UNIVERSITY OF LIVERPOOL

A STUDY OF HALOMETHANES IN WATERS ASSOCIATED WITH THE PRODUCTION OF POTABLE WATER BY DESALINATION, IN KUWAIT.

Thesis submitted in accordance with the requirements of the University of Liverpool for the degree of Doctor in Philosophy

by

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The thesis describes a study of the types and concentrations of halomethanes in the waters utilized in or produced by the desalination process. The study also incorporates experimental investigation of some of the factors affecting the production of halomethenes in chlorinated waters.

The study includes a description of the analytical procedure. This involves extraction of the sample with n-pentane (Henderson **et al.**, 1976) followed by determination of the halomethanes by gas chromatography. Details of the quality assurance procedures are also described.

A limited experimental study has been made of the effects of such factors as chlorine dose, reaction time, the presence of naturally occurring suspended solids, ammonia, chlorophyll (as cells of the alga **Chlorella sp.**) and the water soluble fraction (WSF) of Kuwait crude on the production of halomethanes. The results showed that bromine-containing compounds predominate in the halomethanes produced upon chlorination. Moreover, there was a shift towards the dominance of bromoform as the background bromide concentration increased. The results also suggest that increases in reaction time, chlorine dose and WSF of crude oil have a positive effect on the production of halomethanes, whereas ammonia and naturally occurring suspended solids (comprised of plankton and marine detritus) have a retarding effect. The presence of **Chlorella sp.** cells in chlorinated sea water failed to produce a significant increase in the production of halomethanes.

The results of the field investigations on the distribution of halomethanes are summarised in Chapters 3-5. A study of the coastal waters close to the desalination plants indicated that the concentrations of halomethanes (primarily bromoform and dibromo chloromethane) were highest in the Shuwaikh area, a mean

value of 10.8 ± 18.6 and a maximum of 85 μg/l was detected, whereas the concentrations in Doha and Shuaiba were significantly lower (the maximum concentrations did not exceed 20 μg/l in either areas).

The production of halomethanes during the desalination process is apparently enhanced by the high temperatures and vigorous agitation as evidenced by the detection of concentrations reaching up to 350 μg/l in samples taken from the distillation chambers. However, a large proportion of the halomethanes produced is apparently vented via the air ejectors provided to create the vacuum required for the flash boiling of seawater and to remove corrosive gases (i.e. CO_2 and O_2).

The concentrations of halomethanes in the drinking water supplies of Kuwait also showed a dominance of the bromine-containing halomethanes. The mean concentrations of bromoform in over 100 samples collected from homes and public buildings was 13.6 ± 4.6 μg/l followed by dibromochloromethane (8.8 ± 3.7 μg/l) and dichlorobromomethane (3.3 ± 1.5 μg/l). Chloroform and carbon tetrachloride were detected in few samples in trace concentrations. However, their presence could not be substantiated because of contamination problems.

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CHAPTER 1

General Introduction

Objectives and Methods of Halogenated Organics Analysis

1.1 Background and Objectives of the Study

1.1a Background

Chlorine gas has been used as a bleaching agent in industry since the beginning of the last century and has since become one of the most important industrial chemicals (Davis and Middaugh, 1978). Chlorine was used in 1854 to deodorize London sewage and then as a sewage disinfectant in 1879 (White, 1972). Subsequently, it was used in 1904 to disinfect water supplies on a continuous basis (Laubusch, 1972).

Chlorination is still widely applied in the treatment of domestic water supplies, in sewage treatment plants and in industrial installations. Large quantities of chlorine gas or sodium hypochlorite are used industrially in power plants to prevent the growth of bacteria and microalgae on condenser tubes and the fouling resulting from the settling of barnacles and mussel larvae (Morris, 1971; White, 1972; Burton and Liden, 1978; Waite **et al.**, 1978 and Garey, 1980). The use of chlorine has drastically reduced infections from waterborne diseases and industrially has reduced fouling problems with water used for cooling purposes. However, over the past ten years, intensive research has been revealing that chlorination may have undesirable effects on human health and on the ecology of surface waters receiving chlorinated effluents (Davis and Fava, 1983). Thus, volatile organic compounds containing chlorine and/or bromine were detected in drinking water supplies by Rook (1974), Bellar **et al.**, (1974) and Symons **et al.**, (1975). Moreover, the use of sophisticated extraction and analytical techniques has allowed some less-volatile halogenated organics to be detected in surface waters, chlorinated sewage and cooling water effluents, Jolley (1975), Pitt **et al.**, (1975) and Keith **et al.**, (1976). Such findings have caused concern among health agencies, especially over the effects on human health in terms of potential carcinogenicity and mutagenicity (Simmon and Tardiff, 1978; Cumming, 1978; Wilkins **et al.**, 1979; Shy and Struba, 1980;

Cantor, 1983 and Bull, 1982). Damage to fisheries resources and the ecology of the aquatic systems in general have also been of concern as evidence for the deleterious effect of chlorination has increased. Such effects include changes in behavioural patterns, stress and physiological disorders, inhibition of the photosynthesis of aquatic plants and lethal effects on larvae and adult marine organisms (Gehrs **et al.**, 1974; Whitehouse, 1975; Davis and Middaugh, 1978; Larrick **et al.**, 1978; Laird and Roberts, 1980; Turner and Thayer, 1980; Payne **et al.**, 1980; Sanders and Ryther, 1980; Scott **et al.**, 1982; Davis and Fava, 1983, and Sanders, 1984). This concern has already led to greater efforts to find alternative disinfectants and biofouling-control methods, as well as to the development of methods for the dechlorination of effluents before they are discharged into the aquatic environment (Rook et **al.**, 1978; Burton and Liden, 1978; Waite **et al.**, 1978; Helz and Kosak-Channing, 1980; Garey, 1980 and Helz and Kosak-Channing, 1984).

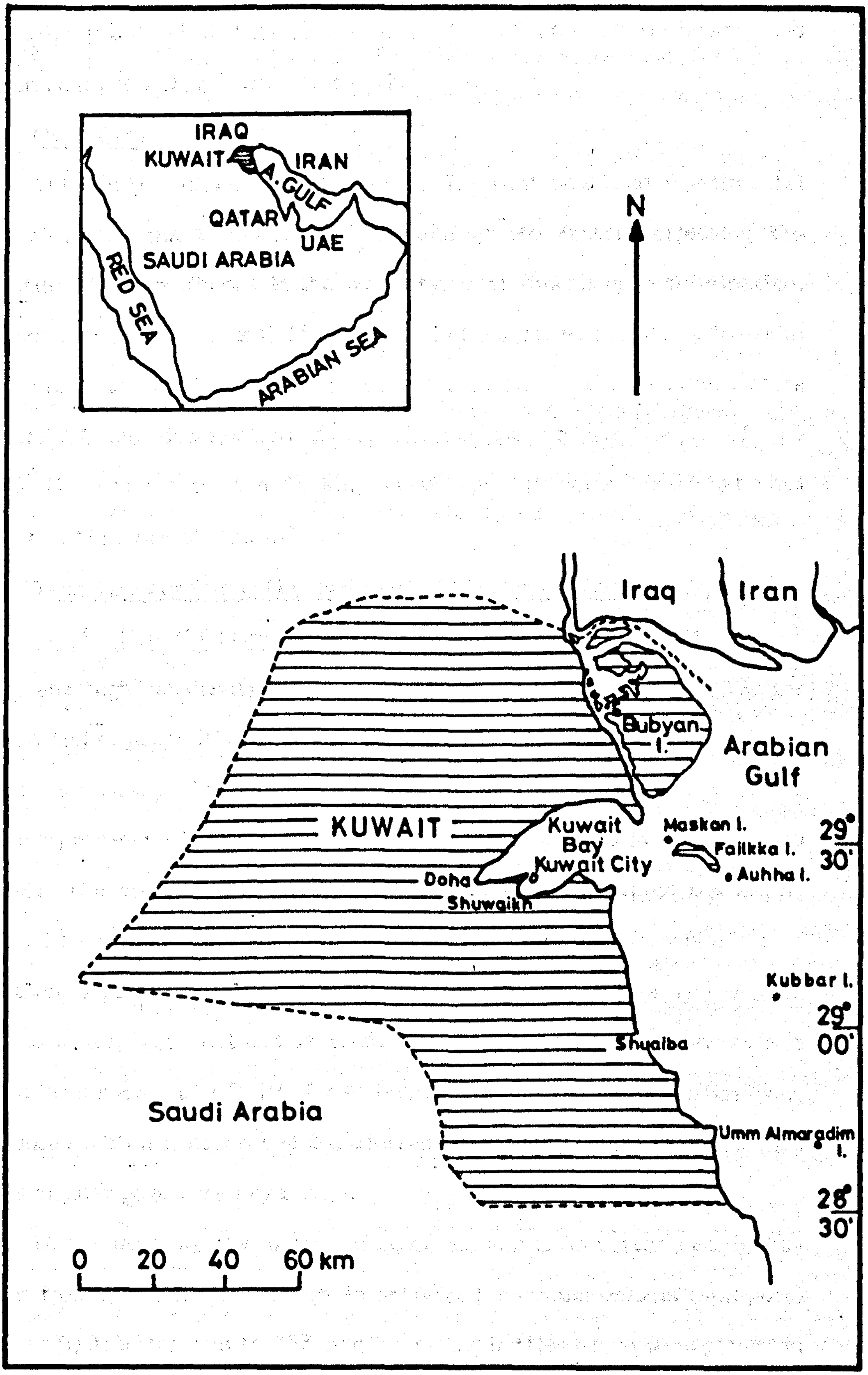
However, it seems that there is a general agreement that it would be premature to alter present disinfection practices (i.e. chlorination) or to seek alternative disinfectants before a better understanding of the pathways, mechanisms and products of chlorination is acquired (Becking and MacGregor, 1978).

Most research on the formation of halogenated organic compounds during chlorination has focused on the interaction between the halogens and the naturally occurring humic materials in surface and ground waters in temperate climates. There have been no detailed studies on the formation or fate of this group of compounds in highly saline and warm marine waters or on their formation during desalination of sea water and in the produced distillate.

Desalination is a method of producing potable water which is utilized mainly in arid countries with cheap fuel supply for the dual purpose of generating electricity and producing distilled water. The produced distillate is usually adjusted by the addition of NaOH and then blended with brackish water to replenish its salt content and render it palatable.

The present study is an attempt to determine the levels of some of the volatile halogenated organics in the waters associated with the desalination process in Kuwait. Kuwait is an arid country located on the north western side of the Arabian Gulf, (Figure 1.1). Until the turn of the century, the population of Kuwait (estimated as 70,000 in 1925) relied mainly on shallow wells which produced limited quantities of drinkable water and on the transport of river water from Iraq by dhows (WRDC, 1973). The discovery of oil in the region, enabled Kuwait and several of the neighbouring Arab countries to invest in desalination-power plants to meet the demand for electricity and fresh water caused by the rapid increase in population and industrial activity. Desalination plants utilize chlorine for the disinfection of sea water used in the desalination process and to combat the high rates of bio-fouling in the warm and oxygen-rich waters of the Gulf. Other heavy industries, mainly the petrochemical plants, also utilize sea water for cooling and hence consume chlorine. The large industrial complexes consisting of desalination-power plants, refineries and other petrochemical industries and harbours represent a consistent pattern among the Gulf states. This input of chlorinated effluents and petroleum-derived pollutants is matched by the release of domestic effluents from coastal cities and agricultural run-off carried down by the rivers from Iraq and Iran (ROPME, 1984). Thus, the formation of halogenated compounds would be expected, not only from the interactions of chlorine with the naturally occurring substances in sea water, but also from its reactions with some of the materials contained in these effluents. The potential effects on the

Figure 1.1 A map of Kuwait showing its location relative to the Arabian Gulf and the Arabian Sea.


IRAQ
KUWAIT
IRAN
A. GULF
QATAR
UAE
SAUDI ARABIA
RED SEA
ARABIAN SEA
N
Iraq
Iran
Bubyan I.
Arabian Gulf
KUWAIT
Kuwait Bay
Kuwait City
Doha
Shuwaikh
Maskan I.
Failkka I.
Auhha I.
29° 30'
Kubbar I.
29° 00'
Shuaiba
Saudi Arabia
Umm Almaradim I.
28° 30'
0 20 40 60 km

ecology of the Gulf and the quality of sea water used for desalination (and hence the produced distillate) are a matter of concern to health and environment protection authorities in the region.

1.1b Objectives

This study is divided into two parts. The first part is an experimental study aimed at the identification of some of the factors affecting the formation of halomethanes in the water types of Kuwait upon chlorination. The second part is a field assessment of the levels of halomethanes in three areas in which chlorine is utilized, including the coastal waters offshore of the desalination power plants, the various stages of the desalination process and the drinking water supply network (including homes and public buildings of Kuwait).

1.2 Techniques of Extraction and Analysis of Halomethanes

1.2a Preparation of Glassware and Other Materials used in the Study

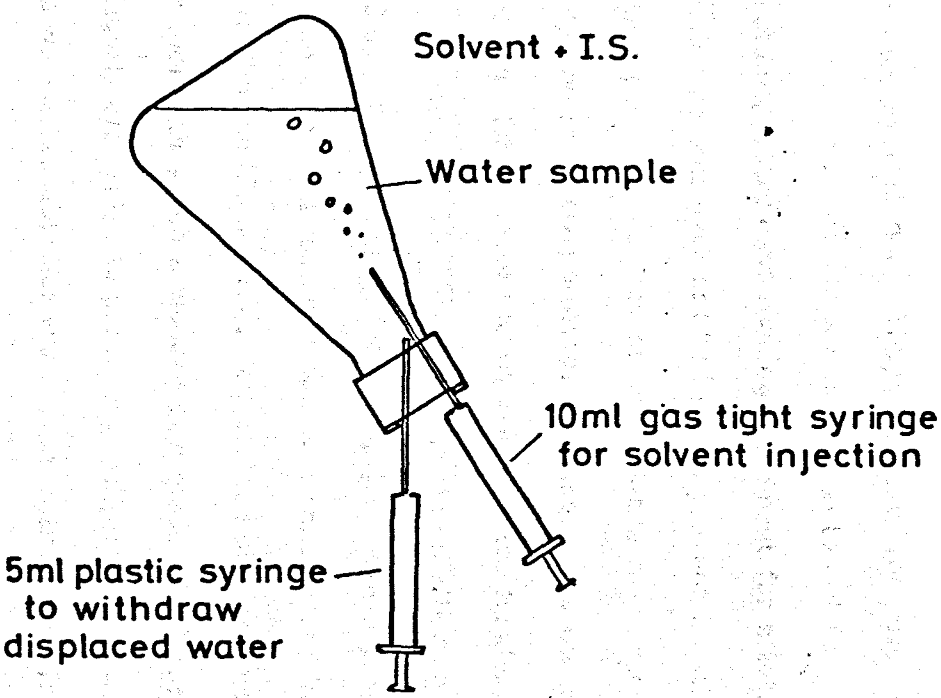
The high sensitivity of the Electron Capture Detector (ECD) for halogenated organics (the detection limit reported by the manufacturer is in the picogram range for lindane) made it necessary to employ a vigorous cleaning procedure for glassware and other materials used in sampling and analysis. This involved washing in hot soapy water, rinsing in hot tap water, followed by rinsing in distilled water. A 20% solution of hydrochloric acid was then used to rinse the items followed by consecutive rinses with distilled water, methanol and acetone. After air drying, most glassware was heated in an oven set at 250°C for 48 hours. Volumetric glassware however, was rinsed with n-pentane and transferred to a drying oven. Items cleaned in this manner gave very low blanks.

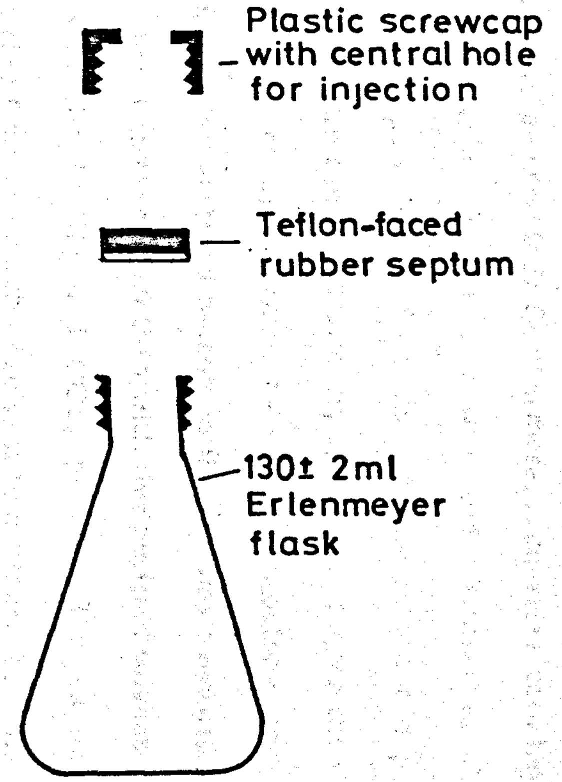
Water used in the preparation of standards was rendered hydrocarbon free by passing it through an activated charcoal column (Millipore) followed by transference to 250 ml gas washing bottles which were placed in a water bath at 80°C and sparging for 20 minutes with purified nitrogen at a flow rate of 30 ml/min. The nitrogen gas used for sparging was passed, before usage, through gas-line purifying bottles (Chrompack), one packed with activated charcoal and the other with silica gel and molecular sieve No. 13. Water cleaned in such a manner gave contamination-free blanks when it was extracted with n-pentane then injected into the gas chromatograph.

1.2b Extraction of Halomethanes

Several techniques for the extraction of halomethanes have been reported in the literature. They include liquid-liquid extraction, liquid-vapour phase extraction and liquid-solid extraction on media such as activated charcoal, Tenax, Amberlites-XAD, gas-chromatographic solid supports coated with adsorbers or polyurethane foam (Burnham **et. al.**, 1973; Bellar and Lichtenberg 1974; Henderson **et. al.**, 1976; Kissinger and Fritz, 1976; Richard and Junk, 1977; Trussell **et al.**, 1978; Quimby **et al.**, 1979; Mieure, 1980 and Keith **et al.**, 1983). For the present work a solvent extraction technique was selected for the determination of halomethanes in samples from desalination plants, drinking water and sea water. The procedure described by Henderson **et al.**, (1976) was selected since it was found to be relatively simple, required no special accessories and achieved a high extraction efficiency. However, it was found to be time consuming. The samples were transferred to a precleaned Erlenmeyer screwcap flask (with a mean volume of 131 ml ± 2.2 ml) closed with a plastic cap lined with a Teflon-faced rubber septum. Care was taken not to allow air bubbles to become trapped. A 5 ml aliquot of glass-distilled GC-grade n-pentane (containing 107.1 ug/l of 1,1,1-trichloroethane as internal standard) was injected using a 10 ml gas-tight syringe while the excess sample was displaced into an empty 5 ml plastic syringe inserted simultaneously. The technique is depicted in Figure (1.2). n-Pentane was selected, despite its low boiling point, since it produced the least amount of interference with

Figure 1.2 Solvent injection technique

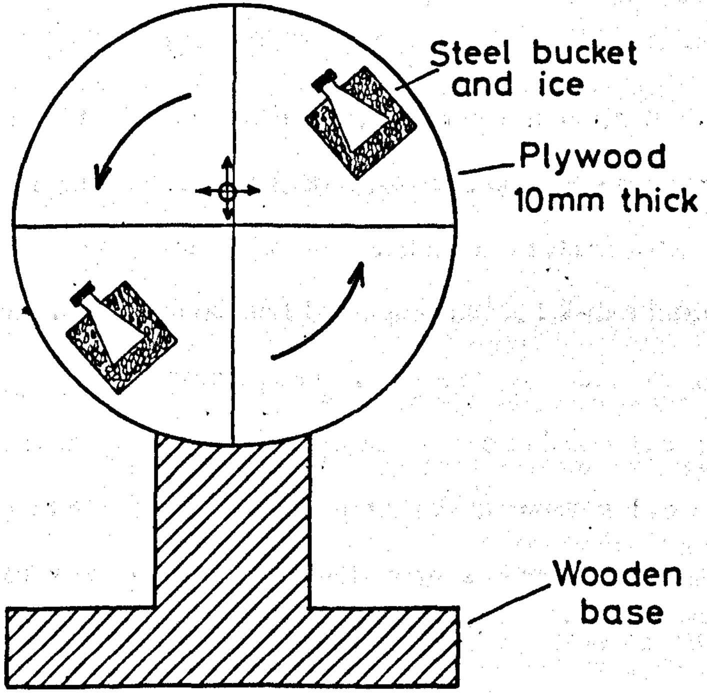

Solvent + I.S.
Water sample
10ml gas tight syringe for solvent injection
5ml plastic syringe to withdraw displaced water


Plastic screwcap with central hole for injection
Teflon-faced rubber septum
130± 2ml Erlenmeyer flask

the halomethanes to be detected. Furthermore, recoveries were higher than when an equivalent volume of n-hexane was used. Trussell **et al.**, (1978) have reported that partition coefficients with n-pentane and petroleum ether (b.p.30-60°C) are similar. However, both were higher than those of other solvents such as cyclohexane, n-hexane, iso-octane and toluene. Commerical grade glass-distilled n-pentane (Fluka) was re-distilled before use for extraction. However, even then with this purified solvent there was interference with the $CHCl_3$ and CCl_4 peaks. The extent of this interference varied from one batch of solvent to another. To minimize such effects, hydrocarbon-free water was used as a blank to enable allowances to be made for the concentrations obtained for these two compounds.

Several shaking techniques were tested to determine the most efficient extraction method. They included the use of a horizontal laboratory shaker, two shakers (one mounted on top of the other) shaking in opposite directions, rotary hand shaking movement for a total of 10 minutes with five cooling periods over crushed ice to prevent bursting the flask by the evaporating pentane and loss of the volatile halomethanes under the effect of body and room temperatures and finally the use of an ultrasonic bath with cooling. Of all these techniques, only the hand shaking technique produced an efficiency of 68-70%, the remaining methods gave efficiencies of about 60%. Beside being laborious, hand-shaking was not always reproducible. So a vertical rotary shaker was constructed in the laboratory by Mr A. Abu-Ghasiba (Figure 1.3). It consisted of a commercial GM wind-screen wiper motor to which a wooden disc made of 10 mm thick plywood was fitted slightly off centre to produce an elliptical motion. Two stainless steel buckets with detachable lids were fixed on the disc. The sample flasks which were filled with crushed ice were placed inside the ice buckets. The lids were then replaced and tightened by two screws. It was found that maximum extraction could be achieved if the flasks were hand-shaken using

Figure 1.3 Vertical Rotary Shaker used in the extraction of halomethanes from water.


Steel bucket and ice
Plywood 10mm thick
Wooden base

rotary motion for two minutes followed by 40 minutes of shaking on the rotary shaker at a speed of about 110 rpm. Data on the efficiency of extraction obtained by the method will be presented in the section dealing with quality assurance.

1.2c Selection of Internal Standard for the Analysis

A number of compounds were tested for possible application as internal standards, but were found to be unsuitable because; (i) their retention times coincided with those compounds of interest, (ii) the sensitivity is low relative to those of the halomethanes (iii) they were present in trace amounts in some of the water samples tested. The samples examined included drinking water, distillate, brine and sea water from the desalination plants intakes. Duplicate samples were examined on three occasions, one of these was extracted with n-pentane only and the other was extracted with n-pentane containing the intended internal standards. On the basis of these criteria, it was found that bromomethane, 1,2-dichloroethane, tetrachloroethylene and trichloroethylene were not suitable as internal standards. 1,1,1-Trichloroethane was selected as internal standard since it was not found in any of the samples examined and because it has an ECD sensitivity similar to that of the halomethanes studied. However, its retention time was not central among those of halomethanes found in the water, since it came second to chloroform, in the mixture of six compounds studied.

A stock solution of the internal standard was prepared by transferring, with a gas-tight syringe, 0.5 ml into 40 ml of glass-distilled ultra pure methanol (Fluka) contained in a 50 ml Volumetric flask and diluting to volume with methanol. This stock solution was used weekly to prepare a working standard. To do this a 0.1 ml aliquot of the methanol stock solution was transferred to a 50 ml volumetric flask containing double distilled n-pentane (Fluka). This solution was further diluted by transferring

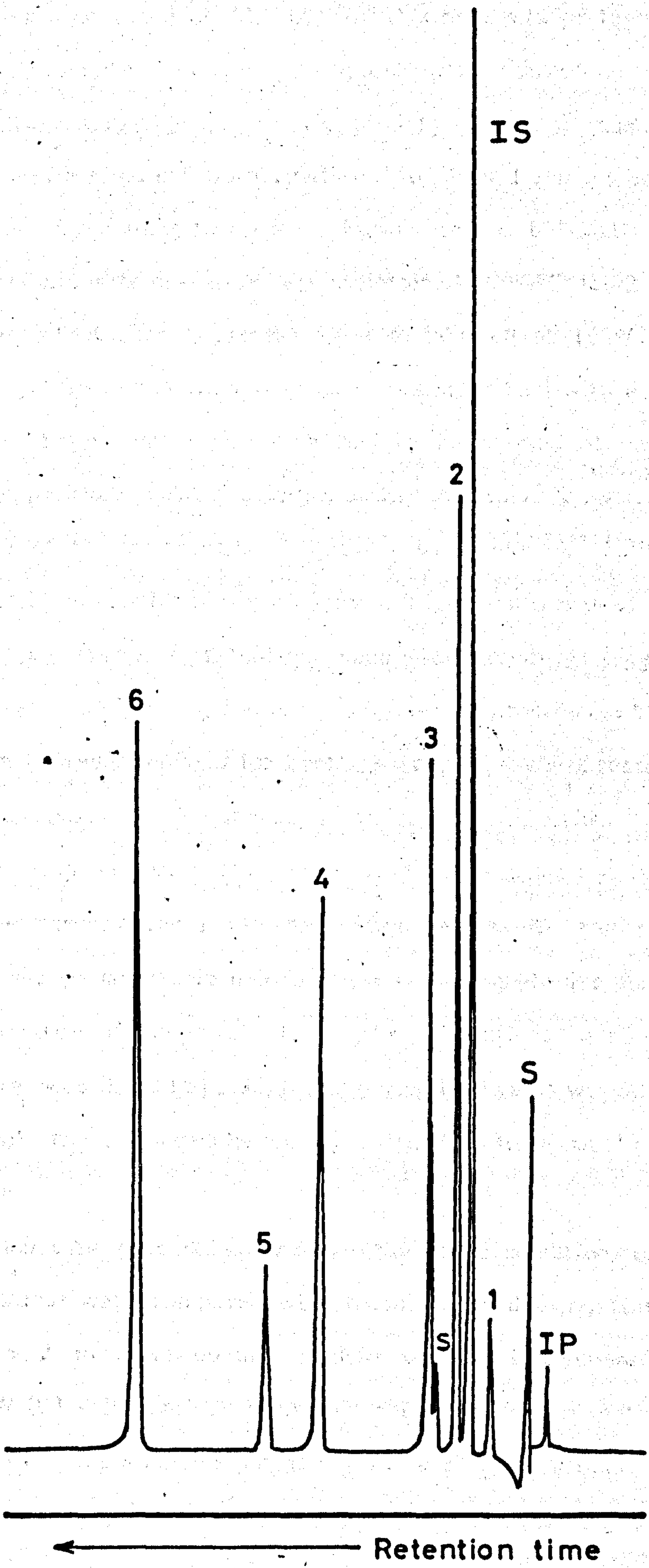
2 ml into 500 ml n-pentane in a volumetric flask. The final working solution contained 107.1 µg/l of the internal standard. The solution was distributed into several 50 and 25 ml volumetric flasks which were filled to the top, capped tightly, transferred to a plastic box and stored in a small refrigerator assigned specially for the storage of the solvent. Each day a new flask was opened and 5 ml aliquots of the solution were used for the extraction of water samples.

1.2d Analysis of Halomethanes

Qualitative determination of halomethanes and tetrachloroethylene present in the water samples were based on comparison of the GC records of the sample extracts in n-pentane containing the internal standard with those of the pure individual compounds of interest. Solutions of chloroform, carbon tetrachloride, dichlorobromomethane, dibromochloromethane, tetrachloroethylene and bromoform (Fluka, Puriss grade) were prepared in n-pentane containing the internal standard and individually injected several times into a Pye Unicam GCV Gas Chromotograph fitted with an ECD using ^{63}Ni as the electron source. The absolute and relative retention time of each was recorded (assigning a value of 100 to the absolute retention time of the internal standard). Then, starting with the bromoform solution, the other compounds were added one at a time and in each case the mixture was injected into the GC at least 12 times using different dilutions. A typical chromatogram obtained with the final mixture is shown in Figure (1.4). The 25 m capillary column used in the analysis was a 3% SE-30 SCOT column (GSC) with 0.5 mm internal diameter. Ultra pure helium gas (99.999%, Matheson), which had been purified by passage through gas-line purifiers (a trap packed with silica gel - Molecular Sieve 13 and acitivated charcoal, Chrompack), was used as carrier gas at a flow rate of 2.8 ml/min. Argon-methane gas mixture (95 to 5%, Matheson) which had also been passed through gas-line purifiers was used both as a quench and a make up gas. The

Figure 1.4 A typical chromatogram of the mixture of standards in n-pentane containing the Internal Standard.

I.P.	Injection peak
S.	Solvent peak
I.S.	Internal Standard
1.	$CHCl_3$
2.	CCl_4
3.	$CHCl_2Br$
4.	$CHBr_2Cl$
5.	$Cl_2C{=}CCl_2$
6.	$CHBr_3$


IS
2
6
3
4
S
5
1
s
IP
Retention time

total gas flow was maintained at 80 ml/min. This high rate of flow was required to ensure complete flushing of the detector which (according to the manufacturer's literature) has a relatively large internal chamber. Chromatography was carried out isothermally at 50°C for 1 minute before using temperature programming to raise the temperature to 80°C at a rate of 2°C/min. Finally, the temperature was maintained at 80°C for 2 min. The injector and detector temperatures were maintained at 100°C and 180°C respectively. Since the GC model used was not fitted with a sub-ambient kit, the temperature programme had to be started at such a relatively high temperature that the columns ability to resolve the solvents' peaks from those of the compounds of interest was reduced. Splitless injection was used in the analysis. An electronic integrator was used (Pye Unicam, CPD1) to measure retention time and areas of peaks. Concentrations were determined by the use of a computer programme based on the calibration curves developed for each compound. A chart recorder was also used to obtain the chromatograms for each injection. The integrator's attenuation was set at 16. The minimum area count was set at 1000 whereas the rest of the parameters (e.g. peak width and slope sensitivity) were set on automatic mode, which was adequate for such a relatively simple mixture of compounds. Under these conditions the number of theoretical plates was found to be 36,000 (the supplier's value was 50,000 for a 40 m column). the calculated height equivalent to a theoretical plate (HETP) was 0.1 mm.

The retention time data obtained under the above conditions using the 3% SE-30 Column were compared with those obtained using similar conditions with a 2 m glass column packed with 10% squalene on Chromosorb C/AW (80 - 100 mesh). With this column an argon methane mixture (95/5) was used as a carrier gas at a flow rate of 60 ml/min. The initial column temperature of 50°C was initially held for 6 minutes and then heated at 2°C/min to a final temperature of 90°C which was maintained for 3 minutes. The injector temperature was set at 120°C and the detector at 200°C. Attenuation was at 16 and the chart speed was 1 cm/min. Absolute and relative retention times found for the halomethanes on both columns are shown in Table (1.1). the table also includes for purposes of comparison the order of elution reported by Suffet **et al.**,(1976). The halomethanes were eluted from both columns (the capillary and the packed columns) in an order approximate to their boiling points and molecular weights. The correlation between the relative retention times and molecular weights of the four haloforms and CCl_4 is shown in Figure 1.5. The five halomethanes were also shown to be eluted in a similar order by Henderson **et al.**,(1976) who used a 2 m glass column packed with 10% squalene on Chromosorb. An attempt was also made to confirm the order of elution by GC-MS. The n-pentane extract of the mixture of standards (and of a sample drinking water) was evaporated with a stream of nitrogen and the concentrate was injected into a Hewlett Packard 5993- GC/MS system, consisting of 5995-Gas chromatograph/Mass Spectrometer and 1000 E series computer. The column used was a 12 m fused silica capillary coated with SE30. However, of the mixture of compounds, the presence of only $CHBr_3$ and $CHBr_2Cl$ could be established by matching their spectra with those in the National Bureau of Standards Library (NBS) of priority pollutants supplied with the system.

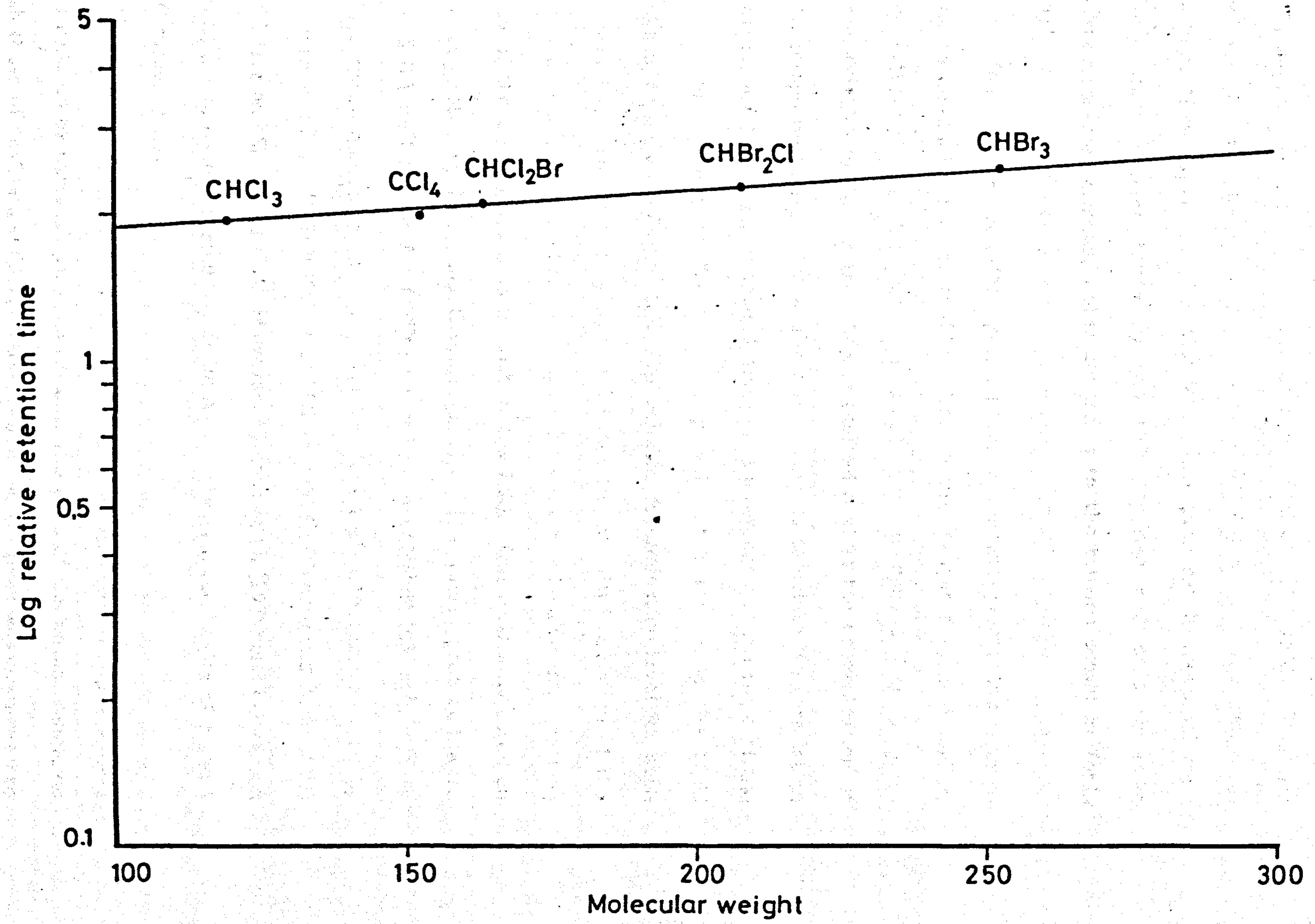
The linear response range of the ECD for $CHCl_3$, CCl_4, $CHCl_2Br$, $CHBr_2Cl$ and $CHBr_3$ was established next. A mixture of the pure compounds was prepared in glass-distilled methanol (Fluka) and from this serial dilutions were prepared in hydrocarbon-free water covering the range from 0.6 to 500 µg/l. The mixtures were extracted in n-pentane, using tetrachloroethylene as internal standard (its use was abandoned later as it was found in trace amounts in some sea water samples). $CHBr_3$ showed a linear response up to 500 µg/l, with a correlation coefficient of 0.9976

Compound	Boiling Point °C (CRC, 1975-1976)	Molecular Weight	Relative Retention Time (RRT) Column 1* (22 Samples)	Relative Retention Time (RRT) Column 2** (16 Samples)	(a) Order of Elution Suffet et al. 1976
			RRT, I.S. = 100	RRT, I.S. = 100	
Chloroform	61.7	119.38	88	31	1
1,1,1-Trichloroethane (I.S.)	74.1	133.41	100	N.A.	2
Carbon Tetrachloride	76.5	153.82	108	54	3
Dichlorobromomethane	90	163.83	123	65	4
Trichloroethane (I.S.)	87	131.39	N.A.	100	N.I.
Dibromochloromethane	119 - 120	208.29	189	123	5
Tetrachloroethylene	121	165.83	216	-	6
Bromoform	149.5	252.75	292	190	7

*3% SE30 Capillary column, 25 meters in length, 0.5 mm in diameter
**10% Squalene 2 m glass column
(a) Numbers indicate the order of elution reported by Suffet et al. (1976)
N.A. Not Applicable
N.I. Not Included

Table 1.1 Absolute and Releative Retention Times of the Standards on Different Columns

Figure 1.5 Correlation between molecular weight and the log. value of the relative retention times for the four halomethanes and carbon tetrachloride used in the study.



5
1
0,5
0.1
Log relative retention time
100
150
200
250
300
Molecular weight
$CHCl_3$
CCl_4
$CHCl_2Br$
$CHBr_2Cl$
$CHBr_3$

whereas, the same level of correlation was achieved for the other components at lower upper limits of concentration (200 µg/l). This was followed by the preparation of calibration curves for the range of concentrations expected. The standards were prepared in methanol from which aliquots were taken by gas tight syringe and used to spike hydrocarbon-free drinking water according to the scheme shown in Table 1.2.

The standard solutions prepared in water were extracted with n-pentane containing the internal standard in the manner described earlier. The ratios of the integrated area of each compound (for a given concentration) to that of the I.S. was plotted against the concentration of each compound. Regression analysis was used to calculate the correlation coefficient (r) for each compound, the y-axis intercept and the slope of the line. The scattergram for each compound was drawn using the SPSS package, as shown in Figure 1.6. The reliable determination level for each compound was calculated by adding 6 times the standard deviation of the lowest concentration used and adding to the y-intercept value (representing ratio of the compound's area to that of the I.S.). This method is based on that suggested by Marr and Cresser (1983). The values produced were around 0.1 µg/l except for $CHBr_3$ which had a value of 0.3 µg/l. These values are in general agreement with the limits of detection reported by Kissinger and Fritz (1976); Kaiser and Oliver (1976); Richard and Junk (1977) and Dietz and Singley (1979). However, Symons **et al.**,(1975) and Henderson **et al.**, (1976) have reported higher limits of detection for $CHBr_3$ of 5 and 1 µg/l respectively.

The effect of solvent peak interference on those of $CHCl_3$ and CCl_4 was reduced by corrections. The ratio of the area of the peaks coinciding with those of $CHCl_3$ and CCl_4 to the area of the I.S. peak was considered to be the background and was therefore subtracted from the values obtained for the pure standards. However, it was realised that different solvent

Dilution Scheme	Concentrations					
	$CHCl_3$	CCl_4	$CHCl_2Br$	$CHBr_2Cl$	$Cl_2C{=}CCl_2$	$CHBr_3$
1. Stock solution in 100 ml MeOH concentrations expressed in µg/ml	4410	1590	3980	4900	1296	16920
2. 1.3 ml of stock solution into 100 ml MeOH (µg/ml)	57.33	20.67	51.74	63.7	16.848	219.69
3. 4 ml of stock solution (2) into 50 ml MeOH (µg/l)	4586.4	1653.6	4139.2	5096.0	1347.8	17596.8
4. 0.2 ml of stock solution (3) (into 1000 ml hydrocarbon-free water (µg/l)	0.9	0.3	0.8	1.0	0.3	3.5
5. 0.5 ml of stock solution (3) into 500 ml water (µg/l)	4.6	1.7	4.1	5.2	1.7	17.6
6. 1.5 ml of stock solution (3) into 500 ml water (µg/l)	13.8	5.0	12.4	15.3	4.0	52.8
7. 2 ml of stock solution (3) into 250 ml water (µg/l)	36.7	13.2	33.1	40.8	10.8	140.8
8. 5 ml of stock solution (3) into 250 ml water (µg/l)	91.7	33.1	82.8	101.9	27.0	351.9

Table 1.2 Preparation of Standard Solution of Halomethanes and Tetrachloroethylene

Figure 1.6 a to f

Calibration curves used in the quantitive analysis of halomethanes

a) $CHCl_3$

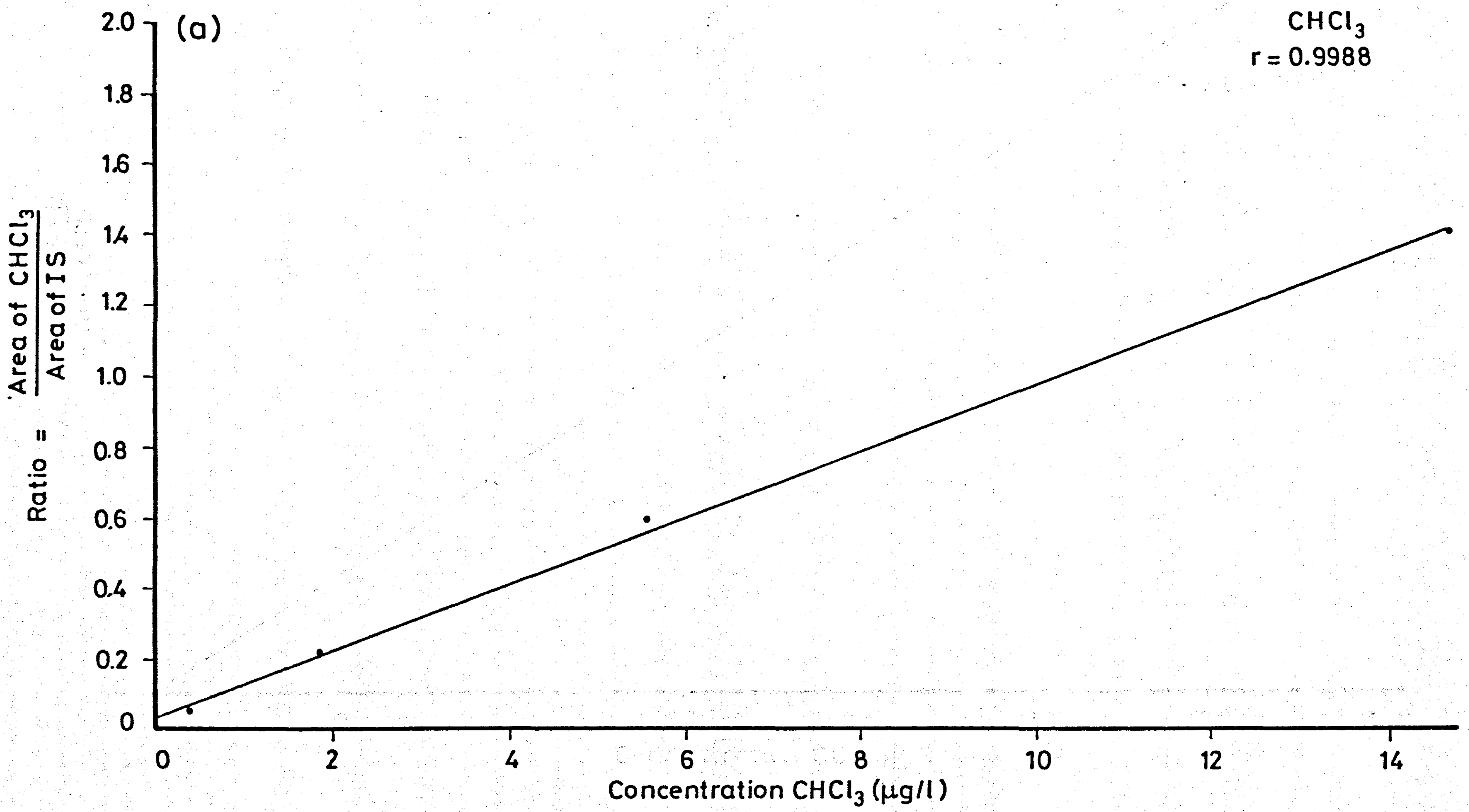
b) CCl_4

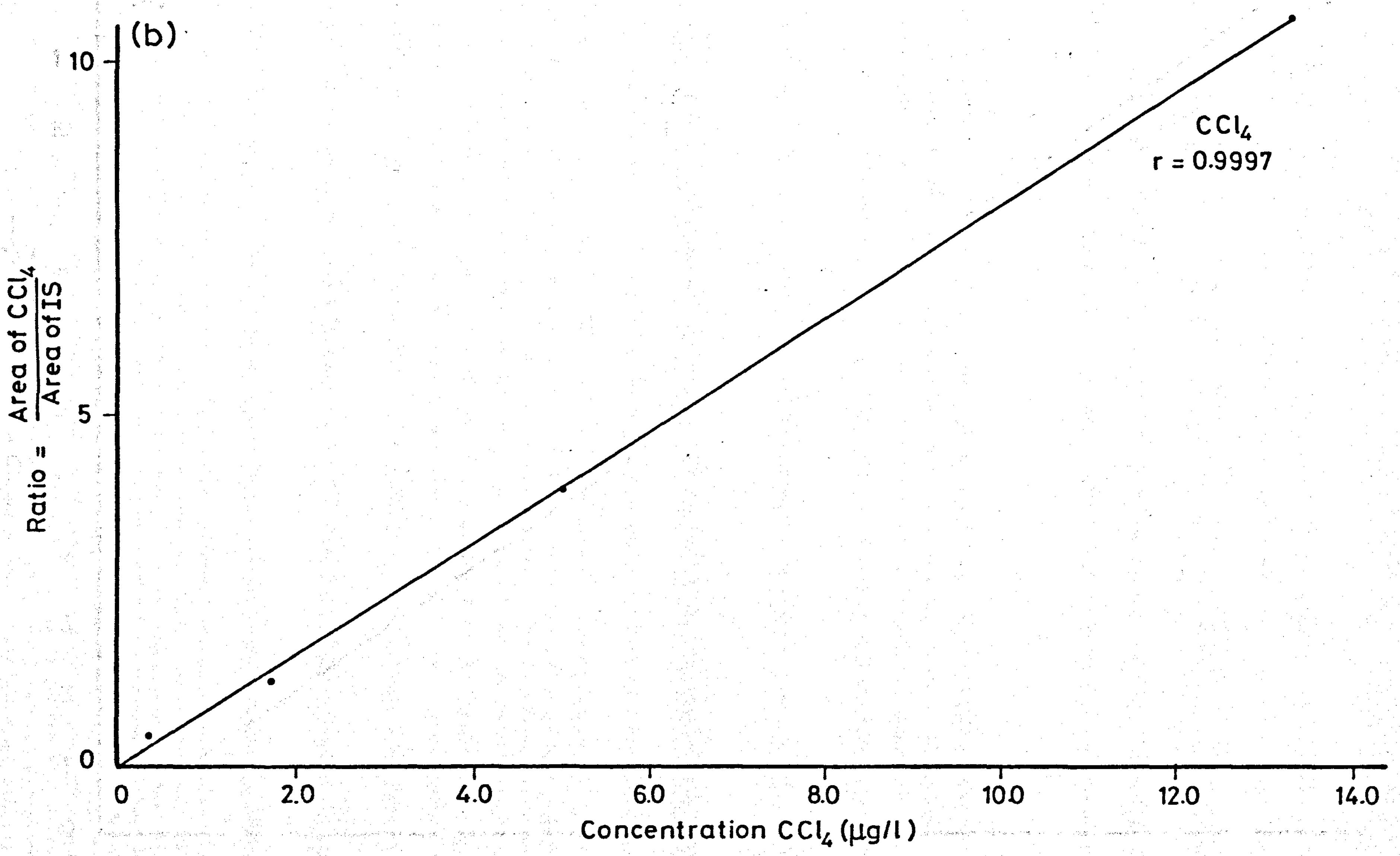
c) $CHCl_2Br$

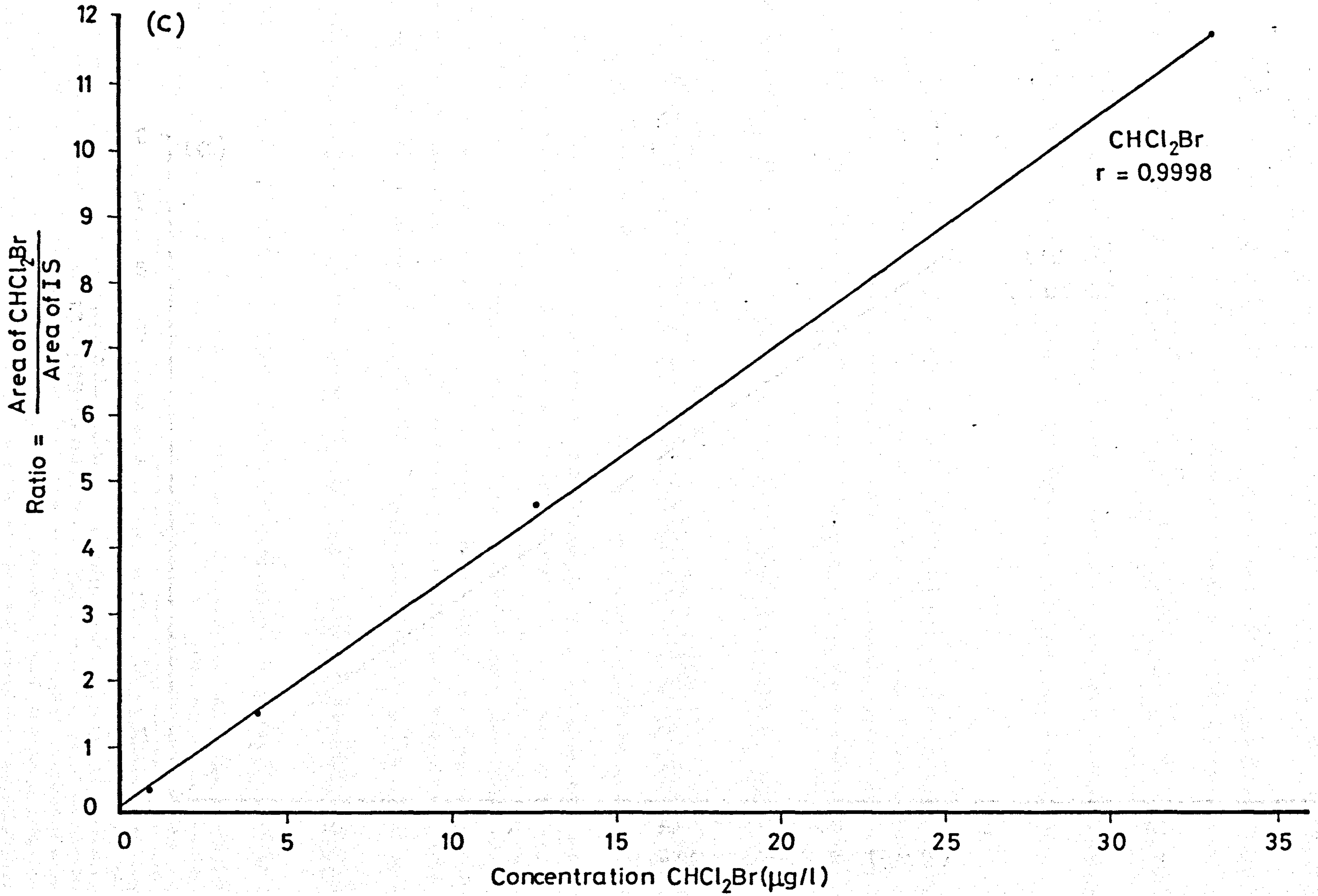
d) $CHCl_2Br$

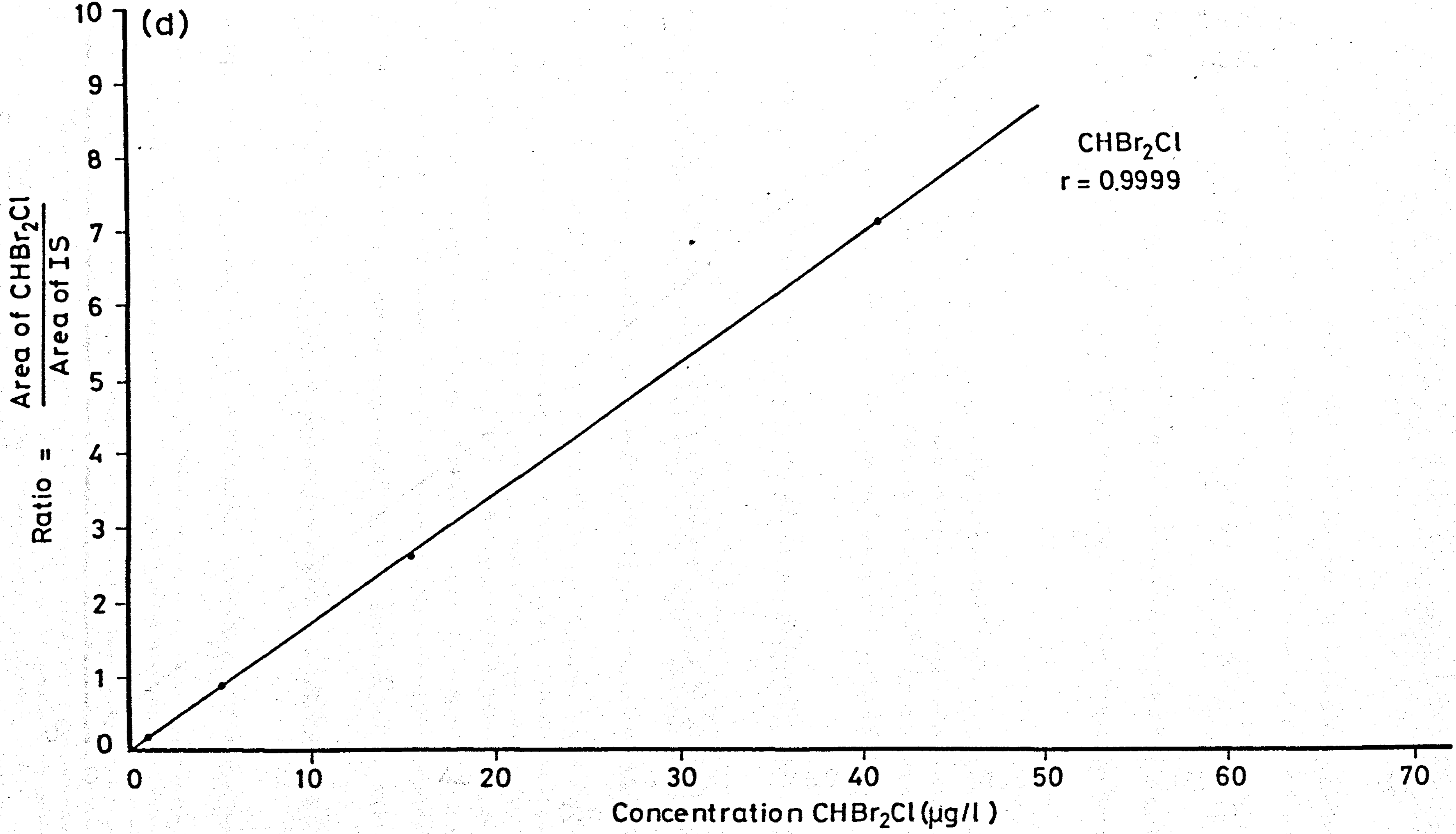
e) $Cl_2C{=}CCl_2$

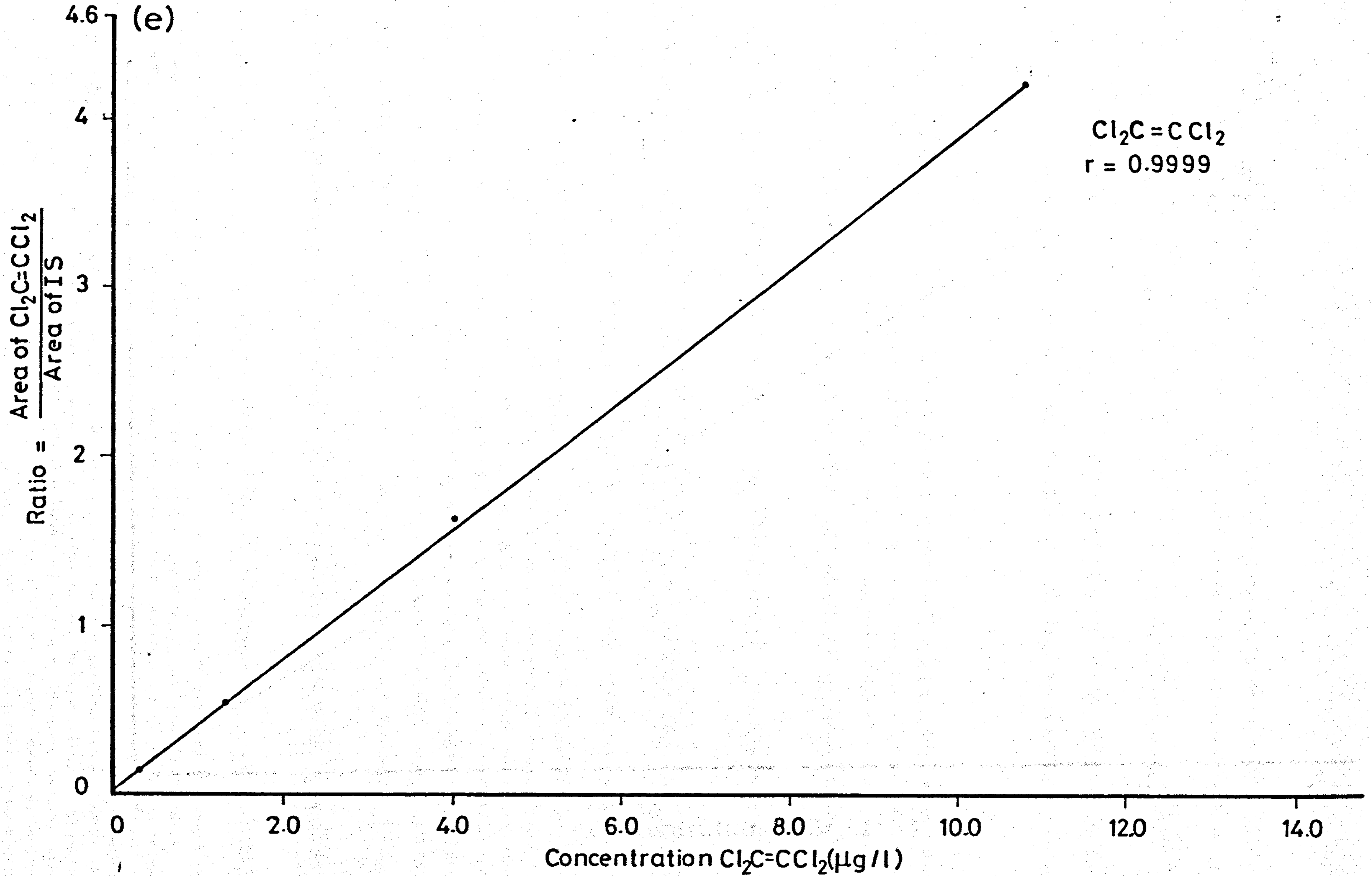
f) $CHBr_3$

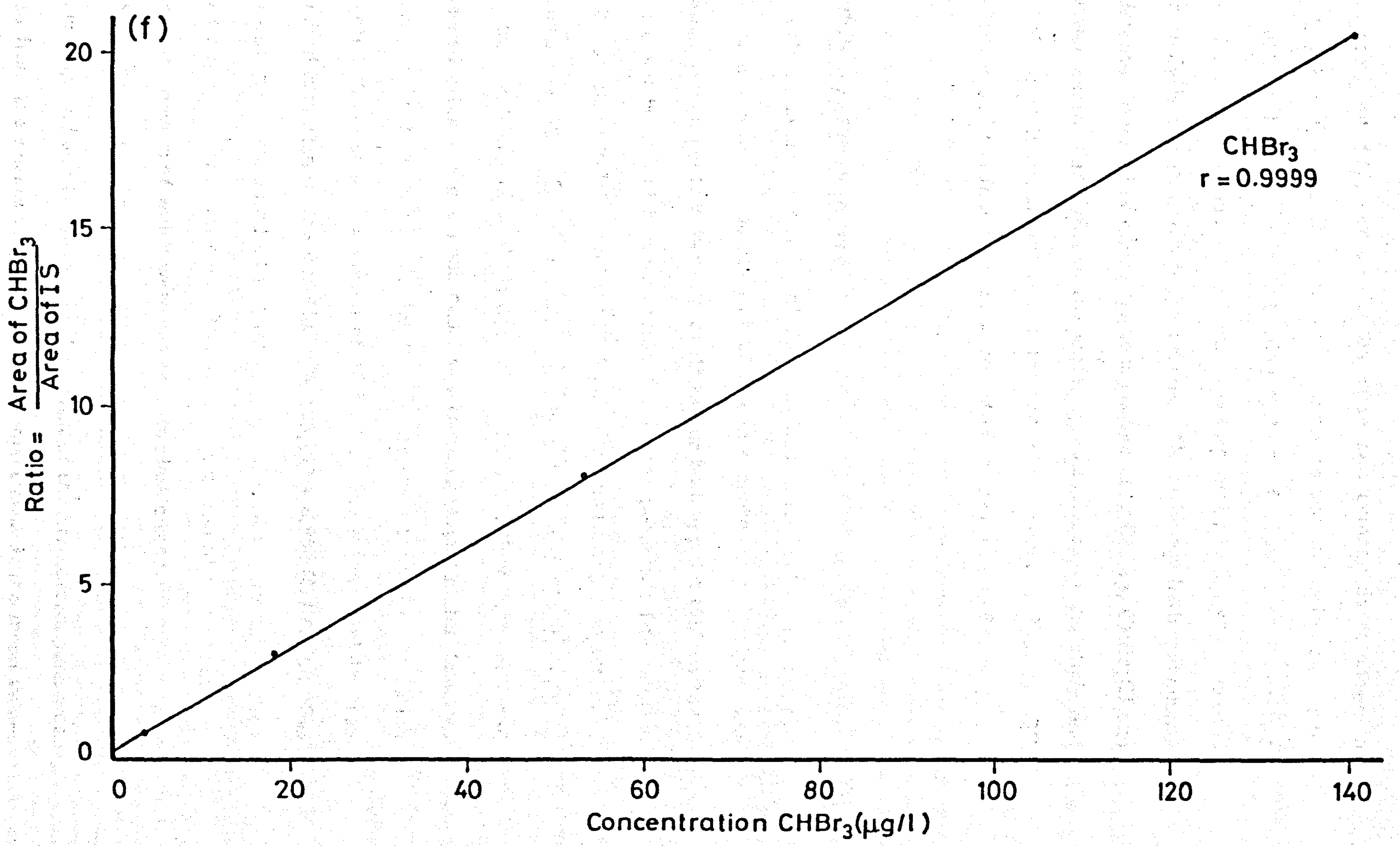

(a)
CHCl3
r = 0.9988
Ratio = Area of CHCl3 / Area of IS
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
12
14
Concentration CHCl3 (µg/l)


(b)
10
5
0
Ratio = $\frac{\text{Area of } CCl_4}{\text{Area of IS}}$
CCl_4
r = 0.9997
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
Concentration CCl_4 (μg/l)


(c)
CHCl$_2$Br
r = 0,9998
Ratio = $\frac{\text{Area of CHCl}_2\text{Br}}{\text{Area of IS}}$
0
1
2
3
4
5
6
7
8
9
10
11
12
0
5
10
15
20
25
30
35
Concentration CHCl$_2$Br(µg/l)


(d)
CHBr₂Cl
r = 0.9999
Ratio = Area of CHBr₂Cl / Area of IS
0
1
2
3
4
5
6
7
8
9
10
0
10
20
30
40
50
60
70
Concentration CHBr₂Cl (µg/l)


(e)
4.6
4
3
2
1
0
Ratio = Area of $Cl_2C=CCl_2$ / Area of I S
$Cl_2C=CCl_2$
r = 0.9999
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
Concentration $Cl_2C=CCl_2$ (µg / l)


(f)
CHBr$_3$
r = 0.9999
Ratio = $\frac{\text{Area of CHBr}_3}{\text{Area of IS}}$
0
5
10
15
20
0
20
40
60
80
100
120
140
Concentration CHBr$_3$(μg/l)

batches produced different effects on these two compounds as shown in Figure 1.7. Part of the problem may also be due to contamination caused by the circulation by the air conditioning system of vapours of these two compounds, which are used in the laboratory (especially CCl_4, which is used for the analysis of petroleum hydrocarbons). Nevertheless both compounds were detected in very low concentrations compared to $CHBr_3$, $CHBr_2Cl$ and to a lesser extent $CHCl_2Br$, in the water types included in the study and thus their contributions to the total were excluded. Typical GC chromatograms of the four types of water studied are shown in Figure 1.8.

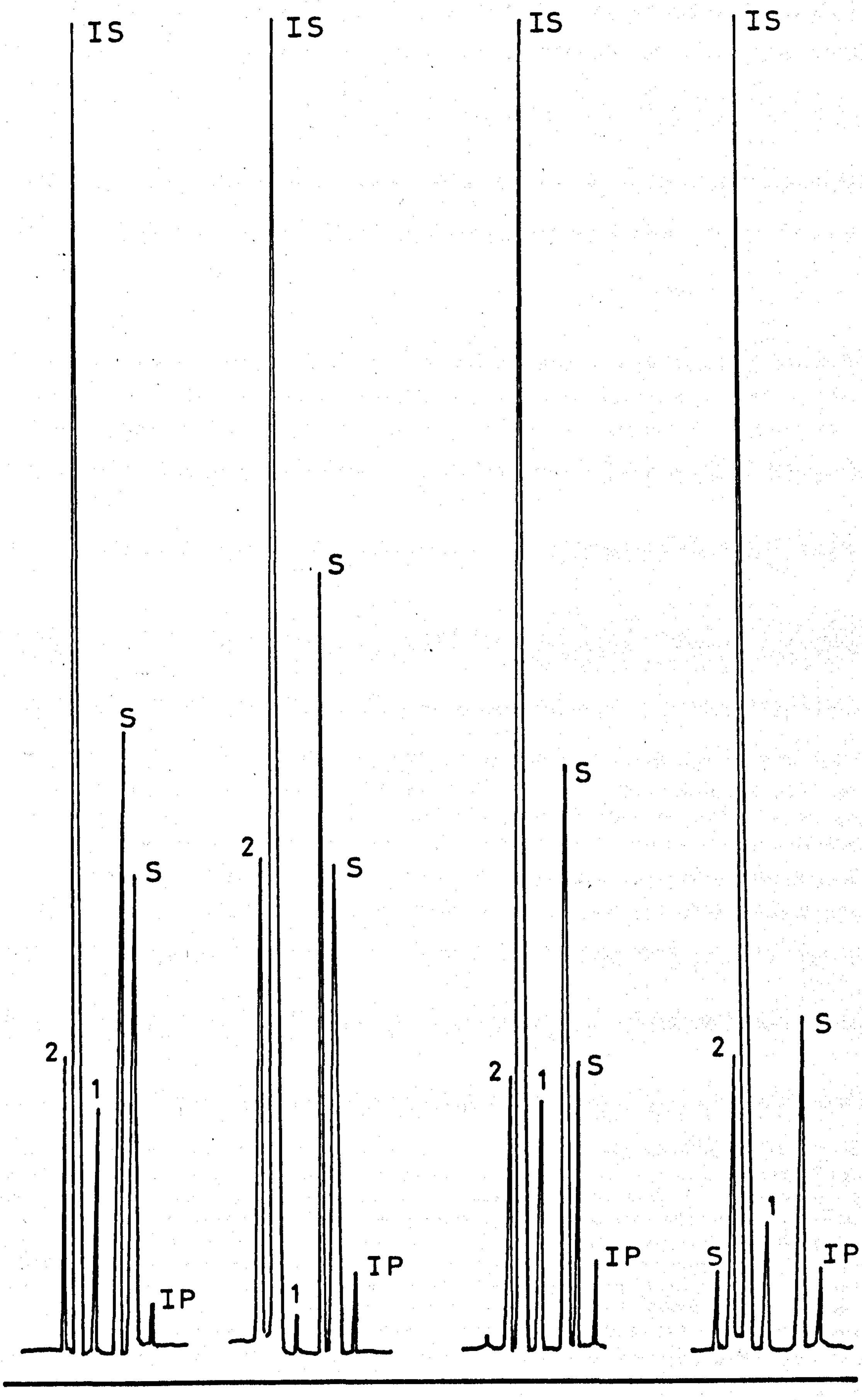
1.3 Stability of Performance

A check on the sensitivity of the ECD was carried out on each day of analysis using a standard solution of $CHBr_3$ in n-heptane. n-Heptane was used rather than n-pentane bacause of its higher boiling point (98° vs 36°C) as it gave solutions which were stable for longer periods. The solution prepared contained 211.5 ng/ml (or 84.6 pg) of bromoform per injection of 0.4 ul into the GC. Starting with a newly conditioned SE-30 capillary column, the conditions of analysis were set and the gas flows were adjusted and checked after the gas lines had been thoroughly tested for leakage. When the baselinehad stabilised, the freshly prepared bromoform solution was injected 30 times over a period of 14 hours. The mean absolute area and standard deviation of the injection was 105,159 $\pm$ 6,851 (CV 6.5%). The solution was then distributed into 10 ml volumetric flasks, care being taken that no head space was formed. The flasks were stored in dark plastic containers, the covers of which were sealed with plastic tape.

At the begining of each day, a new flask of bromoform standard solution was opened and the mean absolute area of the bromoform peak was evaluated from the results of ten consecutive injections. If the mean value

Figure 1.7 Scans of blanks using different solvents during the course of the study

1.P.	Injection peak
S.	Solvent
1.S.	Internal Standard
1.	$CHCl_3$
2.	CCl_4



IS
S
S
2
1
IP
IS
S
2
S
1
IP
IS
S
2
1
S
IP
IS
S
2
S
1
IP
Retention time

Figure 1.8 Typical Chromotograms of halomethanes extracted:

a) Distillate

b) Drinking water

c) C B D (Brine)

d) Sea Water

1.P. Injection Point

S. Solvent Peak

1.S. Internal Standard

1. $CHCl_3$

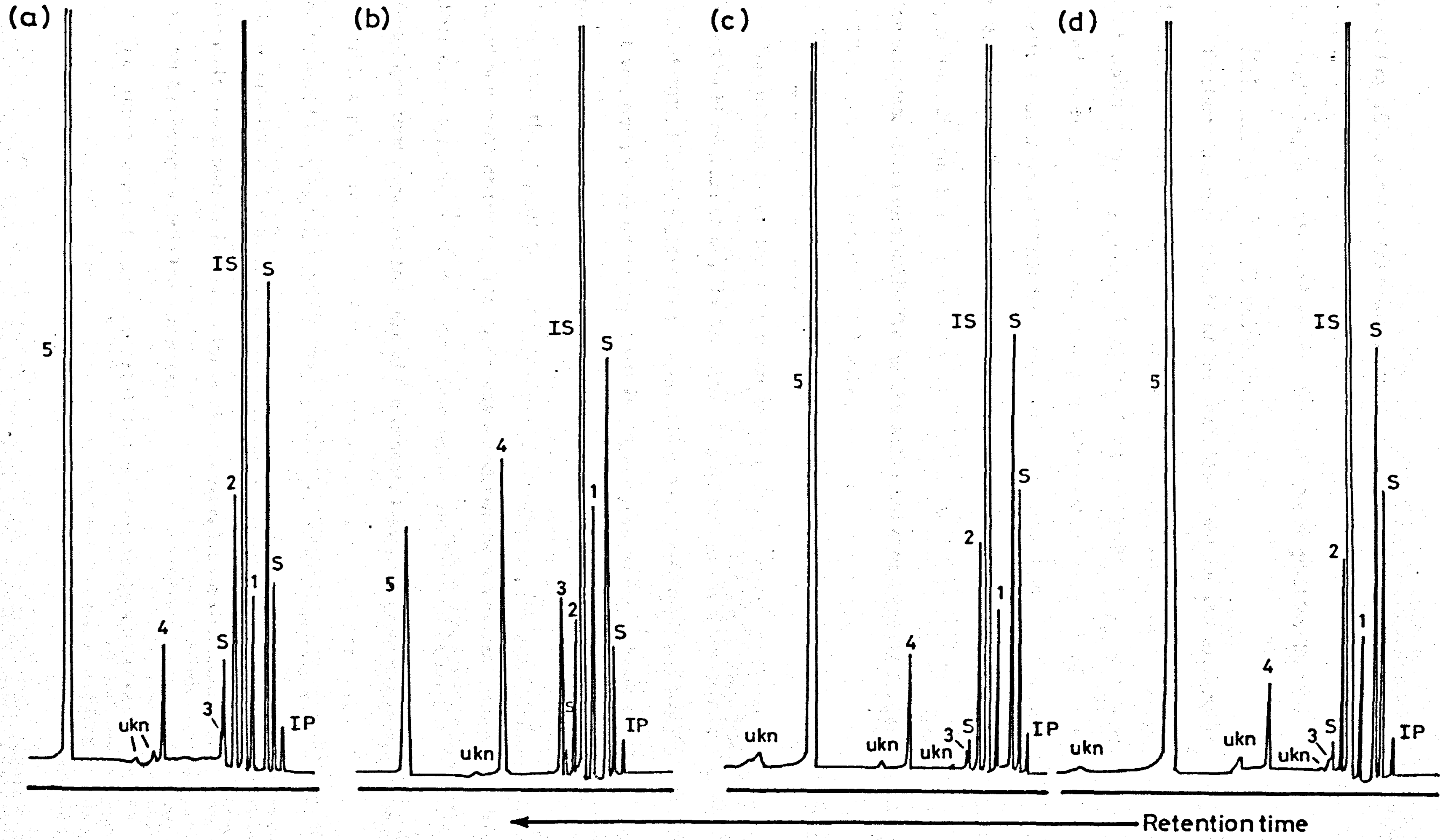
2. CCl_4

3. $CHCl_2Br$

4. $CHBr_2Cl$

5. $CHBr_3$

Uku Unknown


(a)
5
ukn
4
3
S
2
IS
1
S
S
IP
(b)
5
ukn
4
3
S
2
IS
1
S
S
IP
(c)
ukn
5
ukn
4
ukn
3
S
2
IS
1
S
S
IP
(d)
ukn
5
ukn
4
ukn
3
S
2
IS
1
S
S
IP
Retention time

deviated by 10% or more from the original value, more thorough checks on gas flows and leakage were conducted and the column was reconditioned which usually improved the performance to nearly the original levels.

1.4 Test of Reproductability of the Technique

To check the repeatability of the technique used for the extraction and analysis if haloforms, five water samples were collected from the same source (using a cooling coil) and analysed on the same day. This was repeated on two occasions, once using drinking water and once with the concentrate blow down (CBD) from the F-1 desalination unit. The results are shown in Tables 1.3 and 1.4. The overall variability in performance ranged from 2% for the brine concentrate samples to 3% for the drinking water samples. The reproductibility for the individual compounds as better than 5% except for chloroform (15%) and carbon tetrachloride (5%).

1.5 The Efficiency of Extraction

The efficiency of the extraction technique was compared to that reported by Henderson **et al.**, (1976). Assuming an extraction efficiency in excess of 70%, it was decided that a second extraction should remove most of what was not recovered during the first. Samples of distillate, drinking water and sea water were extracted and analysed in the manner described earlier, then the cap of the flask containing the sample was carefully removed and most of the organic layer was withdrawn by a syringe. Using another clean syringe, 5 ml of organic free water was injected below the surface layer thus removing the rest of the organic layer. The cap was refitted with a clean Teflon-faced rubber septum and replaced, care being taken to avoid trapping air bubbles. The extraction and analysis procedure was then repeated on the samples. The results of the extraction efficiency experiments are shown in Tables 1.5 for drinking water, 1.6 for the distillate and 1.7 for the compounds in the sea water.

The mean concentration of total halomethanes extracted from

Name of Compound	Concentrations of Halomethanes per sample (µg/l)					Calculated $\bar{x}$,SD and % of deviation
	1	2	3	4	5	
Chloroform*	1.29	1.09	1.21	1.61	1.38	1.32 (±0.20) (15%)
Carbontetrachloride*	0.18	0.18	0.18	0.20	0.20	0.19 (±0.01) (5%)
Dichlorobromomethane	2.16	2.06	2.19	2.22	2.09	2.14 (±0.07) (3%)
Dibromochloromethane	7.54	7.26	7.69	7.92	7.22	7.53 (±0.29) (4%)
Tetrachloroethylene	0	0	0	0	0	-
Bromoform	12.81	12.58	13.42	12.72	12.46	12.80 (±0.37) (3%)
TOTAL	23.98	23.17	24.69	24.67	23.35	23.97 (±0.71) (3%)

* Values reported without correction for the blank

Table 1.3 Reproducibility of Extraction and Analysis for Drinking Water

Name of Compound	Concentrations of Halomethanes per sample (µg/l)					Calculated $\bar{x}$,SD and % of deviation
	1	2	3	4	5	
Chloroform*	0.80	0.91	0.85	0.81	1.00	0.87 (±0.08) (9%)
Carbontetrachloride*	0.19	0.17	0.17	0.17	0.17	0.17 (±0.01) (4%)
Dichlorobromomethane	0	0	0	0	0	-
Dibromochloromethane	0.40	0.38	0.38	0.38	0.37	0.38 (±0.01) (3%)
Tetrachloroethylene	0	0	0	0	0	-
Bromoform	7.42	6.87	7.00	7.17	6.83	7.1 (±0.24) (3%)
Total	8.81	8.33	8.40	8.53	8.37	8.5 (± .19)(2%)

* Values reported without correcting for the blank

Table 1.4 Reproducibility of Extraction and Analysis for the Concentrate Blow Down (Brine)

Sample	Compound Concs µg/l	$CHCl_3$	CCl_4	$CHCl_2Br$	$CHBr_2Cl$	$Cl_2C{=}CCl_2$	$CHBr_3$	Total	Total Halomethanes Content (µg/l)
OCC-Mains*	1st Ext.	0.55	0.09	3.80	9.71	0	12.87	27.01	31.91
	%	75	64	80	81		90	85	
	2nd Ext.	0.18	0.05	0.95	2.35	0	1.38	4.90	
	%	25	36	20	19		10	15	
OCC-Filter	1st Ext.	0.49	0.10	3.83	9.89	0	13.06	27.36	31.82
	%	69	71	81	82		92	86	
	2nd Ext.	0.22	0.04	0.91	2.18	0	1.11	4.46	
	%	31	29	19	18		8	14	
OCC-Tank	1st Ext.	0.83	0.09	4.04	7.71	0	13.27	25.95	30.33
	%	75	64	81	81		91	86	
	2nd Ext.	0.28	0.05	0.97	1.81	0	1.27	4.38	
	%	25	36	19	19		9	14	
Doha-Tank**	1st Ext.	1.27	0.40	2.90	6.95	0	16.93	28.45	33.07
	%	77	59	87	81		90	86	
	2nd Ext.	0.38	0.28	0.44	1.62	0	1.90	4.62	
	%	23	41	13	19		10	14	
Mean Efficiency for First extraction (%)		74 ±3	65 ±5	82 ±3	81 ±1	-	91 ±1	86 ±1	
Mean Total Halomethanes Content (µg/l)	X̄	1.05	0.28	4.46	10.56		15.45	31.80	
	SD	±0.45	±0.27	±.76	±1.79		±2.26	±1.12	

* OCC refers to the Occupational Health Building in Shuwaikh

** Doha Tank refers to water taken from a roof-top tank in the Doha area

Table 1.5 Efficiency of Extraction from Drinking Water

Sample	Compound Concs. µg/l	$CHCl_3$	CCl_4	$CHCl_2Br$	$CHBr_2Cl$	$Cl_2C=CCl_2$	$CHBr_3$	Total	Total THMS content (µg/l)
F1-Distillate	1st Ext.	0	0.09	0	0.33	0	8.84	9.26	9.49
	%		53		69		100	98	
	2nd Ext.	0	0.08	0	0.15	0	0	0.23	
	%		47		33			2	
F2-Distillate	1st Ext.	0	0.09	0	0.31	0	8.90	9.30	9.51
	%		53		70		100	98	
	2nd Ext.	0	0.08	0	0.13	0	0	0.21	
	%		47		30			2	
F1-Distillate	1st Ext.	0	0.08	0	0.39	0	11.21	11.68	12.24
	%		53		68		97	95	
	2nd Ext.	0	0.07	0	0.18	0	0.31	0.56	
	%		47		32		3	5	
F2-Distillate	1st Ext.	0	0.07	0	0.35	0	10.27	10.69	11.25
	%		54		71		97	95	
	2nd Ext.	0	0.06	0	0.14	0	0.36	0.56	
	%		46		29		3	5	
Mean Efficiency for First Extraction (%)		-	53 ±1	-	70 ±2	-	99 ±2	97 ±2	
Mean Total Halomethanes Content (µg/l)		-	0.16 ±.02	-	0.50 ±.05	- -	9.97 ±1.32	10.62 ±1.36	

*F1 and F2: Desalination Units in the Shuwaikh Desalination Station

Table 1.6 Efficiency of Extraction from Distillate Samples

Sample	Compound Concs. (µg/l)	$CHCl_3$	CCl_4	$CHCl_2Br$	$CHBr_2Cl$	$Cl_2C=CCl_2$	$CHBr_3$	Total	Total Halomethanes (µg/l)
Shuwaikh Screen - 1	1st Ext.	0.18	0.08	0.18	1.48	t	47.33	49.25	61.04
	%	67	62		74		81	81	
	2nd Ext	0.09	0.05	0	0.51	0	11.14	11.79	
	%	33	38		26		19	19	
Shuwaikh Screen - 3	1st Ext.	0	0.21	0.02	1.10	t	33.98	35.31	41.25
	%		81		77		86	86	
	2nd Ext.	0	0.05	0	0.33	0	5.56	5.94	
	%		19		23		14	14	
Shuwaikh Screen - 1	1st Ext.	0.06	0.05	0.04	1.21	0	41.11	42.47	53.63
	%		56		72		79	79	
	2nd Ext.	0	0.04	0	0.47	0	10.66	11.17	
	%		44		28		21	21	
Shuwaikh Screen - 3	1st Ext	0	0.05	0	0.61	0	18.67	19.33	21.76
	%		56		73		90	89	
	2nd Ext.	0	0.04	0	0.23	0	2.16	2.43	
	%		44		27		10	11	
Mean Efficiency of the First Extraction (%)		-	64 ±12		74 ±2	-	84 ±5	84 ±5	
Mean Total Halomethanes Content (µg/l)		-	0.14 ±0.08		1.49 ±0.48	-	42.65 ±16.53	44.42 ±17.17	

Screen = refers to screen located after the intakes, at the Shuwaikh Desalination-Power Plant
t = trace

Table 1.7 Efficiency of Extraction from Sea Water drinking water samples in two rounds of extraction was 31.8 ± 1.1 µg/l, 86% of which was recovered during the first extraction. For $CHBr_3$ which had a mean total of 15.5 ± 2.3 µg/l, the amount recovered in the first extraction was 91%. The percentage of $CHBr_2Cl$ extracted was 81% (for a total of 10.6 ± 1.8 µg/l recovered in the two extractions) whereas 86% of $CHCl_2Br$ was extracted in the first attempt for a total of 4.5 ± 0.8 µg/l. Chloroform and carbon tetrachloride, which were present in very low concentrations that varied greatly from one sample to another, were recovered with an efficiency of extraction of about 70%.

In the distillate samples, which contained a mean total concentration of halomethanes (recovered in the two extractions) of 10.6 ± 1.4 µg/l, the efficiency of extraction exceeded 90%. However, this may be reflecting the high recovery rate of $CHBr_3$ from the distilate (in which it constituted over 90% of the total halomethanes extracted compared to drinking water, where it was one of five compounds extracted and constituted about 50% of the total) rather than a significant difference between the two types of water. Bromoform (10.0 ± 1.3 µg/l) was extracted mostly in the first attempt (99 ± 2%), whereas the efficiency of extraction for $CHBr_2Cl$ was 70 ± 2% (for a total concentration of 0.5 µg/l). Carbon tetrachloride was detected in levels less than 0.2 µg/l and the amount present in the first extraction made up 53% of the total recovered in the two attempts, whereas $CHCl_2Br$ and $CHCl_3$ were not detected.

Sea water samples collected at the screens located after the intake pumps, where intermittent chlorine dosing is applied, had a mean total halomethanes concentration of 44.4 ± 17.2 µg/l, (84 ± 5% of which were recovered in the first extraction). Bromoform had a similar efficiency of extraction (the mean total concentration recovered in the two extractions amounted to 42.7 µg/l). The efficiency of extraction for $CHBr_2Cl$ was 74 ± 2% for a mean concentration of 1.5 µg/l, whereas CCl_4 which was present at a concentration of 0.1 µg/l, the efficiency of extraction was 64%.

To summarise then, the extraction efficiency for the three types of water was generally similar (with an overall mean value of 89 ± 6%). The highest recovery was found for the distillate samples (97%) for which the mean content of halomethanes in the samples was 10.6 µg/l, followed by drinking water (86%) which had a mean content of 31.8 µg/l. The lowest recovery rate was found for the sea water samples (84%) for which the mean content was 44.4 µg/l. Among the individual compounds, the rate of recovery for bromoform was 91%, which was also highest for the distillate and lowest for the sea water samples. This is in accordance with the tendency noticed for the total haloforms for which the extraction efficiency decreased as the concentration increased. However, this was not always the case with the other compounds that were present in much lower concentrations. For example, the overall extraction efficiency of $CHBr_2Cl$ was 75%, the highest recovery rate was for drinking water samples 82%, which had a mean concentration of 10.6 µg/l followed by sea water samples 74% where the concentration was 1.5 µg/l and the lowest rate of recovery was for the distillate samples 76% for which the mean concentration was only 0.5 µg/l. Dichlorobromomethane was not detected in the distillate samples, but high recoveries were found with drinking water samples 82% in which its concentration averaged 4.5 µg/l. Finally, it should be noted that the extraction efficiencies were reported as percent of halomthanes recovered in the first extraction relative to the total amount recovered in the two extraction attempts and not as absolute extraction efficiency.

1.6 Spiking Studies

Spiking of water samples with known quantities of halomethanes was used as another check on the qualitative and quantitative accuracy of the analytical procedure. Standard solutions of halomethanes were prepared in methanol. A 5 l water sample was collected using the cooling coil and apportioned into eight 250 ml volumetric flasks which were kept in the dark at a temperature of about 15°C. The standard halomethane mixture was introduced into four flasks by injection under the water surface using a gas-tight syringe. The flasks were shaken and the extraction and analysis procedures were then carried out in the manner described earlier. All eight samples were analysed on the same day. The process was repeated on another occasion, in which two concentrations were used for spiking. The results of these experiments are summarised in Tables 1.8 and 1.9.

The mean efficency of extraction, as estimated by the spiking experiment of drinking water, amounted to 90 ± 5% which is similar to that obtained during the re-extraction experiments (86 ± 1%) and to the overall efficiency (for the three types of water used), which amounted to 89 ± 6%. The efficiency of extraction for $CHCl_3$ and CCl_4 concentrations improved as their concentration increased (by spiking) over that of the background, from 74 ± 3% to 84 ± 5% for $CHCl_3$ and from 65 ± 5% to 72 ± 5% for CCl_4. It should also be noted that the tend for a slight decrease in the recovery of $CHBr_3$ in the higher concentration ranges was also shown here. For example, $CHBr_3$ recovery was 94% for a total concentration of 15.8 µg/l Table 1.8 whereas it showed a slight decrease to 88% and 84% as the concentrations increased to 37.7 µg/l and 63.8 µg/l respectively. However these differences were not significant.

A summary of the recoveries obtained for drinking water in both types of experiments is shown in Table 1.10.

		Concentrations (µg/l) - Unspiked Samples					Concentrations (µg/l) - Spiked Samples				
	Compound	1	2	3	4	Mean SD	Amount added plus background concentrations	1	2	3	Mean SD
CHCl$_3$	Mean	1.47	1.43	1.53	1.51	1.49	0.91 plus	2.21	2.05	2.00	2.09
	SD	0	±0.08	±0.02	±-0.15	±0.04	Background	+.03	+.01	+.02	+.11
							(+1.49=2.40) R=	(92)	(86)	(83)	(87)
CCl$_4$	Mean	0.24	0.25	0.24	0.25	0.25	0.33 plus	0.43	0.44	0.43	0.43
	SD	0	0	±0	0	±.01	Background	+.01	+0	+ 0	+.01
							(+0.25=0.58) R=	(74)	(76)	(74)	(75)
CHCl$_2$Br	Mean	2.42	2.06	2.40	2.09	2.24	0.82 plus	3.12	2.88	2.88	2.96
	SD	±0.06	0	±0.02	±0.15	±0.19	Background	+.04	+.03	+.02	+.14
							(+2.24=3.06) R=	(102)	(94)	(94)	(97)
CHBr$_2$Cl	Mean	6.71	6.08	6.64	6.03	6.37	1.01 plus	7.45	7.12	7.20	7.26
	SD	± 0	±0.02	±0.11	±0	±0.36	Background	+.13	+.03	+.19	+.17
							(+6.37=7.38) R=	(101	(96)	(98)	(98)
CHBr$_3$	Mean	12.69	11.91	12.62	11.73	12.24	3.56 plus	14.87	14.72	15.04	14.88
	SD	±0.19	±0.08	±0.18	±0.22	±0.49	Background	+.38	+.07	+.66	+.16
							(+12.24=15.80) R=	(94)	(93)	(95)	(94)
Total		23.53	21.73	23.43	21.6	22.58	6.63 plus	28.08	27.22	27.55	27.62
						±1.05	Background				
							(+22.58=29.21) R=	(96)	(93)	(94)	(94)

R = Recovery (%)

Table 1.8 Spiking of Drinking Water Samples

Compound and Recovery %		Concentration (µg/l) - Unspiked Samples (Background Concentration)					Concentrations (µg/l) - Spiked Samples (Low Concentration)						Concentrations (µg/l) - Spiked Samples (High Concentration)				
		1	2	3	Mean SD	Amount added plus background concentrations	1	2	3	4	Mean SD	Amount added plus background concentrations	1	2	3	3	Mean SD
$CHCl_3$	Mean SD	1.11 ±0.01	1.29 ±0.02	1.31 ±0.05	1.24 ±0.11	1.81 plus R= Background (1.24=3.05)	2.63 ±0.01 (85)	2.44 ±0.01 (80)	2.60 ±0.06 (85)	2.83 ±0.08 (93)	2.63 ±0.16 (86)	5.44 plus R= Background (1.24=6.68)	5.27 ±0.18 (79)	5.16 ±0.05 (77)	5.36 ±0.06 (80)	5.57 ±0.29 (83)]	5.34 ±0.17 (80)
CCl_4	Mean SD	0.21 ±0	0.20 ± 0	0.21 ±0.01	0.21 ±0.01	0.65 plus R= Background (0.21=0.86)	0.66 ±0.01 (77)	0.57 ± 0 (66)	0.68 ±0.04 (79)	0.64 ±0.01 (75)	0.64 ±0.05 (74)	1.96 plus R= Background (0.21=2.17)	1.41 ±0.02 (65)	1.53 ±0.03 (71)	1.51 ±0.04 (70)	1.50 ±0.11 (69)	1.49 ±0.05 (69)
$CHCl_2Br$	Mean SD	2.02 ±0.01	2.25 ±0.01	2.57 ±0.01	2.28 ±0.28	1.64 plus R= Background (2.28=3.92)	3.57 ±0.17 (91)	3.32 ±0.01 (85)	3.79 ±0.01 (97)	4.10 ±0.01 (105)	3.70 ±0.33 (94)	4.91 plus R= Background (2.28=7.19)	6.44 ±0.09 (90)	6.41 ±0.08 (89)	6.95 ±0.15 (97)	6.70 ±0.30 (93)	6.63 ±0.25 (92)
$CHBr_2Cl$	Mean SD	6.31 ±0.02	6.75 ±0.10	7.38 ±0.04	6.81 ±0.54	2.01 plus R= Background (6.81=8.82)	8.24 ±0.33 (93)	7.83 ±0.08 (89)	8.76 ±0.45 (99)	9.51 ±0.41 (108)	8.59 ±0.72 (97)	6.04 plus R= Background (6.81=12.85)	12.11 ±0.35 (94)	12.20 ±0.25 (95)	13.14 ±0.18 (102)	12.73 ±0.53 (99)	12.55 ±0.48 (98)
$CHBr_3$	Mean SD	13.41 ± 0.17	13.86 ± 0.55	15.00 ± 0.21	14.09 ± 0.82	6.95 plus R= Background (14.09=21.04)	17.85 ± 1.03 (85)	17.24 ± 0.26 (82)	18.89 ± 1.61 (90)	20.16 ± 0.86 (96)	18.54 ± 1.28 (88)	20.85 plus R= Background (14.09=34.94)	28.50 ±1.56 (82)	29.2 ±0.36 (84)	30.07 ±0.45 (86)	29.62 ±0.62 (85)	28.35 ±2.59 (84)
Total		23.06	24.35	26.47	24.62 ± 1.72	13.06 plus R= Background (24.62=37.68)	32.95 (87)	31.39 (83)	34.72 (91)	37.24 (99)	34.08 ±2.51 (90)	39.20 plus R= Background (24.62=63.82)	53.73 (84)	54.50 (85)	57.03 (89)	56.12 (88)	55.35 (87)

*R = Recovery (%)

Table 1.9 Spiking of Drinking Water

	Efficiency of Extraction Table 1.5) n = 4		Efficiency of Extraction from Spiked Samples Table (1.7) and (1.8)					
			1st Experiment		2nd Experiment (Low conc.)		2nd Experiment (High conc.)	
	Concentration range (μg/l)	Recovery by 1st extraction (%)	Conc. (μg/l)	Recovery (%)	Conc. (μg/l)	Recovery (%)	Conc. (μg/l)	Recovery (%)
$CHCl_3$	1.05 ±0.45	74 ±3	2.40	87 ±5	3.05	86 ±5	6.68	80 ±3
CCl_4	0.28 ±0.27	65 ±5	0.58	75 ±1	0.86	74 ±6	2.17	69 ±3
$CHCl_2Br$	4.46 ±0.76	82 ±3	3.06	97 ±5	3.92	94 ±9	7.19	92 ±4
$CHBr_2Cl$	10.56 ±1.79	81 ±1	7.38	98 ±3	8.82	97 ±8	12.85	98 ±4
$CHBr_3$	15.45 ±2.26	91 ±1	15.80	94 ±1	21.04	88 ±6	34.94	84 ±2
Total	31.80 ±1.12	86 ±1	29.21	94 ±2	37.68	90 ±7	63.82	87 ±2

Table 1.10 A Summary of Comparative Recoveries of Halomethanes by Re-extraction and Spiking Experiments (Drinking Water Samples)

CHAPTER 2

An Experimental Study of the Formation of Halomethanes in Chlorinated Waters of Kuwait

2.1 Introduction

Attention was first drawn to the formation of halomethanes in potable water by Rook (1974) and Bellar **et al.** (1974) and in chlorinated sewage effluents and chlorinated cooling waters by Jolley (1975) and Jolley **et al.** (1975). Since then, experiments on the chlorination of natural waters under various conditions and in the presence of substances that are commonly found in such waters have been described in several papers (Rook, 1977; Rook **et al.**, 1978; Stevens **et al.**, 1978; Helz and Hsu, 1978; Minear and Bird, 1980; Cooper **et al.**, 1983 and Gould **et al.**, 1983). However, there have been no detailed studies on the concentrations of halomethanes in sea water used for desalination, in the brine effluents, or in the produced distillate. This may be because the use of desalination as a major source of potable water is restricted to those arid regions, in which cheap fuel is available. This chapter describes an attempt to investigate some of the factors affecting the formation of halomethanes as a result of the chlorination of the waters associated with the desalination process in Kuwait.

Originally, the main objective of the experimental study was to simulate the conditions in the desalination process in order to determine if halomethanes are being carried over with the distillate during flash evaporation of sea water. Also of interest were the possible effects of naturally occurring substances and those of anthropogenic origin on the levels of halomethanes produced. However, difficulties which were encountered in assembling a reaction vessel that could be maintained leak proof without the formation of a head space, led to the development of a syringe-like vessel. This vessel allowed experiments to be carried out to investigate the effect of reaction time, of chlorine dose and of some of the naturally occurring and industrial contaminants on the formation of halomethanes.

Since the study was of an applied nature, an effort was made to approximate the conditions used for the chlorination of water in Kuwait. However, this had some disadvantages - for example, if the levels of residual chlorine had been increased to values greater than the 2 mg/l dose normally applied, then the uncertainty about the formation of compounds like $CHCl_3$ and CCl_4 might have been resolved. Another limitation of the study was the inability to carry out a sufficient number of replicates to permit the data to be analysed statistically. Nevertheless, the experiments are expected to demonstrate the general trends involved in the formation of halomethanes upon chlorination of the waters of Kuwait.

Calcium hypochlorite, $Ca(ClO)_2$ was used as the source of residual chlorine since it was more stable than NaOCl and readily available, in contrast to chlorine gas which could not be obtained in small cylinders. No attempt was made to study the speciation of chlorine in the waters used, as information about this was available in the literature (see e.g. Wong and Davidson, 1977; Davis and Middaugh, 1978; Morris, 1978; Johnson, 1978; Rook **et al.**, 1978; Sugam and Helz, 1981 and Jolley and Carpenter, 1983).

When chlorine gas is injected into fresh water, it hydrolyses rapidly and almost completely,

$$Cl_2 + H_2O = HOCl + H^+ + Cl^-$$

the HOCl in turn instantly dissociates in the water,

$$HOCl = H^+ + ClO^-$$

This reaction is pH dependant, at pH 7 (20°C), the equilibrium is about 75% HOCl to 25% ClO^-. The percentages are reversed at pH 8. However, HOCl still remains the major reactive species because of its high specific reactivity (r) (relative to OCl^-) which produces a higher net reactivity ($r = \Sigma r_i f_i$), where (f_i) is the fraction of the total stoichiometric reactant concentration of a given molecular form and (r_i) is the specific reactivity of that form (Morris, 1978).

Hypochlorous acid of course, is also produced when calcium hypochlorite dissolves in water,

$$Ca(ClO)_2 \rightarrow Ca^{2+} + 2ClO^-$$

$$ClO^- + H^+ = HOCl$$

In the presence of ammonia or organic amines (and in the absence of Br^-) chloramines are formed. The final products depend on factors such as the pH, the ratio of ammonia to hypochlorous acid and the temperature,

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O$$

The ratio of NH_2Cl to $NHCl_2$ at pH 8 is about 6:1, but it is almost reversed at pH 5. Trichloroamine is only formed in significant amounts at pH values less than (Jolley and Carpenter, 1983)

The addition of chlorine to sea water results in a more complex series of reactions, the products being influenced by several factors such as the ratio of chlorine to the concentration of that of the original bromide ion, the level of ammonia, the temperature, the pH and the presence of other compounds both naturally occurring and anthropogenic. However, under ambient conditions, two classes of substances are sufficiently abundant and reactive to compete with the hydrolysis of chlorine (and the subsequent dissociation described earlier). The first of these are the halide ions, Br^- and I^-. When chlorine is introduced as a gas, it reacts with the bromide ion to form bromine chloride,

$$Cl_2 + Br^- \rightarrow BrCl + Cl^-$$

This reaction is about 300 times faster than that between HOCl and Br^- (Helz and Kosak-Channing, 1980). BrCl would also react rapidly with Br^-,

$$BrCl + Br^- \rightarrow Br_2 + Cl^-$$

In the pH range of sea water, Br_2 is quickly hydrolysed as follows:

$$Br_2 + H_2O \rightarrow HOBr + H^+ + Br^-$$

HOBr is also formed when Br^- reacts with HOCl and ClO^- produced by the hydrolysis of NaOCl or $Ca(ClO)_2$,

$$HOCl + Br^- \rightarrow HOBr + Cl^-$$

and

$$ClO^- + Br^- \rightarrow BrO^- + Cl^-, \text{also } (BrO^- + H^+ = HOBr)$$

Sugam and Helz (1981) have studied the effects of chlorinity on the speciation of oxidants in chlorinated waters. They reported that chlorine-containing oxidants are stable only in fresh and very slightly brackish waters. However, the effect of salinity becomes minor at chlorinity levels above 3g/Kg (salinity above 5‰).

The oxidation of I^-, although it would occur faster than that of Br^-, is of less importance due to the lower concentration of I^- (Helz and Kosak-Channing, 1980).

The second class of compounds that could also compete with hydrolysis in sea water are the amino nitrogen compounds, including ammonia. Thus, chlorine would react with $R\text{-}NH_2$ (R- may be a hydrogen atom as in NH_3 or an organic residue such as that of an amino acid or other organic amine),

$$Cl_2 + R\text{-}NH_2 \rightarrow R\text{-}NHCl + H^+ + Cl^-$$

Under some conditions, ammonia and organic amino nitrogen compounds may compete with Br^- for HOCl in marine waters (Helz and Kosak-Channing, 1980).

$$HOCl + R\text{-}NH_2 \rightarrow RNHCl + H_2O, \text{ followed by}$$

$$HOCl + RNHCl \rightarrow RNCl_2 + H_2O$$

However, normally bromide oxidation will predominate in sea water with the subsequent formation of HOBr and BrO^- which would react with ammonia to form bromamines:

$$NH_3 + HOBr \rightarrow NH_2Br + H_2O$$

$$NH_2Br + BrO^- \rightarrow NHBr_2 + OH \text{ also}$$

$$NH_2Br + HOBr \rightarrow NHBr_2 + H_2O \text{ and}$$

$$NHBr_2 + HOBr \rightarrow NBr_3 + H_2O$$

It has also been established that in sea water of high ammonia concentration, or in estuarine waters of low bromide ion concentration and higher ammonia concentration, a mixture of halamines would be expected,

$$NH_2Cl + HOBr \rightarrow NHBrCl + H_2O$$

$$NHBrCl + HOBr \rightarrow NBr_2Cl$$

The trihalamine (NBr_2Cl) appears to be less stable than the mixed dihalamine (NHBrCl) in the absence of excess halogen. Moreover, in the presence of low concentrations of ammonia, NBr_2Cl and NBr_3, which are formed in chlorinated sea water are relatively stable in the presence of excess HOBr (Haag, 1981; Haag and Jolley, 1983 and Jolley and Carpenter, 1983).

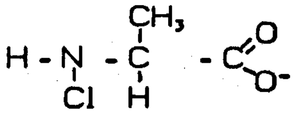
To summarise, it appears that in the presence of Br^-, low concentrations of amino nitrogen compounds and at the pH values of natural waters, what is measured as "total residual chlorine" consists mainly of HOCl, OCl^-, HOBr, OBr^-, NH_2Cl, NH_2Br and $NHBr_2$ (or a mixture of bromochloramines). Thus, a more appropriate term would be "total residual oxidants" (Jolley and Carpenter, 1983). As has been shown for sea water a shift towards the bromine-containing oxidants occurs as the Br^- concentration increases (Helz and Hsu, 1978; Haag, 1981 and Haag and Jolley, 1983).

The formation of halomethanes in chlorinated surface waters was first attributed to the reaction of some of the above described oxidants with naturally occurring humic materials by Rook (1974). Humic materials have been classified by Schnitzer and Khan (1972) according to their solubility in alkali and acid media into fulvic acids, humic acids and humin. They are products of plant decay and are distributed in surface waters, in which they comprise up to 90% of the total soluble organic matter according to some estimates (Helz **et al.**, 1980). Humic materials range in molecular weight from several hundreds to many thousands and are made up of several subunits such as aromatic and alicyclic moieties, containing alcoholic, corbonyl, carboxylic and phenolic functional groups (Schnitzer and Khan, 1972).

If HOCl is the predominant halogenating agent in a dilute aqueous solution, it can react with humic materials and other naturally occurring substances in three different ways (Jolley **et al.**, 1978; Morris, 1978; Carlson and Caple, 1978; and Rook, 1976; 1977 and 1980); viz. by oxidation, additon and substitution reactions. The last of these could lead to the formation of N-chlorinated or C-chlorinated compounds. Oxidation may be the predominant class of reaction between HOCl and organic compounds in natural and process waters (Jolley **et al.**, 1978 and Helz **et al.**, 1980). Carbohydrates and carbohydrate-related compounds would be expected to be subject only to oxidative and not to addition or substitution reactions. However, at the low concentrations at which such compounds occur in the environment, they would be expected to add to the chorine demand, but not to result in the formation of environmentally significant amounts of chloro-organics (Jolley **et al.**, 1978). Other compounds may also undergo oxidative reactions upon chlorination. Thus, in their work with estuarine colloidal matter, Helz **et al.** (1980) reported that amino acids may be subject to oxidative decarboxylation as follows:

$$Cl_2 + R.CH(NH_2).COOH + H_2O \longrightarrow CO_2 + R.CHO + NH_3 + 2Cl^- + 2H^+$$

which is in agreement with the findings of Stanbro and Smith (1979) who have shown that when alanine is chlorinated, N-Chloroalanine is formed mainly in the ionic form of (at higher pH values):



$$\mathrm{H-\underset{Cl}{N}-\overset{CH_3}{\underset{H}{C}}-C(=O)O^-}$$

This subsequently decomposes to form NH_3, CO_2, HCl and acetaldehyde. Alkanes, fatty acids and similar compounds which can be designated by an approximate empirical formula of ($-CH_2$) can also be oxidised (Helz **et al.**, 1980)

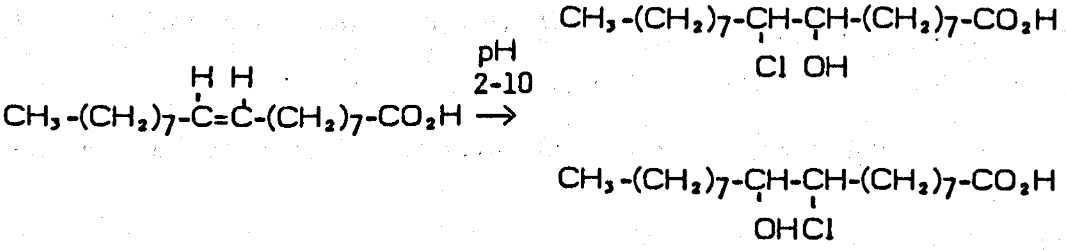
$$3Cl_2 + (CH_2) + 2H_2O \rightarrow CO_2 + 6H^+ + 6Cl^-$$

Oxidation reactions of an inorganic nature involving constituents other than NH_3 and Br^- may also occur. For example, in the oxidation of iron,

$$2Fe^{2+} + HOCl + 5H_2O \rightarrow 2Fe(OH)_3 + 5H^+ + Cl^-$$

manganese (Mn^{2+}), nitrite, sulphide and sulphite may also react in a similar manner (Jolley and Carpenter, 1983).

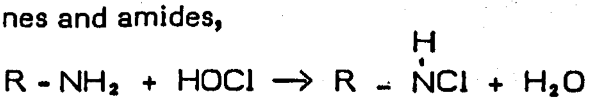
Halogen-addition reactions with organic compounds such as unsaturated fatty acids lead to the formation of chlorohydrins (Carlson and Caple, 1978),



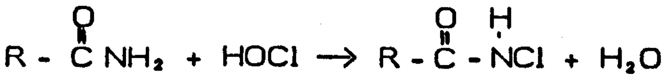
$$\mathrm{CH_3-(CH_2)_7-\overset{H}{C}=\overset{H}{C}-(CH_2)_7-CO_2H \xrightarrow{pH\ 2-10} \begin{cases} CH_3-(CH_2)_7-\underset{Cl}{CH}-\underset{OH}{CH}-(CH_2)_7-CO_2H \\ CH_3-(CH_2)_7-\underset{OH}{CH}-\underset{Cl}{CH}-(CH_2)_7-CO_2H \end{cases}}$$

However, Morris (1975) suggested that additional chlorination and rupture of the chain may also occur.

The formation of N-chlorinated compounds results from the reaction of HOCl with amines and amides,

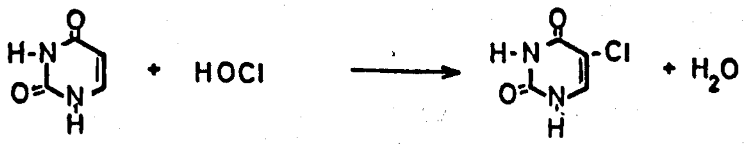


$$\mathrm{R-NH_2 + HOCl \rightarrow R-\overset{H}{N}Cl + H_2O}$$



$$\mathrm{R-\overset{O}{\overset{\|}{C}}NH_2 + HOCl \rightarrow R-\overset{O}{\overset{\|}{C}}-\overset{H}{N}Cl + H_2O}$$

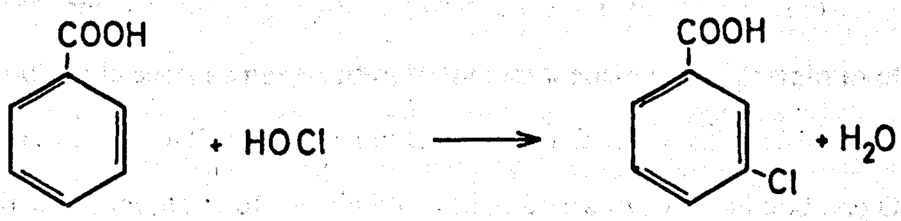
Other organic nitrogenous compounds may also undergo substitution reactions leading to the production of their chlorinated analogues, for example, pyrimidines such as uracil reacts as follows:

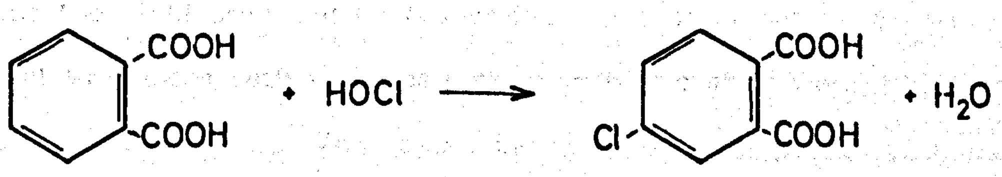


Moreover, proteinaceous material of bacterial cell wall and the purine and pyrimidine bases in the nucleic acids of living cells and decomposing plant and animal matter may also be subject to N-chlorination reactions.

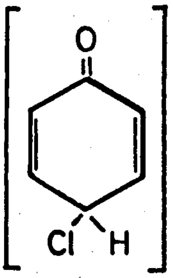
C-chlorinated compounds may also be formed by substitution reactions involving chlorine and organic compounds. Two principal types of such reactions are significant from the point of view of environmental health and ecology. They include substitution into aromatic or heterocyclic compounds and the haloform reaction.

Aromatic compounds such as phenols and aromatic acids (e.g. benzoic and phthalic acids) have been detected in surface waters and sewage effluents (Pitt **et al.**, 1975). Humic substances also contain aromatic moieties as is shown by the fact that on degradation products such as benzoic acid, catechol, 3,4-dihydroxybenzoic acid, 4-hydroxybenzoic acid, 2-methylphenol, 4-methylphenol, resorcinol, syringic acid and vanillin are formed (Christmann and Minear, 1971). These compounds are readily chlorinated to produce chlorine substituted derivatives. The following are examples of such reactions involving benzoic and phthalic acids:

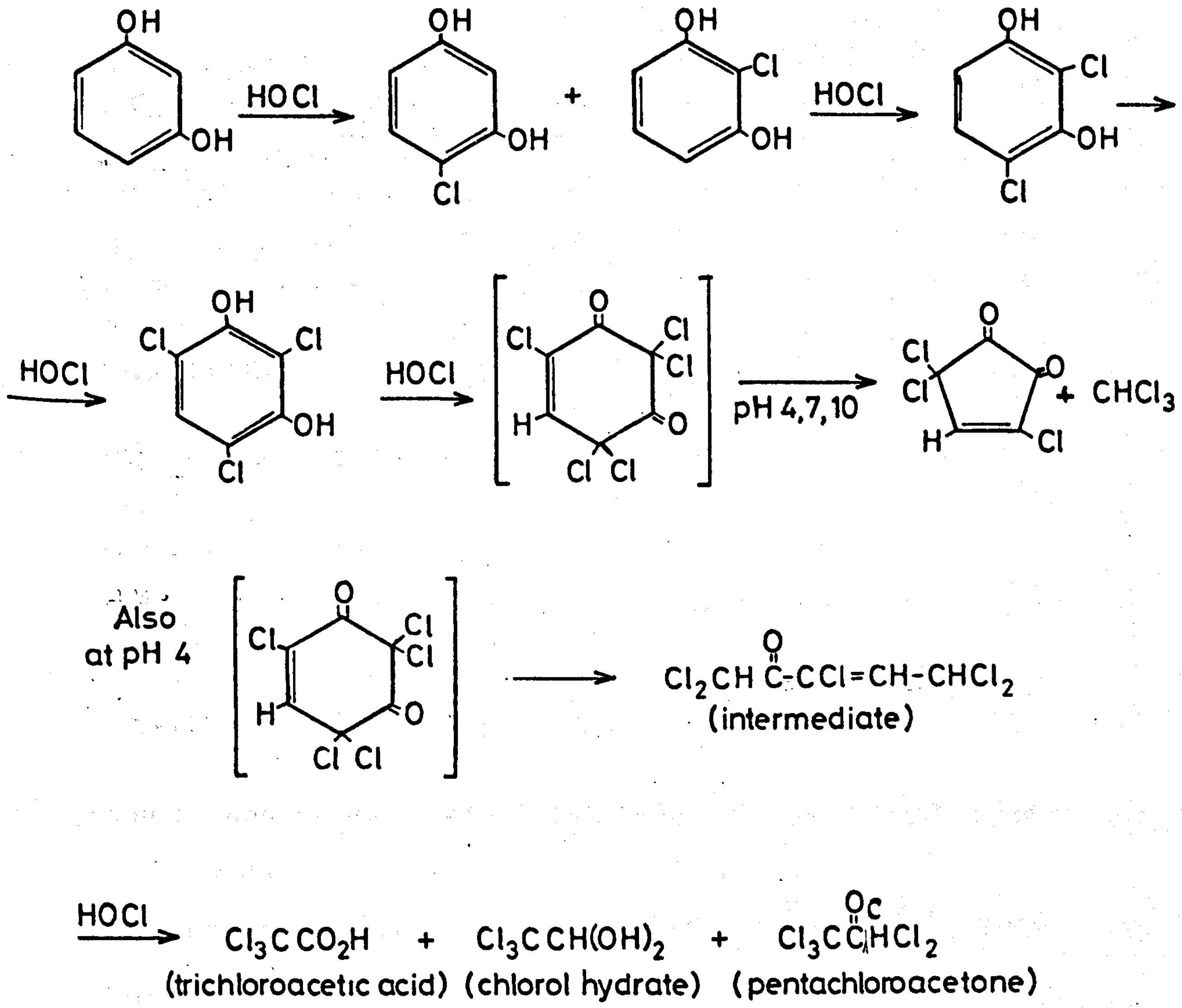




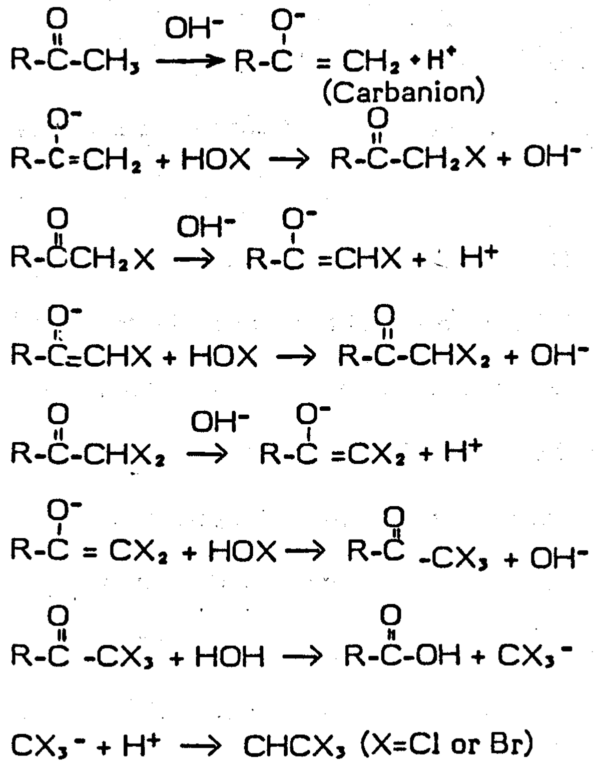
The readiness of these compounds to be chlorinated is attributed to their "activation" by one or more substituents (e.g. OH or CO_2H) in contrast to benzene itself and many of its derivatives which require more active electrophiles than HOCl (e.g. Cl^+ or H_2OCl^+) for chlorine substitution to occur (Morris, 1978). The mechanism involves electrophilic attack by HOCl on the phenoxide which results in the addition of Cl^+ to the aromatic ring in the activated ortho and para positions. A transitory intermediate is formed which, in the formation of p-Chlorophenol (for example), may be represented by the following formula (Morris, 1978):



This is followed by loss of H^+ from the para position to form $ClC_6H_4O^-$. The substitution can proceed until all para and ortho positions are occupied and then to the ring rupture to produce $CHCl_3$ (or $CHBr_3$ if HOBr is used), (Morris, 1978). This was demonstrated by Rook (1977) who used as models substances containing hydroxylated benzene moieties, matching those in fulvic acids such as hesperidin, hesperetin, rutin and phlorizin in chlorination experiments. All of these contained two free meta-positioned OH-groups, with the exception of hesperidin which contains one OH and one O-glucoside group. All gave high yields of $CHCl_3$, ranging from 30 to 90% (expressed as molar percentages). Hesperitin (with two free meta-OH groups) gave nearly twice the yield produced by hesperidin. In another set of experiments, model substances with moieties present in humic acids were subjected to chlorination in water. The results indicated that compounds with meta-substituted carbons gave high yields of $CHCl_3$ which increased as the pH was raised. These compounds included 1,3-dihydroxybenzene (resorcinol), 1,3-dihydroxynaphthalene (naphthoresorcinol), 3,5-dihydroxybenzoic acid, 3,5-dihydroxytoluene and phloroglucinol (1,3,5-trihydroxybenzene). This behaviour is in contrast to that shown by other compounds such as phenol, pyrogallol (1,2,3-trihydroxybenzene), catechol (1,2-dihydroxybenzene) and hydroquinone (1,4-dihydroxybenzene) which produced only low yields of $CHCl_3$ at pH 7. The increase in $CHCl_3$ yields when the pH was raised was attributed to an increase in the proportion of phenoxide ions. It should be noted that the experiments also showed that chlorine consumption in oxidation and substitution reactions of phenolic compounds at pH 12 was much higher than with their methylated counterparts, suggesting that methylation protects phenolic compounds against these reactions. However, at lower pH values, at which hypochlorous acid which is more reactive than OCl^-, becomes the dominant chlorinating species, chlorine consumption increased (Rook, 1980). Working over a wider range of pH, Boyce and Hornig (1980) and Boyce **et al.** (1983) conducted similar experiments which showed that halogenation and subsequent ring rupture and release of $CHCl_3$ and $CHBr_3$ also occur at pH values lower than those reported by Rook. Moreover, the same authors used ^{13}C-labelled resorcinol (2-^{13}C-1,3-dihydroxybenzene) to show that chlorination and bromination proceed via the same pathway and that the production of $^{13}CHCl_3$ and $^{13}CHBr_3$ occurs by electrophillic halogenation leading subsequently to cleavage at the C_2-site in the aromatic ring. They proposed the following reaction chain which shows that halomethanes are not formed from dihydroxybenzenes by a simple haloform mechanism as was implied by Rook's work:



It should be noted that other intermediates have been shown to be formed when resorcinal is chlorinated under different chlorination conditions (Norwood **et al.**, 1980). Rook (1974) was the first to suggest that electrophillic addition of halogens to activated double bonds via the haloform reaction is the major mechanism responsible for the formation of halomethanes in chlorinated waters. The reaction occurs generally in alkaline aqueous solutions with compounds containing the acetyl moiety $(CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-})$ or compounds oxidisable to that structure (Morris, 1975). The reaction sequence has been summarised by Morris (1978) as follows:



$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}CH_3 \xrightarrow{OH^-} R{-}\overset{\overset{O^-}{|}}{C}=CH_2 + H^+}$$

(Carbanion)

(enolizatine step)

$$\mathrm{R{-}\overset{\overset{O^-}{|}}{C}=CH_2 + HOX \rightarrow R{-}\overset{\overset{O}{\|}}{C}{-}CH_2X + OH^-}$$

$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}CH_2X \xrightarrow{OH^-} R{-}\overset{\overset{O^-}{|}}{C}=CHX + H^+}$$

$$\mathrm{R{-}\overset{\overset{O^-}{|}}{C}=CHX + HOX \rightarrow R{-}\overset{\overset{O}{\|}}{C}{-}CHX_2 + OH^-}$$

(Halogenation Steps)

$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}CHX_2 \xrightarrow{OH^-} R{-}\overset{\overset{O^-}{|}}{C}=CX_2 + H^+}$$

$$\mathrm{R{-}\overset{\overset{O^-}{|}}{C}=CX_2 + HOX \rightarrow R{-}\overset{\overset{O}{\|}}{C}{-}CX_3 + OH^-}$$

$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}CX_3 + HOH \rightarrow R{-}\overset{\overset{O}{\|}}{C}{-}OH + CX_3^-}$$

(Hydrolysis Step)

$CX_3^- + H^+ \rightarrow CHCX_3$ (X=Cl or Br)

The mechanism involves an initial dissociation to form a carbanion which is then followed by electrophillic attack by which a halogen is added to the α-carbon atom. Subsequent dissociation and addition continues at the same carbon atom until it is fully halogenated. The halogenation step is then followed by a hydrolysis step to form a halomethane and a carboxylate. The rate determining step in the process is the enolization which at pH values around 7 is too slow to account for the amount of chloroform formed during the chlorination of natural waters (Rook, 1974; Rook, 1976; Morris, 1978 and Stevens **et al.**, 1978). Thus, Rook (1976) has concluded that it would take more highly activated structures than simple methyl ketones to produce chloroform in quantities comparable to those produced upon chlorination of natural waters, a compound having the structure of acetyl acetone in which a methylene group lies between two carbonyl groups (CH_3 $COCH_2$ $COCH_3$). Rook (1976) tested three such compounds, indanedione, cyclohexanedione-1,3 and 5,5-dimethylcyclohexandione-1,3 for chloroform production in aqueous solutions. Relatively high yields of $CHCl_3$ were obtained at pH 7.8 from all of them, compared to acetone which produced only traces of $CHCl_3$. Higher yields were obtained at pH 11, with acetone producing a relatively higher yield as well. Rook's data has been confirmed by the work of others (e.g. Christmann, **et al.**, 1978; Norwood **et al.**, 1980; Boyce and Hornig, 1980; Boyce **et al.**, 1983 and Gurol **et al.**, 1983. However, not all the investigators are in agreement with his conclusion that the haloform reaction is the principal mechanism for halomethanes production.

Although the mechanisms involved in the reactions of HOBr with organic compounds are probably similar to those for HOCl, the rates and extent of the halogen substitutions differ as the bromide ion concentrations of the chlorinated water changes. Using model compounds containing moities matching some of those present in humic acids, Rook **et al.** (1978) and Rook (1980) have conducted experiments utilising HOCl and HOBr separately. The results of these showed that the yields of $CHBr_3$ were higher than those of $CHCl_3$ for most of the compounds tested. The increase was especially apparent for the least activated compounds such as 3- and 4-hydroxybenzoic acids, 3- and 4-methoxybenzoic acids and 3,5-dimethoxybenzoic acid. Rook interpreted these findings as indicating that these compounds, despite the fact that they are only slightly dissociated in water and hence only occur to a small extent as phenolate ions, are still attacked by HOBr because of the superior substitutive powers of bromine compared with chlorine.

In another experiment, $2\text{x}10^{-3}$M of resorcinol was reacted with a combination of chlorine and bromine ($6\text{x}10^{-3}$M of each) at pH 7.4. The total amount of halomethanes produced was 0.77 millimoles, 86% of which was $CHBr_3$, 14% $CHBr_2Cl$, 0.3% $CHCl_2Br$ and no $CHCl_3$ was detected. The effect of the presence of bromide ions on the speciation of halomethanes is further supported by experimental and field measurements (Oliver, 1980;

Minear and Bird, 1980; Sugam and Helz, 1981; Boyce **et al.**, 1983; Gould **et al.**, 1983 and Cooper **et al.**, 1983).

The above summary shows that possible organic sources of the halomethanes found in chlorinated waters are manifold (see also Morris, 1975). The rates and extent of halogen substitution reactions that may lead to the production of halomethanes are influenced by factors such as pH, original concentration of Br^-, type and concentration of substrate and temperature. It is also apparent that the mechanisms responsible for the eventual formation of halomethanes have not been clearly established. However, the ubiquity of these compounds may indicate the existence of several mechanisms, including the haloform reaction suggested by Rook.

2.2 Materials and Methods

Three attempts were made to investigate the factors involved in the formation of halomethanes in the water types of Kuwait. The first attempt was aimed at studying the effect of boiling chlorinated sea water, under reduced pressure, on the formation of halomethanes. Six litres of sea water were boiled under reduced pressure and low temperatures, utilising a 10 litre Büchi rotary evaporator fitted with a vacuum control unit. The temperature in the reaction vessel was maintained by controlling the temperature of the water bath with a contact thermometer. The receiving flask was immersed in an ice bath to minimise the loss of halomethanes. Triplicate experiments were carried out to study the rate of halomethanes formation. The effects of temperature, ammonia, plankton and petroleum hydrocarbons on the concentrations of halomethanes formed were also investigated. However, the system could not be maintained in a leak-proof state and loss of the halomethanes into the vacuum-system resulted in irreproducible results and the data were discarded.

The apparatus used in the second alternative approach consisted of a one litre 3-necked round-bottomed flask. The central neck of the flask was fitted with a condenser and this in turn was connected to a manometer tube filled with mercury which acted as a safety valve and also served to prevent the loss of volatiles. A 10 ml separatory funnel with stopcock was inserted in the second neck of the flask. The top of the funnel was connected to a supply of purified nitrogen gas. The third neck of the flask was fitted with another 10 ml separatory funnel to which the chlorine solution was transferred. The whole assembly was placed in a water bath fitted with a heater which was connected to a contact thermometer. A magnetic stirrer was used to achieve mixing during the reaction. In each experiment, 750 ml of filtered sea water was transferred into the reaction flask. The system was allowed to reach the desired temperature and then purged with N_2. The gas connections were removed and a 2 ml aliquot of 0.1N solution of sodium thiosulphate was transferred to the funnel with the stopcock closed. To start the experiment, chlorine solution was introduced into the reaction vessel and the magnetic stirrer was turned on. At the completion of the experiment, sodium thiosulphate was added in order to stop the reaction by removing the free halogen. The whole system was cooled to about 5°C before a sample of water was transferred from the flask to a 250 ml dark brown glass bottle. Experiments were performed (in triplicate) to investigate the rate of halomethanes formation and the effect of temperature, chlorine dose, particulate matter (biogenic and inorganic), ammonia-nitrogen and petroleum hydrocarbons on the levels of halomethanes formed in chlorinated waters. In these experiments also, the results were irreproducible and thus the data were discarded. It was apparent that the existence of a head space inside the reaction vessel was the primary cause of variability in the results.

To eliminate the head space problem, a gas-tight reaction vessel (Figure 2.1) was constructed at the workshop in the Department by Mr. R.H. Tennant and Mr. J. Murphy. This consisted of a uniform diameter (5 cm) Pyrex glass tube (30 cm long) fitted with an opening for a rubber septum (for the introduction of the chlorine and sodium thiosulphate solutions) and an outlet with a Teflon stopcock to allow the samples to be withdrawn. A plunger, with a Teflon disc fitted with O-rings mounted on a stainless steel rod, served as a piston so as to eliminate the formation of a head space during the experiment and during the removal of the sample.

To start up the experiment, the pre-cleaned vessel was filled with the water sample, a Teflon-coated magnet was placed in the vessel and the plunger was inserted with the outlet stopcock open until it reached a pre-calibrated mark (500 ml), care being taken to ensure that no air bubbles were trapped. The vessel was then placed over a magnetic stirrer and the motor was turned on at a moderate speed that had been previously found (using a dye) to bring about constant gentle mixing. The chlorine solution was taken from a stock solution (500 mg/l) prepared by dissolving calcium hypochlorite in distilled water, free from volatile organic compounds. A blank determination of the chlorine solution showed it to be free from halomethanes. The residual chlorine concentration in the reaction vessel was confirmed by amperometric titration (Fisher),*. The reaction time was measured by use of stopwatch. Once the reaction was completed, 1 ml of 0.1N sodium thiosulphate was injected into the vessel to stop the reaction and the samples were transferred into 200 ml dark brown glass bottles for halomethanes analysis. However, this was not done if the reaction was to be continued and 0.5 ml of the thiosulphate solution was added to the receiving bottle. Once the sample was collected, it was stored over ice until it could be analysed (which took place within six hours). The methods of extraction

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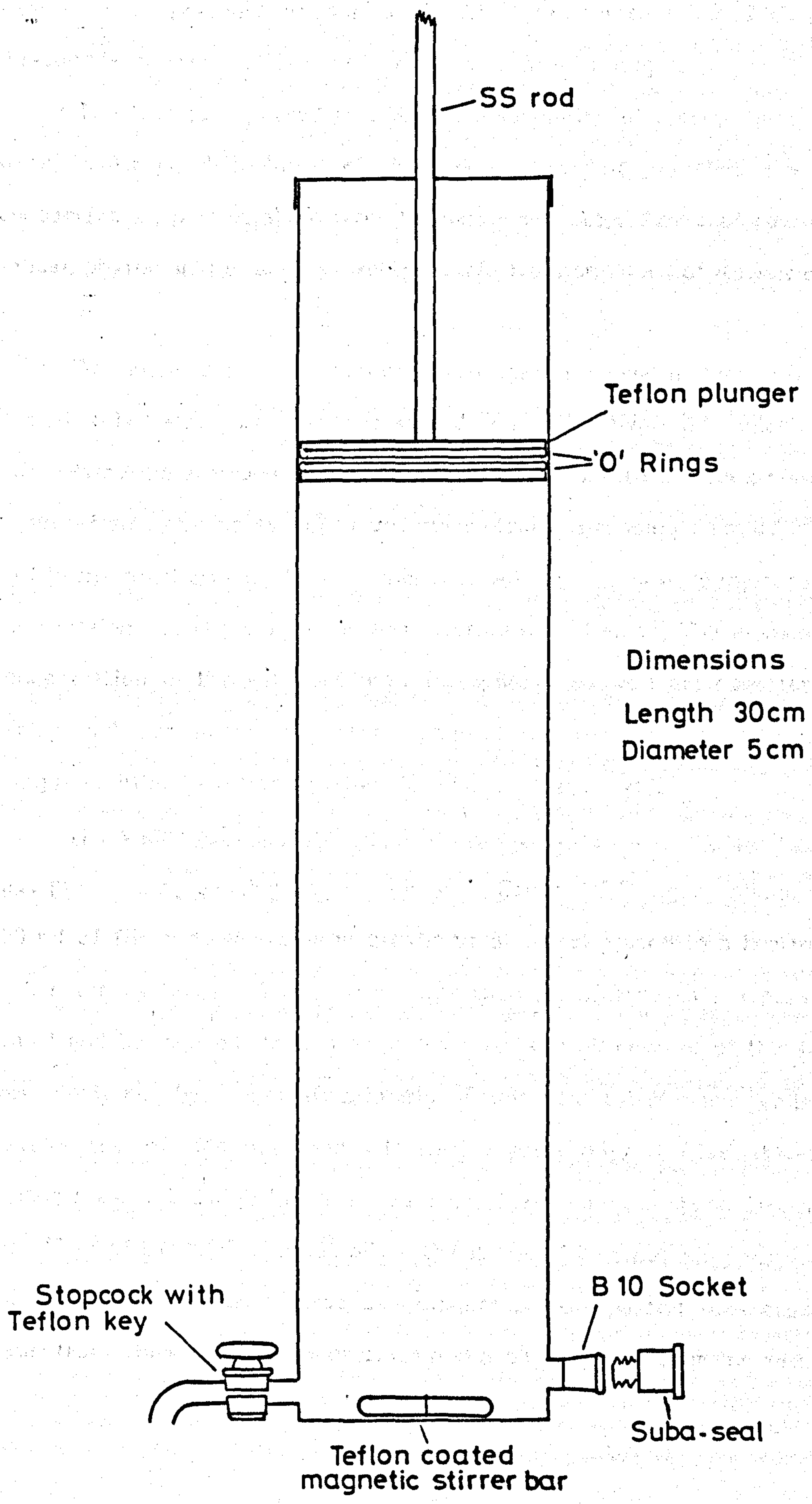
* using a technique based on treatment of the sample with potassium iodide and titration of the resultant iodine with phenylarsine oxide. The endpoint is reached when no further decrease in the current occurs on addition of more titrant (Standard Methods, 1975).

Figure 2.1 Reaction Vessel Used in the Experimental Work


SS rod
Teflon plunger
'O' Rings
Dimensions
Length 30cm
Diameter 5cm
Stopcock with
Teflon key
B 10 Socket
Suba-seal
Teflon coated
magnetic stirrer bar

and analysis of halomethanes described earlier were followed. All experiments were performed at sub-ambient temperature (19-22°C) in an air-conditioned room allowing no exposure to direct sunlight.

The factors expected to affect the formation of halomethanes that were investigated included chlorine dose, time of reaction, ammonia concentration, particulate matter (plankton and other forms of suspended solids), phytoplankton and the water soluble fraction (WSF) of Kuwait crude oil.

Ammonia used for spiking chlorinated sea water was prepared immediately before use from a standard ammonium hydroxide solution (in BDH sealed glass ampoules). Dilutions were made with distilled, volatile-organic-free water so as to produce concentrations ranging from 19.0 - 72 µg/l in the reaction vessel. The amounts used for spiking were injected into the reaction vessel prior to the introduction of chlorine. The ammonia-N concentration in the solutions used for spiking, as well as those for the background level in the sea water used in all experiments, was determined using a modified indophenol method (Liddicoat **et al.**, 1975).

The water soluble fraction of crude oil (WSF) used for spiking was first prepared by shaking 25 ml of Kuwait Crude (KOC export blend) with 250 ml of filtered sea water in a cylindrical vessel placed in a horizontal shaker for 24 hours. The mixture was then transferred to a separatory funnel and the aqueous layer was withdrawn. The oil content of this layer was analysed by spectrofluorimetry (using excitation and emission wavelengths of 365 nm and 415 nm respectively). Five different concentrations (2-200 µg/l) were used in duplicate experiments to determine the effect of the WSF of crude oil on the levels of halomethanes formed in chlorinated sea water. These experiments were repeated with drinking water from which the volatile organics had been purged by sparging with N_2

at 80°C for 30 minutes. However, since the aqueous layer contained not only soluble fractions of oil but also fine droplets of oil-in-water and water-in-oil emulsions, the extract did not represent a truly WSF of crude oil, but more a water accommodated fraction (WAF). For this reasion, the WSF was prepared for the next set of experiments (involving longer reaction times) by filtering the aqueous layer through a Whatman No. 1 filter paper after withdrawal from the separatory funnel. Another difference from the WSF used in the short reaction time experiments was that a 20% ratio of crude oil to sea water was used in the extraction. The long term experiments were carried out using 600 ml dark brown glass bottles as reaction vessels. The volume of the WSF used for spiking was introduced by syringe into the bottle which was then capped allowing no air bubbles to be trapped. The chlorine solution was then injected through the Teflon-faced rubber septum lining the cap. The experiments were performed on drinking water (which had been purged of volatile organics) and on filtered sea water. The reaction times applied were 6, 12, 24 and 48 hours. Control experiments were run on both types of water. Blanks were also run on waters without the addition of chlorine and the results from these were used to correct for the concentrations of halomethanes produced especially those of $CHCl_3$ and CCl_4 whose reaction times coincided with peaks of the solvent (n-pentane) used for the extraction.

Particulate matter (plankton and other suspended matter) used in the experiments was obtained 24 hours earlier by towing a standard phytoplankton net off the Bedaa area, the same location from which the sea water used in the experiments had been collected. After several tows, a concentrate was obtained containing phytoplankton, zooplankton and detrital matter. The concentrate was transferred to a glass bottle and subsamples used for spiking were taken by shaking the bottle and filling a automatic tilting pipette of the desired size in order to get representative samples. Samples were simultaneously collected for chlorophyll-a analysis and the results were taken as an indicator of the amount used for spiking. Chlorophyll-a was determined spectrophotometrically following SCOR/UNESCO procedures, after concentration on a 0.45 µm membrane filter and extraction in 90% acetone (Strickland and Parsons, 1972). Four different concentrations were used to spike sea water which was then chlorinated (2.1 mg/l) and samples were collected for halomethanes analysis after a reaction time of 30 minutes.

The experiments on suspended particulate matter were repeated with pure cultures of a microalga (Chlorella sp.) obtained from the aquaculture station at the Kuwait Institute for Scientific Research (KISR). A concentrate was obtained by using a hand-held plankton net. A sample of the sea water used for the culture was taken for ammonia analysis. The Chlorella suspensions were introduced into the reaction vessel using a tilting pipette of an appropriate size. Equivalent amounts were also taken for chlorphyll-a analysis. Two more sets of experiments on the effect of chlorophyll on halomethanes formed in chlorinated sea water were conducted using 600 ml dark brown glass bottles as reaction vessels, after the previously described vessel broke. The pre-cleaned bottles were fitted with Teflon-faced rubber septa as a liner to the cap, which allowed the introduction of chlorine and sodium thiosulphate solutions. The reaction times applied were 6, 12, 24 and 48 hours.

The waters used in the experimental study were prepared as follows. The distillate was collected from the Blending and Pumping Station at Shuwaikh, it is a mixture of the distillate produced from all the desalination plants in Shuwaikh which has been treated with sodium hydroxide to raise the pH from 6.8 to about 9. The distillate which had been shown previously to contain halomethanes was purged off by sparging with purified N_2 at 80°C for 20 minutes. Drinking water used in the experiments was also treated in the same manner. It was collected from the tap in the laboratory - after allowing the water to flow for 10 minutes. Brackish water was also collected from the Blending and Pumping Station. It is supplied from wells in the Sulaibiya and Shagayah areas, where the water levels range from 15 to 150 metres. The geological age of the waters has been estimated to be 30-50 thousand years (the Dammam formation and the Kuwait groups). Since the brackish water had not been chlorinated it was used without treatment. All three types of water described were used along with sea water in studying the effect of reaction time and chlorine level on the formation of halomethanes. Only drinking water and sea water were used in studying the effect of the WSF of Kuwait Crude on the formation of halomethanes in chlorinated waters. The sea water used in the experiments was freshly collected from 2 m depth off the Bedaa area, which is one of the least polluted areas of the coastal waters of Kuwait. It was filtered by pumping (using a peristaltic pump) through a column containing 2 cm of glass wool, a 7 cm layer of purified sand and another 2 cm layer of glass wool on top. The column and the filtration bed were pre-cleaned by washing with n-pentane and heating at 200°C for 24 hours. This method of filtration was used to remove suspended solids while allowing the soluble organics to be available for the reaction with the halogens. Water pumped in this way was selected in preference to synthetic sea water in order to approximate the natural conditions.*

Parallel to the blanks, 100 ml aliquots of the waters used in the experiments were preserved for DOC analysis by addition of 40 mg/l of mercuric chloride. These samples were analysed in the Oceanography Department by Mr. H. Rogers using the technique described by Parker

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*It should be noted that no anti-foaming and anti-scale agents were added to the seawater used in the experiments in contrast to their use in the desalination plants.

(1978). Results were expressed in mgC/l (Urea). DOC analysis was also carried out on some of the samples following chlorination. The background levels of the bromide ion in the waters used in the study were also determined in the Department, in samples which had not been treated with preservative, using the tentative method adopted by the Standing Committee of Analysts (1981) which is based on the oxidation of bromide to bromate followed by iodometric determination (Morris and Riley, 1966). The pH and water temperature were also measured during the experiments.

2.3 Results and Discussion

2.3.1 The Effect of Chlorine Concentration and Reaction Time on the Formation of Halomethanes:

The effect of chlorine dosage and reaction time intervals on the levels of halomethanes produced in the four types of water in use in Kuwait was investigated in several experiments. The results are presented below according to the types of water.

a) Sea Water

Chlorination experiments on freshly collected and filtered sea water were conducted in three groups, utilizing various residual chlorine levels and reaction times. In the first group, the reaction vessel described in Figure 2.1 was used in running duplicate experiments involving total residual chlorine levels of 1.1, 2.1 and 3.3 mg/l and using reaction times for each chlorine level of 15, 30 and 60 minutes. The experiments on 3.3mg/l residual chlorine were also run for 90 minutes. The water temperature was 22°C and the pH value 8.1. The background DOC level was 2.36 ±0.14 mgC/l and the mean ammonia-nitrogen concentration was 13.2 ± 3.8 μg NH_3 - N/l whereas the bromide ion concentration was 75.0 ±0.25 mg Br^-/l. The results of the halomethanes analysis are summarised in Table 2.1. The levels are expressed as a pooled mean and standard deviation for three GC runs on the sample for each reaction time. The values were rounded off to one decimal point, thus considering concentrations less than 0.05 μg/l to be

Residual Chlorine mg/l	Reaction Time (min)	Halomethanes Concentrations µg/l				
		$\bar{x}$ SD	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total
1.1 mg/l	15	$\bar{x}$	0	1.9	65.3	67.2
		SD		0.1	2.7	2.8
	30	$\bar{x}$	0	2.3	75.4	77.7
		SD		0	1.6	1.7
	60	$\bar{x}$	0	2.8	97.0	99.9
		SD		0.1	1.1	1.1
2.1 mg/l	15	$\bar{x}$	0	2.4	70.7	73.1
		SD		0.2	1.8	2.1
	30	$\bar{x}$	0	2.9	87.7	90.6
		SD		0.1	1.6	1.6
	60	$\bar{x}$	0	3.3	98.7	102.0
		SD		0	0.7	0.7
3.3 mg/l	15	$\bar{x}$	0	2.5	72.2	74.8
		SD		0.1	1.8	1.9
	30	$\bar{x}$	0	3.0	91.6	94.6
		SD		0	1.7	1.8
	60	$\bar{x}$	0	3.5	101.3	104.8
		SD		0.1	4.3	4.4
	90	$\bar{x}$	0	3.9	117.3	121.3
		SD		0.1	4.4	4.5

Table 2.1

Mean Concentrations of Halomethanes Formed in 500 ml of Chlorinated Sea Water According to Levels of Chlorine and Reaction Time. pH = 8.1, Temperature 22°C, Br^- = 75 mg/l and DOC = 2.36 mgC/l

zero. The concentrations indicated were corrected for the blanks. Interference of solvent peaks with those of $CHCl_3$ and CCl_4 and possible contamination by the air conditioning system (especially for CCl_4) made it difficult to ascertain whether they were present in the chlorinated waters. However, their concentrations rarely exceeded 1µg/l after blank corrections. Thus, the discussion of the results will be limited to the three other halomethanes (i.e. $CHBr_3$, $CHBr_2Cl$ and $CHCl_2Br$).

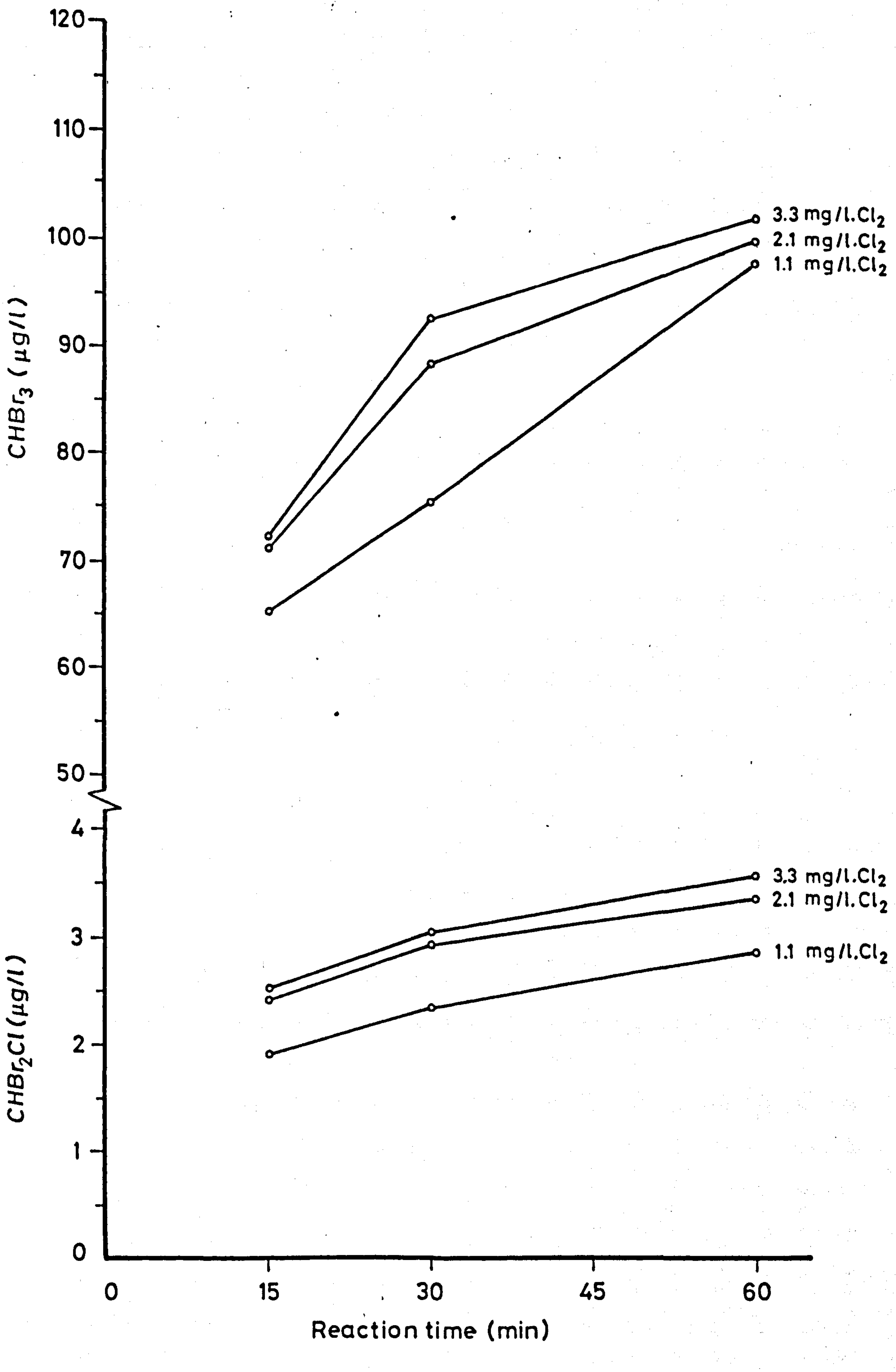
The concentrations of $CHCl_2Br$ in the chlorinated sea water were all below 0.1 µg/l. This is consistent with the field studies of sea water in the coastal areas and intakes of the desalination - power plants. Even when longer reaction times were used $CHCl_2Br$ concentrations were below 1 µg/l. The predominant halomethanes were $CHBr_3$ and $CHBr_2Cl$. The concentrations of both of these compounds increased as the reaction time and concentration of residual chlorine were increased. The halomethane concentrations produced at different reaction times (under similar chlorination conditions) were compared. In all cases, a significant increase in halomethanes was apparent with increased reaction time (Student's t test, $\alpha = 0.01$). However, the concentrations of halomethanes at various residual chlorine concentrations (for similar reaction times) did not always show a significant increase with increased chlorine concentrations as shown below.

The mean $CHBr_2Cl$ concentration produced after 15 minutes reaction time with 1.1 mg Cl_2/l was 1.9 ± 0.1 µg/l, which was significantly lower ($\alpha = 0.05$) than the yield at the same reaction times with 2.1 and 3.3 mgCl_2/l (2.4 ± 0.2 and 2.5 ± 0.1 µg/l respectively). However, the latter two concentrations were not statistically different. With a reaction time of 30 minutes, the mean $CHBr_2Cl$ concentration increased significantly from 2.3 µg/l at 1.1 mgCl_2/l to 2.9 ± 0.1 and 3.0 µg/l at 2.1 and 3.3 mg Cl_2/l ($\alpha = 0.05$). With a reaction time of 60 minutes, the mean concentration of $CHBr_2Cl$ was 2.8 ± 0.1 µg/l at 1.1 mg Cl_2/l, which was significantly lower than the mean concentrations obtained at 2.1 and 3.3 mg Cl_2/l which amounted to 3.3 and 3.5 ± 0.1 µg/l respectively ($\alpha = 0.01$). The latter two concentrations were also significantly different ($\alpha = 0.05$).

The concentrations of $CHBr_3$ produced under similar reaction time but different concentrations of total residual chlorine were also compared. The mean $CHBr_3$ concentration after a 15 minute reaction time and at 1.1 mg Cl_2/l was 65.3 ± 2.7 µg/l which was significantly lower ($\alpha = 0.05$) than the mean concentration produced at 2.1 mg Cl_2/l (70.7 ± 1.8 µg/l) and that produced at 3.3 mg Cl_2/l which amounted to 72.2 ± 1.8 ($\alpha = 0.05$). However, the latter two mean concentrations were not statistically different. This pattern was repeated where the reaction time was 30 minutes for which the mean concentration of $CHBr_3$ increased significantly from 75.4 ± 1.6 µg/l at 1.1 mgCl_2/l to 87.7 ± 1.6 µg/l at 2.1 mg Cl_2/l ($\alpha = 0.05$) and to 91.6 ± 1.7 µg/l at 3.3 mg Cl_2/l ($\alpha = 0.01$). However, the mean concentration of $CHBr_3$ produced at the 2.1 mg Cl_2/l and 3.3 mg Cl_2/l were not statistically different. When the reaction time was 60 minutes, there was no significant difference between the mean $CHBr_3$ concentrations produced which amounted to 97.0 ± 1.1, 98.7 ± 0.7 and 101.3 ± 4.3 µg/l at the three residual chlorine concentrations applied.

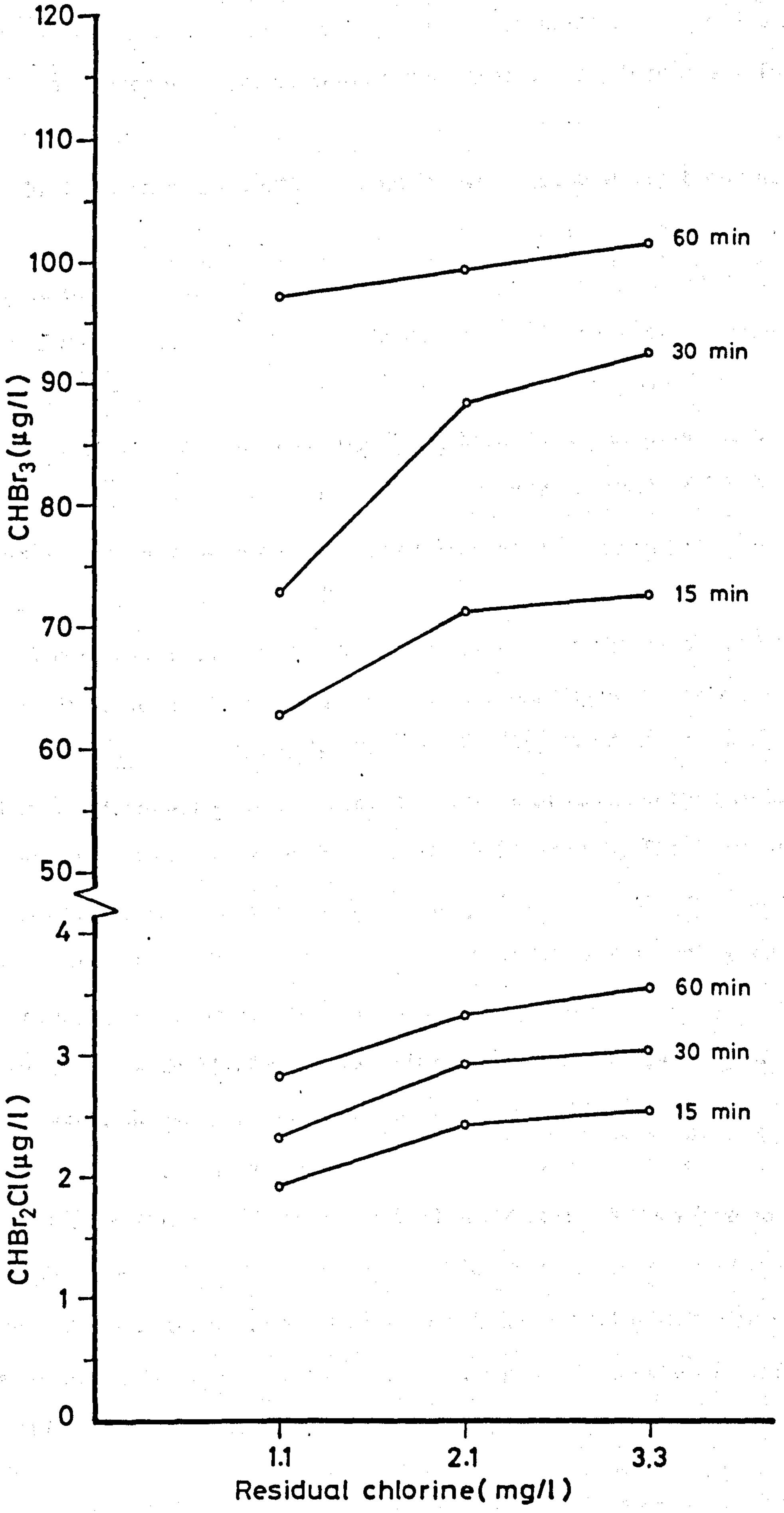
The findings discussed above suggest that under the conditions applied in these experiments, reaction time had a more important effect on the levels of halomethanes formed than did the differences in the levels of chlorine used. The differences in the effects of reaction time and chlorine concentration may also be inferred from the curves in Figure 2.2, indicating a smaller degree of variability between different chlorine levels applied. However, the curves are more scattered in Figure 2.3,suggesting a greater difference in the concentrations of halomethanes at difference reaction times. The curves in the two figures also suggest that the effects of reaction time and chlorine levels are not linear, showing a tendency towards higher rates of halomethane formation at the start of the experiment than towards the completion of the reaction time. Unfortunately, the data are

Figure 2.2 The effect of reaction times on halomethanes formed in sea water at three levels of residual Chlorine.



120
110
100
90
80
70
60
50
4
3
2
1
0
$CHBr_3$ (µg/l)
$CHBr_2Cl$ (µg/l)
3.3 mg/l.Cl_2
2.1 mg/l.Cl_2
1.1 mg/l.Cl_2
3.3 mg/l.Cl_2
2.1 mg/l.Cl_2
1.1 mg/l.Cl_2
0
15
30
45
60
Reaction time (min)

Figure 2.3 The effect of Chlorine levels on the concentrations of halomethanes formed in sea water at three different reaction times.



120
110
100
90
80
70
60
50
4
3
2
1
0
CHBr$_3$(μg/l)
CHBr$_2$Cl(μg/l)
60 min
30 min
15 min
60 min
30 min
15 min
1.1
2.1
3.3
Residual chlorine(mg/l)

insufficient to allow regression lines to be drawn to determine the rates of formation. However, a similar pattern is also apparent from chlorination experiments reported by other workers (e.g. Rook, 1977; Minear and Bird, 1980 and Cooper et al., 1983).

In the second group of experiments involving sea water, the residual chlorine level was maintained at 2.1 mg/l whereas the reaction times were increased to 90 minutes, 3 hours and 6 hours. The same reaction vessel was used and the experiments were run in duplicate. This set of experiments was conducted about three months after the first set. The background concentration of DOC was 1.95 mgC/l the bromide ion concentration was 78.7 ± 1.5 mg/l and the ammonia-nitrogen concentration was 16.2 ± 0.8 µg NH_3-N/l. The water temperature was 21°C and the pH value was 8.2. The results are summarized in Table 2.2.

The concentrations of brominated halomethanes showed a consistent picture with that of the shorter reaction times. $CHCl_2Br$ was only present in traces, not exceeding 0.1 µg/1. The concentrations of $CHBr_2Cl$ increased significantly from 4.4 ± 0.2 µg/l after 90 minutes of reaction time to 5.3 ± 0.6 µg/l after three hours of reaction time ($\alpha = 0.05$). The increase in $CHBr_2Cl$ after 6 hours of reaction time (6.3 ± 0.2 µg/l) was also significantly different from that of the 3 hours reaction time ($\alpha = 0.05$). $CHBr_3$, on the other hand, increased in concentration from 90.5 ± 3.1 µg/l after 90 minutes of reaction time to 117.3 ± 9.5 µg/l after 3 hours and to 140.8 ± 3.2 µg/l after 6 hours, all showing significant differences ($\alpha = 0.01$).

The third group of experiments was conducted using 600 ml dark brown glass bottles as reaction vessels. The chlorine solutions (and sodium thiosulphate) were introduced through the Teflon-faced rubber septa. Two concentrations of residual chlorine were used, 2.1 and 3.3 mg/l for reaction times of 6, 12, 24 and 48 hours respectively. The background levels of DOC were different in the two sets of experiments, 1.65 mgC/l for the 2.1 mg/l

Reaction Time	Halomethanes Concentrations (µg/l)				
	$\bar{x}$ SD	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total
90 min	$\bar{x}$	0	4.4	90.5	95.0
	SD		0.2	3.1	3.3
3 hours	$\bar{x}$	0.1	5.3	117.3	122.7
	SD	0	0.6	9.5	10.2
6 hours	$\bar{x}$	0.1	6.3	140.8	147.2
	SD	0.1	0.2	3.2	3.6

Table 2.2

Mean Concentrations of Halomethanes detected in 500 ml of Chlorinated Sea Water (2.1 mg/l) for Reaction Times of 90 minutes, 3 hours and 6 hours in Duplicate Experiments. pH = 8.2, Temperature = 21°C, DOC = 1.95 mgC/l and Br^- = 78.7 mg/l

of chlorine and 2.40 mgC/l for the 3.3 mg/l of chlorine. This was due to the fact that the two sets were not conducted on the same batches of sea water. They were used as controls for the experiments on the effects of petroleum hydrocarbon and phytoplankton on the formation of halomethanes in sea water. The results are summarized in Table 2.3.

At 2.1 mg/l of total residual chlorine, the concentrations of $CHCl_2Br$ were very low, not exceeding 0.3 µg/l. $CHBr_2Cl$ showed an increase with increased reaction time, from 6.8 ± 0.2 µg/l after 6 hours of reaction time to 8.0 ± 0.1, 9.6 ± 0.4 and 12.0 ± 0.6 after 12, 24 and 48 hours respectively. The concentrations of $CHBr_3$ also showed a steady increase with time, increasing from 155.3 ± 8.2 µg/l after 6 hours of reaction time to 184.3 ± 4.9, 221.6 ± 9.3 and 247.0 ± 11.8 µg/l after 12, 24 and 48 hours respectively.

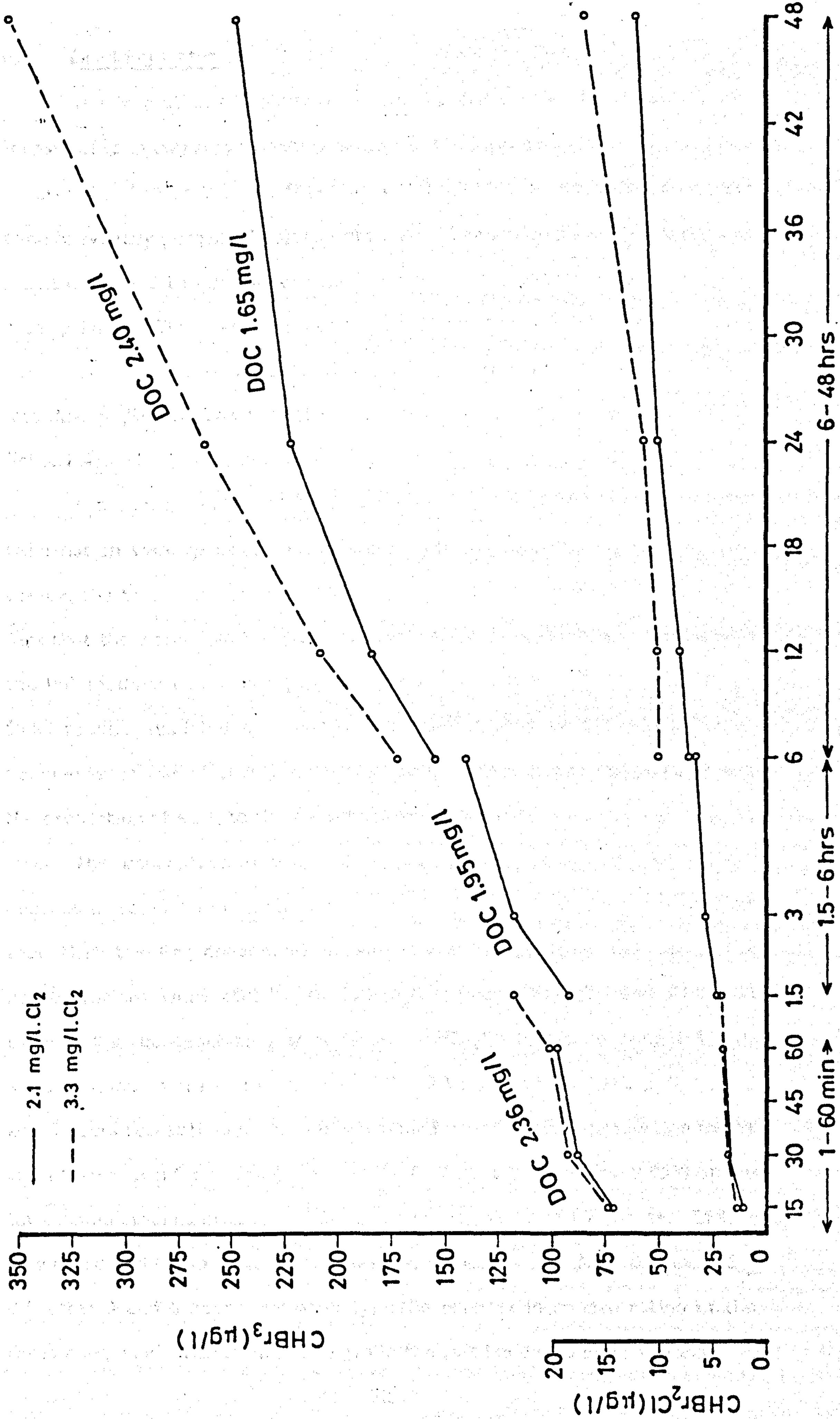
A similar trend in changes of halomethane concentrations with increased reaction time was also apparent at 3.3 mg/l of total residual chlorine. Dichlorobromomethane was detected in trace levels, ranging between 0.3 and 0.5 µg/l. The concentrations of $CHBr_2Cl$ increased from 9.8 ± 0.5 after 6 hours of reaction time to 10.2 ± 0.2, 11.3 ± 1.3 and 17.0 ± 1.0 µg/l after 12, 24 and 48 hours respectively. Bromoform concentrations showed a greater rate of increase with increased time than at 2.1 mg Cl_2/l, from 171.7 ± 8.8 µg/l after 6 hours of reaction time to 206.9 ± 8.0, 261.8 ± 13.0 and 354.8 ± 22.2 µg/l after 12, 24 and 48 hours respectively. It should be noted that the DOC concentration in the sea water used for the 3.3 mg/l of chlorine experiments was relatively higher than that used for the 2.1 mg/l chlorine experiments (i.e. 2.4 mgC/l as opposed to 1.65 mgC/l in the latter). The relative distribution of $CHBr_2Cl$ and $CHBr_3$ over the reaction time range in both sets of experiments is shown in Figure 2.4. The figure also shows the trend in the distribution of both compounds in the shorter reaction times applied in the previous experiments.

Residual Chlorine mg/l	Reaction Time (hrs.)	Halomethanes Concentrations µg/l				
		$\bar{x}$ SD	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total
2.1 mg/l (DOC = 1.65 mgC/l)	6	$\bar{x}$	0.1	6.8	155.3	162.3
		SD	0	0.2	8.2	8.4
	12	$\bar{x}$	0.1	8.0	184.3	192.4
		SD	0	0.1	4.9	5.1
	24	$\bar{x}$	0.3	9.6	221.6	231.5
		SD	0.1	0.4	9.3	9.6
	48	$\bar{x}$	0.2	12.0	247.0	259.2
		SD	0	0.6	11.8	12.4
3.3 mg/l (DOC = 2.40 mgC/l)	6	$\bar{x}$	0.4	9.8	171.7	181.9
		SD	0.1	0.5	8.8	9.4
	12	$\bar{x}$	0.3	10.2	206.9	217.3
		SD	0	0.2	8.0	8.1
	24	$\bar{x}$	0.4	11.3	261.8	273.5
		SD	0.1	1.3	13.0	14.4
	48	$\bar{x}$	0.5	17.0	354.8	372.3
		SD	0.2	1.0	22.2	23.3

Table 2.3

Mean Concentrations of Halomethanes Dectected in 600 ml of Chlorinated Sea Water Reaction Times of 6, 12, 24 and 48 Hours. Two Sets of Experiments with Residual Chlorine Concentrations of 2.1 and 3.3 mg/l Respectively: Temperature = 22°C, pH = 8.1 and Br^- = 78.7 mg/l.

Figure 2.4 Concentrations of $CHBr_2Cl$ and $CHBr_3$ formed in chlorinated sea water at two levels of residual Chlorine and reaction times ranging from 15 minutes to 48 hours. Experiments were performed on different batches of sea water.



2.1 mg/l.Cl_2
3.3 mg/l.Cl_2
DOC 2.36 mg/l
DOC 1.95 mg/l
DOC 2.40 mg/l
DOC 1.65 mg/l
$CHBr_3$ (μg/l)
350
325
300
275
250
225
200
175
150
125
100
75
50
25
0
$CHBr_2Cl$ (μg/l)
20
15
10
5
0
15
30
45
60
1.5
3
6
12
18
24
30
36
42
48
1–60 min
1.5–6 hrs
6–48 hrs
Reaction time

b) Drinking Water

The formation of halomethanes in the drinking water of Kuwait was investigated in two sets of experiments. In the first set, the reaction vessel described in Figure 2.1 was filled with 500 ml of drinking water which had been previously purged of volatile organics. The residual chlorine level was maintained at 2.1 mg/l whereas the reaction times used included 90 minutes, 3 and 6 hours. The pH of the water was 7.9 and the water temperature was 22°C. The background DOC level was 1.85 mgC/l and the Br^- concentration was 0.53 $mgBr^-/l$. The results of halomethane analysis are summarised in Table 2.4.

The concentrations of halomethanes produced in drinking water upon chlorination were generally lower than those encountered during the field survey, the total ranging from 2.9 to 8.1 µg/l. This may be attributed to the fact that the water was "re-chlorinated" in these experiments, after purging the halomethanes produced in the original chlorination. Thus, some of the DOC readily available to undergo reactions leading to the formation of halomethanes was already removed. However, the species composition and the proportion of each to the total remained similar.

The concentration of $CHCl_3$ could not be determined accurately because of solvent interferences and contamination. However, despite the fact that the Br^- concentration was lower than that in sea water the concentrations were still below 1.0 µg/l. Both $CHCl_2Br$ and $CHBr_2Cl$ increased in concentration with time. $CHCl_2Br$ increased from 0.4 µg/l after 90 minutes of reaction time to 0.7 ± 0.1 µg/l and 1.0 ± 0.2 µg/l after 3 and 6 hours respectively. Both compounds formed a larger proportion to the total than shown for sea water for which $CHBr_3$ comprised over 95% of the total halomethanes produced. After a reaction time of 90 minutes, $CHBr_3$ only amounted to 0.5 ± 0.1 µg/l. However, it increased to 3.1 ± 0.1 and 3.6 ± 0.4 after 3 and 6 hours respectively. The changes in concentration of the three compounds with time are shown in the left hand side of Figure 2.5.

Reaction Time	Halomethanes Concentrations (µg/l)				
	$\bar{x}$ SD	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total
90 minutes	$\bar{x}$	0.4	2.0	0.5	2.9
	SD	0	0	0.1	0.1
3 hours	$\bar{x}$	0.7	3.0	3.1	6.8
	SD	0.1	0.2	0.1	0.3
6 hours	$\bar{x}$	1.0	3.5	3.6	8.1
	SD	0.2	0.3	0.4	0.9

Table 2.4

Mean Concentrations of Halomethanes Formed in 500 ml of Chlorinated Drinking Water (2.1 mg/l) for Reaction Times of 90 minutes, 3 hours and 6 hours in Single Experiments.
pH 7.9, Temperature = 22°C, DOC = 1.85 mgC/l and Br^- = 0.53 $mgBr^-/l$

In the second set of experiments, chlorinated drinking water (2.1 mg/l) was left for longer reaction times, from 6 to 48 hours, in 600 ml dark brown glass bottles. The background DOC was slightly lower than in the previous set, 1.65 mgC/l. The pH of the water used was 7.8 and the temperature was 22°C. Samples were not analysed for bromide ion as it was assumed that it would be similar to that of the previous batch (0.53 mgBr$^-$/l). The results of the halomethanes analysis are shown in Table 2.5.

The concentrations of total halomethanes were still lower than those observed in the field study, the maximum value was below 20 µg/l. The concentrations of both $CHCl_2Br$ and $CHBr_2Cl$ increased with time, but at a slower rate than $CHBr_3$. Dichlorobromomethane increased only slightly from 0.9 µg/l after 6 hours of reaction time to 1.0 µg/l and 1.2 µg/l after 12 and 24 hours respectively. It showed no increase as reaction time increased from 24 to 48 hours. Dibromochloromomethane concentrations showed a slightly greater tendency to increase with time (from 3.1 ± 0.2 µg/l after 6 hours of reaction time to 3.5 µg/l, 3.8 µg/l and 4.2 ± 0.3 µg/l after 12, 24 and 48 hours respectively). Both compounds made a higher contribution to the total halomethanes produced (as in the short term experiments) than shown in the sea water experiments. Bromoform concentrations, on the other hand, showed a much greater tendency to increase with time, increasing from 3.8 ± 0.2 µg/l after 6 hours of reaction time to 6.3 ± 0.1 µg/l, 8.9 ± 0.2 µg/l and 11.4 ± 0.8 µg/l after 12, 24, 48 hours respectively.

The change in concentrations of halomethanes with increase in reaction time are presented graphically in Figure 2.5. It was noted that the rise in the curve for both $CHCl_2Br$ and $CHBr_2Cl$ is slight, almost levelling out after 48 hours whereas that for $CHBr_3$ showed a definite tendency to increase with time.

c) Brackish Waters

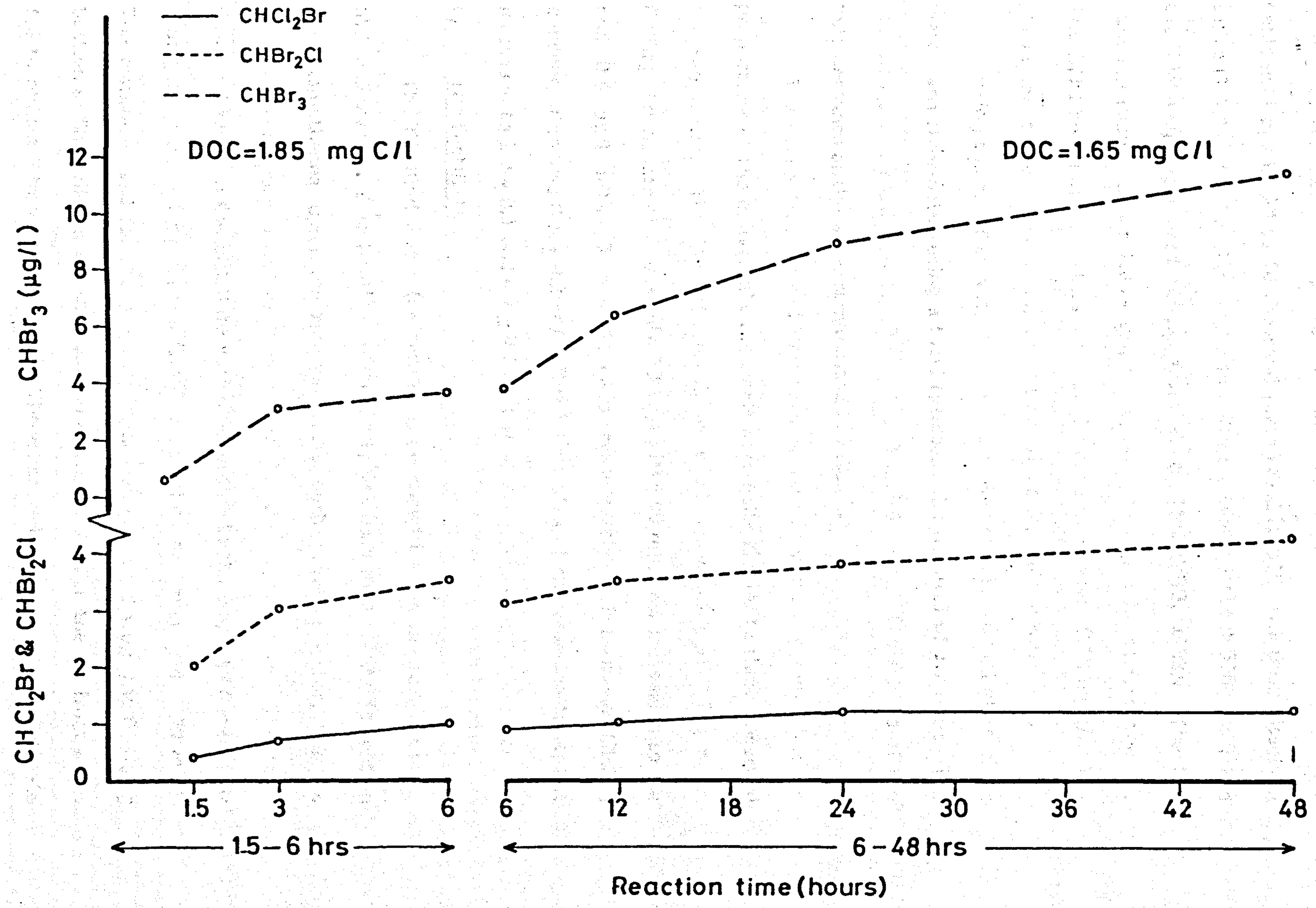
The brackish waters used for blending with the distillate to produce potable water were also investigated for halomethanes production upon

Reaction Time	Halomethanes Concentrations (µg/l)				
	$\bar{x}$ SD	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total
6 hours	$\bar{x}$	0.9	3.1	3.8	7.8
	SD	0	0.2	0.2	0.4
12 hours	$\bar{x}$	1.0	3.5	6.3	10.8
	SD	0	0	0.1	0.1
24 hours	$\bar{x}$	1.2	3.8	8.9	13.9
	SD	0	0	0.2	0.2
48 hours	$\bar{x}$	1.2	4.2	11.4	16.8
	SD	0	0.3	0.8	1.0

Table 2.5

Mean Concentrations of Halomethanes Produced in Chlorinated Drinking Water (2.1 mg/l) for Reaction Times of 6 hrs, 12 hrs and 48 hrs in Single Experiments pH = 7.9 Temperature = 22°C, DOC = 1.65 mgC/l and 0.53 mg Br^-/l

Figure 2.5 Concentrations of halomethanes formed in chlorinated drinking water at reaction times ranging from 90 minutes to 48 hours. Experiments were performed on two different batches of drinking water.


CHCl₂Br
CHBr₂Cl
CHBr₃
DOC=1.85 mg C/l
DOC=1.65 mg C/l
CHBr₃ (µg/l)
12
10
8
6
4
2
0
CHCl₂Br & CHBr₂Cl
4
2
0
1.5
3
6
6
12
18
24
30
36
42
48
1.5 – 6 hrs
6 – 48 hrs
Reaction time (hours)

chlorination. The waters are drawn from aquifers within the Dammam geological formation and Kuwait Groups, which have an estimated geological age of 30 to 50 thousand years (WRDC 1983). The total dissolved solids (TDS) of the brackish waters of Kuwait average about 3500 mg/l and the blending ratio used ranges from 10 to 15% (VBB, 1982). The Br^- concentration is about 1.96 mg/l, but apparently varies for different wells. The DOC levels in the waters used for the experiments was 0.20 mgC/l. The pH value, before chlorination, was 7.6 and the temperature was 22°C.

Using the reaction vessel described in Figure 2.1, 500 ml of brackish water was chlorinated using a total residual chlorine level of 2.1 mg/l. The reaction times applied were 90 minutes, 3 and 6 hours. The results of the halomethanes analysis are summarised in Table 2.6.

The concentrations of halomethanes were very low in general, but the proportions of the individual compounds were quite similar to those observed for sea water. The $CHCl_2Br$ levels were all below 0.1 µg/l. The mean $CHBr_2Cl$ concentration was only 0.3 µg/l after 90 minutes, increasing to 0.4 and 0.6 µg/l after 3 and 6 hours respectively. The mean $CHBr_3$ concentration was 0.5 ± 0.2 µg/l after 90 minutes of the reaction time, but increased to 2.0 ± 0.1 and 4.1 ± 0.1 µg/l after 3 and 6 hours respectively.

d) The Distillate

The distilled water (or distillate) produced by the desalination units at the Shuwaikh. Desalination-power plant, was used to study the formation of halomethanes upon chlorination. As with drinking water, volatile organics were purged before it was used for the experiments. The total dissolved solids in the distillate varied according to the amount of sea water that gets entrained during the flash evaporation, and averaged 30 mg/l. The distillate used for these experiments was collected from the Blending Station at Shuwaikh, after the addition of NaOH to raise the pH from about 6.6 to almost 9 (prior to blending). The measured pH value of the distillate used was 8.9. The Br^- concentration was 0.13 mg/l and the DOC level was

Reaction Time	Halomethanes Concentrations (μg/l)				
	$\bar{x}$ SD	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	Total
90 min	$\bar{x}$	0	0.3	0.5	0.8
	SD		0	0.2	0.2
3 hours	$\bar{x}$	0	0.4	2.0	2.4
	SD		0	0.1	0.1
6 hours	$\bar{x}$	0	0.6	4.1	4.7
	SD		0	0.1	0.1

Table 2.6

Mean Concentrations of Halomethanes Formed in 500 ml of Chlorinated Brackish Water (2.1 mg/l) for Reaction Times of 90 minutes, 3 hours and 6 hours. pH = 7.6 Temperature = 22°C, Br^- = 1.96 mg/l and DOC = 0.2 mgC/l

0.30 mgC/l. The experimental procedure followed was similar to that used for the brackish water study. The results of the halomethane analyses are summarised in Table 2.7.

Although contamination during pumping, storage or handling of the sample prior to the experiments represent possible sources of organic matter in the distillate, carry over of organic matter along with sea water (source of Br^-) should not be ruled out. This is supported by the observation of an oily film in the condensate of the steam sampled from the air ejector (at the Shuwaikh Desalination-power plant) for halomethane analysis. The concentrations of total halomethanes produced were still low, with a trend towards the formation of chlorine - containing halomethanes. A slight increase in $CHCl_3$ concentrations was also apparent. However, solvent interference and contamination makes it difficult to substantiate this conclusion. The distillate also differed from the previous types of water by the fact that only traces of $CHBr_3$ (all below 0.1 µg/l) were produced upon chlorination. $CHBr_2Cl$ became the dominant species, its levels increasing from 1.0 $\pm$ 0.1 µg/l after 90 minutes to 1.5 $\pm$ 0.1 µg/l and 2.3 $\pm$ 0.1 µg/l after 3 and 6 hours respectively. $CHCl_2Br$ also showed a steady increase with time, from 0.3 $\pm$ 0.1 µg/l after 90 minutes to 0.5 and 1.1 µg/l after 3 and 6 hours respectively.

The results of the chlorination experiments on the four types of water can now be compared to assess the effects of Br^- and DOC levels on the types and levels of halomethanes produced. Taking first, the results of the experiments in which all four types of water were chlorinated at 2.1 mg/l of residual chlorine for reaction times of 90 minutes to 6 hours, the proportions of $CHCl_2Br$, $CHBr_2Cl$ and $CHBr_3$ concentrations to the total concentrations of the three compounds was calculated. The results are summarised in Table 2.8.

In general, all compounds showed an increase in concentration with increased reaction time, as discussed earlier. However, their relative

Reaction Time	Halomethanes Concentrations (µg/l)				
	$\bar{x}$ SD	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total
90 minutes	$\bar{x}$	0.2	1.0	0	1.2
	SD	0	0.1		0.2
3 hours	$\bar{x}$	0.5	1.5	0	2.0
	SD	0	0.1		0.1
6 hours	$\bar{x}$	1.1	2.3	0	3.4
	SD	0	0.1	0	0.1

Table 2.7

Mean Concentrations of Halomethanes Formed in 500 ml of the Distillate (2.1 mg/l) for Reaction Times of 90 minutes, 3 hours and 6 hours. pH=8.9, Temperature=23°C, Br^-=0.13 mg/l and DOC=0.3 mgC/l

Water Type	Reaction Time	Halomethanes Concentrations µg/l				
		Mean % of Total	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Sum of the Three Species
Distillate						
Br^- (mg Br^-/l) = 0.13	90 min.	$\bar{x}$	0.2	1.0	0	1.2
		%	(17)	(83)		(100)
DOC (mgC/l), blank = 0.30	3 hours	$\bar{x}$	0.5	1.5	0	2.0
		%	(25)	(75)		(100)
DOC, after 6hr RT*= 0.4	6 hours	$\bar{x}$	1.1	2.1	0	3.2
		%	(34)	(66)		(100)
Drinking Water						
Br^- (mg Br^-/l) = 0.53	90 min.	$\bar{x}$	0.4	2.0	0.5	2.9
		%	(14)	(69)	(17)	(100)
DOC (mgC/l), blank = 1.85	3 hours	$\bar{x}$	0.7	3.0	3.1	6.8
		%	(10)	(44)	(46)	(100)
DOC, after 6hr RT = 1.75	6 hours	$\bar{x}$	1.0	3.5	3.6	8.1
		%	(12)	(43)	(44)	(99)
Brackish Water						
Br^- (mg Br^-/l) = 1.96	90 min.	$\bar{x}$	0	0.3	0.5	0.8
		%		(38)	(63)	(101)
DOC (mgC/l), blank = 0.20	3 hours	$\bar{x}$	0	0.4	2.0	2.4
		%		(17)	(83)	(100)
DOC, after 6hr RT = 0.35	6 hours	$\bar{x}$	0	0.6	4.1	4.7
		%		(13)	(87)	(100)
Sea Water						
Br^- (mg Br^-/l) = 78.7	90 min.	$\bar{x}$	0	4.4	90.5	94.9
		%		(5)	(95)	(100)
DOC (mgC/l), blank = 1.90	3 hours	$\bar{x}$	0.1	5.3	117.3	122.7
		%	(0.1)	(4)	(96)	(100.1)
DOC, after 6hr RT = 1.65	6 hours	$\bar{x}$	0.1	6.3	140.8	147.2
		%	(0.1)	(4)	(96)	(100.1)

*RT = Reaction Time

Table 2.8

Percentage Distribution of the Individual Halomethanes in the Four Types of Water Used in the Experimental Study. Reaction Times of 90 Minutes - 6 Hours

proportions showed changes with time. Starting with the distillate (lowest Br^-), $CHCl_2Br$, constituted 25% of the total. It was the only type of water in which $CHCl_2Br$ showed a proportional increase with time (17 to 34%). The percentage contribution of this compound decreased in drinking water (to about 10%), with a trend to decrease with time. It was around or below 0.1 µg/l in both the brackish and sea water, in which the Br^- ion concentration was highest. Dibromochloromethane concentrations comprised a major proportion of the total in the distillate (about 75%), decreasing with time from 83% to 66%. This, plus the fact that only traces of $CHBr_3$ were produced (whereas the proportional contributions of $CHCl_2Br$ levels increased with time) is further indicative that $CHCl_3$ was produced in the distillate. Dibromochloromethane formed about 50% of the total in drinking water, showing a decrease in percentage contribution to the total with time, from 69% to 43%. It also comprised about 20% of the total in brackish water, also decreasing with time from 38 to 13%, whereas in sea water, it was a minor component (5%) of the total .

The percentage contributions of $CHBr_3$ on the other hand, increased steadily with increased Br^- and reaction time. It went from trace amounts (<0.1 µg/l) in the distillate, to 35% in drinking water, 78% in brackish water and to 95% in sea water (percentage calculated by averaging the three reaction times used). A further indication of the trend towards increased contributions of $CHBr_3$ with increased Br^- and reaction time, was apparent when the results of the longer-reaction time experiments on drinking water and sea water were compared in Table 2.9.

Bromoform concentrations comprised 49% of the total after 6 hours of reaction time in the drinking water experiments and increased to 68% after 48 hours, whereas both $CHCl_2Br$ and $CHBr_2Cl$ showed a decrease in their percentage contributions to the total with time (from 40 to 25% and from 12 to 7% respectively). $CHBr_3$ concentrations again comprised up to

Water Type	Reaction Time	Halomethanes Concentrations $\mu g/l$				
		Mean % of Total	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	Sum of the Three Species
Drinking Water	6 hours	$\bar{x}$	0.9	3.1	3.8	7.8
		%	(12)	(40)	(49)	(101)
Br^- (mg Br^-/l) = 0.53	12 hours	$\bar{x}$	1.0	3.5	6.3	10.8
		%	(9)	(32)	(58)	(99)
DOC (mgC/l), blank = 1.65	24 hours	$\bar{x}$	1.2	3.8	8.9	13.9
		%	(9)	(27)	(64)	(100)
DOC, after 48hr RT* = 1.3	48 hours	$\bar{x}$	1.2	4.2	11.4	16.8
		%	(7)	(25)	(68)	(100)
Sea Water	6 hours	$\bar{x}$	0.1	6.8	155.3	162.2
		%	(0.7)	(4)	(96)	(100.7)
Br^- (mgBr^-/l) = 78.7	12 hours	$\bar{x}$	0.1	8.0	184.3	192.4
		%	(0.1)	(4)	(96)	(100.1)
DOC (mgC/l), blank = 1.65	24 hours	$\bar{x}$	0.3	9.6	221.6	231.5
		%	(0.1)	(4)	(96)	(100.1)
DOC, after 48hr RT = 1.2	48 hours	$\bar{x}$	0.2	12.0	247.0	259.2
		%	(0.1)	(5)	(95)	(101.1)

*RT = Reaction Time

Table 2.9

Percentage Distribution of the Individual Halomethanes in Drinking Water and Sea Water - Reaction Times of 6 - 48 Hours

96% of the sum of the three compounds produced in sea water, whereas the other two made up the balance, 4% from $CHBr_2Cl$ and <1% from $CHCl_2Br$.

The effect of the Br^- ion on the speciation of halomethanes is in general agreement with the findings of Rook (1974), Rook **et el** (1978), Stevens **et al** (1978), Oliver (1980), Minear and Bird (1980), Sugam and Helz (1981) and Cooper **et al** (1983). Based on their findings, it appears that more chlorine-containing halomethanes should have been produced in the distillate and to a certain extent in drinking water. One possible explanation is that both types of Water contained non volatile mostly Br^- substituted compounds from the previous chlorinations at the pumping station (and at the desalination unit for the distillate). These compounds were not removed by sparging with N_2 gas at 80°C. Thus, upon re-chlorination the substitution is continued and halomethanes released. This speculative point of view may be supported by the data on ozonation of water supplies compiled from four water treatment plants (Rook, **et. al.**, 1978). When the water supplies were ozonated after pre-chlorination, the results showed a shift towards the formation of bromine-containing halomethanes. For example, in some cases the concentration of $CHCl_3$ after ozonation (of prechlorinated waters) decreased to half that produced by chlorination only, whereas the concentrations of $CHBr_2Cl$ and $CHBr_3$ increased by a factor of 3 and 6 respectively.

The levels of DOC in the waters used in the experimental study, before and after chlorination, are also shown in Tables 2.8 and 2.9. It is apparent that higher levels of DOC result in the production of greater concentrations of halomethanes upon chlorination, as the distillate (0.3 mgC/l) and brackish water (0.2 mgC/l) produced the lowest concentrations of halomethanes. However, when the concentrations of halomethanes produced in drinking water and sea water were compared (both had similar levels of DOC, 1.65 mgC/l) that conclusion does not appear to be valid since the difference in halomethanes concentrations was very large. Thus, it appears that the composition of organic matter present in the water (and not the levels per se) also exerts a major effect on the levels of halomethanes produced. It should be noted that attempts to relate the concentrations of halomethanes to DOC concentrations in the samples collected during the field studies, also gave inconsistent results (see also Symons et al. 1975). Moreover, comparison of the DOC levels before and after chlorination, gave inconclusive results. DOC levels in drinking water and in sea water showed a decrease after chlorination in both the short term and longer term experiments (Tables 2.8 and 2.9). After a reaction time of 6 hours, DOC levels in drinking water decreased from 1.85 to 1.75 mgC/l whereas, it decreased from 1.90 to 1.65 mgC/l in sea water. In the longer term experiments, the levels decreased from 1.65 mgC/l (for both types of water) to 1.3 mgC/l for drinking water and to 1.2 mgC/l for sea water. However, the DOC levels in the distillate and brackish water, 0.3 and 0.2 mgC/l respectively, showed an increase after chlorination for 6 hours (to 0.4 and 0.35 mgC/l respectively). At such low levels, contamination during handling and transport of the samples may have caused this discrepancy. Thus, it is apparent that changes in DOC concentrations are not sensitive enough to be used as an indicator of the extent of chlorination in water.

2.3.2 The Effects of Petroleum Hydrocarbons on the Formation of Halomethanes in Chlorinated Drinking Water and Sea Water

A study on the effects of adding the water soluble fraction (WSF) of Kuwait crude to chlorinated waters on the production of halomethanes was carried out in two parts.

In the first of these a 10% solution of WSF (containing about 1.9 ppm of total hydrocarbons as determined by spectrofluorometry) was used to spike 500 ml of sea water in the reaction vessel. The total residual chlorine concentration was 2.1 mg/l and the reaction time was maintained at 30 minutes. The background DOC level in the water used was 2.36 mgC/l. The results of the halomethanes analysis are summarized in Table 2.10. Results differing only slightly from those obtained in the control experiments were found in the presence of petroleum hydrocarbons at concentrations from 2 to 100 µg/l in chlorinated sea water. At 100 µg/l of WSF, the $CHBr_2Cl$ concentration showed a significant increase over the control, (5.5 ± 0.1 as compared to 2.9 ± 0.1 µg/l which was significant at $\alpha = 0.01$). However, the $CHBr_3$ concentrations (92.8 ± 4.3 µg/l) were not significantly higher than the control values. At 200 µg/l of WSF, both compounds showed significantly higher levels than those of the control and those formed with 100 ug/l of WSF reaching 7.5 ± 0.2 and 108.9 ± 2.4 µg/l respectively ($\alpha = 0.01$). The failure to produce halomethanes at higher concentrations (than those produced in the control) below 100 µg/l of WSF, may be attributed to the limited availability of compounds that are likely to compete or react as readily with the halogens as those originally present in sea water under the experimental conditions applied. On the other hand, the addition of WSF to drinking water resulted in much higher levels of halomethanes than in the control in which only $CHBr_2Cl$ was detected at a concentration of 0.8 µg/l. With a concentration of 100 µg/l of total hydrocarbons, the concentrations of $CHCl_2Br$, $CHBr_2Cl$ and $CHBr_3$ increased to 0.4 ± 0.1, 5.9 ± 0.3 and 30.1 ± 1.1 µg/l respectively. One possible explanation would be that for the given reaction time, the amount of readily available organics for halogenation in the control experiment was rather limited (producing only 0.8 µg/l of $CHBr_2Cl$). Thus, the amount of halogens available to react with the organic compounds contained in the WSF was relatively greater than what was available in the sea water experiments. The increase in the level of halomethanes in the drinking water experiments may also be due, in part, to the presence of the sea water in which the WSF was prepared (and hence increased the Br^- concentrations). The volume of sea water added constituted about 5% of the total volume of water used in the experiment. A better control for the experiment would have been a 5% solution of sea

Water Type	Conc. of Total Hydrocarbons µg/l	$\bar{X}$ SD	Halomethane Concentrations (µg/l)			
			$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total
Control	0	$\bar{X}$	0	2.9	87.7	90.66
		SD		0.1	1.6	1.6
	2	$\bar{X}$	0	3.1	88.4	91.5
		SD		0.1	3.6	3.8
Sea Water	4	$\bar{X}$	0	3.2	89.1	92.4
		SD		0	0.3	0.3
	8	$\bar{X}$	0	3.2	85.8	89.0
		SD		0.2	1.2	1.4
	20	$\bar{X}$	0	3.2	85.6	88.8
		SD		0	2.5	2.6
	100	$\bar{X}$	0	5.5	92.8	98.3
		SD		0.1	4.3	4.3
	200	$\bar{X}$	0	7.5	108.9	116.4
		SD		0.2	2.4	2.6
Drinking Water						
Control	O	$\bar{X}$	0	0.8	0	0.8
		SD		0		0
	100	$\bar{X}$	0.4	5.9	30.1	36.4
		SD	0.1	0.3	1.1	1.4

Table 2.10

Mean Concentrations of Halomethanes Produced in Chlorinated Drinking Water and Sea Water, According to the Concentrations of WSF of Kuwait Crude. Reaction Time for all Experiments was 30 Minutes, Residual Chlorine Level was 2.1 mg/l. Experiments were Run in Duplicate.

water in drinking water, instead of using drinking water from which volatile organics had been purged.

The experiments on the effect of WSF of Kuwait crude on the production of halomethanes in drinking water and sea water were repeated in two separate sets of experiments. In these, 600 ml dark brown glass bottles were used as reaction vessels and filled with each type of water, which had been treated with WSF of Kuwait crude and allowed to react with chlorine for 6, 12, 24 and 48 hours. Different total residual chlorine concentrations were used, 2.1 mg/l for the drinking water experiments and 3.3 mg/l in the sea water experiments. The WSF used for spiking, before chlorination, was prepared in a different manner from the previous set of experiments. A 20% solution of Kuwait crude in filtered sea water was used in the extraction and the aqueous layer was filtered after withdrawal from the separatory funnel. The extract contained 5.4 mg/l of total hydrocarbons. Two concentrations were used in the drinking water experiments, 90 and 236 µg/l. The background DOC level in the water used for the experiments, after purging the volatile organics, was 1.65 mgC/l. The results are summarised in Table 2.11.

At the 90 µg/l of total petroleum hydrocarbons level, the concentrations of $CHCl_2Br$ showed a slight or no increase with time, from 0.6 to 0.7 µg/l. These concentrations were lower than the corresponding values in the control experiments (see Table 2.5). That may be due to the effect of sea water in the WSF fraction used which increased the concentration of Br^-. However, sea water made up 2% of the total volume of water used in the experiments. The concentrations of $CHBr_2Cl$ showed a slight increase with increased rection time, ranging from 3.3 ± 0.1 µg/l after 6 hours of reaction time to 4.2 ± 0.2 µg/l after 48 hours being either similar to or slightly higher than, the corresponding values in the control experiments. The concentrations of $CHBr_3$, on the other hand, increased from 15.4 ± 0.7 µg/l after six hours to 22.8 ± 1.3, 31.0 ± 0.4 and 40.9 ± 2.5

Total Petroleum Hydrocarbons µg/l	Reaction Time (hrs.)	$\bar{X}$ SD	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total
			Halomethane Concentrations (µg/l)			
90	6	$\bar{X}$	0.6	3.3	15.4	19.4
		SD	0	0.1	0.7	0.8
	12	$\bar{X}$	0.6	3.8	22.8	27.3
		SD	0	0.1	1.3	1.4
	24	$\bar{X}$	0.7	3.9	31.0	35.6
		SD	0	0.1	0.4	0.6
	48	$\bar{X}$	0.7	4.2	40.9	45.8
		SD	0	0.2	2.5	2.7
236	6	$\bar{X}$	1.0	5.5	25.9	32.4
		SD	0	0.4	1.7	2.1
	12	$\bar{X}$	1.2	6.2	33.7	41.0
		SD	0	0.2	1.8	2.0
	24	$\bar{X}$	1.1	6.4	44.6	52.1
		SD	0	0.2	1.9	2.0
	48	$\bar{X}$	1.0	6.7	57.1	64.8
		SD	0.1	0.6	5.8	6.5

Table 2.11

Mean Concentrations of Halomethanes Formed in 600 ml of Chlorinated Drinking Water in the Presence of Petroleum Hydrocarbons. Cl_2 = 2.1 mg/l. Temperature = 22°C

µg/l after 12, 24 and 48 hours respectively, all of which were greater than the corresponding values for the control.

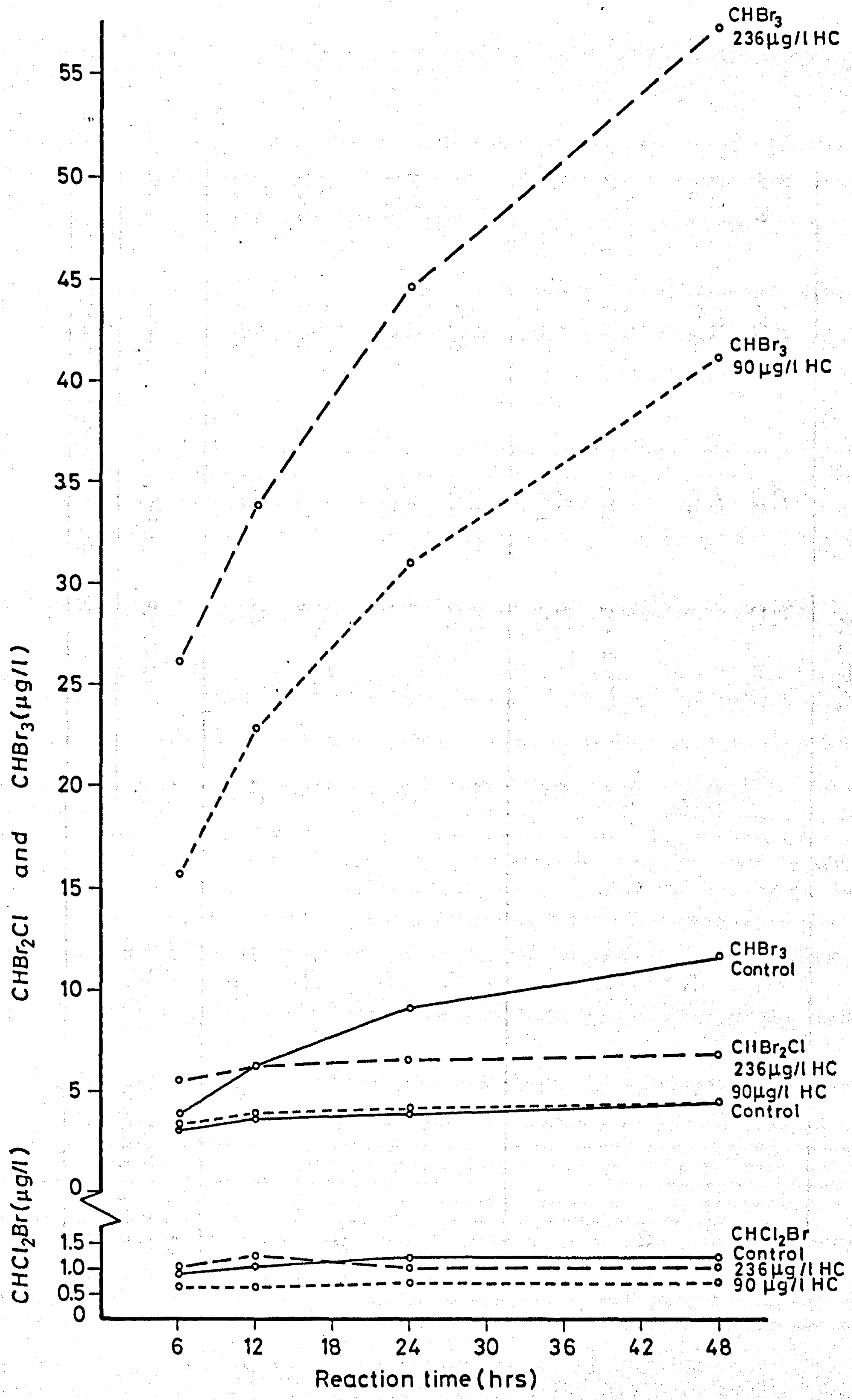
At the level of 236 µg/l of total petroleum hydrocarbons, the concentrations of $CHCl_2Br$ showed a similar pattern to that observed in the previous experiment, being generally similar to the corresponding values in the control. The $CHBr_2Cl$ concentrations were higher than those in the control, increasing from 5.5 ± 0.4 after 6 hours to 6.2 ± 0.2, 6.4 ± 0.2 and 6.7 ± 0.6 µg/l after 12, 24 and 48 hours respectively. The $CHBr_3$ concentrations increased from 25.9 ± 1.7 µg/l after 6 hours of reaction time to 33.7 ± 1.8, 44.6 ± 1.9 and 57.1 ± 5.8 µg/l after 12, 24 and 48 hours respectively, a yield much higher than in the control (see Table 2.5).

The concentrations of the three halomethanes in the chlorination experiments involving hydrocarbons were compared to those in the control experiments in Figure 2.6. The difference between the concentrations of $CHBr_3$ in the presence of petroleum hydrocarbons and that in the control is apparent from the graph, in contrast to the distributions of $CHBr_2Cl$ and $CHCl_2Br$ which were generally closer to the control.

The effect of petroleum hydrocarbons on the production of halomethanes in chlorinated sea water over reaction times ranging from 6 to 48 hours was also studied utilizing 600 ml dark brown glass bottles as reaction vessels. The WSF of petroleum hydrocarbons used for spiking was prepared as described in the drinking water experiments. The stock solution of the WSF was found fluorometrically to contain 4.2 ppm of total petroleum hydrocarbons. The concentration of residual chlorine in the reaction vessels was maintained at 3.3 mg/l. The background DOC level was 2.4 mg/l. The results of halomethanes analysis are summarized in Table 2.12.

At the 105 µg/l level of total petroleum hydrocarbons, $CHCl_2Br$ concentrations were similar to the corresponding values in the control, and did not exceed 0.6 µg/l (see Table 2.3). Dibromochloromethane

Figure 2.6 Distribution of halomethanes detected in chlorinated drinking water in the presence of WSF of Kuwait Crude (expressed as total hydrocarbon concentrations, HC) at 90 and 236 µg/l as compared to the control.


CHBr$_3$ 236µg/l HC
CHBr$_3$ 90µg/l HC
CHBr$_3$ Control
CHBr$_2$Cl 236µg/l HC
90µg/l HC
Control
CHCl$_2$Br Control
236µg/l HC
90 µg/l HC
CHBr$_2$Cl and CHBr$_3$ (µg/l)
CHCl$_2$Br (µg/l)
55
50
45
40
35
30
25
20
15
10
5
0
1.5
1.0
0.5
0
6
12
18
24
30
36
42
48
Reaction time (hrs)

			Halomethane Concentrations (µg/l)			
Total Hydrocarbons Concentration µg/l	Reaction Time (hrs.)	$\bar{X}$ SD	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total
105	6	$\bar{X}$	0.4	10.8	184.9	196.1
		SD	0.2	0.5	8.4	8.9
	12	$\bar{X}$	0.6	12.6	229.2	242.4
		SD	0.2	0.5	7.1	7.8
	24	$\bar{X}$	0.4	16.7	316.0	333.1
		SD	0	0.3	10.8	11.0
	48	$\bar{X}$	0.6	21.5	403.9	425.9
		SD	0.2	1.3	16.1	16.6
410	6	$\bar{X}$	0.5	17.5	222.9	241.0
		SD	0.1	0.5	6.1	6.7
	12	$\bar{X}$	0.7	20.5	267.7	288.8
		SD	0	0.2	6.3	6.5
	24	$\bar{X}$	1.5	32.9	475.0	509.4
		SD	0.1	0.4	11.2	11.3
	48	$\bar{X}$	3.2	38.4	573.8	615.4
			0.1	1.7	20.4	21.5

Table 2.12
Mean Concentrations of Halomethanes Produced in 600 ml of Chlorinated Sea Water (3.3 mg/l) in the Presence of 105 and 410 µg/l of Petroleum Hydrocarbons, Cl_2 = 3.3 mg/l. Temperature = 22°C

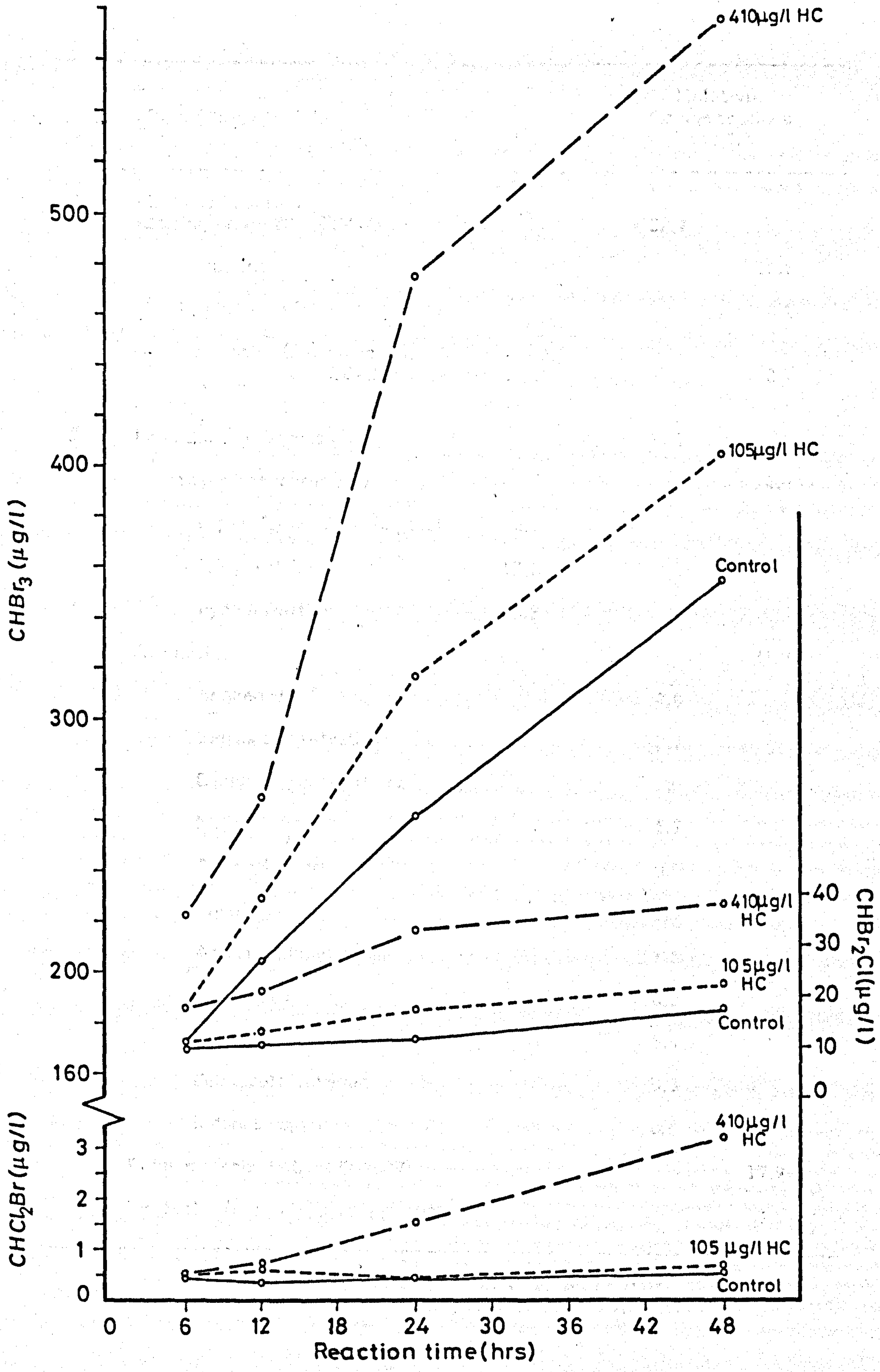
concentrations showed an increase form 10.8 ± 0.5 µg/l after 6 hours to 12.6 ± 0.5, 16.7 ± 0.3 and 21.5 ± 1.3 µg/l after reaction times of 12, 24 and 48 hours respectively. These levels were slightly higher than those detected in the control experiment where the levels ranged from 9.8 ± 0.5 after 6 hours of reaction time to 17.0 ± 1.0 µg/l after 48 hours. The concentrations of $CHBr_3$ after 6 hours of reaction time were 184.9 ± 8.4 µg/l which was similar to the corresponding concentration in the control (171.7 ± 8.8 µg/l). However, the concentration increased at a faster rate than in the control, to 229.2 ± 7.1, 316.0 ± 10.8 and 403.9 ± 16.1 µg/l after 12, 24 and 48 hours respectively.

With 410 µg/l of total petroleum hydrocarbons, the concentrations of halomethanes in chlorinated sea water showed a relatively small increase over the corresponding values as reaction times increased. $CHCl_2Br$ concentrations were only 0.5 ± 0.1 µg/l after a reaction time of 6 hours (similar to the level produced in the control, 0.4 ± 0.1 µg/l). The concentrations increased to 0.7, 1.5 ± 0.1 and 3.2 ± 0.1 µg/l after 12, 24 and 48 hours respectively. The concentrations of $CHBr_2Cl$ increased from 17.5 ± 0.5 µg/l after 6 hours to 20.5 ± 0.2, 32.9 ± 0.4 and 38.4 ± 1.7 µg/l after 12, 24 and 48 hours respectively. Bromoform concentrations also showed a sharp increase in concentration after the first 12 hours of reaction time as did the two other halomethanes. The levels increased from 222.9 ± 6.1 µg/l after a reaction time of 6 hours to 267.7 ± 6.3 after 12 hours and then increased to 475.0 ± 11.2 and 573.8 ± 20.4 µg/l after 24 and 48 hours respectively. This type of performance may indicate that secondary reactions are taking place when the reaction times are prolonged (perhaps involving ring rupture and the release of halomethanes) thus contributing to the overall levels found. Rook (1977) offered such an explanation in his discussion of the chlorination of humic materials (see also Minear and Bird, 1980). The changes in halomethane concentrations with time at the two levels of petroleum hydrocarbons are compared to that shown in the control experiment in Figure 2.7.

The increase in halomethane concentrations in chlorinated drinking water and sea water containing WSF of crude oil may be attributed to the halogenation of some of the compounds in the complex mixture of hydrocarbons, mainly the aromatics. The complexity of the composition of the WSF and subsequently of the possible substitution and degradation processes that may lead to the production of halomethanes may become apparent from the following brief summary on the composition of crude oils (based on a review by Clark and Brown, 1977).

Crude oil is a complex mixture of chemical compounds, of which the most abundant are the hydrocarbons ranging in molecular weight from 16 (CH_4) to 20,000. Minor quantities of sulphur, nitrogen and oxygen-containing compounds and traces of elements and organometallic compounds may also be present. Three classes of hydrocarbons are recognized in crude oils, these comprise up to 98% of the total consituents depending on the type of crude. They include aliphatics, alicyclic and aromatic hydrocarbons. Aliphatics include saturated hydrocarbons (paraffins), unsaturated groups (olefins) which include several homologous series differing in a CH_2 or some other group and compounds with more than one double, triple or both bonds. The alicyclic hydrocarbons or (naphthenes) include saturated and unsaturated compounds in which some or all of the carbon atoms are arranged in a ring. The aromatic hydrocarbons show a wide range of complexity from benzene to the polycyclic aromatic compounds. The nitrogen-containing compounds include mainly pyridines, quinolines, indoles, carbazoles, benzocarbazoles, pyrroles and petroporphyrins. The sulphur-containing compounds include mainly mercaptans and cyclic sulphides, whereas the oxygen containing groups include mainly phenols and carboxylic acids. Table 2.13 summarizes the chemical composition of Kuwait crude.

Figure 2.7 Distribution of halomethanes produced in chlorinated Sea water in the presence of WSF at 105 and 410 µg/l as compared to the control.



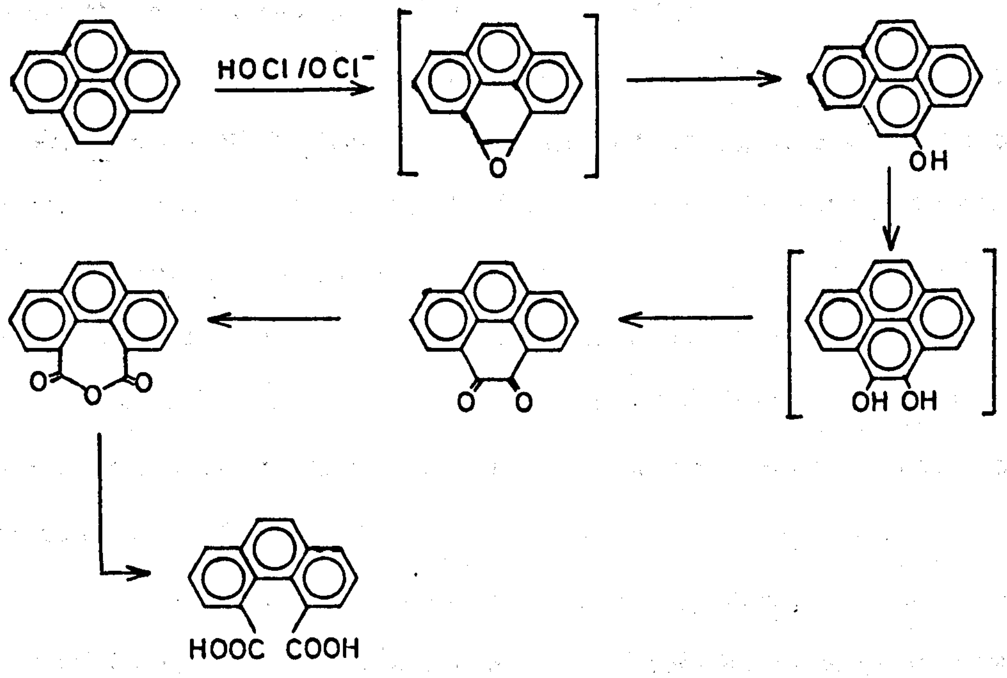
410µg/l HC
105µg/l HC
Control
410µg/l HC
105µg/l HC
Control
410µg/l HC
105 µg/l HC
Control
CHBr$_3$ (µg/l)
500
400
300
200
160
CHCl$_2$Br (µg/l)
3
2
1
0
CHBr$_2$Cl (µg/l)
40
30
20
10
0
0
6
12
18
24
30
36
42
48
Reaction time (hrs)

	Major Components	Relative Concentrations (wt %)		
1 -	Naphtha Fraction (Boiling range 20 - 205°C)		22.7	
	Paraffins			16.2
	Naphthenes (alicyclic)			4.1
	Aromatics (Benzenes = 0.1, Toluene = 0.4 and C8-C11 aromatics = 1.8)			2.4
2. -	High Boiling Fraction		77.3	
	Saturates (paraffins)			34.0
	n-paraffins C11-C32 plus)	4.7		
	iso-paraffins	13.2		
	cycloparaffins	16.2		
	Aromatics			21.9
	Benzenes		4.8	
	Indans and tetralins		2.2	
	Dinaphtheno benzenes		2.0	
	Napthalenes		1.7	
	Acenaphthenes		0.9	
	Phenanthenes		0.3	
	Acenaphthalenes		1.5	
	Chrysenes		0.2	
	Benzothiophenes		5.4	
	Dibenzothiophenes		3.3	
	Indanothiophenes		0.6	
	Polar material (ASTM D-2007)			17.9
	Insolubles (in n -C_5, ASTM D-893)			3.5

Table 2.13 Chemical Composition of Kuwait Crude
(Condensed from Clark and Brown, 1977 after Pancirov, 1974)

The solubilities of petroleum components in brines, sea water and distilled water have been reviewed by McAuliffe (1969), Boylan and Tripp (1971), Clark and MacLeod (1977) and Shaw (1977). It has been shown that aromatic hydrocarbons, which form about 20% of Kuwait Crude, are the most soluble of crude oil components in aqueous solutions. For example, Boylan and Tripp (1971) have shown that in a filtered sea water extract of Kuwait crude, benzene and napthalene and their methyl derivatives consititue about 45% of the total, the rest being mostly high boiling aromatics. Saturated hydrocarbons could be present, as fine droplets incorporated into the solution as a result of agitation during extraction. Rossi and Neff (1978) have also shown that naphthalene and methylnaphthalene isomers have solubilities in sea water in the low ppm range whereas, higher molecular weight (and larger molecular volume) aromatics such as benzo (a) pyrene have solubilities in the lower ppb range. Thus, the sea water extract added in the chlorination experiments discussed above would be expected to contain mainly substituted benzene and naphthalene compounds with the rest being made up of highly polar aromatics, including some of the compounds shown in Table 2.13.

The reactions of some of the aromatic hydrocarbons such as phenols and other aromatics resembling groupings present in humic acids with chlorine have already been discussed in the introductory part of this chapter. Phenol was also shown by Rook (1974) to react with bromine in a dilute aqueous solution to form 2, 4, 6-tribromophenol. Experimental and field data by Harrison et al (1976) and Perry and Harrison (1977) showed that the concentrations of some polynuclear aromatic hydrocarbons (PAH) such as pyrene and benzo (ghi) perylene, in aqueous solutions, decreased after chlorination. However, the products of chlorination were not identified. Moreover, Reinhard et al. (1976), using a GC-MS technique have shown that several components in the aromatic fraction of diesel oil (N0.2 fuel oil) are removed from aqueous solution by chlorination. The disappearance of some of these compounds coincided with the production of chlorinated products, mainly monochlorinated compounds. The aromatic fraction of diesel oil which had been eluted by CH_2Cl_2 from a silica gel column was concentrated and added to buffered water at pH = 7.2. The solution was chlorinated with a chlorine dose of 100 mg/l. The components of the diesel oil extract included mainly benzenes, naphthalenes, indanes, tetralins, acenaphthalenes, anthracenes and phenanthrenes. After one hour of chlorination, 1,3,5-trimethylbenzene concentrations decreased by 30%. Some of the C_2 and C_3 naphthalenes showed a decrease in concentration as well. In the mean time, GC-MS record showed the presence of 2-chloromesitylene and chloro-C_2-andC_3-naphthanlenes. After 30 hours of chlorination, the 3 isomers of trimethylbenzene could no longer be detected and were replaced by a series of chlorinated benzenes. Naphthalene, 1-methylnaphthalene, 2-methylnaphthalene and phenanthrene and its methyl homologues were completely eliminated within 30 hours and no chlorinated analogues were detected, indicating the occurrence of oxidative reactions. 4-methyl indane and 5-methyl indane (with CH_3 on the aromatic ring) were also chlorinated after 30 hours, whereas the 1- and 2-methyl indanes did not react with chlorine. Other compounds which remained stable include n-propyl-, 1-ethyl-2-methyl benzenes and tetralin. The authors concluded that both oxidation and substitution reactions occurred during chlorination. Furthermore, alkyl substituents are activating and ortho- and para-directing, the activation being enhanced if the alkyl groups are in the meta position. Thus, they showed that, for example, 1,3,5-trimethylbenzene reacts with chlorine more readily than 1-methyl-2-ethyl benzene and 4-methylindane reacts more readily than 1-methylindane and tetraline. The authors' conclusions are in agreement with Rook's hypothesis regarding the electrophillic attack by chlorine on the aromatic ring (which was discussed earlier). Unfortunately, the same authors did not indicate if halomethanes would be expected from such reactions. However, Liukkonen et al (1983), utilizing GC-MS techniques, showed that chlorination of pyrene involves the formation of an epoxide which may undergo hydroalysis and rearrangement reactions, forming compounds which may in turn be oxidised.



Thus, it seems likely that halogenation and ring rupture reactions, in view of the superior substitutive powers of bromine shown by Rook and other workers, may be responsible for the observed increase in the production of halomethanes in the chlorinated waters containing WSF of crude oil.

2.3.3 The Effect of Naturally Occurring Suspended Solids on the Formation of Halomethanes in Chlorinated Sea Water

Naturally occurring suspended solids were concentrated from the coastal waters of Al-Bedaa area using a plankton net, and re-suspended in filtered sea water prior to use for spiking. Filtered sea water was transferred into the reaction vessel described in Figure 2.1, volumes of the suspended solids were introduced by a glass dispenser of the appropriate size. The volume was made up to 500 ml by addition of filtered sea water. An aliquot of the chlorine solution equivalent to that used to achieve a residual of 2.1 mg/l, in the control experiment, was then injected into the reaction vessel. However, in the last set of experiments the amount of chlorine was increased to achieve 3.3 mg/l of residual chlorine concentration. The reaction time was maintained at 30 minutes for all experiments. The background DOC level in the filtered sea water was 2.36 mgC/l and the background NH_3-N level was 11 µg/l. The results of the halomethane analyses are summarised in Table 2.14.

The mean concentration of total halomethanes in the control experiment was 90.6 ± 1.6 µg/l. Addition of 5 ml of the suspended solids drastically reduced the levels to below 1 µg/l. Increasing the residual chlorine level to 3.3 mg/l (in the presence of 50 ml of the suspended solids) failed to cause an increase in the level of halomethanes produced. It was apparent that the chlorine added failed to react with the precursor material present in sea water which was responsible for the halomethanes detected in the control.

Microscopic examination of the suspended solids showed it to consist of a mixture of phytoplankton, zooplankton, remains of dead animals and colloidal matter attached to sand particles. On the basis of earlier discussion of reactions of chlorine with organic matter, it is apparent that oxidation and substitution reaction (not leading to the production of halomethanes) are the dominant types of reactions and probably lead to the production of mainly CO_2, NH_3 and R-CHO in the case amino-nitrogen compounds and to the production of mainly CO_2 in the case of fatty materials. These shown by the experimental work on estuarine colloidal matter by Sigleo et al., 1980 and Sigleo et al., 1982.

2.3.4 The Effect of Ammonia-Nitrogen on Halomethanes Production

The effects of the presence of ammonia in chlorinated sea water on the production of halomethanes was studied by spiking filtered sea water with aqueous solution of ammonia of various strengths immediately before chlorination. The reaction vessel described in Figure 2.1 was used in the experiments. The residual chlorine level was 2.1 mg/l and the reaction time was maintained at 30 minutes. The results are summarised in Table 2.15.

Volume of Suspended Solids Added (ml)	Chlorophyll-a Conc. mg/m^3	$\bar{x}$ SD	Halomethane Concentrations (µg/l)			
			$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total
<u>Control</u>						
Filtered Sea Water	N.D.*	$\bar{x}$	0	2.9	87.7	90.6
Cl_2 = 2.1 mg/l		SD		0.1	1.6	1.6
5 ml (Cl_2 = 2.1 mg/l)	4	$\bar{x}$	0	0.4	0	0.4
		SD	0	0	0	0
10 ml (Cl_2 = 2.1 mg/l)	8	$\bar{x}$	0	0.2	0	0.2
		SD	0	0	0	0
25 ml (Cl_2 = 2.1 mg/l)	18	$\bar{x}$	0	0.2	0	0.2
		SD	0	0	0	0.1
50 ml (Cl_2 = 2.1 mg/l)	37	$\bar{x}$	0	0	0	0
		SD	0	0	0	0
50 ml (Cl_2 = 3.3 mg/l)	37	$\bar{x}$	0	0.2	0	0.2
		SD	0	0	0	0

*N.D. = Not Determined

Table 2.14

Mean Concentrations of Halomethanes Produced in 500 ml of Chlorinated Sea Water in the Presence of Various Levels of Naturally Occurring Suspended Solids. DOC Background Level = 2.36 mgc/l, NH_3-N = 11 µg/l, Temperature = 20°C and the Reaction Time was 30 Minutes.

Concentrations of Halomethanes (µg/l)

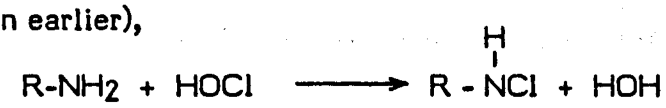
NH_3-N Concentrations µg/l	$\bar{x}$ SD	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total
Control	$\bar{x}$	0	2.8	81.8	84.6
Background = 17	SD		0.1	2.6	2.8
20	$\bar{x}$	0	2.4	74.8	77.8
	SD		0.3	2.6	2.9
36	$\bar{x}$	0	3.0	13.9	15.9
	SD		0	0.2	0.2
72	$\bar{x}$	0	0.6	1.1	1.8
			0	0.4	0.4

Table 2.15

Mean Concentrations of Halomethanes Produced in 500 ml of Chlorinated Sea Water in the Presence of Various Levels of NH_3-N. Background TOC Level 2.20 mgC/l, Temperature = 20°C, Reaction Time = 30 minutes. Residual Chlorine Level was 2.1 mg/l

With a background level of 17 μg/l of NH_3-N, the mean concentration of $CHBr_3$ was 81.8 ± 2.6 μg/l whereas that of $CHBr_2Cl$ was 2.8 ± 0.1 μg/l. No $CHCl_2Br$ or $CHCl_3$ was detected. At 20 μg/l of NH_3-N, the concentration of $CHBr_3$ decreased by 10%, whereas $CHBr_2Cl$ concentration was similar to that of the control. However, when the levels of NH_3-N were nearly doubled to 36 μg/l, concentration of $CHBr_3$ decreased to about 20% of that of the control and $CHBr_2Cl$ decreased by about 30%. Furthermore, at 72 μg/l of NH_3-N, the $CHBr_3$ concentration was only 1.1 ± 0.4 μg/l (about 1% of the level in the control experiment. The concentration of $CHBr_2Cl$ decreased to about 20% of that of the control. It is apparent that ammonia nitrogen competes strongly for halogens which would otherwise react with the organic carbon to produce halomethanes. The reduction in halomethane concentrations observed in this study are in agreement with the experimental data of Sugam and Helz (1981) who demonstrated that the addtion of increasing concentrations of NH_4Cl to Chlorinated sea water resulted in parallel decrease in $CHBr_3$ and $CHBr_2Cl$ concentrations.

The reaction of inorganic nitrogen with halogens in aqueous solution has already been reported in the discussion of the main reactions occurring during chlorination. For example, in the following reaction with amines (shown earlier),



$$R\text{-}NH_2 + HOCl \longrightarrow R - \overset{\overset{H}{|}}{N}Cl + HOH$$

the R - could be another H (thus becoming NH_3) to produce chloramines and dichloramines which would irreversibly bind the available chlorine. However, in the presence of high Br^- concentrations bromamines and bromochloroamines are also formed which also competes with the formation of halomethanes (Haag, 1980 and Luong et al., 1982). It should be noted that bromamines and bromochloroamines are reported to be less stable than chloramines and thus releasing HOBr or Br^- upon decomposition (Jolley and Carpenter, 1983 see also Haag, 1980 and Wajon and Morris, 1980). Which may become available to produce halomethanes (Rook, 1980).

2.3.5 The Effect of Phytoplankton on the Production of Halomethanes

Using the same conditions as in the suspended solids and ammonia experiments the short term effects of the addition of a sea water suspension containing pure culture of **Chlorella sp.** on the production of halomethanes in chlorinated sea water was studied. The total residual chlorine concentration was 2.1 mg/l and the reaction time was 30 minutes. The background DOC level in the filtered sea water was 2.36 mgC/l. The NH_3-N concentration was 11 µg/l. The results of the halomethanes analysis are summarised in Table 2.16.

The concentrations of the halomethanes in both the control and the chlorella containing samples were generally similar. The mean concentration of $CHBr_2Cl$ in the control was 3.9 ± 0.1 µg/l, whereas it ranged from 3.8 ± 0.2 µg/l at 4.8 mg/m^3 of chlorophyll to 3.1 ± 0.2 µg/l at the 95.2 mg/m^3 level of chlorophyll. Bromoform had a mean concentration of 108.3 ± 0.8 µg/l in the control experiment whereas it ranged from 104.5 ± 6 µg/l at 4.8 mg/m^3 of chlorophyll to 95.8 ± 3.5 µg/l at 95.2 mg/m^3 of chlorophyll. Although the mean concentrations of both compounds at 95.2 mg/l of chlorophyll were less than the corresponding values in the control, they were within the ranges exhibited at the other levels of chlorophyll.

The effect of **Chlorella sp.** on the formation of halomethanes in chlorinated sea water was further investigated using 600 ml dark brown glass bottles as reaction vessels. Three levels of chlorophyll were used, 1.6, 3.2 and 4.8 mg/m^3, each was run for 6, 12, 24 and 48 hours. The DOC level in the filtered sea water was 1.65 mgC/l. The results of the halomethanes analysis are summarised in Table 2.17.

The concentrations of halomethanes within each level of chlorophyll used showed an increase with time, except for $CHCl_2Br$ which (as in the control experiment), was present in trace levels that did not exceed 0.3 µg/l. $CHBr_2Cl$ and $CHBr_3$ concentrations showed an increase with increased time. However, in most experiments they were below the corresponding levels in

Volume of Chlorella Added	Chlorophyll-a Levels mg/m^3	$\bar{x}$ SD	Halomethane Concentrations (µg/l)			
			$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total
Control	N.D.*	$\bar{x}$	0	3.9	108.3	112.1
		SD	0	0.1	0.8	0.9
1 ml	4.8	$\bar{x}$	0	3.8	104.5	108.3
		SD	0	0.2	6.0	6.2
5 ml	24.7	$\bar{x}$	0	3.6	101.2	104.8
		SD	0	0.1	3.4	3.5
10 ml	46.7	$\bar{x}$	0	3.3	104.0	107.3
		SD	0	0.2	3.2	3.4
25 ml	95.2	$\bar{x}$	0	3.1	95.8	98.9
		SD	0	0.2	3.5	3.7

*N.D. = Not Determined

Table 2.16

Mean Concentrations of Halomethanes Produced in 500 ml of Chlorinated Sea Water (2.1 mg/l) in the Presence of Various Levels of Chlorella. DOC Background Level = 2.36 mgC/l, Water Temperature = 20°C and the Reaction Time Maintained at 30 Minutes.

Halomethanes Detected		Concentration of Halomethanes (µg/l) According to Chlorophyll Level and Reaction Time											
		1.6 mg/m³				3.2 mg/m³				4.8 mg/m³			
		6h	12	24	48	6h	12	24	48	6h	12	24	48
$CHCl_2Br$	$\bar{x}$	0.1	0.1	0.2	0.3	0.1	0	0.2	0.3	0.1	0	0.2	0.3
	SD	0	0	0.1	0	0.1	0	0.1	0	0	0	0	0
$CHBr_2Cl$	$\bar{x}$	5.1	6.5	9.6	11.2	5.1	7.6	8.4	9.3	4.8	6.3	6.8	8.4
	SD	0	0.2	0.3	0.2	0.1	0.1	0.2	0.2	0	0	0.2	0.4
$CHBr_3$	$\bar{x}$	123.5	144.8	194.2	212.8	127.4	155.7	172.8	206.3	116.7	140.5	147.2	174.2
	SD	1.3	6.2	7.3	5.2	4.2	4.1	5.2	8.6	1.6	2.0	5.5	4.2
Total	$\bar{x}$	128.8	151.4	206.4	224.3	132.6	163.4	181.4	215.9	121.7	146.9	154.1	182.9
	SD	1.3	6.4	7.8	5.5	4.4	4.2	5.5	8.8	1.7	2.1	5.9	4.6

Table 2.17

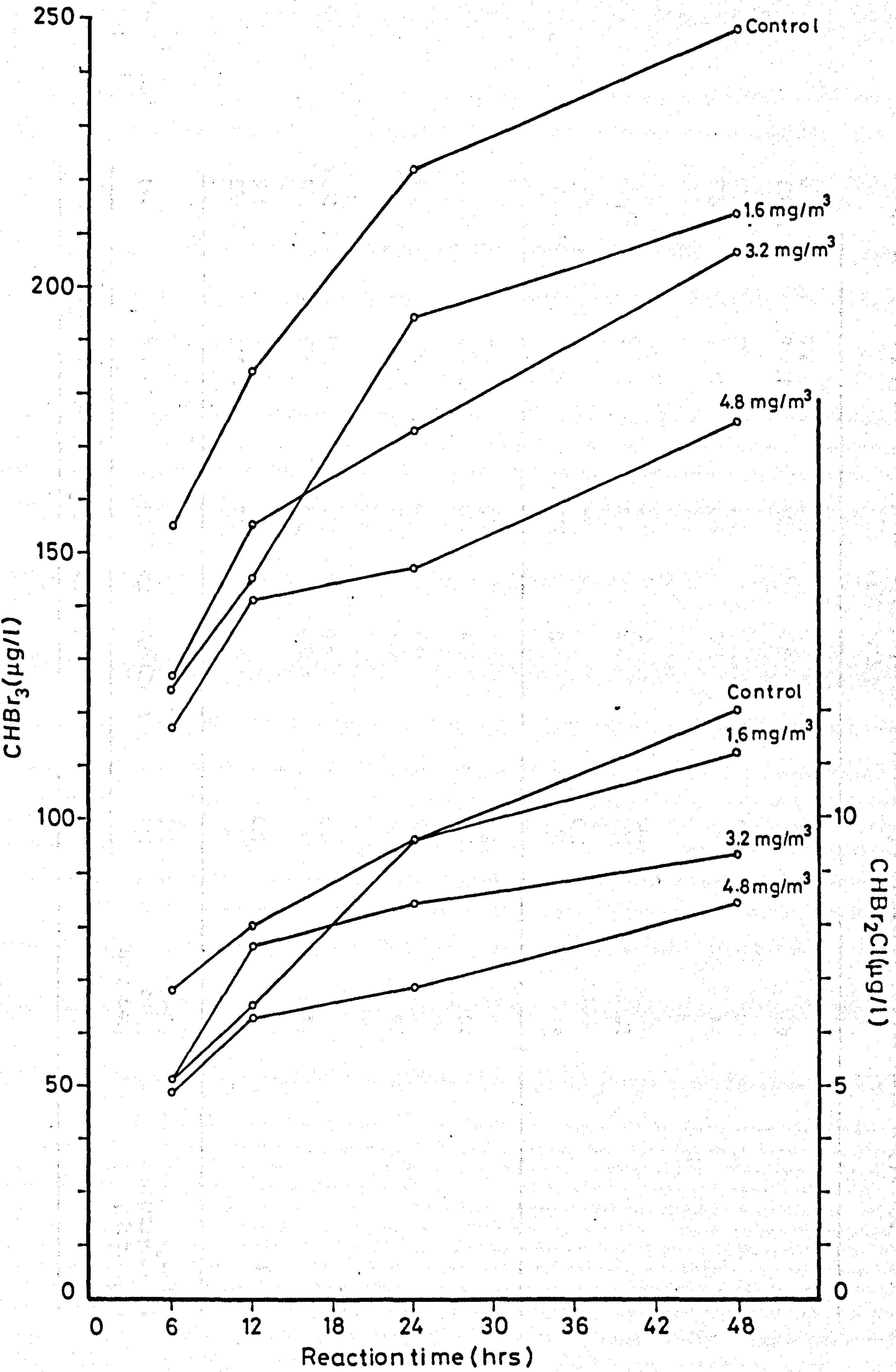
Mean Concentrations of Halomethanes Detected in 600 ml Chlorinated Sea Water (2.1 mg/l) in the Presence of Chlorella. The Background DOC Level was 1.65 mgC/l and Water Temperature was 22°C

the control experiment (see Table 2.3). For example, the $CHBr_2Cl$ concentrations after 6 hours of reaction time (at 1.6 mg/m^3 of chlorophyll) was 5.1 µg/l and increased to 6.5 ± 0.2, 9.6 ± 0.3 and 11.2 ± 0.2 µg/l after 12, 24 and 48 hours respectively, all of which were lower than that of the corresponding reaction times of the control, except at the 24 hours reaction time where they were similar. At 3.2mg/m^3 of chlorophyll, $CHBr_2Cl$ concentration after 6 hours was similar to that at the corresponding reaction time at the 1.6 mg/m^3 of chlorophyll. The levels increased after 12 hours to 7.6 ± 0.1 µg/l which was higher than that for the 1.6 mg/m^3 of chlorophyll, but lower than that produced in the control. The concentration then increased to 8.4 ± 0.2 and 9.3 ± 0.2 after 24 and 48 hours respectively, being less than the corresponding concentrations produced at 1.6 mg/m^3 of chlorophyll. At 4.8 mg/m^3 of chlorophyll, again the concentrations increased with time but remained relatively lower than the concentrations of $CHBr_2Cl$ produced at the corresponding reaction times (at lower levels of chlorophyll). $CHBr_3$ concentrations followed a similar pattern as shown in Table 2.17. The changes in concentrations of $CHBr_2Cl$ and $CHBr_3$ with respect to reaction time and chlorophyll levels applied are shown graphically in Figure 2.8. The concentrations are also compared to the corresponding levels produced in the control bottles.

The chlorination of filtered sea water in the presence of **Chlorella sp.** suspension was repeated under similar conditions, except for changes in the residual chlorine levels and the amount of **Chlorella sp** used for spiking. A concentration residual chlorine of 3.3 mg/l was used and two concentrations of chlorophyll 23 and 95 mg/m^3 were placed in two sets of bottles. The background DOC level was 2.4 mgC/l. The results of halomethane analysis are summarised in Table 2.18.

The changes in the concentrations of halomethanes produced at the two levels of chlorophyll for the various reaction times exhibited a similar trend to that observed in the previous experiments. The concentrations of

Figure 2.8 Comparative distribution of halomethanes detected in chlorinated sea water (2.1 mg/l) in the presence of Chlorella sp. and in the control experiment. The lower set of curves represents the concentrations of $CHBr_2Cl$. The levels of Chlorophyll-a are indicated on the curves.


250
200
150
100
50
0
$CHBr_3(\mu g/l)$
Control
1.6 mg/m^3
3.2 mg/m^3
4.8 mg/m^3
Control
1.6 mg/m^3
3.2 mg/m^3
4.8mg/m^3
10
5
0
$CHBr_2Cl(\mu g/l)$
0
6
12
18
24
30
36
42
48
Reaction time (hrs)

Chlorophyll Concentration mg/m³	Reaction Time (hrs.)	Halomethane Concentrations (µg/l)				
		$\bar{X}$ SD	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total
23	6	$\bar{X}$	0.3	9.2	169.7	179.3
		SD	0	0.1	1.5	1.6
	12	$\bar{X}$	0.2	10.4	197.5	208.0
		SD	0	0.1	2.8	2.9
	24	$\bar{X}$	0.5	12.4	232.4	245.3
		SD	0.2	0.3	5.7	6.3
	48	$\bar{X}$	0.4	13.7	276.2	290.2
		SD	0	0.1	5.4	5.6
95	6	$\bar{X}$	0	5.3	105.7	111.0
		SD		0.2	1.5	1.7
	12	$\bar{X}$	0.2	7.9	124.1	132.3
		SD	0	0.2	3.9	4.2
	24	$\bar{X}$	0.2	9.3	149.5	159.1
		SD	0	0.1	2.2	2.4
	48	$\bar{X}$	0.5	9.1	154.6	164.1
		SD	0	0.2	2.8	3.0

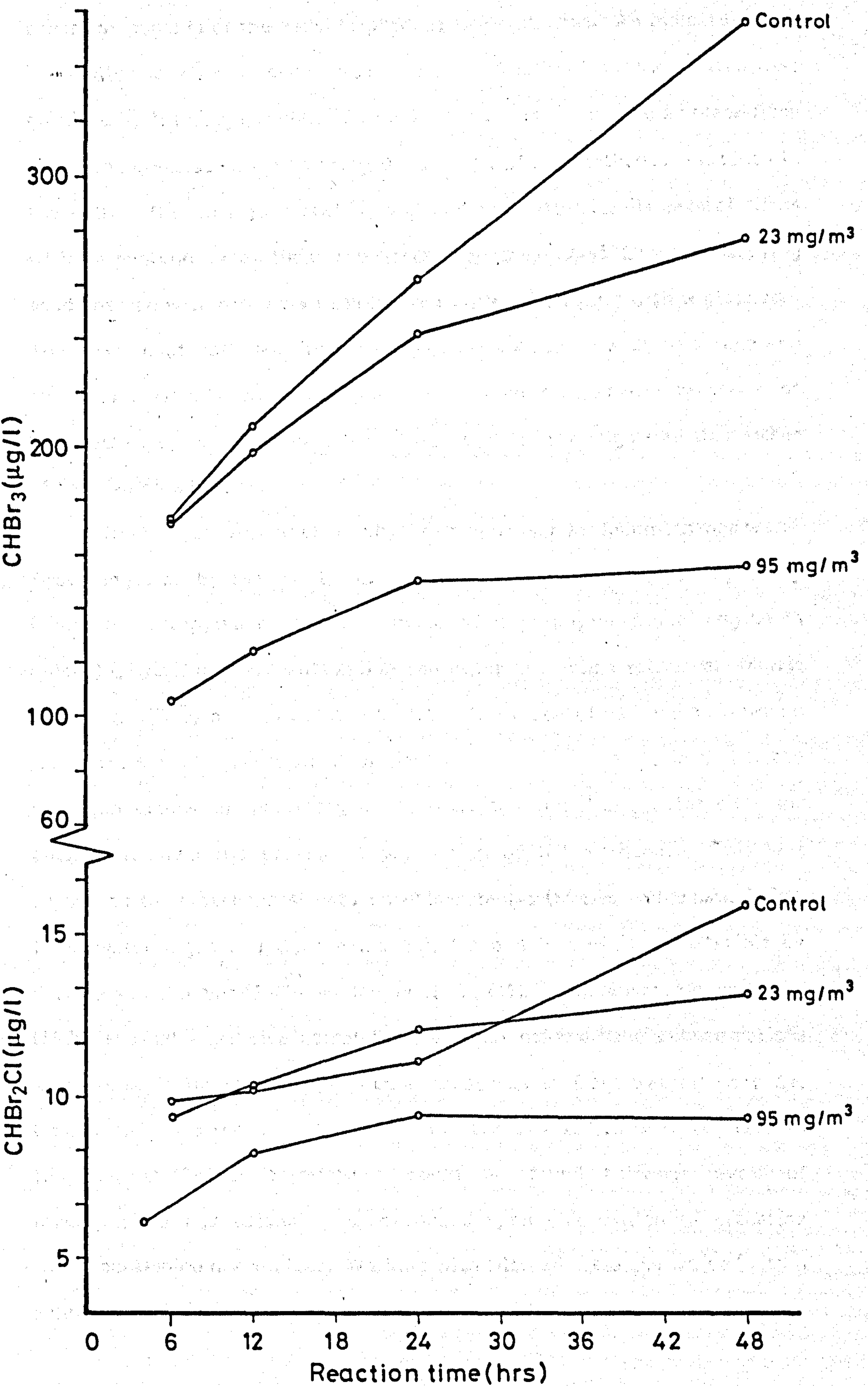
Table 2.18
Mean Concentrations of Halomethanes Produced in 600 ml of Chlorinated Sea Water (3.3 mg/l) in the Presence of Two Different Levels of Chlorella. Background DOC Level 2.4 mgc/l, Water Temperature = 22°C

$CHCl_2Br$ remained at a trace level, not exceeding 0.5 µg/l. With 23 mg/m^3 of chlorophyll, the $CHBr_2Cl$ concentration was 9.2 ± 0.1 µg/l after a reaction time of 6 hours, slightly lower than that of the control experiment. The amount of $CHBr_2Cl$ produced, increased slightly after 12 hours to 10.4 ± 0.1 µg/l and to 12.4 ± 0.3 µg/l after 24 hours. The latter concentration was slightly higher than that in the control, whereas the yield after 48 hours (13.7 ± 0.1 µg/l) was markedly lower than that at a similar reaction time in the control. At 95 mg/m^3 of chlorophyll, the $CHBr_2Cl$ yields at all reaction times were much lower than that produced in the experiment in which 23 mg/m^3 of chlorophyll experiment. However, the concentrations increased from 5.3 ± 0.2 µg/l after a reaction time of 6 hours to 7.9 ± 0.2, 9.3 ± 0.1 and after 12 and 24 hours respectively. The concentration was 9.1 ± 0.2 µg/l after 48 hours.

The concentrations of $CHBr_3$ produced at the 23 mg/m^3 chlorophyll level followed closely those of the control experiment. The concentration was 169.7 ± 1.5 µg/l after 6 hours of reaction time (similar to that of the control) and increased, but at a lower rate than in the control, to 197.5 ± 2.8, 232.4 ± 5.7 and 276.2 ± 5.4 µg/l after 12, 24 and 48 hours respectively. At 95 mg/m^3 of chlorophyll the $CHBr_3$ yields were all much lower than those produced at 23 mg/m^3. They showed a moderately high rate of increase during the first 24 hours and remained nearly constant for the next 24 hours. The comparative distribution of $CHBr_2Cl$ and $CHBr_3$ yields at both levels of chlorophyll and in the control are shown graphically in Figure 2.9.

To summarise the results of the **Chlorella** experiments. It appears that in the presence of **Chlorella** the yield of halomethanes is reduced relative to the control. However, within the reaction time span of each experiment, higher halomethane yields were produced. This may indicate that some of the available halogens were being consumed by oxidation or substitution reactions not leading to the formation of halomethanes whereas

Figure 2.9 Comparative distribution of halomethanes detected in chlorinated sea water (3.3 mg/l in the presence of Chlorella sp. and in the control. The levels of Chlorophyll-a are indicated on the curves.


CHBr$_3$ (µg/l)
300
200
100
60
Control
23 mg/m^3
95 mg/m^3
CHBr$_2$Cl (µg/l)
15
10
5
Control
23 mg/m^3
95 mg/m^3
0
6
12
18
24
30
36
42
48
Reaction time (hrs)

the remaining halogens reacted with the other contents of the water (or other components of the cells) to produce halomethanes. An indication that halomethanes were either being produced or absorbed from the solution was obtained by filtering the cells after chlorination on a pre-cleaned glass-fibre filter and qualitatively measuring the amount of halomethanes contained in the cells. This was conducted by washing the filtered cells several times with n-pentane and then repeatedly freezing (-45°C) and thawing accompanied with attempts to break the cells by grinding with a glass rod. The mixture of cells and filter were then re-extracted with n-pentane and an aliquot was taken for GC analysis which showed the presence of halomethanes. However, no attempt was made to investigate further either of the two possibilities.

The possible role of chlorophyll as a precursor for halomethanes was first suggested by Morris (1975). Chlorophylls were described by Seely (1966) as tetrapyrrolic pigments, made of a porphyrin and a long-chain alcohol (phytol) and that enolization can occur in alkaline solutions. Morris and Baum (1978) have postulated that the formation of carbanion occurs on the pyrrole ring present in chlorophylls , in which the hydrogen ortho- to the nitrogen are activated and thus provide sites for chlorination and the subsequent production of halomethanes. This was supported by experimental data on chlorophyll-a (Morris and Baum, 1978), fresh water algae and their extra cellular and intercellular materials by Olivers and Shindler (1980) and Briley **et al.**, (1980). Moreover, Hoehn **et al.**, (1978) showed a positive correlation between halomethane concentrations and algae blooms (chlorophyll-a concentrations) in fresh water reservoirs. However, it was shown by Crane **et al.**, (1980a) and Crane **et al.**, (1980b) that no statistical correlations could be found between levels of chlorophyll-a and halomethanes produced upon chlorination of estuarine water containing micro algae. Working with filtered estuarine water (with a salinity of 24°/oo), Crane **et al.**, (1980a), showed that the concentrations of

$CHBr_3$ and $CHBr_2Cl$ (comprising total halomethanes) increased significantly in the presence of **Isochrysis galbana** but not **Carteria sp.** or **Thalossiosira pseudonana.** Attempts to relate the increase in halomethanes produced upon chlorination to increase in chlorophyll content produce a low correlation coefficient. It was shown later by Crane **et al.**, (1980b) that the increase in halomethanes production upon chlorination of **I. galbana** may be attributed to D-mannitol which is the principal compound secreted and which was shown to produce significant increase in chloroform concentration in deionized water at high pH values. On the other hand, glycerol and proline, which are the principal secretions of the two other species, **Carteria sp.** and **T. pseudonana** respectively had little or negative effect on chloroform production under similar conditions. Thus, it is apparent that the results of the experiments involving **Chlorella sp.** (this study) cannot be generalized to the waters of Kuwait due to the naturally occurring fluctuations in biomass and growth phases of the many species of marine micro algae, the cellular excretions of which do not have an equal effect on halomethane production upon chlorination.

CHAPTER 3

Halomethanes in Coastal Waters Around the Desalination-Power Stations

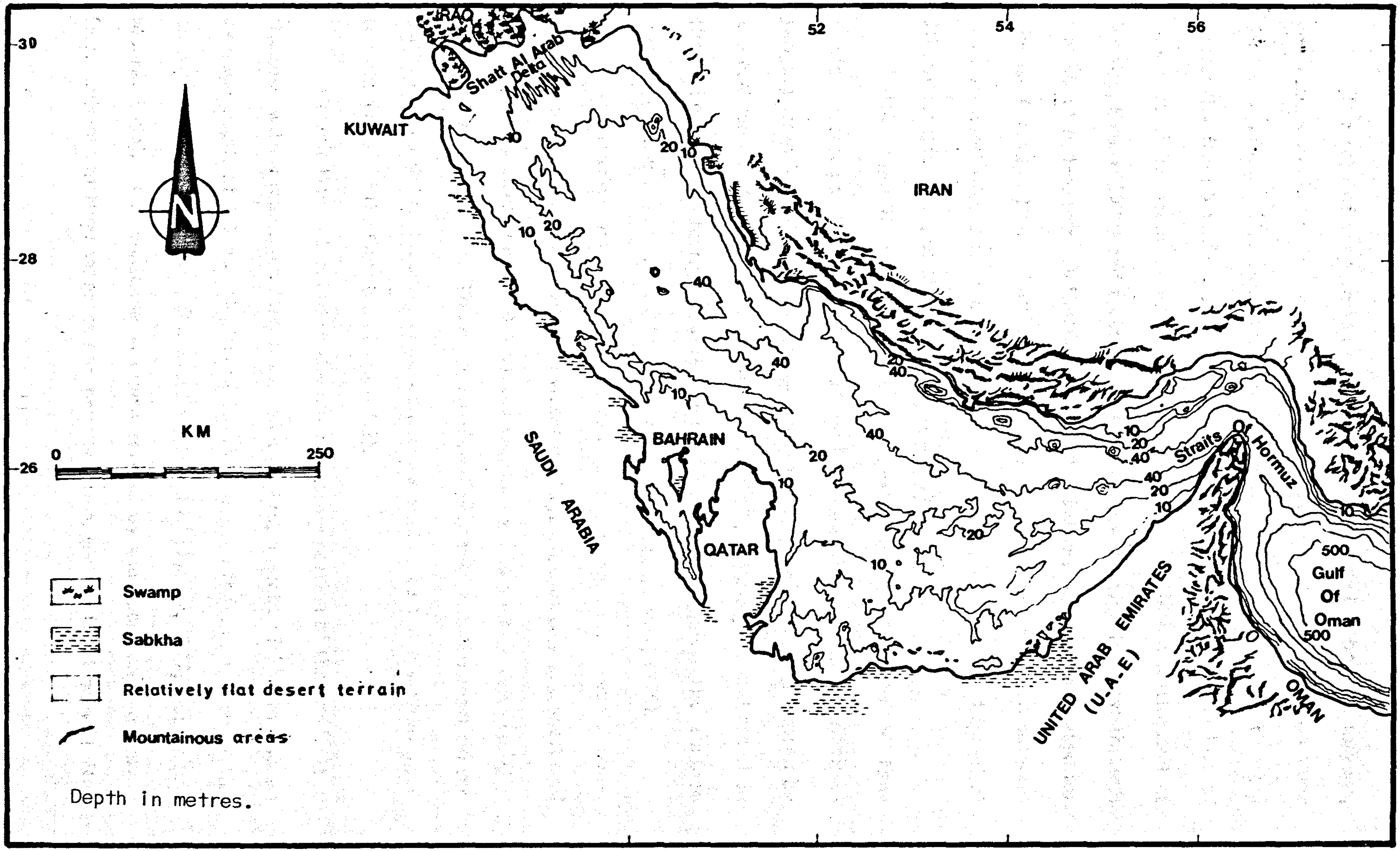
3.1 Introduction

This part of the study describes a field investigation of the levels of halomethanes in sea water in the areas likely to be affected by the release of chlorinated effluents from the desalination-power stations in Kuwait. Since the presence of these compounds has not been reported before, all three areas in which the five major stations are located were included in the survey. They included the Shuwaikh and Doha areas in Kuwait Bay (where the Shuwaikh and the Doha East and West Stations are located) and the Shuaiba Area on the Southern Coast where the Shuaiba North and Shuaiba South Stations are located. The general oceanographic features and sources of environmental pollution that may have an effect on the levels of halomethanes in the areas surveyed are summarised below.

The waters of Kuwait form part of the water masses of the Arabian Gulf, which lies between 24°-31°.30'N and 47°.30'-50°.30'E (Figure 3.1). At its southern end it is separated from the Gulf of Oman by the Strait of Hormuz which is 56 km wide at its narrowest point. It extends in a north-easterly direction for about 990 km, with a maximum width of 338 km (Grasshoff, 1976; Hughes and Hunter, 1980). Estimates of the mean depth range from 31 m to 36.1 m. Its maximum depth is about 90 m (Emery, 1956). The seasonal temperature variation of the surface waters amounts to about 17°C, ranging from 18°C in March to 35°C in August (Grasshoff, 1976).

Because of the high rate of evaporation, the salinity of the surface water tends to be high. Near the entrance to the Gulf the salinity is 36.5$\%_0$, which increases towards the interior (39$\%_0$ near the mid section) and more rapidly in the shallower areas where salinities of 44$\%_0$ have been measured (Purser and Seibold, 1973).

Figure 3.1 Morphological Features and Bathmetry of the Arabian Gulf (After Purser and Seibold, 1973)


IRAQ
Shatt Al Arab Delta
KUWAIT
IRAN
SAUDI ARABIA
BAHRAIN
QATAR
UNITED ARAB EMIRATES (U.A.E)
OMAN
Straits Of Hormuz
Gulf Of Oman
N
KM
0
250
52
54
56
30
28
26
10
20
40
500
Swamp
Sabkha
Relatively flat desert terrain
Mountainous areas
Depth in metres.

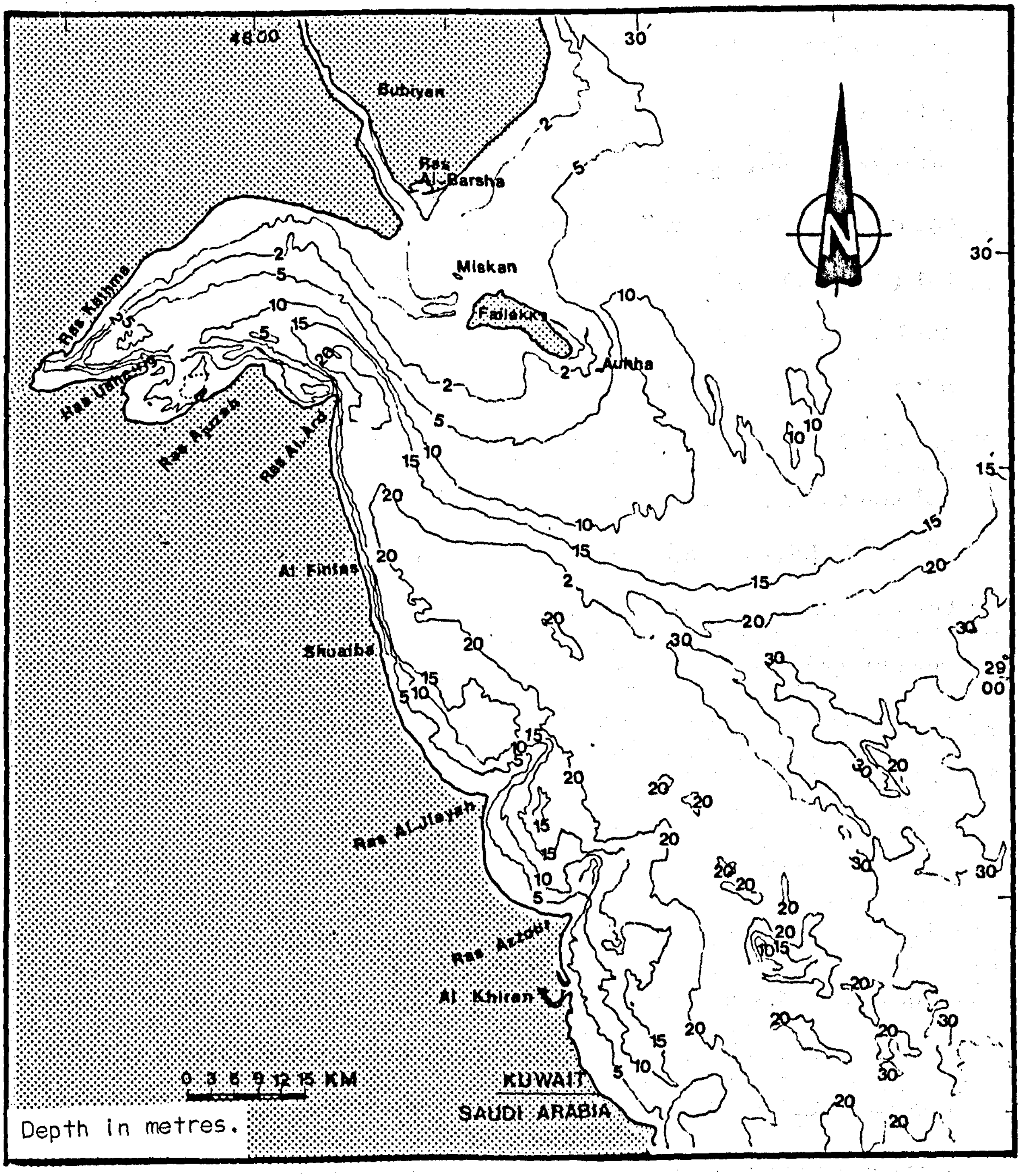
The rate of evaporation in the Gulf is estimated to be 1.44 m/year, reaching a minimum in December and a maximum during May and June (Privett, 1959). The flow from the Shatt-Al-Arab is estimated to vary seasonally from 5 km^3 to 100 km^3/y (Grasshoff, 1976). Thus, the loss of water resulting from excess evaporation over precipitation (estimated at 5 cm/y, Evans, 1970) and river run-off leads to a differential flow through the Strait of Hormuz. A flushing time of 2.5-3 years has been estimated for the Gulf (Koske, 1972). The water flowing from the Gulf of Oman shows a slow anticlockwise drift along the Iranian Coast, at an estimated speed of 10 cm/sec (Hartman, **et al.**, 1971; Grasshoff, 1976).

The limited measurements of tidal currents indicate a flow approximately parallel to the axis of the Gulf near the sea bed at velocities ranging from 50-100 cm/sec. Wind-driven surface currents are produced by the NW "Shamal" winds which blow for about 60% of the year and result in the deposition of terrigenous sediments, and also influence the surface current patterns in the Gulf (Hartman, **et al.**, 1971; Grasshoff, 1976).

The marine waters of Kuwait can be divided into two areas showing differences in terms of energy and water quality. Kuwait Bay is a sheltered coastal area, influenced to a variable degree by fresh water run-off from the Shatt-Al-Arab basin. The more open waters of the southern coast on the other hand, exhibit oceanographic conditions similar to those prevailing in the main body of the Gulf (See Figure 3.2).

Kuwait Bay is located in the north western portion of the Gulf. It is shallow, with a maximum length of about 45 km, a width of 25 km and an average depth of 4.5 m. Depths of 25-34 m occur off Ras Al Ardh at the entrance of the Bay (Babtie Shaw and Morton, 1979; Hayes, 1977; Dames and Moore, 1983). The coastline is characterised by the occurrence of coves (e.g. Sulaibikhat Bay) separated by promontories, such as Ras Ushayrij, Ras

Figure 3.2 Bathymetry of the Coastal Waters of Kuwait (After Al-Bakri et al., 1982)


48 00
30
30
15
29 00
Subiyah
Ras Al-Barsha
Miskan
Failaka
Auhha
Ras Kathma
Ras Ushairij
Ras Ajuzah
Ras Al Ard
Al Fintas
Shuaiba
Ras Al Jilayah
Ras Az-Zor
Al Khiran
KUWAIT
SAUDI ARABIA
N
0 3 6 9 12 15 KM
Depth in metres.

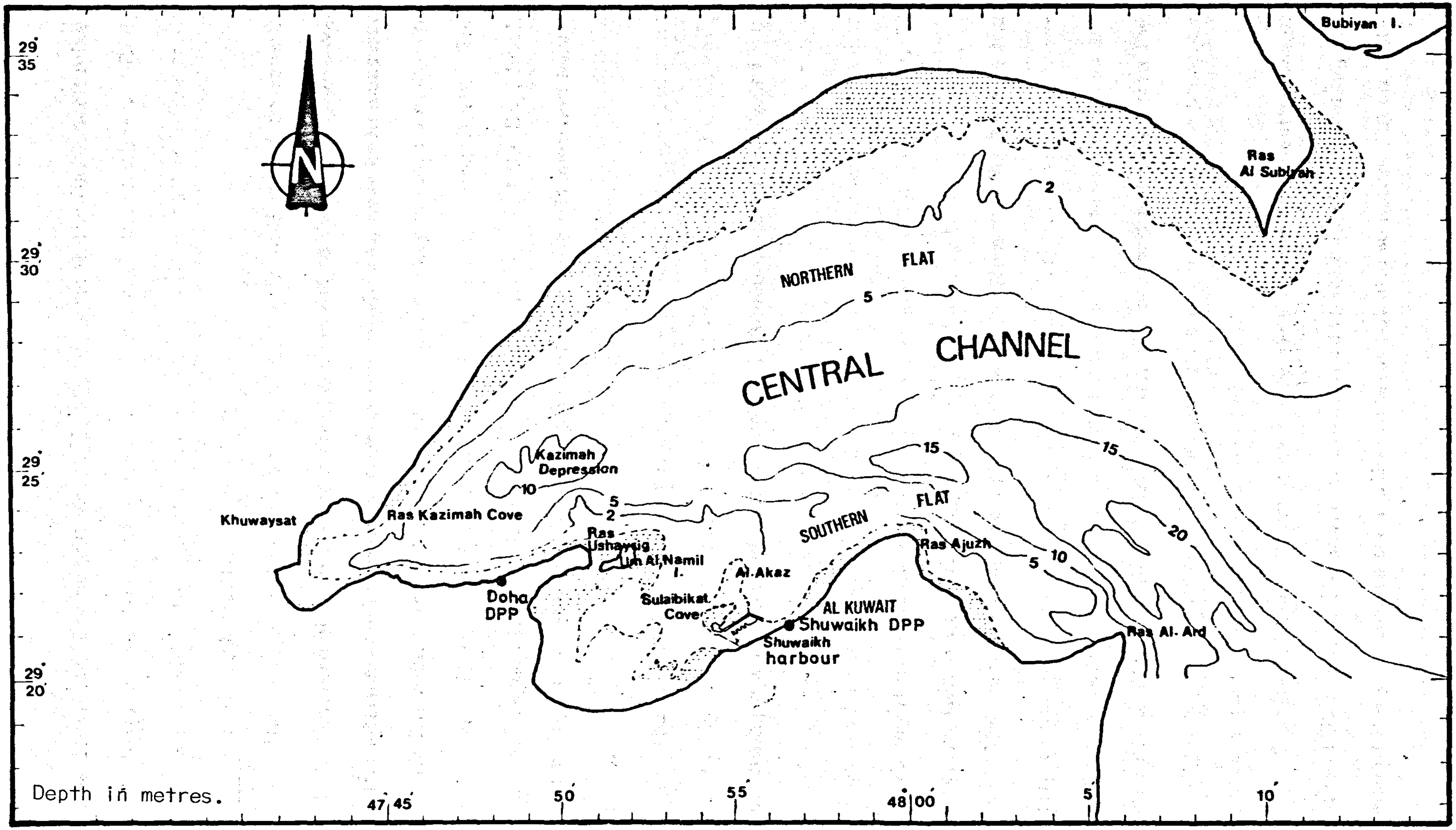
Ajouza and Ras Al Ardh. The interior and northern parts of the Bay are dominated by tidal flats, some of which extend to about 2 km into the sea (Figure 3.3).

The water circulation in Kuwait Bay is predominantly tidal. However, the prevailing north-westerly and, to a lesser extent, the south-easterly winds act as secondary driving forces, influencing the duration and speed of tidal currents. In general, currents are bimodal, reflecting the influence of the tide. The highest current velocities recorded range from 100 to 150 cm/sec in Khor Al Subiyah and off Ras Al Ardh, in contrast the near bottom velocities are on average about 50 cm/sec. Velocities in the central parts of the Bay, off Ras Ajouza, rarely exceed 50 cm/sec and fall to 20-40 cm/sec in the western part of the Bay (Dames and Moore, 1983; Sasaki, 1976). In the open parts of the Bay the direction of the ebb and flood tidal currents generally conforms to the geometry of the Bay, running parallel to the bathymetric contours. Movement of the water in the vicinity of Doha has been reported to be towards the west-southwest on the flood and towards the northeast or east-northeast on the ebb tide (Dames and Moore, 1983).

The tides are of the semi-diurnal type with two highs and two lows, usually unequal in magnitude, occurring within a lunar day of 24.8 hours. Admiralty Chart Datum shows Mean High High Water (MHHW) levels of 4.05 m and Mean Low Low Water (MLLW) of -0.25 m (ACD = KCD - 47 cm) which are confirmed by field measurements (Babtie Shaw and Morton, 1979; Dames and Moore, 1983). Water exchange per tidal cycle is about 20% (approximately 11.5×10^6 m^3) of the Bay's volume (C.T. Main, 1980).

The water temperature in the Bay exhibits a wide seasonal variability estimated to be 20-24°C (Dames and Moore, 1983), ranging from a maximum of 32.4°C (up to 36°C in the shallow coves) in summer to a minimum of

Figure 3.3 Principal Morphological Features and Bathymetry of Kuwait Bay (After Khalaf et al., 1982)


N
Bubiyan I.
Ras
Al Subiyah
29° 35
29° 30
29° 25
29° 20
2
NORTHERN FLAT
5
CENTRAL CHANNEL
Kazimah
Depression
10
15
15
5
2
FLAT
SOUTHERN
20
Khuwaysat
Ras Kazimah Cove
Ras
Ushayrig
Um Al Namil
I.
Al Akaz
Ras Ajuzh
10
5
Doha
DPP
Sulaibikat
Cove
AL KUWAIT
Shuwaikh DPP
Shuwaikh
harbour
Ras Al Ard
Depth in metres.
47 45
50
55
48 00
5
10

12°C in winter (Dames and Moore, 1983). In general, the Bay is well mixed and shows no evidence of permanent or seasonal thermoclines. Daily fluctuations within the upper 2 m are common, reflecting the influence of solar radiation (Dames and Moore, 1983).

The waters of the Bay are also relatively well mixed as regards salinity, showing an increase from the areas near Khor Al Subiyah (33-40‰) to the interior where salinities in the range of 36-43‰ have been measured (Babtie Shaw and Morton, 1979; Lee, 1983). The salinity reaches a maximum in August and then decreases to a minimum in March and April. The dissolved oxygen levels reflect the well mixed character of the Bay, levels of 6-8 mg/l were reported in most parts of the Bay by Dames and Moore (1983).

The levels of other parameters, such as nutrients and suspended solids are highly variable. Levels of chlorophyll-a range from 1-4 mg/m^3, decreasing towards the interior of the Bay. Ammonia-nitrogen levels lie in the range 5-32 µg/l whereas the reported nitrates - nitrogen values range between 98 to 168 µg/l (EPD, 1983). The concentration of suspended solids (10-20 mg/l) increases towards the interior shallower parts of the Bay, as the proportion of fine silt increases (Dames and Moore, 1983).

The southern coastline of Kuwait extends from Ras Al Ardh in the north to the Saudi border in the south (See Figure 3.2) and has several "bow-like" embayments, separated by low promontories. The near-shore areas are generally shallow (maximum depth 36 m), the sea bed extending into the Gulf in a series of terraces. The area is also characterised by the presence of several reefs and islands (Al Bakri **et al.**, 1982).

Currents in the southern area rarely exceed 50 cm/sec, with a mean value of 35 cm/sec. The currents generally run parallel to the shoreline, for much of the year toward the north-northeast but also sometimes in an eastsoutheast direction. The net drift is generally to the south (KISR, 1981). The waves which rarely exceed 2 m have periods of 3-5 seconds. The tides are semi-diurnal with a predicted range of 2.95 m to -0.2 m. However, in practice the range is increased to 3.15 m to -0.6 m during periods of strong north-westerly winds (Cremer and Warner, 1976).

Water temperature measurements in the vicinity of Shuaiba show that the near-shore waters are influenced by cooling water effluents released by the industries in the area and may reach values of 5-6°C above the ambient water temperature in the summer months under relatively calm conditions. Away from the Shuaiba area, ambient water temperature reaches its maximum values in the months of July and August (mean 31.1°C). The strongest thermal stratification is also observed during these months. Minimum temperatures occur in February with a mean value of 15°C. A more homogeneous temperature distribution occurs during the winter months, as a result of extensive mixing (KISR, 1981 and EPD, 1983).

The salinity of the water in the near-shore areas is also influenced by the effluents discharged from the desalintion plant. However, the effect is minimised by mixing the effluents with sea water which has been used for cooling before they are released into the sea. The ambient salinity shows values of about 37‰ during the months of March through April and 40‰ during the rest of the year (KISR, 1981; EPD, 1983).

Other water quality parameters mostly lie within the ranges observed for Kuwait Bay (EPD, 1983). However, the levels of ammonia-nitrogen within the Shuaiba area vicinity may exceed 500 µg/l (Cremer and Warner, 1976 and KISR, 1981).

The desalination-power stations represent the main consumer of sea water for process and cooling purposes in Kuwait Bay. The Shuwaikh Station consumed an estimated 600 x 10^3 m^3/day during 1982 (MEW, 1983) to which

2-3 x 10^3 kg/day of chlorine was added. The discharged sea water (combined cooling sea water and brine) contains higher levels of total dissolved solids (amounting to an increase in salinity of 3-4‰ and is higher in temperature than the ambient water by about 5.4°C (C.T. Main, 1981). The released effluents contain halogenated organics, oil and heavy metals (e.g. Ni and Cu) resulting from corrosion.

Because of their larger capacity, the Doha desalination stations are also expected to have similar but more extreme impact. The Doha East Station consumed about 1600 x 10^3 m^3 of sea water per day in 1982 and 8-9 x 10^3 kg of chlorine. It discharged an estimated total of 1500 x 10^3 m^3 per day. When the Doha West plant is fully operational these amounts are expected to double. Table 3.1 summarises the sea water and chlorine consumption and the amounts of effluents and distillate produced by the four major stations in operation during 1982.

Other effluents released into the Bay contribute mainly to the organic load of the waters. They include those from the Shuwaikh and Doha Harbours, the ship repair yard, effluents from the Kuwait Flour Mill Company and the illegally-connected sewage drains from the Shuwaikh area.

In the Shuaiba area, the desalination-power stations are located in the midst of the largest industrial complex in Kuwait. The amounts of sea water consumed by the two stations (Shuaiba North (SNPS) and South (SSPS) plants) amounts to about 2700 x 10^3 m^3/day. About 7-9 x 10^3 kg of chlorine are also consumed daily (see Table 3.1). The volumes of effluents released by other major industries in the area and the main contaminants in them are summarised in Table 3.2. The table does not include the domestic effluents or contributions from the Shuaiba Harbour, oil loading terminals and ballast waters released into the area. It is apparent that the Shuaiba area receives a greater input of oily discharges and nitrogenous compounds than do either

Station	Number of Desalination Units	Estimate Sea Water Consumption (feed make up & cooling) in $(10^3 m^3/day)$	Estimate Chlorine Consumption (2) $(10^3 kg/day)$	Brine Released $(10^3 m^3/day)$	Distillate Output $(10^3 m^3/day)$
Shuwaikh	10	150 + 450 = 600	2 - 3	100	50
Shuaiba North (3)	7	120 + 360 = 480	2 - 3	80	40
Shuaiba South	6	300 + 900 = 1200	5 - 6	200	100
Doha East (4)	7	390 + 1170 = 1600	8 - 9	260	130

Table 3.1 **Amount of Sea Water and Chlorine Consumed by the Desalination Power Stations and Volume of Effluents and Distillate Produced in 1982**

(1) Estimates were calculated from the performance data of the (D) units in Shuwaikh (Babcock-Hitachi, Japan) in which the ratios of distillate to brine, feed make-up and cooling sea water was found to equal approximately 1:2:3:9.

(2) Data obtained through the WDRC (Ministry of Electricity and Water).

(3) The figures for the SNP and SSP Stations do not include the amount of sea water diverted to other industries to be used for cooling purposes.

(4) The Doha West Station was not in operation until the end of 1983.

Industry	Flow Rate* (m^3/hr)	Average Pollution Load (kg/d)						
		COD	NH_3	Oil	H_2S	Urea	Cr	Cu
Petrochemical Industries Co. (PIC A and B Fertilizer Plants)	46,000	3,000	900	300	-	8,000	0.9	-
Kuwait National Petroleum Co. (KNPC Shuaiba Refinery)	4,000	7,000	1,000	500	600	-	1.6	1.2
Kuwait Oil Co. (KOC Mina Al Ahmadi Refinery & LPG PLant)	92,000	2,000	20	50	2	-	0.2	0.1
Kuwait National Petroleum Co. (KNPC Mina Abdulla Refinery)	300	2,000	100	200	60	-	-	-
Melamine Manufacturing Co.	20	100	700	3	-	100	<0.1	<0.1

*For industries other than desalination plants, the flow rate is for the combined effluents (process water plus cooling sea water).

Table 3.2 Major Sources of Industrial Pollutants into the Shuaiba Area (KISR, 1983) the Shuwaikh or Doha areas. However, the potential for dilution and flushing of effluents in Kuwait Bay is more limited.

The pattern of desalination stations being located in the midst of industrial complexes is repeated throughout the Gulf region. Moreover, the pollution loads released into the Gulf waters are similar to that shown for Kuwait, as can be seen from Table 3.3.

3.2 Materials and Methods

In all, seven sampling trips were conducted using the sampling boat "Sadaf" belonging to the Environment Protection Department. During these about 150 samples were collected for halomethanes analysis from the areas of Shuwaikh, Doha and Shuaiba. The sampling locations in each area are shown in Figures 3.4a to 3.4c inclusive. It should be noted that because the Doha area is very shallow, the sampling points could not be located as close to the desalination-power plant as they were at Shuaiba and to a lesser extent Shuwaikh.

At each sampling location the corrected tide condition and water level were recorded and the wind speed and direction and air temperature were measured by hand-held gauges. A low speed direct-reading current meter and temperature probe (Tsurumi Seiki, Japan) were used to take a profile of the water column just before the samples for the halomethanes analysis were collected. Total residual chlorine analysis was conducted using the DPD Method (Standard Methods, 15th Edition, 1975). This is a titrimetric method using Fe^{2+} ions in the presence of iodide and employing diethyl-p-phenylenediamine as an indicator. The method is specific for residual chlorine and is suitable for field use. It has a range of 0.05 to 5 mg/l chlorine and a detection limit of 0.05 mg/l (Høstgaard et al., 1977).

Sampling of sea water for halomethanes analysis was carried out by lowering a closed 500 ml dark brown glass bottle (placed in a metal frame

		Industrial	Ship Ballast	Domestic	Total
WWV*	$10^3 m^3/yr$	200,000	400,000	70,000	670,000
	%	30	60	10	
BOD	t/yr	16,000		12,000	28,000
	%	60		40	
SS	t/yr	550,000		10,000	560,000
	%	98		2	
Oil	t/yr	60,000	600,000	Relatively small	660,000
	%	9	90		
N	t/yr	211,000		1,000	22,000
	%	95		5	
PO_4-P	t/yr	2,000		1,000	3,000
	%	67		33	
S^{--}	t/yr	200			300
Phenols	t/yr	160			160
Hg	t/yr	20			20
Cr	t/yr	7			7
Cu	t/yr	100			100
F^-	t/yr	4,000			4,000

*WWV = Waste Water Volume

Table 3.3 Annual Releases of Major Effluents into the Gulf (ROPME, 1984)

Figure 3.4a Sampling Locations in Shuwaikh area.

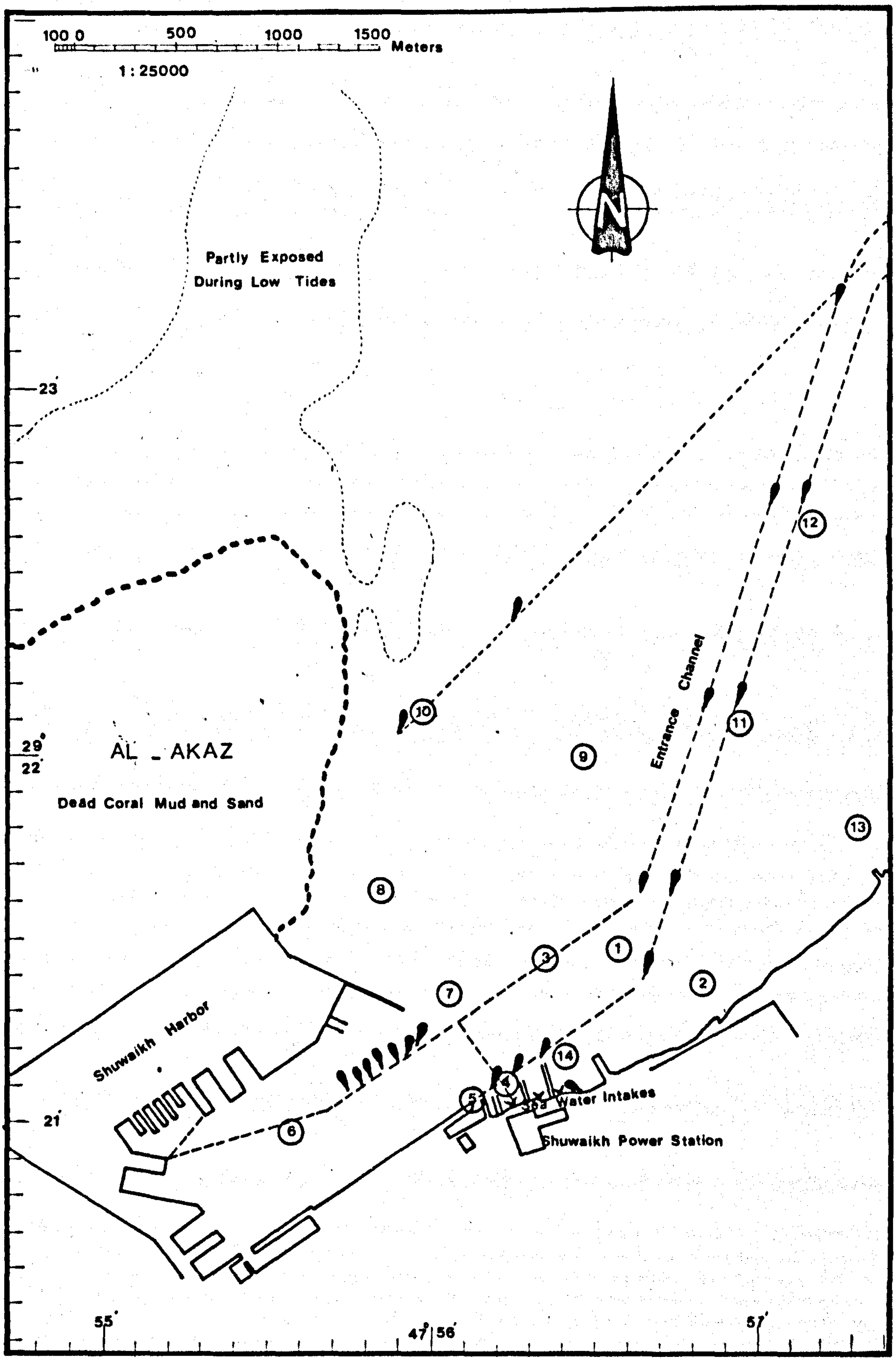
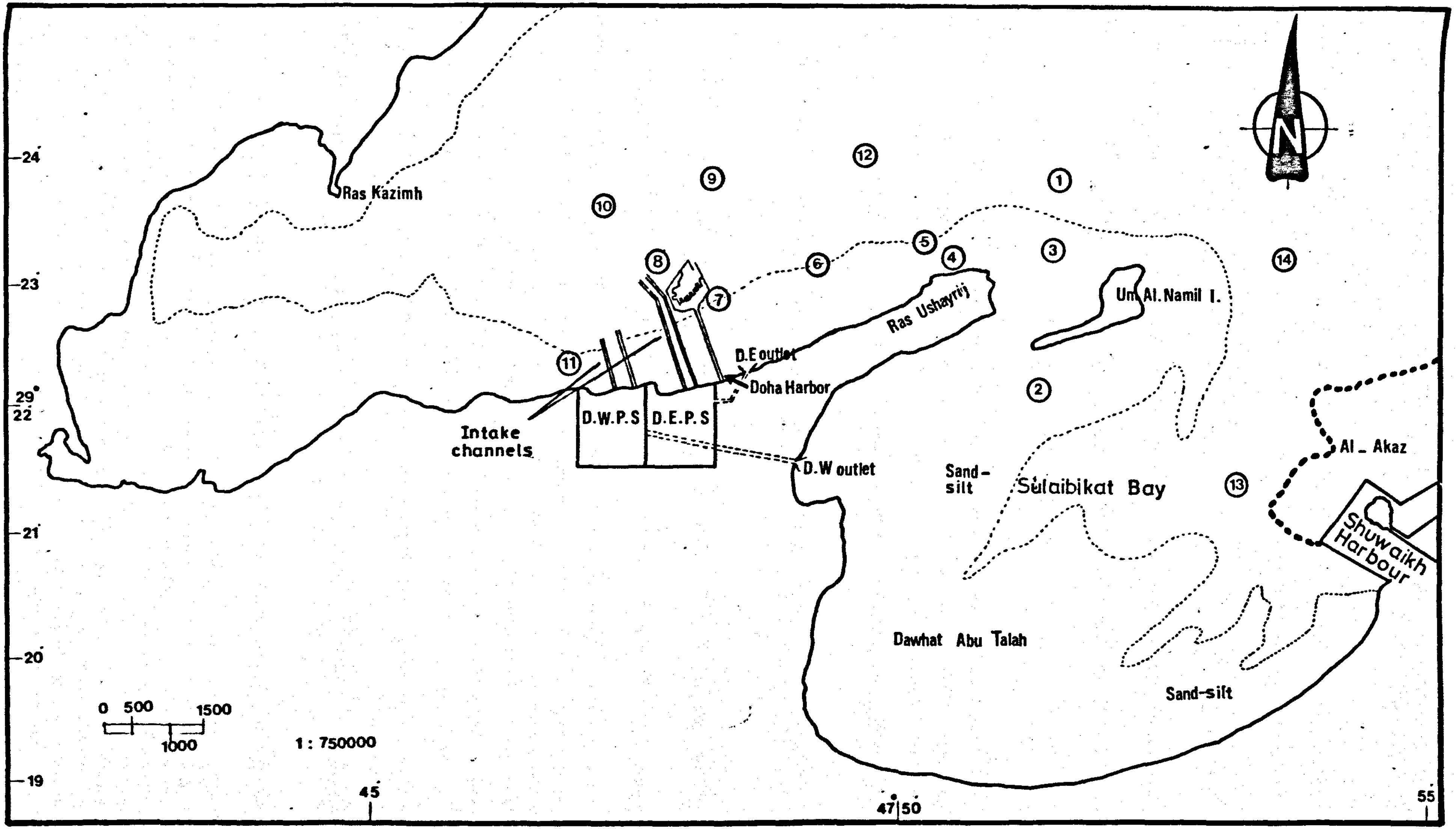
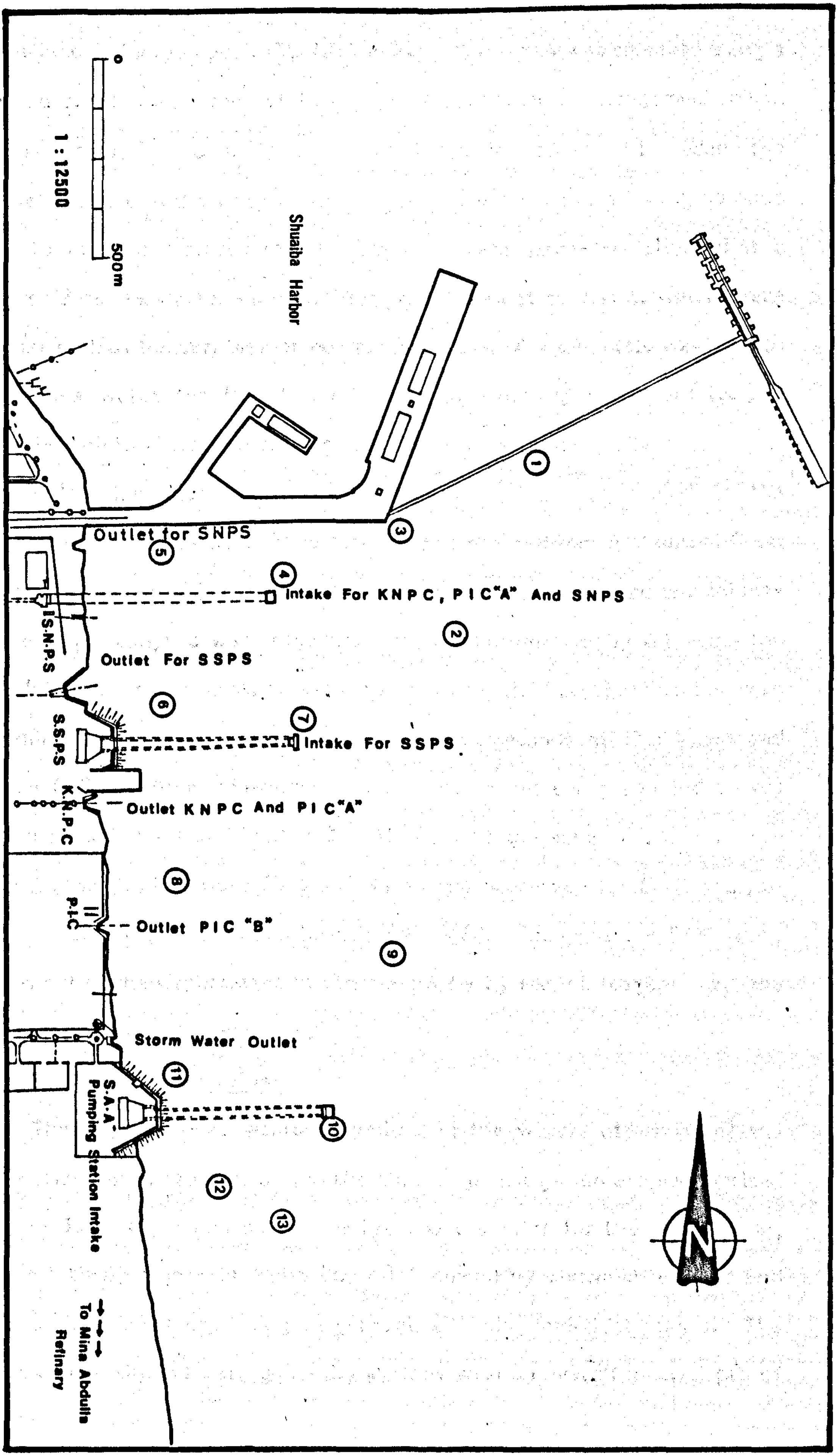

100 0
500
1000
1500
Meters
1:25000
N
Partly Exposed
During Low Tides
23'
29°
22'
AL - AKAZ
Dead Coral Mud and Sand
Entrance Channel
Shuwaikh Harbor
21'
Sea Water Intakes
Shuwaikh Power Station
1
2
3
4
5
6
7
8
9
10
11
12
13
14
55'
47° 56'
57'

Figure 3.4b Sampling Locations in the Doha Area



N
Ras Kazimh
⑫
⑨
①
⑩
⑤
③
⑥
④
⑭
⑧
⑦
Um Al. Namil I.
Ras Ushayrij
D.E outlet
⑪
Doha Harbor
②
D.W.P.S
D.E.P.S
Intake channels
Al _ Akaz
D.W outlet
Sand-silt
Sulaibikat Bay
⑬
Shuwaikh Harbour
Dawhat Abu Talah
Sand-silt
0 500 1500
1000
1 : 750000
24
23
29° 22
21
20
19
45
47|50
55

Figure 3.4c Sampling Locations in the Shuaiba Area



Shuaiba Harbor
1:12500
0
500m
①
②
③
④
⑤
⑥
⑦
⑧
⑨
⑩
⑪
⑫
⑬
Outlet for SNPS
Intake For KNPC, PIC"A" And SNPS
S.N.P.S
Outlet For SSPS
Intake For SSPS
S.S.P.S
K.N.P.C
Outlet KNPC And PIC"A"
P.I.C
Outlet PIC "B"
Storm Water Outlet
S.A.A. Pumping Station Intake
To Mina Abdulla Refinary
N

with a lead-weighted base). To fill the bottle, the cap was released using a nylon cord. However, the bottle was not fitted with a closing mechanism. Upon retrieval, 1 ml of 0.1N sodium thiosulphate was added to reduce the residual chlorine in the water. The bottle was re-capped, allowing no head space to form, and stored in ice. Samples were generally collected at a depth of 2 m. However, samples were also taken at depths at which there were anomalous temperature or current readings. A new bottle was used to collect sea water for the determination of salinity, ammonia-nitrogen, suspended solids, chlorphyll and dissolved organic carbon (DOC).

Extraction and analysis of halomethanes were conducted in the manner described earlier. Salinity was measured on a Tsurumi-Seiki inductive salinometer (Model SK 24) with expanded temperature and salinity ranges. Chlorophyll-a was determined spectophotometrically following the SCOR/UNESCO procedures, described in Chapter 2. Suspended solids were determined gravimetrically according to the methods of Strickland and Parsons (1971). Ammonia-nitrogen was determined using the indophenol method as indicated in Chapter 2. Aliquots of the sample (100 ml) were filtered through glass fibre filters (0.8 µm) and preserved for DOC analysis by the addition of mercuric chloride (40 mg/l). Analyses for DOC were carried out in the Department of Oceanography by Mr. H. Rogers using the techniques described by Parker (1981).

3.3 Results and Discussion

The physical parameters prevailing in the waters off-shore of the desalination-power stations during the time of investigation are summarised in Table 3.4. The mean sea water level was similar for the three areas, being relatively higher at Doha (2.6 m) followed by Shuwaikh (2.4 m) and Shuaiba (2.1 m), corresponding in general with the mid-tidal stages. The locations investigated were generally shallow with an overall mean depth of

Parameter	Locality					
	Shuwaikh (n=60)		Doha (n=34)		Shuaiba (n=54)	
	Mean	SD	Mean	SD	Mean	SD
Water level (m)	2.4	0.4	2.6	0.5	2.1	0.8
Water depth (m)	5.6	3.5	5.0	3.8	5.3	2.4
Wind speed (m/sec)	3.0	3.1	0.6	1.2	4.0	1.8
Current speed (cm/sec)*	18.6	11.8	18.2	7.8	25.7	9.4
Water temperature (°C)*	16.2	2.0	16.7	0.8	18.4	1.2
Salinity (‰)*	39.2	0.8	39.1	0.6	39.4	0.3

*Measured at the upper 2 meters, at the same depths from which samples for halomethanes analysis were taken.

Table 3.4 Physical Parameters Characteristic of the Coastal Areas Offshore of the Desalination-Power Stations at the Time of the Study of the Distribution of Halomethanes (March 1982)

5.3 m, ranging from 5.6 m in Shuwaikh to 5.0 m in Doha. However, the sampling locations in Shuaiba were more uniform in depth than those in the other two areas. The depth of water at some locations near Doha was only about 2 m at low tide.

The mean sea water temperatures ranged from 16.2°C and 16.7°C at Shuwaikh and Doha respectively to 18.4°C at Shuaiba. The effect on the ambient temperature of the released brines and cooling sea water effluents was apparent in locations such as the entrance to Shuwaikh Harbour and around the Shuaiba Harbour structure where values of 2-6°C above ambient values were measured. There was less variation in temperature in the Doha area, since most of the sampling locations were further from the station's outfalls than in the two other areas.

The mean salinity values ranged from 39.1‰ at Doha to 39.4‰ at Shuaiba. The variability was greater at Shuwaikh and Doha (e.g. ranging from 38.1 to 40.2‰ in Shuwaikh) than at Shuaiba. There are probably two reasons for the low variability at Shuaiba (i) the ratio of cooling water to brine is higher there as sea water is also utilised for cooling by the other major industries and (ii) the potential for dilution there is relatively greater. The limited flow of fresh water from Shatt-Al-Arab (in Iraq) via Khor Al-Subiyah may also contribute to the variability of the salinity values measured in Kuwait Bay.

The wind direction was predominantly from the northwest during the sampling period. The wind speed recorded in the Shuwaikh area averaged about 3 m/sec, with short-lived gusts up to 8 m/sec. In the Doha area, the mean wind speed was only 0.6 m/sec, covering a range of 2.5-0.1 m/sec. In the more exposed coastal area at Shuaiba the mean wind speed was 4 m/sec, with a range of 4.7 to 3.1 m/sec.

Current speeds recorded at the time of sampling showed an overall mean of 21 cm/sec, being highest at Shuaiba (25.7 cm/sec), followed by Shuwaikh (18.6 cm/sec) and least at Doha (18.2 cm/sec). However, the values for Shuwaikh showed the greatest variability which is probably attributable to changes in the wind speed. The prevailing current flow in the Shuwaikh area was northerly (35%) followed by easterly and north-westerly directions (16% each). However, all other directions were represented as well, reflecting the wide variability caused by the interaction of the various morphological and hydraulic features discussed earlier. The current direction at Doha was mostly towards the east, north and northeast. The pattern was reversed in Shuaiba where the flow was mostly towards the northwest (57%) followed by northerly and westerly directions (17% each). The frequencies of current directions, expressed as percentages of the total measurements are shown in Table 3.5.

The mean concentrations of total residual chlorine, ammonia-nitrogen, chlorophyll-a, suspended solids and DOC are shown in Table 3.6. The mean concentration of total residual chlorine was significantly higher at Shuwaikh than in the other two areas, 0.5 mg/l compared to 0.1 and 0.03 mg/l in Doha and Shuaiba respectively. This may be attributed to the fact that chlorinated-sea water (produced by the adjacent Chloro-Alkali factory) is injected ahead of the intake-pumps and thus creates a chlorine rich zone around the intakes. The relatively enclosed area in the vicinity of the Shuwaikh Station may be another factor limiting the dissipation of chlorine. The intakes at Doha are located at the end of a dredged channel (see Figure 3.4b). Chlorine gas is injected into the intake pipes located at the end of the channel. The method of chlorination at the Shuaiba North Station is similar to that used for Shuwaikh, except that chlorine gas, instead of chlorinated sea water, is injected at the intakes. In the Shuaiba

Location	Current Direction (%)							
	N	NE	E	SE	S	SW	W	NW
Shuwaikh n = 60	35	12	16	5	5	7	4	16
Doha n = 34	26	24	26	9	3	0	3	9
Shuaiba n = 54	17	2	4	0	2	2	17	57

Table 3.5 Frequency Distribution of Current Directions in the Coastal Areas of Kuwait (March 1982)

Parameter		Locality		
		Shuwaikh	Doha	Shuaiba
Total Residual Chlorine (mg/l)	Mean	0.5	0.1	<0.1(.03±.06)
	SD	0.6	0.2	
	N	54	30	59
Ammonia ($N\text{-}NH_3$ µg/l)	Mean	28	16	83
	SD	27	11	57
	N	25	23	32
Chlorophyll-a (mg/m^3)	Mean	0.8	0.5	0.6
	SD	0.6	0.2	0.2
	N	20	14	9
Suspended Solids (mg/l)	Mean	10	8	4
	SD	4	5	2
	N	21	14	11
DOC (mg C/l)	Mean	2.5	2.6	2.1
	SD	0.7	0.2	0.4
	N	12	7	11

Table 3.6 **The Mean Concentration of Total Residual Chlorine, Ammonia-nitrogen, Chlorophyll-a, and Suspended Solids in Water Samples Collected from the Coastal Areas Offshore of the Desalination-Power Stations in Shuwaikh, Doha and Shuaiba Areas.**

South Station, sea water is pumped into a basin (the Forebay) built inside the station where chlorine gas is injected. However, the levels of residual chlorine measured were relatively lower in the Shuaiba area than at Doha. Although the potential for dilution is greater in the more open Shuaiba area, the input of nitrogen-containing compounds (mainly ammonia and urea from the fertilizer factories) may also contribute to the removal of chlorine. For example, some of the halamines (e.g. $NHBr_2$, NH_2Cl or a mixture) formed by the reaction of ammonia and chlorine, may decompose to produce nitrogen gas, nitrate ion and the halide ion (break point reaction), and thus would not appear as residual chlorine (Høstgaard **et al.**, 1977; Johnson, 1978). However, other reducing species such as S^{2-}, Fe^{2+}, Mn^{2+}, CN^- and NO_2^- may also remove residual chlorine from the water (Høstgaard **et al.**, 1977). The average ammonia-nitrogen levels in the Shuaiba area were 83 µg/l (with a maximum value of 187 µg/l) compared to 28 µg/l and 16 µg/l at Shuwaikh and Doha respectively.

The levels of chlorophyll-a in the Shuwaikh waters were higher than those at Doha and Shuaiba. Organic matter from sewage outfalls and organic matter-rich industrial effluents (e.g. from the flour mills) may be responsible for the relatively high productivity of the Shuwaikh area. The levels of suspended solids there had a mean value of 10 mg/l, compared to 8 mg/l at Doha and 4 mg/l at Shuaiba. In spite of the high turbidity observed in the Doha area, the amount of suspended solids (determined gravimetrically) was lower than in the Shuwaikh area. Thus, the relatively higher proportion of fine particulates in the Doha area, indicated earlier, is not reflected by these measurements. The levels of DOC were generally similar in the three areas, ranging between 2.1 ±0.4 mgC/l in Shuaiba to 2.6 ±0.02 mgC/l in Doha (Shuwaikh samples had a mean value 2.5 ±0.7 mgC/l).

The distribution of halomethanes in the water samples collected from the three areas is summarised in Table 3.7. Of these $CHBr_3$ comprised about 95% of the total, almost all the remainder was $CHBr_2Cl$, the levels of $CHCl_2Br$ being below 0.1 µg/l. The occurrence of $CHCl_3$ and CCl_4 was uncertain as although peaks corresponding to them were found in chromatograms for most samples these also coincided with solvent peaks. In all cases their concentrations would have been less than 1 µg/l. Tetrachloroethylene was detected in four samples from Shuaiba and Shuwaikh at levels not exceeding 0.2 µg/l. It was probably an industrial contaminant rather than a product of chlorination since it was not detected in the experimental work on chlorination. The dominance of $CHBr_3$ in chlorinated sea water has been reported by Helz and Hsu (1978) Bean **et al.** (1978), Sugam and Helz (1981) and Hartwig and Valentine (1983). Most of these investigators have also reported the presence of $CHBr_2$ Cl (about 5% of the total) whereas $CHCl_2Br$ and $CHCl_3$ were either not detected or were found at levels below 0.1 µg/l. The overall mean of total halomethanes in the Shuwaikh area amounted to 10.8 ±18.6 µg/l, ranging from 0.1 to 84.8 µg/l. This was almost double the mean value obtained for Shuaiba (5.7 ±5.7 µg/l with a range of 0.1 to 25.2 µg/l) and about four times the mean value for Doha (2.6 ±4.1 µg/l, ranging from 0.1 to 20.4 µg/l). The limited data available on the dynamics of water movement and detailed composition of the sea water and speciation of the halogens in each area, plus the fact that the geographical coverage of the study differed in the three areas, makes it difficult to attribute the observed differences to a single or a group of factors. However, on the basis of field and experimental data, Grieve **et al.** (1978) Jolley **et al.** (1978) and Jolley and Carpenter (1983), have identified several factors contributing to the production and fate of volatile halogenated organics in cooling water effluents. These include the

Location		Halomethane Concentrations (μg/l)			
		$CHBr_2Cl$	$CHBr_3$	Total	N
Shuwaikh	Mean	0.4	10.3	10.8	60
	SD	0.5	18.0	18.6	
	Range	2.3	82.3	84.7	
Doha	Mean	0.2	2.4	2.6	34
	SD	0.1	4.0	4.1	
	Range	0.5	19.6	20.3	
Shuaiba	Mean	0.2	5.5	5.7	54
	SD	0.1	5.6	5.7	
	Range	0.4	24.8	25.1	

Table 3.7 **The Mean Concentration of the Halomethanes Detected in the Coastal Waters Offshore of the Three Desalination-Power Plants Included in the Investigation (March 1982)**

level of chlorine applied, the quantities of effluents and the rates at which they are released, the dilution capacity of the receiving waters, the presence of materials that may compete for the halogens and factors related to evaporation and natural decay (i.e. U.V. light intensity). Of these factors, dilution and the reaction of the oxidants with materials in the receiving waters seem to have the dominant effect (Jolley and Carpenter 1983).

The mean concentrations of the halomethanes according to sampling locations in the three areas are summarised in Table 3.8. The number of samples taken per station is also shown. The variability in the number of samples indicates that either some of the locations could not be reached in low tides or that more than one sample was taken per trip, wherever stratification was observed. In Shuwaikh, where sampling was conducted for four tidal phases, the highest mean concentration of total halomethanes encountered was at sampling location No. 4 near the intake pumps (49.4 ±25.5 µg/l). The second highest value was at Station No. 14 (33.0 ±20.9 µg/l) about 200 m to the east of Station No. 4. The rest of the stations had levels below 15 µg/l which decreased with increased distance from the station. Variability in halomethanes levels was limited to the upper 2 m. For example, at Station No. 3 the concentration at the depth of 1 m was 12.4 µg/l whereas at 2.5 m, 44.2 µg/l were detected. A similar phenomenon was observed at Station No. 4, thus reflecting the effect of chlorine injection near sea bed rather than a density gradient. The distribution of halomethanes at the ebb and flood stages of the tide are summarised in the left side of Table 3.9 and in Figures 3.5a through 3.5c. The distribution of the overall mean values of halomethanes in Shuwaikh (Figure 3.5a) seems to indicate a flow towards the channel (probably under the influence of the north-westerly wind-induced surface currents). During the ebb phase,

Study Area and Compounds		Concentrations of Halomethanes (µg/l) per Station Number														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	N
Shuwaikh																
CHBr$_2$Cl	$\bar{x}$	0.2	0.3	0.5	1.5	0.4	0.3	0.2	0.2	0.2	0.1	0.2	0.2	0.2	1.0	
	SD	0	0.1	0.5	0.7	0.2	0.1	0.1	0.1	0	0	0.1	0.1	0	0.6	
CHBr$_3$	$\bar{x}$	2.1	4.1	10.8	48.1	11.2	6.5	3.1	2.2	0.7	0.4	0.8	0.8	0.4	32.0	
	SD	1.1	2.1	16.2	24.8	8.0	2.8	3.1	2.6	0.1	0.6	1.4	1.4	0.9	20.3	60
TOTAL	$\bar{x}$	2.3	4.4	11.2	49.5	11.6	6.9	3.3	2.4	0.9	0.5	1.3	1.3	0.6	33.0	
	SD	1.1	2.2	16.7	25.5	8.2	2.8	3.1	2.7	0.1	0.7	1.4	1.3	0.9	20.9	
	n	4	5	6	6	5	3	5	4	3	4	3	3	5	7	
Doha																
CHBr$_2$Cl	$\bar{x}$	0.2	0.1	0.2	0.1	0.2	0.2	0.4	0.3	0.1	0.2	0.2	0.1	0.1	0.1	
	SD	0.1	0	0	0.1	0.1	0.1	0.2	0.1	0	0.1	0	0	0	0	
CHBr$_3$	$\bar{x}$	1.4	0	3.3	1.2	3.4	3.7	9.1	5.5	0	2.3	2.2	0.1	0	0	
	SD	2.5		0	1.6	2.7	2.4	9.9	4.2		2.5	0.7	0.2			34
TOTAL	$\bar{x}$	1.6	0.1	3.5	1.4	3.6	3.9	9.5	5.8	0.1	2.5	3.4	0.3	0.1	0.1	
	SD	2.6	0	0	1.7	2.7	2.4	10.2	4.3	0	2.5	0.7	0.3	0	0	
	n	3	2	1	3	3	2	3	3	3	2	2	3	1	3	
Shuaiba																
CHBr$_2$Cl	$\bar{x}$	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2		
	SD	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0		
CHBr$_3$	$\bar{x}$	2.9	3.8	6.0	6.9	12.9	10.5	5.4	3.8	2.0	1.9	5.0	4.1	3.0		
	SD	4.8	3.5	8.2	2.8	10.5	5.2	5.0	4.6	2.1	1.4	2.7	0.6	1.1		54
TOTAL	$\bar{x}$	3.1	3.9	6.3	7.1	13.2	10.8	5.6	4.0	2.2	2.0	5.2	4.3	3.2		
	SD	4.9	3.6	8.3	2.9	10.6	5.3	5.1	4.7	2.1	1.5	2.8	0.6	1.1		
	n	4	3	5	5	5	4	4	3	4	4	5	4	4		

Table 3.8 The Concentrations of Halomethanes Detected in the Coastal Waters Offshore of the Shuwaikh, Doha and Shuaiba Desalination-Power Stations According to the Sampling Locations

Station No.		Concentrations of Mean Total Halomethanes (µg/l) According to Station No.					
		Shuwaikh		Doha		Shuaiba	
		Ebb	Flood	Ebb	Flood	Ebb	Flood
1	$\bar{x}$	1.63	2.5	0.1	2.3	5.8	0.4
	SD	0	1.3	0	3.1	6.6	0.4
2	$\bar{x}$	4.4	4.4	4.1	0.1	5.8	0.1
	SD	1.0	3.0	0	0	2.1	0
3	$\bar{x}$	3.2	12.8	N.D.	3.5	9.6	1.3
	SD	0	18.1		0	9.9	0.4
4	$\bar{x}$	38.8	60.3	0.7	1.7	6.0	7.8
	SD	27.7	22.7	0	2.2	1.3	3.6
5	$\bar{x}$	13.1	10.7	0.6	5.1	25.2	10.3
	SD	13.2	6.6	0	1.1	0	9.6
6	$\bar{X}$	9.2	5.7	N.D.	3.9	7.8	8.5
	SD	0	2.8		2.4	0	3.2
7	$\bar{x}$	2.3	3.9	20.4	4.1	4.0	7.6
	SD	3.1	3.7	0	5.6	0.9	8.1
8	$\bar{x}$	4.3	1.8	8.1	7.6	1.4	5.3
	SD	0	2.9	0	5.3	0	5.8
9	$\bar{x}$	0.7	1.0	0.1	0.1	4.0	0.3
	SD	0	0	0	0	0.4	0.3
10	$\bar{x}$	0.3	0.6	0.7	4.3	2.2	1.8
	SD	0	0.8	0	0	0.5	2.5
11	$\bar{x}$	0.1	1.4	1.9	2.9	5.1	5.4
	SD	0	1.8	0	0	3.1	3.5
12	$\bar{x}$	0.1	1.9	0.1	0.3	4.3	4.2
	SD	0	2.5	0	0	0.1	1.0
13	$\bar{x}$	1.2	0.2	0.1	0.1	4.2	2.3
	SD	1.5	0	0	0	0.3	0.4
14	$\bar{x}$	47.2	18.9	0.1	0.1		
	SD	21.9	5.0	0	0		

Table 3.9 Mean Concentrations of Halomethanes in Sampling Stations in the Three Study Areas According to Tidal Phase

Figure 3.5a The Distribution of the Overall Mean Concentrations of Total Halomethanes in the Shuwaikh Area (µg/l).

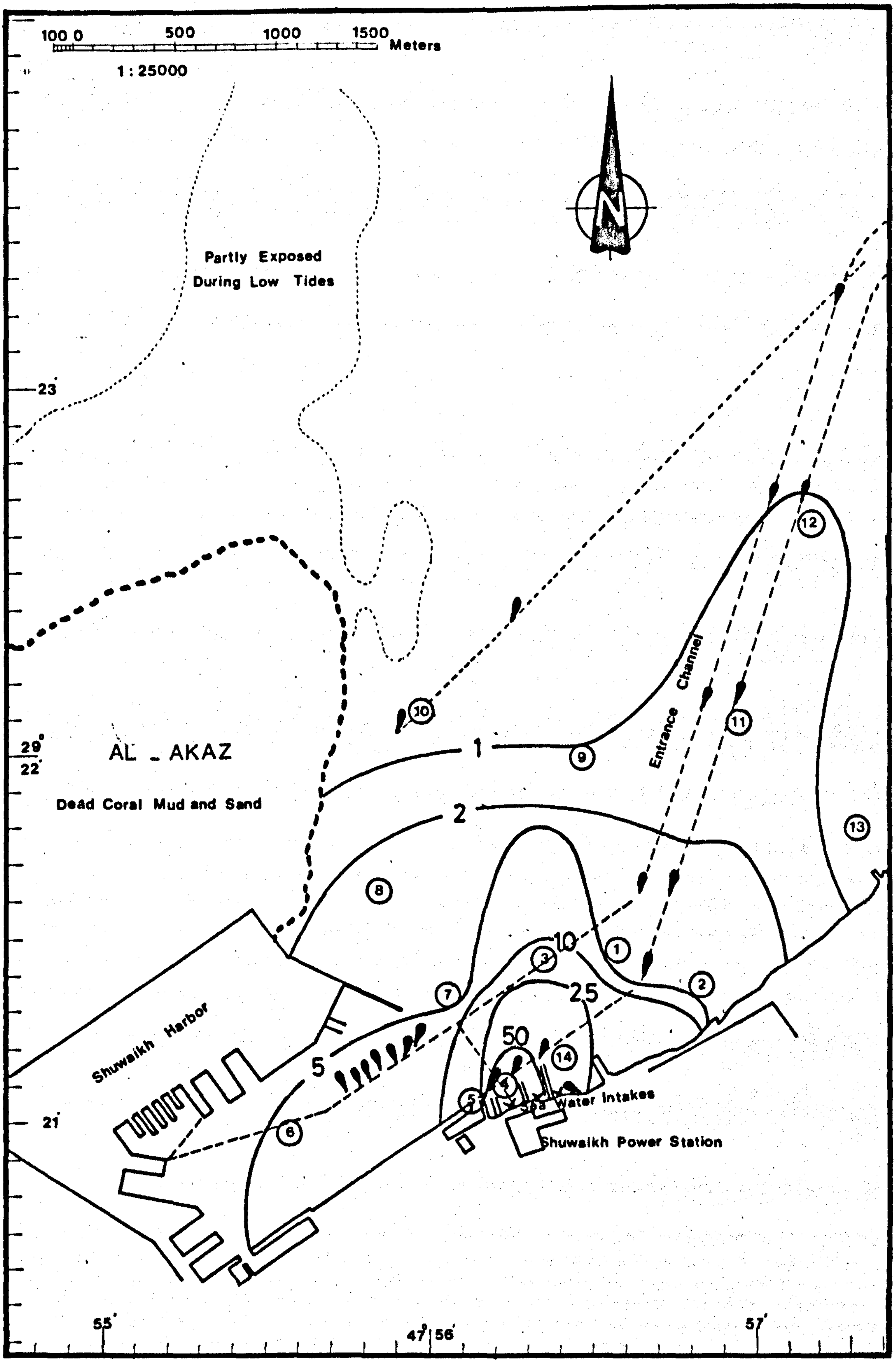

100 0
500
1000
1500
Meters
1:25000
N
Partly Exposed
During Low Tides
AL - AKAZ
Dead Coral Mud and Sand
Entrance Channel
Shuwaikh Harbor
Sea Water Intakes
Shuwaikh Power Station
1
2
5
10
25
50
①
②
③
④
⑤
⑥
⑦
⑧
⑨
⑩
⑪
⑫
⑬
⑭
23
29°
22'
21
55'
47° 56'
57'

Figure 3.5b The Distribution of the Mean Concentrations of total Halomethanes During the Ebb Phase of the Tide in the Shuwaikh Area (µg/l)

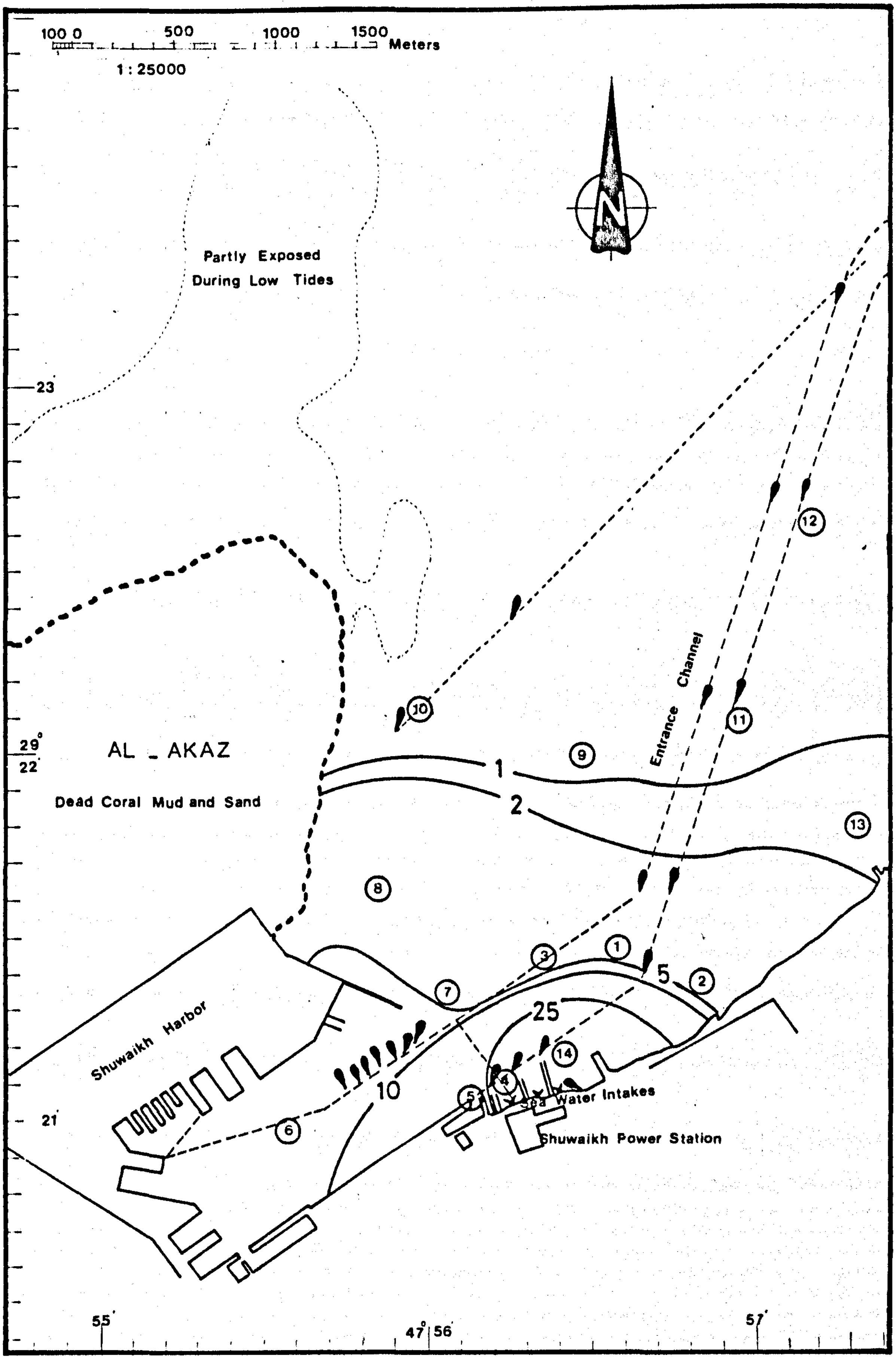
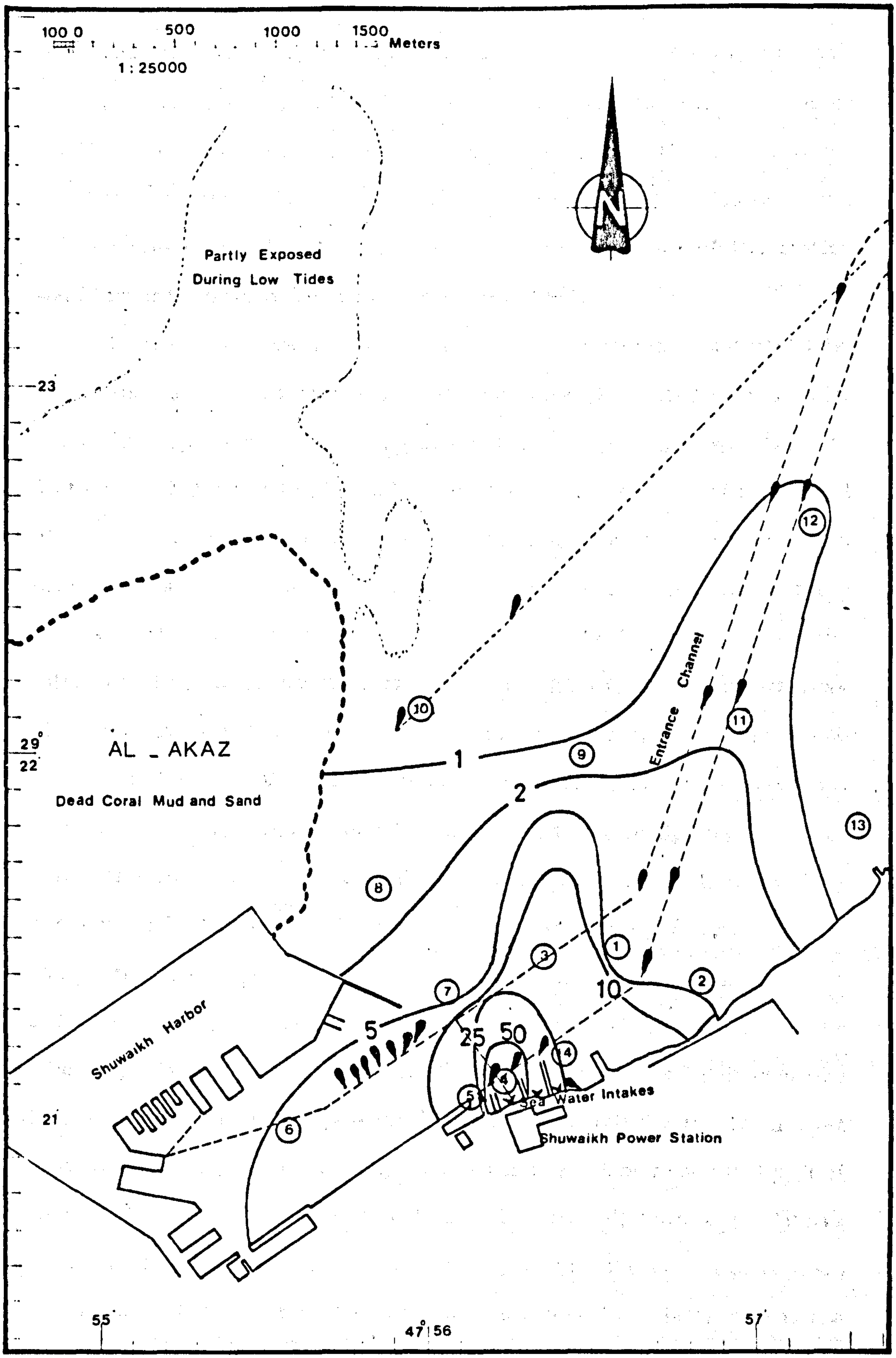

100 0
500
1000
1500
Meters
1:25000
Partly Exposed
During Low Tides
23'
29°
22'
AL _ AKAZ
Dead Coral Mud and Sand
21'
Entrance Channel
Shuwaikh Harbor
Sea Water Intakes
Shuwaikh Power Station
N
1
2
5
25
10
①
②
③
④
⑤
⑥
⑦
⑧
⑨
⑩
⑪
⑫
⑬
⑭
55'
47° 56'
57'

Figure 3.5c The Distribution of the Mean Concentrations of Total Halomethanes During the Flood Phase of the Tide in the Shuwaikh Area (µg/l).


100 0
500
1000
1500
Meters
1 : 25000
N
Partly Exposed
During Low Tides
AL _ AKAZ
Dead Coral Mud and Sand
Shuwaikh Harbor
Entrance Channel
Sea Water Intakes
Shuwaikh Power Station
1
2
5
10
25
50
①
②
③
④
⑤
⑥
⑦
⑧
⑨
⑩
⑪
⑫
⑬
⑭
23
29°
22
21
55
47° 56
57

halomethanes seem to be dispersed towards the NE, N and NW directions, with a greater tendency to move parallel to the shoreline (Figure 3.5b). During the flood stage, on the other hand, they appear to be spread towards the Channel by the anti-clockwise motion of the incoming tide caused by the Al-Akaz submerged island and the harbour structure. However, the concentrations of halomethanes in the immediate vicinity of the station were higher than during the ebb stage (Figure 3.5c).

In the Doha area, which was sampled on three occasions only, halomethanes occurred at lower levels but were distributed over a wider area. The highest mean concentration of total halomethanes was found at Station No. 7 (9.5 µg/l) which is located about 1 km off shore of the outfall of the Doha East Station. The distribution of the overall mean concentrations in the area is shown in Figure 3.6a. It appears that the general pattern of dispersion is mostly towards the E and NE, under the influence of the wind-induced surface current which flows in that direction. The distribution of halomethanes at the sampling locations during the ebb and flood phases of the tide is summarised in Table 3.9 and Figure 3.6b. During the ebb stage halomethanes showed relatively higher mean concentration at Station No. 7 (20.4 µg/l), spreading to the Doha Harbour entrance at Station No. 8 where a concentration of 8.1 µg/l was detected. During the flood stage, the direction of dispersion showed a shift to the E-NE direction, probably as a result of the counter clockwise flow of the incoming tidal waters (Figure 3.6c). It should be noted that Sulaibikhat Bay (between Ras Ushayrij and Al-Akaz) where the outfall for the Doha West Station is located, was practically free of volatile halomethanes (0.1 µg/l of $CHBr_2Cl$). When fully operational, this Station will have a productive capacity of distilled water double that produced by the Doha East. When this happens the levels of halomethanes are therefore likely to show a

Figure 3.6a The Distribution of the Overall Mean Concentrations of Total Halomethanes in the Doha Area (μg/ℓ).

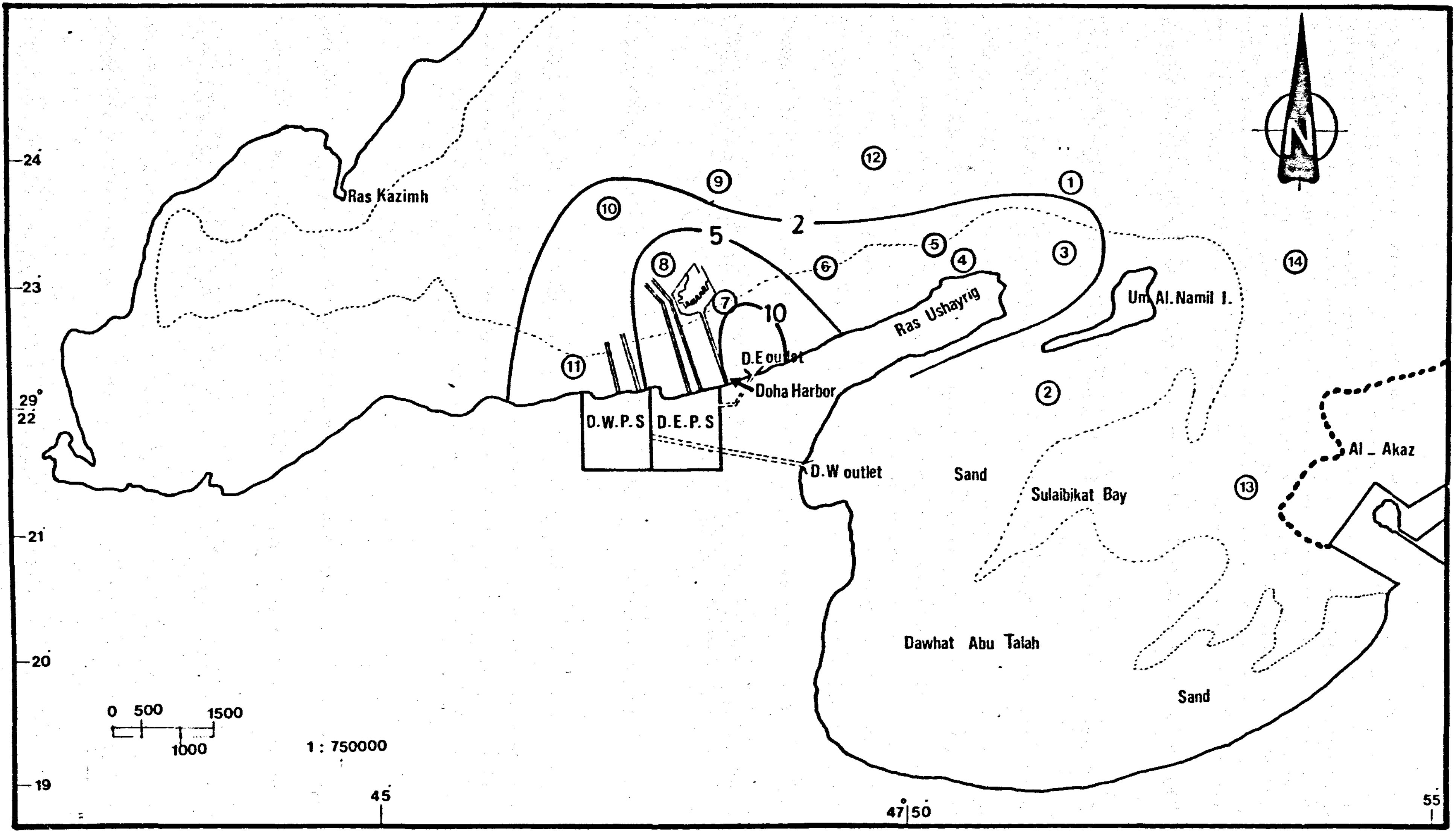

Ras Kazimh
24
23
29°
22
21
20
19
45
47°50
55
N
⑫
⑨
①
⑩
2
5
⑤
④
③
⑭
⑧
⑥
⑦
10
Ras Ushayrig
Um Al.Namil I.
D.E outlet
Doha Harbor
⑪
②
D.W.P.S
D.E.P.S
D.W outlet
Sand
Sulaibikat Bay
Al _ Akaz
⑬
Dawhat Abu Talah
Sand
0 500 1000 1500
1 : 750000

Figure 3.6b The Distribution of the Mean Concentrations of Total Halomethanes During the Ebb Phase of the Tide in the Doha Area (µg/l).

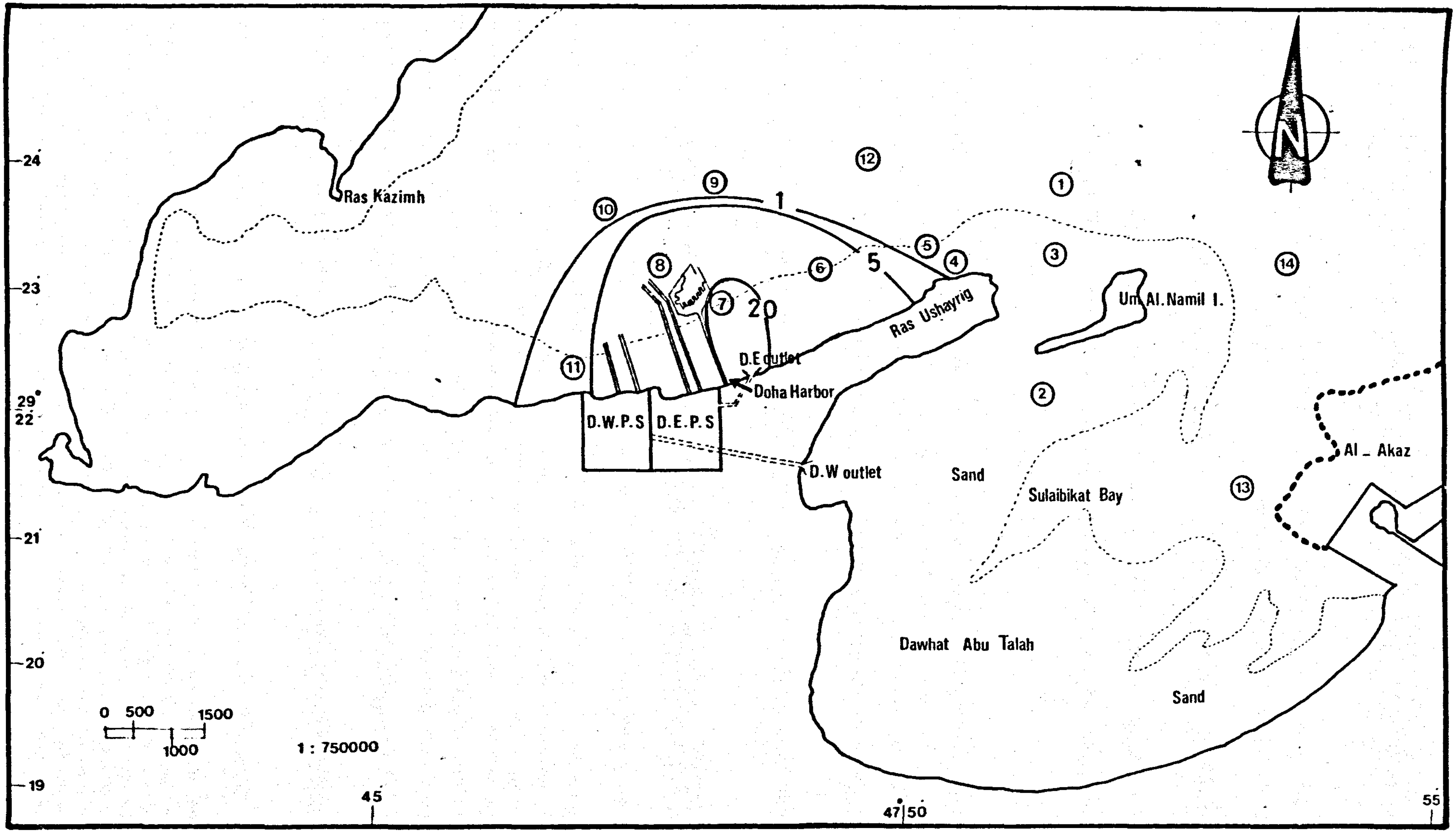
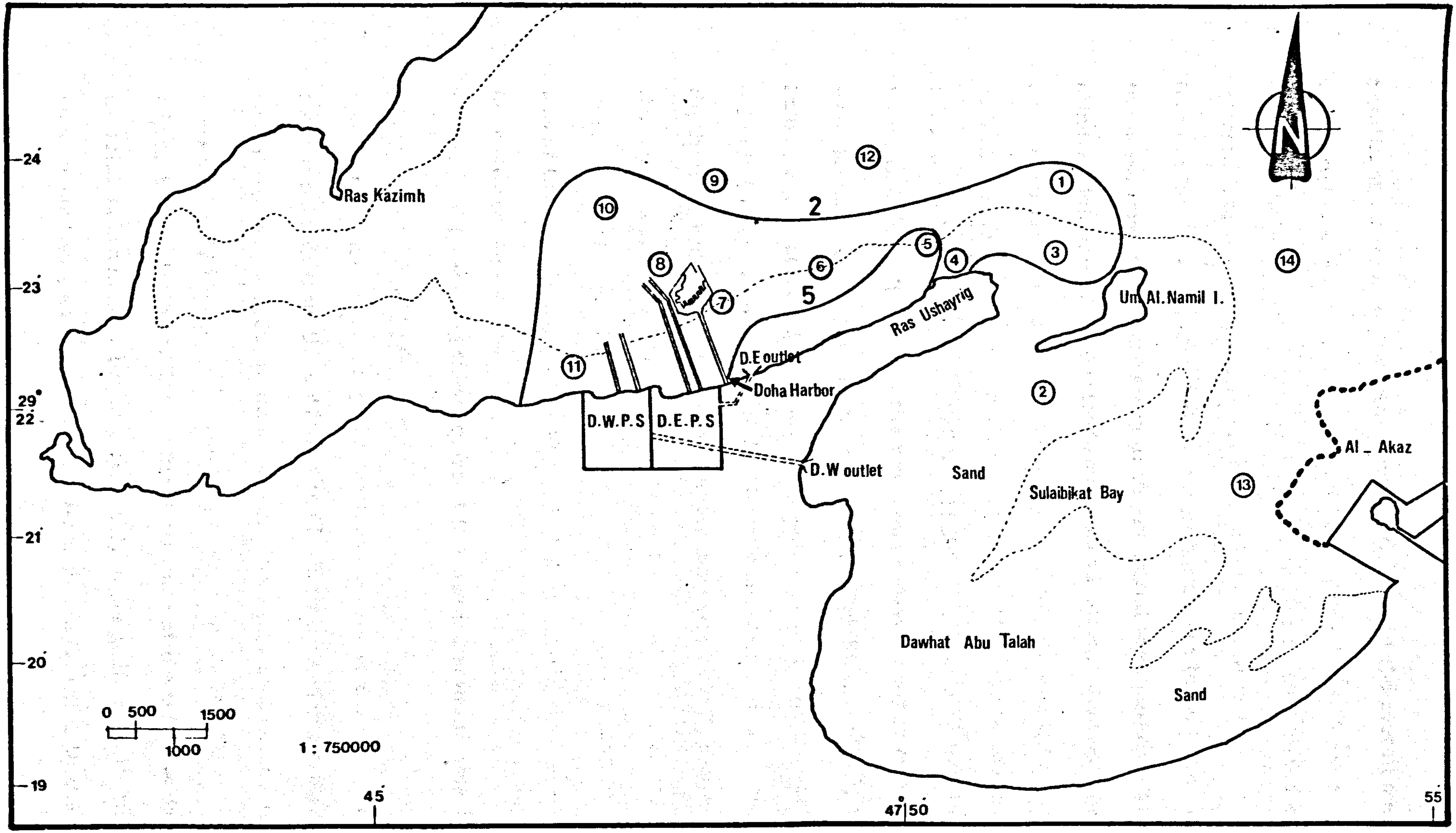

N
Ras Kazimh
⑫
①
⑨
⑩
1
⑤
④
③
⑭
⑧
⑥
5
⑦
20
Um Al. Namil I.
Ras Ushayrig
⑪
D.E outlet
Doha Harbor
②
D.W.P.S
D.E.P.S
D.W outlet
Sand
Sulaibikat Bay
⑬
Al _ Akaz
Dawhat Abu Talah
Sand
24
23
29°
22
21
20
19
0
500
1000
1500
1 : 750000
45
47|50
55

Figure 3.6c The Distribution of the Mean Concentrations of Total Halomethanes During the Flood Phase of the Tide in the Doha Area (µg/ℓ).


24
23
29°
22
21
20
19
45
47|50
55
Ras Kazimh
⑫
⑨
⑩
2
①
⑤
④
③
⑭
⑧
⑥
⑦
5
Ras Ushayrig
Um Al. Namil I.
D.E outlet
⑪
Doha Harbor
②
D.W.P.S
D.E.P.S
Al – Akaz
D.W outlet
Sand
Sulaibikat Bay
⑬
Dawhat Abu Talah
Sand
0 500 1500
1000
1 : 750000
N

significant increase in the area. The distribution of the overall mean total of halomethanes in the Shuaiba area is summarised in Table 3.8 and Figure 3.7a. In spite of the relatively large quantities of chlorinated effluents released into the area, the levels of halomethanes were low compared to those in the Shuwaikh area and their distribution was found to be limited to the areas immediately off shore of the industrial area covering an area of about 2.5 km in width and extending to about 1 km into the sea. The highest mean concentrations of total halomethanes (13.2 and 10.8 µg/l) were found at Stations No. 5 and 6 respectively, which are located near the outfalls of the two desalination stations, SNPS and SSPS. Stratification in halomethane levels was again limited to the top 2 m. However, higher concentrations were found in the upper layer. For example, at Station No. 5, the total halomethanes detected in a sample taken at 2 m below the surface was 4.6 µg/l (water temperature of 18°C) whereas, 24.1 µg/l were found at a depth of 1 m at which the water temperature was 22.7°C, suggesting that the high temperature has more effect on density of the effluents than the increase in salinity. The surfacing of the effluents may lead to a greater loss of the volatile organics by evaporation. The distribution of mean total halomethane concentrations at the various sampling stations in the Shuaiba area during the ebb and flood stages of the tide is shown in Table 3.9 and in the contour maps in Figures 3.7b and 3.7c. At the ebb stage, halomethanes appear to concentrate along the Shuaiba Harbour structure. The 10 µg/l contour extends from the outfall of the SSPS to the end of the Harbour wall which extends about 800 m into the sea. The 5 µg/l contour covers a wider area, extending from the SAA pumping station for about 1200 m in the area adjacent to the Harbour. During the flood stage of the tide, the distribution of total halomethanes became relatively more uniform with the 10 µg/l contour enclosing an area extending from the SSPS outlet to the Harbour,

Figure 3.7a The Distribution of the Overall Mean Concentrations of Total Halomethanes in the Shuaiba Area (μg/ℓ).

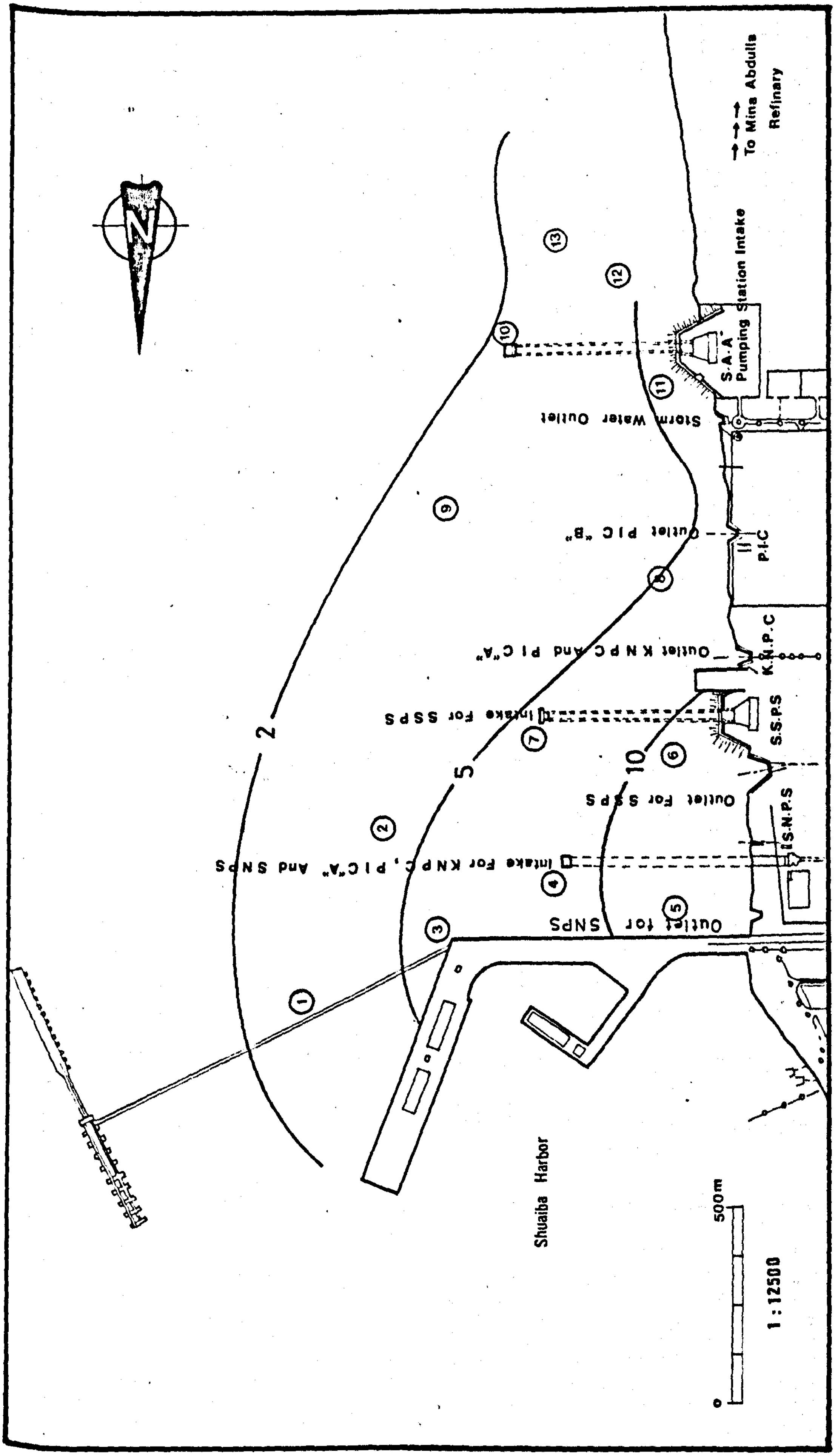

N
To Mina Abdulla Refinary
S.A.A. Pumping Station Intake
Storm Water Outlet
Outlet PIC "B"
P.I.C
K.N.P.C
Outlet KNPC And PIC "A"
Intake For SSPS
S.S.P.S
Outlet For SSPS
S.N.P.S
Intake For KNPC, PIC "A" And SNPS
Outlet for SNPS
Shuaiba Harbor
2
5
10
①
②
③
④
⑤
⑥
⑦
⑧
⑨
⑩
⑪
⑫
⑬
0
500m
1:12500

Figure 3.7b The Distribution of the Mean Concentrations of Total Halomethanes During the Ebb Phase of the Tide in the Shuaiba Area (µg/l).

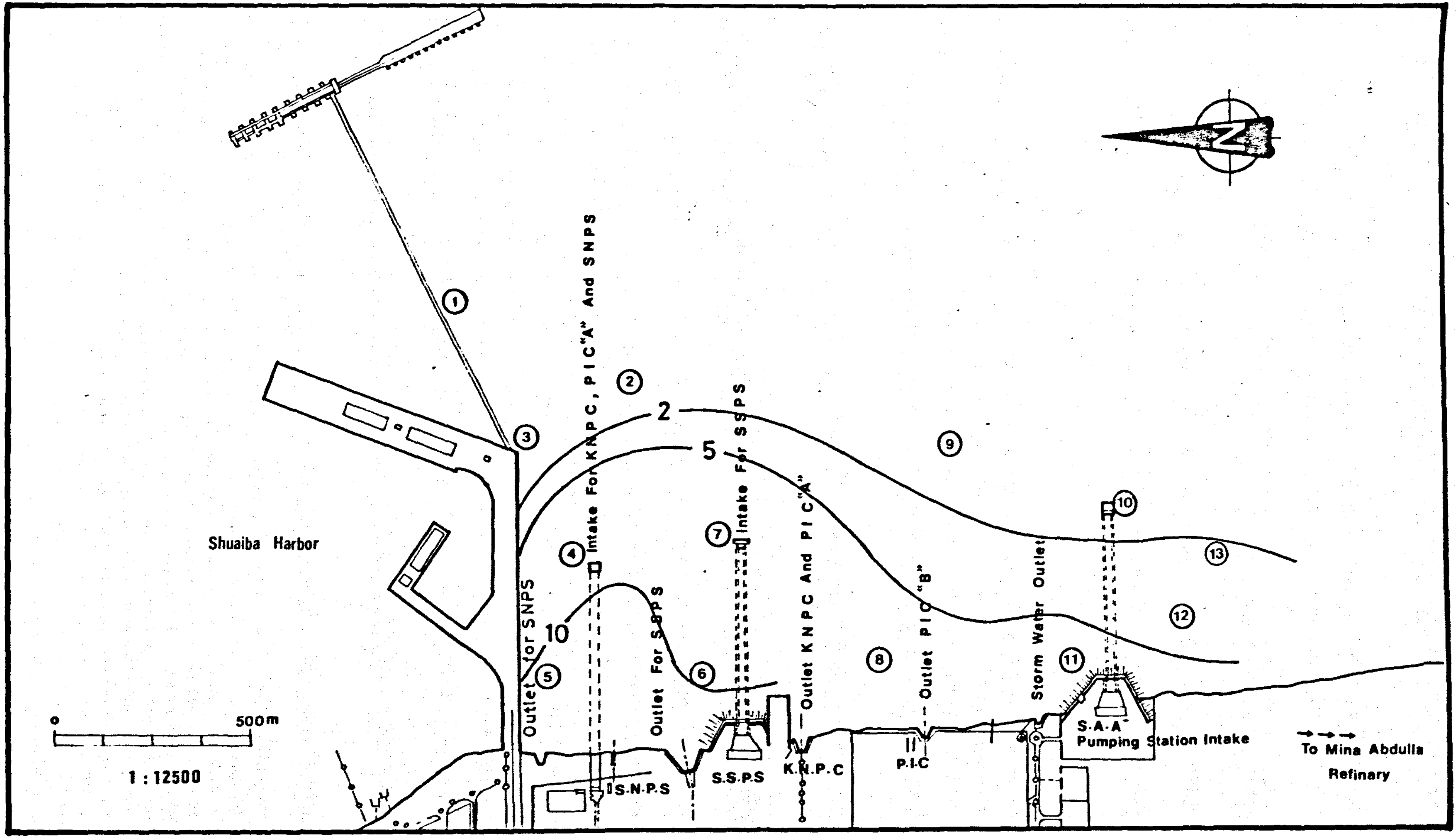
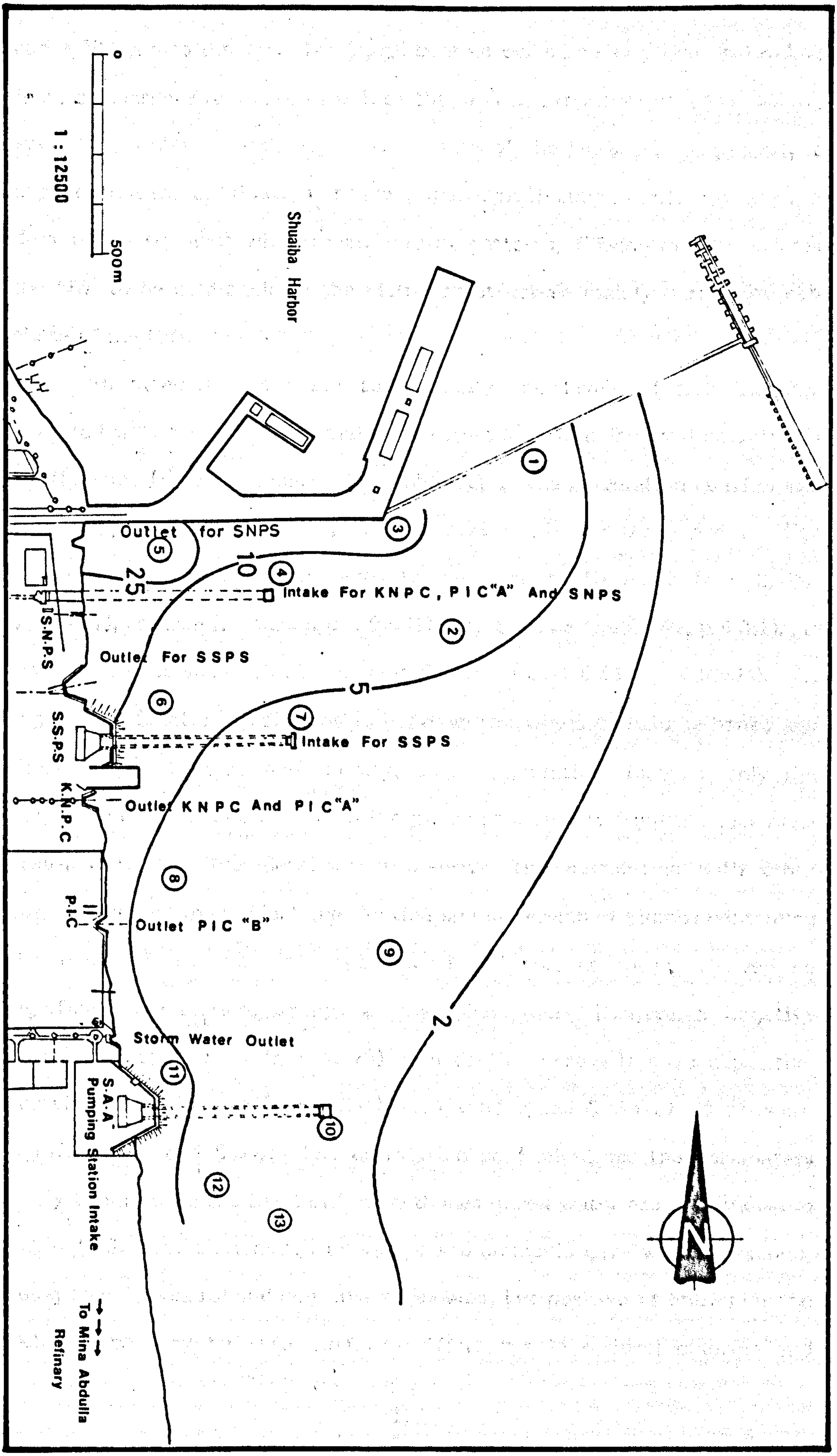

N
①
②
③
④
⑤
⑥
⑦
⑧
⑨
⑩
⑪
⑫
⑬
2
5
10
Shuaiba Harbor
Intake For KNPC, PIC"A" And SNPS
Intake For SSPS
Outlet for SNPS
Outlet For SSPS
Outlet KNPC And PIC"A"
Outlet PIC"B"
Storm Water Outlet
S.N.P.S
S.S.P.S
K.N.P.C
P.I.C
S.A.A
Pumping Station Intake
To Mina Abdulla Refinary
0
500m
1:12500

Figure 3.7c The Distribution of the Mean Concentration of Total Halomethanes During the Flood Phase of the Tide in the Shuaiba Area (ug/l)


1:12500
0
500m
Shuaiba Harbor
Outlet for SNPS
Intake For KNPC, PIC"A" And SNPS
S.N.P.S
Outlet For SSPS
S.S.P.S
Intake For SSPS
K.N.P.C
Outlet KNPC And PIC"A"
P.I.C
Outlet PIC "B"
Storm Water Outlet
S.A.A
Pumping Station Intake
To Mina Abdulla Refinary
N
25
10
5
2
①
②
③
④
⑤
⑥
⑦
⑧
⑨
⑩
⑪
⑫
⑬

about 300 m into the sea. The 5 µg/l contour covers a wider area, extending from the Harbour to an area south of the SAA intake structure and reaching seawards to about 700 m in the area south of the Harbour. In general, it appears that the distribution of halomethanes in Shuaiba is influenced by the dominant north west wind-driven current patterns, flowing mainly towards the NW, to be held back by the Harbour's structure mainly during the ebb phase of the tide.

An attempt was made to correlate the levels of halomethanes detected with the other paramaters measured. The calculated correlation coeffecients (r) are summarised in Table 3.10. The correlation coefficients with temperature and salinity was positive in all the three areas. For example, it was significant with temperature at Shuwaikh ($r = 0.498$, $p < 0.001$), Shuaiba ($r = 0.556$, $p < 0.001$), and at Doha ($r \doteq 0.289$, $p < 0.1$). It was significant with salinity only at Shuwaikh ($r = 0.661$, $p < 0.001$). As there is no functional relationship between the levels of halomethanes and those of temperature and salinity, these correlations indicate only the association of halomethanes with the plume of effluents from the industrial areas, especially the desalination plants. The correlation with other parameters that may affect the dilution and dispersion of plumes containing the halomethanes such as depth, wind and current speeds showed no significant correlation, except at Shuwaikh where it gave a negative correlation coefficient ($r = -0.275$) with depth whereas it gave a positive correlation coefficient ($r = 0.254$) with wind speed (both of which were significant at $p < 0.05$). The correlation coefficient for the parameters likely to influence the level of halomethanes in sea water are also shown in Table 3.10. Correlations with chlorine and ammonia gave variable results, being poor in general and negative at Shuaiba, but positive at Shuwaikh and Doha which may be reflecting the differences in residual chlorine and

Parameter	Location					
	Shuwaikh	(n)	Doha	(n)	Shuaiba	(n)
Temperature	+0.498(4)	(60)	+0.289(1)	(34)	+0.556(4)	(34)
Salinity	+0.661(4)	(60)	+0.222	(34)	+0.055	(54)
Water depth	-0.275(2)	(60)	-0.212	(34)	-0.132	(54)
Current speed	+0.085	(60)	+0.012	(34)	+0.132	(54)
Wind speed	+0.254(2)	(60)	-0.112	(54)	0.091	(54)
Cl_2	+0.181	(54)	+0.211	(30)	-0.230	(54)
NH_3	+0.051	(25)	+0.140	(23)	-0.226	(32)
Chlorophyll-a	+0.309	(20)	+0.099	(14)	+0.223	(9)
Suspended solids	+0.304	(21)	+0.068	(14)	+0.630(3)	(21)
DOC	+0.708(3)	(12)	+0.306	(7)	-0.369	(11)

(1) Significant at $p < 0.1$
(2) Significant at $p < 0.05$
(3) Significant at $p < 0.01$
(4) Significant at $p < 0.001$

Table 3.10 Correlation Coefficients (r) Between Total Halomethane Concentrations Detected in the Coastal Areas Offshore of the Desalination and Power Plants and Various Physical and Chemical Factors ammonia levels between Shuaiba and the two other areas. The correlation coefficient was positive but not significant for chlorophyll and suspended solids, except for suspended solids at Shuaiba where it was 0.630 ($p < 0.01$). This is probably due to the surfacing of effluents (because of their higher temperature) which results in high levels of suspended solids at the upper layers of water where samples for halomethane analysis were taken. Correlation with the DOC levels in Shuwaikh gave a positive correlation coefficient ($r = 0.708$, significant at $p < 0.01$) but poor in Doha and poor and negative in Shuaiba. Thus, it appears that although some of these factors affect the production of halomethanes under experiemental conditions, it is difficult to isolate individual contributions in a dynamic system in which there are many other factors that affect the distribution and fate of halogenated organics.

The formation of halomethanes upon chlorination of the coastal waters of Kuwait is of interest in terms of its possible effects on the quality of the sea water used for desalination and subsequently on the quality of the distillate. This topic will be pursued in the next chapter which deals with the levels of halomethanes produced during the desalination process. The second major point of interest concerns the possible impact on the fisheries resources and ecology of the coastal waters. The ecological impact involves either lethal effects resulting from direct toxicity or long term changes which occur as a result of chronic exposure to pollutants. Relatively limited data is available about the toxicity of $CHBr_3$ and $CHBr_2Cl$, despite the fact that a large number of studies have been conducted on the toxicity of chlorinated water to marine biota (see the reviews by Whitehouse, 1975 and Davis and Middaugh, 1978). However, in most of these studies, factors such as pH, bromide ion concentration, forms and levels of nigrogen-containing compounds and dissolved organic carbon in the test water were not monitored or taken into account during the interpretation of the toxicity results (Davis and Middaugh, 1978; Goldman **et al.**, 1978). Nevertheless, the more recent experimental data available indicate that at the concentrations encountered in this study, lethal effects on most marine organisms by $CHBr_3$ and $CHBr_2Cl$ are not likely to occur beyond the immediate zone of chlorine injection. For example, Gibson **et al.** (1980) have shown that at concentrations approaching 1 mg/l of $CHBr_3$, several nearshore marine species of clams, oysters, shrimp and fish survived. However, the bioaccumulation and depuration rates varied among individual members of a given species, between species and according to the levels of $CHBr_3$ in the water. Trabalka **et al.** (1980) exposed carp embryos to various concentrations of halomethanes. Their data suggests that $CHCl_3$ was least toxic (LC_{50} of 116 mg/l) followed by $CHCl_2Br$ (119 mg/l), $CHBr_3$ (76 mg/l) and $CHBr_2Cl$ (53 mg/l). Moreover, Scott **et al.** (1982) who exposed adult oysters (C. Virginica) to sea water containing on average 25 µg/l of $CHBr_3$, reported that the exposed organisms developed reduced feeding responses, increased rates of respiration and reduced sizes of gonadal tissues. Rapid uptake of $CHBr_3$ into the tissues was observed with a bioaccumulation ratio of 5:1. However, complete depuration occurred within 96 hours. Although the feeding response returned to normal during the depuration period, the damage to gonadal tissues was found to be irreversible. This is in agreement with earlier findings of sensitivity of reproductive tissues and stages, especially sperms, to low levels of chlorination products (Davis and Middaugh, 1978). Other possible effects of low levels of halomethanes in the marine environment include interference with the natural chemical communication system among some of the marine organisms. This is based on the increasing evidence that some halogenated organics, including $CHBr_3$ are being produced by certain marine species as defensive secretions or as sex phermones and thus the release of such compounds into the marine environment may affect the behaviour of these organisms (Jolley **et al.**, 1978; Siuda, 1980 and Fenical, 1981).

CHAPTER 4

The Distribution of Halomethanes in the Various Stages of the Desalination Process

4.1 INTRODUCTION

Dual purpose power generation - desalination plants have become the principal source of potable water in Kuwait since their introduction in 1950 (WRDC, 1973). After 1968 all desalination units in Kuwait where constructed on the multistage flash evaporation (MSF) principle. In this type of plant sea water is introduced through an orifice into the flashing chamber, which is maintained under a reduced pressure. This causes the water to boil vigouroursly at a temperature below its boiling point at atmospheric pressure (Silver, 1967). Flash distillation is maintained by circulating sea water (referred to as recirculating brine) through an array of chambers in which the brine temperature is gradually decreased in 2 to 3°C steps under a progressively increasing vacuum. The vacuum is created by ejecting high pressure steam (part of that used to generate electricity) through nozzels connected to the venting lines as shown in Figure 4.1.

The desalination process requires very large quantities of sea water. It is estimated that for each unit volume of distillate produced, 12 units of sea water are consumed (9 for cooling and 3 for processing). The sea water is chlorinated before usage to control biofouling and to sterilize it. The amount of brine discharged is equivalent to twice the amount of distillate produced representing a sea water-concentration factor of 1.5 (Babcock - Hitachi, 1978).

Since there appears to have been no studies on the fate of chlorinated sea water for desalination-power plants in Kuwait or on the types and levels of halogenated organic compounds produced during the desalination process, this part of the study was initiated to identify the types and levels of halomethanes in the feed sea water, at various stages of desalination, in the brine released into the marine environment and in the distillate. Samples were also taken from the ventilated gases at the air ejection unit to determine whether halomethanes are being released into the atmosphere.

Figure 4.1

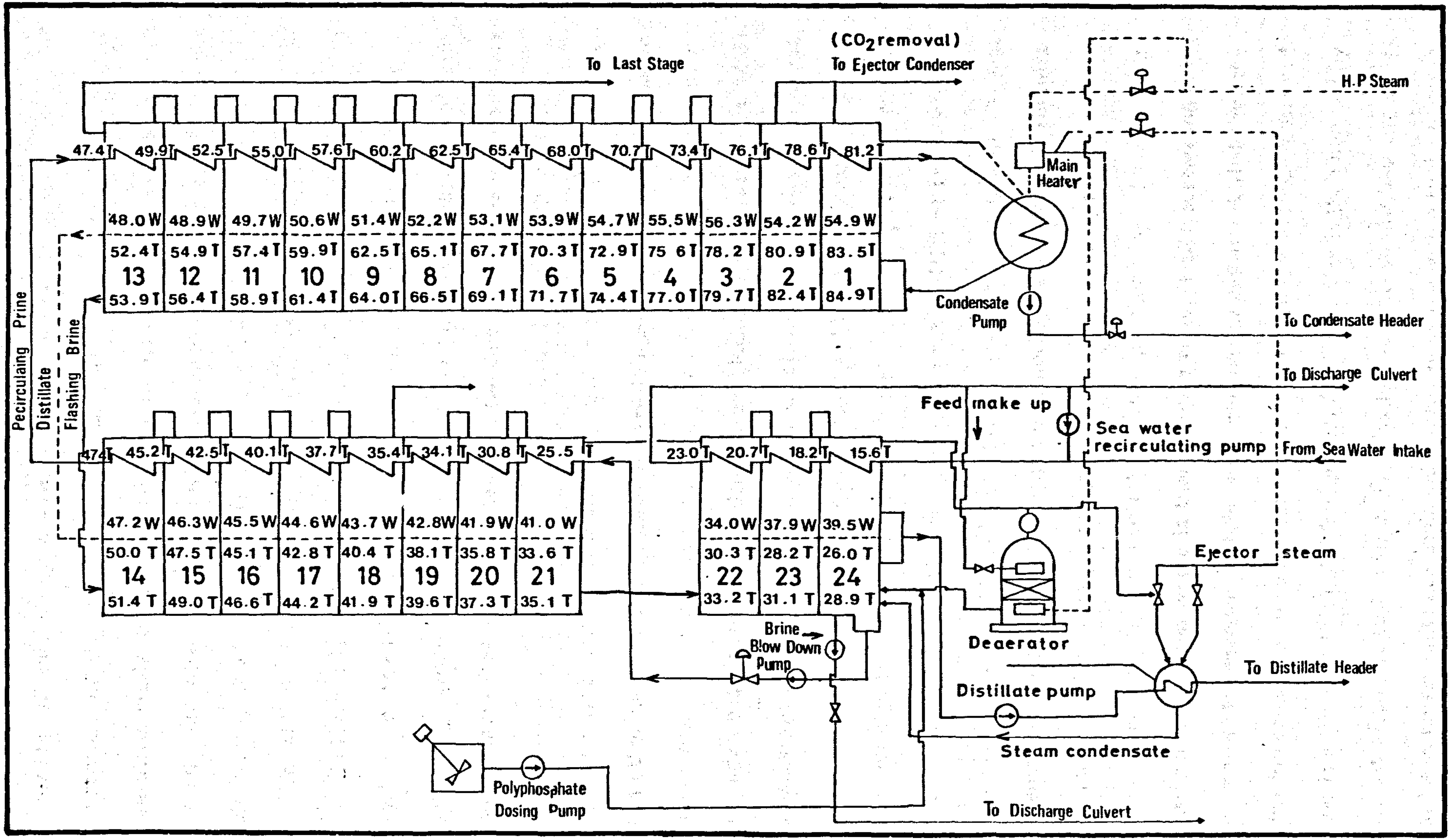
A simplified layout of the "D" Desalination Unit.

Operating Conditions	Summer	Winter *
Distillate output	27300 m^3/day	27300 m^3/day
Performance ratio	8.0 kg/kg	8.4kg/kg
Max. Brine T°C	90.5 C	8.7.4 C
Min.Brine T°C	41.2 C	28.9 C
Sea Water T°C	32.2 C	14.4 C
Recirculating Brine	14439 t/hr	12500 t/hr
Make-up feed sea water	3317 t/hr	3317 t/hr
Brine blow-down	2180 t/hr	218¼ t/hr
Cooling sea water	10420 t/hr	10420 t/hr
TDS in sea water	48500 ppm	48500 ppm
TDS in recircuating Brine	68000 ppm	68000 ppm
Circulation ratio	12.7	11.0

* shown in the diagram

W = Distillate

T = Temperature


(CO2 removal)
To Ejector Condenser
To Last Stage
H.P Steam
Main Heater
Condensate Pump
To Condensate Header
To Discharge Culvert
Feed make up
Sea water recirculating pump
From Sea Water Intake
Pecirculaing Prine
Distillate
Flashing Brine
47.4 T
49.9 T
52.5 T
55.0 T
57.6 T
60.2 T
62.5 T
65.4 T
68.0 T
70.7 T
73.4 T
76.1 T
78.6 T
81.2 T
48.0 W
48.9 W
49.7 W
50.6 W
51.4 W
52.2 W
53.1 W
53.9 W
54.7 W
55.5 W
56.3 W
54.2 W
54.9 W
52.4 T
54.9 T
57.4 T
59.9 T
62.5 T
65.1 T
67.7 T
70.3 T
72.9 T
75 6 T
78.2 T
80.9 T
83.5 T
13
12
11
10
9
8
7
6
5
4
3
2
1
53.9 T
56.4 T
58.9 T
61.4 T
64.0 T
66.5 T
69.1 T
71.7 T
74.4 T
77.0 T
79.7 T
82.4 T
84.9 T
47.4 T
45.2 T
42.5 T
40.1 T
37.7 T
35.4 T
34.1 T
30.8 T
25.5 T
23.0 T
20.7 T
18.2 T
15.6 T
47.2 W
46.3 W
45.5 W
44.6 W
43.7 W
42.8 W
41.9 W
41.0 W
34.0 W
37.9 W
39.5 W
50.0 T
47.5 T
45.1 T
42.8 T
40.4 T
38.1 T
35.8 T
33.6 T
30.3 T
28.2 T
26.0 T
14
15
16
17
18
19
20
21
22
23
24
51.4 T
49.0 T
46.6 T
44.2 T
41.9 T
39.6 T
37.3 T
35.1 T
33.2 T
31.1 T
28.9 T
Ejector steam
Deaerator
Brine Blow Down Pump
Distillate pump
To Distillate Header
Steam condensate
Polyphosphate Dosing Pump
To Discharge Culvert

The results of this study are presented first as a general survey of halomethanes in the desalination units. The second part comprises a comparative study of the distribution of halomethanes in the samples collected from three units located in Shuwaikh, Doha and Shuaiba either simultaneously or within a short time interval of each other.

To aid discussion a brief description of the desalination system utilized in Kuwait is given below. The units selected as representatives of the system (for the first part of the study) are located within the Shuwaikh station. These two plants differ in production capacity and in some of their design features. The "D-1" unit selected for this study is one of three units commissioned in 1980 at the Shuwaikh station. It is a 27,000 m^3/day plant that is quickly becoming the standard unit for desalination in Kuwait. Fifteen other units of similar capacity are in operation at the Doha station and eight more are under construction. The unit incorporates the most recent advances in design resulting from Kuwait's experience in MSF desalination over the past 30 years. A simplified layout of one of these units is shown in Figure 4.1. Sea water is pumped by four submersible pumps installed on a jetty approximately 180 m from the shore, chlorine (in sea water solution) is injected at these pumps at a rate sufficient to maintain a total residual chlorine concentration of approximately 2 mg/l in the sea water entering the plant. The solution of chlorine in sea water is supplied by the adjacent chlor-alkali factory (Kuwait Petrochemical Industries Co.) which uses part of the concentrated brine produced by electrolysis in mercury cells. The sea water is then pumped through 3/8" screen made of Monel metal to remove debris and marine organisms killed by the chlorination process or mechanical stress. An intermittent shock dosing of chlorine is applied at this point (about 6 mg/l). The water is then pumped by another set of pumps to the three D units in the station. Unlike the older plants, these newer units are designed to use sea water with a typical winter temperature of 14.4°C. The result of this is that in summer, when the sea water temperature is around 32°C, the performance ratio (which is defined as amount of distillate in unit weight produced per unit weight of steam applied) is increased from 8:1 to 8.4:1. In order to raise the sea water temperature to that required for flash boiling, the cupro-nickel pipes carrying it are passed first through the "heat rejection section" which includes the stages 22 to 24. The sea water is then split into three fractions, one is used as "feed make-up", a second fraction is mixed with the incoming sea water to raise its temperature and the excess is discharged.

The feed make-up fraction is passed first through the deaerator unit, a newly introduced unit to mechanically remove gases (mainly O_2 and CO_2 to a lesser extent at this stage) by application of both heat and vacuum, which is created at the air ejection unit. Both CO_2 and O_2 are major factors in corrosion of the units internal structurers. Oxygen levels are reduced to about 8 ppb at the deadrator unit whereas most of the CO_2 is released in the first 5 stages at higher temperatures (Babcok and Hitachi, 1978). After deaeration, 4.5 ppm of a mixture of anti-foaming and anti-scaling agents (49% of sodium tripolyphosphate, 49% of sodium lignin sulphonate and 2% of an organic anti-foaming agent) is injected into the feed make-up water. The chemically treated sea water is then pumped to the last stage. Here it is mixed with the brine and comes out as recirculated brine which is pumped by the Brine Re-circulation Pump and passes through stages 21 to 1 (known as the Heat Gain Section) and then to the main heater. The heated recirculated brine (at a temperature of 80.8°C) is then introduced into the first flash distillation chamber (stage 1), from which it passes successively through the other 23 chambers. The distillate produced is then pumped by the Distillate pump to join lines from other units into a mainheader, after passing through the air ejector unit to cool the steam used in the air ejector.

The amount of brine concentrate which is equivalent to about 67% of the sea water introduced as feed make-up (about double the amount of distillate produced) is removed from stage No. 24 via the brine blow down pump to be discharged into a common outfall after mixing with the excess sea water and that used for cooling various parts of the unit. The vacuum which drives the flash evaporation process and purges the deaerator and each stage from corrosive gases (i.e. O_2 and CO_2) is created by ejecting high pressure steam through the air ejector. Part of the distillate produced is used to cool the steam and the condensate is recovered and reintroduced into the last stage at the brine compartment.

The other type of desalination unit investigated in the study was the F-1 unit. This is one of the oldest MSF units installed in Kuwait and most of the experience on desalination has been gained with it. It consists of 30 stages and produces a total of 4500 m^3/d of distillate at a performance ratio of 8:1. The intake pumps and chlorination systems are located at the end of a jetty parallel to that serving the "D" plants. There is no deaeration unit as such, however, it utilises an air ejection system. The plant is designed to operate with warmer intake water (32.2°C) and consequently with higher temperature regimes in the distillation stages, with a range of 87.7 -43.4°C. The anti-foaming and anti-scaling chemicals added are the same as those used in the "D" plants, but are introduced into the 30th stage directly instead of into the feed make-up line. The distillate and brine blow down temperatures are higher by more than 20°C than those in the "D" unit. This necessitates a greater dilution ratio with sea water in order to minimize the impact of the plant's effluents on the marine environment.

The Shuwaikh Power Station comprises in addition to the three "D" plants, 2 (F) units, four 9600 m^3/d units and one 1800 m^3/d unit, all sharing a common intake with the F units and having similar designs except for the number of heat gain stages which ranges between 21 and 23.

The Shuaiba North Station comprises three units similar to the F units (4500 m^3/d), three units with 9000 m^3/d capacity each and one 22,700 m^3/d unit. The Shuaiba South Station comprises six 22,700 m^3/d units. Each of the Shuaiba stations has its own independent intake about 450 m from the shore, each consisting of a 3 m diameter concrete pipe into which sea water flows by gravity. The pipes end in a Basin (called the "Forebay") where chlorine is injected and the water is then pumped via the straining screens into the desalination units.

The desalination power stations at Doha are the largest suppliers of electricity and water in Kuwait. Doha East was commissioned in 1979 with seven 27000 m^3/d plants, similar in capacity to the "D" plants of Shuwaikh. Eight similar units were commissioned at the end of 1983 at the Doha West Station and eight more are expected to start production by the end of 1985. Each of the two stations has a seperate intake system. Since the Doha area is shallow, channels have been dredged for each station each one ending with a forebay area where chlorine gas is injected. The water is then pumped through straining screens to the desalination units. Table 4.1 summarizes the number of units at each station, production capacity and type of chlorination system employed and also gives an estimate of the annual rate of chlorine consumption. In all of the stations the target chlorine level is 2 mg/l as total residual chlorine. Intermittent shock treatment is also applied. In the newly commissioned Doha Stations a level of 6 mg/l of chlorine is maintained for 10 minutes every four hours, whereas in the older stations (e.g. Shuwaikh) shock treatment is controlled manually by applying chlorine gas injections at the screens.

Station	Number and Production Capacity of Units (M^3/d)	Total Production Capacity (M^3/d)	Type of Chlorination System Used	Estimated Chlorine Consumption (t/d)
Shuwaikh	10 Units: 3(27,000), 4 (9,000), 2(4,500) and 1 (18,000)	145,000	Injection of chlorinated sea water at intake pumps	2 - 3
Shuaiba North	7 Units: 3(4,500), 3(9,000) and 1(23,000)	64,000	Chlorine gas is injected at the Pumps and Screeens	2 - 3
Shuaiba South	6 Units, 23,000 m^3/d each	136,000	Chlorine gas is injected into the forebay	5 - 6
Doha East	7 Units, 27,000 m^3/d each	191,000	On-line injection	8 - 9
Doha West	* 8 Units, 27,000 m^3/d each	218,000	On-line injection	Not available

Table 4.1: **A Summery of Number Units, Productive Capacity and Chlorination Methods used in the Desalination Power Stations of Kuwait (MEW 1983).**

* Doha west was commissioned in 1983, 8 more units are to start production by 1985.

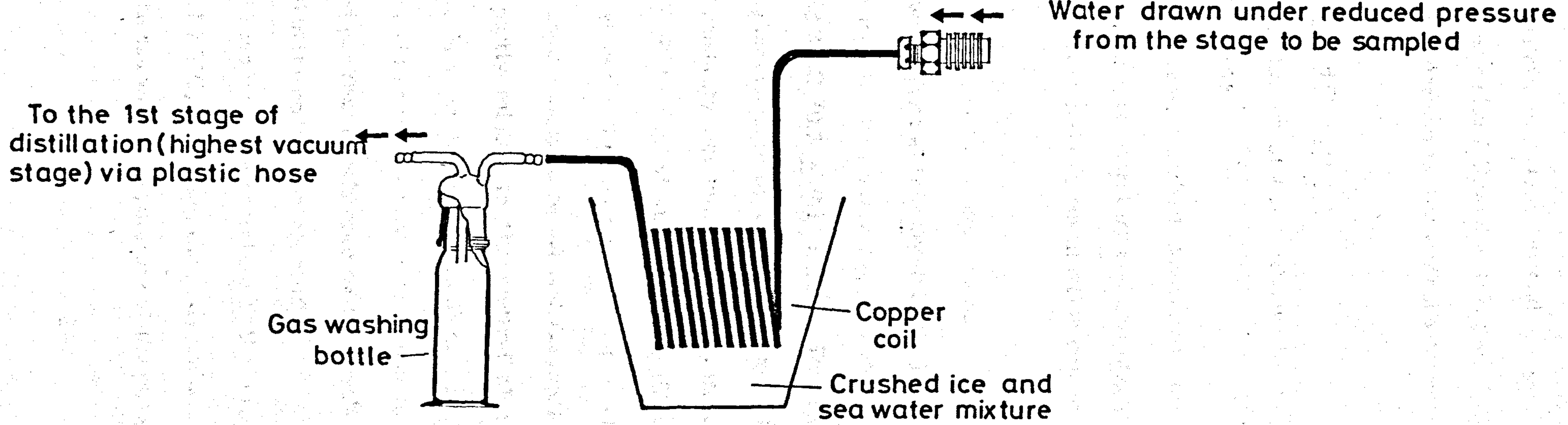
4.2 Sampling and Analysis

In the first part of this study, in which D-1 and F-1 plants were used as models to study the levels of halomethanes produced during desalination, samples were taken from the intake pumps (just after the screens), the sea water feed pumps in the F-1 plant, the deaerator unit in the D-1, stages 1, 5 and 9 , the distillate and from the (concentrate brine blow down valves (CBD) in both plants. The evacuated gases from the air ejector were also sampled for halomethanes.

The second part of the study involved a comparative investigation of halomethanes in selected plants within the desalination stations of Shuwaikh, Doha and Shuaiba. Most samples were taken on the same day, within three hours of each other in order to compare the concentration of halomethanes at the three locations. Samples were taken from the sea water pump (or Forebay at Shuaiba), distillate and CBD valve from the (F-1) plant in Shuwaikh, from a 23,000 m^3/d plant at the Shuaiba South Station (SSPS) and from 2700 m^3/d unit at the Doha East Station (DEPS). Samples of the feed sea water were also taken simultaneously for DOC analysis. In both components of the study, the level of total residual chlorine at each point of sampling and the water temperature were measured in situ. Tidal conditions, sea water level and sky conditions were also noted.

Because of the volatity of halomethanes, special precautions had to be taken in sampling. The lowest water temperatures encounted during the period of sampling was 14°C at the intake of the desalination plants in December. This contrasts with the temperature of up to 30°C at the same locations between May and October. Water temperatures at the distillate discharge point and at the CBD reached 50°C. Samples collected without cooling showed total halomethane levels that were 40% lower than those found for samples collected simultaneously from the same locations when cooling was employed. The copper cooling coil used for collection of samples from the desalination plants is shown in Figure 4.2. The coil is made from 4 m of 5 mm bore copper tubing. One end of the coil was fitted with a brass nut which fitted the sampling outlets of the distillation stages, distillate and CBD valves. The other end of the coil was connected with Teflon tubing to the inlet nozzle of a 300 ml gas washing bottle. When sampling from any of the distillation stages, the pre-cleaned gas washing bottle used for collecting the samples was connected to the sampling coil and both the coil and bottle were placed in a plastic bucket filled with a mixture of crushed ice and sea water, the sampling end of the loop (with the brass nut) was screwed tightly to the outlet valve of the stage being sampled. The outlet nozzle of the gas washing bottle was connected via a plastic hose to the last stage of distillation, thus providing the vacuum required to withdraw the water from the stage being sampled. The temperature of the water after cooling ranged between 9 and 12°C, depending on the initial temperature of the sampled water (from 89°C at stage 1 to 70°C at stage 9). Once the sample was taken the valves at the stage were closed and the water was transferred into a 250 ml dark brown bottle, with a ground glass stopper that allowed no head space to form. The samples were stored in an ice chest until they were analyzed in the laboratory. Sampling of sea water from the screens or forebay (in the case of SSPS), was carried out by lowering a closed 250 ml dark brown glass bottle held at the end of a metal pipe by a flask holder to a depth of about 1 m below the surface. To fill the bottle, the cap was pulled off by the string tied around the cap and then a new cap was replaced immediately upon retrieval and the bottle transfered to the ice chest. No preservatives were added, as all samples were kept on ice until analysis, which was carried out within 8 hours of sample collection.

Figure 4.2 Components of the sampling device used in the study of halomethanes in the destillation stages.


Water drawn under reduced pressure from the stage to be sampled
To the 1st stage of distillation (highest vacuum stage) via plastic hose
Gas washing bottle
Copper coil
Crushed ice and sea water mixture

The methods of extraction and analysis for halomethanes described in Chapter 1 were also followed in this part. The other parameters were also determined according to the methods described in Chapter 2.

4.3 Results and Discussions

4.3.1 Levels of halomethanes in the waters from the desalination units at Shuwaikh:

The means, standard deviations and ranges of the levels of total residual chlorine, temperature and concentrations of halomethanes from the various stages of the F-1 desalination unit at the Shuwaikh Station shown in Table 4.2.

Total residual chlorine was not determined in the distillation stages. Its level was highest at the screen (1.5 ± 1.2 mg/1) followed by the pump (1.0 ± 0.8 mg/1). The level was appreciably lower in the distillate (0.10 ± 0.1 mg/1) and CBD (0.2 ± 0.1 mg/1). The data showed a high degree of variability as indicated by the magnitude of the standard deviation and the range. Variablilty was highest among the samples from the distillate for which the coefficient of viriations was 100% and the range was 0.5 mg/1. Both the screen and pump samples had coefficients of variation of about 80% and their ranges were 5.4 and 2.4 mg/1 respectively. This variability may be partly related to the method of chlorination used, since shock treatment is used to reduce fouling. In fact, the system is operated manually and this results in variable amounts of chlorine being added rather haphazardly. This is reflected by the levels of halomethanes found in this study and in the coastal waters study.

The sea water temperature at the screens averaged 30.4 ± 2.0°C with a range of 7.0°C, reflecting the daily and seasonal variability in the coastal areas. The sea water temperature at the pump averaged 38.5 ± 7.5°C, with

Parameter		Sampling Location						
		Screen	Pump	1st Stage	5th Stage	9th Stage	Dist.	CBD
Total Residual Chlorine (Mg/l)	$\bar{x}$	1.5	1.0	ND	ND	ND	0.1	0.2
	SD	1.2	0.8				0.1	0.1
	R	5.4	2.4				0.5	0.5
Temperature (°C)	$\bar{x}$	30.4	38.5	88	73	70	48.3	46.6
	SD	2.0	7.5				2.9	3.4
	R	7.0	27.0				14.0	18.0
$CHCl_2Br$ (µg/l)	$\bar{x}$	0.0	0.0	0.2	0.0	0.1	0.0	0.00
	SD			0.3		0.2		
	R	0.1	0.2	1.1	0.0	0.6	0.1	0.6
$CHBr_2Cl$ (µg/l)	$\bar{x}$	2.1	2.2	4.4	0.4	0.3	0.4	0.4
	SD	1.1	0.9	2.7	0.2	0.1	0.2	0.1
	R	3.9	3.8	9.0	0.5	0.3	0.8	0.5
$Cl_2C{=}CCl_2$ (µg/l)	$\bar{x}$	0.1	0.0	0.0	0.0	0.0	0.0	0.00
	SD	0.2						
	R	0.9	0.2	0.0	0.0	0.0	0.0	0.1
$CHBr_3$ (µg/l)	$\bar{x}$	79.8	76.6	156.7	16.3	13.6	14.8	** 10.9
	SD	43.6	36.1	95.9	13.1	10.5	8.9	5.5
	R	151.2	143.8	329.1	34.4	30.5	34.0	20.0
Total (µg/l)	$\bar{x}$	82.0	78.9	161.4	16.9	14.0	15.3	11.4
	SD	44.8	36.9	98.4	13.6	10.6	9.1	5.7
	n	21	30	11	10	10	32	30

Table 4.2 **Mean Total Residual Chlorine, Temperature and Halomethane Lavels in The F-1 Unit in Shuwaikh (N = 144)**

R = Range ** Excluding one sample which was unusually high with 123.7 µg/l of total halomethanes
ND = Not Determined
* The water temperature inside the stage was not measured, design values are shown in the table.

a range of 27°C, reflecting the effect of mixing with the returned sea water which apparently varied in amount and/or temperature. The mean temperature of the distillate and brine were 48.3 ± 2.9 and 46.6 ± 3.4°C, with a range of 14 and 18°C respectively. The temperatures of the seawater in the various stages were not measured, however the design values indicate a temperature of 88°C for stage 1 and 70°C for stages 5 and 9 respectively. The mean DOC content of 10 sea water samples collected at the pump (during the comparison of the halomethane levels at the F-1 unit with those at the Doha and Shuiaba units) was 4.7 ± 2.2 mgC/l, ranging from 1.85 to 8.75 mgC/l.

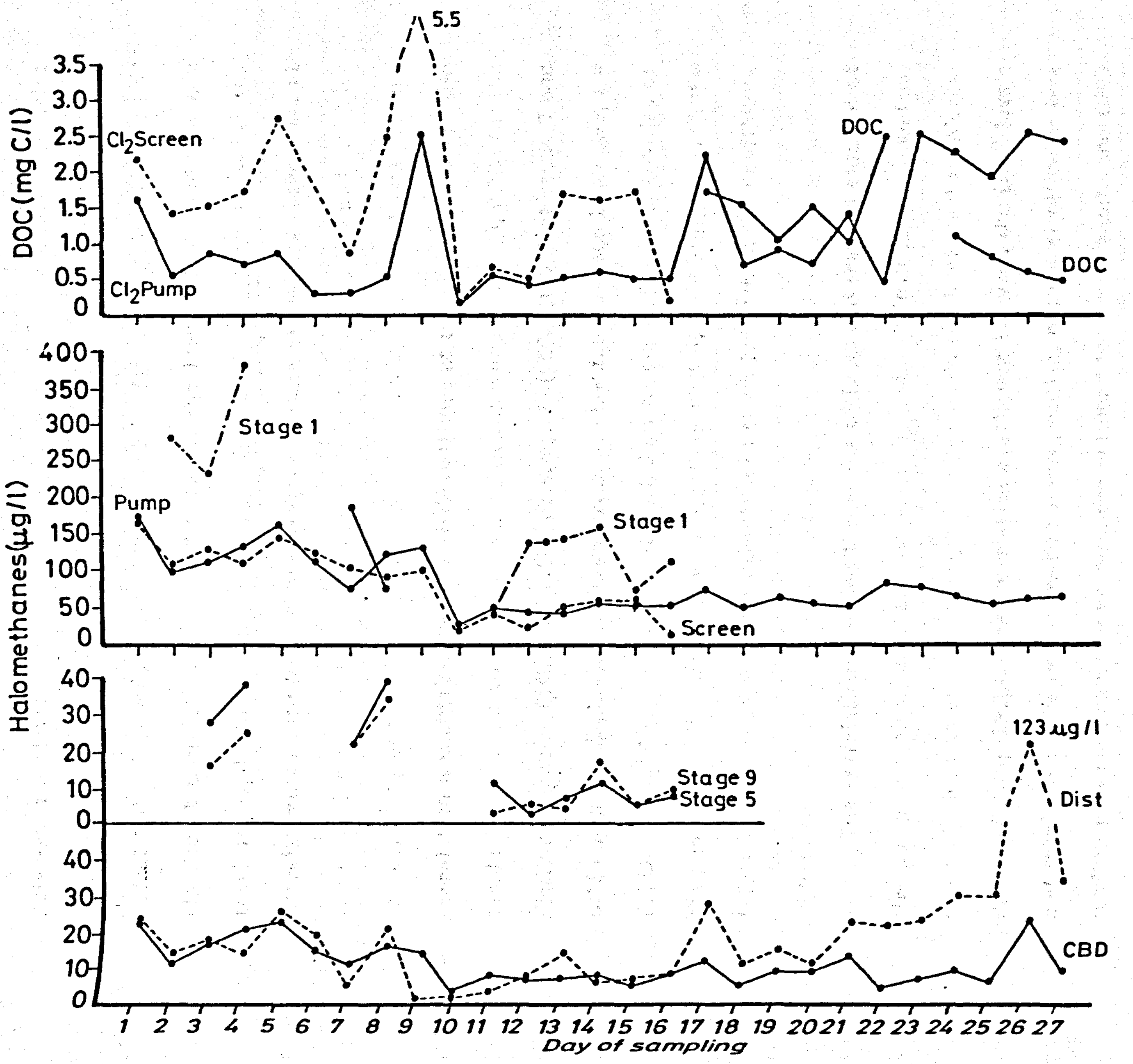
The mean concentration of total halomethanes in the various stages of the desalination process are shown in the last row of the table. The highest mean values were found in samples taken from the first stage (161 ± 98 µg/l). Those at the screen and pump were lower and quite similar to one another being 82 ± 45 µg/l and 79 ± 37 µg/l respectively. The mean concentrations of total halomethanes in samples from 5th and 9th stages were appreciably lower than that at the first stage amounting to almost one tenth of that level, 16.9 ± 13.6 and 14 ± 10.6 µg/l respectively. This is probably attributable to venting the stages. The levels in the distillate had a mean value of 15.3 ± 9.1 µg/l, whereas the total levels for the CBD samples amounted to 11.4 ± 5.7 µg/l.

Bromoform was the dominant component of the total halomethanes detected in all samples, constituting over 95% of the total at all the locations. The highest levels obtained were at stage 1 when the mean value was 157 ± 96 µg/l, with a range of 329 µg/l. The screen and the pump samples showed a mean $CHBr_3$ concentration of 80 ± 44 and 77 ± 36 µg/l respectively, both of which also showed wide ranges amounting to 151 µg/l at the screen and 144 µg/l at the pump. The levels at the 5th and 9th were about 10% of that at stage 1, again showing a high degree of variability. The distillate had a mean concentration of 14.8 ± 8.9 µg/l with a range of 34 µg/l. However one sample showed a level of 123.7 µg/l, this was not included in the calculations as it did not reflect the normal levels obtained in over 30 sampling days. The brine had a mean value slightly lower than that of the distillate, 10.9 ± 5.5 µg/l, with a range of 20 µg/l.

Dibromochloromethane was the second largest component of the total halomethanes detected in all locations. However, it constituted about 3% of the total only. Its levels were similar at the screen and pump, 2.1 ± 1.1 and 2.2 ± 0.9 µg/l respectively, whereas at stage 1 the mean concentration was 4.4 ± 2.7 µg/l. Stages 5 and 9 had only 0.4 ± 0.2 and 0.3 ± 0.1 µg/l respectively. The distillate and CBD samples had similar levels, 0.4 ± 0.2 and 0.4 ± 0.1 µg/l respectively. Dichlorobromomethane was detected at low concentrations (0.1 to 0.2 µg/l) at the screen and pump, especially when chlorine levels were high. Mean concentrations of 0.2 ± 0.3 µg/l and 0.1 ± 0.2 µg/l were found for samples from stages 1 and 9 respectively. In contrast none was detected at stage 5. This compound was also detected in trace amounts in some of the distillate and CBD samples. Tetrachloroethylene was detected in a few samples collected at the screen and (0.1 ± 0.2 µg/l) and to a much lesser extent at the pump. Traces were found at the CBD whereas at the rest of the locations it was not detected. The presence of $CHCl_3$ and CCl_4 could not be ascertained because of solvent interference and the possibility of contamination originating from the laboratory air conditioning system.

The concentrations of total residual chlorine, total halomethanes and DOC in samples collected simultaneously from the various stages of the desalination process in the F-1 unit were compared to determine if a pattern could be established for the high variability observed in the results. It can

Figure 4.3 Comparitive distribution of total residual chlorine, total halomethanes and DOC levels in samples takenfrom the F-1 Unit.


5.5
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
DOC (mg C/l)
Cl₂Screen
Cl₂Pump
DOC
DOC
400
350
300
250
200
150
100
50
0
Halomethanes (µg/l)
Stage 1
Pump
Stage 1
Screen
40
30
20
10
0
Stage 9
Stage 5
123 µg/l
Dist
40
30
20
10
0
CBD
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27
Day of sampling

be seen from the plots in Figure 4.3, that the wide variability in the levels of chlorine applied is generally reflected in the changes of halomethane levels. The levels of residual chlorine at the screen and the pump were apparently in concert ($r=0.804$, $p<0.001$). The correlation coefficient between the levels of total halomethanes and residual chlorine concentrations at the same location, at the screen and at the pump were calculated. The results are summarised in Table 4.3. A possitive and significant correlation was found between the levels of halomethane and total residual chlorine at the screen ($r= 0.523$, $p<0.05$). However the correlation between halomethane levels and residual chlorine determined at the other locations was poor (e.g. $r= 0.039$ at the pump, 0.015 and 0.049 for the distillate and CBD respectively). Statistically significant and positive correlation was obtained between halomethanes at the various locations and residual chlorine at the screen, $r=0.690$ at the pump ($p<0.001$), 0.704 for the distillate samples ($p<0.001$), 0.554 at stage 5, ($p<0.1$), 0.513 at stage 9 and 0.465 at the CBD, ($p<0.05$). However, it was low for the stage 1 samples, $r = 0.203$. Correlation between levels of halomethanes and residual chlorine at the pump generally produced lower coefficients than those obtained with the levels at the screen, with the exception of stage 1, which gave a coefficient of 0.480.

The correlation between the levels of DOC and residual chlorine at the pump was significant and negative ($r = -0.678$, $p<0.05$) as would be expeced, since an increase in organic mater would result in greater chlorine demand (White, 1978). The correlation coefficient between the DOC levels and total halomethanes at the pump was positive, but not significant ($r = 0.432$). However, negative values were obtained for the distillate and CBD samples, ($r = -0.488$ and -0.495) respectively. Thus indicating that in such a dynamic system, the interelationships between the various parameters are

Parameter		Location						
		Screen	Pump	Stage 1	Stage 5	Stage 9	Distillate	CBD
Cl_2 at same location	r	0.523[2]	0.039	ND	ND	ND	0.015	0.049
	n	21	30				30	30
Cl_2 at Screen	r		0.690[4]	0.203	0.554[1]	0.513	0.704[4]*	0.465[2]
	n		30	11	10	10	18	19
Cl_2 at Pump	r			0.480	0.406	0.222	0.525[3]*	0.178
	n			11	10	10	30	30
DOC at Pump	r		0.432				-0.488	-0.495
	n		10				10	10

Table 4.3 **Correlation Coefficients Between the Levels of Total Residual Chlorine, DOC and Total Halomethanes detected at Various Locations Within the F-1 Unit**

*When the value of 123.7 µg/l for the total detected in the distilate on 18/12/82 were included, the value of r decreased to 0.1

1. = significant at $p<0.1$
2. = significant at $p<0.05$
3. = significant at $p<0.01$
4. = significant at $p<0.001$
ND = Not determined

too complex to be revealed by simple correlations. Moreover, it was shown in the experimental section of this study that the levels of DOC as such correlate poorly with the levels of halomethanes produced in chlorinated waters, as only certain components of the DOC (e.g. humic acids) may undergo reactions leading to the production of halomethanes, whereas many others (e.g. lipids) would tend to undergo other reactions which do not lead to the production of haloforms (Morris,1978).

The effect of the tidal conditions on the levels of halomethanes at the various stages of desalination was studied by comparing the levels determined during each phase. No significant difference could be seen in all cases. For example, the mean total halomethane levels detected at the pump and in the distillate samples during ebb stage were 74.1 ± 23.7 mg/l and 16.8 ± 11.1 µg/l respectively, whereas, the levels at both locations during the flood stage were 95.0 ± 45.6 and 18.6 ± 7.5 µg/l respectively.

The mean concentration of total residual chlorine, the temperature and the concentration of the halomethanes in samples collected from the various stages of the desalination process in the D-1 unit of the Shuwaikh plant are shown in Table 4.4. As stated earlier, the productive capacity (27000 m^3/day) of this plant is about six times that of F-1 unit from which it differs in a number of its design features. The total residual chlorine levels were relatively higher in the samples taken from the pump (0.5 ± 0.2 mg/l) and the deaerator (0.3 ± 0.2 mg/l) compared with the distillate and the CBD samples, none of which exceeded 0.1 mg/l. In general the concentrations were lower than those found in the F-1 unit and exhibited a lower degree of variability, as indicated by the magnitudes of the standard deviation and the range. The mean sea water temperature at the pump was similar to that in the F-1 unit, 38.5 ± 1.8°C, but exhibited less variability which may indicate that more regular operating conditions are maintained at D-1 than at the

Parameter		Pump	Deaerator	Stage 1	Stage 5	Stage 9	Distillate	CBD
	x̄	0.5	0.3					
Cl_2	SD	0.2	0.2	ND	ND	ND	0	0
(mg/l)	R	0.5	0.5				0.1	0.1
	x̄	29.8	38.5				40.5	38.2
T	SD	2.0	1.8	85	74	67	1.2	1.2
°C	R	9.0	6.0				4.0	5.0
	x̄	0.1	19.1	0.8	0.1	0	0.1	0.1
$CHCl_2Br$	SD	0.3	21.5	1.8	0.2		0.2	0.3
(µg/l)	R	1.2	68.5	6.0	0.6	0.1	0.8	0.9
	x̄	1.9	1.4	4.0	0.6	0.4	0.3	0.2
$CHBR_2Cl$	SD	0.2	0.4	3.0	0.1	0.1	0.1	0
(µg/l)	R	1.4	1.2	9.0	0.3	0.2	0.2	0.2
	x̄		0	0		0	0	0
$Cl_2C{=}CCl_2$	SD	0			0			
(µg/l)	R		0.2	0.1		0.1	0.1	0.1
	x̄	66.6	52.7	178.1	29.5	17.8	10.4	4.2
$CHBr_3$	SD	13.7	12.8	117.4	6.5	4.8	3.5	1.8
(µg/l)	R	43.5	47.6	356.6	18.8	16.5	11.8	5.9
	x̄	68.6	73.2	182.9	30.1	18.2	10.7	4.5
Total	SD	14.1	20.2	121.7	6.5	4.8	3.6	1.9
(µg/l)	n	17	17	10	10	10	10	10

Table 4.4: Mean Total Residual Chlorine, Temperature and Halomethane Levels at the D - 1 Unit in Shuwaikh (N = 84)

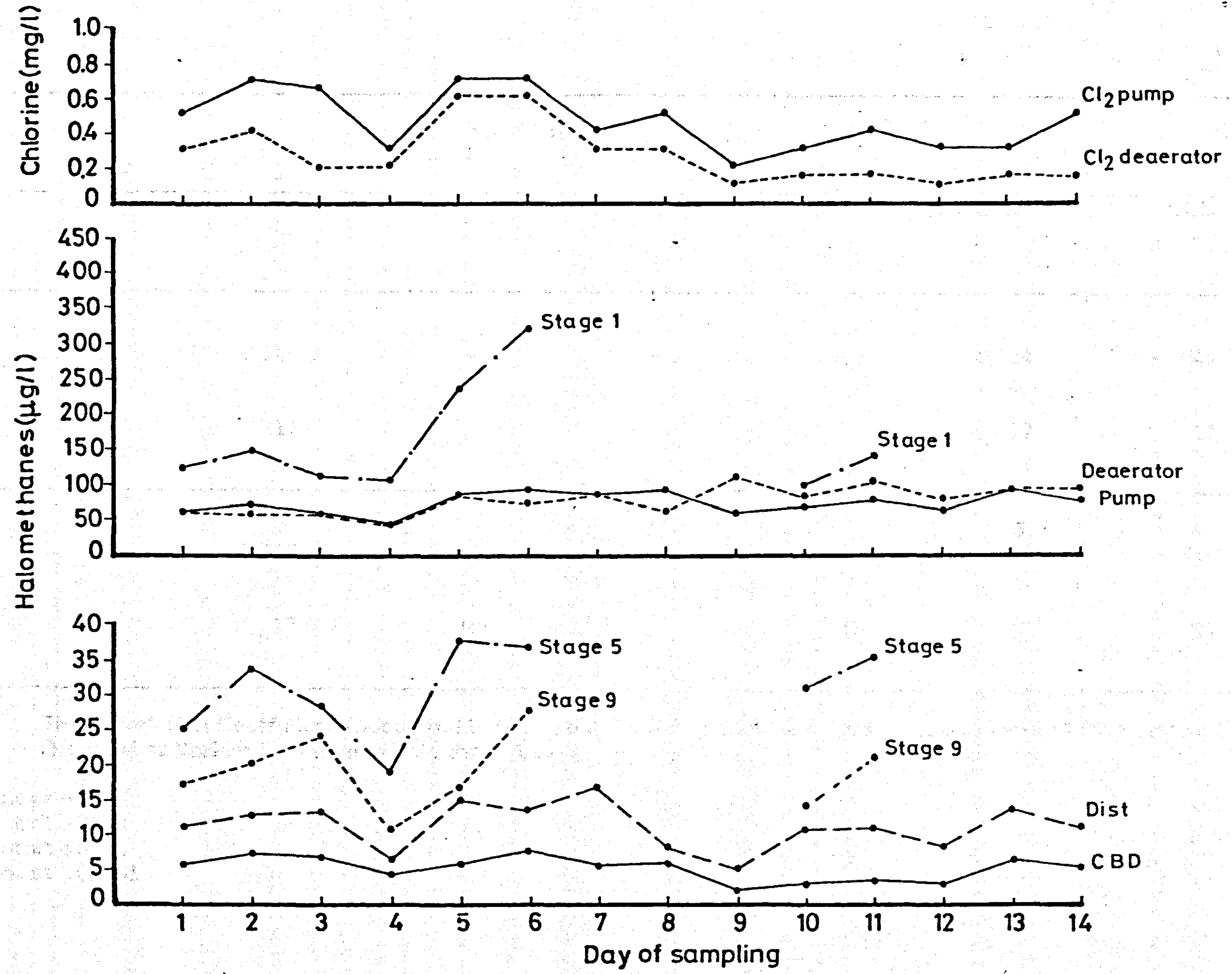
older F-1 unit. The water temperatures of the distillation stages, distillate and CBD were lower than those of the corresponding locations in the F-1 units as had been intended in the design. However a smaller degree of variability was observed (e.g. the temperature of the distillate was 40.5 ± 1.2°C with a range of 4.0°C whereas the CBD samples had a mean temperature of 38.2 ± 1.2°C with a range of 5.0°C), which indicates better control of operating conditions.

The mean concentration of the total halomethanes in the distillation stages was appreciably higher in the D-1 samples than in those from the corresponding stages of the F-1 unit. The general pattern of the distribution seen for F-1 was, however, preserved. The maximum levels were detected at the first stage (183 ± 122 µg/l) followed by the deaerator (73 ± 20 µg/l) and the pump (69 ± 14 µg/l). The coefficient of variation was higher for samples from the first stage (67%) than for those from either the deaerator (28%) or the pump (21%). At stage 5 the mean concentration was 30.1 ± 6.5 µg/l, which is a decrease of over 80% from the levels at the first stage. The levels decrease further to stage 9, for which the mean value was 18.2 ± 4.8 µg/l. The levels of halomethanes in the distillate and the CBD were lower than the corresponding values for F-1, 10.7 ± 3.6 µg/l and 4.5 ± 1.9 µg/l respectively, again with less scatter around the mean as shown by the levels of the coefficients of variation which were 34.1 for the distillate samples and 40% for the CBD samples. Bromoform again constituted the major proportion of the total halomethanes, ranging between 93 and 97% with the exception of the deaerator at which it formed 72% of the total.

Dibromochloromethane was the next most abundant halomethane, making up 2 to 4% of the total at all sampling locations except the deaerator when $CHCl_2Br$ was more concentrated. The concentration of $CHCl_2Br$ was low, in general less than 1 µg/l, except at the deaerator where it reached 19.1 ± 21.5 µg/l, 26% of the total. This may be due to an aberration in the performance of the unit, it was undergoing acceptance tests at the time of sampling. The levels were below 6 µg/l in all the samples collected in the first 10 days and then increased to values ranging between 30 and 60 µg/l for the next 7 consecutive samples, before the unit was decommissioned for repairs. During the period when the concentration of $CHCl_2Br$ increased the total residual chlorine levels at the pump and deaerator showed a slight decrease as did the other halomethanes. No explanation could be found for this change, as it was shown in the experimental part that $CHCl_2Br$ levles in chlorinated sea water were much lower than those of $CHBr_2Cl$ and $CHBr_3$. Only trace levels of tetrachlorethylene, not exceeding 0.1 µg/l were detected in few samples at the various locations. Whereas, the presence of $CHCl_3$ and CCl_4 could not be verified here as well.

The relative distribution of total residual chlorine and total halomethanes is graphically shown in Figure 4.4. It is apparent that the levels of Chlorine at the pump and deaerator and those of halomethanes (except in the deaerator) show a similar pattern of oscillations. A highly significant correlation coefficient between the chlorine levels at the pump and deaerator was shown ($r = 0.769$, $p<0.001$). The correlation coefficients between total halomethanes and the residual chlorine at the same location and at the pump are shown in Table 4.5. A positive and significant correlation coefficient of $r = 0.448$($p<0.1$) was found between the levels of halomethanes and total residual chlorine at the pump. It was negative and poor between the halomethane levels at the deaerator and the residual chlorine levels at the pump and at the dearator (-0.144 and -0.187 respectively). This reflected the effect of the unusually high levels of $CHCl_2Br$ that appeared in some of the samples from the deaerator. This

Figure 4.4 Comparative distribution of total chlorine and totalhalomethanes concentrations in samples taken from theD-1 unit.


Chlorine (mg/l)
1.0
0.8
0.6
0.4
0.2
0
Cl$_2$ pump
Cl$_2$ deaerator
Halomethanes (µg/l)
450
400
350
300
250
200
150
100
50
0
Stage 1
Stage 1
Deaerator
Pump
40
35
30
25
20
15
10
5
0
Stage 5
Stage 5
Stage 9
Stage 9
Dist
CBD
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Day of sampling

Parameter	Location						
	Pump	Deaerator	Stage 1	Stage 5	Stage 9	Distillate	CBD
Cl_2 at Location	0.448[1]	-0.144	-	-	-	0.314	-0.049
n	17	17				17	17
Cl_2 at Pump	-	-0.187	0.088	0.631[1]	0.717[2]	0.678[3]	0.747[4]
n		17	10	10	10	17	17

Table 4.5: **The Correlation Coefficient Calculated Between the Total Residual Chlorine Levels and Total Halomethanes Detected at Various Locations Within the D-1 Unit**

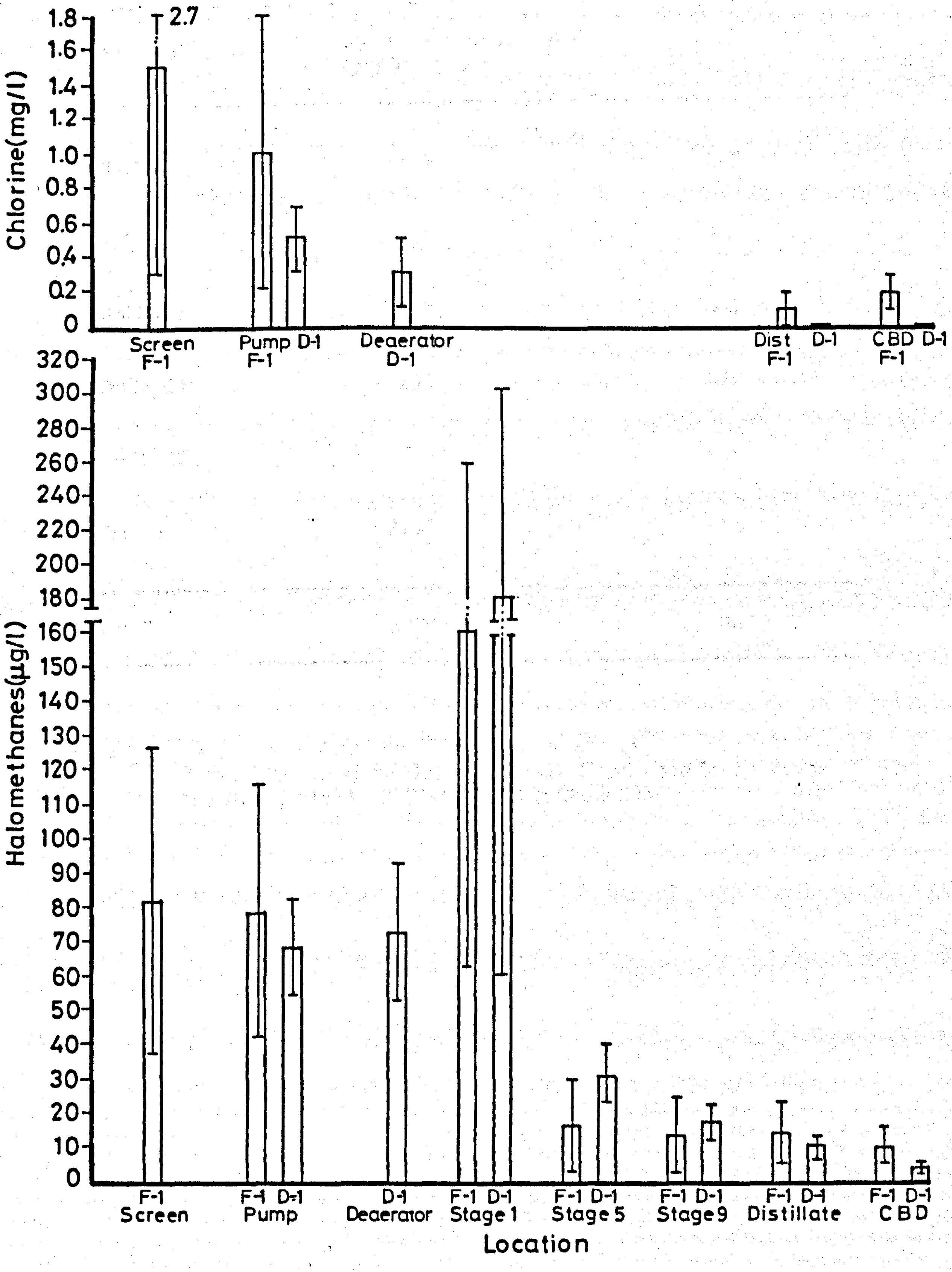
1 = Significant at $p<0.1$
2 = Significant at $p<0.05$
3 = Significant at $p<0.01$
4 = Significant at $p<0.001$

aberration did not effect the levels of $CHBr_3$ and $CHBr_2Cl$ since a significant and positive correlation was obtained with the chlorine levels at the pump ($r=0.688, p<0.01$ and $0.820, p<0.001$ respectlively). The total halomethane levels in the samples from the distillate and the CBD correlated poorly with the levels of residual chlorine at the same locations. However both gave a high and positive correlation coefficient with the levels of residual chlorine at the pump, 0.678 ($p<0.01$) and 0.747 which was also significant ($p<0.001$). The levels of total halomethanes at stages 5 and 9 gave a positive correlation coefficient with the levels of residual chlorine at the pump, 0.631 and 0.717 (both significant, $p<0.1$[illegible] and $p<0.05$ respectively).

A comparison between the mean levels of total halomethanes at the various locations during the ebb and flood phases of the tides showed that as with the F-1 unit, there was no statistical significant difference. For example the mean total halomethanes concentration at the pump was 74.8 ± 11.8 µg/l during the flood phase and 61.7 and 13.7 µg/l during the ebb phase.

The relationship between the mean levels of residual chlorine and total halomethanes at the various locations in units F-1 and D-1 are shown diagrammatically in Figure 4.5. It is apparent that the larger and the more recent D-1 unit showed less variability in water temperatures and in the levels of halomethanes. Moreover, it was more efficient in removing halomethanes from the processed and produced waters. For example, the mean concentrations of halomethanes in the distillate (10.7 ± 3.6 µg/l) and the CBD (4.5 ± 1.9 µg/l) were lower than those at the corresponding stages of the F-1 unit. The difference was significant for the CBD and distillate samples, ($\alpha=0.05$). However, it should be noted that the levels of chlorine dosage applied at the D-1 unit during the period of the study were below the 2 mg/l target generally followed at all other stations. Thus, the differences

Figure 4.5 The relative distribution of the mean concentrationsof total residual chlorine and halomethanes insamples from the various stages of F-1 and D-1 units in shuwaikh.

2.7
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
Chlorine(mg/l)
Screen F-1
Pump F-1
D-1
Deaerator D-1
Dist F-1
D-1
CBD F-1
D-1
320
300
280
260
240
220
200
180
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Halomethanes(μg/l)
F-1 Screen
F-1 D-1 Pump
D-1 Deaerator
F-1 D-1 Stage 1
F-1 D-1 Stage 5
F-1 D-1 Stage 9
F-1 D-1 Distillate
F-1 D-1 CBD
Location

Compound	Mean Concentration (µg/l)	SD
$CHCl_3$	4.4	0.7
CCl_4	5.1	1.0
$CHCl_2Br$	15.4	14.8
$CHBr_2Cl$	136	31
$Cl_2C{=}CCl_2$	0.9	0.1
$CHBr_3$	2747	610
Total	2900	600

Table 4.6 Mean Concentrations of Halomethanes and Tetrachloroethylene Detected in the Condensed Steam from the Air Ejector Unit (D-1 Plant) in Shuwaikh

between halomethane levels at the various stages in both units may become less pronounced than shown by these results.

The removal of halomethanes produced in the chlorinated sea water used for desalination was confirmed by collecting samples of the vented system using a cold trap. The procedure described for the extraction of halomethanes from water was applied with the exception that the volumes of sample and solvent were changed since only a limited quantity of steam could be condensed. The semiquantitative results are summarised in Table 4.6. It is apparent that the amount of halomethanes remaining in the distillate and brine is probably only about 1% of that released into the atmosphere.

4.3.2 Comparison of the distributions of halomethane levels in the desalination units at the Shuwaikh, Shuaiba and Doha Stations

During the second part of the study of halomethane levels produced during the desalination process. Samples were collected regularly over a period of 14 days from the F-1 unit at Shuwaikh (4,500 m^3/d), in the A-3 unit at Shuaiba South (22,700 m^3/d) and the A-1 unit in the Doha East Station (27,300 m^3/d). A summary of data for the mean total residual Chlorine, temperature, DOC and halomethanes is shown in Table 4.7.

The mean levels of total residual chlorine and temperatures for the three sampling points at the F-1 unit were within the ranges shown earlier. The levels of total halomethanes at the pump and the CBD averaged 61.4 ± 10.4 and 9.8 ± 5.3 µg/l respectively, which were also similar to the overall mean values shown in Table 4.2. However the mean total halomethane concentration for the distillate was higher than the value reported earlier, 22.8 ± 8.2 µg/l as opposed to 15.31 ± 9.1 µg/l (significantly different, α = 0.05). However, one sample was excluded from the calculation as it

Parameter		Shuwaikh (F-1)			Shuaiba South (A-3)			Doha East (A-1)		
		Pump	DIST.	CBD	Pump	Dist.	CBD	Pump	Dist.	CBD
Total Resid.	$\bar{x}$	1.6	0.2	0.3	0.9	0.1	0.2	0.7	0.1	0.1
Chlorine	SD	0.8	0.2	0.2	0.7	0.2	0.2	0.5	0.1	0.3
(mg/l)	R	2.1	0.5	0.5	2.7	0.5	0.5	1.4	0.5	0.7
	$\bar{x}$	30.6	47.0	44.8	22.2	39.6	36.9	19.5	32.8	35.4
Temp. °C	SD	6.3	3.5	4.8	2.6	1.6	2.2	4.5	5.0	1.0
	R	16.0	14.0	18.0	8.0	6.0	8.0	12.0	14.0	3.0
	$\bar{x}$	4.7	-	-	4.2	-	-	4.7	-	-
DOC	SD	2.2			1.7			1.4		
(mgC/l)	R	6.9			4.8			3.5		
	$\bar{x}$	0	0	0	0	0	0	0	0.1	0
$CHCl_2Br$	SD								0.4	
(µg/l)	R								1.3	
	$\bar{x}$	2.0	0.6	0.4	0.7	0.1	0	0.6	0.4	0
$CHBr_2Cl$	SD	0.6	0.2	0.1	0.4	0.1		0.03	0.02	
(µg/l)	R	2.2	0.5	0.5	1.1	0.3		0.9	0.8	
	$\bar{x}$	59.4	22.0	9.4	21.0	2.6	0	25.6	18.9	1.4
$CHBr_3$	SD	9.9	7.9	5.1	16.9	4.8		13.2	13.5	4.7
(µg/l)	R	31.5	22.8	18.6	44.9	15.2		44.1	37.9	16.4
	$\bar{x}$	61.4	22.8	9.8	21.7	2.7	0	26.2	19.4	1.4
Total	SD	10.4	8.2	5.3	17.2	4.9		13.5	14.0	4.9
(µg/l)	R	33.5	25.3	19.1	45.9	15.5		45.0	39.9	16.8
n		14	14	14	14	14	14	12	12	12

Table 4.7 Mean Levels of Total Residual Chlorine, Temperature, DOC and Halomethanes Determined in Samples from the Desalination Units in Shuwaikh, Shuaiba and Doha

contained 123.7 µg/l of total halomethanes, which was unusually high. The occurance of high levels of halomethanes was also observed in samples from the Doha and Shuaiba units, ranging from 3 to 5 times the mean halomethane values in the distillate. This may be attributed to the "carry over" of seawater during the flash evaporation process, especially if foaming occurs. However, it would be expected that such an occurrence is rare in view of the addition of anti-foaming agent to the recirculating brine.

The mean concentration of total residual chlorine at the pump in the Shuaiba unit (0.9 ± 0.7 µg/l) was significanty lower than that at the corresponding location in the F-1 unit in Shuwaikh ($\alpha = 0.05$). However, the levels at the distillate and CBD were similar to those in Shuwaikh, 0.1 ±0.2 and 0.2 ± 0.2 mg/l respectively. The mean temperatures at the three sampling locations were all lower than that observed at Shuwaikh. It was 32.3 ± 2.6°C at the pump, compared to 30.6 ± 6.3°C in Shuwaikh, which is probably due to the fact that the samples in Shuaiba where collected immediately after the screen, before the sea water is mixed with the returned fraction (from the seawater feed pump). The lower temperatures of the distillate and CBD reflect the design differences between the newer units at Shuaiba and the F-1 unit in Shuwaikh.

The mean DOC concentration at Shuaiba was 4.2 ± 1.7 mgC/l, which was similar to the levels in Shuwaikh where it averaged 4.7 ± 2.2 mgC/l. Both areas, and also in Doha where 4.7 ± 1.4 mgC/l were determined are influenced by the release of effluents in their vicinity and contamination by organic matter from the adjacent harbours.

The mean levels of total halomethanes at the pump in Shuaiba was 21.7 ± 17.2 µg/l with a range of 45.9 µg/l, which is significantly lower than that at the corresponding position at Shuwaikh ($\alpha = 0.001$). Bromoform still constituted about 97% of the total, with $CHBr_2Cl$ making up the rest having a mean value of 0.7 ± 0.4 µg/l. The levels were aslo significantly lower in the distillate where a mean value of 2.7 ± 4.9 µg/l was obtained compared to 22.8 ± 8.2 µg/l at Shuwaikh (α= 0.001). No halomethanes were detected in the samples collected from the CBD at Shuaiba, indicating that the relativity lower levels of halomethanes formed in sea water were being removed by the venting system with only small amounts transferred into the distillate. The lower levels of halomethanes in the feed sea water may be due mainly to the high levels of ammonia-nitrogen previously referred to. In addition the method of chlorination may play a part, chlorine gas is injected directly into the sea water at Shuaiba whereas a sea water solution of chlorine is injected at the intake jetty at Shuwaikh. Thus at Shuwaikh, chlorine remains in contact with sea water for a longer time (thereby providing a greater chance for halomethanes to form) before introduction into the desalination unit. However this also applies to Doha where the time interval between chlorination and introduction into the unit is short relative to that at Shuwaikh.

The mean concentration of total residual chlorine at the pump in the A-1 unit at Doha was 0.7 ± 0.5 mg/l which was similar to that at the corresponding location at Shuaiba. However it was significantly lower than that at the pump in Shuwaikh (α= 0.001). The levels in the distillate and at the CBD were similar to those in the corresponding locations at Shuwaikh and Shuaiba, 0.1 ± 0.1 and 0.1 ± 0.3 mg/l respectively. The mean temperatures recorded at the pump, distillate and CBD outlets were similar to those at the corresponding locations in Shuaiba, 19.5 ± 4.5, 32.8 ± 5.0 and 35.4 ± 1.0°C respectively.

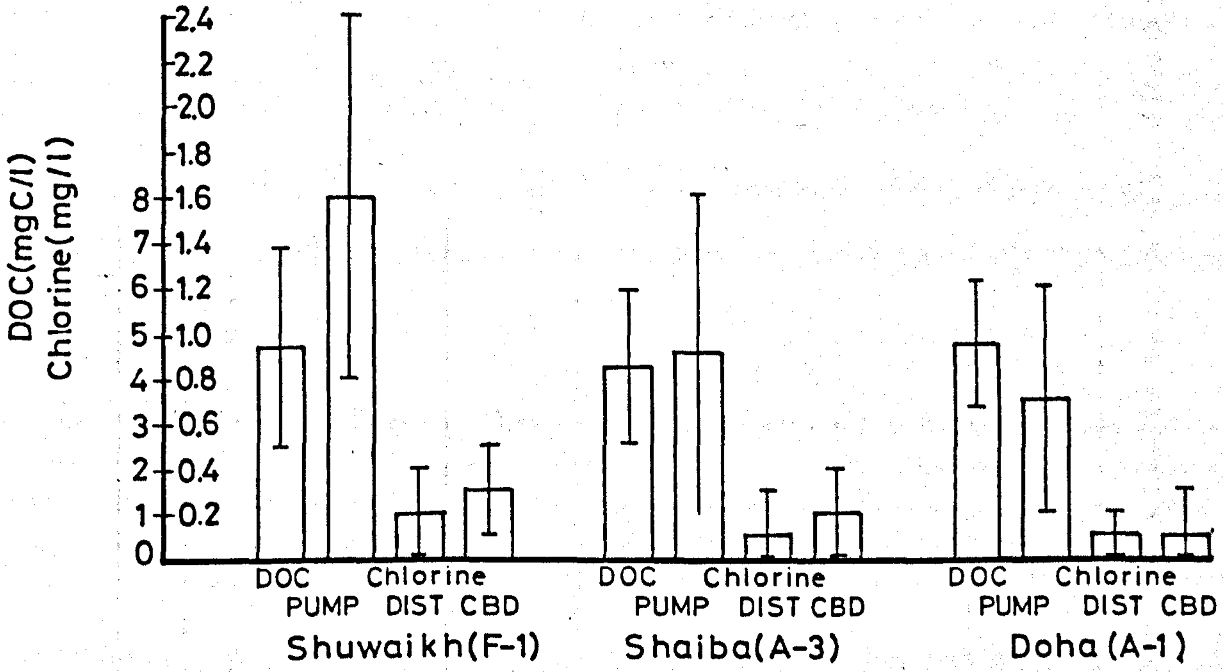
The mean levels of total halomethanes at the pump in the Doha unit was 26.2 ± 13.5 µg/l, the values having a range of 45 µg/l. This was similar to the mean value obtained at the pump in the Shuaiba unit (21.7 µg/l), but was significantly lower than that in the corresponding location at Shuwaikh ($\alpha = 0.001$). The total halomethane concentration in the distillate had a mean value of 19.4 ± 14 µg/l with a range of 39.9 µg/l, which was similar to the mean value obtained for the distillate at Shuwaikh, but significantly higher than that of the distillate in Shuaiba ($\alpha = 0.001$). Samples from the CBD were generally void of halomethanes, with a mean value of 1.4 ± 4.9 µg/l, which was much influenced by the value of 16.8 µg/l found for one sample.

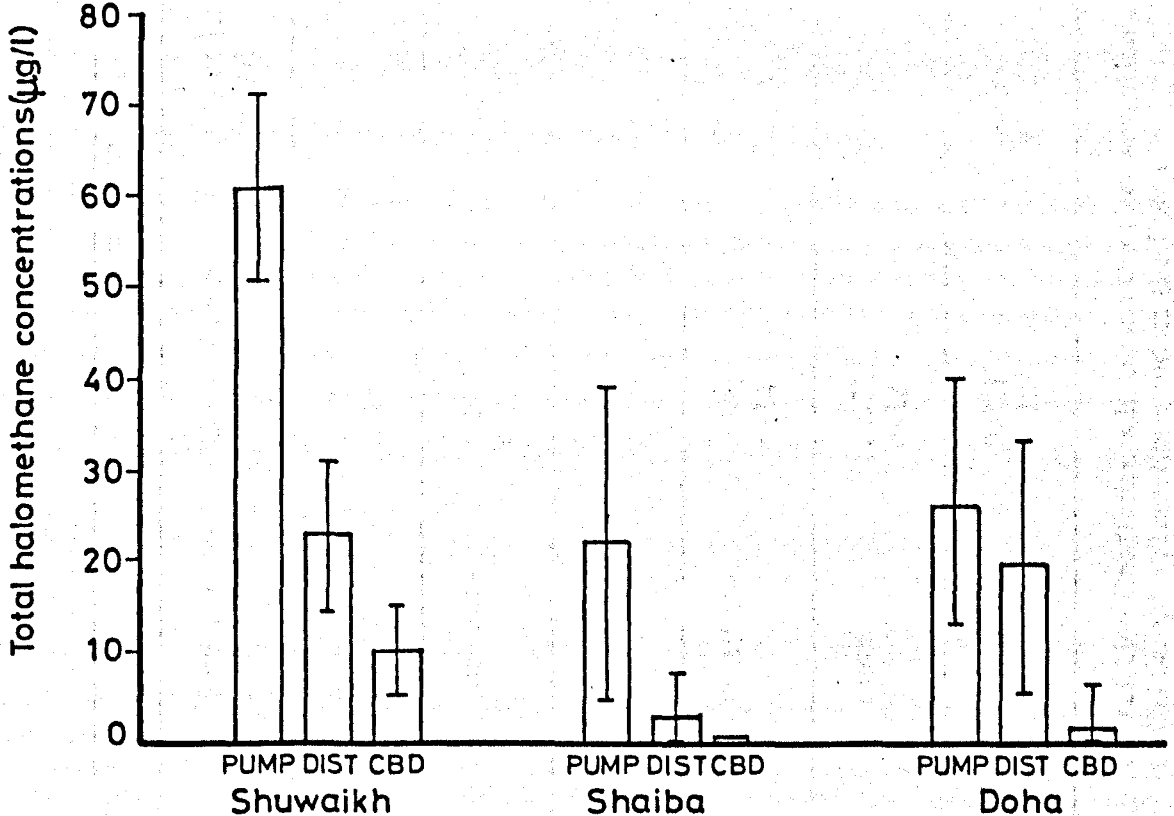
Despite the difference in the levels of halomethanes observed between the three units, the proportion of $CHBr_3$ to the total levels of halomethanes remained at about 97%, the rest being mainly $CHBr_2Cl$. The mean concentration of $CHCl_2Br$ was 0.1 ± 0.7 µg/l in the distillate at Doha,but this compound was not detected in the rest of the locations at the three units.

The mean levels of total residual chlorine, DOC and total halomethanes at the sampling locations in the three units are shown diagrammatically in Figure 4.6. The wide scatter around the mean seems to be characteristic of all sampling locations. Nevertheless an attempt was made to correlate the levels of halomethanes with those of residual chlorine and DOC in the three units. The calculated coefficients are presented in Table (4.8).

Correlations between levels of halomethanes and total residual chlorine at the same sampling location were weak, including that at the pump of the F-1 unit. However the correlation coefficient was positive and significant between total halomethanes at F-1 distillate ($r = 0.522$, $p<0.1$), Shuiaba's pump and distillate ($r = 0.555$ and 0.591 respectively, $P<0.05$) and Doha's pump ($r = 0.521$, $p<0.1$). The levels of halomethanes in the samples from the distillate at the Doha unit give a poor correlation coefficient with residual chlorine levels at the same location and at the pump ($r = -0.005$ and

Figure 4.6 The relative distribution of the mean concentrations oftotal chlorine, total halomethanes and DOC in samples takenfrom the three desalination units.


DOC(mgC/l)
Chlorine(mg/l)
0
1 0.2
2 0.4
3 0.6
4 0.8
5 1.0
6 1.2
7 1.4
8 1.6
1.8
2.0
2.2
2.4
DOC
PUMP
Chlorine
DIST
CBD
Shuwaikh(F-1)
DOC
PUMP
Chlorine
DIST
CBD
Shaiba(A-3)
DOC
PUMP
Chlorine
DIST
CBD
Doha (A-1)


Total halomethane concentrations(µg/l)
0
10
20
30
40
50
60
70
80
PUMP
DIST
CBD
Shuwaikh
PUMP
DIST
CBD
Shaiba
PUMP
DIST
CBD
Doha

Location		Parameter		
Unit	Sampling Location	Cl_2 at Pump (mg/l)	Cl_2 at Location (mg/l)	DOC at Pump (mgC/l)
Shuwaikh F-1	Pump	0.163 n-11	-	0.432 n=10
	Distillate	0.522[1] n=11	-0.053 n=11	-0.488 n=10
Shuaiba South A-3	Pump	0.555[2] n=14	-	-0.003 n=9
	Distillate	0.591[2] n=14	0.231 n=14	-0.182 n=9
Doha East A-1	Pump	0.521[1] n=12	-	-0.001 n=8
	Distillate	0.021 n=12	-0.005 n=12	0.714[2] n=8

Table 4.8: **Correlation Coefficients Between the Concentration of Halomethanes, DOC Levels and with Total Residual Chlorine at the Sampling Locations and at the Pump**

1 = Significant at $p<0.1$
2 = Significant at $p<0.05$

0.021 respectively). However, the levels of halomethanes in the distillate of the Doha Unit gave a positive and significant correlation with the DOC level at the pump (r=0.714, p<0.05). It was also positive at the pump in Shuwaikh, but not significant (r = 0.432). However, correlation with the DOC levels gave a poor and negative coefficient at the pump in Doha (r = -0.001), distillate and pump at Shuaiba (r = -0.182 and -0.003) and distillate at Shuwaikh (r = -0.488).

The generally high correlation coefficients found between halomethane levels and residual chlorine levels for F-1 and D-1 at the pump and screen, rather than at the sampling location itself was unexpected. One possible explanation is that the relatively high levels of chlorine at the intakes (screen and/or pump) are likely to produce such high levels of halomethanes that some will remain at the final stages (after a major fraction is removed by the venting process). If the same rationale is applied to the results of the correlations with the DOC levels at the pump, then higher DOC levels would mean more chlorine demand and lower levels of halomethanes to be formed (given the relatively low chlorination dose of 2 mg/l normally applied). Thus, lower levels of halomethanes would also be expected in the distillate and CBD samples. This was generally the case, except at Doha where a significant correlation coefficient was obtained between the levels of halomethanes and DOC levels at the pump, whereas, it was low with the levels of residual chlorine at the pump. It appears that a larger set of data at shorter in-between sampling time intervals may be required to verify the effects of fluctuations in chlorine levels, DOC concentrations and operating conditions (e.g. temperature) on the levels of halomethanes produced.*

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*It should be noted that the role of the organic compounds added to the recirculating brine as anti-foaming anti-scale agents (e.g. lignin sulphonate) in the formation of halomethanes was not investigated.

CHAPTER 5

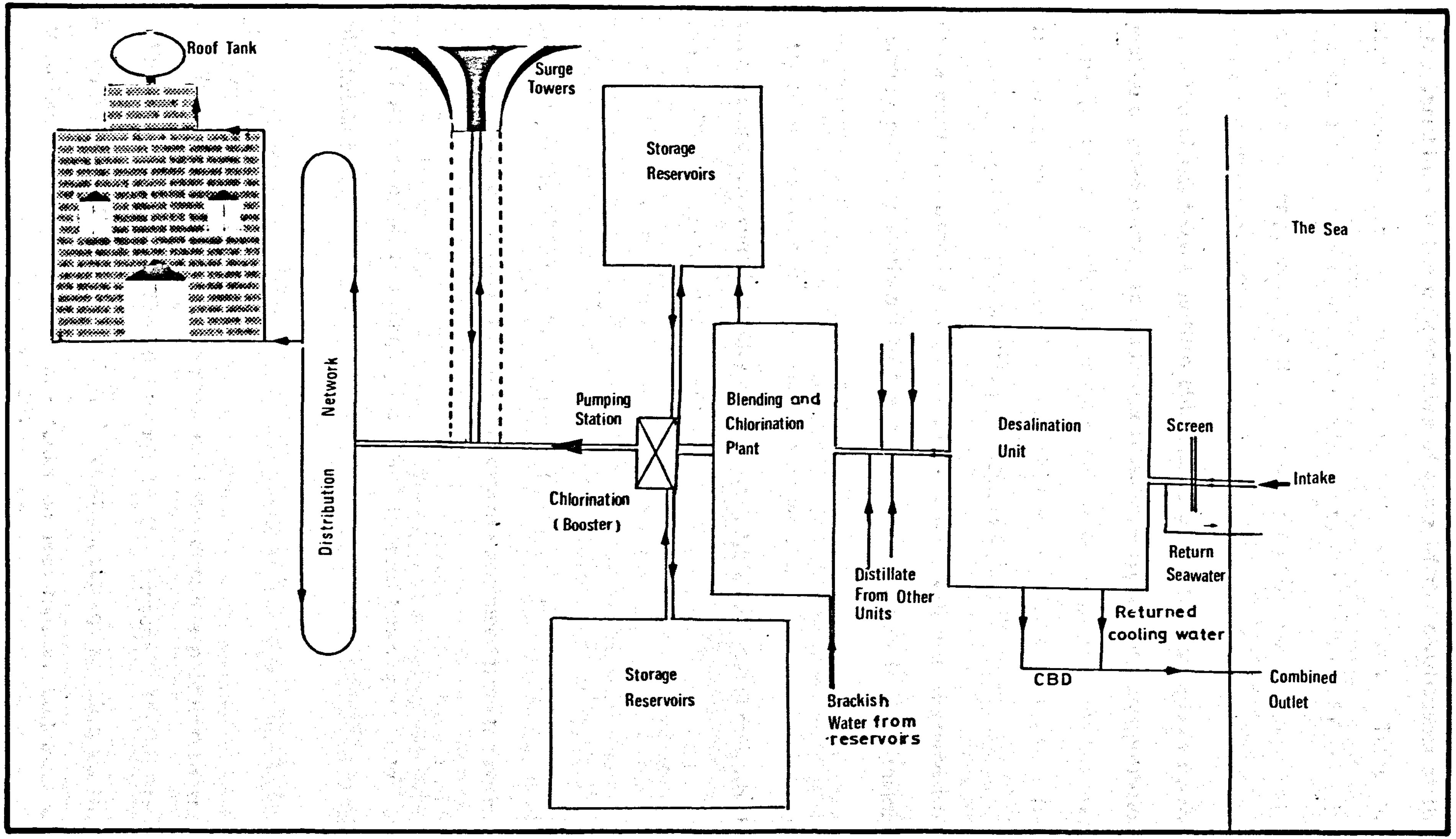
The Distribution of Halomethanes in the Drinking water Supplies

5.1 Introduction

Potable water in Kuwait is a blend made by mixing the distillate produced by the desalination plants with brackish water to render it palatable and to increase the salt content to values within the range recommended by the World Health Organisation (WHO, 1971). As a follow up to the study of halomethanes in the coastal waters and those associated with the desalination process, a limited survey was conducted to determine the types and concentrations of halomethanes in the drinking water supplies in Kuwait. The effects of factors such as type of reservoir, use of household filters and boilers on the levels of halomethanes were also investigated. To aid the discussion, a brief discription of the potable water productions and distribution system is given below. A flow diagram of the system is shown in Figure 5.1.

The distillate produced by the desalination plants is pumped to three blending plants, located in the Shuwaikh, Doha and Shuaiba areas, where the pH is adjusted from a value of about 6 to approximately 9 by the addition of NaOH before it is blended with brackish waters having a geological age of 30,000 to 50,000 years (from the Shagayah and Sulaibiya ground water fields) and with smaller amounts of potable well water (produced mainly from the Um Al-Eish fields). The blending ratios have varied over the past few years as a result of decrease in the supply of potable well waters and variations in the salinity of the brackish water. For example, the amounts of brackish water used in blending in 1982 was about 9% of the volume of distillate used in contrast to 14% in 1977. Over the same period the fraction of potable well water decreased from 3% to 0.5% (MEW, 1983). It has also been reported that there is short term variability in the blending ratios within each plant as well as between the three plants (VBB, 1982). This is reflected

Figure 5.1: Flow of diagram of potable water production and distribution system in Kuwait.


Roof Tank
Surge Towers
Storage Reservoirs
Network
Distribution
Pumping Station
Chlorination (Booster)
Blending and Chlorination Plant
Desalination Unit
Screen
Intake
The Sea
Return Seawater
Distillate From Other Units
Returned cooling water
CBD
Combined Outlet
Storage Reservoirs
Brackish Water from reservoirs

in the variability of the concentrates of some of the constituents of the water produced such as chlorides, calcium and sodium. Table 5.1 summarises the results of analysis conducted by the Ministry of Electricity and Water on water produced at the three blending plants over a period of 9 months (WRDC, 1983).

The blended water is then chlorinated at the blending plants by the injection of chlorine gas, to achieve a total residual chlorine concentration of 2 mg/l. The daily chlorine gas consumption by the three plants has been estimated to range between 800 and 1200 kg/day (WRDC, 1983). The chlorinated water flows by gravity to low-level concrete storage reservoirs (with a combined capacity of 19×10^6 m^3), from which it is pumped by secondary pumping stations into the main network which is made mainly from cement-lined ductile cast iron pipes. The secondary mains are made mostly from asbestos-cement pipes. The network is also connected to high level concrete reservoirs (capacity ranging from 2,000 to 250,000 m^3), which serve both to balance the difference between supply and demand and to act as surge tanks to maintain pressure in the system. The water is subsequently stored in roof tanks made from galvanised metal or glass reinforced plastic (GRP) or in underground concrete reservoirs lined with bitumen or plastic. The use of such reservoirs has continued from the period prior to the construction of the water supply network. They have a wide range of storage capacities ranging from $6m^3$ for roof tanks up to $200m^3$ in public buildings.

5.2 Materials and Methods

The fate of halomethanes present in the distillate produced by the desalination plants was followed through to the consumer, through the blending process with brackish water, chlorination, storage and then via the distribution network to the storage tanks on roof-tops of buildings or

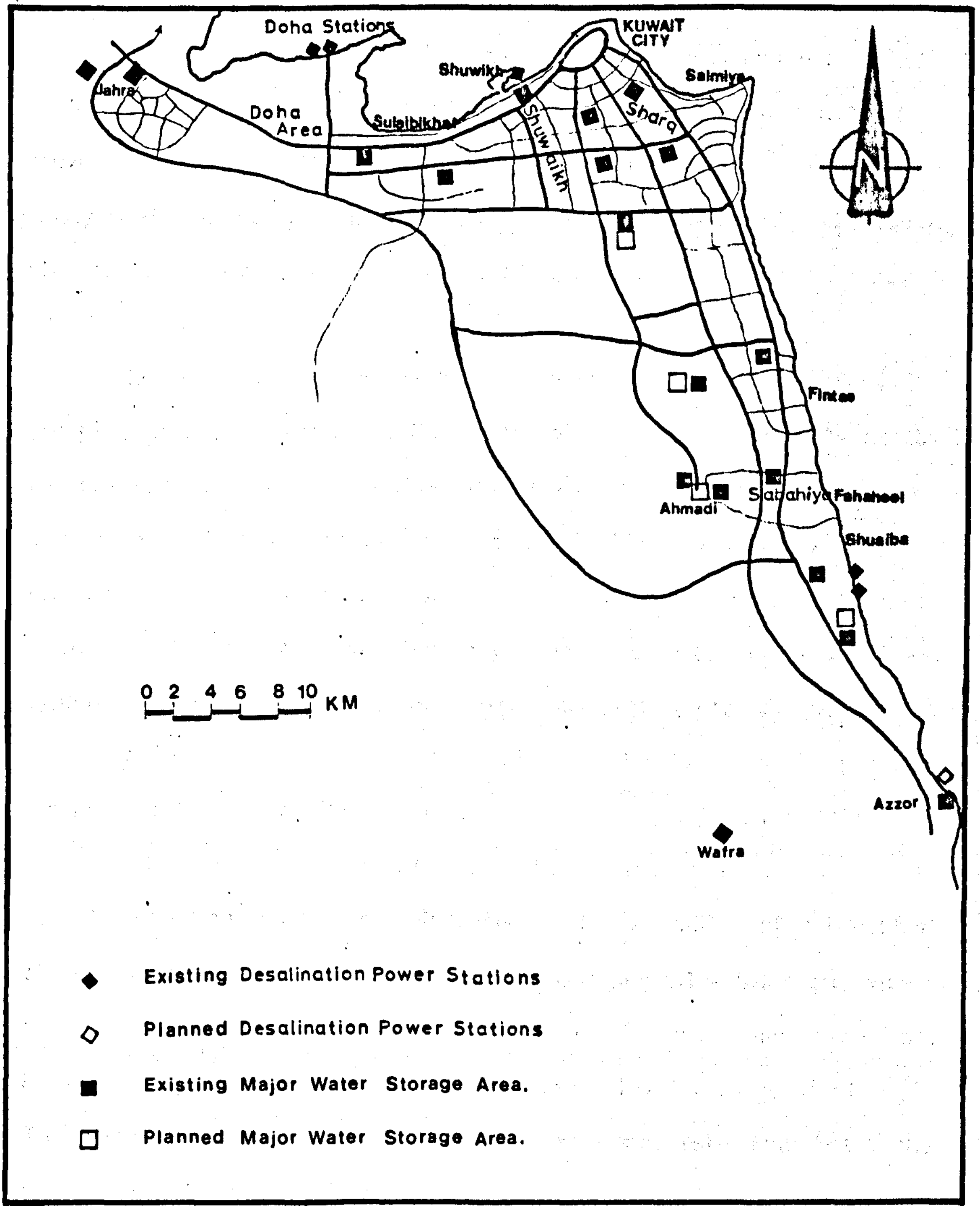
Parameter		Concentration		
		Shuaiba	Shuwaikh	Doha
Conductivity	µmhos/cm	463 ± 96	498 ± 99	472 ± 71
T.D.S.	mg/l	232 ± 52	270 ± 68	256 ± 39
PH		7.4 ± 0.3	7.5 ± 0.3	7.6 ± 0.2
Total Alkilinity	mg/l	8 ± 1	11 ± 2	12 ± 2
Total Hardness	mg/l	95	104	103
$CO_3^=$	mg/l	0	0	0
HCO_3^-	mg/l	10 ± 1	13 ± 3	14 ± 2
$SO_4^=$	mg/l	71 ± 9	78 ± 18	91 ± 13
Cl^-	mg/l	66 ± 15	62 ± 7	57 ± 5
F^-	mg/l	0.17 ± 0.03	0.21 ± 0.04	0.2 ± 0.04
NH_3	mg/l	0.02 ± 0.01	0	0
SiO_2	mg/l	1.2 ± 0.15	1.7 ± 0.3	1.8 ± 0.3
Ca^{++}	mg/l	23 ± 2	25 ± 5	26 ± 3
Mg^{++}	mg/l	9 ± 1	10 ± 1.7	9 ± 1
Na^{++}	mg/l	38 ± 10	42 ± 7	39 ± 5
K^+	mg/l	1 ± 0.4	1.2 ± 0.3	1.2 ± 0.2
Fe, Total	mg/l	0.2 ± 0.2	0.2 ± 0.2	0.2 ± 0.2

Table 5.1: **Chemical Analysis of Potable Water Produced at the Blending Stations in a Nine Month Period (WRDC, 1983). n= 34**

underground. Samples were taken from one of the pumping stations (Shuwaikh) and from two types of reservoirs: (i) residential-size roof tanks made from galvanised iron or glass fibre reinforced plastic (GRP) tanks with a capicity of about 6m^3. Such tanks were sampled in the areas of Shuwaikh (Occupational Health Building, OCC), Doha (two adjacent houses, one with a GRP tank and the other with a metal tank) and from a house in Sabahiya (fitted with a GRP tank); (ii) Public building- size reservoirs built in the form of either a metal water tower (Ibin Cina and Jahra Hospitals) or as an underground concrete reservoir lined with bitumen (the Hilton Hotel and the Mubarak and Adan Hospitals). Samples were also taken from the mains (before the tank) directly from the tank and after the filter. The effects of the water boilers on the levels of halomethanes was also investigated. The geographical distribution of sampling locations is shown in Map Figure 5.2. In all, 120 samples were collected on 31 days spread over almost a three-month period. The OCC-tank location was taken as a reference station (46 samples) whereas the other areas were sampled for a minimum of 4 to a maximum of 13 days. The samples were collected using the cooling coil described earlier to minimize loss of halomethanes by evaporation. The water was collected in dark brown glass bottles, which were stoppered, care being taken to avoid the formation of head space. The bottles were immediately transferred to an ice chest. No preservative was used, as the samples were kept cold (at about 4°C) and analysed within 6 hours of collection.

Before sampling the water was run to waste until its temperature was stable. The thermometer reading was recorded and a sample was then taken for total residual chlorine determination, which was conducted at the site using the DPD method described earlier.

Figure 5.2. Areas of study of the distribution of halomethanes in potable water. Also shown are the locations of the desalination - power stations and major water storage areas.


Doha Stations
KUWAIT CITY
Shuwikh
Salmiya
Jahra
Doha Area
Sulaibikhat
Shuwaikh
Sharq
N
Fintas
Ahmadi
Sabahiya
Fahaheel
Shuaiba
Azzor
Wafra
0 2 4 6 8 10 KM
◆ Existing Desalination Power Stations
◇ Planned Desalination Power Stations
■ Existing Major Water Storage Area.
□ Planned Major Water Storage Area.

5.3 Results and Discussions

The overall mean of the water temperature, total residual chlorine and halomethane concentrations in samples collected from homes and public buildings in several areas extending from Jahra in the western part of Kuwait to Sabahiya in the south are summarised in Table 5.2. The results of analysis of samples taken from the pumping station in Shuwaikh and those of the distillate from the F-1 unit (obtained from data presented in Chapter 4 of this study) are also shown.

The mean water temperature of potable water at the Shuwaikh pumping station was similar to that of the distillate produced at the nearby F-1 unit (50 ± 1°C and 48 ± 3°C respectively). The mean water temperature of samples collected from homes and public buildings was 39 ± 3°C with a range of 14°C. The wide range of temperatures observed is probably due to differences in location of sampling (e.g. mains as opposed to reservoirs) and type of reservoir sampled (e.g. roof tanks or underground reservoirs).

The mean concentrations of total residual chlorine at the pumping station was 2.2 ± 0.4 mg/l ranging from 1.6 to 2.7 mg/l. This variability may be attributed to differences in the chlorine demand of the various waters used for blending and to a certain extent to the variability of the residual chlorine already present in the distillate (averaging 0.1 ± 0.1 mg/l, with a range of 0.5 mg/l). The concentrations of chlorine in samples taken from homes and public buildings averaged 0.8 ± 0.5 mg/l with a range of 2.0 mg/l. The high degree of variability (C.V. = 60%) is probably reflecting that at the source as well as the effects of variable residence time in the various reservoirs in the system. The type and size of reservoirs at the sampling locations may also have an effect on the residual chlorine concentrations.

The mean concentration of total halomethanes at the pumping station was 36.8 ± 4.7 µg/l, which is about double that in the distillate (15.3 ± 9.1 µg/l). The mean concentration of total halomethanes in samples collected

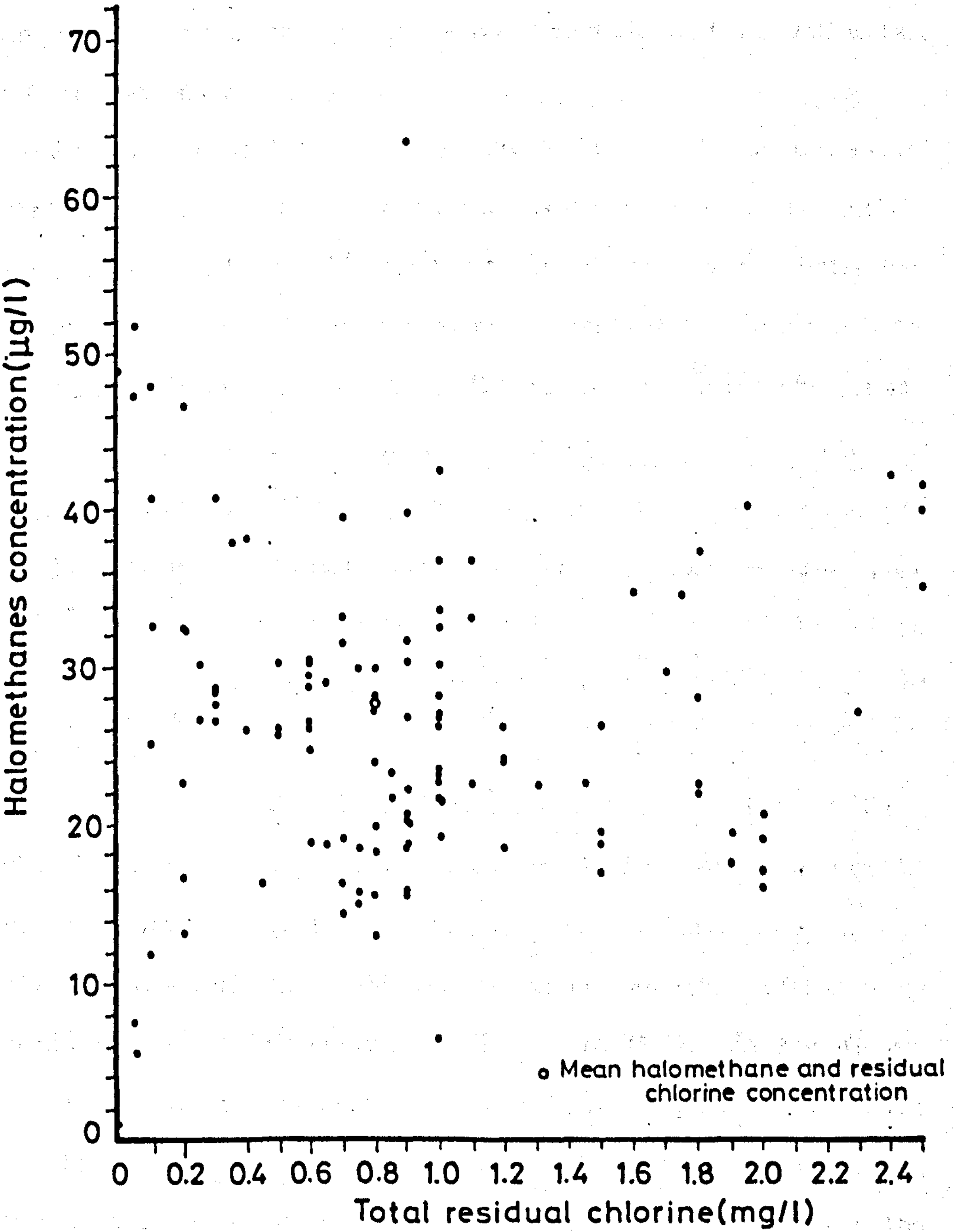
Location	F-1 Unit - Shuwaikh Distillate n=31				Pumping Station Shuwaikh n=9				Homes and Public Buildings n=113			
Parameter	Mean	SD	Range	% of Total	Mean	SD	Range	% of Total	Mean	SD	Range	% of Total
T°C	48	3	10	-	50	1	4	-	39	3	14	-
Total Residual Chlorine (mg/l)	0.1	0.1	0.5	-	2.2	0.4	1.1	-	0.8	0.5	2.0	-
$CHCl_2Br$ (µg/l)	0	0	0	0	5.0	1.0	2.5	14	3.3	1.5	7.1	13
$CHBr_2Cl$ (µg/l)	0.4	0.2	0.8	3	11.4	1.3	4.5	31	8.8	3.7	18.5	34
$CHBr_3$ (µg/l)	14.8	8.9	33.2	97	20.3	2.8	8.7	55	13.6	4.6	23.5	53
Total (µg/l)	15.3	9.1	34.0	100	36.8	4.7	14.9	100	25.6	9.1	50.5	100

Table 5.2: Mean Concentrations of Halomethanes, Total residual Chlorine and Temperature in Samples from the Distillate, Potable Water at the Pumping Station and from Reservoirs in Homes and Public Buildings (June - Sept, 1982)

from homes and public buildings was 25.6 ± 9.1 µg/l, which was significantly lower than the corresponding value at the pumping station ($\alpha<0.05$). However , a greater degree of variability was observed, as is shown by the range (50.5 µg/l) and the coefficient of variation (36% compared to 13% for samples taken from the pumping station). Temporal and spatial variability in the concentrations of halomethanes in water supplies have also been reported in other field studies (Rook, 1974) Symons **et al.**, (1975); Sonneborn and Bohn, 1978 and Trussell **et al.**, 1980). Several factors may affect the concentrations of halomethanes in water, for example, changes in the concentrations of organic matter contained in the waters used for blending as well as in the chlorine demand value - along with the presence of other substances such as iron (Fe^{2+}) Rook (1974); Morris (1975) and Burke **et al** (1983). Temporal variations in the concentrations of halomethanes are also likely to result both from changes in the pH value due to variations in the amount of NaOH added to the distillate and fluctuations in the bromide ion concentration resulting either from the carry over of sea water during the flood evaporation process from changes in the amounts of ground waters used in blending. However changes in the bromide ion concentration are more likely to influence the types of halomethanes formed rather than their absolute concentrations (Rook **et al.**, 1978, Oliver, 1980 and Cooper **et al.**, 1983).

An attempt was made to correlate the concentrations of total halomethanes with those of the total residual chlorine detected at the sampling locations. The correlation, which is shown diagrammatically in Figure 5.3, produced a poor and negative correlation coefficient of 0.294. The correlation coefficient between the concentrations of total halomethanes and residual chlorine at the pumping station was also poor ($r = 0.234$). This may be due to the fact that the distillate (which is forming about 90% of the total) is already chlorinated before reaching the pumping

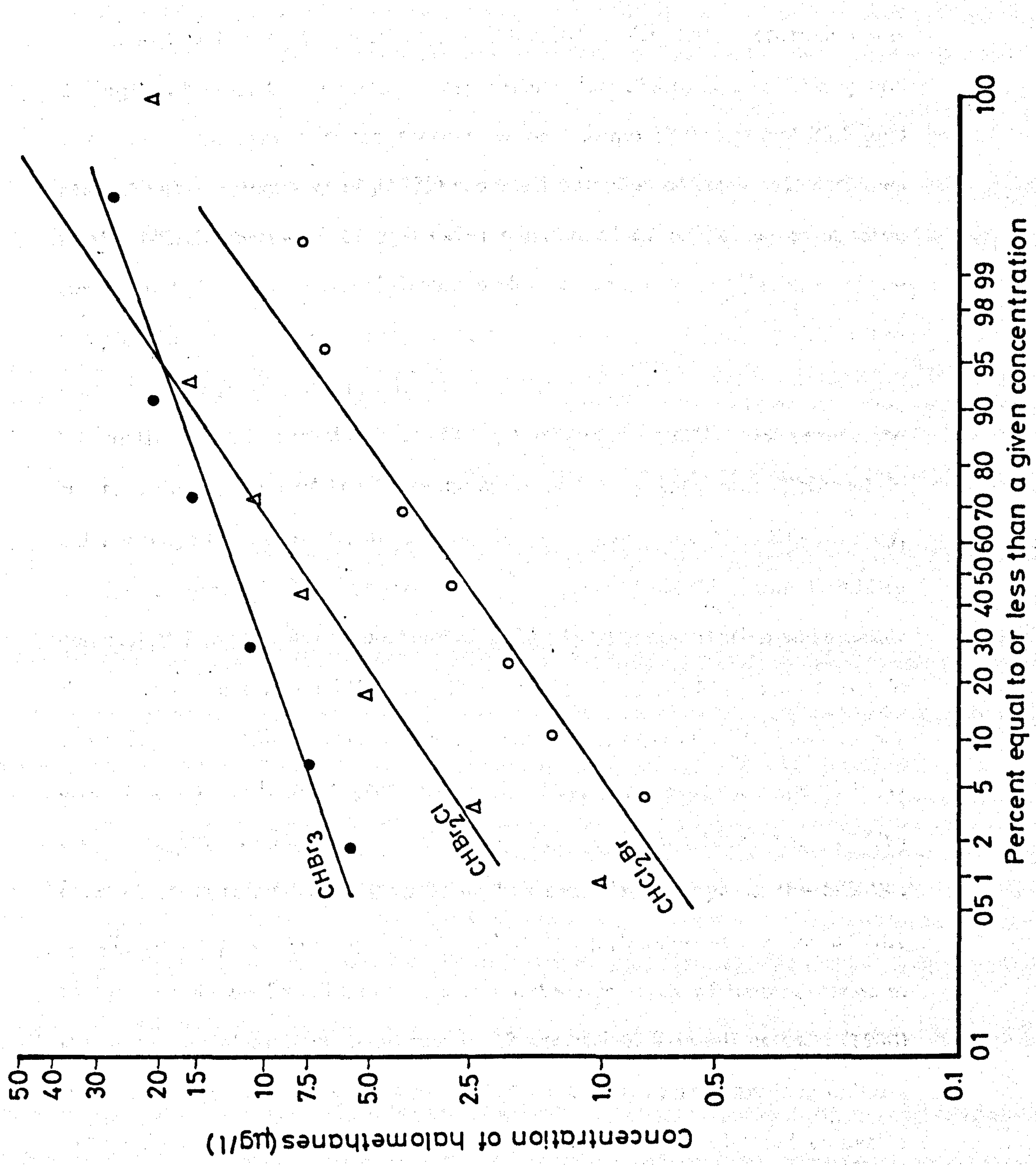
Figure 5.3 Scatter diagram relating the total halomethane concentrations to the total residual chlorine levels in samples collected from homes and public buildings.


Halomethanes concentration (µg/l)
70
60
50
40
30
20
10
0
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
Total residual chlorine (mg/l)
○ Mean halomethane and residual chlorine concentration

station and this may influence the concentrations of both parameters. A better parameter with which to correlate the level of halomethanes might have been the chlorine demand of the waters used for blending as suggested by Morris and Baum (1978). However, that was not possible to monitor during the survey, since the water in the distribution network was a mixture of those produced at the three plants, each utilising distilled and well waters from different sources.

The relevant contributions of the individual halomethanes to the total concentration detected at the various locations is also shown in Table (5.2). Bromoform constituted about 50% of the total halomethane concentrations determined in the potable water samples compared to 90% in the distillate. Its mean concentration was 13.6 ± 4.6 µg/l in samples taken from homes and public buildings in which it formed about 53% of the total halomethanes; this was similar to that at the pumping stations where it constituted 55% of the total and had a mean concentration of 20.3 ± 2.8 µg/l. Dibromochloromomethane constituted about 34% of the total halomethane concentration in the samples, with a mean value of 8.8 ± 3.7 µg/l, which was similar to the percentage of the total it formed at the pumping station (31%). Dichlorobromomethane, which was not detected in the distillate, consituted 13 to 14% of the total in the samples from homes and public buildings and from the pumping station (3.3 ± 1.5 µg/l and 5.0 ± 1.0 µg/l respectively). The variability exhibited by the concentration of the three components shown is diagrammatically in Figure (5.4). In the figure, concentrations of each compound were plotted (on a log scale) against the percent value (probability scale) equal to or less than a given concentration, which provides a better presentation of the concentrations to which the population was exposed to during the time interval covered by the study. Such method was also used in presenting the data of the National Organics Reconnaissance Surveys (NORS) during which the concentrations of

Figure 5.4 The distribution of individual halomethanes in potable water, expressed in terms of percent equal to or less than a given concentration.


Concentration of halomethanes (μg/l)
50
40
30
20
15
10
7.5
5.0
2.5
1.0
0.5
0.1
01
05
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
100
Percent equal to or less than a given concentration
CHBr3
CHBr2Cl
CHCl2Br

halomethanes were determined in water produced by water treatment plants at 80 American cities. On the basis of the frequency distribution pattern shown in the figure, the median value for the $CHCl_2Br$ concentration was 2.7 µg/l, whereas the median concentrations for $CHBr_2Cl$ and $CHBr_3$ and the total halomethane concentrations were 7.5 and 12.0 µg/l and 25.5 µg/l respectively. Symons et al.,(1975) reported a median of total halomethanes in the NORS survey of 27 µg/l (with a mean of 67 µg/l). In an updated survey of 113 cities (National Organics Monitoring Survey, NOMS) where the samples collected from the treatment plants were stored to allow halomethanes production reactions to go to completion. The median total halomethane concentration was 74 µg/l (Cotruvo (1981)). However, the relative distribution of the three compounds to the total was different in both surveys than that shown for Kuwait. For example in the NORS survey, $CHCl_3$ comprised 74% of the total whereas $CHBrCl_2$ and $CHClBr_2$ consituted 21% and 4% respectively. Bromoform concentration were below detection at over 70% of the sampling locations. It should be noted that in the NORS and NOMS surveys, the concentrations of each of the compounds also showed a high degree of variability, for example the $CHCl_3$ concentration varied from <0.1 to 311 µg/l whereas the $CHBr_3$ concentration ranged from 0 to 92 µg/l in the first survey. In the NOMS , $CHCl_3$ concentrations ranged from <0.1 to 540 µg/l whereas a range of <0.1 to 190 was shown for $CHBr_3$. In a less extensive study of halomethanes in the water supplies from locations in 12 countries, Trussell et al., (1980) showed a distribution pattern similar to that shown by the previous authors except in samples taken from southern China, where reclaimed estuaries were used for water catchment and thus, the water contained relatively higher concentrations of Br^-. In samples from that area, $CHBr_3$ formed 21% of the total whereas $CHBr_2Cl$, $CHCl_2Br$ and $CHCl_3$ consituted 43%, 25% and 11% respectively. Other field and experimental data have also given evidence of the increasing dominance of bromine-containing halomethanes as the Cl/Br ratios in the water decreases (Morris, 1975; Rook **et al.**, (1978); Minear and Bird, 1980 and Cooper **et al.**, (1983). The main sources of the Br^- in the potable waters of Kuwait are probably the brackish and potable well water used for blending which contain about 2 mg Br/l. Another possible source is the sea water carried over into the distillate during the flash evaporation process (that this occurs is shown by the occurrence of $\sim$ 14 mg/l of chlorides in the distillate}. Assuming on this basis the fraction of sea water carried over into the distillate is about 0.1% this corresponds with a Br^- concentration in the distillate of 80 µg/l. This conclusion is in general agreement with the results of the analysis of a few water samples taken during the experimental section of this study. The bromide ion concentration in the distillate sample was 0.130 mg/l whereas the potable water contained 0.53 mg/l. At this background level of Br^- and with a chlorination dose of about 2 mg/l, the bromide-containing halomethanes would be expected to dominate. In contrast, $CHCl_3$ would be a minor constituent as indicated by the experimental data of Bunn **et al.**,(1975) (1975), Rook **et al.**,(1978), Minear and Bird (1980) and Cooper **et al.**,(1983). It should be noted that $CHCl_3$ was detected in low concentrations (up to 2 µg/l above the blank) in some of the samples from the pumping stations. However, the values have not been taken into account owing to the uncertainty caused by the contamination problems. *

The concentrations of halomethanes in potable water supplies collected from the districts of Shuwaikh (Occupational Health Building), Doha and Sabahiya, which are all located within a short distance of a pumping station, are shown in Table 5.3 and Figure 5.5a. It should be noted that Sabahiya is the nearest of the three districts to the Shuaiba Station. The water temperature was similar on average at the three locations (38°C). The total residual chlorine concentrations were highest in Shuwaikh (1.2 ±

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* It should be pointed out that the analyses of several samples of potable and brakish well waters showed them to be free of halomethanes. Thus, they are not expected to contribute to the levels of halomethanes found in the final blend until they have been chlorinated.

Parameter	Concentrations of halomethanes according to the location (µg/l)								
	Shuwaikh			Sabahiya			Doha		
	Mean	SD	%	Mean	SD	%	Mean	SD	%
Temperature (°C)	38	3	-	38	2	-	38	1	-
Total Residual Chlorine (mg/l)	1.2	0.4	-	0.5	0.3	-	0.6	0.3	-
$CHCl_2Br$ (µg/l)	3.5	1.0	(14)	3.7	1.3	(12)	1.4	0.6	(8)
$CHBr_2Cl$ (µg/l)	8.7	2.5	(35)	11.2	3.7	(37)	4.9	1.9	(26)
$CHBr_3$ (µg/l)	12.9	3.1	(51)	15.0	5.6	(50)	11.6	4.8	(65)
Total (µg/l)	25.1	5.8	(100)	29.9	10	(99)	17.9	7.1	(99)
(n)	46			18			27		

Table 5.3: **Distribution of the Mean Concentrations of Halomethanes, Total Residual Chlorine and Temperature in Samples of Potable Water from Three Areas in Kuwait.**

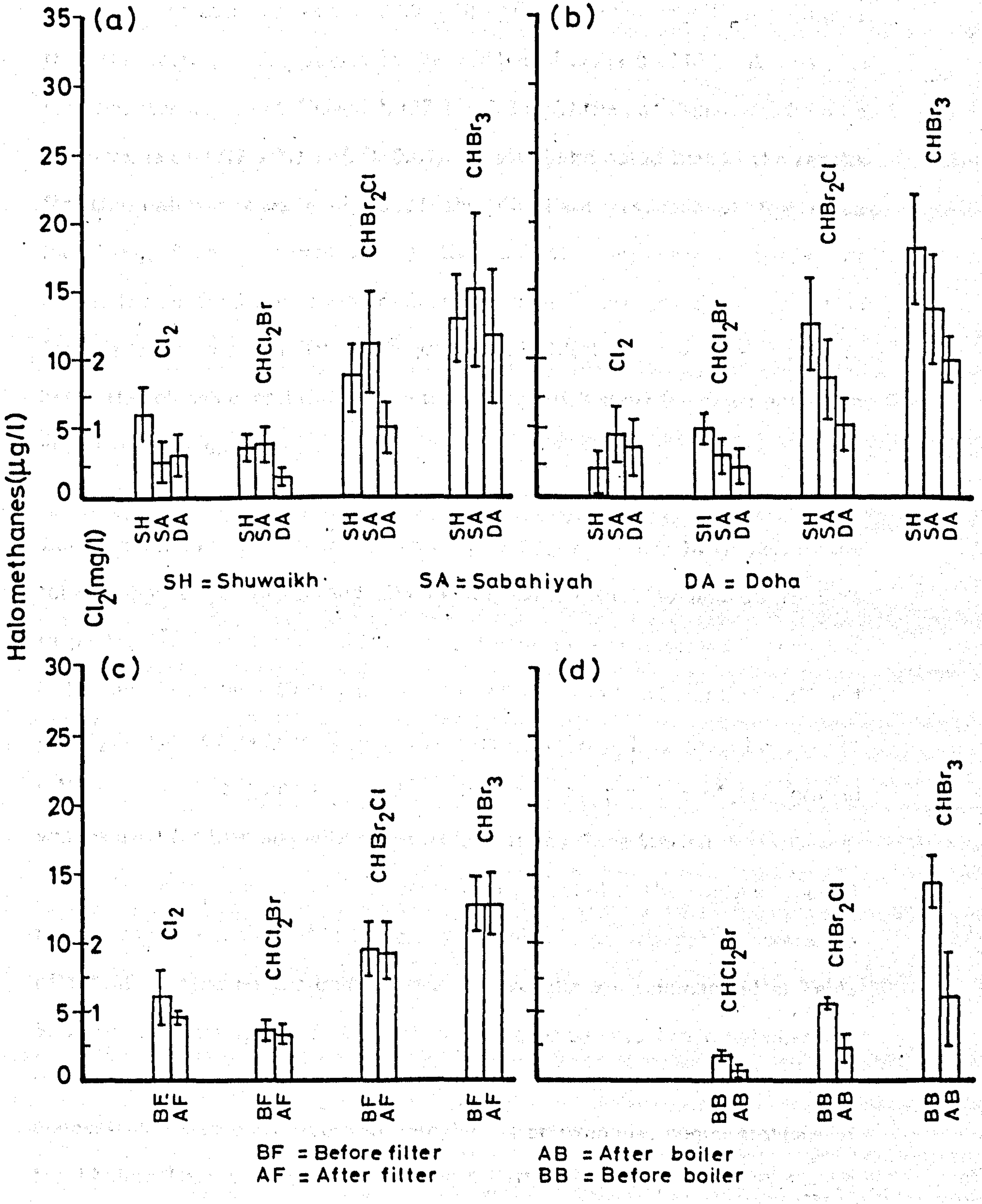
Figure 5.5 Comparitive distribution of mean total residual chlorine and total halomethane concentrations showing the effect of:

a) Location of sampling area

b) Type of reservoir (UG = Underground reservoir, GRP = Glass-reinforced plastic tank and M = Metal tank)

c) Passage through a household filter.

d) Passage through a household boiler


Halomethanes(µg/l)
Cl2(mg/l)
(a)
(b)
(c)
(d)
0
5
10
15
20
25
30
35
1
2
Cl2
CHCl2Br
CHBr2Cl
CHBr3
SH
SA
DA
SII
BF
AF
BB
AB
SH = Shuwaikh
SA = Sabahiyah
DA = Doha
BF = Before filter
AF = After filter
AB = After boiler
BB = Before boiler

0.4 mg/l), whereas it was about half that level at Sabahiya and Doha, (0.5 ± 0.3 and 0.6 ± 0.3 mg/l respectively). The mean total concentration of halomethanes at Sabahiya was 29.9 ± 10 µg/l, which was significantly higher than the corresponding values at Shuwaikh and Doha ($\alpha < 0.01$). It was also significantly higher at Shuwaikh (25.1 ± 5.8 µg/l) than at Doha, which had a mean value of 17.9 ± 7.1 µg/l ($\alpha < 0.01$). It should be noted that in the results for the halomethanes analysis of the distillate produced at the three locations, Shuaiba samples had the lowest mean concentration of halomethanes (and the lowest residual chlorine). One possible explanation for this is that a relativity larger quantity of chlorine gas was being used to bring the chlorine residual concentration up to 2 mg/l (i.e. to satisfy the chlorine demand).

The relative proportions of the individual halomethanes in the total were similar in Shuwaikh and Sabahiyah, $CHCl_2Br$ forming 14 to 12% of the total, whereas $CHBr_2Cl$ and $CHBr_3$ formed 35 to 37% and 51 to 50% respectively. However, a different distribution was observed among the Doha samples, where $CHBr_3$ constituted 65% of the total and $CHBr_2Cl$ and $CHCl_2Br$ formed only 26% and 8% respectively. This may be due to difference in the quantities and/or chemical composition of the ground waters used for blending with the distillate at the Doha Station.

The concentrations of halomethanes detected in the various types of reservoirs were compared to those in the mains in an attempt to assess the effect of storage on the compounds. The results are summarised in Table 5.4. No statistically significant difference could be established between the mean water temperatures, total residual chlorine and halomethane concentrations in both groups of samples. For example, concentrations of total halomethanes in the mains was 26.6 ± 10.5 µg/l, compared to 25.5 ± 8.8 µg/l in the reservoirs. The relative contributions of the individual compounds to the total showed a slight shift towards bromoform, from 48%

Parameter	Halomethane concentrations according to location (µg/l)					
	Mains			Reservoirs		
	Mean	SD	%	Mean	SD	%
Temperature (°C)	40	2	-	38	3	-
Residual Chlorine (mg/l)	1.0	0.7	-	0.8	0.4	-
$CHCl_2Br$ (µg/l)	3.9	1.1	(15)	3.1	1.5	(12)
$CHBr_2Cl$ (µg/l)	9.8	4.2	(37)	8.6	3.6	(34)
$CHBr_3Cl$ (µg/l)	12.9	5.6	(48)	13.8	4.4	(54)
Total (µg/l)	26.6	10.5	(100)	25.5	8.8	(100)

Table 5.4: Distribution of the Mean Concentrations of Halomethanes, Total Residual Chlorine and Temperature in Water Samples from the Mains and various Types of reservoirs

in the mains to 54% in the reservoirs. A similar shift was also observed in the experimental part of this study and analogous effects of time on the speciation of halomethanes have been reported by Rook (1977); Oliver (1980) and Minear and Bird (1980). However, bearing in mind the high degree of variability exhibited by the data, it is unlikely that such differences may not be real.

The effect of the type of reservoir on the concentrations of halomethanes was also studied by comparing underground reservoirs made of bitumen-lined concrete with those made of GRP and galvanised metal. It should be noted that underground reservoirs are normally larger in capacity (and hence have a smaller surface/volume ratio) than the GRP and metal tanks which are usually sited on the roof tops of homes and public buildings. The results are shown in Table 5.5 and Figure 5.5.b. The mean water temperature was higher in the underground reservoirs (41 ± 4°C) than in the GRP and metal tanks, which were 38 ± 2°C and 39 ± 2°C respectively. However, since the samples were collected early in the morning, the temperature difference between the metal and GRP tanks may be greater than is shown. The mean total residual chlorine in the underground reservoirs (0.4 ± 0.4 mg/l) was significantly lower than the corresponding values in the GPR and metal tanks ($\alpha=0.05$), which were 0.9 ± 0.4 and 0.7 ± 0.4 mg/l respectively. Since both types of tanks were connected to the supply pipe, the difference in the residual chlorine concentrations between the GRP and metal tanks may be attributed to differences in the rates of HOCl and HOBr decay to ClO_3^- and BrO_3^-, which would not be detected by the method of analysis used as part of the total residual chlorine. However, iron oxides present in the metal tank are not expected to catalyze the decay of the hypohalous acids (Lister, 1956).

The mean concentration of total halomethanes in the samples taken from the underground reservoirs was 35.4 ± 7.8 µg/l, which was significantly

Parameter	Concentrations of Halomethanes According to type of reservoir (μg/l)								
	Underground			GRP			Metal		
	Mean	SD	%	Mean	SD	%	Mean	SD	%
Temperature (°C)	41	2	-	38	2	-	39	2	-
Residual Chlorine (mg/l)	0.4	0.4	-	0.9	0.4	-	0.7	0.4	-
$CHCl_2Br$ (μg/l)	4.9	1.1	(14)	2.9	1.3	(12)	2.1	1.3	(12)
$CHBr_2Cl$ (μg/l)	12.5	3.3	(35)	8.4	2.9	(34)	5.1	1.9	(30)
$CHBr_3$ (μg/l)	18.0	4.0	(51)	13.6	4.0	(55)	9.9	1.8	(58)
Total (μg/l)	35.4	7.8	(100)	24.9	7.1	(100)	17.1	4.3	(100)
(n)	18			59			17		

Table 5.5: Distribution of the Mean Concentrations of Halomethanes, Total Residual Chlorine and temperature in Water Samples from Three Types of Reservoirs

higher than those of the samples from the GRP and metal tanks ($\alpha = 0.01$). Furthermore, the mean concentration of total halomethanes in the samples from the GRP tanks (24.9 ± 7.1 µg/l) was significantly higher than that for the sample from metal tanks ($\alpha = 0.05$) which amounted to 17.1 ± 4.3 µg/l. Differences in residual chlorine concentration, temperature and in the tank material (GRP as opposed to galvanised iron) may account for the lower levels of total halomethanes in metal tanks. Moreover, since both types of tanks have lids that remain partially open, the levels of halomethanes in both types of tanks are more likely to be influenced by losses due to evaportion and decay due to photoxidation than in the underground reserviors. The higher water temperature in the underground reservoirs may also have had an effect on the concentrations of halomethanes, since experimental evidence suggests that increase of the water temperature of chlorinated waters containing Br^- results in an increase in the yields of brominated halomethanes (Minear and Bird, 1980 and Oliver, 1980).

The effect of using common household filters (porous clay) on the levels of halomethanes contained in potable water was investigated by comparing their concentration in samples collected both from the tank and after filtration. The results are shown in Table 5.6 and Figure 5.5c. A slight decrease in temperature and total residual chlorine was observed which had no apparent effect on the concentration of halomethanes or the proportion of the individual compounds to the total. The mean total halomethane concentration was 26.3 ± 4.2 µg/l in the water before entering the filter, compared to 25.7 ± 4.9 µg/l after filtration. Bromoform constituted 50% of the total in both types of samples whereas $CHBr_2Cl$ and $CHCl_2Br$ formed 37% and 14% respectively.

The effect of household boilers on the concentrations of halomethanes was also investigated by comparing their concentrations in samples from the tap with those after passing through the boiler. The

Parameter	Halomethane Concentrations (μg/l)					
	Before Filtration			After Filtration		
	Mean	SD	%	Mean	SD	%
Temperature (°C)	39	2	-	35	2	-
Residual Chlorine (mg/l)	1.2	0.4	-	0.9	0.1	-
$CHCl_2Br$ (μg/l)	3.7	0.7	(14)	3.4	0.7	(13)
$CHBr_2Cl$ (μg/l)	9.7	2.0	(37)	9.4	2.1	(37)
$CHBr_3$ (μg/l)	12.9	2.0	(50)	12.9	2.2	(50)
Total (μg/l)	26.3	4.2	(101)	25.7	4.9	(100)
n=	9			9		

Table 5.6: Mean Concentrations of Halomethanes, Total Residual Chlorine and Temperature in Water Samples Taken Before and After Filtration

Parameter	Halomethane Concentrations (µg/l)					
	Tap			Boiler		
	Mean	SD	%	Mean	SD	%
Temperature (°C)	13	2	-	64	4	-
$CHCl_2Br$ (µg/l)	1.9	0.2	(9)	0.6	0.4	(7)
$CHBr_2Cl$ (µg/l)	5.6	0.4	(26)	2.3	1.1	(26)
$CHBr_3Cl$ (µg/l)	14.4	1.9	(66)	6.0	3.3	(67)
Total (µg/l)	21.9	2.4	(101)	8.9	4.9	(100)
n=	8			8		

Table 5.7: The Mean Concentrations of Total Halomethanes Detected in Samples Taken From a Household Boiler Compared to Those From the Tap

results are summarised in Tables 5.7 and Figure 5.5.d. The mean water temperature inside the boiler was 64 ± 4°C compared to 13 ± 2°C at the tap. The main concentration of total halomethanes in the samples from the boiler was 8.9 ± 4.9 µg/l which was significantly lower than that of the samples from the tap ($\alpha \leq 0.05$), which had a mean value of 21.9 ± 2.4 µg/l. This was expected due to the high volatility of halomethanes, which were apparently removed through the vent of the boiler. There was however no change in the proportions of the individual compounds perhaps because of the short residence time of the water inside the boiler prior to the collection of samples. Bromoform constituted 67% of the total in both types of samples whereas $CHBr_2Cl$ and $CHCl_2Br$ formed 26% and 8% respectively.

An in depth assessment of the potential health risks posed by the concentrations of halomethanes found in the potable water of Kuwait is clearly beyond the remit of this study. Nevertheless, it may be relevant to consider the following points which are based on the findings of this study and a limited review of the literature i) the concentrations of halomethanes indicated reflect only the levels present during the period of study and not annual averages; ii) although they were lower than the maximum contaminant limit (MCL) set by the U.S. Environmental Protection Agency of 100 µg/l (Federal Register, 1979), they were dominated not by the chloroform, but by the brominated species whose toxicity has not been as well studied. iii) tests conducted on laboratory animals have shown that when $CHCl_3$ is administered at higher doses, there is an increase in the incidence of hepatocellular carcinomas and kidney epithelial tumours (NCI, 1976). These conclusions have been supported by Theiss **et al.**, (1977) who also showed that $CHBr_3$ and $CHCl_2Br$ are more carcinogenic than $CHCl_3$ (see also Pereira **et al.**, 1982 and Morimoto and Koizumi, 1983). The median lethal dose (LD50) for $CHCl_3$, $CHCl_2Br$, $CHBr_2Cl$ and $CHBr_3$ was shown to be in the region of 1g/kg of body weight when administered orally to laboratory animals (Chu **et al.**, 1982a). In a subacute study, using oral doses containing concentrations of $CHCl_3$, $CHCl_2Br$ and $CHBr_3$ ranging from 5 to 500 ppm, an increase in the liver and kidney weights was observed. However, it was also shown that such changes are reversible when the exposure is terminated (Chu **et al.**, 1982b). The findings of other studies are in agreement with this and also suggesting that halomethanes may be tumour promoters rather than initiators (Bull, 1982 and Pereira, 1983). Moreover, Simmon and Tardiff (1978) using the Ames technique, have shown that $CHCl_2Br$ and $CHBr_3$ are both mutagenic, but not $CHCl_3$ (see also Nestmann **et al.**, (1983); iv)in terms of toxicity to man, it has been shown that halogonated organics in drinking water may exert a substantial physiological stress on exposed populations. For example, Neal (1980) has reported the findings by the National Institute of Environmental Health (U.S.A.) that total organic chlorine (TOCl) levels in human milk and blood serum averaged 0.3 ± 0.032 µg/l and 0.88 ± 0.12 µg/l respectively. These results were supported by Pfaffenberger **et al.**, (1980), who reported a median value of 12.4 µg/l of $CHCl_3$ in the serum of women from areas utilising chlorinated water supplies whereas, the median value of 6.9 µg/l was found in the plasma of women from areas utilising non-chlorinated well waters. The same authors attributed the absence of brominated halomethanes in serum to their reactivity which results in rapid metabolic transformation and excretion; v) finally, conclusions about the long term health effects on man are derived from statistical correlations between concentrations of halomethanes in water supplies and cancer mortalities, especially from gastrointestinal and bladder cancers (Page **et al.**, (1976), Cantor and McCabe, 1978; Wilkins **et al.**, (1979), Cantor, 1983, Bull, 1983 and Crump, 1983). It should be emphasised that the findings of epidemiological studies indicate that halogenated organics in drinking water supplies are a well established risk (and not a causal relationship) for gastrointestenal and bladder cancers, which should be considered while keeping in mind the limitations inherent in such studies. Some of these limitations include the temporal and spatial variability of halomethane concentration in chlorinated water supplies, the mobility of populations which complicate exposure records required for such studies (>5 years) and the presence of a large number of compounds in chlorinated waters which are not identified and which may also possess carcinogenic properties. Moreover, the fact that some of these studies have also shown high correlations between chloroform concentrations in water and cancers of biologically implausible anatomic sites such as the lungs reduces confidence in the findings for the gastrointestinal organs and the bladder (see also Burke **et al.**,(1983); Pike, 1980; Shy and Struba, 1980 and Cantor, 1983).

GENERAL CONCLUSIONS AND RECOMMENDATIONS

The results of halomethanes analyses of samples collected during the field surveys indicated that the bromine-containing compounds, especially bromoform, are the principal forms produced upon chlorination. This may be attributed to the presence of bromide ion in the brackish and potable ground waters used for blending, the higher pH value (in drinking water) and the possible carry over sea water into the distillate during the flash boiling of the recirculated brine.

The survey of the distribution of halomethanes in the coastal waters off the desalination plants indicated that the chlorination system used and the dilution potential specific for each area influences the levels and distribution of halomethanes. For example, the higher concentrations of halomethanes were encountered in the vicinity of the Shuwaikh Station where chlorine-enriched sea water is injected ahead of the intake pumps. The potential for dilution is also limited by the layout of the harbour. Changing of the chlorination method to a system similar to that being followed in the Doha and Shuaiba Stations where chlorine gas is injected into the water stream pumped into the station, should result in a reduction in both chlorine consumption and the concentrations of haloemethanes in the surrounding environment. The policy of continuously dosing with 2 mg/l of chlorine in addition to the use of periodical shock treatment with higher doses may require re-assessment. The employment of shock treatment alone may result in a reduction in chlorine consumption and may facilitate dilution of halomethanes into the marine environment. This may be especially true for the Doha area which, because of its morphology and shallowness, may accumulate higher concentration of halomethanes when the Doha West Station becomes fully operational. The results of halomethane analysis in the area show that although the concentrations are generally lower than those encounted at Shuwaikh, the concentration is distributed over a much wider area.

The study of the distribution of halomethanes in several stages of the desalination process indicates that the more recent plants (such as the "D" Units in Shuwaikh) which have a larger distillate-production capacity are likely to produce lower concentrations of halomethanes per unit of distillate produced than their older plants (e.g. the F-1 Unit). A major fraction of halomethanes produced during the process is apparently vented through the air ejectors. This point may be of importance if the vented gases are considered for utilisation as a cheap source of CO_2, the use of which has been suggested in addition to caustic soda or lime in order to increase the bicarbonate (and calcium content), thereby rendering the water less corrosive to the metal pipes and reserviors of the water supply network. Thus, the cost of removal of halomethanes and the monitoring of their levels in the water should be considered.

The concentrations of halomethanes in the drinking water supplies during the survey period averages (25.6 ± 9.1 µg/l) with a maximum of 50.5 µg/l. The principal constituents of the total were bromoform (13.6 ± 4.6 µg/l) dibromochloromethane (8.8 ± 3.7 µg/l) and dichlorobromomethane (3.3 ± 1.5 µg/l). These values are much lower than the mean concentration of halomethanes detected during USEPA's surveys of the drinking water supplies of more than 100 American cities, which indicated the dominance of the chlorine-containing compounds (Cotruvo, 1981). However, it should be noted that the bromine-containing compounds are less studied in terms of toxicity and the long term health effects of low-level exposures than chloroform. Moreover, the limit adopted by the EPA for total halomethane concentration in drinking water (100 µg/l) was based on feasibility of attainment in terms of health risk.

Another point that may need emphasis, concerns the high degree of variability that was apparent in the concentrations of total residual chlorine and halomethanes during the survey on the levels of halomethanes in drinking water. This may be attributed to several factors, among which is the fluctuations in the chlorination dose applied. The use of chlorine demand as a guideline for dosing, assisted with on-line chlorine monitors may reduce chlorine consumption (and hence cost) and consequently produce relatively less variable lower levels of halomethanes in the long run. This also applies to the chlorination practices in the desalination stations, especially in the older units. The ability to utilise the beneficial aspects of chlorination (i.e., control biofouling in the desalination plants and minimise health risks from water-borne diseases in drinking water) while taking the necessary measures to minimise its potential health and environmental deleterious effects should be a matter of policy.

Finally, based on the limited experimental work conducted it appears that petroleum hydrocarbons present in the water soluble fraction of Kuwait Crude, may cause an increase in the concentrations of halomethanes produced upon the chlorination of sea water in drinking water. This may be of special importance in view of the fact that the major petroleum-based industries and harbours of Kuwait are located in the vicinity of the desalination plants. Ammonia, on the other hand, had a strong retarding effect on the production of halomethanes in sea water upon chlorination (probably due to the formation of halamines rather than halomethanes). Thus, due to the relatively high imputs of nitrogen-containing compounds (especially ammonia) in the vicinity of the Shuaiba desalination stations, the chlorination practices may need careful examination. The speciation and fate of chlorine in sea water involves complex intereactions that are influenced by several factors (e.g. the ratio of chlorine to ammonia), which should be considered in order to optimise the utilisation of chlorine as an antifouling measure.

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