Bio-uptake of metalloids (inorganic antimony and arsenic) by plants and development of electroanalytical methods for antimony detection and speciation

A PhD Dissertation

submitted in accordance with the requirements of the University of Liverpool for the

degree of

Doctor of Philosophy

Submitted to

School of Environmental Sciences

by

Dennis San Jose Tuyogon

31 August 2020

DECLARATION

I hereby certify that this dissertation titled "Bio-uptake of metalloids (inorganic antimony and arsenic) by plants and development of electroanalytical methods for antimony detection and speciation" constitutes my own product, that where the language of others is set forth, quotation marks so indicate, and that appropriate credit is given where I have used the language, ideas, expressions or writings of another. Chapters 5 and 6 of this manuscript were edited with the help of P. Salaun.

I declare that the dissertation describes original work that has not previously been presented for the award of any other degree of any institution.

Signed,

Tuyogon

Dennis S.J. Tuyogon

DEDICATION

This dissertation is dedicated to all my friends, family members, and people whom I have met somewhere along the way who encouraged me to pursue my dreams and finish my dissertation.

I dedicate this thesis in the memory of my chemist friend Alex Tardaguila who shares the same dream of becoming a scientist (deceased),

To all my friends here in the UK, Belgium, the Philippines, and all over the world who always believed and supported me.

To my nieces Julia, KC, and my nephews Jayviel, Seb, and Arviel (deceased),.

To my brother Dave, my sisters Daisy and Dannica.

To my parents Mr. and Mrs. Mansueto and Milagros Tuyogon,

And above all, to my Lord and saviour Jesus Christ.

ACKNOWLEDGEMENTS

I thank our Lord God Jesus Christ for everything.

I would like to give my sincerest gratitude to my advisers Prof. Wang (NTHU) and most especially to Dr. Pascal Salaun (UoL) for their continuous guidance and support that made this dissertation successful.

I would also like to thank my other 3 advisers, Prof Wolff (UoL), Prof. Joerg Feldmann (ABDN), and Prof. Sun (NTHU), I also thank our laboratory people here at the University of Liverpool and National Tsing-Hua University for your help that you provide to finish my measurements on time.

Thanks to all my lab mates and office mates here in the UK (Nealy, Mila, Charlie, Valerie, Eugenio, Arthur, Gemma, Leo, etc.)

Thanks to Dr. Yi-Kong for the ICP-MS analysis and literally for all the help, I appreciate it, and the rest of the CFW group, you guys made my stay in the laboratory and Taiwan more enjoyable. To all my Indian, Filipino and Taiwanese friends at NTHU and NCTU.

I also like to thank my IRRI colleagues, especially my former boss/scientist Dr. Sarah Beebout for the big help on my sampling from planning to the collection, to all the laboratory people and the water Science pips for all the support (Ate Ibyang, Ate Mers, Ate Lizzel, etc.). Most notably to Francis and Mia, Ate Ibyang, and Gids for all the help on my rice samples.

Many thanks to Prof. Liu and Prof Sun for allowing me to work with plant growth and microdialysis system. To all laboratory staff, especially Mr. Lin for his patience and sharing of their technical expertise to me during micro-dialysis set-up.

Special thanks to the dual UoL-NTHU PhD scholarship for the opportunity and financial support throughout the program, for without you, I would not witness and experience the best four years of my life so far.

And, last but not least I thank Prof. Tardaguila for his professional advice and support, all of my family members, classmates, JCIM, Carrie, Pastor Carding and Tita Reggie, and the

Su family and professional ministry, all my friends in the Philippines, and all over the world, for their continued support and encouragement. May the almighty God bless you.

ABSTRACT

Metalloids like arsenic (As) and antimony (Sb) are naturally present at low concentrations but the increased use of these metalloids in the environment has led to environmental soil and groundwater contamination issues and understanding their biogeochemical cycling is of prime importance to predict potential contamination issues. Despite its toxicity, Sb received little analytical attention compared to other toxic heavy metals. However, speciation analysis is necessary to understand the toxicity and fate of each metalloid species in the environment. The speciation of metalloids is however often limited to the differentiation of oxidation states and identification of stable organic species by techniques such as ICP and LC-MS. The detection and identification of more reactive, relatively weak complexes that can play a preponderant role in the transport of these elements are however much less known. There is a wide range of available spectroscopic techniques for total Sb and As determination and speciation in real environmental samples. But the equipment often used for such analysis is bulky, expensive, and immobile. The necessity for a cheap, portable, smaller, and simpler analytical technique that can be used in the field were all the reasons for using electrochemical methods. One of the techniques is by using a gold microwire electrode that is well suited for the speciation of inorganic arsenic and antimony that has the advantage of low cost, portability, and may detect weak complex.

The main focus of this study is trying to understand where metalloid species are ending up and how they are being transported. This thesis investigated the bio-uptake of metalloids (inorganic antimony and arsenic) by plants and the development of electroanalytical methods for antimony detection and speciation.

Bio-uptake of metalloids were using a hydroponic experiment of cucumber plant chosen as a model plant to assess the impact of As or Sb species, plant age, exposure duration, and metalloid concentration to overall plant morphology. A new method of microdialysis was developed. Being less destructive and less invasive, it can be a useful tool for xylem sap sampling allowing researchers to simulate nutrient/toxic metal uptake, translocation, and absorption while taking into consideration the effect of transpiration. The other aim of this study is to use voltammetry to study the complexation of such elements with e.g. carboxylic acids, preponderant components of xylem sap that might strongly affect the translocation of As and Sb. Voltammetric methods were developed for (1) complexation studies of Sb(III) with xylem sap samples and determination of stability constants of Sb(III) with low molecular weight ligands and cation mediated reduction of Sb(V) using monovalent, divalent, and trivalent cations. We have demonstrated the feasibility to quantitatively study the complexation of the presence of Sb(III) complex with low molecular weight ligands, specifically EDTA, DTPA, TA, and GSH using a voltammetric method (pseudopolarography on Au electrode) at ppb levels. The technique may also be that will be used to gain insights into the complexation patterns of inorganic and organic bound Sb and highlight the formation of weak, fast dissociating species as well as inert, stable, complexes. Voltammetry may complement nicely the commonly that will be used chromatographic and hyphenated techniques.

TABLE OF CONTENT

ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
AFS	Atomic Fluorescence Spectroscopy
ASV	Anodic Stripping voltammetry
Cond.	Conditioning
CE	Counter electrode
CV	Cyclic voltammetry
DMA	Dimethylarsinic acid
DTPA	Diethylenetriaminepentaacetic acid
EDTA	Ethylenediaminetetraacetic acid
ESI-MS	Electrospray ionization mass spectrometry
Edep	Deposition potential
GC	Gas chromatography
GF-AAS	Graphite Furnace Atomic Absorption Spectroscopy
HPLC	High-performance liquid chromatography
HPLC-FAAS	HPLC-Flame AAS
ICP-MS	Inductively coupled plasma mass spectrometry
IP	Ionization potential
LS	Linear scan
MS	Mass spectrometry
PCA	Principal component analysis
RE	Reference electrode
RF	Radiofrequency
RP	Reversed-phase
SWASV	Square wave anodic stripping voltammetry
SWCSV	Square wave cathodic stripping voltammetry
WE	Working electrode

Experimental symbols

mM	millimolar
µM	micromolar
nM	nanomolar
pM	picomolar
ppb	part per billion
ppm	part per million

CHAPTER 1 INTRODUCTION

Index of Figures

Index of Tables

1.1 Introduction

Metalloids are introduced into the environment as micropollutants anthropogenically from widespread use in different industries, domestic and agriculture. Over the years, trace metalloid pollution has become an environmental problem of concern due to its ecotoxic properties. However, speciation analysis is necessary to understand each metalloid species' toxicity and fate in the environment. Despite its toxicity, antimony (Sb) received little analytical attention compared to other toxic heavy metals. There is limited knowledge in the complexation of Sb with ligands, either for Sb(III) and Sb(V).

Even though a wide range of spectroscopic techniques have been developed to speciate Sb and arsenic (As) species, the equipment used for such analyses is bulky, expensive, and immobile. The necessity for a cheap, portable, smaller, and more straightforward analytical technique used in the field was all the reasons for using electrochemical methods.

A gold microwire electrode that is well suited for inorganic arsenic and antimony speciation has the advantage of low cost, portability, and may detect weak complexes. The technique may also be used to gain insights into the complexation patterns of inorganic and organic bound Sb and highlight the formation of weak, fast dissociating species and inert, stable complexes. Voltammetry may complement chromatographic and hyphenated techniques. It is surprising that even stability constants of Sb with tartaric acid, which has been used for hundreds of years, are not known. This is because analytical methods for measurements in natural conditions of pH are limited in terms of the technical ability to assess the chemical speciation and reactivity of these species, especially when it comes to the formation of relatively weak organic complexes that cannot be analysed through standard chromatographic techniques. Furthermore, it is because of the low solubility of Sb, its strong hydrolysis (Sb(III) is present as $Sb(OH)_3$ and Sb(V) as $Sb(OH)_6^-$) and the fact that previous measurements were carried out in strongly acidic conditions and high concentration.

1.2 Scopes and objectives of the thesis

This thesis is focusing on the metalloids arsenic and antimony and contributes to improving our understanding of the uptake, effect on plant growth, and translocation mechanisms in the plant, as well as expanding the analytical methodology for the determination of these elements. This was achieved by:

- Investigation of the impacts of metalloids like Sb and As in a hydroponic experiment on cucumber plants (*Cucumis Sativa L.)* (Chapter 2),
- Investigation on the xylem sap of the cucumber plants under the impacts of metalloids like Sb and As in a hydroponic experiment (Chapter 3),
- Plant physiological studies of the effect of duration (short- and long-term amendment), concentration, plant age, and species in plants (chapter 2 and 3),
- Devising a new in-vivo less destructive method of collecting plant xylem sap was proposed and examined- microdialysis (chapter 3), In addition,
- Assessment of the metal(loid) in selected Asian brown rice (chapter 4).
- The use of stripping voltammetry for the determination of stability constants of antimonite with model ligands such as EDTA, DTPA, tartaric acid, and glutathione (Ch 5), and
- Development of a new electrochemical method for the determination of antimonate at neutral pH using cation mediated reduction (Ch 6).

1.3 The organisation of the thesis

This thesis is intentionally written as chapters for publication. Every chapter has its introduction part of keeping the right balance in each chapter. **Chapter 1 Introduction.** This chapter will focus on the knowledge of the behaviour of the Sb and As and other metalloids in the environment but more focused on the environment and plants. This chapter will also provide insights on the available analytical techniques for Sb and As species and information on speciation studies.

Chapter 2 Antimony and arsenic species impact on cucumbers – a hydroponic experiment. This chapter will focus on the As and Sb species translocation on cucumber plants grown hydroponically. Xylem saps were collected via the root exudation method. ICP-MS analysis of the xylem saps and plant parts (roots, stems, and leaves) was used to give insights on the translocation of the different metalloid species on cucumber plants. The physiological effects of the amendments were also be studied in this chapter

Chapter 3 A novel method for the determination of antimony and arsenic in cucumber plants *(Cucumis Sativa L.)* using in-vivo microdialysis method (MD). This chapter will focus on the Sb and As translocation on cucumber plants grown hydroponically. ICP-MS techniques on the xylem sap using an in-vivo sampling technique called microdialysis. Different plant parts (i.e., roots, stems, and leaves) will give us insights into the effect of metalloid concentrations and plant age on the translocation of the different metalloids on cucumber plants.

Chapter 4 is about assessing antimony, arsenic, and other heavy metal analysis in rice by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS). Asian brown rice was collected from IRRI (International Rice Research Institute) from three different groups: long-term cropping experiments (control), Asian rice varieties, and rice that were grown in contaminated mining sites in the Philippines will be subjected to ICP-MS analysis. This chapter will give some insights into the heavy metal contents of some Asian brown rice varieties available in the market, the effect of long-term cropping, and mining.

Chapter 5 Determination of stability constants of antimonite with model ligands. This chapter will introduce a voltammetric method for the speciation of Sb(III) species in the presence of model ligands. It is based on the anodic stripping techniques on reducing Sb(III) using vibrated gold with the presence of model ligands at various pH. Most of the experiments have been done only for Sb(III). This chapter will also provide stability constants obtained experimentally from the voltammetric method developed using pseudopolarography (PP). Stability constants obtained experimentally will be compared with the prediction calculations obtained from chemical equilibrium software.

Chapter 6 Cation mediated reduction of antimonate in neutral pH. This chapter will introduce a new voltammetric method for the detection of antimony at neutral pH. It is based on the effect of metal ions that catalyse Sb(V) reduction at neutral pH conditions.

Chapter 7 Conclusions and outlook. This chapter will give the overall idea of the study, including the overall discussions and outlook.

1.4 General aspects

1.4.1 Antimony-General

Antimony (Sb) is a brittle, silvery-white metalloid with atomic number 51 and belongs to group 15 of the periodic table. It has a chemical symbol Sb from the Latin word Stibium with a molecular mass of 121.76 g/mol. It occurs in nature in two isotopes, 121 Sb (57.21%) and 123 Sb (42.79%). The common oxidation numbers for Sb are -3, 0, +3, and +5 (the last two being the most relevant in aqueous solution chemistry). It can form complexes with both hard and soft Lewis bases because of its borderline hardness characteristic as a Lewis acid. Sb(V) has a charge density of more than double that of Sb(III) (and higher than the charge density of, for instance, $Al^{(III)}$) and thus reacts as a hard Lewis acid. Sb(V) exists in an aqueous solution as antimonate $Sb(OH)_6^-$, except under highly acidic conditions. Sb(III) is typically found as antimonite $Sb(OH)_3$ within the pH range from 2 to 11.5 (Figure 1.1).

Sb has been used since ancient times, mainly in cosmetics. Nowadays, it is mostly used in flame retardants as antimony trioxide in many products (e.g., children's clothing, toys, car seat covers, and aircraft). It is also used as an additive of lead and tin to improve hardness and mechanical strength or used in lead-acid batteries to improve the charging characteristics. Sb was used as a perpetual pill or as a laxative in the form of a small Sb ball. Nowadays, Sb is still used for the treatment of the parasitic disease leishmaniasis.

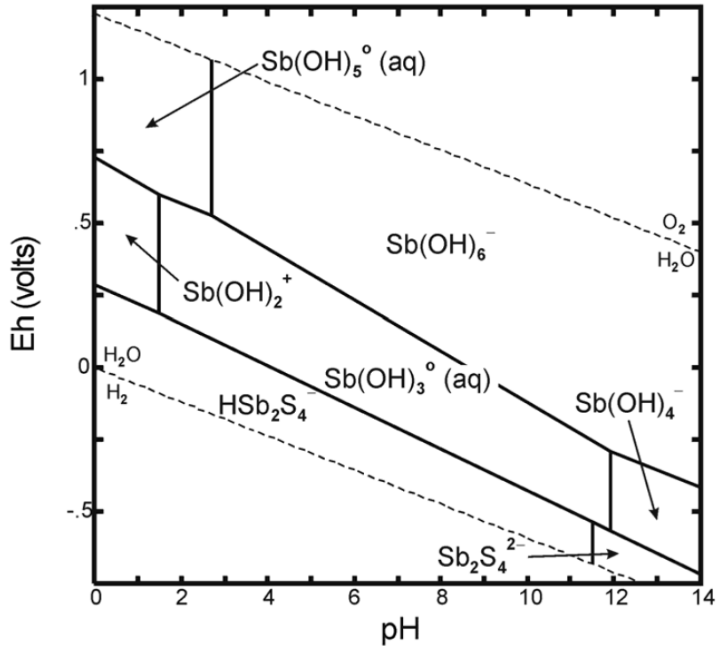


Figure 1. 1. Eh-pH Diagram Showing Dominant Aqueous Species of Antimony [Diagram was calculated at 25 ºC (adapted from Krupka and Serne, 2002).

Another essential use of Sb is as a catalyst in the syntheses of polyethylene terephthalate (PET) plastics which may impose a serious threat to human health. Not only in bottled water, but plastic bottles are also used in juices, coffee, and milk products, which can be contaminated with Sb. Increasing concern about human exposure to Sb through Sb leaching is absorbed from the plastic bottle for the past years (Krachler and Emons, 2001; Bach et al., 2012).

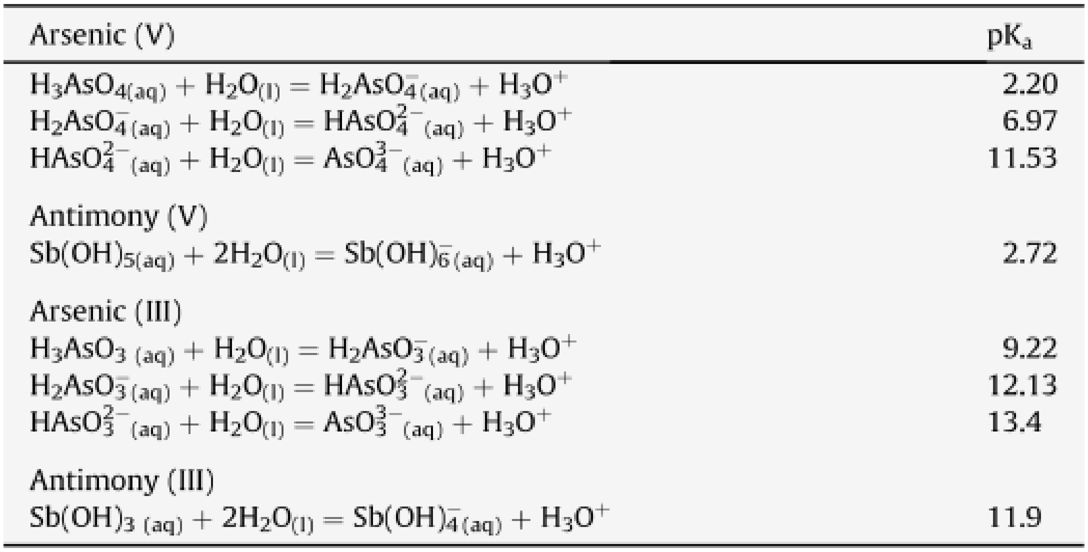
1.4.2 Arsenic - General

Arsenic (As) is a non-essential and carcinogenic element, well known for its acute poisoning effect after acute and chronic exposure (Aposhian and Aposhian, 2006). Arsenic can be released into the environment naturally and anthropogenically by volcanic eruptions and by-products of mining, respectively, to name a few (Welch and Stollenwerk, 2003). Arsenic acid (H_3AsO_4) is the most abundant species in soil but not in soil with pH < 2. The concentration of dihydrogen arsenate ($H_2AsO_4^{-1}$) gradually increases when soil pH increases at around 3 to 6. Both $H_2AsO_4^{-1}$ and hydrogen arsenate ($HAsO_4^{-2}$) species are present at pH 7-8. The most abundant species is $HAsO_4^{-2,}$ around pH 8 to 11 (Sadiq, 1992).

Arsenic does not have many uses by itself but is used in compounds such as wood preservatives, insecticide, semi-conductor, and ammunition production. As exists in four oxidation states: -3, 0, +3 and +5. The various chemical forms and mineral forms are shown in Table 1.4. In soil solution, the inorganic forms arsenite As(III) and arsenate As(V) are the most phytoavailable (Raab et al., 2005). In terms of toxicity, the inorganic forms are the most toxic than the organic counterpart, whereas the trivalent is the most toxic than the pentavalent form (Zhang and Selim, 2005; Wu and Sun, 2016).

In countries such as Bangladesh, India, Pakistan, and the USA are experiencing As contaminated groundwater; that can enter drinking water and the food chain through the soil and during crop irrigation (Finnegan and Chen 2012). World Health Organization (WHO) set the permissible limit of As in drinking water of 10 ug L^{-1} (parts per billion, ppb) and listed As as one of the top ten chemicals of primary public concern together with lead (Pb), mercury (Hg), and benzene (C_6H_6) (Bellido-Martín et al., 2009). Throughout the last 20 years, the extensive nature of acute and chronic human exposure to arsenic in drinking water has become evident in many countries (Finnegan and Chen, 2012). The potential adverse effect is very high such as dermal changes, respiratory, pulmonary, cardiovascular, gastrointestinal, hematological, reproductive, to name a few (Kapaj et al., 2006). Although many As compounds are labeled carcinogenic, the real toxicity of it is not fully understood. This is partly due to the difficulty of speciating a very low concentration of As compounds in food and plants. Table 1.1 shows the equations and pKa values of inorganic As and Sb species commonly found in the environment (Wilson et al., 2010)(Smith et al., 1998; Zakaznova-Iakovleva and Seward, 2000; Puigdomenech, 2002). (Wilson et al., 2010).

Table 1. 1.Equations and pKa values for inorganic As and Sb species (Wilson et al., 2010); Smith et al., 1998; Zakaznova-Lakovleva and Seward, 2000; Puigdomenech, 2002)



Arsenic (V)	pK_a
$H_3AsO_{4(aq)} + H_2O_{(l)} = H_2AsO^-_{4(aq)} + H_3O^+$	2.20
$H_2AsO^-_{4(aq)} + H_2O_{(l)} = HAsO^{2-}_{4\ (aq)} + H_3O^+$	6.97
$HAsO^{2-}_{4\ (aq)} + H_2O_{(l)} = AsO^{3-}_{4\ (aq)} + H_3O^+$	11.53
Antimony (V)	
$Sb(OH)_{5(aq)} + 2H_2O_{(l)} = Sb(OH)^-_{6(aq)} + H_3O^+$	2.72
Arsenic (III)	
$H_3AsO_{3\ (aq)} + H_2O_{(l)} = H_2AsO^-_{3(aq)} + H_3O^+$	9.22
$H_2AsO^-_{3(aq)} + H_2O_{(l)} = HAsO^{2-}_{3\ (aq)} + H_3O^+$	12.13
$HAsO^{2-}_{3\ (aq)} + H_2O_{(l)} = AsO^{3-}_{3\ (aq)} + H_3O^+$	13.4
Antimony (III)	
$Sb(OH)_{3\ (aq)} + 2H_2O_{(l)} = Sb(OH)^-_{4(aq)} + H_3O^+$	11.9

Redox potential (Eh) and pH control arsenic speciation. At higher pH, $HAsO_4^{2-}$ is dominant ($H_3AsO_4$0 and AsO_4^{3-} may be present in strong acid or base conditions, respectively, at low pH (pH 6.9) which is in oxidizing conditions, $H_2ASO_4^-$ dominates. Figure 1.2A shows the Eh-pH diagram, it shows the arsenic species predominating in various pH ranges, and under the reducing conditions (at pH<∼9.2), the uncharged $H_3AsO_4^0$ predominates (Lombi and Holm, 2010). Fig. 1.2B and 1.2C summarise the deprotonations of arsenious (H_3AsO_3) and arsenic (H_3AsO_4) acids under differing conditions (Mohan and Pittman, 2007).

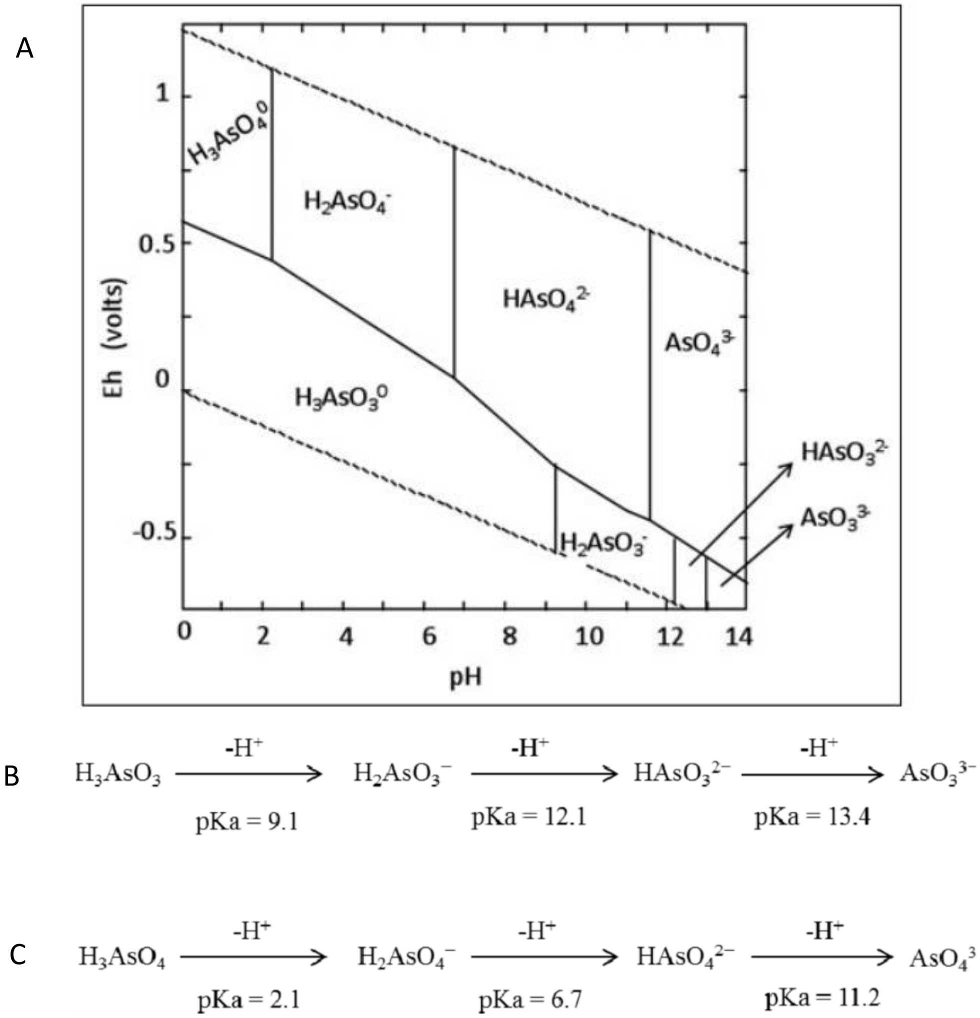


Figure 1. 2. Eh-pH diagram (Lombi and Holm, 2010) **(A) and pKa values and dissociation of As(V) (B, C) (Mohan and Pittman, 2007) for As**

1.5 Sb and As in the environment

In seawater, Sb and As occur at concentrations of 0.4-1.6 nM and 10-20 nM, respectively (Filella, Belzile and Chen, 2002a). Antimonate and arsenate, which are the oxidised inorganic species (V) are predominant in oxic waters, and due to biotic and abiotic reduction process coupled with slow oxidation kinetics, the reduced species (III) (antimonite and arsenite) occurs at much lower levels. Wilson et al., (2010) gave the pertinent redox reaction that occurs in the environment (Table 1.2). Also, the methylated species, dimethyl arsenic acid (DMA), monomethyl arsenic acid (MMA), monomethyl stibonic acid (MMSb), and other organic species (arsenosugars) occur (Quentel and Filella, 2002; Filella et al., 2007; Filella, 2013).

Table 1. 2. Redox reactions in natural systems (adapted from Wilson et al., 2010)

Reaction	pe^{0a}	Eh^0 (V)
$O_2 + 4H^+ + 4e^- = 2H_2O$	20.8	1.23
$2NO_3^- + 12H^+ 10e^- = N_2 + 6H_2O$	21.1	1.25
MnO2 + 4H+ + 2e- = Mn2+ + 2H2O	20.4	1.21
Fe(OH)3 (amorphous) + 3H+ + e- = Fe^{2+} + $3H_2O$	16.6	0.98
a-FeOOH (goethite) + 3H+ + e- = Fe^{2+} + $2H_2O$	13.1	0.77
Sb(OH)6 - + 3H+ + 2e- = $Sb(OH)_3$ + $3H_2O$	12.9	0.76
Sb2O5 + 4H+ + 4e- = Sb2O3 (valentinite) + 2 H_2O	11.0	0.65
Sb2O5 + 6H+ + 4e- = 2Sb(OH)2 + + H_2O	9.8	0.58
H3AsO4 + 2H+ + 2e- = H3AsO3 + H_2O	9.5	0.56
SO4 2- + 10H+ + 8e- = H2S + 4 H_2O	5.3	0.31
Sb(OH)2 + + 2H+ + 3e- = Sb + 2 H_2O	3.6	0.21
CO2 + 8H+ + 8e- = CH4 + 2v	2.9	0.17
Sb2O3 + 6H+ + 6e- = 2Sb + 3 H_2O	-2.5	-0.15
H3AsO3 + 3H+ + 3e- = As + 3 H_2O	-4.2	-0.25
Sb + 3H+ + 3e- = SbH_3	-8.6	-0.51
As + 3H+ + 3e- = AsH_3	-4.0	-0.61

Figure 1.3 shows the pH-dependent dissociation among hydroxylated metalloid acids. The neutral forms of the metalloids with a 0-4 pH range are in the curves in redpoint toward the undissociated portions. Because of the large variability of pKa values of the metalloids in the environment, the species are present in the plant or soil they thrive in uncharged molecular form (Kroukamp et al., 2016; Guerriero et al., 2020).

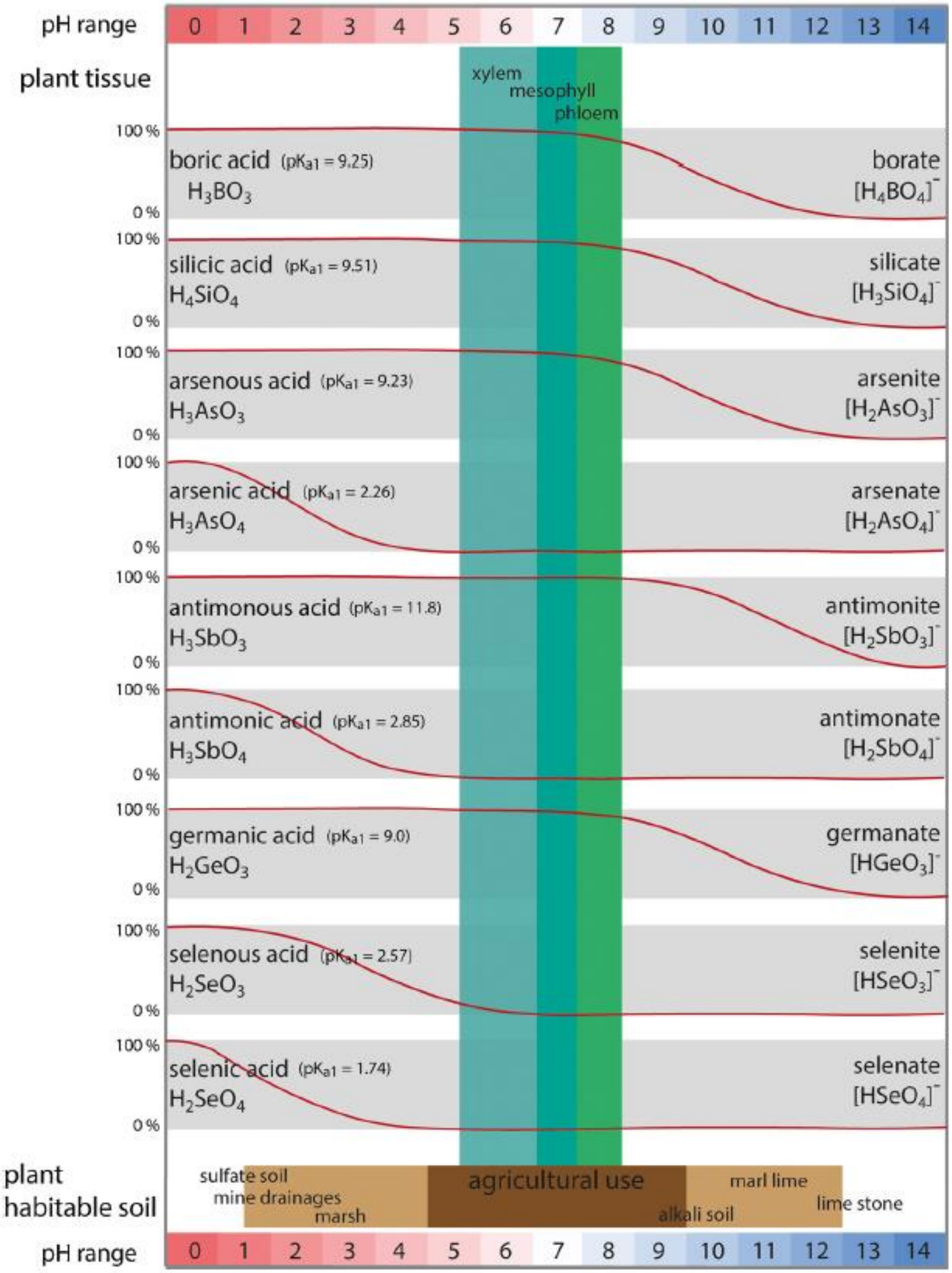

pH range
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
plant tissue
xylem
mesophyll
phloem
100 %
0 %
boric acid (pK$_{a1}$ = 9.25)
H_3BO_3
borate
$[H_4BO_4]^-$
silicic acid (pK$_{a1}$ = 9.51)
H_4SiO_4
silicate
$[H_3SiO_4]^-$
arsenous acid (pK$_{a1}$ = 9.23)
H_3AsO_3
arsenite
$[H_2AsO_3]^-$
arsenic acid (pK$_{a1}$ = 2.26)
H_3AsO_4
arsenate
$[H_2AsO_4]^-$
antimonous acid (pK$_{a1}$ = 11.8)
H_3SbO_3
antimonite
$[H_2SbO_3]^-$
antimonic acid (pK$_{a1}$ = 2.85)
H_3SbO_4
antimonate
$[H_2SbO_4]^-$
germanic acid (pK$_{a1}$ = 9.0)
H_2GeO_3
germanate
$[HGeO_3]^-$
selenous acid (pK$_{a1}$ = 2.57)
H_2SeO_3
selenite
$[HSeO_3]^-$
selenic acid (pK$_{a1}$ = 1.74)
H_2SeO_4
selenate
$[HSeO_4]^-$
plant habitable soil
sulfate soil
mine drainages
marsh
agricultural use
alkali soil
marl lime
lime stone
pH range
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

Figure 1. 3. pH dependent dissociation balance among hydroxylated metalloid acids (adapted from Pommerrenig et al., 2015).

1.5.1 Antimony in the environment

Among the four oxidation states of Sb, the main species that are most frequently present in the environment are Sb(III) and Sb(V) (Filella, 2013; Pla-Vilanova et al., 2019). Sb(V) is the most predominant species and exists in the oxic environment in the form of $Sb(OH)_6^-$ while Sb(III) exists in the form of $Sb(OH)_3$ in anoxic condition.

Antimony's natural concentration in the environment specifically in the Earth's crust is around 0.2-0.3 mg Kg^{-1} (Tschan et al., 2009). In soils, Sb is slightly higher between 0.3 and 8.6 mg Kg^{-1} (Table 1.1). The increased use of Sb in mining and industry has led to widespread environmental soil contamination issues (Tschan et al., 2008). A substantial number of papers have now been published on the element and its behaviour in the natural environment. Sb is present in soils and natural waters (i.e., freshwater systems, oceans, and estuaries) as a result of rock weathering, soil runoff, and anthropogenic activities (Filella et al., 2002) with concentrations ranging from well below 1 ug/L up to 100 ug/L because of anthropogenic activities (Filella et al., 2009). Dissolved Sb concentration in the ocean ranges from ng/L to a ug/L depending on the location and the pollution sources. Information on Sb transformation and transport in the environment is scarce as well as the Sb speciation in various media. This is the reason why further research is needed to understand Sb behaviour and fate in the environment (Filella, Belzile and Chen, 2002a). However, many key aspects of the environmental chemistry of antimony remain poorly understood. These include critical areas such as its ecotoxicology, its global cycling through different environmental compartments, and what chemical form it takes in different environments. The environmental behaviour and toxicological effects of Sb strongly depend on its various forms in the environment, thus developing methods for measuring the various forms of Sb will be depending on the specific form of antimony (Filella et al., 2009).

Table 1. 3. Published values of Sb concentrations in the environment (adapted from (Tschan et al., 2009)

Medium	Source of pollution	Concentration (mg Kg^{-1} unless given otherwise)	References
Igneous rocks	-	0.1-1	US Geological Survey, 2004
Sedimentary rocks	-	0.05-1.5	Bowen, 1979
Soil background	-	0.3-2.3	Kabata-Pendias, 2010
Seawater	-	0.0002	Filella, et. al., 2002
Water near mine	Mercury mine	418	Gemici and Tarcan, 2007
Soils near mine	Mercury mine	0.5-52	Gemici and Tarcan, 2007
Emissions waste deposit	Waste deposit	10 μg m^{-3}	Hirner et al., 2000
Roadside highway (100 m distance)	Traffic pollution	0.53	Cal-Prieto et al., 2001
Needles of trees	Residential area	2.4	Pohl et al., 2003
Orchard soil	Pesticide	0.4-1.5	Wagner et al., 2003
Grass	Antimony smelter	400	Ainsworth et al., 1990a
Garden soil near disused mine	Past mining activities	500	Hammel et al., 2000
Detritivore invertebrates	Smelter	290	Ainsworth et al., 1990b
Ectomycorrhizal fungi	Lead smelter	100-1400	Borovička et al., 2006
Aquatic plants	Mine tailing pond	19	(Hozhina et al., 2001
Garden and crop plants	Spiked pots	399	Hammel et al., 2000
Shooting range	Bullets	13800	Johnson et al., 2005

Figure 1.4 shows the Sb sources, processes transport, and transformation in the environment. The Sb pollution is caused by natural enrichment through weathering of mineralised rocks (Hu et al., 2017) and can be enhanced anthropogenically via historical mining and smelting activities (Lin et al., 2018). The accumulated high Sb concentration was released through the environment by leaching and weathering.

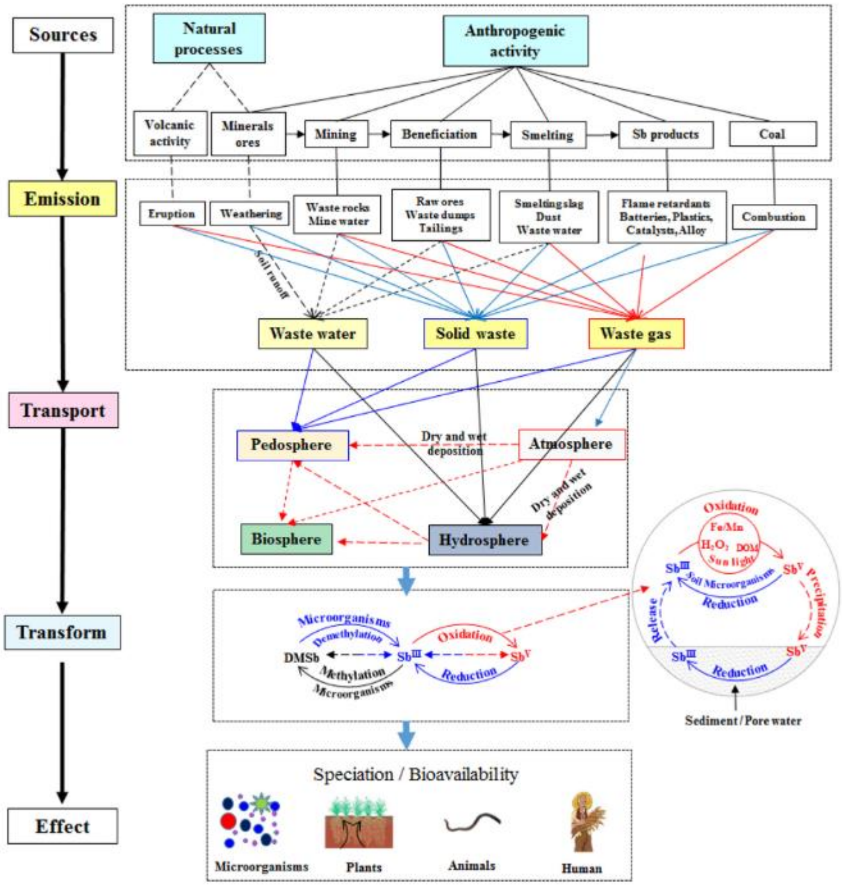


Figure 1. 4. Source of pollution, environmental processes, and ecological effects (adapted from He et al., (2019)).

1.5.2 Arsenic in the environment

As is one of the most abundant, and naturally occurring metalloids in Earth's crust and found in our environment (Moreno-Jiménez et al., 2012; Hettick et al., 2015). It is widely distributed in rocks, soil water, and air. Arsenic can be released into the environment naturally and anthropogenically by volcanic eruptions and by-products of mining, respectively, to name a few (Welch and Stollenwerk, 2003). Mining, smelting of non-ferrous metals, and energy production from fossil fuel are some of the primary anthropogenic sources of As contamination in the environment (Lombi and Holm, 2010). Figure 1.4. shows the summary of important inorganic, organic, and biological forms of arsenic in the environment.

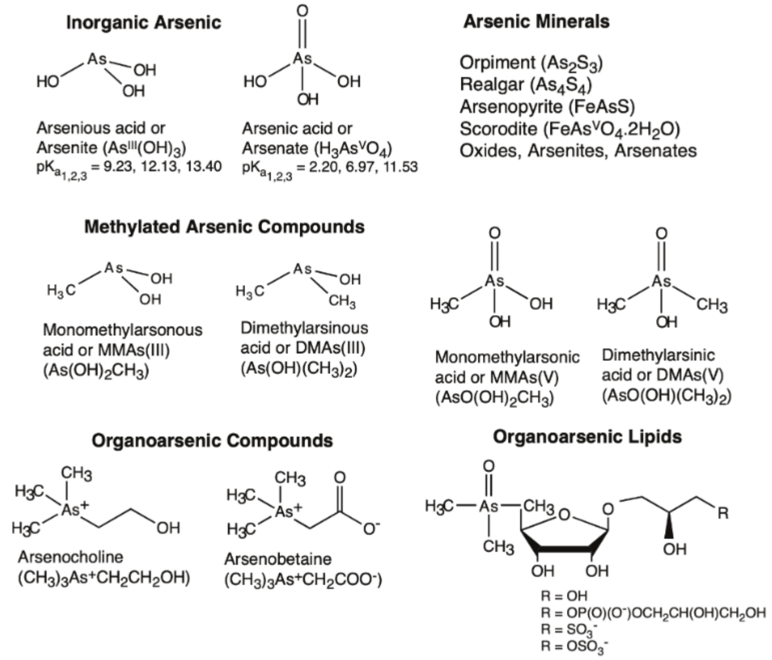


Figure 1. 5 Arsenic speciation in the environment (adapted from O'Day, 2006)

As is widely used as a herbicide and insecticide or wood preservative because of its disinfectant efficacy and resistance to decay, respectively. As is also widely used in manufacturing industries, electronics, and medicine, a high concentration of inorganic As in groundwater has been reported for the past three decades, like in the case of Bangladesh where around 60 million people do not have access to fresh drinking water (Rahman and Hasegawa, 2011), also in different regions like the West Bengal India

(Bengal Delta) (Mandal and Suzuki, 2002) and many countries such as Argentina, China, Chile, Mexico, Taiwan and Vietnam (Smedley and Kinniburgh, 2000).

Table 1.3. Major arsenic minerals occurring in nature composition (adapted from Tschan et al., 2009).

Mineral	Composition	Occurrence
Native arsenic	As	Hydrothermal veins
Niccolite	$NiAs$	Vein deposits and norites
Realgar	AsS	Vein deposits, often associated with orpiment, clays and limestones, also deposits from hot springs
Orpiment	As_2S_3	Hydrothermal veins, hot springs, volcanic sublimation product
Cobaltite	$CoAsS$	High-temperature deposits, metamorphic rocks
Arsenopyrite	$FeAsS$	The most abundant As mineral, dominantly mineral veins
Tennantite	$(Cu, Fe)_{12}As_4S_{13}$	Hydrothermal veins
Enargite	Cu_3AsS_4	Hydrothermal veins
Arsenolite	As_2O_3	Secondary mineral formed by oxidation of arsenopyrite, native arsenic and other As minerals
Claudetite	As_2O_3	Secondary mineral formed by oxidation of realgar, arsenopyrite and other As minerals
Scorodite	$FeAsO_4.2H_2O$	Secondary mineral
Annabergite	$(Ni,Co)_3(AsO_4)_2.8H_2O$	Secondary mineral
Hoernesite	$Mg_3(AsO_4)_2.8H_2O$	Secondary mineral, smelter wastes
Haematolite	$(Mn,Mg)_4Al(AsO_4)(OH)_8$	
Conichalcite	$CaCu(AsO_4)(OH)$	Secondary mineral
Pharmacosiderite	$Fe_3(AsO_4)2(OH)_3.5H_2O$	Ions oxidation product of arsenopyrite and other As minerals

Table 1.4. Standards and Regulations for Inorganic Arsenic (adapted from (ATSDR - Environmental Medicine & Environmental Health Education - CSEM, 2013)

Agency	Focus	Level	Comments
ACGIH	Air-workplace	10 micrograms/m^3	Advisory; TLV/TWA[1]
NIOSH	Air-workplace	2 micrograms/m^3	Advisory; 15-minute ceiling limit
OSHA	Air-workplace	10 micrograms/m^3	Regulation; PEL over 8-hour day
EPA	Air-environment	NA	NA

	Water-drinking water	10 parts per billion	Regulation; maximum contaminant level in public drinking water supplies
	Food	0.5-2 parts per million	Regulation: applies to animals treated with veterinary drugs

ACGIH = American Conference of Governmental Industrial Hygienists EPA = US Environmental Protection Agency
FDA = US Food and Drug Administration NIOSH = National Institute for Occupational Safety and Health OSHA = Occupational Safety and Health Administration, TLV/TWA (Threshold Limit Value/Time Weighted Average) = time-weighted average concentration for a normal 8-hour workday or 40-hour workweek to which nearly all workers may be repeatedly exposed, PEL (Permissible Exposure Limit) = highest level averaged over an 8-hour workday to which a worker may be exposed.

1.6 Sb and As uptake in Plants

1.6.1 Antimony in plants

Sb contamination in soil is caused by anthropogenic sources like mining and industrial activities (Cheng and Sun, 2014). Although Sb is a non-essential element, several studies have reported that plants growing in an Sb polluted environment can uptake large amounts of Sb (Telford et al., 2009; Ren et al., 2014). Very little is known about the mechanisms that lead to the uptake of Sb from the soils to the plant and mechanisms responsible for the translocation of Sb within the plant compartments' uptake.

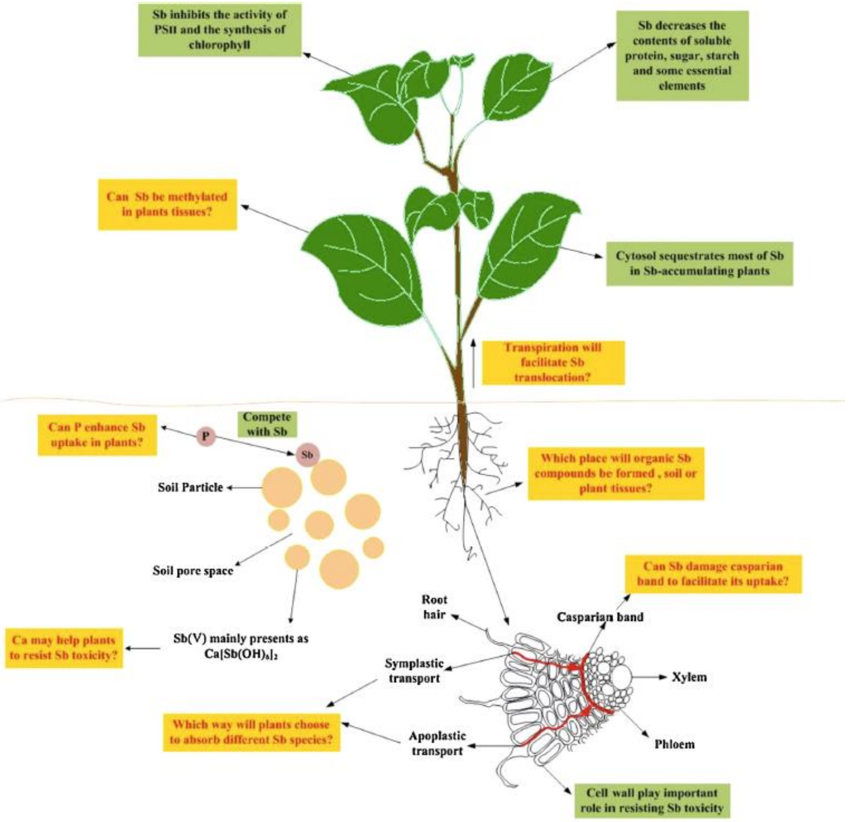


Figure 1. 6. Current understandings (texts in the green box) and gaps (texts in the yellow box) in Sb bio-uptake in plants (adapted from Feng et al., 2013)

Tschan et al. (2009) proposed two Sb uptake mechanism: (1) through anion transporters (i.e., Cl^{-1} or NO_3^-), antimonate enters the root symplast with low selectivity, and (2) through xylem via the apoplastic pathway, antimonate enters the plant by passing in an incompletely sealed or damaged Casparian strip.

1.6.2 Arsenic in plants

The major natural source of As is from desorption from As containing minerals (Hettick et al., 2015). As groundwater contamination is a global problem, it is not only limited to water sources, As contamination in soil has been an environmental problem that is affecting agricultural areas around the world, specifically in countries in Southeast Asia like Bangladesh and Taiwan, and other nations like Hungary, Mexico, USA, Australia, and Argentina (Canepari et al., 2010; Lichtfouse et al., 2012). Soil served as a sink to As and not only can cause considerable harm in microbial processes in the soil that affects plants and other organisms in the soil but can transfer the pollutants to plant roots (Basta, 2006). Table 1.5 and 1.6 show the As concentration in soil and plants, respectively (Panda et al., 2010). As is one of the toxic metalloids and group I carcinogen, it poses a threat to plants, mostly plants that are consumed by human beings that leads to adverse health effects (i.e., cancer) (Panda et al., 2010). As has no known function to plants (Gupta et al., 2011), but maybe toxic even at low concentration (ug L^{-1}) range in plants (Welch and Stollenwerk, 2003; Bastías and Beldarrain, 2016). High As concentration in the soil can cause cell necrosis, chlorosis, growth inhibition, and death (Hettick et al., 2015).

Table 1.5 List of concentrations of Arsenic in typical polluted and non-polluted soils (adapted from Garg et al., 2015)

Type of soil	Concentration of arsenic	Reference
Calcareous soils (uncontaminated)	$5–17\ \mu g\ L^{-1}$	Althobiti et al., 2018
Shallow groundwater	$5–123\ \mu g\ L^{-1}$	Sadiq, 1992
Alluvial aquifers (contaminated)	$50–126\ \mu g\ L^{-1}$	Nimick, 1998
Smelters	$1{,}000\ ng\ m^{-3}$	International programme on chemical safety, 2004
Pesticide manufacturing or mining sites	Up to $5{,}000\ \mu g\ L^{-1}$	International programme on chemical safety, 2004
Volcanic rock or sulfide mineral deposits	$3{,}000\ \mu g\ L^{-1}$	International programme on chemical safety, 2004

Table 1.6. As concentration detected in some plants (adapted from Matschullat, 2000).

Sample	Plants	As concentration (mg Kg^{-1})

1	Cabbage (*Brassica oleracea*)	0.020–0.050
2	Carrot (*Daucus carota*)	0.040–0.080
3	Grass	0.020–0.16
4	Potato (*Solanum tuberosum*)	0.020–0.200
5	Lettuce (*Lactuca sativa*)	0.020–0.25
6	Mosses and lichens	0.26
7	Ferns	1.3

Food chain transport of trace metals and metalloids (i.e., As) poses a threat to human health, and more studies are needed to see the health effects of consuming contaminated crops to humans. Different species have different mechanisms of As transport. For example, Burló et al. (1999) and Rodriguez-Iruretagoiena et al. (2015) showed that tomatoes do not efficiently accumulate As, yet rice is a very efficient As accumulator, making rice potentially unsafe for human consumption (Bhattacharya et al., 2009; Sun et al., 2009).

Despite the firm knowledge of the interaction between As and plant cells, we still don't understand the exact nature of why As is toxic.

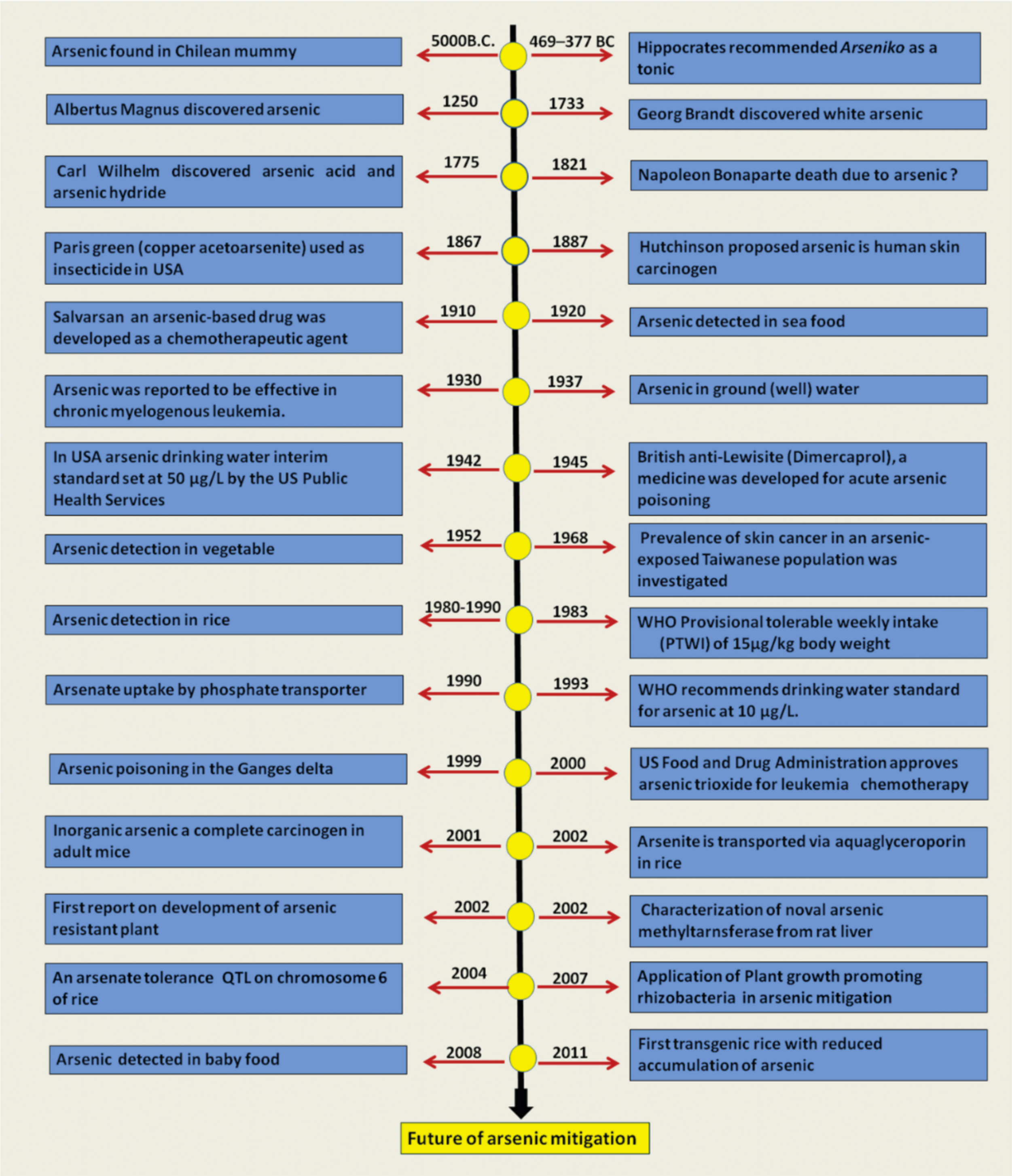


Figure 1. 7. Timeline of some significant proceedings in the toxicology and contamination of arsenic as well as mitigation of arsenic toxicity/accumulation in plants (Adapted from Shri et al., 2019).

What part of the plant metabolism are most vulnerable to As toxicity and why. What are the most critical molecular targets for As, and how to protect these targets through breeding or direct plant engineering (Hettick et al., 2015).

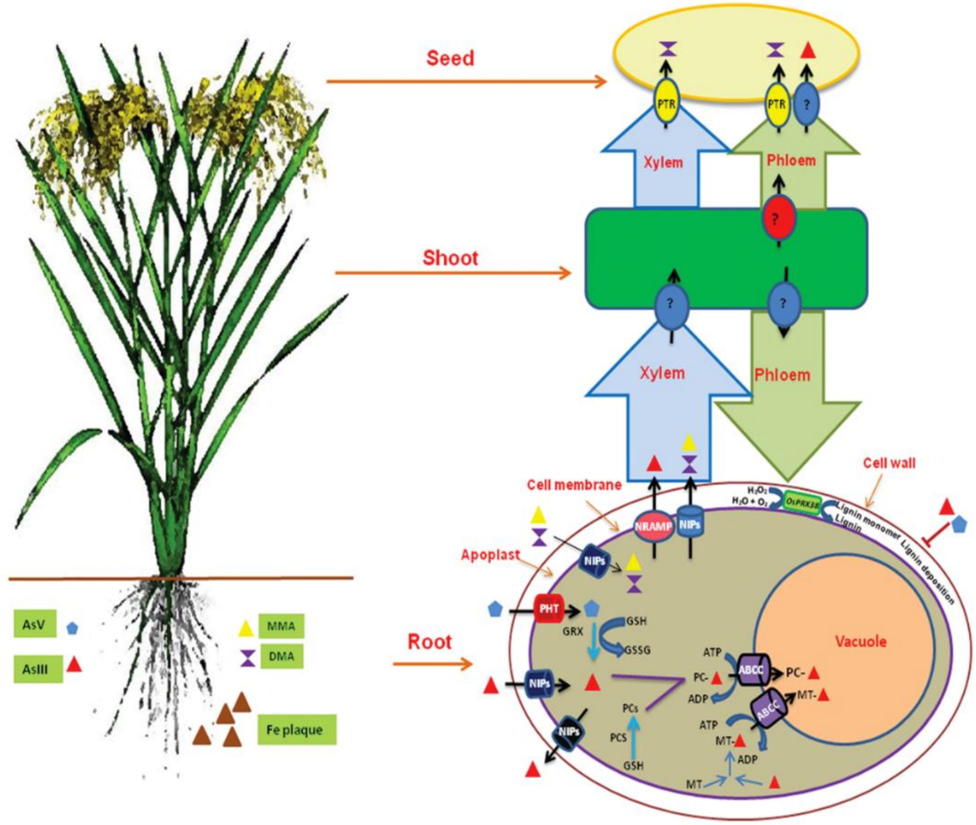


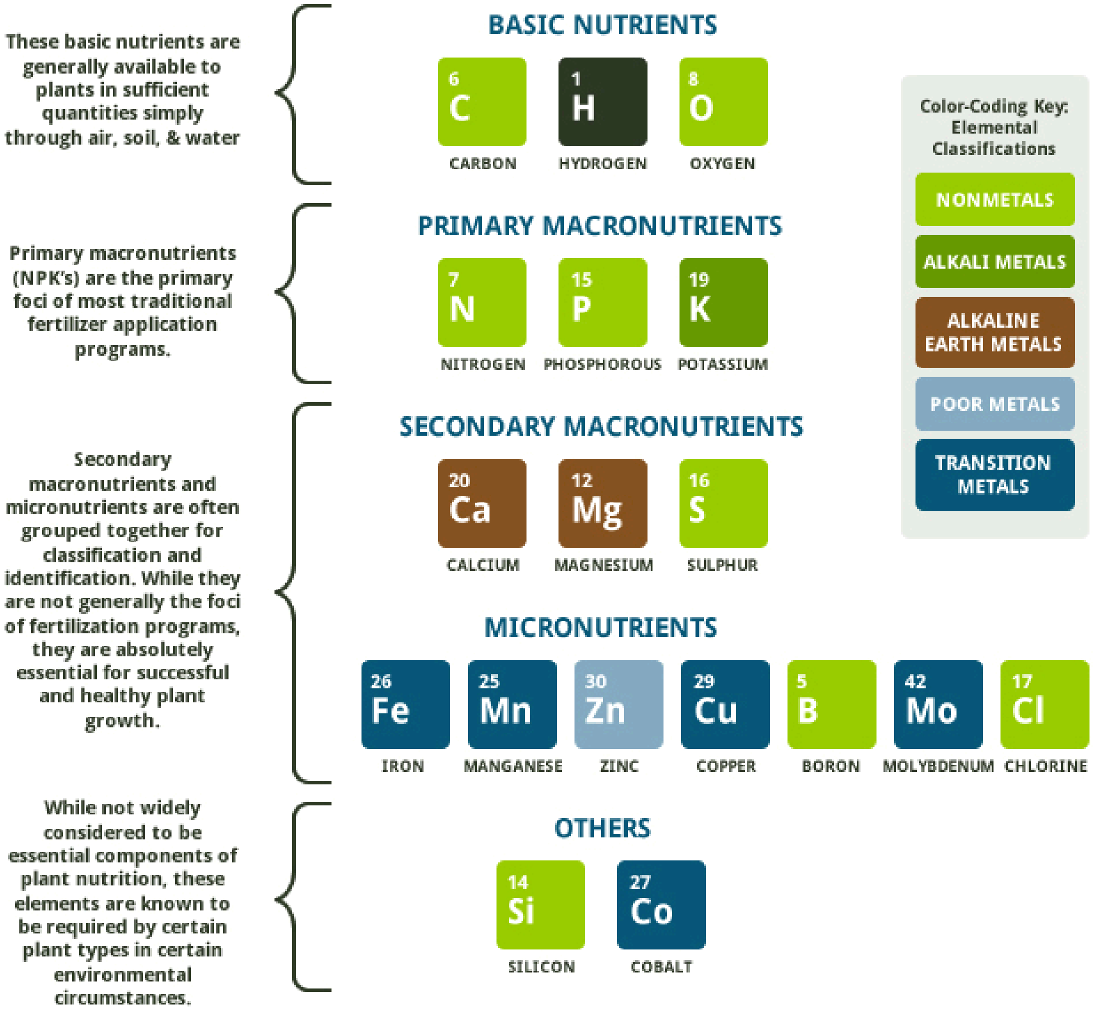
Figure 1. 8. Overview of As uptake, transport, and detoxification in plants (Adapted from Shri et al., 2019).

Figure 1.8 shows Shri et al. (2019) study of As uptake translocation and detoxification in plants. The translocation of As from roots to shoots can be either active or passive. Arsenate (the phosphate analogue) is taken up by Pi transporters, and arsenite and methylated forms of As (MMA and DMA) are taken up by aquaporins. Arsenite forms complexes with glutathione (GSH), phytochelatins (PCs), and metallothionein (MT), which are thiol-rich peptides, and these complexes are sequestered inside the vacuole via ATP-binding transporters (ABCC transporters). Iron (Fe) plaque in the plant roots adsorb and prevents the entry of As via roots. Long-distance transport of arsenite through the xylem/phloem in the shoot to the seed is partially mediated by aquaporins and inositol transporters (INTs).

1.7 Xylem sap, Plant transport, and nutrient and water uptake

Plants obtain water and nutrients from the soil through the roots and carbon and nitrogen from the atmosphere. Micro and macronutrients are essential for all plant species to perform all the needed functions to grow. There are 14 different types of nutrients, among which nitrogen (N), phosphorus (P), potassium (K), sulfur (S), calcium (Ca), and magnesium (Mg) belong to the macronutrients. The second group is the micronutrients or trace metals that are needed in smaller quantities are composed of iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), cobalt (Co), boron (B), chloride (Cl) and molybdenum (Mo) (other additional are sodium (Na) and silicon (Si))

Xylem and phloem are two vascular tissues used by the plant to distribute all the necessary nutrients from the roots. They are involved in a long-distance transport system consisting of vascular bundles that permeate higher plants' whole body. Xylem vessel is primarily used to transport water, nutrients and send signals to different parts of the plants from the roots to the aboveground organs (Alexou and Peuke, 2013).


These basic nutrients are generally available to plants in sufficient quantities simply through air, soil, & water

Primary macronutrients (NPK's) are the primary foci of most traditional fertilizer application programs.

Secondary macronutrients and micronutrients are often grouped together for classification and identification. While they are not generally the foci of fertilization programs, they are absolutely essential for successful and healthy plant growth.

While not widely considered to be essential components of plant nutrition, these elements are known to be required by certain plant types in certain environmental circumstances.

Figure 1. 9. Hierarchy of elemental nutritional requirements for plant life (adapted from http://microfarmgardens.com/blog/2014/1/1/macronutrients-and-micronutrients-for-plants.html)

Xylem water consists of minerals, root metabolites products, and signals transported from the roots to different parts of the upper plant (i.e., leaves). On the other hand, phloem vessels can also transport water, nutrients, and other organic compounds from photosynthetic organs to auxotrophic ones (Figure 1.9)(Alexou and Peuke, 2013; Hawkesford et al., 2013). The driving forces of long-distance transport are based on transport system gradients, like the gradients in hydrostatic pressure, water, and chemical potentials. Xylem can be arguably considered challenging to investigate because of the complex gradients in pressure and potential (Steudle, 2001).

1.7.1 Xylem sap collection methods

One of the crucial aspects of food safety is to study the translocation of nutrients in plants as part of the human diet. The transport of toxic elements (i.e., Sb and As) in low concentration is not always shown by the plants. Moreover, there is a need to study the substances transported in plants as part of food safety. There are several ways to do to study this process. The first one is the total analysis of the metal under study by separating the plants into each part (roots, shoots, leaves, flower, and fruit), use them for extraction, and calculate the translocation factors from these plant parts (Madejón et al., 2006; Rellán-Álvarez et al., 2006). Another method is the collection of xylem sap as the transportation medium. It is the blood equivalent for animals or humans.

The fluid transport (i.e., xylem and phloem) is a closed system, and it is susceptible to outside mechanical disturbances due to air entry. Xylem transport is partially on negative pressure so that air entry will not disturb xylem flow. Many studies about quantification and speciation of metal(loids) in plants reported difficulty of the xylem sap sampling procedure, and most of it involved destructive sampling of xylem sap by cutting the stem of the plant (Pickering et al., 2000; Mihucz et al., 2005; Raab et al., 2005; Xu et al., 2007). Several studies used a destructive way of collecting xylem sap from different plants like cucumber (*Cucumis Sativus L.*), sunflower (*Helianthus annuus*), fern (*Pteris Vittata*), and tomato (*Lycopersicum Esculenthum*). The following are the methods of collecting xylem sap in the plant for speciation and total metal analysis.

1.7.1.1 Destructive techniques

The main disadvantages of destructive xylem sap are that a fair number of samples need to be taken since a plant population is not homogeneous. Also, there are high risk of interferences from the procedure, such as flux rate changes, contamination, or lateral exchange of compounds from xylem to phloem, or vice versa (Schurr, 1998, 1999).

1.7.1.1.1 Root exudate method

This method is the simplest way to collect and sample xylem sap from plants without using sophisticated instrumentation (Satoh, 2006). This method involves cutting off the transpiring shoot of a plant near the root-shoot interface, and the sap is excreted from the decapitated plant part. The advantage of this method is easy to apply and less contamination. Not all plants can be used for this method. Plants that excrete sap after decapitation are suitable (i.e., cucumbers, kiwi fruits, tomato, and soybean plants)(Biles and Abeles, 1991; Tatár et al., 1998; Bennett and Sicher, 2011).

1.7.1.1.2 Centrifugation

This technique involves cutting off the roots, stems and leaves and inserting the stem into a centrifugation vessel with a speed of 4000 rpm at 2-4 °C. This method is simple and easy to use, but the plant sample is limited to woody plants.

1.7.1.1.3 Sampling from other plant parts

This set of methods is based on the notion that exudates can be forced out of the xylem of plant part cuttings by applying pneumatic pressure. The low cost and simplicity of not using other equipment are the advantages of this method (Alexou and Peuke, 2013).

1.7.1.1.3.1 Sampling from other plant parts

This simple method is used when a high amount of xylem sap is expected to be collected from the plants. It uses a handheld portable vacuum pump. This method requires two persons to operate it as its disadvantage. The low cost and simplicity of not using other equipment are the advantages of this method (Alexou and Peuke, 2013).

1.7.1.1.3.2 Pressure Chamber

This is a modified version of the "pressure vessel technique" of Scholander et al. (1965). This technique uses gas pressure applied to a plant causing xylem sap to flow in the opposite direction. This is to compensate for the negative pressure in the xylem vessel. This technique applies to tree and bush twigs and roots and uses a Scholander pressure chamber, which consists of a vertical metal chamber supplied with N_2 gas.

1.7.1.1.3.3 The Passioura method

This method overcomes the xylem tension by the application of pneumatic pressure to the root system. This can only be used in a greenhouse or laboratory set-up (Passioura, 1980). The plants used for the collection must be grown in a unique container/pot, sealed into the pressure chamber with a pressure of 0.2-2.0 MPa. This method is non-destructive, where the plant still survives after the xylem sap collection.

1.7.1.2 Non-Destructive techniques

Non-destructive techniques of sampling xylem saps are used from intact, living, and transpiring plants. In this method, the plants' normal processes are not disturbed (Schurr, 1998).

1.7.1.2.1 Insects feeding on xylem

This method is an indirect technique of sampling xylem sap from the plant using xylem feeding insect (e.g., meadow spittlebug (*Philaenus spumarius L.*)). This bug only feeds on xylem sap, and the excrements represent the inorganic ion concentrations of sap they were fed on. The analysis of xylem sap is through the bug's excrement except for ammonia. This method's disadvantages are that the bug's organic composition might contaminate the xylem sap and the possibility that the bug does not feed on every plant.

1.7.1.2.2 The xylem pressure probe

This method has a less invasive approach in the plant under investigation where a pressure tube is inserted into the xylem, as the name suggests (Schurr, 1999). This method involves the insertion of a microcapillary tube into the xylem vessel, through the stem where the sap is being sampled. An overpressure was applied to compensate for the negative pressure in the vessel. The advantage of this technique is that it can be applied to any intact plant at a specific location and even detect the difference between vessels. The disadvantages are that a high technical effort is required, and mean xylem sap concentration determination is not possible.

1.7.2 Analytical techniques

1.7.2.1 Analytical techniques for Sb determination

Many techniques can now be used for Sb determination commonly present in aqueous and solid samples, depending on the task at hand. This has resulted from the development of a plasma-based analyte system of detection and technological advances in microwave digestion for solid samples (Nash et al., 2000). Inductively Coupled plasma-Mass Spectroscopy (ICP-MS) and (Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) is now commonly used for the measurement of total Sb concentration in soils, aqueous solutions, environmental, and biological samples. ICP-MS has become more popular because of the advantages of reduced spectral interferences and lower analyte detection (pg mL^{-1}).

There is no doubt that these elements' toxicity is related to their chemical speciation, i.e., under which chemical forms they are present. These chemical forms dictate the elements' overall mobility from one compartment to another (e.g., from the dissolved form to adsorbed onto solids), their bioavailability (some forms are more bioavailable than others), and ultimately their toxicity. The determination of that element's speciation is required to better grasp and understand its cycling through the environment. While the determination of total concentrations is no longer an issue, knowledge of the chemical distribution in water and other biological matrices (e.g., sap, leaves) is still challenging. There is a need to emphasize the development of analytical methods for quantification of these metalloids in the environment, food, water, and plants (Francesconi and Kuehnelt, 2004).

The speciation of Sb faces several complex analytical challenges, highly selective separation, and identification before the analysis. Most published studies on typical hydride generation applications are insufficiently selective for determining intrinsic Sb speciation, and often only oxidation data are obtained.

Electrochemical methods with the stripping techniques are also very sensitive and can be used after appropriate treatment of the samples to analyse low Sb levels in, e.g., rivers (Anawar et al., 2011) or soil extract (Telford et al., 2008). In this case, because of Sb(V) electronegativity, a chemical reduction is first achieved using a different reducing agent (SO_2). Spectroscopic techniques are also still used with the formation of a complex with Sb. However, these techniques have the disadvantage of time-consuming and high detection limits. For speciation studies where information about the oxidation states and organo-complex are needed, a coupling of chromatographic with mass spectrometric techniques is the most powerful, robust, and most widely used analytical technique for separation and detection.

Spectroscopic analysis of metals has become obsolete due to the time of time required for sample preparation and analysis but it also has a high limit of detection (Niedzielski and Siepak, 2003). GF-AAS/GF-ICP (Graphite furnace-Atomic Absorption Spectroscopy/Inductively Coupled Plasma) and HG-AAS (Hydride generation-AAS) are the techniques usually used for total Sb (Niedzielski et al., 2002; Wu and Sun, 2016; Grob et al., 2018; Pedron et al., 2019; Wu et al., 2019). A combination with Mass spectrometry (MS) after the wet mineralisation with these techniques gives a good result and good agreement with certified biological standards. Chromatographic techniques in Sb determination, specifically HPLC (High-performance liquid chromatography) and GC (Gas Chromatography) provide more detailed information than spectroscopic analysis explained earlier. Chromatographic techniques require sample pre-treatment, separation of different species in the sample, and detection of the separated species (Zheng et al., 2001).

HPLC has been used in the various analysis of Sb in the surface, or seawater samples (Quentel et al., 2006) contaminated water from mining areas or extracts of mine soil residues, airborne particulate matter, and biological samples like plants (Daus and Hansen, 2016). A typical combination is chromatographic techniques for the separation and spectroscopy as the detector identifies the metalloids such as Sb (HPLC-ICP-MS, HPLC-FAAS ICP-MS) (Niedzielski and Siepak, 2003).

1.7.2.2 Analytical techniques for As determination

There is a need to emphasise the development of analytical methods for quantification of this metalloid in the environment, food, water, and plants (Francesconi and Kuehnelt, 2004). Figure 1.7 shows the analytical methods for arsenic measurements and their relative merits. HPLC-ICP-MS, hydride generation atomic spectrometry, and electrospray MS detection are some of the available methods in As determination, which is based on the hyphenated technique (Ammann, 2011). It can separate different complexes that are stable enough not to be destroyed in the chromatographic column. Hence, it is crucial to determine whether the complexes have been altered during sample preparation/separation or the arsenic species are transported without complexation.

Because of the high-quality speciation work requirements, arsenic speciation remains challenging (Ammann, 2011). The reliability of As elucidation is also a problem because of the interference of less toxic As-species.

The following crucial points should be considered to perform Sb(III) speciation in environmental samples: have a stable complex (like EDTA) of Sb(III) by using the complex-forming agent as eluent, ensure complete complex formation (e.g., by adding EDTA to the samples before analysis), then use a substantial AE column, and use an optimized, element-specific detector (ICP-MS or HG-AFS) (Daus and Hansen, 2016).

1.7.2.3 Electroanalytical Speciation for Sb and As

There is a wide range of spectroscopic techniques for total Sb determination and speciation in real environment samples (Torghill and Compton, 2011). But the equipment often used for such analysis is bulky, expensive, and immobile. The necessity for a cheap, portable, smaller, and more straightforward analytical technique used in the field was to use electrochemical methods. One of the techniques is using a gold micro-wire electrode that is well suited for the speciation of inorganic arsenic and antimony that has the advantage of low cost, portability, and may detect weak complexes (Salaün et al., 2007). The technique may also be used to gain insights into the complexation patterns of inorganic and organic-bound Sb and highlight the formation of weak, fast-dissociating species as well as inert, stable complexes. Voltammetry may be used with chromatographic and hyphenated techniques. This study will give a better understanding of the biogeochemical cycle of Sb in the environment, focusing on the speciation of arsenic in various matrices such as xylem sap to better understand the translocation of Sb in plants or focusing on the complexation of arsenic with humic substances. The speciation of metalloids is often limited to the differentiation of oxidation states, not so much about the complexation of these hydroxy-species with ligands. This is because analytical methods for measurements in natural conditions of pH are lacking. Aside from the matrix effects, poor electroactivity of As and the type of electrode to be used are some of the hindrances in the analysis (Kowalska et al., 1999). However, voltammetry might be able to do it, both for trivalent and pentavalent species (Toghill et al., 2011).

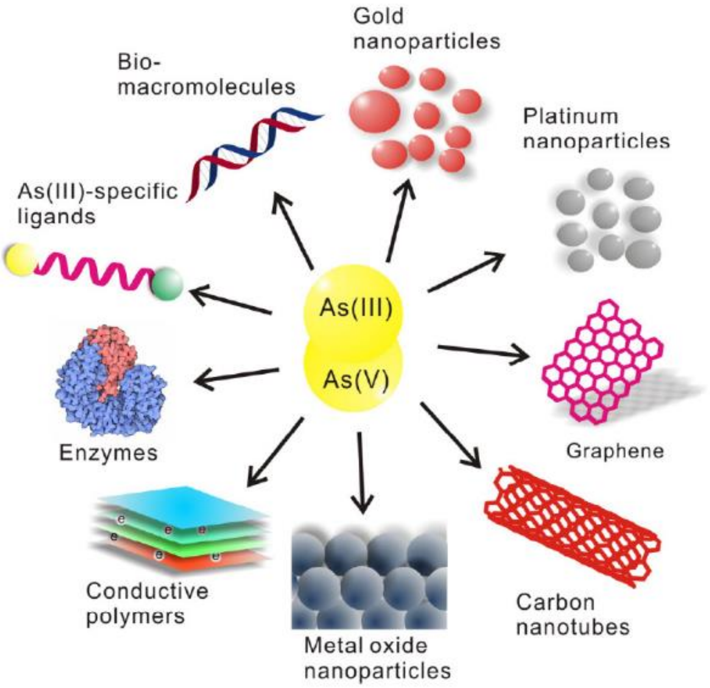


Figure 1.8. The recent development in the construction of modified electrodes aimed at detecting As (adapted from Liu and Huang, 2014).

1.7.2.3.1 Mercury Electrodes

There are several Sb studies with mercury (Hg) electrodes. Sb(III) measurements were possible using this electrode and highly acidic and halide containing electrodes. Due to the Sb(V) inactivity, only the total Sb or Sb(III) is determined in most of the mercury-based electroanalytical techniques. The most common mercury-based electrodes used in Sb determination without complexation or modifiers are Hg film electrodes (MFE) and the hanging Hg drop electrodes (HMDE). The method is based on antimony amalgam formation with the Hg surface, and with this, Differential Pulse-Anodic Stripping Voltammetry (DP-ASV) method is the most frequently used Carbon Electrodes.

1.7.2.3.2 Carbon Electrodes

Sb analysis using Hg electrodes has been used in industries since it is toxic to human beings and the environment despite the control measures being placed during the analysis (Toghill, 2011). Carbon electrodes that have been used in Sb determination include glassy carbon (GC), carbon paste electrodes (CPE), boron-doped diamond (BDD), and screen printed electrodes (SPE) (Niedzielski, 2003). Application of complexing or chelating agents such as triphenylmethane dyes (TPMD) or rhodamine C have been used to form ion-pair complexes with Sb, and in the case of TMPD, it can selectively react only to Sb(V) and not to Sb(III) based on their oxidation states.

1.7.2.3.3 Gold Electrodes

The use of gold micro-wire electrode is well suited for the speciation of antimonate and has the advantage of low cost, portability, and may detect weak complexes (Salaun et al. 2007). The technique may also be used to gain insights into the complexation patterns of inorganic and organic-bound arsenic and highlight the formation of weak, fast-dissociating species as well as inert, stable complexes. Voltammetry may complement chromatographic and hyphenated techniques. This study will give a better understanding of the biogeochemical cycle of arsenic in the environment, focusing on the speciation of arsenic in xylem sap to better understand the translocation of arsenic in plants (Hansen and Pergantis, 2008; Daus and Hansen, 2016).

1.8 References

Abedin, M. J., Feldmann, J. and Meharg, A. A. (2002) ‘Uptake kinetics of arsenic species in rice plants.’ *Plant Physiology*, 128(3) pp. 1120–1128.

Ainsworth, N., Cooke, J. A. and Johnson, M. S. (1990) ‘Distribution of antimony in contaminated grassland: 1- vegetation and soils.’ *Environmental Pollution*. Elsevier, 65(1) pp. 65–77.

Ainsworth, N., Cooke, J.A. and Johnson, M. S. (1990) ‘Distribution of antimony in contaminated grassland: 2— small mammals and invertebrates.’ *Environmental Pollution*. Elsevier, 65(1) pp. 79–87.

Alexou, M. and Peuke, A. D. (2013) *Plant Mineral Nutrients*. Maathuis, F. J. M. (ed.) *Plant Mineral Nutrients*. Totowa, NJ: Humana Press (Methods in Molecular Biology).

Ali, H., Khan, E. and Sajad, M. A. (2013) ‘Phytoremediation of heavy metals—Concepts and applications.’ *Chemosphere*, 91(7) pp. 869–881.

Althobiti, R. A., Sadiq, N. W. and Beauchemin, D. (2018) ‘Realistic risk assessment of arsenic in rice.’ *Food Chemistry*. Elsevier Ltd, 257, August, pp. 230–236.

Álvarez-Fernández, A., Díaz-Benito, P., Abadía, A., And, A.-F. L.-M. and Abadía, J. (2014) ‘Metal species involved in long distance metal transport in plants.’ *Frontiers in Plant Science*, 5(1) p. 105.

Amarasiriwardena, D. and Wu, F. (2011) ‘Antimony: Emerging toxic contaminant in the environment.’ *Microchemical Journal*. Elsevier B.V., 97(1) pp. 1–3.

Ammann, A. A. (2011) ‘Arsenic Speciation Analysis by Ion Chromatography - A Critical Review of Principles and Applications.’ *American Journal of Analytical Chemistry*, 2011(February) pp. 27–45.

Anawar, H. M., Freitas, M. C., Canha, N. and Regina, I. S. (2011) ‘Arsenic, antimony, and other trace element contamination in a mine tailings affected area and uptake by tolerant plant species.’ *Environmental Geochemistry and Health*, 33(4) pp. 353–362.

Aposhian, H. V. and Aposhian, M. M. (2006) ‘Arsenic Toxicology: Five Questions.’ *Chemical Research in Toxicology*, 19(1) pp. 1–15.

Arnold, L. L., Eldan, M., Nyska, A., van Gemert, M. and Cohen, S. M. (2006) ‘Dimethylarsinic acid: Results of chronic toxicity/oncogenicity studies in F344 rats and in B6C3F1 mice.’ *Toxicology*, 223(1–2) pp. 82–100.

Arunakumara, K. K. I. U., Walpola, B. C. and Yoon, M.-H. (2013) ‘Current status of heavy metal contamination in Asia’s rice lands.’ *Reviews in Environmental Science and*

Bio/Technology, 12(4) pp. 355–377.

Ashbrook, P. C. (2014) ‘Standard Operating Procedures.’ *Journal of Chemical Health and Safety*, 21(5) p. 29.

Ashley, P. M., Graham, B. P., Tighe, M. K. and Wolfenden, B. J. (2007) ‘Antimony and arsenic dispersion in the Macleay River catchment, New South Wales: a study of the environmental geochemical consequences.’ *Australian Journal of Earth Sciences*, 54(1) pp. 83–103.

ATSDR - Environmental Medicine & Environmental Health Education - CSEM (2013) ‘Arsenic Toxicity Case Study: What Are the Standards and Regulation for Arsenic Exposure?’ *Encyclopedia of Metalloproteins* pp. 143–143.

Awika, J. M. (2011) ‘Major cereal grains production and use around the world.’ *In ACS Symposium Series*, pp. 1–13.

Bach, C., Dauchy, X., Chagnon, M. C. and Etienne, S. (2012) ‘Chemical compounds and toxicological assessments of drinking water stored in polyethylene terephthalate (PET) bottles: A source of controversy reviewed.’ *Water Research*, 46(3) pp. 571–583.

Baker, A. J. M. (1981) ‘Accumulators and Excluders - Strategies in the Response of Plants to Heavy Metals.’ *Journal of Plant Nutrition*, 3(1–4) pp. 643–654.

Bakhtiari, A. R., Zakaria, M. P., Yaziz, M. I., Lajis, M. N. H. L. and Bi, X. (2014) ‘Environment Asia.’ *Environment Asia*, 7(1) pp. 104–111.

Basta, N. T. (2006) ‘Heavy Metal Contamination of Soil.’ *Soil Science Society of America Journal*, 70(5) p. 1819.

Bastías, J. M. and Beldarrain, T. (2016) ‘Arsenic translocation in rice cultivation and its implication for human health.’ *Chilean Journal of Agricultural Research*. Instituto de Investigaciones Agropecuarias, INIA, 76(1) pp. 114–122.

Bellido-Martín, A., Gómez-Ariza, J. L., Smichowsky, P. and Sánchez-Rodas, D. (2009) ‘Speciation of antimony in airborne particulate matter using ultrasound probe fast extraction and analysis by HPLC-HG-AFS.’ *Analytica Chimica Acta*, 649(2) pp. 191–195.

Benedict, S. R. (1908) *A Reagent For the Detection of Reducing Sugars*. *J. Biol. Chem*.

Bennett, J. O. and Sicher, R. C. (2011) ‘Protein and metabolite composition of xylem sap from field-grown soybeans (Glycine max)’ pp. 921–931.

Bhattacharya, P., Samal, a C., Majumdar, J. and Santra, S. C. (2009) ‘Transfer of Arsenic from Groundwater and Paddy Soil to Rice Plant (Oryza sativa L.): A Micro-Level Study in West Bengal , India.’ *World Journal of Agricultural Sciences*, 5(4) pp. 425–431.

Bi, Z. (2012) *Speciation analysis of trace metals in natural waters using vibrating electrodes*. *Environmental Sciences*. University of Liverpool.

Bielen, A., Remans, T., Vangronsveld, J. and Cuypers, A. (2013) 'The influence of metal stress on the availability and redox state of ascorbate, and possible interference with its cellular functions.' *International Journal of Molecular Sciences* pp. 6382–6413.

Biles, C. L. and Abeles, F. B. (1991) 'Xylem sap proteins.' *Plant Physiology*, 96(July 1991) pp. 597–601.

Billon, G. and Van Den Berg, C. M. G. (2004) 'Gold and silver micro-wire electrodes for trace analysis of metals.' *Electroanalysis*, 16(19) pp. 1583–1591.

Borovička, J., Řanda, Z. and Jelínek, E. (2006) 'Antimony content of macrofungi from clean and polluted areas.' *Chemosphere*, 64(11) pp. 1837–1844.

Bouman, B. A. . and Tuong, T. . (2001) 'Field water management to save water and increase its productivity in irrigated lowland rice.' *Agricultural Water Management*, 49(1) pp. 11–30.

Bowen, H. J. M. (Humphry J. M. (1979) *Environmental chemistry of the elements*. London, New York: Academic Press.

Brackin, R., Näsholm, T., Robinson, N., Guillou, S., Vinall, K., Buckley, S., Lakshmanan, P., Schmidt, S. and Inselsbacher, E. (2016) 'Microdialysis-a new technology for investigating soil nitrogen fluxes in the rhizosphere.' *In Proceedings of the International Nitrogen Initiative 2016 Conference*, pp. 4–8.

Brammer, H. and Ravenscroft, P. (2009) 'Arsenic in groundwater: A threat to sustainable agriculture in South and South-east Asia.' *Environment International*. Elsevier Ltd pp. 647–654.

Brihaye, C. and Duyckaerts, G. (1982) 'Determination of traces of metals by anodic stripping voltammetry at a rotating glassy carbon ring—disc electrode.' *Analytica Chimica Acta*, 143 pp. 111–120.

Broadley, M., Brown, P., Cakmak, I., Rengel, Z. and Zhao, F. (2011) 'Function of Nutrients: Micronutrients.' *In Marschner's Mineral Nutrition of Higher Plants: Third Edition*. Elsevier Inc., pp. 191–248.

Brochu, C., Wang, J., Roy, G., Messier, N., Wang, X.-Y., Saravia, N. G. and Ouellette, M. (2003) 'Antimony Uptake Systems in the Protozoan Parasite Leishmania and Accumulation Differences in Antimony-Resistant Parasites.' *Antimicrobial Agents and Chemotherapy*. American Society for Microbiology (ASM), 47(10) pp. 3073–3079.

Brown, S. D. and Kowalski, B. R. (1979) 'Pseudopolarographic Determination of Metal Complex Stability Constants in Dilute Solution by Rapid Scan Anodic Stripping

Voltammetry.' *Analytical Chemistry*, 51(13) pp. 2133–2139.

Buckley, S., Brackin, Richard, A. and Schmidt, S. (2016) 'Microdialysis-a sensitive method for estimating plant-available N released during litter decomposition.' *Proceedings of the International Nitrogen Initiative Conference 2016*, (December).

Buckley, S., Brackin, R., Jämtgård, S., Näsholm, T. and Schmidt, S. (2020) 'Microdialysis in soil environments: Current practice and future perspectives.' *Soil Biology and Biochemistry*, 143, April, p. 107743.

Buckley, S., Brackin, R., Näsholm, T., Schmidt, S. and Jämtgård, S. (2017) 'Improving in situ recovery of soil nitrogen using the microdialysis technique.' *Soil Biology and Biochemistry*, 114, November, pp. 93–103.

Buckley, S., Brackin, R. and Schmidt, S. (2015) *Microdialysis: an alternative approach to identifying plant-available nitrogen in soils*.

Burló, F., Guijarro, I., Carbonell-Barrachina, A. A., Valero, D. and Martínez-Sánchez, F. (1999) 'Arsenic Species: Effects on and Accumulation by Tomato Plants.' *Journal of Agricultural and Food Chemistry*, 47(3) pp. 1247–1253.

Cabalda, M. V, Banaag, M. A. and Garces, R. B. (2002) *Sustainable Development in The Philippine Minerals Industry: A Baseline Study*. M.V. Cabalda P.N.T. Tidalgo & R.B. Garces, M. A. B. (ed.) *Mining, Minerals and Sustainable Development Project (MMSD)*. England: International Institute for the Environment and Development (IIED).

Cai, Y., Su, J. and Ma, L. Q. (2004) 'Low molecular weight thiols in arsenic hyperaccumulator Pteris Vittata upon exposure to arsenic and other trace elements.' *Environmental Pollution*, 129(1) pp. 69–78.

Cal-Prieto, M. J., Carlosena, A., Andrade, J. M., Martínez, M. L., Muniategui, S., López-Mahía, P. and Prada, D. (2001) 'Antimony as a tracer of the anthropogenic influence on soils and estuarine sediments.' *Water, Air, and Soil Pollution*. Springer, 129(1–4) pp. 333–348.

Canadian Council of Ministers of the Environment (2007) *Canadian soil quality guidelines for the protection of environmental and human health*. Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment. Winnipeg. [Online] http://goo.gl/AePSg4.

Canepari, S., Marconi, E., Astolfi, M. L. and Perrino, C. (2010) 'Relevance of Sb(III), Sb(V), and Sb-containing nano-particles in urban atmospheric particulate matter.' *Analytical and Bioanalytical Chemistry*, 397(6) pp. 2533–2542.

Carey, A.-M., Lombi, E., Donner, E., de Jonge, M. D., Punshon, T., Jackson, B. P., Guerinot, M. Lou, Price, A. H. and Meharg, A. A. (2012) 'A review of recent developments in the speciation and location of arsenic and selenium in rice grain.' *Analytical and Bioanalytical*

Chemistry, 402(10) pp. 3275–3286.

Carneado, S., Hernández-Nataren, E., López-Sánchez, J. F. F. and Sahuquillo, A. (2015) ‘Migration of antimony from polyethylene terephthalate used in mineral water bottles.’ *Food Chemistry*. Elsevier Ltd, 166, January, pp. 544–550.

Carolyn, P., Aqilah, F. A. T., Payus, C., Farhana, A., Talip, A., Carolyn, P., Aqilah, F. A. T., Payus, C., Farhana, A. and Talip, A. (2014) ‘Assessment of heavy metals accumulation in paddy rice (Oryza sativa).’ *African Journal of Agricultural Research*. Academic Journals, 9(41) pp. 3082–3090.

Casiot, C., Ujevic, M., Munoz, M., Seidel, J. L. and Elbaz-Poulichet, F. (2007) ‘Antimony and arsenic mobility in a creek draining an antimony mine abandoned 85 years ago (upper Orb basin, France).’ *Applied Geochemistry*, 22(4) pp. 788–798.

Cavicchioli, A., La-Scalea, M. A., Gutz, G. R., Gutz, I. G. R. and Gutz, G. R. (2004) ‘Analysis and Speciation of Traces of Arsenic in Environmental , Food and Industrial Samples by Voltammetry : a Review.’ *Electroanalysis*, 16(9) pp. 697–711.

Chakraborti, D., Rahman, M. M., Das, B., Nayak, B., Pal, A., Sengupta, M. K., Hossain, M. A., Ahamed, S., Sahu, M., Saha, K. C., Mukherjee, S. C., Pati, S., Dutta, R. N. and Quamruzzaman, Q. (2013) ‘Groundwater arsenic contamination in Ganga–Meghna–Brahmaputra plain, its health effects and an approach for mitigation.’ *Environmental Earth Sciences*, 70(5) pp. 1993–2008.

Chang, C.-Y., Wang, C.-F., Mui, D. T. and Chiang, H.-L. (2009) ‘Application of methods (sequential extraction procedures and high-pressure digestion method) to fly ash particles to determine the element constituents: A case study for BCR 176.’ *Journal of Hazardous Materials*, 163(2–3) pp. 578–587.

Chapman, C. S. and Van Den Berg, C. M. G. G. (2007) ‘Anodic stripping voltammetry using a vibrating electrode.’ *Electroanalysis*, 19(13) pp. 1347–1355.

Chaurasia, C. S., Müller, M., Bashaw, E. D., Benfeldt, E., Bolinder, J., Bullock, R., Bungay, P. M., DeLange, E. C. M., Derendorf, H., Elmquist, W. F., Hammarlund-Udenaes, M., Joukhadar, C., Kellogg, D. L., Lunte, C. E., Nordstrom, C. H., Rollema, H., Sawchuk, R. J., Cheung, B. W. Y., Shah, V. P., Stahle, L., Ungerstedt, U., Welty, D. F. and Yeo, H. (2007) ‘AAPS-FDA workshop white paper: Microdialysis principles, application and regulatory perspectives.’ *In Pharmaceutical Research*, pp. 1014–1025.

Chen, Z. L., Farzana Akter, K., Rahman Mahmudur, M. and Naidu, R. (2006) ‘Speciation of arsenic by ion chromatography inductively coupled plasma mass spectrometry using ammonium eluents.’ *Journal of Separation Science*, 29(17) pp. 2671–2676.

Cheng, T. and Sun, H. (2014) ‘CHAPTER 25. Antimony and Bismuth.’ *In* Maret, W. and Wedd, A. (eds) *Binding, Transport and Storage of Metal Ions in Biological Cells*. London, UK: The Royal Society of Chemistry, pp. 768–799.

Chepkemoi, J. (2017) *What Is The Environmental Impact Of The Mining Industry?* First Break. [Online] worldatlas.com/articles/what-is-the-environmental-impact-of-the-mining-industry.html.

Cheraghi, M., Mosaed, H. P., Lorestani, B. and Yousefi, N. (2012) 'Heavy metal contamination in some rice samples.' *Electronic Journal of Environmental, Agricultural and Food Chemistry*, 11(5) pp. 424–432.

Choudhury, B. U., Malang, A., Webster, R., Mohapatra, K. P., Verma, B. C., Kumar, M., Das, A., Islam, M. and Hazarika, S. (2017) 'Acid drainage from coal mining: Effect on paddy soil and productivity of rice.' *Science of the Total Environment*. Elsevier B.V., 583(August 2018) pp. 344–351.

Ciminelli, V. S. T., Gasparon, M., Ng, J. C., Silva, G. C. and Caldeira, C. L. (2017) 'Dietary arsenic exposure in Brazil: The contribution of rice and beans.' *Chemosphere*. Elsevier Ltd, 168, February, pp. 996–1003.

Çirmi, D., Aydin, R. and Köleli, F. (2015) 'The electrochemical reduction of nitrate ion on polypyrrole coated copper electrode.' *Journal of Electroanalytical Chemistry*, 736 pp. 101–106.

Clark, R. B., Tiffin, L. O. and Brown, J. C. (1973) 'Organic Acids and Iron Translocation in Maize Genotypes.' *Plant Physiology*, 52(2) pp. 147–150.

Clarkson, D. T. (1996) 'Marschner H. 1995. Mineral nutrition of higher plants. second edition. 889pp. London: Academic Press.' *Annals of Botany*, 78(4) pp. 527–528.

Clemens, S. and Ma, J. F. (2016) 'Toxic Heavy Metal and Metalloid Accumulation in Crop Plants and Foods.' *Annual Review of Plant Biology*, 67(1) pp. 489–512.

Correia, M. M., Alves, S., Simões Gonçalves, M. D. L. and Nabais, C. (2006) 'Dynamic modelling of nickel complexation in xylem sap of Quercus ilex: A voltammetric study.' *Electroanalysis*, 18(8) pp. 814–822.

Cullen, W. R. and Reimer, K. J. (2016a) 'CHAPTER 2. Arsenic Is Everywhere.' *In Arsenic is Everywhere: Cause for Concern?*, pp. 8–48.

Cullen, W. R. and Reimer, K. J. (2016b) 'CHAPTER 8. Arsenic and the Evening Meal.' *In Arsenic is Everywhere: Cause for Concern?*, pp. 221–265.

Daniels, R., Rush, C. C. and Bauer, L. (1960) 'The Fehling and Benedict tests.' *Journal of Chemical Education*, 37(4) p. 205.

Daus, B. and Hansen, H. R. (2016) 'Analysis of antimony species – lessons learnt from more than two decades of environmental research.' *Environmental Chemistry*, 13(6) p. 913.

Dawe, B. D., Organisation, A. and Nations, U. (2015) ‘Rice in Asia: Paddy-whacked.’ *Economist (United Kingdom)*, 411(8960).

Dobermann, A., Dawe, D., Roetter, R. P. and Cassman, K. G. (2000) ‘Reversal of rice yield decline in a long-term continuous cropping experiment.’ *Agronomy Journal*, 92(4) pp. 633–643.

Domingo, L. E. and Kyuma, K. (1983) ‘Trace elements in tropical asian paddy soils: I. total trace element status.’ *Soil Science and Plant Nutrition*, 29(4) pp. 439–452.

Dortsiou, M. and Kyriacou, G. (2009) ‘Electrochemical reduction of nitrate on bismuth cathodes.’ *Journal of Electroanalytical Chemistry*, 630(1–2) pp. 69–74.

Duester, L., Diaz-Bone, R. A., Kösters, J. and Hirner, A. V. (2005) ‘Methylated arsenic, antimony and tin species in soils.’ *In Journal of Environmental Monitoring*, pp. 1186–1193.

Dushenkov, S. (2003) ‘Trends in phytoremediation of radionuclides.’ *In Plant and Soil*, pp. 167–175.

Elmquist, W. F. and Sawchuk, R. J. (1997) ‘Application of microdialysis in pharmacokinetic studies.’ *Pharmaceutical Research* pp. 267–288.

Emamverdian, A. and Ding, Y. (2017) ‘Effects of heavy metals’ toxicity on plants and enhancement of plant defense mechanisms of Si-mediation “ Review.”’ *International Journal of Environmental & Agriculture Research*, (4) pp. 41–51.

Emamverdian, A., Ding, Y., Mokhberdoran, F. and Xie, Y. (2015) ‘Heavy Metal Stress and Some Mechanisms of Plant Defense Response.’ *The Scientific World Journal*. Hindawi Publishing Corporation, 2015 pp. 1–18.

EPA (2004) ‘EPA Method 6020A: ICP-MS. Official Name: EPA Method 6020A, Inductively Coupled Plasma-Mass Spectrometry.’ *EPA methods*, 6.

Epstein, E. and and Bloom, A. J. (1972) *Mineral Nutrition of Plants: Principles and Perspectives*. 2nd ed., Sunderland, Massachusetts: Sinauer Associates, Inc.

Fan, Y., Zhu, T., Li, M., He, J., Huang, R. and and Ruixue Huang, T. Z. Y. F. M. L. J. H. (2017) ‘Heavy Metal Contamination in Soil and Brown Rice and Human Health Risk Assessment near Three Mining Areas in Central China.’ *Journal of Healthcare Engineering*. Hindawi, 2017 p. 9.

FAO (2016) *GIEWS - Crop Prospects and Food Situation, No.1,March 2016*.

FAO and WHO (2019) *Report of the 11th session of the codex committee on contaminnants in foods. A joint FAO/WHO food standards programme codex alimentarius commission 40th Session. Codex*. Geneva, Switzerland.

Farid, M., Shakoor, M., Ehsan, S., Ali, S., Zubair, M. and Hanif, M. (2013) ‘Morphological, physiological and biochemical responses of different plant species to Cd stress.’ *Int J Chem Biochem Sci*, 3(March) pp. 53–60.

Farnese, F. S., Oliveira, J. A., Farnese, M. S., Gusman, G. S., Silveira, N. M. and Siman, L. I. (2014) ‘Uptake arsenic by plants: Effects on mineral nutrition, growth and antioxidant capacity.’ *Idesia (Arica)*, 32(1) pp. 99–106.

Fashola, M., Ngole-Jeme, V. and Babalola, O. (2016) ‘Heavy Metal Pollution from Gold Mines: Environmental Effects and Bacterial Strategies for Resistance.’ *International Journal of Environmental Research and Public Health*. MDPI AG, 13(11) p. 1047.

Feldmann, J., Salaün, P. and Lombi, E. (2009) ‘Critical review perspective: elemental speciation analysis methods in environmental chemistry - moving towards methodological integration.’ *Environmental Chemistry*. CSIRO, 6(4) p. 275.

Feng, R., Wei, C., Tu, S., Ding, Y., Wang, R. and Guo, J. (2013) ‘The uptake and detoxification of antimony by plants: A review.’ *Environmental and Experimental Botany*. Elsevier B.V., 96, December, pp. 28–34.

Festin, E. S., Tigabu, M., Chileshe, M. N., Syampungani, S. and Odén, P. C. (2019) ‘Progresses in restoration of post-mining landscape in Africa.’ *Journal of Forestry Research*, 30(2) pp. 381–396.

Filella and May (2003) ‘Computer simulation of the low-molecular-weight inorganic species distribution of antimony (III) and antimony (V) in natural waters.’ *Geochimica et Cosmochimica Acta,* 67(21) pp. 4013–4031.

Filella, M. (2013) ‘Food for thought: A critical overview of current practical and conceptual challenges in trace element analysis in natural waters.’ *Water (Switzerland)*. MDPI AG pp. 1152–1171.

Filella, M., Belzile, N. and Chen, Y.-W. W. (2002) ‘Antimony in the environment: a review focused on natural waters.’ *Earth-Science Reviews*, 57(1–2) pp. 125–176.

Filella, M., Belzile, N. and Lett, M.-C. C. (2007) ‘Antimony in the environment: A review focused on natural waters. III. Microbiota relevant interactions.’ *Earth-Science Reviews*, 80(3–4) pp. 195–217.

Filella, M. and May, P. M. (2005a) ‘Critical appraisal of available thermodynamic data for the complexation of antimony(iii) and antimony(v) by low molecular mass organic ligands.’ *Journal of Environmental Monitoring*, 7(12) p. 1226.

Filella, M. and May, P. M. (2005b) ‘Reflections on the calculation and publication of potentiometrically- determined formation constants.’ *Talanta*, 65(5) pp. 1221–1225.

Filella, M. and Williams, P. A. (2012) ‘Antimony interactions with heterogeneous

complexants in waters, sediments and soils: A review of binding data for homologous compounds.' *Chemie der Erde*. Elsevier GmbH., 72(SUPPL.4) pp. 49–65.

Filella, M., Williams, P. A. and Belzile, N. (2009) 'Antimony in the environment: Knowns and unknowns.' *Environmental Chemistry*, 6(2) pp. 95–105.

Forsberg, G., O'Laughlin, J. W., Megargle, R. G. and Koirtyohann, S. R. (1975) 'Determination of Arsenic by Anodic Stripping Voltammetry and Differential Pulse Anodic Stripping Voltammetry.' *Analytical Chemistry*, 47(9) pp. 1586–1592.

Francesconi, K. A. and Kuehnelt, D. (2004) 'Determination of arsenic species: A critical review of methods and applications, 2000–2003.' *The Analyst*, 129(5) pp. 373–395.

Frantz, J. M. and Epstein, E. (2005) *Nutritional deficiencies: What they look like*. [Online] [Accessed on 16th December 2019] http://www.ces.ncsu.edu/depts/hort/floriculture/def/forfloriculturecropshttp://extension.agron.iastate.edu/soilfertility/nutrienttopics/deficiencies.htmlcornhttp://muextension.missouri.edu/explore/agguides/hort/index.htm.

FSA (2012) *Arsenic speciation in fruit and vegetables grown in the UK.* Aberdeen: University of Aberdeen.

Fu, Z., Wu, F., Mo, C., Deng, Q., Meng, W. and Giesy, J. P. (2016) 'Comparison of arsenic and antimony biogeochemical behavior in water, soil and tailings from Xikuangshan, China.' *Science of the Total Environment*, 539 pp. 97–104.

Garg, N. and Singla, P. (2011) 'Arsenic toxicity in crop plants: physiological effects and tolerance mechanisms.' *Environmental Chemistry Letters*. Springer, 9(3) pp. 303–321.

Garg, N., Singla, P. and Bhandari, P. (2015) 'Metal uptake, oxidative metabolism, and mycorrhization in pigeonpeaand pea under arsenic and cadmium stress.' *Turkish Journal of Agriculture and Forestry*, 39(2) pp. 234–250.

Gebel, T. (1997) 'Arsenic and antimony: comparative approach on mechanistic toxicology.' *Chemico-Biological Interactions*. Elsevier Ireland Ltd, 107(3) pp. 131–144.

Gebel, T. W. (2001) 'Unanswered Questions in Arsenic Toxicology.' *Journal of Environmental Pathology, Toxicology and Oncology*, 20(4) p. 11.

Gemici, Ü. and Tarcan, G. (2007) 'Assessment of the pollutants in farming soils and waters around untreated abandoned Türkönü mercury mine (Turkey).' *Bulletin of Environmental Contamination and Toxicology*, 79(1) pp. 20–24.

Geng, A., Wang, X., Wu, L., Wang, F., Chen, Y., Yang, H., Zhang, Z. and Zhao, X. (2017) 'Arsenic accumulation and speciation in rice grown in arsanilic acid-elevated paddy soil.' *Ecotoxicology and Environmental Safety*, 137 pp. 172–178.

Geng, C. N., Zhu, Y. G., Tong, Y. P., Smith, S. E. and Smith, F. A. (2006) ‘Arsenate (As) uptake by and distribution in two cultivars of winter wheat (Triticum aestivum L.).’ *Chemosphere*, 62(4) pp. 608–615.

Gerényi, A., Czech, V., Fodor, F., Vincze, L. and Szalóki, I. (2017) ‘In vivo XANES measuring technique for studying the arsenic uptake in cucumber plants.’ *X-Ray Spectrometry*, 46(3) pp. 143–150.

German Federal Soil Protection Act (1998) *Federal Law Gazette I p. 502*.

Ghori, N.-H., Ghori, T., Hayat, M. Q., Imadi, S. R., Gul, A., Altay, V. and Ozturk, M. (2019) ‘Heavy metal stress and responses in plants.’ *International Journal of Environmental Science and Technology*. Center for Environmental and Energy Research and Studies, 16(3) pp. 1807–1828.

Gibbon-Walsh, K., Salaün, P. and van den Berg, C. M. G. (2012a) ‘Determination of arsenate in natural pH seawater using a manganese-coated gold microwire electrode.’ *Analytica Chimica Acta*. Elsevier B.V., 710, January, pp. 50–57.

Gibbon-Walsh, K., Salaün, P. and van den Berg, C. M. G. (2012b) ‘Pseudopolarography of Copper Complexes in Seawater Using a Vibrating Gold Microwire Electrode.’ *The Journal of Physical Chemistry A*, 116(25) pp. 6609–6620.

Gibbon-Walsh, K., Salaün, P., Uroic, M. K., Feldmann, J., McArthur, J. M. and Van Den Berg, C. M. G. (2011) ‘Voltammetric determination of arsenic in high iron and manganese groundwaters.’ *Talanta*, 85(3) pp. 1404–1411.

Gidlow, D. A. (2004) ‘Lead toxicity.’ *Occupational Medicine*, 54(2) pp. 76–81.

Goldberg, S. (2011) ‘Chemical Equilibrium and Reaction Modeling of Arsenic and Selenium in Soils.’ *Dynamics and Bioavailability of Heavy Metals in the Rootzone* pp. 65–92.

Grob, M., Wilcke, W. and Mestrot, A. (2018) ‘Release and Biomethylation of Antimony in Shooting Range Soils upon Flooding.’ *Soil Systems*, 2(2) p. 34.

Guerriero, Gea, Deshmukh, R. and Durgesh K., T. (2020) *Metalloids in Plants Advances and Future Prospects*. Deshmukh, R., Tripathi, D. K., and Guerriero, Gia (eds) *Wiley*. John Wiley & Sons Ltd.

Gupta, D. K., Srivastava, S., Huang, H. G., Romero-Puertas, M. C. and Sandalio, L. M. (2011) ‘Arsenic Tolerance and Detoxification Mechanisms in Plants.’ *In*, pp. 169–179.

Ha, N. T. H., Ha, N. T., Nga, T. T. H., Minh, N. N., Anh, B. T. K., Hang, N. T. A., Duc, N. A., Nhuan, M. T. and Kim, K.-W. (2019) ‘Uptake of arsenic and heavy metals by native plants growing near Nui Phao multi-metal mine, northern Vietnam.’ *Applied Geochemistry*. Elsevier Ltd, 108, September, p. 104368.

Hakeem, K. R. (2015) 'Crop production and global environmental issues.' *Crop Production and Global Environmental Issues*, (December) pp. 1–598.

Hall, J. L. L. (2002) 'Cellular mechanisms for heavy metal detoxification and tolerance.' *Journal of experimental botany*, 53(366) pp. 1–11.

Hammel, W., Debus, R. and Steubing, L. (2000) 'Mobility of antimony in soil and its availability to plants.' *Chemosphere*, 41(11) pp. 1791–1798.

Hansen, C. (2011) *Antimony speciation analysis HPLC methods with ICP-MS and ES-MS detection for complex biological matrices*. University of Coppenhagen.

Hansen, H. R. and Pergantis, S. A. (2008) 'Analytical techniques and methods used for antimony speciation analysis in biological matrices.' *Journal of Analytical Atomic Spectrometry*, 23(10) p. 1328.

Hasanuzzaman, M., Nahar, K. and Fujita, M. (2018) *Mechanisms of Arsenic Toxicity and Tolerance in Plants*. Hasanuzzaman, M., Nahar, K., and Fujita, M. (eds) *Mechanisms of Arsenic Toxicity and Tolerance in Plants*. Singapore: Springer Singapore.

Hasanuzzaman, M., Nahar, K., Hakeem, K. R., Öztürk, M. and Fujita, M. (2015) 'Arsenic Toxicity in Plants and Possible Remediation.' *In Soil Remediation and Plants: Prospects and Challenges*. Elsevier Inc., pp. 433–501.

Hawkesford, M. J., Parmar, S. and Buchner, P. (2013) 'Mineral Composition Analysis: Measuring Anion Uptake and Anion Concentrations in Plant Tissues.' *In Plant Mineral Nutrients*. Totowa, NJ: Humana Press, pp. 109–119.

Hazama, K., Nagata, S., Fujimori, T., Yanagisawa, S. and Yoneyama, T. (2015) 'Concentrations of metals and potential metal-binding compounds and speciation of Cd, Zn and Cu in phloem and xylem saps from castor bean plants (Ricinus communis) treated with four levels of cadmium.' *Physiologia Plantarum*, 154(2) pp. 243–255.

He, M., Wang, N., Long, X., Zhang, C., Ma, C., Zhong, Q., Wang, A., Wang, Y., Pervaiz, A. and Shan, J. (2019) 'Antimony speciation in the environment: Recent advances in understanding the biogeochemical processes and ecological effects.' *Journal of Environmental Sciences*. Elsevier B.V., 75, January, pp. 14–39.

Hettick, B. E., Cañas-Carrell, J. E., French, A. D. and Klein, D. M. (2015) 'Arsenic: A Review of the Element's Toxicity, Plant Interactions, and Potential Methods of Remediation.' *Journal of Agricultural and Food Chemistry*, 63(32) pp. 7097–7107.

Hijaz, F. and Killiny, N. (2014) 'Collection and chemical composition of phloem sap from Citrus sinensis L. Osbeck (sweet orange).' *PLoS ONE*. Public Library of Science, 9(7).

Hirner, A. V., Grüter, U. M. and Kresimon, J. (2000) 'Metal(loid)organic compounds in contaminated soil.' *Fresenius' Journal of Analytical Chemistry*. Springer, 368(2–3) pp.

263–267.

Hoagland and Arnon, D., D. (1950) *The water-culture method of growing plants without soil.* Berkeley, Calif. : University of California, College of Agriculture, Agricultural Experiment Station.

Hossain, M. A., Piyatida, P., da Silva, J. A. T. and Fujita, M. (2012) ‘Molecular Mechanism of Heavy Metal Toxicity and Tolerance in Plants: Central Role of Glutathione in Detoxification of Reactive Oxygen Species and Methylglyoxal and in Heavy Metal Chelation.’ *Journal of Botany*. Hindawi Limited, 2012(Cd) pp. 1–37.

Hozhina, E. ., Khramov, A. ., Gerasimov, P. . and Kumarkov, A. . (2001) ‘Uptake of heavy metals, arsenic, and antimony by aquatic plants in the vicinity of ore mining and processing industries.’ *Journal of Geochemical Exploration*, 74(1–3) pp. 153–162.

Hrytsak, L. R., Herts, A. I., Nuzhyna, N. V., Cryk, M. M., Shevchenko, V. V. and Drobyk, N. M. (2018) ‘The influence of light regime on the growth data and pigment composition of the plant Gentiana lutea cultured in vitro.’ *Regulatory Mechanisms in Biosystems*, 9(2) pp. 258–266.

Hu, L., Zhang, B., Wu, D., Fan, H., Tu, J., Liu, W., Huang, R. and Huang, X. (2019) ‘Estimation of arsenic bioaccessibility in raw and cooked radish using simulated in vitro digestion.’ *Food & Function*. Royal Society of Chemistry, 10(3) pp. 1426–1432.

Hu, Y., Cheng, H. and Tao, S. (2016) ‘The Challenges and Solutions for Cadmium-contaminated Rice in China: A Critical Review.’ *Environment International*. Elsevier Ltd pp. 515–532.

Hua, C.-Y., Chen, J.-X., Cao, Y., Li, H.-B., Chen, Y. and Ma, L. Q. (2020) ‘Pteris vittata coupled with phosphate rock effectively reduced As and Cd uptake by water spinach from contaminated soil.’ *Chemosphere*. Elsevier Ltd, 247, May, p. 125916.

Huang, R.-Q., Gao, S.-F., Wang, W.-L., Staunton, S. and Wang, G. (2006) ‘Soil arsenic availability and the transfer of soil arsenic to crops in suburban areas in Fujian Province, southeast China.’ *Science of The Total Environment*, 368(2–3) pp. 531–541.

Huang, Y., Chen, Q., Deng, M., Japenga, J., Li, T., Yang, X. and He, Z. (2018) ‘Heavy metal pollution and health risk assessment of agricultural soils in a typical peri-urban area in southeast China.’ *Journal of Environmental Management*. Academic Press, 207, February, pp. 159–168.

Huang, Z., Pan, X.-D. D., Wu, P.-G. G., Han, J.-L. L. and Chen, Q. (2013) ‘Health Risk Assessment of Heavy Metals in Rice to the Population in Zhejiang, China.’ Scarfi, M. R. (ed.) *PLoS ONE*, 8(9) pp. 1–6.

Huiliang, H., Jagner, D. and Renman, L. (1988) ‘Flow potentiometric and constant-current stripping analysis for arsenic(V) without prior chemical reduction to arsenic(III).’

Analytica Chimica Acta, 207 pp. 37–46.

Humphrey, O. S., Young, S. D., Bailey, E. H., Crout, N. M. J., Ander, E. L., Hamilton, E. M. and Watts, M. J. (2019) 'Investigating the use of microdialysis and SEC-UV-ICP-MS to assess iodine interactions in soil solution.' *Chemosphere*. Elsevier Ltd, 229, August, pp. 41–50.

Hunt, R., Causton, D. R., Shipley, B. and Askew, A. P. (2002) 'A modern tool for classical plant growth analysis.' *Annals of Botany*, 90(4) pp. 485–488.

Inselsbacher, E. (2014) 'Recovery of individual soil nitrogen forms after sieving and extraction.' *Soil Biology and Biochemistry*, 71, April, pp. 76–86.

Inselsbacher, E., Öhlund, J., Jämtgård, S., Huss-Danell, Kerstin, A. and Näsholm, T. (2011) 'The potential of microdialysis to monitor organic and inorganic nitrogen compounds in soil.' *Soil Biology and Biochemistry*, 43(6) pp. 1321–1332.

International Programme on Chemical Safety (2004) 'International programme on chemical safety (IPCS),' (June) pp. 1–34.

IPNI (2002) 'Nutrient Deficiency Symptoms in Rice.' *Better Crops International*, 16(May) pp. 23–25.

IRRI and DFID (2009) 'Scuba rice : breeding flood-tolerance into Asia ' s local mega rice varieties.' *South Asia* pp. 1–6.

Ismail, B., Yap, D., Adezrian, J., Khairiah, J. and Ahmad-Mahir, R. (2009) 'The Uptake of Heavy Metals by Paddy Plants (Oryza sativa) in Kota Marudu, Sabah, Malaysia.' *& Environ. Sci*, 6(1) pp. 16–19.

Jamila Alfaraas, A. M., Khairiah, J., Ismail, B. S. and Noraini, T. (2016) 'Effects of heavy metal exposure on the morphological and microscopical characteristics of the paddy plant.' *Journal of Environmental Biology*, 37(5) pp. 955–963.

Järup, L. (2003) 'Hazards of heavy metal contamination.' *British Medical Bulletin*, 68 pp. 167–182.

JECFA (2016) 'Joint FAO / WHO Expert Committee on Food Additives (JECFA) Call for Experts on Food Additives , Contaminants and toxins ; and Residues of Veterinary Drugs,' (October).

Jentschke, G. and Godbold, D. L. (2000) 'Metal toxicity and ectomycorrhizas.' *Physiologia Plantarum*, 109(2) pp. 107–116.

Ji, Y., Sarret, G., Schulin, R. and Tandy, S. (2017) 'Fate and chemical speciation of antimony (Sb) during uptake, translocation and storage by rye grass using XANES spectroscopy.' *Environmental Pollution*. Elsevier Ltd, 231, December, pp. 1322–1329.

Johnson, C. A., Moench, H., Wersin, P., Kugler, P. and Wenger, C. (2005) ‘Solubility of Antimony and Other Elements in Samples Taken from Shooting Ranges.’ *Journal of Environmental Quality*. Wiley, 34(1) pp. 248–254.

Johnson, C. D. (2014) ‘Phytoremediation of Arsenic Contamination on Vashon-Maury Island METHODS Salix Screening for Arsenic Tolerance.’

Johnston, A. E. and Poulton, P. R. (2018) ‘The importance of long-term experiments in agriculture: their management to ensure continued crop production and soil fertility; the Rothamsted experience.’ *European Journal of Soil Science*, 69(1) pp. 113–125.

Kabata-Pendias, A. (2010) *Trace Elements in Soils and Plants*. 4th ed., CRC Press.

Kalaji, H. M., Jajoo, A., Oukarroum, A., Brestic, M., Zivcak, M., Samborska, I. A., Cetner, M. D., Łukasik, I., Goltsev, V. and Ladle, R. J. (2016) ‘Chlorophyll a fluorescence as a tool to monitor physiological status of plants under abiotic stress conditions.’ *Acta Physiologiae Plantarum*. Polish Academy of Sciences.

Kapaj, S., Peterson, H., Liber, K. and Bhattacharya, P. (2006) ‘Human Health Effects From Chronic Arsenic Poisoning–A Review.’ *Journal of Environmental Science and Health, Part A*. The Safe Drinking Water Foundation, Saskatoon, Saskatchewan, Canada., 41(10) pp. 2399–2428.

Katsounaros, I. and Kyriacou, G. (2007) ‘Influence of the concentration and the nature of the supporting electrolyte on the electrochemical reduction of nitrate on tin cathode.’ *Electrochimica Acta*, 52(23) pp. 6412–6420.

Kehr, J. and Rep, M. (2007) ‘Protein extraction from xylem and phloem sap.’ *Methods in molecular biology (Clifton, N.J.)*, 355 pp. 27–35.

Killiny, N. and Hijaz, F. (1998) ‘Chemical composition of xylem sap of Citrus sinensis L. Osbeck (sweet orange).’ *Trends in Plant Science*, 3(5) pp. 188–195.

Kisan, M., Sangathan, S., Nehru, J. and Pitroda, S. G. (2012) ‘Laboratory Glassware-Volumetric Instruments-Methods for Testing of Capacity and for Use.’ ISO (ed.) *4787*. Geneva: IS pp. 1–29.

Kitagishi, K. (1981) ‘Heavy Metal Pollution in Soils of Japan.’ *Japan Scientific Societies Press, Tokyo, Japan*, 52(4) p. 302.

Koester, R. P., Skoneczka, J. A., Cary, T. R., Diers, B. W. and Ainsworth, E. A. (2014) ‘Historical gains in soybean (Glycine max Merr.) seed yield are driven by linear increases in light interception, energy conversion, and partitioning efficiencies.’ *Journal of Experimental Botany*, 65(12) pp. 3311–3321.

Kolbe, F., Mattusch, J., Wennrich, R., Weiss, H., Sorkau, E., Lorenz, W. and Daus, B. (2012) ‘Analytical investigations of antimony-edta complexes and their use in speciation

analysis.' *Fresenius Environmental Bulletin*, 21(11 C) pp. 3453–3456.

Kowalska, J., Stryjewska, E., Szymański, P. and Golimowski, J. (1999) 'Voltammetric determination of arsenic in plant material.' *Electroanalysis*, 11(17) pp. 1301–1304.

Krachler, M. and Emons, H. (2001) 'Speciation analysis of antimony by high-performance liquid chromatography inductively coupled plasma mass spectrometry using ultrasonic nebulization.' *Analytica Chimica Acta*, 429(1) pp. 125–133.

Kroukamp, E. M., Wondimu, T. and Forbes, P. B. C. (2016) 'Metal and metalloid speciation in plants: Overview, instrumentation, approaches and commonly assessed elements.' *TrAC - Trends in Analytical Chemistry*. Elsevier B.V., 77 pp. 87–99.

Krupka, K. M. and Serne, R. J. (2002) *Geochemical Factors Affecting the Behavior of Antimony, Cobalt, Europium, Technetium, and Uranium in Vadose Zone Sediments*. *Pnnl-14126*. Richland, WA (United States).

Kumar, R., Mishra, R. K., Mishra, V., Qidwai, A., Pandey, A., Shukla, S. K., Pandey, M., Pathak, A. and Dikshit, A. (2015) 'Detoxification and Tolerance of Heavy Metals in Plants.' *In Plant Metal Interaction: Emerging Remediation Techniques*. Elsevier Inc., pp. 335–359.

Kumarathilaka, P., Seneweera, S., Meharg, A. and Bundschuh, J. (2018) 'Arsenic speciation dynamics in paddy rice soil-water environment: sources, physico-chemical, and biological factors - A review.' *Water Research*. Elsevier Ltd pp. 403–414.

Küpper, H. and Andresen, E. (2016) 'Mechanisms of metal toxicity in plants.' *Metallomics*, 8(3) pp. 269–285.

Lansdown, A. B. G. (2013) 'CHAPTER 1. Introduction.' *In The Carcinogenicity of Metals: Human Risk Through Occupational and Environmental Exposure*, pp. 1–18.

Larsen, E. H. and Stürup, S. (1994) 'Carbon-enhanced inductively coupled plasma mass spectrometric detection of arsenic and selenium and its application to arsenic speciation.' *Journal of Analytical Atomic Spectrometry*, 9(10) pp. 1099–1105.

van Leeuwen, H. P., Town, R. M., Buffle, J., Cleven, R. F. M. J., Davison, W., Puy, J., van Riemsdijk, W. H. and Sigg, L. (2005) 'Dynamic Speciation Analysis and Bioavailability of Metals in Aquatic Systems.' *Environmental Science & Technology*, 39(22) pp. 8545–8556.

van Leeuwen, L. C. and Aldenberg, T. (2012) *RIVM Letter Report 601357001/2012: Environmental risk limits for antimony*.

Li, Z. and Cui, Z. (2008) 'Application of microdialysis in tissue engineering monitoring.' *Progress in Natural Science*. Science Press, 18(5) pp. 503–511.

Liang, G., Gong, W., Li, B., Zuo, J., Pan, L. and Liu, X. (2019) 'Analysis of Heavy Metals in Foodstuffs and an Assessment of the Health Risks to the General Public via Consumption

in Beijing, China.' *International Journal of Environmental Research and Public Health*. MDPI AG, 16(6) p. 909.

Lichtfouse, E., Schwarzbauer, J. and Robert, D. (2012) *Environmental chemistry for a sustainable world*. *Environmental Chemistry for a Sustainable World*. Springer Netherlands.

Lintschinger, J., Koch, I., Serves, S., Feldmann, J. and Cullen, W. R. (1997) 'Determination of antimony species with High-Performance Liquid Chromatography using element specific detection.' *Fresenius' Journal of Analytical Chemistry*, 359(6) pp. 484–491.

Liu, Z. G. and Huang, X. J. (2014) 'Voltammetric determination of inorganic arsenic.' *TrAC - Trends in Analytical Chemistry*, 60 pp. 25–35.

Lombi, E. and Holm, P. E. (2010) 'Metalloids, soil chemistry and the environment.' *In Advances in Experimental Medicine and Biology*. Australia: Landes Bioscience and Springer Science+Business Media., pp. 33–44.

Louis, Y., Cmuk, P., Nicolau, R., Omanovi, D., Lenoble, V., Pižeta, I., Mounier, S., and Garde, L. and Garde, L. (2007) 'Pseudopolarography As a Tool for Complexation Studies of Trace Metals With Dissolved Natural Organic Matter,' (January) p. 2007.

Louis, Y., Cmuk, P., Omanović, D., Garnier, C., Lenoble, V., Mounier, S. and Pižeta, I. (2008) 'Speciation of trace metals in natural waters: The influence of an adsorbed layer of natural organic matter (NOM) on voltammetric behaviour of copper.' *Analytica Chimica Acta*. Elsevier Masson, 606(1) pp. 37–44.

Louis, Y., Garnier, C., Lenoble, V., Omanovi, D., Mounier, S., Pižeta, I., Protee, L., Toulon, S., Bp, V., Garde, L., Physico, G. De, Chimie, T., Moléculaires, S. and I, U. B. (2008) 'Electrochemical Study of Major and Trace Metal Interactions With Concentrated Marine Dissolved Organic Matter,' (098) p. 1214910.

Lu, M. and Compton, R. G. (2013) 'Voltammetric Determination of Iron(III) in Water.' *Electroanalysis*, 25(5) pp. 1123–1129.

Lubin, J. H., Moore, L. E., Fraumeni, J. F. and Cantor, K. P. (2008) 'Respiratory Cancer and Inhaled Inorganic Arsenic in Copper Smelters Workers: A Linear Relationship with Cumulative Exposure that Increases with Concentration.' *Environmental Health Perspectives*, 116(12) pp. 1661–1665.

Luo, J. and Shu, W. (2015) 'Arsenic-Induced Developmental Neurotoxicity.' *In* Flora, S. J. S. B. T.-H. of A. T. (ed.) *Handbook of Arsenic Toxicology*. Oxford: Elsevier, pp. 363–386.

Lydic, R., Baghdoyan, H. A. and May, A. L. (2018) 'Chapter Fourteen - Neurochemistry of Anesthetic States.' *In* Eckenhoff, R. G. and Dmochowski, I. J. B. T.-M. in E. (eds) *Chemical and Biochemical Approaches for the Study of Anesthetic Function Part B*. 1st ed., Academic Press, pp. 237–255.

Madejón, P., Marañón, T. and Murillo, J. M. (2006) ‘Biomonitoring of trace elements in the leaves and fruits of wild olive and holm oak trees.’ *Science of the Total Environment*, 355(1–3) pp. 187–203.

Magahud, J. C., Badayos, R. B., Sanchez, P. B. and Sta. Cruz, P. C. (2015) *Levels and Potential Sources of Heavy Metals in Major Irrigated Rice Areas of the Philippines*. *IAMURE International Journal of Ecology and Conservation*.

Mandal, B. K. and Suzuki, K. T. (2002) ‘Arsenic round the world: A review.’ *Talanta*. Elsevier, 58(1) pp. 201–235.

Mareček, V., Jänchenová, H., Samec, Z. and Březina, M. (1986) ‘Voltammetric determination of nitrate, perchlorate and iodide at a hanging electrolyte drop electrode.’ *Analytica Chimica Acta*, 185(C) pp. 359–362.

Marschner, H. (1995) *Mineral Nutrition of High Plants*. Academic Press.

Martin, M., Ferdousi, R., Hossain, K. M. J. and Barberis, E. (2010) ‘Arsenic from groundwater to paddy fields in Bangladesh: Solid-liquid partition, sorption and mobility.’ *Water, Air, and Soil Pollution*, 212(1–4) pp. 27–36.

Martinez, R. E., Marquez, J. E., Hòa, H. T. B. and Gieré, R. (2013) ‘Open-pit coal-mining effects on rice paddy soil composition and metal bioavailability to Oryza sativa L. plants in Cam Pha, northeastern Vietnam.’ *Environmental Science and Pollution Research*, 20(11) pp. 7686–7698.

Massoura, S. T., Echevarria, G., Leclerc-Cessac, E. and Morel, J. L. (2004) ‘Response of excluder, indicator, and hyperaccumulator plants to nickel availability in soils.’ *Australian Journal of Soil Research*, 42(8) pp. 933–938.

Materials, B. (1989) *Analytical Methods*. *WHO*.

Matschullat, J. J. (2000) ‘Arsenic in the geosphere - A review.’ *The Science of the Total Environment*, 249(1–3) pp. 297–312.

Mawia, A. M., Hui, S., Zhou, L., Li, H., Tabassum, J., Lai, C., Wang, J., Shao, G., Wei, X., Tang, S., Luo, J., Hu, S. and Hu, P. (2021) ‘Inorganic arsenic toxicity and alleviation strategies in rice.’ *Journal of Hazardous Materials*. Elsevier B.V. p. 124751.

Mayet, N., Servat, K., Kokoh, K. B. and Napporn, T. W. (2019) ‘Probing the Surface of Noble Metals Electrochemically by Underpotential Deposition of Transition Metals.’ *Surfaces*, 2(2) pp. 257–276.

McLaughlin, M. ., Parker, D. . and Clarke, J. . (1999) ‘Metals and micronutrients – food safety issues.’ *Field Crops Research*, 60(1–2) pp. 143–163.

Mead, M. N. (2005) ‘Arsenic: In search of an antidote to a global poison.’ *Environmental*

Health Perspectives. Public Health Services, US Dept of Health and Human Services, 113(6).

Meadows, R. (2014) ‘How Plants Control Arsenic Accumulation.’ *PLoS Biology*, 12(12) pp. 1002008–1002009.

Meharg, A. A. (2004) ‘Arsenic in rice - Understanding a new disaster for South-East Asia.’ *Trends in Plant Science* pp. 415–417.

Meharg, A. A. and Zhao, F.-J. (2012) *Arsenic & Rice*. *Springer*. Dordrecht: Springer Netherlands.

Mendoza, T. (2012) ‘Estimates of Rice Per Capita Consumption: Its Implications to the Rice Self-Sufficiency Program of the Philippines*.’ *Policy Options*, 4, January.

Mestrot, A., Ji, Y., Tandy, S. and Wilcke, W. (2016) ‘A novel method to determine trimethylantimony concentrations in plant tissue.’ *Environmental Chemistry*, 13(6) pp. 919–926.

Michalski, R., Szopa, S., Jabłońska, M. and Łyko, A. (2012) ‘Application of hyphenated techniques in speciation analysis of arsenic, antimony, and thallium.’ *The Scientific World Journal*. Institute of Environmental Engineering, the Polish Academy of Sciences, 34 Sklodowskiej-Curie Street, 41 819 Zabrze, Poland. michalski@ipis.zabrze.pl, 2012(January 2017) p. 902464.

Miekeley, N., Mortari, S. R. and Schubach, A. O. (2002) ‘Monitoring of total antimony and its species by ICP-MS and on-line ion chromatography in biological samples from patients treated for leishmaniasis.’ *Fresenius’ Journal of Analytical Chemistry*, 372(3) pp. 495–502.

Mihucz, V. G., Tatár, E. E. E., Virág, I., Cseh, E., Fodor, F., Záray, G., Tat??r, E., Vir??g, I., Cseh, E., Fodor, F. and Gyula, Z. (2005) ‘Arsenic speciation in xylem sap of cucumber (Cucumis sativus L.).’ *Analytical and Bioanalytical Chemistry*. Joint Research Group of Environmental Chemistry of the Hungarian Academy of Sciences and L. Eotvos University, PO Box 32, 1518 Budapest, Hungary., 383(3) pp. 461–466.

Mihucz, V. G., Varga, A. and Za, G. (1998) ‘Determination of Organic Acids in Xylem Sap of Cucumber : Effect of Lead Contamination,’ 314(58) pp. 306–314.

Ministerie Van Volkshuisvesting; Ruimtelijke Ordening En Milieu (2000) ‘Dutch Target and Intervention Values; 2000 (the New Dutch List).’ *Netherlands Government Gazette*, 2000 pp. 1–12.

Miró, M., Fitz, W. J., Swoboda, S. and Wenzel, W. W. (2010) ‘In-situ sampling of soil pore water: Evaluation of linear-type microdialysis probes and suction cups at varied moisture contents.’ *Environmental Chemistry*, 7(1) pp. 123–131.

Mishra, S., Srivastava, S., Dwivedi, S. and Tripathi, R. D. (2013) ‘Investigation of

biochemical responses of Bacopa monnieri L. upon exposure to arsenate.' *Environmental Toxicology*, 28(8) pp. 419–430.

Mohan, D. and Pittman, C. U. (2007) 'Arsenic removal from water/wastewater using adsorbents-A critical review.' *Journal of Hazardous Materials* pp. 1–53.

Moles, A. T., Warton, D. I., Warman, L., Swenson, N. G., Laffan, S. W., Zanne, A. E., Pitman, A., Hemmings, F. A. and Leishman, M. R. (2009) 'Global patterns in plant height.' *Journal of Ecology*, 97(5) pp. 923–932.

Moreno-Jiménez, E., Esteban, E. and Peñalosa, J. M. (2012) 'The fate of arsenic in soil-plant systems.' *Reviews of Environmental Contamination and Toxicology*, 215 pp. 1–37.

Morua, M. (2015) 'Investigating various xylem sap extraction techniques from drought-stressed Geijera parviflora trees' pp. 1–26.

Mosetlha, K., Torto, N. and Wibetoe, G. (2007) 'Determination of Cu and Ni in plants by microdialysis sampling: Comparison of dialyzable metal fractions with total metal content.' *Talanta*. Elsevier, 71(2) pp. 766–770.

Nagajyoti, P. C., Lee, K. D. and Sreekanth, T. V. M. (2010) 'Heavy metals, occurrence and toxicity for plants: A review.' *Environmental Chemistry Letters* pp. 199–216.

Nash, M. J., Maskall, J. E. and Hill, S. J. (2000) 'Methodologies for determination of antimony in terrestrial environmental samples.' *Journal of Environmental Monitoring*, 2(2) pp. 97–109.

Natasha, Shahid, M., Khalid, S., Dumat, C., Pierart, A. and Niazi, N. K. (2019) 'Biogeochemistry of antimony in soil-plant system: Ecotoxicology and human health.' *Applied Geochemistry*. Elsevier, 106(April) pp. 45–59.

Netting, A. G., Theobald, J. C. and Dodd, I. C. (2012) 'Xylem sap collection and extraction methodologies to determine in vivo concentrations of ABA and its bound forms by gas chromatography-mass spectrometry (GC-MS).' *Plant Methods*, 8(1) pp. 1–14.

Nicolau, R., Louis, Y., Omanović, D., Garnier, C., Mounier, S. and and, Pižeta, I. (2008) 'Study of interactions of concentrated marine dissolved organic matter with copper and zinc by pseudopolarography.' *Analytica Chimica Acta*, 618(1) pp. 35–42.

Niedzielski, P. and Siepak, M. (2003) 'Analytical methods for determining arsenic, antimony and selenium in environmental samples.' *Polish Journal of Environmental Studies*, 12(6) pp. 653–667.

Niedzielski, P., Siepak, M., Siepak, J. and Przybyłek, J. (2002) 'Determination of Different Forms of Arsenic, Antimony and Selenium in Water Samples Using Hydride Generation.' *Polish Journal of Environmental Studies*, 11(3) pp. 219–224.

Nimick, D. A. (1998) ‘Arsenic hydrogeochemistry in an irrigated river valley-A reevaluation.’ *Journal of groundwater*. Ground Water Publ Co, 36(5) pp. 743–753.

O’Day, P. A. (2006) ‘Chemistry and mineralogy of arsenic.’ *Elements*, 2(2) pp. 77–83.

Obiora, S. C., Chukwu, A. and Davies, T. C. (2016) ‘Heavy metals and health risk assessment of arable soils and food crops around Pb-Zn mining localities in Enyigba, southeastern Nigeria.’ *Journal of African Earth Sciences*. Elsevier Ltd, 116, April, pp. 182–189.

Oda, A., Shimizu, M., Kuroha, T. and Satoh, S. (2005) ‘Induction of xylem sap methylglycine by a drought and rewatering treatment and its inhibitory effects on the growth and development of plant organs.’ *Physiologia Plantarum*, 124(4) pp. 515–523.

Ogawa, K. and Iwabuchi, M. (2001) ‘A mechanism for promoting the germination of Zinnia elegans seeds by hydrogen peroxide.’ *Plant and Cell Physiology*, 42(3) pp. 286–291.

Ohmori, T., El-Deab, M. S. and Osawa, M. (1999) ‘Electroreduction of nitrate ion to nitrite and ammonia on a gold electrode in acidic and basic sodium and cesium nitrate solutions.’ *Journal of Electroanalytical Chemistry*, 470(1) pp. 46–52.

Olsen, S.R., C.V. Cole, F.S. Watanabe, and L. A. D. (1954) *Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circ.No. 939.* U.S. Gov. Print. Office, Washington DC.

Omanović, D. (2006) ‘Pseudopolarography of trace metals. Part III. Determination of stability constants of labile metal complexes.’ *Croatica Chemica Acta*, 79(1) p. 67.

Omanović, D. and Branica, M. (2003) ‘Pseudopolarography of trace metals: Part I. The automatic ASV measurements of reversible electrode reactions.’ *Journal of Electroanalytical Chemistry*, 543(1) pp. 83–92.

Omanović, D. and Branica, M. (2004) ‘Pseudopolarography of trace metals. Part II. The comparison of the reversible, quasireversible and irreversible electrode reactions.’ *Journal of Electroanalytical Chemistry*, 565(1) pp. 37–48.

Onofri, A., Seddaiu, G. and Piepho, H. P. (2016) ‘Long-Term Experiments with cropping systems: Case studies on data analysis.’ *European Journal of Agronomy*, 77, July, pp. 223–235.

Organization, world health (1996) ‘guidelines for drinking water quality - second edition.’ *international programme on chemical safety*.

Özer, U. Y. and Bogucki, R. F. (1971) ‘Equilibrium studies of antimony(III) chelates in aqueous solution.’ *Journal of Inorganic and Nuclear Chemistry*, 33(12) pp. 4143–4153.

Palma-Lara, I., Martínez-Castillo, M., Quintana-Pérez, J. C., Arellano-Mendoza, M. G., Tamay-Cach, F., Valenzuela-Limón, O. L., García-Montalvo, E. A. and Hernández-Zavala, A. (2019) 'Arsenic exposure: A public health problem leading to several cancers.' *Regulatory toxicology and pharmacology : RTP* p. 104539.

Pampolino, M. F., Laureles, E. V., Gines, H. C. and Buresh, R. J. (2008) 'Soil carbon and nitrogen changes in long-term continuous lowland rice cropping.' *Soil Science Society of America Journal*, 72(3) pp. 798–807.

Panda, S. K., Upadhyay, R. K. and Nath, S. (2010) 'Arsenic Stress in Plants.' *Journal of Agronomy and Crop Science*, 196(3) pp. 161–174.

Pandey, P. and Tripathi, A. K. (2014) 'Impact Of Heavy Metals On Morphological And Biochemical Parameters Of Shorea Robusta Plant.' *Ekologia*, 33(2) pp. 116–126.

Passioura, J. B. (1980) 'The transport of water from soil to shoot in wheat seedlings.' *Journal of Experimental Botany*, 31(1) pp. 333–345.

Pedron, T., Segura, F. R., Paniz, F. P., de Moura Souza, F., dos Santos, M. C., de Magalhães Júnior, A. M. and Batista, B. L. (2019) 'Mitigation of arsenic in rice grains by polishing and washing: Evidencing the benefit and the cost.' *Journal of Cereal Science*. Academic Press, 87, May, pp. 52–58.

Penezić, A., Tercier-Waeber, M. Lou, Abdou, M., Bossy, C., Dutruch, L., Bakker, E. and Schäfer, J. (2020) 'Spatial variability of arsenic speciation in the Gironde Estuary: Emphasis on dynamic (potentially bioavailable) inorganic arsenite and arsenate fractions.' *Marine Chemistry*. Elsevier, 223(December 2019) p. 103804.

Pepponi, G., Meirer, F., Streli, C., Wobrauschek, P., Mihucz, V. G., G. Zaray, V. C., Broekaert, J., Fittschen, U. and Falkenberg, G. (2005) 'Arsenic speciation in Cucumber Cucumis Sativus L.) xylem sap by K-edge TXRF-XANES.' *Anal. Bioanal. Chem.*, 383 pp. 461–466.

Peralta-Videa, J. R., Lopez, M. L., Narayan, M., Saupe, G. and Gardea-Torresdey, J. (2009) 'The biochemistry of environmental heavy metal uptake by plants: Implications for the food chain.' *International Journal of Biochemistry and Cell Biology*, 41(8–9) pp. 1665–1677.

Perrino, C., Marconi, E., Canepari, S., Luisa Astolfi, M. and Perrino, C. (2011) 'Determination of Sb(III), Sb(V) and identification of Sb-containing nanoparticles in airborne particulate matter.' *Procedia Environmental Sciences*, 4 pp. 209–217.

Pettine, M., Casentini, B., Mastroianni, D. and Capri, S. (2007) 'Dissolved inorganic carbon effect in the determination of arsenic and chromium in mineral waters by inductively coupled plasma-mass spectrometry.' *Analytica Chimica Acta*. Elsevier, 599(2) pp. 191–198.

Pickering, I. J., Prince, R. C., George, M. J., Smith, R. D., George, G. N. and Salt, D. E. (2000) ‘Reduction and coordination of arsenic in Indian mustard.’ *Plant Physiology*, 122(4) pp. 1171–1177.

Pierart, A., Shahid, M., Séjalon-Delmas, N. and Dumat, C. (2015) ‘Antimony bioavailability: Knowledge and research perspectives for sustainable agricultures.’ *Journal of Hazardous Materials*. Elsevier, 289(February) pp. 219–234.

Pla-Vilanova, P., Galceran, J., Puy, J., Companys, E. and Filella, M. (2019) ‘Antimony speciation in aqueous solution followed with AGNES.’ *Journal of Electroanalytical Chemistry*. Elsevier B.V., 849 p. 113334.

Pohl, P., Lesniewicz, A. and Zyrnicki, W. (2003) ‘Determination of As, Bi, Sb and Sn in conifer needles from various locations in Poland and Norway by hydride generation inductively coupled plasma atomic emission spectrometry.’ *International Journal of Environmental Analytical Chemistry*. Taylor & Francis Group, 83(11) pp. 963–970.

Polunina, O. V., Maiboroda, V. P. and Seleznov, A. Y. (2018) ‘Evaluation methods of estimation of young apple trees leaf area.’ *Bulletin of Uman National University of Horticulture*, (2) pp. 80–82.

Pommerrenig, B., Diehn, T. A. and Bienert, G. P. (2015) ‘Metalloido-porins: Essentiality of Nodulin 26-like intrinsic proteins in metalloid transport.’ *Plant Science*. Elsevier Ireland Ltd, 238 pp. 212–227.

Porra, R. J. (2005) ‘Clorofila Porras 2005’ pp. 633–640.

Postupolski, A. and Golimowski, J. (1991) ‘Trace determination of antimony and bismuth in snow and water samples by stripping voltammetry.’ *Electroanalysis*. Warsaw, Poland, 3(8) pp. 793–797.

Pretti, L., Bazzu, G., Serra, P. A. and Nieddu, G. (2014) ‘A novel method for the determination of ascorbic acid and antioxidant capacity in Opuntia ficus indica using in vivo microdialysis.’ *Food Chemistry*, 147 pp. 131–137.

Punrat, E., Chuanuwatanakul, S., Kaneta, T., Motomizu, S., Chailapakul, O., Zaib, M., Makshoof, M., Saeed, A., Farooq, U., Nearing, M. M., Koch, I., Reimer, K. J., Niedzielski, P., Siepak, M., Day, P. A. O., Mays, D. E., Hussam, A., Welna, M., Szymczycha-Madeja, A., Pohl, P., Ma, J., Sengupta, M. K., Yuan, D., Dasgupta, P. K., Amaral, C. D. B., Nóbrega, J. A., Nogueira, A. R. A., Cavicchioli, A., La-scalea, M. A., Gutz, G. R., Tyson, J., Chen, M. L., Ma, L. Y., Chen, X. W., Punrat, E., Chuanuwatanakul, S., Kaneta, T., Motomizu, S., Chailapakul, O., Hotel, D., Llorente-mirandes, T., Calderón, J., Centrich, F., Rubio, R., López-sánchez, J. F. and Thomas, D. J. (2014) ‘Method development for the determination of arsenic by sequential injection/anodic stripping voltammetry using long-lasting gold-modified screen-printed carbon electrode.’ *Talanta*. Elsevier B.V., 2013(June) pp. 1018–1025.

Quentel, F. and Filella, M. (2002) ‘Determination of inorganic antimony species in seawater by differential pulse anodic stripping voltammetry: Stability of the trivalent state.’ *Analytica Chimica Acta*, 452(2) pp. 237–244.

Quentel, F., Filella, M., Elleouet, C. and Madec, C. (2006) ‘Sb(III) oxidation by iodate in seawater: A cautionary tale.’ *Science of The Total Environment*. Elsevier, 355(1–3) pp. 259–263.

RA (2001) ‘Philippine Mining Act of 1995,.’ Philippines, R. of the (ed.) pp. 1–12.

Raab, A., Feldmann, J. and Meharg, A. A. (2004) ‘The Nature of Arsenic-Phytochelatin Complexes in Holcus lanatus and Pteris cretica.’ *Plant Physiology*. Department of Chemistry, University of Aberdeen, Meston Building, Meston Walk, Aberdeen AB24 3UE, United Kingdom., 134(3) pp. 1113–1122.

Raab, A., Meharg, A. A., Jaspars, M., Genney, D. R. and Feldmann, J. (2004) ‘Arsenic–glutathione complexes—their stability in solution and during separation by different HPLC modes.’ *J. Anal. At. Spectrom.*, 19(1) pp. 183–190.

Raab, A., Schat, H., Meharg, A. A., Feldmann, J., J., A. R. S. H. M. A. A. and F., Raab, A., Schat, H., Meharg, A. A. and Feldmann, J. (2005) ‘Uptake, translocation and transformation of arsenate and arsenite in sunflower (Helianthus annuus): Formation of arsenic-phytochelatin complexes during exposure to high arsenic concentrations.’ *New Phytologist*. Department of Chemistry, University of Aberdeen, Meston Building, Meston Walk, Aberdeen AB24 3UE, UK., 168(3) pp. 551–558.

Rahaman, M. S., Akter, M., Rahman, M. M., Sikder, M. T., Hosokawa, T., Saito, T. and Kurasaki, M. (2020) ‘Investigating the protective actions of D-pinitol against arsenic-induced toxicity in PC12 cells and the underlying mechanism.’ *Environmental Toxicology and Pharmacology*. Elsevier B.V., 74, February, p. 103302.

Rahman, M. A. and Hasegawa, H. (2011) ‘High levels of inorganic arsenic in rice in areas where arsenic-contaminated water is used for irrigation and cooking.’ *Science of The Total Environment*, 409(22) pp. 4645–4655.

Raskin, I., Kumar, P. N., Dushenkov, S. and Salt, D. E. (1994) ‘Bioconcentration of heavy metals by plants.’ *Current Opinion in Biotechnology*, 5(3) pp. 285–290.

Rauser, W. E. (1990) ‘Phytochelatins.’ *Annual Review of Biochemistry*, 59 pp. 61–86.

Reimann, C., Demetriades, A., Eggen, O. A. and Filzmoser, P. (2009) ‘The EuroGeoSurveys geochemical mapping of agricultural and grazing land soils project (GEMAS) -Evaluation of quality control results of aqua regia extraction analysis.’ *EuroGeoSurveys Geochemistry* , (May 2014) p. 94.

Rellán-Álvarez, R., El-Jendoubi, H., Wohlgemuth, G., Abadía, A., Fiehn, O., Abadía, J., Álvarez-Fernández, A., Schjoerring, J. K., Zocchi, G., Degli, U., Di Milano, S., Yoshihara, T.

and Alvarez-Fernández, A. (2011) ‘Metabolite profile changes in xylem sap and leaf extracts of strategy I plants in response to iron deficiency and resupply.’ *Frontiers in plant science*, 2 p. 66.

Rellán-Álvarez, R., Ortega-Villasante, C., Álvarez-Fernández, A., Campo, F. F. del and Hernández, L. E. (2006) ‘Stress Responses of Zea mays to Cadmium and Mercury.’ *Plant and Soil*, 279(1–2) pp. 41–50.

Ren, J. H., Ma, L. Q., Sun, H. J., Cai, F. and Luo, J. (2014) ‘Antimony uptake, translocation and speciation in rice plants exposed to antimonite and antimonate.’ *Science of the Total Environment*. Elsevier B.V., 475 pp. 83–89.

Rodriguez-Iruretagoiena, A., Trebolazabala, J., Martinez-Arkarazo, I., De Diego, A. and Madariaga, J. M. (2015) ‘Metals and metalloids in fruits of tomatoes (Solanum lycopersicum) and their cultivation soils in the Basque Country: Concentrations and accumulation trends.’ *Food Chemistry*. Elsevier Ltd, 173, February, pp. 1083–1089.

Rosas-Castor, J. M., Guzmán-Mar, J. L., Hernández-Ramírez, A., Garza-González, M. T. and Hinojosa-Reyes, L. (2014) ‘Arsenic accumulation in maize crop (Zea mays): A review.’ *Science of The Total Environment*. Elsevier, 488–489(1) pp. 176–187.

Rousk, J. and Jones, D. L. (2010) ‘Loss of low molecular weight dissolved organic carbon (DOC) and nitrogen (DON) in H2O and 0.5M K2SO4 soil extracts.’ *Soil Biology and Biochemistry*, 42(12) pp. 2331–2335.

Sabir, M., Waraich, E. A., Hakeem, K. R., Öztürk, M., Ahmad, H. R. and Shahid, M. (2015) ‘Phytoremediation: Mechanisms and Adaptations. Mechanisms and Adaptations.’ *Soil Remediation and Plants: Prospects and Challenges* pp. 85–105.

Sadiq, M. (1992) *Toxic metal chemistry in marine environments*. *Marcel Dekker*. New York City.

Salama, A. K. and Radwan, M. A. (2005) ‘Heavy metals (Cd,Pb) and trace elements (Cu,Zn) contents in some foodstuffs from the Egyptian market.’ *Emirates Journal of Food and Agriculture*, 17(1) pp. 34–42.

Salaun, P. (2017) ‘Editorial: Environmental Electrochemistry.’ *Current Opinion in Electrochemistry*. Elsevier B.V., 3(1) pp. 75–77.

Salaün, P. and van den Berg, C. M. G. (2006) ‘Voltammetric detection of mercury and copper in seawater using a gold microwire electrode.’ *Analytical chemistry*, 78(14) pp. 5052–60.

Salaün, P. and Frézard, F. (2013) ‘Unexpectedly high levels of antimony (III) in the pentavalent antimonial drug Glucantime: insights from a new voltammetric approach.’ *Analytical and Bioanalytical Chemistry*. Liverpool, 405(15) pp. 5201–5214.

Salaün, P., Gibbon-Walsh, K. B., Alves, G. M. S. S., Soares, H. M. V. M. V. M. and van den Berg, C. M. G. G. (2012) 'Determination of arsenic and antimony in seawater by voltammetric and chronopotentiometric stripping using a vibrated gold microwire electrode.' *Analytica Chimica Acta*. Liverpool: Elsevier B.V., 746(March 2014) pp. 53–62.

Salaün, P., Gibbon-Walsh, K. and van den Berg, C. M. G. (2011) 'Beyond the Hydrogen Wave: New Frontier in the Detection of Trace Elements by Stripping Voltammetry.' *Analytical Chemistry*, 83(10) pp. 3848–3856.

Salaün, P., Planer-Friedrich, B. and van den Berg, C. M. . (2007) 'Inorganic arsenic speciation in water and seawater by anodic stripping voltammetry with a gold microelectrode.' *Analytica Chimica Acta*. Liverpool, 585(2) pp. 312–322.

Samarah, L. Z., Tran, T. H., Stacey, G. and Vertes, A. (2020) 'In Vivo Chemical Analysis of Plant Sap from the Xylem and Single Parenchymal Cells by Capillary Microsampling Electrospray Ionization Mass Spectrometry.' *Analytical Chemistry*, 92(10) pp. 7299–7306.

Samota, M. K., Navnage, N. P. and Bhatt, L. (2017) 'Role of Macro and Micronutrient in Development and Growth of Plant,' 10(18) pp. 3171–3173.

Santos, V. S., Santos, W. de J. R., Kubota, L. T. and Tarley, C. R. T. (2009) 'Speciation of Sb(III) and Sb(V) in meglumine antimoniate pharmaceutical formulations by PSA using carbon nanotube electrode.' *Journal of Pharmaceutical and Biomedical Analysis*, 50(2) pp. 151–157.

Satoh, S. (2006) 'Organic substances in xylem sap delivered to above-ground organs by the roots.' *Journal of Plant Research*, 119(3) pp. 179–187.

Scharifker, B. R., Mostany, J. and Serruya, A. (2000) 'Catalytic reduction of nitrate during electrodeposition of thallium from Tl3+ solution.' *Electrochemistry Communications*, 2(6) pp. 448–451.

Scholander, P. F., Bradstreet, E. D., Hemmingsen, E. A. and Hammel, H. T. (1965) 'Sap Pressure in Vascular Plants: Negative hydrostatic pressure can be measured in plants.' *Science*, 148(3668) pp. 339–346.

Schurr, U. (1998) 'Xylem sap sampling—new approaches to an old topic.' *Trends in Plant Science*. Elsevier Current Trends, 3(8) pp. 293–298.

Schurr, U. (1999) 'Dynamics of Nutrient Transport from the Root to the Shoot.' *In*. Springer, Berlin, Heidelberg, pp. 234–253.

Shahid, M., Khalid, S., Abbas, G., Shahid, N., Nadeem, M., Sabir, M., Aslam, M. and Dumat, C. (2015) 'Heavy metal stress and crop productivity.' *In Crop Production and Global Environmental Issues*. Springer International Publishing, pp. 1–25.

Sharma, S. D. (2013) 'History of Rice in Southeast Asia and Australia.' *Journal of Chemical Information and Modeling*, 53(9) pp. 1689–1699.

Shri, M., Singh, P. K., Kidwai, M., Gautam, N., Dubey, S., Verma, G. and Chakrabarty, D. (2019) 'Recent advances in arsenic metabolism in plants: Current status, challenges and highlighted biotechnological intervention to reduce grain arsenic in rice.' *Metallomics*, 11(3) pp. 519–532.

Simoni, R. D., Hill, R. L. and Vaughan, M. (2005) 'Benedict ' s Solution , a Reagent for Measuring Reducing Sugars : the Clinical Chemistry of Stanley R . Benedict,' 277(16) pp. 10–12.

Slamet-loedin, I., Slamet-loedin, I. H., Johnson-beebout, S. E., Impa, S. and Tsakirpaloglou, N. (2015) 'Enriching rice with Zn and Fe while minimizing Cd risk.' *Frontiers in Plant Science*, 6(MAR).

Smedley, P. L. and Kinniburgh, D. G. (2000) 'Source and behaviour of arsenic in natural waters.' *British Geological Survey* p. 61.

Smedley, P. L. and Kinniburgh, D. G. (2002) 'A review of the source, behaviour and distribution of arsenic in natural waters.' *Applied Geochemistry*, 17(5) pp. 517–568.

Smith, A. H., Lingas, E. O. and Rahman, M. (2000) 'Contamination of drinking-water by arsenic in Bangladesh: A public health emergency.' *Bulletin of the World Health Organization*, 78(9) pp. 1093–1103.

Smith, A. H. and Smith, M. M. H. (2004) 'Arsenic drinking water regulations in developing countries with extensive exposure.' *Toxicology*, 198(1–3) pp. 39–44.

Sobrado, M. A. (2007) 'Relationship of water transport to anatomical features in the mangrove Laguncularia racemosa grown under contrasting salinities.' *New Phytologist*, 173(3) pp. 584–591.

Sørensen, O., Andersen, A., Olsen, H., Alexandr, K., Ekstrøm, P. O., Giercksky, K. E. and Flatmark, K. (2010) 'Validation and use of microdialysis for determination of pharmacokinetic properties of the chemotherapeutic agent mitomycin C - an experimental study.' *BMC Cancer*, 10.

Spurgeon, D. J., Rowland, P., Ainsworth, G., Rothery, P., Long, S. and Black, H. I. J. (2008) 'Geographical and pedological drivers of distribution and risks to soil fauna of seven metals (Cd, Cu, Cr, Ni, Pb, V and Zn) in British soils.' *Environmental Pollution*, 153(2) pp. 273–283.

Sreekanth, T. V. M., Nagajyothi, P. C., Lee, K. D. and Prasad, T. N. V. K. V. (2013) 'Occurrence, physiological responses and toxicity of nickel in plants.' *International Journal of Environmental Science and Technology*. Center for Environmental and Energy Research and Studies pp. 1129–1140.

Stazi, S. R., Cassaniti, C., Marabottini, R., Giuffrida, F. and Leonardi, C. (2016) ‘Arsenic uptake and partitioning in grafted tomato plants.’ *Horticulture, Environment, and Biotechnology*. Korean Society for Horticultural Science, 57(3) pp. 241–247.

Steudle, E. (2001) ‘The cohesion-tension mechanism and the acquisition of water by plant roots.’ *Annual Review of Plant Biology*, 52 pp. 847–875.

Stoeva, N., Berova, M. and Zlatev, Z. (2005) ‘Effect of arsenic on some physiological parameters in bean plants.’ *Biologia Plantarum*, 49(2) pp. 293–296.

Sulyok, M., Miró, M., Stingeder, G. and Koellensperger, G. (2005) ‘The potential of flow-through microdialysis for probing low-molecular weight organic anions in rhizosphere soil solution.’ *Analytica Chimica Acta*. Elsevier, 546(1) pp. 1–10.

Sun, G., Williams, P. N. and Zhu, Y. (2009) ‘Mechanisms of Arsenic Uptake and Metabolism by Plants : Focusing on Rice.’ *Environmental Toxicology*, 134(November) pp. 1–6.

Sun, H., Yan, S. C. and Cheng, W. S. (2000) ‘Interaction of antimony tartrate with the tripeptide glutathione.’ *European Journal of Biochemistry*, 267(17) pp. 5450–5457.

Takarina, N. D. and Pin, T. G. (2017) ‘Bioconcentration Factor (BCF) and Translocation Factor (TF) of Heavy Metals in Mangrove Trees of Blanakan Fish Farm.’ *Makara Journal of Science*, 21(2).

Tamás, M. J. (2016) ‘Cellular and molecular mechanisms of antimony transport, toxicity and resistance.’ *Environmental Chemistry*, 13(6) pp. 955–962.

Tatár, E., Mihucz, V. G., Kmethy, B., Záray, G. and Fodor, F. (2000) ‘Determination of organic acids and their role in nickel transport within cucumber plants.’ *Microchemical Journal*, 67(1–3) pp. 73–81.

Tatár, E., Mihucz, V. G., Varga, A., Záray, G. and Fodor, F. (1998) ‘Determination of Organic Acids in Xylem Sap of Cucumber: Effect of Lead Contamination.’ *Microchemical Journal*. Elsevier Inc., 58(3) pp. 306–314.

Telford, K., Maher, W., Krikowa, F. and Foster, S. (2008) ‘Measurement of total antimony and antimony species in mine contaminated soils by ICPMS and HPLC-ICPMS.’ *Journal of Environmental Monitoring*, 10(1) pp. 136–140.

Telford, K., Maher, W., Krikowa, F., Foster, S., Ellwood, M. J. M. J., Ashley, P. M. P. M., Lockwood, P. V. P. V. and Wilson, S. C. S. C. (2009) ‘Bioaccumulation of antimony and arsenic in a highly contaminated stream adjacent to the Hillgrove Mine, NSW, Australia.’ *Environmental Chemistry*, 6(2) pp. 133–143.

Thomas, G. W. (1996) ‘Soil pH and soil acidity.’ *In* D.L. Sparks et al., editors (ed.) *Methods of soil analysis: Part 3. SSSA Book Series No. 5. SSSA,* pp. 475–490.

Tian, T., Zhou, H., Gu, J., Jia, R., Li, H., Wang, Q., Zeng, M. and Liao, B. (2019) 'Cadmium accumulation and bioavailability in paddy soil under different water regimes for different growth stages of rice (Oryza sativa L.).' *Plant and Soil*. Springer International Publishing, July.

Timofeev, I. and Hutchinson, P. (2008a) 'Microdialysis.' *In Essentials of Neuroanesthesia and Neurointensive Care*. Elsevier, pp. 277–282.

Timofeev, I. and Hutchinson, P. (2008b) 'Microdialysis Learn more about Microdialysis Microdialysis Chemical and Biochemical Approaches for the Study of Anesthetic Function Part B Carrier-mediated and artificial-cell tar-.'

Toghill, K. E., Lu, M., Compton, R. G. and Kathryn E. Toghill, Min Lu, and R. G. C. (2011) 'Electroanalytical Determination of Antimony.' *International Journal of Electrochemical Science*, 6(8) pp. 3057–3076.

Tollestrup, K., Frost, F. J., Harter, L. C. and McMillan, G. P. (2003) 'Mortality among Children Residing near the American Smelting and Refining Company (ASARCO) Copper Smelter in Ruston, Washington.' *Archives of Environmental Health: An International Journal*, 58(11) pp. 683–691.

Torto, N., Mwatseteza, J. and Laurell, T. (2001) 'Microdialysis Sampling: Challenges and New Frontiers.' *LC GC Europe*, 14(9) pp. 536–546.

Torto, N., Mwatseteza, J. and Sawula, G. (2002) 'A study of microdialysis sampling of metal ions.' *Analytica Chimica Acta*. Elsevier, 456(2) pp. 253–261.

Trejo-Téllez, L. I. (2012) 'Nutrient Solutions for Hydroponic Systems.' *In* Asao, F. C. G.-M. E.-T. (ed.). Rijeka: IntechOpen, p. Ch. 1.

Tsang, J. J., Rozan, T. F., Hsu-Kim, H., Mullaugh, K. M. and Luther, G. W. (2006) 'Pseudopolarographic determination of Cd2+ complexation in freshwater.' *Environmental Science and Technology*, 40(17) pp. 5388–5394.

Tschan, M., Robinson, B. H. and Schulin, R. (2009) 'Antimony in the soil - Plant system - A review.' *Environmental Chemistry*, 6(2) pp. 106–115.

Tschan, M., Robinson, B. and Schulin, R. (2008) 'Antimony uptake by Zea mays (L.) and Helianthus annuus (L.) from nutrient solution.' *Environmental Geochemistry and Health*, 30(2) pp. 187–191.

Tsukagoshi, S. and Shinohara, Y. (2015) *Nutrition and Nutrient Uptake in Soilless Culture Systems*. *Plant Factory: An Indoor Vertical Farming System for Efficient Quality Food Production*. Elsevier Inc.

Tuyogon, D. S. J., Impa, S. M., Castillo, O. B., Larazo, W. and Johnson-Beebout, S. E. (2016) 'Enriching rice grain zinc through zinc fertilization and water management.' *Soil Science*

Society of America Journal, 80(1) pp. 121–134.

Tylenda, C. A., Sullivan, D. W. and Fowler, B. A. (2015) *Antimony*. *Handbook on the Toxicology of Metals: Fourth Edition*. Fourth Edi, Elsevier.

U.S. Department of Health and Human (2018) *Revised Draft : Report on Carcinogens Monograph on Antimony Trioxide*.

U.S. Geological Survey (2004) 'Mineral Commodity Profiles-Antimony.' *U.S. Department of the Interior: U.S. Geological Survey* pp. 1–35.

Ugochukwu, G. C., Eneh, F. U., Igwilo, I. . and Aloh, C. H. (2017) 'Comparative study on the heavy metal content of domestic rice (Oryza sativa Comparative study on the heavy metal content of domestic rice (Oryza sativa L) brands common in Awka, Nigeria.' *IOSR Journal of Environmental Science, Toxicology and Food Technology*, 11(8) pp. 67–70.

UN (ed.) (2015) *Crop Prospects and Food Situation*. Rome: FAO.

Ungureanu, G., Santos, S., Boaventura, R. and Botelho, C. (2015) 'Arsenic and antimony in water and wastewater: Overview of removal techniques with special reference to latest advances in adsorption.' *Journal of Environmental Management*, 151, March, pp. 326–342.

Uroic, M. K. (2011) *The impact of arsenic species on the production and composition of xylem sap*. *Environmental & Analytical Chemistry*. University of Aberdeen. Retrieved from internal-pdf://145.35.116.156/PhD thesis The impact of As MK Uroic.pdf.

Uroic, M. K., Salaün, P., Raab, A. and Feldmann, J. (2012) 'Arsenate impact on the metabolite profile, production, and arsenic loading of xylem sap in cucumbers (Cucumis sativus L.).' *Frontiers in Physiology*, 3 APR(March) pp. 1–23.

Varsányi, I., Fodré, Z. and Bartha, A. (1991) 'Arsenic in drinking water and mortality in the Southern Great Plain, Hungary.' *Environmental Geochemistry and Health*. Kluwer Academic Publishers, 13(1) pp. 14–22.

Violante, A., Cozzolino, V., Perelomov, L., Caporale, A. . and Pigna, M. (2010) 'Mobility and bioavailability of heavy metals and metalloids in soil environments.' *Journal of soil science and plant nutrition*. Sociedad Chilena de la Ciencia del Suelo, 10(3) pp. 268–292.

Vithanage, M., Dabrowska, B. B., Mukherjee, A. B., Sandhi, A. and Bhattacharya, P. (2012) 'Arsenic uptake by plants and possible phytoremediation applications: A brief overview.' *Environmental Chemistry Letters* pp. 217–224.

Wagner, S. E., Peryea, F. J. and Filby, R. A. (2003) 'Antimony Impurity in Lead Arsenate Insecticide Enhances the Antimony Content of Old Orchard Soils.' *Journal of Environmental Quality*. Wiley, 32(2) pp. 736–738.

Wan, X. M., Tandy, S., Hockmann, K. and Schulin, R. (2013) ‘Changes in Sb speciation with waterlogging of shooting range soils and impacts on plant uptake.’ *Environmental Pollution*. Elsevier Ltd, 172, January, pp. 53–60.

Wang, S., Shi, X., Sun, H., Chen, Y., Pan, H., Yang, X. and Rafiq, T. (2014) ‘Variations in Metal Tolerance and Accumulation in Three Hydroponically Cultivated Varieties of Salix integra Treated with Lead.’ Reigosa, M. (ed.) *PLoS ONE*. Public Library of Science, 9(9) p. e108568.

Wang, T., Yang, Q., Wang, Y., Wang, J., Zhang, Y. and Pan, W.-P. P. (2020) ‘Arsenic release and transformation in co-combustion of biomass and coal: Effect of mineral elements and volatile matter in biomass.’ *Bioresource technology*. Beijing, PR China: Elsevier Ltd, 297, February, p. 122388.

Wang, Z., Zeng, X., Geng, M., Chen, C., Cai, J., Yu, X., Hou, Y. and Zhang, H. (2015) ‘Health risks of heavy metals uptake by crops grown in a sewage irrigation area in China.’ *Polish Journal of Environmental Studies*, 24(3) pp. 1379–1386.

Welch, A. H. and Stollenwerk, K. G. (eds) (2003) *Arsenic in Ground Water*. *Springer Science Business Media New York*. Boston, MA: Springer US.

White, M. C., Chaney, R. L., Decker, A. M. and R., and M. W. D. A. (1981) ‘Metal Complexation in Xylem Fluid: I. Chemical composition of tomato and soybean stem exudate.’ *Plant Physiology*, 67(2) pp. 292–300.

WHO (2003a) ‘Antimony in Drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality.’ *Who* pp. 1–9.

WHO (2003b) *Background document for preparation of WHO Guidelines for drinking-water quality: Antimony in drinking water.* Geneva, Switzerland.

WHO (2003c) ‘Chromium in drinking-water. Background document for preparation of WHO Guidelines for drinking-water quality.’ *(WHO/SDE/WSH/03.04/4)*, (3) pp. 334–335.

Wickliff, J. L. and Aronoff, S. (1962) *Quantitative measurement of leaf chlorophylss by spectrophotometry of their pheophytins in aqueous alcoholic extracts*. Iowa, USA.

Williams, P. N., Islam, M. R., Adomako, E. E., Raab, A., Hossain, S. A., Zhu, Y. G., Feldmann, J. and Meharg, A. A. (2006) ‘Increase in rice grain arsenic for regions of Bangladesh irrigating paddies with elevated arsenic in groundwaters.’ *Environmental Science and Technology* pp. 4903–4908.

Wilson, S. C., Lockwood, P. V., Ashley, P. M. and Tighe, M. (2010) ‘The chemistry and behaviour of antimony in the soil environment with comparisons to arsenic: A critical review.’ *Environmental Pollution*. Elsevier Ltd, 158(5) pp. 1169–1181.

Woolson, E. A., Axley, J. H. and Kearney, P. C. (1971) ‘Correlation between Available Soil

Arsenic, Estimated by Six Methods, and Response of Corn (Zea mays L.)1.’ *Soil Science Society of America Journal*. Soil Science Society of America, 35(1) p. 101.

Wu, D. and Sun, S. (2016) ‘Speciation analysis of As, Sb and Se.’ *Trends in Environmental Analytical Chemistry*. Elsevier Inc., 11, July, pp. 9–22.

Wu, T.-L. L., Cui, X.-D. D., Cui, P.-X. X., Ata-Ul-Karim, S. T., Sun, Q., Liu, C., Fan, T.-T. T., Gong, H., Zhou, D.-M. M. and Wang, Y.-J. J. (2019) ‘Speciation and location of arsenic and antimony in rice samples around antimony mining area.’ *Environmental Pollution*. Elsevier Ltd, 252, September, pp. 1439–1447.

www.IRRI.org (2019) *Long-Term Continuous Cropping Experiment (LTCCE) | International Rice Research Institute*. [Online] [Accessed on 18th November 2019] https://www.irri.org/long-term-continuous-cropping-experiment-ltcce.

Wyrwicka, A., Urbaniak, M. and Przybylski, M. (2019) ‘ The response of cucumber plants (Cucumis sativus L.) to the application of PCB-contaminated sewage sludge and urban sediment .’ *PeerJ*, 7 p. e6743.

Xu, X. Y., McGrath, S. P. and Zhao, F. J. (2007) ‘Rapid reduction of arsenate in the medium mediated by plant roots.’ *New Phytologist*, 176(3) pp. 590–599.

Yadav, S. K. (2010) ‘Heavy metals toxicity in plants: An overview on the role of glutathione and phytochelatins in heavy metal stress tolerance of plants.’ *South African Journal of Botany*. Elsevier B.V., 76(2) pp. 167–179.

Ye, W.-L. L., Wood, B. A., Stroud, J. L., Andralojc, P. J., Raab, A., McGrath, S. P., Feldmann, J. and Zhao, F.-J. J. (2010) ‘Arsenic speciation in phloem and xylem exudates of castor bean.’ *Plant Physiology*, 154(3) pp. 1505–1513.

Zavala, Y. J. and Duxbury, J. M. (2008) ‘Arsenic in rice: I. Estimating normal levels of total arsenic in rice grain.’ *Environmental Science and Technology*, 42(10) pp. 3856–3860.

Zengin, F. K. and Munzuroglu, O. (2005) ‘Effects of some heavy metals on content of chlorophyll, proline and some antioxidant chemicals in bean (Phaseolus vulgaris L.) seedlings.’ *Acta Biologica Cracoviensia Series Botanica*, 47(2) pp. 157–164.

Zhang, H. and Selim, H. M. (2005) ‘Kinetics of Arsenate Adsorption−Desorption in Soils.’ *Environmental Science & Technology*, 39(16) pp. 6101–6108.

Zhang, T., Ruan, J., Zhang, B., Lu, S., Gao, C., Huang, L., Bai, X., Xie, L., Gui, M. and Qiu, R. (2019) ‘Heavy metals in human urine, foods and drinking water from an e-waste dismantling area: Identification of exposure sources and metal-induced health risk.’ *Ecotoxicology and Environmental Safety*. Academic Press, 169, March, pp. 707–713.

Zhang, W., Cai, Y., Tu, C. and Ma, L. Q. (2002) ‘Arsenic speciation and distribution in an arsenic hyperaccumulating plant.’ *Science of the Total Environment*, 300(1–3) pp. 167–

177.

Zhao, F.-J., Ma, Y., Zhu, Y.-G., Tang, Z. and McGrath, S. P. (2015) ‘Soil Contamination in China: Current Status and Mitigation Strategies.’ *Environmental Science & Technology*. American Chemical Society, 49(2) pp. 750–759.

Zhao, F.-J., McGrath, S. P. and Meharg, A. A. (2010) ‘Arsenic as a Food Chain Contaminant: Mechanisms of Plant Uptake and Metabolism and Mitigation Strategies.’ *Annual Review of Plant Biology*. Annual Reviews, 61(1) pp. 535–559.

Zheng, J., Iijima, A. and Furuta, N. (2001) ‘Complexation effect of antimony compounds with citric acid and its application to the speciation of antimony(III) and antimony(V) using HPLC-ICP-MS.’ *Journal of Analytical Atomic Spectrometry*, 16(8) pp. 812–818.

Zheng, R. L., Sun, G. X. and Zhu, Y. G. (2013) ‘Effects of microbial processes on the fate of arsenic in paddy soil.’ *Chinese Science Bulletin* pp. 186–193.

Zhou, S. N., Ouyang, G. and Pawliszyn, J. (2008) ‘Comparison of microdialysis with solid-phase microextraction for in vitro and in vivo studies.’ *Journal of Chromatography A*, 1196–1197(1–2) pp. 46–56.

Zhou, X., Sun, C., Zhu, P. and Liu, F. (2018) ‘Effects of Antimony Stress on Photosynthesis and Growth of Acorus calamus.’ *Frontiers in Plant Science*. Frontiers Media S.A., 9(May) pp. 1–9.

Zulkafflee, N. S., Redzuan, N. A. M., Hanafi, Z., Selamat, J., Ismail, M. R., Praveena, S. M. and Razis, A. F. A. (2019) ‘Heavy metal in paddy soil and its bioavailability in rice using in vitro digestion model for health risk assessment.’ *International Journal of Environmental Research and Public Health*, 16(23).

CHAPTER 2

ARSENIC AND ANTIMONY SPECIES IMPACT ON CUCUMBERS – HYDROPONIC EXPERIMENT

Index of Figures

Index of Tables

2.1 Introduction

Metalloids like antimony (Sb) and arsenic (As) are naturally present at relatively low levels in the environment (groundwater, rocks, and soils). However, their increased use has led to many environmental soil and groundwater contamination problems, and understanding their biogeochemical cycling is of prime importance to predict potential contamination issues. As toxicity has been recognised worldwide for decades (Lombi and Holm, 2010; Hasanuzzaman et al., 2015, 2018; Tamás, 2016) and has been the subject of many articles because of its epidemic and chronic health effects on both humans and the environment (Mishra et al., 2013). Its hazardous effect is becoming more of a threat due to increasing groundwater contamination that affects nearly 200 million people in over 70 countries (Brammer and Ravenscroft, 2009), more specifically, in South and South-East Asia (Figure 2.1) with an estimated 110 million alone from Bangladesh, Cambodia, China, India, Laos, Myanmar, Nepal, Pakistan, Taiwan and Vietnam (Mandal and Suzuki, 2002; Geng et al., 2006; Brammer and Ravenscroft, 2009; Vithanage et al., 2012). Nevertheless, all continents are suffering from problems, including developed countries such as the United States (US), South America, and Europe (Woolson et al., 1971; Mead, 2005; Amarasiriwardena and Wu, 2011; Moreno-Jiménez et al., 2012)(Woolson et al., 1971; Smedley and Kinniburgh, 2002; Mead, 2005; Amarasiriwardena and Wu, 2011).

As occurs in soil, it is also present in the aquatic environment (freshwater systems, oceans, and estuaries) as a result of rock weathering, soil runoff, microbiological activity, and anthropogenic activities (Gebel, 2001; Smedley and Kinniburgh, 2002; Moreno-Jiménez et al., 2012). The primary mode of environmental exposure to humans is drinking water from human-made deep wells and irrigation water for agriculture like rice farming (Brammer and Ravenscroft, 2009).

In agriculture, As has been used as herbicide, and as Asal medication in chicken in the form of Roxarsone® and organoAs was used as a treatment for *Coccidiosis* (a common parasitic disease in poultry), as feed conversion improvement for faster weight gain for poultry, and meat pigmentation improvement (Jackson and Bertsch, 2001; Garbarino et al., 2003; Nachman et al., 2013). In addition to inorganic As species, methylated species also occur in the environment because of the microbial methylated methylation process (Arnold et al., 2006). Dimethylarsinic acid (DMA), which is the common methylated species in soil, and the sodium salts of monomethyl As acid (MMA) are the most extensively used methylated As species in agriculture (Duester et al., 2005). As is a naturally occurring but carcinogenic pollutant. Its abundant presence in natural and agricultural environments threatens global food security and negatively affects millions worldwide. There have been many studies on the translocation of As in agricultural products like rice (Williams et al., 2006; Martin et al., 2010; Punrat et al., 2014; Ugochukwu et al., 2017; Kumarathilaka et al., 2018) in cereals (Salama and Radwan, 2005), in cucumber (Mihucz et al., 2005; Ye et al., 2010; Gerényi et al., 2017; Wyrwicka et al., 2019), in tomato plants (Xu et al., 2007; Stazi et al., 2016), fruits and vegetables (FSA, 2012; Stazi et al., 2016; Hu et al., 2019). Different As compounds have been identified in the soil-plant systems, but the most common As species are arsenite, arsenate, monomethylarsenate (MMA), and dimethyl arsenate (DMA) (in order of decreasing toxicities) (Huang et al., 2006; Nagajyoti et al., 2010). As can exist in the natural system in four oxidation states: (-3); (0); (+3); and (+5). The main forms in the soils are arsenate (As(V)) and arsenite (As(III))(Peralta-Videa et al., 2009).

Contrary to As, Sb has not received much attention (Filella, Belzile and Chen, 2002a, 2002b; Filella et al., 2009) and very little is known about the behaviour of Sb in plants. There is no legal threshold for Sb in food, but it may pose a potential human health risk (Pierart et al., 2015). In the US and European Union (EU), Sb and its compounds were considered one of the priority pollutants in 1979 (USEPA, 1971) (Filella, Belzile and Chen, 2002c). Sb concentrations can range as little as less than one ug L^{-1} up to 100 ug L^{-1} because of anthropogenic activities (Filella et al., 2009). Dissolved Sb concentration in the ocean ranges from a few ng L^{-1} to a few ug $L^{-1,}$ depending on the location and the pollution sources. The World Health Association (WHO) set a permissible limit of 10 ug L^{-1} (10 parts per billion, ppb) and 20 ug L^{-1} (20 ppb) for As and Sb, respectively (WHO, 2003b; Smith and Smith, 2004). Despite its toxicity, Sb has not received as much attention, mostly due to the relatively low concentrations encountered (nM)(Filella et al., 2009). Sb is typical in small amounts like air, water, and soil. Through groundwater, Sb can pollute soils and other surface waters. Sb-based medicines are used for a parasitic disease in humans called *Leishmaniasis,* with an estimated 14 million human sufferers mainly in developing countries (Miekeley et al., 2002; Brochu et al., 2003; Tylenda et al., 2015). Laboratory tests showed that animals' Sb accumulation in small amounts might kill small animals like rats, rabbits, and guinea pigs. The United States Environmental Protection Agency (USEPA) and the European Union (EU) consider Sb and its compounds as the priority pollutants (Filella, 2013). Information on the Sb transformation and transport in the environment is scarce and the Sb speciation in various media. This is why further research is needed to understand Sb behaviour and fate in the environment (Filella and Williams, 2012).

There is still a significant gap in knowledge on metalloid toxicity (i.e., As and Sb), adsorption, translocation, and bioavailability. A better understanding of the uptake, translocation, effect of exposure duration, and effect on plant growth are crucial for assessing metalloids like Sb and As on crops for human consumption as part of food safety.

2.2 Aims and Objectives

This study's main objective was to understand the toxic effects of the metalloid's exposure (Sb and As) on cucumber plants chosen as model plants by exposing them to different metalloid species at different exposure duration. The hypotheses of this study are: (1) cucumber plant reacts more negatively to the trivalent species for both Sb and As compared to the pentavalent species; (2) the longer the amendment, the more accumulation of the metalloids in the cucumber plants; and (3) micro and macronutrients in the plants will vary as plant defense in counteracting As and Sb translocation in plants.

The specific objectives were:

- To perform hydroponic plant growth experiments where cucumber plants were amended with a constant amount of different species of As or Sb ((III) or (V)) for two exposure duration experiments (short-2 days and long-38 days),
- To quantify the effects of As and Sb species and duration stress on the physiological growth parameters of cucumber (i.e., plant height, number of leaves, number of flowers, leaf area, root mass and biomass and foliar chlorophyll),
- To quantify the total Sb and As concentration in cucumber plant parts (i.e., roots, stems, leaves, flowers, and xylem saps), and
- To carry out correlation analysis to explore the correlation pattern of various nutrients (micro (Ni, Cu, Zn, and Mn) and macro (Mg and Ca)) as a function of As and Sb treatments.

2.3 Materials and Methods

2.3.1 Chemicals

Arsenite (As(III)) and arsenate (As(V)) were from As_2O_3 and $NaAsH_2O_4$, respectively (Sigma-Aldrich, UK) and were of analytical reagent grade. Standard solutions of 100 and 10 μM were prepared from the salt in 50 mL tubes with milli-Q water and acidified to pH 2 with HCl. The As(III) standard solutions were taped and kept in the dark at all times to avoid any photooxidation processes. Solutions were renewed approximately every three months. 70% HNO_3 ACS reagent was used to digestion of plant parts and xylem saps (Sigma Aldrich, UK). Hoagland's nutrient solution was made using MQ water. Chemicals were at least of analytical grade (KNO_3, $Ca(NO_3)_2 \cdot 4\ H_2O$, $MgSO_4$, NH_4NO_3, KH_2PO_4, $FeSO_4 \cdot 7\ H_2O$, $MnCl_2 \cdot 4\ H_2O$, $Na_2B_4O_7 \cdot 10\ H_2O$, $ZnSO_4 \cdot 7\ H_2O$, $CuSO_4 \cdot 3\ H_2O$, $Na_2MoO_4 \cdot 2\ H_2O$ (Sigma Aldrich, UK). A 4-L plastic food container (HDPE) was used for growth experiments. Duct tape was used to cover the outside portion of the container to prevent algae formation, 15 mL centrifuge tubes (without lids and bottom cut open) were used to hold the container's cucumber plants. Cucumber seeds were bought from Real Seed online (http://www.realseeds.co.uk/cucumbers.html). Seedling tray and vermiculite were used to grow cucumber plants until the 2-leaf stage. All materials used were soaked in a 3% bleach solution overnight, followed with acid-washing, and thoroughly rinsed with milli-Q water as used for all hydroponic experiments.

2.3.2 Modified Hoagland's nutrient solution

The following stock solutions (1-6) were prepared, and the amounts indicated were used to prepare 1 litre (final volume) of Hoagland nutrient solution (Hoagland and Arnon, 1950): (1) 2 mL 1.00 M $NH_4H_2PO_4$ (adjusted to pH 6.3 with HCl); (2) 6 mL 1.00 M KNO_3; (3) 4 mL 1.00 M $Ca (NO_3)_2 \cdot 4 H_2O$; (4) 1 mL 1.00 M $MgSO_4$; (5) 1 mL of Micronutrient stocks. The following amount of salts was dissolved in one litre of water 2.86 g H_3BO_3, 1.81 g $MnCl2 \cdot 4H_2O$, 0.22 g $ZnSO_4 \cdot 7H_2O$, 0.08 g $CuSO_4 \cdot 5H_2O$, 0.02 g $H_2MoO_4 \cdot H_2O$ (Assaying 85% MoO_3); and (6) 0.25 mL Iron Stock. The iron stock solution was made by dissolving 26.1 g EDTA in 286 mL MQ water with 19 g KOH giving an EDTA concentration of 64 mM. 24.9 g $FeSO_4 \cdot 7H_2O$ was dissolved in 500 mL MQ water in a separate beaker. This iron sulfate solution was then slowly added to the potassium EDTA solution, and the resulting solution was aerated overnight with stirring. The pH was increased to 7.1 using $HNO_{3,}$ and the solution was wine red with very few precipitations. The solution was made up to 1 litre with MQ water as the final volume and stored in an amber bottle (or covered with foil). Table 2.1 shows the detailed composition of the modified Hoagland solution (Epstein and Bloom, 1972).

Table 2. 1. Composition of a modified Hoagland solution (adapted from Epstein and Bloom, 1972)

Compound	Molecular weight	Concentration of stock solution	Concentration of stock solution	Volume of stock solution per litre of final solution	Element	The final concentration of element	
	g mol^{-1}	mM	g L^{-1}	mL		µM	ppm
Macronutrients							
KNO_3	101.10	1,000	101.10	6.0	**N**	16,000	224
Ca $(NO_3)_2 \cdot 4 H_2O$	236.16	1,000	236.16	4.0	K	6,000	235
$NH_4 H_2PO_4$	115.08	1,000	115.08	2.0	Ca	4,000	160
$MgSO_4 \cdot 7 H_2O$	246.48	1,000	246.49	1.0	P	2,000	62
					S	1,000	32
Macronutrients					Mg	1,000	24
KCl	74.55	25	1.864	2.0	Cl	50	1.77
H_3BO_3	61.83	12.5	0.773		B	25	0.27
$MnSO_4 \cdot H_2O$	169.01	1.0	0.169		Mn	2.0	0.11
$ZnSO_4 \cdot 7 H_2O$	287.54	1.0	0.288		Zn	2.0	0.13
$CuSO_4 \cdot 5 H_2O$	249.68	0.25	0.062		Cu	0.5	0.03
$H_2MoO_4 \cdot 2 H_2O$ (85% MoO_3)	161.97	0.25	0.040		Mo	0.5	0.05
NaFeEDTA	468.20	64	30.0	0.3-1.0	Fe	16.1-53.7	1.00-3.00

2.3.3 Plant growth

2.3.3.1 Seed germination

Cucumber seeds (*Cucumis sativus L.*) were soaked in water for five to 10 hours before draining (1:1 MQ: 3% H_2O_2). The drained seeds were folded into a damp towel with warm water in a plastic bag or box to prevent evaporation. The towel temperature was kept above 21°C (13-35°C). The seeds were checked at least once daily. Seeds with developed roots were transplanted in the Vermiculite®. The germinated seed was transferred until their two-leaf stage, which took approximately two weeks, depending on the environment. The number of seeds that germinated was recorded and were removed from the plastic.

2.3.3.2 Seed Disinfection Method

Seeds are soaked in warm sterilized MQ water with few drops of 3% H_2O_2 for 30 minutes to 1 hour before soaking. This ensured that the seed is free of any pathogens, bacteria, or viruses before planting (Ogawa and Iwabuchi, 2001). All materials, equipment, and surfaces were sterilized by spraying with 3% Hydrogen peroxide and soaking with a 3% bleach solution.

2.3.4 Hydroponic experiments

The chosen model plant is cucumber for the hydroponic experiment to quantify As and Sb's effects on plant growth. The experiments were performed in a randomized complete block design (RCBD, Figure 2.1) located in the Institute of Integrative Biology of the University of Liverpool Bioscience building. All plants were grown in a plant growth room at a photosynthetic flux density (PFD) of 250-300 µmol m^{-2} s^{-1} at plant height, with a 14/10 h light/dark regime, temperatures of 27 °C (±1 °C, day) and 22 °C (±1 °C, night) at air humidity of 60% (±10%, day) and 80% (±10%, night). All cucumber plants were grown from the two-leaf stage until 35 ± two dat, until As and Sb were added to the hydroponic solutions at different exposure duration as described below. Control plants were also grown in the same conditions for short and long-term duration experiments.

The nutrient solutions were renewed every 48 h unless otherwise stated. The loss of nutrient solution by evaporation was less than 10%. All nutrient solutions for the Sb and As the amendment were replenished with only 100 ppb phosphate solution one day before the amendment schedule for short and long-term exposure. This was based on the previous study done by Mihucz et al. (2005b) to exclude the competition between arsenate and phosphate (phosphate and arsenate ratio is 1:1).

2.3.5 Treatments

The two-leaf cucumber plants were transferred into 4-L plastic boxes containing hydroponic nutrient solution (Table 2.1). For the first week, a half-strength solution was used for the hydroponic system; for the rest of the time, a full-strength nutrient solution was used. Two different exposure experiments were conducted. The first experiment (plant set A) was used for studying As uptake and translocation of As(III) and As(V) exposed for only two days. Plant set B was used to repeat parts of the previous experiments but more prolonged exposure (35 days) and the addition of As(V) and Sb(V)species. Plant parts and xylem saps were analysed for As, Sb, and nutrient (micro and macro) determination for the two experiments.

2.3.5.1 Plant set A

Short-term (ST): 6 sets of plants grown until 35 ± two days after transplanting (dat) were allowed to expose for 46 ± 6 hours (2 days) with four plants per condition. Each set was grown in a separate batch (24 plants in total). As(III) or Sb(III) solutions were prepared using 5% HNO_3 solution.

a) Two sets of four plants each (8 plants in total) were challenged with no As and no Sb;

b) Another two sets of four plants each (8 plants in total) were challenged with 100 µg/L As(III).

c) Another two sets of four plants each (8 plants in total) were challenged with 100 µg/L Sb(III).

Short-term amendments (48 h)

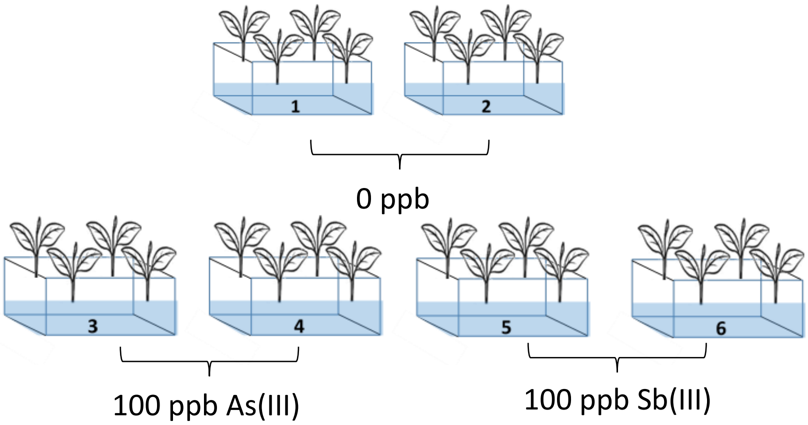


Figure 2. 1.Sprouted cucumber two-leaf seedlings in a 4-L food container (0) 0 ppb (1) 100 ppb As(III), and (2) 100 ppb Sb(III). Four cucumbers in one pot with 1.5 L Hoagland solution.

2.3.5.2 Plant set B

Long-term (LT): 10 sets of plants grown until 35 ± two days after transplanting (dat) were allowed to expose for 40 days with four plants per condition. Each set was grown in a separate batch (40 plants in total).

In total, 40 plants were used in plant set B.

a) Two sets of four plants were challenged with no As (8 plants in total)

b) Two sets of four plants (8 plants) were each challenged with 100 µg/L As(III),100 µg/L As(V), 100 µg/L Sb(III), or 100 µg/L Sb(V) (32 plants in total).

Long-term amendments (38 d)

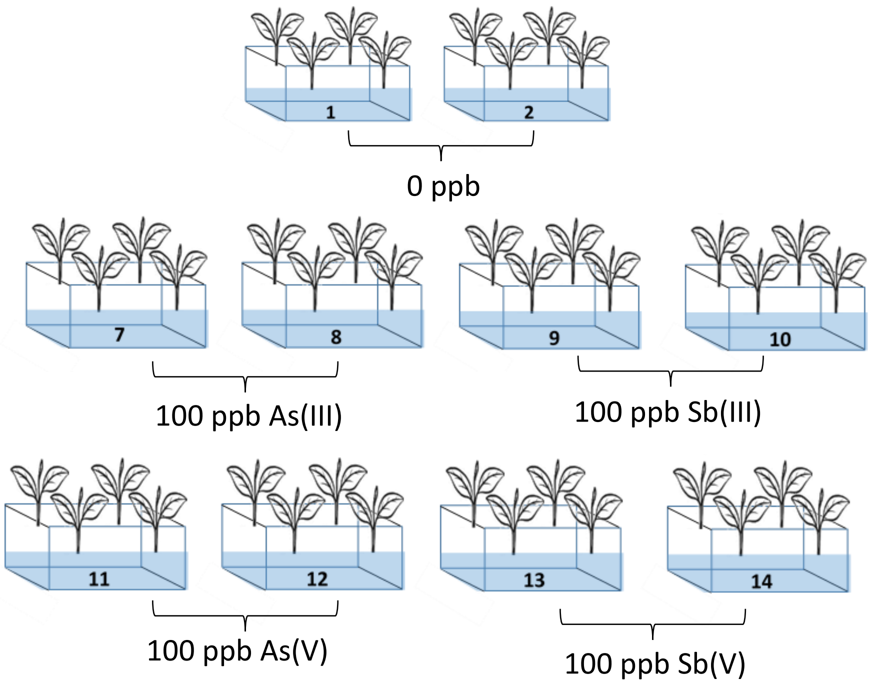


Figure 2. 2. Cucumber hydroponic plant setup (UoL Bioscience plant growth room)

Figures 2.1 and 2.2 show diagrams of four cucumber plants grown hydroponically and the actual set-up inside the plant growth room. The set-up (Fig. 2.3) consists of a 4-L food container covered with duct tape to prevent algae growth by preventing light from entering. Into each lid, four holes were drilled. Into these holes, 15 mL, Greiner tubes without the lid, and bottom cut off were inserted. One container represents one experimental set-up.

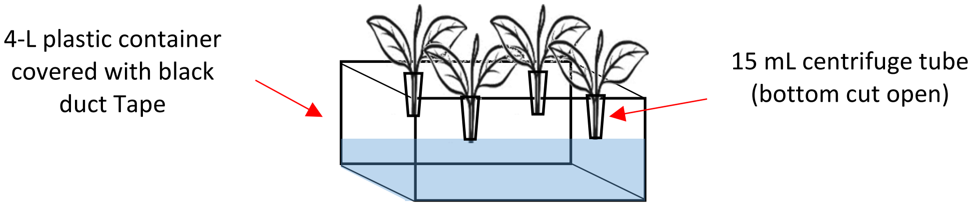


Figure 2. 3. Diagram of a hydroponic plant setup with four cucumber plants in one pot.

2.3.6 Plant sampling and storage

2.3.6.1 Plant Sampling

All plants in each box (both sets) were divided into parts (roots, stems, leaves), washed with tap water followed by distilled water. The washed plant was dried with a paper towel, weighed, and was oven-dried at 70°C in weighed brown envelopes. All dried plant parts were grounded and kept for further analysis with Inductively Coupled Plasma (ICP-MS).

2.3.6.2 Xylem sap sampling – Stem Exudation

This technique is the simplest way to sample xylem sap, which does not require sophisticated instrumentation (Kehr and Rep, 2007; Netting et al., 2012). In this technique, xylem sap was sampled using a micropipette (White et al., 1981), where the stem was cut 2 cm above the roots. The sap (approximately 500-600 uL) was collected after wiping the first few drops from the stem and was collected in a microtube (via micropipette) within the one-hour window period and stored at -80°C freezer until analysis. Benedict's test for reducing sugar was modified with an addition of acid hydrolysis reaction step of the sample to convert the non-reducing sugar into its monosaccharide (Benedict, 1908; Daniels et al., 1960; Simoni et al., 2005). Sucrose analysis was administered to ensure that xylem sap was not contaminated by phloem sap (Killiny and Hijaz, 1998; Uroic et al., 2012; Hijaz and Killiny, 2014).

Figure 2. 4. The hydroponic experiment's actual set-up in the plant growth room (photo taken at 20 days after transplanting (dat), University of Liverpool, Institute of Integrative Biology, Bioscience Building).

2.3.7 Measurement of plant growth parameters

2.3.7.1 Plant Height

Each cucumber plant's average plant height was measured using a ruler starting from the bottom of the stem up to the plant's tip.

2.3.7.2 Leaf Area (Digital Image Analysis Method)

Digital images of 10 randomly selected leaves per treatment were taken against a white background in a well-lighted room using an android smartphone and petiole application (http://petioleapp.com/)(Hrytsak et al., 2018; Polunina et al., 2018). It was calibrated every ten readings using the downloaded calibration pads for different leaf size range (i.e., 8, 11, 15, and 20 cm). A modified stand was made for the analysis based on the suggested set-up by the petiole application website shown in figure 2.6.

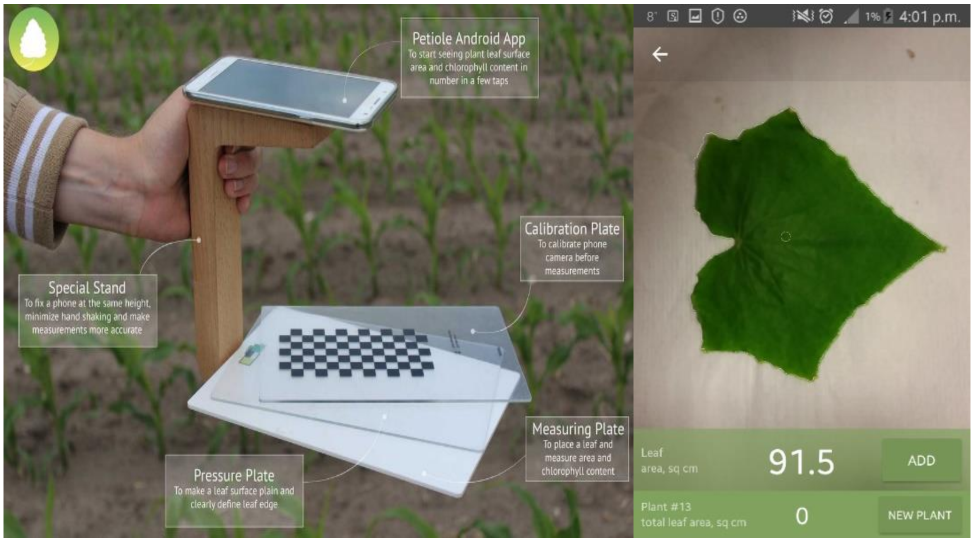


Figure 2. 5. Laboratory set-up for the leaf area analysis (from www.petiole.com) (left) and mobile phone output (right).

2.3.7.3 Number of Leaves and flowers

Leaves and flowers were counted and recorded per plant per treatment, including the control.

2.3.7.4 Biomass and Root mass

Fresh and dry weight biomass was measured per treatment. The plants were divided into roots, stems, and leaves. Plant parts were tapwater washed, followed by distilled water and dried using a paper towel, and put in a pre-weighed brown paper envelope. Fresh weights were measured before oven drying at 70 C overnight. The plants were allowed to cool in a dry environment before weighing the dry weights and measure the moisture content.

2.3.7.5 Foliar Chlorophyll Content

The spectrophotometric method used for chlorophyll extraction was the acetone extraction method (Porra, 2005). The method was based on Hoagland and Arnon (1950), but with modifications, chlorophyll was extracted using 20 % acetone (v/v in distilled water) and quantified using a fluorimeter (Horiba Fluoromax-4 Chem 246, Japan) (Ashbrook, 2014). The extracts were buffered at pH 7.8 to minimise pheophytin formation by losing a Mg atom in the presence of the extracted metabolite (Wickliff and Aronoff, 1962).

2.3.8 Total metal analysis of the plant

ICP-MS analysis of plant samples was adapted with modifications from Cheraghi et al. (2012). Before analysis, digestion pre-treatment was performed using wet acid digestion. Approximately 500 mg of dried plant parts (roots, stem, and leaves) were weighed into digestion tubes; 5 mL of HNO_3 was added to each sample that was inserted into the digestion block. The mixtures were allowed to settle overnight. The digestion tubes were heated for 30 minutes at 60 °C. To ensure all samples were being digested, 1 mL of H_20_2 was added per digestion tube for washing the sides of the tubes. This procedure was repeated two more times (i.e., a total of 3 mL H_2O_2 for each tube). The temperature was raised to 120 °C for 2 hours to evaporate residual acid in the solution until almost dry (2-3 mL). After the cooldown, the digestate was filtered with 540 Whatman filter paper, diluted with MQ water up to 25 mL, and transferred to PTFE tubes, including all the washings from the digestion tubes kept for further ICP-MS analysis. The metals concentration in the plants was calculated from EPA 6020a methods (EPA, 2004). Results of the plant can be from its parts (i.e., roots, stems, and leaves) or the total amount from the whole plant unless otherwise stated.

2.3.9 Quantification of metals in the sap, nutrient solution, and plant parts

A multi-elemental analysis of samples was performed by high resolution inductively coupled plasma mass spectrometer (HR ICP-MS, Element 2, Thermo, Bremen, Germany). Before the analysis, digested samples were diluted up to 5 times using 2 % HNO_3 (ROTIPURAN-Supra, Carl Roth, Germany). Indium (In) was used as an internal standard (IS) for analysis. The quantification of metal concentrations performed using external calibrations.

Table 2. 2. Operation conditions for ICP-MS instrument

ICP-MS	Element 2 (Thermo, Germany)
RF power	1200 W
Coolant	15 Ar L min^{-1} (plasma gas)
Auxiliary	0.92 L min^{-1}
Sample Gas	1.00-1.02 L min^{-1}
Nebulizer	Sea-spray, 0.4 L min^{-1}
Spray chamber	Twister, 50 mL, Cyclonic
Sampling cone	Ni
Skimmer cone	Ni, H model

The validity of HR ICP-MS measurements was confirmed by measuring a river water reference material (SLRS-5, National Research Council Canada); a good agreement with the certified values (within 10% of certified) was always obtained. The instrument's limit of detection is 0.003 and 0.002 ug L^{-1} for Sb and As, respectively. MQ water's procedural blanks were far below the level of concentrations measured in samples. Plant roots, leaves, stem samples were subjected to ICP-MS analysis after the digestion procedure described in section 2.3.3. Digestate (plant parts and xylem sap) were diluted, acidified with HNO_3 at pH2, and subjected to ICP-MS analysis for As, Sb, Ni, Cu, Zn, Mn, Ca, and Mg. The method limit of detection is 0.016 and 0.015 ug Kg^{-1}, for Sb and As, respectively. Each batch was accompanied by a 1 reagent blank, spike, and certified reference material (NIST 1573a).

2.3.10 Statistical Analysis

Data were analyzed using SPSS Statistics for Mac, version 26 (IBM Corp., Armonk, NY, USA). Two-way analysis of variance (ANOVA) was performed to determine the effects of 5 different treatments (control, As(III), Sb(III), As(V), and Sb(V)) and 2 lengths of amendment duration (1: short-2 days and 2: long-38 days) and interactions. A p-value of <0.05 denoted significance. The Tukey (HSD) and subsequent pairwise comparison were employed to compare significant differences (P <0.05) between treatment means. All data presented are expressed as the means of replicates ± standard deviation (SD). A Pearson correlation analysis was carried out for finding the relation between investigated parameters (metalloid treatments, duration, nutrients) using SPSS 26, and a normality check of the variables was done before the analysis using Shapiro-Wilk's test. A Spearman's rank analysis was performed if the data is not normally distributed unless otherwise stated. Principal Component Analysis (PCA) with Varimax normalized rotation was employed to determine the possible concealed relationship on the obtained results. For this analysis, the relevance is identified as the components with eigenvalues of bigger than 1.0, a component that has factor loading > 0.75, from 0.75–0.5, and from 0.5 to 0.3 is taken as strongly, moderately, and weakly relevant, respectively. Principal Component

Analysis (PCA) with Varimax normalized rotation was employed which can reduce the original multi-dimensional spaces of PCs (the principal component). For this analysis, the relevance is identified as the components with eigenvalues of bigger than 1.0, a component that has factor loading > 0.75, from 0.75–0.5, and from 0.5 to 0.3 is taken as strongly, moderately, and weakly relevant, respectively.

2.4 Results

2.4.1 Plant Growth Measurements

This experiment is composed of 2 durations: short-term (2 days) with 3 treatments; (a) control, (b) As(III) (c) Sb(III) and long-term (38 days), with 5 treatments (a) control, (b) As(III) (c) Sb(III) (d) As(V) and (e) Sb(V).

2.4.1.1 Leaf Area

From the leaf area results (Figure 2.7), there were statistically significant differences between different amendments F(4,195)=24.147, *p*=0.0005 and between lengths of amendments F(2,22)=38.077, *p*=0.0005, but there were no interaction effects between the two factors (no correlation). A Tukey post hoc test revealed significantly lower leaf areas between cucumber plants subjected to As and Sb amendments compared to the control plants for short- and long-term treatments. Both the As(III) and Sb(III) species are

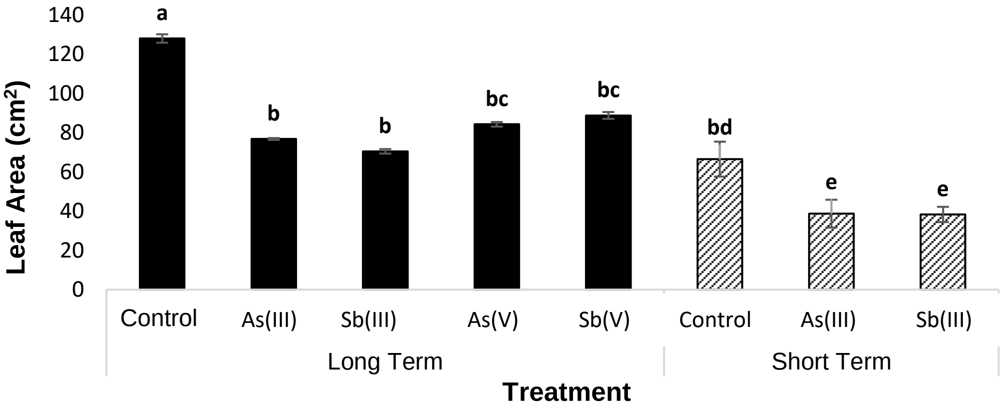


Figure 2. 6. Effect of As and Sb treatments the leaf area among: 5 treatments; (a) control, (b) As(III)(c) Sb(III) (d) As(V) and (e) Sb(V) and the length of amendment; (a) long-term (38 days), (b) short-term (2 days) (a). Data presented are means ± SD of the 10 randomly selected leaves, Bars marked with the same lower-case letters within the treatment are not significantly different at $p < 0.05$.

lesser than the (V) species (not significant). It appears that the As and Sb amendments significantly affected the leaf area of the plants. As(III) and Sb(III) amendments showed a visual less leaf area compared to the As(V) and Sb(V) species exposed plant in the long-term experiment (statistically not significant).

2.4.1.2 Plant height

There were statistically significant differences between the treatments and the lengths of treatment. This observation is similar to the leaf area results (Fig.2.8). Furthermore, in this case, there was an interaction effect between the two factors (metalloid and lengt of treatments are correlated).

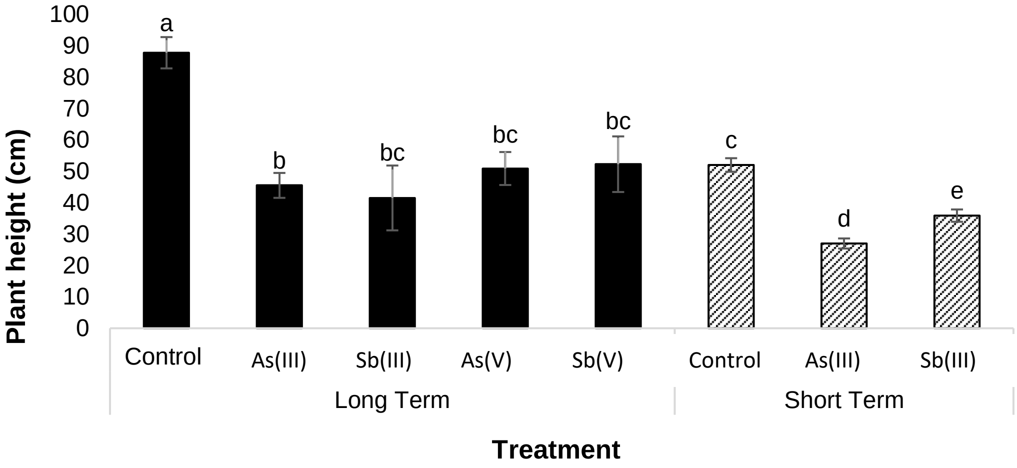


Figure 2. 7. Effect of As and Sb treatments plant height among: (1) 5 treatments; (a) control, (b) As(III) (c) Sb(III) (d) As(V) and (e) Sb(V) and the (2) length of amendment; (a) long-term (38 days), (b) short-term (2 days) (a). Data presented are means ± SD, Bars marked with the same lower-case letters within the treatment are not significantly different at *p* < 0.05.

Based on the results, plants receiving no As nor Sb differ significantly higher plant height with the plants treated with As and Sb both in the short F (2,17) = 240.826 *p*=0.0005 and long-term experiments F (4,35) = 54.044 *p*=0.000. Control cucumber plants are significantly taller compared to the treated plants. In the long-term experiments, different species ((III) and (V)) of As and Sb were not significantly different. In the short-term experiments, plant heights of control, As(III)' and Sb(III) were all significantly different (control>Sb(III)>As(III)).

2.4.1.3 Number of Leaves

Figure 2.9 shows the number of leaves results comparing the control, amendment with As (3 and 5) and Sb (3 and 5) for long-term experiments and only the (III) species with control for the short-term experiment. There were statistically significant differences between the control, As, and Sb amendments F (7,60) = 25.78, p=0.0005 and between lengths of amendments F (2,22) = 38.077, p=0.0005, but there were no interaction effects between the two factors.A Tukey post hoc test revealed a significantly less

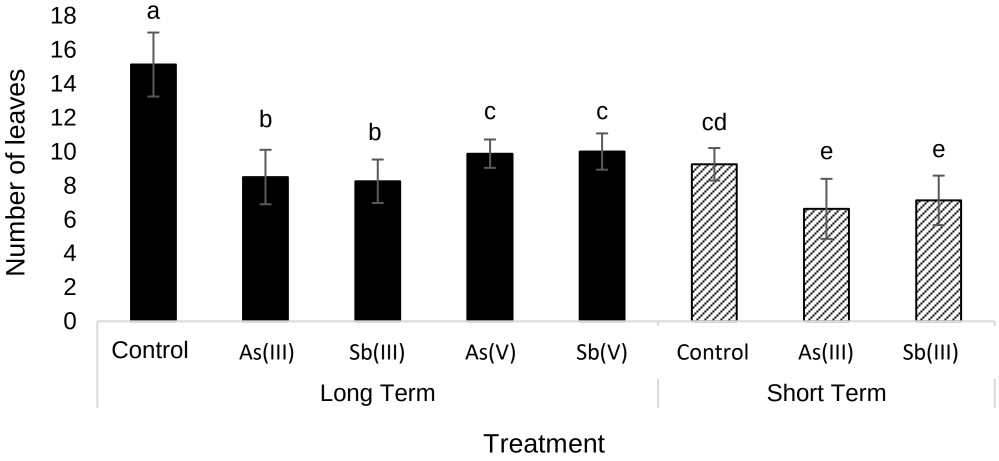


Figure 2. 8. Effect of As and Sb species amendment in the number of leaves among: (1) 5 treatments; (a) control, (b) As(III) (c) Sb(III) (d) As(V) and (e) Sb(V) and the (2) length of amendment; (a) long-term (38 days), (b) short-term (2 days) (a). Data presented are means ± SD, Bars marked with the same lower-case letters within the treatment are not significantly different at *p* < 0.05.

number of leaves between cucumber plants subjected to As and Sb amendments than the control plants for short- and long-term treatments. It appears that the As and Sb amendments significantly reduced the formation of leaves of the plants compared to the control plants. As(III) and Sb(III) amendments showed a statistically lower number of leaves than the As(V) and Sb(V) species in the long-term experiment. There were no statistically significant differences between group means as determined by one-way ANOVA in long experiment F (4,35) = 32.248 p=0.0005 and short experiment F (2,17) = 3.982 p=0.038.

2.4.1.4 Number of Flowers

Figure 2.10 shows the number of flower results comparing the 76control and plants received amendment with As ((III) and (V) species) and Sb ((III) and (V) species) for a long-term experiment.

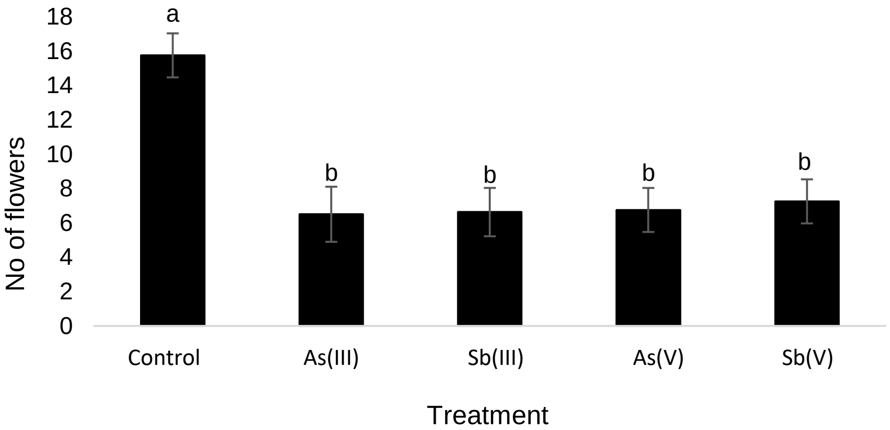


Figure 2. 9. Effect of As and Sb species amendment in the number of flowers among: (1) 5 treatments; (a) control, (b) As(III) (c) Sb(III) (d) As(V) and (e) Sb(V) for long-term (38 days). Data presented are means ± SD (n=4). Bars marked with the same lower-case letters within the treatment are not significantly different at *p* < 0.05.

The test was not measured in the short-term experiments since there were no flowers at 38 dat plants. There was a statistically significant difference between the control, As, and Sb amendments F (2, 4) = 68.3, p=0.0005 but no significant differences between the (III) and (V) both for As and Sb amendments. A Tukey post hoc test revealed a significantly lower number of flowers between cucumber plants subjected to As and Sb amendments than the control. This result showed that As and Sb amendments significantly affected flowers' formation regardless of the species.

2.4.1.5 Foliar Chlorophyll

The Foliar chlorophyll of the plants collected from the hydroponic experiments is shown in Figure 2.11 as a function of the metalloid treatments. It shows the plant foliar chlorophyll count results comparing the control, and plants received amendment with As (III) and (V) and Sb (III) and (V) for long-term experiments.

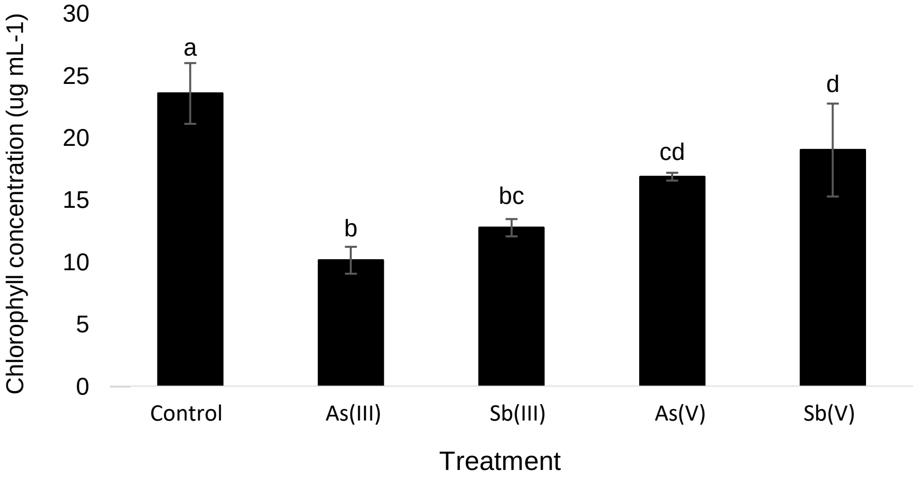


Figure 2. 10. Effect of As and Sb species amendment in the leaf chlorophyll content among (1) 5 treatments; (a) control, (b) As(III) (c) Sb(III) (d) As(V) and (e) Sb(V) for long-term (38 days), Data presented are means ± SD (n=4), Bars marked with the same lower-case letters within the treatment are not significantly different at $p < 0.05$.

There was a statistically significant difference between the control, As, and Sb amendments F (4,15) = 25.535, p=0.0005. A Tukey post hoc test revealed a significantly higher chlorophyll count in the control plant than cucumber plants subjected to As and Sb amendments. This result showed that As and Sb amendments significantly affected chlorophyll formation.

2.4.1.6 Biomass

Figure 2.12a shows the plant dry biomass results comparing the control and plants with As ((III) and (V)) and Sb ((III) and (V)) for long-term experiments and amendment with only the (III) species with control for the short-term experiment.

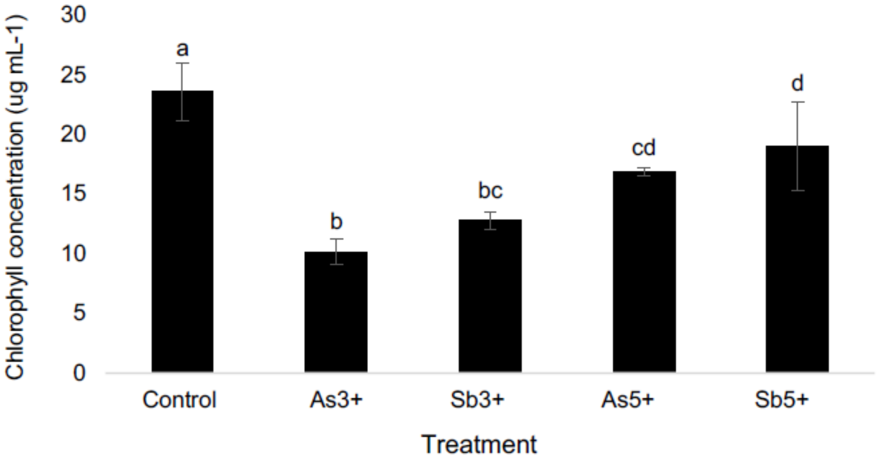


Figure 2. 11. Effect of As and Sb species amendment in the dry biomass (top) and fresh biomass (bottom) among: 1) 5 treatments; (a) control, (b) As(III) (c) Sb(III) (d) As(V) and (e) Sb(V) and the (2) length of amendment; (a) long-term (38 days), (b) short-term (2 days) (a). Data presented are means ± SD (n=4). Bars marked with the same lower-case letters within the treatment are not significantly different at *p* < 0.05. Y-axis is on different scales for short and long-term amendments.

Overall, there was a significant decrease in the dry biomass between the short and long-term experiments, F (1, 14) = 14.18, p=0.002, and a significant interaction between duration and treatments F(2,8)= 21.67, p=0.001.

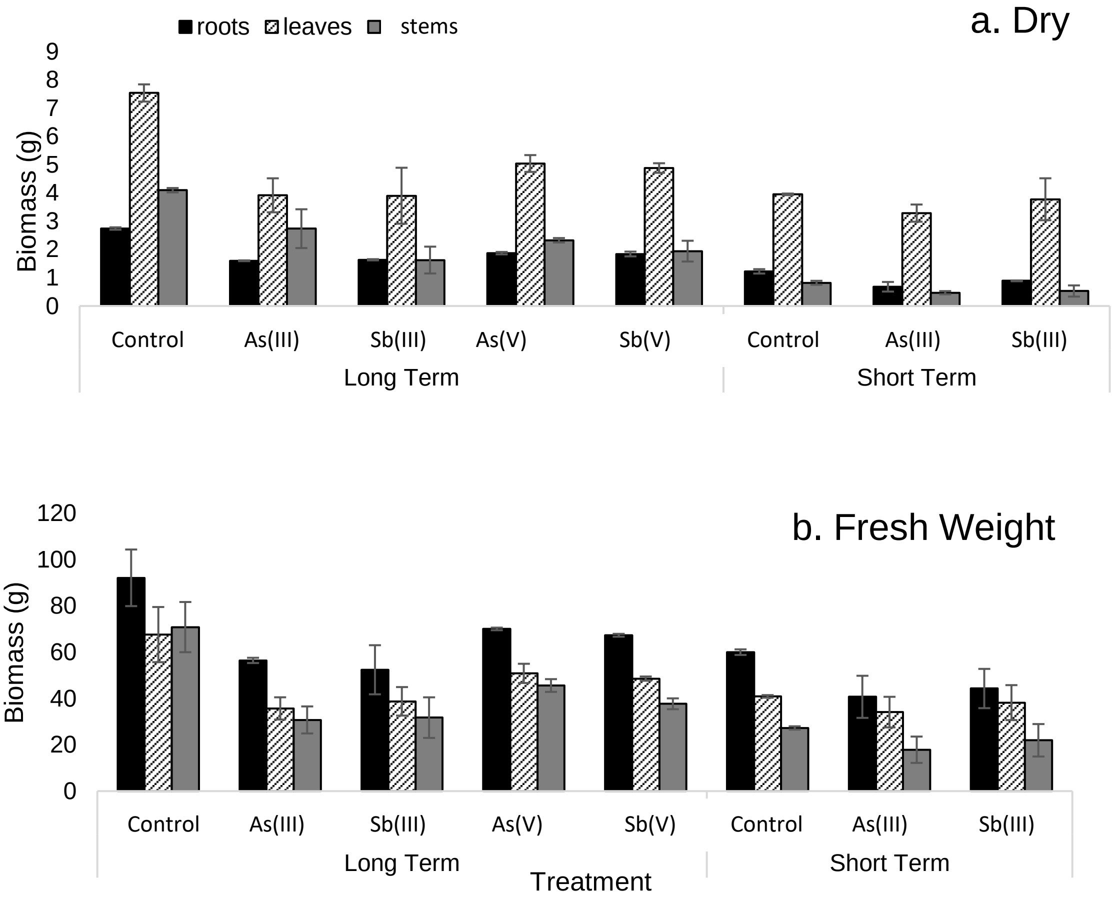


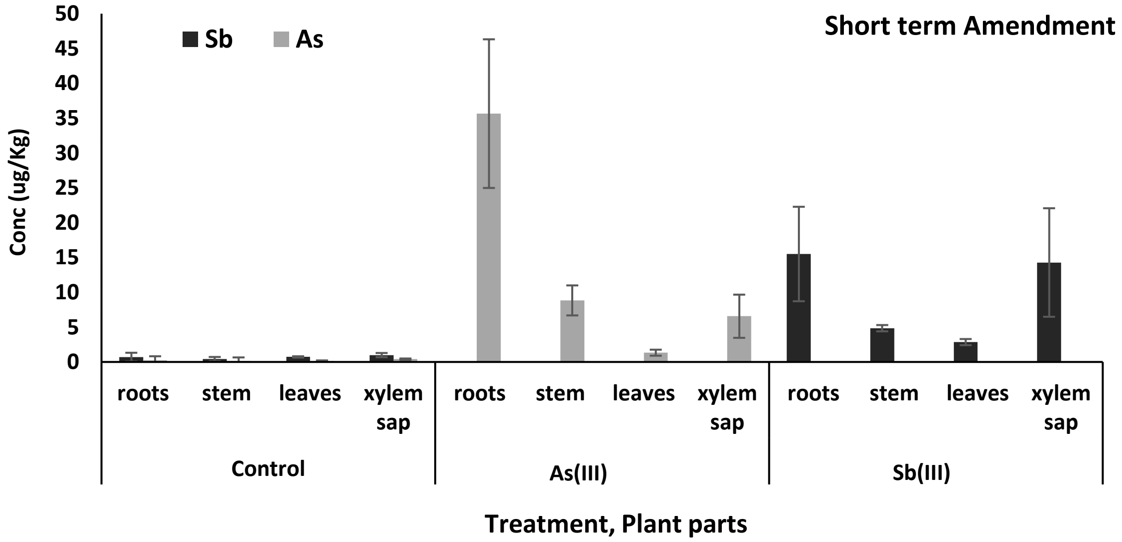
Figure 2. 12. Effect of As and Sb species amendment in the dry biomass (top) and fresh biomass (bottom) in the plant parts: roots, stems and leaves: 1) 5 treatments; (a) control, (b) As(III) (c) Sb(III) (d) As(V) and (e) Sb(V) and the (2) length of amendment; (a) long-term (38 days), (b) short-term (2 days) (a). Data presented are means ± SD (n=4), Y-axis are in different scales for short- and long-term amendments.

In the long-term experiment, there were statistically significant differences between control, (III) species, and (V) species (both for As and Sb) F(4,5) = 27.26, P=0.002. On the other hand, there was no significant difference between control, As(III)' and Sb(III) in the short-term experiment, F (2,3) = 3.160, p=0.183. Figure 2.13b shows the fresh weight plant biomass results comparing the control and plants with the amendment with As ((III) and (V)) and Sb ((III) and (V)) for long-term experiments and amendment (III) species with control for the short-term experiment. There was statistically significant lower biomass between the control, As and Sb amendments F (7,16) = 38.50, p=0.0005 and between lengths of amendments F (1,16) = 132.85, p=0.0005. There was an interaction effect between the two factors. A Tukey post hoc test revealed a significantly lower root mass between cucumber plants subjected to As and Sb amendments compared to the control plants for short and long-term treatments. Figure 2.13 shows the As and Sb species' effect in biomass categorised per plant parts. It shows that leaves have the highest biomass, followed by stems and, lastly, the roots.

2.4.2 Total Sb and As in cucumber plants

This study's Certified Reference Material (CRM) was NIST 1537a (Tomato leaves). The result of total Sb and As were satisfactory with 66.9 ± 2.6 ug Kg^{-1} and 117.7 ± 1.4 ug Kg^{-1}, respectively, although higher than the certified value of 61.9 ± 3.2 and 112.6 ± 2.4 ug Kg^{-1}, respectively. The difference might be due to oxidizing organic compounds in the samples or some interferences from carbon enhancing effect on the As and Sb signals in the ICP-MS (Larsen and Stürup, 1994; Pettine et al., 2007). However, this would not affect the interpretation of the results. Figure 2.14 presents the results of the total As and Sb concentrations in dry matter (d.m) of roots, stems, leaves, and xylem saps after (1) short amendment duration (2d) with As(III) and Sb(III) and control and (2) long amendment duration (38d) with As(III), Sb(III), As(V) and Sb(V), and a control. Cucumber samples subjected to a more extended amendment have higher As and Sb concentrations than the short-term experiments. The As and Sb found in the control plants was due to the low-sub ppb levels of As and Sb from the salts used in the hydroponic nutrient solution for plant feeding.

The highest As and Sb concentrations in the control plants for short and long amendment experiments are less than 1 ppb and less than 7 ppb, respectively. As and Sb concentrations in the plant parts decrease in the following order: roots > stem >= leaves for both short and long-term experiments. In the long-term experiments, the As and Sb concentrations in the plant parts are higher when amended with the trivalent species (As(III) > As(V) and Sb(III) > Sb(V)). When comparing the concentration of As and Sb in the plant parts, higher As concentrations were observed in the roots, stems, and leaves when the nutrient solutions are amended with the trivalent species while, when amended with the pentavalent species, concentrations of As and Sb in the plant parts are similar. However, in the sap, the concentration of Sb is higher than those of As either when comparing As(III)/Sb(III) or As(V)/Sb(V) uptake experiments both for the short



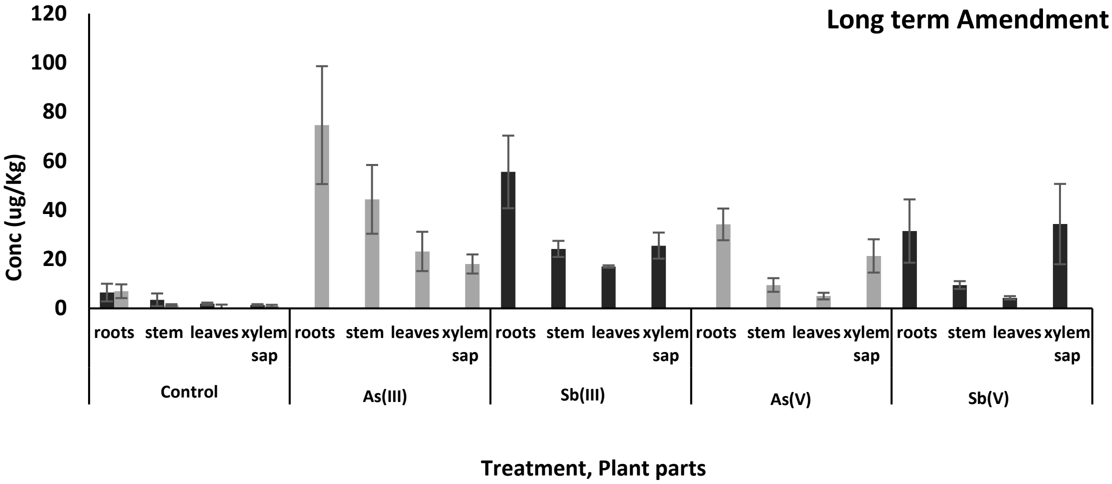


Figure 2. 13. As and Sb concentration of cucumber plants: (top) short-term (2 days) with 3 treatments; (a) control, (b) As(III) (c) Sb(III) and long-term (38 days), with 5 treatments; (a) control, (b) As(III) (c) Sb(III) (d) As(V) and (e) Sb(V) . Data presented are means ± SD (n=4), Y-axis are in different scales for short and long-term amendments.

term and long-term experiments. In the short-term experiment with trivalent species, As concentrations in the roots and stems are significantly higher than those of Sb, but in the leaves, Sb concentrations are higher than those of As.

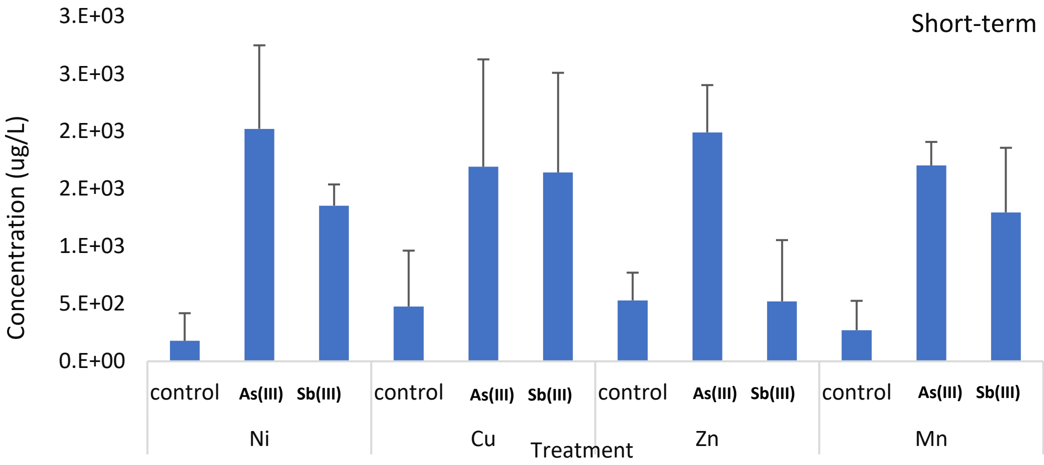
The ratio of average metal concentration in plant biomass to that in the soil/solution is defined as the bioaccumulation factor (BCF) (BCF=Ave. metal conc in plant parts/ metal conc in soil or solution), and translocation factor (TF), is the ratio of metal concentration in aerial parts at different treatments (TF 1=conc stems/conc roots)(Raskin et al., 1994; Wan et al., 2013; Takarina and Pin, 2017) or from shoot to the leaves ((TF 2=conc leaves/conc stems) (Wang et al., 2014).

Table 2. 3. Translocation Factor for As and Sb in hydroponically grown cucumber plants.

Duration	Metalloid	BCF[a]	TF 1[b]	TF 2[c]
Short-Term	As(III)	0.09	0.25	0.40
	Sb(III)	0.05	0.31	0.18
Long-Term	As(III)	0.44	0.59	0.41
	As(V)	0.10	0.28	0.15
	Sb(III)	0.24	0.44	0.31
	Sb(V)	0.11	0.30	0.14

[a] BCF = Ave. metal conc in plant (roots + stems + leaves) / soil or solution)
[b] TF 1 = metal conc in stems/metal conc in roots
[c] TF 2 = metal conc in leaves/metal conc in stems

Overall, the translocation factors between roots and stems (column TF 1, Table 2.3) are all below 1. In TF1, the highest is 0.59 for long-term treatment, and the lowest is 0.25 for the short-term for the As(III) treatment (Table 2.3). It can be observed that the translocation factor for As and Sb treatments are generally higher in the long-term compared to the short-term (TF long > TF short) both for shoot/roots and leaves/stems. In the short-term experiments, TF 1 for the Sb(III) amendment is 0.31, slightly higher than that for As (0.25). The opposite is seen in the long-term experiment; for the III species, the TF values of As is higher than Sb, but for V, As and Sb translocation factors are almost equal. Comparing the two metalloids, the III species are higher than V species, for both metalloids (TF As(III) > Sb(III) > As(V) = Sb(V)). The BCF ranges from 0.05 for ST Sb(III) up to 0.44 for LT As(III). The BCF for the trivalent species both for As and Sb are higher than the pentavalent both for the short and long-term experiments.



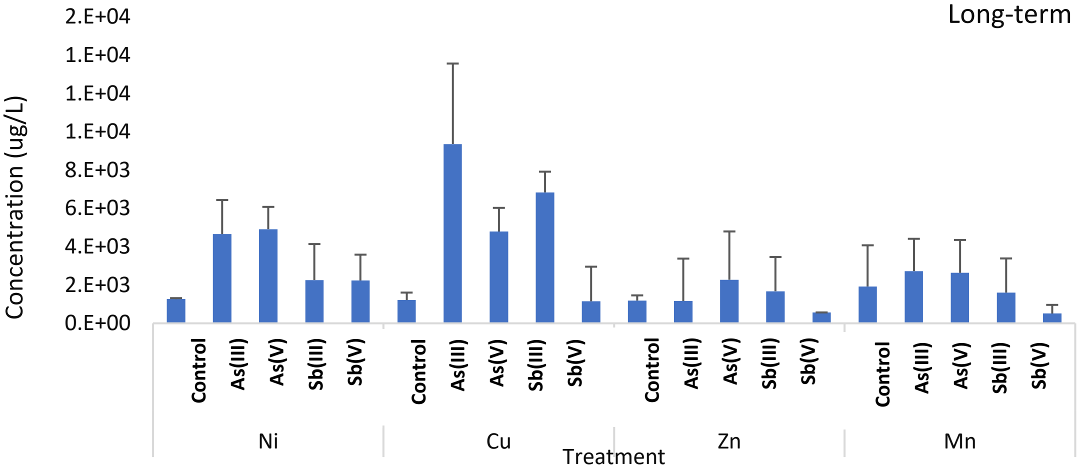
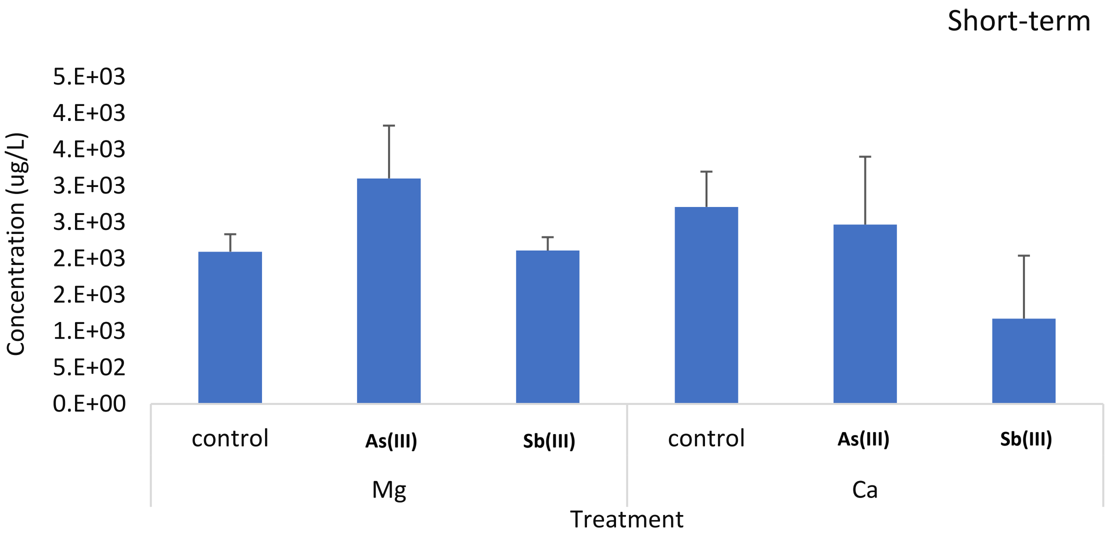


Figure 2. 14. Micronutrients composition of whole cucumber plants among: (top) short-term (2 days) with 3 treatments; (a) control, (b) As(III) (c) Sb(III) and (bottom) long-term (38 days), with 5 treatments; (a) control, (b) As(III) (c) Sb(III) (d) As(V) and (e) Sb(V) . Data presented are means ± SD (n=4). Y-axis are in different scales for short and long-term amendments.

The micro and macronutrients are presented in Figures 2.15 and 2.16, respectively, as a function of (1) duration: short and long-term; and (2) metalloid species exposure ((III) and (V)). These nutrients were analysed together with the Sb and As an analysis by ICP-MS of the digested plant samples. Control plants have nutrient content lower than the exposed to metalloids based on the results. Short-term exposure to metalloids shows much lower concentrations of a nutrient than exposure to the metalloids in the long-term, both for the micro and macronutrients.



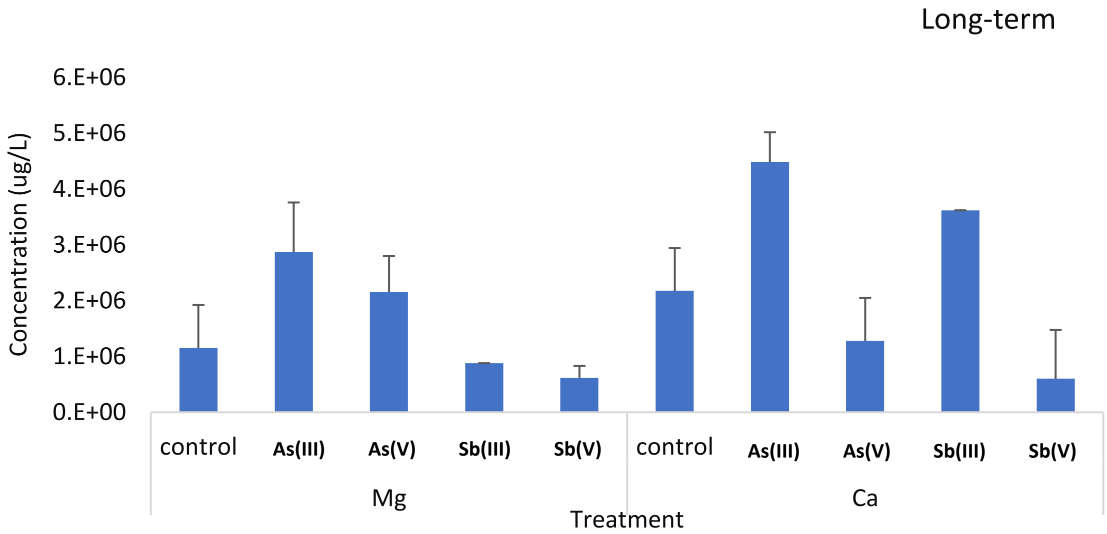


Figure 2. 15. Macronutrients composition of whole cucumber plants among: (top) short-term (2 days) with 3 treatments; (a) control, (b) As(III) (c) Sb(III) and (bottom) long-term (38 days), with 5 treatments; (a) control, (b) As(III) (c) Sb(III) (d) As(V) and (e) Sb(V) . Data presented are means ± SD (n=4). Y-axis are in different scales for short and long-term amendments.

2.4.3 Pearson correlation and principal component analysis (PCA)

In general, absorption of As, Sb, and micro and macronutrients were higher in long-term exposure than the short-term. To observe the changes of the micro (Ni, Cu, Zn, and Mn) and macronutrients (Ca and Mg) as a function of Sb and As stress in the cucumber plant, a Pearson product correlation coefficient was computed. The interaction of Sb (III) and (V) with micronutrients Ni, Cu, Zn, and Mn has a statistically significant linear positive relationship with Sb ($p < 0.001$), meaning that higher Sb concentration is associated with higher micronutrients concentrations (Ni, Cu, Zn, and Mn). In terms of the effect of Sb on macronutrients, Mg has a statistically linear relationship with Sb ($p < .001$), and the direction is negative (the lower Mg concentration is associated with higher Sb concentration). Ca is positively correlated with Sb but not statistically significant at $p < 0.05$.

On the other hand, micronutrients Ni, Cu, and Mn have a statistically significant positive linear relationship with As ($p < 0.001$) and so is Zn but to a less significance ($p < 0.05$), meaning that higher As concentration is associated with higher micronutrients concentrations (Ni, Cu, Zn, and Mn). Mg has a statistically linear relationship with As ($p < 0.05$), and the direction is negative (the lower Mg concentration is associated with higher As concentration). Both Ca, and Fe are positively correlated with As, however not statistically significant at $p < 0.05$.

For the Sb correlations with micronutrients (i.e. Ni, Cu and Zn) among such significant positive correlations, Sb and Cu ($r = 0.617$), Sb and Zn ($r = 0.603$), and Sb and Ni ($r = 0.354$) have been recorded at $p < 0.001$. On the other hand, for the correlation of As with micronutrients, a mild positive correlation was observed, As with Ni (r=0.395), Cu (r=0.273), Zn (r=0.227), and Mn (0.272), all significant at $p < 0.001$). In terms of macronutrients, As has a negative correlation with Ca and Mg.

Moreover, PCA analyses were done to further explain the correlation. The PCA analysis for the long-term experiment yielded three significant components with eigenvalues higher than 1.00, accounting for a total of 87.93 % of the data variation (Table 2.4). The first principal component (PC1), which contained 60.45% of the calculated variance, showed a strongly positive load for Ni, Cu, Pb, Mn, Ca and As but moderately for Zn. Moreover, PC1 showed a moderately negative load for Mg.

Table 2. 4. **Principal component analysis for short-term cucumber plant experiment**

Heavymetals	PC1	PC2	PC3
Ni	0.985	-	-
Cu	0.980	-	-
Zn	0.652	0.637	-
Pb	0.988	-	-
Mn	0.937	-	-
Fe	-	-	-0.835
Mg	-0.483	-0.462	0.546
Ca	0.887	-	-
Sb	-	0.938	-
As	0.868	-	-
Proportion of variances (%)	60.45	15.94	11.54
Cumulative proportion of variances (%)	60.45	76.39	87.93

Note: factor loadings < than 0.4 removed, extraction method: PCA, rotation method: Varimax and Kaiser normalization

On the other hand, the PCA analysis for the short-term experiment yielded three significant components with eigenvalues higher than 1.00, accounting for a total of 71.82 % of the data variation (Table 2.5). The first principal component (PC1), which contained 37.26% of the calculated variance, showed a strongly positive load for Ni, Cu, Pb, Mn, Ca and As but moderately for Zn. Moreover, PC1 showed a moderately negative load for

Mg. Both the long term and short term have a positive load for Ni, Cu, Pb, Mn, Ca, and As. The only difference is that there was a positive load for Zn and the negative load for Mg in the short-term experiment.

Table 2. 5. Principal component analysis for long-term cucumber plant experiment

Heavy metals	PC1	PC2	PC3
Ni	0.848	-	-
Cu	0.949	-	-
Zn	-	0.829	-
Pb	0.656	0.618	-
Mn	0.701	-	-
Fe	-	-	-
Mg	-	-	0.471
Ca	0.774	-	0.487
Sb		-0.464	-0.667
As	0.426	-0.480	-0.420
Proportion of variances (%)	37.26	19.05	15.51
Cumulative proportion of variances (%)	37.26	56.31	71.82

Note: factor loadings < than 0.4 removed, extraction method: PCA, rotation method: Varimax and Kaiser normalization

Plant physiological parameters were significantly affected by the presence of Sb and As ((III) or (V)) in the nutrient solution (100 ppb). Based on the correlation results and the PCA analysis, when a plant is exposed to metalloids like As or Sb (III or V), plant reacted by uploading or downloading of the micronutrients needed to suppress the toxic effects of the metallloids in the system.

2.5 Discussions and Conclusions

High metal(loids) concentrations (i.e., Sb and As) in soils, vegetables, and crops can cause a potential health risk. However, the effect of Sb on the growth and response of crops is not well known, and to date, there is still no Sb limit or standard. Most of the studies available in the literature studied the metal uptake in plants using high concentration levels (or many times higher levels found in contaminated groundwater). There is still a significant gap in Sb toxicity, translocation, and speciation in plants. It is crucial to better understand exposure duration and different metalloid As and Sb species on crops as part of food safety. The study may have practical importance to areas were As, and Sb contamination exceeds the recommended Sb and As levels by the EU for drinking water (and WHO) 5 and 10 ug/mL (Materials, 1989; WHO, 2003a; FAO and WHO, 2019)

The hypothesis for this research is that: (1) cucumber plant reacts more negatively to the (III) species for both Sb and As compared to the (V) species, (2) the longer the amendment, the more accumulation of the metalloids in the cucumber plants and (3) micro and macronutrients in the plants will vary as plant defense in counteracting As and Sb translocation in plants.

The effect of Sb and As in terms of plant physiology, uptake, translocation, and the changes of the micro and macronutrients in the plant under Sb and As stress were investigated. This chapter aimed to explore the effect of Sb and As on the cucumber (*Cucumis Sativa L.)* in a hydroponic experiment.

Hydroponics is a subset of hydroculture, used to grow plants without soil using nutrient solutions in a water solvent (Trejo-Téllez, 2012). Hydroponics was used in uptake trial experiments because of the advantage of designing and controlling what is in the nutrient solution. Furthermore, reliable morphological and chemical analysis of roots and other parts of the plants' translocation studies are possible using hydroponic experiments. The cucumber was chosen because of the large amount of xylem sap collected. Xylem sap investigation has a pivot role in the nutrient and toxic elements transportation from the roots to stems and has the advantage of minimal preparation (Clark et al., 1973; Biles and Abeles, 1991; Tatár et al., 1998; Schurr, 1999). According to Küpper and Andresen (2016) most of the published studies were performed under an artificially high metal concentration since this never occurs even in highly polluted sites, and the exposure time of the toxic metal is too short to see the long-term effect. The chosen concentration of 100 ppb (ug L^{-1}) for As and Sb concentration was based on the studies of Mihucz et al. (2005) and Varsányi et al. (1991). Long-term exposure (38 d) of the metalloids was incorporated with the short-term exposure (2 d) to quantify the effect of more prolonged exposure, as mentioned earlier. Plant growth aimed to explore the physiological effect of the treatments composed of leaf area, plant height, number of leaves, biomass, root mass (dry and fresh wet), number of flowers, and chlorophyll.

The physiological experiments revealed that, in general, there was a significant reduction of the parameters mentioned above (i.e., plant height, number of leaves) compared to the cucumber plant without metalloid amendments both in the short and long experiments. In this study, even a small amount of Sb or As has been allowed to expose to the plants, and these detrimental effects can still be seen in the plant growth. This means that there is a considerable reduction of growth in the plants that are exposed to As or Sb compared to the control plants. The control cucumber plant samples appeared visually healthy and showed the highest plant growth parameters compared to the plants with the As and Sb amendment for all treatments.

Plant growth analyses were used to observe the physiological effects of As and Sb amendments and exposure duration and the species used for both metalloids (III) and (V) species on cucumber plants. According to Hunt et al. (2002), plant growth experiments offer an integrative approach to interpret plant physiological functions when the plant is under stress compared to a control. It uses primary data (i.e., weights, volume, areas) of the plants' contents for investigating processes within the whole plant exposed to individual variables or stimuli.

According to Emamverdian et al. (2015), bioaccumulation of heavy metal in the plant interacts with the cellular biomolecules such as DNA and nuclear proteins in the plants leading to an excessive increase of the reactive oxygen species (ROS). This has serious adverse effects on the plant, such as morphological, metabolic, and physiological irregularities in the plant from chlorosis of stem to lipid peroxidation and protein degradation (Garg and Singla, 2011; Bielen et al., 2013; Kumar et al., 2015; Ghori et al., 2019). Essential nutrients (i.e., micro and macro) play a vital role in plant metabolism and structure. However, the concentration of both the essential and non-essential metals is an important factor in the plant's growth processes, can reduce and inhibit plant growth (Zengin and Munzuroglu, 2005). Heavy metals at a toxic level in plants inhibit the plant's normal processes such as disturbance or displacement of building blocks of protein structure by bonding with sulfhydryl groups (Hall, 2002), deterring functional groups of important cellular molecules (Hossain et al., 2012), disrupting the functions of essential metals in biomolecules such as pigments or enzymes (Farid et al., 2013), and negatively affecting cytoplasmic membrane integrity (Ali et al., 2013). This results in the suppression of vital plant's processes such as photosynthesis, respiration, metabolic, and enzymatic processes (Hossain et al., 2012). Because high levels of HM are associated with reactive oxygen species (ROS), (i.e., superoxide free radicals ($O_2^{\bullet --}$), hydroxyl free radicals ($OH^{\bullet --}$), or non-free radical species (singlet oxygen, O_2*), hydrogen peroxide (H_2O_2) and cytotoxic compounds (methylglyoxal (MG)), cause oxidative stress in plant cells via disturbing the equilibrium between prooxidant and antioxidant homeostasis (Hall, 2002; Zengin and Munzuroglu, 2005; Hossain et al., 2012). According to Clarkson, (1996), xylem sap is mainly an aqueous solution composed of millimolar concentrations of Ca, Mg, K, nitrate, phosphates, amino and carboxylic acids. Furthermore, small molecules like amino acids (Oda et al., 2005), carboxylic acids, and organic acids (Mihucz et al., 1998) are the principal metal-binding ligands in xylem sap in plants (Clarkson, 1996; Correia et al., 2006; Satoh, 2006).

Leaf area growth is an essential parameter in determining plant productivity. It also determines light interception in plants (Koester et al., 2014). Leaf area was also negatively affected by heavy metal treatment. In the study of bean plants, there is a significant negative effect of As its growth, including leaf area (Stoeva et al., 2005). After exposing the plant to As or Sb, chlorophyll reductions were also observed in maize plants studied by Rosas-Castor et al. (2014). Chlorophyll count was used to monitor plants' physiological stress status under abiotic stress (Kalaji et al., 2016). Moles et al. (2009) found that plant height is strongly correlated with life span, seed mass, and time to maturity. It is one of the central plant ecological strategies and a significant determinant of species ability to compete for light. Growth rate and photosynthetic pigments were negatively affected by As in water lettuce (*P. Stratiotes*) (Farnese et al., 2014). Furthermore, it is also related to carbon storage capacity and critical ecosystem variables.

Depending on plant species, As (Sb or other metals), tolerance may result from either exclusion or accumulation (Zhang et al., 2002). The exclusion strategy is the restriction of As transport from roots to stems or As uptake avoidance (Dushenkov, 2003). As the name implies, the accumulation strategy involves accumulation or concentration of As in plant tissues. To determine this, a bioaccumulation factor was used to calculate the content of heavy metals in plants (i.e., stem, leaves) divided by heavy metals in sediments or solution (Carolyn et al., 2014; Zhou et al., 2018). The Sb and As concentration are highest in roots, followed by stems and leaves. These results are similar to Uroic (PhD thesis, 2011) that roots may release ligands, which might complex arsenite or arsenate. This may explain the higher concentrations in the cucumber roots than stems and leaves.

Furthermore, in the same study done by Uroic (2011), the release of ligands in roots to complex As can be another detoxification strategy of plants. Once the As was complexed by ligands (i.e., phytochelatin, PC), PC-As is not available in a form to be taken up by aquaporin channels, which is the proposed of entry into roots. PC are low molecular weight (l.m.w) and glutathione-derived peptide and can be found in root cells (Pickering et al., 2000; Raab, Meharg, et al., 2004; Raab et al., 2005). Up to know, only PC-As complexation is the only mechanism known and responsible for the inorganic As (or Sb) translocation from roots to stems and even in fungi and other organisms (Cai et al., 2004; Raab, Feldmann, et al., 2004; Yadav, 2010; Ji et al., 2017; Shri et al., 2019)

Based on this study's results, there are correlations between metals (i.e., micro and macronutrients) in the plants as a function of As or Sb treatments. The interaction of nutrients was also observed by Farnese et al., (2014), where *Pistia stratiotes* were exposed to different As concentrations, and the influence of this metalloid on growth, mineral nutrition and photosynthesis were analysed. There was an increase in the Cu, Mn, Fe, and P uptake until the As concentration reached 13 uM, and decreased in higher concentrations. The Mg decreased in the same concentration, but no effects in the uptake of K, Ca, and Zn was observed.

The change in nutrients uptake and maintenance of growth in the *P. Stratiotes* indicates the resistance of the plant to the pollutant by an increase in antioxidant capacity of the plant even the As concentrations are up to one hundred times greater than the permissible limit, making it an efficient phytoremediator of As (Farnese et al., 2014).

Plants require 14 essential elements, both macro, and micronutrients, for successful growth, development (i.e., vegetative and reproductive) (Samota et al., 2017). These are obtained from the soil, absorbed through the roots, and absorbed and distributed within various parts of the plants (Frantz and Epstein, 2005; Tsukagoshi and Shinohara, 2015; Samota et al., 2017). Macronutrients (i.e., nitrogen (N), potassium (K), phosphorus (P), calcium (Ca), magnesium (Mg), and sulfur (S)) are generally found in plants in concentrations higher than 0.1% of dry weight.

There is a link between plant defence mechanism and heavy-metal chelators such as phytochelatin (PC) or metallothioneins (MT), however, there is no clear evidence yet on how they act either synergistically or antagonistically concerning plant antioxidant system during metal toxicity (Emamverdian et al., 2015). The plant responds to metal contamination, accordingly, depending on how they respond upon absorption and translocation. Plants can be classified as (a) accumulators when a plant can accumulate metals in above-ground parts regardless of soil concentration; (b) indicators, when uptake and transport increase as a function of soil content; or (c) excluders when plant maintain the elemental concentration in the shoot constantly over a wide range of soil-metal contents (Baker, 1981; Sabir et al., 2015; Shahid et al., 2015; Takarina and Pin, 2017). Hyperaccumulator plants can be used in phytoremediation strategies to uptake toxic metals' contaminated soil. It may also be used as a geobotanical indicator of mineral deposits (Massoura et al., 2004). Based on the results of this study, cucumber plants' translocation factor and bioconcentration factor for As(III)/As(V) and Sb(III)/Sb(V) were all less than 1, indicating that neither it is hyperaccumulator nor excluder. This is the reason why the cucumber plant was chosen as a model plant for this study to observe the plant uptake in the presence of metalloids.

2.6 References

Abedin, M. J., Feldmann, J. and Meharg, A. A. (2002) ‘Uptake kinetics of arsenic species in rice plants.’ *Plant Physiology*, 128(3) pp. 1120–1128.

Ainsworth, N., Cooke, J. A. and Johnson, M. S. (1990) ‘Distribution of antimony in contaminated grassland: 1- vegetation and soils.’ *Environmental Pollution*. Elsevier, 65(1) pp. 65–77.

Ainsworth, N., Cooke, J.A. and Johnson, M. S. (1990) ‘Distribution of antimony in contaminated grassland: 2— small mammals and invertebrates.’ *Environmental Pollution*. Elsevier, 65(1) pp. 79–87.

Alexou, M. and Peuke, A. D. (2013) *Plant Mineral Nutrients*. Maathuis, F. J. M. (ed.) *Plant Mineral Nutrients*. Totowa, NJ: Humana Press (Methods in Molecular Biology).

Ali, H., Khan, E. and Sajad, M. A. (2013) ‘Phytoremediation of heavy metals—Concepts and applications.’ *Chemosphere*, 91(7) pp. 869–881.

Althobiti, R. A., Sadiq, N. W. and Beauchemin, D. (2018) ‘Realistic risk assessment of arsenic in rice.’ *Food Chemistry*. Elsevier Ltd, 257, August, pp. 230–236.

Álvarez-Fernández, A., Díaz-Benito, P., Abadía, A., And, A.-F. L.-M. and Abadía, J. (2014) ‘Metal species involved in long distance metal transport in plants.’ *Frontiers in Plant Science*, 5(1) p. 105.

Amarasiriwardena, D. and Wu, F. (2011) ‘Antimony: Emerging toxic contaminant in the environment.’ *Microchemical Journal*. Elsevier B.V., 97(1) pp. 1–3.

Ammann, A. A. (2011) ‘Arsenic Speciation Analysis by Ion Chromatography - A Critical Review of Principles and Applications.’ *American Journal of Analytical Chemistry*, 2011(February) pp. 27–45.

Anawar, H. M., Freitas, M. C., Canha, N. and Regina, I. S. (2011) ‘Arsenic, antimony, and other trace element contamination in a mine tailings affected area and uptake by tolerant plant species.’ *Environmental Geochemistry and Health*, 33(4) pp. 353–362.

Aposhian, H. V. and Aposhian, M. M. (2006) ‘Arsenic Toxicology: Five Questions.’ *Chemical Research in Toxicology*, 19(1) pp. 1–15.

Arnold, L. L., Eldan, M., Nyska, A., van Gemert, M. and Cohen, S. M. (2006) ‘Dimethylarsinic acid: Results of chronic toxicity/oncogenicity studies in F344 rats and in B6C3F1 mice.’ *Toxicology*, 223(1–2) pp. 82–100.

Arunakumara, K. K. I. U., Walpola, B. C. and Yoon, M.-H. (2013) ‘Current status of heavy metal contamination in Asia’s rice lands.’ *Reviews in Environmental Science and*

Bio/Technology, 12(4) pp. 355–377.

Ashbrook, P. C. (2014) 'Standard Operating Procedures.' *Journal of Chemical Health and Safety*, 21(5) p. 29.

Ashley, P. M., Graham, B. P., Tighe, M. K. and Wolfenden, B. J. (2007) 'Antimony and arsenic dispersion in the Macleay River catchment, New South Wales: a study of the environmental geochemical consequences.' *Australian Journal of Earth Sciences*, 54(1) pp. 83–103.

ATSDR - Environmental Medicine & Environmental Health Education - CSEM (2013) 'Arsenic Toxicity Case Study: What Are the Standards and Regulation for Arsenic Exposure?' *Encyclopedia of Metalloproteins* pp. 143–143.

Awika, J. M. (2011) 'Major cereal grains production and use around the world.' *In ACS Symposium Series*, pp. 1–13.

Bach, C., Dauchy, X., Chagnon, M. C. and Etienne, S. (2012) 'Chemical compounds and toxicological assessments of drinking water stored in polyethylene terephthalate (PET) bottles: A source of controversy reviewed.' *Water Research*, 46(3) pp. 571–583.

Baker, A. J. M. (1981) 'Accumulators and Excluders - Strategies in the Response of Plants to Heavy Metals.' *Journal of Plant Nutrition*, 3(1–4) pp. 643–654.

Bakhtiari, A. R., Zakaria, M. P., Yaziz, M. I., Lajis, M. N. H. L. and Bi, X. (2014) 'Environment Asia.' *Environment Asia*, 7(1) pp. 104–111.

Basta, N. T. (2006) 'Heavy Metal Contamination of Soil.' *Soil Science Society of America Journal*, 70(5) p. 1819.

Bastías, J. M. and Beldarrain, T. (2016) 'Arsenic translocation in rice cultivation and its implication for human health.' *Chilean Journal of Agricultural Research*. Instituto de Investigaciones Agropecuarias, INIA, 76(1) pp. 114–122.

Bellido-Martín, A., Gómez-Ariza, J. L., Smichowsky, P. and Sánchez-Rodas, D. (2009) 'Speciation of antimony in airborne particulate matter using ultrasound probe fast extraction and analysis by HPLC-HG-AFS.' *Analytica Chimica Acta*, 649(2) pp. 191–195.

Benedict, S. R. (1908) *A Reagent For the Detection of Reducing Sugars*. *J. Biol. Chem*.

Bennett, J. O. and Sicher, R. C. (2011) 'Protein and metabolite composition of xylem sap from field-grown soybeans (Glycine max)' pp. 921–931.

Bhattacharya, P., Samal, a C., Majumdar, J. and Santra, S. C. (2009) 'Transfer of Arsenic from Groundwater and Paddy Soil to Rice Plant (Oryza sativa L.): A Micro-Level Study in West Bengal , India.' *World Journal of Agricultural Sciences*, 5(4) pp. 425–431.

Bi, Z. (2012) *Speciation analysis of trace metals in natural waters using vibrating electrodes*. *Environmental Sciences*. University of Liverpool.

Bielen, A., Remans, T., Vangronsveld, J. and Cuypers, A. (2013) 'The influence of metal stress on the availability and redox state of ascorbate, and possible interference with its cellular functions.' *International Journal of Molecular Sciences* pp. 6382–6413.

Biles, C. L. and Abeles, F. B. (1991) 'Xylem sap proteins.' *Plant Physiology*, 96(July 1991) pp. 597–601.

Billon, G. and Van Den Berg, C. M. G. (2004) 'Gold and silver micro-wire electrodes for trace analysis of metals.' *Electroanalysis*, 16(19) pp. 1583–1591.

Borovička, J., Řanda, Z. and Jelínek, E. (2006) 'Antimony content of macrofungi from clean and polluted areas.' *Chemosphere*, 64(11) pp. 1837–1844.

Bouman, B. A. . and Tuong, T. . (2001) 'Field water management to save water and increase its productivity in irrigated lowland rice.' *Agricultural Water Management*, 49(1) pp. 11–30.

Bowen, H. J. M. (Humphry J. M. (1979) *Environmental chemistry of the elements*. London, New York: Academic Press.

Brackin, R., Näsholm, T., Robinson, N., Guillou, S., Vinall, K., Buckley, S., Lakshmanan, P., Schmidt, S. and Inselsbacher, E. (2016) 'Microdialysis-a new technology for investigating soil nitrogen fluxes in the rhizosphere.' *In Proceedings of the International Nitrogen Initiative 2016 Conference*, pp. 4–8.

Brammer, H. and Ravenscroft, P. (2009) 'Arsenic in groundwater: A threat to sustainable agriculture in South and South-east Asia.' *Environment International*. Elsevier Ltd pp. 647–654.

Brihaye, C. and Duyckaerts, G. (1982) 'Determination of traces of metals by anodic stripping voltammetry at a rotating glassy carbon ring—disc electrode.' *Analytica Chimica Acta*, 143 pp. 111–120.

Broadley, M., Brown, P., Cakmak, I., Rengel, Z. and Zhao, F. (2011) 'Function of Nutrients: Micronutrients.' *In Marschner's Mineral Nutrition of Higher Plants: Third Edition*. Elsevier Inc., pp. 191–248.

Brochu, C., Wang, J., Roy, G., Messier, N., Wang, X.-Y., Saravia, N. G. and Ouellette, M. (2003) 'Antimony Uptake Systems in the Protozoan Parasite Leishmania and Accumulation Differences in Antimony-Resistant Parasites.' *Antimicrobial Agents and Chemotherapy*. American Society for Microbiology (ASM), 47(10) pp. 3073–3079.

Brown, S. D. and Kowalski, B. R. (1979) 'Pseudopolarographic Determination of Metal Complex Stability Constants in Dilute Solution by Rapid Scan Anodic Stripping

Voltammetry.' *Analytical Chemistry*, 51(13) pp. 2133–2139.

Buckley, S., Brackin, Richard, A. and Schmidt, S. (2016) 'Microdialysis-a sensitive method for estimating plant-available N released during litter decomposition.' *Proceedings of the International Nitrogen Initiative Conference 2016*, (December).

Buckley, S., Brackin, R., Jämtgård, S., Näsholm, T. and Schmidt, S. (2020) 'Microdialysis in soil environments: Current practice and future perspectives.' *Soil Biology and Biochemistry*, 143, April, p. 107743.

Buckley, S., Brackin, R., Näsholm, T., Schmidt, S. and Jämtgård, S. (2017) 'Improving in situ recovery of soil nitrogen using the microdialysis technique.' *Soil Biology and Biochemistry*, 114, November, pp. 93–103.

Buckley, S., Brackin, R. and Schmidt, S. (2015) *Microdialysis: an alternative approach to identifying plant-available nitrogen in soils*.

Burló, F., Guijarro, I., Carbonell-Barrachina, A. A., Valero, D. and Martínez-Sánchez, F. (1999) 'Arsenic Species: Effects on and Accumulation by Tomato Plants.' *Journal of Agricultural and Food Chemistry*, 47(3) pp. 1247–1253.

Cabalda, M. V, Banaag, M. A. and Garces, R. B. (2002) *Sustainable Development in The Philippine Minerals Industry: A Baseline Study*. M.V. Cabalda P.N.T. Tidalgo & R.B. Garces, M. A. B. (ed.) *Mining, Minerals and Sustainable Development Project (MMSD)*. England: International Institute for the Environment and Development (IIED).

Cai, Y., Su, J. and Ma, L. Q. (2004) 'Low molecular weight thiols in arsenic hyperaccumulator Pteris Vittata upon exposure to arsenic and other trace elements.' *Environmental Pollution*, 129(1) pp. 69–78.

Cal-Prieto, M. J., Carlosena, A., Andrade, J. M., Martínez, M. L., Muniategui, S., López-Mahía, P. and Prada, D. (2001) 'Antimony as a tracer of the anthropogenic influence on soils and estuarine sediments.' *Water, Air, and Soil Pollution*. Springer, 129(1–4) pp. 333–348.

Canadian Council of Ministers of the Environment (2007) *Canadian soil quality guidelines for the protection of environmental and human health*. Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment. Winnipeg. [Online] http://goo.gl/AePSg4.

Canepari, S., Marconi, E., Astolfi, M. L. and Perrino, C. (2010) 'Relevance of Sb(III), Sb(V), and Sb-containing nano-particles in urban atmospheric particulate matter.' *Analytical and Bioanalytical Chemistry*, 397(6) pp. 2533–2542.

Carey, A.-M., Lombi, E., Donner, E., de Jonge, M. D., Punshon, T., Jackson, B. P., Guerinot, M. Lou, Price, A. H. and Meharg, A. A. (2012) 'A review of recent developments in the speciation and location of arsenic and selenium in rice grain.' *Analytical and Bioanalytical*

Chemistry, 402(10) pp. 3275–3286.

Carneado, S., Hernández-Nataren, E., López-Sánchez, J. F. F. and Sahuquillo, A. (2015) ‘Migration of antimony from polyethylene terephthalate used in mineral water bottles.’ *Food Chemistry*. Elsevier Ltd, 166, January, pp. 544–550.

Carolyn, P., Aqilah, F. A. T., Payus, C., Farhana, A., Talip, A., Carolyn, P., Aqilah, F. A. T., Payus, C., Farhana, A. and Talip, A. (2014) ‘Assessment of heavy metals accumulation in paddy rice (Oryza sativa).’ *African Journal of Agricultural Research*. Academic Journals, 9(41) pp. 3082–3090.

Casiot, C., Ujevic, M., Munoz, M., Seidel, J. L. and Elbaz-Poulichet, F. (2007) ‘Antimony and arsenic mobility in a creek draining an antimony mine abandoned 85 years ago (upper Orb basin, France).’ *Applied Geochemistry*, 22(4) pp. 788–798.

Cavicchioli, A., La-Scalea, M. A., Gutz, G. R., Gutz, I. G. R. and Gutz, G. R. (2004) ‘Analysis and Speciation of Traces of Arsenic in Environmental , Food and Industrial Samples by Voltammetry : a Review.’ *Electroanalysis*, 16(9) pp. 697–711.

Chakraborti, D., Rahman, M. M., Das, B., Nayak, B., Pal, A., Sengupta, M. K., Hossain, M. A., Ahamed, S., Sahu, M., Saha, K. C., Mukherjee, S. C., Pati, S., Dutta, R. N. and Quamruzzaman, Q. (2013) ‘Groundwater arsenic contamination in Ganga–Meghna–Brahmaputra plain, its health effects and an approach for mitigation.’ *Environmental Earth Sciences*, 70(5) pp. 1993–2008.

Chang, C.-Y., Wang, C.-F., Mui, D. T. and Chiang, H.-L. (2009) ‘Application of methods (sequential extraction procedures and high-pressure digestion method) to fly ash particles to determine the element constituents: A case study for BCR 176.’ *Journal of Hazardous Materials*, 163(2–3) pp. 578–587.

Chapman, C. S. and Van Den Berg, C. M. G. G. (2007) ‘Anodic stripping voltammetry using a vibrating electrode.’ *Electroanalysis*, 19(13) pp. 1347–1355.

Chaurasia, C. S., Müller, M., Bashaw, E. D., Benfeldt, E., Bolinder, J., Bullock, R., Bungay, P. M., DeLange, E. C. M., Derendorf, H., Elmquist, W. F., Hammarlund-Udenaes, M., Joukhadar, C., Kellogg, D. L., Lunte, C. E., Nordstrom, C. H., Rollema, H., Sawchuk, R. J., Cheung, B. W. Y., Shah, V. P., Stahle, L., Ungerstedt, U., Welty, D. F. and Yeo, H. (2007) ‘AAPS-FDA workshop white paper: Microdialysis principles, application and regulatory perspectives.’ *In Pharmaceutical Research*, pp. 1014–1025.

Chen, Z. L., Farzana Akter, K., Rahman Mahmudur, M. and Naidu, R. (2006) ‘Speciation of arsenic by ion chromatography inductively coupled plasma mass spectrometry using ammonium eluents.’ *Journal of Separation Science*, 29(17) pp. 2671–2676.

Cheng, T. and Sun, H. (2014) ‘CHAPTER 25. Antimony and Bismuth.’ *In* Maret, W. and Wedd, A. (eds) *Binding, Transport and Storage of Metal Ions in Biological Cells*. London, UK: The Royal Society of Chemistry, pp. 768–799.

Chepkemoi, J. (2017) *What Is The Environmental Impact Of The Mining Industry?* First Break. [Online] worldatlas.com/articles/what-is-the-environmental-impact-of-the-mining-industry.html.

Cheraghi, M., Mosaed, H. P., Lorestani, B. and Yousefi, N. (2012) 'Heavy metal contamination in some rice samples.' *Electronic Journal of Environmental, Agricultural and Food Chemistry*, 11(5) pp. 424–432.

Choudhury, B. U., Malang, A., Webster, R., Mohapatra, K. P., Verma, B. C., Kumar, M., Das, A., Islam, M. and Hazarika, S. (2017) 'Acid drainage from coal mining: Effect on paddy soil and productivity of rice.' *Science of the Total Environment*. Elsevier B.V., 583(August 2018) pp. 344–351.

Ciminelli, V. S. T., Gasparon, M., Ng, J. C., Silva, G. C. and Caldeira, C. L. (2017) 'Dietary arsenic exposure in Brazil: The contribution of rice and beans.' *Chemosphere*. Elsevier Ltd, 168, February, pp. 996–1003.

Çirmi, D., Aydin, R. and Köleli, F. (2015) 'The electrochemical reduction of nitrate ion on polypyrrole coated copper electrode.' *Journal of Electroanalytical Chemistry*, 736 pp. 101–106.

Clark, R. B., Tiffin, L. O. and Brown, J. C. (1973) 'Organic Acids and Iron Translocation in Maize Genotypes.' *Plant Physiology*, 52(2) pp. 147–150.

Clarkson, D. T. (1996) 'Marschner H. 1995. Mineral nutrition of higher plants. second edition. 889pp. London: Academic Press.' *Annals of Botany*, 78(4) pp. 527–528.

Clemens, S. and Ma, J. F. (2016) 'Toxic Heavy Metal and Metalloid Accumulation in Crop Plants and Foods.' *Annual Review of Plant Biology*, 67(1) pp. 489–512.

Correia, M. M., Alves, S., Simões Gonçalves, M. D. L. and Nabais, C. (2006) 'Dynamic modelling of nickel complexation in xylem sap of Quercus ilex: A voltammetric study.' *Electroanalysis*, 18(8) pp. 814–822.

Cullen, W. R. and Reimer, K. J. (2016a) 'CHAPTER 2. Arsenic Is Everywhere.' *In Arsenic is Everywhere: Cause for Concern?*, pp. 8–48.

Cullen, W. R. and Reimer, K. J. (2016b) 'CHAPTER 8. Arsenic and the Evening Meal.' *In Arsenic is Everywhere: Cause for Concern?*, pp. 221–265.

Daniels, R., Rush, C. C. and Bauer, L. (1960) 'The Fehling and Benedict tests.' *Journal of Chemical Education*, 37(4) p. 205.

Daus, B. and Hansen, H. R. (2016) 'Analysis of antimony species – lessons learnt from more than two decades of environmental research.' *Environmental Chemistry*, 13(6) p. 913.

Dawe, B. D., Organisation, A. and Nations, U. (2015) ‘Rice in Asia: Paddy-whacked.’ *Economist (United Kingdom)*, 411(8960).

Dobermann, A., Dawe, D., Roetter, R. P. and Cassman, K. G. (2000) ‘Reversal of rice yield decline in a long-term continuous cropping experiment.’ *Agronomy Journal*, 92(4) pp. 633–643.

Domingo, L. E. and Kyuma, K. (1983) ‘Trace elements in tropical asian paddy soils: I. total trace element status.’ *Soil Science and Plant Nutrition*, 29(4) pp. 439–452.

Dortsiou, M. and Kyriacou, G. (2009) ‘Electrochemical reduction of nitrate on bismuth cathodes.’ *Journal of Electroanalytical Chemistry*, 630(1–2) pp. 69–74.

Duester, L., Diaz-Bone, R. A., Kösters, J. and Hirner, A. V. (2005) ‘Methylated arsenic, antimony and tin species in soils.’ *In Journal of Environmental Monitoring*, pp. 1186–1193.

Dushenkov, S. (2003) ‘Trends in phytoremediation of radionuclides.’ *In Plant and Soil*, pp. 167–175.

Elmquist, W. F. and Sawchuk, R. J. (1997) ‘Application of microdialysis in pharmacokinetic studies.’ *Pharmaceutical Research* pp. 267–288.

Emamverdian, A. and Ding, Y. (2017) ‘Effects of heavy metals’ toxicity on plants and enhancement of plant defense mechanisms of Si-mediation “ Review.”’ *International Journal of Environmental & Agriculture Research*, (4) pp. 41–51.

Emamverdian, A., Ding, Y., Mokhberdoran, F. and Xie, Y. (2015) ‘Heavy Metal Stress and Some Mechanisms of Plant Defense Response.’ *The Scientific World Journal*. Hindawi Publishing Corporation, 2015 pp. 1–18.

EPA (2004) ‘EPA Method 6020A: ICP-MS. Official Name: EPA Method 6020A, Inductively Coupled Plasma-Mass Spectrometry.’ *EPA methods*, 6.

Epstein, E. and and Bloom, A. J. (1972) *Mineral Nutrition of Plants: Principles and Perspectives*. 2nd ed., Sunderland, Massachusetts: Sinauer Associates, Inc.

Fan, Y., Zhu, T., Li, M., He, J., Huang, R. and and Ruixue Huang, T. Z. Y. F. M. L. J. H. (2017) ‘Heavy Metal Contamination in Soil and Brown Rice and Human Health Risk Assessment near Three Mining Areas in Central China.’ *Journal of Healthcare Engineering*. Hindawi, 2017 p. 9.

FAO (2016) *GIEWS - Crop Prospects and Food Situation, No.1,March 2016*.

FAO and WHO (2019) *Report of the 11th session of the codex committee on contaminnants in foods. A joint FAO/WHO food standards programme codex alimentarius commission 40th Session. Codex*. Geneva, Switzerland.

Farid, M., Shakoor, M., Ehsan, S., Ali, S., Zubair, M. and Hanif, M. (2013) ‘Morphological, physiological and biochemical responses of different plant species to Cd stress.’ *Int J Chem Biochem Sci*, 3(March) pp. 53–60.

Farnese, F. S., Oliveira, J. A., Farnese, M. S., Gusman, G. S., Silveira, N. M. and Siman, L. I. (2014) ‘Uptake arsenic by plants: Effects on mineral nutrition, growth and antioxidant capacity.’ *Idesia (Arica)*, 32(1) pp. 99–106.

Fashola, M., Ngole-Jeme, V. and Babalola, O. (2016) ‘Heavy Metal Pollution from Gold Mines: Environmental Effects and Bacterial Strategies for Resistance.’ *International Journal of Environmental Research and Public Health*. MDPI AG, 13(11) p. 1047.

Feldmann, J., Salaün, P. and Lombi, E. (2009) ‘Critical review perspective: elemental speciation analysis methods in environmental chemistry - moving towards methodological integration.’ *Environmental Chemistry*. CSIRO, 6(4) p. 275.

Feng, R., Wei, C., Tu, S., Ding, Y., Wang, R. and Guo, J. (2013) ‘The uptake and detoxification of antimony by plants: A review.’ *Environmental and Experimental Botany*. Elsevier B.V., 96, December, pp. 28–34.

Festin, E. S., Tigabu, M., Chileshe, M. N., Syampungani, S. and Odén, P. C. (2019) ‘Progresses in restoration of post-mining landscape in Africa.’ *Journal of Forestry Research*, 30(2) pp. 381–396.

Filella and May (2003) ‘Computer simulation of the low-molecular-weight inorganic species distribution of antimony (III) and antimony (V) in natural waters.’ *Geochimica et Cosmochimica Acta,* 67(21) pp. 4013–4031.

Filella, M. (2013) ‘Food for thought: A critical overview of current practical and conceptual challenges in trace element analysis in natural waters.’ *Water (Switzerland)*. MDPI AG pp. 1152–1171.

Filella, M., Belzile, N. and Chen, Y.-W. W. (2002) ‘Antimony in the environment: a review focused on natural waters.’ *Earth-Science Reviews*, 57(1–2) pp. 125–176.

Filella, M., Belzile, N. and Lett, M.-C. C. (2007) ‘Antimony in the environment: A review focused on natural waters. III. Microbiota relevant interactions.’ *Earth-Science Reviews*, 80(3–4) pp. 195–217.

Filella, M. and May, P. M. (2005a) ‘Critical appraisal of available thermodynamic data for the complexation of antimony(iii) and antimony(v) by low molecular mass organic ligands.’ *Journal of Environmental Monitoring*, 7(12) p. 1226.

Filella, M. and May, P. M. (2005b) ‘Reflections on the calculation and publication of potentiometrically- determined formation constants.’ *Talanta*, 65(5) pp. 1221–1225.

Filella, M. and Williams, P. A. (2012) ‘Antimony interactions with heterogeneous

complexants in waters, sediments and soils: A review of binding data for homologous compounds.' *Chemie der Erde*. Elsevier GmbH., 72(SUPPL.4) pp. 49–65.

Filella, M., Williams, P. A. and Belzile, N. (2009) 'Antimony in the environment: Knowns and unknowns.' *Environmental Chemistry*, 6(2) pp. 95–105.

Forsberg, G., O'Laughlin, J. W., Megargle, R. G. and Koirtyohann, S. R. (1975) 'Determination of Arsenic by Anodic Stripping Voltammetry and Differential Pulse Anodic Stripping Voltammetry.' *Analytical Chemistry*, 47(9) pp. 1586–1592.

Francesconi, K. A. and Kuehnelt, D. (2004) 'Determination of arsenic species: A critical review of methods and applications, 2000–2003.' *The Analyst*, 129(5) pp. 373–395.

Frantz, J. M. and Epstein, E. (2005) *Nutritional deficiencies: What they look like*. [Online] [Accessed on 16th December 2019] http://www.ces.ncsu.edu/depts/hort/floriculture/def/forfloriculturecropshttp://extension.agron.iastate.edu/soilfertility/nutrienttopics/deficiencies.htmlcornhttp://muextension.missouri.edu/explore/agguides/hort/index.htm.

FSA (2012) *Arsenic speciation in fruit and vegetables grown in the UK.* Aberdeen: University of Aberdeen.

Fu, Z., Wu, F., Mo, C., Deng, Q., Meng, W. and Giesy, J. P. (2016) 'Comparison of arsenic and antimony biogeochemical behavior in water, soil and tailings from Xikuangshan, China.' *Science of the Total Environment*, 539 pp. 97–104.

Garg, N. and Singla, P. (2011) 'Arsenic toxicity in crop plants: physiological effects and tolerance mechanisms.' *Environmental Chemistry Letters*. Springer, 9(3) pp. 303–321.

Garg, N., Singla, P. and Bhandari, P. (2015) 'Metal uptake, oxidative metabolism, and mycorrhization in pigeonpeaand pea under arsenic and cadmium stress.' *Turkish Journal of Agriculture and Forestry*, 39(2) pp. 234–250.

Gebel, T. (1997) 'Arsenic and antimony: comparative approach on mechanistic toxicology.' *Chemico-Biological Interactions*. Elsevier Ireland Ltd, 107(3) pp. 131–144.

Gebel, T. W. (2001) 'Unanswered Questions in Arsenic Toxicology.' *Journal of Environmental Pathology, Toxicology and Oncology*, 20(4) p. 11.

Gemici, Ü. and Tarcan, G. (2007) 'Assessment of the pollutants in farming soils and waters around untreated abandoned Türkönü mercury mine (Turkey).' *Bulletin of Environmental Contamination and Toxicology*, 79(1) pp. 20–24.

Geng, A., Wang, X., Wu, L., Wang, F., Chen, Y., Yang, H., Zhang, Z. and Zhao, X. (2017) 'Arsenic accumulation and speciation in rice grown in arsanilic acid-elevated paddy soil.' *Ecotoxicology and Environmental Safety*, 137 pp. 172–178.

Geng, C. N., Zhu, Y. G., Tong, Y. P., Smith, S. E. and Smith, F. A. (2006) 'Arsenate (As) uptake by and distribution in two cultivars of winter wheat (Triticum aestivum L.).' *Chemosphere*, 62(4) pp. 608–615.

Gerényi, A., Czech, V., Fodor, F., Vincze, L. and Szalóki, I. (2017) 'In vivo XANES measuring technique for studying the arsenic uptake in cucumber plants.' *X-Ray Spectrometry*, 46(3) pp. 143–150.

German Federal Soil Protection Act (1998) *Federal Law Gazette I p. 502*.

Ghori, N.-H., Ghori, T., Hayat, M. Q., Imadi, S. R., Gul, A., Altay, V. and Ozturk, M. (2019) 'Heavy metal stress and responses in plants.' *International Journal of Environmental Science and Technology*. Center for Environmental and Energy Research and Studies, 16(3) pp. 1807–1828.

Gibbon-Walsh, K., Salaün, P. and van den Berg, C. M. G. (2012a) 'Determination of arsenate in natural pH seawater using a manganese-coated gold microwire electrode.' *Analytica Chimica Acta*. Elsevier B.V., 710, January, pp. 50–57.

Gibbon-Walsh, K., Salaün, P. and van den Berg, C. M. G. (2012b) 'Pseudopolarography of Copper Complexes in Seawater Using a Vibrating Gold Microwire Electrode.' *The Journal of Physical Chemistry A*, 116(25) pp. 6609–6620.

Gibbon-Walsh, K., Salaün, P., Uroic, M. K., Feldmann, J., McArthur, J. M. and Van Den Berg, C. M. G. (2011) 'Voltammetric determination of arsenic in high iron and manganese groundwaters.' *Talanta*, 85(3) pp. 1404–1411.

Gidlow, D. A. (2004) 'Lead toxicity.' *Occupational Medicine*, 54(2) pp. 76–81.

Goldberg, S. (2011) 'Chemical Equilibrium and Reaction Modeling of Arsenic and Selenium in Soils.' *Dynamics and Bioavailability of Heavy Metals in the Rootzone* pp. 65–92.

Grob, M., Wilcke, W. and Mestrot, A. (2018) 'Release and Biomethylation of Antimony in Shooting Range Soils upon Flooding.' *Soil Systems*, 2(2) p. 34.

Guerriero, Gea, Deshmukh, R. and Durgesh K., T. (2020) *Metalloids in Plants Advances and Future Prospects*. Deshmukh, R., Tripathi, D. K., and Guerriero, Gia (eds) *Wiley*. John Wiley & Sons Ltd.

Gupta, D. K., Srivastava, S., Huang, H. G., Romero-Puertas, M. C. and Sandalio, L. M. (2011) 'Arsenic Tolerance and Detoxification Mechanisms in Plants.' *In*, pp. 169–179.

Ha, N. T. H., Ha, N. T., Nga, T. T. H., Minh, N. N., Anh, B. T. K., Hang, N. T. A., Duc, N. A., Nhuan, M. T. and Kim, K.-W. (2019) 'Uptake of arsenic and heavy metals by native plants growing near Nui Phao multi-metal mine, northern Vietnam.' *Applied Geochemistry*. Elsevier Ltd, 108, September, p. 104368.

Hakeem, K. R. (2015) 'Crop production and global environmental issues.' *Crop Production and Global Environmental Issues*, (December) pp. 1–598.

Hall, J. L. L. (2002) 'Cellular mechanisms for heavy metal detoxification and tolerance.' *Journal of experimental botany*, 53(366) pp. 1–11.

Hammel, W., Debus, R. and Steubing, L. (2000) 'Mobility of antimony in soil and its availability to plants.' *Chemosphere*, 41(11) pp. 1791–1798.

Hansen, C. (2011) *Antimony speciation analysis HPLC methods with ICP-MS and ES-MS detection for complex biological matrices*. University of Coppenhagen.

Hansen, H. R. and Pergantis, S. A. (2008) 'Analytical techniques and methods used for antimony speciation analysis in biological matrices.' *Journal of Analytical Atomic Spectrometry*, 23(10) p. 1328.

Hasanuzzaman, M., Nahar, K. and Fujita, M. (2018) *Mechanisms of Arsenic Toxicity and Tolerance in Plants*. Hasanuzzaman, M., Nahar, K., and Fujita, M. (eds) *Mechanisms of Arsenic Toxicity and Tolerance in Plants*. Singapore: Springer Singapore.

Hasanuzzaman, M., Nahar, K., Hakeem, K. R., Öztürk, M. and Fujita, M. (2015) 'Arsenic Toxicity in Plants and Possible Remediation.' *In Soil Remediation and Plants: Prospects and Challenges*. Elsevier Inc., pp. 433–501.

Hawkesford, M. J., Parmar, S. and Buchner, P. (2013) 'Mineral Composition Analysis: Measuring Anion Uptake and Anion Concentrations in Plant Tissues.' *In Plant Mineral Nutrients*. Totowa, NJ: Humana Press, pp. 109–119.

Hazama, K., Nagata, S., Fujimori, T., Yanagisawa, S. and Yoneyama, T. (2015) 'Concentrations of metals and potential metal-binding compounds and speciation of Cd, Zn and Cu in phloem and xylem saps from castor bean plants (Ricinus communis) treated with four levels of cadmium.' *Physiologia Plantarum*, 154(2) pp. 243–255.

He, M., Wang, N., Long, X., Zhang, C., Ma, C., Zhong, Q., Wang, A., Wang, Y., Pervaiz, A. and Shan, J. (2019) 'Antimony speciation in the environment: Recent advances in understanding the biogeochemical processes and ecological effects.' *Journal of Environmental Sciences*. Elsevier B.V., 75, January, pp. 14–39.

Hettick, B. E., Cañas-Carrell, J. E., French, A. D. and Klein, D. M. (2015) 'Arsenic: A Review of the Element's Toxicity, Plant Interactions, and Potential Methods of Remediation.' *Journal of Agricultural and Food Chemistry*, 63(32) pp. 7097–7107.

Hijaz, F. and Killiny, N. (2014) 'Collection and chemical composition of phloem sap from Citrus sinensis L. Osbeck (sweet orange).' *PLoS ONE*. Public Library of Science, 9(7).

Hirner, A. V., Grüter, U. M. and Kresimon, J. (2000) 'Metal(loid)organic compounds in contaminated soil.' *Fresenius' Journal of Analytical Chemistry*. Springer, 368(2–3) pp.

263–267.

Hoagland and Arnon, D., D. (1950) *The water-culture method of growing plants without soil.* Berkeley, Calif. : University of California, College of Agriculture, Agricultural Experiment Station.

Hossain, M. A., Piyatida, P., da Silva, J. A. T. and Fujita, M. (2012) 'Molecular Mechanism of Heavy Metal Toxicity and Tolerance in Plants: Central Role of Glutathione in Detoxification of Reactive Oxygen Species and Methylglyoxal and in Heavy Metal Chelation.' *Journal of Botany*. Hindawi Limited, 2012(Cd) pp. 1–37.

Hozhina, E. ., Khramov, A. ., Gerasimov, P. . and Kumarkov, A. . (2001) 'Uptake of heavy metals, arsenic, and antimony by aquatic plants in the vicinity of ore mining and processing industries.' *Journal of Geochemical Exploration*, 74(1–3) pp. 153–162.

Hrytsak, L. R., Herts, A. I., Nuzhyna, N. V., Cryk, M. M., Shevchenko, V. V. and Drobyk, N. M. (2018) 'The influence of light regime on the growth data and pigment composition of the plant Gentiana lutea cultured in vitro.' *Regulatory Mechanisms in Biosystems*, 9(2) pp. 258–266.

Hu, L., Zhang, B., Wu, D., Fan, H., Tu, J., Liu, W., Huang, R. and Huang, X. (2019) 'Estimation of arsenic bioaccessibility in raw and cooked radish using simulated in vitro digestion.' *Food & Function*. Royal Society of Chemistry, 10(3) pp. 1426–1432.

Hu, Y., Cheng, H. and Tao, S. (2016) 'The Challenges and Solutions for Cadmium-contaminated Rice in China: A Critical Review.' *Environment International*. Elsevier Ltd pp. 515–532.

Hua, C.-Y., Chen, J.-X., Cao, Y., Li, H.-B., Chen, Y. and Ma, L. Q. (2020) 'Pteris vittata coupled with phosphate rock effectively reduced As and Cd uptake by water spinach from contaminated soil.' *Chemosphere*. Elsevier Ltd, 247, May, p. 125916.

Huang, R.-Q., Gao, S.-F., Wang, W.-L., Staunton, S. and Wang, G. (2006) 'Soil arsenic availability and the transfer of soil arsenic to crops in suburban areas in Fujian Province, southeast China.' *Science of The Total Environment*, 368(2–3) pp. 531–541.

Huang, Y., Chen, Q., Deng, M., Japenga, J., Li, T., Yang, X. and He, Z. (2018) 'Heavy metal pollution and health risk assessment of agricultural soils in a typical peri-urban area in southeast China.' *Journal of Environmental Management*. Academic Press, 207, February, pp. 159–168.

Huang, Z., Pan, X.-D. D., Wu, P.-G. G., Han, J.-L. L. and Chen, Q. (2013) 'Health Risk Assessment of Heavy Metals in Rice to the Population in Zhejiang, China.' Scarfi, M. R. (ed.) *PLoS ONE*, 8(9) pp. 1–6.

Huiliang, H., Jagner, D. and Renman, L. (1988) 'Flow potentiometric and constant-current stripping analysis for arsenic(V) without prior chemical reduction to arsenic(III).'

Analytica Chimica Acta, 207 pp. 37–46.

Humphrey, O. S., Young, S. D., Bailey, E. H., Crout, N. M. J., Ander, E. L., Hamilton, E. M. and Watts, M. J. (2019) 'Investigating the use of microdialysis and SEC-UV-ICP-MS to assess iodine interactions in soil solution.' *Chemosphere*. Elsevier Ltd, 229, August, pp. 41–50.

Hunt, R., Causton, D. R., Shipley, B. and Askew, A. P. (2002) 'A modern tool for classical plant growth analysis.' *Annals of Botany*, 90(4) pp. 485–488.

Inselsbacher, E. (2014) 'Recovery of individual soil nitrogen forms after sieving and extraction.' *Soil Biology and Biochemistry*, 71, April, pp. 76–86.

Inselsbacher, E., Öhlund, J., Jämtgård, S., Huss-Danell, Kerstin, A. and Näsholm, T. (2011) 'The potential of microdialysis to monitor organic and inorganic nitrogen compounds in soil.' *Soil Biology and Biochemistry*, 43(6) pp. 1321–1332.

International Programme on Chemical Safety (2004) 'International programme on chemical safety (IPCS),' (June) pp. 1–34.

IPNI (2002) 'Nutrient Deficiency Symptoms in Rice.' *Better Crops International*, 16(May) pp. 23–25.

IRRI and DFID (2009) 'Scuba rice : breeding flood-tolerance into Asia ' s local mega rice varieties.' *South Asia* pp. 1–6.

Ismail, B., Yap, D., Adezrian, J., Khairiah, J. and Ahmad-Mahir, R. (2009) 'The Uptake of Heavy Metals by Paddy Plants (Oryza sativa) in Kota Marudu, Sabah, Malaysia.' *& Environ. Sci*, 6(1) pp. 16–19.

Jamila Alfaraas, A. M., Khairiah, J., Ismail, B. S. and Noraini, T. (2016) 'Effects of heavy metal exposure on the morphological and microscopical characteristics of the paddy plant.' *Journal of Environmental Biology*, 37(5) pp. 955–963.

Järup, L. (2003) 'Hazards of heavy metal contamination.' *British Medical Bulletin*, 68 pp. 167–182.

JECFA (2016) 'Joint FAO / WHO Expert Committee on Food Additives (JECFA) Call for Experts on Food Additives , Contaminants and toxins ; and Residues of Veterinary Drugs,' (October).

Jentschke, G. and Godbold, D. L. (2000) 'Metal toxicity and ectomycorrhizas.' *Physiologia Plantarum*, 109(2) pp. 107–116.

Ji, Y., Sarret, G., Schulin, R. and Tandy, S. (2017) 'Fate and chemical speciation of antimony (Sb) during uptake, translocation and storage by rye grass using XANES spectroscopy.' *Environmental Pollution*. Elsevier Ltd, 231, December, pp. 1322–1329.

Johnson, C. A., Moench, H., Wersin, P., Kugler, P. and Wenger, C. (2005) ‘Solubility of Antimony and Other Elements in Samples Taken from Shooting Ranges.’ *Journal of Environmental Quality*. Wiley, 34(1) pp. 248–254.

Johnson, C. D. (2014) ‘Phytoremediation of Arsenic Contamination on Vashon-Maury Island METHODS Salix Screening for Arsenic Tolerance.’

Johnston, A. E. and Poulton, P. R. (2018) ‘The importance of long-term experiments in agriculture: their management to ensure continued crop production and soil fertility; the Rothamsted experience.’ *European Journal of Soil Science*, 69(1) pp. 113–125.

Kabata-Pendias, A. (2010) *Trace Elements in Soils and Plants*. 4th ed., CRC Press.

Kalaji, H. M., Jajoo, A., Oukarroum, A., Brestic, M., Zivcak, M., Samborska, I. A., Cetner, M. D., Łukasik, I., Goltsev, V. and Ladle, R. J. (2016) ‘Chlorophyll a fluorescence as a tool to monitor physiological status of plants under abiotic stress conditions.’ *Acta Physiologiae Plantarum*. Polish Academy of Sciences.

Kapaj, S., Peterson, H., Liber, K. and Bhattacharya, P. (2006) ‘Human Health Effects From Chronic Arsenic Poisoning–A Review.’ *Journal of Environmental Science and Health, Part A*. The Safe Drinking Water Foundation, Saskatoon, Saskatchewan, Canada., 41(10) pp. 2399–2428.

Katsounaros, I. and Kyriacou, G. (2007) ‘Influence of the concentration and the nature of the supporting electrolyte on the electrochemical reduction of nitrate on tin cathode.’ *Electrochimica Acta*, 52(23) pp. 6412–6420.

Kehr, J. and Rep, M. (2007) ‘Protein extraction from xylem and phloem sap.’ *Methods in molecular biology (Clifton, N.J.)*, 355 pp. 27–35.

Killiny, N. and Hijaz, F. (1998) ‘Chemical composition of xylem sap of Citrus sinensis L. Osbeck (sweet orange).’ *Trends in Plant Science*, 3(5) pp. 188–195.

Kisan, M., Sangathan, S., Nehru, J. and Pitroda, S. G. (2012) ‘Laboratory Glassware-Volumetric Instruments-Methods for Testing of Capacity and for Use.’ ISO (ed.) *4787*. Geneva: IS pp. 1–29.

Kitagishi, K. (1981) ‘Heavy Metal Pollution in Soils of Japan.’ *Japan Scientific Societies Press, Tokyo, Japan*, 52(4) p. 302.

Koester, R. P., Skoneczka, J. A., Cary, T. R., Diers, B. W. and Ainsworth, E. A. (2014) ‘Historical gains in soybean (Glycine max Merr.) seed yield are driven by linear increases in light interception, energy conversion, and partitioning efficiencies.’ *Journal of Experimental Botany*, 65(12) pp. 3311–3321.

Kolbe, F., Mattusch, J., Wennrich, R., Weiss, H., Sorkau, E., Lorenz, W. and Daus, B. (2012) ‘Analytical investigations of antimony-edta complexes and their use in speciation

analysis.' *Fresenius Environmental Bulletin*, 21(11 C) pp. 3453–3456.

Kowalska, J., Stryjewska, E., Szymański, P. and Golimowski, J. (1999) 'Voltammetric determination of arsenic in plant material.' *Electroanalysis*, 11(17) pp. 1301–1304.

Krachler, M. and Emons, H. (2001) 'Speciation analysis of antimony by high-performance liquid chromatography inductively coupled plasma mass spectrometry using ultrasonic nebulization.' *Analytica Chimica Acta*, 429(1) pp. 125–133.

Kroukamp, E. M., Wondimu, T. and Forbes, P. B. C. (2016) 'Metal and metalloid speciation in plants: Overview, instrumentation, approaches and commonly assessed elements.' *TrAC - Trends in Analytical Chemistry*. Elsevier B.V., 77 pp. 87–99.

Krupka, K. M. and Serne, R. J. (2002) *Geochemical Factors Affecting the Behavior of Antimony, Cobalt, Europium, Technetium, and Uranium in Vadose Zone Sediments*. *Pnnl-14126*. Richland, WA (United States).

Kumar, R., Mishra, R. K., Mishra, V., Qidwai, A., Pandey, A., Shukla, S. K., Pandey, M., Pathak, A. and Dikshit, A. (2015) 'Detoxification and Tolerance of Heavy Metals in Plants.' *In Plant Metal Interaction: Emerging Remediation Techniques*. Elsevier Inc., pp. 335–359.

Kumarathilaka, P., Seneweera, S., Meharg, A. and Bundschuh, J. (2018) 'Arsenic speciation dynamics in paddy rice soil-water environment: sources, physico-chemical, and biological factors - A review.' *Water Research*. Elsevier Ltd pp. 403–414.

Küpper, H. and Andresen, E. (2016) 'Mechanisms of metal toxicity in plants.' *Metallomics*, 8(3) pp. 269–285.

Lansdown, A. B. G. (2013) 'CHAPTER 1. Introduction.' *In The Carcinogenicity of Metals: Human Risk Through Occupational and Environmental Exposure*, pp. 1–18.

Larsen, E. H. and Stürup, S. (1994) 'Carbon-enhanced inductively coupled plasma mass spectrometric detection of arsenic and selenium and its application to arsenic speciation.' *Journal of Analytical Atomic Spectrometry*, 9(10) pp. 1099–1105.

van Leeuwen, H. P., Town, R. M., Buffle, J., Cleven, R. F. M. J., Davison, W., Puy, J., van Riemsdijk, W. H. and Sigg, L. (2005) 'Dynamic Speciation Analysis and Bioavailability of Metals in Aquatic Systems.' *Environmental Science & Technology*, 39(22) pp. 8545–8556.

van Leeuwen, L. C. and Aldenberg, T. (2012) *RIVM Letter Report 601357001/2012: Environmental risk limits for antimony*.

Li, Z. and Cui, Z. (2008) 'Application of microdialysis in tissue engineering monitoring.' *Progress in Natural Science*. Science Press, 18(5) pp. 503–511.

Liang, G., Gong, W., Li, B., Zuo, J., Pan, L. and Liu, X. (2019) 'Analysis of Heavy Metals in Foodstuffs and an Assessment of the Health Risks to the General Public via Consumption

in Beijing, China.’ *International Journal of Environmental Research and Public Health*. MDPI AG, 16(6) p. 909.

Lichtfouse, E., Schwarzbauer, J. and Robert, D. (2012) *Environmental chemistry for a sustainable world*. *Environmental Chemistry for a Sustainable World*. Springer Netherlands.

Lintschinger, J., Koch, I., Serves, S., Feldmann, J. and Cullen, W. R. (1997) ‘Determination of antimony species with High-Performance Liquid Chromatography using element specific detection.’ *Fresenius’ Journal of Analytical Chemistry*, 359(6) pp. 484–491.

Liu, Z. G. and Huang, X. J. (2014) ‘Voltammetric determination of inorganic arsenic.’ *TrAC - Trends in Analytical Chemistry*, 60 pp. 25–35.

Lombi, E. and Holm, P. E. (2010) ‘Metalloids, soil chemistry and the environment.’ *In Advances in Experimental Medicine and Biology*. Australia: Landes Bioscience and Springer Science+Business Media., pp. 33–44.

Louis, Y., Cmuk, P., Nicolau, R., Omanovi, D., Lenoble, V., Pižeta, I., Mounier, S., and Garde, L. and Garde, L. (2007) ‘Pseudopolarography As a Tool for Complexation Studies of Trace Metals With Dissolved Natural Organic Matter,’ (January) p. 2007.

Louis, Y., Cmuk, P., Omanović, D., Garnier, C., Lenoble, V., Mounier, S. and Pižeta, I. (2008) ‘Speciation of trace metals in natural waters: The influence of an adsorbed layer of natural organic matter (NOM) on voltammetric behaviour of copper.’ *Analytica Chimica Acta*. Elsevier Masson, 606(1) pp. 37–44.

Louis, Y., Garnier, C., Lenoble, V., Omanovi, D., Mounier, S., Pižeta, I., Protee, L., Toulon, S., Bp, V., Garde, L., Physico, G. De, Chimie, T., Moléculaires, S. and I, U. B. (2008) ‘Electrochemical Study of Major and Trace Metal Interactions With Concentrated Marine Dissolved Organic Matter,’ (098) p. 1214910.

Lu, M. and Compton, R. G. (2013) ‘Voltammetric Determination of Iron(III) in Water.’ *Electroanalysis*, 25(5) pp. 1123–1129.

Lubin, J. H., Moore, L. E., Fraumeni, J. F. and Cantor, K. P. (2008) ‘Respiratory Cancer and Inhaled Inorganic Arsenic in Copper Smelters Workers: A Linear Relationship with Cumulative Exposure that Increases with Concentration.’ *Environmental Health Perspectives*, 116(12) pp. 1661–1665.

Luo, J. and Shu, W. (2015) ‘Arsenic-Induced Developmental Neurotoxicity.’ *In* Flora, S. J. S. B. T.-H. of A. T. (ed.) *Handbook of Arsenic Toxicology*. Oxford: Elsevier, pp. 363–386.

Lydic, R., Baghdoyan, H. A. and May, A. L. (2018) ‘Chapter Fourteen - Neurochemistry of Anesthetic States.’ *In* Eckenhoff, R. G. and Dmochowski, I. J. B. T.-M. in E. (eds) *Chemical and Biochemical Approaches for the Study of Anesthetic Function Part B*. 1st ed., Academic Press, pp. 237–255.

Madejón, P., Marañón, T. and Murillo, J. M. (2006) ‘Biomonitoring of trace elements in the leaves and fruits of wild olive and holm oak trees.’ *Science of the Total Environment*, 355(1–3) pp. 187–203.

Magahud, J. C., Badayos, R. B., Sanchez, P. B. and Sta. Cruz, P. C. (2015) *Levels and Potential Sources of Heavy Metals in Major Irrigated Rice Areas of the Philippines*. *IAMURE International Journal of Ecology and Conservation*.

Mandal, B. K. and Suzuki, K. T. (2002) ‘Arsenic round the world: A review.’ *Talanta*. Elsevier, 58(1) pp. 201–235.

Mareček, V., Jänchenová, H., Samec, Z. and Březina, M. (1986) ‘Voltammetric determination of nitrate, perchlorate and iodide at a hanging electrolyte drop electrode.’ *Analytica Chimica Acta*, 185(C) pp. 359–362.

Marschner, H. (1995) *Mineral Nutrition of High Plants*. Academic Press.

Martin, M., Ferdousi, R., Hossain, K. M. J. and Barberis, E. (2010) ‘Arsenic from groundwater to paddy fields in Bangladesh: Solid-liquid partition, sorption and mobility.’ *Water, Air, and Soil Pollution*, 212(1–4) pp. 27–36.

Martinez, R. E., Marquez, J. E., Hòa, H. T. B. and Gieré, R. (2013) ‘Open-pit coal-mining effects on rice paddy soil composition and metal bioavailability to Oryza sativa L. plants in Cam Pha, northeastern Vietnam.’ *Environmental Science and Pollution Research*, 20(11) pp. 7686–7698.

Massoura, S. T., Echevarria, G., Leclerc-Cessac, E. and Morel, J. L. (2004) ‘Response of excluder, indicator, and hyperaccumulator plants to nickel availability in soils.’ *Australian Journal of Soil Research*, 42(8) pp. 933–938.

Materials, B. (1989) *Analytical Methods*. *WHO*.

Matschullat, J. J. (2000) ‘Arsenic in the geosphere - A review.’ *The Science of the Total Environment*, 249(1–3) pp. 297–312.

Mawia, A. M., Hui, S., Zhou, L., Li, H., Tabassum, J., Lai, C., Wang, J., Shao, G., Wei, X., Tang, S., Luo, J., Hu, S. and Hu, P. (2021) ‘Inorganic arsenic toxicity and alleviation strategies in rice.’ *Journal of Hazardous Materials*. Elsevier B.V. p. 124751.

Mayet, N., Servat, K., Kokoh, K. B. and Napporn, T. W. (2019) ‘Probing the Surface of Noble Metals Electrochemically by Underpotential Deposition of Transition Metals.’ *Surfaces*, 2(2) pp. 257–276.

McLaughlin, M. ., Parker, D. . and Clarke, J. . (1999) ‘Metals and micronutrients – food safety issues.’ *Field Crops Research*, 60(1–2) pp. 143–163.

Mead, M. N. (2005) ‘Arsenic: In search of an antidote to a global poison.’ *Environmental*

Health Perspectives. Public Health Services, US Dept of Health and Human Services, 113(6).

Meadows, R. (2014) ‘How Plants Control Arsenic Accumulation.’ *PLoS Biology*, 12(12) pp. 1002008–1002009.

Meharg, A. A. (2004) ‘Arsenic in rice - Understanding a new disaster for South-East Asia.’ *Trends in Plant Science* pp. 415–417.

Meharg, A. A. and Zhao, F.-J. (2012) *Arsenic & Rice*. *Springer*. Dordrecht: Springer Netherlands.

Mendoza, T. (2012) ‘Estimates of Rice Per Capita Consumption: Its Implications to the Rice Self-Sufficiency Program of the Philippines*.’ *Policy Options*, 4, January.

Mestrot, A., Ji, Y., Tandy, S. and Wilcke, W. (2016) ‘A novel method to determine trimethylantimony concentrations in plant tissue.’ *Environmental Chemistry*, 13(6) pp. 919–926.

Michalski, R., Szopa, S., Jabłońska, M. and Łyko, A. (2012) ‘Application of hyphenated techniques in speciation analysis of arsenic, antimony, and thallium.’ *The Scientific World Journal*. Institute of Environmental Engineering, the Polish Academy of Sciences, 34 Sklodowskiej-Curie Street, 41 819 Zabrze, Poland. michalski@ipis.zabrze.pl, 2012(January 2017) p. 902464.

Miekeley, N., Mortari, S. R. and Schubach, A. O. (2002) ‘Monitoring of total antimony and its species by ICP-MS and on-line ion chromatography in biological samples from patients treated for leishmaniasis.’ *Fresenius' Journal of Analytical Chemistry*, 372(3) pp. 495–502.

Mihucz, V. G., Tatár, E. E. E., Virág, I., Cseh, E., Fodor, F., Záray, G., Tat??r, E., Vir??g, I., Cseh, E., Fodor, F. and Gyula, Z. (2005) ‘Arsenic speciation in xylem sap of cucumber (Cucumis sativus L.).’ *Analytical and Bioanalytical Chemistry*. Joint Research Group of Environmental Chemistry of the Hungarian Academy of Sciences and L. Eotvos University, PO Box 32, 1518 Budapest, Hungary., 383(3) pp. 461–466.

Mihucz, V. G., Varga, A. and Za, G. (1998) ‘Determination of Organic Acids in Xylem Sap of Cucumber : Effect of Lead Contamination,’ 314(58) pp. 306–314.

Ministerie Van Volkshuisvesting; Ruimtelijke Ordening En Milieu (2000) ‘Dutch Target and Intervention Values; 2000 (the New Dutch List).’ *Netherlands Government Gazette*, 2000 pp. 1–12.

Miró, M., Fitz, W. J., Swoboda, S. and Wenzel, W. W. (2010) ‘In-situ sampling of soil pore water: Evaluation of linear-type microdialysis probes and suction cups at varied moisture contents.’ *Environmental Chemistry*, 7(1) pp. 123–131.

Mishra, S., Srivastava, S., Dwivedi, S. and Tripathi, R. D. (2013) ‘Investigation of

biochemical responses of Bacopa monnieri L. upon exposure to arsenate.' *Environmental Toxicology*, 28(8) pp. 419–430.

Mohan, D. and Pittman, C. U. (2007) 'Arsenic removal from water/wastewater using adsorbents-A critical review.' *Journal of Hazardous Materials* pp. 1–53.

Moles, A. T., Warton, D. I., Warman, L., Swenson, N. G., Laffan, S. W., Zanne, A. E., Pitman, A., Hemmings, F. A. and Leishman, M. R. (2009) 'Global patterns in plant height.' *Journal of Ecology*, 97(5) pp. 923–932.

Moreno-Jiménez, E., Esteban, E. and Peñalosa, J. M. (2012) 'The fate of arsenic in soil-plant systems.' *Reviews of Environmental Contamination and Toxicology*, 215 pp. 1–37.

Morua, M. (2015) 'Investigating various xylem sap extraction techniques from drought-stressed Geijera parviflora trees' pp. 1–26.

Mosetlha, K., Torto, N. and Wibetoe, G. (2007) 'Determination of Cu and Ni in plants by microdialysis sampling: Comparison of dialyzable metal fractions with total metal content.' *Talanta*. Elsevier, 71(2) pp. 766–770.

Nagajyoti, P. C., Lee, K. D. and Sreekanth, T. V. M. (2010) 'Heavy metals, occurrence and toxicity for plants: A review.' *Environmental Chemistry Letters* pp. 199–216.

Nash, M. J., Maskall, J. E. and Hill, S. J. (2000) 'Methodologies for determination of antimony in terrestrial environmental samples.' *Journal of Environmental Monitoring*, 2(2) pp. 97–109.

Natasha, Shahid, M., Khalid, S., Dumat, C., Pierart, A. and Niazi, N. K. (2019) 'Biogeochemistry of antimony in soil-plant system: Ecotoxicology and human health.' *Applied Geochemistry*. Elsevier, 106(April) pp. 45–59.

Netting, A. G., Theobald, J. C. and Dodd, I. C. (2012) 'Xylem sap collection and extraction methodologies to determine in vivo concentrations of ABA and its bound forms by gas chromatography-mass spectrometry (GC-MS).' *Plant Methods*, 8(1) pp. 1–14.

Nicolau, R., Louis, Y., Omanović, D., Garnier, C., Mounier, S. and and, Pižeta, I. (2008) 'Study of interactions of concentrated marine dissolved organic matter with copper and zinc by pseudopolarography.' *Analytica Chimica Acta*, 618(1) pp. 35–42.

Niedzielski, P. and Siepak, M. (2003) 'Analytical methods for determining arsenic, antimony and selenium in environmental samples.' *Polish Journal of Environmental Studies*, 12(6) pp. 653–667.

Niedzielski, P., Siepak, M., Siepak, J. and Przybyłek, J. (2002) 'Determination of Different Forms of Arsenic, Antimony and Selenium in Water Samples Using Hydride Generation.' *Polish Journal of Environmental Studies*, 11(3) pp. 219–224.

Nimick, D. A. (1998) 'Arsenic hydrogeochemistry in an irrigated river valley-A reevaluation.' *Journal of groundwater*. Ground Water Publ Co, 36(5) pp. 743–753.

O'Day, P. A. (2006) 'Chemistry and mineralogy of arsenic.' *Elements*, 2(2) pp. 77–83.

Obiora, S. C., Chukwu, A. and Davies, T. C. (2016) 'Heavy metals and health risk assessment of arable soils and food crops around Pb-Zn mining localities in Enyigba, southeastern Nigeria.' *Journal of African Earth Sciences*. Elsevier Ltd, 116, April, pp. 182–189.

Oda, A., Shimizu, M., Kuroha, T. and Satoh, S. (2005) 'Induction of xylem sap methylglycine by a drought and rewatering treatment and its inhibitory effects on the growth and development of plant organs.' *Physiologia Plantarum*, 124(4) pp. 515–523.

Ogawa, K. and Iwabuchi, M. (2001) 'A mechanism for promoting the germination of Zinnia elegans seeds by hydrogen peroxide.' *Plant and Cell Physiology*, 42(3) pp. 286–291.

Ohmori, T., El-Deab, M. S. and Osawa, M. (1999) 'Electroreduction of nitrate ion to nitrite and ammonia on a gold electrode in acidic and basic sodium and cesium nitrate solutions.' *Journal of Electroanalytical Chemistry*, 470(1) pp. 46–52.

Olsen, S.R., C.V. Cole, F.S. Watanabe, and L. A. D. (1954) *Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circ.No. 939.* U.S. Gov. Print. Office, Washington DC.

Omanović, D. (2006) 'Pseudopolarography of trace metals. Part III. Determination of stability constants of labile metal complexes.' *Croatica Chemica Acta*, 79(1) p. 67.

Omanović, D. and Branica, M. (2003) 'Pseudopolarography of trace metals: Part I. The automatic ASV measurements of reversible electrode reactions.' *Journal of Electroanalytical Chemistry*, 543(1) pp. 83–92.

Omanović, D. and Branica, M. (2004) 'Pseudopolarography of trace metals. Part II. The comparison of the reversible, quasireversible and irreversible electrode reactions.' *Journal of Electroanalytical Chemistry*, 565(1) pp. 37–48.

Onofri, A., Seddaiu, G. and Piepho, H. P. (2016) 'Long-Term Experiments with cropping systems: Case studies on data analysis.' *European Journal of Agronomy*, 77, July, pp. 223–235.

Organization, world health (1996) 'guidelines for drinking water quality - second edition.' *international programme on chemical safety*.

Özer, U. Y. and Bogucki, R. F. (1971) 'Equilibrium studies of antimony(III) chelates in aqueous solution.' *Journal of Inorganic and Nuclear Chemistry*, 33(12) pp. 4143–4153.

Palma-Lara, I., Martínez-Castillo, M., Quintana-Pérez, J. C., Arellano-Mendoza, M. G., Tamay-Cach, F., Valenzuela-Limón, O. L., García-Montalvo, E. A. and Hernández-Zavala, A. (2019) 'Arsenic exposure: A public health problem leading to several cancers.' *Regulatory toxicology and pharmacology : RTP* p. 104539.

Pampolino, M. F., Laureles, E. V., Gines, H. C. and Buresh, R. J. (2008) 'Soil carbon and nitrogen changes in long-term continuous lowland rice cropping.' *Soil Science Society of America Journal*, 72(3) pp. 798–807.

Panda, S. K., Upadhyay, R. K. and Nath, S. (2010) 'Arsenic Stress in Plants.' *Journal of Agronomy and Crop Science*, 196(3) pp. 161–174.

Pandey, P. and Tripathi, A. K. (2014) 'Impact Of Heavy Metals On Morphological And Biochemical Parameters Of Shorea Robusta Plant.' *Ekologia*, 33(2) pp. 116–126.

Passioura, J. B. (1980) 'The transport of water from soil to shoot in wheat seedlings.' *Journal of Experimental Botany*, 31(1) pp. 333–345.

Pedron, T., Segura, F. R., Paniz, F. P., de Moura Souza, F., dos Santos, M. C., de Magalhães Júnior, A. M. and Batista, B. L. (2019) 'Mitigation of arsenic in rice grains by polishing and washing: Evidencing the benefit and the cost.' *Journal of Cereal Science*. Academic Press, 87, May, pp. 52–58.

Penezić, A., Tercier-Waeber, M. Lou, Abdou, M., Bossy, C., Dutruch, L., Bakker, E. and Schäfer, J. (2020) 'Spatial variability of arsenic speciation in the Gironde Estuary: Emphasis on dynamic (potentially bioavailable) inorganic arsenite and arsenate fractions.' *Marine Chemistry*. Elsevier, 223(December 2019) p. 103804.

Pepponi, G., Meirer, F., Streli, C., Wobrauschek, P., Mihucz, V. G., G. Zaray, V. C., Broekaert, J., Fittschen, U. and Falkenberg, G. (2005) 'Arsenic speciation in Cucumber Cucumis Sativus L.) xylem sap by K-edge TXRF-XANES.' *Anal. Bioanal. Chem.*, 383 pp. 461–466.

Peralta-Videa, J. R., Lopez, M. L., Narayan, M., Saupe, G. and Gardea-Torresdey, J. (2009) 'The biochemistry of environmental heavy metal uptake by plants: Implications for the food chain.' *International Journal of Biochemistry and Cell Biology*, 41(8–9) pp. 1665–1677.

Perrino, C., Marconi, E., Canepari, S., Luisa Astolfi, M. and Perrino, C. (2011) 'Determination of Sb(III), Sb(V) and identification of Sb-containing nanoparticles in airborne particulate matter.' *Procedia Environmental Sciences*, 4 pp. 209–217.

Pettine, M., Casentini, B., Mastroianni, D. and Capri, S. (2007) 'Dissolved inorganic carbon effect in the determination of arsenic and chromium in mineral waters by inductively coupled plasma-mass spectrometry.' *Analytica Chimica Acta*. Elsevier, 599(2) pp. 191–198.

Pickering, I. J., Prince, R. C., George, M. J., Smith, R. D., George, G. N. and Salt, D. E. (2000) 'Reduction and coordination of arsenic in Indian mustard.' *Plant Physiology*, 122(4) pp. 1171–1177.

Pierart, A., Shahid, M., Séjalon-Delmas, N. and Dumat, C. (2015) 'Antimony bioavailability: Knowledge and research perspectives for sustainable agricultures.' *Journal of Hazardous Materials*. Elsevier, 289(February) pp. 219–234.

Pla-Vilanova, P., Galceran, J., Puy, J., Companys, E. and Filella, M. (2019) 'Antimony speciation in aqueous solution followed with AGNES.' *Journal of Electroanalytical Chemistry*. Elsevier B.V., 849 p. 113334.

Pohl, P., Lesniewicz, A. and Zyrnicki, W. (2003) 'Determination of As, Bi, Sb and Sn in conifer needles from various locations in Poland and Norway by hydride generation inductively coupled plasma atomic emission spectrometry.' *International Journal of Environmental Analytical Chemistry*. Taylor & Francis Group, 83(11) pp. 963–970.

Polunina, O. V., Maiboroda, V. P. and Seleznov, A. Y. (2018) 'Evaluation methods of estimation of young apple trees leaf area.' *Bulletin of Uman National University of Horticulture*, (2) pp. 80–82.

Pommerrenig, B., Diehn, T. A. and Bienert, G. P. (2015) 'Metalloido-porins: Essentiality of Nodulin 26-like intrinsic proteins in metalloid transport.' *Plant Science*. Elsevier Ireland Ltd, 238 pp. 212–227.

Porra, R. J. (2005) 'Clorofila Porras 2005' pp. 633–640.

Postupolski, A. and Golimowski, J. (1991) 'Trace determination of antimony and bismuth in snow and water samples by stripping voltammetry.' *Electroanalysis*. Warsaw, Poland, 3(8) pp. 793–797.

Pretti, L., Bazzu, G., Serra, P. A. and Nieddu, G. (2014) 'A novel method for the determination of ascorbic acid and antioxidant capacity in Opuntia ficus indica using in vivo microdialysis.' *Food Chemistry*, 147 pp. 131–137.

Punrat, E., Chuanuwatanakul, S., Kaneta, T., Motomizu, S., Chailapakul, O., Zaib, M., Makshoof, M., Saeed, A., Farooq, U., Nearing, M. M., Koch, I., Reimer, K. J., Niedzielski, P., Siepak, M., Day, P. A. O., Mays, D. E., Hussam, A., Welna, M., Szymczycha-Madeja, A., Pohl, P., Ma, J., Sengupta, M. K., Yuan, D., Dasgupta, P. K., Amaral, C. D. B., Nóbrega, J. A., Nogueira, A. R. A., Cavicchioli, A., La-scalea, M. A., Gutz, G. R., Tyson, J., Chen, M. L., Ma, L. Y., Chen, X. W., Punrat, E., Chuanuwatanakul, S., Kaneta, T., Motomizu, S., Chailapakul, O., Hotel, D., Llorente-mirandes, T., Calderón, J., Centrich, F., Rubio, R., López-sánchez, J. F. and Thomas, D. J. (2014) 'Method development for the determination of arsenic by sequential injection/anodic stripping voltammetry using long-lasting gold-modified screen-printed carbon electrode.' *Talanta*. Elsevier B.V., 2013(June) pp. 1018–1025.

Quentel, F. and Filella, M. (2002) ‘Determination of inorganic antimony species in seawater by differential pulse anodic stripping voltammetry: Stability of the trivalent state.’ *Analytica Chimica Acta*, 452(2) pp. 237–244.

Quentel, F., Filella, M., Elleouet, C. and Madec, C. (2006) ‘Sb(III) oxidation by iodate in seawater: A cautionary tale.’ *Science of The Total Environment*. Elsevier, 355(1–3) pp. 259–263.

RA (2001) ‘Philippine Mining Act of 1995,.’ Philippines, R. of the (ed.) pp. 1–12.

Raab, A., Feldmann, J. and Meharg, A. A. (2004) ‘The Nature of Arsenic-Phytochelatin Complexes in Holcus lanatus and Pteris cretica.’ *Plant Physiology*. Department of Chemistry, University of Aberdeen, Meston Building, Meston Walk, Aberdeen AB24 3UE, United Kingdom., 134(3) pp. 1113–1122.

Raab, A., Meharg, A. A., Jaspars, M., Genney, D. R. and Feldmann, J. (2004) ‘Arsenic–glutathione complexes—their stability in solution and during separation by different HPLC modes.’ *J. Anal. At. Spectrom.*, 19(1) pp. 183–190.

Raab, A., Schat, H., Meharg, A. A., Feldmann, J., J., A. R. S. H. M. A. A. and F., Raab, A., Schat, H., Meharg, A. A. and Feldmann, J. (2005) ‘Uptake, translocation and transformation of arsenate and arsenite in sunflower (Helianthus annuus): Formation of arsenic-phytochelatin complexes during exposure to high arsenic concentrations.’ *New Phytologist*. Department of Chemistry, University of Aberdeen, Meston Building, Meston Walk, Aberdeen AB24 3UE, UK., 168(3) pp. 551–558.

Rahaman, M. S., Akter, M., Rahman, M. M., Sikder, M. T., Hosokawa, T., Saito, T. and Kurasaki, M. (2020) ‘Investigating the protective actions of D-pinitol against arsenic-induced toxicity in PC12 cells and the underlying mechanism.’ *Environmental Toxicology and Pharmacology*. Elsevier B.V., 74, February, p. 103302.

Rahman, M. A. and Hasegawa, H. (2011) ‘High levels of inorganic arsenic in rice in areas where arsenic-contaminated water is used for irrigation and cooking.’ *Science of The Total Environment*, 409(22) pp. 4645–4655.

Raskin, I., Kumar, P. N., Dushenkov, S. and Salt, D. E. (1994) ‘Bioconcentration of heavy metals by plants.’ *Current Opinion in Biotechnology*, 5(3) pp. 285–290.

Rauser, W. E. (1990) ‘Phytochelatins.’ *Annual Review of Biochemistry*, 59 pp. 61–86.

Reimann, C., Demetriades, A., Eggen, O. A. and Filzmoser, P. (2009) ‘The EuroGeoSurveys geochemical mapping of agricultural and grazing land soils project (GEMAS) -Evaluation of quality control results of aqua regia extraction analysis.’ *EuroGeoSurveys Geochemistry* , (May 2014) p. 94.

Rellán-Álvarez, R., El-Jendoubi, H., Wohlgemuth, G., Abadía, A., Fiehn, O., Abadía, J., Álvarez-Fernández, A., Schjoerring, J. K., Zocchi, G., Degli, U., Di Milano, S., Yoshihara, T.

and Alvarez-Fernández, A. (2011) ‘Metabolite profile changes in xylem sap and leaf extracts of strategy I plants in response to iron deficiency and resupply.’ *Frontiers in plant science*, 2 p. 66.

Rellán-Álvarez, R., Ortega-Villasante, C., Álvarez-Fernández, A., Campo, F. F. del and Hernández, L. E. (2006) ‘Stress Responses of Zea mays to Cadmium and Mercury.’ *Plant and Soil*, 279(1–2) pp. 41–50.

Ren, J. H., Ma, L. Q., Sun, H. J., Cai, F. and Luo, J. (2014) ‘Antimony uptake, translocation and speciation in rice plants exposed to antimonite and antimonate.’ *Science of the Total Environment*. Elsevier B.V., 475 pp. 83–89.

Rodriguez-Iruretagoiena, A., Trebolazabala, J., Martinez-Arkarazo, I., De Diego, A. and Madariaga, J. M. (2015) ‘Metals and metalloids in fruits of tomatoes (Solanum lycopersicum) and their cultivation soils in the Basque Country: Concentrations and accumulation trends.’ *Food Chemistry*. Elsevier Ltd, 173, February, pp. 1083–1089.

Rosas-Castor, J. M., Guzmán-Mar, J. L., Hernández-Ramírez, A., Garza-González, M. T. and Hinojosa-Reyes, L. (2014) ‘Arsenic accumulation in maize crop (Zea mays): A review.’ *Science of The Total Environment*. Elsevier, 488–489(1) pp. 176–187.

Rousk, J. and Jones, D. L. (2010) ‘Loss of low molecular weight dissolved organic carbon (DOC) and nitrogen (DON) in H2O and 0.5M K2SO4 soil extracts.’ *Soil Biology and Biochemistry*, 42(12) pp. 2331–2335.

Sabir, M., Waraich, E. A., Hakeem, K. R., Öztürk, M., Ahmad, H. R. and Shahid, M. (2015) ‘Phytoremediation: Mechanisms and Adaptations. Mechanisms and Adaptations.’ *Soil Remediation and Plants: Prospects and Challenges* pp. 85–105.

Sadiq, M. (1992) *Toxic metal chemistry in marine environments*. *Marcel Dekker*. New York City.

Salama, A. K. and Radwan, M. A. (2005) ‘Heavy metals (Cd,Pb) and trace elements (Cu,Zn) contents in some foodstuffs from the Egyptian market.’ *Emirates Journal of Food and Agriculture*, 17(1) pp. 34–42.

Salaun, P. (2017) ‘Editorial: Environmental Electrochemistry.’ *Current Opinion in Electrochemistry*. Elsevier B.V., 3(1) pp. 75–77.

Salaün, P. and van den Berg, C. M. G. (2006) ‘Voltammetric detection of mercury and copper in seawater using a gold microwire electrode.’ *Analytical chemistry*, 78(14) pp. 5052–60.

Salaün, P. and Frézard, F. (2013) ‘Unexpectedly high levels of antimony (III) in the pentavalent antimonial drug Glucantime: insights from a new voltammetric approach.’ *Analytical and Bioanalytical Chemistry*. Liverpool, 405(15) pp. 5201–5214.

Salaün, P., Gibbon-Walsh, K. B., Alves, G. M. S. S., Soares, H. M. V. M. V. M. and van den Berg, C. M. G. G. (2012) ‘Determination of arsenic and antimony in seawater by voltammetric and chronopotentiometric stripping using a vibrated gold microwire electrode.’ *Analytica Chimica Acta*. Liverpool: Elsevier B.V., 746(March 2014) pp. 53–62.

Salaün, P., Gibbon-Walsh, K. and van den Berg, C. M. G. (2011) ‘Beyond the Hydrogen Wave: New Frontier in the Detection of Trace Elements by Stripping Voltammetry.’ *Analytical Chemistry*, 83(10) pp. 3848–3856.

Salaün, P., Planer-Friedrich, B. and van den Berg, C. M. . (2007) ‘Inorganic arsenic speciation in water and seawater by anodic stripping voltammetry with a gold microelectrode.’ *Analytica Chimica Acta*. Liverpool, 585(2) pp. 312–322.

Samarah, L. Z., Tran, T. H., Stacey, G. and Vertes, A. (2020) ‘In Vivo Chemical Analysis of Plant Sap from the Xylem and Single Parenchymal Cells by Capillary Microsampling Electrospray Ionization Mass Spectrometry.’ *Analytical Chemistry*, 92(10) pp. 7299–7306.

Samota, M. K., Navnage, N. P. and Bhatt, L. (2017) ‘Role of Macro and Micronutrient in Development and Growth of Plant,’ 10(18) pp. 3171–3173.

Santos, V. S., Santos, W. de J. R., Kubota, L. T. and Tarley, C. R. T. (2009) ‘Speciation of Sb(III) and Sb(V) in meglumine antimoniate pharmaceutical formulations by PSA using carbon nanotube electrode.’ *Journal of Pharmaceutical and Biomedical Analysis*, 50(2) pp. 151–157.

Satoh, S. (2006) ‘Organic substances in xylem sap delivered to above-ground organs by the roots.’ *Journal of Plant Research*, 119(3) pp. 179–187.

Scharifker, B. R., Mostany, J. and Serruya, A. (2000) ‘Catalytic reduction of nitrate during electrodeposition of thallium from Tl3+ solution.’ *Electrochemistry Communications*, 2(6) pp. 448–451.

Scholander, P. F., Bradstreet, E. D., Hemmingsen, E. A. and Hammel, H. T. (1965) ‘Sap Pressure in Vascular Plants: Negative hydrostatic pressure can be measured in plants.’ *Science*, 148(3668) pp. 339–346.

Schurr, U. (1998) ‘Xylem sap sampling—new approaches to an old topic.’ *Trends in Plant Science*. Elsevier Current Trends, 3(8) pp. 293–298.

Schurr, U. (1999) ‘Dynamics of Nutrient Transport from the Root to the Shoot.’ *In*. Springer, Berlin, Heidelberg, pp. 234–253.

Shahid, M., Khalid, S., Abbas, G., Shahid, N., Nadeem, M., Sabir, M., Aslam, M. and Dumat, C. (2015) ‘Heavy metal stress and crop productivity.’ *In Crop Production and Global Environmental Issues*. Springer International Publishing, pp. 1–25.

Sharma, S. D. (2013) ‘History of Rice in Southeast Asia and Australia.’ *Journal of Chemical Information and Modeling*, 53(9) pp. 1689–1699.

Shri, M., Singh, P. K., Kidwai, M., Gautam, N., Dubey, S., Verma, G. and Chakrabarty, D. (2019) ‘Recent advances in arsenic metabolism in plants: Current status, challenges and highlighted biotechnological intervention to reduce grain arsenic in rice.’ *Metallomics*, 11(3) pp. 519–532.

Simoni, R. D., Hill, R. L. and Vaughan, M. (2005) ‘Benedict ’ s Solution , a Reagent for Measuring Reducing Sugars : the Clinical Chemistry of Stanley R . Benedict,’ 277(16) pp. 10–12.

Slamet-loedin, I., Slamet-loedin, I. H., Johnson-beebout, S. E., Impa, S. and Tsakirpaloglou, N. (2015) ‘Enriching rice with Zn and Fe while minimizing Cd risk.’ *Frontiers in Plant Science*, 6(MAR).

Smedley, P. L. and Kinniburgh, D. G. (2000) ‘Source and behaviour of arsenic in natural waters.’ *British Geological Survey* p. 61.

Smedley, P. L. and Kinniburgh, D. G. (2002) ‘A review of the source, behaviour and distribution of arsenic in natural waters.’ *Applied Geochemistry*, 17(5) pp. 517–568.

Smith, A. H., Lingas, E. O. and Rahman, M. (2000) ‘Contamination of drinking-water by arsenic in Bangladesh: A public health emergency.’ *Bulletin of the World Health Organization*, 78(9) pp. 1093–1103.

Smith, A. H. and Smith, M. M. H. (2004) ‘Arsenic drinking water regulations in developing countries with extensive exposure.’ *Toxicology*, 198(1–3) pp. 39–44.

Sobrado, M. A. (2007) ‘Relationship of water transport to anatomical features in the mangrove Laguncularia racemosa grown under contrasting salinities.’ *New Phytologist*, 173(3) pp. 584–591.

Sørensen, O., Andersen, A., Olsen, H., Alexandr, K., Ekstrøm, P. O., Giercksky, K. E. and Flatmark, K. (2010) ‘Validation and use of microdialysis for determination of pharmacokinetic properties of the chemotherapeutic agent mitomycin C - an experimental study.’ *BMC Cancer*, 10.

Spurgeon, D. J., Rowland, P., Ainsworth, G., Rothery, P., Long, S. and Black, H. I. J. (2008) ‘Geographical and pedological drivers of distribution and risks to soil fauna of seven metals (Cd, Cu, Cr, Ni, Pb, V and Zn) in British soils.’ *Environmental Pollution*, 153(2) pp. 273–283.

Sreekanth, T. V. M., Nagajyothi, P. C., Lee, K. D. and Prasad, T. N. V. K. V. (2013) ‘Occurrence, physiological responses and toxicity of nickel in plants.’ *International Journal of Environmental Science and Technology*. Center for Environmental and Energy Research and Studies pp. 1129–1140.

Stazi, S. R., Cassaniti, C., Marabottini, R., Giuffrida, F. and Leonardi, C. (2016) ‘Arsenic uptake and partitioning in grafted tomato plants.’ *Horticulture, Environment, and Biotechnology*. Korean Society for Horticultural Science, 57(3) pp. 241–247.

Steudle, E. (2001) ‘The cohesion-tension mechanism and the acquisition of water by plant roots.’ *Annual Review of Plant Biology*, 52 pp. 847–875.

Stoeva, N., Berova, M. and Zlatev, Z. (2005) ‘Effect of arsenic on some physiological parameters in bean plants.’ *Biologia Plantarum*, 49(2) pp. 293–296.

Sulyok, M., Miró, M., Stingeder, G. and Koellensperger, G. (2005) ‘The potential of flow-through microdialysis for probing low-molecular weight organic anions in rhizosphere soil solution.’ *Analytica Chimica Acta*. Elsevier, 546(1) pp. 1–10.

Sun, G., Williams, P. N. and Zhu, Y. (2009) ‘Mechanisms of Arsenic Uptake and Metabolism by Plants : Focusing on Rice.’ *Environmental Toxicology*, 134(November) pp. 1–6.

Sun, H., Yan, S. C. and Cheng, W. S. (2000) ‘Interaction of antimony tartrate with the tripeptide glutathione.’ *European Journal of Biochemistry*, 267(17) pp. 5450–5457.

Takarina, N. D. and Pin, T. G. (2017) ‘Bioconcentration Factor (BCF) and Translocation Factor (TF) of Heavy Metals in Mangrove Trees of Blanakan Fish Farm.’ *Makara Journal of Science*, 21(2).

Tamás, M. J. (2016) ‘Cellular and molecular mechanisms of antimony transport, toxicity and resistance.’ *Environmental Chemistry*, 13(6) pp. 955–962.

Tatár, E., Mihucz, V. G., Kmethy, B., Záray, G. and Fodor, F. (2000) ‘Determination of organic acids and their role in nickel transport within cucumber plants.’ *Microchemical Journal*, 67(1–3) pp. 73–81.

Tatár, E., Mihucz, V. G., Varga, A., Záray, G. and Fodor, F. (1998) ‘Determination of Organic Acids in Xylem Sap of Cucumber: Effect of Lead Contamination.’ *Microchemical Journal*. Elsevier Inc., 58(3) pp. 306–314.

Telford, K., Maher, W., Krikowa, F. and Foster, S. (2008) ‘Measurement of total antimony and antimony species in mine contaminated soils by ICPMS and HPLC-ICPMS.’ *Journal of Environmental Monitoring*, 10(1) pp. 136–140.

Telford, K., Maher, W., Krikowa, F., Foster, S., Ellwood, M. J. M. J., Ashley, P. M. P. M., Lockwood, P. V. P. V. and Wilson, S. C. S. C. (2009) ‘Bioaccumulation of antimony and arsenic in a highly contaminated stream adjacent to the Hillgrove Mine, NSW, Australia.’ *Environmental Chemistry*, 6(2) pp. 133–143.

Thomas, G. W. (1996) ‘Soil pH and soil acidity.’ *In* D.L. Sparks et al., editors (ed.) *Methods of soil analysis: Part 3. SSSA Book Series No. 5. SSSA,* pp. 475–490.

Tian, T., Zhou, H., Gu, J., Jia, R., Li, H., Wang, Q., Zeng, M. and Liao, B. (2019) ‘Cadmium accumulation and bioavailability in paddy soil under different water regimes for different growth stages of rice (Oryza sativa L.).’ *Plant and Soil*. Springer International Publishing, July.

Timofeev, I. and Hutchinson, P. (2008a) ‘Microdialysis.’ *In Essentials of Neuroanesthesia and Neurointensive Care*. Elsevier, pp. 277–282.

Timofeev, I. and Hutchinson, P. (2008b) ‘Microdialysis Learn more about Microdialysis Microdialysis Chemical and Biochemical Approaches for the Study of Anesthetic Function Part B Carrier-mediated and artificial-cell tar-.’

Toghill, K. E., Lu, M., Compton, R. G. and Kathryn E. Toghill, Min Lu, and R. G. C. (2011) ‘Electroanalytical Determination of Antimony.’ *International Journal of Electrochemical Science*, 6(8) pp. 3057–3076.

Tollestrup, K., Frost, F. J., Harter, L. C. and McMillan, G. P. (2003) ‘Mortality among Children Residing near the American Smelting and Refining Company (ASARCO) Copper Smelter in Ruston, Washington.’ *Archives of Environmental Health: An International Journal*, 58(11) pp. 683–691.

Torto, N., Mwatseteza, J. and Laurell, T. (2001) ‘Microdialysis Sampling: Challenges and New Frontiers.’ *LC GC Europe*, 14(9) pp. 536–546.

Torto, N., Mwatseteza, J. and Sawula, G. (2002) ‘A study of microdialysis sampling of metal ions.’ *Analytica Chimica Acta*. Elsevier, 456(2) pp. 253–261.

Trejo-Téllez, L. I. (2012) ‘Nutrient Solutions for Hydroponic Systems.’ *In* Asao, F. C. G.-M. E.-T. (ed.). Rijeka: IntechOpen, p. Ch. 1.

Tsang, J. J., Rozan, T. F., Hsu-Kim, H., Mullaugh, K. M. and Luther, G. W. (2006) ‘Pseudopolarographic determination of Cd2+ complexation in freshwater.’ *Environmental Science and Technology*, 40(17) pp. 5388–5394.

Tschan, M., Robinson, B. H. and Schulin, R. (2009) ‘Antimony in the soil - Plant system - A review.’ *Environmental Chemistry*, 6(2) pp. 106–115.

Tschan, M., Robinson, B. and Schulin, R. (2008) ‘Antimony uptake by Zea mays (L.) and Helianthus annuus (L.) from nutrient solution.’ *Environmental Geochemistry and Health*, 30(2) pp. 187–191.

Tsukagoshi, S. and Shinohara, Y. (2015) *Nutrition and Nutrient Uptake in Soilless Culture Systems*. *Plant Factory: An Indoor Vertical Farming System for Efficient Quality Food Production*. Elsevier Inc.

Tuyogon, D. S. J., Impa, S. M., Castillo, O. B., Larazo, W. and Johnson-Beebout, S. E. (2016) ‘Enriching rice grain zinc through zinc fertilization and water management.’ *Soil Science*

Society of America Journal, 80(1) pp. 121–134.

Tylenda, C. A., Sullivan, D. W. and Fowler, B. A. (2015) *Antimony*. *Handbook on the Toxicology of Metals: Fourth Edition*. Fourth Edi, Elsevier.

U.S. Department of Health and Human (2018) *Revised Draft : Report on Carcinogens Monograph on Antimony Trioxide*.

U.S. Geological Survey (2004) 'Mineral Commodity Profiles-Antimony.' *U.S. Department of the Interior: U.S. Geological Survey* pp. 1–35.

Ugochukwu, G. C., Eneh, F. U., Igwilo, I. . and Aloh, C. H. (2017) 'Comparative study on the heavy metal content of domestic rice (Oryza sativa Comparative study on the heavy metal content of domestic rice (Oryza sativa L) brands common in Awka, Nigeria.' *IOSR Journal of Environmental Science, Toxicology and Food Technology*, 11(8) pp. 67–70.

UN (ed.) (2015) *Crop Prospects and Food Situation*. Rome: FAO.

Ungureanu, G., Santos, S., Boaventura, R. and Botelho, C. (2015) 'Arsenic and antimony in water and wastewater: Overview of removal techniques with special reference to latest advances in adsorption.' *Journal of Environmental Management*, 151, March, pp. 326–342.

Uroic, M. K. (2011) *The impact of arsenic species on the production and composition of xylem sap*. *Environmental & Analytical Chemistry*. University of Aberdeen. Retrieved from internal-pdf://145.35.116.156/PhD thesis The impact of As MK Uroic.pdf.

Uroic, M. K., Salaün, P., Raab, A. and Feldmann, J. (2012) 'Arsenate impact on the metabolite profile, production, and arsenic loading of xylem sap in cucumbers (Cucumis sativus L.).' *Frontiers in Physiology*, 3 APR(March) pp. 1–23.

Varsányi, I., Fodré, Z. and Bartha, A. (1991) 'Arsenic in drinking water and mortality in the Southern Great Plain, Hungary.' *Environmental Geochemistry and Health*. Kluwer Academic Publishers, 13(1) pp. 14–22.

Violante, A., Cozzolino, V., Perelomov, L., Caporale, A. . and Pigna, M. (2010) 'Mobility and bioavailability of heavy metals and metalloids in soil environments.' *Journal of soil science and plant nutrition*. Sociedad Chilena de la Ciencia del Suelo, 10(3) pp. 268–292.

Vithanage, M., Dabrowska, B. B., Mukherjee, A. B., Sandhi, A. and Bhattacharya, P. (2012) 'Arsenic uptake by plants and possible phytoremediation applications: A brief overview.' *Environmental Chemistry Letters* pp. 217–224.

Wagner, S. E., Peryea, F. J. and Filby, R. A. (2003) 'Antimony Impurity in Lead Arsenate Insecticide Enhances the Antimony Content of Old Orchard Soils.' *Journal of Environmental Quality*. Wiley, 32(2) pp. 736–738.

Wan, X. M., Tandy, S., Hockmann, K. and Schulin, R. (2013) ‘Changes in Sb speciation with waterlogging of shooting range soils and impacts on plant uptake.’ *Environmental Pollution*. Elsevier Ltd, 172, January, pp. 53–60.

Wang, S., Shi, X., Sun, H., Chen, Y., Pan, H., Yang, X. and Rafiq, T. (2014) ‘Variations in Metal Tolerance and Accumulation in Three Hydroponically Cultivated Varieties of Salix integra Treated with Lead.’ Reigosa, M. (ed.) *PLoS ONE*. Public Library of Science, 9(9) p. e108568.

Wang, T., Yang, Q., Wang, Y., Wang, J., Zhang, Y. and Pan, W.-P. P. (2020) ‘Arsenic release and transformation in co-combustion of biomass and coal: Effect of mineral elements and volatile matter in biomass.’ *Bioresource technology*. Beijing, PR China: Elsevier Ltd, 297, February, p. 122388.

Wang, Z., Zeng, X., Geng, M., Chen, C., Cai, J., Yu, X., Hou, Y. and Zhang, H. (2015) ‘Health risks of heavy metals uptake by crops grown in a sewage irrigation area in China.’ *Polish Journal of Environmental Studies*, 24(3) pp. 1379–1386.

Welch, A. H. and Stollenwerk, K. G. (eds) (2003) *Arsenic in Ground Water*. *Springer Science Business Media New York*. Boston, MA: Springer US.

White, M. C., Chaney, R. L., Decker, A. M. and R., and M. W. D. A. (1981) ‘Metal Complexation in Xylem Fluid: I. Chemical composition of tomato and soybean stem exudate.’ *Plant Physiology*, 67(2) pp. 292–300.

WHO (2003a) ‘Antimony in Drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality.’ *Who* pp. 1–9.

WHO (2003b) *Background document for preparation of WHO Guidelines for drinking-water quality: Antimony in drinking water.* Geneva, Switzerland.

WHO (2003c) ‘Chromium in drinking-water. Background document for preparation of WHO Guidelines for drinking-water quality.’ *(WHO/SDE/WSH/03.04/4)*, (3) pp. 334–335.

Wickliff, J. L. and Aronoff, S. (1962) *Quantitative measurement of leaf chlorophylss by spectrophotometry of their pheophytins in aqueous alcoholic extracts*. Iowa, USA.

Williams, P. N., Islam, M. R., Adomako, E. E., Raab, A., Hossain, S. A., Zhu, Y. G., Feldmann, J. and Meharg, A. A. (2006) ‘Increase in rice grain arsenic for regions of Bangladesh irrigating paddies with elevated arsenic in groundwaters.’ *Environmental Science and Technology* pp. 4903–4908.

Wilson, S. C., Lockwood, P. V., Ashley, P. M. and Tighe, M. (2010) ‘The chemistry and behaviour of antimony in the soil environment with comparisons to arsenic: A critical review.’ *Environmental Pollution*. Elsevier Ltd, 158(5) pp. 1169–1181.

Woolson, E. A., Axley, J. H. and Kearney, P. C. (1971) ‘Correlation between Available Soil

Arsenic, Estimated by Six Methods, and Response of Corn (Zea mays L.)1.' *Soil Science Society of America Journal*. Soil Science Society of America, 35(1) p. 101.

Wu, D. and Sun, S. (2016) 'Speciation analysis of As, Sb and Se.' *Trends in Environmental Analytical Chemistry*. Elsevier Inc., 11, July, pp. 9–22.

Wu, T.-L. L., Cui, X.-D. D., Cui, P.-X. X., Ata-Ul-Karim, S. T., Sun, Q., Liu, C., Fan, T.-T. T., Gong, H., Zhou, D.-M. M. and Wang, Y.-J. J. (2019) 'Speciation and location of arsenic and antimony in rice samples around antimony mining area.' *Environmental Pollution*. Elsevier Ltd, 252, September, pp. 1439–1447.

www.IRRI.org (2019) *Long-Term Continuous Cropping Experiment (LTCCE) | International Rice Research Institute*. [Online] [Accessed on 18th November 2019] https://www.irri.org/long-term-continuous-cropping-experiment-ltcce.

Wyrwicka, A., Urbaniak, M. and Przybylski, M. (2019) ' The response of cucumber plants (Cucumis sativus L.) to the application of PCB-contaminated sewage sludge and urban sediment .' *PeerJ*, 7 p. e6743.

Xu, X. Y., McGrath, S. P. and Zhao, F. J. (2007) 'Rapid reduction of arsenate in the medium mediated by plant roots.' *New Phytologist*, 176(3) pp. 590–599.

Yadav, S. K. (2010) 'Heavy metals toxicity in plants: An overview on the role of glutathione and phytochelatins in heavy metal stress tolerance of plants.' *South African Journal of Botany*. Elsevier B.V., 76(2) pp. 167–179.

Ye, W.-L. L., Wood, B. A., Stroud, J. L., Andralojc, P. J., Raab, A., McGrath, S. P., Feldmann, J. and Zhao, F.-J. J. (2010) 'Arsenic speciation in phloem and xylem exudates of castor bean.' *Plant Physiology*, 154(3) pp. 1505–1513.

Zavala, Y. J. and Duxbury, J. M. (2008) 'Arsenic in rice: I. Estimating normal levels of total arsenic in rice grain.' *Environmental Science and Technology*, 42(10) pp. 3856–3860.

Zengin, F. K. and Munzuroglu, O. (2005) 'Effects of some heavy metals on content of chlorophyll, proline and some antioxidant chemicals in bean (Phaseolus vulgaris L.) seedlings.' *Acta Biologica Cracoviensia Series Botanica*, 47(2) pp. 157–164.

Zhang, H. and Selim, H. M. (2005) 'Kinetics of Arsenate Adsorption−Desorption in Soils.' *Environmental Science & Technology*, 39(16) pp. 6101–6108.

Zhang, T., Ruan, J., Zhang, B., Lu, S., Gao, C., Huang, L., Bai, X., Xie, L., Gui, M. and Qiu, R. (2019) 'Heavy metals in human urine, foods and drinking water from an e-waste dismantling area: Identification of exposure sources and metal-induced health risk.' *Ecotoxicology and Environmental Safety*. Academic Press, 169, March, pp. 707–713.

Zhang, W., Cai, Y., Tu, C. and Ma, L. Q. (2002) 'Arsenic speciation and distribution in an arsenic hyperaccumulating plant.' *Science of the Total Environment*, 300(1–3) pp. 167–

177.

Zhao, F.-J., Ma, Y., Zhu, Y.-G., Tang, Z. and McGrath, S. P. (2015) ‘Soil Contamination in China: Current Status and Mitigation Strategies.’ *Environmental Science & Technology*. American Chemical Society, 49(2) pp. 750–759.

Zhao, F.-J., McGrath, S. P. and Meharg, A. A. (2010) ‘Arsenic as a Food Chain Contaminant: Mechanisms of Plant Uptake and Metabolism and Mitigation Strategies.’ *Annual Review of Plant Biology*. Annual Reviews, 61(1) pp. 535–559.

Zheng, J., Iijima, A. and Furuta, N. (2001) ‘Complexation effect of antimony compounds with citric acid and its application to the speciation of antimony(III) and antimony(V) using HPLC-ICP-MS.’ *Journal of Analytical Atomic Spectrometry*, 16(8) pp. 812–818.

Zheng, R. L., Sun, G. X. and Zhu, Y. G. (2013) ‘Effects of microbial processes on the fate of arsenic in paddy soil.’ *Chinese Science Bulletin* pp. 186–193.

Zhou, S. N., Ouyang, G. and Pawliszyn, J. (2008) ‘Comparison of microdialysis with solid-phase microextraction for in vitro and in vivo studies.’ *Journal of Chromatography A*, 1196–1197(1–2) pp. 46–56.

Zhou, X., Sun, C., Zhu, P. and Liu, F. (2018) ‘Effects of Antimony Stress on Photosynthesis and Growth of Acorus calamus.’ *Frontiers in Plant Science*. Frontiers Media S.A., 9(May) pp. 1–9.

Zulkafflee, N. S., Redzuan, N. A. M., Hanafi, Z., Selamat, J., Ismail, M. R., Praveena, S. M. and Razis, A. F. A. (2019) ‘Heavy metal in paddy soil and its bioavailability in rice using in vitro digestion model for health risk assessment.’ *International Journal of Environmental Research and Public Health*, 16(23).

CHAPTER 3 ARSENIC AND ANTIMONY SPECIATION STUDY USING MICRODIALYSIS TECHNIQUE AND ICP-MS

Index of Figures

Index of Tables

3.1 Introduction

The increased use of metalloid arsenic (As) and antimony (Sb) has led to many environmental soils and groundwater contamination problems, and understanding their biogeochemical cycling is of prime importance to predicting potential contamination issues. Antimony and arsenic impact on the xylem sap and its effect on plant growth in vivo has not been reported in detail.

As part of food safety, it is vital to study the transportation of nutrients in plants for human and animal consumption (Meharg, 2004). Moreover, the transportation of the toxic elements is necessary, like Sb, As to name a few. Their presence in low concentration is often not manifested by the plant; therefore, the study of nutrients and toxic elements in the plant is crucial in food safety. There are several ways of determining the total concentration of heavy metal(loid) in plant parts. One of them is ICP-MS analysis by dividing the plant into its parts (i.e., roots, stems, leaves, flowers, and fruits) separately by acid digestion (Jamila et al., 2016; Emamverdian and Ding, 2017; Hua et al., 2020).

Sample preparation innovations result from advances and new insights in separation mechanisms and processes. Recent advancements resulted in a more selective, efficient, and environmentally friendly procedure. Microdialysis (MD) is a passive technique that was initially used in biomedical research, and it was used in monitoring the chemistry of the extracellular space in living tissue (Lydic et al., 2018). It mimics the blood capillary to preview what is happening inside the tissues (Buckley et al., 2016; Lydic et al., 2018). MD is usually constructed as a concentric tube where the perfusate liquid enters the inner tube and exits to the distal ends, and then enters the space between the inner and outer dialysis membrane (Torto et al., 2001; Li and Cui, 2008a; Timofeev and Hutchinson, 2008b). MD is used for monitoring in the medical field (Li and Cui, 2008). It was used predominantly in laboratory research in the 1970s but was applied in the clinical area since the 1990s, specifically in neurointensive care chemistry (Timofeev and Hutchinson, 2008a). Most of the applications are in the biomedical fields, pharmaceutical, pharmacogenetics, and tissue engineering, to name a few (Elmquist and Sawchuk, 1997; Li and Cui, 2008; Lydic et al., 2018).

MD is an emerging sensitive tool in environmental sciences because of such opportunities by the technique and the advantage of sampling with minimal disturbance in soil environments(Buckley et al., 2020). Inselsbacher et al. (2011) used MD as a potential tool for monitoring organic and inorganic nitrogen compounds in the soil. Microdialysis for Ni and Cu's determination in plant suspension made from *Blepharis Aspera* obtained from a Cu and Ni mineralised site was reported 2007 (Mosetlha et al., 2007). Brackin et al. (2016) developed a new technology using MD for investigating soil nitrogen fluxes in the rhizosphere. The advantages of MD include small sampling disturbances making it less destructive/invasive (since inserting the small tube is needed), time efficiency, real-time sampling, high-throughput and efficient collection of dialysate from passive diffusion of solutes across a semi-permeable membrane to be collected over time for nutrient flux dynamic studies (Chaurasia et al., 2007; Timofeev and Hutchinson, 2008b; Zhou et al., 2008; Pretti et al., 2014; Brackin et al., 2016; Lydic et al., 2018a). The MD is becoming popular because of the many drawbacks of conventional sampling methods such as destructive bulk soil sampling, sample degradation or transformation through slow sampling time, and laborious sample clean-up (Miró et al., 2010; Rousk and Jones, 2010; Inselsbacher, 2014).

Appropriate sampling methods are crucial for studying the dynamic variations of xylem sap composition and nutrient fluxes. Currently available techniques have been reviewed by Schurr (1998) and were mainly interested in the nutrient dynamics under natural conditions. The essential requirement is not to interfere with the forces and processes that govern nutrient fluxes in intact plants. Conventional techniques like root pressure exudation and the Scholander bomb method include action destructive to the plant, low-throughput, and thus contain the risk of massive interference with the relevant processes determining nutrient fluxes in intact plants. The conventional techniques mentioned provide useful information, but one must always keep in mind their limitations, and calculations of ion balances based on these are questionable (Schurr, 1999). MD analysis is one way of monitoring biochemical responses to intrinsic and extrinsic factors or stimuli with minimal effects from experimental factors that may change the organism's physiology (Samarah et al., 2020).

Metalloids Sb and As are carcinogenic elements, well-known for acute poisoning effect and insidious toxic effect if consumed over long periods. As and Sb groundwater, contamination is a worldwide problem affecting millions of people through drinking water. Understanding how arsenic is transported through the environment e.g., from water to soils, soil to roots, or translocated from roots to shoot and/or fruits, is thus of importance.

3.2 Aims and Objectives

This chapter presents MD as a novel technique of xylem sap sampling on cucumber plant *Cucumis sativus L*. To examine Sb and As uptake and translocation in plants and understand where inorganic metalloids (Sb and As) are ending up and how they are being transported. An application could be hi-throughput monitoring of metalloids concentration and speciation in the nutrient solution overtime during the treatment. Another application could be monitoring Sb and As in xylem sap of plants by inserting a microdialysis tube into the xylem vessel. This method would have the advantage that no sample preparation is necessary, less invasive to the plant, and the risk of sample alteration.

- The first part of this study will present hydroponic experiments with different levels of As(III) or Sb(III) to quantify the effects of arsenic (As) and antimony (Sb) stress on the growth of cucumber. The differences with chapter 2 are: the concentration is much higher (in ppm levels), the effect of plant age, and only (III) species (both for Sb and As) were used in this experiment to quantify the maximum effect using the proposed sampling method,
- The effect of plant age and the effect of varying concentration of metalloids on the micro- and macro-nutrient consumption of the plant are reported together with selected plant growth experiments (i.e., leaf count, plant height, and biomass),
- To evaluate the potential applicability of the microdialysis sampling technique in collecting xylem sap for the determination (and potential in monitoring) of Sb and

As uptake and translocation were investigated here along with the more traditional approach where the plant was also divided into its components for further analysis,

3.4 Materials and Methods

3.4.1 Chemicals

Arsenite (As_2O_3) and antimonite were purchased from Sigma-Aldrich UK. Hoagland's nutrient solution with MQ water. Chemicals were at least of analytical grade (KNO_3, $Ca(NO_3)_2 \cdot 4 H_2O$, $MgSO_4$, NH_4NO_3, KH_2PO_4, $FeSO_4 \cdot 7 H_2O$, $MnCl_2 \cdot 4 H_2O$, $Na_2B_4O_7 \cdot 10 H_2O$, $ZnSO_4 \cdot 7 H_2O$, $CuSO_4 \cdot 3 H_2O$, $Na_2MoO_4 \cdot 2 H_2O$ (Sigma Aldrich, Singapore)). The set-up for this experiment, compared to Chapter 2, was different. Plants were planted in the hydroponic solution in separate High-Density Polyethylene (HDPE) plastic. A 250-mL HDPE container was used for all hydroponic experiments. Aluminium foil was used to cover the container to prevent algae formation, a small piece of disinfected dishwashing foam inside the small hole was used to hold the cucumber plants in the container, cucumber seeds bought from Taiwan. Seedling tray and vermiculite were used to grow cucumber plants until the 2-leaf stage.

3.4.2 Modified Hoagland's nutrient Solution

The modified Hoagland nutrient solution was prepared, as described in Chapter 2, section 2.3.2.

3.4.3 Plant growth

3.4.3.1 Seed germination and transplantation

Cucumber seeds *Cucumis sativus L.* bought from a local market in Hsinchu town were soaked in water for five to 10 hours before draining them (1:1 MQ:3% H_2O_2). The drained seeds were folded into the towel with warm water in a plastic bag or box to prevent evaporation. The towel temperature was kept above 21 °C (13-35°C). The seeds were checked at least once daily. Seeds with developed roots were transplanted Vermiculite® watered once a day and covered with a black plastic bag. After the seeds sprouted, they were uncovered and a 12 h on/12 h off light regime at 21-24 ° C. The germinated seeds were transferred until their two-leaf stage, which took approximately two weeks depending on the environment. The two-leaf stage plants were thoroughly washed and transferred to a hydroponic set-up (Figure 3.1) with 200 mL Hoagland solution (described in the next section) at pH 6.5.

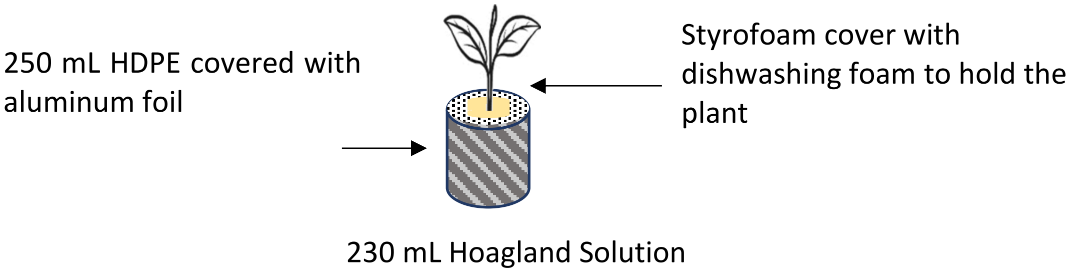


Figure 3. 1.Diagram of a hydroponic plant set-up

Figure 3.1 shows a diagram of an individual cucumber plant grown hydroponically. The set-up consists of a 250-mL HDPE container covered with aluminium foil to prevent algae growth by preventing light from entering. Into each lid, a small Styrofoam with a centre hole was fitted. Into the hole, a dishwashing foam was fitted to hold the cucumber plant. One container represents one experimental set-up.

3.4.3.2 Treatment

The two-leaf cucumber plants were transferred into 250-mL pots containing hydroponic nutrient solution. All plants were grown in an improvised plant growth set-up in BMES (Biomedical Engineering and Environmental Sciences, NTHU) Building at adjusted temperature (27 ± 1 °C). The hydroponic experiment was conducted with a 26-29 °C room temperature and average humidity of 85%. Artificial LED light (Everlight, Taiwan) with a timer plug was used to ensure a 14/10 h light/dark regime. For the first week, half strength nutrient solution only was supplied. For the rest of the time, full strength nutrient solution was used. The solution was replenished every two days (+/- 1 day) for all the plants before the amendment. The water level, pH, and temperature were also constantly checked for each nutrient solution in every container. Two different experiments were conducted for As(III) and Sb(III). Plant parts and xylem sap were used for Sb and determination after a 7-day exposure.

3.4.4 Hydroponic experiments

3.4.4.1 Plant set-up

Figure 3.2 shows three sets of plants were grown for 15 ± 1 days (2-3 leaf stage) with three plants per condition (amended for 7 days). Each set was grown in three separate batches for two stages of the plant (26 and 35 (days after transplanting)).

a) First set plants each box was challenged with no arsenic/antimony (12 plants)

b) The second set of plants each was challenged with 1 mg/L As(III) or 1 mg/L Sb(III) (16 plants in total) for 7 days. (12 plants)

c) The third set of plants each 5 mg/kg As(III) or 5 mg/kg Sb(III) (16 plants in total) for 7 days. (12 plants) In total, 36 plants were used.

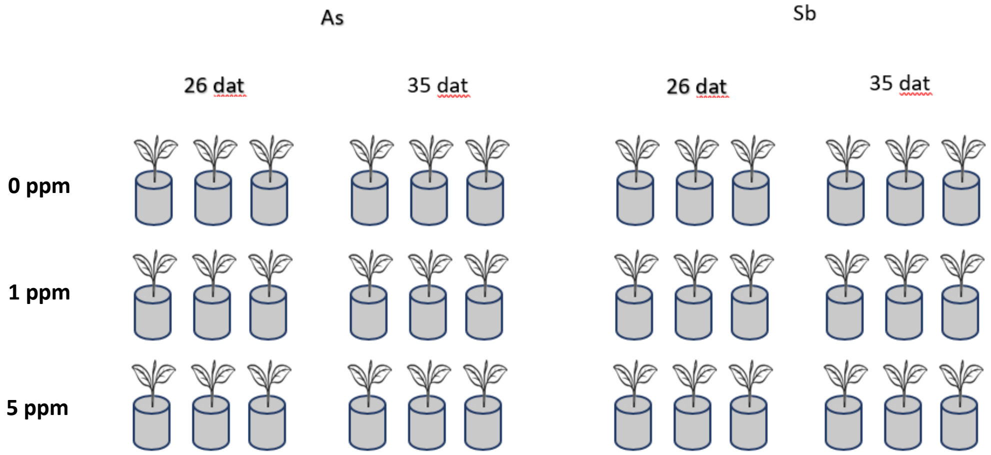


Figure 3. 2.Cucumber hydroponic plant set-up (BMES plant growth room)

3.4.4.2 Amendment with As and Sb

All nutrient solution for the amendment was replenished with only 100 ppb phosphate solution 1 day before the amendment schedule instead of the standard concentration as described in section 3.3.3.2.

3.4.5 Plant Sampling and plant growth parameters

Cucumber plants were harvested 6-7 days after the As/Sb amendments per replicate and per plant growth stage/age. During the harvest, all plants per box (both sets) were separated into roots and above solution parts (stems, leaves), washed several times with distilled water. The hydroponic solutions before and after were also collected for further analysis. The washed plants were dried with a paper towel, weighed, and were oven-dried at 60°C in pre-weighed brown envelops until constant weight. All dried plant parts were weighed again, were ground, and kept for digestion and further analysis with ICP-MS.

3.4.5.1 Biomass

Fresh and dry weight biomass was measured per treatment. The plants were divided into roots, stems, and leaves. Plant parts were washed with tap and followed by distilled water and dried using a paper towel, and put in pre-weighed brown paper envelopes. Fresh weights were measured before oven drying at 60°C overnight. The plants were allowed to cool in a dry environment before weighing the dry weights and measure the moisture content.

3.4.5.2 Plant Height

Each cucumber plant's plant height was measured with a ruler from the bottom of the roots until the tip of the plant.

3.4.5.3 Number of Leaves

Leaves were counted per plant for each trial and the average recorded per plant.

3.4.6 Xylem sap sampling

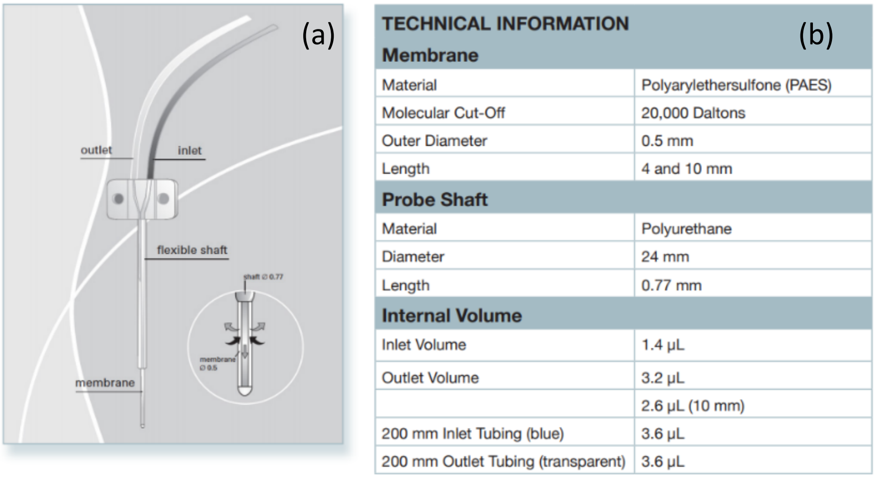
3.4.6.1 Root Exudation

This technique is the simplest way to sample xylem sap, which does not require sophisticated instrumentation. In this technique, xylem sap was sampled using a micropipette (White et al., 1981). The stem was cut 2 cm above the roots. The sap was collected after wiping the first few drops from the stem and was collected in a microtube for one hour (storage at -80°C until analysis) (Kehr and Rep, 2007; Netting et al., 2012).

3.4.6.2 Microdialysis technique

A new microdialysis technique (MD) was developed and performed to monitor metalloid uptake in cucumber plants. MD was performed using CMA-20 Elite MD probes (CMA Microdialysis AB, Sweden) with membrane length 10 mm, diameter 0.5 mm, and molecular cutoff 20 kDa (Table 3.1).

Table 3. 1.CMA 20 elite microdialysis probe for implantation (a) diagram, (b) technical information (CMA, Sweden)



TECHNICAL INFORMATION	
Membrane	
Material	Polyarylethersulfone (PAES)
Molecular Cut-Off	20,000 Daltons
Outer Diameter	0.5 mm
Length	4 and 10 mm
Probe Shaft	
Material	Polyurethane
Diameter	24 mm
Length	0.77 mm
Internal Volume	
Inlet Volume	1.4 µL
Outlet Volume	3.2 µL
	2.6 µL (10 mm)
200 mm Inlet Tubing (blue)	3.6 µL
200 mm Outlet Tubing (transparent)	3.6 µL

3.4.6.2.1 Automatic syringe pump

MD using a portable automatic syringe pump with perfusion liquid was used in xylem sap sampling every 4 hours on the first day and every 8 hours on the following days until 7 days (or until plants show any significant effect). The perfusion liquid used in the study is a Phosphate Buffer Saline (PBS) (UniRegion Bio-Tech Taiwan), at pH 6.5. The PBS solution has the following component: 2.7 mmol L^{-1} KCl; 1.47 mmol L^{-1} KH_2PO_4; 137 mmol L^{-1} NaCl; and 7.7 mmol L^{-1} NaH_2PO_4. The osmolality is 280-315 mOsm Kg^{-1}, isotonic and sterile. The PBS solution was chosen based on a simulation study done beforehand. The composition and pH (pH 6.5) and MQ water and PBS solution were used to clean and activate the membrane (Torto et al., 2001; Li and Cui, 2008; Sørensen et al., 2010).

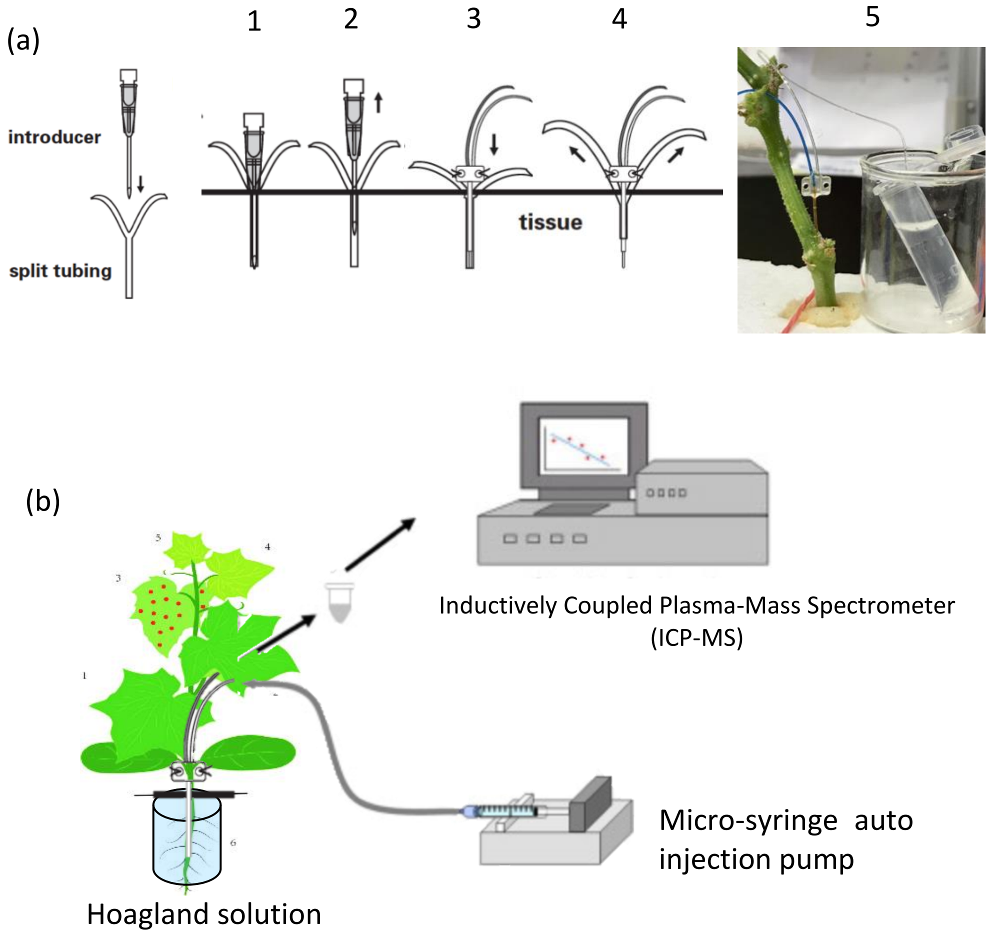


Figure 3. 3. Set-up for the microdialysis sampling and analysis of *Cucumis Sativa L.*

A needle placed in a plastic split tubing was used as the ‘introducer’ to implant the microdialysis probe. As shown in Figure 3.3a (CMA, Sweden), the introducer was inserted into the split tubing (1), the needle was removed (2), the microdialysis probe was pushed forwards through the split tubing (3), the tubing was carefully removed (4), leaving the probe in place, ready to use (5). In Figure 3.3b, an automatic syringe pump (KDS KDS200, Scientific Ltd., Taiwan), equipped with two 10-mL glass micro syringes (Thermo Fischer) at a flow rate of 1 mL min^{-1} were used to administer perfusion solution (PBS, pH 6.5) using the syringe connected to the inlet via polyethylene tubing and handled collected fractions. MD fractions were collected from the outlet in HDPE microtube vials (500 uL), undiluted, and stored at 0°C until ICP-MS analysis. MD set-up was cleaned with MQ water in between sampling (after one week of use).

3.4.6.2.2 Syringe pump calibration

To check the syringe pump's performance, the gravimetric calibration method was applied, which is considered by the National Metrology Institute for calibrating syringe pumps (Kisan et al., 2012). A sufficient amount of MQ water was allowed to pass the tubing to remove air bubbles. The flow to be calibrated together with the specific volume and syringe manufacturer is then programmed in the pump. The water delivered by the 10 mL syringe pump being collected and weighed in a fixed amount of time at 3 different flowrates (3 replicates) using a modified covered microtube in analytical balance. The obtained weight from the microtube is plotted against the corresponding rate (µl min^{-1}) for one minute (Fig. 3.4). Three solutions were tested to be used as perfusate for the microdialysis: Deionised water (DI), Phosphate buffer solution (PBS), and 0.95 % NaCl. The same procedure was applied using 0.95 NaCl solution and phosphate buffer solution (PBS, pH 6.5) results with MQ water.

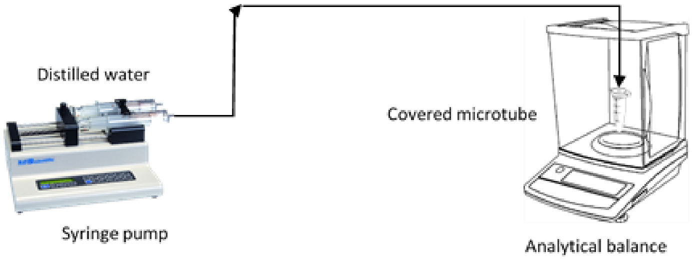


Figure 3. 4. Schematic of the gravimetric calibration of the syringe pump

3.4.7 High-pressure bomb acid digestion

ICP-MS analysis of plant samples was adapted with modifications (Chang et al., 2009). Before analysis, digestion pre-treatment was performed using a high-pressure bomb system. Fig. 3.5 shows the order of the process. Approximately 50 mg of dried plant parts (roots, stem, and leaves) was weighed into Teflon centrifuge tubes; 3 mL of H_2O_2 and 5 mL of HNO_3 were added to each sample and digestion block capped stainless cylinder for acid digestion for 5 hours at 180 °C and cooled down overnight. After the cooldown, the digestate was transferred to a PTFE beaker, including all the washings from the Teflon

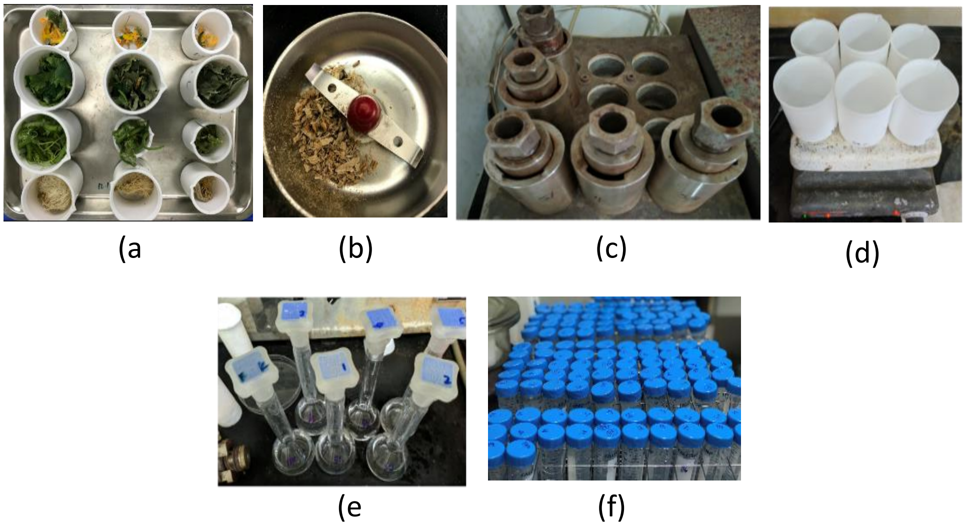


Figure 3. 5. High-pressure bomb acid digestion Set-up (a) drying at 60 °C, (b) grinding, (c) Acid digestion, (d) evaporation, and (e) dilution.

centrifuge tubes and heated gently (85–90 °C) on a hot plate to allow evaporation of residual acid in the solution until almost dry. The residue was diluted to 50 mL of MQ water for further ICP-MS analysis.

3.4.8 Quantification of metals in the sap and plant parts

Total arsenic and antimony analysis were performed using an ICP-MS (Agilent Technologies 7500A). Table 3.2 shows the operational conditions for the ICP-MS instruments. Plant roots, leaves, stem samples were subjected to ICP-MS analysis after the digestion procedure as described in section 2.3.8. Each batch was accompanied by a 1 reagent blank, spike of a known standard concentration, and a certified reference material NIST-1568a rice flour (290 ng/g arsenic). Xylem sap and nutrient solution (before and after) were diluted and ICP-MS analysis for As, Sb, B, Mn, Ni, Cu, Zn, Ca, Mg, and Fe.

Table 3. 2. Operation conditions for ICP-MS instrument used to quantify plants's metal concentrations.

ICP-MS	(Agilent 7500A)
RF power	1500 W
Coolant	15 Ar L min^{-1} (plasma gas)
Auxiliary	2 L min^{-1}
Carrier	1 L min^{-1}
Makeup	0.17 L min^{-1}
Sampling depth	10.6 mm
Sampling cone	Ni (1.1 mm)
Isotopes	B-11, Mg-24, K-39, Ca-43, mn-55, Ni-60, Cu-63, Zn-66, Mo-95, Sb-21, As-75

3.4.9 Statistical Analyses

Data were analysed using SPSS Statistics for MacOS, version 23 (IBM Corp., Armonk, NY, USA). Two-way analysis of variance (ANOVA) was performed to determine the effects of different treatments (control, As(III), Sb(III)) and plant stages (26 and 35) and its interaction effects (treatment*duration). A p-value of <0.05 denoted significance. The Tukey, Dunnett's, and subsequent Pearson correlation coefficients were employed to compare significant difference ($P < 0.05$) between treatment means. All data presented are expressed as the means of 3 replicates ± standard deviation (SD).

3.5 Results

3.5.1 Microdialysis Pump calibration and Recovery

Three solutions were tested to be used as perfusate for the microdialysis: Deionised water (DI), Phosphate buffer solution (PBS), and 0.95 % NaCl (Pretti et al., 2014). Based on the recovery and simulation tests, PBS performed better among the test perfusate solutions with a 92.6% recovery compared to 79.0 % and 77 % for DI and 0.96% NaCl, respectively. Three replicates were performed using PBS at four different flow rates (1, 5, 10, and 20 µl min^{-1}) using a 10 mL glass syringe for 1 minute. The calibration results have excellent repeatability with uncertainties of less than 0.2 %. The flow stabilises after 15 minutes of testing (Figure 3.6).

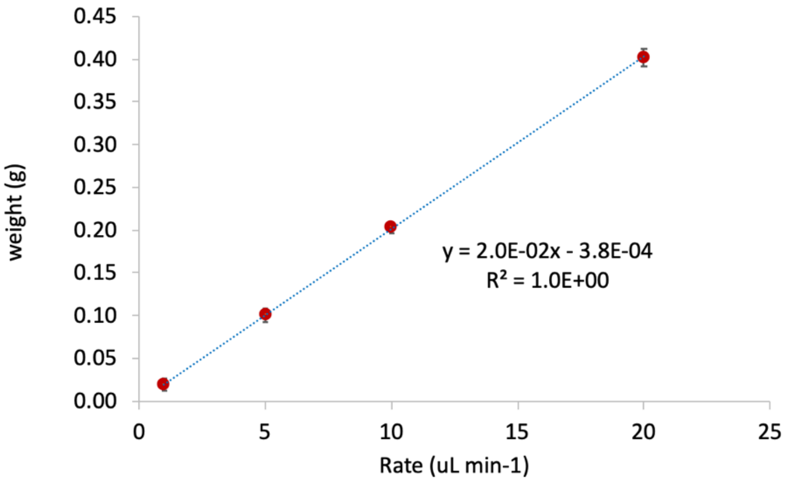
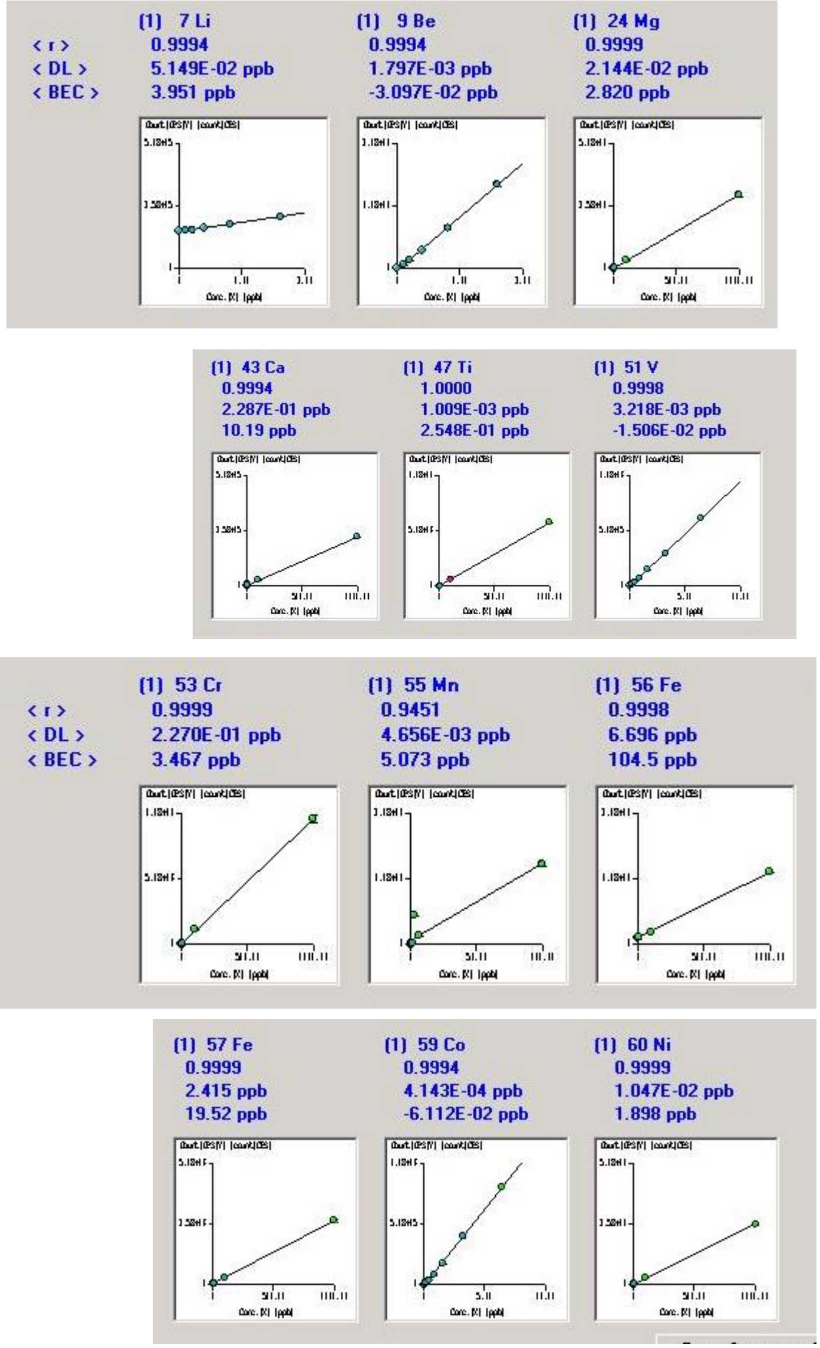


Figure 3. 6. Gravimetric calibration of a syringe pump (average of 3 replicates) to ensure the correct rate in the microdialysis set-up.

3.5.2 Quality control

The certified reference material used in this study was an ICP Multi-element standard XV(III) (with 16 elements in dilute nitric acid) Certipur® (Sigma Aldrich Singapore) and

SRM 1568a (rice flour). The calibration results and the recovery of some elements of the SRM 1568a Rice flour are shown in Figure 3.7 and Table 3.4, respectively.



```
          (1)  7 Li          (1)  9 Be           (1)  24 Mg
< r >      0.9994             0.9994              0.9999
< DL >     5.149E-02 ppb      1.797E-03 ppb       2.144E-02 ppb
< BEC >    3.951 ppb          -3.097E-02 ppb      2.820 ppb
```

```
(1)  43 Ca          (1)  47 Ti          (1)  51 V
 0.9994              1.0000              0.9998
 2.287E-01 ppb       1.009E-03 ppb       3.218E-03 ppb
 10.19 ppb           2.548E-01 ppb       -1.506E-02 ppb
```

```
          (1)  53 Cr          (1)  55 Mn          (1)  56 Fe
< r >      0.9999              0.9451              0.9998
< DL >     2.270E-01 ppb       4.656E-03 ppb       6.696 ppb
< BEC >    3.467 ppb           5.073 ppb           104.5 ppb
```

```
(1)  57 Fe          (1)  59 Co          (1)  60 Ni
 0.9999              0.9994              0.9999
 2.415 ppb           4.143E-04 ppb       1.047E-02 ppb
 19.52 ppb           -6.112E-02 ppb      1.898 ppb
```

Figure 3. 7. Selected ICP-MS calibration results and instrument LOD of ICP Multi-element standard XV(III) (n=5)

Table 3. 3. ICP-MS results of the Certified Reference Material (SRM 1568a Rice flour).

Element	Average Conc*, ug Kg^{-1}	Stdev*	RSD	Recovery, %
Mg	0.04371	0.004	9.22	94
Ca	0.01484	0.000	1.43	99
Mn	24.37	0.582	2.39	97
Fe	6.456	0.298	4.62	105
Zn	16.20	1.072	6.62	101
As	0.2694	0.001	0.44	112

* Sample size of 5

3.5.3 Plant Growth Analysis

Preliminary studies were done using 5 different plant stages of the cucumber plant to know the effect of putting MD in the plants. The following stages are 26, 35, 43, 54, and 63 days after transplanting (dat). Based on the preliminary results, the first two stages (26 and 35 dat) were chosen to see the early effects of the As/Sb treatment using the MD technique. Symptoms of As and Sb phytotoxic effect on plants were observed during the experiment already at the 5 mg L^{-1} amendments (and 10 mg L^{-1} during the initial study) compared to the control plants (0 mg L^{-1} As/Sb). In terms of the plant stages, 26 dat plants showed phytotoxic effects earlier (2 days after amendment) compared to 35 dat plants (4-5 days after amendment). As and Sb effects on plants are browning of leaves resulting in leaves drying. In terms of roots, there is a significant reduction in root mass, blackening in colour, and inhibition of growth. With increasing As and Sb concentration, the symptoms mentioned above were intensifying. The symptoms for Sb are slightly more pronounced visually (e.g., the browning of leaves). The morphology of the plant changed (i.e. plant height, number of leaves), and the effect is more evident at higher metalloid doses in the nutrient system.

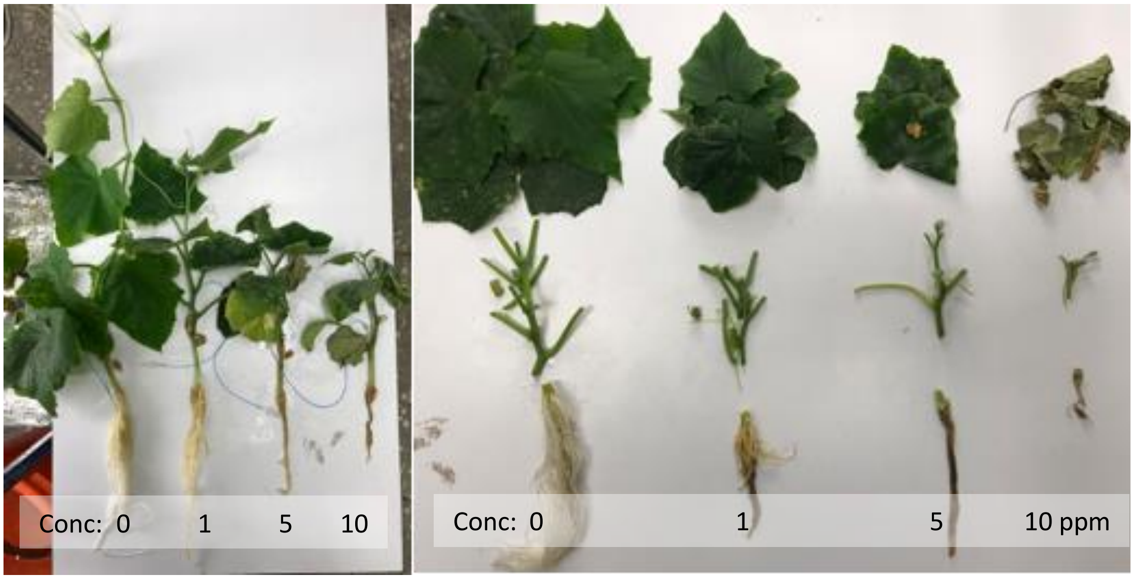


Figure 3. 8. Effect of As(III) and Sb(III) amendment on the physiology of the 26 dat cucumber plant per set: (1) treatments; (a) control (0), (b) 1 ppm (c) 5 ppm (d) 10 ppm.

The experiment is composed of 2 stages: 26 and 35 days after transplanting (dat) with 3 concentration treatments: (a) control (0 ppm), (b) 1 ppm and (c) 5 ppm As(III) or Sb(III).

3.5.3.1 Number of Leaves

From the number of leaves results (Figure 3.9), there were statistically significant differences between different concentration F(2,24)=33.19, *p*=0.0005, between plant stage F(1,24)=731.53, *p*=0.0005, and between metalloid treatment F(1,24)=22.78, *p*=0.0005. There were interaction effects between the two factors (concentration*stage and concentration*treatment) but no interaction effect between stage and treatment.

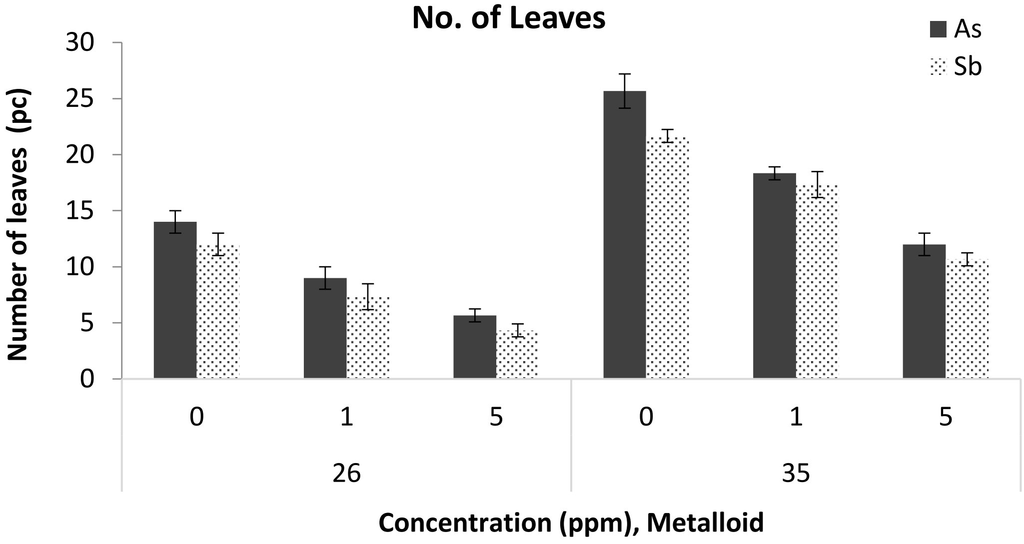


Figure 3. 9. Effect of As(III) and Sb(III) amendment in the number of leaves per set: (1) 3 treatments; control (0), 1 ppm 5 ppm, and (2) plant stage; 26 dat and 35 dat. Data presented are means ± SD.

A Tukey post hoc test revealed that there were a significantly reduced number of leaves between cucumber plants subjected to As and Sb amendments compared to the control plants both for two plant stages. It appears that the As and Sb amendments significantly affected the number of leaves in the early-stage plant samples (26 dat) showed a visually lower leaf area compared to the older plant stage (35 dat).

3.5.3.2 Plant height

From the plant height results (Figure 3.10), there were statistically significant differences between different concentration F(2,24)=1448.44, *p*=0.0005, between plant stage F(1,24)=748.47, *p*=0.0005, and between metalloid treatment F(1,24)=76.98, *p*=0.0005. There were interaction effects between the two factors (concentration*stage and concentration*treatment) but the interaction effect between stage and treatment.

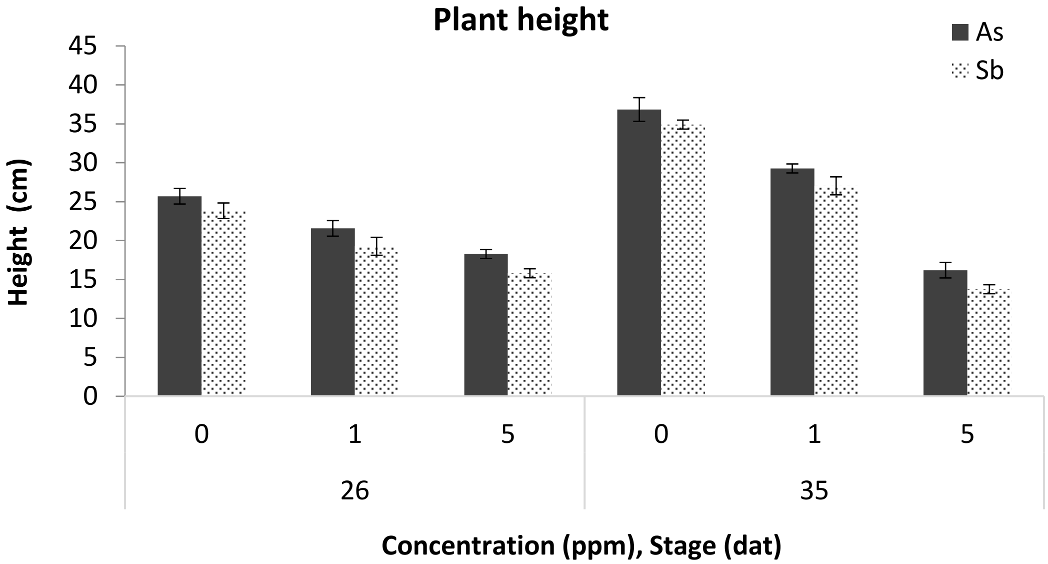


Figure 3. 10. Effect of As(III) and Sb(III) amendment in the number of leaves per set: (1) 3 treatments; 0, 1 ppm 5 ppm, and (2) plant stage; 26 dat and 35 dat. Data presented are means ± SD.

A Tukey post hoc test revealed that there was a significantly lower plant height between cucumber plants subjected to As and Sb amendments compared to the control plants. It appears that the As and Sb amendments significantly affected the plant height in the early stage plant samples (26 dat) showed a visually lower leaf area compared to the older plant stage (35 dat).

3.5.3.3 Biomass

From the biomass (dry) results (Figure 3.11), there were statistically significant differences between concentration F(2,72)=2562.43, *p*=0.0005, between plant stage F(1,72)=961.72, *p*=0.0005, between metalloid treatment F(1,72)=14.74, *p*=0.0005 and between plant parts F(2,72)=650.49, *p*=0.0005 . There were interaction effects between the two factors (concentration*stage and concentration*treatment) but no interaction effect between stage and treatment.

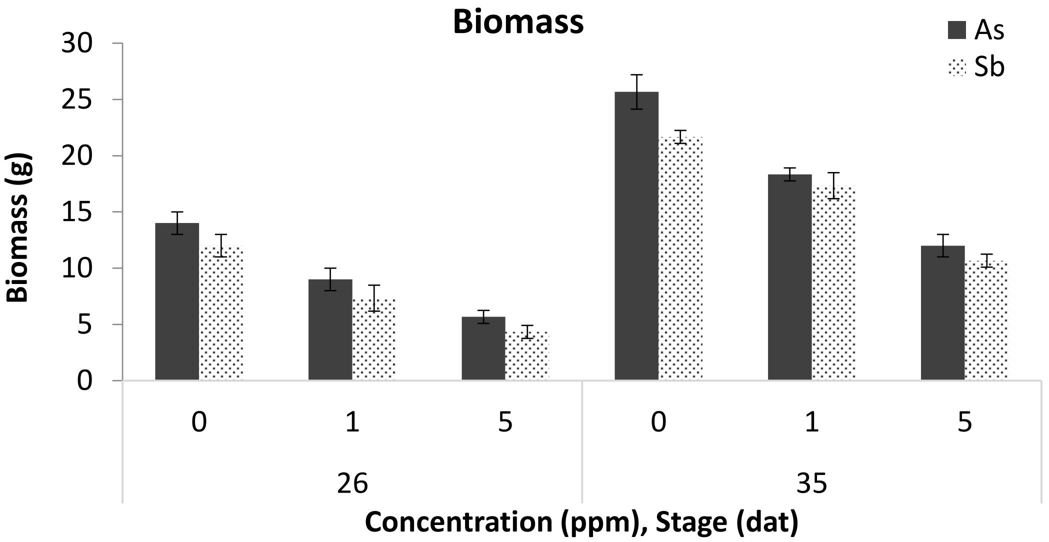


Figure 3. 11. Effect of As(III) and Sb(III) amendment in the number of leaves per set: (1) 3 treatments; 0, 1 ppm 5 ppm, and (2) plant stage; 26 dat and 35 dat. Data presented are means ± SD.

A Tukey post hoc test revealed that there was significantly lower biomass between cucumber plants subjected to As and Sb amendments compared to the control plants. It appears that the As and Sb amendments significantly affected the dry biomass in the early-stage plant samples (26 dat) showed a visually lower leaf area compared to the older plant stage (35 dat). Figure 3.12 shows the effect of As and Sb in cucumber’s dry weight, specifically in roots, shoots, and leaves.

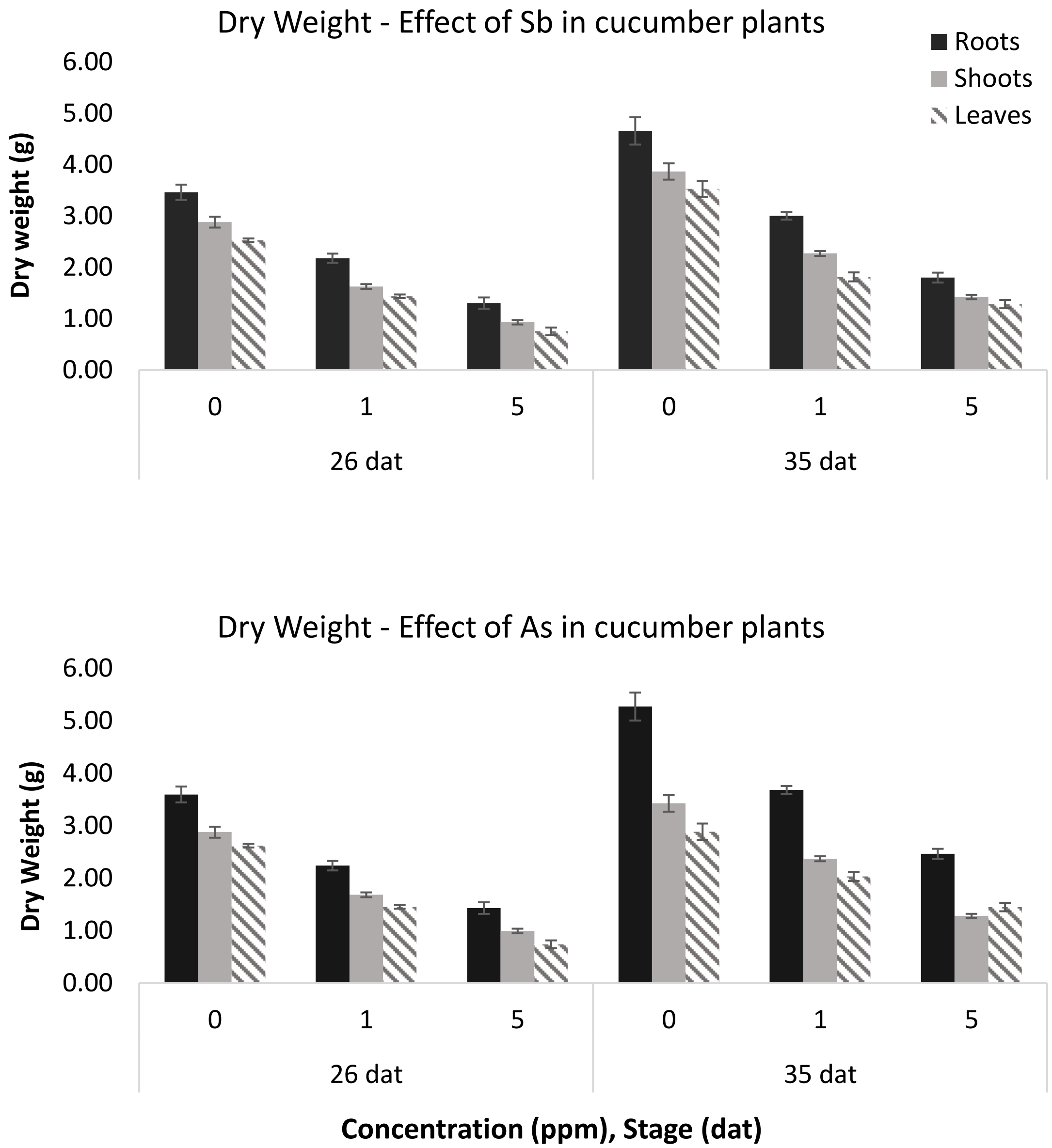
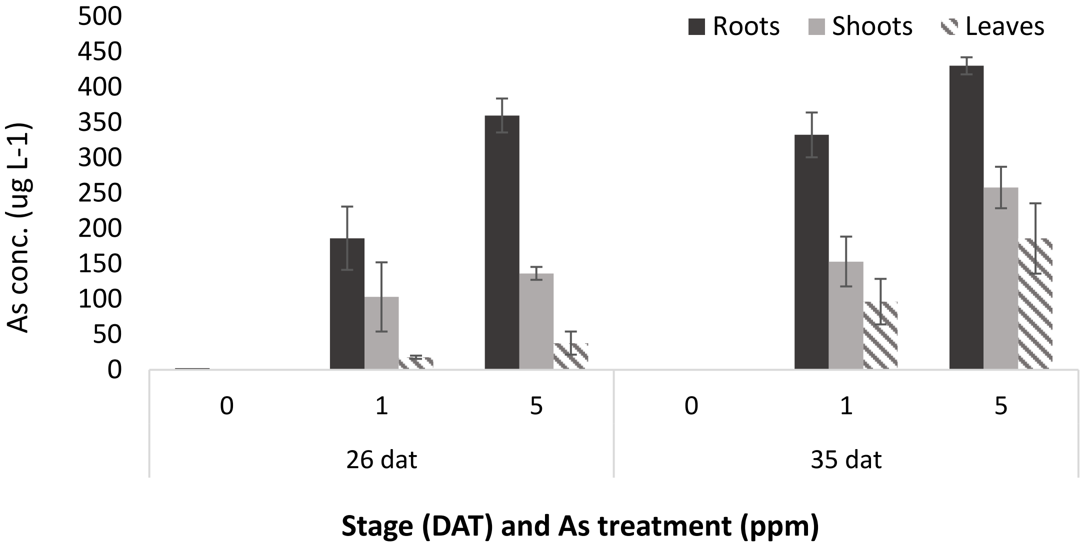


Figure 3. 12. The level of Sb(III) (top) and As(III) (bottom) in roots, shoots and leaves of cucumber exposed to (1) 3 treatments; 0, 1 ppm 5 ppm, and (2) plant stage; 26 dat and 35 dat. Data presented are means ± SD.

3.5.4 Sb and As uptake and translocation

Figure 3.13 shows the Sb and As uptake and translocation in cucumber plants between two plant stages (26 and 35 dat) three levels of As/Sb treatments (0, 1, and 5 ppm). It can be seen that the highest concentration for both Sb and As is found in the roots, followed by the shoots and leaves.



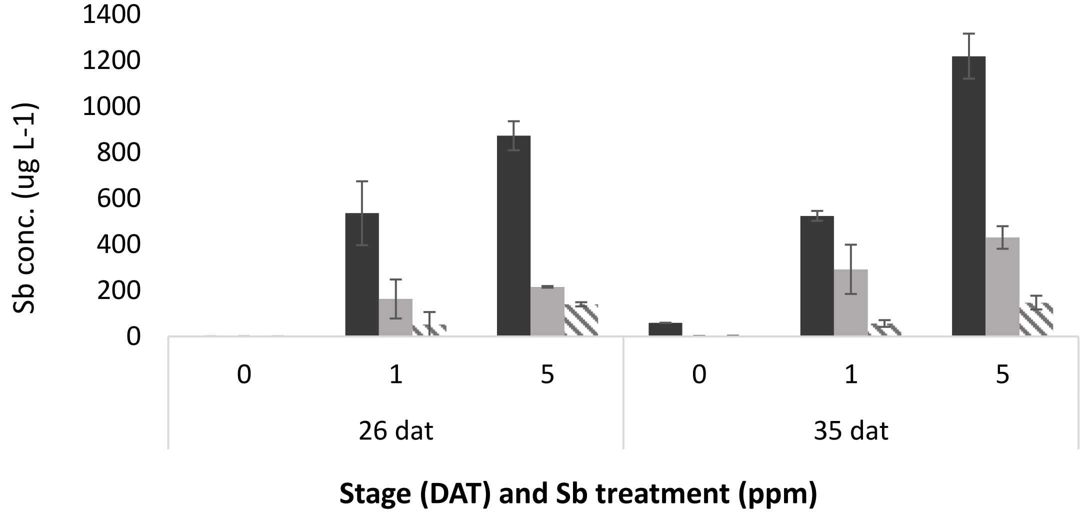


Figure 3. 13. uptake and translocation of Sb(III) (top) and As(III) (bottom) in cucumber plants(1) 3 treatments; 0, 1 ppm 5 ppm, and (2) plant stage; 26 dat and 35 dat. Data presented are means ± SD.

It is also the same pattern for both plant stages. For Sb(III), there were statistically significant differences between different concentrations F(1,144)=66.65, *p*=0.0005 and between plant parts F(2,144)=130.26, *p*=0.000, but no significant difference between plant stage. There were no interaction effects between the two factors (concentration*stage and concentration*treatment). On the other hand, for As(III), there were statistically significant differences between different concentration F(1,144)=28.17, *p*=0.0005, between plant stage F(2,144)=55.33, *p*=0.0005 and between plant parts F(2,144)=33.08, *p*=0.000. There were no interaction effects between the two factors (concentration*stage and concentration*treatment).

The translocation factor between shoot and roots was obtained as the ratio of the concentration in the shoot to the concentration found in the roots (Table 3.4). The same factor was calculated between leaves and shoots. It can be noted that the TF values for roots to shoots at one ppm, both for As and Sb, are always higher than at 5 ppm. For instance, for As treatments: TF of 26 dat plant exposed to 1 ppm is 20% higher than the 5 ppm, and TF of 1 ppm is 60% higher than the 5 ppm in the 35 dat old plants. For Sb treatments, TF of 1 ppm is 45% and 6.7% higher than the 5 ppm in 26 and 35 data plants, respectively.

Table 3. 4. Translocation Factors (shoots/roots, and leaves/shoots) for As and Sb in plants according to plant stage

Metalloid	Plant stage	Concentration, ppm	TF $_{\text{shoots/roots}}$ [a]	TF $_{\text{leaves/shoots}}$ [b]
Sb(III)	26 dat	1	0.30	0.32
		5	0.25	0.65
	35 dat	1	0.56	0.19
		5	0.35	0.34
As(III)	26 dat	1	0.55	0.17
		5	0.38	0.27
	35 dat	1	0.64	0.63
		5	0.60	0.72

[a] TF = metal conc in shoots/metal conc in roots
[b] TF = metal conc in leaves/metal conc in shoots

The opposite was however observed in the TF from shoots to leaves: the TF values for plants exposed with 5 ppm (both 26 or 35 dat plants) are always higher than those for the plants exposed to 1 ppm.

3.5.5 Sb and As uptake in xylem sap- Microdialysis

Figure 3.14 compiled pictures of 26 dat old cucumber plants subjected to 0 (control), 1, and 5 ppm As(III) during 7 days. For each of those set-ups, the xylem sap of the cucumber plants was collected using the MD technique and analysed off-line for total As using ICP-MS (Figure 3.15).

The pictures shown in Fig. 3.14 were representative of the plants per selected sampling times throughout the one-week exposure experiments. Variations in terms of plant morphology were observed between the control and the plants subjected to 1 and 5 ppm metalloids. Control plants look healthy, and no significant negative physiological effect from the first day until the 7th day.

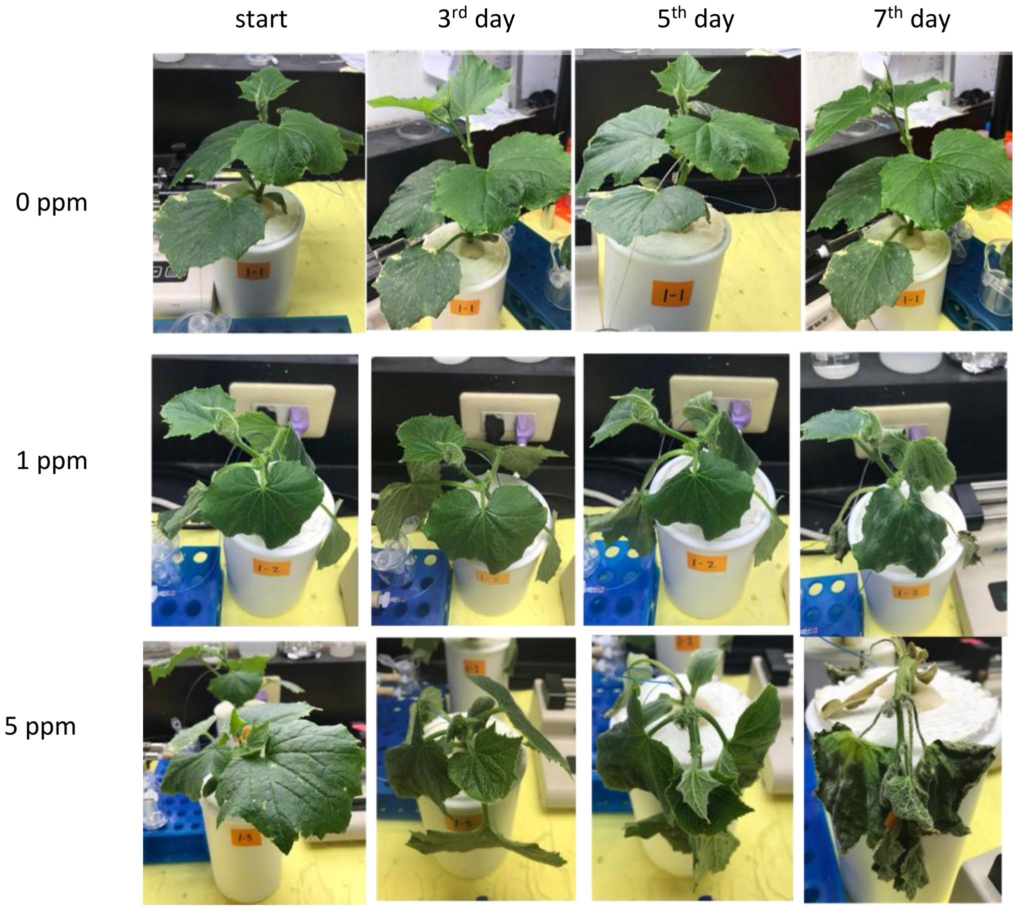


Figure 3. 14. Representative photos were taken at specific times to depict the physiological effect of As/Sb exposure (at the start of the experiment, intermediate, and end of the monitoring). Uptake of As(III) in the xylem sap of 26 dat cucumber for 7 days using in-vivo microdialysis set-up for 3 different treatments;(a) 0 ppm, (b) 1 ppm, and (c) 5 ppm, (left).

Cucumber plants subjected to 5 ppm looked less healthy compared to the plants with 1 ppm, signifying that the health is inversely proportional to the concentration of metalloids. This indicates that the presence of metalloids in plants negatively affected the plant morphology.

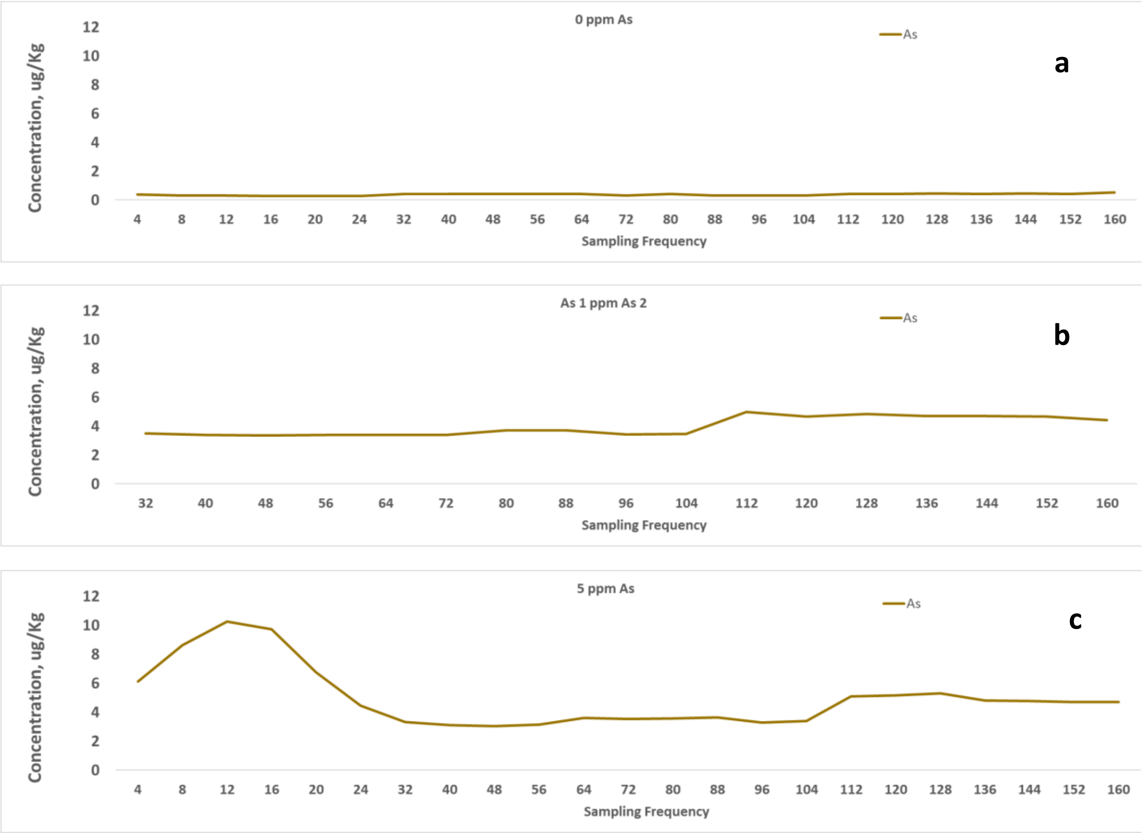


Figure 3. 15. Concentrations of As(III) in the xylem sap of 26 dat cucumber for 7 days using in-vivo microdialysis set-up for 3 different treatments;(a) 0 ppm, (b) 1 ppm, and (c) 5 ppm. Sampling frequency is every four hours.

The data were taken from ICP-MS results of the As analysis of xylem saps collected for 7 days from a micro-dialysis set-up described in section 3.4.6.2.1. Xylem saps were sampled every 2 hours with 3 sets of cucumber subjected for 0 (Fig 3.14a), 1 (Fig 3.14a b), and 5 (Fig 3.14a c) ppm. It can be seen in Figure 3.15a that control plants without As do not show any As readings as expected for a control set. Fig 3.15b shows continuous readings of As around 4 ppb until a slight increase to 5 ppb around 112th sampling and a plateau until the end of the sampling period. Fig 3.15c has a different story where there was a spike increase after a 6 ppb As reading to 10 ppb and decrease to a steady 3-4 ppb and a slight increase until the end of the experiment. Figure 3.16 shows photos from the start to the end of the 7-day amendments of As. Same observations as the 26 dat, the control plants without the metalloid is healthy compared to 1 and 5 ppm plants. The only difference is that the 35 dat plants receiving 1 pm As is healthier compared to the 26 dat plants receiving the same concentration.

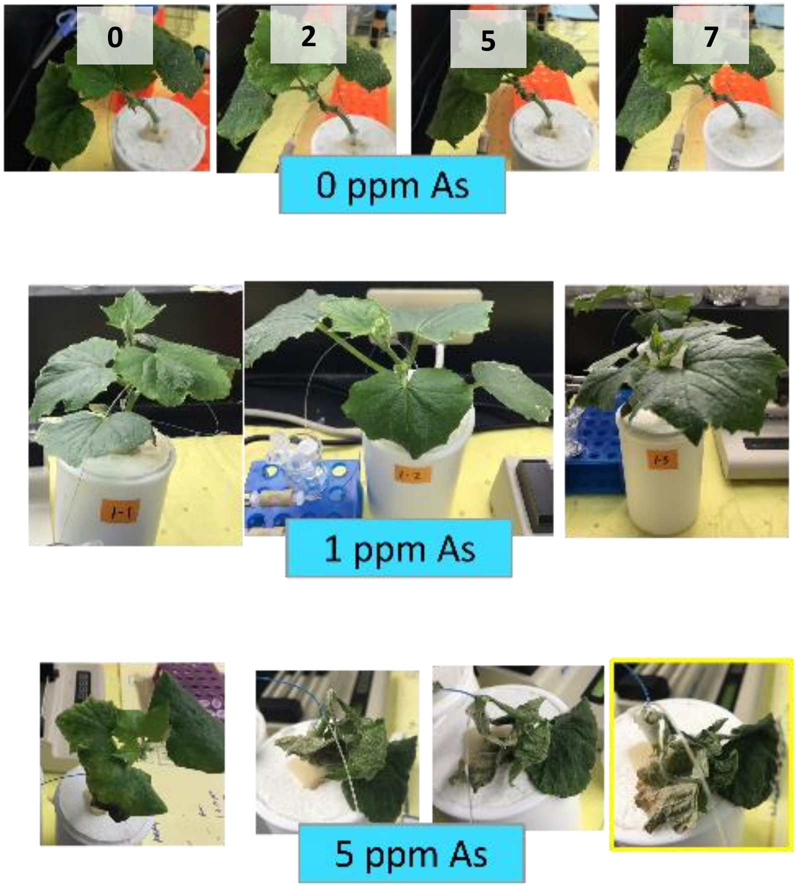


Figure 3. 16. Representative images captured at specific times to depict physiological changes (at the start of the experiment, middle, and end of the monitoring) during the uptake of As(III) in the xylem sap of 35 dat cucumber for 7 days (0, 2, 5 and 7th day) using in-vivo microdialysis set-up for 3 different treatments; 0 ppm, 1 ppm, and 5 ppm

Figure 3.17 shows the 35 dat plant with 0, 1, and 5 ppm As. Fig 3.17a shows that control plants without As do not show any As readings as expected for a control set. Fig 3.15b shows continuous readings of As around 6 ppb and a slight increase at 48th hr sampling time and a constant 6 ppb until the end of the sampling period. Fig 3.15c has a different story where there was a spike increase after the 12th hr sampling time from 0 to 100 ppb until a constant of 80 ppb until 80 hr and a steady 3 ppb and a slight increase until the end of the experiment. Based on the plant pictures, it could be seen that at this time, the plant is already wilted and suffered irreversible damage because of the 5 ppm As concentration.

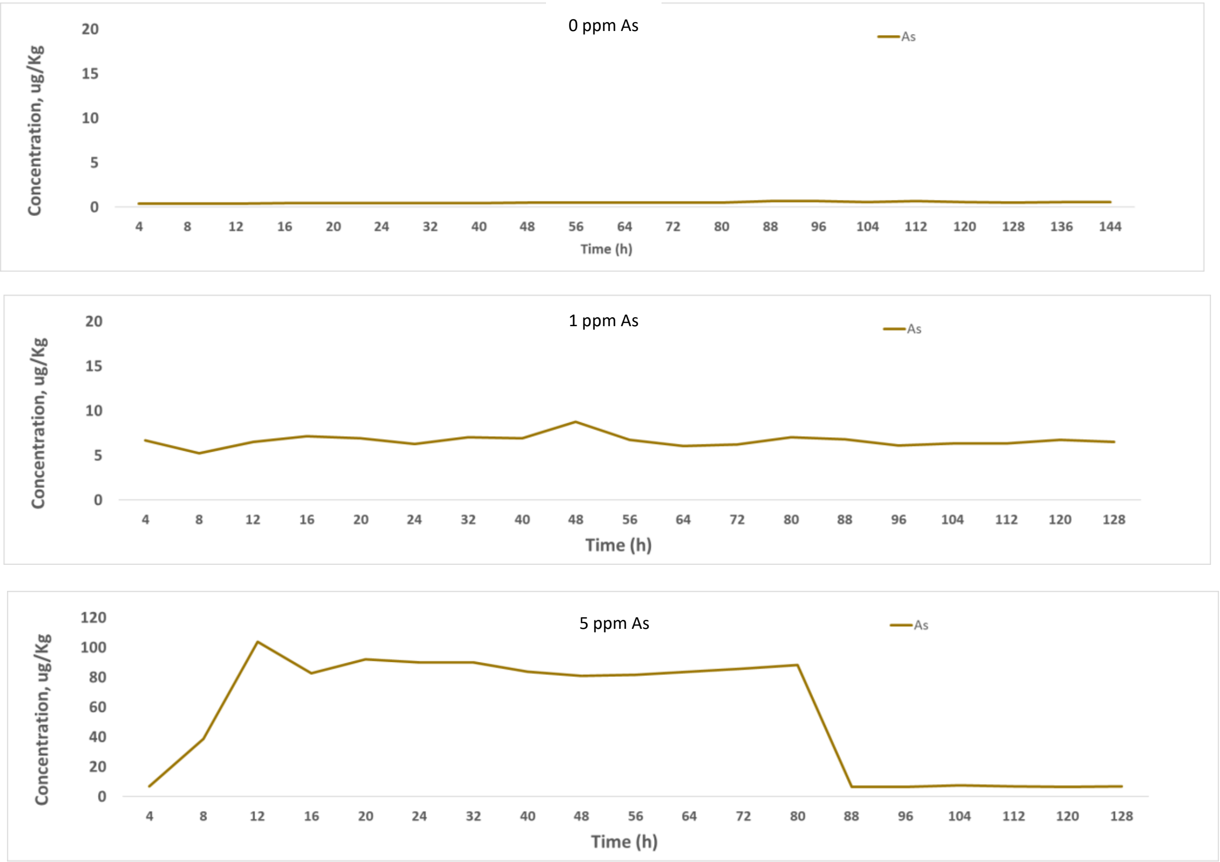
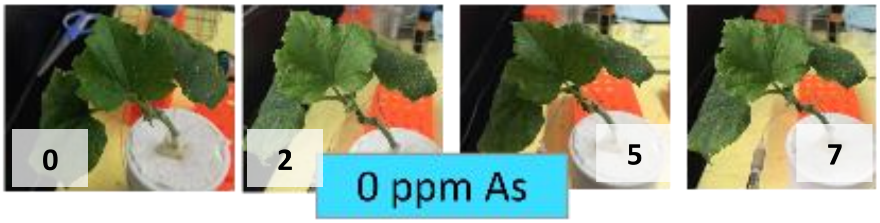
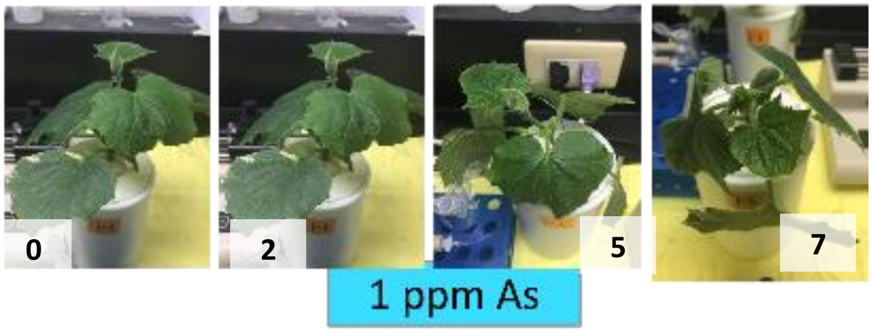


Figure 3. 17. Uptake of As(III) in the xylem sap of 35 dat cucumber for 7 days using in-vivo microdialysis set-up for 3 different treatments;(a) 0 ppm, (b) 1 ppm, and (c) 5 ppm.

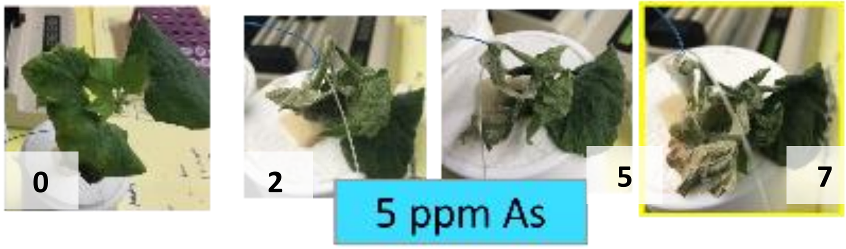
In comparison with the 26 and 35 dat plants in terms of 0 ppm As(III), both of the plant sets has similar results, no As has been detected in the xylem sap showing the control plant sets. In terms of the 26 and 35 data plants exposed to 1 ppm, they almost have the same linear pattern but the 35 data has a slightly higher consumption because of the higher requirement based on the higher plant mass based on age. In terms of the 5 ppm As(III) exposure of the 26 and 35 dat, the older plant (35 dat) showed significantly higher As(III) in the xylem sap (around 100 ppb around 12h sampling period) compared to a maximum of only 10 ppb showed in the xylem sap in the young plant (26 dat). The data showed that there is an effect of age of cucumber plant when exposed to 5 ppm. The 35 data showed a continuous As concentration in the xylem sap of around 85 ppb until 88h sampling time and dropped sharply (at which point, the plant is considered wilted/dried).



0 ppm As



1 ppm As



5 ppm As

Figure 3. 18. Representative images captured at specific times to depict physiological changes (at the start of the expt, middle and end of the monitoring) during the uptake of As(III) in the xylem sap of 35 dat cucumber for 7 days using in-vivo microdialysis set-up for 3 different treatments;(a) 0 ppm, (b) 1 ppm, and (c) 5 ppm,

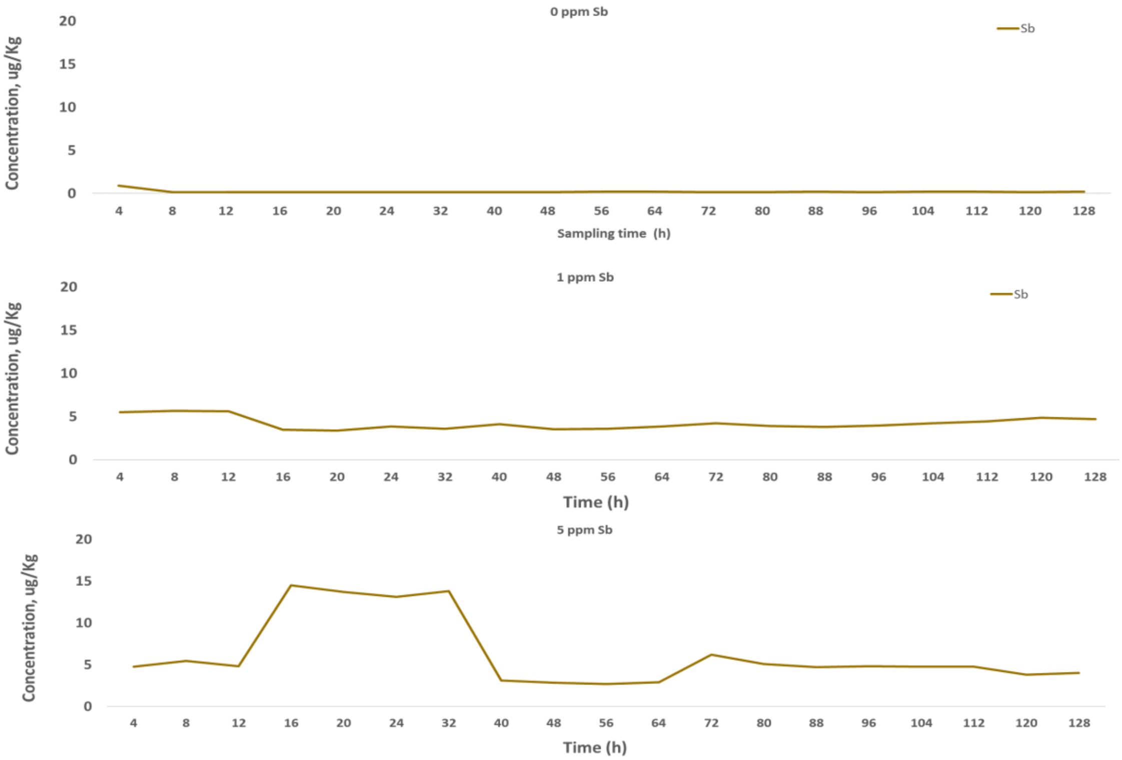


Figure 3. 19. Uptake of Sb(III) in the xylem sap of 26 dat cucumber for 7 days using in-vivo microdialysis set-up for 3 different treatments;(a) 0 ppm, (b) 1 ppm, and (c) 5 ppm.

In terms of the Sb(III) exposure of the 2 cucumber plant age (26 and 35 data), like the data for the 0 ppm As (III), no Sb were detected in both plants. While there was no significant difference in the 26 and 35 data were exposed with 1 ppm As(III), the 35 dat showed a higher Sb(III) detection at the start of the experiment until the 16th sampling hour and a sharp decrease with a constant 5 ppb readings of Sb in the xylem sap, while an approximately 5 ppb Sb readings with the younger 26 dat cucumber plants.

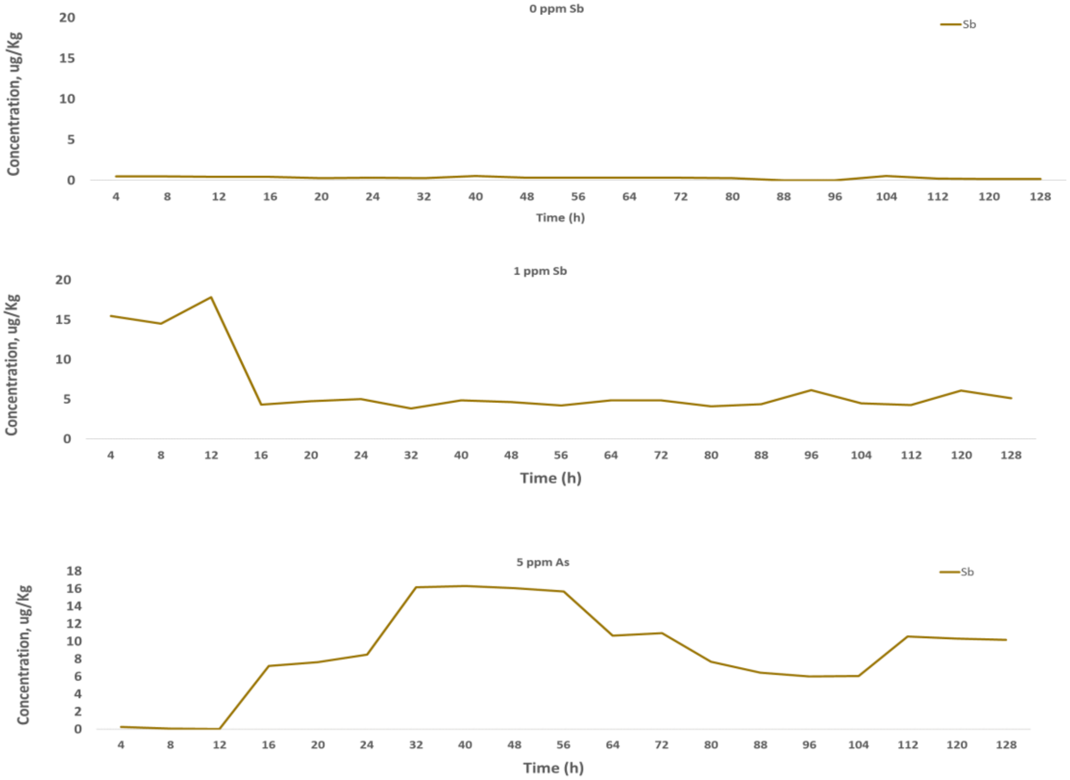


Figure 3. 20. Uptake of Sb(III) in the xylem sap of 35 dat cucumber for 7 days using in-vivo microdialysis set-up for 3 different treatments;(a) 0 ppm, (b) 1 ppm, and (c) 5 ppm.

In terms of the 5 ppm Sb(III) exposure with 26 and 35 dat cucumber plants, there was a steady 5 ppb and an increase to approx. 15 ppb until 32nd sampling hour and a decrease from 15 to 3 ppb and become steady until the last hour sampling. On the other hand for the older 35 dat cucumber plants, exposed with 5 ppm Sb(III), there was a slight increase of Sb in the xylem sap after 12th hour sampling time, and climbing until 16th hour sampling and a slight decrease until the 104th sampling time and a plateau around 8 ppb. Exposure of the plants with 5 ppm As(III) and Sb(III) showed detrimental effects regardless of the age of the cucumber plant when exposed to 5 ppm. Plant physiological parameters were significantly affected by the presence of 5ppm Sb and As ((III) in the nutrient solution.

3.6 Discussions and conclusions

In this chapter, *Cucumis Sativa L.* was used as the model plant to define and test a new microdialysis technique for the detection and quantification of Sb and As in vivo in real-time. The hydroponic experiment was composed of 2 plant stages (26 and 35 data), three treatment concentrations (0, 1, and 5 ppm), and two metalloids Sb and As (both (III) species).

This study aimed to apply microdialysis in the monitoring of metalloids, specifically monitoring of Sb and As in the xylem sap of plants by inserting a microdialysis tube into the xylem vessel. This method would have the advantage that no sample preparation is necessary, less invasive to the plant, high-throughput sampling of xylem sap, and the risk of sample alteration would be minimised, which might result in an alteration of arsenic speciation.

The preliminary morphological study of plant height, number of leaves, and biomass showed that there was a significant negative effect of As and Sb when exposed to the cucumber plant both for the young and older stage plants ($P<0.05$). When plants were exposed to the presence of these 2 inorganic metalloids, there was a significant negative physiological effect on plant’s health (i.e., reduction in biomass, chlorophyll count, number of leaves) compared to a control (no metalloids). These observations were similar to the results in Chapter 2, where As and Sb significantly reduced plant health exposure in terms of morphology, in both short and long duration exposure experiments. According to a similar As study in cucumber plants by Uroic (2011), As was occurring as a free ion in the nutrient solution using RP-HPLC (Reversed Phase-High Performance

Liquid Chromatography) method. There were no methylated As species observed in the nutrient solution using anion exchange LC-ICP-MS, only As(III) (arsenite) and As(V) (arsenate) species. In a similar study done by Mihucz et al. (2005), As(III) is the predominant species in cucumber xylem sap regardless of the As treatment (As(III) > As(V) > DMA). There is only partial oxidation of (<10% in 2 days) As(III) to As(V) in the As(III) containing nutrient solution.

Upon translocation to the shoot, As can severely inhibit plant growth by slowing or arresting expansion and biomass accumulation, as well as compromising plant reproductive capacity through losses fertility, yield, and fruit production (reviewed by (Garg and Singla, 2011). As interferes with critical metabolic processes, which can lead to death (Garg et al., 2015). Most plants possess mechanisms to retain much of their As burden in the root (Jentschke and Godbold, 2000; Hall, 2002; Nagajyoti et al., 2010; Shahid et al., 2015). However, a genotype-dependent proportion of the As is translocated to the shoot and other tissues of the plant.

Several studies have used microdialysis as an emerging sensitive tool in environmental scientific studies. It has been used in different studies in soil N dynamics and root-soil B interactions (Humphrey et al., 2019), sampling of wastewater and soil solution in the laboratory and field settings including metal ions (Torto et al., 2001, 2002), saccharides (Torto et al., 2001), Cu and Ni in plants (Mosetlha et al., 2007), organic acids (Sulyok et al., 2005), and organic and inorganic nitrogen in the soil (Inselsbacher et al., 2011; Buckley et al., 2016, 2017).

In conclusion, it may be suggested that the proposed method is a useful tool for xylem sap sampling for monitoring studies of the plant uptake of metals. Further tests could be recommended using different plants, and different perfusate to fully understand its capabilities in xylem sap sampling with less invasion to the plants. The microdialysis method is less destructive and allows researchers to simulate the plant nutrient/toxic metal uptake, translocation, and absorption compared to the conventional method like root exudation. This method could be a complementary method with the existing method depending on the type of experiments with nutrient analysis with plants.

3.7 References

Abedin, M. J., Feldmann, J. and Meharg, A. A. (2002) ‘Uptake kinetics of arsenic species in rice plants.’ *Plant Physiology*, 128(3) pp. 1120–1128.

Ainsworth, N., Cooke, J. A. and Johnson, M. S. (1990) ‘Distribution of antimony in contaminated grassland: 1- vegetation and soils.’ *Environmental Pollution*. Elsevier, 65(1) pp. 65–77.

Ainsworth, N., Cooke, J.A. and Johnson, M. S. (1990) ‘Distribution of antimony in contaminated grassland: 2— small mammals and invertebrates.’ *Environmental Pollution*. Elsevier, 65(1) pp. 79–87.

Alexou, M. and Peuke, A. D. (2013) *Plant Mineral Nutrients*. Maathuis, F. J. M. (ed.) *Plant Mineral Nutrients*. Totowa, NJ: Humana Press (Methods in Molecular Biology).

Ali, H., Khan, E. and Sajad, M. A. (2013) ‘Phytoremediation of heavy metals—Concepts and applications.’ *Chemosphere*, 91(7) pp. 869–881.

Althobiti, R. A., Sadiq, N. W. and Beauchemin, D. (2018) ‘Realistic risk assessment of arsenic in rice.’ *Food Chemistry*. Elsevier Ltd, 257, August, pp. 230–236.

Álvarez-Fernández, A., Díaz-Benito, P., Abadía, A., And, A.-F. L.-M. and Abadía, J. (2014) ‘Metal species involved in long distance metal transport in plants.’ *Frontiers in Plant Science*, 5(1) p. 105.

Amarasiriwardena, D. and Wu, F. (2011) ‘Antimony: Emerging toxic contaminant in the environment.’ *Microchemical Journal*. Elsevier B.V., 97(1) pp. 1–3.

Ammann, A. A. (2011) ‘Arsenic Speciation Analysis by Ion Chromatography - A Critical Review of Principles and Applications.’ *American Journal of Analytical Chemistry*, 2011(February) pp. 27–45.

Anawar, H. M., Freitas, M. C., Canha, N. and Regina, I. S. (2011) ‘Arsenic, antimony, and other trace element contamination in a mine tailings affected area and uptake by tolerant plant species.’ *Environmental Geochemistry and Health*, 33(4) pp. 353–362.

Aposhian, H. V. and Aposhian, M. M. (2006) ‘Arsenic Toxicology: Five Questions.’ *Chemical Research in Toxicology*, 19(1) pp. 1–15.

Arnold, L. L., Eldan, M., Nyska, A., van Gemert, M. and Cohen, S. M. (2006) ‘Dimethylarsinic acid: Results of chronic toxicity/oncogenicity studies in F344 rats and in B6C3F1 mice.’ *Toxicology*, 223(1–2) pp. 82–100.

Arunakumara, K. K. I. U., Walpola, B. C. and Yoon, M.-H. (2013) ‘Current status of heavy metal contamination in Asia’s rice lands.’ *Reviews in Environmental Science and*

Bio/Technology, 12(4) pp. 355–377.

Ashbrook, P. C. (2014) ‘Standard Operating Procedures.’ *Journal of Chemical Health and Safety*, 21(5) p. 29.

Ashley, P. M., Graham, B. P., Tighe, M. K. and Wolfenden, B. J. (2007) ‘Antimony and arsenic dispersion in the Macleay River catchment, New South Wales: a study of the environmental geochemical consequences.’ *Australian Journal of Earth Sciences*, 54(1) pp. 83–103.

ATSDR - Environmental Medicine & Environmental Health Education - CSEM (2013) ‘Arsenic Toxicity Case Study: What Are the Standards and Regulation for Arsenic Exposure?’ *Encyclopedia of Metalloproteins* pp. 143–143.

Awika, J. M. (2011) ‘Major cereal grains production and use around the world.’ *In ACS Symposium Series*, pp. 1–13.

Bach, C., Dauchy, X., Chagnon, M. C. and Etienne, S. (2012) ‘Chemical compounds and toxicological assessments of drinking water stored in polyethylene terephthalate (PET) bottles: A source of controversy reviewed.’ *Water Research*, 46(3) pp. 571–583.

Baker, A. J. M. (1981) ‘Accumulators and Excluders - Strategies in the Response of Plants to Heavy Metals.’ *Journal of Plant Nutrition*, 3(1–4) pp. 643–654.

Bakhtiari, A. R., Zakaria, M. P., Yaziz, M. I., Lajis, M. N. H. L. and Bi, X. (2014) ‘Environment Asia.’ *Environment Asia*, 7(1) pp. 104–111.

Basta, N. T. (2006) ‘Heavy Metal Contamination of Soil.’ *Soil Science Society of America Journal*, 70(5) p. 1819.

Bastías, J. M. and Beldarrain, T. (2016) ‘Arsenic translocation in rice cultivation and its implication for human health.’ *Chilean Journal of Agricultural Research*. Instituto de Investigaciones Agropecuarias, INIA, 76(1) pp. 114–122.

Bellido-Martín, A., Gómez-Ariza, J. L., Smichowsky, P. and Sánchez-Rodas, D. (2009) ‘Speciation of antimony in airborne particulate matter using ultrasound probe fast extraction and analysis by HPLC-HG-AFS.’ *Analytica Chimica Acta*, 649(2) pp. 191–195.

Benedict, S. R. (1908) *A Reagent For the Detection of Reducing Sugars*. *J. Biol. Chem*.

Bennett, J. O. and Sicher, R. C. (2011) ‘Protein and metabolite composition of xylem sap from field-grown soybeans (Glycine max)’ pp. 921–931.

Bhattacharya, P., Samal, a C., Majumdar, J. and Santra, S. C. (2009) ‘Transfer of Arsenic from Groundwater and Paddy Soil to Rice Plant (Oryza sativa L.): A Micro-Level Study in West Bengal , India.’ *World Journal of Agricultural Sciences*, 5(4) pp. 425–431.

Bi, Z. (2012) *Speciation analysis of trace metals in natural waters using vibrating electrodes*. *Environmental Sciences*. University of Liverpool.

Bielen, A., Remans, T., Vangronsveld, J. and Cuypers, A. (2013) 'The influence of metal stress on the availability and redox state of ascorbate, and possible interference with its cellular functions.' *International Journal of Molecular Sciences* pp. 6382–6413.

Biles, C. L. and Abeles, F. B. (1991) 'Xylem sap proteins.' *Plant Physiology*, 96(July 1991) pp. 597–601.

Billon, G. and Van Den Berg, C. M. G. (2004) 'Gold and silver micro-wire electrodes for trace analysis of metals.' *Electroanalysis*, 16(19) pp. 1583–1591.

Borovička, J., Řanda, Z. and Jelínek, E. (2006) 'Antimony content of macrofungi from clean and polluted areas.' *Chemosphere*, 64(11) pp. 1837–1844.

Bouman, B. A. . and Tuong, T. . (2001) 'Field water management to save water and increase its productivity in irrigated lowland rice.' *Agricultural Water Management*, 49(1) pp. 11–30.

Bowen, H. J. M. (Humphry J. M. (1979) *Environmental chemistry of the elements*. London, New York: Academic Press.

Brackin, R., Näsholm, T., Robinson, N., Guillou, S., Vinall, K., Buckley, S., Lakshmanan, P., Schmidt, S. and Inselsbacher, E. (2016) 'Microdialysis-a new technology for investigating soil nitrogen fluxes in the rhizosphere.' *In Proceedings of the International Nitrogen Initiative 2016 Conference*, pp. 4–8.

Brammer, H. and Ravenscroft, P. (2009) 'Arsenic in groundwater: A threat to sustainable agriculture in South and South-east Asia.' *Environment International*. Elsevier Ltd pp. 647–654.

Brihaye, C. and Duyckaerts, G. (1982) 'Determination of traces of metals by anodic stripping voltammetry at a rotating glassy carbon ring—disc electrode.' *Analytica Chimica Acta*, 143 pp. 111–120.

Broadley, M., Brown, P., Cakmak, I., Rengel, Z. and Zhao, F. (2011) 'Function of Nutrients: Micronutrients.' *In Marschner's Mineral Nutrition of Higher Plants: Third Edition*. Elsevier Inc., pp. 191–248.

Brochu, C., Wang, J., Roy, G., Messier, N., Wang, X.-Y., Saravia, N. G. and Ouellette, M. (2003) 'Antimony Uptake Systems in the Protozoan Parasite Leishmania and Accumulation Differences in Antimony-Resistant Parasites.' *Antimicrobial Agents and Chemotherapy*. American Society for Microbiology (ASM), 47(10) pp. 3073–3079.

Brown, S. D. and Kowalski, B. R. (1979) 'Pseudopolarographic Determination of Metal Complex Stability Constants in Dilute Solution by Rapid Scan Anodic Stripping

Voltammetry.' *Analytical Chemistry*, 51(13) pp. 2133–2139.

Buckley, S., Brackin, Richard, A. and Schmidt, S. (2016) 'Microdialysis-a sensitive method for estimating plant-available N released during litter decomposition.' *Proceedings of the International Nitrogen Initiative Conference 2016*, (December).

Buckley, S., Brackin, R., Jämtgård, S., Näsholm, T. and Schmidt, S. (2020) 'Microdialysis in soil environments: Current practice and future perspectives.' *Soil Biology and Biochemistry*, 143, April, p. 107743.

Buckley, S., Brackin, R., Näsholm, T., Schmidt, S. and Jämtgård, S. (2017) 'Improving in situ recovery of soil nitrogen using the microdialysis technique.' *Soil Biology and Biochemistry*, 114, November, pp. 93–103.

Buckley, S., Brackin, R. and Schmidt, S. (2015) *Microdialysis: an alternative approach to identifying plant-available nitrogen in soils*.

Burló, F., Guijarro, I., Carbonell-Barrachina, A. A., Valero, D. and Martínez-Sánchez, F. (1999) 'Arsenic Species: Effects on and Accumulation by Tomato Plants.' *Journal of Agricultural and Food Chemistry*, 47(3) pp. 1247–1253.

Cabalda, M. V, Banaag, M. A. and Garces, R. B. (2002) *Sustainable Development in The Philippine Minerals Industry: A Baseline Study*. M.V. Cabalda P.N.T. Tidalgo & R.B. Garces, M. A. B. (ed.) *Mining, Minerals and Sustainable Development Project (MMSD)*. England: International Institute for the Environment and Development (IIED).

Cai, Y., Su, J. and Ma, L. Q. (2004) 'Low molecular weight thiols in arsenic hyperaccumulator Pteris Vittata upon exposure to arsenic and other trace elements.' *Environmental Pollution*, 129(1) pp. 69–78.

Cal-Prieto, M. J., Carlosena, A., Andrade, J. M., Martínez, M. L., Muniategui, S., López-Mahía, P. and Prada, D. (2001) 'Antimony as a tracer of the anthropogenic influence on soils and estuarine sediments.' *Water, Air, and Soil Pollution*. Springer, 129(1–4) pp. 333–348.

Canadian Council of Ministers of the Environment (2007) *Canadian soil quality guidelines for the protection of environmental and human health*. Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment. Winnipeg. [Online] http://goo.gl/AePSg4.

Canepari, S., Marconi, E., Astolfi, M. L. and Perrino, C. (2010) 'Relevance of Sb(III), Sb(V), and Sb-containing nano-particles in urban atmospheric particulate matter.' *Analytical and Bioanalytical Chemistry*, 397(6) pp. 2533–2542.

Carey, A.-M., Lombi, E., Donner, E., de Jonge, M. D., Punshon, T., Jackson, B. P., Guerinot, M. Lou, Price, A. H. and Meharg, A. A. (2012) 'A review of recent developments in the speciation and location of arsenic and selenium in rice grain.' *Analytical and Bioanalytical*

Chemistry, 402(10) pp. 3275–3286.

Carneado, S., Hernández-Nataren, E., López-Sánchez, J. F. F. and Sahuquillo, A. (2015) ‘Migration of antimony from polyethylene terephthalate used in mineral water bottles.’ *Food Chemistry*. Elsevier Ltd, 166, January, pp. 544–550.

Carolyn, P., Aqilah, F. A. T., Payus, C., Farhana, A., Talip, A., Carolyn, P., Aqilah, F. A. T., Payus, C., Farhana, A. and Talip, A. (2014) ‘Assessment of heavy metals accumulation in paddy rice (Oryza sativa).’ *African Journal of Agricultural Research*. Academic Journals, 9(41) pp. 3082–3090.

Casiot, C., Ujevic, M., Munoz, M., Seidel, J. L. and Elbaz-Poulichet, F. (2007) ‘Antimony and arsenic mobility in a creek draining an antimony mine abandoned 85 years ago (upper Orb basin, France).’ *Applied Geochemistry*, 22(4) pp. 788–798.

Cavicchioli, A., La-Scalea, M. A., Gutz, G. R., Gutz, I. G. R. and Gutz, G. R. (2004) ‘Analysis and Speciation of Traces of Arsenic in Environmental , Food and Industrial Samples by Voltammetry : a Review.’ *Electroanalysis*, 16(9) pp. 697–711.

Chakraborti, D., Rahman, M. M., Das, B., Nayak, B., Pal, A., Sengupta, M. K., Hossain, M. A., Ahamed, S., Sahu, M., Saha, K. C., Mukherjee, S. C., Pati, S., Dutta, R. N. and Quamruzzaman, Q. (2013) ‘Groundwater arsenic contamination in Ganga–Meghna–Brahmaputra plain, its health effects and an approach for mitigation.’ *Environmental Earth Sciences*, 70(5) pp. 1993–2008.

Chang, C.-Y., Wang, C.-F., Mui, D. T. and Chiang, H.-L. (2009) ‘Application of methods (sequential extraction procedures and high-pressure digestion method) to fly ash particles to determine the element constituents: A case study for BCR 176.’ *Journal of Hazardous Materials*, 163(2–3) pp. 578–587.

Chapman, C. S. and Van Den Berg, C. M. G. G. (2007) ‘Anodic stripping voltammetry using a vibrating electrode.’ *Electroanalysis*, 19(13) pp. 1347–1355.

Chaurasia, C. S., Müller, M., Bashaw, E. D., Benfeldt, E., Bolinder, J., Bullock, R., Bungay, P. M., DeLange, E. C. M., Derendorf, H., Elmquist, W. F., Hammarlund-Udenaes, M., Joukhadar, C., Kellogg, D. L., Lunte, C. E., Nordstrom, C. H., Rollema, H., Sawchuk, R. J., Cheung, B. W. Y., Shah, V. P., Stahle, L., Ungerstedt, U., Welty, D. F. and Yeo, H. (2007) ‘AAPS-FDA workshop white paper: Microdialysis principles, application and regulatory perspectives.’ *In Pharmaceutical Research*, pp. 1014–1025.

Chen, Z. L., Farzana Akter, K., Rahman Mahmudur, M. and Naidu, R. (2006) ‘Speciation of arsenic by ion chromatography inductively coupled plasma mass spectrometry using ammonium eluents.’ *Journal of Separation Science*, 29(17) pp. 2671–2676.

Cheng, T. and Sun, H. (2014) ‘CHAPTER 25. Antimony and Bismuth.’ *In* Maret, W. and Wedd, A. (eds) *Binding, Transport and Storage of Metal Ions in Biological Cells*. London, UK: The Royal Society of Chemistry, pp. 768–799.

Chepkemoi, J. (2017) *What Is The Environmental Impact Of The Mining Industry?* First Break. [Online] worldatlas.com/articles/what-is-the-environmental-impact-of-the-mining-industry.html.

Cheraghi, M., Mosaed, H. P., Lorestani, B. and Yousefi, N. (2012) 'Heavy metal contamination in some rice samples.' *Electronic Journal of Environmental, Agricultural and Food Chemistry*, 11(5) pp. 424–432.

Choudhury, B. U., Malang, A., Webster, R., Mohapatra, K. P., Verma, B. C., Kumar, M., Das, A., Islam, M. and Hazarika, S. (2017) 'Acid drainage from coal mining: Effect on paddy soil and productivity of rice.' *Science of the Total Environment*. Elsevier B.V., 583(August 2018) pp. 344–351.

Ciminelli, V. S. T., Gasparon, M., Ng, J. C., Silva, G. C. and Caldeira, C. L. (2017) 'Dietary arsenic exposure in Brazil: The contribution of rice and beans.' *Chemosphere*. Elsevier Ltd, 168, February, pp. 996–1003.

Çirmi, D., Aydin, R. and Köleli, F. (2015) 'The electrochemical reduction of nitrate ion on polypyrrole coated copper electrode.' *Journal of Electroanalytical Chemistry*, 736 pp. 101–106.

Clark, R. B., Tiffin, L. O. and Brown, J. C. (1973) 'Organic Acids and Iron Translocation in Maize Genotypes.' *Plant Physiology*, 52(2) pp. 147–150.

Clarkson, D. T. (1996) 'Marschner H. 1995. Mineral nutrition of higher plants. second edition. 889pp. London: Academic Press.' *Annals of Botany*, 78(4) pp. 527–528.

Clemens, S. and Ma, J. F. (2016) 'Toxic Heavy Metal and Metalloid Accumulation in Crop Plants and Foods.' *Annual Review of Plant Biology*, 67(1) pp. 489–512.

Correia, M. M., Alves, S., Simões Gonçalves, M. D. L. and Nabais, C. (2006) 'Dynamic modelling of nickel complexation in xylem sap of Quercus ilex: A voltammetric study.' *Electroanalysis*, 18(8) pp. 814–822.

Cullen, W. R. and Reimer, K. J. (2016a) 'CHAPTER 2. Arsenic Is Everywhere.' *In Arsenic is Everywhere: Cause for Concern?*, pp. 8–48.

Cullen, W. R. and Reimer, K. J. (2016b) 'CHAPTER 8. Arsenic and the Evening Meal.' *In Arsenic is Everywhere: Cause for Concern?*, pp. 221–265.

Daniels, R., Rush, C. C. and Bauer, L. (1960) 'The Fehling and Benedict tests.' *Journal of Chemical Education*, 37(4) p. 205.

Daus, B. and Hansen, H. R. (2016) 'Analysis of antimony species – lessons learnt from more than two decades of environmental research.' *Environmental Chemistry*, 13(6) p. 913.

Dawe, B. D., Organisation, A. and Nations, U. (2015) ‘Rice in Asia: Paddy-whacked.’ *Economist (United Kingdom)*, 411(8960).

Dobermann, A., Dawe, D., Roetter, R. P. and Cassman, K. G. (2000) ‘Reversal of rice yield decline in a long-term continuous cropping experiment.’ *Agronomy Journal*, 92(4) pp. 633–643.

Domingo, L. E. and Kyuma, K. (1983) ‘Trace elements in tropical asian paddy soils: I. total trace element status.’ *Soil Science and Plant Nutrition*, 29(4) pp. 439–452.

Dortsiou, M. and Kyriacou, G. (2009) ‘Electrochemical reduction of nitrate on bismuth cathodes.’ *Journal of Electroanalytical Chemistry*, 630(1–2) pp. 69–74.

Duester, L., Diaz-Bone, R. A., Kösters, J. and Hirner, A. V. (2005) ‘Methylated arsenic, antimony and tin species in soils.’ *In Journal of Environmental Monitoring*, pp. 1186–1193.

Dushenkov, S. (2003) ‘Trends in phytoremediation of radionuclides.’ *In Plant and Soil*, pp. 167–175.

Elmquist, W. F. and Sawchuk, R. J. (1997) ‘Application of microdialysis in pharmacokinetic studies.’ *Pharmaceutical Research* pp. 267–288.

Emamverdian, A. and Ding, Y. (2017) ‘Effects of heavy metals’ toxicity on plants and enhancement of plant defense mechanisms of Si-mediation “ Review.”’ *International Journal of Environmental & Agriculture Research*, (4) pp. 41–51.

Emamverdian, A., Ding, Y., Mokhberdoran, F. and Xie, Y. (2015) ‘Heavy Metal Stress and Some Mechanisms of Plant Defense Response.’ *The Scientific World Journal*. Hindawi Publishing Corporation, 2015 pp. 1–18.

EPA (2004) ‘EPA Method 6020A: ICP-MS. Official Name: EPA Method 6020A, Inductively Coupled Plasma-Mass Spectrometry.’ *EPA methods*, 6.

Epstein, E. and and Bloom, A. J. (1972) *Mineral Nutrition of Plants: Principles and Perspectives*. 2nd ed., Sunderland, Massachusetts: Sinauer Associates, Inc.

Fan, Y., Zhu, T., Li, M., He, J., Huang, R. and and Ruixue Huang, T. Z. Y. F. M. L. J. H. (2017) ‘Heavy Metal Contamination in Soil and Brown Rice and Human Health Risk Assessment near Three Mining Areas in Central China.’ *Journal of Healthcare Engineering*. Hindawi, 2017 p. 9.

FAO (2016) *GIEWS - Crop Prospects and Food Situation, No.1,March 2016*.

FAO and WHO (2019) *Report of the 11th session of the codex committee on contaminnants in foods. A joint FAO/WHO food standards programme codex alimentarius commission 40th Session. Codex*. Geneva, Switzerland.

Farid, M., Shakoor, M., Ehsan, S., Ali, S., Zubair, M. and Hanif, M. (2013) 'Morphological, physiological and biochemical responses of different plant species to Cd stress.' *Int J Chem Biochem Sci*, 3(March) pp. 53–60.

Farnese, F. S., Oliveira, J. A., Farnese, M. S., Gusman, G. S., Silveira, N. M. and Siman, L. I. (2014) 'Uptake arsenic by plants: Effects on mineral nutrition, growth and antioxidant capacity.' *Idesia (Arica)*, 32(1) pp. 99–106.

Fashola, M., Ngole-Jeme, V. and Babalola, O. (2016) 'Heavy Metal Pollution from Gold Mines: Environmental Effects and Bacterial Strategies for Resistance.' *International Journal of Environmental Research and Public Health*. MDPI AG, 13(11) p. 1047.

Feldmann, J., Salaün, P. and Lombi, E. (2009) 'Critical review perspective: elemental speciation analysis methods in environmental chemistry - moving towards methodological integration.' *Environmental Chemistry*. CSIRO, 6(4) p. 275.

Feng, R., Wei, C., Tu, S., Ding, Y., Wang, R. and Guo, J. (2013) 'The uptake and detoxification of antimony by plants: A review.' *Environmental and Experimental Botany*. Elsevier B.V., 96, December, pp. 28–34.

Festin, E. S., Tigabu, M., Chileshe, M. N., Syampungani, S. and Odén, P. C. (2019) 'Progresses in restoration of post-mining landscape in Africa.' *Journal of Forestry Research*, 30(2) pp. 381–396.

Filella and May (2003) 'Computer simulation of the low-molecular-weight inorganic species distribution of antimony (III) and antimony (V) in natural waters.' *Geochimica et Cosmochimica Acta,* 67(21) pp. 4013–4031.

Filella, M. (2013) 'Food for thought: A critical overview of current practical and conceptual challenges in trace element analysis in natural waters.' *Water (Switzerland)*. MDPI AG pp. 1152–1171.

Filella, M., Belzile, N. and Chen, Y.-W. W. (2002) 'Antimony in the environment: a review focused on natural waters.' *Earth-Science Reviews*, 57(1–2) pp. 125–176.

Filella, M., Belzile, N. and Lett, M.-C. C. (2007) 'Antimony in the environment: A review focused on natural waters. III. Microbiota relevant interactions.' *Earth-Science Reviews*, 80(3–4) pp. 195–217.

Filella, M. and May, P. M. (2005a) 'Critical appraisal of available thermodynamic data for the complexation of antimony(iii) and antimony(v) by low molecular mass organic ligands.' *Journal of Environmental Monitoring*, 7(12) p. 1226.

Filella, M. and May, P. M. (2005b) 'Reflections on the calculation and publication of potentiometrically- determined formation constants.' *Talanta*, 65(5) pp. 1221–1225.

Filella, M. and Williams, P. A. (2012) 'Antimony interactions with heterogeneous

complexants in waters, sediments and soils: A review of binding data for homologous compounds.' *Chemie der Erde*. Elsevier GmbH., 72(SUPPL.4) pp. 49–65.

Filella, M., Williams, P. A. and Belzile, N. (2009) 'Antimony in the environment: Knowns and unknowns.' *Environmental Chemistry*, 6(2) pp. 95–105.

Forsberg, G., O'Laughlin, J. W., Megargle, R. G. and Koirtyohann, S. R. (1975) 'Determination of Arsenic by Anodic Stripping Voltammetry and Differential Pulse Anodic Stripping Voltammetry.' *Analytical Chemistry*, 47(9) pp. 1586–1592.

Francesconi, K. A. and Kuehnelt, D. (2004) 'Determination of arsenic species: A critical review of methods and applications, 2000–2003.' *The Analyst*, 129(5) pp. 373–395.

Frantz, J. M. and Epstein, E. (2005) *Nutritional deficiencies: What they look like*. [Online] [Accessed on 16th December 2019] http://www.ces.ncsu.edu/depts/hort/floriculture/def/forfloriculturecropshttp://extension.agron.iastate.edu/soilfertility/nutrienttopics/deficiencies.htmlcornhttp://muextension.missouri.edu/explore/agguides/hort/index.htm.

FSA (2012) *Arsenic speciation in fruit and vegetables grown in the UK.* Aberdeen: University of Aberdeen.

Fu, Z., Wu, F., Mo, C., Deng, Q., Meng, W. and Giesy, J. P. (2016) 'Comparison of arsenic and antimony biogeochemical behavior in water, soil and tailings from Xikuangshan, China.' *Science of the Total Environment*, 539 pp. 97–104.

Garg, N. and Singla, P. (2011) 'Arsenic toxicity in crop plants: physiological effects and tolerance mechanisms.' *Environmental Chemistry Letters*. Springer, 9(3) pp. 303–321.

Garg, N., Singla, P. and Bhandari, P. (2015) 'Metal uptake, oxidative metabolism, and mycorrhization in pigeonpeaand pea under arsenic and cadmium stress.' *Turkish Journal of Agriculture and Forestry*, 39(2) pp. 234–250.

Gebel, T. (1997) 'Arsenic and antimony: comparative approach on mechanistic toxicology.' *Chemico-Biological Interactions*. Elsevier Ireland Ltd, 107(3) pp. 131–144.

Gebel, T. W. (2001) 'Unanswered Questions in Arsenic Toxicology.' *Journal of Environmental Pathology, Toxicology and Oncology*, 20(4) p. 11.

Gemici, Ü. and Tarcan, G. (2007) 'Assessment of the pollutants in farming soils and waters around untreated abandoned Türkönü mercury mine (Turkey).' *Bulletin of Environmental Contamination and Toxicology*, 79(1) pp. 20–24.

Geng, A., Wang, X., Wu, L., Wang, F., Chen, Y., Yang, H., Zhang, Z. and Zhao, X. (2017) 'Arsenic accumulation and speciation in rice grown in arsanilic acid-elevated paddy soil.' *Ecotoxicology and Environmental Safety*, 137 pp. 172–178.

Geng, C. N., Zhu, Y. G., Tong, Y. P., Smith, S. E. and Smith, F. A. (2006) ‘Arsenate (As) uptake by and distribution in two cultivars of winter wheat (Triticum aestivum L.).’ *Chemosphere*, 62(4) pp. 608–615.

Gerényi, A., Czech, V., Fodor, F., Vincze, L. and Szalóki, I. (2017) ‘In vivo XANES measuring technique for studying the arsenic uptake in cucumber plants.’ *X-Ray Spectrometry*, 46(3) pp. 143–150.

German Federal Soil Protection Act (1998) *Federal Law Gazette I p. 502*.

Ghori, N.-H., Ghori, T., Hayat, M. Q., Imadi, S. R., Gul, A., Altay, V. and Ozturk, M. (2019) ‘Heavy metal stress and responses in plants.’ *International Journal of Environmental Science and Technology*. Center for Environmental and Energy Research and Studies, 16(3) pp. 1807–1828.

Gibbon-Walsh, K., Salaün, P. and van den Berg, C. M. G. (2012a) ‘Determination of arsenate in natural pH seawater using a manganese-coated gold microwire electrode.’ *Analytica Chimica Acta*. Elsevier B.V., 710, January, pp. 50–57.

Gibbon-Walsh, K., Salaün, P. and van den Berg, C. M. G. (2012b) ‘Pseudopolarography of Copper Complexes in Seawater Using a Vibrating Gold Microwire Electrode.’ *The Journal of Physical Chemistry A*, 116(25) pp. 6609–6620.

Gibbon-Walsh, K., Salaün, P., Uroic, M. K., Feldmann, J., McArthur, J. M. and Van Den Berg, C. M. G. (2011) ‘Voltammetric determination of arsenic in high iron and manganese groundwaters.’ *Talanta*, 85(3) pp. 1404–1411.

Gidlow, D. A. (2004) ‘Lead toxicity.’ *Occupational Medicine*, 54(2) pp. 76–81.

Goldberg, S. (2011) ‘Chemical Equilibrium and Reaction Modeling of Arsenic and Selenium in Soils.’ *Dynamics and Bioavailability of Heavy Metals in the Rootzone* pp. 65–92.

Grob, M., Wilcke, W. and Mestrot, A. (2018) ‘Release and Biomethylation of Antimony in Shooting Range Soils upon Flooding.’ *Soil Systems*, 2(2) p. 34.

Guerriero, Gea, Deshmukh, R. and Durgesh K., T. (2020) *Metalloids in Plants Advances and Future Prospects*. Deshmukh, R., Tripathi, D. K., and Guerriero, Gia (eds) *Wiley*. John Wiley & Sons Ltd.

Gupta, D. K., Srivastava, S., Huang, H. G., Romero-Puertas, M. C. and Sandalio, L. M. (2011) ‘Arsenic Tolerance and Detoxification Mechanisms in Plants.’ *In*, pp. 169–179.

Ha, N. T. H., Ha, N. T., Nga, T. T. H., Minh, N. N., Anh, B. T. K., Hang, N. T. A., Duc, N. A., Nhuan, M. T. and Kim, K.-W. (2019) ‘Uptake of arsenic and heavy metals by native plants growing near Nui Phao multi-metal mine, northern Vietnam.’ *Applied Geochemistry*. Elsevier Ltd, 108, September, p. 104368.

Hakeem, K. R. (2015) ‘Crop production and global environmental issues.’ *Crop Production and Global Environmental Issues*, (December) pp. 1–598.

Hall, J. L. L. (2002) ‘Cellular mechanisms for heavy metal detoxification and tolerance.’ *Journal of experimental botany*, 53(366) pp. 1–11.

Hammel, W., Debus, R. and Steubing, L. (2000) ‘Mobility of antimony in soil and its availability to plants.’ *Chemosphere*, 41(11) pp. 1791–1798.

Hansen, C. (2011) *Antimony speciation analysis HPLC methods with ICP-MS and ES-MS detection for complex biological matrices*. University of Coppenhagen.

Hansen, H. R. and Pergantis, S. A. (2008) ‘Analytical techniques and methods used for antimony speciation analysis in biological matrices.’ *Journal of Analytical Atomic Spectrometry*, 23(10) p. 1328.

Hasanuzzaman, M., Nahar, K. and Fujita, M. (2018) *Mechanisms of Arsenic Toxicity and Tolerance in Plants*. Hasanuzzaman, M., Nahar, K., and Fujita, M. (eds) *Mechanisms of Arsenic Toxicity and Tolerance in Plants*. Singapore: Springer Singapore.

Hasanuzzaman, M., Nahar, K., Hakeem, K. R., Öztürk, M. and Fujita, M. (2015) ‘Arsenic Toxicity in Plants and Possible Remediation.’ *In Soil Remediation and Plants: Prospects and Challenges*. Elsevier Inc., pp. 433–501.

Hawkesford, M. J., Parmar, S. and Buchner, P. (2013) ‘Mineral Composition Analysis: Measuring Anion Uptake and Anion Concentrations in Plant Tissues.’ *In Plant Mineral Nutrients*. Totowa, NJ: Humana Press, pp. 109–119.

Hazama, K., Nagata, S., Fujimori, T., Yanagisawa, S. and Yoneyama, T. (2015) ‘Concentrations of metals and potential metal-binding compounds and speciation of Cd, Zn and Cu in phloem and xylem saps from castor bean plants (Ricinus communis) treated with four levels of cadmium.’ *Physiologia Plantarum*, 154(2) pp. 243–255.

He, M., Wang, N., Long, X., Zhang, C., Ma, C., Zhong, Q., Wang, A., Wang, Y., Pervaiz, A. and Shan, J. (2019) ‘Antimony speciation in the environment: Recent advances in understanding the biogeochemical processes and ecological effects.’ *Journal of Environmental Sciences*. Elsevier B.V., 75, January, pp. 14–39.

Hettick, B. E., Cañas-Carrell, J. E., French, A. D. and Klein, D. M. (2015) ‘Arsenic: A Review of the Element’s Toxicity, Plant Interactions, and Potential Methods of Remediation.’ *Journal of Agricultural and Food Chemistry*, 63(32) pp. 7097–7107.

Hijaz, F. and Killiny, N. (2014) ‘Collection and chemical composition of phloem sap from Citrus sinensis L. Osbeck (sweet orange).’ *PLoS ONE*. Public Library of Science, 9(7).

Hirner, A. V., Grüter, U. M. and Kresimon, J. (2000) ‘Metal(loid)organic compounds in contaminated soil.’ *Fresenius’ Journal of Analytical Chemistry*. Springer, 368(2–3) pp.

263–267.

Hoagland and Arnon, D., D. (1950) *The water-culture method of growing plants without soil.* Berkeley, Calif. : University of California, College of Agriculture, Agricultural Experiment Station.

Hossain, M. A., Piyatida, P., da Silva, J. A. T. and Fujita, M. (2012) 'Molecular Mechanism of Heavy Metal Toxicity and Tolerance in Plants: Central Role of Glutathione in Detoxification of Reactive Oxygen Species and Methylglyoxal and in Heavy Metal Chelation.' *Journal of Botany*. Hindawi Limited, 2012(Cd) pp. 1–37.

Hozhina, E. ., Khramov, A. ., Gerasimov, P. . and Kumarkov, A. . (2001) 'Uptake of heavy metals, arsenic, and antimony by aquatic plants in the vicinity of ore mining and processing industries.' *Journal of Geochemical Exploration*, 74(1–3) pp. 153–162.

Hrytsak, L. R., Herts, A. I., Nuzhyna, N. V., Cryk, M. M., Shevchenko, V. V. and Drobyk, N. M. (2018) 'The influence of light regime on the growth data and pigment composition of the plant Gentiana lutea cultured in vitro.' *Regulatory Mechanisms in Biosystems*, 9(2) pp. 258–266.

Hu, L., Zhang, B., Wu, D., Fan, H., Tu, J., Liu, W., Huang, R. and Huang, X. (2019) 'Estimation of arsenic bioaccessibility in raw and cooked radish using simulated in vitro digestion.' *Food & Function*. Royal Society of Chemistry, 10(3) pp. 1426–1432.

Hu, Y., Cheng, H. and Tao, S. (2016) 'The Challenges and Solutions for Cadmium-contaminated Rice in China: A Critical Review.' *Environment International*. Elsevier Ltd pp. 515–532.

Hua, C.-Y., Chen, J.-X., Cao, Y., Li, H.-B., Chen, Y. and Ma, L. Q. (2020) 'Pteris vittata coupled with phosphate rock effectively reduced As and Cd uptake by water spinach from contaminated soil.' *Chemosphere*. Elsevier Ltd, 247, May, p. 125916.

Huang, R.-Q., Gao, S.-F., Wang, W.-L., Staunton, S. and Wang, G. (2006) 'Soil arsenic availability and the transfer of soil arsenic to crops in suburban areas in Fujian Province, southeast China.' *Science of The Total Environment*, 368(2–3) pp. 531–541.

Huang, Y., Chen, Q., Deng, M., Japenga, J., Li, T., Yang, X. and He, Z. (2018) 'Heavy metal pollution and health risk assessment of agricultural soils in a typical peri-urban area in southeast China.' *Journal of Environmental Management*. Academic Press, 207, February, pp. 159–168.

Huang, Z., Pan, X.-D. D., Wu, P.-G. G., Han, J.-L. L. and Chen, Q. (2013) 'Health Risk Assessment of Heavy Metals in Rice to the Population in Zhejiang, China.' Scarfi, M. R. (ed.) *PLoS ONE*, 8(9) pp. 1–6.

Huiliang, H., Jagner, D. and Renman, L. (1988) 'Flow potentiometric and constant-current stripping analysis for arsenic(V) without prior chemical reduction to arsenic(III).'

Analytica Chimica Acta, 207 pp. 37–46.

Humphrey, O. S., Young, S. D., Bailey, E. H., Crout, N. M. J., Ander, E. L., Hamilton, E. M. and Watts, M. J. (2019) 'Investigating the use of microdialysis and SEC-UV-ICP-MS to assess iodine interactions in soil solution.' *Chemosphere*. Elsevier Ltd, 229, August, pp. 41–50.

Hunt, R., Causton, D. R., Shipley, B. and Askew, A. P. (2002) 'A modern tool for classical plant growth analysis.' *Annals of Botany*, 90(4) pp. 485–488.

Inselsbacher, E. (2014) 'Recovery of individual soil nitrogen forms after sieving and extraction.' *Soil Biology and Biochemistry*, 71, April, pp. 76–86.

Inselsbacher, E., Öhlund, J., Jämtgård, S., Huss-Danell, Kerstin, A. and Näsholm, T. (2011) 'The potential of microdialysis to monitor organic and inorganic nitrogen compounds in soil.' *Soil Biology and Biochemistry*, 43(6) pp. 1321–1332.

International Programme on Chemical Safety (2004) 'International programme on chemical safety (IPCS),' (June) pp. 1–34.

IPNI (2002) 'Nutrient Deficiency Symptoms in Rice.' *Better Crops International*, 16(May) pp. 23–25.

IRRI and DFID (2009) 'Scuba rice : breeding flood-tolerance into Asia ' s local mega rice varieties.' *South Asia* pp. 1–6.

Ismail, B., Yap, D., Adezrian, J., Khairiah, J. and Ahmad-Mahir, R. (2009) 'The Uptake of Heavy Metals by Paddy Plants (Oryza sativa) in Kota Marudu, Sabah, Malaysia.' *& Environ. Sci*, 6(1) pp. 16–19.

Jamila Alfaraas, A. M., Khairiah, J., Ismail, B. S. and Noraini, T. (2016) 'Effects of heavy metal exposure on the morphological and microscopical characteristics of the paddy plant.' *Journal of Environmental Biology*, 37(5) pp. 955–963.

Järup, L. (2003) 'Hazards of heavy metal contamination.' *British Medical Bulletin*, 68 pp. 167–182.

JECFA (2016) 'Joint FAO / WHO Expert Committee on Food Additives (JECFA) Call for Experts on Food Additives , Contaminants and toxins ; and Residues of Veterinary Drugs,' (October).

Jentschke, G. and Godbold, D. L. (2000) 'Metal toxicity and ectomycorrhizas.' *Physiologia Plantarum*, 109(2) pp. 107–116.

Ji, Y., Sarret, G., Schulin, R. and Tandy, S. (2017) 'Fate and chemical speciation of antimony (Sb) during uptake, translocation and storage by rye grass using XANES spectroscopy.' *Environmental Pollution*. Elsevier Ltd, 231, December, pp. 1322–1329.

Johnson, C. A., Moench, H., Wersin, P., Kugler, P. and Wenger, C. (2005) 'Solubility of Antimony and Other Elements in Samples Taken from Shooting Ranges.' *Journal of Environmental Quality*. Wiley, 34(1) pp. 248–254.

Johnson, C. D. (2014) 'Phytoremediation of Arsenic Contamination on Vashon-Maury Island METHODS Salix Screening for Arsenic Tolerance.'

Johnston, A. E. and Poulton, P. R. (2018) 'The importance of long-term experiments in agriculture: their management to ensure continued crop production and soil fertility; the Rothamsted experience.' *European Journal of Soil Science*, 69(1) pp. 113–125.

Kabata-Pendias, A. (2010) *Trace Elements in Soils and Plants*. 4th ed., CRC Press.

Kalaji, H. M., Jajoo, A., Oukarroum, A., Brestic, M., Zivcak, M., Samborska, I. A., Cetner, M. D., Łukasik, I., Goltsev, V. and Ladle, R. J. (2016) 'Chlorophyll a fluorescence as a tool to monitor physiological status of plants under abiotic stress conditions.' *Acta Physiologiae Plantarum*. Polish Academy of Sciences.

Kapaj, S., Peterson, H., Liber, K. and Bhattacharya, P. (2006) 'Human Health Effects From Chronic Arsenic Poisoning–A Review.' *Journal of Environmental Science and Health, Part A*. The Safe Drinking Water Foundation, Saskatoon, Saskatchewan, Canada., 41(10) pp. 2399–2428.

Katsounaros, I. and Kyriacou, G. (2007) 'Influence of the concentration and the nature of the supporting electrolyte on the electrochemical reduction of nitrate on tin cathode.' *Electrochimica Acta*, 52(23) pp. 6412–6420.

Kehr, J. and Rep, M. (2007) 'Protein extraction from xylem and phloem sap.' *Methods in molecular biology (Clifton, N.J.)*, 355 pp. 27–35.

Killiny, N. and Hijaz, F. (1998) 'Chemical composition of xylem sap of Citrus sinensis L. Osbeck (sweet orange).' *Trends in Plant Science*, 3(5) pp. 188–195.

Kisan, M., Sangathan, S., Nehru, J. and Pitroda, S. G. (2012) 'Laboratory Glassware-Volumetric Instruments-Methods for Testing of Capacity and for Use.' ISO (ed.) *4787*. Geneva: IS pp. 1–29.

Kitagishi, K. (1981) 'Heavy Metal Pollution in Soils of Japan.' *Japan Scientific Societies Press, Tokyo, Japan*, 52(4) p. 302.

Koester, R. P., Skoneczka, J. A., Cary, T. R., Diers, B. W. and Ainsworth, E. A. (2014) 'Historical gains in soybean (Glycine max Merr.) seed yield are driven by linear increases in light interception, energy conversion, and partitioning efficiencies.' *Journal of Experimental Botany*, 65(12) pp. 3311–3321.

Kolbe, F., Mattusch, J., Wennrich, R., Weiss, H., Sorkau, E., Lorenz, W. and Daus, B. (2012) 'Analytical investigations of antimony-edta complexes and their use in speciation analysis.’ *Fresenius Environmental Bulletin*, 21(11 C) pp. 3453–3456.

Kowalska, J., Stryjewska, E., Szymański, P. and Golimowski, J. (1999) ‘Voltammetric determination of arsenic in plant material.’ *Electroanalysis*, 11(17) pp. 1301–1304.

Krachler, M. and Emons, H. (2001) ‘Speciation analysis of antimony by high-performance liquid chromatography inductively coupled plasma mass spectrometry using ultrasonic nebulization.’ *Analytica Chimica Acta*, 429(1) pp. 125–133.

Kroukamp, E. M., Wondimu, T. and Forbes, P. B. C. (2016) ‘Metal and metalloid speciation in plants: Overview, instrumentation, approaches and commonly assessed elements.’ *TrAC - Trends in Analytical Chemistry*. Elsevier B.V., 77 pp. 87–99.

Krupka, K. M. and Serne, R. J. (2002) *Geochemical Factors Affecting the Behavior of Antimony, Cobalt, Europium, Technetium, and Uranium in Vadose Zone Sediments*. *Pnnl-14126*. Richland, WA (United States).

Kumar, R., Mishra, R. K., Mishra, V., Qidwai, A., Pandey, A., Shukla, S. K., Pandey, M., Pathak, A. and Dikshit, A. (2015) ‘Detoxification and Tolerance of Heavy Metals in Plants.’ *In Plant Metal Interaction: Emerging Remediation Techniques*. Elsevier Inc., pp. 335–359.

Kumarathilaka, P., Seneweera, S., Meharg, A. and Bundschuh, J. (2018) ‘Arsenic speciation dynamics in paddy rice soil-water environment: sources, physico-chemical, and biological factors - A review.’ *Water Research*. Elsevier Ltd pp. 403–414.

Küpper, H. and Andresen, E. (2016) ‘Mechanisms of metal toxicity in plants.’ *Metallomics*, 8(3) pp. 269–285.

Lansdown, A. B. G. (2013) ‘CHAPTER 1. Introduction.’ *In The Carcinogenicity of Metals: Human Risk Through Occupational and Environmental Exposure*, pp. 1–18.

Larsen, E. H. and Stürup, S. (1994) ‘Carbon-enhanced inductively coupled plasma mass spectrometric detection of arsenic and selenium and its application to arsenic speciation.’ *Journal of Analytical Atomic Spectrometry*, 9(10) pp. 1099–1105.

van Leeuwen, H. P., Town, R. M., Buffle, J., Cleven, R. F. M. J., Davison, W., Puy, J., van Riemsdijk, W. H. and Sigg, L. (2005) ‘Dynamic Speciation Analysis and Bioavailability of Metals in Aquatic Systems.’ *Environmental Science & Technology*, 39(22) pp. 8545–8556.

van Leeuwen, L. C. and Aldenberg, T. (2012) *RIVM Letter Report 601357001/2012: Environmental risk limits for antimony*.

Li, Z. and Cui, Z. (2008) ‘Application of microdialysis in tissue engineering monitoring.’ *Progress in Natural Science*. Science Press, 18(5) pp. 503–511.

Liang, G., Gong, W., Li, B., Zuo, J., Pan, L. and Liu, X. (2019) ‘Analysis of Heavy Metals in Foodstuffs and an Assessment of the Health Risks to the General Public via Consumption

in Beijing, China.’ *International Journal of Environmental Research and Public Health*. MDPI AG, 16(6) p. 909.

Lichtfouse, E., Schwarzbauer, J. and Robert, D. (2012) *Environmental chemistry for a sustainable world*. *Environmental Chemistry for a Sustainable World*. Springer Netherlands.

Lintschinger, J., Koch, I., Serves, S., Feldmann, J. and Cullen, W. R. (1997) ‘Determination of antimony species with High-Performance Liquid Chromatography using element specific detection.’ *Fresenius’ Journal of Analytical Chemistry*, 359(6) pp. 484–491.

Liu, Z. G. and Huang, X. J. (2014) ‘Voltammetric determination of inorganic arsenic.’ *TrAC - Trends in Analytical Chemistry*, 60 pp. 25–35.

Lombi, E. and Holm, P. E. (2010) ‘Metalloids, soil chemistry and the environment.’ *In Advances in Experimental Medicine and Biology*. Australia: Landes Bioscience and Springer Science+Business Media., pp. 33–44.

Louis, Y., Cmuk, P., Nicolau, R., Omanovi, D., Lenoble, V., Pižeta, I., Mounier, S., and Garde, L. and Garde, L. (2007) ‘Pseudopolarography As a Tool for Complexation Studies of Trace Metals With Dissolved Natural Organic Matter,’ (January) p. 2007.

Louis, Y., Cmuk, P., Omanović, D., Garnier, C., Lenoble, V., Mounier, S. and Pižeta, I. (2008) ‘Speciation of trace metals in natural waters: The influence of an adsorbed layer of natural organic matter (NOM) on voltammetric behaviour of copper.’ *Analytica Chimica Acta*. Elsevier Masson, 606(1) pp. 37–44.

Louis, Y., Garnier, C., Lenoble, V., Omanovi, D., Mounier, S., Pižeta, I., Protee, L., Toulon, S., Bp, V., Garde, L., Physico, G. De, Chimie, T., Moléculaires, S. and I, U. B. (2008) ‘Electrochemical Study of Major and Trace Metal Interactions With Concentrated Marine Dissolved Organic Matter,’ (098) p. 1214910.

Lu, M. and Compton, R. G. (2013) ‘Voltammetric Determination of Iron(III) in Water.’ *Electroanalysis*, 25(5) pp. 1123–1129.

Lubin, J. H., Moore, L. E., Fraumeni, J. F. and Cantor, K. P. (2008) ‘Respiratory Cancer and Inhaled Inorganic Arsenic in Copper Smelters Workers: A Linear Relationship with Cumulative Exposure that Increases with Concentration.’ *Environmental Health Perspectives*, 116(12) pp. 1661–1665.

Luo, J. and Shu, W. (2015) ‘Arsenic-Induced Developmental Neurotoxicity.’ *In* Flora, S. J. S. B. T.-H. of A. T. (ed.) *Handbook of Arsenic Toxicology*. Oxford: Elsevier, pp. 363–386.

Lydic, R., Baghdoyan, H. A. and May, A. L. (2018) ‘Chapter Fourteen - Neurochemistry of Anesthetic States.’ *In* Eckenhoff, R. G. and Dmochowski, I. J. B. T.-M. in E. (eds) *Chemical and Biochemical Approaches for the Study of Anesthetic Function Part B*. 1st ed., Academic Press, pp. 237–255.

Madejón, P., Marañón, T. and Murillo, J. M. (2006) 'Biomonitoring of trace elements in the leaves and fruits of wild olive and holm oak trees.' *Science of the Total Environment*, 355(1–3) pp. 187–203.

Magahud, J. C., Badayos, R. B., Sanchez, P. B. and Sta. Cruz, P. C. (2015) *Levels and Potential Sources of Heavy Metals in Major Irrigated Rice Areas of the Philippines*. *IAMURE International Journal of Ecology and Conservation*.

Mandal, B. K. and Suzuki, K. T. (2002) 'Arsenic round the world: A review.' *Talanta*. Elsevier, 58(1) pp. 201–235.

Mareček, V., Jänchenová, H., Samec, Z. and Březina, M. (1986) 'Voltammetric determination of nitrate, perchlorate and iodide at a hanging electrolyte drop electrode.' *Analytica Chimica Acta*, 185(C) pp. 359–362.

Marschner, H. (1995) *Mineral Nutrition of High Plants*. Academic Press.

Martin, M., Ferdousi, R., Hossain, K. M. J. and Barberis, E. (2010) 'Arsenic from groundwater to paddy fields in Bangladesh: Solid-liquid partition, sorption and mobility.' *Water, Air, and Soil Pollution*, 212(1–4) pp. 27–36.

Martinez, R. E., Marquez, J. E., Hòa, H. T. B. and Gieré, R. (2013) 'Open-pit coal-mining effects on rice paddy soil composition and metal bioavailability to Oryza sativa L. plants in Cam Pha, northeastern Vietnam.' *Environmental Science and Pollution Research*, 20(11) pp. 7686–7698.

Massoura, S. T., Echevarria, G., Leclerc-Cessac, E. and Morel, J. L. (2004) 'Response of excluder, indicator, and hyperaccumulator plants to nickel availability in soils.' *Australian Journal of Soil Research*, 42(8) pp. 933–938.

Materials, B. (1989) *Analytical Methods*. *WHO*.

Matschullat, J. J. (2000) 'Arsenic in the geosphere - A review.' *The Science of the Total Environment*, 249(1–3) pp. 297–312.

Mawia, A. M., Hui, S., Zhou, L., Li, H., Tabassum, J., Lai, C., Wang, J., Shao, G., Wei, X., Tang, S., Luo, J., Hu, S. and Hu, P. (2021) 'Inorganic arsenic toxicity and alleviation strategies in rice.' *Journal of Hazardous Materials*. Elsevier B.V. p. 124751.

Mayet, N., Servat, K., Kokoh, K. B. and Napporn, T. W. (2019) 'Probing the Surface of Noble Metals Electrochemically by Underpotential Deposition of Transition Metals.' *Surfaces*, 2(2) pp. 257–276.

McLaughlin, M. ., Parker, D. . and Clarke, J. . (1999) 'Metals and micronutrients – food safety issues.' *Field Crops Research*, 60(1–2) pp. 143–163.

Mead, M. N. (2005) 'Arsenic: In search of an antidote to a global poison.' *Environmental*

Health Perspectives. Public Health Services, US Dept of Health and Human Services, 113(6).

Meadows, R. (2014) ‘How Plants Control Arsenic Accumulation.’ *PLoS Biology*, 12(12) pp. 1002008–1002009.

Meharg, A. A. (2004) ‘Arsenic in rice - Understanding a new disaster for South-East Asia.’ *Trends in Plant Science* pp. 415–417.

Meharg, A. A. and Zhao, F.-J. (2012) *Arsenic & Rice*. *Springer*. Dordrecht: Springer Netherlands.

Mendoza, T. (2012) ‘Estimates of Rice Per Capita Consumption: Its Implications to the Rice Self-Sufficiency Program of the Philippines*.’ *Policy Options*, 4, January.

Mestrot, A., Ji, Y., Tandy, S. and Wilcke, W. (2016) ‘A novel method to determine trimethylantimony concentrations in plant tissue.’ *Environmental Chemistry*, 13(6) pp. 919–926.

Michalski, R., Szopa, S., Jabłońska, M. and Łyko, A. (2012) ‘Application of hyphenated techniques in speciation analysis of arsenic, antimony, and thallium.’ *The Scientific World Journal*. Institute of Environmental Engineering, the Polish Academy of Sciences, 34 Sklodowskiej-Curie Street, 41 819 Zabrze, Poland. michalski@ipis.zabrze.pl, 2012(January 2017) p. 902464.

Miekeley, N., Mortari, S. R. and Schubach, A. O. (2002) ‘Monitoring of total antimony and its species by ICP-MS and on-line ion chromatography in biological samples from patients treated for leishmaniasis.’ *Fresenius’ Journal of Analytical Chemistry*, 372(3) pp. 495–502.

Mihucz, V. G., Tatár, E. E. E., Virág, I., Cseh, E., Fodor, F., Záray, G., Tat??r, E., Vir??g, I., Cseh, E., Fodor, F. and Gyula, Z. (2005) ‘Arsenic speciation in xylem sap of cucumber (Cucumis sativus L.).’ *Analytical and Bioanalytical Chemistry*. Joint Research Group of Environmental Chemistry of the Hungarian Academy of Sciences and L. Eotvos University, PO Box 32, 1518 Budapest, Hungary., 383(3) pp. 461–466.

Mihucz, V. G., Varga, A. and Za, G. (1998) ‘Determination of Organic Acids in Xylem Sap of Cucumber : Effect of Lead Contamination,’ 314(58) pp. 306–314.

Ministerie Van Volkshuisvesting; Ruimtelijke Ordening En Milieu (2000) ‘Dutch Target and Intervention Values; 2000 (the New Dutch List).’ *Netherlands Government Gazette*, 2000 pp. 1–12.

Miró, M., Fitz, W. J., Swoboda, S. and Wenzel, W. W. (2010) ‘In-situ sampling of soil pore water: Evaluation of linear-type microdialysis probes and suction cups at varied moisture contents.’ *Environmental Chemistry*, 7(1) pp. 123–131.

Mishra, S., Srivastava, S., Dwivedi, S. and Tripathi, R. D. (2013) ‘Investigation of

biochemical responses of Bacopa monnieri L. upon exposure to arsenate.' *Environmental Toxicology*, 28(8) pp. 419–430.

Mohan, D. and Pittman, C. U. (2007) 'Arsenic removal from water/wastewater using adsorbents-A critical review.' *Journal of Hazardous Materials* pp. 1–53.

Moles, A. T., Warton, D. I., Warman, L., Swenson, N. G., Laffan, S. W., Zanne, A. E., Pitman, A., Hemmings, F. A. and Leishman, M. R. (2009) 'Global patterns in plant height.' *Journal of Ecology*, 97(5) pp. 923–932.

Moreno-Jiménez, E., Esteban, E. and Peñalosa, J. M. (2012) 'The fate of arsenic in soil-plant systems.' *Reviews of Environmental Contamination and Toxicology*, 215 pp. 1–37.

Morua, M. (2015) 'Investigating various xylem sap extraction techniques from drought-stressed Geijera parviflora trees' pp. 1–26.

Mosetlha, K., Torto, N. and Wibetoe, G. (2007) 'Determination of Cu and Ni in plants by microdialysis sampling: Comparison of dialyzable metal fractions with total metal content.' *Talanta*. Elsevier, 71(2) pp. 766–770.

Nagajyoti, P. C., Lee, K. D. and Sreekanth, T. V. M. (2010) 'Heavy metals, occurrence and toxicity for plants: A review.' *Environmental Chemistry Letters* pp. 199–216.

Nash, M. J., Maskall, J. E. and Hill, S. J. (2000) 'Methodologies for determination of antimony in terrestrial environmental samples.' *Journal of Environmental Monitoring*, 2(2) pp. 97–109.

Natasha, Shahid, M., Khalid, S., Dumat, C., Pierart, A. and Niazi, N. K. (2019) 'Biogeochemistry of antimony in soil-plant system: Ecotoxicology and human health.' *Applied Geochemistry*. Elsevier, 106(April) pp. 45–59.

Netting, A. G., Theobald, J. C. and Dodd, I. C. (2012) 'Xylem sap collection and extraction methodologies to determine in vivo concentrations of ABA and its bound forms by gas chromatography-mass spectrometry (GC-MS).' *Plant Methods*, 8(1) pp. 1–14.

Nicolau, R., Louis, Y., Omanović, D., Garnier, C., Mounier, S. and and, Pižeta, I. (2008) 'Study of interactions of concentrated marine dissolved organic matter with copper and zinc by pseudopolarography.' *Analytica Chimica Acta*, 618(1) pp. 35–42.

Niedzielski, P. and Siepak, M. (2003) 'Analytical methods for determining arsenic, antimony and selenium in environmental samples.' *Polish Journal of Environmental Studies*, 12(6) pp. 653–667.

Niedzielski, P., Siepak, M., Siepak, J. and Przybyłek, J. (2002) 'Determination of Different Forms of Arsenic, Antimony and Selenium in Water Samples Using Hydride Generation.' *Polish Journal of Environmental Studies*, 11(3) pp. 219–224.

Nimick, D. A. (1998) ‘Arsenic hydrogeochemistry in an irrigated river valley-A reevaluation.’ *Journal of groundwater*. Ground Water Publ Co, 36(5) pp. 743–753.

O’Day, P. A. (2006) ‘Chemistry and mineralogy of arsenic.’ *Elements*, 2(2) pp. 77–83.

Obiora, S. C., Chukwu, A. and Davies, T. C. (2016) ‘Heavy metals and health risk assessment of arable soils and food crops around Pb-Zn mining localities in Enyigba, southeastern Nigeria.’ *Journal of African Earth Sciences*. Elsevier Ltd, 116, April, pp. 182–189.

Oda, A., Shimizu, M., Kuroha, T. and Satoh, S. (2005) ‘Induction of xylem sap methylglycine by a drought and rewatering treatment and its inhibitory effects on the growth and development of plant organs.’ *Physiologia Plantarum*, 124(4) pp. 515–523.

Ogawa, K. and Iwabuchi, M. (2001) ‘A mechanism for promoting the germination of Zinnia elegans seeds by hydrogen peroxide.’ *Plant and Cell Physiology*, 42(3) pp. 286–291.

Ohmori, T., El-Deab, M. S. and Osawa, M. (1999) ‘Electroreduction of nitrate ion to nitrite and ammonia on a gold electrode in acidic and basic sodium and cesium nitrate solutions.’ *Journal of Electroanalytical Chemistry*, 470(1) pp. 46–52.

Olsen, S.R., C.V. Cole, F.S. Watanabe, and L. A. D. (1954) *Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circ.No. 939.* U.S. Gov. Print. Office, Washington DC.

Omanović, D. (2006) ‘Pseudopolarography of trace metals. Part III. Determination of stability constants of labile metal complexes.’ *Croatica Chemica Acta*, 79(1) p. 67.

Omanović, D. and Branica, M. (2003) ‘Pseudopolarography of trace metals: Part I. The automatic ASV measurements of reversible electrode reactions.’ *Journal of Electroanalytical Chemistry*, 543(1) pp. 83–92.

Omanović, D. and Branica, M. (2004) ‘Pseudopolarography of trace metals. Part II. The comparison of the reversible, quasireversible and irreversible electrode reactions.’ *Journal of Electroanalytical Chemistry*, 565(1) pp. 37–48.

Onofri, A., Seddaiu, G. and Piepho, H. P. (2016) ‘Long-Term Experiments with cropping systems: Case studies on data analysis.’ *European Journal of Agronomy*, 77, July, pp. 223–235.

Organization, world health (1996) ‘guidelines for drinking water quality - second edition.’ *international programme on chemical safety*.

Özer, U. Y. and Bogucki, R. F. (1971) ‘Equilibrium studies of antimony(III) chelates in aqueous solution.’ *Journal of Inorganic and Nuclear Chemistry*, 33(12) pp. 4143–4153.

Palma-Lara, I., Martínez-Castillo, M., Quintana-Pérez, J. C., Arellano-Mendoza, M. G., Tamay-Cach, F., Valenzuela-Limón, O. L., García-Montalvo, E. A. and Hernández-Zavala, A. (2019) 'Arsenic exposure: A public health problem leading to several cancers.' *Regulatory toxicology and pharmacology : RTP* p. 104539.

Pampolino, M. F., Laureles, E. V., Gines, H. C. and Buresh, R. J. (2008) 'Soil carbon and nitrogen changes in long-term continuous lowland rice cropping.' *Soil Science Society of America Journal*, 72(3) pp. 798–807.

Panda, S. K., Upadhyay, R. K. and Nath, S. (2010) 'Arsenic Stress in Plants.' *Journal of Agronomy and Crop Science*, 196(3) pp. 161–174.

Pandey, P. and Tripathi, A. K. (2014) 'Impact Of Heavy Metals On Morphological And Biochemical Parameters Of Shorea Robusta Plant.' *Ekologia*, 33(2) pp. 116–126.

Passioura, J. B. (1980) 'The transport of water from soil to shoot in wheat seedlings.' *Journal of Experimental Botany*, 31(1) pp. 333–345.

Pedron, T., Segura, F. R., Paniz, F. P., de Moura Souza, F., dos Santos, M. C., de Magalhães Júnior, A. M. and Batista, B. L. (2019) 'Mitigation of arsenic in rice grains by polishing and washing: Evidencing the benefit and the cost.' *Journal of Cereal Science*. Academic Press, 87, May, pp. 52–58.

Penezić, A., Tercier-Waeber, M. Lou, Abdou, M., Bossy, C., Dutruch, L., Bakker, E. and Schäfer, J. (2020) 'Spatial variability of arsenic speciation in the Gironde Estuary: Emphasis on dynamic (potentially bioavailable) inorganic arsenite and arsenate fractions.' *Marine Chemistry*. Elsevier, 223(December 2019) p. 103804.

Pepponi, G., Meirer, F., Streli, C., Wobrauschek, P., Mihucz, V. G., G. Zaray, V. C., Broekaert, J., Fittschen, U. and Falkenberg, G. (2005) 'Arsenic speciation in Cucumber Cucumis Sativus L.) xylem sap by K-edge TXRF-XANES.' *Anal. Bioanal. Chem.*, 383 pp. 461–466.

Peralta-Videa, J. R., Lopez, M. L., Narayan, M., Saupe, G. and Gardea-Torresdey, J. (2009) 'The biochemistry of environmental heavy metal uptake by plants: Implications for the food chain.' *International Journal of Biochemistry and Cell Biology*, 41(8–9) pp. 1665–1677.

Perrino, C., Marconi, E., Canepari, S., Luisa Astolfi, M. and Perrino, C. (2011) 'Determination of Sb(III), Sb(V) and identification of Sb-containing nanoparticles in airborne particulate matter.' *Procedia Environmental Sciences*, 4 pp. 209–217.

Pettine, M., Casentini, B., Mastroianni, D. and Capri, S. (2007) 'Dissolved inorganic carbon effect in the determination of arsenic and chromium in mineral waters by inductively coupled plasma-mass spectrometry.' *Analytica Chimica Acta*. Elsevier, 599(2) pp. 191–198.

Pickering, I. J., Prince, R. C., George, M. J., Smith, R. D., George, G. N. and Salt, D. E. (2000) 'Reduction and coordination of arsenic in Indian mustard.' *Plant Physiology*, 122(4) pp. 1171–1177.

Pierart, A., Shahid, M., Séjalon-Delmas, N. and Dumat, C. (2015) 'Antimony bioavailability: Knowledge and research perspectives for sustainable agricultures.' *Journal of Hazardous Materials*. Elsevier, 289(February) pp. 219–234.

Pla-Vilanova, P., Galceran, J., Puy, J., Companys, E. and Filella, M. (2019) 'Antimony speciation in aqueous solution followed with AGNES.' *Journal of Electroanalytical Chemistry*. Elsevier B.V., 849 p. 113334.

Pohl, P., Lesniewicz, A. and Zyrnicki, W. (2003) 'Determination of As, Bi, Sb and Sn in conifer needles from various locations in Poland and Norway by hydride generation inductively coupled plasma atomic emission spectrometry.' *International Journal of Environmental Analytical Chemistry*. Taylor & Francis Group, 83(11) pp. 963–970.

Polunina, O. V., Maiboroda, V. P. and Seleznov, A. Y. (2018) 'Evaluation methods of estimation of young apple trees leaf area.' *Bulletin of Uman National University of Horticulture*, (2) pp. 80–82.

Pommerrenig, B., Diehn, T. A. and Bienert, G. P. (2015) 'Metalloido-porins: Essentiality of Nodulin 26-like intrinsic proteins in metalloid transport.' *Plant Science*. Elsevier Ireland Ltd, 238 pp. 212–227.

Porra, R. J. (2005) 'Clorofila Porras 2005' pp. 633–640.

Postupolski, A. and Golimowski, J. (1991) 'Trace determination of antimony and bismuth in snow and water samples by stripping voltammetry.' *Electroanalysis*. Warsaw, Poland, 3(8) pp. 793–797.

Pretti, L., Bazzu, G., Serra, P. A. and Nieddu, G. (2014) 'A novel method for the determination of ascorbic acid and antioxidant capacity in Opuntia ficus indica using in vivo microdialysis.' *Food Chemistry*, 147 pp. 131–137.

Punrat, E., Chuanuwatanakul, S., Kaneta, T., Motomizu, S., Chailapakul, O., Zaib, M., Makshoof, M., Saeed, A., Farooq, U., Nearing, M. M., Koch, I., Reimer, K. J., Niedzielski, P., Siepak, M., Day, P. A. O., Mays, D. E., Hussam, A., Welna, M., Szymczycha-Madeja, A., Pohl, P., Ma, J., Sengupta, M. K., Yuan, D., Dasgupta, P. K., Amaral, C. D. B., Nóbrega, J. A., Nogueira, A. R. A., Cavicchioli, A., La-scalea, M. A., Gutz, G. R., Tyson, J., Chen, M. L., Ma, L. Y., Chen, X. W., Punrat, E., Chuanuwatanakul, S., Kaneta, T., Motomizu, S., Chailapakul, O., Hotel, D., Llorente-mirandes, T., Calderón, J., Centrich, F., Rubio, R., López-sánchez, J. F. and Thomas, D. J. (2014) 'Method development for the determination of arsenic by sequential injection/anodic stripping voltammetry using long-lasting gold-modified screen-printed carbon electrode.' *Talanta*. Elsevier B.V., 2013(June) pp. 1018–1025.

Quentel, F. and Filella, M. (2002) ‘Determination of inorganic antimony species in seawater by differential pulse anodic stripping voltammetry: Stability of the trivalent state.’ *Analytica Chimica Acta*, 452(2) pp. 237–244.

Quentel, F., Filella, M., Elleouet, C. and Madec, C. (2006) ‘Sb(III) oxidation by iodate in seawater: A cautionary tale.’ *Science of The Total Environment*. Elsevier, 355(1–3) pp. 259–263.

RA (2001) ‘Philippine Mining Act of 1995,.’ Philippines, R. of the (ed.) pp. 1–12.

Raab, A., Feldmann, J. and Meharg, A. A. (2004) ‘The Nature of Arsenic-Phytochelatin Complexes in Holcus lanatus and Pteris cretica.’ *Plant Physiology*. Department of Chemistry, University of Aberdeen, Meston Building, Meston Walk, Aberdeen AB24 3UE, United Kingdom., 134(3) pp. 1113–1122.

Raab, A., Meharg, A. A., Jaspars, M., Genney, D. R. and Feldmann, J. (2004) ‘Arsenic–glutathione complexes—their stability in solution and during separation by different HPLC modes.’ *J. Anal. At. Spectrom.*, 19(1) pp. 183–190.

Raab, A., Schat, H., Meharg, A. A., Feldmann, J., J., A. R. S. H. M. A. A. and F., Raab, A., Schat, H., Meharg, A. A. and Feldmann, J. (2005) ‘Uptake, translocation and transformation of arsenate and arsenite in sunflower (Helianthus annuus): Formation of arsenic-phytochelatin complexes during exposure to high arsenic concentrations.’ *New Phytologist*. Department of Chemistry, University of Aberdeen, Meston Building, Meston Walk, Aberdeen AB24 3UE, UK., 168(3) pp. 551–558.

Rahaman, M. S., Akter, M., Rahman, M. M., Sikder, M. T., Hosokawa, T., Saito, T. and Kurasaki, M. (2020) ‘Investigating the protective actions of D-pinitol against arsenic-induced toxicity in PC12 cells and the underlying mechanism.’ *Environmental Toxicology and Pharmacology*. Elsevier B.V., 74, February, p. 103302.

Rahman, M. A. and Hasegawa, H. (2011) ‘High levels of inorganic arsenic in rice in areas where arsenic-contaminated water is used for irrigation and cooking.’ *Science of The Total Environment*, 409(22) pp. 4645–4655.

Raskin, I., Kumar, P. N., Dushenkov, S. and Salt, D. E. (1994) ‘Bioconcentration of heavy metals by plants.’ *Current Opinion in Biotechnology*, 5(3) pp. 285–290.

Rauser, W. E. (1990) ‘Phytochelatins.’ *Annual Review of Biochemistry*, 59 pp. 61–86.

Reimann, C., Demetriades, A., Eggen, O. A. and Filzmoser, P. (2009) ‘The EuroGeoSurveys geochemical mapping of agricultural and grazing land soils project (GEMAS) -Evaluation of quality control results of aqua regia extraction analysis.’ *EuroGeoSurveys Geochemistry* , (May 2014) p. 94.

Rellán-Álvarez, R., El-Jendoubi, H., Wohlgemuth, G., Abadía, A., Fiehn, O., Abadía, J., Álvarez-Fernández, A., Schjoerring, J. K., Zocchi, G., Degli, U., Di Milano, S., Yoshihara, T.

and Alvarez-Fernández, A. (2011) 'Metabolite profile changes in xylem sap and leaf extracts of strategy I plants in response to iron deficiency and resupply.' *Frontiers in plant science*, 2 p. 66.

Rellán-Álvarez, R., Ortega-Villasante, C., Álvarez-Fernández, A., Campo, F. F. del and Hernández, L. E. (2006) 'Stress Responses of Zea mays to Cadmium and Mercury.' *Plant and Soil*, 279(1–2) pp. 41–50.

Ren, J. H., Ma, L. Q., Sun, H. J., Cai, F. and Luo, J. (2014) 'Antimony uptake, translocation and speciation in rice plants exposed to antimonite and antimonate.' *Science of the Total Environment*. Elsevier B.V., 475 pp. 83–89.

Rodriguez-Iruretagoiena, A., Trebolazabala, J., Martinez-Arkarazo, I., De Diego, A. and Madariaga, J. M. (2015) 'Metals and metalloids in fruits of tomatoes (Solanum lycopersicum) and their cultivation soils in the Basque Country: Concentrations and accumulation trends.' *Food Chemistry*. Elsevier Ltd, 173, February, pp. 1083–1089.

Rosas-Castor, J. M., Guzmán-Mar, J. L., Hernández-Ramírez, A., Garza-González, M. T. and Hinojosa-Reyes, L. (2014) 'Arsenic accumulation in maize crop (Zea mays): A review.' *Science of The Total Environment*. Elsevier, 488–489(1) pp. 176–187.

Rousk, J. and Jones, D. L. (2010) 'Loss of low molecular weight dissolved organic carbon (DOC) and nitrogen (DON) in H2O and 0.5M K2SO4 soil extracts.' *Soil Biology and Biochemistry*, 42(12) pp. 2331–2335.

Sabir, M., Waraich, E. A., Hakeem, K. R., Öztürk, M., Ahmad, H. R. and Shahid, M. (2015) 'Phytoremediation: Mechanisms and Adaptations. Mechanisms and Adaptations.' *Soil Remediation and Plants: Prospects and Challenges* pp. 85–105.

Sadiq, M. (1992) *Toxic metal chemistry in marine environments*. *Marcel Dekker*. New York City.

Salama, A. K. and Radwan, M. A. (2005) 'Heavy metals (Cd,Pb) and trace elements (Cu,Zn) contents in some foodstuffs from the Egyptian market.' *Emirates Journal of Food and Agriculture*, 17(1) pp. 34–42.

Salaun, P. (2017) 'Editorial: Environmental Electrochemistry.' *Current Opinion in Electrochemistry*. Elsevier B.V., 3(1) pp. 75–77.

Salaün, P. and van den Berg, C. M. G. (2006) 'Voltammetric detection of mercury and copper in seawater using a gold microwire electrode.' *Analytical chemistry*, 78(14) pp. 5052–60.

Salaün, P. and Frézard, F. (2013) 'Unexpectedly high levels of antimony (III) in the pentavalent antimonial drug Glucantime: insights from a new voltammetric approach.' *Analytical and Bioanalytical Chemistry*. Liverpool, 405(15) pp. 5201–5214.

Salaün, P., Gibbon-Walsh, K. B., Alves, G. M. S. S., Soares, H. M. V. M. V. M. and van den Berg, C. M. G. G. (2012) 'Determination of arsenic and antimony in seawater by voltammetric and chronopotentiometric stripping using a vibrated gold microwire electrode.' *Analytica Chimica Acta*. Liverpool: Elsevier B.V., 746(March 2014) pp. 53–62.

Salaün, P., Gibbon-Walsh, K. and van den Berg, C. M. G. (2011) 'Beyond the Hydrogen Wave: New Frontier in the Detection of Trace Elements by Stripping Voltammetry.' *Analytical Chemistry*, 83(10) pp. 3848–3856.

Salaün, P., Planer-Friedrich, B. and van den Berg, C. M. . (2007) 'Inorganic arsenic speciation in water and seawater by anodic stripping voltammetry with a gold microelectrode.' *Analytica Chimica Acta*. Liverpool, 585(2) pp. 312–322.

Samarah, L. Z., Tran, T. H., Stacey, G. and Vertes, A. (2020) 'In Vivo Chemical Analysis of Plant Sap from the Xylem and Single Parenchymal Cells by Capillary Microsampling Electrospray Ionization Mass Spectrometry.' *Analytical Chemistry*, 92(10) pp. 7299–7306.

Samota, M. K., Navnage, N. P. and Bhatt, L. (2017) 'Role of Macro and Micronutrient in Development and Growth of Plant,' 10(18) pp. 3171–3173.

Santos, V. S., Santos, W. de J. R., Kubota, L. T. and Tarley, C. R. T. (2009) 'Speciation of Sb(III) and Sb(V) in meglumine antimoniate pharmaceutical formulations by PSA using carbon nanotube electrode.' *Journal of Pharmaceutical and Biomedical Analysis*, 50(2) pp. 151–157.

Satoh, S. (2006) 'Organic substances in xylem sap delivered to above-ground organs by the roots.' *Journal of Plant Research*, 119(3) pp. 179–187.

Scharifker, B. R., Mostany, J. and Serruya, A. (2000) 'Catalytic reduction of nitrate during electrodeposition of thallium from Tl3+ solution.' *Electrochemistry Communications*, 2(6) pp. 448–451.

Scholander, P. F., Bradstreet, E. D., Hemmingsen, E. A. and Hammel, H. T. (1965) 'Sap Pressure in Vascular Plants: Negative hydrostatic pressure can be measured in plants.' *Science*, 148(3668) pp. 339–346.

Schurr, U. (1998) 'Xylem sap sampling—new approaches to an old topic.' *Trends in Plant Science*. Elsevier Current Trends, 3(8) pp. 293–298.

Schurr, U. (1999) 'Dynamics of Nutrient Transport from the Root to the Shoot.' *In*. Springer, Berlin, Heidelberg, pp. 234–253.

Shahid, M., Khalid, S., Abbas, G., Shahid, N., Nadeem, M., Sabir, M., Aslam, M. and Dumat, C. (2015) 'Heavy metal stress and crop productivity.' *In Crop Production and Global Environmental Issues*. Springer International Publishing, pp. 1–25.

Sharma, S. D. (2013) ‘History of Rice in Southeast Asia and Australia.’ *Journal of Chemical Information and Modeling*, 53(9) pp. 1689–1699.

Shri, M., Singh, P. K., Kidwai, M., Gautam, N., Dubey, S., Verma, G. and Chakrabarty, D. (2019) ‘Recent advances in arsenic metabolism in plants: Current status, challenges and highlighted biotechnological intervention to reduce grain arsenic in rice.’ *Metallomics*, 11(3) pp. 519–532.

Simoni, R. D., Hill, R. L. and Vaughan, M. (2005) ‘Benedict ’ s Solution , a Reagent for Measuring Reducing Sugars : the Clinical Chemistry of Stanley R . Benedict,’ 277(16) pp. 10–12.

Slamet-loedin, I., Slamet-loedin, I. H., Johnson-beebout, S. E., Impa, S. and Tsakirpaloglou, N. (2015) ‘Enriching rice with Zn and Fe while minimizing Cd risk.’ *Frontiers in Plant Science*, 6(MAR).

Smedley, P. L. and Kinniburgh, D. G. (2000) ‘Source and behaviour of arsenic in natural waters.’ *British Geological Survey* p. 61.

Smedley, P. L. and Kinniburgh, D. G. (2002) ‘A review of the source, behaviour and distribution of arsenic in natural waters.’ *Applied Geochemistry*, 17(5) pp. 517–568.

Smith, A. H., Lingas, E. O. and Rahman, M. (2000) ‘Contamination of drinking-water by arsenic in Bangladesh: A public health emergency.’ *Bulletin of the World Health Organization*, 78(9) pp. 1093–1103.

Smith, A. H. and Smith, M. M. H. (2004) ‘Arsenic drinking water regulations in developing countries with extensive exposure.’ *Toxicology*, 198(1–3) pp. 39–44.

Sobrado, M. A. (2007) ‘Relationship of water transport to anatomical features in the mangrove Laguncularia racemosa grown under contrasting salinities.’ *New Phytologist*, 173(3) pp. 584–591.

Sørensen, O., Andersen, A., Olsen, H., Alexandr, K., Ekstrøm, P. O., Giercksky, K. E. and Flatmark, K. (2010) ‘Validation and use of microdialysis for determination of pharmacokinetic properties of the chemotherapeutic agent mitomycin C - an experimental study.’ *BMC Cancer*, 10.

Spurgeon, D. J., Rowland, P., Ainsworth, G., Rothery, P., Long, S. and Black, H. I. J. (2008) ‘Geographical and pedological drivers of distribution and risks to soil fauna of seven metals (Cd, Cu, Cr, Ni, Pb, V and Zn) in British soils.’ *Environmental Pollution*, 153(2) pp. 273–283.

Sreekanth, T. V. M., Nagajyothi, P. C., Lee, K. D. and Prasad, T. N. V. K. V. (2013) ‘Occurrence, physiological responses and toxicity of nickel in plants.’ *International Journal of Environmental Science and Technology*. Center for Environmental and Energy Research and Studies pp. 1129–1140.

Stazi, S. R., Cassaniti, C., Marabottini, R., Giuffrida, F. and Leonardi, C. (2016) ‘Arsenic uptake and partitioning in grafted tomato plants.’ *Horticulture, Environment, and Biotechnology*. Korean Society for Horticultural Science, 57(3) pp. 241–247.

Steudle, E. (2001) ‘The cohesion-tension mechanism and the acquisition of water by plant roots.’ *Annual Review of Plant Biology*, 52 pp. 847–875.

Stoeva, N., Berova, M. and Zlatev, Z. (2005) ‘Effect of arsenic on some physiological parameters in bean plants.’ *Biologia Plantarum*, 49(2) pp. 293–296.

Sulyok, M., Miró, M., Stingeder, G. and Koellensperger, G. (2005) ‘The potential of flow-through microdialysis for probing low-molecular weight organic anions in rhizosphere soil solution.’ *Analytica Chimica Acta*. Elsevier, 546(1) pp. 1–10.

Sun, G., Williams, P. N. and Zhu, Y. (2009) ‘Mechanisms of Arsenic Uptake and Metabolism by Plants : Focusing on Rice.’ *Environmental Toxicology*, 134(November) pp. 1–6.

Sun, H., Yan, S. C. and Cheng, W. S. (2000) ‘Interaction of antimony tartrate with the tripeptide glutathione.’ *European Journal of Biochemistry*, 267(17) pp. 5450–5457.

Takarina, N. D. and Pin, T. G. (2017) ‘Bioconcentration Factor (BCF) and Translocation Factor (TF) of Heavy Metals in Mangrove Trees of Blanakan Fish Farm.’ *Makara Journal of Science*, 21(2).

Tamás, M. J. (2016) ‘Cellular and molecular mechanisms of antimony transport, toxicity and resistance.’ *Environmental Chemistry*, 13(6) pp. 955–962.

Tatár, E., Mihucz, V. G., Kmethy, B., Záray, G. and Fodor, F. (2000) ‘Determination of organic acids and their role in nickel transport within cucumber plants.’ *Microchemical Journal*, 67(1–3) pp. 73–81.

Tatár, E., Mihucz, V. G., Varga, A., Záray, G. and Fodor, F. (1998) ‘Determination of Organic Acids in Xylem Sap of Cucumber: Effect of Lead Contamination.’ *Microchemical Journal*. Elsevier Inc., 58(3) pp. 306–314.

Telford, K., Maher, W., Krikowa, F. and Foster, S. (2008) ‘Measurement of total antimony and antimony species in mine contaminated soils by ICPMS and HPLC-ICPMS.’ *Journal of Environmental Monitoring*, 10(1) pp. 136–140.

Telford, K., Maher, W., Krikowa, F., Foster, S., Ellwood, M. J. M. J., Ashley, P. M. P. M., Lockwood, P. V. P. V. and Wilson, S. C. S. C. (2009) ‘Bioaccumulation of antimony and arsenic in a highly contaminated stream adjacent to the Hillgrove Mine, NSW, Australia.’ *Environmental Chemistry*, 6(2) pp. 133–143.

Thomas, G. W. (1996) ‘Soil pH and soil acidity.’ *In* D.L. Sparks et al., editors (ed.) *Methods of soil analysis: Part 3. SSSA Book Series No. 5. SSSA,* pp. 475–490.

Tian, T., Zhou, H., Gu, J., Jia, R., Li, H., Wang, Q., Zeng, M. and Liao, B. (2019) ‘Cadmium accumulation and bioavailability in paddy soil under different water regimes for different growth stages of rice (Oryza sativa L.).’ *Plant and Soil*. Springer International Publishing, July.

Timofeev, I. and Hutchinson, P. (2008a) ‘Microdialysis.’ *In Essentials of Neuroanesthesia and Neurointensive Care*. Elsevier, pp. 277–282.

Timofeev, I. and Hutchinson, P. (2008b) ‘Microdialysis Learn more about Microdialysis Microdialysis Chemical and Biochemical Approaches for the Study of Anesthetic Function Part B Carrier-mediated and artificial-cell tar-.’

Toghill, K. E., Lu, M., Compton, R. G. and Kathryn E. Toghill, Min Lu, and R. G. C. (2011) ‘Electroanalytical Determination of Antimony.’ *International Journal of Electrochemical Science*, 6(8) pp. 3057–3076.

Tollestrup, K., Frost, F. J., Harter, L. C. and McMillan, G. P. (2003) ‘Mortality among Children Residing near the American Smelting and Refining Company (ASARCO) Copper Smelter in Ruston, Washington.’ *Archives of Environmental Health: An International Journal*, 58(11) pp. 683–691.

Torto, N., Mwatseteza, J. and Laurell, T. (2001) ‘Microdialysis Sampling: Challenges and New Frontiers.’ *LC GC Europe*, 14(9) pp. 536–546.

Torto, N., Mwatseteza, J. and Sawula, G. (2002) ‘A study of microdialysis sampling of metal ions.’ *Analytica Chimica Acta*. Elsevier, 456(2) pp. 253–261.

Trejo-Téllez, L. I. (2012) ‘Nutrient Solutions for Hydroponic Systems.’ *In* Asao, F. C. G.-M. E.-T. (ed.). Rijeka: IntechOpen, p. Ch. 1.

Tsang, J. J., Rozan, T. F., Hsu-Kim, H., Mullaugh, K. M. and Luther, G. W. (2006) ‘Pseudopolarographic determination of Cd2+ complexation in freshwater.’ *Environmental Science and Technology*, 40(17) pp. 5388–5394.

Tschan, M., Robinson, B. H. and Schulin, R. (2009) ‘Antimony in the soil - Plant system - A review.’ *Environmental Chemistry*, 6(2) pp. 106–115.

Tschan, M., Robinson, B. and Schulin, R. (2008) ‘Antimony uptake by Zea mays (L.) and Helianthus annuus (L.) from nutrient solution.’ *Environmental Geochemistry and Health*, 30(2) pp. 187–191.

Tsukagoshi, S. and Shinohara, Y. (2015) *Nutrition and Nutrient Uptake in Soilless Culture Systems*. *Plant Factory: An Indoor Vertical Farming System for Efficient Quality Food Production*. Elsevier Inc.

Tuyogon, D. S. J., Impa, S. M., Castillo, O. B., Larazo, W. and Johnson-Beebout, S. E. (2016) ‘Enriching rice grain zinc through zinc fertilization and water management.’ *Soil Science*

Society of America Journal, 80(1) pp. 121–134.

Tylenda, C. A., Sullivan, D. W. and Fowler, B. A. (2015) *Antimony*. *Handbook on the Toxicology of Metals: Fourth Edition*. Fourth Edi, Elsevier.

U.S. Department of Health and Human (2018) *Revised Draft : Report on Carcinogens Monograph on Antimony Trioxide*.

U.S. Geological Survey (2004) 'Mineral Commodity Profiles-Antimony.' *U.S. Department of the Interior: U.S. Geological Survey* pp. 1–35.

Ugochukwu, G. C., Eneh, F. U., Igwilo, I. . and Aloh, C. H. (2017) 'Comparative study on the heavy metal content of domestic rice (Oryza sativa Comparative study on the heavy metal content of domestic rice (Oryza sativa L) brands common in Awka, Nigeria.' *IOSR Journal of Environmental Science, Toxicology and Food Technology*, 11(8) pp. 67–70.

UN (ed.) (2015) *Crop Prospects and Food Situation*. Rome: FAO.

Ungureanu, G., Santos, S., Boaventura, R. and Botelho, C. (2015) 'Arsenic and antimony in water and wastewater: Overview of removal techniques with special reference to latest advances in adsorption.' *Journal of Environmental Management*, 151, March, pp. 326–342.

Uroic, M. K. (2011) *The impact of arsenic species on the production and composition of xylem sap*. *Environmental & Analytical Chemistry*. University of Aberdeen. Retrieved from internal-pdf://145.35.116.156/PhD thesis The impact of As MK Uroic.pdf.

Uroic, M. K., Salaün, P., Raab, A. and Feldmann, J. (2012) 'Arsenate impact on the metabolite profile, production, and arsenic loading of xylem sap in cucumbers (Cucumis sativus L.).' *Frontiers in Physiology*, 3 APR(March) pp. 1–23.

Varsányi, I., Fodré, Z. and Bartha, A. (1991) 'Arsenic in drinking water and mortality in the Southern Great Plain, Hungary.' *Environmental Geochemistry and Health*. Kluwer Academic Publishers, 13(1) pp. 14–22.

Violante, A., Cozzolino, V., Perelomov, L., Caporale, A. . and Pigna, M. (2010) 'Mobility and bioavailability of heavy metals and metalloids in soil environments.' *Journal of soil science and plant nutrition*. Sociedad Chilena de la Ciencia del Suelo, 10(3) pp. 268–292.

Vithanage, M., Dabrowska, B. B., Mukherjee, A. B., Sandhi, A. and Bhattacharya, P. (2012) 'Arsenic uptake by plants and possible phytoremediation applications: A brief overview.' *Environmental Chemistry Letters* pp. 217–224.

Wagner, S. E., Peryea, F. J. and Filby, R. A. (2003) 'Antimony Impurity in Lead Arsenate Insecticide Enhances the Antimony Content of Old Orchard Soils.' *Journal of Environmental Quality*. Wiley, 32(2) pp. 736–738.

Wan, X. M., Tandy, S., Hockmann, K. and Schulin, R. (2013) ‘Changes in Sb speciation with waterlogging of shooting range soils and impacts on plant uptake.’ *Environmental Pollution*. Elsevier Ltd, 172, January, pp. 53–60.

Wang, S., Shi, X., Sun, H., Chen, Y., Pan, H., Yang, X. and Rafiq, T. (2014) ‘Variations in Metal Tolerance and Accumulation in Three Hydroponically Cultivated Varieties of Salix integra Treated with Lead.’ Reigosa, M. (ed.) *PLoS ONE*. Public Library of Science, 9(9) p. e108568.

Wang, T., Yang, Q., Wang, Y., Wang, J., Zhang, Y. and Pan, W.-P. P. (2020) ‘Arsenic release and transformation in co-combustion of biomass and coal: Effect of mineral elements and volatile matter in biomass.’ *Bioresource technology*. Beijing, PR China: Elsevier Ltd, 297, February, p. 122388.

Wang, Z., Zeng, X., Geng, M., Chen, C., Cai, J., Yu, X., Hou, Y. and Zhang, H. (2015) ‘Health risks of heavy metals uptake by crops grown in a sewage irrigation area in China.’ *Polish Journal of Environmental Studies*, 24(3) pp. 1379–1386.

Welch, A. H. and Stollenwerk, K. G. (eds) (2003) *Arsenic in Ground Water*. *Springer Science Business Media New York*. Boston, MA: Springer US.

White, M. C., Chaney, R. L., Decker, A. M. and R., and M. W. D. A. (1981) ‘Metal Complexation in Xylem Fluid: I. Chemical composition of tomato and soybean stem exudate.’ *Plant Physiology*, 67(2) pp. 292–300.

WHO (2003a) ‘Antimony in Drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality.’ *Who* pp. 1–9.

WHO (2003b) *Background document for preparation of WHO Guidelines for drinking-water quality: Antimony in drinking water.* Geneva, Switzerland.

WHO (2003c) ‘Chromium in drinking-water. Background document for preparation of WHO Guidelines for drinking-water quality.’ *(WHO/SDE/WSH/03.04/4)*, (3) pp. 334–335.

Wickliff, J. L. and Aronoff, S. (1962) *Quantitative measurement of leaf chlorophylss by spectrophotometry of their pheophytins in aqueous alcoholic extracts*. Iowa, USA.

Williams, P. N., Islam, M. R., Adomako, E. E., Raab, A., Hossain, S. A., Zhu, Y. G., Feldmann, J. and Meharg, A. A. (2006) ‘Increase in rice grain arsenic for regions of Bangladesh irrigating paddies with elevated arsenic in groundwaters.’ *Environmental Science and Technology* pp. 4903–4908.

Wilson, S. C., Lockwood, P. V., Ashley, P. M. and Tighe, M. (2010) ‘The chemistry and behaviour of antimony in the soil environment with comparisons to arsenic: A critical review.’ *Environmental Pollution*. Elsevier Ltd, 158(5) pp. 1169–1181.

Woolson, E. A., Axley, J. H. and Kearney, P. C. (1971) ‘Correlation between Available Soil

Arsenic, Estimated by Six Methods, and Response of Corn (Zea mays L.)1.' *Soil Science Society of America Journal*. Soil Science Society of America, 35(1) p. 101.

Wu, D. and Sun, S. (2016) 'Speciation analysis of As, Sb and Se.' *Trends in Environmental Analytical Chemistry*. Elsevier Inc., 11, July, pp. 9–22.

Wu, T.-L. L., Cui, X.-D. D., Cui, P.-X. X., Ata-Ul-Karim, S. T., Sun, Q., Liu, C., Fan, T.-T. T., Gong, H., Zhou, D.-M. M. and Wang, Y.-J. J. (2019) 'Speciation and location of arsenic and antimony in rice samples around antimony mining area.' *Environmental Pollution*. Elsevier Ltd, 252, September, pp. 1439–1447.

www.IRRI.org (2019) *Long-Term Continuous Cropping Experiment (LTCCE) | International Rice Research Institute*. [Online] [Accessed on 18th November 2019] https://www.irri.org/long-term-continuous-cropping-experiment-ltcce.

Wyrwicka, A., Urbaniak, M. and Przybylski, M. (2019) ' The response of cucumber plants (Cucumis sativus L.) to the application of PCB-contaminated sewage sludge and urban sediment .' *PeerJ*, 7 p. e6743.

Xu, X. Y., McGrath, S. P. and Zhao, F. J. (2007) 'Rapid reduction of arsenate in the medium mediated by plant roots.' *New Phytologist*, 176(3) pp. 590–599.

Yadav, S. K. (2010) 'Heavy metals toxicity in plants: An overview on the role of glutathione and phytochelatins in heavy metal stress tolerance of plants.' *South African Journal of Botany*. Elsevier B.V., 76(2) pp. 167–179.

Ye, W.-L. L., Wood, B. A., Stroud, J. L., Andralojc, P. J., Raab, A., McGrath, S. P., Feldmann, J. and Zhao, F.-J. J. (2010) 'Arsenic speciation in phloem and xylem exudates of castor bean.' *Plant Physiology*, 154(3) pp. 1505–1513.

Zavala, Y. J. and Duxbury, J. M. (2008) 'Arsenic in rice: I. Estimating normal levels of total arsenic in rice grain.' *Environmental Science and Technology*, 42(10) pp. 3856–3860.

Zengin, F. K. and Munzuroglu, O. (2005) 'Effects of some heavy metals on content of chlorophyll, proline and some antioxidant chemicals in bean (Phaseolus vulgaris L.) seedlings.' *Acta Biologica Cracoviensia Series Botanica*, 47(2) pp. 157–164.

Zhang, H. and Selim, H. M. (2005) 'Kinetics of Arsenate Adsorption−Desorption in Soils.' *Environmental Science & Technology*, 39(16) pp. 6101–6108.

Zhang, T., Ruan, J., Zhang, B., Lu, S., Gao, C., Huang, L., Bai, X., Xie, L., Gui, M. and Qiu, R. (2019) 'Heavy metals in human urine, foods and drinking water from an e-waste dismantling area: Identification of exposure sources and metal-induced health risk.' *Ecotoxicology and Environmental Safety*. Academic Press, 169, March, pp. 707–713.

Zhang, W., Cai, Y., Tu, C. and Ma, L. Q. (2002) 'Arsenic speciation and distribution in an arsenic hyperaccumulating plant.' *Science of the Total Environment*, 300(1–3) pp. 167–

177.

Zhao, F.-J., Ma, Y., Zhu, Y.-G., Tang, Z. and McGrath, S. P. (2015) ‘Soil Contamination in China: Current Status and Mitigation Strategies.’ *Environmental Science & Technology*. American Chemical Society, 49(2) pp. 750–759.

Zhao, F.-J., McGrath, S. P. and Meharg, A. A. (2010) ‘Arsenic as a Food Chain Contaminant: Mechanisms of Plant Uptake and Metabolism and Mitigation Strategies.’ *Annual Review of Plant Biology*. Annual Reviews, 61(1) pp. 535–559.

Zheng, J., Iijima, A. and Furuta, N. (2001) ‘Complexation effect of antimony compounds with citric acid and its application to the speciation of antimony(III) and antimony(V) using HPLC-ICP-MS.’ *Journal of Analytical Atomic Spectrometry*, 16(8) pp. 812–818.

Zheng, R. L., Sun, G. X. and Zhu, Y. G. (2013) ‘Effects of microbial processes on the fate of arsenic in paddy soil.’ *Chinese Science Bulletin* pp. 186–193.

Zhou, S. N., Ouyang, G. and Pawliszyn, J. (2008) ‘Comparison of microdialysis with solid-phase microextraction for in vitro and in vivo studies.’ *Journal of Chromatography A*, 1196–1197(1–2) pp. 46–56.

Zhou, X., Sun, C., Zhu, P. and Liu, F. (2018) ‘Effects of Antimony Stress on Photosynthesis and Growth of Acorus calamus.’ *Frontiers in Plant Science*. Frontiers Media S.A., 9(May) pp. 1–9.

Zulkafflee, N. S., Redzuan, N. A. M., Hanafi, Z., Selamat, J., Ismail, M. R., Praveena, S. M. and Razis, A. F. A. (2019) ‘Heavy metal in paddy soil and its bioavailability in rice using in vitro digestion model for health risk assessment.’ *International Journal of Environmental Research and Public Health*, 16(23).

CHAPTER 4

ARSENIC AND OTHER HEAVYMETALS ANALYSIS IN RICE BY ICP-MS

Index of Figures

Index of Tables

4.1 Introduction

One of the crucial concerns in agriculture nowadays is food safety and security. It is a severe issue and considered one of the major concerns of the United Nation's Millennium Development Goals ((UN-MDG) (JECFA, 2016). It is essential to reduce the accumulation of toxic elements in crops.

Plants acquire vital and beneficial elements from the soil, but they can also take up non-essential ones that are bio-available to them because of their imperfect selectivity (Clemens and Ma, 2016). Some of these unintentionally accumulated elements are highly toxic, like As, Sb, Pb, Cd, and Hg (Järup, 2003). Exposure to toxic heavy metals and metalloids is associated with the main threats to human health (Järup, 2003). Heavy metals have been used for a long time, and their adverse health effects have been extensively reported. Continuous monitoring and assessment of agricultural products are needed to enhance food safety and security. Rice is the world's second most important cereal in the world, according to FAO (Food Agricultural Office) next to maise, and it provides half of the world's energy (Carey et al., 2012; FAO, 2016).

Paddy rice is considered the primary source of heavy metal contamination for human exposure because of its efficient heavy metal accumulation primarily when cultivated in contaminated areas ((Salama and Radwan, 2005; Zhao et al., 2010; Zheng et al., 2013; Clemens and Ma, 2016; Cullen and Reimer, 2016b; Jamila Alfaraas et al., 2016; Wang et al., 2020). Rice (Oryza sativa L.) is the most economically important food crop in the world and provides more than half of the world's population. Predominantly in Asia, it remains the most critical crop because of its political, economic, and social significance

(Awika, 2011; Meharg and Zhao, 2012; Bakhtiari et al., 2014). Rice provides 35-80% of the caloric intake and 15% of per capita protein for more than 3 billion people in Asia Zhu et al., 2008; Bhattacharya et al., 2010; Hu et al., 2016). Particularly in the Philippines, according to the Philippine Carabao Center (PCC), an estimated 0.225 Kg of rice per day (93 Kg per capita year) was estimated rice consumption (Mendoza, 2012). Rice consumption has also increased in other developing countries in North America and the European Union (EU) due to food diversification and immigration (Broadley et al., 2011). The present high population pressure, food insecurity, increasing competition for energy and water, high production cost, and the demands for income enhancement have encouraged rice farmers to increase yield with limited sources to provide adequate food for the world. Asia, in particular, where about 60% of the world's population lives, is challenged by increasing food demand and, at the same time, threatened by food insecurity and water scarcity. Also, climate change further adds to the complexity of the problem.

In Asia, 90 % of the world's rice is consumed as rice itself, flour, noodles, and bread (Sharma, 2013). Apart from its culinary importance, it also has religious and cultural uses across the continent (Dawe et al., 2015), and alcoholic drink is also made from it (i.e., sake in Japan, and rice whiskey in Thailand). Rice represents the agricultural commodity in Asia, with the third-highest worldwide production next to sugarcane and maise (FAO, 2011). World rice production needs to be increased as the population has grown tremendously (Bouman and Tuong, 2001). Rice cultivation has a lot of significant challenges like global warming (Mohanty et al., 2013), water scarcity (Bouman and Tuong, 2001; Chakraborti et al., 2013), micronutrient deficiencies (IPNI, 2002; Frantz and

Epstein, 2005; Tuyogon et al., 2016), salinity (Sobrado, 2007), and flooding (IRRI and DFID, 2009). Assessing rice sustainability and productivity in the future, a study like the long-term continuous cropping experiment (LTCCE) was set-up (Dobermann et al., 2000; Pampolino et al., 2008; Onofri et al., 2016; www.IRRI.org, 2019). Long term experiments are essential for checking the sustainability of land and cropping management (Johnston and Poulton, 2018; www.IRRI.org, 2019). It is also invaluable in detecting possible slow changes produced by the rice cropping system and may reveal possible threats to the environment and future fertility on the agricultural land. It was the most intensively cultivated and the longest-running field trial on rice in the world in increasing soil health and productivity of rice crops (Pampolino et al., 2008; Onofri et al., 2016).

Figure 4. 1. IRRI's Long-term Continuous Cropping Experiment (LTCCE) is the world's longest-running rice research project. It celebrated its 150th crop last 2014; that is three seasons each year for 50 years (Los Banos, Laguna, Philippines) (www.irri.org).

Studies showed that rice is a significant dietary source of toxic metals like arsenic (As), cadmium (Cd), and lead (Pb) (Ismail et al., 2009; Huang et al., 2013; Clemens and Ma, 2016). There is a growing need to understand toxic heavy metal(loids) concentrations in food, specifically cereals like rice. Heavy metals are introduced into the environment as pollutants from anthropogenic activities and widespread use in different industries such as mining (Casiot et al., 2007; Festin et al., 2019), smelting (Fu et al., 2016) and burning of fossil fuels (Johnson, 2014), domestic (Lansdown, 2013) and agriculture (Violante et al., 2010). Over the years, trace metal(loid) pollution has become an environmental problem of concern due to their ecotoxic properties (Lombi and Holm, 2010). Industrial development and modern technologies adversely affect the environment by an increase in pollution (i.e., soil, water, air), loss of biodiversity, soil, and water contamination (Chepkemoi, 2017). Mining, where minerals are being extracted from the deposits of earth, causes a lot of environmental problems to the surrounding community. Air and water pollution, damage to land, and loss of biodiversity are some of the environmental impacts of mining. Waste discharge from metal mining leads to soil contamination to nearby rice fields that could lead to heavy metal contamination of the nearby soil, water supply and crops (Tollestrup et al., 2003; Johnson, 2014; Fan et al., 2017). Air quality is also affected by releasing unrefined materials from mining operations (Lubin et al., 2008). Heavy metals (e.g., lead, cadmium, arsenic) were also present in air particles that become airborne caused by wind erosion, nearby vehicular traffic (Chepkemoi, 2017), and from open coal mining sites (Martinez et al., 2013; Choudhury et al., 2017). These pollutants have adverse effects on the people living near the mining area. Diseases associated with mining site activities like skin allergies, respiratory, and even cancer (e.g., lung and kidney) due to prolonged exposure. Mining also causes water pollution which includes acid mine drainage ((Ashley et al., 2007; Mestrot et al., 2016), metal contamination and increased sediment levels in streams affecting aquatic wildlife and animals nearby (Hettick et al., 2015; Hu et al., 2016). Fields near the mining site and fields that once were used as one of the mining sites are now being rehabilitated and converted to rice fields due to the government mandate for rehabilitation (e.g., In the Philippines, Republic Act no. 7942 Philippine mining act of 1995 (RA, 2001; Cabalda et al., 2002; Bastías and Beldarrain, 2016).

The lack of scientific reports about possible heavy metal contamination in rice in old mining site areas of the Philippines, as well in the Asian rice that is available in the market, create the need to assess the concentration of heavy metals. A possible threat to consumer's health or public safety is indicative of the presence of heavy metals in soil and rice. Strategies for the reduction or soil remediation can be accurately formulated if toxic or high metal concentrations are found. This study is also vital as a reference for future studies that will monitor the heavy metal levels of paddy soil and rice in polluted rice fields of the country.

4.2 Aims and objectives

The research question of this monitoring study is whether the rice harvested from old mining sites were safe for human consumption based on the available maximum tolerable limits.

- This chapter is aimed to investigate the total antimony and other heavy metals in rice and soil used in the Philippines using ICP-MS,
- to provide information and identify gaps in knowledge about the current concentration in the Philippines of antimony and other heavy metals,
- to compare heavy metal concentrations of rice grown between mine impacted and non-impacted soils,
- Furthermore, to establish trends, or correlation on the heavy metal concentration in rice samples with the content of macronutrients (Mg, Ca) and micronutrients (Cu, Ni, Zn, and Mo) in rice samples.

4.3 Materials and Methods

4.3.1 Chemicals

All chemicals used for the study were supplied by Merck (analytical reagent grade). All the extraction solutions were prepared with deionised water (high purity water of resistance >16 MΩ cm). Concentrated nitric acid was used in the digestion of samples (Sigma-Aldrich, 70%, ACS), and standard calibration solutions of the elements of interest (1000 g mL^{-1}) were prepared from stock concentrations (Merck Millipore ICP XVIII) by diluting to volume with deionised water. The polytetrafluoroethylene (PTFE), polyethylene, and propylene containers were cleaned by immersing the vessels in concentrated HNO_3 overnight and then washing successively with deionised water before use.

4.3.2 Soil preparation, collection, and basic characterisation

In-house fabricated plastic ware pots (PVC pipes glued and sealed with plastic caps with polymer silicone) measuring 20 cm (height) x 15 cm (internal diameter) was filled with 2.5 kg of soils from the Philippines: (1) Bay, Laguna, (2) Agusan del Sur, and (3) Puerto Princesa, Palawan were used for the study. Soil samples were collected from the plough layer (0-15 cm) during fallow (Figure 4.2). Soils were air-dried and sieved to 2 mm. Non-soil debris was removed, and homogenisation was done to the soil before transferring the soil to individual pots.

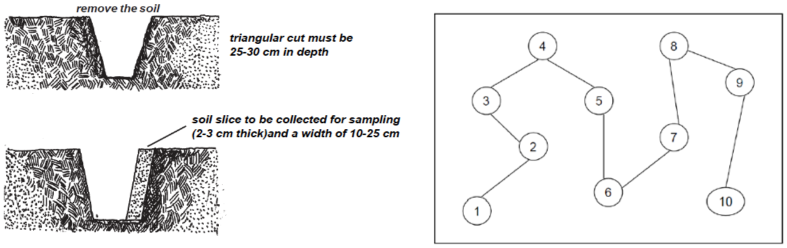


Figure 4. 2.The soil sampling method used in the experiment (a) plough layer and (b) ten different places in the field where soil sample should be collected (Olsen, S.R., C.V. Cole, F.S. Watanabe, 1954).

Two composite samples were collected and analysed for essential characterisation. Figure 4.3. shows the different sampling sites for the three groups of rice for this study. The first sampling site is in the long term cropping experiments started from 1965 up to

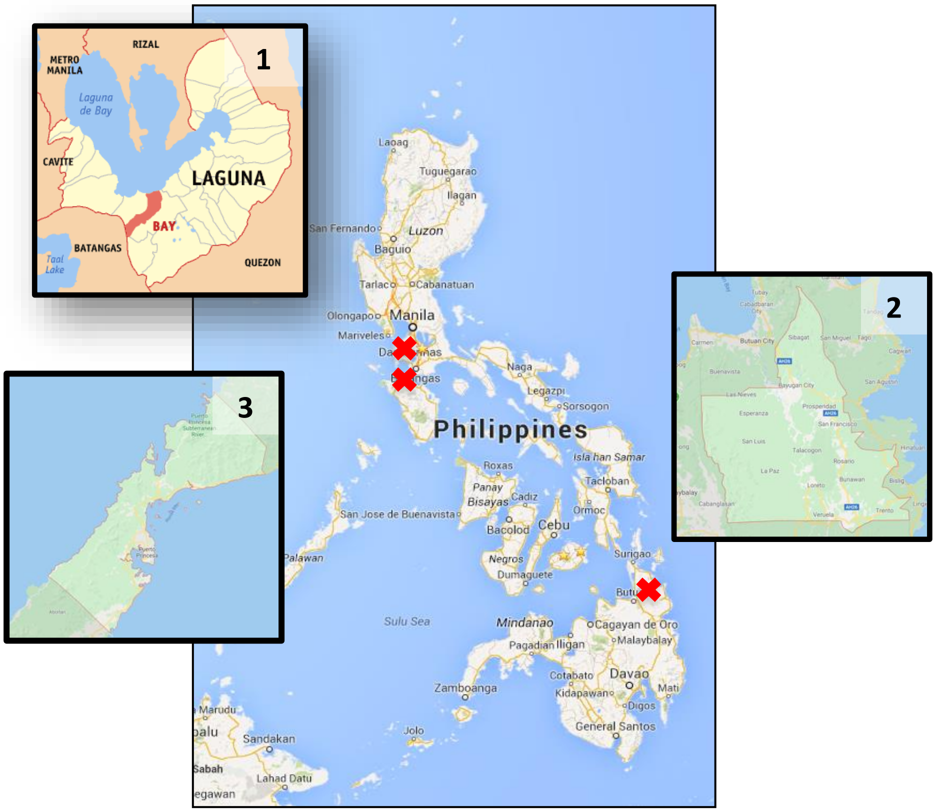


Figure 4. 3. Philippine map showing the 3-rice field sampling locations: (1) IRRI, Laguna (2) Agusan del Sur, and (3) IRRI Experiment Station (screenshot from Google).

the present, and the second one is an old mining site turned into a rice field, and the third is the experimental site using local farmer's method using different Asian varieties for Philippine market. A sub-sample was analysed for each of the soil after air-drying. Soil pH was analysed using a glass electrode by the KCl solution method. Cation exchange capacity (CEC) and available K were determined by the NH_4O-Ac extraction method at pH 7 (Thomas, 1996). Exchangeable bases (K, Mg, and Ca) were measured by the NH_4-OAc extraction method at pH 7. Total organic C (TOC) was determined using an automated dry combustion method (elemental analyser-TCD method). Available Zn was determined by DTPA-TEA (Diethylenetriaminepentaacetic acid-Triethylamine) method using ICP analysis (Slamet-loedin et al., 2015; Tuyogon et al., 2016). Available P was measured using both the Olsen and Bray Methods (Olsen, S.R., C.V. Cole, F.S. Watanabe, 1954). Total Fe and Mn were measured by XRF analysis. Other metals were analysed using ICP-OES. Particle size analysis for sand, silt, and clay was done by the hydrometer method (Thomas, 1996).

4.3.3 Rice sample collection

A total of 23 different varieties and three different brown Asian rice were obtained from the 2018 IRRI harvest. They were from three different groups namely: (1) from the LTCCE experiment (6 varieties), as a control (2) from a rice field near an old mining site in the Philippines (7 varieties) and (3) from IRRI field experiments representing different varieties of rice available in the Philippines' market (10 varieties). Rough rice was dehulled using rubber husk roller to obtain rice (Satake Inc., Japan). The obtained rice was dried at 60 °C, dehulled, polished, ground, and kept at a desiccator until further analysis (Figure 4.4).

4.3.4 High-pressure bomb acid digestion

For the determination of heavy metals, samples were digested as follows. All plastic and glassware used in contact with the samples were thoroughly washed with non-sulphate detergents, soaked in a 10% HNO_3 bath for at least 24 h, rinsed twice with MilliQ water (18.2 Mohms cm) (Millipore, USA).

Figure 4. 4. Rice pre-treatment. (a) Hard Rice, (b) dehulled and (c) polished and ground rice

The levels of As, Sb, and other heavy metals in rice samples were measured by ICP-MS analysis with modifications from Chang et al., (2009). Before analysis, digestion treatment was performed using a high-pressure bomb system. Approximately 50 mg of dried ground rice was accurately weighed into a Teflon centrifuge tube; 3 mL of H_20_2 and 5 mL of 70% concentrated HNO_3 were added to each sample and inserted to the digestion block through a capped stainless cylinder for acid digestion for 5 hours at 180 °C and cooled down overnight. After the cooldown, the digestate was transferred to a PTFE beaker including all the washings from the Teflon centrifuge tubes and heated gently (85–90°C) on a hot plate to allow evaporation of residual acid in the solution until almost dry. The residue was diluted to 50 mL of distilled water for further ICP-MS analysis (see also as described in Chapter 3, section 3.3.7).

4.3.5 ICP-MS

Total arsenic and antimony analysis were performed using an ICP-MS (Agilent Technologies 7500A). The operational conditions for the ICP-MS instruments are the same as in Table 3.3 of section 3.3.8 in Chapter 3. Each batch was accompanied by a 1 reagent blank, spike, and a certified reference material NIST-1568a rice flour (290 ng/g arsenic). Xylem sap and nutrient solution (before and after nutrient solution change once a week) were diluted and analysed by ICP-MS for As, Sb, B, Mn, Ni, Cu, Zn, Ca, Mg, and Fe contents.

4.3.6 Quality control and assurance

The relative standard deviation (RSD) for each metal repeated analysis was maintained below 5%. The detection limits for the elements were 0.4 mg kg^{-1} for Cd, 5 mg kg^{-1} for Pb, 30 mg kg^{-1} for Cu, and 850 mg kg^{-1} for Fe. A spiked sample using a known amount of metal standard was examined via acid digestion for verification of the accuracy of the analytical procedure. Recoveries of the heavy metals ranged between 85 and 110%. All reagents used were analytical reagent grade. A pre-cleaning regime, i.e., acid-washed, was applied for each glassware apparatus before use. High purity water (water sensitivity ~ 18.2 Mohms·cm at 25 °C; Millipore, MA, USA) was used throughout this study for laboratory applications, including reagents, blanks, and standard preparation.

4.3.7 Statistical Analysis

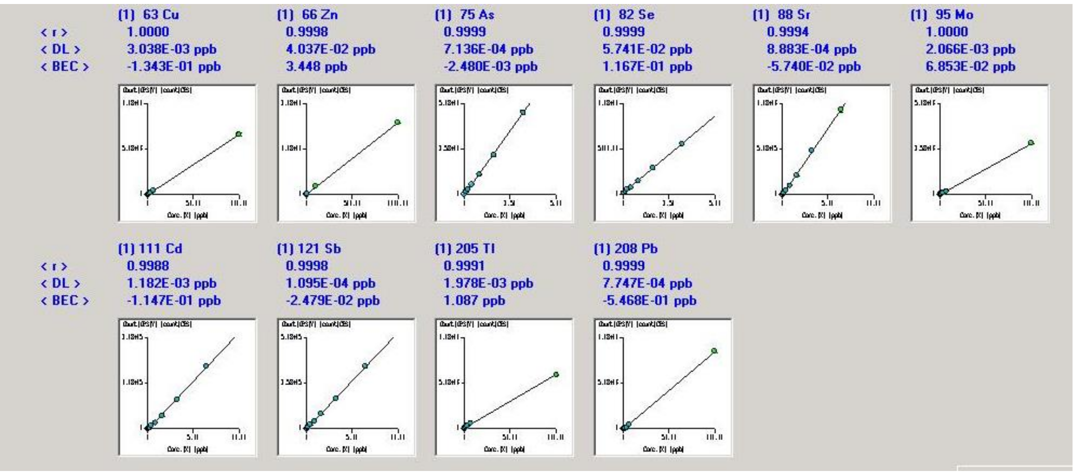
Data were analysed using SPSS Statistics for Windows, version 24 (IBM Corp., Armonk, NY, USA). One-way analysis of variance (ANOVA) was performed to determine the effects of different treatments (control, As^3, Sb^3) and plant stages (26 and 35 dat) and their interaction. A p-value of <0.05 denoted significance. The Tukey, Dunnett's, and subsequent pairwise comparisons were employed to compare significant differences ($P <0.05$) between treatment means. A Pearson correlation analysis was carried out for finding the relation between investigated parameters (metalloid treatments, duration, nutrients) using SPSS 26, and a normality check of the variables was done before the analysis using Shapiro-Wilk's test. A Spearman's rank analysis was performed if the data is not generally distributed unless otherwise stated. All data presented are expressed as the means of replicates ± standard deviation (SD).

Principal Component Analysis (PCA) with Varimax normalized rotation was employed, was used to determine the possible concealed relationship on the obtained results, which can reduce the original multi-dimensional spaces of PCs (the principal component). For this analysis, the relevance is identified as the components with eigenvalues of bigger than 1.0, a component that has factor loading > 0.75, from 0.75–0.5, and from 0.5 to 0.3 is taken as strongly, moderately, and weakly relevant, respectively.

4.4 Results

4.4.1 Calibration

The accuracy of the analytical procedure was checked by the analysis of the CRM SRM 1568a (rice flour). The calibration results using ICP Multi-element standard XVIII (with 16 elements in dilute nitric acid) Certipur® (Sigma Aldrich Singapore) and the recovery of some elements of the SRM 1568a Rice flour (with instrument limit of detection) are shown in figure 4.5 and table 4.1, respectively.



```
          (1)  63 Cu         (1)  66 Zn         (1)  75 As          (1)  82 Se         (1)  88 Sr          (1)  95 Mo
< r >       1.0000             0.9998             0.9999              0.9999             0.9994              1.0000
< DL >      3.038E-03 ppb      4.037E-02 ppb      7.136E-04 ppb       5.741E-02 ppb      8.883E-04 ppb       2.066E-03 ppb
< BEC >     -1.343E-01 ppb     3.448 ppb          -2.480E-03 ppb      1.167E-01 ppb      -5.740E-02 ppb      6.853E-02 ppb

          (1) 111 Cd         (1) 121 Sb         (1) 205 Tl          (1) 208 Pb
< r >       0.9988             0.9998             0.9991              0.9999
< DL >      1.182E-03 ppb      1.095E-04 ppb      1.978E-03 ppb       7.747E-04 ppb
< BEC >     -1.147E-01 ppb     -2.479E-02 ppb     1.087 ppb           -5.468E-01 ppb
```

Figure 4. 5. Selected ICP-MS calibration results and instrument LOD of ICP Multi-element standard XVIII (n=5)

Quantitative results (within 10% of the certified value) were obtained for each metal in the CRM. Recovery results were ranged from 98-105%. Limits of detection (LOD) were defined as 3 times the standard deviation of 10 blank measurements. Instrument LODs of As and Sb were $7.13e^{-4}$ ppb and $1.10e^{-4}$ ppb, respectively.

Table 4. 1. Chemical composition between certified SRM 1568a (Rice flour).

	Ave[a] (ppb)	STDEV	RSD[b]	% Recovery
As	0.2730	± 0.011	4.2	105
Ca	0.0148	± 0.002	1.4	99
Fe	6.4563	± 0.298	4.62	102
Zn	16.1963	± 1.072	6.62	101
Mg	0.0437	± 0.004	7.22	98

a sample size of 6

b Relative standard deviation (RSD) = (standard error/mean) x 100%.

4.4.2 Soil properties

The soils used in the experiment were taken from 3 different irrigated rice fields in the Philippines with contrasting soil properties. The areas had been under lowland rice cultivation with at least 2 croppings (rice-rice) season per year. Non-soil debris was retained (e.g. straw residues from the last cropping season) upon homogenisation by

Table 4. 2. Selected physicochemical properties of the soils used in the experiment, as measured on samples that had been air-dried before routine analysis.

Chemical properties	Soil 1	Soil 2	Soil 3
Location source	Bay, Laguna	Rosario, Agusan del Sur	IRRI Experiment Station
Coordinates	14°10'07.7"N 121°15'21.1"E	8°18'42.9"N 125°59'47.2"E	14°09'35.4"N 121°15'34.5"E
pH (KCl)	6.1	6.3	5.9
Organic C (%)	2.88	4.65	5.83
CEC (cmolc Kg-1)	31.3	27.6	32.8
DTPA-TEA Extractable			
Fe	8.82	5.51	40.4
Cu	0.774	0.802	14.1
Mn	10.1	4.70	37.7
Zn	0.751	1.29	19.0
Olsen P (mg Kg-1)	9.6	2.5	25
USDA Soil Texture	Loam	Sandy loam	Silty clay loam
Particle Size (%)			
Sand	42	64	18
Silt	37	28	47
Clay	21	8	35

hand mixing in a large trough. The following analysis results were provided with the following analysis procedures. Soils were air-dried during the homogenisation procedure, which was done in a greenhouse at 30-35°C air temperature at 60-75% relative humidity.

Table 4. 3.Safe limits guidelines of selected heavy metals in plants and soil.

Standards		Permissible Limits (mg Kg^{-1})							
		Cd	Cu	Pb	Zn	As	Cr	Sb	Hg
Plant	**WHO/FAO[1]**	0.2	40	0.2	60	0.2	0.129	-	0.02
	EU (629/2008)[2]	0.2	-	0.2	-	0.1	-	1	0.02
	Chinese (GB 2762-2005)[3]	0.2	10	0.2	50	0.15	-	-	0.02
Soil	**WHO/FAO**	-	-	-	-		-	-	-
	EU (629/2008)	3.0	140	300	300		150	37[4]	-
	Chinese (GB 15618-1995)	0.6	100	350	300	20	250	-	1.0

[1](WHO, 2003b; FAO and WHO, 2019) [2](Obiora et al., 2016) [3](Wang et al., 2015) [4](van Leeuwen and Aldenberg, 2012)

- No guideline set

4.4.3 Heavy metal analysis in rice

Three groups of rice were subjected to ICP-MS analysis of the mentioned metals from Group 1 (LTCCE) as control; Group 2 rice from the old mining site and Group 3, Asian rice that is available in the market. Figure 4.6 to 4.8 shows the ICP-MS results that are divided into macronutrients (Ca, Mg), micronutrients (Ni, Cu, Zn, Mn, Mo), as well as the toxic metals like As, Sb, Cr, Cd, and Pb for each group, in ug L^{-1}.

Figure 4.6 shows the Ca and Mg contents of the rice from 23 rice samples categorised into three groups. Ca and Mg contents of the rice from three different groups are not significantly different from each other at $P<0.05$. The Ca and Mg content is ranging from

42.9 to 124.5 ppb and 1270 to 2568 ppb, respectively. It can be noted that the lowest Ca and Mg came from group 2 which is rice from the near mining industry, and the highest Ca and Mg concentration comes from group 3 (Asian varieties) and control group (1 LTCCE), respectively.

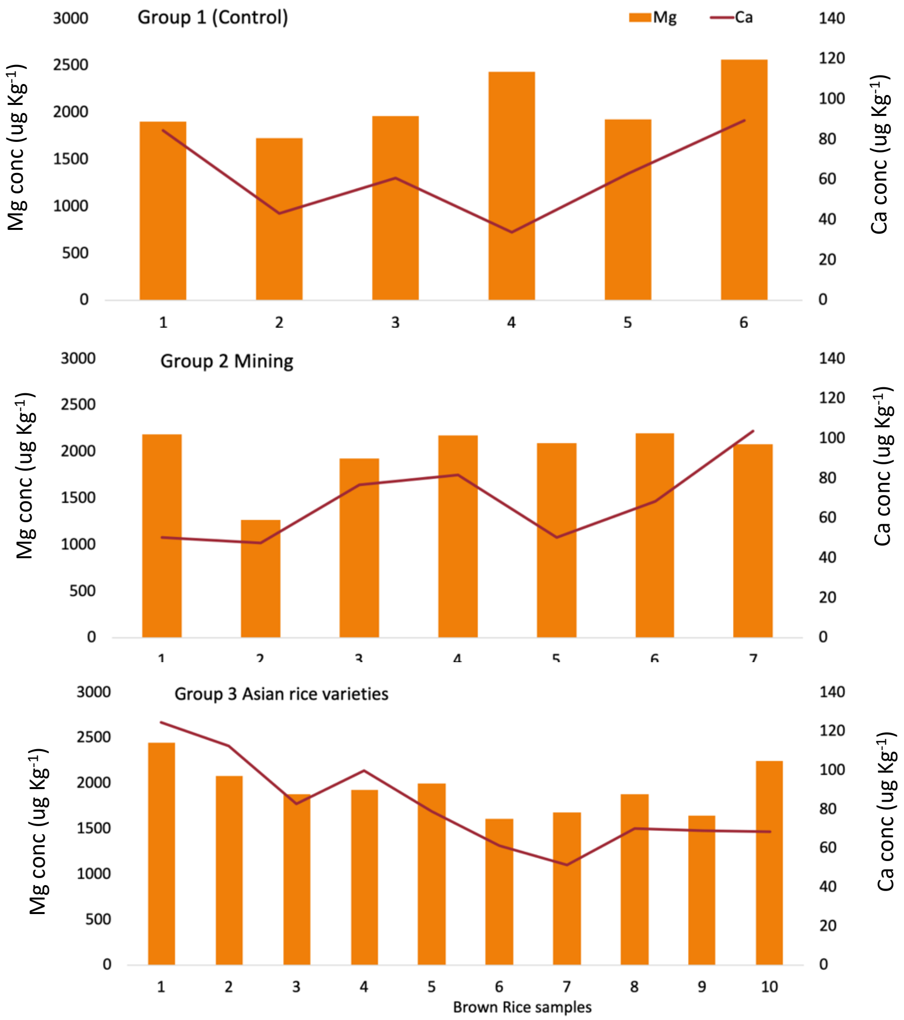


Figure 4. 6. ICP-MS results of macronutrient contents (Ca and Mg) for the three rice groups

Micronutrient contents (Mn, Fe, Ni, Cu, Zn, and Mo) of the rice samples are shown in Figure 4.7. It can be seen that the concentration of Fe, Ni, and Mo in rice in group 2 are significantly higher compared to groups 1 and 3, respectively. Specifically, Fe is the most abundant in the majority of the 7 rice samples in group 2, ranging from 139.7 – 517.6 ug Kg^{-1}. It is followed by Ni from 8.08 – 121.7 ug Kg^{-1} and Mo from 2.52 – 53.6 ug Kg^{-1}. Moreover, Zn, Ni, and Mn show no significant differences between the 3 groups.

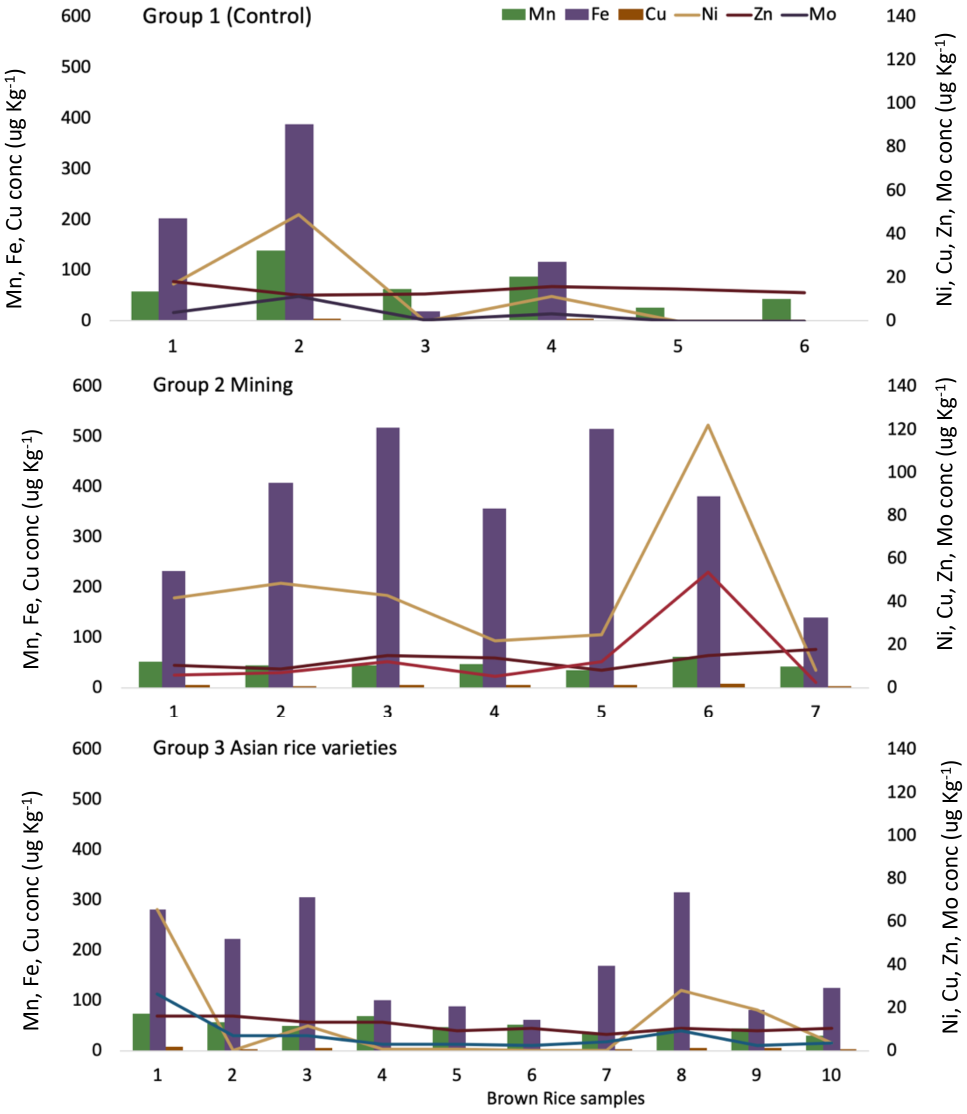


Figure 4. 7. ICP-MS results of micronutrient contents (Mn, Ni Cu, Fe, Zn, and Mo) for the three rice groups

Toxic metal contents Cr, As, Sb, Se, Cd, and Pb in rice are shown in Figure 4.8. It shows that Cr is significantly higher in group 2 rice compared to groups 1 and 3 (group2>3>1).

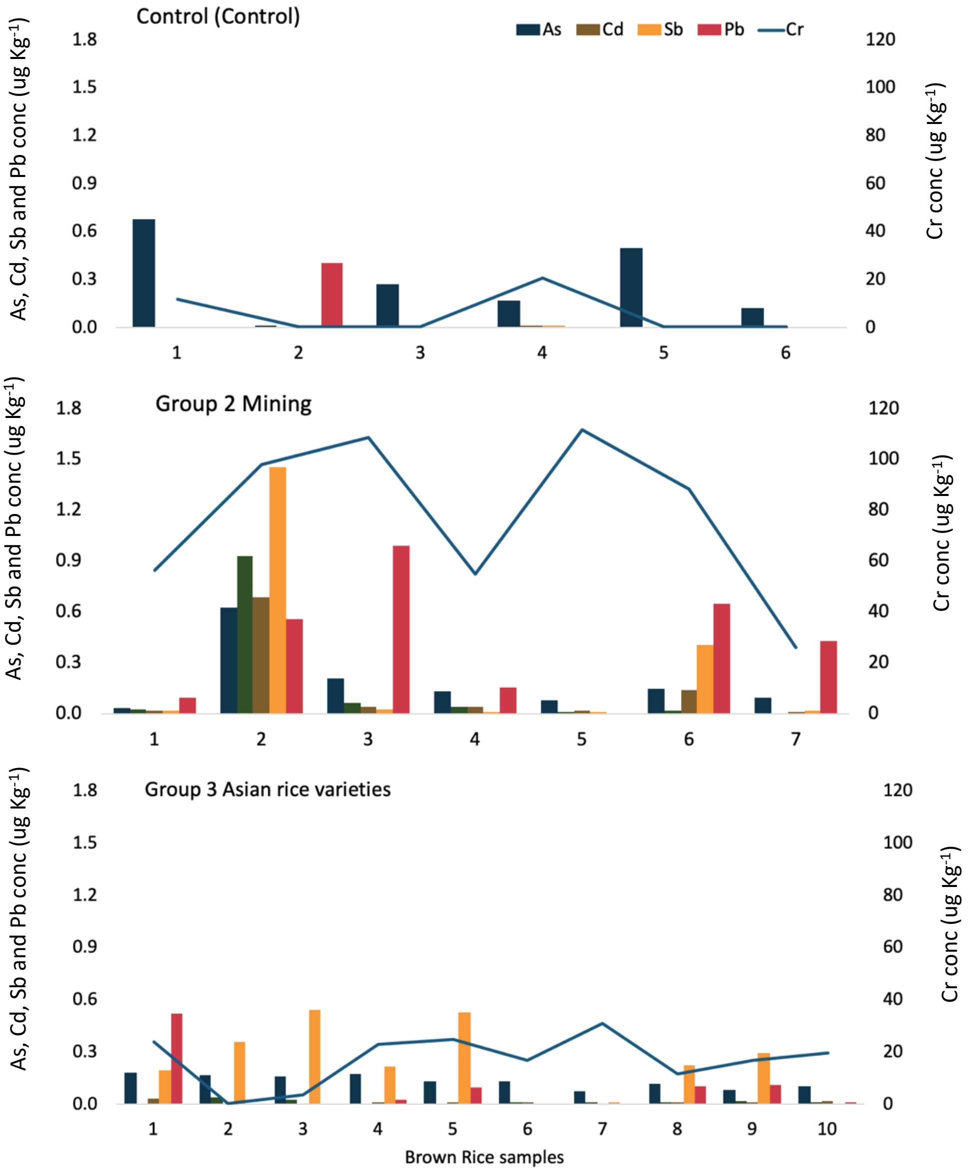


Figure 4. 8. ICP-MS results of heavy metal contents (Cr, As, Se, Cd, Sb, and Pb) for the three rice groups

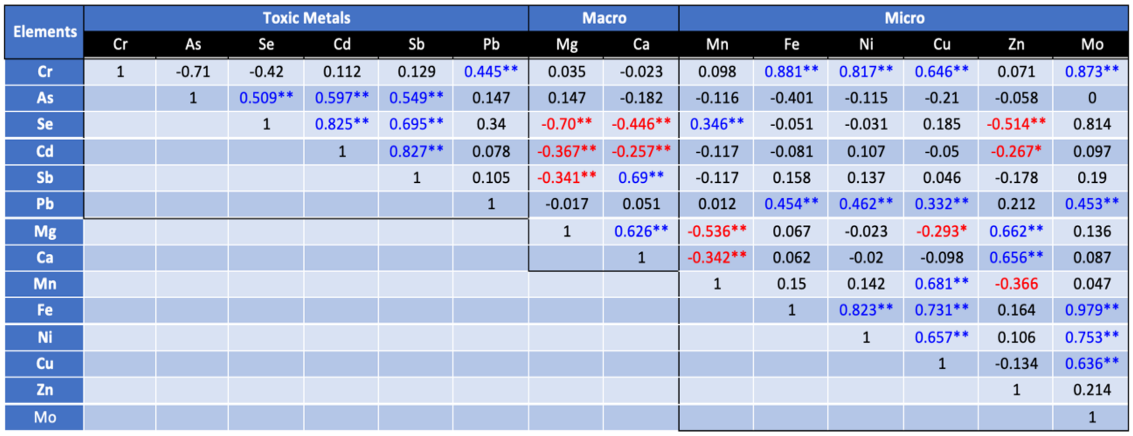
The heavy metal contents for group 1 rice samples were 0 for Cd, Sb, and Cd. Results showed that the Cr and As levels were 0-20.7 and 0-0.50 ug Kg^{-1}, respectively. It can be noted that even though As and Sb contents are not significantly different within the 3 groups ($P<0.05$), rice from group 2 has the highest Sb content.

There is significantly higher Pb (F(2,1)=3.224), Cr F(2,1)=6.934, Cd F(2,1)=3.329 and Se F(2,1)=3.842 in rice in group 2 compared to group 1 and 2. Cr contents of 25.7 to 111.4 ug/Kg in rice from group 2 were significantly higher compared to the other rice groups. The following values in ug Kg^{-1}were also obtained: As has a range of 0.03 to 0.62; Sb and Pb have 0 to 1.45 ug Kg^{-1}; and Cd with a range of 0.01 to 0.68 ug Kg^{-1}. Rice in group 3 was in between the heavy metal values of group 1 and 2. Although soil samples from the 3 different groups were not analysed for heavy metals, according to Magahud et al., (2015), the average Cr, Ni, Cu, Zn and Mo are 130, 20.0, 37.0, 81.0, 1nd 3.1 mg Kg^{-1} respectively.

4.4.4 Correlation of metal content in rice

To be able to assess if there is a correlation on the heavy metal concentration in rice samples, the Pearson correlation was used with a p-value of 0.05 and 0.001 shown in Table 4.4. Pearson correlation was used to quantify the strength or relationship degree between heavy metals using SPSS 24. The Pearson correlation matrix with r>0.7 is

Table 4. 4. Spearman correlation matrix of heavy metals in Rice (n=23 samples).



Elements	Toxic Metals						Macro		Micro					
	Cr	As	Se	Cd	Sb	Pb	Mg	Ca	Mn	Fe	Ni	Cu	Zn	Mo
Cr	1	-0.71	-0.42	0.112	0.129	0.445**	0.035	-0.023	0.098	0.881**	0.817**	0.646**	0.071	0.873**
As		1	0.509**	0.597**	0.549**	0.147	0.147	-0.182	-0.116	-0.401	-0.115	-0.21	-0.058	0
Se			1	0.825**	0.695**	0.34	-0.70**	-0.446**	0.346**	-0.051	-0.031	0.185	-0.514**	0.814
Cd				1	0.827**	0.078	-0.367**	-0.257**	-0.117	-0.081	0.107	-0.05	-0.267*	0.097
Sb					1	0.105	-0.341**	0.69**	-0.117	0.158	0.137	0.046	-0.178	0.19
Pb						1	-0.017	0.051	0.012	0.454**	0.462**	0.332**	0.212	0.453**
Mg							1	0.626**	-0.536**	0.067	-0.023	-0.293*	0.662**	0.136
Ca								1	-0.342**	0.062	-0.02	-0.098	0.656**	0.087
Mn									1	0.15	0.142	0.681**	-0.366	0.047
Fe										1	0.823**	0.731**	0.164	0.979**
Ni											1	0.657**	0.106	0.753**
Cu												1	-0.134	0.636**
Zn													1	0.214
Mo														1

*Significant correlation at the 0.05 level (both sides)

** Significant correlation at the 0.01 level (both sides) strongly correlated, and r values of <0.5-0.7 are moderately correlated. The metals were divided into toxic (i.e. As, Sb, Cd, Pb, and Cr), macronutrients (Ca, and Mg), and micronutrients (Ni, Cu, Zn, and Mo). Text in blue is significantly positively correlated, and red texts are significantly negatively correlated. All correlation in coloured texts is significant at P<0.001 other than the one with Mg and Cu.

Moreover, the PCA analysis (Table 4.5.) yielded four significant components with eigenvalues higher than 1.00, accounting for a total of 81.24% of the data variation (Table 4.5). The first principal component (PC1), which contained 30.49% of the calculated variance, showed a strongly positive load for Mn, Co, Cu, Se, and Sr but moderately for Cr, Ni and Fe. Moreover, PC1 showed a strongly negative load for Mg and a moderately negative load for Ca and Zn. Chromium and Nickel are known to be mutually associated with several sorts of rocks and, hence, into any soil-driven of these strata (Spurgeon et al., 2008). The same was reconfirmed in the study, obtaining a Pearson correlation coefficient of r = 0.817 between them. Also, the As was positively related to Cr (r = 0.432) and Ni (r = 0.751), which indicates that As might be driven from parent rock materials. Moreover, the second principal component (PC2) yielded 26.54% which showed a strongly positive load for Cr, Ni, Mo, and Fe, and a moderately positive load for Mg, Cu, and Pb. The third and the last PC (PC3 and PC4), yielded 17.46% and 6.74, respectively. PC3 yielded a strongly positive load for As, Sb, and Cd, and moderately negatively loaded for Mn, Co, and Sr. And lastly, PC4 yielded positively loaded for Ca and Sr.

Table 4. 5. Principal component analysis for heavy metals in rice from 3 different groups

Heavymetals	PC1	PC2	PC3	PC4
Mg	-0.782	0.454	-	-
Ca	-0.529	-	-	0.626
Ti	-	0.523	-	-
Cr	0.408	0.804	-	-
Mn	0.753	-	-0.545	-
Fe	0.411	0.867	-	-
Co	0.846	-	-0.433	-
Ni	0.409	0.771	-	-
Cu	0.747	0.534	-	-
Zn	-0.568	0.493	-	-
As	-	-	0.718	-
Se	0.698	-0.434	0.469	-
Sr	0.741	-	-0.447	0.406
Mo	-	0.865	-	-
Cd	-	-	0.832	-
Sb	-	-	0.801	-
Pb	-	0.533	-	-
Proportion of variances (%)	**30.49**	**26.54**	**17.46**	**6.74**
Cumulative proportion of variances (%)	**30.49**	**57.03**	**74.50**	**81.24**

Note: factor loadings < than 0.4 removed, extraction method: PCA, rotation method: Varimax and Kaiser normalization

4.4.5 Heavy metal contents in soils

Background of the total heavy metal contents in plant and soil samples from 3 different groups were compared to the natural abundance and guidelines of countries (Table 4.6). Soil 1 came from the control group of the long-term cropping experiment, soil 2 was from the rice field from the rehabilitated mining area, and soil 3 was one of the farmer’s fields.

Table 4. 6 Heavy metal content in soil samples in comparison with background values and guidelines of some selected countries

	Values (mg Kg^{-1})									
Metal Guidelines	**As**	**Cr**	**Cd**	**Hg**	**Pb**	**Ni**	**Cu**	**Zn**	**Mo**	**Sb**
Natural abundance in Japanese rice soils (N=97-408)[a]	9	64	0.5	0.3	29	39	32	99	na	na
Mean for Philippine rice soils (N=54)[b]	na	130	na	na	na	20	37	81	3.1	na
Canadian soil quality guidelines for agricultural soils[c]	12	64	1.4	6.6	70	50	63	200	5	na
Netherlands target values for soils (2000)[d]	29	100	0.8	0.3	85	35	36	140	3	na
Netherlands intervention values for soils (2009)[d]	76	180.0[e]	13	4.0[f]	530	100	190	720	190	na
Soil 1 (control)	na	36.8	na	na	18.8	29.8	93	76	na	na
Soil 2 (Mining site)	na	126.5	na	na	28.4	224.1	25	15	na	na
Soil 3 (Asian Market)	na	52.7	na	na	24.1	50	59.2	98.2	na	na

[a](Kitagishi, 1981), [b](Domingo and Kyuma, 1983), [c] (Canadian Council of Ministers of the Environment, 2007)
[d] (Ministerie Van Volkshuisvesting; Ruimtelijke Ordening En Milieu, 2000), [e]Cr$^{(III)}$, organic Hg, na-non-analysed or no data available

Generally, the Cr content in the 3 soil samples is less than the mean soil guidelines of Cr in Philippine soil of 130 mg Kg^{-1}. In soil 2, Cr concentration was two times, and Ni level is around 6 times higher than the Japanese soil guideline values. These soil Cr values are higher compared to Japanese, Canadian (both 64 mg Kg^{-1}), and lesser compared with the Netherlands guidelines (2000). It can be noted that soil 1 heavy metal contents are the least of the 3 soil samples followed by soil 3, and soil 2 has the highest content, particularly in Cr and Ni content. However, soil 1 Cu content has the highest of the three, and three times the Japanese rice soil, 2.5 times the Philippines, and 2.6 times the Netherlands soil guidelines. Soil 2 Zn content was the lowest, which is 660%, 540%, 1,333%, 933% lower than the Japanese, Philippines, Canadian, and Netherlands soil guidelines. In terms of Ni content of 224.1 mg/Kg in soil from group 2 exceeded the maximum allowable limits of the different countries. Precisely 2.2 times the Netherlands, 5.7 times Japan, and 11.2 x the Philippines soil guidelines.

4.5 Discussions and Conclusion

One of the world's most pressing environmental problems in recent years is the agricultural food safety concerns caused by heavy metal and metalloids pollution (Nagajyoti et al., 2010; Arunakumara et al., 2013; Hakeem, 2015; Liang et al., 2019). Toxic heavy metals and metalloids tend to accumulate in crops rather than being metabolised nor excreted (Zhao et al., 2015; Fashola et al., 2016) and enter the food chain via human consumption, posing human health problems (Tian et al., 2019). Among the heavy metals and metalloids, As, Cd, Cr, and Pb are mostly of grave concern because of accumulation prone to accumulate in rice (Zavala and Duxbury, 2008; Palma-Lara et al., 2019). Sb, like As, is a non-essential toxic metalloid (Filella et al., 2009; Lombi and Holm, 2010), of increasing environmental and health concerns due to being increasingly used in industry (i.e., mining) (Nash et al., 2000). In contrast to the popularity of widespread interest in As, Sb received relatively little attention. Toxic effects of these heavy metals and metalloids ranging from the liver, reproductive, bone, nerve damage, spontaneous miscarriages in pregnant women, and kidney diseases (i.e., cancer) to name a few (Mandal and Suzuki, 2002; Gidlow, 2004; Kapaj et al., 2006; Sreekanth et al., 2013; Pandey and Tripathi, 2014; Luo and Shu, 2015). Based on previous studies, limited information about the health risk assessment for rice consumption as well as the heavy metal content in paddy soils and rice (Ciminelli et al., 2017; Huang et al., 2018; Zhang et al., 2019; Zulkafflee et al., 2019).

Different rice and its paddy soil were sampled and analysed for the total heavy metal contents grouped into three: long term cropping experiment as the control rice, rice from previously old mining site turned into a rice field and selected different Asian rice available in the market. The findings showed that group 2 rice (from mining area) has the highest heavy metals, particularly As, Sb, Pb, and Cd, compared to rice from the control group and Philippine market Asian rice. Similar results have been found in the heavy metal contents in soil from the mining site. Furthermore, ICP-MS results showed that Ni levels of soils from group 2 exceeded different maximum levels set by the Philippines of 20 mg/Kg as well as different countries (i.e., 100 for Netherland, 39 for Japan, and 50 for Canada, mg/Kg). Cr soil contents in group 2 were the highest compared with the other 2 groups. The rice sampled from group 2 (mining area) is considered contaminated compared the Philippines standard as well as Asian neihboring country's allowable limit. The average As in world's soils is 7.2 mg Kg^{-1} (Cullen and Reimer, 2016a).

Soil As concentration varies from 4.4 mg Kg^{-1} in podzols to 9.3 mg Kg^{-1} in histosols, where the highest As concentration where found in clay soils and lowest in sandy soils (Kabata-Pendias, 2010; Goldberg, 2011). Based on GEMAS (Geochmeical mapping of agrigultural and graziing land soils project), the median soil As value is 5.7 mg Kg^{-1} in aqua regia extraction were a little below the global average of 6 $mgKg^{-1}$ (Bowen, 1979; Reimann et al., 2009). In terms of agricultural land use, the guide values varies in selected countries from 20 $mgKg^{-1}$ (Argentina, Canada, Norway, New Jersey, USA) (Obiora et al., 2016) to 200 mg Kg^{-1} (Germany) (*German Federal Soil Protection Act*, 1998). In average, As concentration in non-contaminated soils ranges from 0.1 to 40 mg Kg^{-1} (Mawia et al., 2021). In Asia, particularly in peaty and peaty clay sediments in southwest Bangladesh, arsenic content is 20 to 111 mg Kg^{-1} (Smith et al., 2000), 4 to 45 mg Kg^{-1} in the sediments of Mekong river delta (Ha et al., 2019), and 0.6 to 33 ug Kg^{-1}in Red river delta.

In this study, different varieties have been grown in different environment, different soil properties, different bioavailability, and comparison of metal concentrations cannot be achieved. It shows that soils from an old mining site can be used for agriculture use as long as proper assessment has been facilitated. This study showed that plants upload or download micronutrients when exposed to heavymetals (i.e. Sb, as etc.) based for the correlation and PCA analysis. This study would help in monitoring of heavymetals for rice in different parts of the Philippines, that could give valuable information for awareness, consumer safety, and possible heavymetal mitigation to set a maximum level in the Philippines.

The WHO set 0.2 mg Kg^{-1} as the limit or legal standards for As in rice and rice derived products, and no set limit yet for EU and USA. Although the As and other heavymetal values that was observed in this study were below the maximum allowable concentration values specified by the Japanese and Canadian soil guidelines, it can pose potential health hazards since these metals can accumulate chronically. The amount of rice consumption determines the risk of human exposure (Yost et al., 2004; Huang et al., 2018; Nguyen et al., 2020), and health concern of As exposure from rice is the due to large quantity of average daily intake per capita rice consumption. In Asia 400 mg of rice was the average daily intake (Biswas et al., 2020), particularly in the Philippines, 300 mg day per day (or 110 Kg or ice per year) (PSA, 2017).

In terms of the heavymetals found in the rice in the samples from the Philippines, particulary as, it is significantly lower than South and Southeast Asia like India, Pakistan, Vietnam, China and Bangladesh where the groundwater is contaminated with As (Shri et al., 2019). Philippines soil guidelines do not have set limits for As, Sb, Pb, and Cd at the time of writing, and there is a need to address this accordingly by the regulatory agency to ensure consumer’s safety and public health. Speciation of Sb and As was not determined, but recent studies have reported that arsenate (As(V)) once taken up by rice via phosphate transporters through roots to xylem, rice will convert it to the form (arsenite, As(III)) that no longer resembles phosphate and is transported back to the soil through its root (McLaughlin et al., 1999; Abedin et al., 2002; Meadows, 2014; Geng et al., 2017).

In terms of consumer protection and food safety, there is a need to efficiently assess rice as well as paddy soils in the Philippines as the staple food of the country. In countries where rice is the source of carbohydrates such as Asian countries, this may result in significant health concern. Heavy metals accumulate chronically, and the levels detected in rice fields near mining sites was relatively high even though it passed the safety limit set by WHO or FAO. Other factors such as water source, air, soil, and another possible contaminant source should be tested by regulatory agencies to ensure consumer safety. Laws in the rehabilitation of old mining sites turned into agricultural areas such as rice fields that should be stringent. A further test is to be performed to all rice varieties is recommended to ensure public safety. It is highly recommended to have a regular monitoring of heavymetal in rice and soil especially near or on the mining areas.

4.6 References

Abedin, M. J., Feldmann, J. and Meharg, A. A. (2002) 'Uptake kinetics of arsenic species in rice plants.' *Plant Physiology*, 128(3) pp. 1120–1128.

Ainsworth, N., Cooke, J. A. and Johnson, M. S. (1990) 'Distribution of antimony in contaminated grassland: 1- vegetation and soils.' *Environmental Pollution*. Elsevier, 65(1) pp. 65–77.

Ainsworth, N., Cooke, J.A. and Johnson, M. S. (1990) 'Distribution of antimony in contaminated grassland: 2— small mammals and invertebrates.' *Environmental Pollution*. Elsevier, 65(1) pp. 79–87.

Alexou, M. and Peuke, A. D. (2013) *Plant Mineral Nutrients*. Maathuis, F. J. M. (ed.) *Plant Mineral Nutrients*. Totowa, NJ: Humana Press (Methods in Molecular Biology).

Ali, H., Khan, E. and Sajad, M. A. (2013) 'Phytoremediation of heavy metals—Concepts and applications.' *Chemosphere*, 91(7) pp. 869–881.

Althobiti, R. A., Sadiq, N. W. and Beauchemin, D. (2018) 'Realistic risk assessment of arsenic in rice.' *Food Chemistry*. Elsevier Ltd, 257, August, pp. 230–236.

Álvarez-Fernández, A., Díaz-Benito, P., Abadía, A., And, A.-F. L.-M. and Abadía, J. (2014) 'Metal species involved in long distance metal transport in plants.' *Frontiers in Plant Science*, 5(1) p. 105.

Amarasiriwardena, D. and Wu, F. (2011) 'Antimony: Emerging toxic contaminant in the environment.' *Microchemical Journal*. Elsevier B.V., 97(1) pp. 1–3.

Ammann, A. A. (2011) 'Arsenic Speciation Analysis by Ion Chromatography - A Critical Review of Principles and Applications.' *American Journal of Analytical Chemistry*, 2011(February) pp. 27–45.

Anawar, H. M., Freitas, M. C., Canha, N. and Regina, I. S. (2011) 'Arsenic, antimony, and other trace element contamination in a mine tailings affected area and uptake by tolerant plant species.' *Environmental Geochemistry and Health*, 33(4) pp. 353–362.

Aposhian, H. V. and Aposhian, M. M. (2006) 'Arsenic Toxicology: Five Questions.' *Chemical Research in Toxicology*, 19(1) pp. 1–15.

Arnold, L. L., Eldan, M., Nyska, A., van Gemert, M. and Cohen, S. M. (2006) 'Dimethylarsinic acid: Results of chronic toxicity/oncogenicity studies in F344 rats and in B6C3F1 mice.' *Toxicology*, 223(1–2) pp. 82–100.

Arunakumara, K. K. I. U., Walpola, B. C. and Yoon, M.-H. (2013) 'Current status of heavy metal contamination in Asia's rice lands.' *Reviews in Environmental Science and*

Bio/Technology, 12(4) pp. 355–377.

Ashbrook, P. C. (2014) 'Standard Operating Procedures.' *Journal of Chemical Health and Safety*, 21(5) p. 29.

Ashley, P. M., Graham, B. P., Tighe, M. K. and Wolfenden, B. J. (2007) 'Antimony and arsenic dispersion in the Macleay River catchment, New South Wales: a study of the environmental geochemical consequences.' *Australian Journal of Earth Sciences*, 54(1) pp. 83–103.

ATSDR - Environmental Medicine & Environmental Health Education - CSEM (2013) 'Arsenic Toxicity Case Study: What Are the Standards and Regulation for Arsenic Exposure?' *Encyclopedia of Metalloproteins* pp. 143–143.

Awika, J. M. (2011) 'Major cereal grains production and use around the world.' *In ACS Symposium Series*, pp. 1–13.

Bach, C., Dauchy, X., Chagnon, M. C. and Etienne, S. (2012) 'Chemical compounds and toxicological assessments of drinking water stored in polyethylene terephthalate (PET) bottles: A source of controversy reviewed.' *Water Research*, 46(3) pp. 571–583.

Baker, A. J. M. (1981) 'Accumulators and Excluders - Strategies in the Response of Plants to Heavy Metals.' *Journal of Plant Nutrition*, 3(1–4) pp. 643–654.

Bakhtiari, A. R., Zakaria, M. P., Yaziz, M. I., Lajis, M. N. H. L. and Bi, X. (2014) 'Environment Asia.' *Environment Asia*, 7(1) pp. 104–111.

Basta, N. T. (2006) 'Heavy Metal Contamination of Soil.' *Soil Science Society of America Journal*, 70(5) p. 1819.

Bastías, J. M. and Beldarrain, T. (2016) 'Arsenic translocation in rice cultivation and its implication for human health.' *Chilean Journal of Agricultural Research*. Instituto de Investigaciones Agropecuarias, INIA, 76(1) pp. 114–122.

Bellido-Martín, A., Gómez-Ariza, J. L., Smichowsky, P. and Sánchez-Rodas, D. (2009) 'Speciation of antimony in airborne particulate matter using ultrasound probe fast extraction and analysis by HPLC-HG-AFS.' *Analytica Chimica Acta*, 649(2) pp. 191–195.

Benedict, S. R. (1908) *A Reagent For the Detection of Reducing Sugars*. *J. Biol. Chem*.

Bennett, J. O. and Sicher, R. C. (2011) 'Protein and metabolite composition of xylem sap from field-grown soybeans (Glycine max)' pp. 921–931.

Bhattacharya, P., Samal, a C., Majumdar, J. and Santra, S. C. (2009) 'Transfer of Arsenic from Groundwater and Paddy Soil to Rice Plant (Oryza sativa L.): A Micro-Level Study in West Bengal , India.' *World Journal of Agricultural Sciences*, 5(4) pp. 425–431.

Bi, Z. (2012) *Speciation analysis of trace metals in natural waters using vibrating electrodes*. *Environmental Sciences*. University of Liverpool.

Bielen, A., Remans, T., Vangronsveld, J. and Cuypers, A. (2013) 'The influence of metal stress on the availability and redox state of ascorbate, and possible interference with its cellular functions.' *International Journal of Molecular Sciences* pp. 6382–6413.

Biles, C. L. and Abeles, F. B. (1991) 'Xylem sap proteins.' *Plant Physiology*, 96(July 1991) pp. 597–601.

Billon, G. and Van Den Berg, C. M. G. (2004) 'Gold and silver micro-wire electrodes for trace analysis of metals.' *Electroanalysis*, 16(19) pp. 1583–1591.

Borovička, J., Řanda, Z. and Jelínek, E. (2006) 'Antimony content of macrofungi from clean and polluted areas.' *Chemosphere*, 64(11) pp. 1837–1844.

Bouman, B. A. . and Tuong, T. . (2001) 'Field water management to save water and increase its productivity in irrigated lowland rice.' *Agricultural Water Management*, 49(1) pp. 11–30.

Bowen, H. J. M. (Humphry J. M. (1979) *Environmental chemistry of the elements*. London, New York: Academic Press.

Brackin, R., Näsholm, T., Robinson, N., Guillou, S., Vinall, K., Buckley, S., Lakshmanan, P., Schmidt, S. and Inselsbacher, E. (2016) 'Microdialysis-a new technology for investigating soil nitrogen fluxes in the rhizosphere.' *In Proceedings of the International Nitrogen Initiative 2016 Conference*, pp. 4–8.

Brammer, H. and Ravenscroft, P. (2009) 'Arsenic in groundwater: A threat to sustainable agriculture in South and South-east Asia.' *Environment International*. Elsevier Ltd pp. 647–654.

Brihaye, C. and Duyckaerts, G. (1982) 'Determination of traces of metals by anodic stripping voltammetry at a rotating glassy carbon ring—disc electrode.' *Analytica Chimica Acta*, 143 pp. 111–120.

Broadley, M., Brown, P., Cakmak, I., Rengel, Z. and Zhao, F. (2011) 'Function of Nutrients: Micronutrients.' *In Marschner's Mineral Nutrition of Higher Plants: Third Edition*. Elsevier Inc., pp. 191–248.

Brochu, C., Wang, J., Roy, G., Messier, N., Wang, X.-Y., Saravia, N. G. and Ouellette, M. (2003) 'Antimony Uptake Systems in the Protozoan Parasite Leishmania and Accumulation Differences in Antimony-Resistant Parasites.' *Antimicrobial Agents and Chemotherapy*. American Society for Microbiology (ASM), 47(10) pp. 3073–3079.

Brown, S. D. and Kowalski, B. R. (1979) 'Pseudopolarographic Determination of Metal Complex Stability Constants in Dilute Solution by Rapid Scan Anodic Stripping

Voltammetry.' *Analytical Chemistry*, 51(13) pp. 2133–2139.

Buckley, S., Brackin, Richard, A. and Schmidt, S. (2016) 'Microdialysis-a sensitive method for estimating plant-available N released during litter decomposition.' *Proceedings of the International Nitrogen Initiative Conference 2016*, (December).

Buckley, S., Brackin, R., Jämtgård, S., Näsholm, T. and Schmidt, S. (2020) 'Microdialysis in soil environments: Current practice and future perspectives.' *Soil Biology and Biochemistry*, 143, April, p. 107743.

Buckley, S., Brackin, R., Näsholm, T., Schmidt, S. and Jämtgård, S. (2017) 'Improving in situ recovery of soil nitrogen using the microdialysis technique.' *Soil Biology and Biochemistry*, 114, November, pp. 93–103.

Buckley, S., Brackin, R. and Schmidt, S. (2015) *Microdialysis: an alternative approach to identifying plant-available nitrogen in soils*.

Burló, F., Guijarro, I., Carbonell-Barrachina, A. A., Valero, D. and Martínez-Sánchez, F. (1999) 'Arsenic Species: Effects on and Accumulation by Tomato Plants.' *Journal of Agricultural and Food Chemistry*, 47(3) pp. 1247–1253.

Cabalda, M. V, Banaag, M. A. and Garces, R. B. (2002) *Sustainable Development in The Philippine Minerals Industry: A Baseline Study*. M.V. Cabalda P.N.T. Tidalgo & R.B. Garces, M. A. B. (ed.) *Mining, Minerals and Sustainable Development Project (MMSD)*. England: International Institute for the Environment and Development (IIED).

Cai, Y., Su, J. and Ma, L. Q. (2004) 'Low molecular weight thiols in arsenic hyperaccumulator Pteris Vittata upon exposure to arsenic and other trace elements.' *Environmental Pollution*, 129(1) pp. 69–78.

Cal-Prieto, M. J., Carlosena, A., Andrade, J. M., Martínez, M. L., Muniategui, S., López-Mahía, P. and Prada, D. (2001) 'Antimony as a tracer of the anthropogenic influence on soils and estuarine sediments.' *Water, Air, and Soil Pollution*. Springer, 129(1–4) pp. 333–348.

Canadian Council of Ministers of the Environment (2007) *Canadian soil quality guidelines for the protection of environmental and human health*. Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment. Winnipeg. [Online] http://goo.gl/AePSg4.

Canepari, S., Marconi, E., Astolfi, M. L. and Perrino, C. (2010) 'Relevance of Sb(III), Sb(V), and Sb-containing nano-particles in urban atmospheric particulate matter.' *Analytical and Bioanalytical Chemistry*, 397(6) pp. 2533–2542.

Carey, A.-M., Lombi, E., Donner, E., de Jonge, M. D., Punshon, T., Jackson, B. P., Guerinot, M. Lou, Price, A. H. and Meharg, A. A. (2012) 'A review of recent developments in the speciation and location of arsenic and selenium in rice grain.' *Analytical and Bioanalytical*

Chemistry, 402(10) pp. 3275–3286.

Carneado, S., Hernández-Nataren, E., López-Sánchez, J. F. F. and Sahuquillo, A. (2015) ‘Migration of antimony from polyethylene terephthalate used in mineral water bottles.’ *Food Chemistry*. Elsevier Ltd, 166, January, pp. 544–550.

Carolyn, P., Aqilah, F. A. T., Payus, C., Farhana, A., Talip, A., Carolyn, P., Aqilah, F. A. T., Payus, C., Farhana, A. and Talip, A. (2014) ‘Assessment of heavy metals accumulation in paddy rice (Oryza sativa).’ *African Journal of Agricultural Research*. Academic Journals, 9(41) pp. 3082–3090.

Casiot, C., Ujevic, M., Munoz, M., Seidel, J. L. and Elbaz-Poulichet, F. (2007) ‘Antimony and arsenic mobility in a creek draining an antimony mine abandoned 85 years ago (upper Orb basin, France).’ *Applied Geochemistry*, 22(4) pp. 788–798.

Cavicchioli, A., La-Scalea, M. A., Gutz, G. R., Gutz, I. G. R. and Gutz, G. R. (2004) ‘Analysis and Speciation of Traces of Arsenic in Environmental , Food and Industrial Samples by Voltammetry : a Review.’ *Electroanalysis*, 16(9) pp. 697–711.

Chakraborti, D., Rahman, M. M., Das, B., Nayak, B., Pal, A., Sengupta, M. K., Hossain, M. A., Ahamed, S., Sahu, M., Saha, K. C., Mukherjee, S. C., Pati, S., Dutta, R. N. and Quamruzzaman, Q. (2013) ‘Groundwater arsenic contamination in Ganga–Meghna–Brahmaputra plain, its health effects and an approach for mitigation.’ *Environmental Earth Sciences*, 70(5) pp. 1993–2008.

Chang, C.-Y., Wang, C.-F., Mui, D. T. and Chiang, H.-L. (2009) ‘Application of methods (sequential extraction procedures and high-pressure digestion method) to fly ash particles to determine the element constituents: A case study for BCR 176.’ *Journal of Hazardous Materials*, 163(2–3) pp. 578–587.

Chapman, C. S. and Van Den Berg, C. M. G. G. (2007) ‘Anodic stripping voltammetry using a vibrating electrode.’ *Electroanalysis*, 19(13) pp. 1347–1355.

Chaurasia, C. S., Müller, M., Bashaw, E. D., Benfeldt, E., Bolinder, J., Bullock, R., Bungay, P. M., DeLange, E. C. M., Derendorf, H., Elmquist, W. F., Hammarlund-Udenaes, M., Joukhadar, C., Kellogg, D. L., Lunte, C. E., Nordstrom, C. H., Rollema, H., Sawchuk, R. J., Cheung, B. W. Y., Shah, V. P., Stahle, L., Ungerstedt, U., Welty, D. F. and Yeo, H. (2007) ‘AAPS-FDA workshop white paper: Microdialysis principles, application and regulatory perspectives.’ *In Pharmaceutical Research*, pp. 1014–1025.

Chen, Z. L., Farzana Akter, K., Rahman Mahmudur, M. and Naidu, R. (2006) ‘Speciation of arsenic by ion chromatography inductively coupled plasma mass spectrometry using ammonium eluents.’ *Journal of Separation Science*, 29(17) pp. 2671–2676.

Cheng, T. and Sun, H. (2014) ‘CHAPTER 25. Antimony and Bismuth.’ *In* Maret, W. and Wedd, A. (eds) *Binding, Transport and Storage of Metal Ions in Biological Cells*. London, UK: The Royal Society of Chemistry, pp. 768–799.

Chepkemoi, J. (2017) *What Is The Environmental Impact Of The Mining Industry?* First Break. [Online] worldatlas.com/articles/what-is-the-environmental-impact-of-the-mining-industry.html.

Cheraghi, M., Mosaed, H. P., Lorestani, B. and Yousefi, N. (2012) 'Heavy metal contamination in some rice samples.' *Electronic Journal of Environmental, Agricultural and Food Chemistry*, 11(5) pp. 424–432.

Choudhury, B. U., Malang, A., Webster, R., Mohapatra, K. P., Verma, B. C., Kumar, M., Das, A., Islam, M. and Hazarika, S. (2017) 'Acid drainage from coal mining: Effect on paddy soil and productivity of rice.' *Science of the Total Environment*. Elsevier B.V., 583(August 2018) pp. 344–351.

Ciminelli, V. S. T., Gasparon, M., Ng, J. C., Silva, G. C. and Caldeira, C. L. (2017) 'Dietary arsenic exposure in Brazil: The contribution of rice and beans.' *Chemosphere*. Elsevier Ltd, 168, February, pp. 996–1003.

Çirmi, D., Aydin, R. and Köleli, F. (2015) 'The electrochemical reduction of nitrate ion on polypyrrole coated copper electrode.' *Journal of Electroanalytical Chemistry*, 736 pp. 101–106.

Clark, R. B., Tiffin, L. O. and Brown, J. C. (1973) 'Organic Acids and Iron Translocation in Maize Genotypes.' *Plant Physiology*, 52(2) pp. 147–150.

Clarkson, D. T. (1996) 'Marschner H. 1995. Mineral nutrition of higher plants. second edition. 889pp. London: Academic Press.' *Annals of Botany*, 78(4) pp. 527–528.

Clemens, S. and Ma, J. F. (2016) 'Toxic Heavy Metal and Metalloid Accumulation in Crop Plants and Foods.' *Annual Review of Plant Biology*, 67(1) pp. 489–512.

Correia, M. M., Alves, S., Simões Gonçalves, M. D. L. and Nabais, C. (2006) 'Dynamic modelling of nickel complexation in xylem sap of Quercus ilex: A voltammetric study.' *Electroanalysis*, 18(8) pp. 814–822.

Cullen, W. R. and Reimer, K. J. (2016a) 'CHAPTER 2. Arsenic Is Everywhere.' *In Arsenic is Everywhere: Cause for Concern?*, pp. 8–48.

Cullen, W. R. and Reimer, K. J. (2016b) 'CHAPTER 8. Arsenic and the Evening Meal.' *In Arsenic is Everywhere: Cause for Concern?*, pp. 221–265.

Daniels, R., Rush, C. C. and Bauer, L. (1960) 'The Fehling and Benedict tests.' *Journal of Chemical Education*, 37(4) p. 205.

Daus, B. and Hansen, H. R. (2016) 'Analysis of antimony species – lessons learnt from more than two decades of environmental research.' *Environmental Chemistry*, 13(6) p. 913.

Dawe, B. D., Organisation, A. and Nations, U. (2015) ‘Rice in Asia: Paddy-whacked.’ *Economist (United Kingdom)*, 411(8960).

Dobermann, A., Dawe, D., Roetter, R. P. and Cassman, K. G. (2000) ‘Reversal of rice yield decline in a long-term continuous cropping experiment.’ *Agronomy Journal*, 92(4) pp. 633–643.

Domingo, L. E. and Kyuma, K. (1983) ‘Trace elements in tropical asian paddy soils: I. total trace element status.’ *Soil Science and Plant Nutrition*, 29(4) pp. 439–452.

Dortsiou, M. and Kyriacou, G. (2009) ‘Electrochemical reduction of nitrate on bismuth cathodes.’ *Journal of Electroanalytical Chemistry*, 630(1–2) pp. 69–74.

Duester, L., Diaz-Bone, R. A., Kösters, J. and Hirner, A. V. (2005) ‘Methylated arsenic, antimony and tin species in soils.’ *In Journal of Environmental Monitoring*, pp. 1186–1193.

Dushenkov, S. (2003) ‘Trends in phytoremediation of radionuclides.’ *In Plant and Soil*, pp. 167–175.

Elmquist, W. F. and Sawchuk, R. J. (1997) ‘Application of microdialysis in pharmacokinetic studies.’ *Pharmaceutical Research* pp. 267–288.

Emamverdian, A. and Ding, Y. (2017) ‘Effects of heavy metals’ toxicity on plants and enhancement of plant defense mechanisms of Si-mediation “ Review.”’ *International Journal of Environmental & Agriculture Research*, (4) pp. 41–51.

Emamverdian, A., Ding, Y., Mokhberdoran, F. and Xie, Y. (2015) ‘Heavy Metal Stress and Some Mechanisms of Plant Defense Response.’ *The Scientific World Journal*. Hindawi Publishing Corporation, 2015 pp. 1–18.

EPA (2004) ‘EPA Method 6020A: ICP-MS. Official Name: EPA Method 6020A, Inductively Coupled Plasma-Mass Spectrometry.’ *EPA methods*, 6.

Epstein, E. and and Bloom, A. J. (1972) *Mineral Nutrition of Plants: Principles and Perspectives*. 2nd ed., Sunderland, Massachusetts: Sinauer Associates, Inc.

Fan, Y., Zhu, T., Li, M., He, J., Huang, R. and and Ruixue Huang, T. Z. Y. F. M. L. J. H. (2017) ‘Heavy Metal Contamination in Soil and Brown Rice and Human Health Risk Assessment near Three Mining Areas in Central China.’ *Journal of Healthcare Engineering*. Hindawi, 2017 p. 9.

FAO (2016) *GIEWS - Crop Prospects and Food Situation, No.1,March 2016*.

FAO and WHO (2019) *Report of the 11th session of the codex committee on contaminnants in foods. A joint FAO/WHO food standards programme codex alimentarius commission 40th Session. Codex*. Geneva, Switzerland.

Farid, M., Shakoor, M., Ehsan, S., Ali, S., Zubair, M. and Hanif, M. (2013) ‘Morphological, physiological and biochemical responses of different plant species to Cd stress.’ *Int J Chem Biochem Sci*, 3(March) pp. 53–60.

Farnese, F. S., Oliveira, J. A., Farnese, M. S., Gusman, G. S., Silveira, N. M. and Siman, L. I. (2014) ‘Uptake arsenic by plants: Effects on mineral nutrition, growth and antioxidant capacity.’ *Idesia (Arica)*, 32(1) pp. 99–106.

Fashola, M., Ngole-Jeme, V. and Babalola, O. (2016) ‘Heavy Metal Pollution from Gold Mines: Environmental Effects and Bacterial Strategies for Resistance.’ *International Journal of Environmental Research and Public Health*. MDPI AG, 13(11) p. 1047.

Feldmann, J., Salaün, P. and Lombi, E. (2009) ‘Critical review perspective: elemental speciation analysis methods in environmental chemistry - moving towards methodological integration.’ *Environmental Chemistry*. CSIRO, 6(4) p. 275.

Feng, R., Wei, C., Tu, S., Ding, Y., Wang, R. and Guo, J. (2013) ‘The uptake and detoxification of antimony by plants: A review.’ *Environmental and Experimental Botany*. Elsevier B.V., 96, December, pp. 28–34.

Festin, E. S., Tigabu, M., Chileshe, M. N., Syampungani, S. and Odén, P. C. (2019) ‘Progresses in restoration of post-mining landscape in Africa.’ *Journal of Forestry Research*, 30(2) pp. 381–396.

Filella and May (2003) ‘Computer simulation of the low-molecular-weight inorganic species distribution of antimony (III) and antimony (V) in natural waters.’ *Geochimica et Cosmochimica Acta,* 67(21) pp. 4013–4031.

Filella, M. (2013) ‘Food for thought: A critical overview of current practical and conceptual challenges in trace element analysis in natural waters.’ *Water (Switzerland)*. MDPI AG pp. 1152–1171.

Filella, M., Belzile, N. and Chen, Y.-W. W. (2002) ‘Antimony in the environment: a review focused on natural waters.’ *Earth-Science Reviews*, 57(1–2) pp. 125–176.

Filella, M., Belzile, N. and Lett, M.-C. C. (2007) ‘Antimony in the environment: A review focused on natural waters. III. Microbiota relevant interactions.’ *Earth-Science Reviews*, 80(3–4) pp. 195–217.

Filella, M. and May, P. M. (2005a) ‘Critical appraisal of available thermodynamic data for the complexation of antimony(iii) and antimony(v) by low molecular mass organic ligands.’ *Journal of Environmental Monitoring*, 7(12) p. 1226.

Filella, M. and May, P. M. (2005b) ‘Reflections on the calculation and publication of potentiometrically- determined formation constants.’ *Talanta*, 65(5) pp. 1221–1225.

Filella, M. and Williams, P. A. (2012) ‘Antimony interactions with heterogeneous

complexants in waters, sediments and soils: A review of binding data for homologous compounds.' *Chemie der Erde*. Elsevier GmbH., 72(SUPPL.4) pp. 49–65.

Filella, M., Williams, P. A. and Belzile, N. (2009) 'Antimony in the environment: Knowns and unknowns.' *Environmental Chemistry*, 6(2) pp. 95–105.

Forsberg, G., O'Laughlin, J. W., Megargle, R. G. and Koirtyohann, S. R. (1975) 'Determination of Arsenic by Anodic Stripping Voltammetry and Differential Pulse Anodic Stripping Voltammetry.' *Analytical Chemistry*, 47(9) pp. 1586–1592.

Francesconi, K. A. and Kuehnelt, D. (2004) 'Determination of arsenic species: A critical review of methods and applications, 2000–2003.' *The Analyst*, 129(5) pp. 373–395.

Frantz, J. M. and Epstein, E. (2005) *Nutritional deficiencies: What they look like*. [Online] [Accessed on 16th December 2019] http://www.ces.ncsu.edu/depts/hort/floriculture/def/forfloriculturecropshttp://extension.agron.iastate.edu/soilfertility/nutrienttopics/deficiencies.htmlcornhttp://muextension.missouri.edu/explore/agguides/hort/index.htm.

FSA (2012) *Arsenic speciation in fruit and vegetables grown in the UK.* Aberdeen: University of Aberdeen.

Fu, Z., Wu, F., Mo, C., Deng, Q., Meng, W. and Giesy, J. P. (2016) 'Comparison of arsenic and antimony biogeochemical behavior in water, soil and tailings from Xikuangshan, China.' *Science of the Total Environment*, 539 pp. 97–104.

Garg, N. and Singla, P. (2011) 'Arsenic toxicity in crop plants: physiological effects and tolerance mechanisms.' *Environmental Chemistry Letters*. Springer, 9(3) pp. 303–321.

Garg, N., Singla, P. and Bhandari, P. (2015) 'Metal uptake, oxidative metabolism, and mycorrhization in pigeonpeaand pea under arsenic and cadmium stress.' *Turkish Journal of Agriculture and Forestry*, 39(2) pp. 234–250.

Gebel, T. (1997) 'Arsenic and antimony: comparative approach on mechanistic toxicology.' *Chemico-Biological Interactions*. Elsevier Ireland Ltd, 107(3) pp. 131–144.

Gebel, T. W. (2001) 'Unanswered Questions in Arsenic Toxicology.' *Journal of Environmental Pathology, Toxicology and Oncology*, 20(4) p. 11.

Gemici, Ü. and Tarcan, G. (2007) 'Assessment of the pollutants in farming soils and waters around untreated abandoned Türkönü mercury mine (Turkey).' *Bulletin of Environmental Contamination and Toxicology*, 79(1) pp. 20–24.

Geng, A., Wang, X., Wu, L., Wang, F., Chen, Y., Yang, H., Zhang, Z. and Zhao, X. (2017) 'Arsenic accumulation and speciation in rice grown in arsanilic acid-elevated paddy soil.' *Ecotoxicology and Environmental Safety*, 137 pp. 172–178.

Geng, C. N., Zhu, Y. G., Tong, Y. P., Smith, S. E. and Smith, F. A. (2006) 'Arsenate (As) uptake by and distribution in two cultivars of winter wheat (Triticum aestivum L.).' *Chemosphere*, 62(4) pp. 608–615.

Gerényi, A., Czech, V., Fodor, F., Vincze, L. and Szalóki, I. (2017) 'In vivo XANES measuring technique for studying the arsenic uptake in cucumber plants.' *X-Ray Spectrometry*, 46(3) pp. 143–150.

German Federal Soil Protection Act (1998) *Federal Law Gazette I p. 502*.

Ghori, N.-H., Ghori, T., Hayat, M. Q., Imadi, S. R., Gul, A., Altay, V. and Ozturk, M. (2019) 'Heavy metal stress and responses in plants.' *International Journal of Environmental Science and Technology*. Center for Environmental and Energy Research and Studies, 16(3) pp. 1807–1828.

Gibbon-Walsh, K., Salaün, P. and van den Berg, C. M. G. (2012a) 'Determination of arsenate in natural pH seawater using a manganese-coated gold microwire electrode.' *Analytica Chimica Acta*. Elsevier B.V., 710, January, pp. 50–57.

Gibbon-Walsh, K., Salaün, P. and van den Berg, C. M. G. (2012b) 'Pseudopolarography of Copper Complexes in Seawater Using a Vibrating Gold Microwire Electrode.' *The Journal of Physical Chemistry A*, 116(25) pp. 6609–6620.

Gibbon-Walsh, K., Salaün, P., Uroic, M. K., Feldmann, J., McArthur, J. M. and Van Den Berg, C. M. G. (2011) 'Voltammetric determination of arsenic in high iron and manganese groundwaters.' *Talanta*, 85(3) pp. 1404–1411.

Gidlow, D. A. (2004) 'Lead toxicity.' *Occupational Medicine*, 54(2) pp. 76–81.

Goldberg, S. (2011) 'Chemical Equilibrium and Reaction Modeling of Arsenic and Selenium in Soils.' *Dynamics and Bioavailability of Heavy Metals in the Rootzone* pp. 65–92.

Grob, M., Wilcke, W. and Mestrot, A. (2018) 'Release and Biomethylation of Antimony in Shooting Range Soils upon Flooding.' *Soil Systems*, 2(2) p. 34.

Guerriero, Gea, Deshmukh, R. and Durgesh K., T. (2020) *Metalloids in Plants Advances and Future Prospects*. Deshmukh, R., Tripathi, D. K., and Guerriero, Gia (eds) *Wiley*. John Wiley & Sons Ltd.

Gupta, D. K., Srivastava, S., Huang, H. G., Romero-Puertas, M. C. and Sandalio, L. M. (2011) 'Arsenic Tolerance and Detoxification Mechanisms in Plants.' *In*, pp. 169–179.

Ha, N. T. H., Ha, N. T., Nga, T. T. H., Minh, N. N., Anh, B. T. K., Hang, N. T. A., Duc, N. A., Nhuan, M. T. and Kim, K.-W. (2019) 'Uptake of arsenic and heavy metals by native plants growing near Nui Phao multi-metal mine, northern Vietnam.' *Applied Geochemistry*. Elsevier Ltd, 108, September, p. 104368.

Hakeem, K. R. (2015) ‘Crop production and global environmental issues.’ *Crop Production and Global Environmental Issues*, (December) pp. 1–598.

Hall, J. L. L. (2002) ‘Cellular mechanisms for heavy metal detoxification and tolerance.’ *Journal of experimental botany*, 53(366) pp. 1–11.

Hammel, W., Debus, R. and Steubing, L. (2000) ‘Mobility of antimony in soil and its availability to plants.’ *Chemosphere*, 41(11) pp. 1791–1798.

Hansen, C. (2011) *Antimony speciation analysis HPLC methods with ICP-MS and ES-MS detection for complex biological matrices*. University of Coppenhagen.

Hansen, H. R. and Pergantis, S. A. (2008) ‘Analytical techniques and methods used for antimony speciation analysis in biological matrices.’ *Journal of Analytical Atomic Spectrometry*, 23(10) p. 1328.

Hasanuzzaman, M., Nahar, K. and Fujita, M. (2018) *Mechanisms of Arsenic Toxicity and Tolerance in Plants*. Hasanuzzaman, M., Nahar, K., and Fujita, M. (eds) *Mechanisms of Arsenic Toxicity and Tolerance in Plants*. Singapore: Springer Singapore.

Hasanuzzaman, M., Nahar, K., Hakeem, K. R., Öztürk, M. and Fujita, M. (2015) ‘Arsenic Toxicity in Plants and Possible Remediation.’ *In Soil Remediation and Plants: Prospects and Challenges*. Elsevier Inc., pp. 433–501.

Hawkesford, M. J., Parmar, S. and Buchner, P. (2013) ‘Mineral Composition Analysis: Measuring Anion Uptake and Anion Concentrations in Plant Tissues.’ *In Plant Mineral Nutrients*. Totowa, NJ: Humana Press, pp. 109–119.

Hazama, K., Nagata, S., Fujimori, T., Yanagisawa, S. and Yoneyama, T. (2015) ‘Concentrations of metals and potential metal-binding compounds and speciation of Cd, Zn and Cu in phloem and xylem saps from castor bean plants (Ricinus communis) treated with four levels of cadmium.’ *Physiologia Plantarum*, 154(2) pp. 243–255.

He, M., Wang, N., Long, X., Zhang, C., Ma, C., Zhong, Q., Wang, A., Wang, Y., Pervaiz, A. and Shan, J. (2019) ‘Antimony speciation in the environment: Recent advances in understanding the biogeochemical processes and ecological effects.’ *Journal of Environmental Sciences*. Elsevier B.V., 75, January, pp. 14–39.

Hettick, B. E., Cañas-Carrell, J. E., French, A. D. and Klein, D. M. (2015) ‘Arsenic: A Review of the Element’s Toxicity, Plant Interactions, and Potential Methods of Remediation.’ *Journal of Agricultural and Food Chemistry*, 63(32) pp. 7097–7107.

Hijaz, F. and Killiny, N. (2014) ‘Collection and chemical composition of phloem sap from Citrus sinensis L. Osbeck (sweet orange).’ *PLoS ONE*. Public Library of Science, 9(7).

Hirner, A. V., Grüter, U. M. and Kresimon, J. (2000) ‘Metal(loid)organic compounds in contaminated soil.’ *Fresenius’ Journal of Analytical Chemistry*. Springer, 368(2–3) pp.

263–267.

Hoagland and Arnon, D., D. (1950) *The water-culture method of growing plants without soil.* Berkeley, Calif. : University of California, College of Agriculture, Agricultural Experiment Station.

Hossain, M. A., Piyatida, P., da Silva, J. A. T. and Fujita, M. (2012) 'Molecular Mechanism of Heavy Metal Toxicity and Tolerance in Plants: Central Role of Glutathione in Detoxification of Reactive Oxygen Species and Methylglyoxal and in Heavy Metal Chelation.' *Journal of Botany*. Hindawi Limited, 2012(Cd) pp. 1–37.

Hozhina, E. ., Khramov, A. ., Gerasimov, P. . and Kumarkov, A. . (2001) 'Uptake of heavy metals, arsenic, and antimony by aquatic plants in the vicinity of ore mining and processing industries.' *Journal of Geochemical Exploration*, 74(1–3) pp. 153–162.

Hrytsak, L. R., Herts, A. I., Nuzhyna, N. V., Cryk, M. M., Shevchenko, V. V. and Drobyk, N. M. (2018) 'The influence of light regime on the growth data and pigment composition of the plant Gentiana lutea cultured in vitro.' *Regulatory Mechanisms in Biosystems*, 9(2) pp. 258–266.

Hu, L., Zhang, B., Wu, D., Fan, H., Tu, J., Liu, W., Huang, R. and Huang, X. (2019) 'Estimation of arsenic bioaccessibility in raw and cooked radish using simulated in vitro digestion.' *Food & Function*. Royal Society of Chemistry, 10(3) pp. 1426–1432.

Hu, Y., Cheng, H. and Tao, S. (2016) 'The Challenges and Solutions for Cadmium-contaminated Rice in China: A Critical Review.' *Environment International*. Elsevier Ltd pp. 515–532.

Hua, C.-Y., Chen, J.-X., Cao, Y., Li, H.-B., Chen, Y. and Ma, L. Q. (2020) 'Pteris vittata coupled with phosphate rock effectively reduced As and Cd uptake by water spinach from contaminated soil.' *Chemosphere*. Elsevier Ltd, 247, May, p. 125916.

Huang, R.-Q., Gao, S.-F., Wang, W.-L., Staunton, S. and Wang, G. (2006) 'Soil arsenic availability and the transfer of soil arsenic to crops in suburban areas in Fujian Province, southeast China.' *Science of The Total Environment*, 368(2–3) pp. 531–541.

Huang, Y., Chen, Q., Deng, M., Japenga, J., Li, T., Yang, X. and He, Z. (2018) 'Heavy metal pollution and health risk assessment of agricultural soils in a typical peri-urban area in southeast China.' *Journal of Environmental Management*. Academic Press, 207, February, pp. 159–168.

Huang, Z., Pan, X.-D. D., Wu, P.-G. G., Han, J.-L. L. and Chen, Q. (2013) 'Health Risk Assessment of Heavy Metals in Rice to the Population in Zhejiang, China.' Scarfi, M. R. (ed.) *PLoS ONE*, 8(9) pp. 1–6.

Huiliang, H., Jagner, D. and Renman, L. (1988) 'Flow potentiometric and constant-current stripping analysis for arsenic(V) without prior chemical reduction to arsenic(III).'

Analytica Chimica Acta, 207 pp. 37–46.

Humphrey, O. S., Young, S. D., Bailey, E. H., Crout, N. M. J., Ander, E. L., Hamilton, E. M. and Watts, M. J. (2019) 'Investigating the use of microdialysis and SEC-UV-ICP-MS to assess iodine interactions in soil solution.' *Chemosphere*. Elsevier Ltd, 229, August, pp. 41–50.

Hunt, R., Causton, D. R., Shipley, B. and Askew, A. P. (2002) 'A modern tool for classical plant growth analysis.' *Annals of Botany*, 90(4) pp. 485–488.

Inselsbacher, E. (2014) 'Recovery of individual soil nitrogen forms after sieving and extraction.' *Soil Biology and Biochemistry*, 71, April, pp. 76–86.

Inselsbacher, E., Öhlund, J., Jämtgård, S., Huss-Danell, Kerstin, A. and Näsholm, T. (2011) 'The potential of microdialysis to monitor organic and inorganic nitrogen compounds in soil.' *Soil Biology and Biochemistry*, 43(6) pp. 1321–1332.

International Programme on Chemical Safety (2004) 'International programme on chemical safety (IPCS),' (June) pp. 1–34.

IPNI (2002) 'Nutrient Deficiency Symptoms in Rice.' *Better Crops International*, 16(May) pp. 23–25.

IRRI and DFID (2009) 'Scuba rice : breeding flood-tolerance into Asia ' s local mega rice varieties.' *South Asia* pp. 1–6.

Ismail, B., Yap, D., Adezrian, J., Khairiah, J. and Ahmad-Mahir, R. (2009) 'The Uptake of Heavy Metals by Paddy Plants (Oryza sativa) in Kota Marudu, Sabah, Malaysia.' *& Environ. Sci*, 6(1) pp. 16–19.

Jamila Alfaraas, A. M., Khairiah, J., Ismail, B. S. and Noraini, T. (2016) 'Effects of heavy metal exposure on the morphological and microscopical characteristics of the paddy plant.' *Journal of Environmental Biology*, 37(5) pp. 955–963.

Järup, L. (2003) 'Hazards of heavy metal contamination.' *British Medical Bulletin*, 68 pp. 167–182.

JECFA (2016) 'Joint FAO / WHO Expert Committee on Food Additives (JECFA) Call for Experts on Food Additives , Contaminants and toxins ; and Residues of Veterinary Drugs,' (October).

Jentschke, G. and Godbold, D. L. (2000) 'Metal toxicity and ectomycorrhizas.' *Physiologia Plantarum*, 109(2) pp. 107–116.

Ji, Y., Sarret, G., Schulin, R. and Tandy, S. (2017) 'Fate and chemical speciation of antimony (Sb) during uptake, translocation and storage by rye grass using XANES spectroscopy.' *Environmental Pollution*. Elsevier Ltd, 231, December, pp. 1322–1329.

Johnson, C. A., Moench, H., Wersin, P., Kugler, P. and Wenger, C. (2005) ‘Solubility of Antimony and Other Elements in Samples Taken from Shooting Ranges.’ *Journal of Environmental Quality*. Wiley, 34(1) pp. 248–254.

Johnson, C. D. (2014) ‘Phytoremediation of Arsenic Contamination on Vashon-Maury Island METHODS Salix Screening for Arsenic Tolerance.’

Johnston, A. E. and Poulton, P. R. (2018) ‘The importance of long-term experiments in agriculture: their management to ensure continued crop production and soil fertility; the Rothamsted experience.’ *European Journal of Soil Science*, 69(1) pp. 113–125.

Kabata-Pendias, A. (2010) *Trace Elements in Soils and Plants*. 4th ed., CRC Press.

Kalaji, H. M., Jajoo, A., Oukarroum, A., Brestic, M., Zivcak, M., Samborska, I. A., Cetner, M. D., Łukasik, I., Goltsev, V. and Ladle, R. J. (2016) ‘Chlorophyll a fluorescence as a tool to monitor physiological status of plants under abiotic stress conditions.’ *Acta Physiologiae Plantarum*. Polish Academy of Sciences.

Kapaj, S., Peterson, H., Liber, K. and Bhattacharya, P. (2006) ‘Human Health Effects From Chronic Arsenic Poisoning–A Review.’ *Journal of Environmental Science and Health, Part A*. The Safe Drinking Water Foundation, Saskatoon, Saskatchewan, Canada., 41(10) pp. 2399–2428.

Katsounaros, I. and Kyriacou, G. (2007) ‘Influence of the concentration and the nature of the supporting electrolyte on the electrochemical reduction of nitrate on tin cathode.’ *Electrochimica Acta*, 52(23) pp. 6412–6420.

Kehr, J. and Rep, M. (2007) ‘Protein extraction from xylem and phloem sap.’ *Methods in molecular biology (Clifton, N.J.)*, 355 pp. 27–35.

Killiny, N. and Hijaz, F. (1998) ‘Chemical composition of xylem sap of Citrus sinensis L. Osbeck (sweet orange).’ *Trends in Plant Science*, 3(5) pp. 188–195.

Kisan, M., Sangathan, S., Nehru, J. and Pitroda, S. G. (2012) ‘Laboratory Glassware-Volumetric Instruments-Methods for Testing of Capacity and for Use.’ ISO (ed.) *4787*. Geneva: IS pp. 1–29.

Kitagishi, K. (1981) ‘Heavy Metal Pollution in Soils of Japan.’ *Japan Scientific Societies Press, Tokyo, Japan*, 52(4) p. 302.

Koester, R. P., Skoneczka, J. A., Cary, T. R., Diers, B. W. and Ainsworth, E. A. (2014) ‘Historical gains in soybean (Glycine max Merr.) seed yield are driven by linear increases in light interception, energy conversion, and partitioning efficiencies.’ *Journal of Experimental Botany*, 65(12) pp. 3311–3321.

Kolbe, F., Mattusch, J., Wennrich, R., Weiss, H., Sorkau, E., Lorenz, W. and Daus, B. (2012) ‘Analytical investigations of antimony-edta complexes and their use in speciation

analysis.’ *Fresenius Environmental Bulletin*, 21(11 C) pp. 3453–3456.

Kowalska, J., Stryjewska, E., Szymański, P. and Golimowski, J. (1999) ‘Voltammetric determination of arsenic in plant material.’ *Electroanalysis*, 11(17) pp. 1301–1304.

Krachler, M. and Emons, H. (2001) ‘Speciation analysis of antimony by high-performance liquid chromatography inductively coupled plasma mass spectrometry using ultrasonic nebulization.’ *Analytica Chimica Acta*, 429(1) pp. 125–133.

Kroukamp, E. M., Wondimu, T. and Forbes, P. B. C. (2016) ‘Metal and metalloid speciation in plants: Overview, instrumentation, approaches and commonly assessed elements.’ *TrAC - Trends in Analytical Chemistry*. Elsevier B.V., 77 pp. 87–99.

Krupka, K. M. and Serne, R. J. (2002) *Geochemical Factors Affecting the Behavior of Antimony, Cobalt, Europium, Technetium, and Uranium in Vadose Zone Sediments*. *Pnnl-14126*. Richland, WA (United States).

Kumar, R., Mishra, R. K., Mishra, V., Qidwai, A., Pandey, A., Shukla, S. K., Pandey, M., Pathak, A. and Dikshit, A. (2015) ‘Detoxification and Tolerance of Heavy Metals in Plants.’ *In Plant Metal Interaction: Emerging Remediation Techniques*. Elsevier Inc., pp. 335–359.

Kumarathilaka, P., Seneweera, S., Meharg, A. and Bundschuh, J. (2018) ‘Arsenic speciation dynamics in paddy rice soil-water environment: sources, physico-chemical, and biological factors - A review.’ *Water Research*. Elsevier Ltd pp. 403–414.

Küpper, H. and Andresen, E. (2016) ‘Mechanisms of metal toxicity in plants.’ *Metallomics*, 8(3) pp. 269–285.

Lansdown, A. B. G. (2013) ‘CHAPTER 1. Introduction.’ *In The Carcinogenicity of Metals: Human Risk Through Occupational and Environmental Exposure*, pp. 1–18.

Larsen, E. H. and Stürup, S. (1994) ‘Carbon-enhanced inductively coupled plasma mass spectrometric detection of arsenic and selenium and its application to arsenic speciation.’ *Journal of Analytical Atomic Spectrometry*, 9(10) pp. 1099–1105.

van Leeuwen, H. P., Town, R. M., Buffle, J., Cleven, R. F. M. J., Davison, W., Puy, J., van Riemsdijk, W. H. and Sigg, L. (2005) ‘Dynamic Speciation Analysis and Bioavailability of Metals in Aquatic Systems.’ *Environmental Science & Technology*, 39(22) pp. 8545–8556.

van Leeuwen, L. C. and Aldenberg, T. (2012) *RIVM Letter Report 601357001/2012: Environmental risk limits for antimony*.

Li, Z. and Cui, Z. (2008) ‘Application of microdialysis in tissue engineering monitoring.’ *Progress in Natural Science*. Science Press, 18(5) pp. 503–511.

Liang, G., Gong, W., Li, B., Zuo, J., Pan, L. and Liu, X. (2019) ‘Analysis of Heavy Metals in Foodstuffs and an Assessment of the Health Risks to the General Public via Consumption

in Beijing, China.’ *International Journal of Environmental Research and Public Health*. MDPI AG, 16(6) p. 909.

Lichtfouse, E., Schwarzbauer, J. and Robert, D. (2012) *Environmental chemistry for a sustainable world*. *Environmental Chemistry for a Sustainable World*. Springer Netherlands.

Lintschinger, J., Koch, I., Serves, S., Feldmann, J. and Cullen, W. R. (1997) ‘Determination of antimony species with High-Performance Liquid Chromatography using element specific detection.’ *Fresenius’ Journal of Analytical Chemistry*, 359(6) pp. 484–491.

Liu, Z. G. and Huang, X. J. (2014) ‘Voltammetric determination of inorganic arsenic.’ *TrAC - Trends in Analytical Chemistry*, 60 pp. 25–35.

Lombi, E. and Holm, P. E. (2010) ‘Metalloids, soil chemistry and the environment.’ *In Advances in Experimental Medicine and Biology*. Australia: Landes Bioscience and Springer Science+Business Media., pp. 33–44.

Louis, Y., Cmuk, P., Nicolau, R., Omanovi, D., Lenoble, V., Pižeta, I., Mounier, S., and Garde, L. and Garde, L. (2007) ‘Pseudopolarography As a Tool for Complexation Studies of Trace Metals With Dissolved Natural Organic Matter,’ (January) p. 2007.

Louis, Y., Cmuk, P., Omanović, D., Garnier, C., Lenoble, V., Mounier, S. and Pižeta, I. (2008) ‘Speciation of trace metals in natural waters: The influence of an adsorbed layer of natural organic matter (NOM) on voltammetric behaviour of copper.’ *Analytica Chimica Acta*. Elsevier Masson, 606(1) pp. 37–44.

Louis, Y., Garnier, C., Lenoble, V., Omanovi, D., Mounier, S., Pižeta, I., Protee, L., Toulon, S., Bp, V., Garde, L., Physico, G. De, Chimie, T., Moléculaires, S. and I, U. B. (2008) ‘Electrochemical Study of Major and Trace Metal Interactions With Concentrated Marine Dissolved Organic Matter,’ (098) p. 1214910.

Lu, M. and Compton, R. G. (2013) ‘Voltammetric Determination of Iron(III) in Water.’ *Electroanalysis*, 25(5) pp. 1123–1129.

Lubin, J. H., Moore, L. E., Fraumeni, J. F. and Cantor, K. P. (2008) ‘Respiratory Cancer and Inhaled Inorganic Arsenic in Copper Smelters Workers: A Linear Relationship with Cumulative Exposure that Increases with Concentration.’ *Environmental Health Perspectives*, 116(12) pp. 1661–1665.

Luo, J. and Shu, W. (2015) ‘Arsenic-Induced Developmental Neurotoxicity.’ *In* Flora, S. J. S. B. T.-H. of A. T. (ed.) *Handbook of Arsenic Toxicology*. Oxford: Elsevier, pp. 363–386.

Lydic, R., Baghdoyan, H. A. and May, A. L. (2018) ‘Chapter Fourteen - Neurochemistry of Anesthetic States.’ *In* Eckenhoff, R. G. and Dmochowski, I. J. B. T.-M. in E. (eds) *Chemical and Biochemical Approaches for the Study of Anesthetic Function Part B*. 1st ed., Academic Press, pp. 237–255.

Madejón, P., Marañón, T. and Murillo, J. M. (2006) ‘Biomonitoring of trace elements in the leaves and fruits of wild olive and holm oak trees.’ *Science of the Total Environment*, 355(1–3) pp. 187–203.

Magahud, J. C., Badayos, R. B., Sanchez, P. B. and Sta. Cruz, P. C. (2015) *Levels and Potential Sources of Heavy Metals in Major Irrigated Rice Areas of the Philippines*. *IAMURE International Journal of Ecology and Conservation*.

Mandal, B. K. and Suzuki, K. T. (2002) ‘Arsenic round the world: A review.’ *Talanta*. Elsevier, 58(1) pp. 201–235.

Mareček, V., Jänchenová, H., Samec, Z. and Březina, M. (1986) ‘Voltammetric determination of nitrate, perchlorate and iodide at a hanging electrolyte drop electrode.’ *Analytica Chimica Acta*, 185(C) pp. 359–362.

Marschner, H. (1995) *Mineral Nutrition of High Plants*. Academic Press.

Martin, M., Ferdousi, R., Hossain, K. M. J. and Barberis, E. (2010) ‘Arsenic from groundwater to paddy fields in Bangladesh: Solid-liquid partition, sorption and mobility.’ *Water, Air, and Soil Pollution*, 212(1–4) pp. 27–36.

Martinez, R. E., Marquez, J. E., Hòa, H. T. B. and Gieré, R. (2013) ‘Open-pit coal-mining effects on rice paddy soil composition and metal bioavailability to Oryza sativa L. plants in Cam Pha, northeastern Vietnam.’ *Environmental Science and Pollution Research*, 20(11) pp. 7686–7698.

Massoura, S. T., Echevarria, G., Leclerc-Cessac, E. and Morel, J. L. (2004) ‘Response of excluder, indicator, and hyperaccumulator plants to nickel availability in soils.’ *Australian Journal of Soil Research*, 42(8) pp. 933–938.

Materials, B. (1989) *Analytical Methods*. *WHO*.

Matschullat, J. J. (2000) ‘Arsenic in the geosphere - A review.’ *The Science of the Total Environment*, 249(1–3) pp. 297–312.

Mawia, A. M., Hui, S., Zhou, L., Li, H., Tabassum, J., Lai, C., Wang, J., Shao, G., Wei, X., Tang, S., Luo, J., Hu, S. and Hu, P. (2021) ‘Inorganic arsenic toxicity and alleviation strategies in rice.’ *Journal of Hazardous Materials*. Elsevier B.V. p. 124751.

Mayet, N., Servat, K., Kokoh, K. B. and Napporn, T. W. (2019) ‘Probing the Surface of Noble Metals Electrochemically by Underpotential Deposition of Transition Metals.’ *Surfaces*, 2(2) pp. 257–276.

McLaughlin, M. ., Parker, D. . and Clarke, J. . (1999) ‘Metals and micronutrients – food safety issues.’ *Field Crops Research*, 60(1–2) pp. 143–163.

Mead, M. N. (2005) ‘Arsenic: In search of an antidote to a global poison.’ *Environmental*

Health Perspectives. Public Health Services, US Dept of Health and Human Services, 113(6).

Meadows, R. (2014) ‘How Plants Control Arsenic Accumulation.’ *PLoS Biology*, 12(12) pp. 1002008–1002009.

Meharg, A. A. (2004) ‘Arsenic in rice - Understanding a new disaster for South-East Asia.’ *Trends in Plant Science* pp. 415–417.

Meharg, A. A. and Zhao, F.-J. (2012) *Arsenic & Rice*. *Springer*. Dordrecht: Springer Netherlands.

Mendoza, T. (2012) ‘Estimates of Rice Per Capita Consumption: Its Implications to the Rice Self-Sufficiency Program of the Philippines*.’ *Policy Options*, 4, January.

Mestrot, A., Ji, Y., Tandy, S. and Wilcke, W. (2016) ‘A novel method to determine trimethylantimony concentrations in plant tissue.’ *Environmental Chemistry*, 13(6) pp. 919–926.

Michalski, R., Szopa, S., Jabłońska, M. and Łyko, A. (2012) ‘Application of hyphenated techniques in speciation analysis of arsenic, antimony, and thallium.’ *The Scientific World Journal*. Institute of Environmental Engineering, the Polish Academy of Sciences, 34 Sklodowskiej-Curie Street, 41 819 Zabrze, Poland. michalski@ipis.zabrze.pl, 2012(January 2017) p. 902464.

Miekeley, N., Mortari, S. R. and Schubach, A. O. (2002) ‘Monitoring of total antimony and its species by ICP-MS and on-line ion chromatography in biological samples from patients treated for leishmaniasis.’ *Fresenius’ Journal of Analytical Chemistry*, 372(3) pp. 495–502.

Mihucz, V. G., Tatár, E. E. E., Virág, I., Cseh, E., Fodor, F., Záray, G., Tat??r, E., Vir??g, I., Cseh, E., Fodor, F. and Gyula, Z. (2005) ‘Arsenic speciation in xylem sap of cucumber (Cucumis sativus L.).’ *Analytical and Bioanalytical Chemistry*. Joint Research Group of Environmental Chemistry of the Hungarian Academy of Sciences and L. Eotvos University, PO Box 32, 1518 Budapest, Hungary., 383(3) pp. 461–466.

Mihucz, V. G., Varga, A. and Za, G. (1998) ‘Determination of Organic Acids in Xylem Sap of Cucumber : Effect of Lead Contamination,’ 314(58) pp. 306–314.

Ministerie Van Volkshuisvesting; Ruimtelijke Ordening En Milieu (2000) ‘Dutch Target and Intervention Values; 2000 (the New Dutch List).’ *Netherlands Government Gazette*, 2000 pp. 1–12.

Miró, M., Fitz, W. J., Swoboda, S. and Wenzel, W. W. (2010) ‘In-situ sampling of soil pore water: Evaluation of linear-type microdialysis probes and suction cups at varied moisture contents.’ *Environmental Chemistry*, 7(1) pp. 123–131.

Mishra, S., Srivastava, S., Dwivedi, S. and Tripathi, R. D. (2013) ‘Investigation of

biochemical responses of Bacopa monnieri L. upon exposure to arsenate.' *Environmental Toxicology*, 28(8) pp. 419–430.

Mohan, D. and Pittman, C. U. (2007) 'Arsenic removal from water/wastewater using adsorbents-A critical review.' *Journal of Hazardous Materials* pp. 1–53.

Moles, A. T., Warton, D. I., Warman, L., Swenson, N. G., Laffan, S. W., Zanne, A. E., Pitman, A., Hemmings, F. A. and Leishman, M. R. (2009) 'Global patterns in plant height.' *Journal of Ecology*, 97(5) pp. 923–932.

Moreno-Jiménez, E., Esteban, E. and Peñalosa, J. M. (2012) 'The fate of arsenic in soil-plant systems.' *Reviews of Environmental Contamination and Toxicology*, 215 pp. 1–37.

Morua, M. (2015) 'Investigating various xylem sap extraction techniques from drought-stressed Geijera parviflora trees' pp. 1–26.

Mosetlha, K., Torto, N. and Wibetoe, G. (2007) 'Determination of Cu and Ni in plants by microdialysis sampling: Comparison of dialyzable metal fractions with total metal content.' *Talanta*. Elsevier, 71(2) pp. 766–770.

Nagajyoti, P. C., Lee, K. D. and Sreekanth, T. V. M. (2010) 'Heavy metals, occurrence and toxicity for plants: A review.' *Environmental Chemistry Letters* pp. 199–216.

Nash, M. J., Maskall, J. E. and Hill, S. J. (2000) 'Methodologies for determination of antimony in terrestrial environmental samples.' *Journal of Environmental Monitoring*, 2(2) pp. 97–109.

Natasha, Shahid, M., Khalid, S., Dumat, C., Pierart, A. and Niazi, N. K. (2019) 'Biogeochemistry of antimony in soil-plant system: Ecotoxicology and human health.' *Applied Geochemistry*. Elsevier, 106(April) pp. 45–59.

Netting, A. G., Theobald, J. C. and Dodd, I. C. (2012) 'Xylem sap collection and extraction methodologies to determine in vivo concentrations of ABA and its bound forms by gas chromatography-mass spectrometry (GC-MS).' *Plant Methods*, 8(1) pp. 1–14.

Nicolau, R., Louis, Y., Omanović, D., Garnier, C., Mounier, S. and and, Pižeta, I. (2008) 'Study of interactions of concentrated marine dissolved organic matter with copper and zinc by pseudopolarography.' *Analytica Chimica Acta*, 618(1) pp. 35–42.

Niedzielski, P. and Siepak, M. (2003) 'Analytical methods for determining arsenic, antimony and selenium in environmental samples.' *Polish Journal of Environmental Studies*, 12(6) pp. 653–667.

Niedzielski, P., Siepak, M., Siepak, J. and Przybyłek, J. (2002) 'Determination of Different Forms of Arsenic, Antimony and Selenium in Water Samples Using Hydride Generation.' *Polish Journal of Environmental Studies*, 11(3) pp. 219–224.

Nimick, D. A. (1998) ‘Arsenic hydrogeochemistry in an irrigated river valley-A reevaluation.’ *Journal of groundwater*. Ground Water Publ Co, 36(5) pp. 743–753.

O’Day, P. A. (2006) ‘Chemistry and mineralogy of arsenic.’ *Elements*, 2(2) pp. 77–83.

Obiora, S. C., Chukwu, A. and Davies, T. C. (2016) ‘Heavy metals and health risk assessment of arable soils and food crops around Pb-Zn mining localities in Enyigba, southeastern Nigeria.’ *Journal of African Earth Sciences*. Elsevier Ltd, 116, April, pp. 182–189.

Oda, A., Shimizu, M., Kuroha, T. and Satoh, S. (2005) ‘Induction of xylem sap methylglycine by a drought and rewatering treatment and its inhibitory effects on the growth and development of plant organs.’ *Physiologia Plantarum*, 124(4) pp. 515–523.

Ogawa, K. and Iwabuchi, M. (2001) ‘A mechanism for promoting the germination of Zinnia elegans seeds by hydrogen peroxide.’ *Plant and Cell Physiology*, 42(3) pp. 286–291.

Ohmori, T., El-Deab, M. S. and Osawa, M. (1999) ‘Electroreduction of nitrate ion to nitrite and ammonia on a gold electrode in acidic and basic sodium and cesium nitrate solutions.’ *Journal of Electroanalytical Chemistry*, 470(1) pp. 46–52.

Olsen, S.R., C.V. Cole, F.S. Watanabe, and L. A. D. (1954) *Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circ.No. 939.* U.S. Gov. Print. Office, Washington DC.

Omanović, D. (2006) ‘Pseudopolarography of trace metals. Part III. Determination of stability constants of labile metal complexes.’ *Croatica Chemica Acta*, 79(1) p. 67.

Omanović, D. and Branica, M. (2003) ‘Pseudopolarography of trace metals: Part I. The automatic ASV measurements of reversible electrode reactions.’ *Journal of Electroanalytical Chemistry*, 543(1) pp. 83–92.

Omanović, D. and Branica, M. (2004) ‘Pseudopolarography of trace metals. Part II. The comparison of the reversible, quasireversible and irreversible electrode reactions.’ *Journal of Electroanalytical Chemistry*, 565(1) pp. 37–48.

Onofri, A., Seddaiu, G. and Piepho, H. P. (2016) ‘Long-Term Experiments with cropping systems: Case studies on data analysis.’ *European Journal of Agronomy*, 77, July, pp. 223–235.

Organization, world health (1996) ‘guidelines for drinking water quality - second edition.’ *international programme on chemical safety*.

Özer, U. Y. and Bogucki, R. F. (1971) ‘Equilibrium studies of antimony(III) chelates in aqueous solution.’ *Journal of Inorganic and Nuclear Chemistry*, 33(12) pp. 4143–4153.

Palma-Lara, I., Martínez-Castillo, M., Quintana-Pérez, J. C., Arellano-Mendoza, M. G., Tamay-Cach, F., Valenzuela-Limón, O. L., García-Montalvo, E. A. and Hernández-Zavala, A. (2019) 'Arsenic exposure: A public health problem leading to several cancers.' *Regulatory toxicology and pharmacology : RTP* p. 104539.

Pampolino, M. F., Laureles, E. V., Gines, H. C. and Buresh, R. J. (2008) 'Soil carbon and nitrogen changes in long-term continuous lowland rice cropping.' *Soil Science Society of America Journal*, 72(3) pp. 798–807.

Panda, S. K., Upadhyay, R. K. and Nath, S. (2010) 'Arsenic Stress in Plants.' *Journal of Agronomy and Crop Science*, 196(3) pp. 161–174.

Pandey, P. and Tripathi, A. K. (2014) 'Impact Of Heavy Metals On Morphological And Biochemical Parameters Of Shorea Robusta Plant.' *Ekologia*, 33(2) pp. 116–126.

Passioura, J. B. (1980) 'The transport of water from soil to shoot in wheat seedlings.' *Journal of Experimental Botany*, 31(1) pp. 333–345.

Pedron, T., Segura, F. R., Paniz, F. P., de Moura Souza, F., dos Santos, M. C., de Magalhães Júnior, A. M. and Batista, B. L. (2019) 'Mitigation of arsenic in rice grains by polishing and washing: Evidencing the benefit and the cost.' *Journal of Cereal Science*. Academic Press, 87, May, pp. 52–58.

Penezić, A., Tercier-Waeber, M. Lou, Abdou, M., Bossy, C., Dutruch, L., Bakker, E. and Schäfer, J. (2020) 'Spatial variability of arsenic speciation in the Gironde Estuary: Emphasis on dynamic (potentially bioavailable) inorganic arsenite and arsenate fractions.' *Marine Chemistry*. Elsevier, 223(December 2019) p. 103804.

Pepponi, G., Meirer, F., Streli, C., Wobrauschek, P., Mihucz, V. G., G. Zaray, V. C., Broekaert, J., Fittschen, U. and Falkenberg, G. (2005) 'Arsenic speciation in Cucumber Cucumis Sativus L.) xylem sap by K-edge TXRF-XANES.' *Anal. Bioanal. Chem.*, 383 pp. 461–466.

Peralta-Videa, J. R., Lopez, M. L., Narayan, M., Saupe, G. and Gardea-Torresdey, J. (2009) 'The biochemistry of environmental heavy metal uptake by plants: Implications for the food chain.' *International Journal of Biochemistry and Cell Biology*, 41(8–9) pp. 1665–1677.

Perrino, C., Marconi, E., Canepari, S., Luisa Astolfi, M. and Perrino, C. (2011) 'Determination of Sb(III), Sb(V) and identification of Sb-containing nanoparticles in airborne particulate matter.' *Procedia Environmental Sciences*, 4 pp. 209–217.

Pettine, M., Casentini, B., Mastroianni, D. and Capri, S. (2007) 'Dissolved inorganic carbon effect in the determination of arsenic and chromium in mineral waters by inductively coupled plasma-mass spectrometry.' *Analytica Chimica Acta*. Elsevier, 599(2) pp. 191–198.

Pickering, I. J., Prince, R. C., George, M. J., Smith, R. D., George, G. N. and Salt, D. E. (2000) 'Reduction and coordination of arsenic in Indian mustard.' *Plant Physiology*, 122(4) pp. 1171–1177.

Pierart, A., Shahid, M., Séjalon-Delmas, N. and Dumat, C. (2015) 'Antimony bioavailability: Knowledge and research perspectives for sustainable agricultures.' *Journal of Hazardous Materials*. Elsevier, 289(February) pp. 219–234.

Pla-Vilanova, P., Galceran, J., Puy, J., Companys, E. and Filella, M. (2019) 'Antimony speciation in aqueous solution followed with AGNES.' *Journal of Electroanalytical Chemistry*. Elsevier B.V., 849 p. 113334.

Pohl, P., Lesniewicz, A. and Zyrnicki, W. (2003) 'Determination of As, Bi, Sb and Sn in conifer needles from various locations in Poland and Norway by hydride generation inductively coupled plasma atomic emission spectrometry.' *International Journal of Environmental Analytical Chemistry*. Taylor & Francis Group, 83(11) pp. 963–970.

Polunina, O. V., Maiboroda, V. P. and Seleznov, A. Y. (2018) 'Evaluation methods of estimation of young apple trees leaf area.' *Bulletin of Uman National University of Horticulture*, (2) pp. 80–82.

Pommerrenig, B., Diehn, T. A. and Bienert, G. P. (2015) 'Metalloido-porins: Essentiality of Nodulin 26-like intrinsic proteins in metalloid transport.' *Plant Science*. Elsevier Ireland Ltd, 238 pp. 212–227.

Porra, R. J. (2005) 'Clorofila Porras 2005' pp. 633–640.

Postupolski, A. and Golimowski, J. (1991) 'Trace determination of antimony and bismuth in snow and water samples by stripping voltammetry.' *Electroanalysis*. Warsaw, Poland, 3(8) pp. 793–797.

Pretti, L., Bazzu, G., Serra, P. A. and Nieddu, G. (2014) 'A novel method for the determination of ascorbic acid and antioxidant capacity in Opuntia ficus indica using in vivo microdialysis.' *Food Chemistry*, 147 pp. 131–137.

Punrat, E., Chuanuwatanakul, S., Kaneta, T., Motomizu, S., Chailapakul, O., Zaib, M., Makshoof, M., Saeed, A., Farooq, U., Nearing, M. M., Koch, I., Reimer, K. J., Niedzielski, P., Siepak, M., Day, P. A. O., Mays, D. E., Hussam, A., Welna, M., Szymczycha-Madeja, A., Pohl, P., Ma, J., Sengupta, M. K., Yuan, D., Dasgupta, P. K., Amaral, C. D. B., Nóbrega, J. A., Nogueira, A. R. A., Cavicchioli, A., La-scalea, M. A., Gutz, G. R., Tyson, J., Chen, M. L., Ma, L. Y., Chen, X. W., Punrat, E., Chuanuwatanakul, S., Kaneta, T., Motomizu, S., Chailapakul, O., Hotel, D., Llorente-mirandes, T., Calderón, J., Centrich, F., Rubio, R., López-sánchez, J. F. and Thomas, D. J. (2014) 'Method development for the determination of arsenic by sequential injection/anodic stripping voltammetry using long-lasting gold-modified screen-printed carbon electrode.' *Talanta*. Elsevier B.V., 2013(June) pp. 1018–1025.

Quentel, F. and Filella, M. (2002) 'Determination of inorganic antimony species in seawater by differential pulse anodic stripping voltammetry: Stability of the trivalent state.' *Analytica Chimica Acta*, 452(2) pp. 237–244.

Quentel, F., Filella, M., Elleouet, C. and Madec, C. (2006) 'Sb(III) oxidation by iodate in seawater: A cautionary tale.' *Science of The Total Environment*. Elsevier, 355(1–3) pp. 259–263.

RA (2001) 'Philippine Mining Act of 1995,.' Philippines, R. of the (ed.) pp. 1–12.

Raab, A., Feldmann, J. and Meharg, A. A. (2004) 'The Nature of Arsenic-Phytochelatin Complexes in Holcus lanatus and Pteris cretica.' *Plant Physiology*. Department of Chemistry, University of Aberdeen, Meston Building, Meston Walk, Aberdeen AB24 3UE, United Kingdom., 134(3) pp. 1113–1122.

Raab, A., Meharg, A. A., Jaspars, M., Genney, D. R. and Feldmann, J. (2004) 'Arsenic–glutathione complexes—their stability in solution and during separation by different HPLC modes.' *J. Anal. At. Spectrom.*, 19(1) pp. 183–190.

Raab, A., Schat, H., Meharg, A. A., Feldmann, J., J., A. R. S. H. M. A. A. and F., Raab, A., Schat, H., Meharg, A. A. and Feldmann, J. (2005) 'Uptake, translocation and transformation of arsenate and arsenite in sunflower (Helianthus annuus): Formation of arsenic-phytochelatin complexes during exposure to high arsenic concentrations.' *New Phytologist*. Department of Chemistry, University of Aberdeen, Meston Building, Meston Walk, Aberdeen AB24 3UE, UK., 168(3) pp. 551–558.

Rahaman, M. S., Akter, M., Rahman, M. M., Sikder, M. T., Hosokawa, T., Saito, T. and Kurasaki, M. (2020) 'Investigating the protective actions of D-pinitol against arsenic-induced toxicity in PC12 cells and the underlying mechanism.' *Environmental Toxicology and Pharmacology*. Elsevier B.V., 74, February, p. 103302.

Rahman, M. A. and Hasegawa, H. (2011) 'High levels of inorganic arsenic in rice in areas where arsenic-contaminated water is used for irrigation and cooking.' *Science of The Total Environment*, 409(22) pp. 4645–4655.

Raskin, I., Kumar, P. N., Dushenkov, S. and Salt, D. E. (1994) 'Bioconcentration of heavy metals by plants.' *Current Opinion in Biotechnology*, 5(3) pp. 285–290.

Rauser, W. E. (1990) 'Phytochelatins.' *Annual Review of Biochemistry*, 59 pp. 61–86.

Reimann, C., Demetriades, A., Eggen, O. A. and Filzmoser, P. (2009) 'The EuroGeoSurveys geochemical mapping of agricultural and grazing land soils project (GEMAS) -Evaluation of quality control results of aqua regia extraction analysis.' *EuroGeoSurveys Geochemistry* , (May 2014) p. 94.

Rellán-Álvarez, R., El-Jendoubi, H., Wohlgemuth, G., Abadía, A., Fiehn, O., Abadía, J., Álvarez-Fernández, A., Schjoerring, J. K., Zocchi, G., Degli, U., Di Milano, S., Yoshihara, T.

and Alvarez-Fernández, A. (2011) ‘Metabolite profile changes in xylem sap and leaf extracts of strategy I plants in response to iron deficiency and resupply.’ *Frontiers in plant science*, 2 p. 66.

Rellán-Álvarez, R., Ortega-Villasante, C., Álvarez-Fernández, A., Campo, F. F. del and Hernández, L. E. (2006) ‘Stress Responses of Zea mays to Cadmium and Mercury.’ *Plant and Soil*, 279(1–2) pp. 41–50.

Ren, J. H., Ma, L. Q., Sun, H. J., Cai, F. and Luo, J. (2014) ‘Antimony uptake, translocation and speciation in rice plants exposed to antimonite and antimonate.’ *Science of the Total Environment*. Elsevier B.V., 475 pp. 83–89.

Rodriguez-Iruretagoiena, A., Trebolazabala, J., Martinez-Arkarazo, I., De Diego, A. and Madariaga, J. M. (2015) ‘Metals and metalloids in fruits of tomatoes (Solanum lycopersicum) and their cultivation soils in the Basque Country: Concentrations and accumulation trends.’ *Food Chemistry*. Elsevier Ltd, 173, February, pp. 1083–1089.

Rosas-Castor, J. M., Guzmán-Mar, J. L., Hernández-Ramírez, A., Garza-González, M. T. and Hinojosa-Reyes, L. (2014) ‘Arsenic accumulation in maize crop (Zea mays): A review.’ *Science of The Total Environment*. Elsevier, 488–489(1) pp. 176–187.

Rousk, J. and Jones, D. L. (2010) ‘Loss of low molecular weight dissolved organic carbon (DOC) and nitrogen (DON) in H2O and 0.5M K2SO4 soil extracts.’ *Soil Biology and Biochemistry*, 42(12) pp. 2331–2335.

Sabir, M., Waraich, E. A., Hakeem, K. R., Öztürk, M., Ahmad, H. R. and Shahid, M. (2015) ‘Phytoremediation: Mechanisms and Adaptations. Mechanisms and Adaptations.’ *Soil Remediation and Plants: Prospects and Challenges* pp. 85–105.

Sadiq, M. (1992) *Toxic metal chemistry in marine environments*. *Marcel Dekker*. New York City.

Salama, A. K. and Radwan, M. A. (2005) ‘Heavy metals (Cd,Pb) and trace elements (Cu,Zn) contents in some foodstuffs from the Egyptian market.’ *Emirates Journal of Food and Agriculture*, 17(1) pp. 34–42.

Salaun, P. (2017) ‘Editorial: Environmental Electrochemistry.’ *Current Opinion in Electrochemistry*. Elsevier B.V., 3(1) pp. 75–77.

Salaün, P. and van den Berg, C. M. G. (2006) ‘Voltammetric detection of mercury and copper in seawater using a gold microwire electrode.’ *Analytical chemistry*, 78(14) pp. 5052–60.

Salaün, P. and Frézard, F. (2013) ‘Unexpectedly high levels of antimony (III) in the pentavalent antimonial drug Glucantime: insights from a new voltammetric approach.’ *Analytical and Bioanalytical Chemistry*. Liverpool, 405(15) pp. 5201–5214.

Salaün, P., Gibbon-Walsh, K. B., Alves, G. M. S. S., Soares, H. M. V. M. V. M. and van den Berg, C. M. G. G. (2012) 'Determination of arsenic and antimony in seawater by voltammetric and chronopotentiometric stripping using a vibrated gold microwire electrode.' *Analytica Chimica Acta*. Liverpool: Elsevier B.V., 746(March 2014) pp. 53–62.

Salaün, P., Gibbon-Walsh, K. and van den Berg, C. M. G. (2011) 'Beyond the Hydrogen Wave: New Frontier in the Detection of Trace Elements by Stripping Voltammetry.' *Analytical Chemistry*, 83(10) pp. 3848–3856.

Salaün, P., Planer-Friedrich, B. and van den Berg, C. M. . (2007) 'Inorganic arsenic speciation in water and seawater by anodic stripping voltammetry with a gold microelectrode.' *Analytica Chimica Acta*. Liverpool, 585(2) pp. 312–322.

Samarah, L. Z., Tran, T. H., Stacey, G. and Vertes, A. (2020) 'In Vivo Chemical Analysis of Plant Sap from the Xylem and Single Parenchymal Cells by Capillary Microsampling Electrospray Ionization Mass Spectrometry.' *Analytical Chemistry*, 92(10) pp. 7299–7306.

Samota, M. K., Navnage, N. P. and Bhatt, L. (2017) 'Role of Macro and Micronutrient in Development and Growth of Plant,' 10(18) pp. 3171–3173.

Santos, V. S., Santos, W. de J. R., Kubota, L. T. and Tarley, C. R. T. (2009) 'Speciation of Sb(III) and Sb(V) in meglumine antimoniate pharmaceutical formulations by PSA using carbon nanotube electrode.' *Journal of Pharmaceutical and Biomedical Analysis*, 50(2) pp. 151–157.

Satoh, S. (2006) 'Organic substances in xylem sap delivered to above-ground organs by the roots.' *Journal of Plant Research*, 119(3) pp. 179–187.

Scharifker, B. R., Mostany, J. and Serruya, A. (2000) 'Catalytic reduction of nitrate during electrodeposition of thallium from Tl3+ solution.' *Electrochemistry Communications*, 2(6) pp. 448–451.

Scholander, P. F., Bradstreet, E. D., Hemmingsen, E. A. and Hammel, H. T. (1965) 'Sap Pressure in Vascular Plants: Negative hydrostatic pressure can be measured in plants.' *Science*, 148(3668) pp. 339–346.

Schurr, U. (1998) 'Xylem sap sampling—new approaches to an old topic.' *Trends in Plant Science*. Elsevier Current Trends, 3(8) pp. 293–298.

Schurr, U. (1999) 'Dynamics of Nutrient Transport from the Root to the Shoot.' *In*. Springer, Berlin, Heidelberg, pp. 234–253.

Shahid, M., Khalid, S., Abbas, G., Shahid, N., Nadeem, M., Sabir, M., Aslam, M. and Dumat, C. (2015) 'Heavy metal stress and crop productivity.' *In Crop Production and Global Environmental Issues*. Springer International Publishing, pp. 1–25.

Sharma, S. D. (2013) 'History of Rice in Southeast Asia and Australia.' *Journal of Chemical Information and Modeling*, 53(9) pp. 1689–1699.

Shri, M., Singh, P. K., Kidwai, M., Gautam, N., Dubey, S., Verma, G. and Chakrabarty, D. (2019) 'Recent advances in arsenic metabolism in plants: Current status, challenges and highlighted biotechnological intervention to reduce grain arsenic in rice.' *Metallomics*, 11(3) pp. 519–532.

Simoni, R. D., Hill, R. L. and Vaughan, M. (2005) 'Benedict ' s Solution , a Reagent for Measuring Reducing Sugars : the Clinical Chemistry of Stanley R . Benedict,' 277(16) pp. 10–12.

Slamet-loedin, I., Slamet-loedin, I. H., Johnson-beebout, S. E., Impa, S. and Tsakirpaloglou, N. (2015) 'Enriching rice with Zn and Fe while minimizing Cd risk.' *Frontiers in Plant Science*, 6(MAR).

Smedley, P. L. and Kinniburgh, D. G. (2000) 'Source and behaviour of arsenic in natural waters.' *British Geological Survey* p. 61.

Smedley, P. L. and Kinniburgh, D. G. (2002) 'A review of the source, behaviour and distribution of arsenic in natural waters.' *Applied Geochemistry*, 17(5) pp. 517–568.

Smith, A. H., Lingas, E. O. and Rahman, M. (2000) 'Contamination of drinking-water by arsenic in Bangladesh: A public health emergency.' *Bulletin of the World Health Organization*, 78(9) pp. 1093–1103.

Smith, A. H. and Smith, M. M. H. (2004) 'Arsenic drinking water regulations in developing countries with extensive exposure.' *Toxicology*, 198(1–3) pp. 39–44.

Sobrado, M. A. (2007) 'Relationship of water transport to anatomical features in the mangrove Laguncularia racemosa grown under contrasting salinities.' *New Phytologist*, 173(3) pp. 584–591.

Sørensen, O., Andersen, A., Olsen, H., Alexandr, K., Ekstrøm, P. O., Giercksky, K. E. and Flatmark, K. (2010) 'Validation and use of microdialysis for determination of pharmacokinetic properties of the chemotherapeutic agent mitomycin C - an experimental study.' *BMC Cancer*, 10.

Spurgeon, D. J., Rowland, P., Ainsworth, G., Rothery, P., Long, S. and Black, H. I. J. (2008) 'Geographical and pedological drivers of distribution and risks to soil fauna of seven metals (Cd, Cu, Cr, Ni, Pb, V and Zn) in British soils.' *Environmental Pollution*, 153(2) pp. 273–283.

Sreekanth, T. V. M., Nagajyothi, P. C., Lee, K. D. and Prasad, T. N. V. K. V. (2013) 'Occurrence, physiological responses and toxicity of nickel in plants.' *International Journal of Environmental Science and Technology*. Center for Environmental and Energy Research and Studies pp. 1129–1140.

Stazi, S. R., Cassaniti, C., Marabottini, R., Giuffrida, F. and Leonardi, C. (2016) 'Arsenic uptake and partitioning in grafted tomato plants.' *Horticulture, Environment, and Biotechnology*. Korean Society for Horticultural Science, 57(3) pp. 241–247.

Steudle, E. (2001) 'The cohesion-tension mechanism and the acquisition of water by plant roots.' *Annual Review of Plant Biology*, 52 pp. 847–875.

Stoeva, N., Berova, M. and Zlatev, Z. (2005) 'Effect of arsenic on some physiological parameters in bean plants.' *Biologia Plantarum*, 49(2) pp. 293–296.

Sulyok, M., Miró, M., Stingeder, G. and Koellensperger, G. (2005) 'The potential of flow-through microdialysis for probing low-molecular weight organic anions in rhizosphere soil solution.' *Analytica Chimica Acta*. Elsevier, 546(1) pp. 1–10.

Sun, G., Williams, P. N. and Zhu, Y. (2009) 'Mechanisms of Arsenic Uptake and Metabolism by Plants : Focusing on Rice.' *Environmental Toxicology*, 134(November) pp. 1–6.

Sun, H., Yan, S. C. and Cheng, W. S. (2000) 'Interaction of antimony tartrate with the tripeptide glutathione.' *European Journal of Biochemistry*, 267(17) pp. 5450–5457.

Takarina, N. D. and Pin, T. G. (2017) 'Bioconcentration Factor (BCF) and Translocation Factor (TF) of Heavy Metals in Mangrove Trees of Blanakan Fish Farm.' *Makara Journal of Science*, 21(2).

Tamás, M. J. (2016) 'Cellular and molecular mechanisms of antimony transport, toxicity and resistance.' *Environmental Chemistry*, 13(6) pp. 955–962.

Tatár, E., Mihucz, V. G., Kmethy, B., Záray, G. and Fodor, F. (2000) 'Determination of organic acids and their role in nickel transport within cucumber plants.' *Microchemical Journal*, 67(1–3) pp. 73–81.

Tatár, E., Mihucz, V. G., Varga, A., Záray, G. and Fodor, F. (1998) 'Determination of Organic Acids in Xylem Sap of Cucumber: Effect of Lead Contamination.' *Microchemical Journal*. Elsevier Inc., 58(3) pp. 306–314.

Telford, K., Maher, W., Krikowa, F. and Foster, S. (2008) 'Measurement of total antimony and antimony species in mine contaminated soils by ICPMS and HPLC-ICPMS.' *Journal of Environmental Monitoring*, 10(1) pp. 136–140.

Telford, K., Maher, W., Krikowa, F., Foster, S., Ellwood, M. J. M. J., Ashley, P. M. P. M., Lockwood, P. V. P. V. and Wilson, S. C. S. C. (2009) 'Bioaccumulation of antimony and arsenic in a highly contaminated stream adjacent to the Hillgrove Mine, NSW, Australia.' *Environmental Chemistry*, 6(2) pp. 133–143.

Thomas, G. W. (1996) 'Soil pH and soil acidity.' *In* D.L. Sparks et al., editors (ed.) *Methods of soil analysis: Part 3. SSSA Book Series No. 5. SSSA,* pp. 475–490.

Tian, T., Zhou, H., Gu, J., Jia, R., Li, H., Wang, Q., Zeng, M. and Liao, B. (2019) 'Cadmium accumulation and bioavailability in paddy soil under different water regimes for different growth stages of rice (Oryza sativa L.).' *Plant and Soil*. Springer International Publishing, July.

Timofeev, I. and Hutchinson, P. (2008a) 'Microdialysis.' *In Essentials of Neuroanesthesia and Neurointensive Care*. Elsevier, pp. 277–282.

Timofeev, I. and Hutchinson, P. (2008b) 'Microdialysis Learn more about Microdialysis Microdialysis Chemical and Biochemical Approaches for the Study of Anesthetic Function Part B Carrier-mediated and artificial-cell tar-.'

Toghill, K. E., Lu, M., Compton, R. G. and Kathryn E. Toghill, Min Lu, and R. G. C. (2011) 'Electroanalytical Determination of Antimony.' *International Journal of Electrochemical Science*, 6(8) pp. 3057–3076.

Tollestrup, K., Frost, F. J., Harter, L. C. and McMillan, G. P. (2003) 'Mortality among Children Residing near the American Smelting and Refining Company (ASARCO) Copper Smelter in Ruston, Washington.' *Archives of Environmental Health: An International Journal*, 58(11) pp. 683–691.

Torto, N., Mwatseteza, J. and Laurell, T. (2001) 'Microdialysis Sampling: Challenges and New Frontiers.' *LC GC Europe*, 14(9) pp. 536–546.

Torto, N., Mwatseteza, J. and Sawula, G. (2002) 'A study of microdialysis sampling of metal ions.' *Analytica Chimica Acta*. Elsevier, 456(2) pp. 253–261.

Trejo-Téllez, L. I. (2012) 'Nutrient Solutions for Hydroponic Systems.' *In* Asao, F. C. G.-M. E.-T. (ed.). Rijeka: IntechOpen, p. Ch. 1.

Tsang, J. J., Rozan, T. F., Hsu-Kim, H., Mullaugh, K. M. and Luther, G. W. (2006) 'Pseudopolarographic determination of Cd2+ complexation in freshwater.' *Environmental Science and Technology*, 40(17) pp. 5388–5394.

Tschan, M., Robinson, B. H. and Schulin, R. (2009) 'Antimony in the soil - Plant system - A review.' *Environmental Chemistry*, 6(2) pp. 106–115.

Tschan, M., Robinson, B. and Schulin, R. (2008) 'Antimony uptake by Zea mays (L.) and Helianthus annuus (L.) from nutrient solution.' *Environmental Geochemistry and Health*, 30(2) pp. 187–191.

Tsukagoshi, S. and Shinohara, Y. (2015) *Nutrition and Nutrient Uptake in Soilless Culture Systems*. *Plant Factory: An Indoor Vertical Farming System for Efficient Quality Food Production*. Elsevier Inc.

Tuyogon, D. S. J., Impa, S. M., Castillo, O. B., Larazo, W. and Johnson-Beebout, S. E. (2016) 'Enriching rice grain zinc through zinc fertilization and water management.' *Soil Science*

Society of America Journal, 80(1) pp. 121–134.

Tylenda, C. A., Sullivan, D. W. and Fowler, B. A. (2015) *Antimony*. *Handbook on the Toxicology of Metals: Fourth Edition*. Fourth Edi, Elsevier.

U.S. Department of Health and Human (2018) *Revised Draft : Report on Carcinogens Monograph on Antimony Trioxide*.

U.S. Geological Survey (2004) 'Mineral Commodity Profiles-Antimony.' *U.S. Department of the Interior: U.S. Geological Survey* pp. 1–35.

Ugochukwu, G. C., Eneh, F. U., Igwilo, I. . and Aloh, C. H. (2017) 'Comparative study on the heavy metal content of domestic rice (Oryza sativa Comparative study on the heavy metal content of domestic rice (Oryza sativa L) brands common in Awka, Nigeria.' *IOSR Journal of Environmental Science, Toxicology and Food Technology*, 11(8) pp. 67–70.

UN (ed.) (2015) *Crop Prospects and Food Situation*. Rome: FAO.

Ungureanu, G., Santos, S., Boaventura, R. and Botelho, C. (2015) 'Arsenic and antimony in water and wastewater: Overview of removal techniques with special reference to latest advances in adsorption.' *Journal of Environmental Management*, 151, March, pp. 326–342.

Uroic, M. K. (2011) *The impact of arsenic species on the production and composition of xylem sap*. *Environmental & Analytical Chemistry*. University of Aberdeen. Retrieved from internal-pdf://145.35.116.156/PhD thesis The impact of As MK Uroic.pdf.

Uroic, M. K., Salaün, P., Raab, A. and Feldmann, J. (2012) 'Arsenate impact on the metabolite profile, production, and arsenic loading of xylem sap in cucumbers (Cucumis sativus L.).' *Frontiers in Physiology*, 3 APR(March) pp. 1–23.

Varsányi, I., Fodré, Z. and Bartha, A. (1991) 'Arsenic in drinking water and mortality in the Southern Great Plain, Hungary.' *Environmental Geochemistry and Health*. Kluwer Academic Publishers, 13(1) pp. 14–22.

Violante, A., Cozzolino, V., Perelomov, L., Caporale, A. . and Pigna, M. (2010) 'Mobility and bioavailability of heavy metals and metalloids in soil environments.' *Journal of soil science and plant nutrition*. Sociedad Chilena de la Ciencia del Suelo, 10(3) pp. 268–292.

Vithanage, M., Dabrowska, B. B., Mukherjee, A. B., Sandhi, A. and Bhattacharya, P. (2012) 'Arsenic uptake by plants and possible phytoremediation applications: A brief overview.' *Environmental Chemistry Letters* pp. 217–224.

Wagner, S. E., Peryea, F. J. and Filby, R. A. (2003) 'Antimony Impurity in Lead Arsenate Insecticide Enhances the Antimony Content of Old Orchard Soils.' *Journal of Environmental Quality*. Wiley, 32(2) pp. 736–738.

Wan, X. M., Tandy, S., Hockmann, K. and Schulin, R. (2013) ‘Changes in Sb speciation with waterlogging of shooting range soils and impacts on plant uptake.’ *Environmental Pollution*. Elsevier Ltd, 172, January, pp. 53–60.

Wang, S., Shi, X., Sun, H., Chen, Y., Pan, H., Yang, X. and Rafiq, T. (2014) ‘Variations in Metal Tolerance and Accumulation in Three Hydroponically Cultivated Varieties of Salix integra Treated with Lead.’ Reigosa, M. (ed.) *PLoS ONE*. Public Library of Science, 9(9) p. e108568.

Wang, T., Yang, Q., Wang, Y., Wang, J., Zhang, Y. and Pan, W.-P. P. (2020) ‘Arsenic release and transformation in co-combustion of biomass and coal: Effect of mineral elements and volatile matter in biomass.’ *Bioresource technology*. Beijing, PR China: Elsevier Ltd, 297, February, p. 122388.

Wang, Z., Zeng, X., Geng, M., Chen, C., Cai, J., Yu, X., Hou, Y. and Zhang, H. (2015) ‘Health risks of heavy metals uptake by crops grown in a sewage irrigation area in China.’ *Polish Journal of Environmental Studies*, 24(3) pp. 1379–1386.

Welch, A. H. and Stollenwerk, K. G. (eds) (2003) *Arsenic in Ground Water*. *Springer Science Business Media New York*. Boston, MA: Springer US.

White, M. C., Chaney, R. L., Decker, A. M. and R., and M. W. D. A. (1981) ‘Metal Complexation in Xylem Fluid: I. Chemical composition of tomato and soybean stem exudate.’ *Plant Physiology*, 67(2) pp. 292–300.

WHO (2003a) ‘Antimony in Drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality.’ *Who* pp. 1–9.

WHO (2003b) *Background document for preparation of WHO Guidelines for drinking-water quality: Antimony in drinking water.* Geneva, Switzerland.

WHO (2003c) ‘Chromium in drinking-water. Background document for preparation of WHO Guidelines for drinking-water quality.’ *(WHO/SDE/WSH/03.04/4)*, (3) pp. 334–335.

Wickliff, J. L. and Aronoff, S. (1962) *Quantitative measurement of leaf chlorophylss by spectrophotometry of their pheophytins in aqueous alcoholic extracts*. Iowa, USA.

Williams, P. N., Islam, M. R., Adomako, E. E., Raab, A., Hossain, S. A., Zhu, Y. G., Feldmann, J. and Meharg, A. A. (2006) ‘Increase in rice grain arsenic for regions of Bangladesh irrigating paddies with elevated arsenic in groundwaters.’ *Environmental Science and Technology* pp. 4903–4908.

Wilson, S. C., Lockwood, P. V., Ashley, P. M. and Tighe, M. (2010) ‘The chemistry and behaviour of antimony in the soil environment with comparisons to arsenic: A critical review.’ *Environmental Pollution*. Elsevier Ltd, 158(5) pp. 1169–1181.

Woolson, E. A., Axley, J. H. and Kearney, P. C. (1971) ‘Correlation between Available Soil

Arsenic, Estimated by Six Methods, and Response of Corn (Zea mays L.)1.' *Soil Science Society of America Journal*. Soil Science Society of America, 35(1) p. 101.

Wu, D. and Sun, S. (2016) 'Speciation analysis of As, Sb and Se.' *Trends in Environmental Analytical Chemistry*. Elsevier Inc., 11, July, pp. 9–22.

Wu, T.-L. L., Cui, X.-D. D., Cui, P.-X. X., Ata-Ul-Karim, S. T., Sun, Q., Liu, C., Fan, T.-T. T., Gong, H., Zhou, D.-M. M. and Wang, Y.-J. J. (2019) 'Speciation and location of arsenic and antimony in rice samples around antimony mining area.' *Environmental Pollution*. Elsevier Ltd, 252, September, pp. 1439–1447.

www.IRRI.org (2019) *Long-Term Continuous Cropping Experiment (LTCCE) | International Rice Research Institute*. [Online] [Accessed on 18th November 2019] https://www.irri.org/long-term-continuous-cropping-experiment-ltcce.

Wyrwicka, A., Urbaniak, M. and Przybylski, M. (2019) ' The response of cucumber plants (Cucumis sativus L.) to the application of PCB-contaminated sewage sludge and urban sediment .' *PeerJ*, 7 p. e6743.

Xu, X. Y., McGrath, S. P. and Zhao, F. J. (2007) 'Rapid reduction of arsenate in the medium mediated by plant roots.' *New Phytologist*, 176(3) pp. 590–599.

Yadav, S. K. (2010) 'Heavy metals toxicity in plants: An overview on the role of glutathione and phytochelatins in heavy metal stress tolerance of plants.' *South African Journal of Botany*. Elsevier B.V., 76(2) pp. 167–179.

Ye, W.-L. L., Wood, B. A., Stroud, J. L., Andralojc, P. J., Raab, A., McGrath, S. P., Feldmann, J. and Zhao, F.-J. J. (2010) 'Arsenic speciation in phloem and xylem exudates of castor bean.' *Plant Physiology*, 154(3) pp. 1505–1513.

Zavala, Y. J. and Duxbury, J. M. (2008) 'Arsenic in rice: I. Estimating normal levels of total arsenic in rice grain.' *Environmental Science and Technology*, 42(10) pp. 3856–3860.

Zengin, F. K. and Munzuroglu, O. (2005) 'Effects of some heavy metals on content of chlorophyll, proline and some antioxidant chemicals in bean (Phaseolus vulgaris L.) seedlings.' *Acta Biologica Cracoviensia Series Botanica*, 47(2) pp. 157–164.

Zhang, H. and Selim, H. M. (2005) 'Kinetics of Arsenate Adsorption−Desorption in Soils.' *Environmental Science & Technology*, 39(16) pp. 6101–6108.

Zhang, T., Ruan, J., Zhang, B., Lu, S., Gao, C., Huang, L., Bai, X., Xie, L., Gui, M. and Qiu, R. (2019) 'Heavy metals in human urine, foods and drinking water from an e-waste dismantling area: Identification of exposure sources and metal-induced health risk.' *Ecotoxicology and Environmental Safety*. Academic Press, 169, March, pp. 707–713.

Zhang, W., Cai, Y., Tu, C. and Ma, L. Q. (2002) 'Arsenic speciation and distribution in an arsenic hyperaccumulating plant.' *Science of the Total Environment*, 300(1–3) pp. 167–

177.

Zhao, F.-J., Ma, Y., Zhu, Y.-G., Tang, Z. and McGrath, S. P. (2015) ‘Soil Contamination in China: Current Status and Mitigation Strategies.’ *Environmental Science & Technology*. American Chemical Society, 49(2) pp. 750–759.

Zhao, F.-J., McGrath, S. P. and Meharg, A. A. (2010) ‘Arsenic as a Food Chain Contaminant: Mechanisms of Plant Uptake and Metabolism and Mitigation Strategies.’ *Annual Review of Plant Biology*. Annual Reviews, 61(1) pp. 535–559.

Zheng, J., Iijima, A. and Furuta, N. (2001) ‘Complexation effect of antimony compounds with citric acid and its application to the speciation of antimony(III) and antimony(V) using HPLC-ICP-MS.’ *Journal of Analytical Atomic Spectrometry*, 16(8) pp. 812–818.

Zheng, R. L., Sun, G. X. and Zhu, Y. G. (2013) ‘Effects of microbial processes on the fate of arsenic in paddy soil.’ *Chinese Science Bulletin* pp. 186–193.

Zhou, S. N., Ouyang, G. and Pawliszyn, J. (2008) ‘Comparison of microdialysis with solid-phase microextraction for in vitro and in vivo studies.’ *Journal of Chromatography A*, 1196–1197(1–2) pp. 46–56.

Zhou, X., Sun, C., Zhu, P. and Liu, F. (2018) ‘Effects of Antimony Stress on Photosynthesis and Growth of Acorus calamus.’ *Frontiers in Plant Science*. Frontiers Media S.A., 9(May) pp. 1–9.

Zulkafflee, N. S., Redzuan, N. A. M., Hanafi, Z., Selamat, J., Ismail, M. R., Praveena, S. M. and Razis, A. F. A. (2019) ‘Heavy metal in paddy soil and its bioavailability in rice using in vitro digestion model for health risk assessment.’ *International Journal of Environmental Research and Public Health*, 16(23).

CHAPTER 5

DETERMINATION OF STABILITY CONSTANTS OF SB SPECIES WITH MODEL LIGANDS

Index of Figures

Index of Tables

5.1 Introduction

The increased use of antimony (Sb) has led to many environmental soils and groundwater contamination problems, and understanding their biogeochemical cycling is of prime importance to predict potential contamination issues. Sb is traditionally used in a wide range of industrial applications including insecticides (Wagner et al., 2003), ceramic and glass making (Wu and Sun, 2016), fire retardants fabrication (Filella, Belzile, and Y.-W. Chen, 2002a), lead-antimony based alloy batteries (US Geological Survey, 2004), ball bearings and ammunition (US Geological Survey, 2004), automobile linings (US Geological Survey, 2004), in medicine because of its anti-cancer and anti-parasitic activities (Leishmaniasis) (Brochu et al., 2003; Cheng and Sun, 2014) and recently in microelectronics (Natasha et al., 2019). Sb has also been used as a catalyst in the polyethene terephthalate (PET) fabrication, and recent studies showed that Sb had been found in water and fruit juices contained in PET bottles at levels exceeding the EU set limit (Carneado et al., 2015; US Department of Health and Human, 2018). Sb is poisonous to humans and animals at high dosage analogous to As poisoning (Gebel, 1997; WHO, 2003a; Lombi and Holm, 2010). Despite its toxicity, Sb received little attention relatively with other toxic heavy metal and other metalloids (i.e., As) (Filella et al., 2002; Toghill et al., 2011; Daus and Hansen, 2016).

Trace metal speciation is aimed at determining all chemical species formed by that element in the environment (Filella et al., 2009). Identification of stable organic species by techniques such as Inductively Coupled Plasma- Mass Spectrometry (ICP-MS) and Liquid Chromatography-Mass Spectroscopy (LC-MS) is commonly achieved with sufficiently stable species to undergo the chromatographic separation step without change. The detection and identification of more reactive, relatively weak complexes, that can play a preponderant role in the transport of these elements are, however, much less known (Filella and May, 2005a). Michalski et al. (2012) summarised several chromatographic analysis of Sb speciation. In LC, a complexing agent was needed to preserve the Sb trivalent state to obtain a well-defined peak shape and quantitatively elute Sb in the anion exchange column (Perrino et al., 2011). In the last few years, several complexes were suggested, and phthalic acid was found to be the best (Daus and Hansen, 2016). EDTA was first used as a complexing agent of Sb (Lintschinger et al., 1997) and from then on was used in different variations (Chen et al., 2006; Hansen, 2011; Kolbe et al., 2012). It was found out that the accepted range of stable Sb(III) with EDTA can be analysed at a pH range of only 4.3-5 (acidic) (Filella and May, 2003; Hansen and Pergantis, 2008). In the case of environmental analysis or biological media (i.e. plants) where pH is at around 6-7 (neutral). Figure 5.1 shows that despite the high concentrations of carboxylic acids, chromatographic studies predict that Sb are present as not complexed (i.e. free ion). An alternative possibility is that these metalloids form weak complexes that are too weak to undergo the chromatographic process at neutral pH (e.g. 6.5). These weak complexes may be destroyed during the chromatographic step and the use of other analytical techniques might be required (Feldmann et al., 2009). The answer to the question of whether metalloids (i.e. Sb, As) cannot be transported from the roots to the shoots when bound to ligands must be addressed by using a sensitive and selective analytical method to identify weak arsenic complexes at neutral pH like those that may exist in the xylem sap matrix.

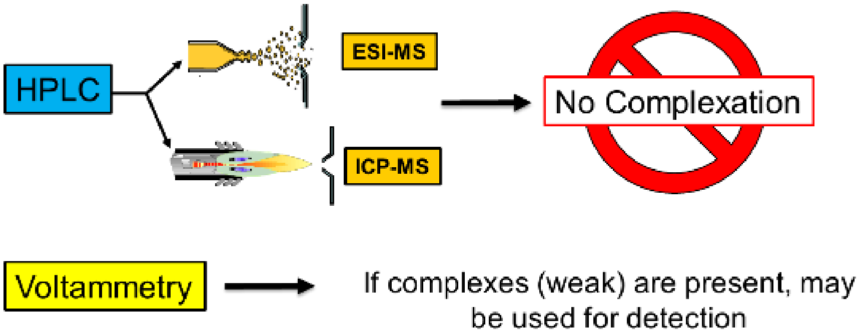


Figure 5. 1. Research hypothesis stating that voltammetry may complement hyphenated techniques (i.e. HPLC) in metalloid speciation in the environment

Many metal speciation is predominantly controlled by ligand interactions (or active sites of natural organic matter)(Louis et al., 2008). The speciation of metalloids (i.e. Sb) is often limited to the differentiation of oxidation states, not so much about the complexation of these hydroxy species with ligands. Sb chemical speciation with low molecular weight ligands (l.m.w) has not previously modelled comprehensively, even though Sb is toxic and of increasing environmental significance (Filella and May, 2005; Filella et al., 2009; Filella, 2013). The scarcity of thermodynamic data of Sb complexation with l.m.w in environmental or biological media may be attributed to challenging issues in the analysis, such as the following. This lack of data can also be attributed to the difficulty to study the free Sb ions in solutions other than very dilute ones because Sb (+3 and +5) are easily hydrolysed in aqueous solutions (Filella and May, 2005). In terms of the experimental procedure, the current method used (i.e. glass potentiometry) either done in very acidic media or the limitation of not being able to measure at low concentrations (Filella and May, 2005a, 2005b). Available thermodynamic data are either old or sparse and rarely measured in natural conditions (often too acidic or high concentration) (Filella and May, 2005a), the required information is not available or given in the publication (Filella and May, 2003); redundant information in the data compilation, and are measured in the same condition background electrolyte media (Filella and May, 2005b). Furthermore, significant errors are repeatedly produced from repeated experimental measurements without further analysis or discussions. Among several methods for the chemical speciation, using voltammetry, lower concentrations can be measured at neutral pH. Voltammetric approaches have been used in the past to determine whether there is complexation of other ligands to Sb in the plants. However, the voltammetric analysis of this metalloid is not straight forward, aside from the matrix effects, sample preparation, and the type of electrode to be used are some of the hindrances in the analysis (Kowalska et al., 1999). (Cavicchioli et al., 2004). Available voltammetric methods for Sb measurements are done in acidic conditions and not so much in natural conditions of pH are lacking.

Voltammetry, specifically anodic stripping voltammetry (ASV), is an attractive method in terms of satisfying the requirement concerning sensitivity and selectivity. Also, it has the advantage of low contamination and low risk of sample alteration during analysis (van Leeuwen et al., 2005). The limitation of the ASV technique is a kinetically dependent technique (i.e. underestimation of complexing parameters due to dissociation of inert complexes during the accumulation period). This limitation, however, can be seen as a good point since, in natural biological processes, such processes might also occur in the solution around the cell membrane (van Leeuwen et al., 2005). One of the techniques is by using a gold micro-wire electrode that is well suited for the speciation of inorganic arsenic and has the advantage of low cost, portability, and may detect weak complexes

(Billon and Van Den Berg, 2004; Salaün et al., 2007; Feldmann et al., 2009; Salaun, 2017). The technique may also be used to gain insights into the complexation patterns of inorganic and organic-bound arsenic and highlight the formation of weak, fast-dissociating species as well as inert, stable, complexes. Voltammetry may complement nicely the commonly used chromatographic and hyphenated techniques.

Pseudopolarography (PP) is an electroanalytical method based on ASV that is suitable for metal speciation at natural concentrations, capable of measuring complex thermodynamic stability which is pH and ligand concentration-independent (Omanović and Branica, 2003; Louis et al., 2007). The advantages of the PP method include (1) the ability to differentiate between labile and inert metal complexes; (2) minimise problems associated with a high metal concentration in stability constant determination (e.g. precipitation, sufficient ligand excess) and, (3) the experimental procedure can be fully automated making the method appealing (Omanović and Branica, 2003, 2004; Omanović, 2006; Louis et al., 2007). PP has been used in several studies for the speciation of Pb in freshwater (Omanović and Branica, 2003; Billon and Van Den Berg, 2004), Zn in seawater (Brown and Kowalski, 1979; Filella et al., 2002), Cd (Tsang et al., 2006; Bi, 2012), and Cu in seawater (Louis, Cmuk, et al., 2008; Nicolau et al., 2008; Gibbon-Walsh et al., 2012b). To the best of our knowledge, PP has only been used once for metalloids speciation, specifically to look at Sb speciation in anti-leishmaniasis drug (Salaün and Frézard, 2013).

5.2 Aims and objectives

The general aim of this study is to assess if Sb(III) is complexed or not in the xylem sap of cucumbers. To achieve this primary aim, the following points list specific objectives:

- To develop and optimise a pseudopolarographic procedure for the determination of Sb(III) at the gold electrode, ready to be used for complexation studies,
- To validate the voltammetric method by looking at the complexation of Sb(III) with low molecular weight ligands (Ethylenediaminetetraacetic acid (EDTA), Diethylenetriamine-pentaaacetic acid (DTPA), tartaric acid (TA) and glutathione (GSH)); these ligands have known stability constants with Sb(III) but GSH (Filella & May, (2005)), and
- To use the method to assess if any complexation of Sb(III) in xylem sap can be observed.

5.3 Materials and Methods

5.3.1 Reagents and instrumentation

All chemicals were of analytical quality unless otherwise stated. Water that has been used to prepare reagents and preliminary working solutions was 18 MΩ cm^{-1} purified using a Millipore-Elix system. Standard Sb solutions were prepared by dilution with water of 1000 ppm standard solutions, EDTA, DTPA, TA, and GSH were also from Sigma Aldrich. Standard solutions (LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$, and $BaCl_2$) were kept at room temperature.

Voltammetric experiments were made using a µAutolabIII potentiostat (EcoChemie, now Metrohm AG, Switzerland) computer-controlled using GPES software (version 4.9). A three-electrode cell containing the gold microwire working electrode (WE), an iridium counter electrode (CE) (150 µm diameter, ~3 mm length), and a double-junction reference electrode, Ag/AgCl/KCl (3 M)//$NaNO_3$ (0.1 M), was placed in a voltammetric cell (Teflon), which was placed in a Faraday cage (Windsor Scientific, UK). The salt bridge was filled with 0.1 M $NaNO_3$ to avoid leakage of chloride in the voltammetric cell. Gold microwires (Purity: 99.99%, temper: hard) of 10 and 25 µm diameter (Goodfellow, UK) were used as working electrodes. A vibrator rotor (150 Hz) was attached to the microwire WE. The vibrator, which was used in place of a standard magnetic stirrer, was powered by an IME663 (EcoChemie) and controlled by GPES software (version 4.9). The vibrated gold microwire electrodes were prepared as described previously (Salaün and van den Berg, 2006; Gibbon-Walsh et al., 2012b) and stored in air or Milli-Q water.

5.3.2 Au microwire fabrication

Gold (Au) microwire electrodes (10 and 25 uM) were fabricated according to the procedure described by Salaün and Van Den Berg, (2006). An approximately 10-cm length of 100-um diameter copper wire was passed through a 100-uL pipet tip (polyethene, Corning Inc.). Its end was dipped in a freshly mixed conductive silver solution (Leitsilber L100, Maplin, UK), used as a conductive adhesive. The copper wire was then attached to approximately 10-mm length gold microwire (10 or 25 um) (Goodfellow) by gently touching it. The copper wire was then carefully pulled through the pipet tip until the microwire passed halfway through. The microwire tip was sealed by holding it for a few seconds at 400 °C horizontal tube oven to melt and seal the gap uniformly (Figure 5.2). The microwire electrodes were converted to a vibrating electrode by insertion a vibrator in the microwire holder at the top (Chapman and Van Den Berg, 2007). Electrodes were stored vertically using an empty pipette tips holder until use. This particular electrode does not need continuous polishing and can be cleaned electrochemically before each measurement. By doing this method improves the sensitivity of the microwire electrode during analysis (Chapman and Van Den Berg, 2007).

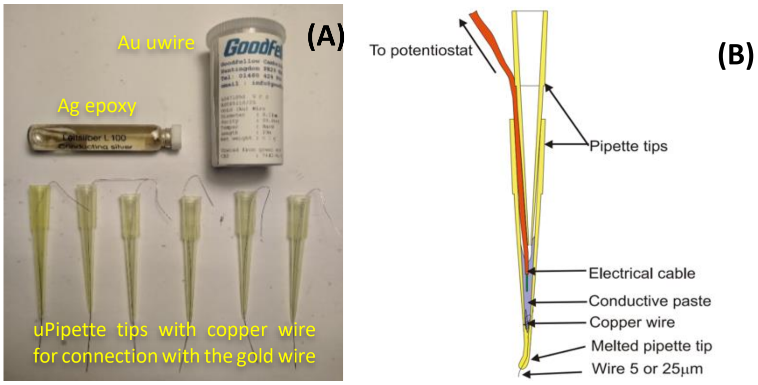


Figure 5. 2. Fabrication of Au microwire (a) and schematic diagram of the Au microwire fabricated from a micropipette tips finished product adapted from Salaün and Van Den Berg, (2006).

5.3.3 Pre-treatment

The Au microwire electrode was conditioned with 0.5 M H_2SO_4 with the application of a negative potential of -2.5 V for 30-60s to produce hydrogen gas to clean the wire surface and to desorb any species that might have remained to adsorb (Salaün and van den Berg, 2006). This process was done twice daily (before and after use). A cyclic voltammetric scan (CV) was followed at 10 mV.s^{-1} between 0 and +1.5 or 1.6 V to form the oxide layer at c.a at 1.1 V reversibly during the anodic scan and reduce it back at c.a 0.8 V in the cathodic scan. The shape of this CV was used to assess the behaviour of the electrode and the charge of the oxide reduction peak was monitored to detect any change in surface area of the electrode (Salaün and van den Berg, 2006).

5.3.4 Voltammetric parameters used for the PP experiments

Twenty millilitres of MQ water with 20 nM of Sb(III) were transferred to the voltammetric cell together with 50 mM $NaClO_4$ and 1 mM $HClO_4$, giving a pH of around 3 (or in 0.1.M phosphate solution or Hoagland solution at pH 6.5). The solution was purged with N_2 for

15 mins. The experimental procedure (Table 5.1) consisted of a first stage for the stabilisation of the electrode before proceeding with the PP. This stabilisation step consisted of a sequence of 15 ASV scans with 20s deposition below -1.1V and a 60 s cleaning step at +0.5V. The intensity of the Sb peak was monitored, and it was observed that the peak generally stabilised within 15 scans. The PP procedure was then achieved by running successive ASV scans at different deposition potentials. Each ASV measurement was obtained as follow: a background scan (the same as the analytical scan but without the deposition step) was first recorded followed by an analytical scan; the background scan was then subtracted from the analytical scan, and the intensity of the Sb peak was measured from this background-subtracted scan. The peak derivative was used as a measure of the peak intensity because it is independent of an often-subjective choice of baseline. All procedure was fully automated through the GPES software. During conditioning, deposition, and desorption steps, the electrode was vibrated; during equilibrium and stripping, the electrode was stagnant. Finally, at the end of each stripping scan, a potential of +0.5 V was always imposed until a new scan was started. The various steps were automated using GPES software. Figure 5.3 shows the voltammetric equipment set-up for the experiment, and Figure 5.4 shows a typical subtracted scan.

Table 5. 1.Voltammetric conditions for the stabilisation, analytical, and background scans. The same stripping parameters were used.

Mode	Parameter	Values
Purging		15 min
Stabilisation of the WE (minimum of 15 times)	Conditioning potential	0.5 V
	Conditioning time	60s
	Desorption Potential	-1.1 V
	Desorption time	20s
	Equilibrium time	1s
Analytical	Deposition Potential	+0.4 V to -0.4 V
	Deposition time	20 s
	Desorption Potential	-1.1V
	Desorption time	1s
	Equilibrium time	1 s
Background	Conditioning potential	0.5 V
	Conditioning time	5s
	Desorption Potential	-1.1V
	Desorption time	1s
	Equilibrium time	1 s
Stripping	Range	From -0.2 to +0.25 V
	Step	4 mV
	Amplitude	100 mV
	Pulse time	6 ms
	Interval time	100 ms

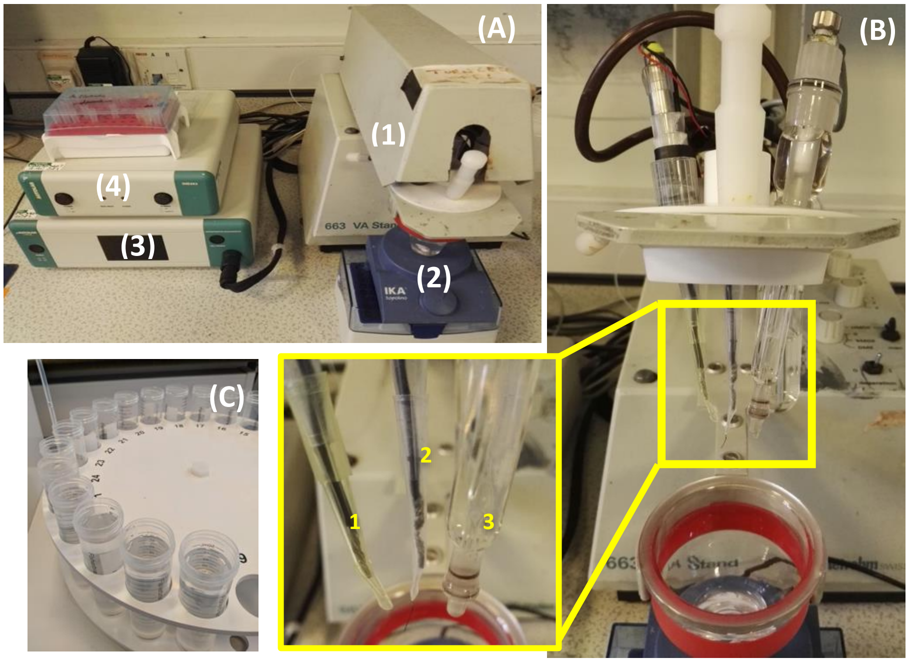


Figure 5. 3. (a) Voltammetric equipment set-up; (1) Instrument: 696 VA electrode stand, (2) electrochemical cell (3) connected via an interface IME663, Autolab, (4) a uAutolab(III) potentiostat (Metrohm, Switzerland), using GPeS software (b) Anodic stripping voltammetric set-up: (1) Working Electrode (WE): Au wire (10 uM); (2) Counter Electrode (CE): Iridium wire; (3) Reference Electrode (RE): Ag/AgCl/KCl (3M) // $NaNO_3$ (0.1M) and (c) autosampler used for the pseudopolarography experiments.

5.3.5 Pseudopolarographic method (PP)

Pseudopolarograms were obtained for Sb(III) with and without the presence of the following model ligands: (a) EDTA; (b) DTPA; (c) tartaric acid (TA) and (d) glutathione (GSH). Before recording any pseudopolarograms, the signal stability was checked and obtained by running the same ASV scans of a solution of known Sb(III) concentration until the signal was found stable.

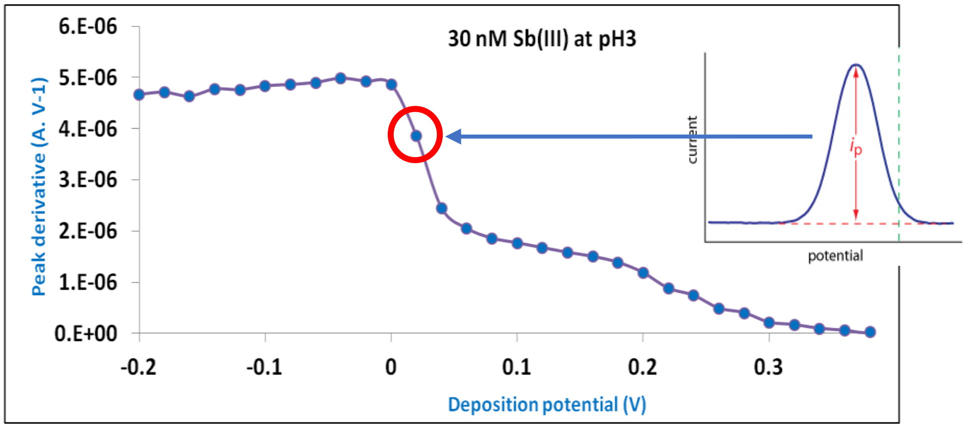


Figure 5. 4. Typical pseudopolarography scan (each point represents one background-subtracted ASV signal for Sb(III)).

5.3.6 Determination of stability constants of Sb with l.m.w. model ligands

Stability constants were estimated experimentally using PP by titrating low nM levels of $Sb(OH)_3$ with EDTA, DTPA, TA and GSH. These ligands are known to complex Sb(III) and their optimum stability constants have been derived from a compilation of all the published values Filella and May, (2005). These values were entered manually (see section 5.7 Annex for the procedure) into Visual Minteq®, a freeware equilibrium model used for calculation of metal speciation in natural waters. Visual Minteq® was used here to predict the concentration of all aqueous species at various pH when $Sb(OH)_3$ is in the presence of the low molecular weight ligands. The stability constants between ligands and Sb(OH)$_3$ are given in Table 5.2. These stability constants were derived at a temperature of 25 C and for a ionic strength of 0 mol.L^{-1} and correspond to the formation of the species in bold. For instance, the stability constants for SbEDTA- is:

$$\mathrm{K} = \frac{[SbEDTA^{-}]}{[Sb(OH)_3].[EDTA^{4-}].[H^{+}]^{3}} = 10^{26.77} \qquad \text{Equation 5.1.}$$

Table 5. 2. Stability constants between Sb(OH)$_3$ and l.m.w. ligands at 25 C and ionic strength of 0 mol.L-1. Taken from Filella and May (2005)

Ligands	Equation	Stability constant (log K)
EDTA^{4-}	Sb(OH)$_3$0 + EDTA4- + 3H+ → **SbEDTA-** + 3H2O	26.77
	Sb(OH)$_3$0 + EDTA4- + 4H+ → **SbHEDTA0** + 3H2O	28.00
	Sb(OH)$_3$0 + EDTA4- + 2H+ → **SbEDTA(OH)2-** + 2H2O	20.76
	Sb(OH)$_3$0 + EDTA4- + H+ → **SbEDTA(OH)23-** + H2O	12.676
DTPA^{5-}	Sb(OH)$_3$0 + DTPA5- + 3H+ → **SbDTPA2-** + 3H2O	30.70
	Sb(OH)$_3$0 + DTPA4- + 4H+ → **SbHDTPA-** + 3H2O	31.67
TA	Sb(OH)$_3$0 + TA2- + 3H+ → **SbTA+** + 3H2O	9.855
	Sb(OH)$_3$0 + 2TA2- + 3H+ → **SbTA2-** + 3H2O	17.184
	Sb(OH)$_3$0 + TA2- + 2H+ → **SbTA(OH)-** + 2H2O	9.408
	2 Sb(OH)$_3$0 + 2TA2- + 2H+ → **Sb**2**H**-2**(OH)**2**TA**22**-** + 4H2O	22.17
	Sb(OH)$_3$0 + TA2- → **SbH-2(OH)TA2-** + 2H2O	2.045

The experimental determination of stability constant was done here by recording PPs of 30 nM Sb(OH)$_3$ in presence/absence of various concentrations of ligands. Conditions of pH were chosen so that complexation is predominant and if possible, only one complex is formed. Upon addition of the ligand, Sb(OH)$_3$ is expected to decrease because of Sb(III) complexation. In the case represented by Equation 5.1, when the peak due to Sb(OH)$_3$ is half its original value, it is assumed that [SbEDTA$^-$] = [Sb(OH)$_3$] and the experimental stability constant can then be determined by:

$$K_{exp} = \frac{1}{\{\mathrm{EDTA}^{4-}\}.\{\mathrm{H}^{+}\}^{3}} \qquad \text{Equation 5.2.}$$

where { } represents the activity at the particular ionic strength used experimentally (I = 0.05 M). $\{EDTA^{4-}\}$ and $\{H^{+}\}$ (i.e. pH) are obtained directly from the output file in Visual Minteq, using the total concentration of ligand at which the $Sb(OH)_3$ voltammetric signal is half its original value (i.e. that without any ligand).

5.4 Results

5.4.1 Pseudopolarography of Sb(OH)3 on a gold electrode in non-complexing media

Before proceeding with the PP measurements in the presence of ligands, the general behaviour of the gold electrode for Sb(III) determination was first checked by running calibration curves, determination of the linear range at various pH, determination of the detection limit as well as assessing the variation of deposition time and concentrations on PPs.

5.4.2 Calibration and electrode stability

A pseudopolarogram is obtained by running successive ASV measurements at different deposition potentials and plotting the intensity of the peak of interest vs deposition potential (Edep) (Figure 5.5). The calibration curve of Sb(III) at pH3 has a linear response until from 0 to 40 nM (R^2=0.9998). Figure 5.6 shows the stacked ASV voltammograms of the calibration curve from 0 to 320 nM (top) and the blow-up figure of the linear range (bottom). Calibration curves of the various pH are shown in Figure 5.7. It shows that acidic pH (i.e. 1) gives a higher response.

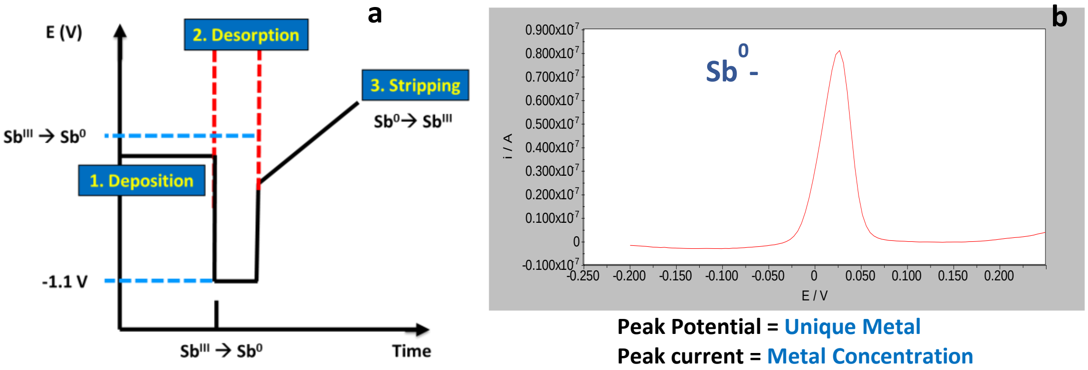


Figure 5. 5. Steps in voltammetric analysis (a) and Typical background-subtracted ASV (anodic stripping voltammetry) signal of Sb(III) (b).

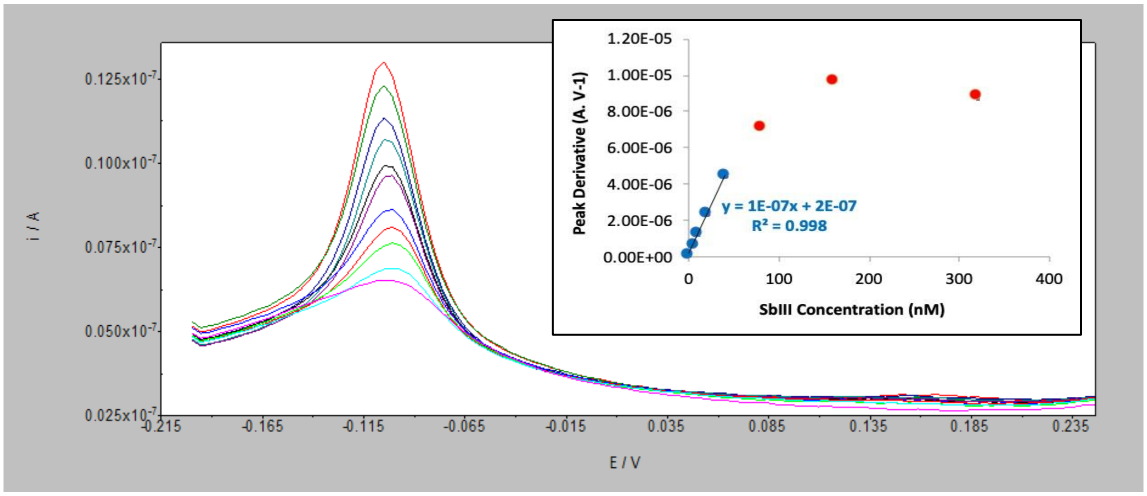


Figure 5. 6. Stacked As(III) voltammograms of the calibration curve of Sb(III) in 0.1 M Phosphate solution at pH6.0 from 0 to 320 nM and (inset) Peak derivatives vs. Sb(III) showing the linear range concentration 0-40 nM. Method: DPASV -0.2V (30s) A; -2.2V (1s), Scan: -0.1 V to +0.4V, Step Potential: 0.00405V ,Modulation Potential: 0.02505 V Standby pot: +0.75V. Electrodes: Working Elect; Au wire (10 uM), Iridium counter electrode and Ref. electrode; Double junction Ag/AgCl/KCl (3M)//NaNO3 (0.1M)

The same Au microwire electrode was used to measure the calibration curve at different pH. Figure 5.7 shows the graphs of the Sb calibration curve at selected different pH (1, 2, and 5). The peak potential varies cathodically (c.a. 60 mV/pH) in agreement with the reaction: $Sb^0 + 3H_2O \rightarrow Sb(OH)_3 + 3e^- + 3H^+$.

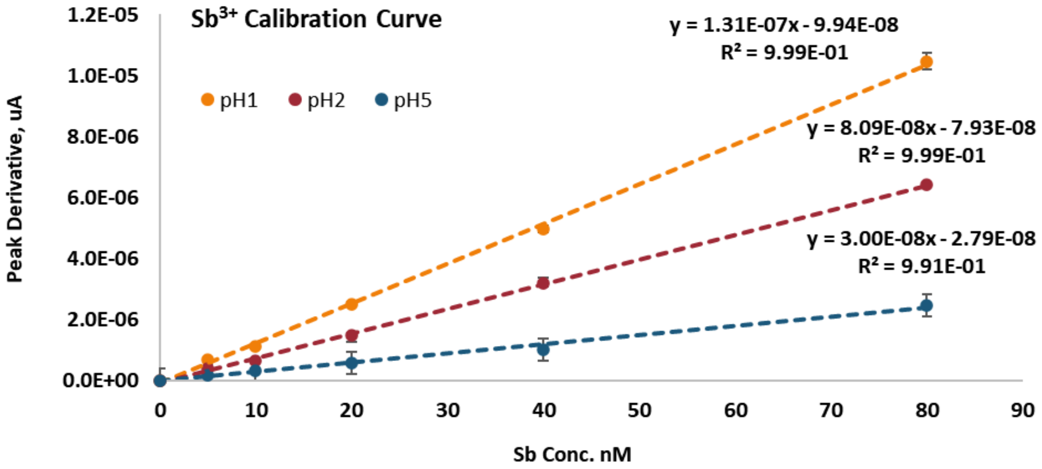


Figure 5. 7. Sb(III) calibration curves at different pH (n=3). Sb(III) solution (0, 5, 10, 20, 40 and 80 nM) (1) pH1: 0.1 M HCl; (2) pH2: 10 mM HCl; (3) pH5: 10 mM Na-Ac+ 8 mM HCl. Method: DPASV -0.2V (30s) A; -1.5V (1s), Scan: -0.1 V to +0.4V, Step Potential: 0.00405V ,Modulation Potential: 0.02505 V Standby pot: +0.75V. Electrodes: Working Elect; same Au wire (10 uM), Iridium counter electrode and Ref. electrode; Double junction Ag/AgCl/KCl (3M)//NaNO3 (0.1M)

Table 5. 3. Calibration parameters obtained for electrode repeatability calculation for each pH.

	pH1	pH2	pH5
Ave % recovery [1]	100.8	99.6	101.1
Stdev of response (Sy)	7.6E-09	6.26E-09	3.8E-09
Slope (S)	1.31e-7	8.09e-8	3.00e-8
LOD[2] (nM)	1.91	2.55	0.980
LOQ[3] (nM)	5.80	7.74	2.97
Linear range (nM)	0-80	0-80	0-80
Coefficient of Determination (R^2)	0.999	0.999	0.991

[1] Average recovery is obtained by comparing the actual concentration of the standard computed from the calibration curve and multiplied by 100 (n=3), [2] LOD=3.3 x (Sy/S), [3] LOQ=10 x (Sy/S)

In any measurements, it is essential to have a stable peak before starting the pseudopolarogram. As shown in Figure 5.8, after 15-20 scans, the signal becomes stable. Each stability sequences (before and in between individual PP experiments) serve as a reset of the electrode before each new PP experiment. Without this stability sequence, the less reproducible shape of the pseudopolarograms and an overall gradual loss of the signal were being observed.

Recovery measurements were also done to check the accuracy of the Au working electrode, shown in Table 5.2. A standard addition procedure was achieved in a blank solution containing 20 nM Sb(III). The recovery percentage was calculated from Recovery % = $(x_s-x)/x_{add}$ x 100%, where x_s =calculated concentration of spiked samples, x=calculated concentration of unspiked samples and x_{add} = amount of added analyte (Lu and Compton, 2013). The % recovery range obtained was from 99.6 to 101.1.

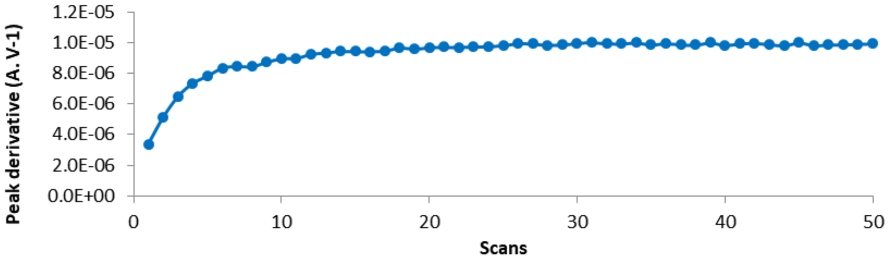


Figure 5. 8. Stability ASV scans before PP experiments. Solution: 20 nM Sb(III) + 50 mM $NaClO_4$ + 1 mM $HClO_4$, pH 3.0 Method: DPASV Deposition potential: -0.2V/30s; Desorption potential: -1.5V/1s; Step Potential: 0.00405V, Modulation Potential: 0.02505 V Standby pot: +0.75V. Electrodes: Working Elect; Au wire (10 uM), Iridium counter electrode and Ref. electrode; Double junction Ag/AgCl/KCl (3M)//NaNO3 (0.1M)

5.4.3 Pseudopolarograms (PP) of $Sb(OH)_3$ at pH 3.

Testing of the pseudolarographic method was done at pH around 3 to visualise any complexation effect best (see section 5.4.2). Measurements were done in 50 mM $NaClO_4$ with 1 mM $HCl0_4$. Figure 5.9 (top) shows that a reproducible PP signal was obtained and that the overall shape of the PP was unaltered with $Sb(OH)_3$ concentrations, although the relative intensities of the signals were. Each PP presented 4 different sections :

1- Edep > 0.3 V: no Sb signal in this region because there is no accumulation of Sb at the gold surface during the deposition step;

2- 0.3 > Edep > 0.08 V: adsorption of $Sb(OH)_3$ on the gold electrode is occurring during the deposition step: $Sb(OH)_3 \rightarrow Sb(OH)_{3ads}$; this adsorbed species is reduced to Sb^0 when the desorption potential is applied ($Sb(OH)_{3ads} + 3e^- + 3H^+ \rightarrow Sb^0 + 3H_2O$);

3- 0.08 > Edep > -0.02 V: this is the reduction wave of $Sb(OH)_3$; here the species is directly reduced during the deposition time, and the reduction rate increases with decreasing the deposition potential; the half-wave potential in these conditions was estimated at $E^{1/2}$ = 0.02-0.03 V.

4- Edep < -0.02 V: diffusion-limited conditions; the deposition potential is sufficiently low so that the reduction rate is sufficiently fast and the amount of Sb^0 accumulated at the gold electrode surface is now only limited by the diffusion of $Sb(OH)_3$ in the solution (i.e. the flux of $Sb(OH)_3$ towards the electrode).

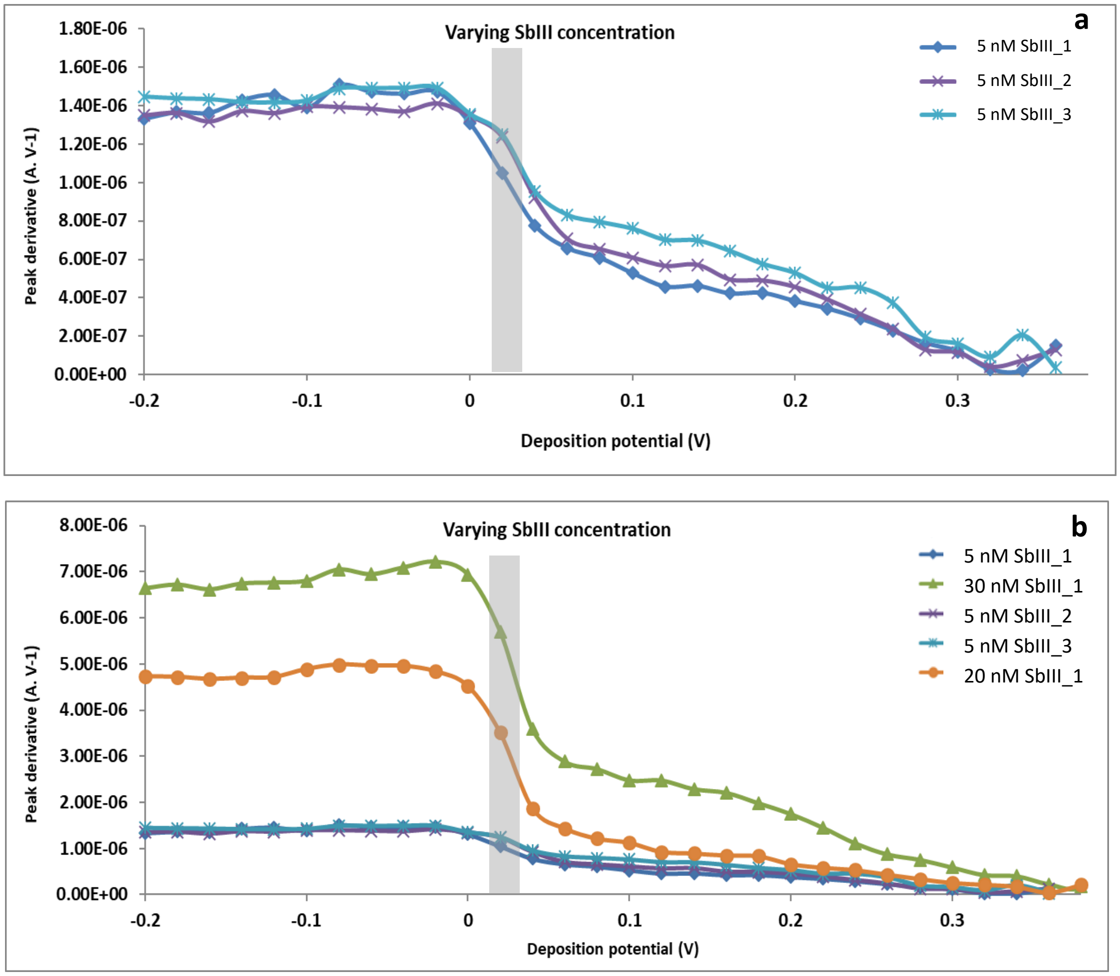


Figure 5. 9. Pseudo graphs (peak intensity vs peak derivative) of varying Sb(III) concentrations (a) three scans of 5 nM Sb(III) + and (b) 10, 20 and 30 nM nM Sb(III), both in 50 mM $NaClO_4$ + 1 mM $HClO_4$ (Deposition potential: 0.4 to -0.2V/30s; Desorption potential: -1.5V/1s).

5.4.4 Varying deposition time

Figure 5.10 shows normalised PPs obtained at varying deposition times (from 10s to 300s) for deposition potentials decreasing from 0.4 to -0.2 V. The intensity of the individual PPs were normalised to the intensity obtained at Edep = -0.2 V because electrodes of different lengths (i.e. sensitivities) were used.

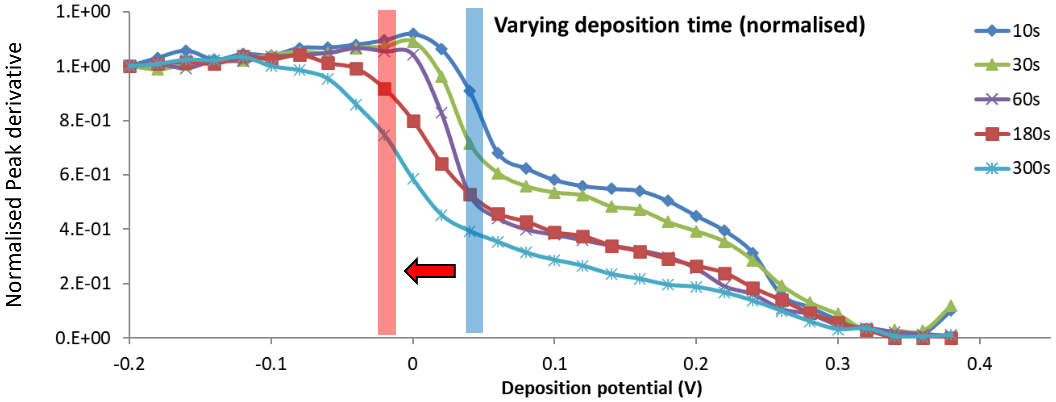


Figure 5. 10. Graph of the intensity of the peak against deposition potential (10, 30, 60, 180 and 300s). Original data (top) normalised (bottom). 30 nM nM Sb(III), in 50 mM $NaClO_4$ + 1 mM $HClO_4$ (pH3) (Conditioning potential: 0.4 to -0.2V/30s; Deposition potential: -1.5V/1s).

There is a c.a. 60 mV shift in the half-wave potential from c.a. 0.04V (@10s) to -0.02V (@300s). It seems that an increase of deposition time results in a less reversible behaviour, as shown by the lower slope of the reduction wave with increasing deposition time. It can be noted from the graph the relative proportion of the maximum signal where no reduction is occurring (measured at 0.1V) tends to decrease with increasing deposition time. The variation of the wave at increasing deposition times on the gold electrode was also previously observed for Cu (Gibbon-Walsh et al., 2012b) and can be explained for reversible systems (where electrons transfer is not limiting/fast). In this work, the same deposition time was used for all experiments.

5.4.5 Stability constant determination

5.4.5.1 Sb(III)- EDTA system

5.4.5.1.1Visual Minteq modelling

Figure 5.11 shows the distribution of Sb-EDTA species as a function of pH for EDTA concentrations of 1, 10, 100 and 1,000 μM. It can be seen that complexation and formation of Sb-EDTA- is best seen at pH of around 3. At higher pH, $[OH^-]$ increases and hydrolysis of Sb(III) becomes predominant while at lower pH, protonation of EDTA and protonation of $Sb(OH)_3$ becomes predominant, thus decreasing the formation of $SbEDTA^-$. Also, at pH 3, the voltammetric signal is predominantly from $Sb(OH)_3$, $Sb(OH)_2^+$ accounting only for less than 5% while $SbEDTA^-$ is the only complex being formed, SbHEDTA being only present at the negligible amount. Measurements were made here in a solution of 50 mM $HClO_4$ + 1 mM $HClO_4$ giving an approximate pH of 3.08 (Visual Minteq). This pH was used for calculation.

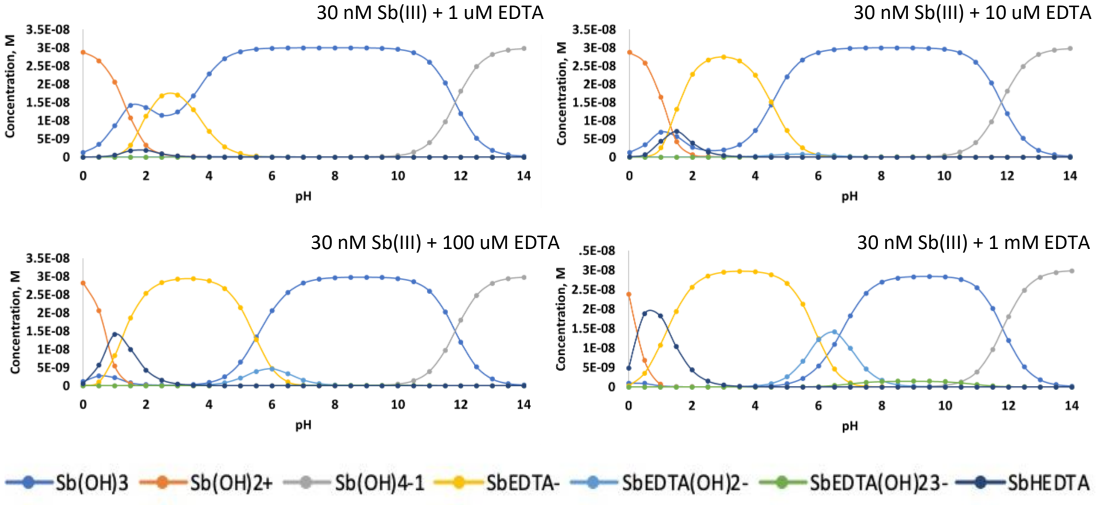


Figure 5. 11.Predicted distributions of all Sb species to be considered as a function of pH (Sb-EDTA) for various concentrations of EDTA. Solution: 30 nM Sb(III) + 1, 10 uM, 100 uM or 1mM EDTA.

5.4.5.1.2 Voltammetry (Experimental)

Figure 5.12 shows the PP obtained between -0.4 and +0.4 V at different concentrations of EDTA in a pH 3 $NaClO_4$ solution. When increasing EDTA concentrations, the following observations can be made: the half-wave reduction potential of $Sb(OH)_3$ reduction (at c.a. +20 mV) remains constant while the half-wave amplitude sharply decreases; this is consistent with a reduction of $Sb(OH)_3$ upon addition with EDTA. A second wave appears at a potential of c.a. -0.1 V was suggesting the presence of a complex; this wave is attributed to the presence of the $SbEDTA^-$ complex and its reduction wave is c.a. 120 mV more cathodic than the reduction wave of $Sb(OH)_3$ (Figure 5.13). At a deposition potential below ~ -0.2 V, the waves reach a plateau, and this plateau decreases in intensity upon addition of EDTA until reaching a stable value that becomes more or less independent of [EDTA]tot (Note that PP scan at [EDTA] = 100 μM seems to be an outlier, as significantly lower than that for EDTA = 8, 10, 30, or 500 μM). The decrease in the plateau value between no ligand and 500 uM EDTA suggest that the complex $Sb\text{-}EDTA^-$ has a diffusion coefficient that is 54% that of $Sb(OH)_3$. It is interesting to note that the adsorption of $Sb(OH)_3$ that occurs at Edep between 0.02 V and 0.38 V in the absence of EDTA completely disappears at 500 μM EDTA, strongly suggesting that $SbEDTA^-$ does not adsorb on the gold electrode before its reduction.

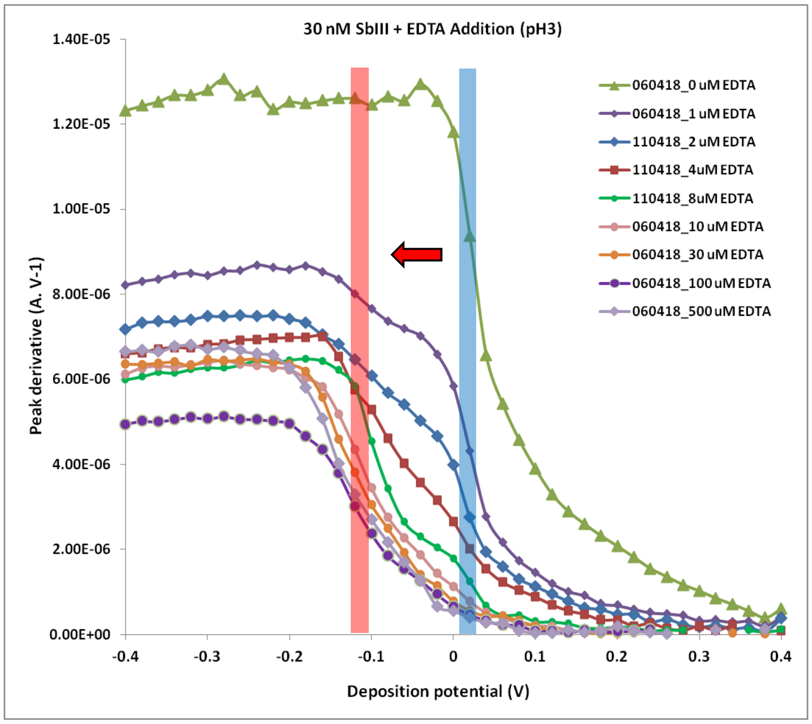


Figure 5. 12. Pseudopolarograms of 30 nM Sb(III) in 50 mM $NaClO_4$ + 1 mM $NaClO_4$ with stepwise addition of EDTA (1 uM to 500 uM). DPASV: Deposition potential: 0.4 to -0.4 (30s); Desorption potential: -1.5V/1s. The shaded areas represent the approximate half-wave reduction potential of $Sb(OH)_3$ (blue) and the half-wave reduction potential of the complex SbEDTA- (red) with an approximate cathodic shift of 120 mV.

Assuming that the signal obtained at potentials above -0.02 V and above is only due to $Sb(OH)_3$, the decrease of the signal as a function of $[EDTA]_{total}$ can be compared to modelling predictions. The peak intensity given in Figure 5.12 is transformed to a concentration by normalising the signal to the 30 nM Sb(III) signal in the absence of ligands. Figure 5.13 shows the variation of inorganic antimony ($[Sb(OH)_3] + [Sb(OH)_2^+]$) at different deposition potentials (-20 mV, 0, +20 and +40 mV) together.

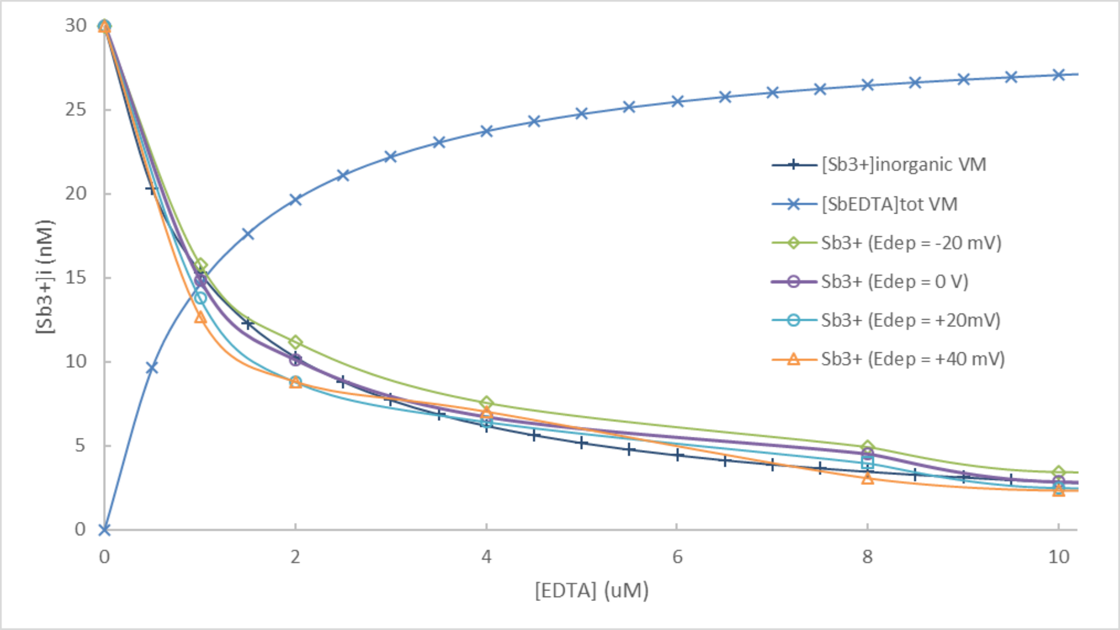


Figure 5. 13. Modelled and experimental variations of inorganic Sb(III) as a function of the total concentration of EDTA. VM: Visual Minteq.

When the voltammetric signal is half the original value (15 nM in Figure 5.13), the stability constants can be estimated from Equation 5.1. The total concentration of EDTA at which inorganic Sb(III) is 15 nM was determined graphically and found to be 0.82, 0.9, 0.98 and 1.08 μM at Edep of +40, +20, 0 and -20 mV respectively. The corresponding log K were obtained from the activity of {EDTA^{4-}} at each of these total concentrations at a fixed pH of 3.087 and were found to be 26.97, 26.92, 26.88 and 26.84 respectively, in excellent agreement with the value of 26.77 (Filella and May, 2005).

5.4.5.2 Sb(III)- DTPA system

5.4.5.2.1 Visual Minteq modelling

Figure 5.14 shows the modelling predictions for DTPA concentrations varying from 1 μM to 1 mM. Similar to EDTA, complexation is best seen at a pH of 3 to 5, with higher pH presenting less complexation due to the strong hydrolysis of $Sb(OH)_3$ and at lower pH, the formation of $Sb(OH)_2^+$. Voltammetric measurements were achieved in the same solution as for EDTA, i.e. in 50 mM $NaClO_4$ + 1 mM $HClO_4$ giving a predicted pH of 3.086. In these conditions, only the $SbDTPA^{2-}$ is being formed, the other species $SbHDTPA^-$ being only present at negligible amounts (<1%).

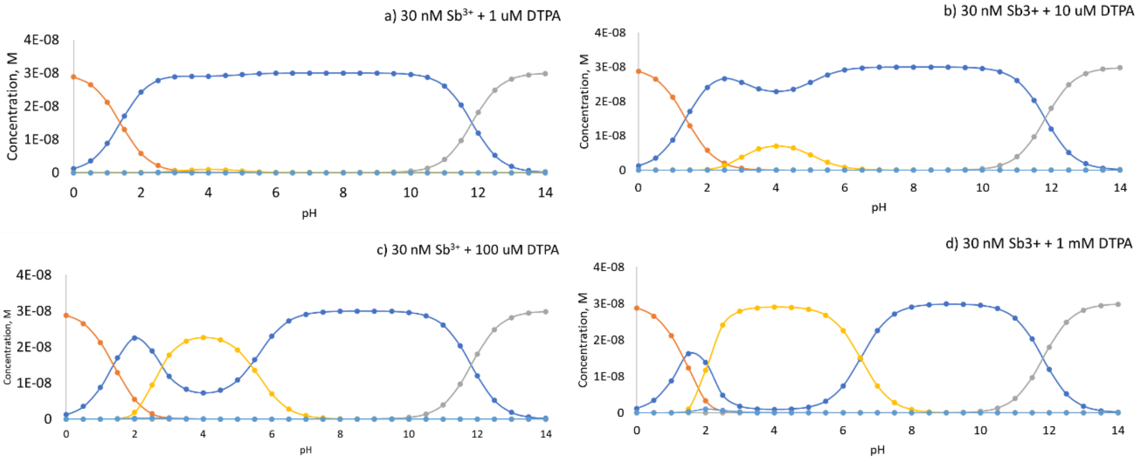


Figure 5. 14. Predicted distribution graphs of all the species to be considered as a function of pH (Sb-EDTA) using Visual MINTEQ® software (top) thermodynamic data (bottom) prediction Solution: 30 nM Sb(III) + (a) 1 uM, (b) 10 uM, (c) 100 uM, and (d) 1mM.DTPA. Red: $Sb(OH)_2^+$, Blue: $Sb(OH)_3$, Grey: $Sb(OH)_4$, Yellow: Sb-$DTPA^{2-}$.

5.4.5.2.2 Voltammetry (Experimental)

Figure 5.15 shows the pseudopolarograms obtained between -0.4 and +0.4 V at different concentrations of DTPA in a pH 3 $NaClO_4$ solution. When increasing DTPA concentrations, the following observations can be made. The half-wave potential of the $Sb(OH)_3$

reduction (at c.a. +20 mV) remains constant while the half-wave amplitude sharply decreases; this is consistent with a reduction of $Sb(OH)_3$ upon addition with DTPA. A second wave appears at a potential of c.a. -0.1 V suggesting the presence of a complex, this wave is attributed to the presence of the $Sb\text{-}DTPA^{2-}$ complex. At high DTPA concentration (500 uM and 1 mM), a further shift of the complex reduction wave is noted associated with a substantial decrease of the amplitude, suggesting a strong interference effect at these higher concentrations. At deposition potential below -0.1 V, the pseudopolarograms reach a plateau that is similar in amplitude for 10, 30, and 100 μM DTPA suggesting that interferences only occur at higher concentrations. By comparing the plateau value with no ligand and at 100 uM DTPA and assuming that the difference in intensity only originates from a change in diffusion coefficient, it suggests that the diffusion coefficient of Sb-DTPA2- is ~ 40% that of $Sb(OH)_3$.

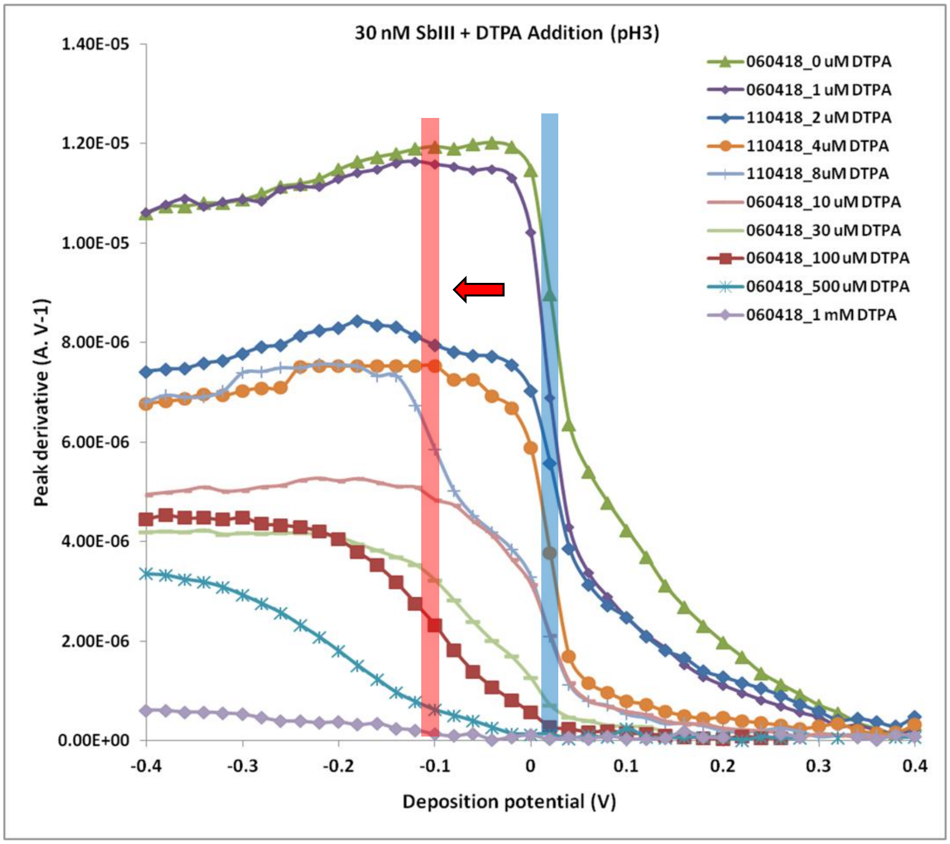


Figure 5. 15. Pseudopolarograms of 30 nM Sb(III) in 50 mM $NaClO_4$ + 1 mM $NaClO_4$ with stepwise addition of DTPA (1 uM to 1mM). DPASV: Deposition potential: 0.4 to -0.4 (30s); Desorption potential: -1.5V/1s. The shaded areas represent the approximate half-wave reduction potential of $Sb(OH)_3$ (blue) and the half-wave reduction potential of the complex $SbDTPA^{2-}$ (red) with an approximate cathodic shift of 120 mV.

Plotting the concentration of $Sb(OH)_3$ obtained experimentally at Edep = -20 mV and 0 V as a function of total concentration allows a visual comparison between experimental and modelling results (Figure 5.16). There is an apparent mismatch, and a stronger complexation is obtained experimentally than predicted. Using the concentration of DTPA at which $Sb(OH)_3$ is half its original value, log K values of 31.95 and 32.05 are estimated for Edep = -20 mV and 0 V respectively. These values are more than one order of magnitude higher than the value given in the literature (log K = 30.70 – Filella and May, 2005).

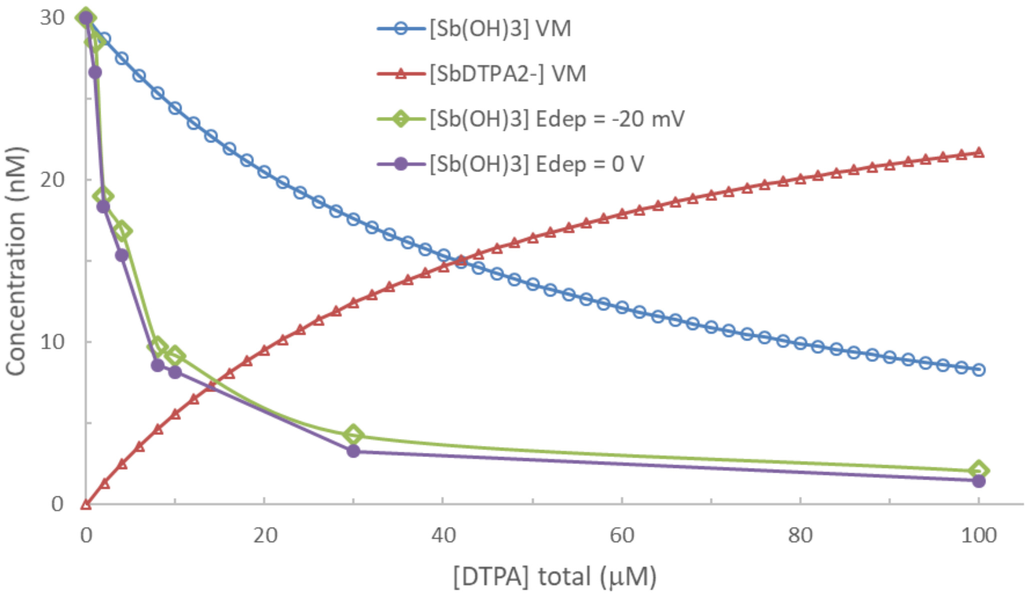


Figure 5. 16. Modelled and experimental variations of inorganic $Sb(OH)_3$ as a function of the total concentration of EDTA. VM: Visual Minteq.

5.4.5.3 Sb(III)- Tartaric acid (TA) system

5.4.5.3.1 Visual Minteq modelling

The Sb-tartaric system promotes the formation of up to 5 Sb complexes (see Table 5.2), depending on the pH and concentration of tartrate (Figure 5.17). In contrast to EDTA and DTPA systems, tartrate forms a complex at neutral and alkaline pH. Stronger complexation is observed at pH around 4 with the formation of 3 different Sb(III)-TA species.

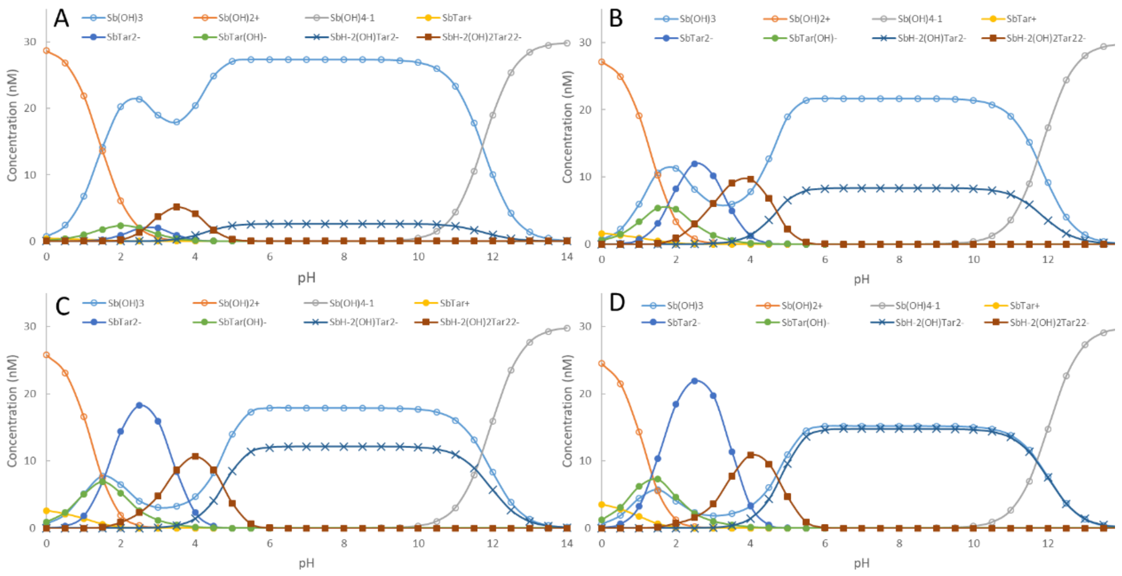


Figure 5. 17. Predicted distributions of all Sb(III) species to be considered as a function of pH in presence of various concentrations of tartaric acid. Solution: 30 nM Sb(III) + 1, 4, 7 and 10 mM TA (A, B, C and D respectively).

5.4.5.3.2 Voltammetry (Experimental)

Pseudopolarograms were obtained at pH 4 in a solution of 50 mM $NaClO_4$ in the presence of various concentrations of tartaric acid (Figure 5.18). Upon addition of TA, a strong decrease of the reduction wave is observed but in contrast to EDTA and DTPA systems, no second wave is apparent, down to -1 V suggesting that the complex(es) being formed is(are) electro-inactive (i.e. cannot be reduced). Other interesting observations are: the half-wave reduction potential in the absence of ligand is c.a. -20 mV which is around 40 mV more cathodic than at pH 3. The strong adsorption observed at pH 3 for deposition potentials comprised between c.a. +80 and +360 mV has almost disappeared here (pH 4).

When plotting $Sb(OH)_3$ obtained experimentally as a function of TA and comparing with modelling predictions (Figure 5.18), a rather good agreement is obtained. However, because of the formation of 3 different Sb(III)-TA complexes at pH 4, comparison of stability constants cannot be achieved. For that, the study should have been done at pH of, e.g. 8 where only one complex is predicted. However, the study here confirms again that the voltammetric determination of Sb(III) by ASV allows to clearly assess if complexation occurs. Different pH (i.e., pH 4) were used based on the recommendations from the Visual Minteq modelling results done prior the experimental procedure. Figure 5.19 shows the comparison of the experimental voltammetric results with the results obtained from the modelling predictions using Visual Minteq at pH4.

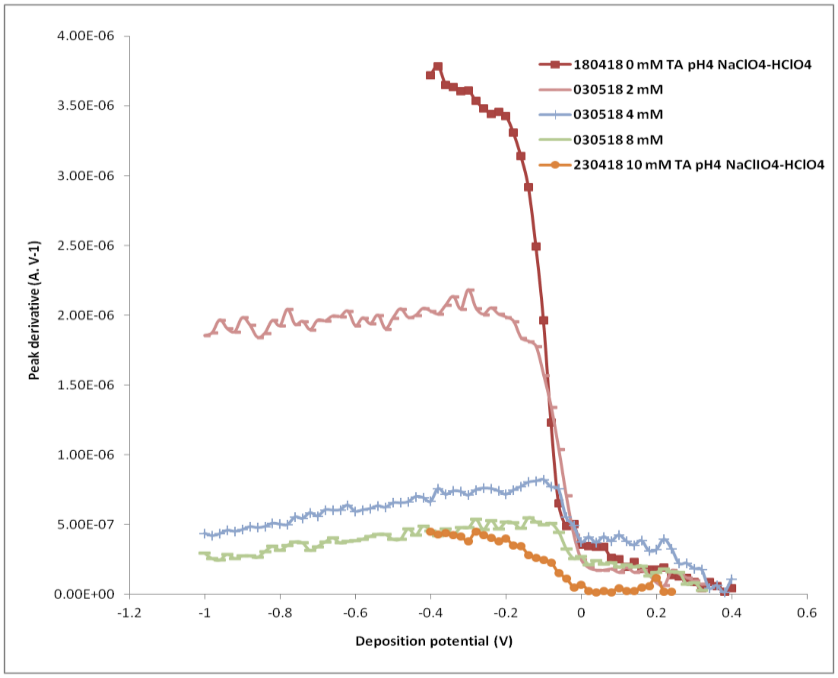


Figure 5. 18. Pseudopolarograms of 30 nM Sb(III) in 50 mM NaClO$_4$ adjusted to pH 4 with HClO4 after addition of tartaric acid (0, 2, 4, 8 and 10 mM). DPASV: Deposition potential: 0.4 to -0.4 (or to -1V) for 30s; Desorption potential: -1.5V/1s

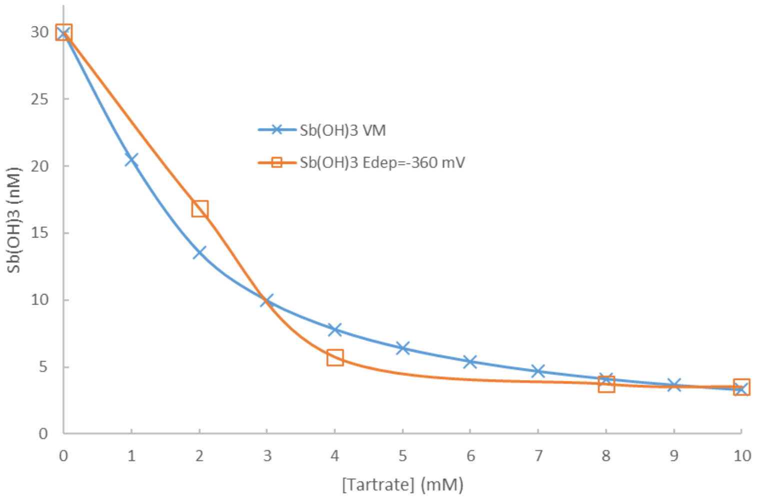


Figure 5. 19. Comparison between Sb(OH)$_3$ obtained experimentally (Edep = -360 mV, from Figure 5.18) with modelling predictions. VM: Visual Minteq.

5.4.5.4 Sb(III)- glutathione (GSH) system

5.4.5.4.1 Visual Minteq modelling

There is no known stability constant published.

5.4.5.4.2 Voltammetry (Experimental)

PP of Sb(III) and GSH were studied to show whether there was a complexation between the two. Figure 5.20 shows the PP graphs (top) and voltammograms (bottom) of 30 nM Sb(III) with/without and addition of GSH (0, 50, 100, 500 nM, 1, and 5 uM) at pH3. Similar to tartrate, a decrease of the pseudopolarogram plateau without any reduction wave of the complex indicates the formation of strong, inert complexes, electrochemically inactive. When plotting the intensity of the peak as a function of [GSH] and normalising to concentration, it is found that half of the original Sb(OH)$_3$ signal is lost when the concentration of glutathione added was 100 nM. Supposing that the complex formed is $Sb(GS)_3$: $Sb(OH)_3 + 3GSH \rightarrow Sb(GS)_3 + 3H_2O$

with $K'_{(Sb(GS)_3)} = \frac{[\mathrm{Sb(GS)_3}]}{[Sb(OH)_3].[GSH]^3}$ Equation 5.3.

Where K' is the conditional stability constant, and [GSH] is the concentration of free glutathione.

$[GSH]_{tot} = [GSH]_f + 3[Sb(GS)_3]$ Equation 5.4.

When $[Sb(GS)_3] = [Sb(OH)_3] = 15$ nM, [GSH] = 55 nM and $\log K'_{Sb(GS)_3} = 21.55$. This value is in the same order as the only other conditional stability constant reported in the literature (log K'=20.6), which was obtained by NMR spectroscopy (Sun et al., 2000). Figure 5.20, 5.21 and 5.22 shows the pseudopolarograms, voltammograms and graphs, respectively of 30 nM Sb(III) at different depositions showing a decrease of signal in response of the increase addition of GSH in the solution.

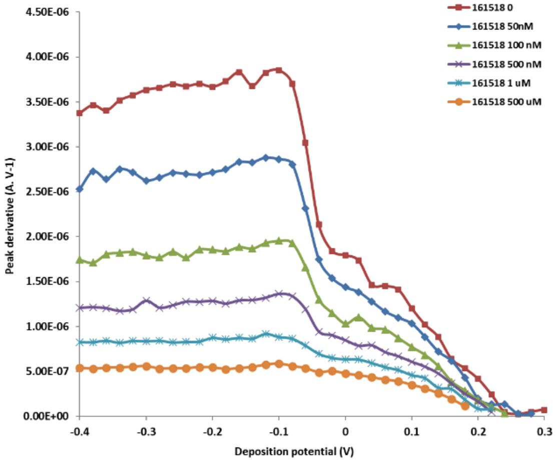


Figure 5. 20. Pseudopolarograms of 30 nM Sb(III) in 50 mM $NaClO_4$ + 1 mM $HClO_4$ after addition of GSH (0, 50 nM, 100 nM, 1 uM and 5 uM). DPASV: Deposition potential: 0.4 to -0.4 for 30s; Desorption potential: -1.5V/1s.

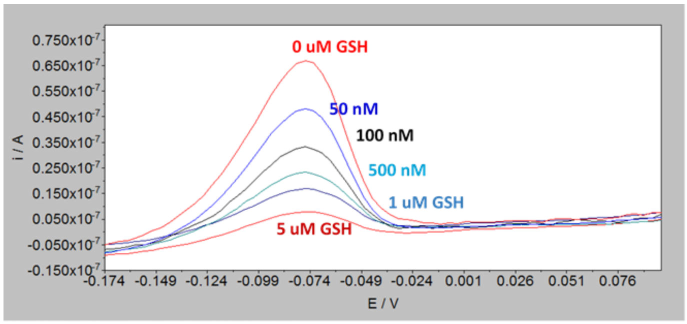


Figure 5. 21. Voltammograms of selected scan from Figure 5.20a at Edep = -0.4 V showing the $Sb(OH)_3$ DPASV signal.

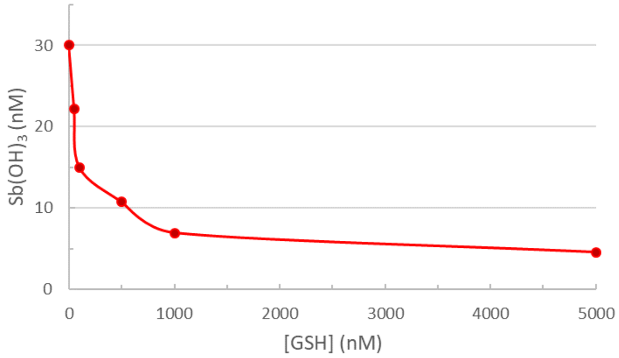


Figure 5. 22. Variation of $Sb(OH)_3$ as a function of GSH concentration.

5.4.6 Complexation of Sb(III) in xylem sap

Cucumber xylem sap obtained from Chapter 2 were used to test if complexation of antimonite is occurring upon addition of the sap. Figure 5.23 (top) shows the PP scans upon the stepwise addition of 25 uL sap (4 times, total of 100 uL) in 20 mL Hoagland solution (pH 6) with 100 nM Sb(III).

PP experiments were done in this solution which has a similar background matrix as the xylem sap and nutrient solution which has a pH of 6.0 (Mihucz et al., 2005; Uroic, 2011; Uroic et al., 2012). The chosen pH 6 was chosen as near to the pH of the xylem sap. The shape of the pseudopolarograms in this Hoagland solution before addition of the sap consists in one well-defined reduction wave at Edep ~ -30 mV followed by a plateau value down to Edep = -0.8 V. At positive values of Edep, there is no adsorption occurring. Upon addition of the sap, two main changes occur: 1- the intensity of the plateau decreases linearly with sap volume (r2= 0.998) and 2- a positive shift of the reduction wave can be observed (Figure 5.22 bottom). A positive potential shift usually indicates adsorption of organics on the electrode surface that may affect the sensitivity of the electrode towards Sb(III) by the decrease of the electroactive surface; this would have the net effect to decrease the intensity of the plateau value, as observed. However, if this is the case, such loss should also be observed for Cu, since it is also present in the Hoagland solution at levels of 0.5 uM. Figure 5.23 displays the Cu PP scans obtained during the same experiment, and they clearly show that this is not the case: the Cu peak intensity is unaffected by the addition of xylem sap showing that adsorption of organics on the electrode surface is not responsible for the loss of the $Sb(OH)_3$ signal. Therefore, we conclude here that this loss can only be due to the formation of inert/electroinactive complexes, even though the sap has been diluted extensively (up to 250 times). However, when 100 uL addition of sap is added to the Hoagland solution, an ~ 80% loss of signal was occurring at Edep = -0.8 V for (Figure 5.22) while a 40% decrease only is obtained at Edep = -1.3 V (Figure 5.24); this difference possibly suggests that some of the complexes being formed are electroactive at this low deposition potential.

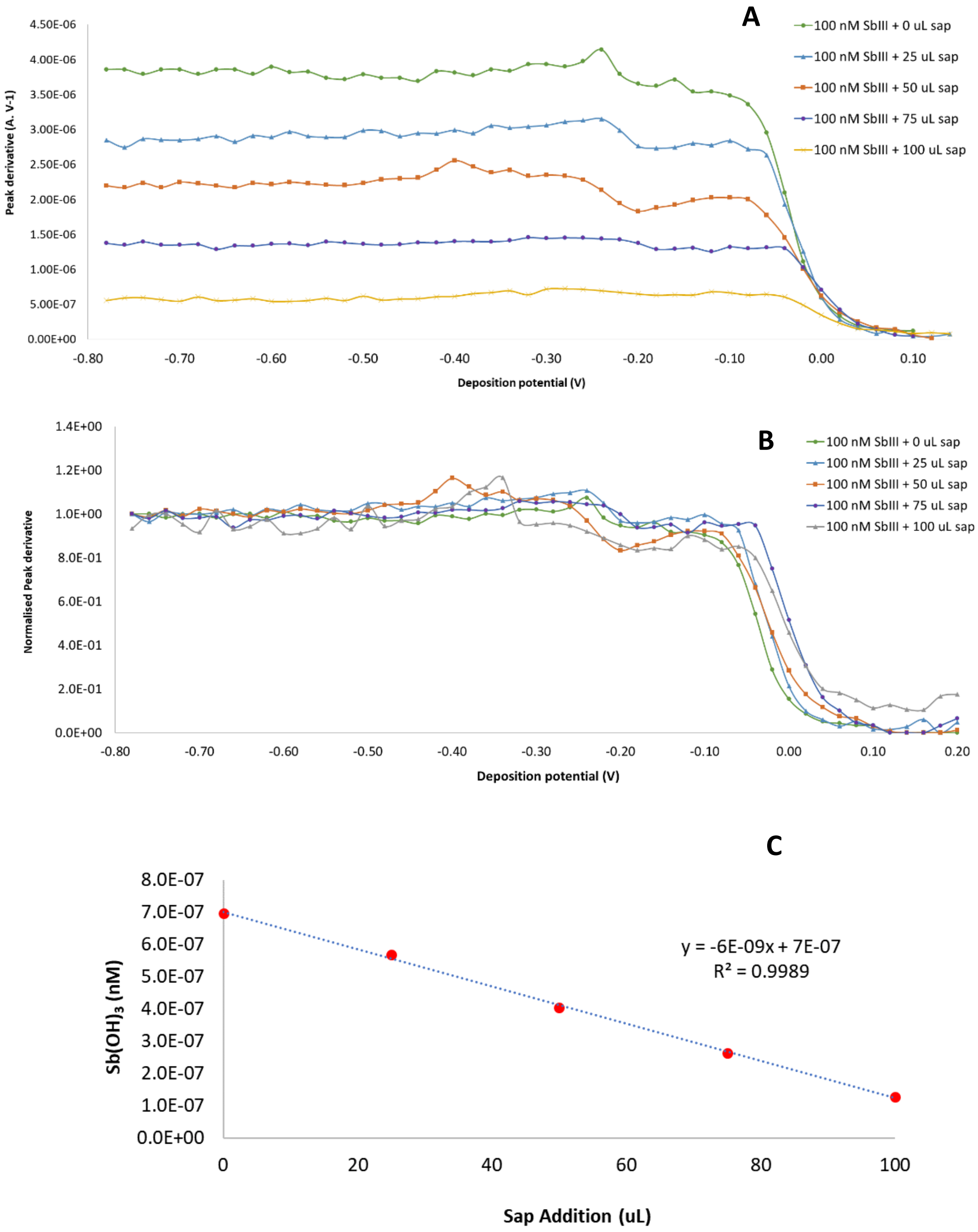


Figure 5. 23. Pseudopolarograms of 100 nM Sb(III) in Hoagland solution (pH 6) with stepwise addition of 25 uL xylem sap (total 100 uL sap). (A) original signal, (B) normalised signal, and (C) Variation of $Sb(OH)_3$ as a function of xylem sap addition (0-100 uL sap),. DPASV: Deposition potential: 0.2 to -0.8V (30s); Desorption potential: -1.5V/1s.

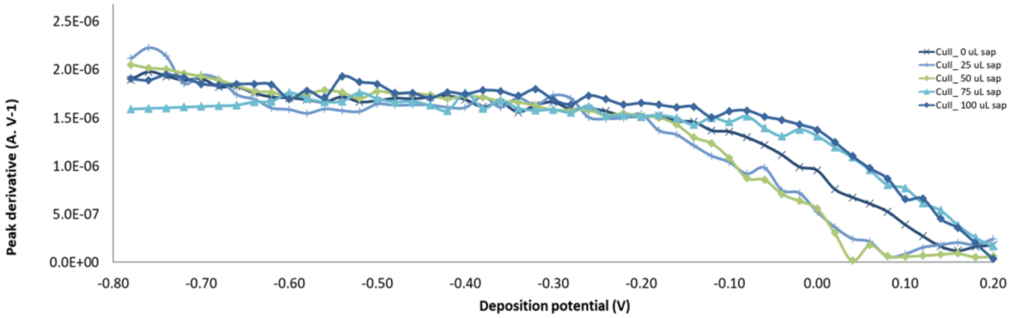


Figure 5. 24. Pseudopolarograms of 0.5 uMCu(II) in Hoagland solution with 4 stepwise additions of 25 uL xylem sap each (total 100 uL sap (pH6). DPASV: Deposition potential: 0.2 to -0.8V (30s); Desorption potential: -1.5V/1s.

A kinetic experiment was done where the same ASV scan was repeated using a deposition potential of -1.3 V, as low as possible in this Hoagland solution (Figure 5.25). The aim here was to assess if these Sb-complexes are still electroinactive at such low deposition potential. Upon addition of the xylem sap, similar observations were made with a decrease of the $Sb(OH)_3$ signal and a constant Cu signal (Figure 5.24). Unfortunately, a PP down to -1.3 V was not recorded to confirm this. For information, Figure 5.25 also displays the variation of the Zn peak intensity upon addition of the sap; a decrease is also observed, probably indicating the formation of complexes.

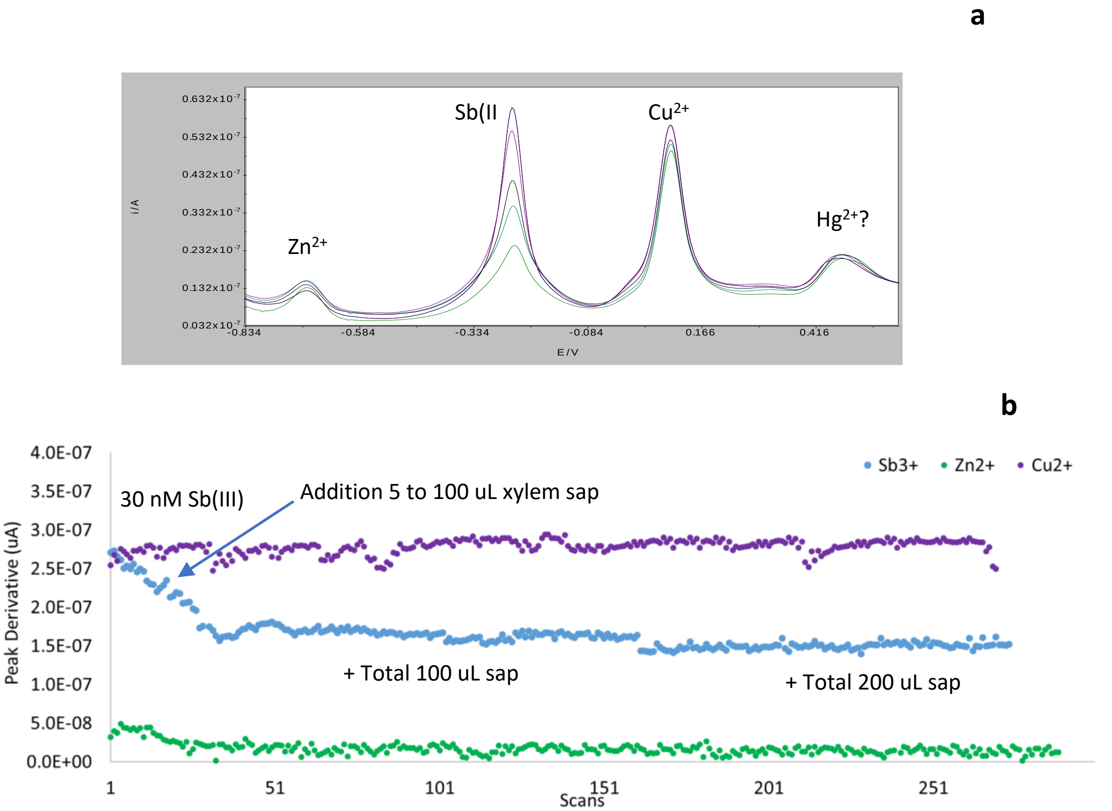


Figure 5. 25. (A) Graph of peak intensity against deposition potential (background subtracted). Solution: 30 nM Sb(III) in 0.1M phosphate solution (pH6) + xylem sap (up to 100 uL) and (C) background subtracted voltammograms showing Zn^{2+} (-0.683V), Sb(III) (-0.267V) and Cu^{2+} (0.092V). DPASV Econd 1.5V(30s) Edep -1.3V(30s) (-1v to 0.6V) step potential: 4 mV modulation amplitude:50 mV (Background subtracted).

5.5 Discussions and Conclusion

Knowledge of Sb complexation in biological matrices is far limited, either for +3 or +5. So far, only four complexes of Sb(V) with lactate and citrate ligands and two complexes of Sb(III) with glutathione have been identified (Hansen and Pergantis, 2008; Daus and Hansen, 2016). The following are few of the challenges and problems why there is limited progress in Sb analysis in biological media: the lack of analytical methodologies; difficulties in quantitative extraction from biological samples; instability and preservation of Sb species sampling and processing; low recoveries (i.e. chromatography); and trace level Sb species are too low for spectrometric identification, (Quentel et al., 2006; Filella et al., 2009). In this study, the suitability of the PP method for the determination of stability constants of Sb complexes at low metal concentrations and mildly to neutral pH were explored.

Preliminary studies on the DPASV method using Au microwire showed a stable signal upon 15-20 scans and was found here to be required to perform before each PP experiments so that reproducible results can be obtained. Sb(III) calibration at different pH showed a linear range of 0 to 40 nM (using a 30 s deposition time), and the peak potential varies cathodically (c.a. 60 mV/pH) as pH increases, in agreement with previous observations (Salaün et al., 2012). The position of the wave is reproducible, independent on the concentration but dependent on the deposition time, as previously observed, e.g. for Cu in marine systems (Gibbon-Walsh et al., 2012).

The ability of PP to visualise complexation and retrieve stability constants is best exemplified with measurements in the presence of EDTA. Complexation is clearly observed with the presence of two distinct waves, one for inorganic Sb(III) (consisting mostly of $Sb(OH)_3$ at pH 3) and one for the reduction of the complex itself (without prior dissociation in the diffusion layer). Stability constants for the formation of $Sb\text{-}EDTA^-$ determined experimentally here agrees very well with literature values. Similarly, the extent of complexation in the presence of tartaric acid also agrees well with modelling predictions, but this not the case for the formation of the $Sb\text{-}DTPA^{2-}$ complex. In that case, although the presence of the complex is evident from the presence of a second wave (Figure 5.15), our experimental value is 20 times higher than the recommended literature value. It could be that such discrepancy comes from the experimental conditions that were used, with, e.g. concentrations of Sb(III) in the order of 10 mM used by Özer and Bogucki (1971) which might be prone to solubility and precipitation issues (Filella and May, 2005b).

The PP procedure developed here can assess the complexation of Sb(III) at low nM concentrations, i.e., at environmentally relevant concentrations at less acidic to neutral pH. To the best of our knowledge, this is the first time that complexation of antimony is visualised with well-known ligands using anodic stripping voltammetry. One exciting aspect is the observation that complexes of Sb(III) with EDTA, DTPA, TA and GSH are inert, i.e. they do not dissociate in the diffusion layer of the gold electrode during the deposition step. While EDTA and DTPA complexes display a cathodic shift of the reduction wave by c.a. 120 mV, complexes with tartaric acid and glutathione are looking like they are electroinactive in the deposition potential range used here (down to -0.4 V). This is similar to what was observed in the xylem samples: complexation is occurring as seen by the decrease in the plateau value at higher sap concentration, but no reduction wave of the complex is seen, suggesting a strong complexation. The research hypothesis is that glutathione, phytochelatin (PC) or sulphur-containing molecules like cysteine might be responsible for the complexation of Sb in the plant xylem sap.

It was also observed here that the adsorption of $Sb(OH)_3$ on the gold electrode surface at relatively high deposition potentials occurs in perchlorate solutions (similar to previously reported in acetate solution (Salaün et al., 2012)). This adsorption does not occur in Hoagland solution at pH 6 (Figure 5.22) and does not occur when complexation is extensive in the presence of EDTA (Figure 5.12), DTPA (Figure 5.15) and TA (Figure 5.17), showing unambiguously that these complexes do not adsorb on the gold electrode at these high deposition potentials. However, in the presence of GSH, even though complexation is evidenced by the decrease of the plateau value (Figure 5.22), an adsorption signal (Edep > 0.1 V) is still observed suggesting the complexes (presumably $Sb(GS)_3$ in this case) may adsorb on the gold electrode surface and get reduced during the desorption step, before the stripping step. This adsorption at high potential region might open new analytical possibilities.

The research hypothesis is that glutathione, phytochelatin (PC) or sulphur-containing molecules like cysteine might be responsible for the complexation of Sb in the plant xylem sap. Xylem sap consists of organic ligands (e.g., glutathione (GSH), low molecular ligands, phytochelatins (PC) and other sulphur containing compounds (e.g. cysteine)) that may be responsible in metal translocation (Tatár et al., 2000; Raab et al., 2005; Álvarez-Fernández et al., 2014; Morua, 2015, Rellán-Álvarez et al., 2011). According to Hazama et al. (2015), 1–2 uM reduced glutathione were found in xylem sap, and 30–150 µM in phloem saps, but oxidised glutathione concentrations were similar using (using capillary electrophoresis- MS).

Until now, the occurrence of the Sb-glutathione complexes (also even in the case of As) in biological media is still unknown, most of the studies are indirect derivation by comparison of results from experimental with and without GSH inhibitors and synthesised in the laboratory (Raab, Meharg, et al., 2004). Hazama et al. (2015) found out that reduced glutathione (GSH) concentrations differed in xylem and phloem saps of castor bean plant (*Ricinus Communis*) (1–2 and 30–150 µM, respectively), but oxidised glutathione concentrations were similar using (capillary electrophoresis- MS). Phloem sap phytochelatin concentration increased from 0.8 µM in controls to 8 µM in the presence of 10 µM Cd. Free citrate was 2–4 µM in xylem sap and 70–100 µM in phloem sap in the absence of Cd. In the presence of 10 uM Cd, free citrate increased from 0.8 uM (control) to 8 uM.

To validate the hypothesis mentioned above, PP of Sb(III) and GSH were studied to show whether there was a complexation between the two since literature often mentioned the complexation of metals with phytochelatins (PC) or GSH in plants (Rauser, 1990; Cai et al., 2004; Emamverdian and Ding, 2017; Rahaman et al., 2020). From our results, it is apparent that there is a strong complexation between Sb(III) and GSH forming electroinactive complexes similar to what is observed in the sap. It is thus possible that glutathione (as well as other sulphur containing compounds) might complex Sb(III) in xylem sap samples, thus facilitating the translocation of this metalloid. The complexation is seen by voltammetric means, and other issues might explain why it is not detected by chromatographic techniques.

5.6 References

Abedin, M. J., Feldmann, J. and Meharg, A. A. (2002) ‘Uptake kinetics of arsenic species in rice plants.’ *Plant Physiology*, 128(3) pp. 1120–1128.

Ainsworth, N., Cooke, J. A. and Johnson, M. S. (1990) ‘Distribution of antimony in contaminated grassland: 1- vegetation and soils.’ *Environmental Pollution*. Elsevier, 65(1) pp. 65–77.

Ainsworth, N., Cooke, J.A. and Johnson, M. S. (1990) ‘Distribution of antimony in contaminated grassland: 2— small mammals and invertebrates.’ *Environmental Pollution*. Elsevier, 65(1) pp. 79–87.

Alexou, M. and Peuke, A. D. (2013) *Plant Mineral Nutrients*. Maathuis, F. J. M. (ed.) *Plant Mineral Nutrients*. Totowa, NJ: Humana Press (Methods in Molecular Biology).

Ali, H., Khan, E. and Sajad, M. A. (2013) ‘Phytoremediation of heavy metals—Concepts and applications.’ *Chemosphere*, 91(7) pp. 869–881.

Althobiti, R. A., Sadiq, N. W. and Beauchemin, D. (2018) ‘Realistic risk assessment of arsenic in rice.’ *Food Chemistry*. Elsevier Ltd, 257, August, pp. 230–236.

Álvarez-Fernández, A., Díaz-Benito, P., Abadía, A., And, A.-F. L.-M. and Abadía, J. (2014) ‘Metal species involved in long distance metal transport in plants.’ *Frontiers in Plant Science*, 5(1) p. 105.

Amarasiriwardena, D. and Wu, F. (2011) ‘Antimony: Emerging toxic contaminant in the environment.’ *Microchemical Journal*. Elsevier B.V., 97(1) pp. 1–3.

Ammann, A. A. (2011) ‘Arsenic Speciation Analysis by Ion Chromatography - A Critical Review of Principles and Applications.’ *American Journal of Analytical Chemistry*, 2011(February) pp. 27–45.

Anawar, H. M., Freitas, M. C., Canha, N. and Regina, I. S. (2011) ‘Arsenic, antimony, and other trace element contamination in a mine tailings affected area and uptake by tolerant plant species.’ *Environmental Geochemistry and Health*, 33(4) pp. 353–362.

Aposhian, H. V. and Aposhian, M. M. (2006) ‘Arsenic Toxicology: Five Questions.’ *Chemical Research in Toxicology*, 19(1) pp. 1–15.

Arnold, L. L., Eldan, M., Nyska, A., van Gemert, M. and Cohen, S. M. (2006) ‘Dimethylarsinic acid: Results of chronic toxicity/oncogenicity studies in F344 rats and in B6C3F1 mice.’ *Toxicology*, 223(1–2) pp. 82–100.

Arunakumara, K. K. I. U., Walpola, B. C. and Yoon, M.-H. (2013) ‘Current status of heavy metal contamination in Asia’s rice lands.’ *Reviews in Environmental Science and Bio/Technology*, 12(4) pp. 355–377.

Ashbrook, P. C. (2014) 'Standard Operating Procedures.' *Journal of Chemical Health and Safety*, 21(5) p. 29.

Ashley, P. M., Graham, B. P., Tighe, M. K. and Wolfenden, B. J. (2007) 'Antimony and arsenic dispersion in the Macleay River catchment, New South Wales: a study of the environmental geochemical consequences.' *Australian Journal of Earth Sciences*, 54(1) pp. 83–103.

ATSDR - Environmental Medicine & Environmental Health Education - CSEM (2013) 'Arsenic Toxicity Case Study: What Are the Standards and Regulation for Arsenic Exposure?' *Encyclopedia of Metalloproteins* pp. 143–143.

Awika, J. M. (2011) 'Major cereal grains production and use around the world.' *In ACS Symposium Series*, pp. 1–13.

Bach, C., Dauchy, X., Chagnon, M. C. and Etienne, S. (2012) 'Chemical compounds and toxicological assessments of drinking water stored in polyethylene terephthalate (PET) bottles: A source of controversy reviewed.' *Water Research*, 46(3) pp. 571–583.

Baker, A. J. M. (1981) 'Accumulators and Excluders - Strategies in the Response of Plants to Heavy Metals.' *Journal of Plant Nutrition*, 3(1–4) pp. 643–654.

Bakhtiari, A. R., Zakaria, M. P., Yaziz, M. I., Lajis, M. N. H. L. and Bi, X. (2014) 'Environment Asia.' *Environment Asia*, 7(1) pp. 104–111.

Basta, N. T. (2006) 'Heavy Metal Contamination of Soil.' *Soil Science Society of America Journal*, 70(5) p. 1819.

Bastías, J. M. and Beldarrain, T. (2016) 'Arsenic translocation in rice cultivation and its implication for human health.' *Chilean Journal of Agricultural Research*. Instituto de Investigaciones Agropecuarias, INIA, 76(1) pp. 114–122.

Bellido-Martín, A., Gómez-Ariza, J. L., Smichowsky, P. and Sánchez-Rodas, D. (2009) 'Speciation of antimony in airborne particulate matter using ultrasound probe fast extraction and analysis by HPLC-HG-AFS.' *Analytica Chimica Acta*, 649(2) pp. 191–195.

Benedict, S. R. (1908) *A Reagent For the Detection of Reducing Sugars*. *J. Biol. Chem*.

Bennett, J. O. and Sicher, R. C. (2011) 'Protein and metabolite composition of xylem sap from field-grown soybeans (Glycine max)' pp. 921–931.

Bhattacharya, P., Samal, a C., Majumdar, J. and Santra, S. C. (2009) 'Transfer of Arsenic from Groundwater and Paddy Soil to Rice Plant (Oryza sativa L.): A Micro-Level Study in West Bengal , India.' *World Journal of Agricultural Sciences*, 5(4) pp. 425–431.

Bi, Z. (2012) *Speciation analysis of trace metals in natural waters using vibrating electrodes*. *Environmental Sciences*. University of Liverpool.

Bielen, A., Remans, T., Vangronsveld, J. and Cuypers, A. (2013) ‘The influence of metal stress on the availability and redox state of ascorbate, and possible interference with its cellular functions.’ *International Journal of Molecular Sciences* pp. 6382–6413.

Biles, C. L. and Abeles, F. B. (1991) ‘Xylem sap proteins.’ *Plant Physiology*, 96(July 1991) pp. 597–601.

Billon, G. and Van Den Berg, C. M. G. (2004) ‘Gold and silver micro-wire electrodes for trace analysis of metals.’ *Electroanalysis*, 16(19) pp. 1583–1591.

Borovička, J., Řanda, Z. and Jelínek, E. (2006) ‘Antimony content of macrofungi from clean and polluted areas.’ *Chemosphere*, 64(11) pp. 1837–1844.

Bouman, B. A. . and Tuong, T. . (2001) ‘Field water management to save water and increase its productivity in irrigated lowland rice.’ *Agricultural Water Management*, 49(1) pp. 11–30.

Bowen, H. J. M. (Humphry J. M. (1979) *Environmental chemistry of the elements*. London, New York: Academic Press.

Brackin, R., Näsholm, T., Robinson, N., Guillou, S., Vinall, K., Buckley, S., Lakshmanan, P., Schmidt, S. and Inselsbacher, E. (2016) ‘Microdialysis-a new technology for investigating soil nitrogen fluxes in the rhizosphere.’ *In Proceedings of the International Nitrogen Initiative 2016 Conference*, pp. 4–8.

Brammer, H. and Ravenscroft, P. (2009) ‘Arsenic in groundwater: A threat to sustainable agriculture in South and South-east Asia.’ *Environment International*. Elsevier Ltd pp. 647–654.

Brihaye, C. and Duyckaerts, G. (1982) ‘Determination of traces of metals by anodic stripping voltammetry at a rotating glassy carbon ring—disc electrode.’ *Analytica Chimica Acta*, 143 pp. 111–120.

Broadley, M., Brown, P., Cakmak, I., Rengel, Z. and Zhao, F. (2011) ‘Function of Nutrients: Micronutrients.’ *In Marschner’s Mineral Nutrition of Higher Plants: Third Edition*. Elsevier Inc., pp. 191–248.

Brochu, C., Wang, J., Roy, G., Messier, N., Wang, X.-Y., Saravia, N. G. and Ouellette, M. (2003) ‘Antimony Uptake Systems in the Protozoan Parasite Leishmania and Accumulation Differences in Antimony-Resistant Parasites.’ *Antimicrobial Agents and Chemotherapy*. American Society for Microbiology (ASM), 47(10) pp. 3073–3079.

Brown, S. D. and Kowalski, B. R. (1979) ‘Pseudopolarographic Determination of Metal Complex Stability Constants in Dilute Solution by Rapid Scan Anodic Stripping Voltammetry.’ *Analytical Chemistry*, 51(13) pp. 2133–2139.

Buckley, S., Brackin, Richard, A. and Schmidt, S. (2016) ‘Microdialysis-a sensitive method for estimating plant-available N released during litter decomposition.' *Proceedings of the International Nitrogen Initiative Conference 2016*, (December).

Buckley, S., Brackin, R., Jämtgård, S., Näsholm, T. and Schmidt, S. (2020) 'Microdialysis in soil environments: Current practice and future perspectives.' *Soil Biology and Biochemistry*, 143, April, p. 107743.

Buckley, S., Brackin, R., Näsholm, T., Schmidt, S. and Jämtgård, S. (2017) 'Improving in situ recovery of soil nitrogen using the microdialysis technique.' *Soil Biology and Biochemistry*, 114, November, pp. 93–103.

Buckley, S., Brackin, R. and Schmidt, S. (2015) *Microdialysis: an alternative approach to identifying plant-available nitrogen in soils*.

Burló, F., Guijarro, I., Carbonell-Barrachina, A. A., Valero, D. and Martínez-Sánchez, F. (1999) 'Arsenic Species: Effects on and Accumulation by Tomato Plants.' *Journal of Agricultural and Food Chemistry*, 47(3) pp. 1247–1253.

Cabalda, M. V, Banaag, M. A. and Garces, R. B. (2002) *Sustainable Development in The Philippine Minerals Industry: A Baseline Study*. M.V. Cabalda P.N.T. Tidalgo & R.B. Garces, M. A. B. (ed.) *Mining, Minerals and Sustainable Development Project (MMSD)*. England: International Institute for the Environment and Development (IIED).

Cai, Y., Su, J. and Ma, L. Q. (2004) 'Low molecular weight thiols in arsenic hyperaccumulator Pteris Vittata upon exposure to arsenic and other trace elements.' *Environmental Pollution*, 129(1) pp. 69–78.

Cal-Prieto, M. J., Carlosena, A., Andrade, J. M., Martínez, M. L., Muniategui, S., López-Mahía, P. and Prada, D. (2001) 'Antimony as a tracer of the anthropogenic influence on soils and estuarine sediments.' *Water, Air, and Soil Pollution*. Springer, 129(1–4) pp. 333–348.

Canadian Council of Ministers of the Environment (2007) *Canadian soil quality guidelines for the protection of environmental and human health*. Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment. Winnipeg. [Online] http://goo.gl/AePSg4.

Canepari, S., Marconi, E., Astolfi, M. L. and Perrino, C. (2010) 'Relevance of Sb(III), Sb(V), and Sb-containing nano-particles in urban atmospheric particulate matter.' *Analytical and Bioanalytical Chemistry*, 397(6) pp. 2533–2542.

Carey, A.-M., Lombi, E., Donner, E., de Jonge, M. D., Punshon, T., Jackson, B. P., Guerinot, M. Lou, Price, A. H. and Meharg, A. A. (2012) 'A review of recent developments in the speciation and location of arsenic and selenium in rice grain.' *Analytical and Bioanalytical Chemistry*, 402(10) pp. 3275–3286.

Carneado, S., Hernández-Nataren, E., López-Sánchez, J. F. F. and Sahuquillo, A. (2015)

‘Migration of antimony from polyethylene terephthalate used in mineral water bottles.’ *Food Chemistry*. Elsevier Ltd, 166, January, pp. 544–550.

Carolyn, P., Aqilah, F. A. T., Payus, C., Farhana, A., Talip, A., Carolyn, P., Aqilah, F. A. T., Payus, C., Farhana, A. and Talip, A. (2014) ‘Assessment of heavy metals accumulation in paddy rice (Oryza sativa).’ *African Journal of Agricultural Research*. Academic Journals, 9(41) pp. 3082–3090.

Casiot, C., Ujevic, M., Munoz, M., Seidel, J. L. and Elbaz-Poulichet, F. (2007) ‘Antimony and arsenic mobility in a creek draining an antimony mine abandoned 85 years ago (upper Orb basin, France).’ *Applied Geochemistry*, 22(4) pp. 788–798.

Cavicchioli, A., La-Scalea, M. A., Gutz, G. R., Gutz, I. G. R. and Gutz, G. R. (2004) ‘Analysis and Speciation of Traces of Arsenic in Environmental , Food and Industrial Samples by Voltammetry : a Review.’ *Electroanalysis*, 16(9) pp. 697–711.

Chakraborti, D., Rahman, M. M., Das, B., Nayak, B., Pal, A., Sengupta, M. K., Hossain, M. A., Ahamed, S., Sahu, M., Saha, K. C., Mukherjee, S. C., Pati, S., Dutta, R. N. and Quamruzzaman, Q. (2013) ‘Groundwater arsenic contamination in Ganga–Meghna–Brahmaputra plain, its health effects and an approach for mitigation.’ *Environmental Earth Sciences*, 70(5) pp. 1993–2008.

Chang, C.-Y., Wang, C.-F., Mui, D. T. and Chiang, H.-L. (2009) ‘Application of methods (sequential extraction procedures and high-pressure digestion method) to fly ash particles to determine the element constituents: A case study for BCR 176.’ *Journal of Hazardous Materials*, 163(2–3) pp. 578–587.

Chapman, C. S. and Van Den Berg, C. M. G. G. (2007) ‘Anodic stripping voltammetry using a vibrating electrode.’ *Electroanalysis*, 19(13) pp. 1347–1355.

Chaurasia, C. S., Müller, M., Bashaw, E. D., Benfeldt, E., Bolinder, J., Bullock, R., Bungay, P. M., DeLange, E. C. M., Derendorf, H., Elmquist, W. F., Hammarlund-Udenaes, M., Joukhadar, C., Kellogg, D. L., Lunte, C. E., Nordstrom, C. H., Rollema, H., Sawchuk, R. J., Cheung, B. W. Y., Shah, V. P., Stahle, L., Ungerstedt, U., Welty, D. F. and Yeo, H. (2007) ‘AAPS-FDA workshop white paper: Microdialysis principles, application and regulatory perspectives.’ *In Pharmaceutical Research*, pp. 1014–1025.

Chen, Z. L., Farzana Akter, K., Rahman Mahmudur, M. and Naidu, R. (2006) ‘Speciation of arsenic by ion chromatography inductively coupled plasma mass spectrometry using ammonium eluents.’ *Journal of Separation Science*, 29(17) pp. 2671–2676.

Cheng, T. and Sun, H. (2014) ‘CHAPTER 25. Antimony and Bismuth.’ *In* Maret, W. and Wedd, A. (eds) *Binding, Transport and Storage of Metal Ions in Biological Cells*. London, UK: The Royal Society of Chemistry, pp. 768–799.

Chepkemoi, J. (2017) *What Is The Environmental Impact Of The Mining Industry?* First Break. [Online] worldatlas.com/articles/what-is-the-environmental-impact-of-the-mining-industry.html.

Cheraghi, M., Mosaed, H. P., Lorestani, B. and Yousefi, N. (2012) ‘Heavy metal contamination in some rice samples.’ *Electronic Journal of Environmental, Agricultural and Food Chemistry*, 11(5) pp. 424–432.

Choudhury, B. U., Malang, A., Webster, R., Mohapatra, K. P., Verma, B. C., Kumar, M., Das, A., Islam, M. and Hazarika, S. (2017) ‘Acid drainage from coal mining: Effect on paddy soil and productivity of rice.’ *Science of the Total Environment*. Elsevier B.V., 583(August 2018) pp. 344–351.

Ciminelli, V. S. T., Gasparon, M., Ng, J. C., Silva, G. C. and Caldeira, C. L. (2017) ‘Dietary arsenic exposure in Brazil: The contribution of rice and beans.’ *Chemosphere*. Elsevier Ltd, 168, February, pp. 996–1003.

Çirmi, D., Aydin, R. and Köleli, F. (2015) ‘The electrochemical reduction of nitrate ion on polypyrrole coated copper electrode.’ *Journal of Electroanalytical Chemistry*, 736 pp. 101–106.

Clark, R. B., Tiffin, L. O. and Brown, J. C. (1973) ‘Organic Acids and Iron Translocation in Maize Genotypes.’ *Plant Physiology*, 52(2) pp. 147–150.

Clarkson, D. T. (1996) ‘Marschner H. 1995. Mineral nutrition of higher plants. second edition. 889pp. London: Academic Press.’ *Annals of Botany*, 78(4) pp. 527–528.

Clemens, S. and Ma, J. F. (2016) ‘Toxic Heavy Metal and Metalloid Accumulation in Crop Plants and Foods.’ *Annual Review of Plant Biology*, 67(1) pp. 489–512.

Correia, M. M., Alves, S., Simões Gonçalves, M. D. L. and Nabais, C. (2006) ‘Dynamic modelling of nickel complexation in xylem sap of Quercus ilex: A voltammetric study.’ *Electroanalysis*, 18(8) pp. 814–822.

Cullen, W. R. and Reimer, K. J. (2016a) ‘CHAPTER 2. Arsenic Is Everywhere.’ *In Arsenic is Everywhere: Cause for Concern?*, pp. 8–48.

Cullen, W. R. and Reimer, K. J. (2016b) ‘CHAPTER 8. Arsenic and the Evening Meal.’ *In Arsenic is Everywhere: Cause for Concern?*, pp. 221–265.

Daniels, R., Rush, C. C. and Bauer, L. (1960) ‘The Fehling and Benedict tests.’ *Journal of Chemical Education*, 37(4) p. 205.

Daus, B. and Hansen, H. R. (2016) ‘Analysis of antimony species – lessons learnt from more than two decades of environmental research.’ *Environmental Chemistry*, 13(6) p. 913.

Dawe, B. D., Organisation, A. and Nations, U. (2015) ‘Rice in Asia: Paddy-whacked.’ *Economist (United Kingdom)*, 411(8960).

Dobermann, A., Dawe, D., Roetter, R. P. and Cassman, K. G. (2000) ‘Reversal of rice yield decline in a long-term continuous cropping experiment.’ *Agronomy Journal*, 92(4) pp. 633–643.

Domingo, L. E. and Kyuma, K. (1983) ‘Trace elements in tropical asian paddy soils: I. total trace element status.’ *Soil Science and Plant Nutrition*, 29(4) pp. 439–452.

Dortsiou, M. and Kyriacou, G. (2009) ‘Electrochemical reduction of nitrate on bismuth cathodes.’ *Journal of Electroanalytical Chemistry*, 630(1–2) pp. 69–74.

Duester, L., Diaz-Bone, R. A., Kösters, J. and Hirner, A. V. (2005) ‘Methylated arsenic, antimony and tin species in soils.’ *In Journal of Environmental Monitoring*, pp. 1186–1193.

Dushenkov, S. (2003) ‘Trends in phytoremediation of radionuclides.’ *In Plant and Soil*, pp. 167–175.

Elmquist, W. F. and Sawchuk, R. J. (1997) ‘Application of microdialysis in pharmacokinetic studies.’ *Pharmaceutical Research* pp. 267–288.

Emamverdian, A. and Ding, Y. (2017) ‘Effects of heavy metals’ toxicity on plants and enhancement of plant defense mechanisms of Si-mediation “ Review.”’ *International Journal of Environmental & Agriculture Research*, (4) pp. 41–51.

Emamverdian, A., Ding, Y., Mokhberdoran, F. and Xie, Y. (2015) ‘Heavy Metal Stress and Some Mechanisms of Plant Defense Response.’ *The Scientific World Journal*. Hindawi Publishing Corporation, 2015 pp. 1–18.

EPA (2004) ‘EPA Method 6020A: ICP-MS. Official Name: EPA Method 6020A, Inductively Coupled Plasma-Mass Spectrometry.’ *EPA methods*, 6.

Epstein, E. and and Bloom, A. J. (1972) *Mineral Nutrition of Plants: Principles and Perspectives*. 2nd ed., Sunderland, Massachusetts: Sinauer Associates, Inc.

Fan, Y., Zhu, T., Li, M., He, J., Huang, R. and and Ruixue Huang, T. Z. Y. F. M. L. J. H. (2017) ‘Heavy Metal Contamination in Soil and Brown Rice and Human Health Risk Assessment near Three Mining Areas in Central China.’ *Journal of Healthcare Engineering*. Hindawi, 2017 p. 9.

FAO (2016) *GIEWS - Crop Prospects and Food Situation, No.1,March 2016*.

FAO and WHO (2019) *Report of the 11th session of the codex committee on contaminnants in foods. A joint FAO/WHO food standards programme codex alimentarius commission 40th Session. Codex*. Geneva, Switzerland.

Farid, M., Shakoor, M., Ehsan, S., Ali, S., Zubair, M. and Hanif, M. (2013) ‘Morphological, physiological and biochemical responses of different plant species to Cd stress.’ *Int J*

Chem Biochem Sci, 3(March) pp. 53–60.

Farnese, F. S., Oliveira, J. A., Farnese, M. S., Gusman, G. S., Silveira, N. M. and Siman, L. I. (2014) 'Uptake arsenic by plants: Effects on mineral nutrition, growth and antioxidant capacity.' *Idesia (Arica)*, 32(1) pp. 99–106.

Fashola, M., Ngole-Jeme, V. and Babalola, O. (2016) 'Heavy Metal Pollution from Gold Mines: Environmental Effects and Bacterial Strategies for Resistance.' *International Journal of Environmental Research and Public Health*. MDPI AG, 13(11) p. 1047.

Feldmann, J., Salaün, P. and Lombi, E. (2009) 'Critical review perspective: elemental speciation analysis methods in environmental chemistry - moving towards methodological integration.' *Environmental Chemistry*. CSIRO, 6(4) p. 275.

Feng, R., Wei, C., Tu, S., Ding, Y., Wang, R. and Guo, J. (2013) 'The uptake and detoxification of antimony by plants: A review.' *Environmental and Experimental Botany*. Elsevier B.V., 96, December, pp. 28–34.

Festin, E. S., Tigabu, M., Chileshe, M. N., Syampungani, S. and Odén, P. C. (2019) 'Progresses in restoration of post-mining landscape in Africa.' *Journal of Forestry Research*, 30(2) pp. 381–396.

Filella and May (2003) 'Computer simulation of the low-molecular-weight inorganic species distribution of antimony (III) and antimony (V) in natural waters.' *Geochimica et Cosmochimica Acta,* 67(21) pp. 4013–4031.

Filella, M. (2013) 'Food for thought: A critical overview of current practical and conceptual challenges in trace element analysis in natural waters.' *Water (Switzerland)*. MDPI AG pp. 1152–1171.

Filella, M., Belzile, N. and Chen, Y.-W. W. (2002) 'Antimony in the environment: a review focused on natural waters.' *Earth-Science Reviews*, 57(1–2) pp. 125–176.

Filella, M., Belzile, N. and Lett, M.-C. C. (2007) 'Antimony in the environment: A review focused on natural waters. III. Microbiota relevant interactions.' *Earth-Science Reviews*, 80(3–4) pp. 195–217.

Filella, M. and May, P. M. (2005a) 'Critical appraisal of available thermodynamic data for the complexation of antimony(iii) and antimony(v) by low molecular mass organic ligands.' *Journal of Environmental Monitoring*, 7(12) p. 1226.

Filella, M. and May, P. M. (2005b) 'Reflections on the calculation and publication of potentiometrically- determined formation constants.' *Talanta*, 65(5) pp. 1221–1225.

Filella, M. and Williams, P. A. (2012) 'Antimony interactions with heterogeneous complexants in waters, sediments and soils: A review of binding data for homologous compounds.' *Chemie der Erde*. Elsevier GmbH., 72(SUPPL.4) pp. 49–65.

Filella, M., Williams, P. A. and Belzile, N. (2009) 'Antimony in the environment: Knowns and unknowns.' *Environmental Chemistry*, 6(2) pp. 95–105.

Forsberg, G., O'Laughlin, J. W., Megargle, R. G. and Koirtyohann, S. R. (1975) 'Determination of Arsenic by Anodic Stripping Voltammetry and Differential Pulse Anodic Stripping Voltammetry.' *Analytical Chemistry*, 47(9) pp. 1586–1592.

Francesconi, K. A. and Kuehnelt, D. (2004) 'Determination of arsenic species: A critical review of methods and applications, 2000–2003.' *The Analyst*, 129(5) pp. 373–395.

Frantz, J. M. and Epstein, E. (2005) *Nutritional deficiencies: What they look like*. [Online] [Accessed on 16th December 2019] http://www.ces.ncsu.edu/depts/hort/floriculture/def/forfloriculturecropshttp://extension.agron.iastate.edu/soilfertility/nutrienttopics/deficiencies.htmlcornhttp://muextension.missouri.edu/explore/agguides/hort/index.htm.

FSA (2012) *Arsenic speciation in fruit and vegetables grown in the UK.* Aberdeen: University of Aberdeen.

Fu, Z., Wu, F., Mo, C., Deng, Q., Meng, W. and Giesy, J. P. (2016) 'Comparison of arsenic and antimony biogeochemical behavior in water, soil and tailings from Xikuangshan, China.' *Science of the Total Environment*, 539 pp. 97–104.

Garg, N. and Singla, P. (2011) 'Arsenic toxicity in crop plants: physiological effects and tolerance mechanisms.' *Environmental Chemistry Letters*. Springer, 9(3) pp. 303–321.

Garg, N., Singla, P. and Bhandari, P. (2015) 'Metal uptake, oxidative metabolism, and mycorrhization in pigeonpeaand pea under arsenic and cadmium stress.' *Turkish Journal of Agriculture and Forestry*, 39(2) pp. 234–250.

Gebel, T. (1997) 'Arsenic and antimony: comparative approach on mechanistic toxicology.' *Chemico-Biological Interactions*. Elsevier Ireland Ltd, 107(3) pp. 131–144.

Gebel, T. W. (2001) 'Unanswered Questions in Arsenic Toxicology.' *Journal of Environmental Pathology, Toxicology and Oncology*, 20(4) p. 11.

Gemici, Ü. and Tarcan, G. (2007) 'Assessment of the pollutants in farming soils and waters around untreated abandoned Türkönü mercury mine (Turkey).' *Bulletin of Environmental Contamination and Toxicology*, 79(1) pp. 20–24.

Geng, A., Wang, X., Wu, L., Wang, F., Chen, Y., Yang, H., Zhang, Z. and Zhao, X. (2017) 'Arsenic accumulation and speciation in rice grown in arsanilic acid-elevated paddy soil.' *Ecotoxicology and Environmental Safety*, 137 pp. 172–178.

Geng, C. N., Zhu, Y. G., Tong, Y. P., Smith, S. E. and Smith, F. A. (2006) 'Arsenate (As) uptake by and distribution in two cultivars of winter wheat (Triticum aestivum L.).' *Chemosphere*, 62(4) pp. 608–615.

Gerényi, A., Czech, V., Fodor, F., Vincze, L. and Szalóki, I. (2017) 'In vivo XANES measuring technique for studying the arsenic uptake in cucumber plants.' *X-Ray Spectrometry*, 46(3) pp. 143–150.

German Federal Soil Protection Act (1998) *Federal Law Gazette I p. 502*.

Ghori, N.-H., Ghori, T., Hayat, M. Q., Imadi, S. R., Gul, A., Altay, V. and Ozturk, M. (2019) 'Heavy metal stress and responses in plants.' *International Journal of Environmental Science and Technology*. Center for Environmental and Energy Research and Studies, 16(3) pp. 1807–1828.

Gibbon-Walsh, K., Salaün, P. and van den Berg, C. M. G. (2012a) 'Determination of arsenate in natural pH seawater using a manganese-coated gold microwire electrode.' *Analytica Chimica Acta*. Elsevier B.V., 710, January, pp. 50–57.

Gibbon-Walsh, K., Salaün, P. and van den Berg, C. M. G. (2012b) 'Pseudopolarography of Copper Complexes in Seawater Using a Vibrating Gold Microwire Electrode.' *The Journal of Physical Chemistry A*, 116(25) pp. 6609–6620.

Gibbon-Walsh, K., Salaün, P., Uroic, M. K., Feldmann, J., McArthur, J. M. and Van Den Berg, C. M. G. (2011) 'Voltammetric determination of arsenic in high iron and manganese groundwaters.' *Talanta*, 85(3) pp. 1404–1411.

Gidlow, D. A. (2004) 'Lead toxicity.' *Occupational Medicine*, 54(2) pp. 76–81.

Goldberg, S. (2011) 'Chemical Equilibrium and Reaction Modeling of Arsenic and Selenium in Soils.' *Dynamics and Bioavailability of Heavy Metals in the Rootzone* pp. 65–92.

Grob, M., Wilcke, W. and Mestrot, A. (2018) 'Release and Biomethylation of Antimony in Shooting Range Soils upon Flooding.' *Soil Systems*, 2(2) p. 34.

Guerriero, Gea, Deshmukh, R. and Durgesh K., T. (2020) *Metalloids in Plants Advances and Future Prospects*. Deshmukh, R., Tripathi, D. K., and Guerriero, Gia (eds) *Wiley*. John Wiley & Sons Ltd.

Gupta, D. K., Srivastava, S., Huang, H. G., Romero-Puertas, M. C. and Sandalio, L. M. (2011) 'Arsenic Tolerance and Detoxification Mechanisms in Plants.' *In*, pp. 169–179.

Ha, N. T. H., Ha, N. T., Nga, T. T. H., Minh, N. N., Anh, B. T. K., Hang, N. T. A., Duc, N. A., Nhuan, M. T. and Kim, K.-W. (2019) 'Uptake of arsenic and heavy metals by native plants growing near Nui Phao multi-metal mine, northern Vietnam.' *Applied Geochemistry*. Elsevier Ltd, 108, September, p. 104368.

Hakeem, K. R. (2015) 'Crop production and global environmental issues.' *Crop Production and Global Environmental Issues*, (December) pp. 1–598.

Hall, J. L. L. (2002) ‘Cellular mechanisms for heavy metal detoxification and tolerance.’ *Journal of experimental botany*, 53(366) pp. 1–11.

Hammel, W., Debus, R. and Steubing, L. (2000) ‘Mobility of antimony in soil and its availability to plants.’ *Chemosphere*, 41(11) pp. 1791–1798.

Hansen, C. (2011) *Antimony speciation analysis HPLC methods with ICP-MS and ES-MS detection for complex biological matrices*. University of Coppenhagen.

Hansen, H. R. and Pergantis, S. A. (2008) ‘Analytical techniques and methods used for antimony speciation analysis in biological matrices.’ *Journal of Analytical Atomic Spectrometry*, 23(10) p. 1328.

Hasanuzzaman, M., Nahar, K. and Fujita, M. (2018) *Mechanisms of Arsenic Toxicity and Tolerance in Plants*. Hasanuzzaman, M., Nahar, K., and Fujita, M. (eds) *Mechanisms of Arsenic Toxicity and Tolerance in Plants*. Singapore: Springer Singapore.

Hasanuzzaman, M., Nahar, K., Hakeem, K. R., Öztürk, M. and Fujita, M. (2015) ‘Arsenic Toxicity in Plants and Possible Remediation.’ *In Soil Remediation and Plants: Prospects and Challenges*. Elsevier Inc., pp. 433–501.

Hawkesford, M. J., Parmar, S. and Buchner, P. (2013) ‘Mineral Composition Analysis: Measuring Anion Uptake and Anion Concentrations in Plant Tissues.’ *In Plant Mineral Nutrients*. Totowa, NJ: Humana Press, pp. 109–119.

Hazama, K., Nagata, S., Fujimori, T., Yanagisawa, S. and Yoneyama, T. (2015) ‘Concentrations of metals and potential metal-binding compounds and speciation of Cd, Zn and Cu in phloem and xylem saps from castor bean plants (Ricinus communis) treated with four levels of cadmium.’ *Physiologia Plantarum*, 154(2) pp. 243–255.

He, M., Wang, N., Long, X., Zhang, C., Ma, C., Zhong, Q., Wang, A., Wang, Y., Pervaiz, A. and Shan, J. (2019) ‘Antimony speciation in the environment: Recent advances in understanding the biogeochemical processes and ecological effects.’ *Journal of Environmental Sciences*. Elsevier B.V., 75, January, pp. 14–39.

Hettick, B. E., Cañas-Carrell, J. E., French, A. D. and Klein, D. M. (2015) ‘Arsenic: A Review of the Element’s Toxicity, Plant Interactions, and Potential Methods of Remediation.’ *Journal of Agricultural and Food Chemistry*, 63(32) pp. 7097–7107.

Hijaz, F. and Killiny, N. (2014) ‘Collection and chemical composition of phloem sap from Citrus sinensis L. Osbeck (sweet orange).’ *PLoS ONE*. Public Library of Science, 9(7).

Hirner, A. V., Grüter, U. M. and Kresimon, J. (2000) ‘Metal(loid)organic compounds in contaminated soil.’ *Fresenius’ Journal of Analytical Chemistry*. Springer, 368(2–3) pp. 263–267.

Hoagland and Arnon, D., D. (1950) *The water-culture method of growing plants without* *soil.* Berkeley, Calif. : University of California, College of Agriculture, Agricultural Experiment Station.

Hossain, M. A., Piyatida, P., da Silva, J. A. T. and Fujita, M. (2012) 'Molecular Mechanism of Heavy Metal Toxicity and Tolerance in Plants: Central Role of Glutathione in Detoxification of Reactive Oxygen Species and Methylglyoxal and in Heavy Metal Chelation.' *Journal of Botany*. Hindawi Limited, 2012(Cd) pp. 1–37.

Hozhina, E. ., Khramov, A. ., Gerasimov, P. . and Kumarkov, A. . (2001) 'Uptake of heavy metals, arsenic, and antimony by aquatic plants in the vicinity of ore mining and processing industries.' *Journal of Geochemical Exploration*, 74(1–3) pp. 153–162.

Hrytsak, L. R., Herts, A. I., Nuzhyna, N. V., Cryk, M. M., Shevchenko, V. V. and Drobyk, N. M. (2018) 'The influence of light regime on the growth data and pigment composition of the plant Gentiana lutea cultured in vitro.' *Regulatory Mechanisms in Biosystems*, 9(2) pp. 258–266.

Hu, L., Zhang, B., Wu, D., Fan, H., Tu, J., Liu, W., Huang, R. and Huang, X. (2019) 'Estimation of arsenic bioaccessibility in raw and cooked radish using simulated in vitro digestion.' *Food & Function*. Royal Society of Chemistry, 10(3) pp. 1426–1432.

Hu, Y., Cheng, H. and Tao, S. (2016) 'The Challenges and Solutions for Cadmium-contaminated Rice in China: A Critical Review.' *Environment International*. Elsevier Ltd pp. 515–532.

Hua, C.-Y., Chen, J.-X., Cao, Y., Li, H.-B., Chen, Y. and Ma, L. Q. (2020) 'Pteris vittata coupled with phosphate rock effectively reduced As and Cd uptake by water spinach from contaminated soil.' *Chemosphere*. Elsevier Ltd, 247, May, p. 125916.

Huang, R.-Q., Gao, S.-F., Wang, W.-L., Staunton, S. and Wang, G. (2006) 'Soil arsenic availability and the transfer of soil arsenic to crops in suburban areas in Fujian Province, southeast China.' *Science of The Total Environment*, 368(2–3) pp. 531–541.

Huang, Y., Chen, Q., Deng, M., Japenga, J., Li, T., Yang, X. and He, Z. (2018) 'Heavy metal pollution and health risk assessment of agricultural soils in a typical peri-urban area in southeast China.' *Journal of Environmental Management*. Academic Press, 207, February, pp. 159–168.

Huang, Z., Pan, X.-D. D., Wu, P.-G. G., Han, J.-L. L. and Chen, Q. (2013) 'Health Risk Assessment of Heavy Metals in Rice to the Population in Zhejiang, China.' Scarfi, M. R. (ed.) *PLoS ONE*, 8(9) pp. 1–6.

Huiliang, H., Jagner, D. and Renman, L. (1988) 'Flow potentiometric and constant-current stripping analysis for arsenic(V) without prior chemical reduction to arsenic(III).' *Analytica Chimica Acta*, 207 pp. 37–46.

Humphrey, O. S., Young, S. D., Bailey, E. H., Crout, N. M. J., Ander, E. L., Hamilton, E. M.

and Watts, M. J. (2019) ‘Investigating the use of microdialysis and SEC-UV-ICP-MS to assess iodine interactions in soil solution.’ *Chemosphere*. Elsevier Ltd, 229, August, pp. 41–50.

Hunt, R., Causton, D. R., Shipley, B. and Askew, A. P. (2002) ‘A modern tool for classical plant growth analysis.’ *Annals of Botany*, 90(4) pp. 485–488.

Inselsbacher, E. (2014) ‘Recovery of individual soil nitrogen forms after sieving and extraction.’ *Soil Biology and Biochemistry*, 71, April, pp. 76–86.

Inselsbacher, E., Öhlund, J., Jämtgård, S., Huss-Danell, Kerstin, A. and Näsholm, T. (2011) ‘The potential of microdialysis to monitor organic and inorganic nitrogen compounds in soil.’ *Soil Biology and Biochemistry*, 43(6) pp. 1321–1332.

International Programme on Chemical Safety (2004) ‘International programme on chemical safety (IPCS),’ (June) pp. 1–34.

IPNI (2002) ‘Nutrient Deficiency Symptoms in Rice.’ *Better Crops International*, 16(May) pp. 23–25.

IRRI and DFID (2009) ‘Scuba rice : breeding flood-tolerance into Asia ’ s local mega rice varieties.’ *South Asia* pp. 1–6.

Ismail, B., Yap, D., Adezrian, J., Khairiah, J. and Ahmad-Mahir, R. (2009) ‘The Uptake of Heavy Metals by Paddy Plants (Oryza sativa) in Kota Marudu, Sabah, Malaysia.’ *& Environ. Sci*, 6(1) pp. 16–19.

Jamila Alfaraas, A. M., Khairiah, J., Ismail, B. S. and Noraini, T. (2016) ‘Effects of heavy metal exposure on the morphological and microscopical characteristics of the paddy plant.’ *Journal of Environmental Biology*, 37(5) pp. 955–963.

Järup, L. (2003) ‘Hazards of heavy metal contamination.’ *British Medical Bulletin*, 68 pp. 167–182.

JECFA (2016) ‘Joint FAO / WHO Expert Committee on Food Additives (JECFA) Call for Experts on Food Additives , Contaminants and toxins ; and Residues of Veterinary Drugs,’ (October).

Jentschke, G. and Godbold, D. L. (2000) ‘Metal toxicity and ectomycorrhizas.’ *Physiologia Plantarum*, 109(2) pp. 107–116.

Ji, Y., Sarret, G., Schulin, R. and Tandy, S. (2017) ‘Fate and chemical speciation of antimony (Sb) during uptake, translocation and storage by rye grass using XANES spectroscopy.’ *Environmental Pollution*. Elsevier Ltd, 231, December, pp. 1322–1329.

Johnson, C. A., Moench, H., Wersin, P., Kugler, P. and Wenger, C. (2005) ‘Solubility of Antimony and Other Elements in Samples Taken from Shooting Ranges.’ *Journal of*

Environmental Quality. Wiley, 34(1) pp. 248–254.

Johnson, C. D. (2014) ‘Phytoremediation of Arsenic Contamination on Vashon-Maury Island METHODS Salix Screening for Arsenic Tolerance.’

Johnston, A. E. and Poulton, P. R. (2018) ‘The importance of long-term experiments in agriculture: their management to ensure continued crop production and soil fertility; the Rothamsted experience.’ *European Journal of Soil Science*, 69(1) pp. 113–125.

Kabata-Pendias, A. (2010) *Trace Elements in Soils and Plants*. 4th ed., CRC Press.

Kalaji, H. M., Jajoo, A., Oukarroum, A., Brestic, M., Zivcak, M., Samborska, I. A., Cetner, M. D., Łukasik, I., Goltsev, V. and Ladle, R. J. (2016) ‘Chlorophyll a fluorescence as a tool to monitor physiological status of plants under abiotic stress conditions.’ *Acta Physiologiae Plantarum*. Polish Academy of Sciences.

Kapaj, S., Peterson, H., Liber, K. and Bhattacharya, P. (2006) ‘Human Health Effects From Chronic Arsenic Poisoning–A Review.’ *Journal of Environmental Science and Health, Part A*. The Safe Drinking Water Foundation, Saskatoon, Saskatchewan, Canada., 41(10) pp. 2399–2428.

Katsounaros, I. and Kyriacou, G. (2007) ‘Influence of the concentration and the nature of the supporting electrolyte on the electrochemical reduction of nitrate on tin cathode.’ *Electrochimica Acta*, 52(23) pp. 6412–6420.

Kehr, J. and Rep, M. (2007) ‘Protein extraction from xylem and phloem sap.’ *Methods in molecular biology (Clifton, N.J.)*, 355 pp. 27–35.

Killiny, N. and Hijaz, F. (1998) ‘Chemical composition of xylem sap of Citrus sinensis L. Osbeck (sweet orange).’ *Trends in Plant Science*, 3(5) pp. 188–195.

Kisan, M., Sangathan, S., Nehru, J. and Pitroda, S. G. (2012) ‘Laboratory Glassware-Volumetric Instruments-Methods for Testing of Capacity and for Use.’ ISO (ed.) *4787*. Geneva: IS pp. 1–29.

Kitagishi, K. (1981) ‘Heavy Metal Pollution in Soils of Japan.’ *Japan Scientific Societies Press, Tokyo, Japan*, 52(4) p. 302.

Koester, R. P., Skoneczka, J. A., Cary, T. R., Diers, B. W. and Ainsworth, E. A. (2014) ‘Historical gains in soybean (Glycine max Merr.) seed yield are driven by linear increases in light interception, energy conversion, and partitioning efficiencies.’ *Journal of Experimental Botany*, 65(12) pp. 3311–3321.

Kolbe, F., Mattusch, J., Wennrich, R., Weiss, H., Sorkau, E., Lorenz, W. and Daus, B. (2012) ‘Analytical investigations of antimony-edta complexes and their use in speciation analysis.’ *Fresenius Environmental Bulletin*, 21(11 C) pp. 3453–3456.

Kowalska, J., Stryjewska, E., Szymański, P. and Golimowski, J. (1999) 'Voltammetric determination of arsenic in plant material.' *Electroanalysis*, 11(17) pp. 1301–1304.

Krachler, M. and Emons, H. (2001) 'Speciation analysis of antimony by high-performance liquid chromatography inductively coupled plasma mass spectrometry using ultrasonic nebulization.' *Analytica Chimica Acta*, 429(1) pp. 125–133.

Kroukamp, E. M., Wondimu, T. and Forbes, P. B. C. (2016) 'Metal and metalloid speciation in plants: Overview, instrumentation, approaches and commonly assessed elements.' *TrAC - Trends in Analytical Chemistry*. Elsevier B.V., 77 pp. 87–99.

Krupka, K. M. and Serne, R. J. (2002) *Geochemical Factors Affecting the Behavior of Antimony, Cobalt, Europium, Technetium, and Uranium in Vadose Zone Sediments*. *Pnnl-14126*. Richland, WA (United States).

Kumar, R., Mishra, R. K., Mishra, V., Qidwai, A., Pandey, A., Shukla, S. K., Pandey, M., Pathak, A. and Dikshit, A. (2015) 'Detoxification and Tolerance of Heavy Metals in Plants.' *In Plant Metal Interaction: Emerging Remediation Techniques*. Elsevier Inc., pp. 335–359.

Kumarathilaka, P., Seneweera, S., Meharg, A. and Bundschuh, J. (2018) 'Arsenic speciation dynamics in paddy rice soil-water environment: sources, physico-chemical, and biological factors - A review.' *Water Research*. Elsevier Ltd pp. 403–414.

Küpper, H. and Andresen, E. (2016) 'Mechanisms of metal toxicity in plants.' *Metallomics*, 8(3) pp. 269–285.

Lansdown, A. B. G. (2013) 'CHAPTER 1. Introduction.' *In The Carcinogenicity of Metals: Human Risk Through Occupational and Environmental Exposure*, pp. 1–18.

Larsen, E. H. and Stürup, S. (1994) 'Carbon-enhanced inductively coupled plasma mass spectrometric detection of arsenic and selenium and its application to arsenic speciation.' *Journal of Analytical Atomic Spectrometry*, 9(10) pp. 1099–1105.

van Leeuwen, H. P., Town, R. M., Buffle, J., Cleven, R. F. M. J., Davison, W., Puy, J., van Riemsdijk, W. H. and Sigg, L. (2005) 'Dynamic Speciation Analysis and Bioavailability of Metals in Aquatic Systems.' *Environmental Science & Technology*, 39(22) pp. 8545–8556.

van Leeuwen, L. C. and Aldenberg, T. (2012) *RIVM Letter Report 601357001/2012: Environmental risk limits for antimony*.

Li, Z. and Cui, Z. (2008) 'Application of microdialysis in tissue engineering monitoring.' *Progress in Natural Science*. Science Press, 18(5) pp. 503–511.

Liang, G., Gong, W., Li, B., Zuo, J., Pan, L. and Liu, X. (2019) 'Analysis of Heavy Metals in Foodstuffs and an Assessment of the Health Risks to the General Public via Consumption in Beijing, China.' *International Journal of Environmental Research and Public Health*. MDPI AG, 16(6) p. 909.

Lichtfouse, E., Schwarzbauer, J. and Robert, D. (2012) *Environmental chemistry for a sustainable world*. *Environmental Chemistry for a Sustainable World*. Springer Netherlands.

Lintschinger, J., Koch, I., Serves, S., Feldmann, J. and Cullen, W. R. (1997) 'Determination of antimony species with High-Performance Liquid Chromatography using element specific detection.' *Fresenius' Journal of Analytical Chemistry*, 359(6) pp. 484–491.

Liu, Z. G. and Huang, X. J. (2014) 'Voltammetric determination of inorganic arsenic.' *TrAC - Trends in Analytical Chemistry*, 60 pp. 25–35.

Lombi, E. and Holm, P. E. (2010) 'Metalloids, soil chemistry and the environment.' *In Advances in Experimental Medicine and Biology*. Australia: Landes Bioscience and Springer Science+Business Media., pp. 33–44.

Louis, Y., Cmuk, P., Nicolau, R., Omanovi, D., Lenoble, V., Pižeta, I., Mounier, S., and Garde, L. and Garde, L. (2007) 'Pseudopolarography As a Tool for Complexation Studies of Trace Metals With Dissolved Natural Organic Matter,' (January) p. 2007.

Louis, Y., Cmuk, P., Omanović, D., Garnier, C., Lenoble, V., Mounier, S. and Pižeta, I. (2008) 'Speciation of trace metals in natural waters: The influence of an adsorbed layer of natural organic matter (NOM) on voltammetric behaviour of copper.' *Analytica Chimica Acta*. Elsevier Masson, 606(1) pp. 37–44.

Louis, Y., Garnier, C., Lenoble, V., Omanovi, D., Mounier, S., Pižeta, I., Protee, L., Toulon, S., Bp, V., Garde, L., Physico, G. De, Chimie, T., Moléculaires, S. and I, U. B. (2008) 'Electrochemical Study of Major and Trace Metal Interactions With Concentrated Marine Dissolved Organic Matter,' (098) p. 1214910.

Lu, M. and Compton, R. G. (2013) 'Voltammetric Determination of Iron(III) in Water.' *Electroanalysis*, 25(5) pp. 1123–1129.

Lubin, J. H., Moore, L. E., Fraumeni, J. F. and Cantor, K. P. (2008) 'Respiratory Cancer and Inhaled Inorganic Arsenic in Copper Smelters Workers: A Linear Relationship with Cumulative Exposure that Increases with Concentration.' *Environmental Health Perspectives*, 116(12) pp. 1661–1665.

Luo, J. and Shu, W. (2015) 'Arsenic-Induced Developmental Neurotoxicity.' *In* Flora, S. J. S. B. T.-H. of A. T. (ed.) *Handbook of Arsenic Toxicology*. Oxford: Elsevier, pp. 363–386.

Lydic, R., Baghdoyan, H. A. and May, A. L. (2018) 'Chapter Fourteen - Neurochemistry of Anesthetic States.' *In* Eckenhoff, R. G. and Dmochowski, I. J. B. T.-M. in E. (eds) *Chemical and Biochemical Approaches for the Study of Anesthetic Function Part B*. 1st ed., Academic Press, pp. 237–255.

Madejón, P., Marañón, T. and Murillo, J. M. (2006) 'Biomonitoring of trace elements in the leaves and fruits of wild olive and holm oak trees.' *Science of the Total Environment*, 355(1–3) pp. 187–203.

Magahud, J. C., Badayos, R. B., Sanchez, P. B. and Sta. Cruz, P. C. (2015) *Levels and Potential Sources of Heavy Metals in Major Irrigated Rice Areas of the Philippines*. *IAMURE International Journal of Ecology and Conservation*.

Mandal, B. K. and Suzuki, K. T. (2002) 'Arsenic round the world: A review.' *Talanta*. Elsevier, 58(1) pp. 201–235.

Mareček, V., Jänchenová, H., Samec, Z. and Březina, M. (1986) 'Voltammetric determination of nitrate, perchlorate and iodide at a hanging electrolyte drop electrode.' *Analytica Chimica Acta*, 185(C) pp. 359–362.

Marschner, H. (1995) *Mineral Nutrition of High Plants*. Academic Press.

Martin, M., Ferdousi, R., Hossain, K. M. J. and Barberis, E. (2010) 'Arsenic from groundwater to paddy fields in Bangladesh: Solid-liquid partition, sorption and mobility.' *Water, Air, and Soil Pollution*, 212(1–4) pp. 27–36.

Martinez, R. E., Marquez, J. E., Hòa, H. T. B. and Gieré, R. (2013) 'Open-pit coal-mining effects on rice paddy soil composition and metal bioavailability to Oryza sativa L. plants in Cam Pha, northeastern Vietnam.' *Environmental Science and Pollution Research*, 20(11) pp. 7686–7698.

Massoura, S. T., Echevarria, G., Leclerc-Cessac, E. and Morel, J. L. (2004) 'Response of excluder, indicator, and hyperaccumulator plants to nickel availability in soils.' *Australian Journal of Soil Research*, 42(8) pp. 933–938.

Materials, B. (1989) *Analytical Methods*. *WHO*.

Matschullat, J. J. (2000) 'Arsenic in the geosphere - A review.' *The Science of the Total Environment*, 249(1–3) pp. 297–312.

Mawia, A. M., Hui, S., Zhou, L., Li, H., Tabassum, J., Lai, C., Wang, J., Shao, G., Wei, X., Tang, S., Luo, J., Hu, S. and Hu, P. (2021) 'Inorganic arsenic toxicity and alleviation strategies in rice.' *Journal of Hazardous Materials*. Elsevier B.V. p. 124751.

Mayet, N., Servat, K., Kokoh, K. B. and Napporn, T. W. (2019) 'Probing the Surface of Noble Metals Electrochemically by Underpotential Deposition of Transition Metals.' *Surfaces*, 2(2) pp. 257–276.

McLaughlin, M. ., Parker, D. . and Clarke, J. . (1999) 'Metals and micronutrients – food safety issues.' *Field Crops Research*, 60(1–2) pp. 143–163.

Mead, M. N. (2005) 'Arsenic: In search of an antidote to a global poison.' *Environmental Health Perspectives*. Public Health Services, US Dept of Health and Human Services, 113(6).

Meadows, R. (2014) ‘How Plants Control Arsenic Accumulation.’ *PLoS Biology*, 12(12) pp. 1002008–1002009.

Meharg, A. A. (2004) ‘Arsenic in rice - Understanding a new disaster for South-East Asia.’ *Trends in Plant Science* pp. 415–417.

Meharg, A. A. and Zhao, F.-J. (2012) *Arsenic & Rice*. *Springer*. Dordrecht: Springer Netherlands.

Mendoza, T. (2012) ‘Estimates of Rice Per Capita Consumption: Its Implications to the Rice Self-Sufficiency Program of the Philippines*.’ *Policy Options*, 4, January.

Mestrot, A., Ji, Y., Tandy, S. and Wilcke, W. (2016) ‘A novel method to determine trimethylantimony concentrations in plant tissue.’ *Environmental Chemistry*, 13(6) pp. 919–926.

Michalski, R., Szopa, S., Jabłońska, M. and Łyko, A. (2012) ‘Application of hyphenated techniques in speciation analysis of arsenic, antimony, and thallium.’ *The Scientific World Journal*. Institute of Environmental Engineering, the Polish Academy of Sciences, 34 Sklodowskiej-Curie Street, 41 819 Zabrze, Poland. michalski@ipis.zabrze.pl, 2012(January 2017) p. 902464.

Miekeley, N., Mortari, S. R. and Schubach, A. O. (2002) ‘Monitoring of total antimony and its species by ICP-MS and on-line ion chromatography in biological samples from patients treated for leishmaniasis.’ *Fresenius’ Journal of Analytical Chemistry*, 372(3) pp. 495–502.

Mihucz, V. G., Tatár, E. E. E., Virág, I., Cseh, E., Fodor, F., Záray, G., Tat??r, E., Vir??g, I., Cseh, E., Fodor, F. and Gyula, Z. (2005) ‘Arsenic speciation in xylem sap of cucumber (Cucumis sativus L.).’ *Analytical and Bioanalytical Chemistry*. Joint Research Group of Environmental Chemistry of the Hungarian Academy of Sciences and L. Eotvos University, PO Box 32, 1518 Budapest, Hungary., 383(3) pp. 461–466.

Mihucz, V. G., Varga, A. and Za, G. (1998) ‘Determination of Organic Acids in Xylem Sap of Cucumber : Effect of Lead Contamination,’ 314(58) pp. 306–314.

Ministerie Van Volkshuisvesting; Ruimtelijke Ordening En Milieu (2000) ‘Dutch Target and Intervention Values; 2000 (the New Dutch List).’ *Netherlands Government Gazette*, 2000 pp. 1–12.

Miró, M., Fitz, W. J., Swoboda, S. and Wenzel, W. W. (2010) ‘In-situ sampling of soil pore water: Evaluation of linear-type microdialysis probes and suction cups at varied moisture contents.’ *Environmental Chemistry*, 7(1) pp. 123–131.

Mishra, S., Srivastava, S., Dwivedi, S. and Tripathi, R. D. (2013) ‘Investigation of biochemical responses of Bacopa monnieri L. upon exposure to arsenate.’ *Environmental Toxicology*, 28(8) pp. 419–430.

Mohan, D. and Pittman, C. U. (2007) ‘Arsenic removal from water/wastewater using adsorbents-A critical review.’ *Journal of Hazardous Materials* pp. 1–53.

Moles, A. T., Warton, D. I., Warman, L., Swenson, N. G., Laffan, S. W., Zanne, A. E., Pitman, A., Hemmings, F. A. and Leishman, M. R. (2009) ‘Global patterns in plant height.’ *Journal of Ecology*, 97(5) pp. 923–932.

Moreno-Jiménez, E., Esteban, E. and Peñalosa, J. M. (2012) ‘The fate of arsenic in soil-plant systems.’ *Reviews of Environmental Contamination and Toxicology*, 215 pp. 1–37.

Morua, M. (2015) ‘Investigating various xylem sap extraction techniques from drought-stressed Geijera parviflora trees’ pp. 1–26.

Mosetlha, K., Torto, N. and Wibetoe, G. (2007) ‘Determination of Cu and Ni in plants by microdialysis sampling: Comparison of dialyzable metal fractions with total metal content.’ *Talanta*. Elsevier, 71(2) pp. 766–770.

Nagajyoti, P. C., Lee, K. D. and Sreekanth, T. V. M. (2010) ‘Heavy metals, occurrence and toxicity for plants: A review.’ *Environmental Chemistry Letters* pp. 199–216.

Nash, M. J., Maskall, J. E. and Hill, S. J. (2000) ‘Methodologies for determination of antimony in terrestrial environmental samples.’ *Journal of Environmental Monitoring*, 2(2) pp. 97–109.

Natasha, Shahid, M., Khalid, S., Dumat, C., Pierart, A. and Niazi, N. K. (2019) ‘Biogeochemistry of antimony in soil-plant system: Ecotoxicology and human health.’ *Applied Geochemistry*. Elsevier, 106(April) pp. 45–59.

Netting, A. G., Theobald, J. C. and Dodd, I. C. (2012) ‘Xylem sap collection and extraction methodologies to determine in vivo concentrations of ABA and its bound forms by gas chromatography-mass spectrometry (GC-MS).’ *Plant Methods*, 8(1) pp. 1–14.

Nicolau, R., Louis, Y., Omanović, D., Garnier, C., Mounier, S. and and, Pižeta, I. (2008) ‘Study of interactions of concentrated marine dissolved organic matter with copper and zinc by pseudopolarography.’ *Analytica Chimica Acta*, 618(1) pp. 35–42.

Niedzielski, P. and Siepak, M. (2003) ‘Analytical methods for determining arsenic, antimony and selenium in environmental samples.’ *Polish Journal of Environmental Studies*, 12(6) pp. 653–667.

Niedzielski, P., Siepak, M., Siepak, J. and Przybyłek, J. (2002) ‘Determination of Different Forms of Arsenic, Antimony and Selenium in Water Samples Using Hydride Generation.’ *Polish Journal of Environmental Studies*, 11(3) pp. 219–224.

Nimick, D. A. (1998) ‘Arsenic hydrogeochemistry in an irrigated river valley-A reevaluation.’ *Journal of groundwater*. Ground Water Publ Co, 36(5) pp. 743–753.

O'Day, P. A. (2006) 'Chemistry and mineralogy of arsenic.' *Elements*, 2(2) pp. 77–83.

Obiora, S. C., Chukwu, A. and Davies, T. C. (2016) 'Heavy metals and health risk assessment of arable soils and food crops around Pb-Zn mining localities in Enyigba, southeastern Nigeria.' *Journal of African Earth Sciences*. Elsevier Ltd, 116, April, pp. 182–189.

Oda, A., Shimizu, M., Kuroha, T. and Satoh, S. (2005) 'Induction of xylem sap methylglycine by a drought and rewatering treatment and its inhibitory effects on the growth and development of plant organs.' *Physiologia Plantarum*, 124(4) pp. 515–523.

Ogawa, K. and Iwabuchi, M. (2001) 'A mechanism for promoting the germination of Zinnia elegans seeds by hydrogen peroxide.' *Plant and Cell Physiology*, 42(3) pp. 286–291.

Ohmori, T., El-Deab, M. S. and Osawa, M. (1999) 'Electroreduction of nitrate ion to nitrite and ammonia on a gold electrode in acidic and basic sodium and cesium nitrate solutions.' *Journal of Electroanalytical Chemistry*, 470(1) pp. 46–52.

Olsen, S.R., C.V. Cole, F.S. Watanabe, and L. A. D. (1954) *Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circ.No. 939.* U.S. Gov. Print. Office, Washington DC.

Omanović, D. (2006) 'Pseudopolarography of trace metals. Part III. Determination of stability constants of labile metal complexes.' *Croatica Chemica Acta*, 79(1) p. 67.

Omanović, D. and Branica, M. (2003) 'Pseudopolarography of trace metals: Part I. The automatic ASV measurements of reversible electrode reactions.' *Journal of Electroanalytical Chemistry*, 543(1) pp. 83–92.

Omanović, D. and Branica, M. (2004) 'Pseudopolarography of trace metals. Part II. The comparison of the reversible, quasireversible and irreversible electrode reactions.' *Journal of Electroanalytical Chemistry*, 565(1) pp. 37–48.

Onofri, A., Seddaiu, G. and Piepho, H. P. (2016) 'Long-Term Experiments with cropping systems: Case studies on data analysis.' *European Journal of Agronomy*, 77, July, pp. 223–235.

Organization, world health (1996) 'guidelines for drinking water quality - second edition.' *international programme on chemical safety*.

Özer, U. Y. and Bogucki, R. F. (1971) 'Equilibrium studies of antimony(III) chelates in aqueous solution.' *Journal of Inorganic and Nuclear Chemistry*, 33(12) pp. 4143–4153.

Palma-Lara, I., Martínez-Castillo, M., Quintana-Pérez, J. C., Arellano-Mendoza, M. G., Tamay-Cach, F., Valenzuela-Limón, O. L., García-Montalvo, E. A. and Hernández-Zavala, A. (2019) 'Arsenic exposure: A public health problem leading to several cancers.'

Regulatory toxicology and pharmacology : RTP p. 104539.

Pampolino, M. F., Laureles, E. V., Gines, H. C. and Buresh, R. J. (2008) 'Soil carbon and nitrogen changes in long-term continuous lowland rice cropping.' *Soil Science Society of America Journal*, 72(3) pp. 798–807.

Panda, S. K., Upadhyay, R. K. and Nath, S. (2010) 'Arsenic Stress in Plants.' *Journal of Agronomy and Crop Science*, 196(3) pp. 161–174.

Pandey, P. and Tripathi, A. K. (2014) 'Impact Of Heavy Metals On Morphological And Biochemical Parameters Of Shorea Robusta Plant.' *Ekologia*, 33(2) pp. 116–126.

Passioura, J. B. (1980) 'The transport of water from soil to shoot in wheat seedlings.' *Journal of Experimental Botany*, 31(1) pp. 333–345.

Pedron, T., Segura, F. R., Paniz, F. P., de Moura Souza, F., dos Santos, M. C., de Magalhães Júnior, A. M. and Batista, B. L. (2019) 'Mitigation of arsenic in rice grains by polishing and washing: Evidencing the benefit and the cost.' *Journal of Cereal Science*. Academic Press, 87, May, pp. 52–58.

Penezić, A., Tercier-Waeber, M. Lou, Abdou, M., Bossy, C., Dutruch, L., Bakker, E. and Schäfer, J. (2020) 'Spatial variability of arsenic speciation in the Gironde Estuary: Emphasis on dynamic (potentially bioavailable) inorganic arsenite and arsenate fractions.' *Marine Chemistry*. Elsevier, 223(December 2019) p. 103804.

Pepponi, G., Meirer, F., Streli, C., Wobrauschek, P., Mihucz, V. G., G. Zaray, V. C., Broekaert, J., Fittschen, U. and Falkenberg, G. (2005) 'Arsenic speciation in Cucumber Cucumis Sativus L.) xylem sap by K-edge TXRF-XANES.' *Anal. Bioanal. Chem.*, 383 pp. 461–466.

Peralta-Videa, J. R., Lopez, M. L., Narayan, M., Saupe, G. and Gardea-Torresdey, J. (2009) 'The biochemistry of environmental heavy metal uptake by plants: Implications for the food chain.' *International Journal of Biochemistry and Cell Biology*, 41(8–9) pp. 1665–1677.

Perrino, C., Marconi, E., Canepari, S., Luisa Astolfi, M. and Perrino, C. (2011) 'Determination of Sb(III), Sb(V) and identification of Sb-containing nanoparticles in airborne particulate matter.' *Procedia Environmental Sciences*, 4 pp. 209–217.

Pettine, M., Casentini, B., Mastroianni, D. and Capri, S. (2007) 'Dissolved inorganic carbon effect in the determination of arsenic and chromium in mineral waters by inductively coupled plasma-mass spectrometry.' *Analytica Chimica Acta*. Elsevier, 599(2) pp. 191–198.

Pickering, I. J., Prince, R. C., George, M. J., Smith, R. D., George, G. N. and Salt, D. E. (2000) 'Reduction and coordination of arsenic in Indian mustard.' *Plant Physiology*, 122(4) pp. 1171–1177.

Pierart, A., Shahid, M., Séjalon-Delmas, N. and Dumat, C. (2015) ‘Antimony bioavailability: Knowledge and research perspectives for sustainable agricultures.’ *Journal of Hazardous Materials*. Elsevier, 289(February) pp. 219–234.

Pla-Vilanova, P., Galceran, J., Puy, J., Companys, E. and Filella, M. (2019) ‘Antimony speciation in aqueous solution followed with AGNES.’ *Journal of Electroanalytical Chemistry*. Elsevier B.V., 849 p. 113334.

Pohl, P., Lesniewicz, A. and Zyrnicki, W. (2003) ‘Determination of As, Bi, Sb and Sn in conifer needles from various locations in Poland and Norway by hydride generation inductively coupled plasma atomic emission spectrometry.’ *International Journal of Environmental Analytical Chemistry*. Taylor & Francis Group, 83(11) pp. 963–970.

Polunina, O. V., Maiboroda, V. P. and Seleznov, A. Y. (2018) ‘Evaluation methods of estimation of young apple trees leaf area.’ *Bulletin of Uman National University of Horticulture*, (2) pp. 80–82.

Pommerrenig, B., Diehn, T. A. and Bienert, G. P. (2015) ‘Metalloido-porins: Essentiality of Nodulin 26-like intrinsic proteins in metalloid transport.’ *Plant Science*. Elsevier Ireland Ltd, 238 pp. 212–227.

Porra, R. J. (2005) ‘Clorofila Porras 2005’ pp. 633–640.

Postupolski, A. and Golimowski, J. (1991) ‘Trace determination of antimony and bismuth in snow and water samples by stripping voltammetry.’ *Electroanalysis*. Warsaw, Poland, 3(8) pp. 793–797.

Pretti, L., Bazzu, G., Serra, P. A. and Nieddu, G. (2014) ‘A novel method for the determination of ascorbic acid and antioxidant capacity in Opuntia ficus indica using in vivo microdialysis.’ *Food Chemistry*, 147 pp. 131–137.

Punrat, E., Chuanuwatanakul, S., Kaneta, T., Motomizu, S., Chailapakul, O., Zaib, M., Makshoof, M., Saeed, A., Farooq, U., Nearing, M. M., Koch, I., Reimer, K. J., Niedzielski, P., Siepak, M., Day, P. A. O., Mays, D. E., Hussam, A., Welna, M., Szymczycha-Madeja, A., Pohl, P., Ma, J., Sengupta, M. K., Yuan, D., Dasgupta, P. K., Amaral, C. D. B., Nóbrega, J. A., Nogueira, A. R. A., Cavicchioli, A., La-scalea, M. A., Gutz, G. R., Tyson, J., Chen, M. L., Ma, L. Y., Chen, X. W., Punrat, E., Chuanuwatanakul, S., Kaneta, T., Motomizu, S., Chailapakul, O., Hotel, D., Llorente-mirandes, T., Calderón, J., Centrich, F., Rubio, R., López-sánchez, J. F. and Thomas, D. J. (2014) ‘Method development for the determination of arsenic by sequential injection/anodic stripping voltammetry using long-lasting gold-modified screen-printed carbon electrode.’ *Talanta*. Elsevier B.V., 2013(June) pp. 1018–1025.

Quentel, F. and Filella, M. (2002) ‘Determination of inorganic antimony species in seawater by differential pulse anodic stripping voltammetry: Stability of the trivalent state.’ *Analytica Chimica Acta*, 452(2) pp. 237–244.

Quentel, F., Filella, M., Elleouet, C. and Madec, C. (2006) ‘Sb(III) oxidation by iodate in seawater: A cautionary tale.’ *Science of The Total Environment*. Elsevier, 355(1–3) pp. 259–263.

RA (2001) ‘Philippine Mining Act of 1995,.’ Philippines, R. of the (ed.) pp. 1–12.

Raab, A., Feldmann, J. and Meharg, A. A. (2004) ‘The Nature of Arsenic-Phytochelatin Complexes in Holcus lanatus and Pteris cretica.’ *Plant Physiology*. Department of Chemistry, University of Aberdeen, Meston Building, Meston Walk, Aberdeen AB24 3UE, United Kingdom., 134(3) pp. 1113–1122.

Raab, A., Meharg, A. A., Jaspars, M., Genney, D. R. and Feldmann, J. (2004) ‘Arsenic–glutathione complexes—their stability in solution and during separation by different HPLC modes.’ *J. Anal. At. Spectrom.*, 19(1) pp. 183–190.

Raab, A., Schat, H., Meharg, A. A., Feldmann, J., J., A. R. S. H. M. A. A. and F., Raab, A., Schat, H., Meharg, A. A. and Feldmann, J. (2005) ‘Uptake, translocation and transformation of arsenate and arsenite in sunflower (Helianthus annuus): Formation of arsenic-phytochelatin complexes during exposure to high arsenic concentrations.’ *New Phytologist*. Department of Chemistry, University of Aberdeen, Meston Building, Meston Walk, Aberdeen AB24 3UE, UK., 168(3) pp. 551–558.

Rahaman, M. S., Akter, M., Rahman, M. M., Sikder, M. T., Hosokawa, T., Saito, T. and Kurasaki, M. (2020) ‘Investigating the protective actions of D-pinitol against arsenic-induced toxicity in PC12 cells and the underlying mechanism.’ *Environmental Toxicology and Pharmacology*. Elsevier B.V., 74, February, p. 103302.

Rahman, M. A. and Hasegawa, H. (2011) ‘High levels of inorganic arsenic in rice in areas where arsenic-contaminated water is used for irrigation and cooking.’ *Science of The Total Environment*, 409(22) pp. 4645–4655.

Raskin, I., Kumar, P. N., Dushenkov, S. and Salt, D. E. (1994) ‘Bioconcentration of heavy metals by plants.’ *Current Opinion in Biotechnology*, 5(3) pp. 285–290.

Rauser, W. E. (1990) ‘Phytochelatins.’ *Annual Review of Biochemistry*, 59 pp. 61–86.

Reimann, C., Demetriades, A., Eggen, O. A. and Filzmoser, P. (2009) ‘The EuroGeoSurveys geochemical mapping of agricultural and grazing land soils project (GEMAS) -Evaluation of quality control results of aqua regia extraction analysis.’ *EuroGeoSurveys Geochemistry* , (May 2014) p. 94.

Rellán-Álvarez, R., El-Jendoubi, H., Wohlgemuth, G., Abadía, A., Fiehn, O., Abadía, J., Álvarez-Fernández, A., Schjoerring, J. K., Zocchi, G., Degli, U., Di Milano, S., Yoshihara, T. and Alvarez-Fernández, A. (2011) ‘Metabolite profile changes in xylem sap and leaf extracts of strategy I plants in response to iron deficiency and resupply.’ *Frontiers in plant science*, 2 p. 66.

Rellán-Álvarez, R., Ortega-Villasante, C., Álvarez-Fernández, A., Campo, F. F. del and Hernández, L. E. (2006) 'Stress Responses of Zea mays to Cadmium and Mercury.' *Plant and Soil*, 279(1–2) pp. 41–50.

Ren, J. H., Ma, L. Q., Sun, H. J., Cai, F. and Luo, J. (2014) 'Antimony uptake, translocation and speciation in rice plants exposed to antimonite and antimonate.' *Science of the Total Environment*. Elsevier B.V., 475 pp. 83–89.

Rodriguez-Iruretagoiena, A., Trebolazabala, J., Martinez-Arkarazo, I., De Diego, A. and Madariaga, J. M. (2015) 'Metals and metalloids in fruits of tomatoes (Solanum lycopersicum) and their cultivation soils in the Basque Country: Concentrations and accumulation trends.' *Food Chemistry*. Elsevier Ltd, 173, February, pp. 1083–1089.

Rosas-Castor, J. M., Guzmán-Mar, J. L., Hernández-Ramírez, A., Garza-González, M. T. and Hinojosa-Reyes, L. (2014) 'Arsenic accumulation in maize crop (Zea mays): A review.' *Science of The Total Environment*. Elsevier, 488–489(1) pp. 176–187.

Rousk, J. and Jones, D. L. (2010) 'Loss of low molecular weight dissolved organic carbon (DOC) and nitrogen (DON) in H2O and 0.5M K2SO4 soil extracts.' *Soil Biology and Biochemistry*, 42(12) pp. 2331–2335.

Sabir, M., Waraich, E. A., Hakeem, K. R., Öztürk, M., Ahmad, H. R. and Shahid, M. (2015) 'Phytoremediation: Mechanisms and Adaptations. Mechanisms and Adaptations.' *Soil Remediation and Plants: Prospects and Challenges* pp. 85–105.

Sadiq, M. (1992) *Toxic metal chemistry in marine environments*. *Marcel Dekker*. New York City.

Salama, A. K. and Radwan, M. A. (2005) 'Heavy metals (Cd,Pb) and trace elements (Cu,Zn) contents in some foodstuffs from the Egyptian market.' *Emirates Journal of Food and Agriculture*, 17(1) pp. 34–42.

Salaun, P. (2017) 'Editorial: Environmental Electrochemistry.' *Current Opinion in Electrochemistry*. Elsevier B.V., 3(1) pp. 75–77.

Salaün, P. and van den Berg, C. M. G. (2006) 'Voltammetric detection of mercury and copper in seawater using a gold microwire electrode.' *Analytical chemistry*, 78(14) pp. 5052–60.

Salaün, P. and Frézard, F. (2013) 'Unexpectedly high levels of antimony (III) in the pentavalent antimonial drug Glucantime: insights from a new voltammetric approach.' *Analytical and Bioanalytical Chemistry*. Liverpool, 405(15) pp. 5201–5214.

Salaün, P., Gibbon-Walsh, K. B., Alves, G. M. S. S., Soares, H. M. V. M. V. M. and van den Berg, C. M. G. G. (2012) 'Determination of arsenic and antimony in seawater by voltammetric and chronopotentiometric stripping using a vibrated gold microwire electrode.' *Analytica Chimica Acta*. Liverpool: Elsevier B.V., 746(March 2014) pp. 53–62.

Salaün, P., Gibbon-Walsh, K. and van den Berg, C. M. G. (2011) 'Beyond the Hydrogen Wave: New Frontier in the Detection of Trace Elements by Stripping Voltammetry.' *Analytical Chemistry*, 83(10) pp. 3848–3856.

Salaün, P., Planer-Friedrich, B. and van den Berg, C. M. . (2007) 'Inorganic arsenic speciation in water and seawater by anodic stripping voltammetry with a gold microelectrode.' *Analytica Chimica Acta*. Liverpool, 585(2) pp. 312–322.

Samarah, L. Z., Tran, T. H., Stacey, G. and Vertes, A. (2020) 'In Vivo Chemical Analysis of Plant Sap from the Xylem and Single Parenchymal Cells by Capillary Microsampling Electrospray Ionization Mass Spectrometry.' *Analytical Chemistry*, 92(10) pp. 7299–7306.

Samota, M. K., Navnage, N. P. and Bhatt, L. (2017) 'Role of Macro and Micronutrient in Development and Growth of Plant,' 10(18) pp. 3171–3173.

Santos, V. S., Santos, W. de J. R., Kubota, L. T. and Tarley, C. R. T. (2009) 'Speciation of Sb(III) and Sb(V) in meglumine antimoniate pharmaceutical formulations by PSA using carbon nanotube electrode.' *Journal of Pharmaceutical and Biomedical Analysis*, 50(2) pp. 151–157.

Satoh, S. (2006) 'Organic substances in xylem sap delivered to above-ground organs by the roots.' *Journal of Plant Research*, 119(3) pp. 179–187.

Scharifker, B. R., Mostany, J. and Serruya, A. (2000) 'Catalytic reduction of nitrate during electrodeposition of thallium from Tl3+ solution.' *Electrochemistry Communications*, 2(6) pp. 448–451.

Scholander, P. F., Bradstreet, E. D., Hemmingsen, E. A. and Hammel, H. T. (1965) 'Sap Pressure in Vascular Plants: Negative hydrostatic pressure can be measured in plants.' *Science*, 148(3668) pp. 339–346.

Schurr, U. (1998) 'Xylem sap sampling—new approaches to an old topic.' *Trends in Plant Science*. Elsevier Current Trends, 3(8) pp. 293–298.

Schurr, U. (1999) 'Dynamics of Nutrient Transport from the Root to the Shoot.' *In*. Springer, Berlin, Heidelberg, pp. 234–253.

Shahid, M., Khalid, S., Abbas, G., Shahid, N., Nadeem, M., Sabir, M., Aslam, M. and Dumat, C. (2015) 'Heavy metal stress and crop productivity.' *In Crop Production and Global Environmental Issues*. Springer International Publishing, pp. 1–25.

Sharma, S. D. (2013) 'History of Rice in Southeast Asia and Australia.' *Journal of Chemical Information and Modeling*, 53(9) pp. 1689–1699.

Shri, M., Singh, P. K., Kidwai, M., Gautam, N., Dubey, S., Verma, G. and Chakrabarty, D. (2019) 'Recent advances in arsenic metabolism in plants: Current status, challenges and highlighted biotechnological intervention to reduce grain arsenic in rice.' *Metallomics*, 11(3) pp. 519–532.

Simoni, R. D., Hill, R. L. and Vaughan, M. (2005) 'Benedict ' s Solution , a Reagent for Measuring Reducing Sugars : the Clinical Chemistry of Stanley R . Benedict,' 277(16) pp. 10–12.

Slamet-loedin, I., Slamet-loedin, I. H., Johnson-beebout, S. E., Impa, S. and Tsakirpaloglou, N. (2015) 'Enriching rice with Zn and Fe while minimizing Cd risk.' *Frontiers in Plant Science*, 6(MAR).

Smedley, P. L. and Kinniburgh, D. G. (2000) 'Source and behaviour of arsenic in natural waters.' *British Geological Survey* p. 61.

Smedley, P. L. and Kinniburgh, D. G. (2002) 'A review of the source, behaviour and distribution of arsenic in natural waters.' *Applied Geochemistry*, 17(5) pp. 517–568.

Smith, A. H., Lingas, E. O. and Rahman, M. (2000) 'Contamination of drinking-water by arsenic in Bangladesh: A public health emergency.' *Bulletin of the World Health Organization*, 78(9) pp. 1093–1103.

Smith, A. H. and Smith, M. M. H. (2004) 'Arsenic drinking water regulations in developing countries with extensive exposure.' *Toxicology*, 198(1–3) pp. 39–44.

Sobrado, M. A. (2007) 'Relationship of water transport to anatomical features in the mangrove Laguncularia racemosa grown under contrasting salinities.' *New Phytologist*, 173(3) pp. 584–591.

Sørensen, O., Andersen, A., Olsen, H., Alexandr, K., Ekstrøm, P. O., Giercksky, K. E. and Flatmark, K. (2010) 'Validation and use of microdialysis for determination of pharmacokinetic properties of the chemotherapeutic agent mitomycin C - an experimental study.' *BMC Cancer*, 10.

Spurgeon, D. J., Rowland, P., Ainsworth, G., Rothery, P., Long, S. and Black, H. I. J. (2008) 'Geographical and pedological drivers of distribution and risks to soil fauna of seven metals (Cd, Cu, Cr, Ni, Pb, V and Zn) in British soils.' *Environmental Pollution*, 153(2) pp. 273–283.

Sreekanth, T. V. M., Nagajyothi, P. C., Lee, K. D. and Prasad, T. N. V. K. V. (2013) 'Occurrence, physiological responses and toxicity of nickel in plants.' *International Journal of Environmental Science and Technology*. Center for Environmental and Energy Research and Studies pp. 1129–1140.

Stazi, S. R., Cassaniti, C., Marabottini, R., Giuffrida, F. and Leonardi, C. (2016) 'Arsenic uptake and partitioning in grafted tomato plants.' *Horticulture, Environment, and Biotechnology*. Korean Society for Horticultural Science, 57(3) pp. 241–247.

Steudle, E. (2001) ‘The cohesion-tension mechanism and the acquisition of water by plant roots.’ *Annual Review of Plant Biology*, 52 pp. 847–875.

Stoeva, N., Berova, M. and Zlatev, Z. (2005) ‘Effect of arsenic on some physiological parameters in bean plants.’ *Biologia Plantarum*, 49(2) pp. 293–296.

Sulyok, M., Miró, M., Stingeder, G. and Koellensperger, G. (2005) ‘The potential of flow-through microdialysis for probing low-molecular weight organic anions in rhizosphere soil solution.’ *Analytica Chimica Acta*. Elsevier, 546(1) pp. 1–10.

Sun, G., Williams, P. N. and Zhu, Y. (2009) ‘Mechanisms of Arsenic Uptake and Metabolism by Plants : Focusing on Rice.’ *Environmental Toxicology*, 134(November) pp. 1–6.

Sun, H., Yan, S. C. and Cheng, W. S. (2000) ‘Interaction of antimony tartrate with the tripeptide glutathione.’ *European Journal of Biochemistry*, 267(17) pp. 5450–5457.

Takarina, N. D. and Pin, T. G. (2017) ‘Bioconcentration Factor (BCF) and Translocation Factor (TF) of Heavy Metals in Mangrove Trees of Blanakan Fish Farm.’ *Makara Journal of Science*, 21(2).

Tamás, M. J. (2016) ‘Cellular and molecular mechanisms of antimony transport, toxicity and resistance.’ *Environmental Chemistry*, 13(6) pp. 955–962.

Tatár, E., Mihucz, V. G., Kmethy, B., Záray, G. and Fodor, F. (2000) ‘Determination of organic acids and their role in nickel transport within cucumber plants.’ *Microchemical Journal*, 67(1–3) pp. 73–81.

Tatár, E., Mihucz, V. G., Varga, A., Záray, G. and Fodor, F. (1998) ‘Determination of Organic Acids in Xylem Sap of Cucumber: Effect of Lead Contamination.’ *Microchemical Journal*. Elsevier Inc., 58(3) pp. 306–314.

Telford, K., Maher, W., Krikowa, F. and Foster, S. (2008) ‘Measurement of total antimony and antimony species in mine contaminated soils by ICPMS and HPLC-ICPMS.’ *Journal of Environmental Monitoring*, 10(1) pp. 136–140.

Telford, K., Maher, W., Krikowa, F., Foster, S., Ellwood, M. J. M. J., Ashley, P. M. P. M., Lockwood, P. V. P. V. and Wilson, S. C. S. C. (2009) ‘Bioaccumulation of antimony and arsenic in a highly contaminated stream adjacent to the Hillgrove Mine, NSW, Australia.’ *Environmental Chemistry*, 6(2) pp. 133–143.

Thomas, G. W. (1996) ‘Soil pH and soil acidity.’ *In* D.L. Sparks et al., editors (ed.) *Methods of soil analysis: Part 3. SSSA Book Series No. 5. SSSA,* pp. 475–490.

Tian, T., Zhou, H., Gu, J., Jia, R., Li, H., Wang, Q., Zeng, M. and Liao, B. (2019) ‘Cadmium accumulation and bioavailability in paddy soil under different water regimes for different growth stages of rice (Oryza sativa L.).’ *Plant and Soil*. Springer International Publishing, July.

Timofeev, I. and Hutchinson, P. (2008a) 'Microdialysis.' *In Essentials of Neuroanesthesia and Neurointensive Care*. Elsevier, pp. 277–282.

Timofeev, I. and Hutchinson, P. (2008b) 'Microdialysis Learn more about Microdialysis Microdialysis Chemical and Biochemical Approaches for the Study of Anesthetic Function Part B Carrier-mediated and artificial-cell tar-.'

Toghill, K. E., Lu, M., Compton, R. G. and Kathryn E. Toghill, Min Lu, and R. G. C. (2011) 'Electroanalytical Determination of Antimony.' *International Journal of Electrochemical Science*, 6(8) pp. 3057–3076.

Tollestrup, K., Frost, F. J., Harter, L. C. and McMillan, G. P. (2003) 'Mortality among Children Residing near the American Smelting and Refining Company (ASARCO) Copper Smelter in Ruston, Washington.' *Archives of Environmental Health: An International Journal*, 58(11) pp. 683–691.

Torto, N., Mwatseteza, J. and Laurell, T. (2001) 'Microdialysis Sampling: Challenges and New Frontiers.' *LC GC Europe*, 14(9) pp. 536–546.

Torto, N., Mwatseteza, J. and Sawula, G. (2002) 'A study of microdialysis sampling of metal ions.' *Analytica Chimica Acta*. Elsevier, 456(2) pp. 253–261.

Trejo-Téllez, L. I. (2012) 'Nutrient Solutions for Hydroponic Systems.' *In* Asao, F. C. G.-M. E.-T. (ed.). Rijeka: IntechOpen, p. Ch. 1.

Tsang, J. J., Rozan, T. F., Hsu-Kim, H., Mullaugh, K. M. and Luther, G. W. (2006) 'Pseudopolarographic determination of Cd2+ complexation in freshwater.' *Environmental Science and Technology*, 40(17) pp. 5388–5394.

Tschan, M., Robinson, B. H. and Schulin, R. (2009) 'Antimony in the soil - Plant system - A review.' *Environmental Chemistry*, 6(2) pp. 106–115.

Tschan, M., Robinson, B. and Schulin, R. (2008) 'Antimony uptake by Zea mays (L.) and Helianthus annuus (L.) from nutrient solution.' *Environmental Geochemistry and Health*, 30(2) pp. 187–191.

Tsukagoshi, S. and Shinohara, Y. (2015) *Nutrition and Nutrient Uptake in Soilless Culture Systems*. *Plant Factory: An Indoor Vertical Farming System for Efficient Quality Food Production*. Elsevier Inc.

Tuyogon, D. S. J., Impa, S. M., Castillo, O. B., Larazo, W. and Johnson-Beebout, S. E. (2016) 'Enriching rice grain zinc through zinc fertilization and water management.' *Soil Science Society of America Journal*, 80(1) pp. 121–134.

Tylenda, C. A., Sullivan, D. W. and Fowler, B. A. (2015) *Antimony*. *Handbook on the*

Toxicology of Metals: Fourth Edition. Fourth Edi, Elsevier.

U.S. Department of Health and Human (2018) *Revised Draft : Report on Carcinogens Monograph on Antimony Trioxide*.

U.S. Geological Survey (2004) 'Mineral Commodity Profiles-Antimony.' *U.S. Department of the Interior: U.S. Geological Survey* pp. 1–35.

Ugochukwu, G. C., Eneh, F. U., Igwilo, I. . and Aloh, C. H. (2017) 'Comparative study on the heavy metal content of domestic rice (Oryza sativa Comparative study on the heavy metal content of domestic rice (Oryza sativa L) brands common in Awka, Nigeria.' *IOSR Journal of Environmental Science, Toxicology and Food Technology*, 11(8) pp. 67–70.

UN (ed.) (2015) *Crop Prospects and Food Situation*. Rome: FAO.

Ungureanu, G., Santos, S., Boaventura, R. and Botelho, C. (2015) 'Arsenic and antimony in water and wastewater: Overview of removal techniques with special reference to latest advances in adsorption.' *Journal of Environmental Management*, 151, March, pp. 326–342.

Uroic, M. K. (2011) *The impact of arsenic species on the production and composition of xylem sap*. *Environmental & Analytical Chemistry*. University of Aberdeen. Retrieved from internal-pdf://145.35.116.156/PhD thesis The impact of As MK Uroic.pdf.

Uroic, M. K., Salaün, P., Raab, A. and Feldmann, J. (2012) 'Arsenate impact on the metabolite profile, production, and arsenic loading of xylem sap in cucumbers (Cucumis sativus L.).' *Frontiers in Physiology*, 3 APR(March) pp. 1–23.

Varsányi, I., Fodré, Z. and Bartha, A. (1991) 'Arsenic in drinking water and mortality in the Southern Great Plain, Hungary.' *Environmental Geochemistry and Health*. Kluwer Academic Publishers, 13(1) pp. 14–22.

Violante, A., Cozzolino, V., Perelomov, L., Caporale, A. . and Pigna, M. (2010) 'Mobility and bioavailability of heavy metals and metalloids in soil environments.' *Journal of soil science and plant nutrition*. Sociedad Chilena de la Ciencia del Suelo, 10(3) pp. 268–292.

Vithanage, M., Dabrowska, B. B., Mukherjee, A. B., Sandhi, A. and Bhattacharya, P. (2012) 'Arsenic uptake by plants and possible phytoremediation applications: A brief overview.' *Environmental Chemistry Letters* pp. 217–224.

Wagner, S. E., Peryea, F. J. and Filby, R. A. (2003) 'Antimony Impurity in Lead Arsenate Insecticide Enhances the Antimony Content of Old Orchard Soils.' *Journal of Environmental Quality*. Wiley, 32(2) pp. 736–738.

Wan, X. M., Tandy, S., Hockmann, K. and Schulin, R. (2013) 'Changes in Sb speciation with waterlogging of shooting range soils and impacts on plant uptake.' *Environmental Pollution*. Elsevier Ltd, 172, January, pp. 53–60.

Wang, S., Shi, X., Sun, H., Chen, Y., Pan, H., Yang, X. and Rafiq, T. (2014) 'Variations in Metal Tolerance and Accumulation in Three Hydroponically Cultivated Varieties of Salix integra Treated with Lead.' Reigosa, M. (ed.) *PLoS ONE*. Public Library of Science, 9(9) p. e108568.

Wang, T., Yang, Q., Wang, Y., Wang, J., Zhang, Y. and Pan, W.-P. P. (2020) 'Arsenic release and transformation in co-combustion of biomass and coal: Effect of mineral elements and volatile matter in biomass.' *Bioresource technology*. Beijing, PR China: Elsevier Ltd, 297, February, p. 122388.

Wang, Z., Zeng, X., Geng, M., Chen, C., Cai, J., Yu, X., Hou, Y. and Zhang, H. (2015) 'Health risks of heavy metals uptake by crops grown in a sewage irrigation area in China.' *Polish Journal of Environmental Studies*, 24(3) pp. 1379–1386.

Welch, A. H. and Stollenwerk, K. G. (eds) (2003) *Arsenic in Ground Water*. *Springer Science Business Media New York*. Boston, MA: Springer US.

White, M. C., Chaney, R. L., Decker, A. M. and R., and M. W. D. A. (1981) 'Metal Complexation in Xylem Fluid: I. Chemical composition of tomato and soybean stem exudate.' *Plant Physiology*, 67(2) pp. 292–300.

WHO (2003a) 'Antimony in Drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality.' *Who* pp. 1–9.

WHO (2003b) *Background document for preparation of WHO Guidelines for drinking-water quality: Antimony in drinking water.* Geneva, Switzerland.

WHO (2003c) 'Chromium in drinking-water. Background document for preparation of WHO Guidelines for drinking-water quality.' *(WHO/SDE/WSH/03.04/4)*, (3) pp. 334–335.

Wickliff, J. L. and Aronoff, S. (1962) *Quantitative measurement of leaf chlorophylss by spectrophotometry of their pheophytins in aqueous alcoholic extracts*. Iowa, USA.

Williams, P. N., Islam, M. R., Adomako, E. E., Raab, A., Hossain, S. A., Zhu, Y. G., Feldmann, J. and Meharg, A. A. (2006) 'Increase in rice grain arsenic for regions of Bangladesh irrigating paddies with elevated arsenic in groundwaters.' *Environmental Science and Technology* pp. 4903–4908.

Wilson, S. C., Lockwood, P. V., Ashley, P. M. and Tighe, M. (2010) 'The chemistry and behaviour of antimony in the soil environment with comparisons to arsenic: A critical review.' *Environmental Pollution*. Elsevier Ltd, 158(5) pp. 1169–1181.

Woolson, E. A., Axley, J. H. and Kearney, P. C. (1971) 'Correlation between Available Soil Arsenic, Estimated by Six Methods, and Response of Corn (Zea mays L.)1.' *Soil Science Society of America Journal*. Soil Science Society of America, 35(1) p. 101.

Wu, D. and Sun, S. (2016) 'Speciation analysis of As, Sb and Se.' *Trends in Environmental*

Analytical Chemistry. Elsevier Inc., 11, July, pp. 9–22.

Wu, T.-L. L., Cui, X.-D. D., Cui, P.-X. X., Ata-Ul-Karim, S. T., Sun, Q., Liu, C., Fan, T.-T. T., Gong, H., Zhou, D.-M. M. and Wang, Y.-J. J. (2019) 'Speciation and location of arsenic and antimony in rice samples around antimony mining area.' *Environmental Pollution*. Elsevier Ltd, 252, September, pp. 1439–1447.

www.IRRI.org (2019) *Long-Term Continuous Cropping Experiment (LTCCE) | International Rice Research Institute*. [Online] [Accessed on 18th November 2019] https://www.irri.org/long-term-continuous-cropping-experiment-ltcce.

Wyrwicka, A., Urbaniak, M. and Przybylski, M. (2019) ' The response of cucumber plants (Cucumis sativus L.) to the application of PCB-contaminated sewage sludge and urban sediment .' *PeerJ*, 7 p. e6743.

Xu, X. Y., McGrath, S. P. and Zhao, F. J. (2007) 'Rapid reduction of arsenate in the medium mediated by plant roots.' *New Phytologist*, 176(3) pp. 590–599.

Yadav, S. K. (2010) 'Heavy metals toxicity in plants: An overview on the role of glutathione and phytochelatins in heavy metal stress tolerance of plants.' *South African Journal of Botany*. Elsevier B.V., 76(2) pp. 167–179.

Ye, W.-L. L., Wood, B. A., Stroud, J. L., Andralojc, P. J., Raab, A., McGrath, S. P., Feldmann, J. and Zhao, F.-J. J. (2010) 'Arsenic speciation in phloem and xylem exudates of castor bean.' *Plant Physiology*, 154(3) pp. 1505–1513.

Zavala, Y. J. and Duxbury, J. M. (2008) 'Arsenic in rice: I. Estimating normal levels of total arsenic in rice grain.' *Environmental Science and Technology*, 42(10) pp. 3856–3860.

Zengin, F. K. and Munzuroglu, O. (2005) 'Effects of some heavy metals on content of chlorophyll, proline and some antioxidant chemicals in bean (Phaseolus vulgaris L.) seedlings.' *Acta Biologica Cracoviensia Series Botanica*, 47(2) pp. 157–164.

Zhang, H. and Selim, H. M. (2005) 'Kinetics of Arsenate Adsorption−Desorption in Soils.' *Environmental Science & Technology*, 39(16) pp. 6101–6108.

Zhang, T., Ruan, J., Zhang, B., Lu, S., Gao, C., Huang, L., Bai, X., Xie, L., Gui, M. and Qiu, R. (2019) 'Heavy metals in human urine, foods and drinking water from an e-waste dismantling area: Identification of exposure sources and metal-induced health risk.' *Ecotoxicology and Environmental Safety*. Academic Press, 169, March, pp. 707–713.

Zhang, W., Cai, Y., Tu, C. and Ma, L. Q. (2002) 'Arsenic speciation and distribution in an arsenic hyperaccumulating plant.' *Science of the Total Environment*, 300(1–3) pp. 167–177.

Zhao, F.-J., Ma, Y., Zhu, Y.-G., Tang, Z. and McGrath, S. P. (2015) 'Soil Contamination in China: Current Status and Mitigation Strategies.' *Environmental Science & Technology*.

American Chemical Society, 49(2) pp. 750–759.

Zhao, F.-J., McGrath, S. P. and Meharg, A. A. (2010) ‘Arsenic as a Food Chain Contaminant: Mechanisms of Plant Uptake and Metabolism and Mitigation Strategies.’ *Annual Review of Plant Biology*. Annual Reviews, 61(1) pp. 535–559.

Zheng, J., Iijima, A. and Furuta, N. (2001) ‘Complexation effect of antimony compounds with citric acid and its application to the speciation of antimony(III) and antimony(V) using HPLC-ICP-MS.’ *Journal of Analytical Atomic Spectrometry*, 16(8) pp. 812–818.

Zheng, R. L., Sun, G. X. and Zhu, Y. G. (2013) ‘Effects of microbial processes on the fate of arsenic in paddy soil.’ *Chinese Science Bulletin* pp. 186–193.

Zhou, S. N., Ouyang, G. and Pawliszyn, J. (2008) ‘Comparison of microdialysis with solid-phase microextraction for in vitro and in vivo studies.’ *Journal of Chromatography A*, 1196–1197(1–2) pp. 46–56.

Zhou, X., Sun, C., Zhu, P. and Liu, F. (2018) ‘Effects of Antimony Stress on Photosynthesis and Growth of Acorus calamus.’ *Frontiers in Plant Science*. Frontiers Media S.A., 9(May) pp. 1–9.

Zulkafflee, N. S., Redzuan, N. A. M., Hanafi, Z., Selamat, J., Ismail, M. R., Praveena, S. M. and Razis, A. F. A. (2019) ‘Heavy metal in paddy soil and its bioavailability in rice using in vitro digestion model for health risk assessment.’ *International Journal of Environmental Research and Public Health*, 16(23).

CHAPTER 6

CATION MEDIATED REDUCTION OF ANTIMONATE SB(V) IN MILDLY ACIDIC AND NEUTRAL PH

Index of Figures

Index of Tables

6.1 Introduction

Antimony (Sb) is a naturally occurring element in the environment (groundwater, rocks, and soils). It is naturally present at low concentrations, but the increased use of Sb in activities such as mining, fire-retardants, or microelectronic industry has led to increased environmental soil and water contamination issues. Despite its toxicity, Sb has not received as much attention compared to other toxic heavy metals and/or metalloids such as arsenic, mostly due to the relatively low concentrations (low nM) encountered in natural waters. In oxygenated water, it is mostly present as the anionic species arsenate $Sb(OH)_6^-$, while the neutral antimonite $Sb(OH)_3$ is predominant in anoxic conditions (Filella and May, 2003). While the determination of total concentrations is not an issue anymore, the determination of individual species is still challenging, and Sb speciation is still mostly restricted to the differentiation of oxidation states (Wu and Sun, 2016), similar to what was already stated 20 years ago (Nash et al., 2000). Low concentration of Sb naturally present in environmental systems, low recovery on chromatographic columns, species instability in terms of oxidation/reduction and formation of weak complexes that are easily destroyed during sample treatment are some of the reasons identified in the challenges facing Sb speciation (Hansen and Pergantis, 2008).

One of the available methods in Sb determination is the hyphenated technique method based on chromatography coupled with spectroscopy. The most common techniques are HPLC-ICP-MS, hydride generation atomic spectrometry (HG-AAS), Graphite Furnace-Atomic Absorption Spectroscopy (GF-AAS), electrospray MS detection, and Inductively

Coupled Plasma-Mass Spectrometry (ICP-MS) (Ammann, 2011). In addition, aside from the matrix effects, laborious and expensive chemical analysis are some of the hindrances in the Sb analysis.

Similar to other techniques, all electrochemical methods are focusing on the determination of inorganic Sb(III) and/or inorganic Sb(V) with speciation being limited to the differentiation of oxidation states; one of the main reason for such limitation is that the electroanalytical determination of metalloids is often achieved in acidic conditions. These acidic conditions have been commonly used to facilitate the reduction, chemical and/or electrochemical reduction of the oxy-hydroxy species even though the reduction of the trivalent species arsenite had been reported at all pH as early as 1975 (Forsberg et al., 1975). For pentavalent species, this is different. Both antimonate Sb(V) and arsenate As(V) are often considered as electroinactive, i.e., they cannot be reduced electrochemically. In these cases, their detection is conditional on a chemical reduction step to form the trivalent species that can be detected more easily. Several reducing agents have been used (e.g., cysteine (Santos et al., 2009), SO_2 (Brihaye and Duyckaerts, 1982) or hydrazine in boiling water (Postupolski and Golimowski, 1991), but this chemical step introduces several disadvantages: challenging to implement, time-consuming, limiting sample throughput, and a potential source of contamination. Although rarely used, a direct electrochemical reduction is a preferred option as more straightforward and faster to implement. It has been used on several occasions for arsenate detection (see (Salaün et al., 2007) and references therein) but rarely for antimonate where reduction can only be achieved in strongly acidic conditions (3-6 M) on Hg electrodes (e.g. (Quentel and Filella, 2002)). Hydrogen generation through the reduction of protons at the electrode surface is usually avoided because (1) it affects the mechanical stability of the mercury drop electrode (vibrations created by the generation of the gas tend to dislodge the drop), (2) the hydrogen blocks the electrode surface (e.g., on a gold disc electrode) during the deposition step or 3- it creates noisy voltammograms, unsuitable for analytical determination. Hydrogen generation at a gold wire electrode was found to be a reproducible process allowing the use of low pH and low deposition potential (Salaün et al., 2011). However, the issue of these analytical conditions is that only the valency of the ions can be determined, while information on speciation in terms of complexation is not accessible due to the required change in pH. The importance of developing analytical methods that can measure analytes in environmentally relevant conditions of pH is a well-known challenge (Toghill et al., 2011; Salaün et al., 2012; Ungureanu et al., 2015).

The determination of As(V) in neutral conditions of pH was first reported in 2011 by Gibbon-Walsh et al., (2011). At neutral pH of 7-8, arsenate is present as a mix of dihydrogen and hydrogen arsenate anions ($H_2AsO_4^-$ or $HAsO_4^{2-}$ respectively). The direct electrochemical reduction could not be achieved at a pH lower than 4 at a gold electrode, irrespective of the deposition potential that was used (Salaün et al., 2007, 2012). Interestingly, the authors found that the presence of an excess of Mn^{2+} ions (uM level) favours the detection of As(V) in neutral conditions of pH. They found that Mn^{2+} is first reduced to Mn^0, and this layer of reduced manganese favors the chemical reduction of arsenate to arsenite at the electrode surface during the deposition step. Similar observations were also made using Fe(III) or Fe(II) in place of Mn(II). In both cases, the reduction and deposition of Mn and/or Fe facilitate the overall electron transfer from the electrode to As(V), inducing its deposition and allowing stripping analysis in conditions of pH that are not favorable for a direct reduction. The manganese mediated reduction was very recently used to study the cycling of arsenic in estuarine conditions (Penezić et al., 2020); by looking at the difference of arsenic detected in acidic and neutral conditions, the authors reached the conclusion that As(V) is probably transported as adsorbed onto colloidal materials (probably iron oxides), which strongly affects its bioavailability. This latter study exemplifies the importance of measuring speciation in conditions as close as possible from those encountered in environmental systems.

Preliminary experiments made by Salaun et al. (unpublished results) suggest that a similar "cation mediated reduction" process can be used for the determination of Sb(V) in non-acidic conditions; such a method could provide a new analytical methodology to gain further insights into antimony cycling in the environment.

6.2 Aims and objectives

This chapter presents preliminary experiments performed with the effect of monovalent (Na^+, K^+), divalent (Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+}) and trivalent ($La^{(III)}$, $Y^{(III)}$) cations on antimonate reduction in acidic (pH = 1), mildly acidic (pH 2) and neutral conditions of pH. The aim was to assess the influence of the presence of these cations on the electrochemical reduction of Sb(V) at a gold electrode. The specific objectives were to:

- Compile the results obtained with preliminary experiments,
- Assess the influence of the presence of copper at trace levels (sub uM),
- To assess the analytical capability of this cation mediated reduction process,
- To propose a schematic representation of this cation mediated process, and
- To develop a voltammetric analysis for Sb(V) in commercially available bottled mineral water.

6.3 Materials and Methods

6.3.1 Reagents and Materials

All chemicals were of analytical quality unless otherwise stated. Water used to prepare reagents and preliminary working solutions was 18 MΩ cm−1 purified using a Millipore-Elix system. Standard Sb(V) (10 uM and 100 uM) and Cu^{2+} (10 uM) solutions were prepared by dilution of a 1,000-ppm atomic absorption standard solution from Aldrich. Standard solutions were kept at room temperature and used for several months.

6.3.2 Instrumentation

Voltammetric experiments were made using a μAutolabIII potentiostat (EcoChemie, now Metrohm AG, Switzerland) computer-controlled using GPES software (version 4.9). A three-electrode cell containing the gold microwire working electrode (WE), an iridium counter electrode (CE) (150 μm diameter, ∼3 mm length), and a double-junction, Ag/AgCl/KCl (3 M)//NaNO3 (0.1 M), a reference electrode was placed in a voltammetric cell (Teflon), which was placed in a Faraday cage (Windsor Scientific, UK). The salt bridge was filled with 0.1 M NaNO3. Gold microwires (Purity: 99.99%, temper: hard) of 10 and 25 μm diameter (Goodfellow, UK) used for the electrodes. A vibrator rotor was attached to the microwire WE. The vibrator, which was used in place of a standard magnetic stirrer, was powered by an IME663 (EcoChemie) controlled by GPES software. The vibrated gold microwire electrodes were prepared as described in Chapter 5 (5.3.2, pp 287) and stored in air or Milli-Q water. The surface of the electrode was cleaned electrochemically in 0.5 M H_2SO_4 by hydrogen generation at −2.5 V for 30 s prior to use twice daily. The reduction peak of the oxide monolayer obtained in 0.5 M H_2SO_4 was that was used to monitor the surface area and check on the good behavior of the electrode (Salaün and van den Berg, 2006).

6.3.2.1 Determination of Sb(V) using DPASV (Differential Pulse Anodic Stripping Voltammetry)

Sb(V) was measured by DPASV using the background methodology procedure, as described in Chapter 5. Typical DP conditions were 100ms interval time, 4-20 ms pulse time, 25-50 mV amplitude, and 4-6 mV step. The peak potential and the peak intensity (as given by the peak derivative in $A.V^{-1}$) was measured automatically by the GPES software using the peak derivative. All measurements, unless specified, were done in deaerated solutions with hydrated N_2 gas. Pseudopolarographic measurements were typically achieved by varying the deposition potentials from -2.4 to -0.1 V with 0.05V increments. Typical voltammetric conditions are given in Table 6.1.

Table 6. 1.Voltammetric conditions used for measurements at pH 2.0 (10 mM HCl) and pH 5.0 (10 mM $CH_3COO^-Na^+$ + 2.5 mM HCl).

Mode	DPASV
Conditioning potential	-2.4 V
Conditioning time	15 s
Deposition potential	-2 V
Deposition time sample	1 s
Deposition time blank	1 s
Scan	-0.2 V – 0.4 V
Step	0.00405 V
Amplitude	50 mV
Frequency	50Hz

6.3.2.2 Electrode Fabrication

Ten and 25 uM Au microwire electrodes were fabricated according to the procedure described by (Salaün and van den Berg, 2006). A 10-cm length of 100-um copper wire was passed through a 100-uL pipet tip (polyethylene, Corning Inc.). Its end was dipped in a conductive silver solution (Leitsilber L100, Maplin, UK), which had been freshly agitated and acted as a conductive adhesive. The copper wire was then attached to a 10- mm length of gold microwire (10 or 25 um) by gently touching it. The copper wire was then carefully pulled through the pipet tip until the microwire passed halfway through. The microwire was sealed in the tip by holding it in the top of the oven, which had been set to 400 °C, during approximately 8 s to melt it uniformly.

6.3.2.3 Gold microwire electrode surface area measurement

The surface of the Au microwire was measured along the procedure described in (Salaün and van den Berg, 2006). Briefly, after the cleaning stage (-2.5 V for 30-60s), a CV between 0 and 1.5 V was repeated 3-4 times until the scan was stable (normally after the second scan). The potential at which a current minimum is observed after the formation of the gold oxide is a proxy for the completion of a gold oxide monolayer at the surface of the gold (Mareček et al., 1986). By measuring the charge of the reduction peak of this oxide monolayer and normalising to length using the coefficient of 450 $\mu C.cm^{-2}$, the surface area could be obtained. Using an average roughness of 1.2, the length of the electrode was estimated (Salaün and van den Berg, 2006). This was done to normailse the peak intensity to the length of the electrode (Figure 6.3).

6.3.2.4 Analytical capability of the cation mediated reduction process for determination of Sb(V) in mineral water.

Mineral water samples were collected from a Tesco store. For pH 1, 19.6 mL of the sample aliquot were mixed with 400 uL of 5M HCl (0.1M HCl) and 3 mM $CaCl_2$ and for pH 2, 19.6 mL of the samples were mixed with 40 uL of 5M HCl (10 mM HCl) and 3 mM $CaCl_2$. For pH 5, measurements were done in 10 mM NaAc with pH being adjusted with addition of c.a. 8 mM HCl. The samples were placed in a voltammetric cell, with 15 minutes deaeration with nitrogen gas before ASV analysis using the standard addition method only at pH5.

6.4 Results

6.4.1 Influence of cations on the reduction of Sb(V) in 10 mM HCl

6.4.1.1 Effect of Na, K, Mg and Ca ions

The effect of the addition of sodium nitrate on the voltammetric detection of 10 nM Sb(V) is shown in 10 mM HCl (Figure 6.1) with a low deposition potential of E_{dep} = -2.4 V. In HCl only, no Sb(V) peak is apparent (red voltammograms). However, upon the addition of mM levels of $NaNO_3$, a well-defined Sb peak appears at a potential of c.a. + 59 mV, and the peak intensity increases with additions of $NaNO_3$ in the studied range of 1-9 mM. This range were chosen from the results of unpublished preliminary studies (not shown).

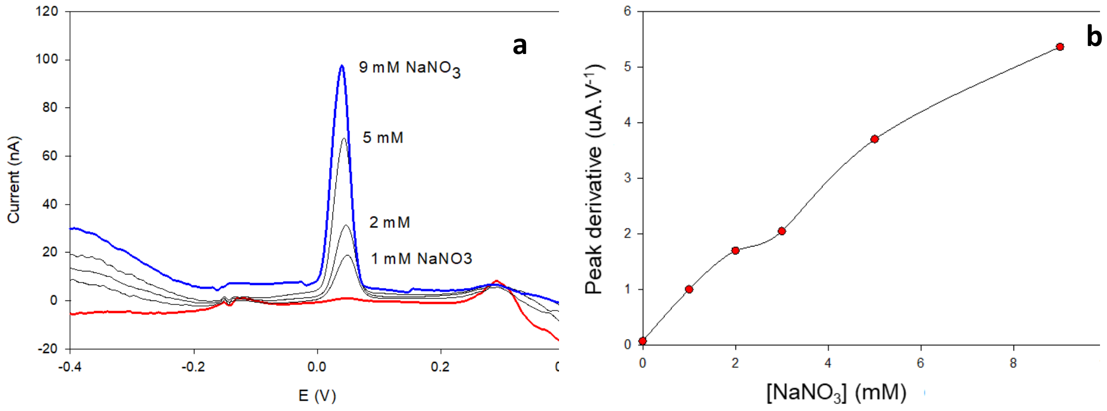


Figure 6. 1.Effect of addition of $NaNO_3$ on the DPASV peak intensity of 10 nM Sb(V) in 10 mM HCl (a). Voltammetric parameters: Deposition at -2.4 V for 30s, -1 V for 2s, stripping from -0.4 to 0.4 V (b). Experiment performed with P. Salaun and confirmed by D. Tuyogon.

Similar effects were also observed for sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), or magnesium (Mg^{2+}), each cation having its own characteristic pseudopolarograms (PP). Figure 6.2 shows the influence of the deposition potential on the Sb peak intensity of 10 nM Sb(V) in 10 mM HCl in the absence and in the presence of these cations. In 10 mM HCl only, no Sb signal can be detected, apart from a deposition potential comprised from

-2.6 to -2.9 V where a small Sb(V) peak is apparent. In the presence of 3 mM of Na^+, K^+, Ca^{2+}, or Mg^{2+}, the Sb(V) peak increases significantly at deposition potentials that are dependent on the nature of the cation. For K+ and Na+, the Sb peak appears at potentials lower than -2.05 V, while for Ca^{2+} and Mg^{2+}, it appears for Edep ≤ -1.5 V and Edep ≤ -1.2 V, respectively. The same pseudopolarograms are obtained irrespective of the salt being used (e.g., $CaCl_2$ or $Ca(NO_3)_2$ salts), clearly evidencing that this enhancement of the antimonate peak is due to the presence of the cation, not that of the anion.

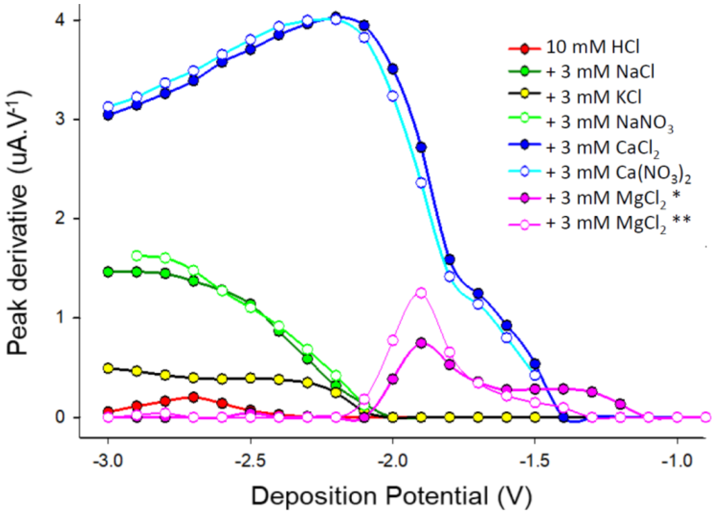


Figure 6. 2. Influence of the addition of 3 mM $MgCl_2$ (*anhydrous and ** heptahydrate), 3mM $CaCl_2$, 3 mM $Ca(NO_3)_2$, 3 mM NaNO3, 3 mM NaCl or 3mM KCl on the DPASV peak intensity of 10 nM Sb(V) in 10 mM HCl. Electrode: 10 um diameter gold wire electrode. Voltammetric parameters: Edep for 15s, 1s at -1 V, 1s equilibrium, stripping from -0.2 V to 0.4 V – 100 ms interval time, 4ms pulse time, 4 mV step, 50 mV amplitude. Note: preliminary experiment performed with P. Salaun and confirmed by D. Tuyogon.

Out of Mg, Ca, Na, and K, calcium enhanced the reduction rate of antimonate the most. Reproducibility of this Ca^{2+} catalysis on Sb(V) reduction was evaluated using 3 identical (Figure 6.3A) or 3 different 10 μm ∅ electrodes (Figure 6.3B), 3 identical (Figure 6.3C) or 3 different (Figure 6.3D) 25 μm ∅ electrodes. Relatively good reproducibility was obtained (+/- 10%) on both the position of the reduction wave and the intensity of the wave, suggesting a very reproducible mechanism. However, although the reproducibility within an experimental set up was acceptable, there were differences between experiments. Figures 6.2, 6.3A, and 6.3B all have similar conditions: the same electrode, similar preparation methodology, and similar measuring conditions, but produce significantly different results (i.e., different shapes of the pseudopolarograms with different positions of the waves).

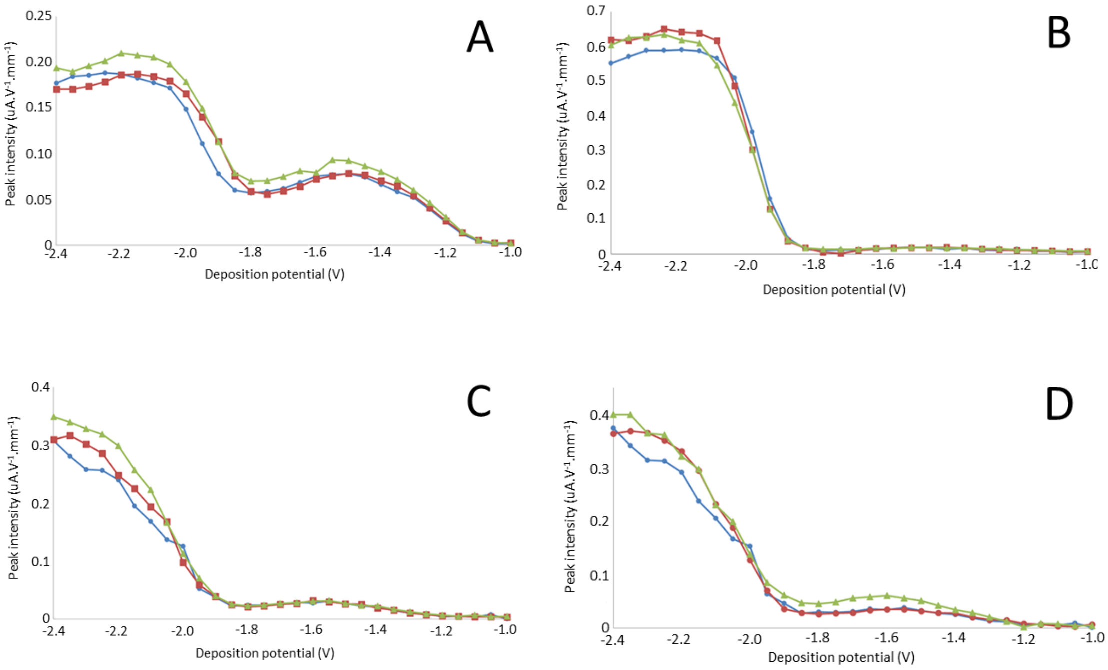


Figure 6. 3. Reproducibility of the Influence of 3 mM calcium on the normalised DPASV peak intensity of 10 nM antimonate in 10 mM HCl in presence of 40 nM Cu. A/B: 10 um electrodes; C/D: 25 um electrodes; A/C: 3 identical electrodes; B/D: 3 different electrodes. Voltammetric parameters: Econ: +0.75V (5s) Edep for 15s, -2.4V (1s), 1s equilibrium, stripping scan from -0.1 V to +0.4V. Step: 4 mV, amplitude: 25 mV; standby pot.: +0.75V; Electrodes: gold working electrodes, Iridium counter electrode and Ag/AgCl/KCl (3M)//3M KCl reference electrode. (red, green and blue lines are replicates analysis)

Differences in potentials could be related to different reference electrodes with slightly different junction potentials. Comparing the responses obtained at the 10 and 25 um diameter electrodes (Figure 6.3B and 6.3D respectively), the reduction of antimonate seems to be facilitated at the smaller size electrode because of a plateau value at c.a. -2.1 V, while the signal is still increasing at -2.4 V for 25 um, ∅ electrodes.Repeated measurement gave an excellent reproducibility of the Sb signal. For instance, an RSD of less than 2% was obtained for almost 90 successive measurements (Conditions: 10 mM HCl, Edep = -2.5 V (30s), 10 nM Sb(V) + 3 mM $CaCl_2$). Alternate analysis at different potentials also proved to be reproducible over several cycles (e.g., Figure 6.4).

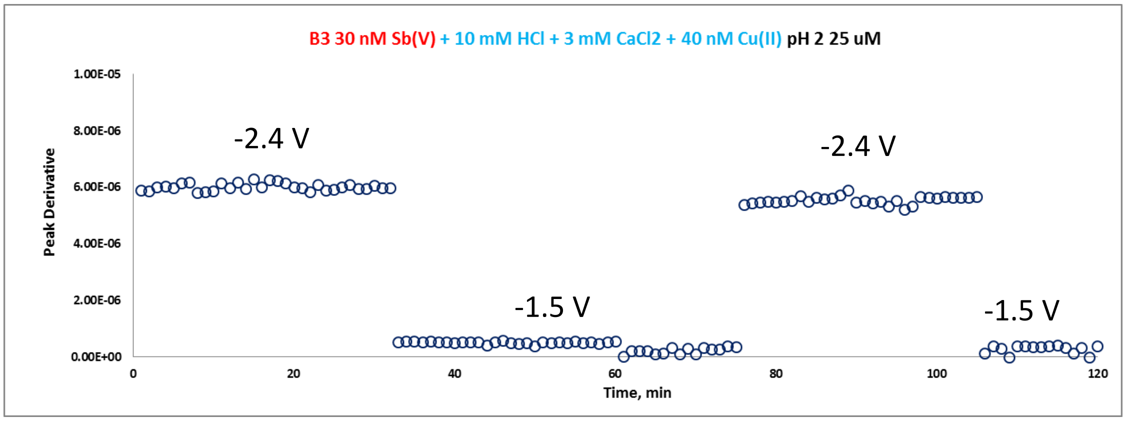


Figure 6. 4. Stability of Sb(V) DPASV peak intensity obtained at a 25-um Au microwire electrode. Solution: 30 nM Sb(V) in 10 mM HCl (pH2) + 40 nM Cu + 3 mM CaCl2. Voltammetric parameters: Econ: +0.75V (5s) Edep (-2.4 V or -1.5 V) for 15s, -2.4V (1s), 1s equilibrium, stripping scan from -0.1 V to +0.4V. Step: 4 mV, amplitude: 25 mV; standby pot.: +0.75V; Electrodes: gold working electrodes, Iridium counter electrode and Ag/AgCl/KCl (3M)//3M KCl reference electrode

6.4.1.2 Effect of concentrations of cations on pseudopolarograms

In contrast to typical pseudopolarograms where the potential at half-wave is insensitive to the concentration of the metal being reduced, the effect of the cation concentration on the potential at which Sb(V) reduction is occurring is essential. This is shown in Figure 6.5 for magnesium and Figure 6.6 for calcium, sodium, and potassium. For instance, at lower Mg concentration (e.g., 1 μM), and Sb signal is only observed at relatively low Edep

(-2.3 V for [Mg]= 1 μM). When increasing Mg, the Sb peak appears at higher Edep (-1.7 V for [Mg]= 10 mM). At any concentration, the pseudopolarogram goes through a maximum, and this bell shape behavior was also observed for calcium, sodium, and potassium (Figure 6.6). In every case, increasing the concentration of the cations and reducing the deposition potential to extreme values (i.e., -3.0 V) not only resulted in a complete loss of the signal, but it also affected the mechanical stability of the gold wire electrode. Repeated measurements in such conditions (i.e., high concentrations of cations and low deposition potentials) inevitably led to a complete dissolution of the gold wire electrode.

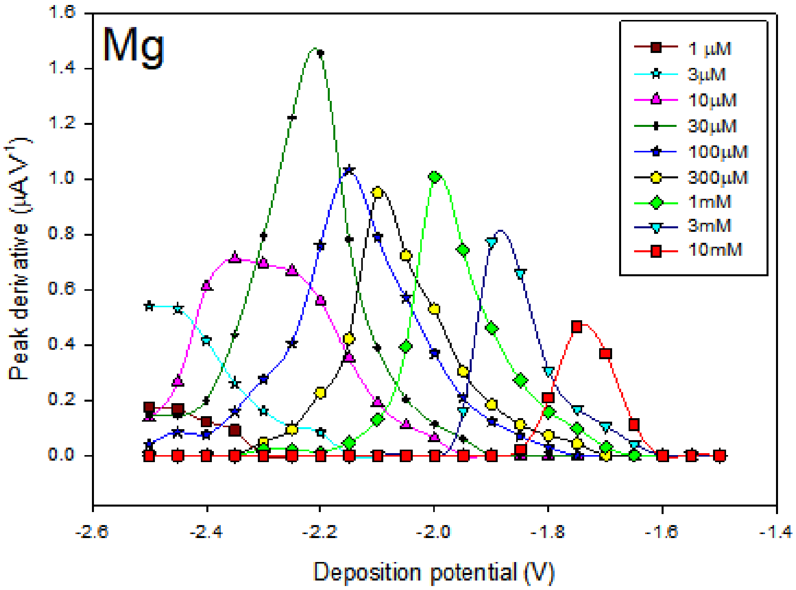
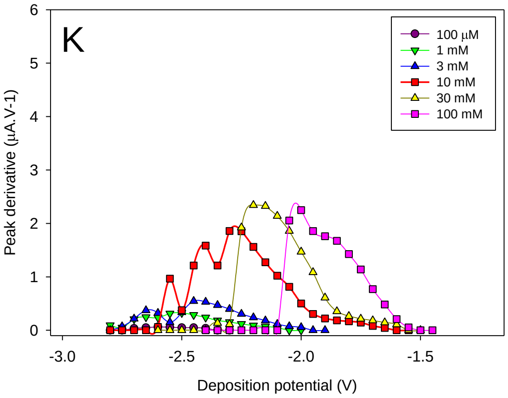
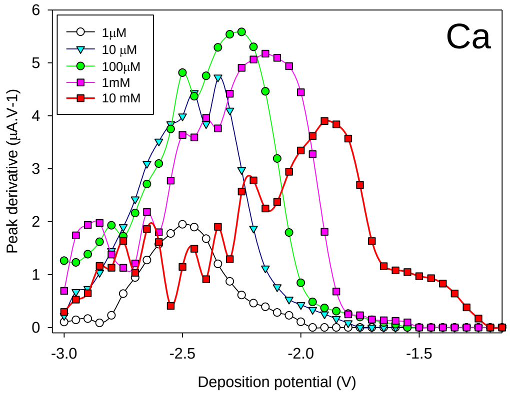


Figure 6. 5. Effect of concentration of magnesium on the PP of 10 nM Sb(V). Background electrolyte: 10 mM HCl.





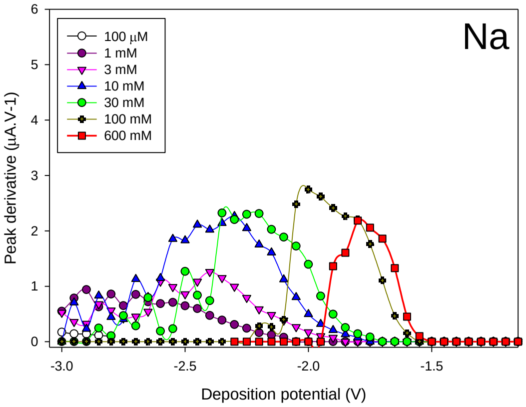


Figure 6. 6. Effect of concentration of potassium, calcium, and sodium on the pseudopolarogram of 10 nM Sb(V). Background electrolyte: 10 mM HCl. Relative intensities can be compared since the same gold wire electrode was used for all these experiments (including Figure 6.3). Note: Experiments performed by P. Salaun and confirmed by D. Tuyogon.

For K, Na, and especially Ca, a "double wave" is sometimes observed. For instance, for Ca = 10 mM (Fig. 6.6), a first increase is observed for -1.1 V ≥ Edep ≥ -1.3 V followed by a plateau (-1.3 V ≥ Edep ≥ -1.65 V) before a second increase at -1.65 V ≥ Edep ≥ -1.85 V. This double wave is also observed in Figure 6.2 for [Ca]= 3mM.

The effect of the divalent barium and strontium cations, as well as the trivalent yttrium and lanthanum cations, all added from the corresponding chloride salts were also studied (Figure 6.7) (Benkaddour, 2016). Pseudopolarograms were obtained in similar conditions (10 nM Sb(V) in 10 mM HCl) but with deposition potentials varied between -0.8 and -2.5 V to avoid extensive damage to the gold electrode.

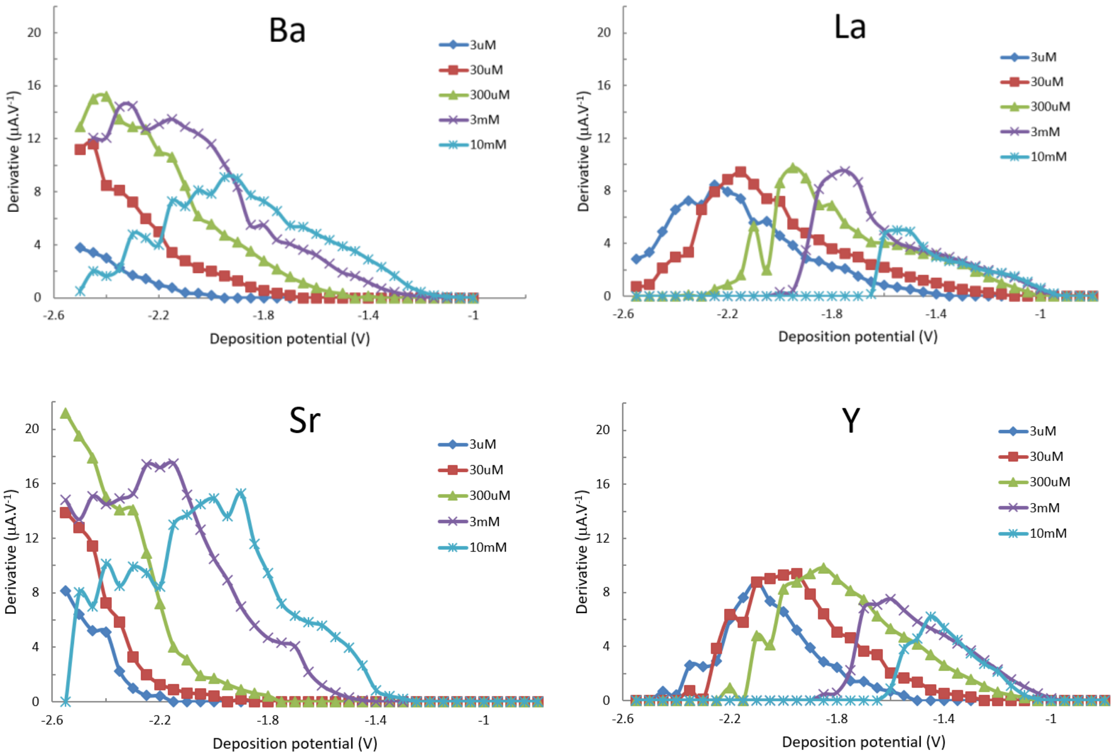


Figure 6. 7. Effect of concentration of barium, strontium, lanthanum, and yttrium (all taken from chloride salts) on the pseudopolarogram of 10 nM Sb(V). Background electrolyte: 10 mM HCl. Relative intensities can be compared since the same gold wire electrode was used for these experiments. Note: Pseudopolarograms obtained by Sassi Benkaddour (Master project, 2016, University of Toulon).

6.4.1.3 Comparison of pseudopolarograms (PP)

Different systems (gold wire electrodes, actual reference and auxiliary electrodes, vibrating device) were used for obtaining Figure 6.5/6.6 and Figure 6.7, which prevent any direct comparison of intensities. Nevertheless, the reproducibility on the potential of the Sb(V) reduction wave obtained for different electrodes (as exemplified in Figure 6.3) indicates that the inherent characteristics of the pseudopolarograms can be compared. Figure 6.8 displays a definite order with the valency of the cations being involved: the higher the valency the more positive is the potential at which the reduction of antimonate is being enhanced. The potentials given in Figure 6.8 are the potentials at which the signal is maximal, and they are also given in Table 6.1, along with the potentials at which the Sb(V) reduction is beginning to be observed (last column) when going from positive to negative values. The enhancement effect of the added cation on the reduction of antimonate is observed at potentials that are much more positive than the standard reduction potentials, clearly indicating that the reduction of these cations is not the driving force for antimonate reduction.

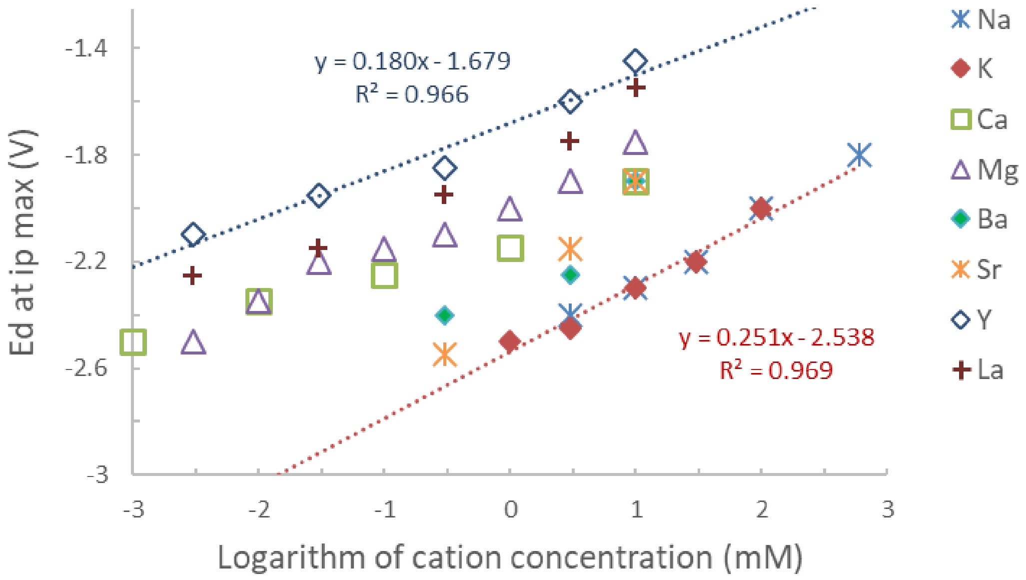


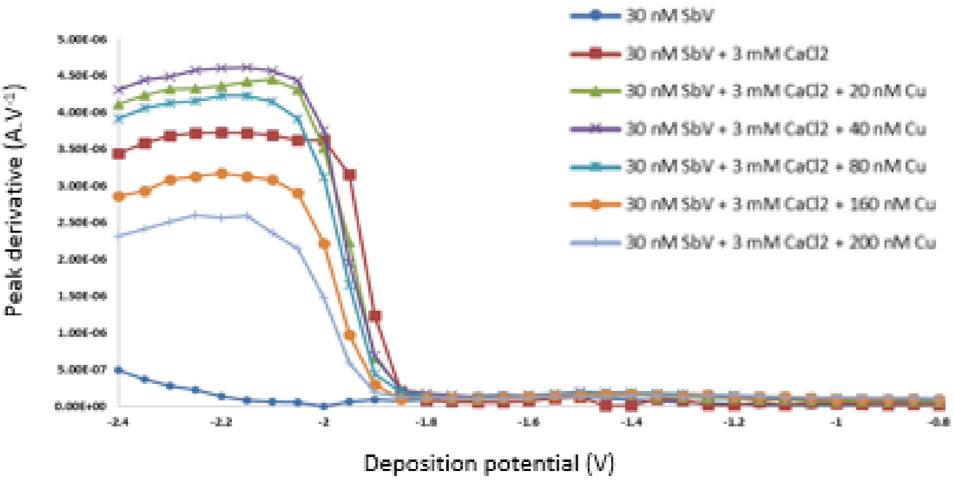
Figure 6. 8. Variation of Edepmax (potential at which peak intensity of 10 nM Sb(V) is maximal) at various concentrations of cations. Background electrolyte: 10 mM HCl. Potential range studied (-0.8 to -3.0 V for Na, K, Ca and Mg; -0.8 to -2.5 V for Ba, Sr, La and Y). Slopes given for yttrium and potassium.

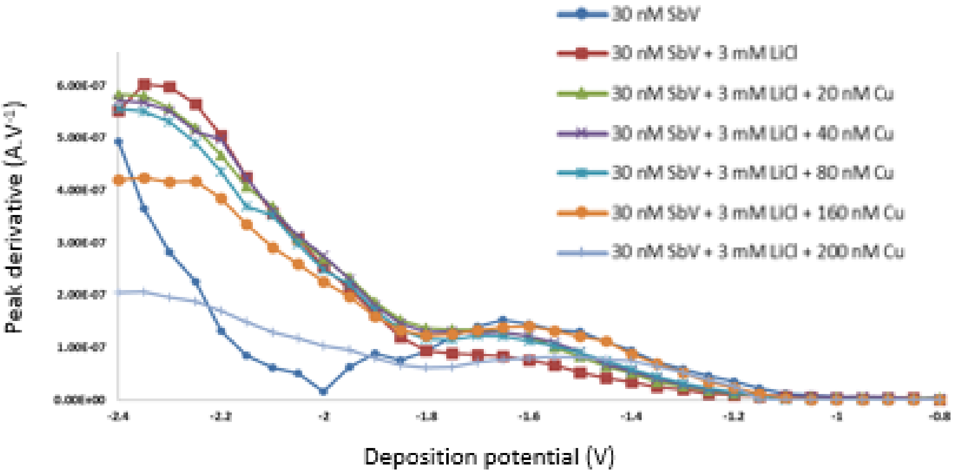
Table 6. 2. Potential and concentration features of DPASV pseudopolarograms of 10 nM Sb(V) in 10 mM HCl

Metal M	Valency	Standard reduction potential (vs Ag/AgCl)	[M] of maximum Sb(V) signal	Edep for maximum Sb(V) signal at 10 mM	Edep for start signal at [M] = 10 mM
Potassium	1	-3.16	30-100 mM	-2.25	-1.85
Sodium	1	-2.95	100 mM	-2.25	-1.85
Calcium	2	-3.0	100 uM	-1.9	-1.25
Strontium	2	-3.13	300 uM	-1.9	-1.4
Magnesium	2	-2.61	30 uM	-1.75	-1.65
Barium	2	-3.14	300 uM	-1.9	-1.2
Yttrium	3	-2.60	30 -300 uM	-1.45	-1.1
Lanthanum	3	-2.61	30uM – 3 mM	-1.5	-1.0

6.4.1.4 Influence of Cu to Sb(V)

The effect of transition trace metals that are present at nM, low uM levels (i.e., much lower concentration than the major elements) was assessed by looking at the effect of Cu on the reduction of antimonate in 10 mM HCl + 3 mM of various cations (Ca, Li and K; Figure 6.9). Upon addition of Cu from 0 up to 200 nM, the Sb(V) reduction wave was found to shift cathodically by c.a. 100 mV for Ca, to shift anodically by c.a. 100 mV for K and to remain almost unchanged for Li. The intensity of the peak was also affected with a lower intensity at higher Cu levels for Ca and Li, while a higher one was observed for K. Nevertheless, the shape of the Sb(V) peak remains sharp although the potential was slightly affected by the presence of copper (Figure 6.10).


30 nM SbV
30 nM SbV + 3 mM CaCl2
30 nM SbV + 3 mM CaCl2 + 20 nM Cu
30 nM SbV + 3 mM CaCl2 + 40 nM Cu
30 nM SbV + 3 mM CaCl2 + 80 nM Cu
30 nM SbV + 3 mM CaCl2 + 160 nM Cu
30 nM SbV + 3 mM CaCl2 + 200 nM Cu
Peak derivative (A.V⁻¹)
5.00E-06
4.50E-06
4.00E-06
3.50E-06
3.00E-06
2.50E-06
2.00E-06
1.50E-06
1.00E-06
5.00E-07
0.00E+00
-2.4
-2.2
-2
-1.8
-1.6
-1.4
-1.2
-1
-0.8
Deposition potential (V)


30 nM SbV
30 nM SbV + 3 mM LiCl
30 nM SbV + 3 mM LiCl + 20 nM Cu
30 nM SbV + 3 mM LiCl + 40 nM Cu
30 nM SbV + 3 mM LiCl + 80 nM Cu
30 nM SbV + 3 mM LiCl + 160 nM Cu
30 nM SbV + 3 mM LiCl + 200 nM Cu
Peak derivative (A.V⁻¹)
6.00E-07
5.00E-07
4.00E-07
3.00E-07
2.00E-07
1.00E-07
0.00E+00
-2.4
-2.2
-2
-1.8
-1.6
-1.4
-1.2
-1
-0.8
Deposition potential (V)

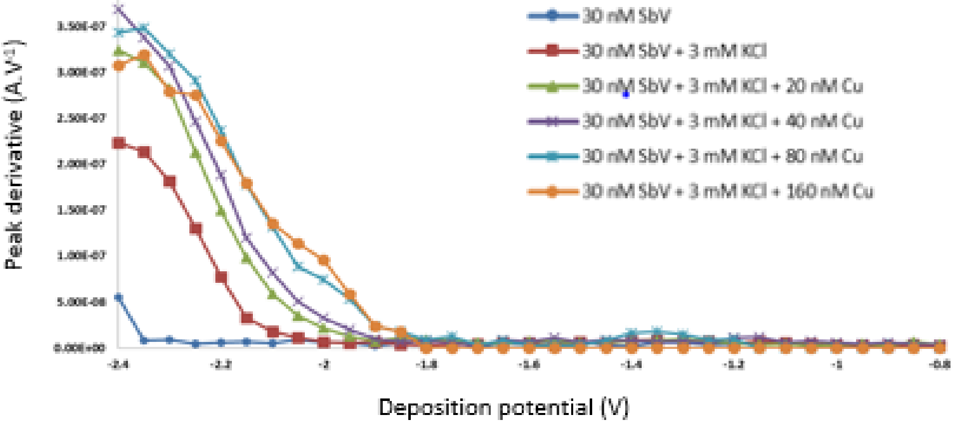

30 nM SbV
30 nM SbV + 3 mM KCl
30 nM SbV + 3 mM KCl + 20 nM Cu
30 nM SbV + 3 mM KCl + 40 nM Cu
30 nM SbV + 3 mM KCl + 80 nM Cu
30 nM SbV + 3 mM KCl + 160 nM Cu
Peak derivative (A.V⁻¹)
3.50E-07
3.00E-07
2.50E-07
2.00E-07
1.50E-07
1.00E-07
5.00E-08
0.00E+00
-2.4
-2.2
-2
-1.8
-1.6
-1.4
-1.2
-1
-0.8
Deposition potential (V)

Figure 6. 9. Effect of Cu on the pseudoplarogram of 30 nM Sb(V). Background electrolye: 10 mM HCl + top: 3 mM $CaCl_2$; middle: 3 mM LiCl and bottom: 3 mM KCl. Electrode diameter: 10 um.

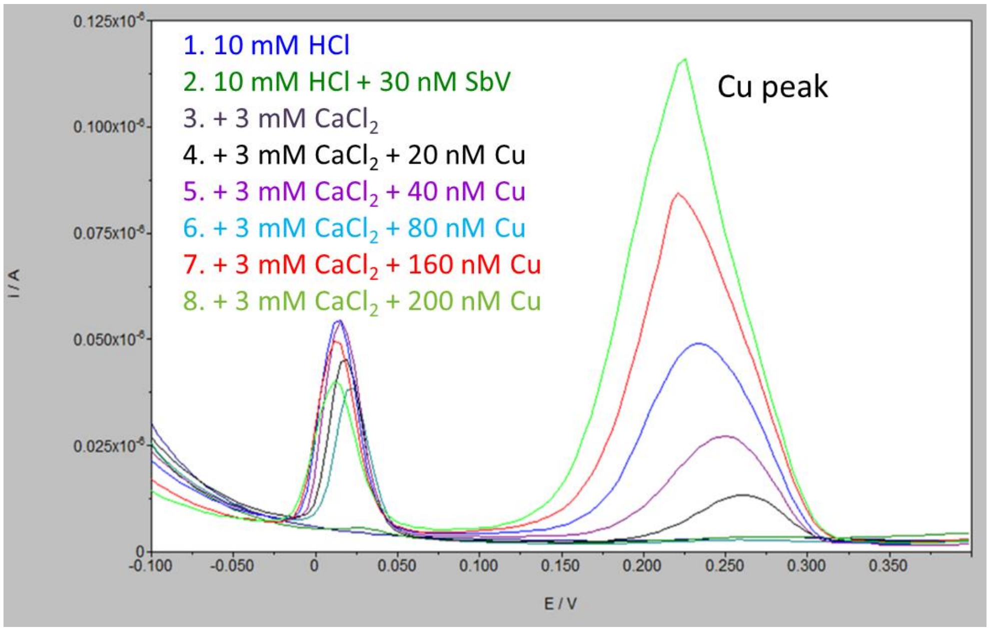


Figure 6.10: Sb(V) peak at various concentrations of Cu. Background electrolyte: 10 mM HCl + 3 mM CaCl2 + 30 nM Sb(V). Electrode diameter: 10 um.

6.4.2 Influence of cations on the reduction of Sb(V) in 100 mM HCl

The effect of cations on the reduction of Sb(V) was also assessed at pH 1. Figure 6.11 shows the influence of Ca, Mg, Li, Na, and K on the Sb(V) peak in 0.1 M HCl. In contrast to pH 2 where a strong enhancement in the Sb(V) peak intensity was observed for any cations, at pH 1, only calcium and magnesium significantly improved the peak intensity while no significant differences were obtained after addition of the monovalent cations (lithium, potassium, and sodium).

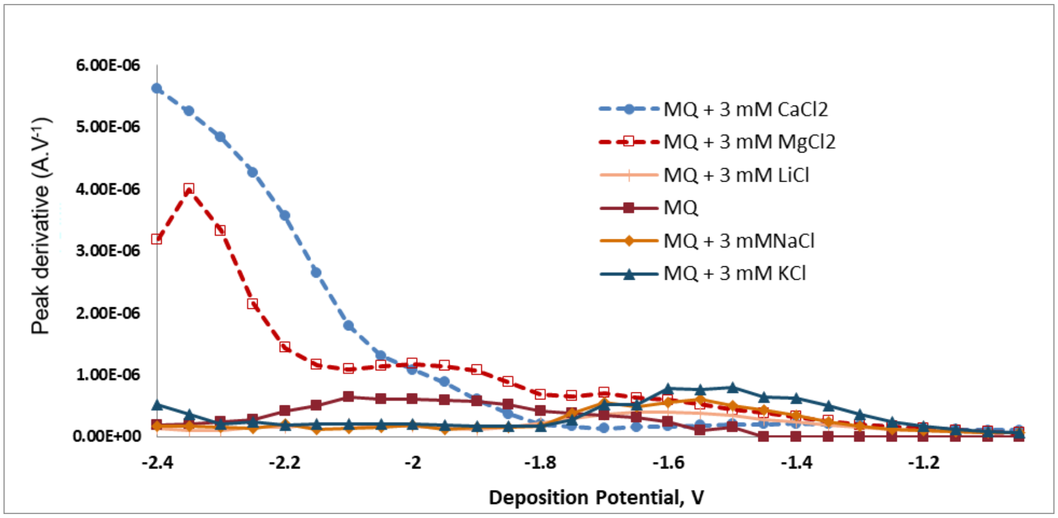


Figure 6.11: Influence of 3 mM NaCl, KCl, LiCl, CaCl2 and MgCl2 on the DPASV peak of 40 nM Sb(V) in 0.1 M HCl.

6.4.3 Influence of cations on the reduction of Sb(V) at neutral and alkaline pH

The same effect of enhancement was observed at pH 4.75 in 10 mM acetate buffer (Figure 6.12). Here, sodium acetate was used, and the background electrolyte already contained 10 mM Na which is the reason why Sb(V) is giving a peak at Edep < -1.5 V. For comparison, at pH 2 and for 10 mM Na^+, a peak was observed for Edep < -1.8 V (Figure 6.6). Interestingly, the wave reaches a stable plateau, at least down to Edep = -2.5 V. This is different than at pH 2 were a bell shape PP was obtained (Figure 6.6). Upon additions of $CaCl_2$, a double wave appears with Sb(V) being detected now from Edep < -1.2 V.

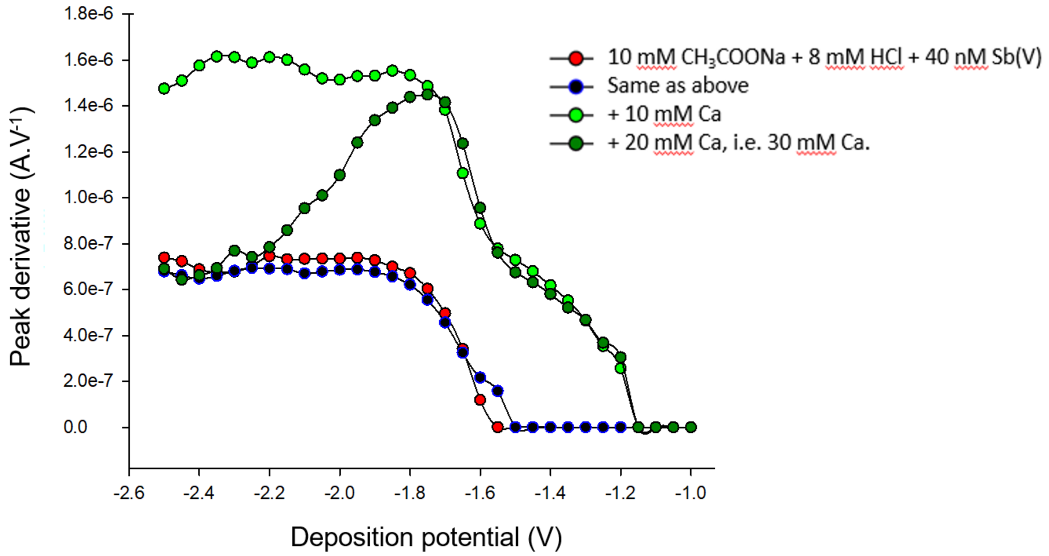


Figure 6.12: Pseudopolarograms of 40 nM Sb(V) in 10 mM acetate buffer (pH 4.75 adjusted with 8 mM HCl) in absence and presence of 10 mM and 30 mM $CaCl_2$.

It was also observed (not shown here) that this cation enhancement of the Sb(V) signal was also observed in a borate buffer at pH 9 in the presence of Na and Ca, suggesting that this cation mediated reduction is a process that occurs at all pH. However, the peaks were sluggish, and the sensitivity relatively low so no further effort was made to optimize the detection at that pH.

6.4.4 Analytical capability of the cation mediated reduction process for determination of Sb(V) in mineral water.

To assess the analytical usefulness of the cation mediated method, determination of Sb(V) in purchased mineral water was attempted. Four different brands of bottled mineral water used in the UK were examined for their Sb(V) analysis. The pH of the bottled water ranged from 6.2 (Tesco®) to 7.41 (Buxton®). There were cations less than

20 ppm for most of the samples. The highest cation comes with the bicarbonates in the Evian sample, followed by Buxton, Volvic, and Tesco has the least bicarbonate content. Determination was attempted at pH 1, pH 2 and pH 5 by the method of standard additions with a minimum of 3 additions and 3 repeats for the blank and for each addition. At pH 1, 0.1 M HCl acid was added to the mineral water and determination was done using a deposition potential of -1.8 V; this Sb determination method was validated by comparison to ICP-MS in a previous study (Salaün et al., 2011) and was used here as the reference method. At pH 2, determination was done after addition 10 mM HCl and 3 mM $CaCl_2$ using a deposition potential of -2.2 V, irrespective of the original Ca content in these waters (Table 6.3). At pH 5, the determination was done after the addition of 10 mM sodium acetate with the pH adjusted at 4.75 with HCl. Each standard addition was repeated 3 times and the average and standard deviations are given in Table 6.4 below. Surprisingly, no reliable results could be obtained at pH 5 with a signal that was unstable and irreproducible, thus making the standard addition procedure unreliable. Although "good" standard addition curves were obtained at pH 1 and 2, significant different concentrations of Sb(V) were calculated, with those at pH 1 being much higher than those obtained at pH 2. It is currently unknown why such differences occur, but they might be related to the presence of other cations in the mineral water. Comparison with an ICP-MS analysis were not done due to technical difficulties during the analysis.

Table 6. 3. Cation contents of different bottled mineral waters (plastic container composition: PET (polyethylene terephthalate). Concentrations are given in mg.L-1 and mM between brackets.

Cations, mg L^{-1}	Bottled mineral water samples			
	Evian	**Buxton**	**Tesco**	**Volvic**
Ca	80 (2)	55 (1.38)	10 (0.25)	12 (0.30)
Mg	26 (0.65)	19 (0.48)	2.5 (0.06)	8 (0.20)
Na	6.5 (0.16)	24 (0.60)	9 (0.23)	12 (0.30)
K	1 (0.03)	1 (0.03)	2 (0.05)	6 (0.15)
Bicarbonates	360 (9)	248 (6.2)	25 (0.63)	74 (1.85)
Sulfates	14 (0.35)	13 (0.33)	10(0.25)	-
Chlorides	10 (0.25)	37 (0.93)	12 (0.30)	15 (0.38)
Nitrates	3.8 (0.10)	<0.1	11 (0.28)	7.3 (0.18)
Dry Residue @ 180 C	345	280	80	130
pH at source	7.2	7.4	6.2	7
Actual pH	7.21	7.41	6.2	7.36

Table 6. 4. Determination of SbV in bottled mineral water samples DPASV method (pH1:-2.2V (, pH2: -2.2V (10s)/-2V (1s), pH5: -2.4V (15s)/-2.4V (1s)).

Water Samples	SbV content (nM)	
	pH1	**pH2**
Evian	3.6 ± 0.106	0.78 ± 0.091
Buxton	3.16 ± 0.031	0.96 ± 0.074
Tesco	3.40 ± 0.372	1.42 ± 0.187
Volvic	3.38 ± 0.435	1.64 ± 0.290

6.5 Discussion and Conclusion

Alkali and alkali-earth metal cations are often used as electrolytes in electrochemical experiments because considered as inactive. However, when using low deposition potentials (ultracathodic deposition), this inactivity does not stand anymore, and this is observed here by looking at the effect of these cations on the anodic stripping signal of antimonate. The process by which cations influence the reduction of anionic species is known as "cationic catalysis" (Katsounaros and Kyriacou, 2007) and it has been studied mostly for nitrate reduction (see below for references) to assess the possibility to remove this pollutant from aqueous media through electrochemical reduction to nitrogen gas. Cationic catalysis has also been studied for the reduction of other anions such as persulfate (Nazmutdinov et al., 2002) but also for the reduction of oxygen on gold-catalysed by the presence of Rb^+ (Kajii et al., 2010). Cationic catalysis is a standard process: it occurs on many different materials and through many different cations. Cationic catalysis of nitrate has been achieved on carbon (Scharifker et al., 2000), gold (Huiliang et al., 1988), palladium (Safonova and Petrii, 1998), bismuth (Dortsiou and Kyriacou, 2009), tin (Katsounaros and Kyriacou, 2007) or silver (Liu and Huang, 2014). Like for other anions, the reduction rate of nitrate was found dependent on the concentration and the nature of the cation. For instance, the reduction rate of nitrate on a tin cathode increases with an increase of the radius of the monovalent cation $Li^+ < Na^+ < K^+ < Cs^+$ and with an increase in valencies of the cation (monovalent < divalent, trivalent) (Katsounaros and Kyriacou, 2007).

The process involved in favoring and increasing the reduction rate is complex and different for various anions, depending on the number of electrons being transferred, on the rate-limiting step, and the requirement of hydrogenation or not. There are several hypotheses to explain the observed rate increase: the presence of the cations may induce a change in the electrical double layer decreasing the potential at the plane where the anion reduction occurs (known as the Frumkin theory (Frumkin et al., 1975)); formation of ion pairs and ion bridges between the adsorbed cation and the anion (Dogonadz.Rr et al., 1972) which decreases the repulsion between the anion and the similarly charged electrode; cation-assisted surface reconstruction of the electrode (Kajii et al. 2010) and formation of adatoms, positively charged (i.e., partially reduced) deposited by underpotential mechanism (UPD) that favour electrostatic attraction of the anion (Ohmori et al., 1999; Çirmi et al., 2015).

The reduction of antimonate is shown here to be enhanced by the presence of monovalent, divalent, and trivalent cations; all cations tested from sub uM levels, were found to have a positive effect on its reduction rate. The valency of the cation plays an important role; for the same concentration (10 mM), trivalent cations are enhancing the Sb(V) signal at the least cathodic potential (i.e., they facilitate the most the reduction), followed by divalent cations and monovalent cations (Table 6.2). This facilitation is consistent with previous findings for nitrate reduction (Katsounaros and Kyriacou, 2007), where a higher reduction rate was obtained with trivalent cations. In our case, the nature of the associate anion (chloride and nitrate) does not play a significant role in the Sb(V) reduction rate (Figure 6.4). This is different from the cationic catalysis of nitrate, where anions of the electrolyte were found to influence the reduction rate, influence attributed to their specific adsorption on the electrode surface(Pletcher and Poorabedi, 1979; Horanyi and Rizmayer, 1982; Katsounaros and Kyriacou, 2007).

Antimonate has an acidity constant of 2.8 and is thus present as the neutral species $Sb(OH)_5^0$ at pH ≤ 1, as the anion $Sb(OH)_6^-$ at pH ≥ 4.5 and as a mix of the two at the intermediate pH of 2 (69% and 31% as $Sb(OH)_5$ and $Sb(OH)_6^-$ respectively). Strong enhancement of the reduction rate was observed at pH 1 in the presence of calcium and magnesium; at this pH, antimonate is present as a neutral species showing for the first time that this cation catalysis process is not specific to anions as previously suggested (Katsounaros and Kyriacou, 2007).

All pseudopolarograms obtained at pH 2 are presenting a bell shape with a loss of the signal at low deposition potentials. When increasing the concentration of the cation, a strong anodic shift of the bell occurs, shift that is dependent on the nature of the cation and linear when plotted against the logarithm of the concentration (see Figure 6.8) with a slope ranging from 180 mV for $La^{(III)}$ to 269 mV for Na^+. Finally, both for $La^{(III)}$ and $Y^{(III)}$, an increase of the concentration from 3 to 10 mM did not result in the appearance of the signal at potentials higher than ~ -1 V. These observations suggest:

- The nature and concentration of the cation appear to be the main reason for the bell shape since similar shapes, albeit with an anodic shift, are obtained when cation concentrations are increased. At such low deposition potentials, hydrogen generation is occurring, but its influence seems to be minimal and/or reproducible and cannot explain the loss of the signal at potentials lower than Edep max. Instead, this loss seems to be related to the surface concentration of the cation at the gold electrode: an optimum coverage seems to exist, sufficient to promote Sb(V) reduction but not too high to prevent blockage of the surface.

- Deposition potentials of less than -1 V are required. Coincidentally, this is the same potential as for the reduction of Sb(V) in acidic conditions, with no other cations than protons (Salaün et al., 2011). This potential corresponds to the formation of nascent hydrogen at the surface of the gold electrode along the so-called Volmer reaction:

  $$Au + H_3O^+ + e^- \rightarrow Au\text{-}H^0 + H_2O \qquad \text{Equation 6.1}$$

  It is thus likely that the presence of nascent hydrogen is still required in this cation catalysis process.

- The linear relation between the logarithm of the cation concentration and the shift in potentials of the bell (as taken from Edepmax, see Figure 6.8) suggests a Nernstian relationship. This behavior is consistent with an underpotential deposition (UPD) mechanism. UPD is a process by which full or partial reduction of up to a monolayer of the metal occurs at a potential that is more anodic than the standard reduction potential (see e.g. (Mayet et al., 2019)). This anodic shift is due to the attraction between the metal and the substrate, here gold, and the added metal on the substrate is called an adatom. For instance, the UPD process of sodium on gold can be represented as:

  $$Au + Na^+ + ze^- --> Au - Na_{upd}^{(1-z)+} \qquad \text{Equation 6.2}$$

  where z is the number of electrons exchanged, Au represents the gold electrode and $Au - Na_{upd}^{(1-z)+}$ represents the underpotentially deposited sodium adatom on the gold surface. If the reduction of Sb(V) is only dependent on the sub-monolayer of UPD cations, we can expect a variation of potentials as a function of the cation concentrations that conforms the Nernst equation:

$$\mathbf{E_{eq} = E^0_{upd} + 2.3\ RT/zF\ log(\{M+\}/\{M\})} \qquad \text{Equation 6. 3.}$$

where E_{eq} is the equilibrium potential (V), E^0_{upd} is the reversible potential of the upd reaction of individual cation on the substrate, R is the universal gas constant, F is the Faraday constant,T is the temperature, {M+} is the activity of the metal in solution and {M} is the activity of the reduced or fully reduced) metal adatom on the substrate.

Assuming that the optimum surface coverage of adatoms is constant at different cation concentrations (i.e. {M} in Equation 6.3 is constant), the variation of E_{depmax} with cation concentrations should follow the following relation:

$$\mathbf{E_{depmax} = A + 2.3\ RT/zF\ log\{M^+\} = K + 0.059.1/z\ log\{M^+\}} \qquad \text{Equation 6.4.}$$

Where A is a constant that includes E^0_{upd} and 2.3 RT/zF log{M}. In that case, the slope of the linear relationships obtained in Figure 6.8 allows us to estimate the number of electrons being transferred and the remaining charge on each adatom. Those are given in Table 6.5.

Table 6. 5. Estimation of the number of electrons exchanged for each upd process and remaining charge on each adatom from the slope of E_{depmax} vs ($\log[M^+]$) in Figure 6.8.

Cation	Slope (mV/decade)	Number of electrons exchanged	Remaining charge on adatom
Sodium	269	0.22	+ 0.78
Potassium	251	0.24	+ 0.76
Magnesium	194	0.30	+ 1.70
Calcium	145	0.41	+ 1.59
Strontium	433	0.14	+ 1.86
Barium	Not linear	-	-
Lanthanum	196	0.30	+ 2.70
Yttrium	180	0.33	+ 2.67

From those values, it is apparent that the remaining charge on adatoms formed from the partial reduction of trivalent ions are significantly higher than those from monovalent ions.

We suggest that the overall process of Sb(V) reduction proceed as follows: during the deposition, cations are partially reduced to positively charged adatoms on the negatively charged gold surface, the surface coverage being dependent both on the cation concentration and the deposition potential. These adatoms become preferential sites of attraction for anions such as $Sb(OH)_6^-$ in a similar process as previously invoked for the electrochemical reduction of nitrate at gold electrodes in the presence of sodium or cesium ions (Ohmori et al., 1999). Concomitantly with adatoms formation, hydrogen reduction occurs at these low cathodic deposition potentials, with adsorption of nascent hydrogen at the gold surface. This hydrogen is a strong reducing agent able to chemically reduce Sb(V) to Sb(III) at the adatom site. Once Sb(III) is formed, it is reduced electrochemically at the gold surface and deposited as Sb^0 before its detection by oxidation during the stripping step.

To the best of our knowledge, this is the first time that cation catalysis is reported to enhance the reduction rate of antimonate. The effect is strong, allowing a reduction in conditions of pH where no reduction would be expected. A similar observation had been made for the reduction of arsenate with manganese (Gibbon-Walsh et al., 2012) or iron (Noskova et al., 2012). Here, antimonate reduction seems to be enhanced with any cations, and positive effects are observed at all pH. Although most of the experiments presented in this chapter have been made at pH 2, preliminary experiments (see Figure 6.12) strongly suggest that the process may also apply at neutral pH, potentially raising the possibility of using this method to gain insights into the biogeochemical cycling of Sb(V) in naturally relevant conditions (e.g., looking at its complexation with humic substances, adsorption onto colloids). Another important aspect of this work is that detection of antimonate might provide a unique route to look at the underpotential deposition of so-called "electroinactive" cations in a region where the hydrogen evolution occurs, which is usually avoided. There are reports in the literature that mention the Under Potential Deposition (UPD) process of metals other than transition metals, and this could possibly open new electrochemical and analytical possibilities. It is not yet understood why the quantification of Sb(V) in mineral waters at pH 1 and pH 2 did not agree but it is likely that the composition of mineral waters, both in major and trace components, might have an influence. For instance, it was shown here that the presence of even trace levels of Cu affects the response. It is evident that cationic catalysis of antimonate is occurring, but the process is highly complex, with many steps involved and more work needs to be done to move from this process study to develop a reliable analytical method.

6.6 References

Abedin, M. J., Feldmann, J. and Meharg, A. A. (2002) ‘Uptake kinetics of arsenic species in rice plants.’ *Plant Physiology*, 128(3) pp. 1120–1128.

Ainsworth, N., Cooke, J. A. and Johnson, M. S. (1990) ‘Distribution of antimony in contaminated grassland: 1- vegetation and soils.’ *Environmental Pollution*. Elsevier, 65(1) pp. 65–77.

Ainsworth, N., Cooke, J.A. and Johnson, M. S. (1990) ‘Distribution of antimony in contaminated grassland: 2— small mammals and invertebrates.’ *Environmental Pollution*. Elsevier, 65(1) pp. 79–87.

Alexou, M. and Peuke, A. D. (2013) *Plant Mineral Nutrients*. Maathuis, F. J. M. (ed.) *Plant Mineral Nutrients*. Totowa, NJ: Humana Press (Methods in Molecular Biology).

Ali, H., Khan, E. and Sajad, M. A. (2013) ‘Phytoremediation of heavy metals—Concepts and applications.’ *Chemosphere*, 91(7) pp. 869–881.

Althobiti, R. A., Sadiq, N. W. and Beauchemin, D. (2018) ‘Realistic risk assessment of arsenic in rice.’ *Food Chemistry*. Elsevier Ltd, 257, August, pp. 230–236.

Álvarez-Fernández, A., Díaz-Benito, P., Abadía, A., And, A.-F. L.-M. and Abadía, J. (2014) ‘Metal species involved in long distance metal transport in plants.’ *Frontiers in Plant Science*, 5(1) p. 105.

Amarasiriwardena, D. and Wu, F. (2011) ‘Antimony: Emerging toxic contaminant in the environment.’ *Microchemical Journal*. Elsevier B.V., 97(1) pp. 1–3.

Ammann, A. A. (2011) ‘Arsenic Speciation Analysis by Ion Chromatography - A Critical Review of Principles and Applications.’ *American Journal of Analytical Chemistry*, 2011(February) pp. 27–45.

Anawar, H. M., Freitas, M. C., Canha, N. and Regina, I. S. (2011) ‘Arsenic, antimony, and other trace element contamination in a mine tailings affected area and uptake by tolerant plant species.’ *Environmental Geochemistry and Health*, 33(4) pp. 353–362.

Aposhian, H. V. and Aposhian, M. M. (2006) ‘Arsenic Toxicology: Five Questions.’ *Chemical Research in Toxicology*, 19(1) pp. 1–15.

Arnold, L. L., Eldan, M., Nyska, A., van Gemert, M. and Cohen, S. M. (2006) ‘Dimethylarsinic acid: Results of chronic toxicity/oncogenicity studies in F344 rats and in B6C3F1 mice.’ *Toxicology*, 223(1–2) pp. 82–100.

Arunakumara, K. K. I. U., Walpola, B. C. and Yoon, M.-H. (2013) ‘Current status of heavy metal contamination in Asia’s rice lands.’ *Reviews in Environmental Science and*

Bio/Technology, 12(4) pp. 355–377.

Ashbrook, P. C. (2014) 'Standard Operating Procedures.' *Journal of Chemical Health and Safety*, 21(5) p. 29.

Ashley, P. M., Graham, B. P., Tighe, M. K. and Wolfenden, B. J. (2007) 'Antimony and arsenic dispersion in the Macleay River catchment, New South Wales: a study of the environmental geochemical consequences.' *Australian Journal of Earth Sciences*, 54(1) pp. 83–103.

ATSDR - Environmental Medicine & Environmental Health Education - CSEM (2013) 'Arsenic Toxicity Case Study: What Are the Standards and Regulation for Arsenic Exposure?' *Encyclopedia of Metalloproteins* pp. 143–143.

Awika, J. M. (2011) 'Major cereal grains production and use around the world.' *In ACS Symposium Series*, pp. 1–13.

Bach, C., Dauchy, X., Chagnon, M. C. and Etienne, S. (2012) 'Chemical compounds and toxicological assessments of drinking water stored in polyethylene terephthalate (PET) bottles: A source of controversy reviewed.' *Water Research*, 46(3) pp. 571–583.

Baker, A. J. M. (1981) 'Accumulators and Excluders - Strategies in the Response of Plants to Heavy Metals.' *Journal of Plant Nutrition*, 3(1–4) pp. 643–654.

Bakhtiari, A. R., Zakaria, M. P., Yaziz, M. I., Lajis, M. N. H. L. and Bi, X. (2014) 'Environment Asia.' *Environment Asia*, 7(1) pp. 104–111.

Basta, N. T. (2006) 'Heavy Metal Contamination of Soil.' *Soil Science Society of America Journal*, 70(5) p. 1819.

Bastías, J. M. and Beldarrain, T. (2016) 'Arsenic translocation in rice cultivation and its implication for human health.' *Chilean Journal of Agricultural Research*. Instituto de Investigaciones Agropecuarias, INIA, 76(1) pp. 114–122.

Bellido-Martín, A., Gómez-Ariza, J. L., Smichowsky, P. and Sánchez-Rodas, D. (2009) 'Speciation of antimony in airborne particulate matter using ultrasound probe fast extraction and analysis by HPLC-HG-AFS.' *Analytica Chimica Acta*, 649(2) pp. 191–195.

Benedict, S. R. (1908) *A Reagent For the Detection of Reducing Sugars*. *J. Biol. Chem*.

Bennett, J. O. and Sicher, R. C. (2011) 'Protein and metabolite composition of xylem sap from field-grown soybeans (Glycine max)' pp. 921–931.

Bhattacharya, P., Samal, a C., Majumdar, J. and Santra, S. C. (2009) 'Transfer of Arsenic from Groundwater and Paddy Soil to Rice Plant (Oryza sativa L.): A Micro-Level Study in West Bengal , India.' *World Journal of Agricultural Sciences*, 5(4) pp. 425–431.

Bi, Z. (2012) *Speciation analysis of trace metals in natural waters using vibrating electrodes*. *Environmental Sciences*. University of Liverpool.

Bielen, A., Remans, T., Vangronsveld, J. and Cuypers, A. (2013) 'The influence of metal stress on the availability and redox state of ascorbate, and possible interference with its cellular functions.' *International Journal of Molecular Sciences* pp. 6382–6413.

Biles, C. L. and Abeles, F. B. (1991) 'Xylem sap proteins.' *Plant Physiology*, 96(July 1991) pp. 597–601.

Billon, G. and Van Den Berg, C. M. G. (2004) 'Gold and silver micro-wire electrodes for trace analysis of metals.' *Electroanalysis*, 16(19) pp. 1583–1591.

Borovička, J., Řanda, Z. and Jelínek, E. (2006) 'Antimony content of macrofungi from clean and polluted areas.' *Chemosphere*, 64(11) pp. 1837–1844.

Bouman, B. A. . and Tuong, T. . (2001) 'Field water management to save water and increase its productivity in irrigated lowland rice.' *Agricultural Water Management*, 49(1) pp. 11–30.

Bowen, H. J. M. (Humphry J. M. (1979) *Environmental chemistry of the elements*. London, New York: Academic Press.

Brackin, R., Näsholm, T., Robinson, N., Guillou, S., Vinall, K., Buckley, S., Lakshmanan, P., Schmidt, S. and Inselsbacher, E. (2016) 'Microdialysis-a new technology for investigating soil nitrogen fluxes in the rhizosphere.' *In Proceedings of the International Nitrogen Initiative 2016 Conference*, pp. 4–8.

Brammer, H. and Ravenscroft, P. (2009) 'Arsenic in groundwater: A threat to sustainable agriculture in South and South-east Asia.' *Environment International*. Elsevier Ltd pp. 647–654.

Brihaye, C. and Duyckaerts, G. (1982) 'Determination of traces of metals by anodic stripping voltammetry at a rotating glassy carbon ring—disc electrode.' *Analytica Chimica Acta*, 143 pp. 111–120.

Broadley, M., Brown, P., Cakmak, I., Rengel, Z. and Zhao, F. (2011) 'Function of Nutrients: Micronutrients.' *In Marschner's Mineral Nutrition of Higher Plants: Third Edition*. Elsevier Inc., pp. 191–248.

Brochu, C., Wang, J., Roy, G., Messier, N., Wang, X.-Y., Saravia, N. G. and Ouellette, M. (2003) 'Antimony Uptake Systems in the Protozoan Parasite Leishmania and Accumulation Differences in Antimony-Resistant Parasites.' *Antimicrobial Agents and Chemotherapy*. American Society for Microbiology (ASM), 47(10) pp. 3073–3079.

Brown, S. D. and Kowalski, B. R. (1979) 'Pseudopolarographic Determination of Metal Complex Stability Constants in Dilute Solution by Rapid Scan Anodic Stripping

Voltammetry.’ *Analytical Chemistry*, 51(13) pp. 2133–2139.

Buckley, S., Brackin, Richard, A. and Schmidt, S. (2016) ‘Microdialysis-a sensitive method for estimating plant-available N released during litter decomposition.’ *Proceedings of the International Nitrogen Initiative Conference 2016*, (December).

Buckley, S., Brackin, R., Jämtgård, S., Näsholm, T. and Schmidt, S. (2020) ‘Microdialysis in soil environments: Current practice and future perspectives.’ *Soil Biology and Biochemistry*, 143, April, p. 107743.

Buckley, S., Brackin, R., Näsholm, T., Schmidt, S. and Jämtgård, S. (2017) ‘Improving in situ recovery of soil nitrogen using the microdialysis technique.’ *Soil Biology and Biochemistry*, 114, November, pp. 93–103.

Buckley, S., Brackin, R. and Schmidt, S. (2015) *Microdialysis: an alternative approach to identifying plant-available nitrogen in soils*.

Burló, F., Guijarro, I., Carbonell-Barrachina, A. A., Valero, D. and Martínez-Sánchez, F. (1999) ‘Arsenic Species: Effects on and Accumulation by Tomato Plants.’ *Journal of Agricultural and Food Chemistry*, 47(3) pp. 1247–1253.

Cabalda, M. V, Banaag, M. A. and Garces, R. B. (2002) *Sustainable Development in The Philippine Minerals Industry: A Baseline Study*. M.V. Cabalda P.N.T. Tidalgo & R.B. Garces, M. A. B. (ed.) *Mining, Minerals and Sustainable Development Project (MMSD)*. England: International Institute for the Environment and Development (IIED).

Cai, Y., Su, J. and Ma, L. Q. (2004) ‘Low molecular weight thiols in arsenic hyperaccumulator Pteris Vittata upon exposure to arsenic and other trace elements.’ *Environmental Pollution*, 129(1) pp. 69–78.

Cal-Prieto, M. J., Carlosena, A., Andrade, J. M., Martínez, M. L., Muniategui, S., López-Mahía, P. and Prada, D. (2001) ‘Antimony as a tracer of the anthropogenic influence on soils and estuarine sediments.’ *Water, Air, and Soil Pollution*. Springer, 129(1–4) pp. 333–348.

Canadian Council of Ministers of the Environment (2007) *Canadian soil quality guidelines for the protection of environmental and human health*. Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment. Winnipeg. [Online] http://goo.gl/AePSg4.

Canepari, S., Marconi, E., Astolfi, M. L. and Perrino, C. (2010) ‘Relevance of Sb(III), Sb(V), and Sb-containing nano-particles in urban atmospheric particulate matter.’ *Analytical and Bioanalytical Chemistry*, 397(6) pp. 2533–2542.

Carey, A.-M., Lombi, E., Donner, E., de Jonge, M. D., Punshon, T., Jackson, B. P., Guerinot, M. Lou, Price, A. H. and Meharg, A. A. (2012) ‘A review of recent developments in the speciation and location of arsenic and selenium in rice grain.’ *Analytical and Bioanalytical*

Chemistry, 402(10) pp. 3275–3286.

Carneado, S., Hernández-Nataren, E., López-Sánchez, J. F. F. and Sahuquillo, A. (2015) 'Migration of antimony from polyethylene terephthalate used in mineral water bottles.' *Food Chemistry*. Elsevier Ltd, 166, January, pp. 544–550.

Carolyn, P., Aqilah, F. A. T., Payus, C., Farhana, A., Talip, A., Carolyn, P., Aqilah, F. A. T., Payus, C., Farhana, A. and Talip, A. (2014) 'Assessment of heavy metals accumulation in paddy rice (Oryza sativa).' *African Journal of Agricultural Research*. Academic Journals, 9(41) pp. 3082–3090.

Casiot, C., Ujevic, M., Munoz, M., Seidel, J. L. and Elbaz-Poulichet, F. (2007) 'Antimony and arsenic mobility in a creek draining an antimony mine abandoned 85 years ago (upper Orb basin, France).' *Applied Geochemistry*, 22(4) pp. 788–798.

Cavicchioli, A., La-Scalea, M. A., Gutz, G. R., Gutz, I. G. R. and Gutz, G. R. (2004) 'Analysis and Speciation of Traces of Arsenic in Environmental , Food and Industrial Samples by Voltammetry : a Review.' *Electroanalysis*, 16(9) pp. 697–711.

Chakraborti, D., Rahman, M. M., Das, B., Nayak, B., Pal, A., Sengupta, M. K., Hossain, M. A., Ahamed, S., Sahu, M., Saha, K. C., Mukherjee, S. C., Pati, S., Dutta, R. N. and Quamruzzaman, Q. (2013) 'Groundwater arsenic contamination in Ganga–Meghna–Brahmaputra plain, its health effects and an approach for mitigation.' *Environmental Earth Sciences*, 70(5) pp. 1993–2008.

Chang, C.-Y., Wang, C.-F., Mui, D. T. and Chiang, H.-L. (2009) 'Application of methods (sequential extraction procedures and high-pressure digestion method) to fly ash particles to determine the element constituents: A case study for BCR 176.' *Journal of Hazardous Materials*, 163(2–3) pp. 578–587.

Chapman, C. S. and Van Den Berg, C. M. G. G. (2007) 'Anodic stripping voltammetry using a vibrating electrode.' *Electroanalysis*, 19(13) pp. 1347–1355.

Chaurasia, C. S., Müller, M., Bashaw, E. D., Benfeldt, E., Bolinder, J., Bullock, R., Bungay, P. M., DeLange, E. C. M., Derendorf, H., Elmquist, W. F., Hammarlund-Udenaes, M., Joukhadar, C., Kellogg, D. L., Lunte, C. E., Nordstrom, C. H., Rollema, H., Sawchuk, R. J., Cheung, B. W. Y., Shah, V. P., Stahle, L., Ungerstedt, U., Welty, D. F. and Yeo, H. (2007) 'AAPS-FDA workshop white paper: Microdialysis principles, application and regulatory perspectives.' *In Pharmaceutical Research*, pp. 1014–1025.

Chen, Z. L., Farzana Akter, K., Rahman Mahmudur, M. and Naidu, R. (2006) 'Speciation of arsenic by ion chromatography inductively coupled plasma mass spectrometry using ammonium eluents.' *Journal of Separation Science*, 29(17) pp. 2671–2676.

Cheng, T. and Sun, H. (2014) 'CHAPTER 25. Antimony and Bismuth.' *In* Maret, W. and Wedd, A. (eds) *Binding, Transport and Storage of Metal Ions in Biological Cells*. London, UK: The Royal Society of Chemistry, pp. 768–799.

Chepkemoi, J. (2017) *What Is The Environmental Impact Of The Mining Industry?* First Break. [Online] worldatlas.com/articles/what-is-the-environmental-impact-of-the-mining-industry.html.

Cheraghi, M., Mosaed, H. P., Lorestani, B. and Yousefi, N. (2012) ‘Heavy metal contamination in some rice samples.’ *Electronic Journal of Environmental, Agricultural and Food Chemistry*, 11(5) pp. 424–432.

Choudhury, B. U., Malang, A., Webster, R., Mohapatra, K. P., Verma, B. C., Kumar, M., Das, A., Islam, M. and Hazarika, S. (2017) ‘Acid drainage from coal mining: Effect on paddy soil and productivity of rice.’ *Science of the Total Environment*. Elsevier B.V., 583(August 2018) pp. 344–351.

Ciminelli, V. S. T., Gasparon, M., Ng, J. C., Silva, G. C. and Caldeira, C. L. (2017) ‘Dietary arsenic exposure in Brazil: The contribution of rice and beans.’ *Chemosphere*. Elsevier Ltd, 168, February, pp. 996–1003.

Çirmi, D., Aydin, R. and Köleli, F. (2015) ‘The electrochemical reduction of nitrate ion on polypyrrole coated copper electrode.’ *Journal of Electroanalytical Chemistry*, 736 pp. 101–106.

Clark, R. B., Tiffin, L. O. and Brown, J. C. (1973) ‘Organic Acids and Iron Translocation in Maize Genotypes.’ *Plant Physiology*, 52(2) pp. 147–150.

Clarkson, D. T. (1996) ‘Marschner H. 1995. Mineral nutrition of higher plants. second edition. 889pp. London: Academic Press.’ *Annals of Botany*, 78(4) pp. 527–528.

Clemens, S. and Ma, J. F. (2016) ‘Toxic Heavy Metal and Metalloid Accumulation in Crop Plants and Foods.’ *Annual Review of Plant Biology*, 67(1) pp. 489–512.

Correia, M. M., Alves, S., Simões Gonçalves, M. D. L. and Nabais, C. (2006) ‘Dynamic modelling of nickel complexation in xylem sap of Quercus ilex: A voltammetric study.’ *Electroanalysis*, 18(8) pp. 814–822.

Cullen, W. R. and Reimer, K. J. (2016a) ‘CHAPTER 2. Arsenic Is Everywhere.’ *In Arsenic is Everywhere: Cause for Concern?*, pp. 8–48.

Cullen, W. R. and Reimer, K. J. (2016b) ‘CHAPTER 8. Arsenic and the Evening Meal.’ *In Arsenic is Everywhere: Cause for Concern?*, pp. 221–265.

Daniels, R., Rush, C. C. and Bauer, L. (1960) ‘The Fehling and Benedict tests.’ *Journal of Chemical Education*, 37(4) p. 205.

Daus, B. and Hansen, H. R. (2016) ‘Analysis of antimony species – lessons learnt from more than two decades of environmental research.’ *Environmental Chemistry*, 13(6) p. 913.

Dawe, B. D., Organisation, A. and Nations, U. (2015) ‘Rice in Asia: Paddy-whacked.’ *Economist (United Kingdom)*, 411(8960).

Dobermann, A., Dawe, D., Roetter, R. P. and Cassman, K. G. (2000) ‘Reversal of rice yield decline in a long-term continuous cropping experiment.’ *Agronomy Journal*, 92(4) pp. 633–643.

Domingo, L. E. and Kyuma, K. (1983) ‘Trace elements in tropical asian paddy soils: I. total trace element status.’ *Soil Science and Plant Nutrition*, 29(4) pp. 439–452.

Dortsiou, M. and Kyriacou, G. (2009) ‘Electrochemical reduction of nitrate on bismuth cathodes.’ *Journal of Electroanalytical Chemistry*, 630(1–2) pp. 69–74.

Duester, L., Diaz-Bone, R. A., Kösters, J. and Hirner, A. V. (2005) ‘Methylated arsenic, antimony and tin species in soils.’ *In Journal of Environmental Monitoring*, pp. 1186–1193.

Dushenkov, S. (2003) ‘Trends in phytoremediation of radionuclides.’ *In Plant and Soil*, pp. 167–175.

Elmquist, W. F. and Sawchuk, R. J. (1997) ‘Application of microdialysis in pharmacokinetic studies.’ *Pharmaceutical Research* pp. 267–288.

Emamverdian, A. and Ding, Y. (2017) ‘Effects of heavy metals’ toxicity on plants and enhancement of plant defense mechanisms of Si-mediation “ Review.”’ *International Journal of Environmental & Agriculture Research*, (4) pp. 41–51.

Emamverdian, A., Ding, Y., Mokhberdoran, F. and Xie, Y. (2015) ‘Heavy Metal Stress and Some Mechanisms of Plant Defense Response.’ *The Scientific World Journal*. Hindawi Publishing Corporation, 2015 pp. 1–18.

EPA (2004) ‘EPA Method 6020A: ICP-MS. Official Name: EPA Method 6020A, Inductively Coupled Plasma-Mass Spectrometry.’ *EPA methods*, 6.

Epstein, E. and and Bloom, A. J. (1972) *Mineral Nutrition of Plants: Principles and Perspectives*. 2nd ed., Sunderland, Massachusetts: Sinauer Associates, Inc.

Fan, Y., Zhu, T., Li, M., He, J., Huang, R. and and Ruixue Huang, T. Z. Y. F. M. L. J. H. (2017) ‘Heavy Metal Contamination in Soil and Brown Rice and Human Health Risk Assessment near Three Mining Areas in Central China.’ *Journal of Healthcare Engineering*. Hindawi, 2017 p. 9.

FAO (2016) *GIEWS - Crop Prospects and Food Situation, No.1,March 2016*.

FAO and WHO (2019) *Report of the 11th session of the codex committee on contaminnants in foods. A joint FAO/WHO food standards programme codex alimentarius commission 40th Session. Codex*. Geneva, Switzerland.

Farid, M., Shakoor, M., Ehsan, S., Ali, S., Zubair, M. and Hanif, M. (2013) ‘Morphological, physiological and biochemical responses of different plant species to Cd stress.’ *Int J Chem Biochem Sci*, 3(March) pp. 53–60.

Farnese, F. S., Oliveira, J. A., Farnese, M. S., Gusman, G. S., Silveira, N. M. and Siman, L. I. (2014) ‘Uptake arsenic by plants: Effects on mineral nutrition, growth and antioxidant capacity.’ *Idesia (Arica)*, 32(1) pp. 99–106.

Fashola, M., Ngole-Jeme, V. and Babalola, O. (2016) ‘Heavy Metal Pollution from Gold Mines: Environmental Effects and Bacterial Strategies for Resistance.’ *International Journal of Environmental Research and Public Health*. MDPI AG, 13(11) p. 1047.

Feldmann, J., Salaün, P. and Lombi, E. (2009) ‘Critical review perspective: elemental speciation analysis methods in environmental chemistry - moving towards methodological integration.’ *Environmental Chemistry*. CSIRO, 6(4) p. 275.

Feng, R., Wei, C., Tu, S., Ding, Y., Wang, R. and Guo, J. (2013) ‘The uptake and detoxification of antimony by plants: A review.’ *Environmental and Experimental Botany*. Elsevier B.V., 96, December, pp. 28–34.

Festin, E. S., Tigabu, M., Chileshe, M. N., Syampungani, S. and Odén, P. C. (2019) ‘Progresses in restoration of post-mining landscape in Africa.’ *Journal of Forestry Research*, 30(2) pp. 381–396.

Filella and May (2003) ‘Computer simulation of the low-molecular-weight inorganic species distribution of antimony (III) and antimony (V) in natural waters.’ *Geochimica et Cosmochimica Acta,* 67(21) pp. 4013–4031.

Filella, M. (2013) ‘Food for thought: A critical overview of current practical and conceptual challenges in trace element analysis in natural waters.’ *Water (Switzerland)*. MDPI AG pp. 1152–1171.

Filella, M., Belzile, N. and Chen, Y.-W. W. (2002) ‘Antimony in the environment: a review focused on natural waters.’ *Earth-Science Reviews*, 57(1–2) pp. 125–176.

Filella, M., Belzile, N. and Lett, M.-C. C. (2007) ‘Antimony in the environment: A review focused on natural waters. III. Microbiota relevant interactions.’ *Earth-Science Reviews*, 80(3–4) pp. 195–217.

Filella, M. and May, P. M. (2005a) ‘Critical appraisal of available thermodynamic data for the complexation of antimony(iii) and antimony(v) by low molecular mass organic ligands.’ *Journal of Environmental Monitoring*, 7(12) p. 1226.

Filella, M. and May, P. M. (2005b) ‘Reflections on the calculation and publication of potentiometrically- determined formation constants.’ *Talanta*, 65(5) pp. 1221–1225.

Filella, M. and Williams, P. A. (2012) ‘Antimony interactions with heterogeneous

complexants in waters, sediments and soils: A review of binding data for homologous compounds.' *Chemie der Erde*. Elsevier GmbH., 72(SUPPL.4) pp. 49–65.

Filella, M., Williams, P. A. and Belzile, N. (2009) 'Antimony in the environment: Knowns and unknowns.' *Environmental Chemistry*, 6(2) pp. 95–105.

Forsberg, G., O'Laughlin, J. W., Megargle, R. G. and Koirtyohann, S. R. (1975) 'Determination of Arsenic by Anodic Stripping Voltammetry and Differential Pulse Anodic Stripping Voltammetry.' *Analytical Chemistry*, 47(9) pp. 1586–1592.

Francesconi, K. A. and Kuehnelt, D. (2004) 'Determination of arsenic species: A critical review of methods and applications, 2000–2003.' *The Analyst*, 129(5) pp. 373–395.

Frantz, J. M. and Epstein, E. (2005) *Nutritional deficiencies: What they look like*. [Online] [Accessed on 16th December 2019] http://www.ces.ncsu.edu/depts/hort/floriculture/def/forfloriculturecropshttp://extension.agron.iastate.edu/soilfertility/nutrienttopics/deficiencies.htmlcornhttp://muextension.missouri.edu/explore/agguides/hort/index.htm.

FSA (2012) *Arsenic speciation in fruit and vegetables grown in the UK.* Aberdeen: University of Aberdeen.

Fu, Z., Wu, F., Mo, C., Deng, Q., Meng, W. and Giesy, J. P. (2016) 'Comparison of arsenic and antimony biogeochemical behavior in water, soil and tailings from Xikuangshan, China.' *Science of the Total Environment*, 539 pp. 97–104.

Garg, N. and Singla, P. (2011) 'Arsenic toxicity in crop plants: physiological effects and tolerance mechanisms.' *Environmental Chemistry Letters*. Springer, 9(3) pp. 303–321.

Garg, N., Singla, P. and Bhandari, P. (2015) 'Metal uptake, oxidative metabolism, and mycorrhization in pigeonpeaand pea under arsenic and cadmium stress.' *Turkish Journal of Agriculture and Forestry*, 39(2) pp. 234–250.

Gebel, T. (1997) 'Arsenic and antimony: comparative approach on mechanistic toxicology.' *Chemico-Biological Interactions*. Elsevier Ireland Ltd, 107(3) pp. 131–144.

Gebel, T. W. (2001) 'Unanswered Questions in Arsenic Toxicology.' *Journal of Environmental Pathology, Toxicology and Oncology*, 20(4) p. 11.

Gemici, Ü. and Tarcan, G. (2007) 'Assessment of the pollutants in farming soils and waters around untreated abandoned Türkönü mercury mine (Turkey).' *Bulletin of Environmental Contamination and Toxicology*, 79(1) pp. 20–24.

Geng, A., Wang, X., Wu, L., Wang, F., Chen, Y., Yang, H., Zhang, Z. and Zhao, X. (2017) 'Arsenic accumulation and speciation in rice grown in arsanilic acid-elevated paddy soil.' *Ecotoxicology and Environmental Safety*, 137 pp. 172–178.

Geng, C. N., Zhu, Y. G., Tong, Y. P., Smith, S. E. and Smith, F. A. (2006) 'Arsenate (As) uptake by and distribution in two cultivars of winter wheat (Triticum aestivum L.).' *Chemosphere*, 62(4) pp. 608–615.

Gerényi, A., Czech, V., Fodor, F., Vincze, L. and Szalóki, I. (2017) 'In vivo XANES measuring technique for studying the arsenic uptake in cucumber plants.' *X-Ray Spectrometry*, 46(3) pp. 143–150.

German Federal Soil Protection Act (1998) *Federal Law Gazette I p. 502*.

Ghori, N.-H., Ghori, T., Hayat, M. Q., Imadi, S. R., Gul, A., Altay, V. and Ozturk, M. (2019) 'Heavy metal stress and responses in plants.' *International Journal of Environmental Science and Technology*. Center for Environmental and Energy Research and Studies, 16(3) pp. 1807–1828.

Gibbon-Walsh, K., Salaün, P. and van den Berg, C. M. G. (2012a) 'Determination of arsenate in natural pH seawater using a manganese-coated gold microwire electrode.' *Analytica Chimica Acta*. Elsevier B.V., 710, January, pp. 50–57.

Gibbon-Walsh, K., Salaün, P. and van den Berg, C. M. G. (2012b) 'Pseudopolarography of Copper Complexes in Seawater Using a Vibrating Gold Microwire Electrode.' *The Journal of Physical Chemistry A*, 116(25) pp. 6609–6620.

Gibbon-Walsh, K., Salaün, P., Uroic, M. K., Feldmann, J., McArthur, J. M. and Van Den Berg, C. M. G. (2011) 'Voltammetric determination of arsenic in high iron and manganese groundwaters.' *Talanta*, 85(3) pp. 1404–1411.

Gidlow, D. A. (2004) 'Lead toxicity.' *Occupational Medicine*, 54(2) pp. 76–81.

Goldberg, S. (2011) 'Chemical Equilibrium and Reaction Modeling of Arsenic and Selenium in Soils.' *Dynamics and Bioavailability of Heavy Metals in the Rootzone* pp. 65–92.

Grob, M., Wilcke, W. and Mestrot, A. (2018) 'Release and Biomethylation of Antimony in Shooting Range Soils upon Flooding.' *Soil Systems*, 2(2) p. 34.

Guerriero, Gea, Deshmukh, R. and Durgesh K., T. (2020) *Metalloids in Plants Advances and Future Prospects*. Deshmukh, R., Tripathi, D. K., and Guerriero, Gia (eds) *Wiley*. John Wiley & Sons Ltd.

Gupta, D. K., Srivastava, S., Huang, H. G., Romero-Puertas, M. C. and Sandalio, L. M. (2011) 'Arsenic Tolerance and Detoxification Mechanisms in Plants.' *In*, pp. 169–179.

Ha, N. T. H., Ha, N. T., Nga, T. T. H., Minh, N. N., Anh, B. T. K., Hang, N. T. A., Duc, N. A., Nhuan, M. T. and Kim, K.-W. (2019) 'Uptake of arsenic and heavy metals by native plants growing near Nui Phao multi-metal mine, northern Vietnam.' *Applied Geochemistry*. Elsevier Ltd, 108, September, p. 104368.

Hakeem, K. R. (2015) ‘Crop production and global environmental issues.’ *Crop Production and Global Environmental Issues*, (December) pp. 1–598.

Hall, J. L. L. (2002) ‘Cellular mechanisms for heavy metal detoxification and tolerance.’ *Journal of experimental botany*, 53(366) pp. 1–11.

Hammel, W., Debus, R. and Steubing, L. (2000) ‘Mobility of antimony in soil and its availability to plants.’ *Chemosphere*, 41(11) pp. 1791–1798.

Hansen, C. (2011) *Antimony speciation analysis HPLC methods with ICP-MS and ES-MS detection for complex biological matrices*. University of Coppenhagen.

Hansen, H. R. and Pergantis, S. A. (2008) ‘Analytical techniques and methods used for antimony speciation analysis in biological matrices.’ *Journal of Analytical Atomic Spectrometry*, 23(10) p. 1328.

Hasanuzzaman, M., Nahar, K. and Fujita, M. (2018) *Mechanisms of Arsenic Toxicity and Tolerance in Plants*. Hasanuzzaman, M., Nahar, K., and Fujita, M. (eds) *Mechanisms of Arsenic Toxicity and Tolerance in Plants*. Singapore: Springer Singapore.

Hasanuzzaman, M., Nahar, K., Hakeem, K. R., Öztürk, M. and Fujita, M. (2015) ‘Arsenic Toxicity in Plants and Possible Remediation.’ *In Soil Remediation and Plants: Prospects and Challenges*. Elsevier Inc., pp. 433–501.

Hawkesford, M. J., Parmar, S. and Buchner, P. (2013) ‘Mineral Composition Analysis: Measuring Anion Uptake and Anion Concentrations in Plant Tissues.’ *In Plant Mineral Nutrients*. Totowa, NJ: Humana Press, pp. 109–119.

Hazama, K., Nagata, S., Fujimori, T., Yanagisawa, S. and Yoneyama, T. (2015) ‘Concentrations of metals and potential metal-binding compounds and speciation of Cd, Zn and Cu in phloem and xylem saps from castor bean plants (Ricinus communis) treated with four levels of cadmium.’ *Physiologia Plantarum*, 154(2) pp. 243–255.

He, M., Wang, N., Long, X., Zhang, C., Ma, C., Zhong, Q., Wang, A., Wang, Y., Pervaiz, A. and Shan, J. (2019) ‘Antimony speciation in the environment: Recent advances in understanding the biogeochemical processes and ecological effects.’ *Journal of Environmental Sciences*. Elsevier B.V., 75, January, pp. 14–39.

Hettick, B. E., Cañas-Carrell, J. E., French, A. D. and Klein, D. M. (2015) ‘Arsenic: A Review of the Element’s Toxicity, Plant Interactions, and Potential Methods of Remediation.’ *Journal of Agricultural and Food Chemistry*, 63(32) pp. 7097–7107.

Hijaz, F. and Killiny, N. (2014) ‘Collection and chemical composition of phloem sap from Citrus sinensis L. Osbeck (sweet orange).’ *PLoS ONE*. Public Library of Science, 9(7).

Hirner, A. V., Grüter, U. M. and Kresimon, J. (2000) ‘Metal(loid)organic compounds in contaminated soil.’ *Fresenius’ Journal of Analytical Chemistry*. Springer, 368(2–3) pp.

263–267.

Hoagland and Arnon, D., D. (1950) *The water-culture method of growing plants without soil.* Berkeley, Calif. : University of California, College of Agriculture, Agricultural Experiment Station.

Hossain, M. A., Piyatida, P., da Silva, J. A. T. and Fujita, M. (2012) 'Molecular Mechanism of Heavy Metal Toxicity and Tolerance in Plants: Central Role of Glutathione in Detoxification of Reactive Oxygen Species and Methylglyoxal and in Heavy Metal Chelation.' *Journal of Botany*. Hindawi Limited, 2012(Cd) pp. 1–37.

Hozhina, E. ., Khramov, A. ., Gerasimov, P. . and Kumarkov, A. . (2001) 'Uptake of heavy metals, arsenic, and antimony by aquatic plants in the vicinity of ore mining and processing industries.' *Journal of Geochemical Exploration*, 74(1–3) pp. 153–162.

Hrytsak, L. R., Herts, A. I., Nuzhyna, N. V., Cryk, M. M., Shevchenko, V. V. and Drobyk, N. M. (2018) 'The influence of light regime on the growth data and pigment composition of the plant Gentiana lutea cultured in vitro.' *Regulatory Mechanisms in Biosystems*, 9(2) pp. 258–266.

Hu, L., Zhang, B., Wu, D., Fan, H., Tu, J., Liu, W., Huang, R. and Huang, X. (2019) 'Estimation of arsenic bioaccessibility in raw and cooked radish using simulated in vitro digestion.' *Food & Function*. Royal Society of Chemistry, 10(3) pp. 1426–1432.

Hu, Y., Cheng, H. and Tao, S. (2016) 'The Challenges and Solutions for Cadmium-contaminated Rice in China: A Critical Review.' *Environment International*. Elsevier Ltd pp. 515–532.

Hua, C.-Y., Chen, J.-X., Cao, Y., Li, H.-B., Chen, Y. and Ma, L. Q. (2020) 'Pteris vittata coupled with phosphate rock effectively reduced As and Cd uptake by water spinach from contaminated soil.' *Chemosphere*. Elsevier Ltd, 247, May, p. 125916.

Huang, R.-Q., Gao, S.-F., Wang, W.-L., Staunton, S. and Wang, G. (2006) 'Soil arsenic availability and the transfer of soil arsenic to crops in suburban areas in Fujian Province, southeast China.' *Science of The Total Environment*, 368(2–3) pp. 531–541.

Huang, Y., Chen, Q., Deng, M., Japenga, J., Li, T., Yang, X. and He, Z. (2018) 'Heavy metal pollution and health risk assessment of agricultural soils in a typical peri-urban area in southeast China.' *Journal of Environmental Management*. Academic Press, 207, February, pp. 159–168.

Huang, Z., Pan, X.-D. D., Wu, P.-G. G., Han, J.-L. L. and Chen, Q. (2013) 'Health Risk Assessment of Heavy Metals in Rice to the Population in Zhejiang, China.' Scarfi, M. R. (ed.) *PLoS ONE*, 8(9) pp. 1–6.

Huiliang, H., Jagner, D. and Renman, L. (1988) 'Flow potentiometric and constant-current stripping analysis for arsenic(V) without prior chemical reduction to arsenic(III).'

Analytica Chimica Acta, 207 pp. 37–46.

Humphrey, O. S., Young, S. D., Bailey, E. H., Crout, N. M. J., Ander, E. L., Hamilton, E. M. and Watts, M. J. (2019) 'Investigating the use of microdialysis and SEC-UV-ICP-MS to assess iodine interactions in soil solution.' *Chemosphere*. Elsevier Ltd, 229, August, pp. 41–50.

Hunt, R., Causton, D. R., Shipley, B. and Askew, A. P. (2002) 'A modern tool for classical plant growth analysis.' *Annals of Botany*, 90(4) pp. 485–488.

Inselsbacher, E. (2014) 'Recovery of individual soil nitrogen forms after sieving and extraction.' *Soil Biology and Biochemistry*, 71, April, pp. 76–86.

Inselsbacher, E., Öhlund, J., Jämtgård, S., Huss-Danell, Kerstin, A. and Näsholm, T. (2011) 'The potential of microdialysis to monitor organic and inorganic nitrogen compounds in soil.' *Soil Biology and Biochemistry*, 43(6) pp. 1321–1332.

International Programme on Chemical Safety (2004) 'International programme on chemical safety (IPCS),' (June) pp. 1–34.

IPNI (2002) 'Nutrient Deficiency Symptoms in Rice.' *Better Crops International*, 16(May) pp. 23–25.

IRRI and DFID (2009) 'Scuba rice : breeding flood-tolerance into Asia ' s local mega rice varieties.' *South Asia* pp. 1–6.

Ismail, B., Yap, D., Adezrian, J., Khairiah, J. and Ahmad-Mahir, R. (2009) 'The Uptake of Heavy Metals by Paddy Plants (Oryza sativa) in Kota Marudu, Sabah, Malaysia.' *& Environ. Sci*, 6(1) pp. 16–19.

Jamila Alfaraas, A. M., Khairiah, J., Ismail, B. S. and Noraini, T. (2016) 'Effects of heavy metal exposure on the morphological and microscopical characteristics of the paddy plant.' *Journal of Environmental Biology*, 37(5) pp. 955–963.

Järup, L. (2003) 'Hazards of heavy metal contamination.' *British Medical Bulletin*, 68 pp. 167–182.

JECFA (2016) 'Joint FAO / WHO Expert Committee on Food Additives (JECFA) Call for Experts on Food Additives , Contaminants and toxins ; and Residues of Veterinary Drugs,' (October).

Jentschke, G. and Godbold, D. L. (2000) 'Metal toxicity and ectomycorrhizas.' *Physiologia Plantarum*, 109(2) pp. 107–116.

Ji, Y., Sarret, G., Schulin, R. and Tandy, S. (2017) 'Fate and chemical speciation of antimony (Sb) during uptake, translocation and storage by rye grass using XANES spectroscopy.' *Environmental Pollution*. Elsevier Ltd, 231, December, pp. 1322–1329.

Johnson, C. A., Moench, H., Wersin, P., Kugler, P. and Wenger, C. (2005) 'Solubility of Antimony and Other Elements in Samples Taken from Shooting Ranges.' *Journal of Environmental Quality*. Wiley, 34(1) pp. 248–254.

Johnson, C. D. (2014) 'Phytoremediation of Arsenic Contamination on Vashon-Maury Island METHODS Salix Screening for Arsenic Tolerance.'

Johnston, A. E. and Poulton, P. R. (2018) 'The importance of long-term experiments in agriculture: their management to ensure continued crop production and soil fertility; the Rothamsted experience.' *European Journal of Soil Science*, 69(1) pp. 113–125.

Kabata-Pendias, A. (2010) *Trace Elements in Soils and Plants*. 4th ed., CRC Press.

Kalaji, H. M., Jajoo, A., Oukarroum, A., Brestic, M., Zivcak, M., Samborska, I. A., Cetner, M. D., Łukasik, I., Goltsev, V. and Ladle, R. J. (2016) 'Chlorophyll a fluorescence as a tool to monitor physiological status of plants under abiotic stress conditions.' *Acta Physiologiae Plantarum*. Polish Academy of Sciences.

Kapaj, S., Peterson, H., Liber, K. and Bhattacharya, P. (2006) 'Human Health Effects From Chronic Arsenic Poisoning–A Review.' *Journal of Environmental Science and Health, Part A*. The Safe Drinking Water Foundation, Saskatoon, Saskatchewan, Canada., 41(10) pp. 2399–2428.

Katsounaros, I. and Kyriacou, G. (2007) 'Influence of the concentration and the nature of the supporting electrolyte on the electrochemical reduction of nitrate on tin cathode.' *Electrochimica Acta*, 52(23) pp. 6412–6420.

Kehr, J. and Rep, M. (2007) 'Protein extraction from xylem and phloem sap.' *Methods in molecular biology (Clifton, N.J.)*, 355 pp. 27–35.

Killiny, N. and Hijaz, F. (1998) 'Chemical composition of xylem sap of Citrus sinensis L. Osbeck (sweet orange).' *Trends in Plant Science*, 3(5) pp. 188–195.

Kisan, M., Sangathan, S., Nehru, J. and Pitroda, S. G. (2012) 'Laboratory Glassware-Volumetric Instruments-Methods for Testing of Capacity and for Use.' ISO (ed.) *4787*. Geneva: IS pp. 1–29.

Kitagishi, K. (1981) 'Heavy Metal Pollution in Soils of Japan.' *Japan Scientific Societies Press, Tokyo, Japan*, 52(4) p. 302.

Koester, R. P., Skoneczka, J. A., Cary, T. R., Diers, B. W. and Ainsworth, E. A. (2014) 'Historical gains in soybean (Glycine max Merr.) seed yield are driven by linear increases in light interception, energy conversion, and partitioning efficiencies.' *Journal of Experimental Botany*, 65(12) pp. 3311–3321.

Kolbe, F., Mattusch, J., Wennrich, R., Weiss, H., Sorkau, E., Lorenz, W. and Daus, B. (2012) 'Analytical investigations of antimony-edta complexes and their use in speciation

analysis.' *Fresenius Environmental Bulletin*, 21(11 C) pp. 3453–3456.

Kowalska, J., Stryjewska, E., Szymański, P. and Golimowski, J. (1999) 'Voltammetric determination of arsenic in plant material.' *Electroanalysis*, 11(17) pp. 1301–1304.

Krachler, M. and Emons, H. (2001) 'Speciation analysis of antimony by high-performance liquid chromatography inductively coupled plasma mass spectrometry using ultrasonic nebulization.' *Analytica Chimica Acta*, 429(1) pp. 125–133.

Kroukamp, E. M., Wondimu, T. and Forbes, P. B. C. (2016) 'Metal and metalloid speciation in plants: Overview, instrumentation, approaches and commonly assessed elements.' *TrAC - Trends in Analytical Chemistry*. Elsevier B.V., 77 pp. 87–99.

Krupka, K. M. and Serne, R. J. (2002) *Geochemical Factors Affecting the Behavior of Antimony, Cobalt, Europium, Technetium, and Uranium in Vadose Zone Sediments*. *Pnnl-14126*. Richland, WA (United States).

Kumar, R., Mishra, R. K., Mishra, V., Qidwai, A., Pandey, A., Shukla, S. K., Pandey, M., Pathak, A. and Dikshit, A. (2015) 'Detoxification and Tolerance of Heavy Metals in Plants.' *In Plant Metal Interaction: Emerging Remediation Techniques*. Elsevier Inc., pp. 335–359.

Kumarathilaka, P., Seneweera, S., Meharg, A. and Bundschuh, J. (2018) 'Arsenic speciation dynamics in paddy rice soil-water environment: sources, physico-chemical, and biological factors - A review.' *Water Research*. Elsevier Ltd pp. 403–414.

Küpper, H. and Andresen, E. (2016) 'Mechanisms of metal toxicity in plants.' *Metallomics*, 8(3) pp. 269–285.

Lansdown, A. B. G. (2013) 'CHAPTER 1. Introduction.' *In The Carcinogenicity of Metals: Human Risk Through Occupational and Environmental Exposure*, pp. 1–18.

Larsen, E. H. and Stürup, S. (1994) 'Carbon-enhanced inductively coupled plasma mass spectrometric detection of arsenic and selenium and its application to arsenic speciation.' *Journal of Analytical Atomic Spectrometry*, 9(10) pp. 1099–1105.

van Leeuwen, H. P., Town, R. M., Buffle, J., Cleven, R. F. M. J., Davison, W., Puy, J., van Riemsdijk, W. H. and Sigg, L. (2005) 'Dynamic Speciation Analysis and Bioavailability of Metals in Aquatic Systems.' *Environmental Science & Technology*, 39(22) pp. 8545–8556.

van Leeuwen, L. C. and Aldenberg, T. (2012) *RIVM Letter Report 601357001/2012: Environmental risk limits for antimony*.

Li, Z. and Cui, Z. (2008) 'Application of microdialysis in tissue engineering monitoring.' *Progress in Natural Science*. Science Press, 18(5) pp. 503–511.

Liang, G., Gong, W., Li, B., Zuo, J., Pan, L. and Liu, X. (2019) 'Analysis of Heavy Metals in Foodstuffs and an Assessment of the Health Risks to the General Public via Consumption

in Beijing, China.’ *International Journal of Environmental Research and Public Health*. MDPI AG, 16(6) p. 909.

Lichtfouse, E., Schwarzbauer, J. and Robert, D. (2012) *Environmental chemistry for a sustainable world*. *Environmental Chemistry for a Sustainable World*. Springer Netherlands.

Lintschinger, J., Koch, I., Serves, S., Feldmann, J. and Cullen, W. R. (1997) ‘Determination of antimony species with High-Performance Liquid Chromatography using element specific detection.’ *Fresenius’ Journal of Analytical Chemistry*, 359(6) pp. 484–491.

Liu, Z. G. and Huang, X. J. (2014) ‘Voltammetric determination of inorganic arsenic.’ *TrAC - Trends in Analytical Chemistry*, 60 pp. 25–35.

Lombi, E. and Holm, P. E. (2010) ‘Metalloids, soil chemistry and the environment.’ *In Advances in Experimental Medicine and Biology*. Australia: Landes Bioscience and Springer Science+Business Media., pp. 33–44.

Louis, Y., Cmuk, P., Nicolau, R., Omanovi, D., Lenoble, V., Pižeta, I., Mounier, S., and Garde, L. and Garde, L. (2007) ‘Pseudopolarography As a Tool for Complexation Studies of Trace Metals With Dissolved Natural Organic Matter,’ (January) p. 2007.

Louis, Y., Cmuk, P., Omanović, D., Garnier, C., Lenoble, V., Mounier, S. and Pižeta, I. (2008) ‘Speciation of trace metals in natural waters: The influence of an adsorbed layer of natural organic matter (NOM) on voltammetric behaviour of copper.’ *Analytica Chimica Acta*. Elsevier Masson, 606(1) pp. 37–44.

Louis, Y., Garnier, C., Lenoble, V., Omanovi, D., Mounier, S., Pižeta, I., Protee, L., Toulon, S., Bp, V., Garde, L., Physico, G. De, Chimie, T., Moléculaires, S. and I, U. B. (2008) ‘Electrochemical Study of Major and Trace Metal Interactions With Concentrated Marine Dissolved Organic Matter,’ (098) p. 1214910.

Lu, M. and Compton, R. G. (2013) ‘Voltammetric Determination of Iron(III) in Water.’ *Electroanalysis*, 25(5) pp. 1123–1129.

Lubin, J. H., Moore, L. E., Fraumeni, J. F. and Cantor, K. P. (2008) ‘Respiratory Cancer and Inhaled Inorganic Arsenic in Copper Smelters Workers: A Linear Relationship with Cumulative Exposure that Increases with Concentration.’ *Environmental Health Perspectives*, 116(12) pp. 1661–1665.

Luo, J. and Shu, W. (2015) ‘Arsenic-Induced Developmental Neurotoxicity.’ *In* Flora, S. J. S. B. T.-H. of A. T. (ed.) *Handbook of Arsenic Toxicology*. Oxford: Elsevier, pp. 363–386.

Lydic, R., Baghdoyan, H. A. and May, A. L. (2018) ‘Chapter Fourteen - Neurochemistry of Anesthetic States.’ *In* Eckenhoff, R. G. and Dmochowski, I. J. B. T.-M. in E. (eds) *Chemical and Biochemical Approaches for the Study of Anesthetic Function Part B*. 1st ed., Academic Press, pp. 237–255.

Madejón, P., Marañón, T. and Murillo, J. M. (2006) 'Biomonitoring of trace elements in the leaves and fruits of wild olive and holm oak trees.' *Science of the Total Environment*, 355(1–3) pp. 187–203.

Magahud, J. C., Badayos, R. B., Sanchez, P. B. and Sta. Cruz, P. C. (2015) *Levels and Potential Sources of Heavy Metals in Major Irrigated Rice Areas of the Philippines*. *IAMURE International Journal of Ecology and Conservation*.

Mandal, B. K. and Suzuki, K. T. (2002) 'Arsenic round the world: A review.' *Talanta*. Elsevier, 58(1) pp. 201–235.

Mareček, V., Jänchenová, H., Samec, Z. and Březina, M. (1986) 'Voltammetric determination of nitrate, perchlorate and iodide at a hanging electrolyte drop electrode.' *Analytica Chimica Acta*, 185(C) pp. 359–362.

Marschner, H. (1995) *Mineral Nutrition of High Plants*. Academic Press.

Martin, M., Ferdousi, R., Hossain, K. M. J. and Barberis, E. (2010) 'Arsenic from groundwater to paddy fields in Bangladesh: Solid-liquid partition, sorption and mobility.' *Water, Air, and Soil Pollution*, 212(1–4) pp. 27–36.

Martinez, R. E., Marquez, J. E., Hòa, H. T. B. and Gieré, R. (2013) 'Open-pit coal-mining effects on rice paddy soil composition and metal bioavailability to Oryza sativa L. plants in Cam Pha, northeastern Vietnam.' *Environmental Science and Pollution Research*, 20(11) pp. 7686–7698.

Massoura, S. T., Echevarria, G., Leclerc-Cessac, E. and Morel, J. L. (2004) 'Response of excluder, indicator, and hyperaccumulator plants to nickel availability in soils.' *Australian Journal of Soil Research*, 42(8) pp. 933–938.

Materials, B. (1989) *Analytical Methods*. *WHO*.

Matschullat, J. J. (2000) 'Arsenic in the geosphere - A review.' *The Science of the Total Environment*, 249(1–3) pp. 297–312.

Mawia, A. M., Hui, S., Zhou, L., Li, H., Tabassum, J., Lai, C., Wang, J., Shao, G., Wei, X., Tang, S., Luo, J., Hu, S. and Hu, P. (2021) 'Inorganic arsenic toxicity and alleviation strategies in rice.' *Journal of Hazardous Materials*. Elsevier B.V. p. 124751.

Mayet, N., Servat, K., Kokoh, K. B. and Napporn, T. W. (2019) 'Probing the Surface of Noble Metals Electrochemically by Underpotential Deposition of Transition Metals.' *Surfaces*, 2(2) pp. 257–276.

McLaughlin, M. ., Parker, D. . and Clarke, J. . (1999) 'Metals and micronutrients – food safety issues.' *Field Crops Research*, 60(1–2) pp. 143–163.

Mead, M. N. (2005) 'Arsenic: In search of an antidote to a global poison.' *Environmental*

Health Perspectives. Public Health Services, US Dept of Health and Human Services, 113(6).

Meadows, R. (2014) 'How Plants Control Arsenic Accumulation.' *PLoS Biology*, 12(12) pp. 1002008–1002009.

Meharg, A. A. (2004) 'Arsenic in rice - Understanding a new disaster for South-East Asia.' *Trends in Plant Science* pp. 415–417.

Meharg, A. A. and Zhao, F.-J. (2012) *Arsenic & Rice*. *Springer*. Dordrecht: Springer Netherlands.

Mendoza, T. (2012) 'Estimates of Rice Per Capita Consumption: Its Implications to the Rice Self-Sufficiency Program of the Philippines*.' *Policy Options*, 4, January.

Mestrot, A., Ji, Y., Tandy, S. and Wilcke, W. (2016) 'A novel method to determine trimethylantimony concentrations in plant tissue.' *Environmental Chemistry*, 13(6) pp. 919–926.

Michalski, R., Szopa, S., Jabłońska, M. and Łyko, A. (2012) 'Application of hyphenated techniques in speciation analysis of arsenic, antimony, and thallium.' *The Scientific World Journal*. Institute of Environmental Engineering, the Polish Academy of Sciences, 34 Sklodowskiej-Curie Street, 41 819 Zabrze, Poland. michalski@ipis.zabrze.pl, 2012(January 2017) p. 902464.

Miekeley, N., Mortari, S. R. and Schubach, A. O. (2002) 'Monitoring of total antimony and its species by ICP-MS and on-line ion chromatography in biological samples from patients treated for leishmaniasis.' *Fresenius' Journal of Analytical Chemistry*, 372(3) pp. 495–502.

Mihucz, V. G., Tatár, E. E. E., Virág, I., Cseh, E., Fodor, F., Záray, G., Tat??r, E., Vir??g, I., Cseh, E., Fodor, F. and Gyula, Z. (2005) 'Arsenic speciation in xylem sap of cucumber (Cucumis sativus L.).' *Analytical and Bioanalytical Chemistry*. Joint Research Group of Environmental Chemistry of the Hungarian Academy of Sciences and L. Eotvos University, PO Box 32, 1518 Budapest, Hungary., 383(3) pp. 461–466.

Mihucz, V. G., Varga, A. and Za, G. (1998) 'Determination of Organic Acids in Xylem Sap of Cucumber : Effect of Lead Contamination,' 314(58) pp. 306–314.

Ministerie Van Volkshuisvesting; Ruimtelijke Ordening En Milieu (2000) 'Dutch Target and Intervention Values; 2000 (the New Dutch List).' *Netherlands Government Gazette*, 2000 pp. 1–12.

Miró, M., Fitz, W. J., Swoboda, S. and Wenzel, W. W. (2010) 'In-situ sampling of soil pore water: Evaluation of linear-type microdialysis probes and suction cups at varied moisture contents.' *Environmental Chemistry*, 7(1) pp. 123–131.

Mishra, S., Srivastava, S., Dwivedi, S. and Tripathi, R. D. (2013) 'Investigation of biochemical responses of Bacopa monnieri L. upon exposure to arsenate.’ *Environmental Toxicology*, 28(8) pp. 419–430.

Mohan, D. and Pittman, C. U. (2007) ‘Arsenic removal from water/wastewater using adsorbents-A critical review.’ *Journal of Hazardous Materials* pp. 1–53.

Moles, A. T., Warton, D. I., Warman, L., Swenson, N. G., Laffan, S. W., Zanne, A. E., Pitman, A., Hemmings, F. A. and Leishman, M. R. (2009) ‘Global patterns in plant height.’ *Journal of Ecology*, 97(5) pp. 923–932.

Moreno-Jiménez, E., Esteban, E. and Peñalosa, J. M. (2012) ‘The fate of arsenic in soil-plant systems.’ *Reviews of Environmental Contamination and Toxicology*, 215 pp. 1–37.

Morua, M. (2015) ‘Investigating various xylem sap extraction techniques from drought-stressed Geijera parviflora trees’ pp. 1–26.

Mosetlha, K., Torto, N. and Wibetoe, G. (2007) ‘Determination of Cu and Ni in plants by microdialysis sampling: Comparison of dialyzable metal fractions with total metal content.’ *Talanta*. Elsevier, 71(2) pp. 766–770.

Nagajyoti, P. C., Lee, K. D. and Sreekanth, T. V. M. (2010) ‘Heavy metals, occurrence and toxicity for plants: A review.’ *Environmental Chemistry Letters* pp. 199–216.

Nash, M. J., Maskall, J. E. and Hill, S. J. (2000) ‘Methodologies for determination of antimony in terrestrial environmental samples.’ *Journal of Environmental Monitoring*, 2(2) pp. 97–109.

Natasha, Shahid, M., Khalid, S., Dumat, C., Pierart, A. and Niazi, N. K. (2019) ‘Biogeochemistry of antimony in soil-plant system: Ecotoxicology and human health.’ *Applied Geochemistry*. Elsevier, 106(April) pp. 45–59.

Netting, A. G., Theobald, J. C. and Dodd, I. C. (2012) ‘Xylem sap collection and extraction methodologies to determine in vivo concentrations of ABA and its bound forms by gas chromatography-mass spectrometry (GC-MS).’ *Plant Methods*, 8(1) pp. 1–14.

Nicolau, R., Louis, Y., Omanović, D., Garnier, C., Mounier, S. and and, Pižeta, I. (2008) ‘Study of interactions of concentrated marine dissolved organic matter with copper and zinc by pseudopolarography.’ *Analytica Chimica Acta*, 618(1) pp. 35–42.

Niedzielski, P. and Siepak, M. (2003) ‘Analytical methods for determining arsenic, antimony and selenium in environmental samples.’ *Polish Journal of Environmental Studies*, 12(6) pp. 653–667.

Niedzielski, P., Siepak, M., Siepak, J. and Przybyłek, J. (2002) ‘Determination of Different Forms of Arsenic, Antimony and Selenium in Water Samples Using Hydride Generation.’ *Polish Journal of Environmental Studies*, 11(3) pp. 219–224.

Nimick, D. A. (1998) 'Arsenic hydrogeochemistry in an irrigated river valley-A reevaluation.' *Journal of groundwater*. Ground Water Publ Co, 36(5) pp. 743–753.

O'Day, P. A. (2006) 'Chemistry and mineralogy of arsenic.' *Elements*, 2(2) pp. 77–83.

Obiora, S. C., Chukwu, A. and Davies, T. C. (2016) 'Heavy metals and health risk assessment of arable soils and food crops around Pb-Zn mining localities in Enyigba, southeastern Nigeria.' *Journal of African Earth Sciences*. Elsevier Ltd, 116, April, pp. 182–189.

Oda, A., Shimizu, M., Kuroha, T. and Satoh, S. (2005) 'Induction of xylem sap methylglycine by a drought and rewatering treatment and its inhibitory effects on the growth and development of plant organs.' *Physiologia Plantarum*, 124(4) pp. 515–523.

Ogawa, K. and Iwabuchi, M. (2001) 'A mechanism for promoting the germination of Zinnia elegans seeds by hydrogen peroxide.' *Plant and Cell Physiology*, 42(3) pp. 286–291.

Ohmori, T., El-Deab, M. S. and Osawa, M. (1999) 'Electroreduction of nitrate ion to nitrite and ammonia on a gold electrode in acidic and basic sodium and cesium nitrate solutions.' *Journal of Electroanalytical Chemistry*, 470(1) pp. 46–52.

Olsen, S.R., C.V. Cole, F.S. Watanabe, and L. A. D. (1954) *Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circ.No. 939.* U.S. Gov. Print. Office, Washington DC.

Omanović, D. (2006) 'Pseudopolarography of trace metals. Part III. Determination of stability constants of labile metal complexes.' *Croatica Chemica Acta*, 79(1) p. 67.

Omanović, D. and Branica, M. (2003) 'Pseudopolarography of trace metals: Part I. The automatic ASV measurements of reversible electrode reactions.' *Journal of Electroanalytical Chemistry*, 543(1) pp. 83–92.

Omanović, D. and Branica, M. (2004) 'Pseudopolarography of trace metals. Part II. The comparison of the reversible, quasireversible and irreversible electrode reactions.' *Journal of Electroanalytical Chemistry*, 565(1) pp. 37–48.

Onofri, A., Seddaiu, G. and Piepho, H. P. (2016) 'Long-Term Experiments with cropping systems: Case studies on data analysis.' *European Journal of Agronomy*, 77, July, pp. 223–235.

Organization, world health (1996) 'guidelines for drinking water quality - second edition.' *international programme on chemical safety*.

Özer, U. Y. and Bogucki, R. F. (1971) 'Equilibrium studies of antimony(III) chelates in aqueous solution.' *Journal of Inorganic and Nuclear Chemistry*, 33(12) pp. 4143–4153.

Palma-Lara, I., Martínez-Castillo, M., Quintana-Pérez, J. C., Arellano-Mendoza, M. G., Tamay-Cach, F., Valenzuela-Limón, O. L., García-Montalvo, E. A. and Hernández-Zavala, A. (2019) 'Arsenic exposure: A public health problem leading to several cancers.' *Regulatory toxicology and pharmacology : RTP* p. 104539.

Pampolino, M. F., Laureles, E. V., Gines, H. C. and Buresh, R. J. (2008) 'Soil carbon and nitrogen changes in long-term continuous lowland rice cropping.' *Soil Science Society of America Journal*, 72(3) pp. 798–807.

Panda, S. K., Upadhyay, R. K. and Nath, S. (2010) 'Arsenic Stress in Plants.' *Journal of Agronomy and Crop Science*, 196(3) pp. 161–174.

Pandey, P. and Tripathi, A. K. (2014) 'Impact Of Heavy Metals On Morphological And Biochemical Parameters Of Shorea Robusta Plant.' *Ekologia*, 33(2) pp. 116–126.

Passioura, J. B. (1980) 'The transport of water from soil to shoot in wheat seedlings.' *Journal of Experimental Botany*, 31(1) pp. 333–345.

Pedron, T., Segura, F. R., Paniz, F. P., de Moura Souza, F., dos Santos, M. C., de Magalhães Júnior, A. M. and Batista, B. L. (2019) 'Mitigation of arsenic in rice grains by polishing and washing: Evidencing the benefit and the cost.' *Journal of Cereal Science*. Academic Press, 87, May, pp. 52–58.

Penezić, A., Tercier-Waeber, M. Lou, Abdou, M., Bossy, C., Dutruch, L., Bakker, E. and Schäfer, J. (2020) 'Spatial variability of arsenic speciation in the Gironde Estuary: Emphasis on dynamic (potentially bioavailable) inorganic arsenite and arsenate fractions.' *Marine Chemistry*. Elsevier, 223(December 2019) p. 103804.

Pepponi, G., Meirer, F., Streli, C., Wobrauschek, P., Mihucz, V. G., G. Zaray, V. C., Broekaert, J., Fittschen, U. and Falkenberg, G. (2005) 'Arsenic speciation in Cucumber Cucumis Sativus L.) xylem sap by K-edge TXRF-XANES.' *Anal. Bioanal. Chem.*, 383 pp. 461–466.

Peralta-Videa, J. R., Lopez, M. L., Narayan, M., Saupe, G. and Gardea-Torresdey, J. (2009) 'The biochemistry of environmental heavy metal uptake by plants: Implications for the food chain.' *International Journal of Biochemistry and Cell Biology*, 41(8–9) pp. 1665–1677.

Perrino, C., Marconi, E., Canepari, S., Luisa Astolfi, M. and Perrino, C. (2011) 'Determination of Sb(III), Sb(V) and identification of Sb-containing nanoparticles in airborne particulate matter.' *Procedia Environmental Sciences*, 4 pp. 209–217.

Pettine, M., Casentini, B., Mastroianni, D. and Capri, S. (2007) 'Dissolved inorganic carbon effect in the determination of arsenic and chromium in mineral waters by inductively coupled plasma-mass spectrometry.' *Analytica Chimica Acta*. Elsevier, 599(2) pp. 191–198.

Pickering, I. J., Prince, R. C., George, M. J., Smith, R. D., George, G. N. and Salt, D. E. (2000) ‘Reduction and coordination of arsenic in Indian mustard.’ *Plant Physiology*, 122(4) pp. 1171–1177.

Pierart, A., Shahid, M., Séjalon-Delmas, N. and Dumat, C. (2015) ‘Antimony bioavailability: Knowledge and research perspectives for sustainable agricultures.’ *Journal of Hazardous Materials*. Elsevier, 289(February) pp. 219–234.

Pla-Vilanova, P., Galceran, J., Puy, J., Companys, E. and Filella, M. (2019) ‘Antimony speciation in aqueous solution followed with AGNES.’ *Journal of Electroanalytical Chemistry*. Elsevier B.V., 849 p. 113334.

Pohl, P., Lesniewicz, A. and Zyrnicki, W. (2003) ‘Determination of As, Bi, Sb and Sn in conifer needles from various locations in Poland and Norway by hydride generation inductively coupled plasma atomic emission spectrometry.’ *International Journal of Environmental Analytical Chemistry*. Taylor & Francis Group, 83(11) pp. 963–970.

Polunina, O. V., Maiboroda, V. P. and Seleznov, A. Y. (2018) ‘Evaluation methods of estimation of young apple trees leaf area.’ *Bulletin of Uman National University of Horticulture*, (2) pp. 80–82.

Pommerrenig, B., Diehn, T. A. and Bienert, G. P. (2015) ‘Metalloido-porins: Essentiality of Nodulin 26-like intrinsic proteins in metalloid transport.’ *Plant Science*. Elsevier Ireland Ltd, 238 pp. 212–227.

Porra, R. J. (2005) ‘Clorofila Porras 2005’ pp. 633–640.

Postupolski, A. and Golimowski, J. (1991) ‘Trace determination of antimony and bismuth in snow and water samples by stripping voltammetry.’ *Electroanalysis*. Warsaw, Poland, 3(8) pp. 793–797.

Pretti, L., Bazzu, G., Serra, P. A. and Nieddu, G. (2014) ‘A novel method for the determination of ascorbic acid and antioxidant capacity in Opuntia ficus indica using in vivo microdialysis.’ *Food Chemistry*, 147 pp. 131–137.

Punrat, E., Chuanuwatanakul, S., Kaneta, T., Motomizu, S., Chailapakul, O., Zaib, M., Makshoof, M., Saeed, A., Farooq, U., Nearing, M. M., Koch, I., Reimer, K. J., Niedzielski, P., Siepak, M., Day, P. A. O., Mays, D. E., Hussam, A., Welna, M., Szymczycha-Madeja, A., Pohl, P., Ma, J., Sengupta, M. K., Yuan, D., Dasgupta, P. K., Amaral, C. D. B., Nóbrega, J. A., Nogueira, A. R. A., Cavicchioli, A., La-scalea, M. A., Gutz, G. R., Tyson, J., Chen, M. L., Ma, L. Y., Chen, X. W., Punrat, E., Chuanuwatanakul, S., Kaneta, T., Motomizu, S., Chailapakul, O., Hotel, D., Llorente-mirandes, T., Calderón, J., Centrich, F., Rubio, R., López-sánchez, J. F. and Thomas, D. J. (2014) ‘Method development for the determination of arsenic by sequential injection/anodic stripping voltammetry using long-lasting gold-modified screen-printed carbon electrode.’ *Talanta*. Elsevier B.V., 2013(June) pp. 1018–1025.

Quentel, F. and Filella, M. (2002) 'Determination of inorganic antimony species in seawater by differential pulse anodic stripping voltammetry: Stability of the trivalent state.' *Analytica Chimica Acta*, 452(2) pp. 237–244.

Quentel, F., Filella, M., Elleouet, C. and Madec, C. (2006) 'Sb(III) oxidation by iodate in seawater: A cautionary tale.' *Science of The Total Environment*. Elsevier, 355(1–3) pp. 259–263.

RA (2001) 'Philippine Mining Act of 1995,.' Philippines, R. of the (ed.) pp. 1–12.

Raab, A., Feldmann, J. and Meharg, A. A. (2004) 'The Nature of Arsenic-Phytochelatin Complexes in Holcus lanatus and Pteris cretica.' *Plant Physiology*. Department of Chemistry, University of Aberdeen, Meston Building, Meston Walk, Aberdeen AB24 3UE, United Kingdom., 134(3) pp. 1113–1122.

Raab, A., Meharg, A. A., Jaspars, M., Genney, D. R. and Feldmann, J. (2004) 'Arsenic–glutathione complexes—their stability in solution and during separation by different HPLC modes.' *J. Anal. At. Spectrom.*, 19(1) pp. 183–190.

Raab, A., Schat, H., Meharg, A. A., Feldmann, J., J., A. R. S. H. M. A. A. and F., Raab, A., Schat, H., Meharg, A. A. and Feldmann, J. (2005) 'Uptake, translocation and transformation of arsenate and arsenite in sunflower (Helianthus annuus): Formation of arsenic-phytochelatin complexes during exposure to high arsenic concentrations.' *New Phytologist*. Department of Chemistry, University of Aberdeen, Meston Building, Meston Walk, Aberdeen AB24 3UE, UK., 168(3) pp. 551–558.

Rahaman, M. S., Akter, M., Rahman, M. M., Sikder, M. T., Hosokawa, T., Saito, T. and Kurasaki, M. (2020) 'Investigating the protective actions of D-pinitol against arsenic-induced toxicity in PC12 cells and the underlying mechanism.' *Environmental Toxicology and Pharmacology*. Elsevier B.V., 74, February, p. 103302.

Rahman, M. A. and Hasegawa, H. (2011) 'High levels of inorganic arsenic in rice in areas where arsenic-contaminated water is used for irrigation and cooking.' *Science of The Total Environment*, 409(22) pp. 4645–4655.

Raskin, I., Kumar, P. N., Dushenkov, S. and Salt, D. E. (1994) 'Bioconcentration of heavy metals by plants.' *Current Opinion in Biotechnology*, 5(3) pp. 285–290.

Rauser, W. E. (1990) 'Phytochelatins.' *Annual Review of Biochemistry*, 59 pp. 61–86.

Reimann, C., Demetriades, A., Eggen, O. A. and Filzmoser, P. (2009) 'The EuroGeoSurveys geochemical mapping of agricultural and grazing land soils project (GEMAS) -Evaluation of quality control results of aqua regia extraction analysis.' *EuroGeoSurveys Geochemistry* , (May 2014) p. 94.

Rellán-Álvarez, R., El-Jendoubi, H., Wohlgemuth, G., Abadía, A., Fiehn, O., Abadía, J., Álvarez-Fernández, A., Schjoerring, J. K., Zocchi, G., Degli, U., Di Milano, S., Yoshihara, T.

and Alvarez-Fernández, A. (2011) 'Metabolite profile changes in xylem sap and leaf extracts of strategy I plants in response to iron deficiency and resupply.' *Frontiers in plant science*, 2 p. 66.

Rellán-Álvarez, R., Ortega-Villasante, C., Álvarez-Fernández, A., Campo, F. F. del and Hernández, L. E. (2006) 'Stress Responses of Zea mays to Cadmium and Mercury.' *Plant and Soil*, 279(1–2) pp. 41–50.

Ren, J. H., Ma, L. Q., Sun, H. J., Cai, F. and Luo, J. (2014) 'Antimony uptake, translocation and speciation in rice plants exposed to antimonite and antimonate.' *Science of the Total Environment*. Elsevier B.V., 475 pp. 83–89.

Rodriguez-Iruretagoiena, A., Trebolazabala, J., Martinez-Arkarazo, I., De Diego, A. and Madariaga, J. M. (2015) 'Metals and metalloids in fruits of tomatoes (Solanum lycopersicum) and their cultivation soils in the Basque Country: Concentrations and accumulation trends.' *Food Chemistry*. Elsevier Ltd, 173, February, pp. 1083–1089.

Rosas-Castor, J. M., Guzmán-Mar, J. L., Hernández-Ramírez, A., Garza-González, M. T. and Hinojosa-Reyes, L. (2014) 'Arsenic accumulation in maize crop (Zea mays): A review.' *Science of The Total Environment*. Elsevier, 488–489(1) pp. 176–187.

Rousk, J. and Jones, D. L. (2010) 'Loss of low molecular weight dissolved organic carbon (DOC) and nitrogen (DON) in H2O and 0.5M K2SO4 soil extracts.' *Soil Biology and Biochemistry*, 42(12) pp. 2331–2335.

Sabir, M., Waraich, E. A., Hakeem, K. R., Öztürk, M., Ahmad, H. R. and Shahid, M. (2015) 'Phytoremediation: Mechanisms and Adaptations. Mechanisms and Adaptations.' *Soil Remediation and Plants: Prospects and Challenges* pp. 85–105.

Sadiq, M. (1992) *Toxic metal chemistry in marine environments*. *Marcel Dekker*. New York City.

Salama, A. K. and Radwan, M. A. (2005) 'Heavy metals (Cd,Pb) and trace elements (Cu,Zn) contents in some foodstuffs from the Egyptian market.' *Emirates Journal of Food and Agriculture*, 17(1) pp. 34–42.

Salaun, P. (2017) 'Editorial: Environmental Electrochemistry.' *Current Opinion in Electrochemistry*. Elsevier B.V., 3(1) pp. 75–77.

Salaün, P. and van den Berg, C. M. G. (2006) 'Voltammetric detection of mercury and copper in seawater using a gold microwire electrode.' *Analytical chemistry*, 78(14) pp. 5052–60.

Salaün, P. and Frézard, F. (2013) 'Unexpectedly high levels of antimony (III) in the pentavalent antimonial drug Glucantime: insights from a new voltammetric approach.' *Analytical and Bioanalytical Chemistry*. Liverpool, 405(15) pp. 5201–5214.

Salaün, P., Gibbon-Walsh, K. B., Alves, G. M. S. S., Soares, H. M. V. M. V. M. and van den Berg, C. M. G. G. (2012) 'Determination of arsenic and antimony in seawater by voltammetric and chronopotentiometric stripping using a vibrated gold microwire electrode.' *Analytica Chimica Acta*. Liverpool: Elsevier B.V., 746(March 2014) pp. 53–62.

Salaün, P., Gibbon-Walsh, K. and van den Berg, C. M. G. (2011) 'Beyond the Hydrogen Wave: New Frontier in the Detection of Trace Elements by Stripping Voltammetry.' *Analytical Chemistry*, 83(10) pp. 3848–3856.

Salaün, P., Planer-Friedrich, B. and van den Berg, C. M. . (2007) 'Inorganic arsenic speciation in water and seawater by anodic stripping voltammetry with a gold microelectrode.' *Analytica Chimica Acta*. Liverpool, 585(2) pp. 312–322.

Samarah, L. Z., Tran, T. H., Stacey, G. and Vertes, A. (2020) 'In Vivo Chemical Analysis of Plant Sap from the Xylem and Single Parenchymal Cells by Capillary Microsampling Electrospray Ionization Mass Spectrometry.' *Analytical Chemistry*, 92(10) pp. 7299–7306.

Samota, M. K., Navnage, N. P. and Bhatt, L. (2017) 'Role of Macro and Micronutrient in Development and Growth of Plant,' 10(18) pp. 3171–3173.

Santos, V. S., Santos, W. de J. R., Kubota, L. T. and Tarley, C. R. T. (2009) 'Speciation of Sb(III) and Sb(V) in meglumine antimoniate pharmaceutical formulations by PSA using carbon nanotube electrode.' *Journal of Pharmaceutical and Biomedical Analysis*, 50(2) pp. 151–157.

Satoh, S. (2006) 'Organic substances in xylem sap delivered to above-ground organs by the roots.' *Journal of Plant Research*, 119(3) pp. 179–187.

Scharifker, B. R., Mostany, J. and Serruya, A. (2000) 'Catalytic reduction of nitrate during electrodeposition of thallium from Tl3+ solution.' *Electrochemistry Communications*, 2(6) pp. 448–451.

Scholander, P. F., Bradstreet, E. D., Hemmingsen, E. A. and Hammel, H. T. (1965) 'Sap Pressure in Vascular Plants: Negative hydrostatic pressure can be measured in plants.' *Science*, 148(3668) pp. 339–346.

Schurr, U. (1998) 'Xylem sap sampling—new approaches to an old topic.' *Trends in Plant Science*. Elsevier Current Trends, 3(8) pp. 293–298.

Schurr, U. (1999) 'Dynamics of Nutrient Transport from the Root to the Shoot.' *In*. Springer, Berlin, Heidelberg, pp. 234–253.

Shahid, M., Khalid, S., Abbas, G., Shahid, N., Nadeem, M., Sabir, M., Aslam, M. and Dumat, C. (2015) 'Heavy metal stress and crop productivity.' *In Crop Production and Global Environmental Issues*. Springer International Publishing, pp. 1–25.

Sharma, S. D. (2013) 'History of Rice in Southeast Asia and Australia.' *Journal of Chemical Information and Modeling*, 53(9) pp. 1689–1699.

Shri, M., Singh, P. K., Kidwai, M., Gautam, N., Dubey, S., Verma, G. and Chakrabarty, D. (2019) 'Recent advances in arsenic metabolism in plants: Current status, challenges and highlighted biotechnological intervention to reduce grain arsenic in rice.' *Metallomics*, 11(3) pp. 519–532.

Simoni, R. D., Hill, R. L. and Vaughan, M. (2005) 'Benedict ' s Solution , a Reagent for Measuring Reducing Sugars : the Clinical Chemistry of Stanley R . Benedict,' 277(16) pp. 10–12.

Slamet-loedin, I., Slamet-loedin, I. H., Johnson-beebout, S. E., Impa, S. and Tsakirpaloglou, N. (2015) 'Enriching rice with Zn and Fe while minimizing Cd risk.' *Frontiers in Plant Science*, 6(MAR).

Smedley, P. L. and Kinniburgh, D. G. (2000) 'Source and behaviour of arsenic in natural waters.' *British Geological Survey* p. 61.

Smedley, P. L. and Kinniburgh, D. G. (2002) 'A review of the source, behaviour and distribution of arsenic in natural waters.' *Applied Geochemistry*, 17(5) pp. 517–568.

Smith, A. H., Lingas, E. O. and Rahman, M. (2000) 'Contamination of drinking-water by arsenic in Bangladesh: A public health emergency.' *Bulletin of the World Health Organization*, 78(9) pp. 1093–1103.

Smith, A. H. and Smith, M. M. H. (2004) 'Arsenic drinking water regulations in developing countries with extensive exposure.' *Toxicology*, 198(1–3) pp. 39–44.

Sobrado, M. A. (2007) 'Relationship of water transport to anatomical features in the mangrove Laguncularia racemosa grown under contrasting salinities.' *New Phytologist*, 173(3) pp. 584–591.

Sørensen, O., Andersen, A., Olsen, H., Alexandr, K., Ekstrøm, P. O., Giercksky, K. E. and Flatmark, K. (2010) 'Validation and use of microdialysis for determination of pharmacokinetic properties of the chemotherapeutic agent mitomycin C - an experimental study.' *BMC Cancer*, 10.

Spurgeon, D. J., Rowland, P., Ainsworth, G., Rothery, P., Long, S. and Black, H. I. J. (2008) 'Geographical and pedological drivers of distribution and risks to soil fauna of seven metals (Cd, Cu, Cr, Ni, Pb, V and Zn) in British soils.' *Environmental Pollution*, 153(2) pp. 273–283.

Sreekanth, T. V. M., Nagajyothi, P. C., Lee, K. D. and Prasad, T. N. V. K. V. (2013) 'Occurrence, physiological responses and toxicity of nickel in plants.' *International Journal of Environmental Science and Technology*. Center for Environmental and Energy Research and Studies pp. 1129–1140.

Stazi, S. R., Cassaniti, C., Marabottini, R., Giuffrida, F. and Leonardi, C. (2016) ‘Arsenic uptake and partitioning in grafted tomato plants.’ *Horticulture, Environment, and Biotechnology*. Korean Society for Horticultural Science, 57(3) pp. 241–247.

Steudle, E. (2001) ‘The cohesion-tension mechanism and the acquisition of water by plant roots.’ *Annual Review of Plant Biology*, 52 pp. 847–875.

Stoeva, N., Berova, M. and Zlatev, Z. (2005) ‘Effect of arsenic on some physiological parameters in bean plants.’ *Biologia Plantarum*, 49(2) pp. 293–296.

Sulyok, M., Miró, M., Stingeder, G. and Koellensperger, G. (2005) ‘The potential of flow-through microdialysis for probing low-molecular weight organic anions in rhizosphere soil solution.’ *Analytica Chimica Acta*. Elsevier, 546(1) pp. 1–10.

Sun, G., Williams, P. N. and Zhu, Y. (2009) ‘Mechanisms of Arsenic Uptake and Metabolism by Plants : Focusing on Rice.’ *Environmental Toxicology*, 134(November) pp. 1–6.

Sun, H., Yan, S. C. and Cheng, W. S. (2000) ‘Interaction of antimony tartrate with the tripeptide glutathione.’ *European Journal of Biochemistry*, 267(17) pp. 5450–5457.

Takarina, N. D. and Pin, T. G. (2017) ‘Bioconcentration Factor (BCF) and Translocation Factor (TF) of Heavy Metals in Mangrove Trees of Blanakan Fish Farm.’ *Makara Journal of Science*, 21(2).

Tamás, M. J. (2016) ‘Cellular and molecular mechanisms of antimony transport, toxicity and resistance.’ *Environmental Chemistry*, 13(6) pp. 955–962.

Tatár, E., Mihucz, V. G., Kmethy, B., Záray, G. and Fodor, F. (2000) ‘Determination of organic acids and their role in nickel transport within cucumber plants.’ *Microchemical Journal*, 67(1–3) pp. 73–81.

Tatár, E., Mihucz, V. G., Varga, A., Záray, G. and Fodor, F. (1998) ‘Determination of Organic Acids in Xylem Sap of Cucumber: Effect of Lead Contamination.’ *Microchemical Journal*. Elsevier Inc., 58(3) pp. 306–314.

Telford, K., Maher, W., Krikowa, F. and Foster, S. (2008) ‘Measurement of total antimony and antimony species in mine contaminated soils by ICPMS and HPLC-ICPMS.’ *Journal of Environmental Monitoring*, 10(1) pp. 136–140.

Telford, K., Maher, W., Krikowa, F., Foster, S., Ellwood, M. J. M. J., Ashley, P. M. P. M., Lockwood, P. V. P. V. and Wilson, S. C. S. C. (2009) ‘Bioaccumulation of antimony and arsenic in a highly contaminated stream adjacent to the Hillgrove Mine, NSW, Australia.’ *Environmental Chemistry*, 6(2) pp. 133–143.

Thomas, G. W. (1996) ‘Soil pH and soil acidity.’ *In* D.L. Sparks et al., editors (ed.) *Methods of soil analysis: Part 3. SSSA Book Series No. 5. SSSA,* pp. 475–490.

Tian, T., Zhou, H., Gu, J., Jia, R., Li, H., Wang, Q., Zeng, M. and Liao, B. (2019) 'Cadmium accumulation and bioavailability in paddy soil under different water regimes for different growth stages of rice (Oryza sativa L.).' *Plant and Soil*. Springer International Publishing, July.

Timofeev, I. and Hutchinson, P. (2008a) 'Microdialysis.' *In Essentials of Neuroanesthesia and Neurointensive Care*. Elsevier, pp. 277–282.

Timofeev, I. and Hutchinson, P. (2008b) 'Microdialysis Learn more about Microdialysis Microdialysis Chemical and Biochemical Approaches for the Study of Anesthetic Function Part B Carrier-mediated and artificial-cell tar-.'

Toghill, K. E., Lu, M., Compton, R. G. and Kathryn E. Toghill, Min Lu, and R. G. C. (2011) 'Electroanalytical Determination of Antimony.' *International Journal of Electrochemical Science*, 6(8) pp. 3057–3076.

Tollestrup, K., Frost, F. J., Harter, L. C. and McMillan, G. P. (2003) 'Mortality among Children Residing near the American Smelting and Refining Company (ASARCO) Copper Smelter in Ruston, Washington.' *Archives of Environmental Health: An International Journal*, 58(11) pp. 683–691.

Torto, N., Mwatseteza, J. and Laurell, T. (2001) 'Microdialysis Sampling: Challenges and New Frontiers.' *LC GC Europe*, 14(9) pp. 536–546.

Torto, N., Mwatseteza, J. and Sawula, G. (2002) 'A study of microdialysis sampling of metal ions.' *Analytica Chimica Acta*. Elsevier, 456(2) pp. 253–261.

Trejo-Téllez, L. I. (2012) 'Nutrient Solutions for Hydroponic Systems.' *In* Asao, F. C. G.-M. E.-T. (ed.). Rijeka: IntechOpen, p. Ch. 1.

Tsang, J. J., Rozan, T. F., Hsu-Kim, H., Mullaugh, K. M. and Luther, G. W. (2006) 'Pseudopolarographic determination of Cd2+ complexation in freshwater.' *Environmental Science and Technology*, 40(17) pp. 5388–5394.

Tschan, M., Robinson, B. H. and Schulin, R. (2009) 'Antimony in the soil - Plant system - A review.' *Environmental Chemistry*, 6(2) pp. 106–115.

Tschan, M., Robinson, B. and Schulin, R. (2008) 'Antimony uptake by Zea mays (L.) and Helianthus annuus (L.) from nutrient solution.' *Environmental Geochemistry and Health*, 30(2) pp. 187–191.

Tsukagoshi, S. and Shinohara, Y. (2015) *Nutrition and Nutrient Uptake in Soilless Culture Systems*. *Plant Factory: An Indoor Vertical Farming System for Efficient Quality Food Production*. Elsevier Inc.

Tuyogon, D. S. J., Impa, S. M., Castillo, O. B., Larazo, W. and Johnson-Beebout, S. E. (2016) 'Enriching rice grain zinc through zinc fertilization and water management.' *Soil Science*

Society of America Journal, 80(1) pp. 121–134.

Tylenda, C. A., Sullivan, D. W. and Fowler, B. A. (2015) *Antimony*. *Handbook on the Toxicology of Metals: Fourth Edition*. Fourth Edi, Elsevier.

U.S. Department of Health and Human (2018) *Revised Draft : Report on Carcinogens Monograph on Antimony Trioxide*.

U.S. Geological Survey (2004) ‘Mineral Commodity Profiles-Antimony.’ *U.S. Department of the Interior: U.S. Geological Survey* pp. 1–35.

Ugochukwu, G. C., Eneh, F. U., Igwilo, I. . and Aloh, C. H. (2017) ‘Comparative study on the heavy metal content of domestic rice (Oryza sativa Comparative study on the heavy metal content of domestic rice (Oryza sativa L) brands common in Awka, Nigeria.’ *IOSR Journal of Environmental Science, Toxicology and Food Technology*, 11(8) pp. 67–70.

UN (ed.) (2015) *Crop Prospects and Food Situation*. Rome: FAO.

Ungureanu, G., Santos, S., Boaventura, R. and Botelho, C. (2015) ‘Arsenic and antimony in water and wastewater: Overview of removal techniques with special reference to latest advances in adsorption.’ *Journal of Environmental Management*, 151, March, pp. 326–342.

Uroic, M. K. (2011) *The impact of arsenic species on the production and composition of xylem sap*. *Environmental & Analytical Chemistry*. University of Aberdeen. Retrieved from internal-pdf://145.35.116.156/PhD thesis The impact of As MK Uroic.pdf.

Uroic, M. K., Salaün, P., Raab, A. and Feldmann, J. (2012) ‘Arsenate impact on the metabolite profile, production, and arsenic loading of xylem sap in cucumbers (Cucumis sativus L.).’ *Frontiers in Physiology*, 3 APR(March) pp. 1–23.

Varsányi, I., Fodré, Z. and Bartha, A. (1991) ‘Arsenic in drinking water and mortality in the Southern Great Plain, Hungary.’ *Environmental Geochemistry and Health*. Kluwer Academic Publishers, 13(1) pp. 14–22.

Violante, A., Cozzolino, V., Perelomov, L., Caporale, A. . and Pigna, M. (2010) ‘Mobility and bioavailability of heavy metals and metalloids in soil environments.’ *Journal of soil science and plant nutrition*. Sociedad Chilena de la Ciencia del Suelo, 10(3) pp. 268–292.

Vithanage, M., Dabrowska, B. B., Mukherjee, A. B., Sandhi, A. and Bhattacharya, P. (2012) ‘Arsenic uptake by plants and possible phytoremediation applications: A brief overview.’ *Environmental Chemistry Letters* pp. 217–224.

Wagner, S. E., Peryea, F. J. and Filby, R. A. (2003) ‘Antimony Impurity in Lead Arsenate Insecticide Enhances the Antimony Content of Old Orchard Soils.’ *Journal of Environmental Quality*. Wiley, 32(2) pp. 736–738.

Wan, X. M., Tandy, S., Hockmann, K. and Schulin, R. (2013) ‘Changes in Sb speciation with waterlogging of shooting range soils and impacts on plant uptake.’ *Environmental Pollution*. Elsevier Ltd, 172, January, pp. 53–60.

Wang, S., Shi, X., Sun, H., Chen, Y., Pan, H., Yang, X. and Rafiq, T. (2014) ‘Variations in Metal Tolerance and Accumulation in Three Hydroponically Cultivated Varieties of Salix integra Treated with Lead.’ Reigosa, M. (ed.) *PLoS ONE*. Public Library of Science, 9(9) p. e108568.

Wang, T., Yang, Q., Wang, Y., Wang, J., Zhang, Y. and Pan, W.-P. P. (2020) ‘Arsenic release and transformation in co-combustion of biomass and coal: Effect of mineral elements and volatile matter in biomass.’ *Bioresource technology*. Beijing, PR China: Elsevier Ltd, 297, February, p. 122388.

Wang, Z., Zeng, X., Geng, M., Chen, C., Cai, J., Yu, X., Hou, Y. and Zhang, H. (2015) ‘Health risks of heavy metals uptake by crops grown in a sewage irrigation area in China.’ *Polish Journal of Environmental Studies*, 24(3) pp. 1379–1386.

Welch, A. H. and Stollenwerk, K. G. (eds) (2003) *Arsenic in Ground Water*. *Springer Science Business Media New York*. Boston, MA: Springer US.

White, M. C., Chaney, R. L., Decker, A. M. and R., and M. W. D. A. (1981) ‘Metal Complexation in Xylem Fluid: I. Chemical composition of tomato and soybean stem exudate.’ *Plant Physiology*, 67(2) pp. 292–300.

WHO (2003a) ‘Antimony in Drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality.’ *Who* pp. 1–9.

WHO (2003b) *Background document for preparation of WHO Guidelines for drinking-water quality: Antimony in drinking water.* Geneva, Switzerland.

WHO (2003c) ‘Chromium in drinking-water. Background document for preparation of WHO Guidelines for drinking-water quality.’ *(WHO/SDE/WSH/03.04/4)*, (3) pp. 334–335.

Wickliff, J. L. and Aronoff, S. (1962) *Quantitative measurement of leaf chlorophylss by spectrophotometry of their pheophytins in aqueous alcoholic extracts*. Iowa, USA.

Williams, P. N., Islam, M. R., Adomako, E. E., Raab, A., Hossain, S. A., Zhu, Y. G., Feldmann, J. and Meharg, A. A. (2006) ‘Increase in rice grain arsenic for regions of Bangladesh irrigating paddies with elevated arsenic in groundwaters.’ *Environmental Science and Technology* pp. 4903–4908.

Wilson, S. C., Lockwood, P. V., Ashley, P. M. and Tighe, M. (2010) ‘The chemistry and behaviour of antimony in the soil environment with comparisons to arsenic: A critical review.’ *Environmental Pollution*. Elsevier Ltd, 158(5) pp. 1169–1181.

Woolson, E. A., Axley, J. H. and Kearney, P. C. (1971) ‘Correlation between Available Soil

Arsenic, Estimated by Six Methods, and Response of Corn (Zea mays L.)1.' *Soil Science Society of America Journal*. Soil Science Society of America, 35(1) p. 101.

Wu, D. and Sun, S. (2016) 'Speciation analysis of As, Sb and Se.' *Trends in Environmental Analytical Chemistry*. Elsevier Inc., 11, July, pp. 9–22.

Wu, T.-L. L., Cui, X.-D. D., Cui, P.-X. X., Ata-Ul-Karim, S. T., Sun, Q., Liu, C., Fan, T.-T. T., Gong, H., Zhou, D.-M. M. and Wang, Y.-J. J. (2019) 'Speciation and location of arsenic and antimony in rice samples around antimony mining area.' *Environmental Pollution*. Elsevier Ltd, 252, September, pp. 1439–1447.

www.IRRI.org (2019) *Long-Term Continuous Cropping Experiment (LTCCE) | International Rice Research Institute*. [Online] [Accessed on 18th November 2019] https://www.irri.org/long-term-continuous-cropping-experiment-ltcce.

Wyrwicka, A., Urbaniak, M. and Przybylski, M. (2019) ' The response of cucumber plants (Cucumis sativus L.) to the application of PCB-contaminated sewage sludge and urban sediment .' *PeerJ*, 7 p. e6743.

Xu, X. Y., McGrath, S. P. and Zhao, F. J. (2007) 'Rapid reduction of arsenate in the medium mediated by plant roots.' *New Phytologist*, 176(3) pp. 590–599.

Yadav, S. K. (2010) 'Heavy metals toxicity in plants: An overview on the role of glutathione and phytochelatins in heavy metal stress tolerance of plants.' *South African Journal of Botany*. Elsevier B.V., 76(2) pp. 167–179.

Ye, W.-L. L., Wood, B. A., Stroud, J. L., Andralojc, P. J., Raab, A., McGrath, S. P., Feldmann, J. and Zhao, F.-J. J. (2010) 'Arsenic speciation in phloem and xylem exudates of castor bean.' *Plant Physiology*, 154(3) pp. 1505–1513.

Zavala, Y. J. and Duxbury, J. M. (2008) 'Arsenic in rice: I. Estimating normal levels of total arsenic in rice grain.' *Environmental Science and Technology*, 42(10) pp. 3856–3860.

Zengin, F. K. and Munzuroglu, O. (2005) 'Effects of some heavy metals on content of chlorophyll, proline and some antioxidant chemicals in bean (Phaseolus vulgaris L.) seedlings.' *Acta Biologica Cracoviensia Series Botanica*, 47(2) pp. 157–164.

Zhang, H. and Selim, H. M. (2005) 'Kinetics of Arsenate Adsorption−Desorption in Soils.' *Environmental Science & Technology*, 39(16) pp. 6101–6108.

Zhang, T., Ruan, J., Zhang, B., Lu, S., Gao, C., Huang, L., Bai, X., Xie, L., Gui, M. and Qiu, R. (2019) 'Heavy metals in human urine, foods and drinking water from an e-waste dismantling area: Identification of exposure sources and metal-induced health risk.' *Ecotoxicology and Environmental Safety*. Academic Press, 169, March, pp. 707–713.

Zhang, W., Cai, Y., Tu, C. and Ma, L. Q. (2002) 'Arsenic speciation and distribution in an arsenic hyperaccumulating plant.' *Science of the Total Environment*, 300(1–3) pp. 167–

177.

Zhao, F.-J., Ma, Y., Zhu, Y.-G., Tang, Z. and McGrath, S. P. (2015) ‘Soil Contamination in China: Current Status and Mitigation Strategies.’ *Environmental Science & Technology*. American Chemical Society, 49(2) pp. 750–759.

Zhao, F.-J., McGrath, S. P. and Meharg, A. A. (2010) ‘Arsenic as a Food Chain Contaminant: Mechanisms of Plant Uptake and Metabolism and Mitigation Strategies.’ *Annual Review of Plant Biology*. Annual Reviews, 61(1) pp. 535–559.

Zheng, J., Iijima, A. and Furuta, N. (2001) ‘Complexation effect of antimony compounds with citric acid and its application to the speciation of antimony(III) and antimony(V) using HPLC-ICP-MS.’ *Journal of Analytical Atomic Spectrometry*, 16(8) pp. 812–818.

Zheng, R. L., Sun, G. X. and Zhu, Y. G. (2013) ‘Effects of microbial processes on the fate of arsenic in paddy soil.’ *Chinese Science Bulletin* pp. 186–193.

Zhou, S. N., Ouyang, G. and Pawliszyn, J. (2008) ‘Comparison of microdialysis with solid-phase microextraction for in vitro and in vivo studies.’ *Journal of Chromatography A*, 1196–1197(1–2) pp. 46–56.

Zhou, X., Sun, C., Zhu, P. and Liu, F. (2018) ‘Effects of Antimony Stress on Photosynthesis and Growth of Acorus calamus.’ *Frontiers in Plant Science*. Frontiers Media S.A., 9(May) pp. 1–9.

Zulkafflee, N. S., Redzuan, N. A. M., Hanafi, Z., Selamat, J., Ismail, M. R., Praveena, S. M. and Razis, A. F. A. (2019) ‘Heavy metal in paddy soil and its bioavailability in rice using in vitro digestion model for health risk assessment.’ *International Journal of Environmental Research and Public Health*, 16(23).

CHAPTER 7

CONCLUSIONS AND OUTLOOK

7.1 Conclusions and outlooks

This thesis investigated the bio-uptake of metalloids (inorganic antimony and arsenic) by plants and the development of electroanalytical methods for antimony detection and speciation.

Bio-uptake of metalloids were using a hydroponic experiment of cucumber plant chosen as a model plant to assess the impact of As or Sb species, plant age, exposure duration, and metalloid concentration to overall plant morphology (Chapter 2). A new method of microdialysis was developed (Chapter 3). Being less destructive and less invasive (e.g. than decapitation), it can be a useful tool for in-vivo xylem sap sampling allowing researchers to simulate nutrient/toxic metal uptake, translocation, and absorption while taking into consideration the effect of transpiration. The following observations were made:

- Inorganic As/Sb significantly reduces the health in terms of the morphology of the cucumber plant, which leads to drying and eventually dying of the plants.
- Plant physiological parameters were significantly affected by the presence of Sb and As ((III) or (V)) in the nutrient solution, either a small amount (100 ppb) or more considerable amount (5 ppm),
- Younger plants were significantly affected by the presence of the inorganic metalloids, compared to older plants,
- The Sb and As concentration in roots were the highest followed by stem and leaves,
- There are interesting correlations found in micro and macronutrients in the plants as a function of Sb or As treatments,

Voltammetric methods were developed for (1) complexation studies of Sb(III) with xylem sap samples and determination of stability constants of Sb(III) with low molecular weight ligands (Chapter 5), and (2) cation mediated reduction of Sb(V) using monovalent, divalent and trivalent cations (Chapter 6)We have demonstrated the feasibility to quantitatively study the complexation of the presence of Sb(III) complex with low molecular weight ligands, specifically EDTA, DTPA, TA, and GSH using a voltammetric method (pseudopolarography on Au electrode) at ppb levels.

Importantly, results obtained in the complexation studies with the sap on Sb(III) seem to show that Sb(III) is indeed complexed and the voltammetric signal of this complexation suggests that glutathione could be one of the ligands involved in complexing Sb(III) in that media. Other sulfur compounds could likely behave similarly.

There is still a substantial gap in metalloid toxicity scientific literature (i.e., As and Sb), adsorption, translocation, and bioavailability. A better understanding of the uptake, translocation, effect of exposure duration, and effect on the plant growth are very crucial for the assessment of metalloids on crops for human consumption as part of food safety. Since many Sb contaminated sites are being used for agriculture, it is crucial to assess the risks of Sb transfer from such soils into food and feed crop plants, and therefore understand how Sb accumulation, allocation, and speciation in crop plants relates to Sb speciation in the soil (Ji et al., 2018). Figure 7 shows a general eye view of what the critical experiments and results obtained from this PhD thesis are.

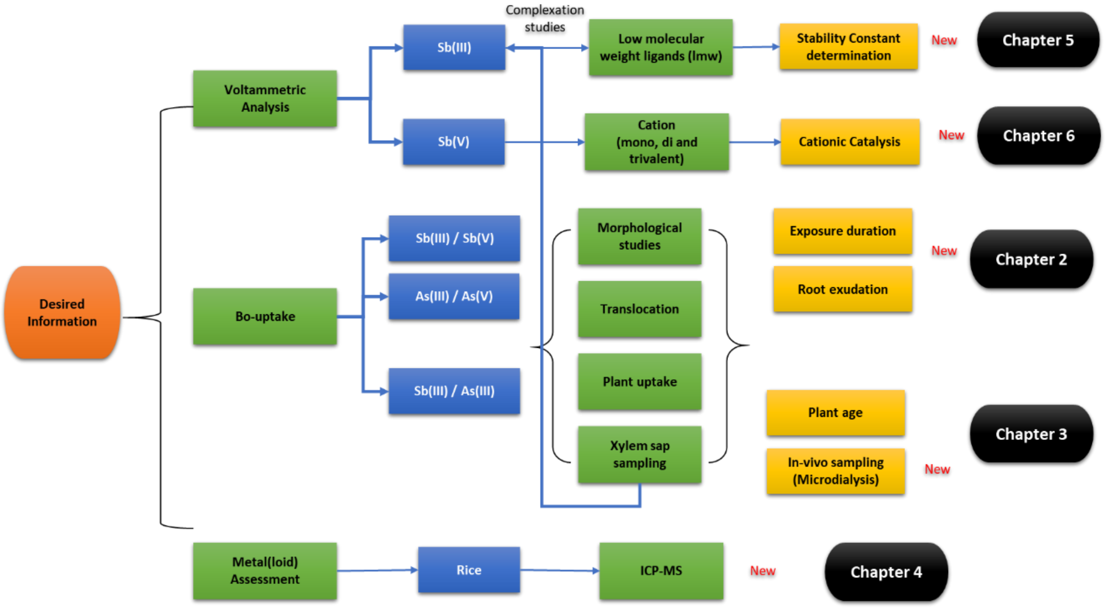


Figure 7. 1. Schematic diagram of the PhD thesis from Chapter 1 (not shown) to Chapter 6.

In comparison to arsenic that has been extensively studied, not a lot is known in regard to Sb speciation and complexation. The lack of analytical methodologies, difficulties in quantitative extraction from biological samples, instability and preservation of Sb species sampling and processing, low recoveries due to adsorption problems to the column (i.e., chromatography), and trace level Sb species are too low for spectrometric identification, are few of the challenges and problems why there is limited progress in Sb analysis in biological media. The strong limitation on chromatography on Sb(III) is that the compound is strongly adsorbed to the stainless steel column and is irreversibly retained on the HPLC column. The incorporation of a potent chelating agent in the mobile phase will be able to solve this problem however, by doing this, original information on the ligand is lost. In this study presented here, speciation of Sb(III) in the sap was attempted by HPLC-ES-MS in Aberdeen (in the group of Prof. Feldmann) but unfortunately, due to technical problems, the obtained results were unreliable, and not enough sap remained

for us to proceed again with this speciation study. This was a real shame as such intercomparison would have given us insights into the advantages and disadvantages of both voltammetry and chromatography. It is still unknown, and not appreciated, that relatively weak complexes might be destroyed during the chromatographic process, while they might be detected by voltammetry. More studies combining chromatography and voltammetry should likely be promoted to gain insights into the “detection window” of each technique, i.e. what can and cannot be detected?
Chapter 6 presents a new cation mediated reduction of antimonate; this cationic catalysis had never been reported before although similar observations were made for arsenate. It provides a new concept that needs to be further developed, fully assess its application range in terms of e.g. pH, concentrations, and assess if it can be applied to other trace analytes such as germanium or selenium for instance. It is possible that attractive analytical methods, easily implementable for some matrix, can be developed and possibly used for routine monitoring studies as part of food safety.

The last part (Chapter 4) is an assessment study. The lack of scientific reports about possible heavy metal contamination in rice grown in old mining site areas of the Philippines, as well as in the Asian rice that is available in the market, creates the need to assess the concentration of heavy metals. A possible threat to consumer’s health or public safety is indicative of the presence of heavy metals in soil and rice. Strategies for the reduction or soil remediation can be accurately formulated if toxic or high metal concentrations are found. This study is important as a reference for future studies that will monitor the heavy metal levels of paddy soil and rice in polluted rice fields of the country. In terms of consumer protection through food security measures, there is a need to efficiently assess rice as well as paddy soils in the Philippines as the staple food of the country. In countries where rice is the source of carbohydrates such as Asian countries, this may result in significant health concerns. Laws in the rehabilitation of old mining sites turned into agricultural areas such as rice fields that should be stringent. A further test is to be performed on all rice varieties is recommended to ensure public safety.

APPENDICES

8.1 Visual minteq procedure

8.1.1 Modifications

a. The modification of the database of the components. C: \ Vminteq30 \ comp_2008.vdb or a copy (eg LEG \ Xylenol \ comp_2008_Xylenol.vdb and then point it to the VMINTEQ through the Database management menu, Database selection). We open the components database (comp_2008.vdb or a copy if we want to work safer) with the notepad (WordPad or Notepad).

b. To the new component (eg XO) we must give you an identifying number that does not exist yet. Once this number is chosen, we add a new line in the components database by filling out the data as follows: No. identifier, "Symbol", load (of the totally deprotonated ligand), 0.0, Mass Molar, Save changes: File-Save as Then, in order to introduce the new constants to the base of constants C: \ Vminteq30 \ thermo.vdb or a copy (eg LEG \ Xylenol \ thermo_Xylenol.vdb and then point it to the VMINTEQ through the Database management menu, Database selection), return to VMINTEQ. We have to make sure that we are working with the component database where we have introduced the new component. Therefore, executing VMINTEQ checked in: Database management Database selection-Component database (what we generated with the notebook). Save to this problem and Quit

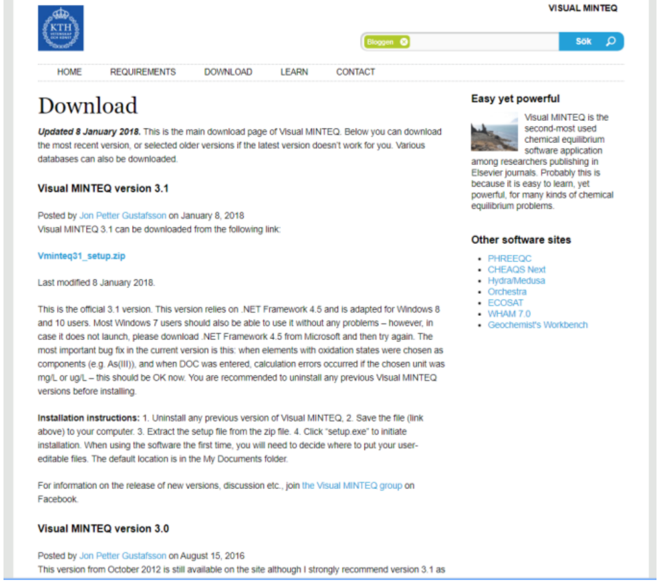
c. In the VMINTEQ Main Menu, the new linked link is selected and added to the list (add to list), then the same is done with the metal that you want to work with.

Then, in the Database management menu, choose the Aqueous species option. Once here, we have to add the new species that we want to introduce (Add new species). In Species name, the name of the species you want to add (eg if we want the first protonation of the XO we put, HXO5-), the first stoichiometric factor (eg 1) and the first component (p. ex. H). Thus each of the components of the new species that is wanted to be added must be placed. To do this, you must choose from the eyelash where Component does not. I. Once selected, click Next.

d. Then, a little further up, the components that are selected are leaving and where Stoichiometry of 1st component is released, it must be checked that the stoichiometry of all the components has been well established. Indicate the resulting load of the new species (eg for HXO5- would -5). Finally, click on Suggest ID number and mol. Wt You must enter the log of the constant log K (at ionic strength zero, or constant thermodynamics for the formation from the components, often called), the load of the new added species. If you do not know, ΔH can be zero. You can indicate date of incorporation of the new constants, bibliography or whatever you want (in References) When everything seems correct, it is recorded with Save changes to database.

8.1.2 Visual Minteq Procedure

Downloaded Visual Minteq from the university or the link https://vminteq.lwr.kth.se/download/



Download

Updated 8 January 2018. This is the main download page of Visual MINTEQ. Below you can download the most recent version, or selected older versions if the latest version doesn't work for you. Various databases can also be downloaded.

Visual MINTEQ version 3.1

Posted by Jon Petter Gustafsson on January 8, 2018
Visual MINTEQ 3.1 can be downloaded from the following link:

Vminteq31_setup.zip

Last modified 8 January 2018.

This is the official 3.1 version. This version relies on .NET Framework 4.5 and is adapted for Windows 8 and 10 users. Most Windows 7 users should also be able to use it without any problems – however, in case it does not launch, please download .NET Framework 4.5 from Microsoft and then try again. The most important bug fix in the current version is this: when elements with oxidation states were chosen as components (e.g. As(III)), and when DOC was entered, calculation errors occurred if the chosen unit was mg/L or ug/L – this should be OK now. You are recommended to uninstall any previous Visual MINTEQ versions before installing.

Installation instructions: 1. Uninstall any previous version of Visual MINTEQ, 2. Save the file (link above) to your computer. 3. Extract the setup file from the zip file. 4. Click "setup.exe" to initiate installation. When using the software the first time, you will need to decide where to put your user-editable files. The default location is in the My Documents folder.

For information on the release of new versions, discussion etc., join the Visual MINTEQ group on Facebook.

Visual MINTEQ version 3.0

Posted by Jon Petter Gustafsson on August 15, 2016
This version from October 2012 is still available on the site although I strongly recommend version 3.1 as

Easy yet powerful

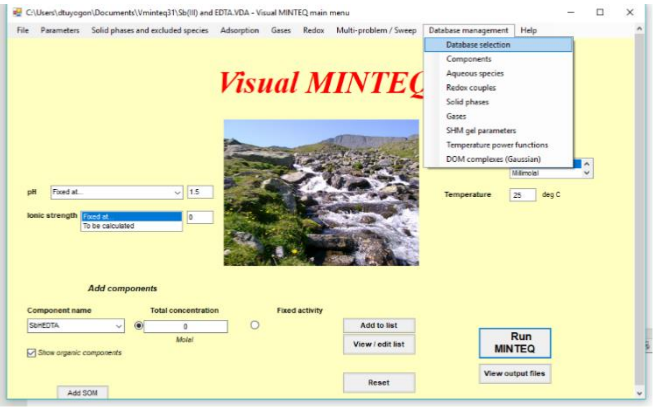
Visual MINTEQ is the second-most used chemical equilibrium software application among researchers publishing in Elsevier journals. Probably this is because it is easy to learn, yet powerful, for many kinds of chemical equilibrium problems.

Other software sites

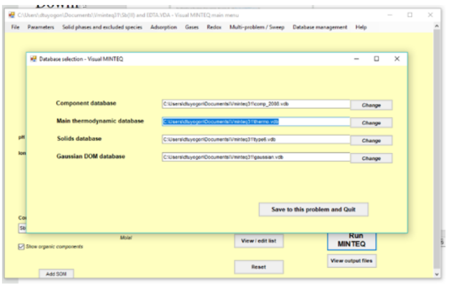
- PHREEQC
- CHEAQS Next
- Hydra/Medusa
- Orchestra
- ECOSAT
- WHAM 7.0
- Geochemist's Workbench

2. Visual Minteq –database selection-component database

Component database: C:\Users\dtuyogon\Documents\Vminteq31\comp_2008.vdb
Main thermodynamic database:



pH: Fixed at... 1.5
Ionic strength: Fixed at... 0
Temperature: 25 deg C
Component name: SbHEDTA
Total concentration: 0 Molal

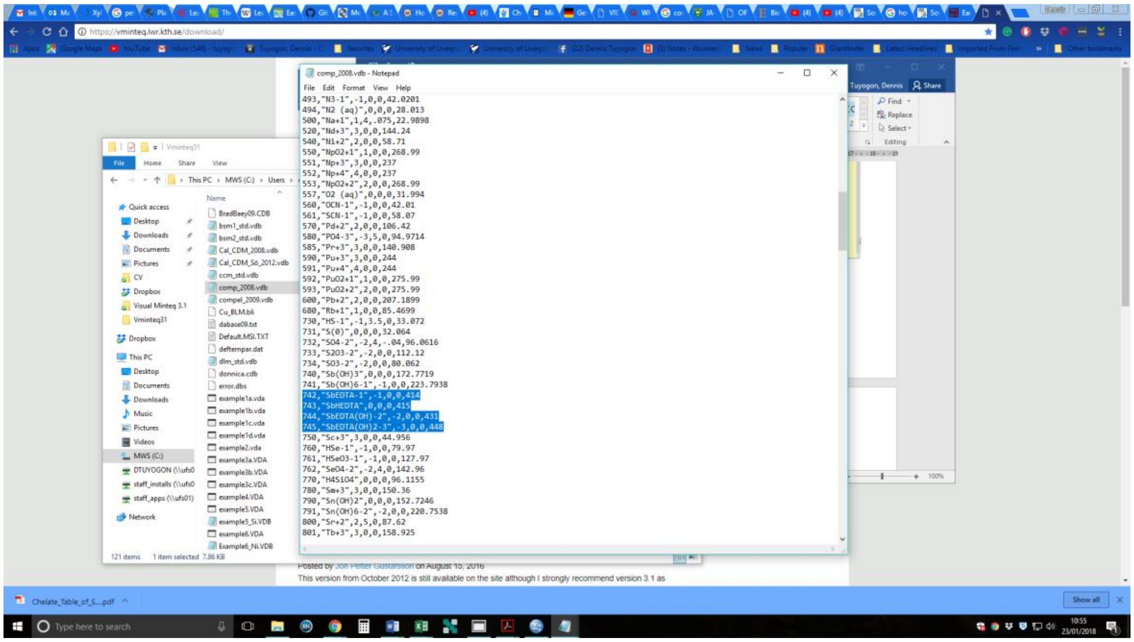


Component database: C:\Users\dtuyogon\Documents\Vminteq31\comp_2008.vdb
Main thermodynamic database: C:\Users\dtuyogon\Documents\Vminteq31\thermo.vdb
Solids database: C:\Users\dtuyogon\Documents\Vminteq31\type6.vdb
Gaussian DOM database: C:\Users\dtuyogon\Documents\Vminteq31\gaussian.vdb

C:\Users\dtuyogon\Documents\Vminteq31\thermo.vdb

Addition of components

Component database: C:\Users\dtuyogon\Documents\Vminteq31\comp_2008.vdb



```
493,"N3-1",-1,0,0,42.0201
494,"N2 (aq)",0,0,0,28.013
500,"Na+1",1,4,.075,22.9898
520,"Nd+3",3,0,0,144.24
540,"Ni+2",2,0,0,58.71
550,"NpO2+1",1,0,0,268.99
551,"Np+3",3,0,0,237
552,"Np+4",4,0,0,237
553,"NpO2+2",2,0,0,268.99
557,"O2 (aq)",0,0,0,31.994
560,"OCN-1",-1,0,0,42.01
561,"SCN-1",-1,0,0,58.07
570,"Pd+2",2,0,0,106.42
580,"PO4-3",-3,5,0,94.9714
585,"Pr+3",3,0,0,140.908
590,"Pu+3",3,0,0,244
591,"Pu+4",4,0,0,244
592,"PuO2+1",1,0,0,275.99
593,"PuO2+2",2,0,0,275.99
600,"Pb+2",2,0,0,207.1899
680,"Rb+1",1,0,0,85.4699
730,"HS-1",-1,3.5,0,33.072
731,"S(0)",0,0,0,32.064
732,"SO4-2",-2,4,-.04,96.0616
733,"S2O3-2",-2,0,0,112.12
734,"SO3-2",-2,0,0,80.062
740,"Sb(OH)3",0,0,0,172.7719
741,"Sb(OH)6-1",-1,0,0,223.7938
742,"SbEDTA-1",-1,0,0,414
743,"SbHEDTA",0,0,0,415
744,"SbEDTA(OH)-2",-2,0,0,431
745,"SbEDTA(OH)2-3",-3,0,0,448
750,"Sc+3",3,0,0,44.956
760,"HSe-1",-1,0,0,79.97
761,"HSeO3-1",-1,0,0,127.97
762,"SeO4-2",-2,4,0,142.96
770,"H4SiO4",0,0,0,96.1155
780,"Sm+3",3,0,0,150.36
790,"Sn(OH)2",0,0,0,152.7246
791,"Sn(OH)6-2",-2,0,0,220.7538
800,"Sr+2",2,5,0,87.62
801,"Tb+3",3,0,0,158.925
```

Posted by Jon Petter Gustafsson on August 15, 2016

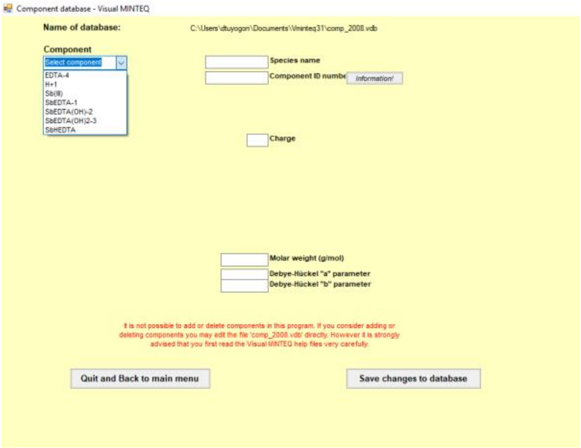
This version from October 2012 is still available on the site although I strongly recommend version 3.1 as

742,"SbEDTA-1",-1,0,0,414

743,"SbHEDTA",0,0,0,415

744,"SbEDTA(OH)-2",-2,0,0,431

745,"SbEDTA(OH)2-3",-3,0,0,448



Name of database: C:\Users\dtuyogon\Documents\Vminteq31\comp_2008.vdb

It is not possible to add or delete components in this program. If you consider adding or deleting components you may edit the file 'comp_2008.vdb' directly. However it is strongly advised that you first read the Visual MINTEQ help files very carefully.

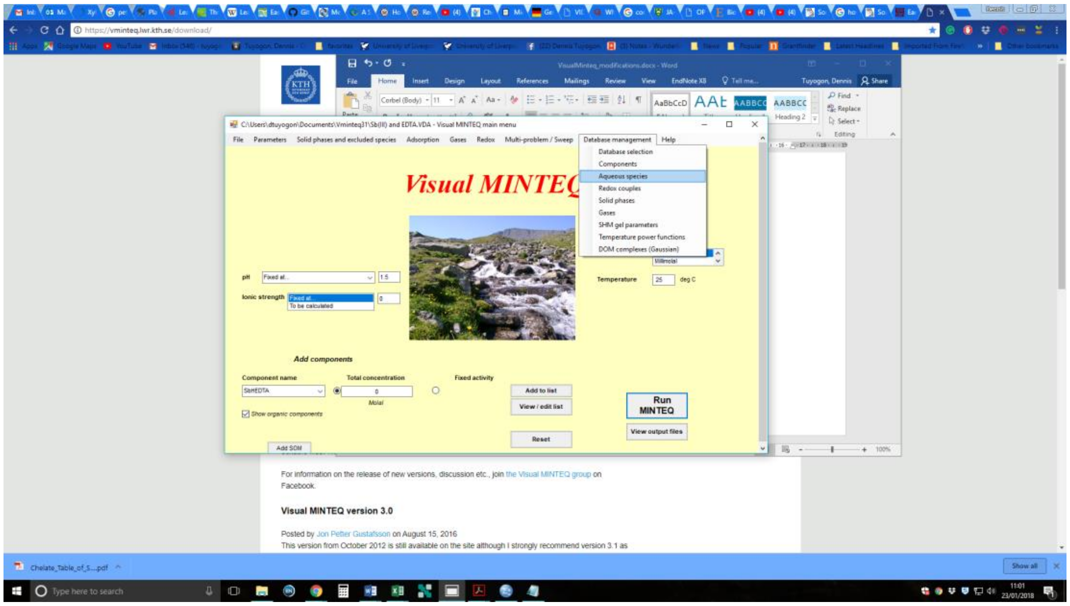
Addition of thermodynamic data

Main thermodynamic database:

C:\Users\dtuyogon\Documents\Vminteq31\thermo.vdb

Decided to add the species 3309596 (after the EDTA series)

Visual Minteq –database selection-aqueous species-add new species



C:\Users\dtuyogon\Documents\Vminteq31\Sb(III) and EDTA.VDA - Visual MINTEQ main menu

pH: Fixed at... 1.5

Ionic strength: Fixed at... 0 (To be calculated)

Millimolal

Temperature: 25 deg C

Component name: SbHEDTA

Total concentration: ● 0 Molal

Fixed activity: ○

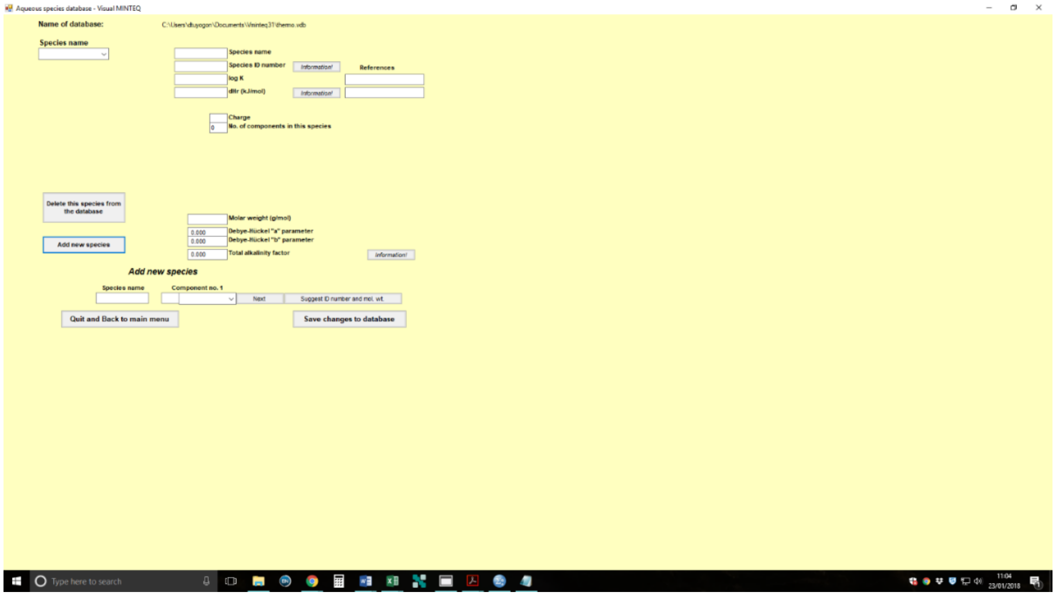
☑ Show organic components

For information on the release of new versions, discussion etc., join the Visual MINTEQ group on Facebook.

Visual MINTEQ version 3.0

Posted by Jon Petter Gustafsson on August 15, 2016

This version from October 2012 is still available on the site although I strongly recommend version 3.1 as



Aqueous species database - Visual MINTEQ

Name of database: C:\Users\dtuyogon\Documents\Vminteq31\thermo.vdb

Species name:

Species ID number:

log K:

dHr (kJ/mol):

Charge:

No. of components in this species: 0

Molar weight (g/mol):

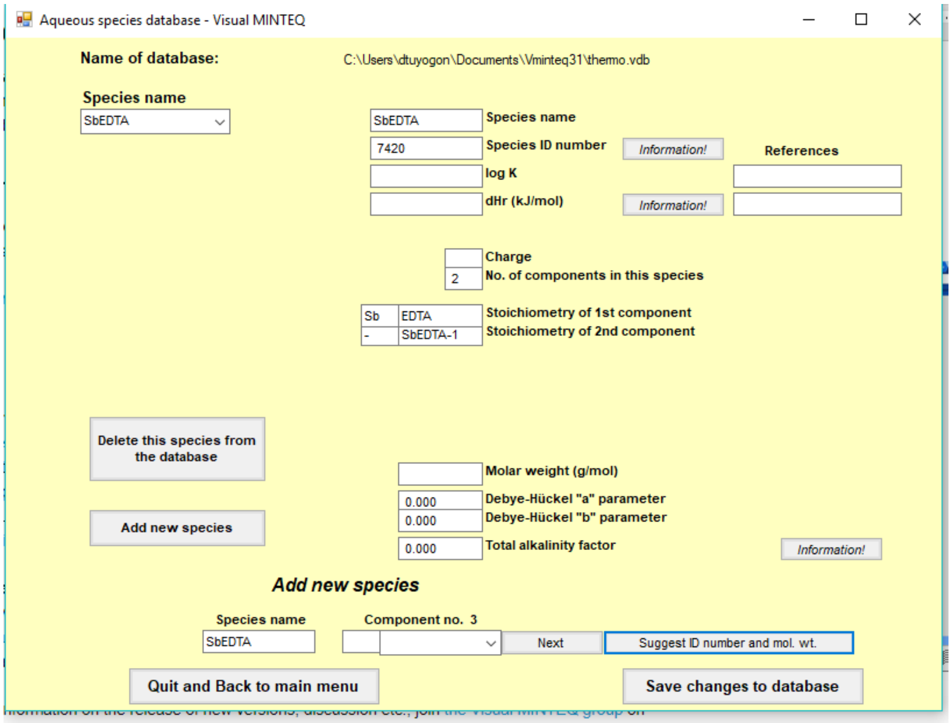
Debye-Hückel "a" parameter: 0.000

Debye-Hückel "b" parameter: 0.000

Total alkalinity factor: 0.000

Species name:

Component no. 1:



Name of database: C:\Users\dtuyogon\Documents\Vminteq31\thermo.vdb

Species name: SbEDTA

Species name: SbEDTA

Species ID number: 7420

log K:

dHr (kJ/mol):

References:

Charge:

No. of components in this species: 2

Stoichiometry of 1st component: Sb EDTA

Stoichiometry of 2nd component: - SbEDTA-1

Molar weight (g/mol):

Debye-Hückel "a" parameter: 0.000

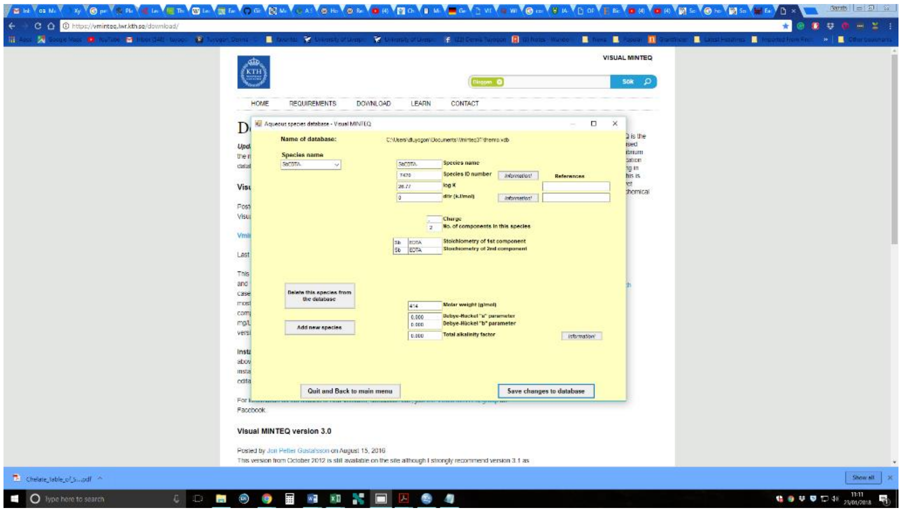
Debye-Hückel "b" parameter: 0.000

Total alkalinity factor: 0.000

Add new species

Species name: SbEDTA

Component no. 3



Name of database: C:\Users\dtuyogon\Documents\Vminteq31\thermo.vdb

Species name: SbEDTA

Species name: SbEDTA

Species ID number: 7420

log K: 26.77

dHr (kJ/mol): 0

References:

Charge: -

No. of components in this species: 2

Stoichiometry of 1st component: Sb EDTA

Stoichiometry of 2nd component: Sb EDTA

Molar weight (g/mol): 414

Debye-Hückel "a" parameter: 0.000

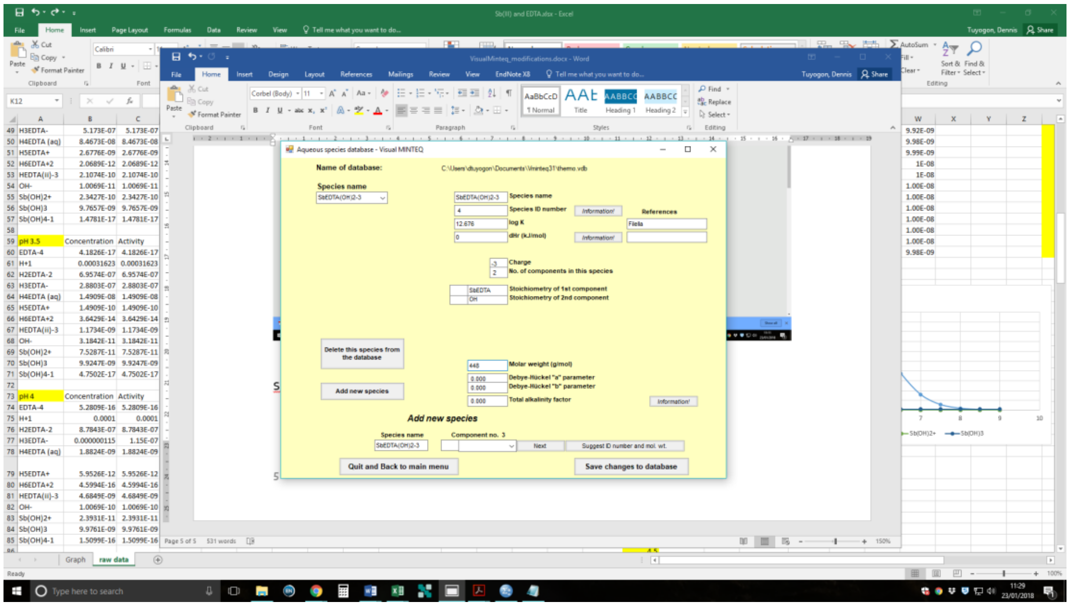
Debye-Hückel "b" parameter: 0.000

Total alkalinity factor: 0.000

Posted by Jon Petter Gustafsson on August 15, 2016

This version from October 2012 is still available on the site although I strongly recommend version 3.1 as

SbHEDTA(OH)2-3



	A	B	C	W
49	H3EDTA-	5.173E-07	5.173E-07	9.92E-09
50	H4EDTA (aq)	8.4673E-08	8.4673E-08	9.98E-09
51	H5EDTA+	2.6776E-09	2.6776E-09	9.99E-09
52	H6EDTA+2	2.0689E-12	2.0689E-12	1E-08
53	HEDTA(iii)-3	2.1074E-10	2.1074E-10	1E-08
54	OH-	1.0069E-11	1.0069E-11	1.00E-08
55	Sb(OH)2+	2.3427E-10	2.3427E-10	1.00E-08
56	Sb(OH)3	9.7657E-09	9.7657E-09	1.00E-08
57	Sb(OH)4-1	1.4781E-17	1.4781E-17	1.00E-08
58				1.00E-08
59	pH 3.5	Concentration	Activity	1.00E-08
60	EDTA-4	4.1826E-17	4.1826E-17	9.98E-09
61	H+1	0.00031623	0.00031623	
62	H2EDTA-2	6.9574E-07	6.9574E-07	
63	H3EDTA-	2.8803E-07	2.8803E-07	
64	H4EDTA (aq)	1.4909E-08	1.4909E-08	
65	H5EDTA+	1.4909E-10	1.4909E-10	
66	H6EDTA+2	3.6429E-14	3.6429E-14	
67	HEDTA(iii)-3	1.1734E-09	1.1734E-09	
68	OH-	3.1842E-11	3.1842E-11	
69	Sb(OH)2+	7.5287E-11	7.5287E-11	
70	Sb(OH)3	9.9247E-09	9.9247E-09	
71	Sb(OH)4-1	4.7502E-17	4.7502E-17	
72				
73	pH 4	Concentration	Activity	
74	EDTA-4	5.2809E-16	5.2809E-16	
75	H+1	0.0001	0.0001	
76	H2EDTA-2	8.7843E-07	8.7843E-07	
77	H3EDTA-	0.000000115	1.15E-07	
78	H4EDTA (aq)	1.8824E-09	1.8824E-09	
79	H5EDTA+	5.9526E-12	5.9526E-12	
80	H6EDTA+2	4.5994E-16	4.5994E-16	
81	HEDTA(iii)-3	4.6849E-09	4.6849E-09	
82	OH-	1.0069E-10	1.0069E-10	
83	Sb(OH)2+	2.3931E-11	2.3931E-11	
84	Sb(OH)3	9.9761E-09	9.9761E-09	
85	Sb(OH)4-1	1.5099E-16	1.5099E-16	

Aqueous species database - Visual MINTEQ

Name of database: C:\Users\dtuyogon\Documents\Vminteq31\thermo.vdb

Species name: SbEDTA(OH)2-3

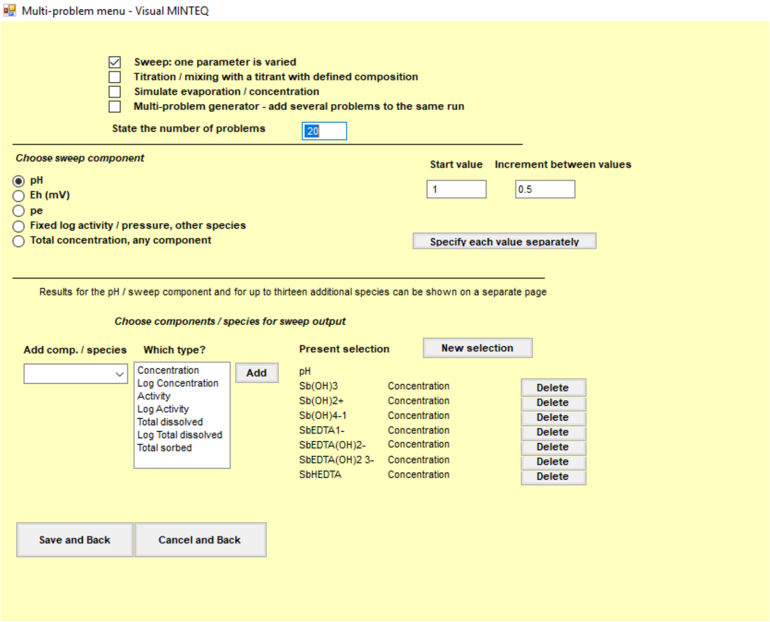
SbEDTA(OH)2-3 Species name
4 Species ID number
12.676 log K
0 dHr (kJ/mol)
References: Filella
-3 Charge
2 No. of components in this species
SbEDTA Stoichiometry of 1st component
OH Stoichiometry of 2nd component
448 Molar weight (g/mol)
0.000 Debye-Hückel "a" parameter
0.000 Debye-Hückel "b" parameter
0.000 Total alkalinity factor

March 20

C:\Users\dtuyogon\Documents\Vminteq31\comp_2008_v1.vdb

Multi-problem sweep

Reference: Filella 2005 Critical appraisal of available thermodynamic data for the compleaxtion……


Multi-problem menu - Visual MINTEQ

☑ Sweep: one parameter is varied
☐ Titration / mixing with a titrant with defined composition
☐ Simulate evaporation / concentration
☐ Multi-problem generator - add several problems to the same run

State the number of problems: 20

Choose sweep component

● pH
○ Eh (mV)
○ pe
○ Fixed log activity / pressure, other species
○ Total concentration, any component

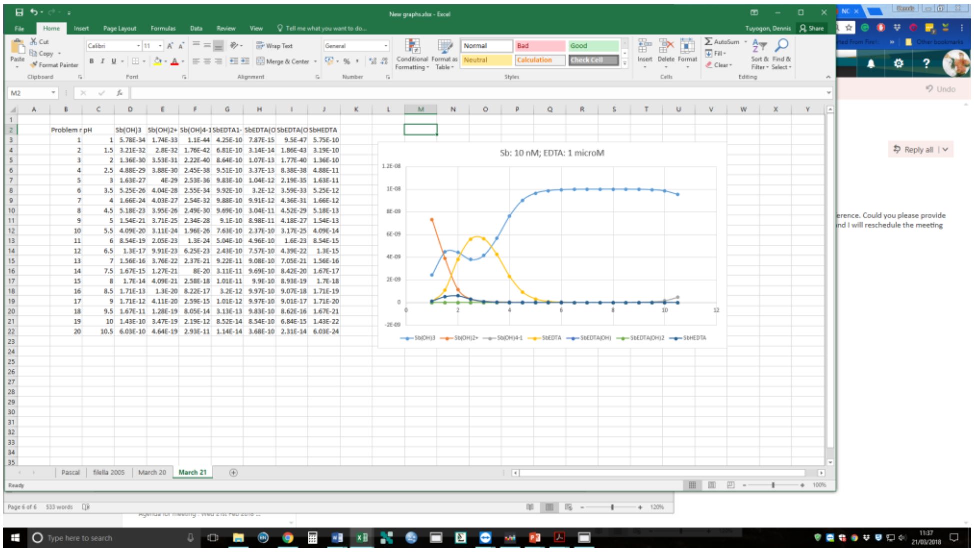
Start value: 1
Increment between values: 0.5

Results for the pH / sweep component and for up to thirteen additional species can be shown on a separate page

Choose components / species for sweep output

Present selection:

pH	
Sb(OH)3	Concentration
Sb(OH)2+	Concentration
Sb(OH)4-1	Concentration
SbEDTA1-	Concentration
SbEDTA(OH)2-	Concentration
SbEDTA(OH)2 3-	Concentration
SbHEDTA	Concentration



Problem r	pH	Sb(OH)3	Sb(OH)2+	Sb(OH)4-1	SbEDTA1-	SbEDTA(O	SbEDTA(O	SbHEDTA
1	1	5.78E-34	1.74E-33	1.1E-44	4.25E-10	7.87E-15	9.5E-47	5.75E-10
2	1.5	3.21E-32	2.8E-32	1.76E-42	6.81E-10	3.14E-14	1.86E-43	3.19E-10
3	2	1.36E-30	3.53E-31	2.22E-40	8.64E-10	1.07E-13	1.77E-40	1.36E-10
4	2.5	4.88E-29	3.88E-30	2.45E-38	9.51E-10	3.37E-13	8.38E-38	4.88E-11
5	3	1.63E-27	4E-29	2.53E-36	9.83E-10	1.04E-12	2.19E-35	1.63E-11
6	3.5	5.25E-26	4.04E-28	2.55E-34	9.92E-10	3.2E-12	3.59E-33	5.25E-12
7	4	1.66E-24	4.03E-27	2.54E-32	9.88E-10	9.91E-12	4.36E-31	1.66E-12
8	4.5	5.18E-23	3.95E-26	2.49E-30	9.69E-10	3.04E-11	4.52E-29	5.18E-13
9	5	1.54E-21	3.71E-25	2.34E-28	9.1E-10	8.98E-11	4.18E-27	1.54E-13
10	5.5	4.09E-20	3.11E-24	1.96E-26	7.63E-10	2.37E-10	3.17E-25	4.09E-14
11	6	8.54E-19	2.05E-23	1.3E-24	5.04E-10	4.96E-10	1.6E-23	8.54E-15
12	6.5	1.3E-17	9.91E-23	6.25E-23	2.43E-10	7.57E-10	4.39E-22	1.3E-15
13	7	1.56E-16	3.76E-22	2.37E-21	9.22E-11	9.08E-10	7.05E-21	1.56E-16
14	7.5	1.67E-15	1.27E-21	8E-20	3.11E-11	9.69E-10	8.42E-20	1.67E-17
15	8	1.7E-14	4.09E-21	2.58E-18	1.01E-11	9.9E-10	8.93E-19	1.7E-18
16	8.5	1.71E-13	1.3E-20	8.22E-17	3.2E-12	9.97E-10	9.07E-18	1.71E-19
17	9	1.71E-12	4.11E-20	2.59E-15	1.01E-12	9.97E-10	9.01E-17	1.71E-20
18	9.5	1.67E-11	1.28E-19	8.05E-14	3.13E-13	9.83E-10	8.62E-16	1.67E-21
19	10	1.43E-10	3.47E-19	2.19E-12	8.52E-14	8.54E-10	6.84E-15	1.43E-22
20	10.5	6.03E-10	4.64E-19	2.93E-11	1.14E-14	3.68E-10	2.31E-14	6.03E-24

M:\Dennis\Dissertation\Visual Minteq 3.1\new graphs.xls

8.2 Research Plan

Activities	2016							2017												2018												
	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	
1. Electroanalytical method training -As	■	■																														
2. Au microwire fabrication (10 and 25 uM)		■	■																													
3. Method Development-Arsenic (SW, DP, LSV and PSA techniques)			■	■	■																											
4. Calibration Curves						■	■																									
5. Stability and Reproducibility Tests								■	■	■										■	■	■										
6.Method Development-Antimony III and V										■	■	■										■	■	■								
7. Sb(V) with humic acid, and stability contant determination													■	■											■	■						
8. Hydroponic experiment- cucumbers a. plant growth analysis b. sample collection and storage													■	■											■	■						
9. Sb(III) with ligands and stability constant determination a. calculations b. experimental													■	■											■	■						
10. Measurements with real samples a. LC-ICP-MS b. voltammetry												■	■	■										■	■	■						
11 Write-up Introduction and Related Literature													■	■											■	■						

(SW) Square Wave voltammetry, (DP ASV) Differential Pulse Anodic Stripping Voltammetry, (LSV) Linear Sweep Voltammetry and (PSA) Potentiometric Stripping Analysis

Activities	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M
NTHU- Taiwan Hydroponic experiment- cucumbers A. preparation B. set-up	■	■	■	■	■	■	■	■													
Germination		■	■	■	■	■	■	■													
Sample collection: roots/stem/leaves/sap								■	■	■											
As(III) 26 and 35 dat (x3)								■	■	■											
Sb(III) 26 and 35 dat (x3)								■	■	■											
Se(IV) 26 and 35 dat (x3)								■	■	■											
ICP-MS analysis of xylem sap								■	■	■											
Plant sample drying									■	■											
Grinding and Acid digestion									■	■											
Plant growth parameters										■	■	■									
Statistics										■	■	■									
Write-up (Back to UK)													■	■	■	■	■	■			
Thesis Submission																			■		
VIVA																					■