THE DISTRIBUTION, SEA WATER SOLUBILITY AND SOLID STATE SPECIATION OF SOME TRACE ELEMENTS FROM THE NORTH SEA ATMOSPHERE.

PhD THESIS

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Submitted in accordance with the regulations
of the University of Liverpool for the
degree of Doctor of Philosophy.

January 1992

Acknowledgements.

I would like to express my sincere thanks to my supervisor Prof. R. Chester for the tremendous amount of time and effort he put into helping guide me throughout my studentship.

I would also like to thank Dr K. J. T. Murphy for his support in the earlier stages of my studentship. To Dr H. Leach for helping me with the statistics and for spending much off his valuable time in discussion with myself (this was much appreciated!).

I would especially like to give thanks to Chris Ottley and Andy Rendell for helping me collect the samples on board ship. Also to Dr R. Procter for providing the air mass trajectories and Dr R. Lowry for providing the rainfall contour maps. All the Principle Scientists, Officers and Crew on board RRS Challenger throughout the North Sea Project.

Finally, and most importantly I give my thanks to the Pos♥ (Jane Louise Merrett), the lads (all fifteen) and the Plum☺ (Maxwell Hansom Academic), for all those possy + plummy moments.

To the Pos ♥ and Plum ☺.

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Chapter 1

1.1 Introduction.

The dispersion of solid or liquid particles in a gaseous media is defined as an aerosol, where particles correspond to a small discrete mass of solid or liquid matter (Harrison and Perry, 1986). This particulate matter has a lower size limit of $1\times10^{-3}\mu m$ and an upper size limit of $100\mu m$ diameter (Lodge et al, 1981).

On average, the world aerosol consists of ~80 - 90% inorganic material: mainly sulphate, nitrate, crustal dust and sea salt. Factors influencing the concentrations of particles in the atmosphere include the following: (a) particle sources and emission rates; (b) chemical reactions in the atmosphere, (c) the location and time, and (d) the efficiency of particle removal processes by wet (rainfall) and dry deposition (see e.g.: Duffus, 1980; Dehairs et al., 1983; Brimblecombe, 1986). As a result of the interplay of these various factors the concentrations of particles in the atmosphere can vary considerably in both space and time.

1.2 The Composition of the Marine Aerosol.

Prospero et al., (1983), defined a number of aerosol types on the basis of their compositions and sources, and a summary of their classifications is given in Table 1.1. The components that make up the world aerosol originate

Table 1.1 The classification of aerosols on the basis of their composition or sources*.

1. **Natural Aerosols.**
    - 1.1 Sea spray residue.
    - 1.2 Windblown mineral dust.
    - 1.3 Volcanic effluvia.
    - 1.4 Biogenic materials.
    - 1.5 Smoke from the burning of land biota.
    - 1.6 Natural gas-to-particle conversion products.
2. **Anthropogenic Aerosols.**
    - 2.1 Direct anthropogenic particle emissions.
    - 2.2 Products from the conversion of anthropogenic gases.

* based on Prospero et al., (1983).

from two different kinds of processes: (a) direct formation (e.g. crustal weathering, sea salt generation and volcanic emissions), and (b) indirect formation of particles in the atmosphere by chemical reactions, and by the condensation of gases and vapours. Sources of atmospheric particulate material have been listed by Riley and Chester (1971), and Sanders (1983), and estimates of the contributions made by these sources to the trace element constituent of the atmospheric aerosol have been made by Niragu (1989) and Pacyna (1986b), both of whom summarised the available world wide emission data for both natural and anthropogenic atmospheric sources. These data are summarised in Table 1.2, and indicate that man-made, (i.e. anthropogenic) sources contribute large quantities of trace elements to the atmosphere. However, there are differences between the various estimates. For example Niragu (1989), gives lower anthropogenic atmospheric Pb emission rates, due to the reduction of Pb emissions and a substantially larger natural input of Zn, because of the revised estimate of natural biogenic emissions than does Pacyna (1986b). Important factors controlling the emissions of anthropogenic particles into the atmosphere include the volatility of the elements, and their usage in industrial applications.

1.3 The Size Distribution of Aerosol Particles

The shapes of atmospheric particles are rarely uniform (Brimblecombe, 1986). Expressions used to describe the size

Table 1.2 A comparison of natural and anthropogenic emissions of trace elements to the atmosphere in 1979 (Pacyna, 1986b), and in 1983 (Nriagu, 1989).

	Pacyna (1986b) Annual emission x 10^9 gyr^{-1}		Nriagu (1989) Annual emission x 10^9 gyr^{-1}	
Element	Natural	Anthropogenic	Natural	Anthropogenic
Cd	0.96	7.3	1.3	7.6
Cu	18.9	56	28	35
Mn	516	-	317	38
Ni	26	47	30	56
Pb	18.6	449	12	332
Zn	0.6	314	45	132

Taken from Yaqqub (1989).

of aerosols are geometric size, optical size and aerodynamic size (Lodge et al., 1981; Harrison and Perry, 1986). Due to the variation in the shape and density of an aerosol particle it is convenient to define an equivalent aerodynamic radius (Brimblecombe, 1986); this is, the radius of a sphere of unit specific gravity having the same fall velocity as the particle in question. Studies by Whitby (1977), Willeke and Whitby (1975) and Slinn (1983), have suggested that atmospheric particles in general have a multi-modal distribution. A generalised relationship between (a) The processes responsible for the generation of aerosol particles, and (b) The size spectra of particles is illustrated in Figure 1.1. The Figure shows three modal peaks, together with the particle formation and removal mechanisms. These peaks are associated with the following particles:

(1) Particles < 0.1μm in diameter.

These atmospheric particles always have a combustion source (Whitby, 1977; Pacyna et al., 1984a; Oblad and Selin, 1986). The aerosol sub-population is known as the nuclei mode, in which particles are formed by condensation and disappear quickly by coagulation (Lodge et al., 1981; Whitby, 1977). Particles of this size are important in affecting the visibility of the atmosphere (Hopke et al., 1984).

(2) Particles with the size range of 0.1-2μm diameter.

This population of atmospheric particles is known as the accumulation mode (Noller et al., 1981, Lodge et al.,

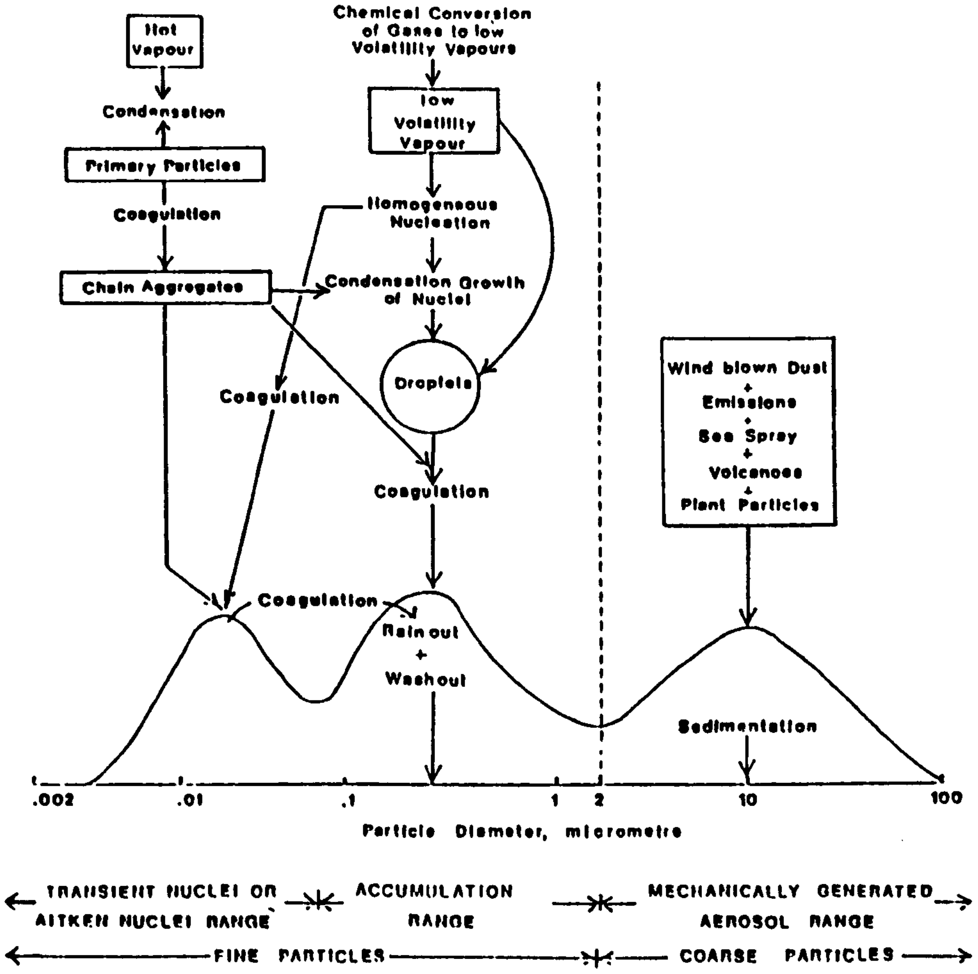

Figure 1.1 Schematic digram of the processes involved in the formation of the three modes of atmospheric particles and an example of a surface area distribution of the particles (Whitby, 1977).

1981), and is usually formed either by the coagulation of primary particles, or by the condensation of reaction products, or water, onto primary particles (Whitby 1977).

The nuclei and accumulation mode particles are termed 'fine particles' and their predominant man-made source is the combustion, or condensation, of chemical or photochemical reaction products on nuclei from combustion (Whitby, 1977, Harrison and Perry, 1986).

(3) Particles > 2.0μm in diameter.

This type of atmospheric particle can be formed in a number of ways, which include the following. (1) as a result of mechanical processes, e.g. erosion and sea spray (Martinson et el. 1984; Oblad and Selin, 1986), (2) as the result of the incomplete combustion of other particles (Wadge et at. 1986), and (3) as a result of the re-suspension of precipitated dust in the free atmosphere (Nicholson, 1988a). The > 2μm sized particle population is known as the coarse particle mode. These particles have a limited residence time in the atmosphere (typically only a few days), as a result of their high settling velocities (Arimoto and Duce, 1987). However, it should be noted that unstable weather, e.g. high wind speeds, can prolong the lifetime of coarse particles in the atmosphere and can transport them over greater than normal distances.

Each of these three particle classes can be described by a log normal size distribution in terms of the particle number, mass or volume (Lodge et al., 1981; Whitby, 1977).

The formula with respect to the number is given by the equation;

$$dN = \frac{C\ r^{-b}}{d\log_{(r)}} \qquad \text{Equation 1.1}$$

Where; N = the number of particles.

r = the radius.

C and B = constants.

A plot of $dN/d\log_{(r)}$ against the size gives the log normal distribution and is shown in Figure 1.2 (Junge, 1963; Brimblecombe, 1986). This figure illustrates that the number concentration decreases very rapidly with size. Slinn (1983), plotted a surface area distribution for aerosol particles. This is illustrated in Figure 1.3, and shows a multi modal distribution for atmospheric particles of different origins. (1) Aerosols having a continental origin show a bimodal distribution, the smaller particles being in the nuclei mode, and the larger particles in the accumulation mode. (2) Urban aerosol particles have a tri-modal distribution arising from different particle sources.

Close to the source, the composition of a specific aerosol component, such as a mineral dust, will be closely related to that of the parent material. However, during their residence time in the atmosphere both coarse and fine particles can undergo physical and chemical modifications, and as a result the character of an aerosol will change with increasing distance from the source, this is termed

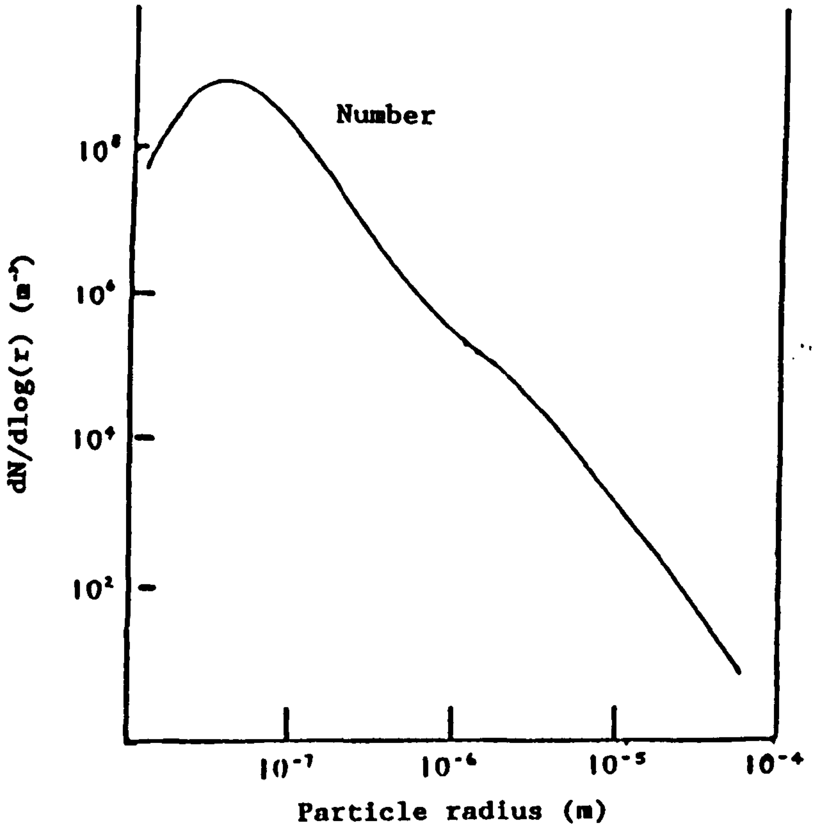

Figure 1.2 A concentration distribution for a typical continental aerosol (taken from Brimblecombe, 1986).

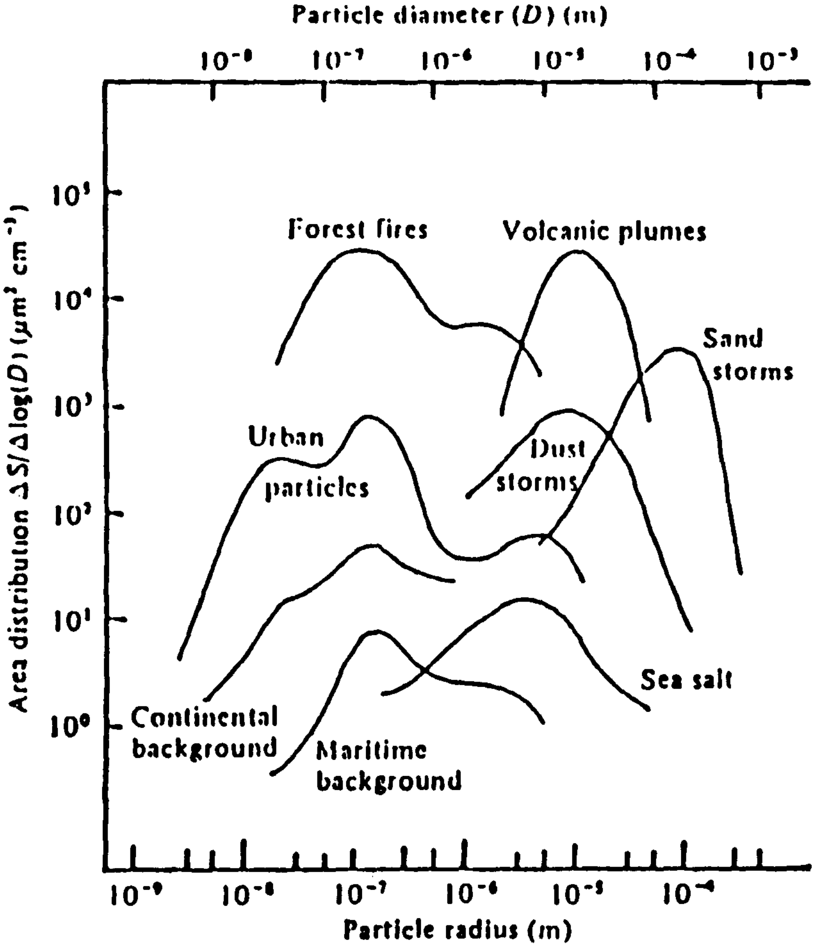

Figure 1.3 The area distribution proposed by Slinn (1983) for different types of atmospheric particles (taken from Brimblecombe, 1986).

'ageing'. For example, as the concentration falls off, the particle size distribution is altered, and the chemical composition tends to become more uniform. As a consequence aerosols are the end product of a complex series of processes and should be regarded as a 'dynamic aerosol continuum' (Prospero et al., 1983).

The particle size distribution at any one location can vary with time; e.g. a shift towards a smaller size distribution from summer to winter was reported by Oblad and Selin (1986), for aerosols off the west coast of Sweden. The authors related this shift to three principle factors; (1) A longer transport route for the winter particle, (2) The faster removal of the larger particles by rain or snow in winter, and (3) Less convection activity in the winter which causes the large particles to have shorter residence times in the atmosphere.

1.4 The Transport of Atmospheric Aerosols.

A particle emitted into the atmosphere will have its behaviour influenced by the physical and chemical nature of the atmosphere. Dilution, dispersion transport, chemical transformation and deposition will define the pathway of the particle through the atmosphere. Factors effecting the dispersion and transportation of the particles include the depth of the mixing layer, precipitation, the stability of the atmosphere, and wind speed and direction.

The transport of aerosols within the troposphere takes place via the major wind systems, which operate on a global

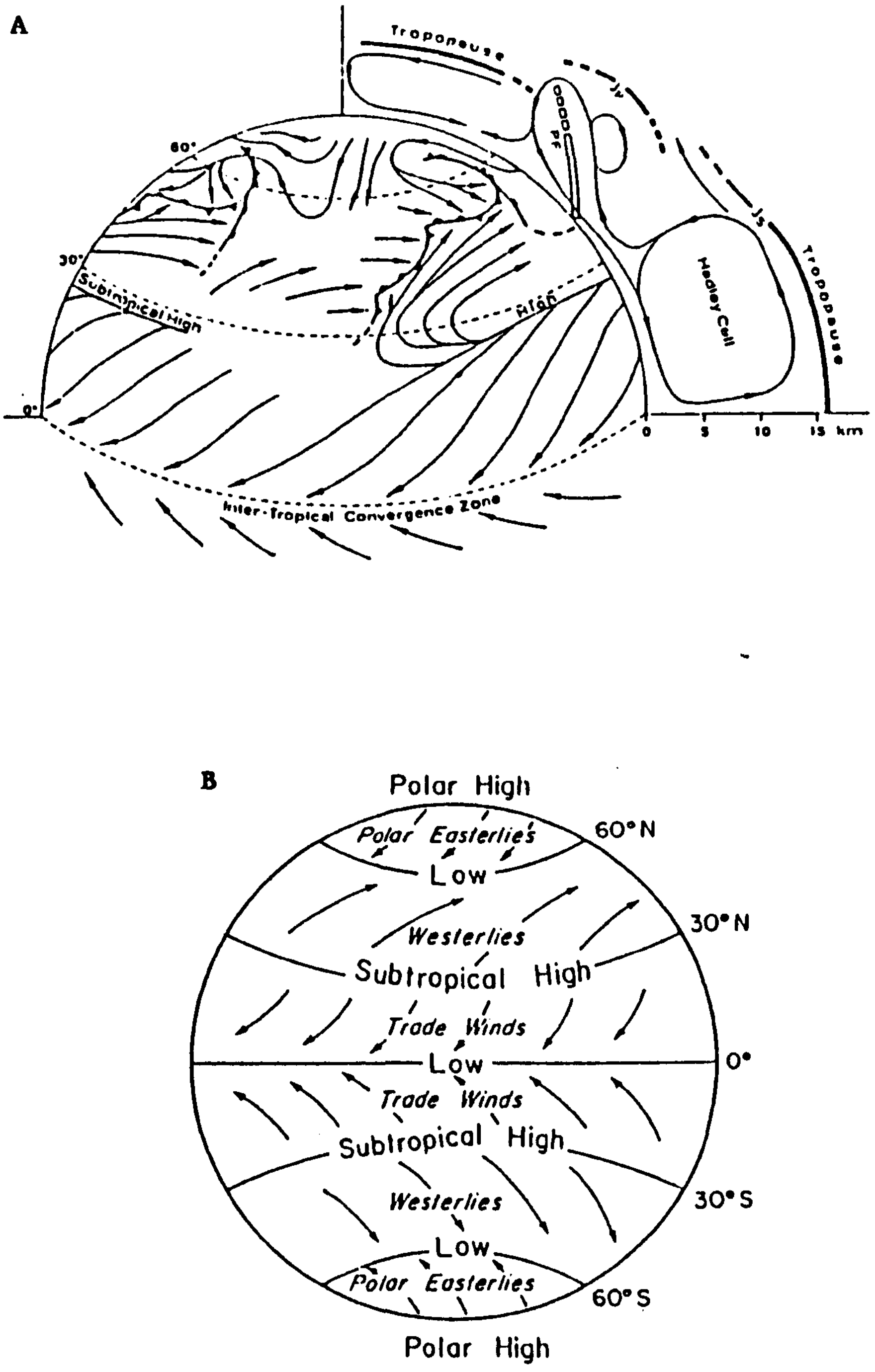

Figure 1.4 Circulation in the atmosphere. A) Schematic representation of the general circulation in the atmosphere at the surface and a meridional cross section (from Hasse 1983, after Defant and Defant 1958). J_p and J_s indicate the average positions of the Polar Front (PF) and the Subtropical Jet Streams. B) Schematic representation of the surface wind distribution (from Iribarne and Cho, 1980).

scale. Figure 1.4 gives a schematic representation of the general circulation of the atmosphere. Most of the continentally-derived material (both natural and anthropogenic), which contributes to the World Aerosol is initially injected into the planetary boundary layer of the atmosphere. This layer has a height of ~1000 to ~1500 m over the land and ~300 to ~600 m over the sea, and is directly influenced by the underlying surface (Hasse, 1983). The upper surface of the boundary layer is defined by an inversion, which inhibits the transfer of material to the upper atmosphere (Prospero 1981). According to Prospero (1981), the primary path for the transport of continentally-derived material reaching the sea surface, within tens to hundreds of kilometres from the continents, is via this marine boundary layer. Over longer distances, however, the major transport path is probably via the free troposphere above the marine boundary layer. As a result, at remote marine regions continentally-derived material in the boundary layer will have been transferred from the overlying atmosphere. It is apparent, therefore, that the rate of exchange between the free troposphere and the boundary layer will affect the distance an aerosol component can be transported in the atmosphere. It is worth mentioning at this point that most collections of marine aerosols are made in the boundary layer, and are thus probably not representative of the concentrations at higher levels in the troposphere.

The long-range transport of particulate material has been well documented. For example, Duce et al., (1980, 1983a), and Suzuki and Tsunugai (1988), observed a significant transport of contaminated aerosol from Asian sources to a large area of the North Pacific. Similarly Rahn et al., (1982), revealed that Arctic aerosols during the winter comprised a high proportion of particulate material transported from Eurasia. Another example of long-range atmospheric sampling is that the red soil sometimes appearing on the European continent can be attributed to dust from Africa (Reiff et al., 1986). Thus, Dedeurwarder (1988), used air mass back trajectories to identify air flow patterns which indicated the long-range transport of Sahara dust to the Southern Bight of the North Sea. However, the North Sea can be considered as a 'coastal Sea' with the majority of the atmospheric particulate material being transported and deposited from the marine boundary layer.

1.5 The Chemistry of the Marine Aerosol.

1.5.1. The Chemical Composition of the Marine Aerosol.

The concentrations of particulate elements in the marine atmosphere can vary over several orders of magnitude, see Table 1.3. At any specific location the concentrations of elements in the marine aerosol are dependant on a number of factors. According to Chester (1990), these include; the efficiency with which host components are mobilised into, transported through, and

Table 1.3 The concentration ranges of some elements in the marine aerosol.

Element	Estimated concentration range* (ng m^{-3} of air)
Al	1 - 10^4
Fe	1 - 10^4
Mn	0.1 - 10^2
Cu	0.1 - 10^1
Zn	0.1 - 10^2
Pb	0.1 - 10^2

* Approximate values only.
Taken from Chester 1990.

removed from the atmosphere, and the extent to which the parent aerosol has 'aged'. Berg and Winchester (1978), suggested that the composition of the marine aerosol resembles that expected from the mixing of small sized material from large scale sources.

The three principle sources of most elements to the marine aerosol are; (1) the Earth's crust, (2) the sea surface, and (3) anthropogenic activity.

1.5.2 Methods of Identifying the Sources of Elements in Aerosols.

1.5.2.1 Assessment of Elemental Source Contributions to an Aerosol Using the E.F. Concept.

The most commonly used method of relating an element in an aerosol to its source is to use a source indicator which is derived from one specific source. This source indicator is then used in an enrichment factor (EF), which is calculated by an equation of the type;

$$EF_{source} = \frac{(E/I)_{air}}{(E/I)_{source}} \qquad \text{Equation 1.2}$$

where $(E/I)_{air}$ = the ratio of the concentration of an element E and the indicator element in the aerosol.

$(E/I)_{source}$ = the ratio of their concentrations in the source material.

The two most important natural sources for the low temperature generation of material to the atmosphere are the Earth's crust and the sea surface. Crust-derived continental dusts, and ocean-derived sea salts, are ubiquitous components of the marine aerosol and are usually present in varying concentrations in the atmosphere at all marine locations. It is important therefore, to assess the contribution of these two sources to the chemistry of the marine aerosol, and this can be done using Enrichment Factors (EF's).

1.5.2.1.1 The Earths Crust as a Source of Trace Elements to the Marine Aerosol.

Al is normally used as the crustal indicator element, although Fe has been used in some studies (see e.g.; Adams et al., 1980). However, there are problems in the selection of a reference composition for the crustal source material. Crustal material is supplied to the atmosphere as a result of the wind erosion of surface soil deposits, and ideally these soils would be used as a reference composition. In practice, however, more reliable data are available for the composition of average crustal rocks, and it is these which are usually used in the calculation of EF_{crust} values. There are several compilations of elemental abundances in crustal rocks available, and in the present work that of Taylor (1964), has been used in the EF_{crust} calculations. However, there are several uncertainties associated with this approach. For example, the physical and chemical processes which occur during the transformation of crustal material to soils are complex, and may result in considerable chemical alterations (see e.g.; Hunt 1972). Furthermore, the fractionation of crust-derived soil material will also occur in the atmosphere itself. For example, in general, small-sized particles will be transported greater distances than large-sized particles, and this may lead to differences in concentration for elements which are associated with host materials of specific particulate sizes. Despite these difficulties EF_{crust} values are usually calculated using the average composition of crustal rock as a reference material according to the equation;

$$EF_{crust} = \frac{([E]/[Al])_{air}}{([E]/[Al])_{crust}} \qquad \text{Equation 1.3}$$

where; $([E]/[Al])_{air}$ = the element to Al concentration in the aerosol.

$([E]/[Al])_{crust}$ = the element to Al concentration in average crustal rock.

Because of the uncertainties discussed above EF_{crust} values are best viewed as only order of magnitude indicators of a crustal source. That is; (1) EF_{crust} values close to unity are taken to indicate that an element has a predominantly crustal origin, and these elements are termed the non-enriched elements (NEE), and (2) EF_{crust} values > 10 are taken to indicate that a substantial portion of the element is of non-crustal origin, and these elements are termed the anomalously-enriched elements (AEE).

1.5.2.1.2 The Sea as a Source of Trace Elements to the Marine Aerosol.

The surface of the sea can be an important source of particulate material to the marine aerosol. To assess the importance of this source Na can be used as the marine indicator element and the composition of bulk sea water can be used as the source composition.

The EF_{sea} can then be calculated using the equation;

$$EF_{sea} = \frac{[E/Na]_{air}}{[E/Na]_{sea\ water}} \qquad \text{Equation 1.4}$$

where; $[E/Na]_{air}$ = the ratio of the concentrations of an element E and Na in the aerosol.

$[E/Na]_{sea\ water}$ = the ratio of their concentrations in bulk sea water.

The EF_{sea} values for aerosols in a number of marine regions, ranked on a basis of their increasing distance from the continents is given in Table 1.4. However, it must be pointed out that the calculation of EF_{sea} values present problems that are considerably more complicated than those associated with EF_{crust} values. These problems involve the selection of a composition for the precursor material,

Table 1.4 EF_{sea} values for a number of elements in the marine aerosol*.

Element	EF_{sea}		
	North Atlantic	North Pacific Hawaii	North Pacific Enetwak
K	1.3	1.1	1.3
Mg	0.9	1.0	1.1
Al	1×10^6	3×10^5	1×10^5
Co	8×10^3	$<1 \times 10^3$	1×10^3
Cu	6×10^4	7×10^3	3×10^3
Fe	4×10^7	6×10^5	3×10^4
Mn	4×10^5	8×10^3	2×10^4
Pb	5×10^5	5×10^5	3×10^4
V	9×10^3	4×10^2	2×10^2
Zn	2×10^6	4×10^2	2×10^2
Sc	1×10^5	-	4×10^4

Mo	U.K. coastal aerosol	N.Atlantic Westerlies	Atlantic N.E. trades	Atlantic S.E trades	South Atlantic westerlies
	116	20	13	9.5	1.4

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* Data for Mo from Chester et al., (1984); data for all other elements from Weisel et al., (1984).

particularly in response to the nature of the processes involved in the generation of sea salts.

During the bursting of bubbles, which is the principle mechanism in sea salt formation, part of the sea surface microlayer can be skimmed off to be incorporated into the salt particles. This microlayer can contain concentrations of some trace elements which are enhanced up to $1x10^3$ - $1x10^7$ times relative to bulk sea water. As a result, considerable fractionation of these trace elements can take place during formation of sea salts, so that bulk sea water is not the immediate oceanic source of the trace elements. There have been a number of attempts made to evaluate a more realistic source composition for material generated from the sea surface by relating the material directly to the microlayer itself. One of these involves the collection and analysis of bubble-produced sea salts using the Bubble Interfacial Microlayer Sampler (BIMS) (see e.g.: Fasching et al., 1974; Piotrowicz et al., 1979).

BIMS EF_{sea} values take account of the enrichment of trace elements on sea salt with respect to sea water. In a recent study, Weisel et al., (1984), presented data for BIMS EF_{sea} values over the North Atlantic and a summary of these is given Table 1.5. From studying the data in Table 1.5, it can be seen that there are broadly two groups of trace elements, and these are described as follows;

<u>Group 1</u> contains K and Mg. These elements have average Bims EF_{sea} values of unity as they did in bulk sea water. That is

Table 1.5 BIMS EF_{sea} values determined over the North Atlantic Ocean*

Element	BIMS EF_{sea}
K	1.0
Mg	1.0
Al	5×10^3
Co	6×10^2
Cu	8×10^2
Fe	1×10^4
Mn	1×10^3
Pb	4×10^3
V	1×10^2
Zn	2×10^4

* Data from Weisel et al., (1984).
Taken from Chester 1990.

these elements, together with Na, retain their original bulk sea water ratios on bubble-generated salts, and <u>Group 2</u> contains Al, Fe, Mn, Co, V, Cu, Zn, Pb and Sc. These elements have relatively high BIMS EF_{sea} values, ranging from 10 for Sc to 20,000 for Zn, and apparently undergo fractionation at the sea surface.

Despite the difficulties inherent in assessing the fractionation of elements at the air/sea interface, the BIMS EF_{sea} data provide at least a first approximation of the degree to which fractionation has taken place. Further, by making the assumption that BIMS EF_{sea} values found for the North Atlantic apply globally, Weisel et al., (1984), introduced the important concept of relative oceanic enrichment factor (REF_{sea}), which is the aerosol EF_{sea} value (calculated with respect to bulk sea water) divided by the BIMS EF_{sea} value. The REF_{sea} values therefore directly relate the enrichment of an element in a marine aerosol to the fractionation that occurs at the sea surface, and so offer a more realistic assessment of the ocean as a source material. The REF_{sea} values will approach unity if the sea surface is a significant source of trace element and this is evaluated with respect to a number of marine aerosol regions in Table 1.6. In the Table the BIMS EF_{sea} values are expressed as a percentage of the EF_{sea} value (i.e that obtained using bulk sea water), and the REF_{sea} values are also given. From these data it can be seen that for Al, Co, Mn, and Pb, the BIMS EF_{sea} values are < 10% of the EF_{sea} values, and for these elements the sea surface is a trivial

Table 1.6 Sea surface sources of trace elements in marine aerosol populations.

Element	North Atlantic		North Pacific			
			Hawaii		Enewetak	
	BIMS EF_{sea} as a % of aerosol EF_{sea}	REF_{sea}	BIMS EF_{sea} as a % of aerosol EF_{sea}	REF_{sea}	BIMS EF_{sea} as a % of aerosol EF_{sea}	REF_{sea}
Al	0.5	200	1.6	6	5	20
Co	0.75	133	6	17	6	17
Mn	0.25	400	12	8	5	20
Cu	1.3	75	11	8.75	27	3.75
V	1.1	90	25	4	50	2
Zn	1	100	3	30	20	5
Pb	0.8	125	0.8	125	10	7.5

[*] Original data from Wiesel et al., (1984).
Taken from Chester 1990.

source even at the remote site Enewetak. For V, Cu and Zn, however, the BIMS EF_{sea} values are > 20% of the EF_{sea} values for the Enewetak population, indicating that at some remote sites the sea surface becomes a non-trivial source for these elements; this was later confirmed by Arimoto et al., (1987), for aerosols at the remote Samoa (South Pacific) site. However, extreme caution must be taken when attempting to interpret the enrichment of elements on sea salts. One reason for this being that particulates deposited onto the sea surface from the atmosphere can be recycled back into the air during sea salt production. For example, Settle and Patterson (1982), showed that much of the Pb in the sea salt aerosol may have originated from Pb-rich atmospheric particles that have been recycled from the microlayer. Recycling of this kind therefore makes it difficult to estimate the true net flux of elements from the ocean surface to the atmosphere. Another factor that can complicate the assessment of fluxes of elements from the sea surface is the formation of particulate components from gaseous emissions from sea water, since these will have a small particle, and not a sea salt particle size (see Section 1.5.3). For example, Mosher et al., (1987), gave data on the distribution of Se in the Pacific atmosphere. Although the element is concentrated on particles with a Mass Median Diameter (MMD), of 1.5μm, the authors concluded that the enrichment of the element on the marine aerosols is a sea surface phenomenon, and can be explained by the gas-to-particle conversion of a natural vapour-phase flux generated by biologically mediated reactions associated with primary production. The ocean-to-atmosphere vapour phase selenium flux was estimated to be ~(5-8) x 10^9 g yr^{-1}, ~ 40% of which is derived from highly productive upwelling waters of the equatorial and sub-polar regions. This natural ocean-to-atmosphere Se flux is the same order of magnitude as the total anthropogenic emissions of atmospheric Se, i.e. ~7 x 10^9 g yr^{-1}, thus demonstrating the important role played by the sea-surface recycling in the atmospheric budget of Se.

1.5.2.1.3 Pollution as a Source of Trace Elements to the Marine Aerosol.

Material of anthropogenic origin is released to the atmosphere by a variety of industrial, social and agricultural activities. These include the combustion of fossil fuels, the incineration of wastes, the smelting of ores and the combustion of leaded petrol in automobiles (see e.g.: Patterson et al., 1976; Greenberg et al., 1978).

A combination of EF_{crust}, and EF_{sea} enrichment factors can be used to identify those elements which are enriched in the marine aerosol relative to both crustal and sea surface sources. These are termed the Anomously Enriched Elements (AEEs, see Section 1.5.2.1.1), and are assumed to have originated largely from anthropogenic sources. However, there is no indicator element which can be used to characterise the anthropogenic source composition; i.e. there is no element that is specific to this source alone.

However, two other parameters can be used to characterise the anthropogenic source. These are particle size and the solid state speciation of elements in the marine aerosol.

1.5.3 The Size Distribution of Elements in the Marine Aerosol.

The size of an atmospheric particulate containing an element is controlled by the manner in which the element is incorporated into its host component, which in turn is a function of its source. Figure 1.1 identifies two general particle populations. (a) Mechanically generated "coarse" particles with diameters ≥ 2μm. This population includes sea salts and crust generated components, which acquire their elements directly from the precursor material. (b) Particles in the "accumulation", or Aitken nuclei, with diameters ≤ 2μm, which are formed by processes such as condensations and gas-to-particle conversions. Elements can become associated with these particles during high-temperature processes (e.g. volcanic activity, fossil fuel combustion, waste incineration and the processing of ore materials). This aerosol population also includes elements that can be volatilised directly from the parent material into the vapour phase. Gas-to-particle and condensation processes remove volatilised elements from the vapour phase, during which the elements can be adsorbed onto ambient aerosol surfaces. These processes are size dependant because, in general, small particle condensation nuclei will have a large surface area to volume ratio (see e.g.; Rahn 1976). Consequently, many of the elements released during high-temperature processes will associate with small particles in the accumulation range; i.e. with diameters of ≤ 0.1 - 2μm (see Section 1.3).

Because of the different processes involved in the generation of their host particles, elements having a crustal, or an oceanic, source should be present in association with larger (≥ 2μm diameter) particles, whereas those having a high-temperature source should be found on smaller (≤ 2μm diameter) particles. There are also differences in the particle size distributions of the mechanically-generated crustal and sea salt generated aerosols.

The particle size distribution of an element in an aerosol population should therefore offer an insight into its source. This has been demonstrated in a number of studies. For example, Figure 1.5 illustrates the mass particle size distributions of; (a) ^{210}Pb, which altough not originating from high temperature processes can be used as an example of an element that has a mass predominantly associated with submicrometer-derived particles typical of many high-temperature-generated, pollutant-derived elements, (b) Al, which is typical of crust-derived elements, and (c) Na, which is typical of sea salt derived elements. From data such as these, three general conclusions can be drawn regarding the particle size distributions of elements in the marine aerosol (see Chester 1990), and these are summarised as follows;

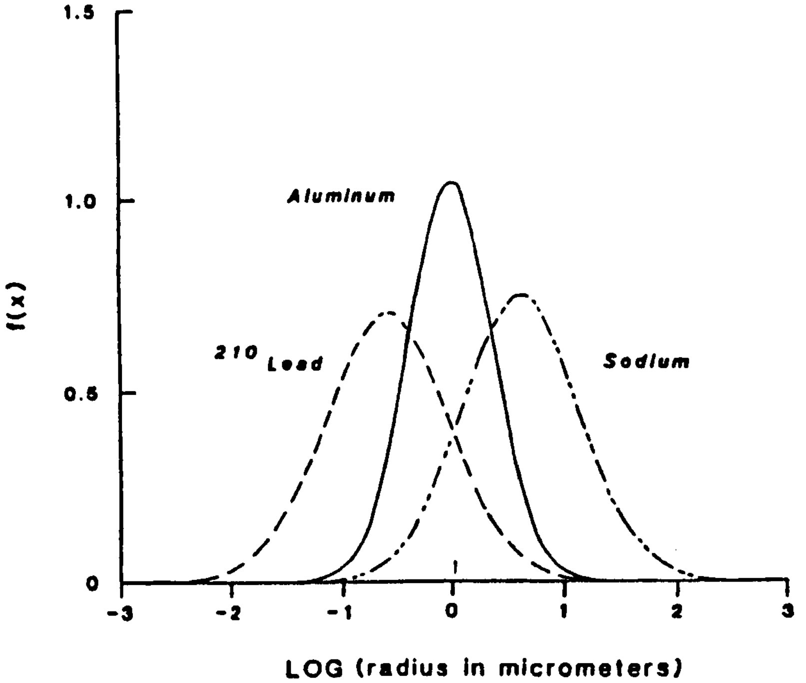

Figure 1.5 Mass size distributions of Pb^{210}, Al and Na in aerosols from the marine atmosphere (from Arimoto and Duce 1986).

(1) Sea salt associated elements have most of their mass on particles with MMD in the range 3~7μm; these elements include Na, Ca, Mg and K.

(2) Crust-derived elements have most of their total mass on particles in the range MMD 1~3μm; these elements include the NEE Al, Sc, Fe, Co, V, Cs, Ce, Rb, Eu, Hf.

(3) Elements associated with high-temperature sources (mainly anthropogenic) have most of their total mass on particles with MMDs ~ of < 0.5μm; these elements include the AEE Pb, Zn, Cu, Cd and Sb.

It must be stressed, however, that the particle size characteristics of some elements in an aerosol can change as source influences change. For example, under certain circumstances, (e.g. a Saharan pulse), some of the AEE can be crust controlled, resulting in their size distribution being dominated by particles with a MMD in the 1-3μm crustal range. In remote regions, some trace elements in aerosols have a significant source from the sea surface, which will be concentrated on particles with MMD in the 3-7μm sea salt range. An example of how the size distribution of the AEEs changed in response to changes in their sources was demonstrated for the aerosol collected at Enewetak (North Pacific) by Duce et al, (1983a). These authors showed that during the wet, 'low dust' season, when crust-derived components were at a minimum, Cu and Zn were associated predominantly with sea salt and anthropogenic sized particles. However, during the dry, 'high dust' season, when the concentrations of the crust-derived material was highest, the Cu and Zn were associated mainly with crustal and anthropogenic sized particles.

It may be concluded that the distributions of elements between the three particle classes within an aerosol population, combined with EF data, can be used to establish the relative importance of their anthropogenic, crustal and sea salt sources.

1.5.4 The Solid State Speciation of Elements in the Marine Aerosol.

Information on the sources of elements in the marine aerosol can be revealed by solid state speciation studies; i.e. by the partitioning of elements among the components of an aerosol. This can be illustrated by two recent studies carried out on the speciation of elements in urban and crustal end-member aerosols. (1) Lum et al., (1982), used urban particulate material (UPM) collected at St. Louis USA as an example of a pollution-dominated (high-temperature-generated) urban aerosol end-member, and (2) Chester et al., (1986), used a series of soil-sized particulates collected in the north east trades off the coast of west Africa as an example of the crustal low-temperature generated end-member aerosol. The speciation schemes employed in the two studies were generally similar, and both identified a 'least mobile' residual fraction and a 'most mobile' loosely-held fraction. Figure 1.6 illustrates the partitioning signatures of a number of elements in the two end-member aerosols. From this figure

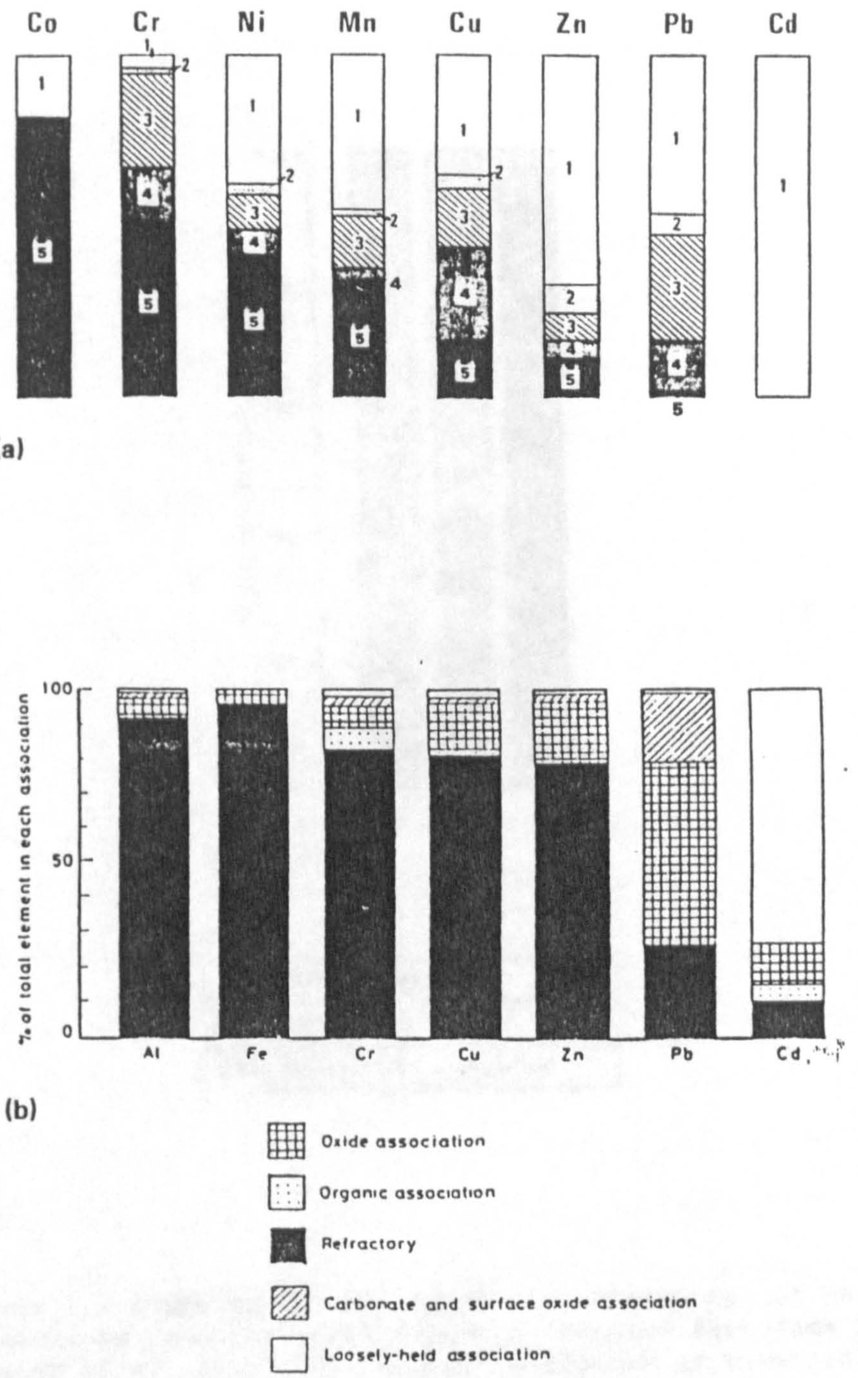

Figure 1.6 The partitioning of elements in aerosols. (a) High-temperature-generated aerosols (modified from Salomons and Forstner 1984; original data from Lum et al. 1982). 1 Exchangeable (or loosely held) association. 2 Surface oxide and carbonate association. 3 Oxide association. 4 Organic association. 5 Residual, or refractory, association. (b) Low-temperature-generated crustal aerosols (from Chester et al. 1986).

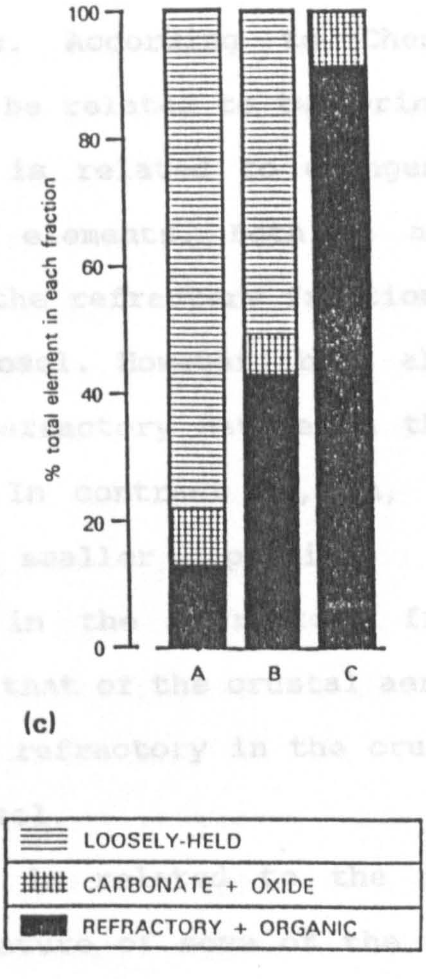

Figure 1.6 (cont'd) (c) The speciation signatures of Zn in aerosols from the North Atlantic (adapted from data in Chester et al. 1988). A, Aerosols collected at Liverpool, representative of a European coastal urban-dominated population. B, Aerosols collected around Cape Verde, representative of a mixed North Atlantic population. C, Aerosols collected in the Atlantic North East trades, representative of a crust-dominated population. Note how the proportion of the loosely-bound Zn decreases in the sequence urban-dominated > mixed > crust-dominated aerosols. Taken from Chester (1990).

it can be seen that the speciation signatures of some elements are considerably different between the two end-member aerosols. According to Chester (1990), these differences can be related to two principle trends.

(1) This trend is related to changes in the refractory nature of some elements. Both Al and Fe have smaller percentages in the refractory fraction of the UPM than in the crustal aerosol. However, both elements still retain their overall refractory nature in the anthropogenically generated UPM. In contrast Pb, Zn, Cu and Cd all have substantially smaller portions of their total concentrations in the refractory fraction of the UPM aerosol than in that of the crustal aerosol. Thus, Zn falls from being ~80% refractory in the crustal aerosol to ~15% in the UPM aerosol.

(2) This trend is related to the manner in which the loosely-bound nature of some of the elements varies. For Al, Fe and Cr, < 5% of their total concentrations are held in this association in both aerosol end-members. However, Cu, Zn, Pb and Cd show relatively large increases in the percentages of the loosely-bound associations in the UPM. Zn shows the strongest effect with ~65% of its total concentration found in the loosely-bound fraction in the UPM, compared to ~ 5% found in the loosely bound fraction in the crustal material.

In summary; the more volatile elements (e.g. Cd, Pb, Zn and Cu), become increasingly more loosely-bound in character in the UPM relative to the crustal aerosol end-member. This is consistent with the release of these elements into the vapour phase, and their subsequent uptake onto ambient particles, during high-temperature processes. The extent to which the volatile elements are in the loosely-bound associations in the marine aerosol will vary with the extent to which the end-member aerosols are mixed in the marine atmosphere. This was demonstrated by Chester et al., (1988), who provided speciation data on a number of elements in the North Atlantic aerosol. These authors applied a three stage leaching technique to a series of filter-collected aerosol particles on a north-south transect from the European coast to the north east trades off the coast of West Africa. The data showed a decrease in the loosely-bound nature of Zn, Pb and Cu along the transect. This was illustrated with respect to Zn, for which the loosely-bound fraction of the element in the aerosol decreased away from the european pollutant sources. Thus, the solid state speciation of some elements in the marine aerosol can provide data on these sources.

1.5.5 The Source Strength of Elements to the Marine Aerosol.

There have been a number of attempts to estimate the global source strengths of elements to the atmosphere. Large uncertainties are involved in making these estimates, but a number of overall trends in the elemental atmospheric source strengths can be identified from published data. Lantzy and Mallard (1979), compiled data on the natural and anthropogenic global source strengths of elements released into the atmosphere and used an atmospheric interference factor (AIF) to compare the strengths of natural and anthropogenic sources. The AIF was calculated using the equation;

$$AIF = (E_a/E_n) \times 100 \qquad \text{Equation 1.5}$$

where; E_a = the total anthropogenic emission of an element E.

E_n = the total natural emission of that element.

An AIF of 100 indicates the anthropogenic flux of an element is equal to its natural flux. Table 1.7 lists data for the global atmospheric source strengths, and the AIF values, for a series of elements. The elements in this table fall into three main groups, and these are as follows;

(1) Al, Ti, Fe, Mn and Co have AIF values < 100 and are dominated by natural fluxes to the atmosphere.

(2) Cr, V and Ni have AIF values in the range 100-500 indicating that anthropogenic fluxes are in excess of natural fluxes, but only by factors < 5.

(3) Sn, Cu, Cd, Zn, As, Se, Mo, Hg, and Pb have AIF values ranging from 500-35,000, and are dominated by anthropogenic fluxes.

When considering the World Aerosol, however, it must be remembered that ~90% of anthropogenic fluxes are

Table 1.7 Natural and anthropogenic sources of atmospheric emissions[a] (units, 10^8 gyr^{-1}).

Element	Continental Dust Flux	Volcanic Dust Flux	Volcanic Gas Flux	Industrial Particulate Emissions	Fossil Fuel Flux	Total Emissions Industrial Fossil Fuel	Atmospheric[b] Interference Factor (%).
Al	356,500	132,750	8.4	40,000	32,000	72,000	15
Ti	23,000	12,000	-	3,600	1,600	5,200	15
Sm	32	9	-	7	5	12	29
Fe	190,000	87,750	3.7	75,000	32,000	107,000	39
Mn	4,250	1,800	2.1	3,000	160	3,160	52
Co	40	30	0.04	24	20	44	63
Cr	500	84	0.005	650	290	940	161
V	500	150	0.05	1,000	1,100	2,100	323
Ni	200	83	0.0009	600	380	980	346
Sn	50	2.4	0.005	400	30	430	821
Cu	100	93	0.012	2,200	430	2,630	1,363
Cd	2.5	0.4	0.001	40	15	55	1,897
Zn	250	108	0.14	7,000	1,400	8,400	2,346
As	25	3	0.10	620	160	780	2,786
Se	3	1	0.13	50	90	140	3,390
Sb	9.5	0.3	0.013	200	180	380	3,878
Mo	10	1.4	0.02	100	410	510	4,474
Ag	0.5	0.1	0.0006	40	10	50	8,333
Hg	0.3	0.1	0.001	50	60	110	27,500
Pb	50	8.7	0.012	16,000	4,300	20,300	34,583

---

[a] From Lantzy and Mackenzie (1979).

[b] Interference factor = (total emissions/continental + volcanic fluxes) x 100. Taken from Chester (1990).

Table 1.8 Global source strengths for atmospheric trace elements[a] (units, 10^9 gy $^{-1}$).

	Natural				Anthropogenic	
Element	Ocean (mean)[b]	Crust	Volcanoes	Vegetation	Fossil fuel	Others
Al	200	20000	700	40	2000	2000
Co	0.2	7	0.1	0.04	0.9	2
Cu	5	10	6	0.9	2	50
K	30000	6000	200	100	2	50
Fe	50	10000	300	20	2000	4000
Mg	100000	3000	80	20	300	200
Mn	7	200	9	5	8	400
Pb	8	3	0.4	0.2	4	400
Sc	5×10^{-4}	7	0.2	0.002	0.8	0.4
V	10	30	0.7	0.2	20	2
Zn	8	80	10	10	80	200
Cd	0.4	0.05	0.1	0.05	0.2	5

[a] Data from Weisel et al., (1984): except Cd, which is from Buat-Menard (1983).

[b] Based on BIMS EF_{sea} data from all bubble depths.

Taken from Chester 1990.

released into the Northern hemisphere and ~10% in the Southern hemisphere (Robinson and Robins, 1971).

Weisel et al., (1984), estimated the global source strengths of a number of elements in the atmosphere and the data are given in Table 1.8. These data offer a breakdown of some of the individual sources, and include the ocean surface as a potential source. The following general conclusions can be drawn from the data presented by Weisel et al., (1984), and these are summarised as follows;

(1) > 90% of Al, Fe, Mn and Co in atmospheric particulates have natural sources, and are supplied to the atmosphere by the injection of crustal dust.

(2) ~80% of the K and Mg are associated with sea salt generation.

(3) BIMS REF$_{sea}$ values were used rather than those calculated using bulk sea water to asses the importance of the ocean surface as a source for trace elements. On the basis of the mean BIMS data ~24% of the V, ~23% of the Cu, and as much as 69% of the Pb released to the atmosphere from natural processes have an oceanic source.

(4) According to Weisel et al., (1984), only Cu has a volcanic source which contributes ≥ 5% of its natural atmospheric input. However, Walsh et al., (1979 a,b), have shown that volcanic sources dominate the release of As into the atmosphere, and Niragu (1979), has suggested that volcanic processes may be a significant source of atmospheric Cd.

(5) From the data presented by Weisel et al., (1984), vegetation does not appear to be an important source for most elements to the marine aerosol. However, Niragu (1979), estimated that vegetative release can be important in the atmospheric cycles of some elements, contributing for example ~20% of the Zn released naturally into the atmosphere.

On the basis of the data available at present it can be concluded that the natural inputs of some NEE elements (e.g. Al, Fe, Mn, Co and Sc), are dominated by the injection of crustal material into the atmosphere, and that those of other elements (e.g. Na, K, Mg and possibly some trace elements), are dominated by the generation of sea salts. Volcanic activity and vegetative processes may also be significant sources in the natural fluxes of some elements to the atmosphere. However, these are difficult to quantify at present. Although the sea surface can be important in the release of V, Cu, Zn and Pb to the atmosphere by natural processes the data in Table 1.8 indicates that at present the natural sources of these AEE are dwarfed on a global scale by their anthropogenic inputs, and only in regions remote enough from the influence of these inputs can the ocean be a significant source of the trace elements to the atmosphere. It must also be remembered that elements originating from the sea surface have been recycled into the air, and consequently do not take part in the net input of elements to the atmosphere from the oceans.

Table 1.9 Concentration (1) and EF values (2) of trace metals in marine aerosols

		Coastal seas; close to pollution sources				Coastal seas and open ocean; close to crust sources										Open ocean													
Conc. units; m^{-3} of air		North Sea[a]		Keil Bight[b]		Western Med.[c]		Eastern Med.[d]		N.Atlantic (northeast trades)[e]		N.Arabian Sea[f]		Tropical N.Atlantic[g]		N.Atlantic (Bermuda)[h]		N.Atlantic westerlies[e]		S.Atlantic westerlies[e]		N.Pacific (Enewetak)[i]		S.Pacific (Samoa)[j]	
		1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Al	ng	159	1.0	394	1.0	324	1.0	915	1.0	5925	1.0	1184	1.0	160	1.0	140	1.0	48	1.0	2.7	1.0	21	1.0	0.72	1.0
Fe	ng	330	3.0	369	1.4	-	-	570	0.9	3865	1.0	908	1.1	100	0.9	94	1.0	36	1.1	2.6	1.4	17	1.2	0.21	0.4
Sc	pg	82	1.9	-	-	-	-	-	-	-	-	-	-	35	0.8	20	0.5	-	-	-	-	5	0.9	0.04	0.2
Mn	ng	21	11	15	3.3	-	-	12	1.1	65	1.0	15	1.1	2.2	1.2	1.2	0.7	1.7	3.1	0.11	3.5	0.29	1.2	0.005	0.6
Ni	ng	10	69	4	11	-	-	-	-	6.6	1.2	3.9	3.6	0.64	4.4	0.08	0.6	0.51	12	0.02	8.1	-	-	-	-
Co	pg	360	7	-	-	-	-	-	-	2100	1.2	670	1.9	80	1.6	-	-	50	3.4	10	12	8	1.3	0.37	1.7
Cr	ng	4.5	23	-	-	-	-	1.6	1.4	10	1.4	4.3	3.0	0.43	2.2	0.28	1.6	0.49	8.4	0.17	52	0.09	3.5	-	-
V	ng	12	46	9.7	15	-	-	-	-	15	1.5	-	-	0.54	2.1	-	-	1.0	13	0.03	6.8	0.08	2.3	-	-
Cu	ng	-	-	7.7	29	-	-	4.9	8.0	4.5	1.1	3.2	4.0	0.79	7.4	0.90	10	1.0	31	0.29	161	0.045	3.2	0.013	27
Zn	ng	153	1132	57	170	-	-	-	-	16	3.2	4.3	4.3	4.4	32	3.2	27	7.5	184	1.8	784	0.17	9.5	0.07	114
Cd	ng	-	-	-	-	1.9	2413	-	-	0.12	8.3	0.05	17	-	-	0.19	558	0.11	943	0.02	3048	0.004	78	-	-
Se	ng	1.5	15466	1.6	6657	-	-	-	-	-	-	-	-	0.43	4405	0.13	1522	-	-	-	-	0.13	10148	0.09	20491
Sb	pg	2900	7600	-	-	-	-	-	-	-	-	-	-	110	286	30	89	-	-	-	-	4.0	79	0.20	116
Pb	ng	147	6082	53	885	40	812	7.4	53	6.9	7.7	2.9	16	9.9	407	3.5	164	6.0	882	0.97	2364	0.12	38	0.016	146

[a] Cambray et al. (1975)
[b] Schneider (1987)
[c] Dulac et al. (1987)
[d] Saydam (1981)
[e] Murphy (1985)
[f] Sanders (1983)
[g] Buat-Menard & Chesselet (1979).
[h] Duce et al. (1976)
[i] Duce et al. (1983a)
[j] Arimoto et al. (1987)

Taken from Chester (1990).

1.5.6 Geographical Variations in the Elemental Composition of the Marine Aerosol.

According to Chester (1990), the overall composition of the marine aerosol is controlled by the extent to which components derived from various sources are mixed together in the atmosphere. As a result, the concentrations of many elements in the marine atmosphere can vary over several orders of magnitude between different regions. Table 1.9 gives a compilation of some of the more recent data for the concentrations of elements in marine aerosols from a variety of marine environments. In the Table marine locations are arranged in increasing order of remoteness from primary continental, i.e. non-oceanic, source. Following Chester (1990), trends in the atmospheric concentrations of the elements emerging from the data set can be summarised as follows.

(1) Coastal seas close to the continental anthropogenic sources have the highest concentration of the AEE.

(2) Regions close to the continental arid land and desert sources have the highest concentrations of the NEE.

(3) Concentrations of both the NEE and the AEE decrease with remoteness from the continental sources. For regions with sufficient available data, the general rank order of the concentrations of both the NEE and the AEE is as follows; coastal seas > North Atlantic > North Pacific > South Pacific.

(4) The highest EF_{crust} values are found for coastal seas. However, for the Samoa aerosol the EF_{crust} values are higher than those for the less remote Enewatak aerosol. This suggests that the residence time of the small sized AEE-containing anthropogenic particles are longer than those of the larger NEE-containing mineral particles.

1.6 Processes for the Removal of Aerosol Particles from the Atmosphere.

The removal of particulates from the atmosphere takes place by two main mechanisms; i.e. dry and wet deposition.

1.6.1 Dry Deposition.

The processes involved in dry deposition are gravitational settling, turbulent diffusion, Brownian diffusion, interception and impaction (Slinn, 1983; ERL, 1983). The dry removal of particles from the atmosphere is a continuous process, and is affected by a number of factors, which include wind speed and particle size. Particle size is especially important. For example, M^cDonald et al., (1982) showed that the dry deposition of sea salts is dominated by large particles (MMD > 10μm), which accounted for ~70% of the total salt deposition, although they only made up ~13% of the total salt mass. Dry deposition is therefore especially important for large particles.

The dry deposition flux (F_d) of an aerosol particle to the sea surface is given by Equation 1.6, which is the product of the dry deposition velocity (V_d) of the particle and its corresponding concentration in air (C), at about 1m above the ground (Davies and Nicholson, 1982).

$$F_d = V_d \times c \qquad \text{Equation 1.6}$$

Yaqqub (1990), has discussed the different techniques used to measure the dry deposition velocity of particles; e.g. the eddy flux model, micro meteorological techniques, gradient model, wind tunnel and field measurements, (see also: Nicholson 1988a; Davies and Nicholson, 1982; Margaranda and Flothman, 1982). The results obtained from the various techniques show inconsistencies due to both a variability in environmental influences, and to inadequacies in the adopted measurement technique (see e.g.: Nicholson, 1988a; Marggrander and Flothman, 1982). As a result dry deposition velocity measurement have a great deal of uncertainty; this is particularly true for smaller sized particles, for which the deposition velocity depends on the size and shape of the particle (Slinn, 1983).

1.6.2 Wet Deposition.

Wet deposition is the removal of substances from the atmosphere by precipitation scavenging, a process that is random in time. Generally, wet deposition rates depend on the concentration of the component in rain and the total amount of that rain which falls onto a surface. Junge (1963), indicated two principle mechanisms for the removal of particulates from the atmosphere by precipitation, and these are summarised as follows;

(1) Rain out processes occurring within a cloud, as a result of the nucleation of material onto pre-existing cloud elements.

(2) Wash out processes occurring below the cloud due to impaction, and/or, the interception of aerosols by falling precipitation such as raindrops and snowflakes.

Washout factors, or scavenging rates, are often employed to determine the degree to which a component is removed from the air by rain. The washout factor (WF) is calculated from an equation of the general type.

$$WF = C_r/C_a \qquad \text{Equation 1.7}$$

where; C_r = the concentration of a component in the rain.

C_a = the concentration of the element in low level air.

somtimes an air density term is included in the equation.

WF values for the most commonly studied elements lie in the range $10x10^2$ - $10x10^3$. However, it must be noted that problems arise when rain concentrations are employed in the estimation of trace element wet deposition using washout factors. The principle reason for this is that the concentration of the elements in the rain can change during the course of a rainfall event, as a result of variations in the efficiencies with which aerosols of different sizes are scavenged. However, at remote sites where the number of particles in the air is relatively low, the frequency of rainfall is an important factor in removing aerosols from the atmosphere (see e.g. Remoudaki et al., 1991), further, the rainfall may scavenge aerosols of different sizes with nearly equal efficiencies (see e.g; Arimoto et al., 1985).

The importance of wet deposition relative to dry deposition is dependant upon the volume and duration of the rainfall. Rohbock (1982) used a mass balance equation, and determined that elements bound on sub-micron particles are more likely to be removed primarily by wet deposition, whereas elements bound on coarse particles are mainly removed by dry deposition. Thus, the relative importance of dry versus wet deposition is essentially dependant upon the distance from the source. The closer to the source, the more likely dry deposition is to be dominant (ERL, 1983), depending on the particle size of the aerosol and the meterological conditions.

1.7 Fluxes of Atmospherically Transported Elements to the Sea Surface.

The recycling of particulate components across the sea surface can occur during the generation of sea salts. The degree to which some elements are fractionated at the ocean surface with respect to bulk sea water has been discussed in section 1.5.2.1.2. The extent of recycling across the air/sea interface can now be estimated with some degree of certainty. For example, Arimoto et al., (1985) used a combination of aerosol, rain and sea water data to estimate the percentage of wet deposition associated with recycled sea salts at Enewetak (North Pacific). Values for individual elements included 15% (Zn), 30% (V) and 48%(Cu). Recycling must be taken into account when estimates are made of the total deposition fluxes of some elements to the sea surface from the atmosphere.

Buat-Menard (1983), concluded that in general, the net atmospheric fluxes of the AEEs to the sea surface are primarily due to wet deposition over most marine regions, but that dry deposition is significant for sea salt and mineral (large particle size) aerosols. These overall trends tend to be confirmed by the literature values, although anomalies do occur. For example at Enewatak, flux data (corrected for sea surface recycling) showed that, although wet deposition did exceed dry deposition for Pb, V, Cd and Se, this was not the case for Cu and Zn. Further, at Enewatak wet deposition was more important than dry deposition for Fe, although for Al dry deposition was an order of magnitude higher than wet removal.

Recently, advanced 'wet and dry' flux deposition models have become available (see e.g.: Arimoto et al., 1985, 1987). Their use offers the best available estimates of the net deposition of trace elements to the sea surface. A summary of some data given in the literature for the fluxes of trace elements to the sea surface is given in Table 1.10. However, with the exceptions of the data sets

Table 1.10 Atmospheric fluxes of trace metals to the sea surface (units, ng cm^{-2} yr^{-1})

	New York Bight[a]	North Sea[b]	Western Med.[c]	South Atlantic Bight[d]	Bermuda[e]	North Atlantic; north-east trades[f]	Tropical North Atlantic[g]	Tropical North Pacific; total net deposition[h]	South Pacific; total net deposition[i]	North Atlantic[j]; westerlies	North Pacific; westerlies	South Pacific[j]; easterlies
Al	6000	30000	5000	2900	3900	97000	5000	1200	132 - 1800	-	-	-
Sc	-	5	1	-	0.6	-	1.1	0.18	0.06	-	-	-
V	-	480	-	-	5	-	17	7.8	-	-	-	-
Cr	-	210	49	-	9	111	14	-	-	-	-	-
Mn	-	920	-	60	45	570	70	9.0	3.6	-	-	-
Fe	5700	25500	5100	5900	3000	48000	3200	560	47 - 337	-	-	-
Co	-	39	3.5	-	1.2	12	2.7	-	0.25	-	-	-
Ni	-	260	-	390	3	67	20	-	-	-	-	-
Cu	-	1300	96	220	30	48	25	8.9	4.4 - 7.9	-	-	-
Zn	1400	8950	1080	750	75	152	130	67	5.8 - 2.4	-	-	-
As	-	280	54	45	3	-	-	-	-	-	-	-
Se	-	22	48	-	3	-	14	4.2	0.8	-	-	-
Ag	-	-	3	-	-	-	0.9	-	-	-	-	-
Cd	30	43	13	9	4.5	-	5	0.35	-	-	-	-
Sb	-	58	48	-	1.0	-	3.5	-	-	-	-	-
Au	-	-	0.05	-	-	-	0.1	-	-	-	-	-
Hg	-	-	5	24	-	-	2.1	-	-	-	-	-
Pb	3900	2650	1050	660	100	32	310	7.0	1.4 - 2.8	170	50	3
Th	-	4	1.2	-	-	-	0.9	0.61	0.036	-	-	-

[a] Duce et al. (1976).
[b] Cambray et al. (1975).
[c] Arnold et al. (1982).
[d] Windom (1981).
[e] Duce et al. (1976).
[f] Chester et al. (1979).
[g] Buat-Menard & Chesselet (1979).
[h] Arimoto et al. (1985).
[i] Arimoto et al. (1987).
[j] Settle and Patterson (1982).

Taken from Chester (1990).

for Enewetak and Samoa, most of the calculations do not take account of sea surface recycling. As a result, the fluxes, especially those for the AEE, will tend to be overestimated. Further, the fluxes have been obtained by different methods. Despite this there is a strong geographical trend which can be identified from the data in Table 1.10, which indicate that the strengths of the air-to-sea fluxes decrease by orders of magnitude as the degree of remoteness of a site from the major aerosol sources increases. For example, a well established trend is apparent for Pb, where the atmospheric flux for the North Atlantic Westerlies is over 50 times greater than that for the South Pacific Westerlies.

1.8 Fates of Atmospherically-Transported Trace Elements in Sea water.

The initial constraint on the behaviour of atmospherically-transported trace elements in the mixed layer is imposed by the extent to which they are solubilised in sea water. This is of importance since the physical state (i.e. particulate or dissolved) of the elements affects both their subsequent involvement in the biochemical cycles, and their residence times in sea water.

Hodge et al., (1978), studied the sea water solubility of trace elements from a [illegible] an urban aerosol, and a summary of their data is given in Table 1.11. From the data in the Table 1.11 it can be seen there are considerable differences between the solubility of the

Table 1.11 The solubility of atmospheric trace elements in sea water from anthropogenic-rich, and crust-rich aerosols (% total element).

Atmospheric population	Al	Fe	Mn	Ni	Co	Cr	V	Ag	Zn	Cu	Pb	Cd
Anthropogenic-rich[b]												
Mean concentration (ng m^{-3} of air)	900	610	11	11	<0.4	<1.6	13	<0.05	25	16	560	0.25
Mean % soluble in sea water	0.56	1.1	47	47	25	12.5	31	80	68	28	39	84
Mean EF_{crust}	1	0.99	1	14	1.5	1.5	9	-	33	26	4148	16
Dust-rich[c]												
Mean concentration (ng m^{-3} of air)	3380	2100	46	2.8	<0.5	4	<11	<0.03	18	20	150	0.2
Mean % soluble in sea water	0.09	0.19	34	28	20	10	18	67	24	14.5	13	80
Mean EF_{crust}	1	0.91	1.2	0.92	0.49	0.99	2	-	6.2	8.4	296	25

[a] Data taken from Hodge et al., (1978).
[b] Southern California.
[c] Baja California.
Taken from Chester (1990).

elements from the two different aerosol groups. This is reflected in the differing solubility of Pb, Zn and Cu which are solubilised to a much greater extent from the polluted aerosols, associated with relatively high EF_{crust} values, than from the crustal aerosols, with correspondingly lower EF_{crust} values. In general, these trends can be related to the partitioning of the elements among the aerosol components. Thus, in Section 1.5.4 it was shown that the contaminated end-member aerosols have relatively large amounts of the total concentrations of Pb(~46%), Zn (~67%) and Cu (~37%), in the loosely-bound form compared to the crustal end member aerosols, which have < 5% of the total concentrations of these elements present in this fraction. Therefore upon contact with sea water there will be a greater release of these elements from the polluted aerosols which is entirely consistent with their solubilisation from the loosely-held fraction with which they become associated during high-temperature volatilisation processes. However, Cd is found mainly in the loosely-held fractions of both the contaminated and the crustal end member aerosols, and is therefore relatively soluble from both types of aerosol. These general relationships, i.e. between the solid state speciation and sea water solubilities of elements from aerosols have been confirmed by Chester et al., (1988).

1.9 The Present Investigation.

The present investigation is concerned with the sources, distributions and fates of a series of trace elements transported via the atmosphere to the North Sea. This is a coastal sea close to sources of aerosol contamination, and should provide a representative example of the importance of atmospheric transport in trace element budgets in this type of sea.

The investigation was carried out as part of the Natural Environmental Research Council (NERC) North Sea Programme. This programme is described in Chapter 2, which also includes a description of the aims of the investigation.

Chapter 2

The North Sea Project.

2.1 Introduction.

The North Sea encompasses a surface area of 575,000 Km^2 with a volume of 40.3 m^3 (ICES 1983). The region is subject to oceanic influences in the north, and to a minor extent via the Dover Straits in the south. However, it is strongly influenced on the remaining three sides by terrestrial inputs.

As a result of the strong input of contaminants from both the British Isles and the European continent, and a limited dilution on account of the shallow water, the southern part of the North Sea is one of the most heavily polluted marine areas in the world (Goldberg 1976). A particularly high degree of contamination can be observed in the river estuaries around the mouths of the Rhine, Maas and Scheldt Rivers (Holland/Belgium), Humber, Tyne, and Firth of Forth (United Kingdom), Wester and Elbe (Federal Republic of Germany), and Oslo Fjord (Norway). In addition, dumping of waste materials is practised in several areas, which also contributes to the increase in pollution, for example Golberg (1976) has estimated that 4.5 million tons of sewage sludge from London are dumped in the outer Thames estuary each year.

Trace elements can also be introduced into the North Sea by atmospheric fallout. This type of transport, which contributes to the wide distribution of these pollutants, has reached considerable proportions in recent years; e.g. Hg and Pb, which have relatively high atmospheric source strengths, are introduced into the North Sea predominantly as a result of air pollution from the surrounding mainland (Cambray et al., 1975).

The North Sea is thus surrounded by some of the most industrialised nations in the world, and in recent years considerable concern has arisen over the extent to which it is polluted by several classes of contaminants, including trace elements. In an attempt to accurately quantify these terrestrial inputs into the North Sea, the United Kingdom Natural Environmental Research Council (NERC) funded a North Sea Programme, involving a number of multi-disciplinary studies. These studies were directed towards the formulation of 3D hydrodynamical and transport models for predicting water quality in the North Sea, which involved an understanding of chemical (including marine aerosol studies), biological and sedimentary processes.

2.2 The Climatology of the North Sea.

Because of its geographical location, the North Sea atmosphere is dominated by variable, prevailing westerly, winds which extend, in a zone 2000 - 3000km breadth, from North America over the North Atlantic Ocean and North West and Central Europe to Siberia. The North Sea is part of the temperate humid climate belt of the Northern Hemisphere. The dominance of the westerly winds which transport the air from the Atlantic Ocean over the European region produces a climate with high rainfall, but without extreme temperature variations. Within this climatic region, the North Sea has its own special character. Like a large bight of the North Atlantic Ocean, the North Sea pushes itself forward into the land masses of Europe. As a result, the climate of the North Sea is classified as being that of a transition area because the surrounding land prevents a pure oceanic climate from arising. The influence of the continent on the climate of the North Sea increases from the north to the south, and from the west to the east.

An essential feature of the climate of the North Sea is the variability which is found at all seasons, which results from its location in the range of the Atlantic depressions which most often pass north of Scotland, but not in frequently cross the North Sea. These depressions may bring about relatively large changes in all elements of the weather, even within a few hours. The conflicting air masses in the depressions are the cause of most of the storms, strong winds, and rainfall which are typical of the North Sea region in the winter, and which also occur in the summer.

2.3 The Pressure and Wind Systems Over the North Sea.

2.3.1 The Pressure Systems Over the North Sea.

Maps which present the long-term averages of the pressure distribution over the North Sea have been presented by Höhn (1971), and the conclusions determined from them are summarised below. Höhn (1971) has shown that in all seasons the average pressure is relatively high in the southern part of the North Sea and in the west of Central Europe, and is relatively low to the North where there are numerous depressions which have passed north east or eastward from the vicinity of Iceland. This general distribution is modified in the course of the year by the varying interactions between the low pressure near Iceland, the high pressure near the Azores, and the alternating high and low pressures in Asia, which result in seasonal pressure changes over the North Sea. The pressure changes for the individual months, however, vary greatly from year to year, and almost any collection of synoptic weather charts will indicate that the distribution of pressure on any given occasion may differ widely from the average. These variations are caused by the passing of depressions which may cause considerable changes, even in the course of a day.

2.3.2 The Wind Systems Over the North Sea.

In agreement with the average pressure distribution, south westerly to weserly winds of Atlantic origin prevail over the North Sea in nearly all seasons, although in summer north westerly winds can become predominant over some parts of the North Sea. However, it must stressed that all wind directions are possible in each month or season at any location over the North Sea.

The average wind force in nearly all areas of the North Sea is about 5 on the Beaufort (Bft) Scale in November to February, and about 3 Bft in May to August. The differences in wind force between the northern, southern, western, and eastern parts are small in any month. The fact that the average wind force is 3 Bft in the summer months and more in the winter months, means that the air stream at most times is dynamically turbulent since an air stream with a speed of 2 Bft or more is dynamically unstable, even if the stratification of the air itself is stable. This may be of importance for the fallout of contaminants from the atmosphere to the sea since in turbulent winds the fallout of particles is reduced.

The transport of both natural and contaminant material via the atmosphere and the ocean depends on number of factors which, in addition to the direction and force of the wind, include the stability of the air over the North Sea. There is an important difference between summer and winter conditions with respect to the stability of the air. In the summer months, continental winds bring in air having a higher temperature than the sea surface, which causes the lower level air (i.e. that below the boundary layer), to be generally stable and results in relatively small vertical turbulent exchange of any components in the air across the air/sea interface. In the winter months, the conditions are reversed, and the air temperature is lower than the sea surface temperature, producing less stability in the lower air. As a result there is an increased vertical turbulent exchange of components across the air/sea surface. Thus, the vertical turbulent exchange of material across the North Sea air/sea interface will be generally higher in the winter than in the summer.

2.4 The Atmospheric Inputs Into the North Sea.

The atmosphere is an important pathway for the transport of trace elements to the oceans, and over the past decade or so it has become increasingly recognized that atmospheric transport plays a critical role in the input of these atmospheric constituents to the sea surface. This is particularly the case for coastal receiving zones, and is especially important for the North Sea which is close to the major European land-based pollution sources. It has been estimated that for some trace elements the atmospheric input to the North Sea considerably exceeds that from fluvial sources; e.g. it has been estimated that about seven times as much Pb reaches the North Sea from the atmosphere than from the feeder rivers (Cambray et al., 1975). A knowledge of these atmospheric inputs is therefore essential to gain an understanding of the budgets of pollutants to the North Sea.

2.4.1 Previous Work Carried Out on the North Sea Aerosol.

Much of the data on the concentrations of trace elements in the atmosphere over the North Sea has been extrapolated from collections made at stations on the edges of the surrounding land masses, or from fixed platforms at single locations in the North Sea itself. However, model calculations have indicated that fluxes of trace elements to the North Sea based on data collected at coastal stations in continental Europe and the United Kingdom (UK) are probably 2-4 times higher than the actual fluxes into the open North Sea (van Jaarsveld et al., 1986). It is important, therefore, to establish the concentrations of the atmospheric trace elements over various open sea regions of the North Sea itself. Recently, collections of atmospheric particulates (aerosols) have been made over the open North Sea from an aeroplane (Otten et al., 1989); however, they were confined to a limited sector over the southern North Sea, and relatively few data have been obtained for the concentrations of particulate atmospheric trace elements over large areas of the rest of the North Sea. Because the input of contaminants, such as trace elements changes with time as precautions are taken to control their use, data of this kind are necessary in order to provide a baseline for future monitoring.

2.5 Description of the Research Project.

During a fifteen month sampling period, covering August 1988 to October 1989, regular oceanographic observations were made from the RRS Challenger along a set survey track as part of the NERC North Sea Programme. The survey track is represented in Figure 2.1, and was ~3300 Km

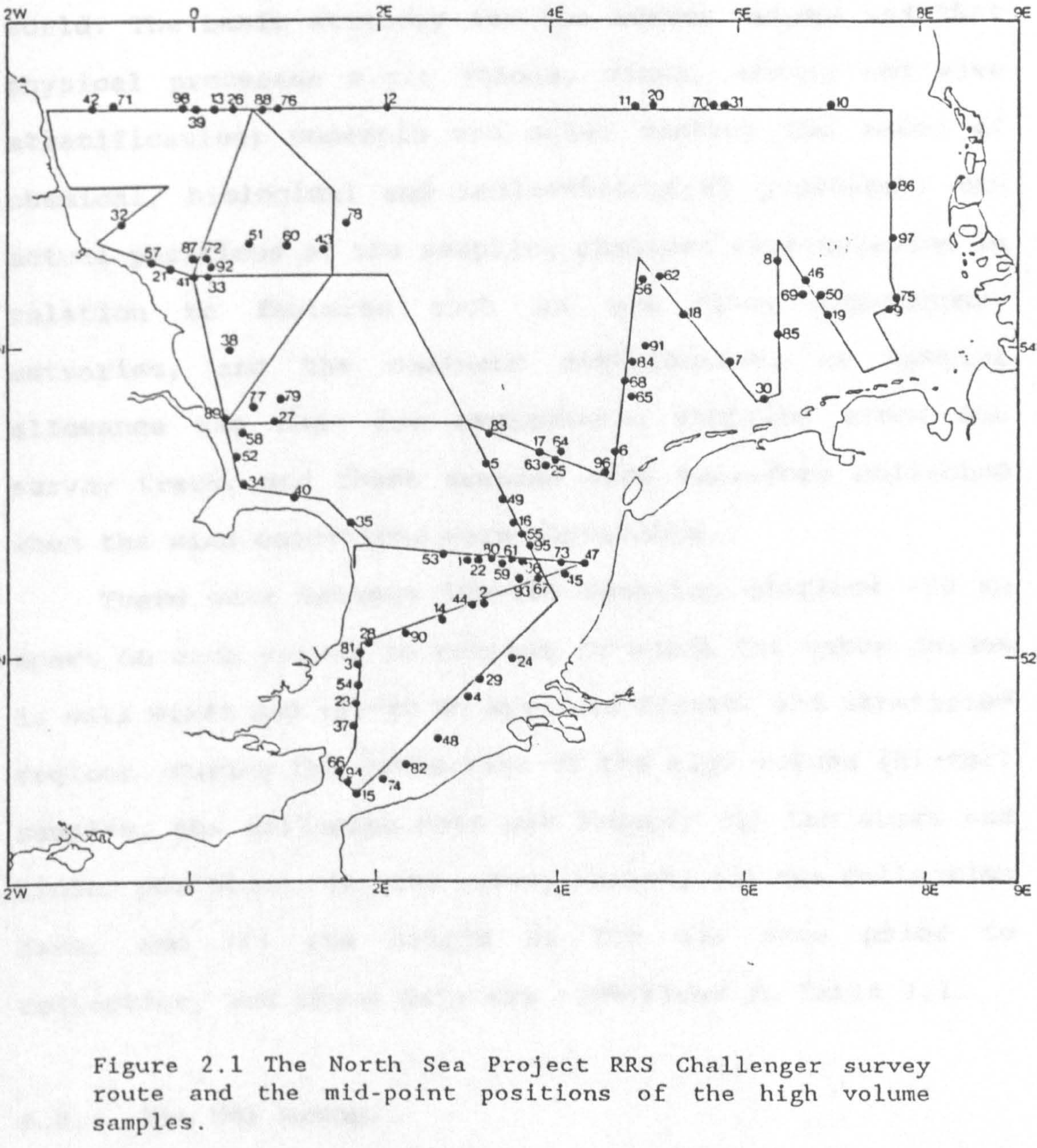

Figure 2.1 The North Sea Project RRS Challenger survey route and the mid-point positions of the high volume samples.

long and was confined to the southern region of the North Sea, which is surrounded by one of the most densely populated and most heavily industrialised parts of the world. The basic strategy for the survey design was that physical processes e.g.; (tides, winds, storms and wave stratification) underpin and often control the rates of chemical, biological and sedimentological processes. The actual positions of the sampling stations were selected in relation to features such as sea flow, topography, estuaries, and the sediment distribution. No special allowance was made for atmospheric sampling along the survey track, and these samples were therefore collected when the wind conditions were favourable.

There were between 100-150 sampling stations ~70 Km apart on each survey in regions in which the water column is well mixed and ~20-40 Km apart in frontal and stratified regions. During the collection of the high volume (hi-vol) samples, the following data was logged: (1) the start and finish positions, (2) the survey number, (3) the collection date, and (4) the origin of the air mass prior to collection, and these data are summarised in Table 2.1.

2.5.1 The NSA Group.

There were a number of United Kingdom Universities involved with NSA collections. As a result the interpretation of the data itself can be conveniently sub-divided into a number of sections, depending upon the aerosol collection. These groups were as follows;

Table 2.1 NSA hi-vol sample collection details, from August 1988 to October 1989.

Sample number	Survey number	Collection dates, start-finish	Time (GMT)	Position start finish		ú wind speed Km hr^{-1}	Air mass origin	Sampling comments
1	CH33	04.08.88 05.08.88	18.18 09.38	52°43′N 52°38′N	01°59′E 04°05′E	5	-	good sampling weather.
2	CH33	05.08.88 06.08.88	12.55 00.34	52°37′N 52°10′N	03°51′E 02°20′E	9	-	"
3	CH33	06.08.88 06.08.88	01.12 07.28	52°09′N 51°30′N	02°12′E 01°45′E	9	-	"
4	CH33	06.08.88 07.08.88	08.50 00.27	51°23′N 52°08′N	01°42′E 03°30′E	9	-	fog towards end of sample.
5	CH33	07.08.88 08.08.88	11.39 03.33	52°58′N 53°10′N	03°28′E 04°37′E	9	-	good sampling weather.
6	CH33	08.08.88 08.08.88	04.20 17.00	53°10′N 54°31′N	04°35′E 04°56′E	9	-	"
7	CH33	08.08.88 09.08.88	17.51 07.14	54°23′N 53°59′N	05°10′E 06°26′E	9	-	"
8	CH33	09.08.88 09.08.88	07.54 20.09	54°38′N 54°00′N	06°06′E 07°14′E	5	-	"

9	CH33	10.08.88	10.36	55°05'N	07°40'E	9	-	"
		10.08.88	22.35	55°30'N	05°46'E			
10	CH33	10.08.88	23.34	55°30'N	06°00'E	9	-	good sampling weather.
		11.08.88	13.00	55°30'N	04°30'E			
11	CH33	11.08.88	15.20	55°30'N	03°45'E	18	-	occasional spray.
		12.08.88	03.00	55°30'N	01°25'E			
12	CH33	12.08.88	03.45	55°30'N	01°24'E	19	-	"
		12.08.88	21.20	55°30'N	01°13'W			
13	CH33	12.08.88	23.12	55°29'N	01°34'W	11	UK	rain at the end of sample.
		13.08.88	18.17	54°26'N	00°01'W			
14	CH35	04.09.88	06.01	52°36'N	04°17'E	16	UK	occasional sea spray.
		04.09.88	19.50	52°04'N	01°49'E			
15	CH35	04.09.88	21.10	51°54'N	01°48'E	10	UK	occasional spray and patchy rain.
		05.09.88	15.30	51°48'N	03°11'E			
16	CH35	05.09.88	18.30	52°00'N	03°32'E	5	UK	good sampling weather.
		06.09.88	13.20	53°30'N	02°59'E			
17	CH35	06.09.88	15.47	53°30'N	03°03'E	5	UK	"
		07.09.88	07.15	53°39'N	04°51'E			
18	CH35	07.09.88	14.33	54°32'N	04°54'E	13	Eu+UK	occasional spray.
		08.09.88	02.30	53°44'N	06°33'E			
19	CH35	08.09.88	08.45	54°35'N	06°26'E	12	Eu	"
		08.09.88	18.50	53°55'N	07°40'E			

20	CH35	08.09.88	21.50	54°14′N	07°39′E	15	Eu	"
		10.09.88	10.55	55°30′N	03°10′E			
21	CH35	11.09.88	08.30	55°29′N	01°09′W	16	UK	spray + gale warning.
		12.09.88	05.19	54°20′N	00°25′E			
22	CH37	02.10.88	03.07	52°43′N	01°49′E	8	Eu	good sampling weather.
		02.10.88	18.59	52°13′N	02°53′E			
23	CH37	02.10.88	20.09	52°38′N	04°06′E	6	Eu	"
		03.10.88	20.27	51°05′N	01°46′E			
24	CH37	03.10.88	21.38	51°05′N	01°46′E	9	Eu	fog at end of sample.
		05.10.88	02.06	53°14′N	03°14′E			
25	CH37	05.10.88	09.34	52°30′N	03°00′E	10	Eu+UK	rain at start of sample.
		06.10.88	00.16	53°39′N	04°50′E			
26	CH37	09.10.88	12.53	54°20′N	00°26′E	6	UK+OS	"
		10.10.88	21.50	55°30′N	01°33′W			
27	CH37	12.10.88	09.19	53°43′N	00°24′E	10	Eu	occasional spray.
		12.10.88	22.00	53°49′N	00°49′E			
28	CH39	02.11.88	08.43	52°35′N	04°04′E	11	OS	"
		03.11.88	09.15	51°07′N	01°50′E			
29	CH39	03.11.88	10.18	51°13′N	02°49′E	7	Eu	good sampling weather.
		04.11.88	01.25	52°26′N	03°57′E			
30	CH39	04.11.88	16.10	52°28′N	03°09′E	9	Eu+UK	rain at end of sample.
		06.11.88	17.00	54°18′N	07°43′E			

31	CH39	07.11.88	05.50	55°30'N	06°30'E	8	UK	good sampling weather.
		07.11.88	20.10	55°30'N	04°27'E			
32	CH39	08.11.88	01.45	55°30'N	03°08'E	10	Eu+UK	heavy rain samples wet.
		10.11.88	01.45	54°30'N	00°19'W			
33	CH39	10.11.88	03.35	54°26'N	00°01'E	11	Eu+UK	rain in vicinity.
		11.11.88	23.45	53°44'N	00°24'E			
34	CH39	12.11.88	00.30	53°40'N	02°41'E	9	UK	"
		12.11.88	18.30	53°01'N	01°27'E			
35	CH39	12.11.88	19.35	52°52'N	01°42'E	12	Eu+UK	occasional spray.
		13.11.88	06.30	52°44'N	02°24'E			
36	CH41	01.12.88	16.30	52°38'N	01°46'E	14	Eu	rain.
		02.12.88	19.50	52°22'N	03°20'E			
37	CH41	03.12.88	00.25	52°14'N	02°34'E	12	Eu+UK	rain.
		03.12.88	20.48	51°44'N	02°58'E			
38	CH41	07.12.88	13.11	54°23'N	02°26'E	10	UK	good sampling weather.
		08.12.88	08.13	55°00'N	01°08'E			
39	CH41	08.12.88	15.47	55°30'N	01°25'W	5	UK	"
		09.12.88	10.53	55°31'N	01°04'E			
40	CH43	30.12.88	22.40	52°41'N	02°59'E	6	Eu+UK	"
		31.12.88	19.56	53°43'N	00°43'E			
41	CH43	01.01.89	03.40	54°20'N	01°29'E	8	UK	"
		02.01.89	04.11	55°00'N	00°57'W			

42	CH43	02.01.89	05.10	55°00'N	01°08'W	7	UK	"
		02.01.89	19.47	55°30'N	00°09'E			
43	CH43	03.01.89	00.22	55°30'N	00°54'E	12	UK+Eu	occasional spay.
		03.01.89	17.05	54°05'N	02°22'E			
44	CH43	03.01.89	18.43	53°59'N	02°12'E	8	Eu+UK	rain.
		06.01.89	19.58	51°50'N	03°22'E			
45	CH43	06.01.89	21.08	51°53'N	03°29'E	12	Eu+UK	rain.
		07.01.89	13.52	53°18'N	04°00'E			
46	CH43	07.01.89	18.07	53°15'N	04°36'E	13	UK	ocassional spray.
		10.01.89	12.17	55°30'N	03°41'E			
47	CH45	28.01.89	23.06	52°40'N	02°36'E	12	UK	good sampling weather.
		30.01.89	04.04	52°05'N	01°50'E			
48	CH45	30.01.89	04.30	52°05'N	01°50'E	9	UK	"
		31.01.89	05.05	52°08'N	03°30'E			
49	CH45	31.01.89	06.28	52°14'N	03°54'E	8	UK	fog at end of sample.
		01.02.89	01.18	53°14'N	04°15'E			
50	CH45	01.02.89	22.51	53°53'N	05°55'E	10	Eu+UK	foggy.
		03.02.89	15.28	54°02'N	07°08'E			
51	CH45	03.02.89	09.11	55°27'N	07°39'E	9	UK	mist.
		07.02.89	05.16	53°40'N	02°40'E			
52	CH45	07.02.89	05.41	53°40'N	02°10'E	11	-	thick fog at end of sample.
		09.02.89	19.37	52°37'N	01°46'E			

53	CH47	27.02.89	16.55	53°48'N	02°05'E	7	-	good sampling weather.
		01.03.89	17.51	52°37'N	04°17'E			
54	CH47	28.02.89	05.20	52°36'N	04°13'E	18	UK	spray.
		01.03.89	08.42	51°07'N	01°49'E			
55	CH47	02.03.89	00.31	52°22'N	03°59'E	11	Eu+UK	rain at begining of sample.
		02.03.89	10.57	53°24'N	03°06'E			
56	CH47	03.03.89	08.43	53°42'N	04°50'E	9	Eu	rain.
		04.03.89	16.45	54°06'N	07°01'E			
57	CH47	07.03.89	05.14	54°29'N	00°28'E	9	Eu+UK	good sampling weather.
		08.03.89	00.04	55°00'N	01°12'W			
58	CH47	08.03.89	01.04	55°00'N	01°18'W	12	UK	"
		11.03.89	12.20	53°01'N	01°04'E			
59	CH49	29.03.89	14.50	52°43'N	01°49'E	12	Eu+UK	"
		30.03.89	18.17	52°13'N	02°40'E			
60	CH49	08.04.89	08.24	54°20'N	00°24'E	11	UK	heavy rain before sample.
		09.04.89	17.59	53°10'N	00°31'E			
61	CH52	12.05.89	08.22	52°39'N	03°40'E	7	UK	heavy spray.
		12.05.89	18.44	52°55'N	03°42'E			
62	CH52	14.05.89	13.00	54°35'N	04°51'E	9	UK	
		15.05.89	10.00	54°35'N	04°49'E			
63	CH52	16.05.89	06.53	52°47'N	03°40'E	7	Eu+UK	mist/fog.
		16.05.89	22.50	52°38'N	03°38'E			

64	CH52	18.05.89	06.55	52°39’N	03°40’E	6	Eu+UK	good sampling
		18.05.89	19.50	52°41’N	03°40’E			weather.
65	CH52	19.05.89	09.48	54°35’N	04°51’E	8	Eu+OS	"
		21.05.89	14.45	52°40’N	03°40’E			
66	CH53	26.05.89	20.50	52°54’N	02°26’E	12	OS	occasional
		28.05.89	18.07	51°46’N	03°03’E			spray.
67	CH53	28.05.89	18.34	51°48’N	03°13’E	10	OS	good sampling
		29.05.89	16.49	52°29’N	03°06’E			weather.
68	CH53	29.05.89	17.21	53°27’N	03°16’E	8	OS+UK	"
		30.05.89	11.27	54°15’N	05°50’E			
69	CH53	31.05.89	13.24	53°55’N	07°16’E	11	OS	rain forcast.
		01.06.89	19.41	53°30’N	05°06’E			
70	CH53	01.06.89	23.04	55°30’N	04°25’E	9	OS+UK	rain.
		03.06.89	16.52	54°60’N	00°16’W			
71	CH53	03.06.89	17.59	54°47’N	00°29’W	11	OS+UK	rain on ship
		04.06.89	14.45	55°06’N	00°44’E			radar.
72	CH53	04.06.89	15.20	55°06’N	00°44’E	10	OS+UK	good sampling
		05.06.89	14.08	53°35’N	01°02’E			weather.
73	CH55	24.06.89	15.26	52°43’N	02°02’E	12	UK	"
		25.06.89	17.00	52°10’N	02°20’E			
74	CH55	25.06.89	17.58	52°09’N	02°14’E	13	UK+Eu	"
		26.05.89	19.58	52°13’N	03°52’E			

75	CH55	28.06.89 30.06.89	14.25 11.06	53°50’N 55°30’N	06°01’E 05°30’E	12	UK	rain.
76	CH55	30.06.89 02.07.89	14.34 02.26	55°31’N 55°30’N	05°28’E 01°12’W	10	Eu+UK	rain.
77	CH55	02.07.89 03.07.89	12.11 16.23	55°00’N 55°05’N	00°40’W 00°04’E	9	Eu	good sampling weather.
78	CH55	03.07.89 04.07.89	18.08 10.48	55°00’N 54°05’N	02°01’E 02°23’E	8	Eu+OS	"
79	CH55	04.07.89 05.07.89	15.48 22.40	53°35’N 53°15’N	02°35’E 00°41’E	9	OS	good sampling weather.
80	CH57	24.07.89 25.07.89	13.16 11.25	52°37’N 52°27’N	01°46’E 03°41’E	9	Eu	"
81	CH57	25.07.89 26.07.89	12.02 04.17	52°27’N 51°12’N	03°41’E 01°36’E	7	Eu+UK	fog at end.
82	CH57	26.07.89 27.07.89	05.07 04.45	51°12’N 52°37’N	01°35’E 03°46’E	11	UK	fog patches.
83	CH57	27.07.89 27.07.89	05.36 23.10	52°37’N 53°14’N	03°46’E 04°24’E	9	UK	good sampling weather.
84	CH57	27.07.89 28.07.89	23.40 16.49	53°14’N 54°19’N	04°24’E 05°15’E	6	UK	"
85	CH57	28.07.89 29.07.89	17.17 16.30	54°12’N 53°52’N	05°27’E 07°19’E	10	Eu+UK	"

86	CH57	29.07.89 30.07.89	17.23 18.23	53°52′N 55°30′N	07°19′E 05°31′E	8	Eu+UK	rain at end.
87	CH57	02.08.89 03.08.89	11.47 16.48	55°01′N 55°30′N	01°17′W 00°59′W	10	UK	good sampling weather.
88	CH57	03.08.89 04.08.89	17.23 23.40	55°30′N 54°10′N	01°10′W 01°16′E	9	UK	"
89	CH57	04.08.89 06.08.89	00.05 00.05	54°10′N 52°45′N	01°16′E 01°53′E	6	UK	"
90	CH59	23.08.89 24.08.89	16.14 22.10	52°43′N 51°47′N	01°58′E 01°47′E	12	UK	rain at end.
91	CH59	25.08.89 29.08.89	17.22 16.43	51°60′N 55°30′N	03°32′E 05°30′E	9	OS	rain at start.
92	CH59	31.08.89 01.09.89	06.56 17.41	55°09′N 55°14′N	01°24′W 01°11′E	12	UK	rain at end.
93	CH61	21.09.89 22.09.89	16.16 11.54	52°43′N 52°22′N	01°57′E 03°17′E	11	Eu	good sampling weather.
94	CH61	22.09.89 23.09.89	12.53 09.04	52°19′N 51°28′N	03°07′E 02°40′E	17	Eu+UK	spray.
95	CH61	23.09.89 24.09.89	10.12 14.34	51°36′N 53°14′N	02°49′E 04°16′E	10	UK	good sampling weather.
96	CH61	24.09.89 25.09.89	15.22 00.15	53°13′N 53°38′N	04°24′E 04°40′E	9	UK	heavy rain.

97	CH61	26.09.89	11.02	53°44′N	06°29′E	13	UK	rain on ships radar.
		27.09.89	15.25	55°28′N	07°33′E			
98	CH61	27.09.89	16.50	55°30′N	07°12′E	10	UK	"
		29.09.89	23.11	55°00′N	01°18′E			

ú = arithmetic mean.
- = no data.

University of Liverpool (R. Chester and G. Bradshaw, trace elements [present work]: M. Preston and J. Merrett, trace Organics); University of East Anglia (T. Jickells and A. Rendell, rain water collection), and University of Essex (R. Harrison and C. Ottley, large particles).

2.6 The Aims of the Current Investigation.

A recent paper by Chester and Bradshaw (1991), presented data relating to the atmospheric trace element input to the North Sea. These data were used to: (1) provide 'baseline concentrations', which can be used in future monitoring studies, and (2) assess the extent to which local sources on the surrounding land masses control the geographical distributions of the trace elements over the open North Sea. This thesis expands on the paper and addresses: (1) the influence of air mass origin on the trace element loading over the North Sea aerosol (NSA), (2) the chemical reactivity of some trace elements in the NSA, by applying a series of sequential leaching, sea water and rain water solubility experiments, developed at the University of Liverpool Oceanography Laboratories, (3) a preliminary assessment of the fates of these trace elements in the water column, and (4) a crude estimate of the fluxes of atmospherically transported trace elements to the North Sea surface.

Chapter 3

Sampling The North Sea Aerosol.

3.1 Introduction

The numerous techniques available for sampling atmospheric particles have been reviewed by Hochrainer (1978), and they include: impactors (e.g. Anderson samplers), filters, electric precipitators, centrifuges, and instruments based on sedimentation. In considering the use of these techniques for the present project the following requirements were taken into consideration.

(1) Sampling would be carried out on board ship.

(2) An amount of sample sufficient for the analysis of several elements by atomic absorption spectrophotometry was to be collected in the minimum possible time (usually ~14 hours).

(3) A representative sample (i.e. all size fractions) of the total aerosol was required.

Samplers of the impactor, electric precipitator and centrifuge types generally have low flow rates and, given the above requirements, would result in correspondingly low sample yields. Analysis of these small amounts of sample is generally carried out by neutron activation analysis, a facility not available for the present project. Sedimentation methods would also result in small sample yields and would have the disadvantage that it would be difficult to accurately carry out solid state speciation, sea water and rain water solubility experiments, since matrix effects encountered in the analysis make it advantageous to have larger amounts of sample to commence with. Filtration techniques, particularly those involving hi-vol and cascade impactor (CI) sampler systems, meet all the requirements listed above.

In view of the sampler properties and project requirements briefly discussed above, two aerosol sampling techniques were therefore selected for the present investigation. These were:

(1) Filter sampling, using a hi-vol pump assembly (see Section 3.2), and

(2) Sierra Anderson CI filtration system (see Section 3.3).

In the subsequent sections, these air filtration devices will be discussed individually.

3.2 The Hi-Vol Filter Collection Technique.

The filter technique employed in the present work was essentially that developed and used by Saydam (1981), Sanders (1983) and Murphy (1985), although some modifications were necessary (i.e. the position of the air-filtration apparatus, see Figure 3.1). Similar hi-vol collection techniques have been employed by many other investigators at sea (see e.g. : Prospero, 1979; Buart-Menard and Chesselet, 1979; Murphy, 1985 and Berry, 1990).

3.2.1 Theory of the Hi-Vol Collection Technique.

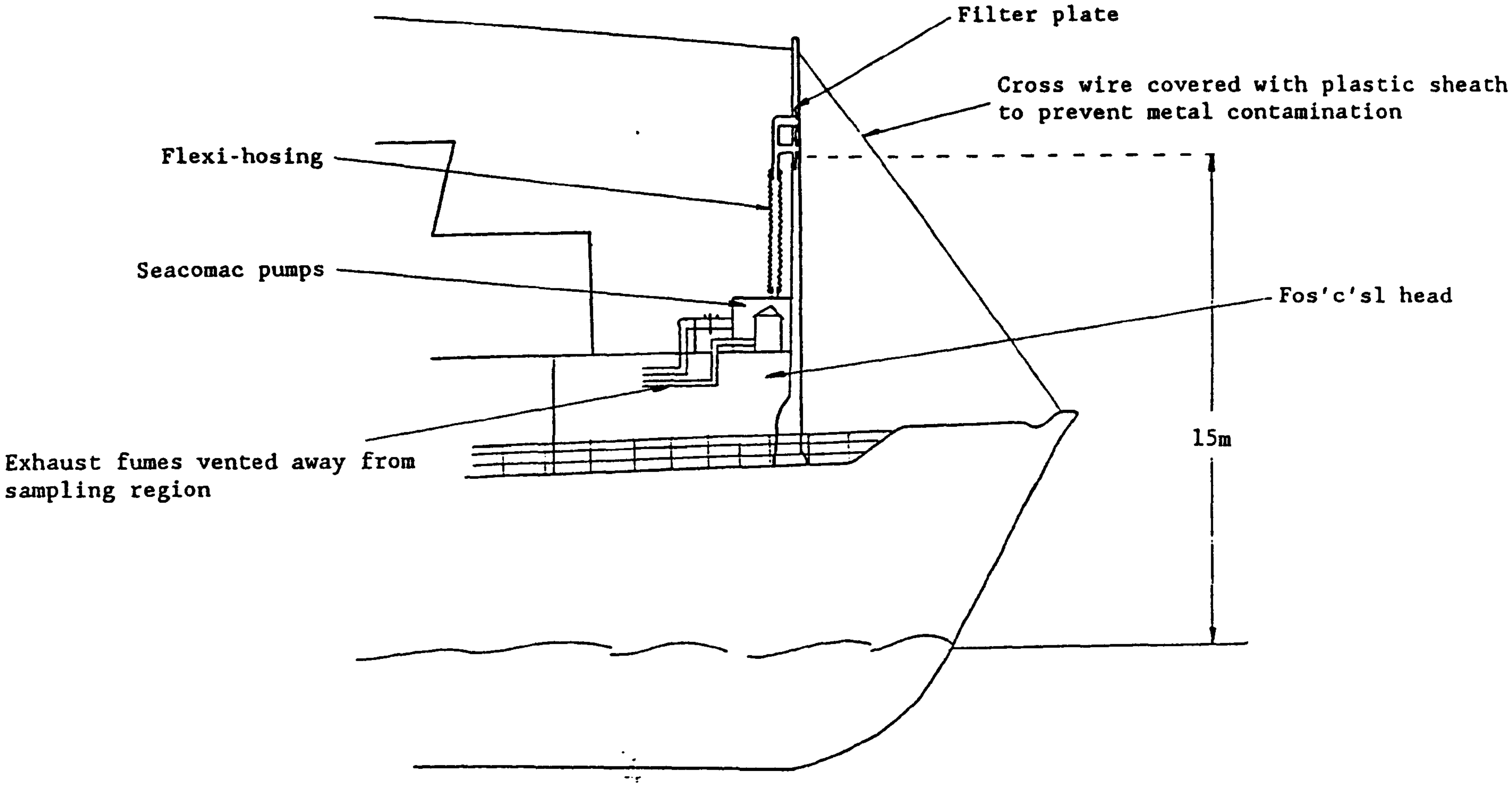

Figure 3.1 The position of the high volume and cascade impactor on board RRS Challenger.

The sampling of aerosols is based on the assumption that a particle moving in an airstream will have an inertia which is determined by the product of its velocity and its mass. The ideal sampling condition is one which does not induce perturbations in the atmospheric flow; i.e. the sample flow velocity should match the ambient air flow velocity, and this condition is termed iso-kinetic sampling Hudrey (1977). This will result in a minimal perturbation of the flow into and around the sampler, and will give an accurate estimation of the air volumes and thus particle concentrations. If the sampling flow rate is less than that of the ambient flow, the gas flow will be diverted around the sides of the sampler. Under these conditions the larger sized particles will deposit onto the sampler because of their inertia, and this will lead to an over estimation of the atmospheric concentrations of the particles. Finally if the sampling flow velocity is greater than the ambient flow velocity, more air will be drawn into the sampler. The particles will then tend to miss the sampler surface as they cannot accelerate towards it as fast as gas molecules, and an underestimation of the air concentration of particles will therefore result.

Due to the relationship between the size of a particle and its inertia, non iso-kinetic effects are more pronounced for large particle sizes. This results in a size bias during periods of non iso-kinetic sampling. However, according to Hudrey (1977) the inertial effects upon particles of less than 3-5μm is not sufficient to cause any meaningful error. Another consideration in relation to inertial effects is the orientation of the sampler into the oncoming air mass. Wedding et al., (1977), found that hi-vol samplers are extremely sensitive to the angle of sampling and that the collection efficiency falls off as the angle of approach veers from a direct headwind to a wind blowing across the face of the sampler, which will result in both an underestimation of the particle concentration. To minimise non iso-kinetic effects, would require the following conditions: (1) some means of orienting the sampler into the wind, (2) the maintenance of a constant ships course into the wind, and (3) sampling only in a direct wind.

Unfortunately, it was not possible to conform strictly to any of the above criteria. This was due to; (1) the hi-vol sampling plate being fixed in a set position (see Figure 3.1, and (2) the complex structure of the ships survey track (see Figure 2.1) resulted in a change of course approximately every hour. These two criteria resulted in a frequent change in the orientation of the sampler to the oncoming wind. As a result it was therefore decided that the small errors resulting with sampling under non-headwind conditions were acceptable in order to obtain as large a sample base as was possible.

The sampling flow rate used as in the North Sea project was ~0.8 ms^{-1}, depending on the pump characteristics. Sampling occurred in wind speeds ranging from 1 ms^{-1}-25 ms^{-1}, with the result that non-iso-kinetic sampling was unavoidable in some cases.

3.3 The Theory of the CI Technique.

CI's fractionate airborne particles according to their aerodynamic diameter, and operate by a mechanism of inertia (Davidson and Osborne 1986). Figure 3.2 represents a diagrammatic view of the Sierra Anderson Model 236 CI. In practice, the aerosol is drawn through the series of jets. Particles with a large aerodynamic size, i.e. large diameters, are deposited on the first stage, smaller diameter particles are deposited on successive stages down to the back up filter. The CI stages 2,3,4 and 5 have ten parallel slotted impaction jets, and stage 1 has nine slots. Particles which pass through the slotted jets in the impactor stages impact on the collection substrate and are deposited. The collection substrate also act as the pressure seals between the impactor stages. The stages stack on top of a clear anodized aluminium base plate, and are secured by two stainless steel studs. The base plate fits on top of a filter holder, which also contains a filter which acts as the backup filter for the CI, and collects all particles smaller than the cut off size of the last impactor stage, in this case $< 0.5\mu m$.

The experimental particle size collection will deviate from the predicted values if the design and operation of the impactor does not correspond exactly to theoretical values. There are several factors which must be taken into

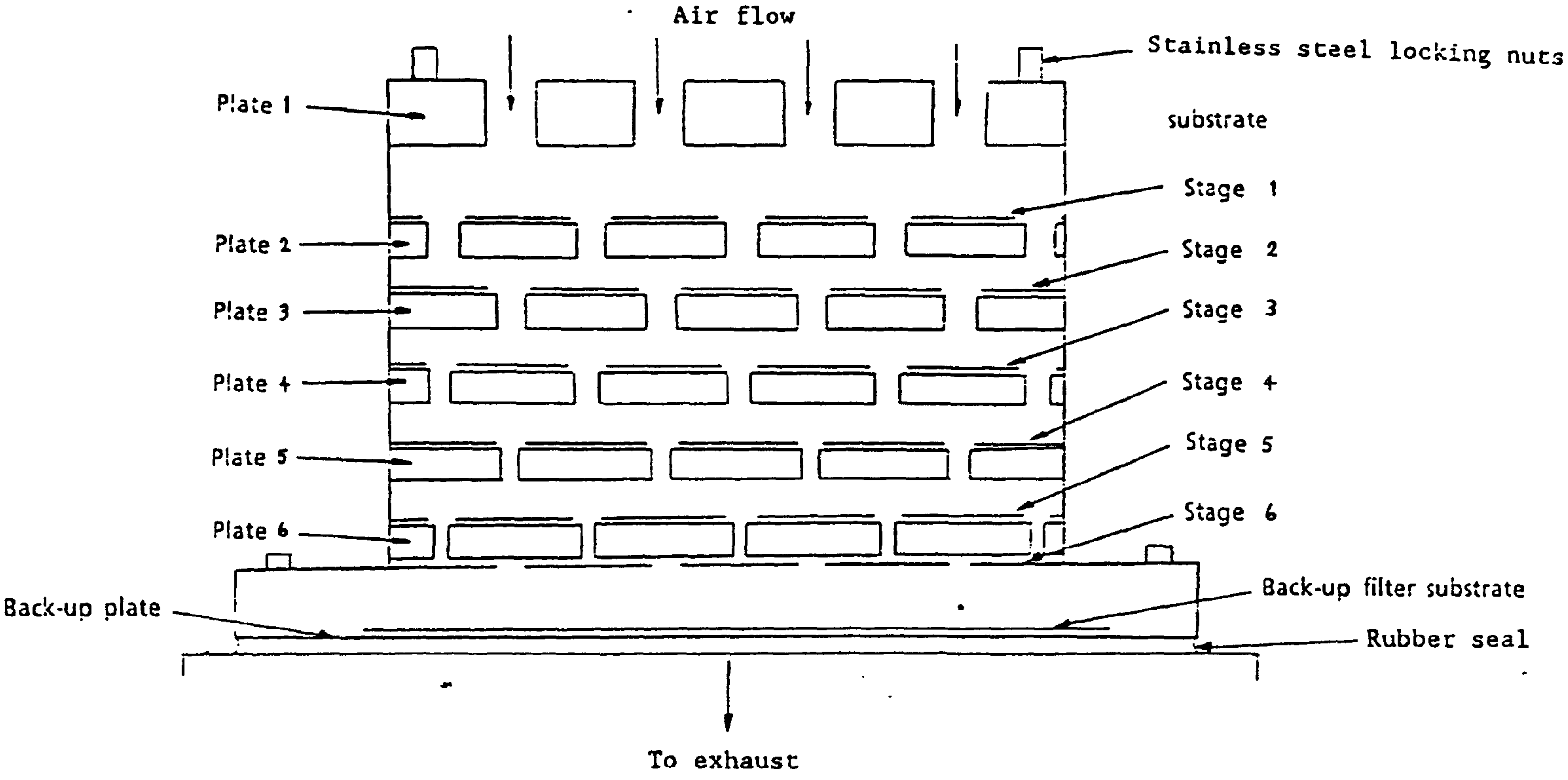

Figure 3.2 A cross section illustrating the cascade impactor housing assembly.

consideration when assessing the efficiency of the CI. Isokinetic sampling requires the air velocity at the impactor inlet to be approximately the same as the ambient wind speed, and the inlet must be directionally aligned with the wind (Liu and Pui, 1981). Large-particle loss on the inner walls of impactors can occur as reported by Cushing et al,. (1979), and Chan and Lawson (1981). Wall loses tend to decrease with particle size and are negligible for particles less than 1-2μm. Problems also arise with changes in the flow rate which essentially diminish the sharpness of the particle collection efficiency. Ultimately the accuracy with which the sampler measures the true average concentration depends upon the consistency of the airflow.

The Sierra Anderson Model 236 used in the present work was fitted with a constant flow controller which maintains a constant flow rate once calibrated (see Section 3.5.3) within the Environmental Protection Agency, U.S.A (EPA's) required accuracy of +/- 0.03 SCMM. The constant flow controller also provides correction for filter loading and changes in the line voltage, over a wide range of ambient temperature and ambient pressure conditions.

3.4 The Selection of Filters.

There are several criteria that must be taken into consideration in the selection of a filter for sampling marine atmospheric particles which are subsequently to be used for trace element analysis. The selection of Whatman 41 filters for use with a shipboard hi-vol system has been discussed in detail by Sanders (1983), and Murphy(1985), and a these selection criteria can be summarised as follows: (1) the filter should have a high collection efficiency for a wide range of particle sizes, especially for particle diameters < 1μm. (2) the filter should cause minimal restriction to the flow of air, so as to allow as large as possible volume of air to be sampled. (3) the filter must be relatively trace metal free. (4) the filter must be flexible and robust enough to enable sampling at high flow rates. (5) the filter must be completely solubilised in a mixture of nitric and hydrofluoric acids. (6) the filter must be readily available and relatively inexpensive.

Numerous types of filters have been used in atmospheric particulate studies, the two main types being; (1) Membrane filters, e.g. Millipore (0.45μm rated pore size), and (2) Fibrous filters of the glass fibre or cellulose fibre types. These filters will now be discussed.

Membrane filters have closely controlled pore sizes and high filtration efficiencies, but tend to exhibit relatively high flow resistance. In addition, they tend to be fragile in comparison with fibrous filters. Glass fibre filters are generally coarse, difficult to dissolve and posses low collection efficiencies for smaller sized particles. Furthermore, the level of impurities in glass fibre filters tends to be high (see Table 3.1). Glass fibre filters could therefore be rejected since they failed to meet criteria (1), (3), and (5) above. Membrane filters

Table 3.1 Metallic impurities in filters, ng cm^{-2}

Trace Element	Millipore 0.4μm	Whatman No. 41	Glass Fibre
Al	10	12	-
Co	<1	0.1	-
Cr	14	3	80
Cu	40	<4	20
Fe	300	40	4000
Hg	<1	0.5	-
Mn	2	0.5	400
Ni	<50	<10	<80
Pb	-	-	800
Ti	5	<10	800
V	0.09	<0.03	30
Zn	20	<25	160000

Taken from Harrison (1977).

failed to meet criteria (2) and (4), and were inferior to cellulose filters with respect to criterion (3) (see Table 3.1).

The most widely used cellulose fibre filters are the Whatman 41 and the IPC 1478. According to Savoie and Prospero (1977), the IPC 1478 filter has the advantage over the Whatman 41 filter with regard to flow resistance. However, the Whatman 41 is more readily available and has been commonly used for air sampling by many workers (see e.g. : Duce et al., 1976, Buart-Menard and Chesselet, 1979; Murphy, 1985; Schneider, 1987; Dulac et al., 1987 Duce et al., 1976a; Yaqqub, 1989; and Berry, 1990). It should also be pointed out that Whatman 41 filters were used for the collection of atmospheric particulates throughout the major SEAREX (Sea-Air exchange Program) in the Pacific Ocean (see e.g.: Duce et al., 1983; Arimoto et al., 1987). However, a number of criticisms have been made against the use of Whatman 41 filters for air sampling (see e.g.: Kitto and Anderson, 1988; Harrison, 1987). The efficiency of Whatman 41 filter paper media as an air sampling medium has been discussed in detail by Sanders (1983), and can be summarised as follows. Under conditions of hi-vol sampling the efficiency of the Whatman 41 is > 80% for particles over the radii range 1.0 - 2μm. As the loading on the filter increases the efficiency of the filter sampling also increases, so that the value given above is a minimum estimate of the particle collection efficiency.

Lowenthal and Rahn (1987), carried out a large-scale field study on the use of 47mm diameter Whatman 41 filters for the collection of atmospheric particles. The results indicated that under the sampling conditions used the collection efficiency of the filters was ~90%, or better. The authors concluded that the absolute errors associated with the sampling efficiency of the Whatman 41 filters were similar to those associated with uncertainties in the chemical analysis of the samples.

Despite the problems discussed above the Whatman 41 filter fulfils most of the necessary criteria for atmospheric particulate sampling in that it has a high collection efficiency, low blank values for the elements analyzed is readily available, and is strong and durable. Only criterion (2) (i.e. restriction of air flow) remained a problem, but the selection of a suitable pump allowed large volumes of air based on the selection criteria 1-6, to be sampled.

Whatman 41 filters were also selected for the use in the CI size fractionated aerosol collections see 1-6 above, and have been used for sampling of the marine aerosol by other workers (see e.g. : Duce et al., 1983; Arimoto et al., 1987; Dulac et al., 1987; Dulac et al., 1989; Bayens and Deudewarder, 1991). According to Arimoto et al., (1987), there is evidence that the mass size distributions of trace elements calculated from CI samplers may be shifted towards smaller particles because some particles bounce off the dry impaction surfaces and are deposited in the subsequent stages of the impactor; this does not apply to sea salt particles, however, because their hydroscopic nature reduces their potential for bouncing off the filter surface. In addition, the bouncing off effect for non sea salt particles may be less important for the marine aerosol because of the relatively high humidity in the air over the sea which will moisten the filters, thereby providing a more efficient impaction surface (Walsh et al., 1978).

3.5 Description of the Hi-Vol and CI Sampling Systems.

3.5.1.1 The Hi-Vol Sampling System.

The hi-vol sampling assembly used on board ship was developed in the Oceanography Laboratories at the University of Liverpool, and at the Research Vessel Services Barry. The system was originally built and tested by Sanders (1983), and incorporated a orifice plate which may be used to calibrate the flow rate (see Section 3.5.3). The positioning of the sampling equipment is shown in Figure 3.1. The filters were raised from deck level to the sampling position, ~15 m above the surface of the sea, by means of a pulley system consisting of a shackle at the top of the mast and high quality synthetic climbing rope. The sampling assembly was located as far forward on the ship as was possible, to minimise any contamination by funnel smoke or the structure of the ship. Contamination from the stay wire was reduced by covering with a plastic sheath.

The sampling equipment comprised a Seacomac high velocity fan Model 492/2, 415 volt, 3 phase, 50 hz. Two filter holders were mounted on an aluminium plate which had been painted with an anti-corrosive metal-free paint to prevent filter contamination (see Figure 3.3). The air which was drawn through the filters was directed through a PVC T intersection into a single length of tough plastic flexi hosing (75 mm internal diameter) stretching ~14m from the pumps to the filter plate. The exhaust from the pumps was diverted using thick PVC piping, which also contained the orifice plate mechanism, to the starboard, and rear of the ship to reduce filter contamination from exhaust fumes.

3.5.1.2 The Filter Assembly.

The Whatman 41 filters were clamped tightly between two perspex filter holders, using four perspex locking screws. The filter holder had terylene mesh at the rear, to support the filter (see Figure 3.4). PVC tape was then bound around sides of the two plates to ensure an airtight seal. In operation, each filter gave an exposed sampling diameter of 0.156 m; this produced a combined sampling area of 0.0428 m^2 and resulted in adequate flow rates.

3.5.1.3 Mounting the System and Connections.

The mounting system was designed and constructed by Research Vessel Services, Barry, for use on board ship. It consisted of ~12 m of 75 mm I.D. heavy duty flexible PVC tubing connecting the filter plate assembly to the Seacomac pumps. A T-shaped section of rigid PVC tubing connected the filter plate assembly to the end of the flexible hosing.

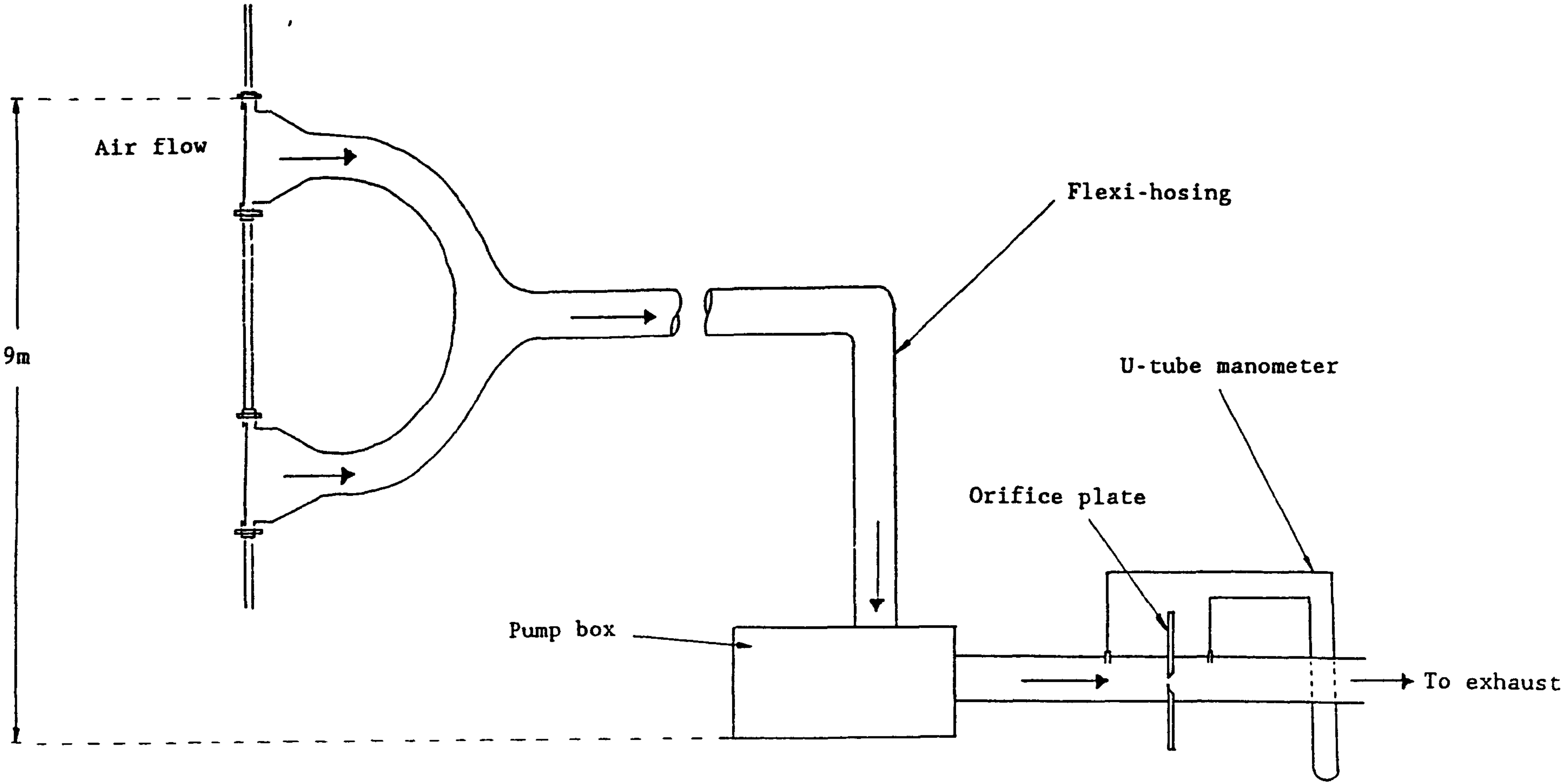

Figure 3.3 The high volume filter plate assembly.

The air flow through the filter plates was assumed to be the same for each sample and therefore, no attempt was made to investigate any differences in particulat concentrations between any pair of collected filters (see Sanders 1983). The steel filter plate was painted with epoxy resin to prevent metal contamination of the filters.

The flexible PVC tubing was connected to the T-intersection and pump assembly using a steel expandable clip, and further sealed using plastic sticky tape. The metal casing containing the Seacomac pumps was painted regularly with standard weather-proof paint preceding each voyage to prevent rusting and was positioned on top of the fo'c'slehead (see Figure 3.5).

3.5.1.4 The Hi-Vol Sampling Arrangement on Board Ship.

The air-sampling position and equipment arrangement on board ship is illustrated in Figures 3.1 and 3.5, and was designed and constructed by Research Vessel Services Barry. It consisted of two rigid anodised steel wires, one either side of the filter plate, which ran from the cross trees to the base of the pump housing. The filter plate was mounted onto the anodised steel wires by means of four anodised shackles, and was hoisted into position by means of a pulley arrangement constructed of a steel shackle and a heavy duty PVC rope. Contamination from the steel cross wire was reduced by encasing it in plastic hosing during the surveys.

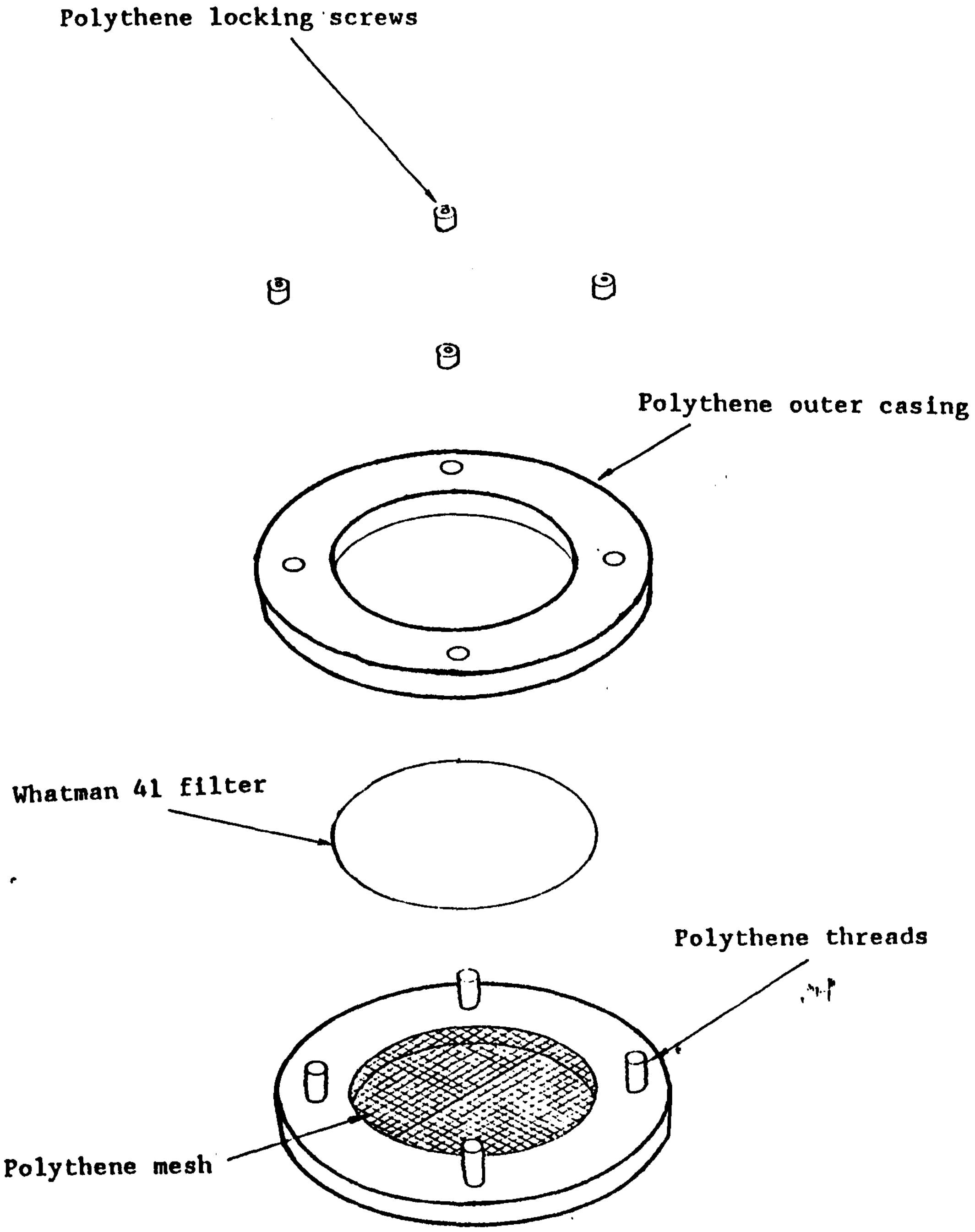

Figure 3.4 The high volume holder assembly.

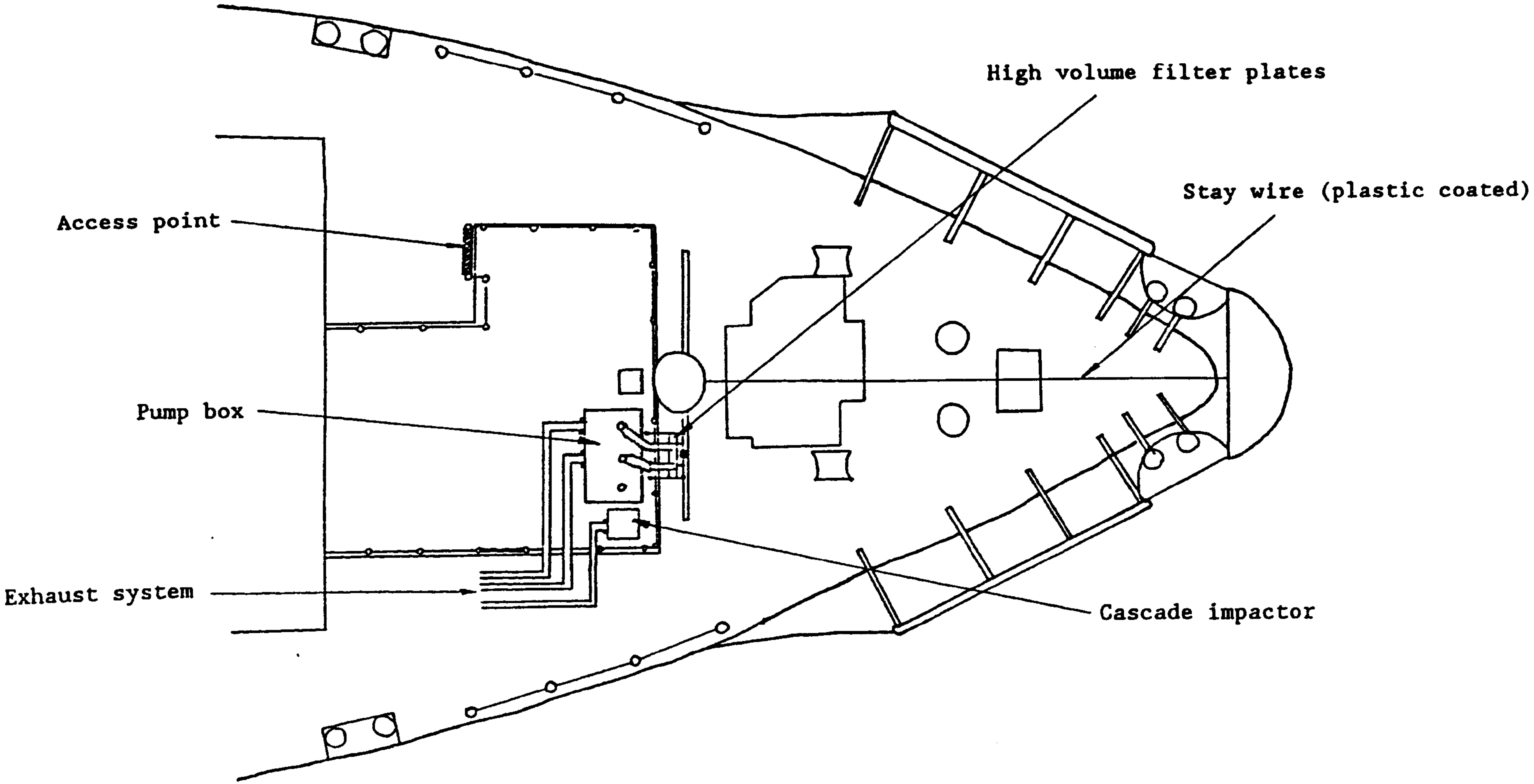

Figure 3.5 An overview of the sampling equipment.

3.5.2 The CI Sampling System.

The CI sampling system used on board ship was incorporated into a wooden protective housing constructed by Research Vessel Services Barry. The housing containing the CI was positioned on the starboard section of the fo'c'slehead, ~9 m above the surface of the sea.

The exhaust from the pump was diverted using thick PVC piping, to the starboard, and rear of the ship to reduce filter contamination from exhaust fumes. The CI was calibrated at the beginning and end of each survey (see Section 3.5.3).

3.5.2.1 The CI Sampling Technique.

The most commonly used instrument for the size fractionation of the marine aerosol is the Sierra Anderson slotted CI with flow rates of 1.0 $m^3 min^{-1}$ ~ 1.13 $m^3 min^{-1}$.

The CI used for the collection of size separated atmospheric aerosols for the North Sea project was a Sierra Anderson six stage hi-vol sampling impactor Model 236 with a flow rate of approximately 1.13 $m^3 min^{-1}$. This is a popular model and has also been used by several other workers, for example Duce et al (1976, 1983); Arimoto et al., (1985); Dulac et al., (1989), and Bayens and Deudewarder 1991.

3.5.2.2 The CI Sampling Arrangement on Board Ship.

The air-sampling position and arrangement for the CI on board ship is illustrated in Figure 3.5. At the beginning of each survey the CI filter plate containing the impactor stages and filters was mounted inside the container housing of the Aluminium casing, and sealed into position using four locking screws (see Figure 3.2).

3.5.3 The Calibration of the Air Flow Rates.

The assembly for measuring both the flow rate across the hi-vol filters and through the CI consisted of an orifice plate mounted between flanges in a 2.5 m length of the 75 mm diameter rigid PVC tubing. The orifice plate was located ~1 m from the relevant exhaust outlets; the pressure drop across the orifice was measured by means of a water-filled U tube manometer connected to brass tappings. These are situated at distances of 75 mm upstream, and 37.5 mm down stream of the front face of the orifice plate. The difference between the manometer readings is related to the flow rate by the formula for a straight edged orifice given by Francis (1971).

$$Q = \frac{6\mathrm{x}10^{-5}\ C\ a\ (2g[p_1 - p_2]/r_a\ g)^{1/2}}{[1-a/A^2]^{1/2}} \qquad \text{Equation 3.1}$$

$$Q = \frac{6\mathrm{x}10^{-5}\ C\ \pi\ d^2\ (2r_w g\ [h_1-h_2]/r_a)^{1/2}}{4(1-[d/D]^4)^{1/2}} \qquad \text{Equation 3.2}$$

Where;

Q = flow rate ($m^3\ min^{-1}$);

C = coefficient of discharge for an orifice = 0.62;

a = orifice cross-sectional area;

g = acceleration due to gravity = 981 cms^{-1};

p_1-p_2 = pressure drop across the orifice;

r_a = density of air at 20°C = 1.2×10^{-3}g cm^{-3};

A = pipe cros-sectional area;

d = orifice diameter cm (3.5);

r_w = density of water at 20°C;

$h_1 - h_2$ = difference of manometer limb readings, (cm);

D = pipe diameter, 7.5 cm;

$6x10^{-5}$ = factor to correct for centimetres into meters and seconds into minutes.

For the hi-vol and CI collectors Equation 3.2 reduces to:

$$Q = 0.4658 \; ([h_1 - h_2])^{1/2} \qquad \text{Equation 3.3}$$

The value for the volume of air sampled can be calculated by substituting the appropriate values of (h_1 - h_2) into Equation 3.3 and multiplying the obtained number by the sampling time (in minutes). In the calculation no corrections were made for the variation in air and water density since these errors will be relatively small compared with the errors in reading the manometer. In heavy swells the manometer readings (h_1 and h_2) can introduce errors of up to ~20%, although a figure of ~10% is more typical (Sanders 1983).

The calibration of the hi-vol filters was checked every hour during sampling and at the start and finish times during the sample collection. The CI, however, once calibrated, automatically adjusts to maintain a constant flow rate when the filters become loaded, and was therefore calibrated at the beginning of the survey.

3.5.4 Sampling Procedure at Sea.

In order to obtain as accurate as possible representative air sample, which is free from contamination, a strict protocol must be followed very closely. Hence the sampling procedure undertaken for the hi-vol collection technique was carried out as follows; steps 1-4 were carried out under a laminar flow hood air cabinet:

(1) A fresh pair of disposable plastic gloves were put on by the operator.

(2) The filter holders were rinsed with doubly quartz distilled water and allowed to dry.

(3) Using a pair plastic 0.1N acid-cleaned tweezers, an acid washed Whatman 41 was removed from its sealed plastic carrier and centred by eye on the terylene mesh of the hi-vol assembly filter holder. The filter holder was then assembled and sealed by two plastic locking nuts (see Figure 3.5).

(4) A protective plastic cover was placed over the filter holder assembly and firmly secured into position. The filter assembly was then placed into a polythene bag, and transported by hand onto the fo'c'slehead, ready to be fitted into position on the filter plate.

(5) A fresh pair of disposable plastic gloves were put on by the operator and the filter assembly was removed from

the polythene carrier bag. Using plastic locking screws the filter holders were then clamped into position on the filter plate.

(6) When sampling conditions were favourable, the protective plastic cover was removed from the filter holder assembly, the filters were raised to the sampling position (see Figure 3.1), and sampling commenced. At the beginning, and at regular hourly intervals during deployment, the following data were collected. (a) date and time GMT, (b) ships position, and course heading, (c) real wind speed, and direction, (d) weather conditions, and (e) the manometer readings.

(7) At the end of each sampling run the filter plate was lowered from the sampling position. The protective cover was then placed in position by the operator who wore plastic gloves, and the filter holders were then removed from the filter plate and placed into fresh polythene bags and transported to the laminar flow hood for packaging. Once inside the laminar flow hood, the operator put on a fresh pair of disposable gloves and the filter assembly was carefully opened to expose the filtered sample. The filter paper was then carefully folded, with the exposed faces together and sealed individually inside a clean, labelled, polythene bag. The perspex filter holders were then rinsed with redistilled water ready for reuse.

The sampling procedure undertaken for the CI was essentially the same as that for the Hi-vols, and is described below: Again steps 1-4 were carried out under a laminar flow hood air cabinet;

(1) A fresh pair of disposable plastic gloves were put on by the operator.

(2) The CI aluminum filter plates for each CI stage were rinsed with doubly quartz distilled water and allowed to dry.

(3) Using a pair plastic 0.1N acid-cleaned tweezers, an acid washed slotted Whatman 41 filter, was removed from its sealed plastic carrier and centred by eye on the corresponding CI stage plate. The CI filter assembly was then assembled and sealed by two stainless steel locking screws.

(4) The CI filter assembly was then placed into a polythene bag, and transported by hand onto the fo'c'slehead, ready to be fitted into position in the CI housing.

(5) A fresh pair of plastic disposable gloves were put on by the operator and the CI filter assembly was removed from the polythene carrier bag. Using the plastic locking screws the filter holder was then clamped into position inside the CI housing.

(6) A aluminium cover was placed over the top of the CI filter assembly to prevent contamination due to gravitational fallout etc.

(6) During the survey when sampling conditions were favourable, i.e. (a) there was no possibility of contamination from the ships funnel smoke, (b) there was an abscence of rain, and (c) an abscence of heavy sea swells.

Then air filtration commenced. At the beginning, and at regular hourly intervals during deployment, the following data were collected. (a) date and time GMT, (b) ships position, and course heading, (c) real wind speed and direction, and (d) weather conditions.

(7) At the end of each sampling run the CI filter assembly recovered and placed into fresh polythene bags and transported to the laminar flow hood for packaging. Once inside the laminar flow hood, the operator put on a fresh pair of disposable gloves and the filter assembly was carefully opened to expose the filtered sample. The filter papers were then carefully folded, with the exposed faces together and sealed individually inside a clean, labelled, polythene bag. The CI filter assembly was then rinsed with redistilled water ready for reuse.

3.6 Procedure in Bad Weather.

On the majority of occasions the officer of the watch on the bridge was able, by use of radar, to give advanced warning of imminent rain, snow, heavy seas, etc. In the event of advanced warning of events of this type one of the following procedures was adopted. (1) If sampling had already been carried out for sufficiently long periods then the hi-vol filters and CI was recovered in the standard manner and stored for analysis. (2) If the exposure period had been insufficient to collect a large enough quantity of sample, then the filter assembly was brought down. The plastic covers were then placed over the filter plates, and the assembly was encased in a polythene sheet and securely tied into position until the conditions for sampling became suitable again when the assembly was re-deployment occurred. Whenever sampling ceased, or resumed, all relevant readings were recorded with a note in the log book of the reason for the break in sampling.

In this chapter the calibration and the deployment of the NSA sampling equipment has been described. In Chapter 4 the analytical techniques used to determine total trace element concentrations and solubilities of the NSA are given.

Chapter 4

4.1 Analytical Techniques for Atmospheric Particles.

There are a number of analytical techniques that have been used to investigate the trace element composition of atmospheric particles. These include:

1) Instrumental neutron activation analysis (see e.g.: Dams et al., 1975).

2) X-ray photoelectron spectroscopy (see e.g.: Barbaray et al., 1979).

43) X-Ray florescence (see e.g.; Wedberg et al., 1974), and

4) Atomic absorption spectrophotometry (AAS) (see e.g.; Slavin, 1978).

In the present study the analytical technique employed to determine the concentration of the elements Al, Fe, Mn, Cr, Cu, Ni, Co, Cd, Pb and Zn in the NSA was atomic absorbtion spectrophotometry (AAS) in either the flame or the flameless mode. In addition Na and K were analyzed by emission using a flame photometer.

Prior to analysis by AAS, the elements were dissolved into solution by treatment of the aerosol samples with a mixture of concentrated nitric and hydrofluoric acids. The hydrofluoric acid is required to breakdown the aluminosilicate material, e.g. clays, thus releasing lattice bound elements into solution. The experimental procedure is described in Section 4.2.2. In addition to the total digestion of the samples, sub-samples were selected in order to carry out a series of sequential leaching, sea water and rain water solubilities using a selection of reagents.

4.2 Hi-Vol Sample Digest Procedure.

4.2.1 Reagents and Equipment.

Redistilled water. This was obtained from a Fisons Fi-stream water still connected to a Sybron/Barnstead NANOpure system, and was used throughout the project for the making of standards, the preparation of reagents and for the final washing of equipment.

0.1N Acid bath. This consisted of a plastic container, and lid, filled with a 0.1N acid solution, made up by diluting concentrated nitric acid in the appropriate volume of distilled water.

Redistilled concentrated nitric acid. This was obtained by distilation of BDH Analar grade nitric acid in a quartz still. The redistiled acid was then stored in a acid-cleaned polythene bottle.

40% Hydrofluoric acid, BDH Analar grade.

0.1N Redistilled nitric acid. this was prepared by dilution of redistilled concentrated acid with redistilled water.

Standard solutions were made up by dilution of the relevant BDH spectrosol grade 1000ppm solutions, using 0.1N redistilled nitric acid. Sodium and potassium standards were prepared from BDH Analar grade sodium and potassium chloride.

100ml capacity PTFE beakers/lids for the digestion of the filters. The beakers were cleaned using acetone, and washed thoroughly using detergent and a scourer. 20mls of concentrated nitric acid was then added and the beakers were placed on a hotplate to clean overnight. The acid was then discarded and the beaker and lid washed three times in redistilled water.

25ml Volumetric flasks were stored prior to use in a 0.1N nitric acid bath and were used for making up to volume standards, samples and blanks.

New 30ml Polystyrene Sterilin vials were used to store standards, samples and blanks.

4.2.2 Digestion of the Filters.

One of each pair of exposed Whatman 41 filters was used for the determination of the total atmospheric trace element loadings. The relevant filters and blanks were carefully removed from the sealed plastic bag used to store them, in a laminar flow hood using a pair of acid cleaned plastic tweezers. During this procedure the operator wore plastic disposable gloves. Each filter was then folded several times, placed into a cleaned PTFE beaker, and moistened with a little 0.1N redistilled nitric acid. 15ml of redistilled concentrated nitric acid was then added and the beakers, with lids, were placed on the hotplate to reflux at 60-70°C for 1-2 days. The PTFE lids were then removed using acid washed plastic tweezers, and approximately half the nitric acid was evaporated away prior to the addition of 10ml of hydrofluoric acid. The PTFE lids were then replaced and the mixture was allowed to reflux for a further 2-3 days at ~120°C to dissolve any remaining material. The lids were then removed and the mixture was allowed to evaporate to near dryness. 2ml of redistilled nitric acid was then added, followed by evaporation to near dryness again. This process was repeated twice more to drive off the hydrofluoric acid. After the final evaporation, 5ml of redistilled 0.1N nitric acid was added, the lids were replaced and the beakers transported to the laminar flow cabinet where the samples were made up to volume using 0.1N nitric acid in clean acid washed 25ml capacity volumetric flasks. The samples were then transferred to a new 30ml capacity Sterilin vile for storage prior to analysis.

4.2.3 Procedure for the Digestion of the CI Filters.

The exposed CI samples consisted of filters from the 5 stages, and a back-up filter stage. For each CI filter the analytical digestion procedure followed was that used for the digestion of the hi-vol collected samples (see Section 4.2.2).

4.3 Sequential Analysis of the Filters.

The complete dissolution of particulate material only gives information on the total amounts of the elements present in each sample. However, solid state speciation can provide information on the manner in which elements are partitioned among different host fractions in aerosols. In turn, this can provide information on the 'environmental mobility' of the elements following the deposition of the aerosols to the sea surface. Chemists can use sequential leaching techniques to investigate the solid state speciation of elements in aerosols. One of these techniques, involving a five stage leaching procedure was used by Chester et al., (1986), to investigate the solid state speciation of elements in crust dominated aerosols. However these authors used mesh-collected samples, which had the advantage that the material could be shaken from the meshes and used as discrete solids. Filter-collected samples cannot be readily removed from the filter substrate and collect much smaller quantities of sample than do meshes. Chester et al., (1989), designed a solid state speciation technique for direct application to filter-collected marine aerosols, but because of the relatively small amount of material they restricted their technique to only three stages. The three stages were selected in order to provide information on the most important host fractions in marine aerosols with respect to their 'environmental mobility'. The three stages are described below.

(1) Stage 1. Reagent 1M NH_4OA_c at pH7. Elements released at this stage are classified as being loosely-held. These elements are mainly derived from high temperature anthropogenic processes, and/or volcanic activity, and are important because they are the most 'environmentally mobile' elements associated with marine aerosols.

(2) Stage 2. Reagent 1M hydroxylamine hydrochloride + 25% acetic acid (the Chester-Hughes reagent). Elements released at this stage are classified as being in the carbonate, surface oxide and oxide associations. In particular, the oxide association is important because once the aerosol has been deposited in sea water the oxide fraction can act as a 'scavenging surface' for dissolved trace elements.

(3) Stage 3. Reagent nitric and hydrofluoric acids. Elements released at this stage are classified as being residual, or refractory, in character. These elements are associated with the crystalline lattices of minerals. Because of the limited amount of sample it was not possible to include a stage in the sequential leaching scheme which separated elements in organic associations from those in other associations. Stage 3 therefore includes elements found in such organic associations. The elements associated with stage 3 are the least 'environmentally mobile' of all the aerosol elements.

4.3.1 Reagents and Equipment.

Ion-exchange column. The column contained chelex 100 resin, and was cleaned prior to use by passing 100mls of 1N ammonium solution followed by 100mls of 1N nitric acid solution through the column. Excess ultra pure water was then passed through the column until the pH of the water leaving the column was ~7.

1M BDH Analar ammonium acetate pH7. The reagent was prepared by dissolving 77.08 g of Analar grade ammonium acetate in 1L of distilled deionized water, and was purified by passing through the ion-exchange column at pH ~7. This reagent was prepared immediately prior to its use.

1M hydroxylamine hydrochloride + 25% acetic acid. The combined reagent was prepared by dissolving 69.49 g Analar grade hydroxylamine hydrochloride in 750 ml distilled-deionised water, and adding 250 ml Aristar grade acetic acid to a final volume of 1L. The reagent was prepared immediately prior to its use.

Nitric and hydrofluoric acids. Redistilled nitric acid and Aristar hydrofluoric acid were used.

25 ml capacity glass pipettes. 0.1N nitric acid-soaked glass pipettes were used to transfer the reagent solutions into the sample.

BDH stock standard solutions. These were used to make up the relevant standards in, (1) the ammonium acetate, (2) the hydroxylamine hydrochloride + 25% acetic acid, and (3) 0.1N nitric acid for the final conc. nitric acid and HF acid stage.

30ml capacity polystyrene Sterilin vials. New acid-cleaned vials were used to carry out the leaching experiments, and for the subsequent storing of the three sample stages.

A Centaur MSE centrifuge. Was used for centrifugation at 2000 r.p.m.

A KS500 orbital variable speed shaker. Variable speed was used for shaking the filter/reagent combination.

4.3.2 Experimental Procedure.

All procedures were carried out under the laminar flow cabinet, with the operator wearing disposable plastic gloves. A pair of acid cleaned plastic tweezers was used to remove the selected filters from their sealed bags. Each filter was then carefully torn in half, and both halves were folded in on themselves so as not to expose the particle-loaded face to the air. One half of each filter was replaced in its plastic container, re-sealed and stored for later use. The remaining half filter was folded in on its-self again several times before ripping into smaller pieces which were placed into a clean Sterilin vile. This procedure was repeated for blank filters, using a fresh pair of disposable gloves for each new filter.

25mls of pH7-adjusted 1M ammonium acetate was added to the Sterilin vial using an acid-cleaned volumetric pipette and the vile was sealed with the lid and placed onto an orbital shaker for 20 minutes, after which it was centrifuged at ~2000 rpm for 15 minutes. The sample was then returned to the laminar flow cabinet where the ammonium acetate was decanted into a fresh Sterilin vile and labelled. 20mls of the 1M hydroxylamine hydrochloride + 25% acetic acid reagent was then added, and the vial was shaken on the orbital shaker for 6 hours. After centrifuging and decanting, the second Stage 2 reagent was placed into a new labelled Sterilin vial. The filter was then washed into a clean PTFE beaker using 0.1N redistilled nitric acid, and the beaker was placed on the hotplate to completely digest the sample in nitric and hydrofluoric acids following the procedure described in Section 4.2.2.

4.4 Sea Water Solubility Experiments.

A series of experiments were carried out to asses the extent to which elements in the NSA are soluble in sea water.

4.4.1 Reagents and Equipment.

Filtered sea water. Sea water collected from the North Sea at a depth of 10 m was used for the solubility experiments. The sea water was N_2 filtered through a 0.45μm Nucleopore membrane filter under a pressure of 1 atmosphere in a acid cleaned Sartorius polycarbonate filter assembly. The sea water was then cleaned by shaking with a 0.0125M MnO_2 solution to remove trace elements (van den Berg, 1984). The sea water was then filtered again through an acid cleaned 0.45μm Nucleopore membrane filter and finally through a regenerated ion-exchange column and stored in an acid cleaned Nalgene bottle prior to use.

Nalgene bottles. These were acid cleaned for the storage of the cleaned sea water.

Ion-exchange column. (see Section 4.3.1).

0.1N nitric acid. This was added to the sea water sample following the dissolution experiments to prevent trace element desorption onto the container walls.

10% L-ascorbic acid. This was freshly prepared from analytical grade L-ascorbic acid powder by dilution with distilled water to give a final solution of 10% (w/v) and, was used as a matrix modifier for the analysis of Pb.

Standard solutions. These were prepared as described in Section 4.2.1, but using sea water instead of distilled water.

30ml capacity polystyrene Steralin vials. These were used for the storage of the samples.

Filtration assembly. For the filtration of the sea water, an acid washed 2.5 cm diameter membrane filter was clamped in a filter holder constructed of perspex. A plastic screw cap which was connected to the N_2 gas supply, sealed the filter assembly.

0.45μm membrane filters. A 47mm diameter membrane filter was used in the filter system. The filters were cut in a perspex press to give a diameter of 2.5 cm, and were then acid washed in 0.1N nitric acid for 24 hours. The filters were removed from the acid bath using acid cleaned plastic tweezers and thoroughly rinsed using distilled water before being used to filter the sample solutions.

25ml glass pipettes. These were acid cleaned before use.

Gilson autopipettes and plastic disposable tips. (200 μl, 1 ml, 5 ml capacity), these were acid cleaned prior to use.

KS500 orbital variable speed shaker.

4.4.2 Experimental Procedure.

All the sea water procedures were carried out under the laminar flow hood with the operator wearing a pair of plastic disposable gloves. The exposed Whatman 41 (half) filters, and blanks, were carefully removed from their sealed plastic bag containers using a pair of acid cleaned plastic tweezers. The filters were folded several times and then torn into small pieces and placed in new freshly labelled polystyrene Steralin vials. 25ml of sea water was then added to each of the filters in the vials using the acid-cleaned glass pipette. With the lid firmly in place, the vials were given a good shake by hand in order to ensure all parts of the filter were wetted by the sea water. The vials were then transported to the orbital shaker and agitated for one hour. The filtration apparatus was removed from the acid bath and thoroughly rinsed with distilled water. Under the laminar flow hood, the acid washed 0.45μm membrane filter was rinsed thoroughly with distilled water and secured into position in the filter holder. Following the agitation period the sea water solution was filtered under a pressure of 1 atmosphere using N_2 gas. The filter was then carefully rinsed into a cleaned PTFE beaker using as little as possible 0.1N nitric acid solution. Finally, a mixture of concentrated redistilled nitric and hydrofluoric acids was added in order to totally digest the remaining substrate, which was then stored. The total digestion of the filter was used to give an indication of the concentration of the residual material which was not soluble in sea water. At the normal pH range of sea water most trace elements are metastable, which can result in a loss from solution by element precipitation and absorption on to the container walls as the solution ages. To prevent the potential loss of trace element in this way the processed samples and blanks were spiked with redistilled concentrated nitric acid to give a final concentration of 0.1N.

4.5 Rain Water Solubility Experiments.

A series of experiments were carried out to asses the extent to which elements in the NSA are soluble in rain water at pH ~4.0.

4.5.1 Reagents and Equipment.

Artificial rain water. Rain water was prepared in ultra pure water following a recipe from Statham and Chester (1988), and had a composition as follows;

(a) Cations (μM) Na^+ (5), K^+ (2), Ca^+ (5), Mg^+ (2), NH_4^+ (20) and H^+ (23).

(b) Anions (μM) Cl^{-1} (9), NO_3^- (35) and SO_4^{2-} (10).

Ion-exchange column. (see Section 4.3.1).

Standard solutions. These were prepared as described in Section 4.2.1, but using artificial rain water instead of distilled water.

30ml capacity polystyrene Steralin vials. These were used for the storage of the samples.

25ml glass pipettes. These were acid cleaned before use.

Gilson autopipettes and plastic disposable tips. (200 μl, 1 ml, 5 ml capacity), these were acid cleaned prior to use.

KS500 orbital variable speed shaker.

4.5.2 Experimental Procedure.

A concentrated stock solution 1000 times the final concentration of the rain water was prepared and trace element contaminants were removed by passing through a ion-exchange column. Sub-samples of the rain water concentrate were diluted 1000 fold with ultra pure water and were acidified to pH ~4.0, using 0.3M sulphuric acid. This solution was stored in acid cleaned Nalgene bottles,

The rain water solubilitie experiments were carried out under the laminar flow hood with the operator wearing a pair of plastic disposable gloves. The exposed Whatman 41 (half) filters, and blanks, were carefully removed from their sealed plastic bag containers using a pair of acid cleaned plastic tweezers. The filters were folded several times and then torn into small pieces and placed in new freshly labelled polystyrene Steralin vials. 25ml of rain water was then added to each of the filters in the vials using the acid-cleaned glass pipette. With the lid firmly in place, the vials were given a good shake by hand to ensure that all parts of the filter were wetted by the rain water. The vials were then transported to the orbital shaker and agitated for 20 minutes. The filtration apparatus was removed from the acid bath and thoroughly rinsed with distilled water. Under the laminar flow hood, the acid washed 0.45μm membrane filter was rinsed thoroughly with distilled water and secured into position on the filter holder. Following the agitation period the rain water solution was then filtered under a pressure of

1 atmosphere using N_2 gas. The filter was then carefully rinsed into a cleaned PTFE beaker using as little as possible 0.1N nitric acid solution. Finally, a mixture of concentrated redistilled nitric and hydrofluoric acids was added to totally digest the remaining substrate which was then stored. The total digestion of the filter was used to give an indication of the concentration of the residual material which was not soluble in the rain water. Absorption on to the container walls was prevented by addition of redistilled concentrated nitric acid to give a final concentration of 0.1N.

4.6 Determination of the Trace Elements by Flame (AA) and Flameless (AAS).

The theory and general procedures involved in AAS and flame photometry are well documented (see e.g.: Slavin, 1978), and will not be described in detail in the present work. All flame analyses were performed on a Perkin Elmer model 2380 atomic absorption spectrophotometer, whilst the flameless work was carried out on a Perkin Elmer model 1100B (HGA-700/AS70) graphite furnace spectrophotometer, using a single element hollow cathode lamp and a deuterium background corrector lamp. The instruments were operated in accordance with the manufactures instruction manual. Instrument settings for slit width and wavelength were used as given in the manual, and recommended evaporation of the solvent, pre-char (in the case of a heavy matrix), char and atomization temperature steps were used as guidelines. The optimum ramp and hold times for the corresponding temperature steps were determined by experimentation. Sample injection volumes of between 5-50μl, carrier gas flow rates and graphite tube quality (non-coated or coated) were selected on the basis of the sensitivity required. When necessary, aliquots of the samples were diluted using the blank solution to bring them within the linear range of the instrument for the particular element.

Flame and flameless trace element concentrations were determined by comparison of the concentrations in the samples with those in the standard solutions. The standards were made up in the same medium as the samples immediately prior to the analysis.

For the analysis of Al, a solution of BDH Analar grade potassium chloride was added to the samples to give a concentration of 2000ppm, with respect to potassium. This was necessary to prevent loss of sensitivity due to the ionisation of Al in the high temperature nitrous oxide/acetylene flame.

Sodium and potassium were determined in both hi-vol and CI samples by atomic emission using an Evans Electroselenium Ltd, EEL flame photometer. The instrument was operated as per manufactures guidelines. When determining Na the samples generally required dilution of up to 100 times, using 0.1N redistilled nitric acid. The concentrations of the samples were determined by comparison with standard solutions.

The direct analysis of trace elements in sea water by AA presents a number of problems due to the heavy chloride/matrix properties of the sea water which reduce analytical sensitivity. Pre-concentration is normally required when detecting trace elements in sea water because of the very low concentrations; i.e. in the range ~ 10^{-6} - 10^{-12} gl^{-1}. However, in the present study pre-concentration was not necessary because of the relatively high concentration of trace elements in the sea water leaching solutions. However, the use of matrix modifiers was required in order to increase the sensitivity of the technique. (1) Interference from chloride was overcome by the addition of 200μl of conc redistilled nitric acid to the sea water leaching sample in the graphite tube prior to the charing step in order to drive off the chloride as HCl during thermal pretreatment. (2) The addition of 20μl of 10% ascorbic acid was used as a matrix modifier for Pb. The matrix modifiers change the wetting properties of the mixture and spread the injected sample over the interior of the graphite tube. This results in much smaller salt crystals being formed on the surface of the tube after the drying stage, and allows for more efficient and reproducible thermal pre-treatment and atomization of the sample. Analysis by Flame AA was generally possible for the following elements:

(1) Al, Fe, Mn, Cr, Cu, Ni, Pb and Zn in total digests on hi-vol samples placed into the European (Eu), the United Kingdom (UK) and the Mixed European and United Kingdom

(UK+Eu) groupings, (see Section 6.2.2.1.1 for a description of the grouping selection criteria).

(2) Fe, Mn, Cu, Cr, Pb and Zn in total digests on hi-vol samples placed in the Open Sea (OS) grouping.

(3) Al, Fe, Mn, Cr, Cu, Ni, Zn and Pb for stages 1-5, and the back up filter, in both CI samples.

(4) Fe, Cu, Zn and Pb in most of the ammonium acetate sequential leaching, sea water and rain water solubilities on filters for the groupings Eu, UK and Eu + UK.

(5) Pb and Zn in the hydroxylamine hydrochloride + 25% acetic acid reagent sequential leaching extracts for some samples extracts.

(6) Al and Fe in the final stage of the solid state speciation, sea water and rain water solubilities for most of the samples analyzed.

Analysis by flameless AAS was used for the following elements:

(1) Cd and Co in all the hi-vol total digests and CI samples (all the stages).

(2) Al and Ni in hi-vol samples placed in the (OS) grouping, and for all the sea water and rain water solubility experiments.

(3) Al, Mn and Cd in the both the solid state speciation, sea water and rain water solubilities experiments.

(4) Al, Fe, Mn, Cu, Zn and Pb in the hydroxylamine hydrochloride + 25% acetic acid sequential leaching extracts.

(5) Cu, Zn, Pb and Cd in the final stages of the solid state speciation, sea water and rain water solubilities experiments.

4.7 Analytical Blanks and the Detection Limits of the Analysis.

4.7.1 The Analytical Blank.

The hi-vol and CI filter samples used in the present work were assessed for analytical blanks by adopting the following procedure. For each set of air samples collected on each survey, three blank filters which had not been exposed to air sampling, were run through the total digest procedures described in Section 4.2.2 for the hi-vol and CI samples, and through the solid state speciation, sea water and rain water solubility experiments. The blank concentration obtained was then subtracted from the sample concentration, to give the concentration of the element of interest.

4.7.2 The Detection Limits of the Analysis.

In order to set the detection limit for the analysis of an element the following Equation 4.1 was used.

$$A_{bs} = Blk_{bs} + 3 \times S_{d\ blk} \qquad \text{Equation 4.1}$$

where; A_{bs} = the minimum absorbance of the detection limit.

Blk_{bs} = the mean value of the blank absorbance.

S_d = the standard deviation of the blank absorbances used to calculate the mean absorbance value.

Any sample which gave an absorbance reading less than A_{bs} in Equation 4.1 was classified as being below the detection limit.

4.8 Accuracy and Precision of the Determinations.

4.8.1 The Accuracy of the Determinations for the Hi-Vol and CI Samples.

The accuracy of the trace element determinations in the present work was estimated using U.S.G.S. standard rocks AGV-1 and G-2. The standard rocks were digested and analyzed as described in Section 4.2.2. The results are presented in Table 4.1 which also shows the results obtained by Flanagan (1973), Rantala and Loring (1975), and Murphy (1985) for the analysis of the same standard rocks. Further, a comparison of the results show reasonable agreement for the trace elements analyzed.

4.8.2 The Precision of the Determinations for the Hi-Vol and CI Samples.

10 sub-samples of a mesh collected dust taken by Murphy (1985), were digested and analyzed as described in Sections 4.2.2, in order to estimate the precision of the analytical method. Table 4.2 presents the ranges of the

concentrations, mean concentration, standard deviation and coefficient of variation.

4.8.3 The Accuracy, and the Precision of the Determinations for the Solid State Speciation, Sea Water and Rain Water Solubilities.

4.8.3.1 The Solid State Speciation.

Chester et al., (1989), pointed out that it was not possible to check directly the precision of the three-stage sequential leaching technique on filter-collected aerosols because insufficient amounts of a single sample were available. Nor was it possible to check directly the accuracy of the technique since appropriate filter-collected aerosol standards are not available. The authors concluded, therefore, that ultimately the assessment of the accuracy of the technique must rely on a 'geochemical consistency' test. The same approach was adopted in the present work.

4.8.3.2 The Sea Water and Rain Water Solubility Experiments.

The same general conclusions reached by Chester et al., (1989), regarding the determination of the accuracy and reproducibility of the sequential leaching experiments, also apply to the sea water and rain water solubility experiments carried out in the present study. Thus, insufficient quantities of individual samples were available to check reproducibility, and no appropriate sea

Table 4.1 Trace element concentrations in standard rocks, (concentrations in ppm).

TRACE ELEMENT	STANDARD ROCK	PRESENT WORK	FLANAGAN (1973)	RANTALI AND LORING (1975)	MURPHY (1985)
AL	AGV-1	93215	91298	-	94735
	G-2	82489	81506	81100	83433
Fe	AGV-1	54127	47282	-	52593
	G-2	20085	18535	19000	21079
MN	AGV-1	727	763	-	713
	G-2	275	260	250	231
Cd	AGV-1	0.069	0.090	-	0.060
	G-2	0.023	0.039	-	0.019
Co	AGV-1	14.8	14.1	18.0	15.0
	G-2	6.7	5.5	7.0	5.1
Cr	AGV-1	12.1	12.2	9.0	12.5
	G-2	7.2	7.0	7.0	7.1
Cu	AGV-1	55.3	59.7	59.0	54.7
	G-2	11.4	11.7	12.0	11.5
Ni	AGV-1	18.9	18.5	12.0	19.6
	G-2	3.9	5.1	<12.0	4.4
Pb	AGV-1	35.4	35.1	40.0	32.1
	G-2	30.5	31.2	34.0	28.8
Zn	AGV-1	87.2	84.0	90.0	88.9
	G-2	82.9	85.0	87.0	83.9
Na	AGV-1	31745	31600	-	31936
	G-2	29485	30194	29400	29339

- no data.

Table 4.2 Reproducibility of analysis (concentrations in ppm).

METAL	CONCENTRATION RANGE	MEAN CONCENTRATION	STANDARD DEVIATION	VARIATION COEFFICIENT
Al	79106 - 86142	82944	2280	2.75
Fe	49950 - 53200	51274	768.3	1.49
Mn	951 - 1073	1002	43.6	4.36
Cd	0.194 - 0.226	0.207	0.013	6.42
Co	23.4 - 27.9	25.9	1.6	6.05
Cr	74.2 - 85.9	79.3	4.05	5.11
Cu	42.1 - 44.0	43.2	0.67	1.55
Ni	63.9 - 76.3	69.2	4.05	5.86
Pb	43.2 - 49.1	46.7	1.94	4.15
Zn	79.4 - 86.9	82.7	2.65	3.19
Na	5219 - 5870	5571	198.4	3.56

water and rain water standards were available to check the accuracy of the sea water analysis. It was therefore decided to apply the 'geochemical consistency' approach to the sea water and rain water solubility data.

In the previous sections the analytical techniques employed to determine (a) total atmospheric particulate concentrations, and (b) speciation studies have been described. In the next chapter the results obtained from these experiments are presented.

Chapter 5

The Calculation of Results.

5.1 Introduction.

During the present investigation data were obtained on the following; (a) total aerosol trace element concentrations (hi-vol filters); (b) size-fractionated trace element concentrations (CI's); (c) aerosol trace element solid state speciation; (d) aerosol sea water solubility experiments and (e) aerosol rain water solubility experiments.

All the calculations were carried out on the initial raw data (μg trace element per filter), using Minitab release 7.2. Table 5.1 supplements the collection details for the hi-vol aerosol samples given in Table 2.1, and is included in this chapter because the table contains additional information used in the calculation of the results.

Concentrations in $\mu g\ g^{-1}$ for the hi-vol samples were calculated by relating the concentration of the digested final soloution (25mls), and comparing this to that of the relevant standard concentration. These data are given in Table 5.2.

Tables 5.3a and 5.3b present the raw data in $\mu g\ g^{-1}$, and the % of the total trace element concentration on the CI stages.

Table 5.1 The sampling time, volume of air sampled, and the average manometer readings for the NSA hi-vol samples.

Sample number.	Sampling time (mins).	Volume of air sampled (m^3).	Mean manometer reading.
1	456	749.5	12.4
2	649	1089.9	13
3	288	473.3	12.4
4	871	1348.8	12.4
5	804	1309.2	12.2
6	760	1276.9	13
7	803	1349.1	13
8	653	1125	13.6
9	565	1105.3	12.0
10	620	992.5	11.8
11	700	1150.5	12.4
12	534	877.7	12.4
13	790	1301	12.5
14	829	857.3	39.2*
15	575	588.5	38.4*
16	800	792.3	35.9*
17	648	697.8	42.5*
18	717	746.1	39.7*
19	605	625.5	39.2*
20	896	914.5	38.2*
21	716	740	39.2*
22	581	1062	15.4
23	819	1437.6	14.2
24	660	1160.9	14.2
25	502	864.9	13.6[1]
26	795	1369.7	13.6[1]
27	667	1229.1	13.6[1]
28	685	1180.1	13.6[1]
29	907	1562.6	13.6[1]
30	680	1171.5	13.6[1]
31	685	1180.1	13.6[1]
32	808	1387.9	13.6[1]
33	740	1271.2	13.6[1]
34	850	1464.4	13.6[1]
35	395	870	13.6[1]
36	579	976.1	13.1
37	531	914.8	13.6
38	878	1518.7	13.8
39	1146	1974.4	13.7
40	863	1486.5	13.8
41	807	1661.6	13.1
42	656	1077.3	12.4
43	678	1168.1	13.7

Con'td.

44	914	1697.6	15.9
45	730	1257.7	13.7
46	829	1428.2	13.7
47	1223	2191.6	14.8
48	936	1631.3	14
49	1020	1777.7	13.6[1]
50	811	1413.5	13.6[1]
51	1212	2112.4	13.6[1]
52	746	1300.1	14
53	506	798.6	11.5
54	1642	2556.2	11.2
55	626	1121.8	14.8
56	1146	1916.5	12.9
57	857	1445.4	13.1
58	1448	2523.7	13.6[1]
59	961	1519.3	11.5
60	934	1462.5	11.3
61	868	1578.9	15.3
62	839	1518.6	15.1
63	957	1613.4	13.1
64	775	1311.6	13.2
65	835	1470.8	14.3
66	994	1666.2	12.9
67	1006	1685	12.9
68	809	1316.2	12.2
69	1068	1971.2	15.7
70	1000	1874.8	16.2
71	1062	1783.6	13
72	972	1753.5	15
73	961	1339.2	13.6[1]
74	823	1212.3	10.9
75	951	1515.2	11.7
76	164	264.6	12
77	931	1343.7	13.6[1]
78	862	1288	10.9
79	878	1312.5	10.9
80	1137	2006.3	14.4
81	936	1648.7	14.6
82	856	1491.9	14
83	917	1598.2	14
84	933	1628.8	13.7
85	1055	1825.5	13.8
86	698	1194.6	13.5
87	1093	1884.4	13.7
88	984	1705.2	13.8
89	1380	2431.6	14.3
90	957	1406.1	10.9
91	999	1464	11.7
92	945	1448	10.8
93	978	1416.2	13.6[1]
94	954	1310.9	13.6[1]
95	896	1523.2	13.9
96	993	1688.8	13.9

Cont'td.

97	981	1667.7	13.7
98	1022	1839.4	13.6

[1] averaged manometer reading used.

* orifice plate diameter used = 2.1 cm, all others were 3.5 cm.

Table 5.2. Atmospheric particulate concentrations ($\mu g\ g^{-1}$) for the NSA hi-vol samples.

Sample Number	Al	Fe	Mn	Ni	Cd	Co	Cr	Cu	Pb	Zn	Na
1	512	304	11	2.4	0.28	0.23	6.4	4.8	55.5	-	-
2	289	158	3.8	7	0.28	0.39	6.6	3.8	41	38	3035
3	222	159	4.1	2.3	0.22	0.14	5.6	4.1	41	41.5	360
4	100	96	2.2	0	0.46	0.29	4.9	4.8	40	33.5	1175
5	211	163	3.6	4.7	0.43	0.3	6.6	5.4	42.5	38	1785
6	39	1.5	0.2	2	0.01	0.07	3.1	1.7	13.5	7.3	2080
7	228	119	5.4	2.6	0.03	0.11	5.7	3.1	12.5	11.5	2140
8	312	144	5.9	3.	0.09	0.19	6.8	4.8	9.3	9.9	-
9	116.5	80	3.2	2.3	0.2	0.29	5.5	1.6	23	18	2590
10	100	202	10	4.8	0.01	0.23	4.9	6	56	34.5	-
11	433.5	214	13	1.7	0.73	0.18	5.8	5.4	57.5	34.5	10270
12	294.5	186	6.4	2.2	0.21	0.25	3.3	4.1	38.5	15	4844
13	350	1050	14.5	2.3	0.14	0.38	6.3	4.1	18.5	25	6453
14	72	35.5	4.8	0.52	0.15	0.11	1.3	1.3	7.8	3.2	7680
15	144	68	36.5	1.9	0.28	0.17	4.6	8.2	8.7	25	3035
16	300	238	21	4.1	0.19	0.19	3.6	3.3	16	26	1250
17	72.5	40	1.8	1.5	0.14	0.15	2.9	1.1	0.5	1.2	2410
18	278	219	7.9	2.	0.21	0.11	5.9	3.7	5.9	18	209820
19	394.5	560	18	1.9	0.59	0.23	7.7	7.7	53	32.5	5270
20	489	616.5	22	1.9	0.53	0.31	6.9	13.5	47.5	42	3390
21	189	-	21	7.4	0.21	0.17	1.1	3	6.3	17.5	5270
22	244.5	929	36.5	3.8	0.72	0.51	10.5	12	114.5	85.5	15180
23	1205	1784	82	18.5	2.4	0.4	36	28.5	216	239	30000
24	494.5	1279	40.5	1.8	0.29	0.78	28	20	166	139	7500
25	306	213	8.7	1	0.44	0.45	3.9	7.7	17	18	9285
26	200	50	3.6	3.7	0.07	0.08	6.2	10	5.2	3.4	55360
27	216.5	385.5	21	1.6	0.22	0.24	4.8	5.1	54	54	9460

Con'td.

28	39	166	6.4	3.5	0.09	0.14	0.1	1.8	7.7	4.2	9075
29	322	287.5	14	9.8	0.17	0.44	3.2	5.2	37	41	4350
30	455.5	716.5	36	9.1	0.38	0.64	18.5	44	163.5	83	11880
31	200	128	9.5	1.8	0.16	0.16	4.8	4.5	15.5	15.5	3900
32	294.5	366.5	23	5.7	0.93	0.34	4.4	6.9	43	64.5	11850
33	516.5	666.5	36	8.4	0.42	0.5	10	5	62	77.5	8700
34	566.5	554	32	9.8	0.71	0.46	7.3	21.5	201	185	3750
35	227.5	185.5	9	5.7	0.28	0.19	2	0.4	24	53.5	6075
36	400	541.5	16.5	5.1	0.43	0.4	5	18.6	49	39	12000
37	122	120.5	77.5	5.1	0.45	0.27	2.4	5.3	18	59	2325
38	216.5	916.5	51	5.1	0.26	0.24	17.3	6.6	71	33	109500
39	161	153	3.3	0.99	0.05	0.09	1.2	1.3	6.4	12.5	21000
40	450	817	30.5	11.47	0.95	0.73	3.6	14.5	85	123.5	30000
41	839	1034	41.5	9.8	0.45	0.43	4.8	9.3	78	81.5	3150
42	560.5	321	14	5.9	0.53	0.41	5.7	8.4	40.5	64.5	1326
43	372	438.5	16.5	6.7	0.72	0.27	2.4	5.5	67.5	62	3075
44	71.5	439	24.5	9.8	0.61	0.29	3.2	14.5	26.5	1.1	31500
45	72	94.5	6.9	5.1	0.67	0.12	2.4	3.3	27	36	2685
46	261	209	7.6	4.8	0.17	0.18	2	2.7	26.5	21.5	12540
47	295.5	231	3.6	5.7	0.91	0.25	2.8	5.5	41.5	81.5	6600
48	283	456.5	10.6	11.6	1.5	0.59	3.6	43	93.5	85	3010
49	522	511	15	9.1	1.1	0.58	6.5	15	59.5	72	2420
50	390	699.5	25.8	11.1	2.5	0.63	4.9	17	129.5	161.5	2815
51	1489.5	1560	41.9	16.5	1.9	1.3	12	28	164	138	29125
52	623	1272.5	39.2	11.8	5.1	0.73	6.9	17	237	196.5	2525
53	136.5	254	6.4	3	0.11	0.17	6.4	5.8	33	18.5	3885
54	425	357	5.1	8.9	0.71	0.4	6.1	5.9	41.5	58.5	25245
55	137	201	5.4	4	0.36	0.19	7.9	2.6	17.5	14	2585
56	321.5	700.5	30.5	15	2	0.77	11.5	17.5	118	96.5	3840
57	1076.5	933.5	24	7.1	0.64	0.63	6.9	9.5	63	30.5	4370
58	1313	1258.5	27	10.8	1.2	0.76	6.9	16.5	151.5	79.5	75000
59	714	770	20.5	12.2	0.7	0.46	3	13.5	65.5	74	5050
60	201	356	6.4	5.4	0.75	0.38	4	5.8	58.5	60	3300

Con’td.

61	266	321	10.5	3.8	0.35	0.28	2.6	6.1	51	33.5	11260
62	243.5	261	5.6	8.4	0.41	0.16	1.6	3.2	34	44	3010
63	271	1973	48.5	28	0.89	0.35	26.5	6.2	142.5	68	990
64	554	1694	37	6.5	0.44	0.39	5.9	7.3	52.5	39.5	595
65	565	755.5	17	7.8	0.49	0.27	4	7.1	47.5	43	2280
66	180	341	6.1	0.76	0.12	0.07	2.5	2.2	10.5	11.5	52430
67	63	137.5	4.4	0.53	0.16	0.08	2	1.5	17.5	7.9	3060
68	244	228	5.3	0.29	0.33	0.07	0.8	1.5	12	9.6	83495
69	41.5	53	4.2	0.07	0.04	0.01	0.3	1.5	3.9	3.1	5440
70	42	64	2.5	0.09	0.05	0.03	0.5	1.9	17	2.2	7525
71	53.5	56.5	4.6	0.07	0.01	0.04	1.9	0.7	5.1	1.5	3250
72	127	922	26	0.61	1.9	0.13	3.1	3.6	43.5	41	3030
73	522.5	738	30	1.7	0.68	0.42	10	8.1	51.5	46	2670
74	180.5	288.5	7.9	1.3	0.19	0.3	3.2	7.1	33.5	22	4125
75	547	216.5	4.6	0.66	0.03	0.16	3.2	4.5	7.7	3.5	6505
76	53	45.5	1.9	0.02	0.08	0.03	0.1	2.6	22	3.1	4760
77	201.5	169	4.7	1.5	0.09	0.48	4	6.5	15	9.6	2235
78	201	153.5	4.4	1.8	0.01	0.53	3.2	5.8	8.5	3.5	1750
79	650	201	7.6	0.79	0.1	0.27	2.5	5.8	45.5	11.5	3930
80	992.5	784	30.5	7.4	1.12	0.57	7.9	11.5	130	76	3155
81	1462.5	1439	35	14.5	0.92	0.59	13	15.5	110.5	67	3785
82	714	515	19.5	10.5	0.18	0.38	4	10.5	38	22	3640
83	757	542.5	22	2.6	0.47	0.66	6	5.9	66.5	29	2620
84	778	521.5	17	6.5	0.45	0.48	3	6.8	56.5	28	5340
85	736.5	1042	28	10	0.57	0.43	3.5	7.7	49	53.5	3835
86	723	301	20	4.7	0.23	0.24	13	6.4	46	27	2720
87	501	646	22	3.2	0.26	0.36	16.5	3.9	60	20.5	5050
88	458.5	149	6.3	1.8	0.08	0.13	3.5	3.6	14	3.4	4415
89	928	1508	62	17.6	0.9	0.64	28	11	126.5	49	3885
90	1059	828	19.5	10	0.66	0.51	5.7	10	70.5	56	4980
91	69	58.5	2.1	0.31	0.01	0.04	3.1	0.7	6.6	4.4	10560
92	286	251.5	11.5	4.0	0.25	0.23	4.8	4.4	35	32	4725
93	1210	2216	76.5	18.5	3.2	0.3	24.5	37.5	446	268.5	1330

Con‘td.

94	275	224.5	10.5	8.1	0.39	0.22	1.6	2.7	44.1	32	9020
95	371.5	328.5	9.3	2.8	0.21	0.02	2.4	2.7	26	21.5	1905
96	41	25	3.3	2.0	0.01	0.06	0.1	1.1	9.9	5.6	7960
97	782	521	10.2	1.7	0.63	0.45	3.7	9.5	38	63.5	16590
98	171	105.5	3.7	1.4	0.09	0.11	0.1	3.8	18.5	7.8	4210

- = no data.

Table 5.3a The average concentrations of trace elements (μg g^{-1}), and % of total concentration stage by stage for the NSA, survey CH39 (November 1988).

$D_{p\,50}$ (μm)	Al		Fe		Mn		Cd		Cr		Ni	
	μg	%	μg	%	μg	%	μg	%	μg	%	μg	%
>9.3	254	27.4	142.5	20.8	5.7	13.1	0.17	7.1	1.3	14.1	2.5	11.4
3.9 - 9.3	278	29.9	238	35	7.9	18.2	0.14	5.8	2.1	22.8	3.3	15
1.97 - 3.9	103	11	15.5	2.2	1.1	2.5	0.01	0.4	0.32	3.5	2.1	9.5
1.28 - 1.97	93	9.9	34	5	3.6	8.4	0.09	3.8	0.99	10.7	2.5	11.4
0.61 - 1.28	140	15	158.5	23.5	14.5	33.5	0.26	10.8	2.9	31.5	4.6	20.9
<0.67	63	6.8	91	13.5	10.5	24.3	1.73	72.1	1.6	17.4	7	31.8
Total	931	100	679.5	100	43.3	100	2.4	100	9.21	100	22	100

$D_{p\,50}$ (μm)	Pb		Zn		Na	
	μg	%	μg	%	μg	%
>9.3	5.7	3.5	20	4.4	5250	36.9
3.9 - 9.3	13.8	8.5	53.8	11.4	4900	34.5
1.97 - 3.9	1.9	1.1	8.4	1.8	250	1.7
1.28 - 1.97	9.5	6	23	4.9	400	2.8
0.61 - 1.28	66.5	41	234.5	50	1300	9.4
<0.67	63.3	39	129	27.5	2100	14.7
Total	160.7	100	468.7	100	14200	100

Table 5.3b The average concentrations of trace elements (μg g^{-1}), and % of total concentration stage by stage for the NSA, survey CH53 (June 1989).

$D_{p\,50}$ (μm)	Al		Fe		Mn		Cd		Cr		Ni	
	μg	%	μg	%	μg	%	μg	%	μg	%	μg	%
>9.3	85	24.2	13.9	21.3	0.68	22.4	0.014	12.4	0.31	5.5	0.25	17.1
3.9 - 9.3	33	9.3	5	7.7	0.36	11.8	0.011	9.7	0.99	17.4	0.08	5.5
1.97 - 3.9	61.5	17.4	4.1	6.3	0.12	3.9	0.003	2.7	3.5	61.6	0.08	5.5
1.28 - 1.97	63	17.9	32.7	50.1	0.85	27.9	0.049	43.4	0.4	7	0.82	56.1
0.61 - 1.28	33	9.4	5	7.7	0.52	17	0.011	9.7	0.21	3.6	0.08	5.5
<0.67	77	21.8	4.5	6.9	0.52	17	0.025	22.1	0.27	4.9	0.15	10.3
Total	352.5	100	65.2	100	3.05	100	0.113	100	5.68	100	1.46	100

$D_{p\,50}$ (μm)	Pb		Zn		Na	
	μg	%	μg	%	μg	%
>9.3	0.43	17.7	0.29	1.2	1950	55.6
3.9 - 9.3	0.08	3.3	*	-	950	27.1
1.97 - 3.9	0.15	6.2	*	-	125	3.6
1.28 - 1.97	0.77	31.6	5.9	24.9	300	8.5
0.61 - 1.28	0.22	9.1	*	-	100	2.8
<0.67	0.78	32.1	17.5	73.9	85	2.4
Total	2.43	100	23.69	100	3510	100

* = Below detection.

Table 5.4. present the atmospheric concentrations (ng m^3 of air) for the elements from the hi-vol samples. However, due to difficulties in accurately calculating the volumes of air and the flow rates through the CI's; the atmospheric concentrations (ng m^3 of air) for these samples are not presented.

Table 5.5a presents the results for the EF_{crust} values for the hi-vol samples using element crustal values taken from Table 5.5b.

Tables 5.6a, and 5.6b present the EF_{crust} values for the CI's using elemental crustal values taken from Table 5.5b.

Table 5.7 presents the EF_{sea} values for the hi-vol samples, using sea water trace element concentration data taken from Table 6.12.

Tables 5.8a - 5.8g present the average % partitioning data for some elements selected from the hi-vol samples.

Table 5.9 presents the average % sea water solubility data for some elements selected from the hi-vol samples.

Table 5.10 presents the average % rain water solubility data for some elements selected from the hi-vol samples.

Sources of error and their importance are discussed at the end of this chapter.

5.2 Calculation of Results.

5.2.1 The Hi-Vol Trace Element Concentrations.

Table 5.4 Trace Element Concentrations (ng m^{-3} of air), for the NSA hi-vol samples.

Sample Number	Al	Fe	Mn	Cd	Co	Cr	Cu	Ni	Pb	Zn	Na
1	683.5	405.5	59.5	2.1	0.79	8.5	4.4	2.1	10.5	-	-
2	265	145	3.5	0.26	0.36	6.1	3.5	6.4	35	37.5	2785
3	469	336	8.7	0.46	0.30	12	8.7	4.8	87.5	86.5	760
4	74	71	1.6	0.34	0.22	3.6	3.6	4.6	25	30	870
5	161	125	2.7	0.33	0.23	5.0	4.1	3.6	29	32.5	1365
6	31	2	0.2	0.01	0.05	2.4	1.3	1.6	5.7	10.5	1630
7	169	88	4	0.02	0.08	4.2	2.3	1.9	8.5	9.1	1585
8	277	128	5.2	0.08	0.17	6.0	4.3	2.7	8.8	8.3	-
9	106	72	2.9	0.18	0.26	5.0	1.4	2.1	16.5	21	1400
10	101	204	10.5	0.01	0.23	5.0	6.0	4.8	35	56.5	-
11	376	186	11	0.63	0.16	5.0	4.7	1.4	20	50	8930
12	335	212	7.3	0.24	0.28	3.8	4.7	2.5	17	44	5520
13	269	807	11	0.11	0.29	4.8	3.2	1.7	19	14.5	4960
14	84	41	5.6	0.17	0.13	1.5	1.5	0.61	3.7	9.1	8960
15	245	116	62	0.48	0.29	7.8	14	3.3	42.5	15	5160
16	379	300	27	0.24	0.24	4.5	4.2	5.2	33	20	1580
17	105	57	2.6	0.2	0.21	4.2	1.6	2.1	1.7	0.7	3455
18	373	294	10.5	0.28	0.15	7.9	5.0	2.7	24	7.9	281210
19	630	895	29	0.94	0.37	12	12.5	2.9	52	84.5	8430
20	535	675	24	0.58	0.34	7.5	15	2.1	46	51.5	3705
21	255	-	28.5	0.28	0.23	1.5	4.1	9.9	24	8.5	7120
22	230	875	34.5	0.68	0.48	9.9	11.5	3.6	81	107.5	14295
23	838	1241	57	1.7	0.29	25.0	20	13	166	150	20870

Con'td.

24	426	1102	35	0.25	0.67	24.5	17	1.6	120	143	6460
25	354	246	10	0.51	0.52	4.5	8.9	1.2	21	19.5	10735
26	146	37	2.6	0.05	0.06	4.5	7.4	2.7	2.5	3.8	40420
27	177	313	17	0.18	0.20	3.9	4.1	1.3	43.5	44	7700
28	33	141	5.4	0.08	0.10	20	1.5	2.9	3.6	6.5	7690
29	206	184	8.8	0.11	0.28	2	3.3	6.3	26.5	23.5	2785
30	389	612	31	0.32	0.55	16	37.5	7.8	71	139.5	10140
31	169	108	8	0.14	0.14	4.1	3.8	1.3	13	13	3305
32	211	264	16.5	0.67	0.24	3.2	5	4.1	46	31	8515
33	341	440	24	0.28	0.33	6.9	7.4	5.6	51	41	5740
34	387	378	22	0.48	0.31	5	15	6.7	126	137	2560
35	262	213	10.5	0.32	0.22	2.3	12	6.6	61.5	27.5	6985
36	410	555	17	0.44	0.40	15	8.9	5.2	40.5	50	12295
37	133	132	84.5	0.49	0.30	2.6	5.8	5.5	64.5	19.5	2540
38	143	604	33.5	0.17	0.16	11.5	4.3	3.3	21.5	47	72100
39	82	77	1.7	0.03	0.05	0.6	0.7	0.5	6.3	3.2	10635
40	303	550	20.5	0.64	0.49	2.4	9.9	7.7	83	57	20180
41	616	759	30.5	0.33	0.32	3.5	6.8	7.2	60	57	2315
42	520	298	13	0.49	0.38	5.3	7.8	5.5	60	37.5	1230
43	318	376	14	0.62	0.23	2.1	4.7	5.8	53	57.5	2635
44	42	259	14.5	0.36	0.17	1.9	8.4	5.8	0.6	15.5	18555
45	57	75	5.5	0.53	0.1	1.9	2.6	4	28.5	21.5	2135
46	183	146	5.3	0.12	0.13	1.4	1.9	3.4	15	18.5	8780
47	140	105	1.6	0.42	0.11	1.3	2.5	2.6	37	19	3010
48	173	280	6.5	0.89	0.36	2.2	26.5	7	52	57.5	1845
49	294	288	8.5	0.64	0.33	3.7	8.6	5.1	40.5	33.5	1370
50	276	495	18.5	1.7	0.45	3.5	12	7.9	114	91.5	1990
51	705	739	20	0.94	0.61	5.6	13.5	7.8	65.5	77.5	13790
52	479	979	30	3.9	0.56	5.3	13	9.1	151	182	1940
53	172	318	8	0.14	0.16	8	7.3	3.8	23	41	4000

Con‘td.

54	166	140	2	0.28	0.17	2.4	2.3	3.5	23	16	9875
55	122	179	4.8	0.32	0.4	7.0	2.3	3.6	12.5	16	2305
56	167	366	16	1.1	0.44	5.9	9.2	7.8	50.5	61.5	2005
57	745	646	16.5	0.44	0.5	4.8	6.6	4.9	21	43.5	3025
58	520	498	10.5	0.48	0.26	2.7	6.6	4.3	31.5	60	29720
59	470	507	13.5	0.46	0.18	2	9	8	49	43	3325
60	137	243	4.4	0.51	0.11	2.7	4	3.7	41	40	2255
61	168	203	6.5	0.22	0.22	1.6	3.9	2.4	21	32.5	7130
62	161	172	3.7	0.27	0.30	1.1	2.1	5.6	29	22.5	1980
63	168	1223	30	0.55	0.18	16.5	3.8	6	42	88.5	615
64	422	1292	28.5	0.34	0.04	4.5	5.6	4.9	30	40	455
65	384	514	11.5	0.33	0.05	2.7	4.8	5.3	29	32	1550
66	108	205	3.7	0.07	0.05	1.5	1.3	0.48	6.8	6.3	31470
67	37	82	2.6	0.1	0.01	1.2	0.9	0.31	4.7	10.5	1820
68	185	173	4	0.25	0.02	0.6	1.1	0.22	7.3	9	63435
69	21	27	2.1	0.02	0.02	0.2	0.8	0.04	1.6	2	2760
70	22	34	1.5	0.03	0.07	0.3	1	0.05	1.2	9	4015
71	30	32	2.6	0.01	0.31	1.1	0.4	0.04	0.8	2.9	1820
72	72	526	14.5	1.1	0.25	1.8	2.1	0.35	23.5	25	1730
73	390	551	22.5	0.51	0.11	7.5	6	1.3	34.5	38.5	1995
74	148	238	6.5	0.16	0.11	2.6	5.9	1.1	18	28	3405
75	361	143	3	0.02	0.36	2.1	3	0.44	2.3	5.1	4295
76	200	174	7.2	0.3	0.41	0.4	9.8	0.08	11.5	83.5	17990
77	150	126	3.5	0.07	0.21	3.0	4.8	1.2	7	11	1665
78	156	119	3.4	0.01	0.28	2.5	4.5	1.4	2.7	6.6	1360
79	495	153	5.8	0.08	0.36	1.9	4.4	0.6	8.7	34.5	2995
80	494	391	15.5	0.56	0.25	3.9	5.7	3.7	38	65	1575
81	887	873	21.5	0.56	0.41	7.8	9.4	8.9	40.5	67	2300
82	479	345	13	0.12	0.30	2.7	6.9	7.1	14.5	25.5	2440
83	474	339	14	0.29	0.24	3.8	3.7	1.7	18	41.5	1640

Con'td.

84	467	313	10	0.27	0.20	1.8	4.1	3.9	17	40	3285
85	403	571	15.5	0.31	0.19	1.9	4.2	5.5	29.5	27	2100
86	605	252	16.5	0.19	0.08	11	5.4	3.9	22.5	38.5	2275
87	266	343	11.5	0.14	0.26	8.7	2.1	1.7	11	32	2680
88	269	87	3.7	0.05	0.36	2.1	2.1	1.0	2	8.3	2590
89	382	620	25.5	0.37	0.49	11.5	4.6	7.3	20	52	1600
90	753	589	14	0.47	0.16	4.1	7.1	7.2	40	50	3540
91	149	125	4.5	0.02	0.21	2.1	1.5	0.67	9.5	14	22760
92	197	174	8	0.17	0.17	3.3	3	2.8	22	24	3260
93	854	1565	54	2.2	0.01	17.5	26.5	10	189.5	250	940
94	210	172	8.2	0.30	0.04	1.2	2.1	6.2	24.5	33.5	6880
95	244	215	6.1	0.14	0.27	1.6	1.8	1.9	14	17	1250
96	24	15	2	0.10	0.01	0.1	0.7	1.2	3.3	5.9	4715
97	469	312	6.1	0.38	0.04	2.2	5.7	1	38	22.5	9950
98	97	59	2.1	0.05	0.06	0.1	2.1	0.79	4.4	10.5	2375

- = no data.

Table 5.5a EF_{crust} values using Al as the indicator element for the NSA hi-vol samples.

Sample Number.	Al	Fe	Mn	Cd	Co	Cr	Cu	Ni	Pb	Zn	Na
1	1	0.9	7.5	1259	3.8	10	9.6	3.4	100	-	-
2	1	0.8	1.1	404	4.4	19	19.5	26.5	866.5	166.5	36.5
3	1	1.0	1.6	404	2.1	20.5	27.5	11	1224.5	217	5.6
4	1	1.4	1.8	1891	9.7	40	73	68	2205	471.5	41
5	1	1.2	1.4	844	4.6	25.5	38	24	1185	237	29.5
6	1	0.1	0.56	133	5.3	63.5	62.5	56	1209.5	398	183
7	1	0.8	2.0	49	1.5	20	20	12.5	331	63	33
8	1	0.7	1.6	119	2.0	17.5	23	10.5	209	35	-
9	1	0.9	2.3	699	8.0	38.5	19.5	21.5	1024	230.5	46
10	1	2.9	8.8	41	7.4	40.5	89	52	2280	657.5	-
11	1	0.7	2.5	689	1.3	11	18.5	4.2	528.5	156.5	83
12	1	0.9	1.8	295	2.7	9	21	8.1	332	154.5	57.5
13	1	4.4	3.6	168	3.5	14.5	18	7.1	467	63	64
14	1	0.7	5.7	833	5.0	14.5	26.5	7.9	290	127	372
15	1	0.7	22	806	3.8	26	85	14.5	1141	71	73
16	1	1.2	6.1	261	2.0	9.7	16.5	15	574.5	62.5	14.5
17	1	0.8	2.1	784	6.5	32.5	23	22	106.5	7.8	114.5
18	1	1.2	2.4	309	1.3	17	20	8	423	25	2627
19	1	2.1	3.9	614	1.9	16	29	5	544	157.5	46.5
20	1	1.8	3.8	446	2.0	11.5	42	4	562	113.5	24
21	1	-	9.7	452	2.9	4.8	24	42.5	614	39	97
22	1	5.6	13	1217	6.8	35	75	17	2308.5	549.5	216.5
23	1	2.2	5.9	835	1.1	24.5	35.5	17	1303	210	87

Con'td.

24	1	3.8	7.1	242	5.1	46.5	59.5	3.9	1853	394	53
25	1	1.0	2.4	593	4.8	10.5	38	3.7	384.5	64.5	105.5
26	1	0.4	1.5	141	1.3	25	76	20	112.5	30.5	964.5
27	1	2.6	8.4	419	3.7	18	34.5	7.9	1620.5	291	151.5
28	1	6.2	14	998	12	2.4	68	99	717.5	231.5	812
29	1	1.3	3.7	220	4.4	7.9	24	33.5	840	135	47
30	1	2.3	6.8	339	4.6	33	144.5	22	1197.5	421.5	91
31	1	0.9	4.1	341	2.7	20	33.5	9.9	506	90.5	68
32	1	1.8	6.7	1307	3.7	12.5	35.5	21	1440.5	172	140.5
33	1	1.9	6.0	338	3.1	16.5	32.5	18	988	141	58
34	1	1.4	4.9	510	2.6	10.5	57	19	2145.5	417	23
35	1	1.2	3.4	503	2.7	7.1	68.5	27.5	1547	123	93
36	1	1.9	3.5	442	3.2	10	32.5	14	646.5	143.5	105
37	1	1.5	55	1516	7.4	16	65	45.5	3185.5	174	66.5
38	1	6.2	20	489	3.6	65	45	25.5	998	384.5	1757
39	1	1.4	1.8	151	2.0	5.9	13	6.7	505.5	46	452
40	1	2.7	5.9	869	5.3	6.4	49	28	1800	221.5	232
41	1	1.8	4.3	221	1.7	4.6	16.5	13	639.5	109	13
42	1	0.8	2.2	388	2.4	8.3	22.5	11.5	756.5	85	8.2
43	1	1.7	3.8	802	2.3	5.4	22	20	1096.5	213	29
44	1	9.0	30	3527	13	37	299.5	150.5	94	436.5	1539
45	1	1.9	8.3	3826	5.7	27	68	77.5	3289.5	439	130.5
46	1	1.2	2.5	270	2.3	6.2	15.5	20	543	118	167
47	1	1.1	0.99	1235	2.5	7.6	26.5	20.5	1748	158	75
48	1	2.4	3.2	2117	6.8	10.5	227.5	44.5	1985	390	37
49	1	1.4	2.5	896	3.6	10	44	19	908.5	134	16
50	1	2.6	5.7	2594	5.3	10	65	31	2722	389.5	25
51	1	1.5	2.4	549	2.8	6.5	28	12	610	129.5	68
52	1	2.9	5.4	3368	3.8	9	40.5	21	2077	437	14
53	1	2.7	4.0	335	3.0	38	63.5	24	879.5	281.5	81

Con‘td.

54	1	1.2	1.0	694	3.3	12	20.5	23	903.5	113	207
55	1	2.1	3.4	1079	10.5	47	28	32.5	679.5	152	66
56	1	3.2	8.2	2587	8.6	29	82.5	51.5	1995.5	432.5	42
57	1	1.2	1.9	243	2.2	5.2	13	7.2	187	68.5	14
58	1	1.4	1.7	380	1.6	4.2	19	9.0	398.5	135.5	199
59	1	1.6	2.4	403	1.2	3.4	28.5	18.5	683	107.5	25
60	1	2.6	2.7	1532	2.6	16	43.5	29.5	1973.5	342	57
61	1	1.8	3.3	539	4.3	7.8	35	15.5	826	226.5	148
62	1	1.6	1.9	690	6.1	5.6	19.5	38	1181	164	43
63	1	10.5	15.5	1347	3.5	80.5	34	39	1648.5	617.5	13
64	1	4.5	5.8	332	0.3	8.7	20	13	467.5	111.4	3.8
65	1	1.9	2.6	354	0.4	5.7	18.5	15	500	98.5	14
66	1	2.8	2.9	267	1.5	11	18	4.7	414	68.5	1015
67	1	3.2	6.1	1112	0.8	26.5	36.5	9.2	835.5	333.5	171
68	1	1.4	1.8	556	0.3	2.6	8.9	1.3	259.5	57	1195
69	1	1.9	8.6	392	3.1	7.8	57	2.1	501	112	458
70	1	2.3	5.9	561	10.5	11	68	2.	359	481	636
71	1	1.6	7.5	137	34	30	20	1.	175.5	113.5	211
72	1	10.5	17.5	6059	11.5	20	43.	5.	2138	406.5	84
73	1	2.1	5.0	538	0.9	16	23	3.5	580	115.5	17
74	1	2.4	3.8	445	2.4	14	59.5	7.9	804.5	220.5	80
75	1	0.6	0.7	23	3.2	4.7	12.5	1.3	42	16.5	41
76	1	1.3	3.1	617	6.7	1.6	73.5	0.4	385	490.5	313
77	1	1.2	2.0	192	4.6	16	48	8.6	311.5	87	39
78	1	1.1	1.8	26	5.9	13	43	9.8	114	49.5	30
79	1	0.5	1.0	67	2.3	3.1	13	1.3	115.5	82	21
80	1	1.2	2.6	467	1.6	6.4	17	8.1	504.5	154	11
81	1	1.4	2.0	260	1.5	7.2	16	11	300	89	9
82	1	1.1	2.3	103	2.0	4.6	21.5	16	202	62	18
83	1	1.0	2.5	252	1.6	6.5	12	3.8	252.5	103	12

Con'td.

84	1	0.9	1.8	238	1.4	3.1	13	9.1	236.5	87	24.5
85	1	2.1	3.3	317	1.5	3.8	15.5	17	480	79	18
86	1	0.6	2.3	129	0.4	15	13.5	7.1	244.5	74.5	13
87	1	1.9	3.8	217	3.2	27	12	7.1	267	140.5	35
88	1	0.5	1.1	77	4.4	6.3	12	4.2	49	36	33.5
89	1	2.4	5.8	399	4.2	24	18	21	346	160	14.5
90	1	1.1	1.6	257	0.6	4.4	14	10.5	348.5	78	16
91	1	1.2	2.6	55	4.6	11.5	15	4.9	419.5	112	532
92	1	1.3	3.5	355	2.8	13.5	23	15.5	741.5	143	57.5
93	1	2.7	5.4	1075	0.0	16	46	13	1460	344	3.8
94	1	1.2	3.3	588	0.6	4.6	15	32	770.5	188	114
95	1	1.3	2.1	236	3.6	5.3	11	8.3	383	81.5	18
96	1	0.9	7.2	1715	1.3	3.4	44	55	904.5	289	684.5
97	1	0.9	1.1	333	0.2	3.8	18	2.4	533	57	74
98	1	0.9	1.8	212	2.0	0.8	32.5	8.9	298.5	126	85

- = no data.

Table 5.5b The average concentrations of elements in the crust and their ratios to Al, from Taylor (1964).

Element	Concentration (ppm)	Crustal Ratio
Al	82,300	1
Fe	56,300	0.684
Mn	950	1.15×10^{-2}
Cd	0.2	2.43×10^{-6}
Co	25	3.04×10^{-4}
Cr	100	1.22×10^{-3}
Cu	55	6.68×10^{-4}
Mo	1.5	1.82×10^{-5}
Ni	75	9.11×10^{-4}
Pb	12.5	1.52×10^{-4}
Ti	5700	6.93×10^{-2}
V	135	1.64×10^{-3}
Zn	70	8.51×10^{-4}
K	20,900	0.254
Na	23,600	0.287

Table 5.6a Crustal Enrichment Factors of NSA elements using Al as a source indicator, for the CI CH53 (June 1989).

Impactor Stage	Fe	Mn	Cd	Zn	Pb	Ni	Cu	Cr	Na
1	0.2	0.7	48.5	4	32.5	3.2	5.8	2.9	80
2	0.2	0.9	124	-	16	2.6	5.4	24.5	100
3	0.1	0.2	-	-	15.5	1.4	4	6.4	-
4	0.8	1.2	337.5	113.5	83	15	216	5.4	17
5	0.2	1.4	125.5	-	44	2.7	164.5	5.2	10.5
6	0.1	0.6	106.5	7.9	66.5	2.1	85	2.9	3.8

- = no data.

Table 5.6b Crustal Enrichment Factors of elements in the NSA using Al as a source indicator, for the CI CH39 (November 1989).

Impactor Stage	FE	Mn	Cd	Zn	Pb	Ni	Cu	Cr	Na
1	0.8	1.9	275.5	92.5	147.5	11	42	4.2	72
2	1.3	2.5	207	227.5	326.5	13	130	6.2	61.5
3	0.2	0.9	40	95.5	121	22.5	39	2.4	8.5
4	0.5	3.4	398	290.5	671.5	29.5	85	7.9	15
5	1.6	9.1	761	1958	111.5	43.5	456	17	32
6	2.1	14.5	11070	2395	6589.5	121.5	384.5	20.5	115.5

Table 5.7 EF_{sea} values for the NSA hi-vol samples.

Sample Number	Fex10^5	Mnx10^4	Nix10^3	Cdx10^4	Cox10^4	Cux10^4	Pbx10^5	Znx10^4
1	-	-	-	-	-	-	-	-
2	3.5	0.46	18.8	1.2	1.9	1.2	12.3	6
3	29.9	4.2	51.9	8	5.9	10.9	112.5	51
4	5.5	0.68	43	5.2	3.8	3.9	27.9	15.5
5	6.2	0.73	21.5	3.2	2.5	2.9	21	10.5
6	0.08	0.05	7.9	0.08	0.46	0.76	3.4	2.9
7	3.8	0.93	9.9	0.17	0.76	1.4	5.3	2.6
8	-	-	-	-	-	-	-	-
9	3.5	0.77	12	1.7	2.8	0.96	11.5	6.7
10	-	-	-	-	-	-	-	-
11	1.4	0.46	1.3	0.93	0.27	0.50	3.3	2.5
12	2.6	0.49	3.6	0.58	0.77	0.82	2.9	3.6
13	11	0.83	2.8	0.29	0.88	0.62	3.8	1.3
14	0.31	0.23	0.56	0.25	0.22	0.16	0.41	0.45
15	1.5	4.4	5.1	1.2	0.85	2.6	8.1	1.3
16	12.8	6.3	27	2	2.3	2.5	20.5	5.7
17	1.1	0.28	5	0.77	0.92	0.44	0.48	0.09
18	0.07	0.01	0.08	0.01	0.00805	0.02	0.08	0.01
19	7.2	1.3	2.9	1.5	0.66	1.4	6.1	4.5
20	12.3	2.4	4.6	2.1	1.4	3.9	12.1	6.3
21	-	1.5	11.4	0.5	0.5	0.55	3.3	0.54
22	4.1	0.89	2	0.63	0.51	0.77	5.5	3.4
23	4	1	5	1.1	0.21	0.91	7.7	3.2
24	11.5	1.9	1.9	0.51	1.5	2.5	18	9.9

25	1.6	0.35	0.9	0.63	0.73	0.79	1.9	0.82
26	0.06	0.02	0.53	0.03	0.02	0.18	0.06	0.04
27	2.7	0.83	1.4	0.31	0.39	0.51	5.5	2.6
28	1.2	0.26	3.2	0.14	0.24	0.19	0.46	0.38
29	4.5	1.2	18.5	0.53	1.5	1.1	9.3	3.8
30	4	1.1	6.3	0.42	0.82	3.6	6.8	6.2
31	2.2	0.89	3.8	0.56	0.64	1.1	3.9	1.8
32	2.1	0.71	3.9	1	0.43	0.56	5.5	1.6
33	5.2	1.5	7.9	0.65	0.87	1.23	8.7	3.2
34	9.9	3.2	21	2.5	1.8	5.5	48	24
35	2	0.55	7.7	0.61	0.48	1.6	8.6	1.8
36	3	0.51	3.4	0.48	0.50	0.69	3.2	1.8
37	3.5	12.5	17.5	2.6	1.8	2.2	25	3.5
38	0.57	0.17	0.38	0.03	0.03	0.06	0.29	0.29
39	0.49	0.06	0.38	0.04	0.07	0.06	0.58	0.14
40	1.8	0.38	3.1	0.42	0.37	0.47	4	1.3
41	22	4.9	25	1.9	2	2.8	25.5	11
42	16.5	3.9	36.5	5.3	4.7	6.1	47.5	14
43	9.7	1.9	18	3.1	1.3	1.7	19.5	9.8
44	0.94	0.29	2.5	0.26	0.14	0.43	0.03	0.38
45	2.4	0.95	15.5	3.3	0.71	1.2	13	4.5
46	1.1	0.22	3.1	0.18	0.22	0.21	1.7	0.94
47	2.4	0.19	7.1	1.9	0.55	0.79	12	2.8
48	10	1.3	31	6.4	2.9	13.5	27.5	14
49	14	2.3	30.5	6.2	3.6	6	29	11
50	17	3.4	32	11.5	3.4	5.8	56	20.5
51	3.6	0.53	4.6	0.9	0.67	0.92	4.6	2.5
52	34	5.8	38	27	4.4	6.4	76.5	42
53	5.4	0.74	7.7	0.47	0.60	1.7	5.6	4.5
54	0.96	0.07	2.9	0.38	0.26	0.22	2.3	0.73

Con'td.

55	5.3	0.77	12.5	1.8	2.6	0.96	5.4	3.1
56	12	2.9	32	6.9	3.3	4.4	24.5	14
57	14.5	2	13	1.9	2.5	2.1	6.9	6.4
58	1.1	0.13	1.2	0.21	0.13	0.21	1	0.91
59	10.5	1.5	19.5	1.8	0.82	2.6	14.5	5.9
60	7.3	0.72	13.5	3	0.74	1.7	18	7.9
61	1.9	0.34	2.8	0.41	0.47	0.53	2.9	2
62	5.9	0.69	22.9	1.8	2.3	1	14	5.1
63	134.5	18	79.5	12	4.4	5.9	67	64.5
64	192	23	89.5	9.9	1.3	12	64.5	39.5
65	22.5	2.8	27.8	2.8	0.49	2.9	18.5	9.3
66	0.44	0.04	0.12	0.03	0.02	0.04	0.21	0.09
67	3	0.53	1.4	0.73	0.08	0.47	2.5	2.6
68	0.18	0.02	0.03	0.05	0.005	0.02	0.11	0.06
69	0.66	0.28	0.12	0.09	0.11	0.28	0.57	0.3
70	0.57	0.14	0.10	0.09	0.26	0.24	0.29	1
71	1.2	0.53	0.18	0.07	2.6	0.21	0.43	0.72
72	20.5	3.1	1.7	8.1	2.2	1.2	13	6.5
73	18.5	4.2	5	3.5	0.83	2.9	17	8.6
74	4.7	0.71	2.5	0.62	0.49	1.7	5.2	3.6
75	2.3	0.26	0.84	0.06	1.3	0.67	0.53	0.53
76	0.65	0.15	0.04	0.22	0.34	0.52	0.64	2.1
77	5.1	0.78	5.6	0.56	1.9	2.8	4.2	2.9
78	5.9	0.92	8.3	0.09	3.1	3.2	1.9	2.2
79	3.5	0.72	1.6	0.36	1.8	1.4	2.8	5.2
80	17	3.6	19	4.7	2.4	3.5	23.5	18.5
81	25.5	3.4	31.5	3.2	2.7	3.9	17	13
82	9.5	1.9	23.5	0.65	1.9	2.7	5.9	4.7
83	14	3.1	8.2	2.4	2.2	2.2	11	11.5
84	6.4	1.1	9.6	1.1	0.92	1.2	5	4.6

Con'td.

85	18.5	2.7	21.5	1.9	1.4	1.9	13.5	5.8
86	7.5	2.7	14	1.1	0.53	2.3	9.7	7.6
87	8.7	1.6	5	0.69	1.5	0.75	3.9	5.3
88	2.2	0.53	3.2	0.26	2.1	0.78	0.78	1.4
89	26	5.9	37	3	4.6	2.8	12.5	14.5
90	11	1.5	16.5	1.8	0.68	1.9	11	6.5
91	0.37	0.07	0.24	0.01	0.14	0.06	0.41	0.28
92	3.6	0.91	6.9	0.69	0.79	0.88	6.7	3.3
93	112.5	21	87	31.5	0.16	27	197.5	119.5
94	1.7	0.44	7.3	0.58	0.09	0.29	3.5	2.1
95	11.5	1.8	12.1	1.5	3.3	1.4	11	6
96	0.22	0.16	2.1	0.28	0.03	0.14	0.69	0.56
97	2.1	0.23	0.85	0.51	0.06	0.55	3.7	1
98	1.7	0.33	2.7	0.28	0.38	0.85	1.8	1.9

- = no data.

Table 5.8a The sequential extraction of Al in the NSA.

Sample Number	Stage%		
	1	2	3
14	0.6	4.8	94.6
15	5.7	13.1	81.2
16	4.4	7.1	89.7
17	1.6	13.8	84.6
18	6.8	12.3	80.9
19	3	20.1	76.9
20	2	25.9	72.1
21	2.2	20.6	77.2
22	20	20.7	59.3
23	5.2	11.5	83.3
24	7.3	7.3	85.6
25	4.3	7	89.7
26	6.4	6.7	86.9
27	6.7	8.6	84.5
28	3.4	7.9	88.7
29	1.9	10	88.1
30	7.4	8	84.6
31	3.8	4.6	91.6
32	2.1	3.3	94.6
33	1.3	6.9	91.8
34	1.9	7.4	90.3
35	2.6	5.8	91.6
37	15	19.3	65.7
39	3.2	2.6	94.2
48	9.2	5.6	86.2
63	4.4	17.1	78.5
66	16.6	12.1	71.3
67	5.4	21.1	73.5
68	4.4	8.4	87.2
69	2.4	5.5	92.1
70	4.4	8.4	87.2
71	1	19.5	79.7
72	12.4	21.9	65.7
93	2.8	5.1	92.1

1 = Ammonium acetate shake.
2 = Hydroxlyammonium hydrochloride + acetic acid shake.
3 = Conc. nitric and hydrofluoric acids.

Table 5.8b The sequential exstraction of Fe in the NSA.

Sample Number	Stage%		
	1	2	3
14	2	3.9	94.1
15	9.9	11.9	78.2
16	0.6	31.1	68.3
17	4.3	7	88.7
18	10.9	10.5	78.6
19	1.6	13.8	84.6
20	1.4	27.5	71.1
21	0.1	0.1	99.8
22	3.2	19.3	77.5
23	7.7	21.3	70
24	7.4	14	78.6
25	3.2	6.8	90
26	2.5	2.5	95
27	1	8.2	90.8
28	0.1	5.6	94.3
29	0.1	22.8	77.1
30	1.3	9.1	89.6
31	0.1	5	94.9
32	5.2	13.9	80.9
33	0.9	10.7	88.4
34	0.9	18.3	80.8
35	3.8	14.8	81.4
37	15	19.3	65.7
39	22	26.2	51.8
48	10.8	12.5	76.7
63	0.4	5.9	93.7
66	11.9	1.8	86.3
67	22.8	0.8	76.4
68	20	6.6	73.4
69	16.3	1.4	82.3
70	18.5	0.1	81.4
71	7.8	0.1	92.1
72	0.8	9.3	89.9
93	2.3	14.6	83.1

1 = Ammonium acetate shake.
2 = Hydroxlyammonium hydrochloride + acetic acid shake.
3 = Conc. nitric and hydroflouric acids.

Table 5.8c The sequential exstraction of Mn in the NSA.

Sample Number	Stage%		
	1	2	3
14	15	20.1	64.9
15	81.3	2	16.7
16	66.5	1.2	32.3
17	75.4	3	21.6
18	28	8.5	63.5
19	45.2	3.9	50.9
20	57.2	1.7	41.1
21	14.8	8.4	76.8
22	61.9	5.4	32.7
23	77.9	2.1	20
24	71.6	2.5	25.9
25	45.8	3.9	50.3
26	41.2	2.5	56.3
27	54.8	3	42.2
28	41.8	6.5	51.7
29	45.5	12.5	41.9
30	57.2	12.7	30.1
31	49.6	20.8	29.6
32	43.1	9.4	47.5
33	42.8	4.1	53.1
34	51.7	1.2	47.1
35	59.1	7.6	33.3
37	77.7	15.8	6.5
39	26.9	10.1	63
48	53.3	12.4	34.3
63	15.2	7.1	77.7
66	46.3	6.9	46.8
67	45.6	2.6	51.8
68	92.7	7.2	0.1
69	86.1	11.4	2.5
70	95	2.6	2.4
71	94.7	2.7	2.6
72	95	4.5	0.5
93	43.6	13.4	53

1 = Ammonium acetate shake.
2 = Hydroxyammonium chloride shake + acetic acid.
3 = Conc. nitric and hydroflouric acids.

Table 5.8d The sequential extraction of Cd in the NSA.

Sample Number.	Stage %		
	1	2	3
14	95.8	3.2	1
15	69.7	11.9	18.4
16	69.2	15.9	14.9
17	48.1	31.1	20.8
18	82.1	13.1	4.8
19	55.8	36.4	7.8
20	29.5	67.2	3.3
21	41.7	34.1	24.2
22	56	37.8	6.2
23	61.6	32.7	5.7
24	58.1	35.9	6
25	70.1	11.4	18.5
26	44.4	53.6	2
27	60.1	33.2	6.7
28	82.2	5	12.8
29	84.2	7.6	8.2
30	76.4	8.3	15.3
31	91.4	1.3	7.3
32	78.5	7.3	14.2
33	67.3	18.1	14.6
34	19.2	45.7	35.1
35	77.3	12.3	10.4
37	76.8	13.5	9.7
39	88.7	1.3	10
48	19.3	73.6	7.1
63	46.9	42.7	10.4
66	91.3	8.6	0.1
67	87.1	12.8	0.1
68	BD	BD	BD
69	99.8	0.1	0.1
70	99.8	0.1	0.1
71	96.1	2.7	1.2
72	31.3	56.7	12
93	71.6	24.4	4

1 = Ammonium acetate shake.
2 = Hydroxyammonium hydrochloride + acetic acid shake.
3 = Conc. nitric and hydroflouric acids.
BD = below detection limit.

Table 5.8e The sequential extraction of Cu in the NSA.

Sample Number.	Stage% 1	2	3
14	29.3	19.5	51.2
15	38	17.1	44.9
16	21.7	27.2	51.1
17	19.6	39.8	40.6
18	26.2	30.9	42.9
19	39.1	33.2	27.7
20	48.4	34.1	17.5
21	34	33.8	32.2
22	49.2	26.6	24.2
23	47.7	26.4	25.9
24	34.4	39.2	26.4
25	26	22.9	51.1
26	41.3	28.7	30
27	46.2	25.3	28.5
28	30.2	28.4	41.4
29	27.8	33.1	39.1
30	54.9	19	26.1
31	70.6	16.8	12.6
32	72.1	18.7	9.2
33	42.7	26.4	30.9
34	47.1	28.9	21
35	27.2	40.9	32.8
37	60.5	22.1	17.4
39	65.5	18.5	16
48	44.4	24.5	31.1
63	38.7	41.3	20
66	62.6	20.5	16.9
67	29.7	33.8	36.5
68	75	15.3	9.7
69	62.6	15	22.4
70	65.3	16.4	18.3
71	76.3	19.5	4.2
72	55.3	21.9	22.8
93	24.4	71.6	4

1 = Ammonium acetate shake.
2 = Hydroxyammonium hydrochloride + acetic acid shake.
3 = Conc. nitric and hydroflouric acid.

Table 5.8f The sequential extraction of Pb in the NSA.

Sample Number	Stage%		
	1	2	3
14	84.1	12.1	3.8
15	78.4	19.1	2.5
16	77.3	16.2	6.5
17	91.8	8	0.2
18	78.1	15.7	6.2
19	73.6	18.4	8
20	72.5	21.3	2.1
21	71	14.5	13.5
22	48.2	48.3	3.5
23	68.7	25.9	5.4
24	67.1	26.4	6.5
25	77.5	15	7.5
26	95	0.2	4.8
27	84.7	9.6	5.7
28	72.9	11.3	15.7
29	87.8	3.9	8.3
30	91.3	0.6	8.1
31	57.6	37.9	4.5
32	81.4	11.7	6.9
33	63.2	26.8	10.9
34	91.6	0.1	8.3
35	80	12.2	7.8
37	71	28.8	0.2
39	81.9	0.3	11.7
48	90.3	2	6.7
63	54.1	40.6	5.3
66	83.3	7.9	8.8
67	74.5	17.4	8
68	81	10.2	8.8
69	84.7	8.3	7
70	79.6	2.2	18.2
71	96.7	2.1	1.2
72	82.9	8.8	8.1
93	64.1	29.2	6.7

1 = Ammonium acetate shake.
2 = Hydroxyammonium hydrochloride + acetic acid shake.
3 = Conc. nitric and hydroflouric acids.

Table 5.8g The sequential extraction of Zn in the NSA.

Sample Number	Stage% 1	2	3
14	79.1	2.5	18
15	69.7	11.9	18.4
16	69.2	15.9	14.9
17	76.3	12	11.7
18	79.5	15	5.5
19	75.3	10.6	14.1
20	84.2	6.7	9.1
21	41.7	34.1	24.2
22	81.3	7.5	11.2
23	79.8	8	87.8
24	79.9	9.8	10.3
25	68.3	22	90.3
26	93.7	0.1	6.2
27	84.2	7.1	8.7
28	92.2	6	1.8
29	68.5	19	87.5
30	74.3	14	11.7
31	71.4	13	15.6
32	61.9	18.1	20
33	67.3	18.1	14.6
34	19.2	45.7	35.1
35	77.3	12.3	10.4
37	71.2	22	6.8
39	81.2	16	2.8
48	77.2	13.6	9.2
63	71.5	15.3	13.2
66	92.1	3	4.9
67	80.1	15.2	4.7
68	93.7	4	2.7
69	97.1	0.1	2.8
70	91.4	0.7	7.9
71	95.1	0.5	4.4
72	91.8	2.6	5.6
93	71.5	12.7	15.8

1 = Ammonium acetate shake.
2 = Hydroxlyammonium hydrochloride + acetic acid.
3 = Conc. nitric and hydroflouric acids.

Table 5.9 The % sea water solubility of the NSA.

	Al		Fe		Cu	
Sample number	Sea water shake	Residual	Sea water shake	Residual	Sea water shake	Residual
15	1.2	98.8	8.5	91.5	59.6	40.4
16	1.9	98.1	12.8	87.2	42.5	57.5
19	3.7	96.3	3.1	96.9	27.1	72.9
20	6.9	93.1	7.2	92.8	17.5	82.5
22	5.9	94.1	5.6	94.4	51.2	48.8
24	3.8	96.2	11.9	88.1	39.4	60.6
27	1.6	98.4	2.2	97.8	41.1	58.9
33	1.9	98.1	6.7	93.3	20.3	79.7
34	1.3	98.7	4.7	95.3	18.4	81.6
35	8.5	91.5	15.3	84.7	19.7	80.3
66	7.5	92.5	10.5	89.5	41.1	58.9
67	6.8	93.2	7.9	92.1	52.6	47.4
68	6.9	93.1	8.1	91.9	63.1	36.9
69	4.1	95.9	8.3	91.7	72.8	27.2
70	2.7	97.3	7.9	92.1	37.2	62.8

Con'td.

Table 5.9 continued.

	Pb		Zn	
Sample number	Sea water shake	Residual	Sea water shake	Residual
15	84.6	15.4	98.4	1.6
16	54	46	86.7	13.3
19	35.3	64.7	58.3	41.7
20	69.7	30.3	79.9	20.1
22	55.8	44.2	64.9	35.1
24	60.1	39.9	64	36
27	33.5	56.5	66.1	33.9
33	30.9	69.1	55.5	44.5
34	42.1	57.9	67.7	32.3
35	42.1	57.9	92.8	7.2
66	91.5	8.5	95.9	4.1
67	60	40	97.2	2.8
68	55.4	44.6	91.5	8.5
69	97.5	2.5	97.5	2.5
70	62.1	37.9	93.6	6.4

Table 5.10 The solubilities of Cu, Zn and Pb from the NSA into artificial rain water (ph 4).

Sample number	%age of total element soluble		
	Cu	Pb	Zn
30	54	66	80
60	51	80	87
64	60	77	76
65	50	76.5	71
70	59	77	84
71	43	71	53
78	19	70	78
79	42	78	41
80	34	74.5	69
81	50	77	70
82	31	73	68
83	42	76	74
84	49	62	65
85	40	78	69.5
89	40	81	73
mean; rain water solubility[1]	44	74.5	70.5
mean; sea water solubility[2]	~40	~80	~60

[1] Mean, NSA data in present table.
[2] Mean, from NSA data in Section 6.4.3.

The raw trace element concentrations μg^{-1} deposited on the filter for both the hi-vol, and the CI samples were calculated using equation 5.1.

$$C = \frac{A_{spl} \times C_{std} \times V}{A_{std}} \qquad \text{Equation 5.1}$$

where: C = the concentration of the metal in μg^{-1}.

A_{spl} = the absorbance of the sample.

A_{std} = the absorbance of the standard.

C_{std} = the concentration of the standard in μg^{-1}.

V = the final volume in mls of sample.

The trace element loading ng m^3 of air for these samples is then calculated using equation 5.2.

$$E_l = \frac{C \times 1000 \times 2}{V_a} \qquad \text{Equation 5.2}$$

where: E_l = the element loading ng m^{-3} of air.

C = the concentration in μg^{-1}.

V_a = the volume of air sampled.

1000 = a factor to convert from μg to ng.

2 = is a factor to correct for the use of two filters.

5.2.2 Crustal Enrichment Factors.

The element crustal enrichment factors for the hi-vol, and CI samples are calculated using equation 5.3.

$$EF_{crust} = \frac{[(x_e)/(Al_e)]s}{[(x_r)/(Al_r)]_{rm}} \qquad \text{Equation 5.3}$$

where: EF_{crust} = the element crustal enrichment factor, x_e = the concentration of the trace element in the aerosol, Al_e = the concentration of aluminium in the aerosol, $[(x_r)/(Al_r)]_{rm}$ = the crustal ratio of the trace element (see Table 5.5a).

5.2.3 EF_{sea} values.

The element EF_{sea} values for the hi-vol samples are calculated using equation 5.4.

$$EF_{sea} = \frac{(E/Na)_{air}}{(E/Na)_{sea}} \qquad \text{Equation 5.4}$$

where: EF_{sea} = the enrichment of the element relative to the sea.

$(E/Na)_{air}$ = the ratio of the concentrations of an element E and Na in the aerosol.

$(E/Na)_{sea\ water}$ = the ratio of the concentrations of an element E and Na in bulk sea water (see Table 6.12).

5.2.4 Relative Oceanic Enrichment Factors.

The mean relative oceanic enrichment factors for the hi-vols are presented in Table 6.14, and these are calculated using equation 5.5.

$$REF_{sea} = \frac{EF_{sea}}{\text{BIMS } EF_{sea}} \qquad \text{Equation 5.5}$$

where: REF_{sea} = the relative oceanic enrichment factor, EF_{sea} = the enrichment of the element relative to the sea (see Table 5.7, and BIMS EF_{sea} = values relate the material generated at the sea surface directly to the microlayer itself, (see Table 1.5).

The EF_{sea}, BIMS EF_{sea} and REF_{sea}, are explained in Section 1.5.2.1.2.

5.3 Solubility Experiments.

5.3.1 Solid State Speciation Solubilities.

For each extraction stage, the amount of trace element extracted was calculated in relation to the total amount (T) of trace element in all three stages; (i.e. the concentration of the element in each of the three stages were added together to give a total concentration T), then Equation 5.6, was used to calculate the % trace element in each stage.

$$\%_{Se} = C_{Se}/T_x \qquad \text{Equation 5.6}$$

where: $\%_{S_e}$ = the percentage of the trace element in the selected stage (1, 2 or 3).

C_{S_e} = the concentration of the trace element in the stage.

T_x = the sum of the trace element concentrations in stages 1,2 + 3.

5.3.2 Sea Water and Rain Water Solubilities.

The concentration of the trace element was determined in; (a) The sea water/rain water shake, and (b) The remaining residual material. The % soluble of a trace element in the sea water/rain water shake was then determined using Equation 5.7.

$$\%S_e = \frac{C_{E1}}{C_{E1} + C_{E2}} \times 100 \qquad \text{Equation 5.7}$$

where: $\%S_e$ = the % soluble of the trace element in the sea water/rain water shake.

C_{E1} = the concentration of the trace element in the sea water/rain water shake.

C_{E2} = the concentration of the trace element in the residual material.

5.4 Sources of Error.

There are two sources of errors in the estimation of the atmospheric trace element loadings and enrichment factors. These are associated with; (a) Collection procedures, and (b) Analytical procedures.

5.4.1 Filter Collection Errors.

The errors that are associated with filter collection are discussed in Section 3.5.3, and were estimated to be between 20% for the worst cases and ~10% on average with respect to the volume of air sampled.

An indication of the analytical errors are given in Table 4.2 (Reproducibility of analysis). The variation coefficient associated with these analysis range from 1.55 for Cu, to 6.42 for Cd.

In the calculation of EF_{values} the main source of errors will be analytical. Any remaining errors are effectively cancelled out since for example with EF_{crust} values, the calculation involves the division of atmospheric element loading by the atmospheric Al loading (see Equation 5.3). For the purpose of EF comparisons only order of magnitude results are required. It is therefore unlikely that these errors will be significant.

5.4.2 Errors Associated with the Solid State Speciation and the Sea Water/Rain Water Solubilities.

The errors associated with the solid state speciation, and the sea and rain water solubility work can be summarised as follows: (a) loss of colloidal material which does not centrifuge out (b) carry over of elements from the preceding stage. (c) analytical errors.

The loss of colloidal material, and the carry over of trace element concentrations from one stage to the next cannot be easily accounted for. One method of preventing carry over, would be to collect the 1st extract then re-shake the particulate material with a fresh solution of reagent. This technique would effectively prevent carry over of soluble trace elements into the next reagent stage. However, the added problem of particulate loss due to decanting-off of this second 'wash reagent' would be again encountered. Since the aim of carrying out solid state speciation, sea and rain water solubilities was to establish a first order estimation of the potential environmental mobility of some trace elements from the NSA. These errors will be ignored from the interpretation of results.

An indication of the analytical errors are given in Table 4.2 (Reproducibility of analysis). It should be noted that these errors are associated with the analysis of trace elements in a 1% acidic medium. The solid state speciation and the sea and rain water solubility experiments were conducted in different matrix solutions. Therefore, the data from Table 4.2 will only give an approximate indication of the analytical errors associated with the speciation and solubility work.

In this chapter the results of the current work have been presented. These results will now be discussed in the Chapter six.

Chapter 6

The Interpretation of Results

6.1 Introduction.

In the present work data have been provided in Chapter 5 for the following parameters; (a) total aerosol trace element concentrations (hi-vol filters); (b) aerosol trace element solid state speciation signatures; (c) aerosol sea water and rain water solubilities, and (d) size fractionated trace element concentrations (CI filters).

These various data for the NSA will be interpreted within the following overall framework.

(1) The distributions of particulate trace elements over the North Sea. The data from (a) above will be used to estimate the average trace element composition of the NSA, and this will be compared to other estimates given in the literature.

(2) Controls on the sources of particulate trace elements over the North Sea. The data from (a) above will be assessed in terms of air mass back trajectories and trace element emission rates, inter-element relationships, EF_{values}, CI measurements, and model generated rainfall patterns to determine the factors which control the trace element concentrations in the atmosphere over the North Sea.

(3) The fates of the atmospherically transported trace elements in the mixed layer of the North Sea. The data from

(b) and (c) above will be interpreted to provide an assessment of the fates of the elements once they have been deposited at the sea surface.

6.2 The Distribution of Particulate Trace Elements Over the North Sea.

6.2.1 Trace Element Concentrations.

A summary of the concentrations of particulate trace elements over the southern North Sea obtained in the present work is given in Table 6.1. In Table 6.2 the data obtained from the present study are compared with those reported by other workers. These data sets have been selected in order to illustrate geographical variations in the atmospheric input of trace elements to the North Sea. The locations of the sampling stations surrounding the North Sea from which the collections were made are illustrated in Figure 6.1.

Two important points emerge from a study of the data in Table 6.2.

(1) From the data obtained from land stations surrounding the North Sea, it is apparent that there is a general south to north decrease in the atmospheric concentrations of some trace elements along the length of the North Sea. For example there is a an overall decrease in the concentrations of Pb on a south to north transect in the following order; Haamstede > Leiston > West-Hinder > Keil Bight > Hemsby > Collafirth. This general south to north trend in the atmospheric concentrations of some trace

Table 6.1 Data on particulate atmospheric trace element concentrations over the North Sea; present study (conc. units ng m^{-3} of air).

Element	N	Arithmetic Mean concentration	Range	σ	Geometric mean concentration
Al	98	294.5	21 - 887	205	219
Fe	97	353.0	2 - 1565	316.5	230.5
Mn	98	14.5	0.2 - 84.7	14.5	9.1
Cd	98	0.42	0.01 - 3.9	0.54	0.39
Co	98	0.25	0.01 - 0.8	0.19	0.19
Cr	98	4.7	0.1 - 25	4.58	3.1
Cu	98	6.3	0.4 - 37.6	5.87	4.4
Ni	98	3.8	0.04 - 12.9	2.75	2.5
Pb	98	34.5	0.6 - 189.5	35.3	20
Zn	97	41.0	0.7 - 250	41.1	26
Na	95	10128	455 - 281210	30315	990

N = number of observations
σ = standard deviation.

Table 6.2 Data on particulate atmospheric trace element concentrations over the North Sea and surrounding areas (conc. units ng m^{-3} of air).

	Surrounding land areas					North Sea				
Element	Collafirth[1]	Wraymires 1772-72[2]	Kiel Bight[3]	Leiston 1972-73[2]	Haamstede[4]	West* Hinder[5]	Hemsby[6]	Aero-plane[7]	Helgoland[8]	Present Data
Al	-	120.5	394	235	-	140	-	-	210	294.5
Fe	54	175	369	335	-	300	216	160	201	353
Mn	-	10.5	15	21	-	15	10	-	7.2	14.5
Cd										
Ni	<3.7	4.5	4	5.3	22	-	2.7	-	2.6	3.8
Cr	0.7	2	2.9	5.7	7.5	-	-	-	1.7	4.7
Co	-	0.14	-	0.38	-	-	-	-	0.24	0.25
Cu	20	<6	7.7	<10	22	14.7	-	7.8	3.9	6.3
Zn	15	60	57	137.5	130	67.4	41	69	33	41
Pb	21	64	53	127.5	190	96	34	33	29	34.5

- denotes no data available.

[1]Cambray et al. (1975) [2]Cawse (1974) [3]Schneider (1987) [4]Diederen & Guichert (1981)
[5]Bayens & Dedeurwaerder (1991) [6]Yaaqub et al. (1991) [7]Otten et al. (1989) [8] Kersten et al. (1988)

* geometric mean data.

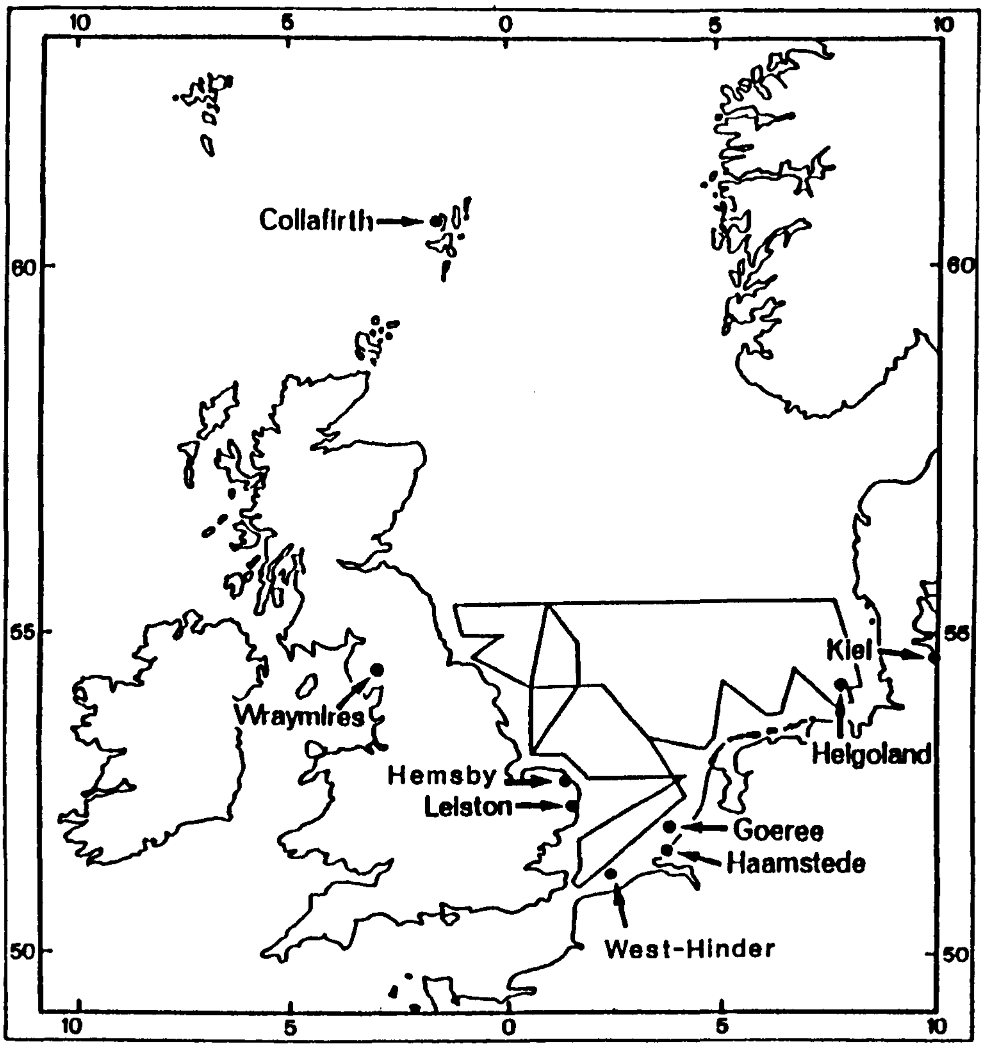

Figure 6.1 Locations at which aerosols have been calculated in, and around, the North Sea. The aeroplane collections extended for 100 km seaward from the Goeree platform. The solid black line indicates the track over which samples were collected from on board ship in the present study.

elements generally follows variations in the element source strengths on the surrounding land masses. This will be considered in more detail later, with particular reference to the emission rates of Pb in the UK and Continental Europe.

(2) The mean atmospheric trace element concentrations found for atmospheric particulates collected during aeroplane flights over the southern North Sea (Otten et al., 1989), in the general open sea region between Leiston and Haamstede, are lower than those that are reported for the two land stations. This situation is also found further north in the survey region, when the data reported for Helgoland and Keil Bight stations are compared. For example, the average concentrations of Zn (33 ng m^{-3} of air), and Pb (29 ng m^{-3} of air) at Helgoland are only about half those reported for the Kiel Bight; i.e. Zn (57 ng m^{-3} of air) and Pb (53 ng m^{-3} of air). However, the average trace element concentrations found in the present study for Zn (41 ng m^{-3} of air) and Pb (34.5 ng m^{-3} of air) are very similar to those reported for Helgoland and more recently for Hemsby; i.e. Zn (41 ng m^{-3} of air), and Pb (34 ng m^{-3} of air); references given in Table 6.2.

From the data in Table 6.2, it can be seen that there is a good agreement between the atmospheric concentrations of Zn and Pb reported by Yaaqub et al., (1991) over a one year sampling period for a rural site at Hemsby, and those for the current data set. The samples reported by Yaaqub et al., (1991) were also collected using a hi-vol collection technique, employing Whatman 41 filters and flow rates of ~0.8 ms^{-1} which are similar to the flow rates used in the present study (i.e. 0.75 - 0.85 ms^{-1}).

It is interesting to note the general similarity between the average atmospheric concentrations of Zn and Pb reported at Helgoland, Hemsby and the current data set. This is despite the fact that measurements were carried out during different sampling periods and at different sites. It may be concluded that these comparisons further support suggestion made by Dehairs et al., (1983) that on a long term basis the aerosol burden of the whole North Sea troposphere has a fairly homogeneous composition. However, short term variations in the aerosol composition do exist, and a clear indication of this is given by the standard deviations of the trace element concentrations reported in the present study (see Table 6.1). It may be concluded therefore that although the average trace element composition of the NSA appears to be similar at many sites, variations can occur and some of these have been related to a decreasing south - north concentration gradient. Because of these variations in aerosol trace element concentrations, is it is necessary to establish the extent to which air mass transport from different source regions can exert a control on the geographical distributions of particulate atmospheric trace elements over the North Sea.

6.2.2 Controls On the Sources of Particulate Trace Elements Over the North Sea.

6.2.2.1 The Application of Air Mass Back Trajectories to Establish the Origin of an Aerosol.

6.2.2.1.1 Air masses.

Information on the transport history of an air parcel can be obtained from air mass back trajectories, which can be used to define the pathway along which the parcel has moved prior to the point at which it was sampled. For the air masses sampled during the North Sea Programme 36 hourly air mass back trajectories at a height of 10m above the sea surface were provide by the UK Meteorological Office. It has been pointed out in (Section 2.3), that the wind regime over the North Sea can vary over relatively short periods of time, and consequently winds often changed direction during individual sample collections. Despite this, it was possible to identify a number of end-member aerosols on the basis of their sources using the 36 hourly air mass back trajectories (see Appendix A for sample air mass back trajectories). Three end-member air masses were identified according to the following criteria.

(1) Type A aerosols, i.e. those that had passed over the United Kingdom (UK) mainland.

(2) Type B aerosols, i.e. those that had passed over continental Europe (EU).

(3) Type C aerosols, i.e. those that in the previous 36 hours to collection had not passed over land areas, and were mostly confined to 'open sea' regions (OS).

It is important to point out, however, that the aerosol classifications should not be considered to be highly specific, e.g. air masses that have passed over the more northerly regions of the UK are likely to carry a mixture of UK and OS aerosols. Further, aerosols for which the air mass origin changed significantly during the sampling collection, e.g. giving a mixture of UK and European sources were discarded from the end-member classifications.

From the original sample set of 98 samples it was possible to classify 55 samples into the three aerosol end-member types, and these were as follows. (1) Type A aerosols, UK (n = 36). (2) Type B aerosols, EU (n = 13), and (3) Type C aerosols, OS (n = 6). Following the classification of the samples into the three categories it can be seen that transport to the North Sea is dominated by air masses having a UK origin. The collection of samples from the present data set covered an eighteen month period and it has been pointed out by Miller and Harris (1985), and Davies et al., (1986), that long term climatoligies will reveal inter-annual variability within a region. Further, Davies et al., (1990), pointed out that seasonal variations can confound interpretations of the annual cycle with respect to the strengths of some sources and to meteorological variables; e.g. precipitation (Yaaqub et al., 1991). Factors such as these could have an effect on the relative numbers of samples attributable to the three aerosol end-member types during any specific sampling period. However, the dominance of westerlies is a consistent feature of the North Sea atmosphere (Lamb, 1950;

Barry and Chorley, 1982), and it is suggested here that any differences found between the trace element concentrations of the three end-member aerosols will occur irrespective of the sampling period providing, that is, that the sampling period is of sufficient duration; e.g. ≥ one year.

Despite probable annual variations in the source strengths of trace elements, it is the intention here to use the trace elements to distinguish between the three NSA end-members, and to compare the results with those reported by Yaaqub et al., (1991). Further, it is assumed that any short term variations in the source strengths of trace elements from the UK and the European end-member aerosol populations, will be effectively smoothed out over the sampling period (~15 months) to the same extent in both sample populations.

The samples which have been classified into the three end-member aerosol types are listed in Table 6.3. In Table 6.4 the atmospheric particulate arithmetic mean, range, standard deviation and geometric mean values for the three end-member aerosol types are presented. In Table 6.5 the arithmetic mean concentrations of the three end-member aerosol sample populations (present study) are compared to those reported by Yaaqub et al., (1991). It must be pointed out, however, that Yaaqub et al., (1991), defined four aerosol end-member types: i.e. UK, Remote, East Europe and West Europe, and for the purpose of the present comparison data for the East and West Europe aerosol end-members have been averaged.

Table 6.3 Sample number classification for the UK, EU and OS end-member aerosols, based on air mass back trajectories.

Aerosol end-member.	Sample Number.
UK n=36	13-17, 21 31 34 38 39 41 42 46 47-49, 51 54 58 60-62, 73.75 82-84, 87-90, 92 95-97
European n=13	19 20 22-24 27 29 36 56 77 80 86 93
Open Sea n=6	28 66 67 69 79 91

Table 6.4 The arithmetic mean, range, standard deviation and geometric mean values of the NSA taken from the three end-member sample populations (present study).

Element	UK (n=36)			Europe (n=13)			Open Sea (n=6)		
	Arithmetic mean / σ	Range	Geo. mean	Arithmetic mean / σ	Range	Geo. mean	Arithmetic mean / σ	Range	Geo. mean
Al	300 ± 182	24 - 753	243.5	440 ± 247	150 - 854	372	84 ± 61	21 - 156	63
Fe	304 ± 217	15 - 807	223	657 ± 449	126 - 1565	512	116.5 ± 59.5	27 - 205	99
Mn	13 ± 12	1.6 - 62	8.5	25 ± 16	3.5 - 57	20	3.6 ± 1.2	2.1 - 5.4	3.4
Ni	3.7 ± 2.5	0.4 - 7.8	2.9	4.8 ± 3.6	1.2 - 13	3.7	0.97 ± 1.1	0.04 - 2.9	0.5
Co	0.24 ± 0.13	0.01 - 0.6	0.2	0.31 ± 0.17	0.01 - 0.67	0.2	0.12 ± 0.11	0.01 - 0.28	0.1
Cd	0.31 ± 0.22	0.02 - 0.95	0.2	0.69 ± 0.65	0.07 - 2.2	0.4	0.05 ± 0.04	0.1 - 0.04	0.03
Cr	3.8 ± 2.8	0.1 - 11.5	2.8	10 ± 7.8	2 - 25	7.6	1.3 ± 0.9	0.1 - 2.5	0.8
Cu	5.3 ± 5	0.7 - 26	3.9	11 ± 6.9	3.3 - 26	9.1	1.8 ± 1.4	0.8 - 4.5	1.5
Zn	31 ± 26	0.7 - 138	21	83 ± 65.5	11 - 250	62.5	7.7 ± 4.2	2 - 14	6.6
Pb	28 ± 24	1.7 - 126	19	68 ± 56	7 - 189.5	49.5	4.8 ± 2.9	1.6 - 9.5	4.1
Na	6910 ± 12379	1230 - 72100	3940	6538 ± 6084	940 - 20870	4315	11580 ± 12510	1820 - 31470	6607

σ = standard deviation.

Table 6.5 The arithmetic mean concentrations of the three end-member aerosols (present data) compared with those of Yaaqub et al., (1991).

Element	Present data			Yaaqub et al., (1991)		
	UK	EU	O.Sea	UK	EU*	O.Sea
Al	300	440	84	-	-	-
Fe	304	657	116.5	186	371	133
Mn	13	25	3.6	8.5	19.5	7
Ni	3.7	4.8	0.97	-	-	-
Co	0.24	0.31	0.12	-	-	-
Cd	0.31	0.69	0.05	1.1	1.4	0.75
Cr	3.8	10	1.3	-	-	-
Cu	5.3	11	1.8	-	-	-
Zn	31	83	7.7	33	76	28
Pb	28	68	4.8	31	48	20
Na	6910	6538	11580	-	-	-

* data averaged from West and East Europe. For original classifications see Yaaqub et al., (1991).

Two main conclusions can be drawn from the data in Tables 6.4 and 6.5, and these are summarised below.

(1) The average trace element concentrations of the three end-member aerosol populations found in the present study can be ranked in the decreasing order, European > UK >> Open Sea. This can be illustrated with particular reference to the trace elements Pb and Zn which have arithmetic mean end-member atmospheric concentrations (ng m^{-3} of air), as follows; European (Pb = 70, Zn = 83), UK (Pb = 28, Zn = 31) and Open Sea (Pb = 4.8, Zn = 7.7).

(2) The average concentrations (ng m^{-3} of air) of Pb (28) and Zn (31) in the UK end-member aerosol population (present study) are very similar to those values found for the whole sample population (n = 98), which has average atmospheric concentrations of Pb (34.5) and Zn (41). This probably arises because the numbers of samples from the three end-member aerosol types is heavily biased towards the UK group; i.e. UK = 36, EU = 13 and OS = 6, and 43 = unclassified.

Data for the average trace element concentrations of the NSA end-member aerosols may be compared to those reported by Yaqqub et al., (1991), for the Hemsby aerosol (HA) - see Table 6.5.

(a) <u>The UK end-member aerosol.</u> The average concentrations (ng m^{-3} of air) of Pb (28 (NSA) and 33 (HA)), and Zn (31 (NSA) and 33 (HA)), are similar in the UK end-members from both studies. However, the average concentration of Fe is much higher in the NSA (304), than in the HA (186), and the average concentration of Cd in the NSA (0.31), is lower than in the HA (1.1).

(b) The EU end-member aerosol. The average concentrations of Pb (68 (NSA) and 48 (HA)) and Zn (83 (NSA) and 76 (HA)), are generally similar in the EU end-members from both studies. However, as with the UK end-member, the average concentration of Fe is higher in the NSA (657), than in the HA (371), and the average concentration of Cd in the NSA(0.69) is lower than in the HA (1.4).

(c) The OS (North) end-member aerosol. The average concentration of Fe is similar in the two OS end-members (116.5 (NSA), and 133 (HA)). However, the average concentrations of (Pb 4.8 (NSA), and 20 (HA)), (Zn (7.7 (NSA), and 28 (HA)), and (Cd 0.05 (NSA), and 0.75 (HA)) are lower in the NSA than in the HA. The reason for this may be that the Hemsby site is not ideal for the collection of open sea samples, as Pb, Zn and Cd which are predominantly anthropogenic in origin, may have suffered local pollution effects.

In general, the relatively high trace element concentrations in the European end-member aerosol population is consistent with the high emissions of pollutant trace elements from the European source areas (see e.g.; Pacyna, 1985) which the air masses have passed over prior to collection. Further, according to Yaaqub et al., (1991), the development of high pressure systems over Europe allows aerosols to accumulate in the atmosphere because of reduced vertical mixing. As this polluted

European air is transported towards the UK the continuing relative stability of the air, and the general absence of wet removal processes, can lead to high aerosol concentrations over the southern North Sea. By comparing the arithmetic mean concentrations (ng m^{-3} of air) in the EU end-member aerosols for Pb (68 ng) and Zn (83), with those for the OS end-member Pb (4.8) and Zn (7.7), it is apparent that when a high pressure system is predominant over Europe the trace element concentrations of the NSA are approximately 15 times higher for Pb and Zn than when a northerly wind system (OS) is predominant over the North Sea.

It was shown above that the transport of trace elements to the North Sea is dominated by the UK end-member aerosol population (n=36), which accounts for 65% of the samples for which end-member sample classification was possible. According to Yaaqub et al., (1991), aerosol transport from the west is generally associated with greater wind speeds, and often with frontal systems and rainfall which will effectively clean the atmosphere of trace elements, and so will generally result in lower concentrations of elements collected over the North Sea than from air masses which have crossed the European source area. This can be further emphasised by comparing the average trace element concentrations of the UK and EU end-member aerosol populations found in the present study see Table 6.4. From the table it can be seen that the average trace element concentrations (ng m^{-3} of air), of Pb and Zn

(28 and 31 respectively) for the UK end-member aerosol population are only about half the average values for the EU end-member aerosol; i.e. (68) for Pb and (83) for Zn.

It is suggested therefore that the lower trace element concentrations of the UK end-member aerosol, relative to the EU end-member, are primarily due to two controlling factors, and these are summarised as follows.

(1) According to van Aalst et al., (1982), the emission pattern for Pb in the UK varies between 35 t yr^{-1} in the far north to 725 t yr^{-1} in the south, with intermediate values in between (see Figure 6.2). In contrast, the emission pattern for Pb in Europe is relatively more compact, i.e. it has a smaller range of emission values, and generally the European sources have higher Pb emission rates (typically, 180 - 614 t yr^{-1}) than the UK sources. As a result, it may be expected that the lower emission rates for the UK will result in a air masses crossing the region having generally lower Pb concentrations than those crossing Europe.

(2) The transport of aerosols to the North Sea from the west is usually associated with frontal systems which will have the effect of lowering the particulate trace element concentrations of samples collected at sea because of the associated rainfall scavenging. In contrast, air masses originating over Europe are generally linked with high pressure systems which often do not have rainfall associated with them, and aerosol samples collected from them will therefore have correspondingly higher trace

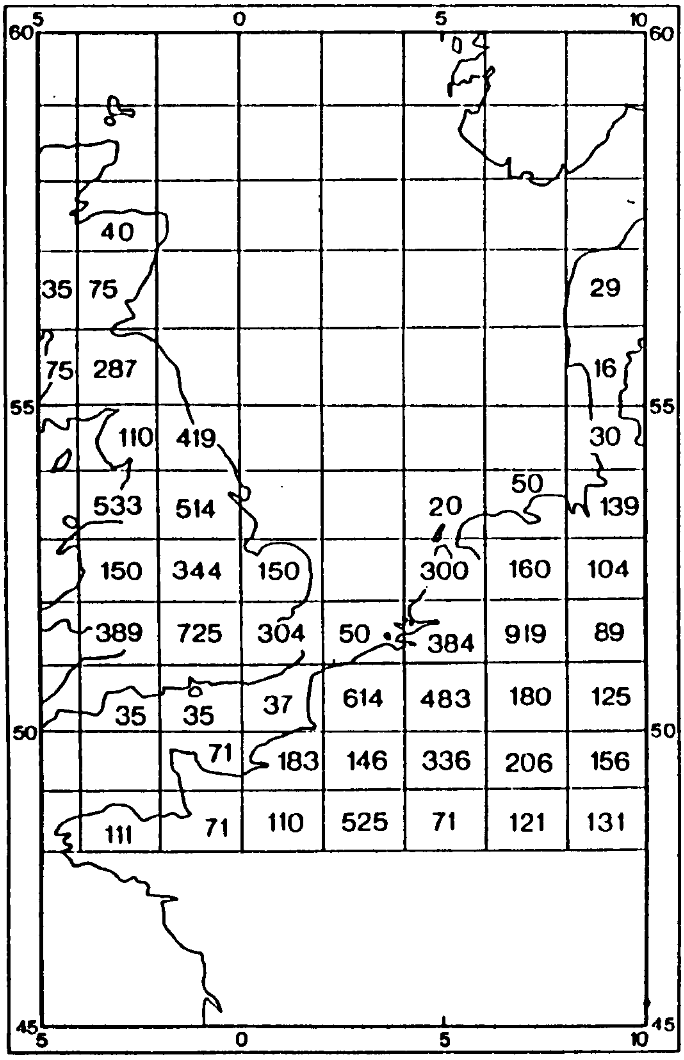

Figure 6.2 Grid cell emissions of Pb from source regions surrounding the North Sea (units; t yr^{-1}; after van Aalst et al., 1982.)

element concentrations than those collected from air masses which have crossed the UK.

It is apparent, therefore, that the concentration of particulate trace elements in the North Sea atmosphere is strongly related to the origin of the air mass which transports them. This can be illustrated with respect to a number of samples which have been selected from each of the three end-member aerosol classifications. The concentration data for the various samples are given in Table 6.6, and the sample locations and associated air mass back trajectories are illustrated in Figure 6.3 (a-c). It must be stressed, however, that these examples of end-member aerosols have been selected to specifically illustrate how the origin of an air mass can exert a control on the relative compositions of aerosols, and that there are other important factors that constrain the atmospheric concentration of trace elements; e.g. the degree of rainfall (rain-out) that has occurred during the history of an air mass from its source to the point of collection. The rainfall can perturb the 'air mass source/trace element concentration' relationship. For example, the atmosphere can be cleaned of aerosols by precipitation scavenging, with the result that air masses flowing into the North Sea can have low trace element burdens irrespective of their source.

Van Aalst et al., (1982) produced a grid cell map showing the emission of Pb on the land areas surrounding the North Sea, and to facilitate the interpretation of the

Table 6.6 Data on the atmospheric particulate trace element concentrations associated with the three end-member sample populations (conc. units ng m^{-3} of air).

Element	U.K.		Europe			Open Sea	
	Sample 48	Sample 92	Sample 93	Sample 19	Sample 80	Sample 28	Sample 66
Al	173	107	854	630	494	33	108
Fe	280	174	1565	895	391	141	205
Mn	6.5	8	54	29	15.5	5.5	3.7
Ni	7	2.8	10	2.9	3.7	2.9	0.5
Cd	0.89	0.17	2.2	0.94	0.56	0.08	0.07
Co	0.36	0.17	0.01	0.37	0.25	0.12	0.05
Cr	2.2	3.3	17.5	12.5	3.9	0.1	1.5
Cu	26	3	26.5	12.5	5.7	1.5	1.3
Zn	57.5	24	250	84.5	65	6.6	6.3
Pb	52	22	189.5	52	38	3.6	6.8
Na	1845	3260	940	8430	1575	5740	31470

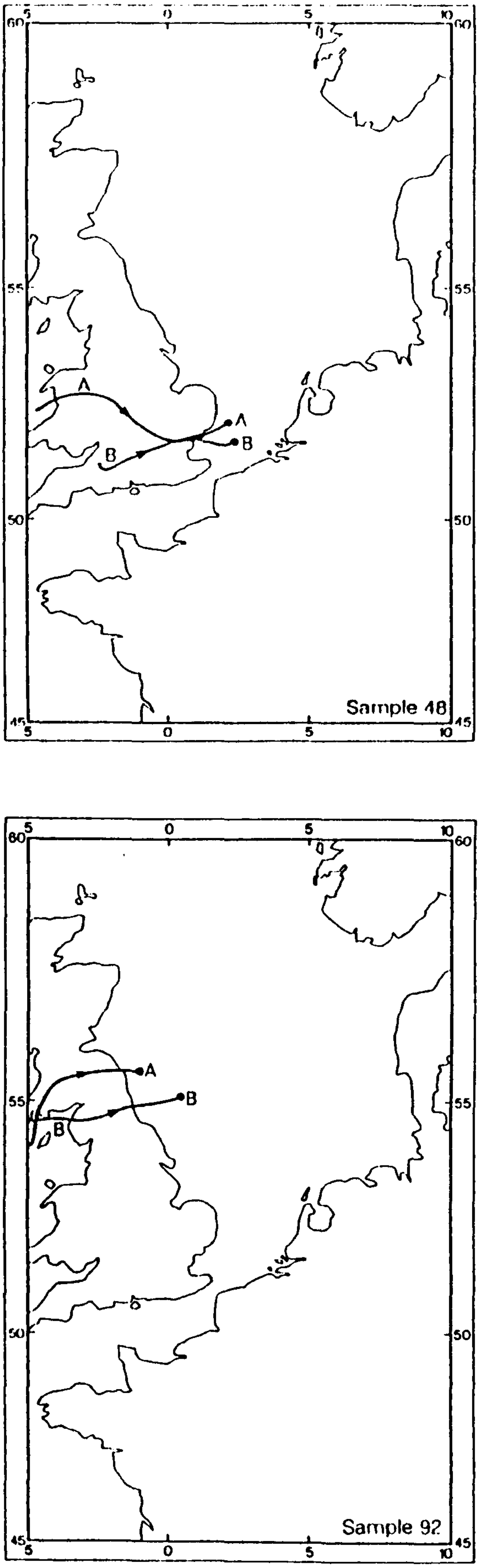

Figure 6.3a UK end-member air mass back trajectory types. Trajectories are indicated from the start (A) and finish (B) of a sampling run.

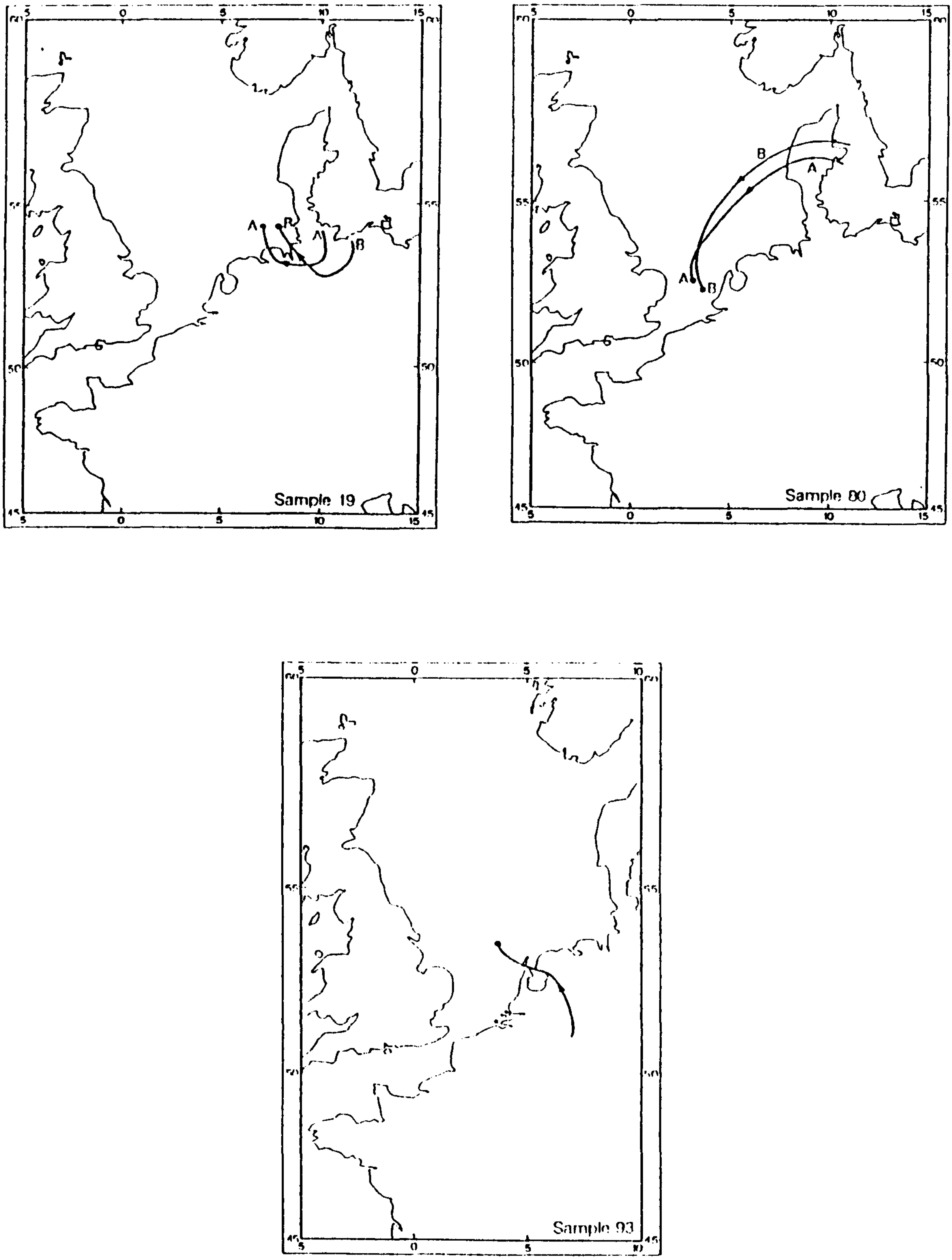

Figure 6.3b Europe end-member air mass back trajectory types. Trajectories are indicated from the start (A) and finish (B) of a sampling run; only one trajectory was available for Sample 93.

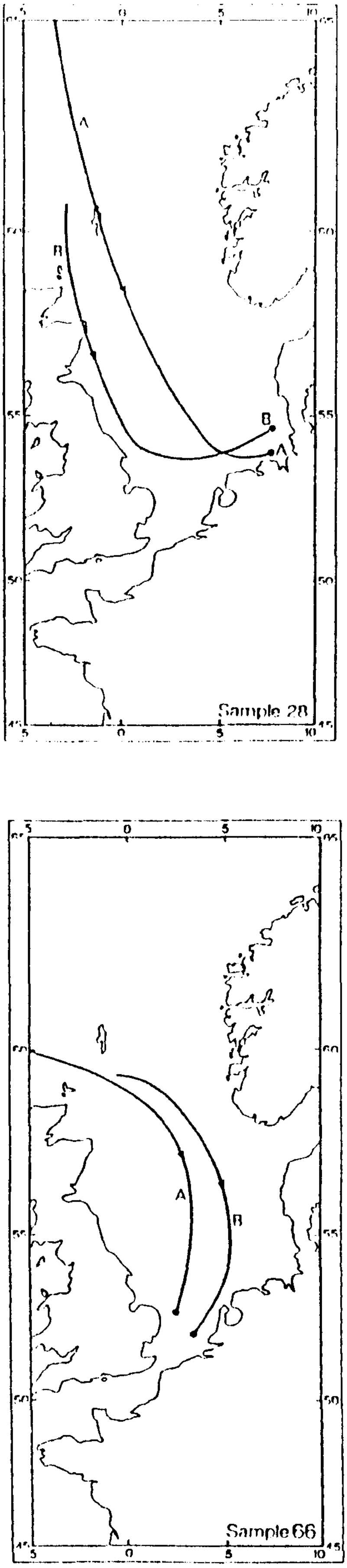

Figure 6.3c Open sea end-member air mass back trajectory types. Trajectories are indicated from the start (A) and finish (B) of a sampling run.

'air mass source/trace element concentration' relationship with respect to the end-member samples identified in Table 6.6, a representative selection of these Pb emission data are illustrated in Figure 6.2. The trace element concentrations associated with each of the selected 'end-member' aerosols are described below.

(1) <u>Type A aerosols; those that have crossed the UK mainland.</u> Two examples of the Type A aerosols have been selected (samples 48 and 92), and the trajectory of the air masses transporting them for the 48 hours previous to collection is illustrated in Figure 6.3a. For Sample 48 the air mass has crossed the southern UK and the concentrations of the most enriched trace elements Cd, Cu, Zn and Pb in the atmosphere are higher than those for Sample 92, for which the air mass has crossed the northern UK. For Pb the concentrations in the atmosphere can be related to the general pattern of emissions in the UK source area; thus, Sample 48, which has crossed a part of the UK for which the Pb emissions are the highest (reaching 725 t yr^{-1}) has a atmospheric Pb concentration of 52 ng m^{-3} of air, compared to 22 ng m^{-3} of air for Sample 92 for which the air mass has crossed regions with considerably lower Pb emissions (maximum, 419 t yr^{-1}).

(2) <u>Type B aerosols; those that have crossed continental Europe.</u> Three examples of Type B aerosols have been selected and these can be arranged in a north - south sequence (samples 19, 80 and 93); the trajectories for the samples are illustrated in Figure 6.3b. Sample 93 collected

from an air mass that has reached the North Sea after passing over a strong trace element source region on the continental mainland. Samples 19 and 80 were collected from air masses that has crossed over progressively more northern regions of the continental mainland. This has resulted in a distinct decrease in the atmospheric concentrations of Cu, Zn and Pb in the south to north transect in the order; Sample 93 > Sample 19 > Sample 80. This relationship for Pb can be related to emissions in the source regions crossed by the air masses in the following manner. (1) Sample 93, which has a Pb atmospheric loading of 189.5 ng m^{-3} of air, has crossed the region for which the Pb emissions reach a high of 919 t yr^{-1}; (2) Sample 19, which has a Pb atmospheric loading of 52 ng m^{-3} of air, has crossed a region for which the Pb emissions drop to 139 t yr^{-1}; and (3) Sample 80, which has a Pb atmospheric loading of 38 ng m^{-3} of air, has crossed a region for which the Pb emissions are even lower, with values ~30 t yr^{-1}.

(3) <u>Type C aerosols; those that have not passed over land areas and are confined to mainly open ocean areas.</u> Two examples of Type C aerosol have been selected (28 and 66), and the trajectories of their host air masses are illustrated in Figure 6.3c. From the concentration data in Table 6.4 it can be seen that the atmospheric concentrations of trace elements associated with the Type C aerosols over the North Sea atmosphere are considerably lower in concentration than in those associated with either

Type A or Type B aerosols, particularly for the trace elements Pb, Zn, Cd and Cu.

Clearly, therefore, an 'air mass source/trace element' relationship is strongly evident for the end-member-type air mass trajectories; this is particularly evident for Pb, for which the atmospheric concentrations have been related to an emission grid on the land masses surrounding the North Sea. Further, the dominant feature in this 'air mass source/trace element concentration' relationship is a South - North decrease in particulate trace element concentration reflected in samples collected at the land stations surrounding the North Sea. Thus, the South - North increasing gradient in trace element sources is confirmed by the present data. However, it can be seen from Figures 6.3 (a-c), air masses of the Type A, B, C and indeed a mixture of all three Types can be transported to any part of the North Sea. Therefore, although the strength of the source emissions for an atmospheric particulate controls the initial atmospheric concentration, it is the origin of the air masses themselves, and not the location at which a sample was collected which constrains the concentrations of trace elements in the NSA. This is an important conclusion and can be further illustrated with respect to: (1) samples collected at different locations from an air mass of the same general source, and (2) samples collected at the same general location from air masses having different sources.
(1) Samples collected during the Survey CH53, in June 1989 can be used to illustrate how aerosols collected at

different locations over the North Sea from air masses having the same general source can have similar atmospheric concentrations of trace elements. A total of seven samples (66, 67, 68, 69, 70, 71, and 72), were taken over the twelve day sampling period. All the samples were collected from air masses which had largely been confined to open ocean regions of the North Sea (see Appendix A for individual air mass back trajectories)). For the latter part of the survey rain was detected on the ships radar (radius 50 nautical miles) during the collection of samples 70 - 72. However, samples 66, 67 and 68 were collected before the rain moved in, and will serve to illustrate how the origin of an air mass puts constraints on the atmospheric concentrations of particulate trace elements over the NSA. The mid-points of the track over which the samples were taken is illustrated in Figure 6.4a, and the corresponding trace element concentrations are listed in Table 6.7. It is apparent from Figure 6.4a, that the samples cover a South - North transect, with samples 67 and 66 being in a region were trace element land sources are specially strong. However, it is evident from the data in Table 6.7, that even the most southerly sample (Sample 66) has relatively low concentrations of Cu, Zn and Pb, despite its position close to the major sources of elements on the surrounding landmasses. Further, it has virtually the same concentrations as Sample 68, which was taken from a position considerably more to the north.

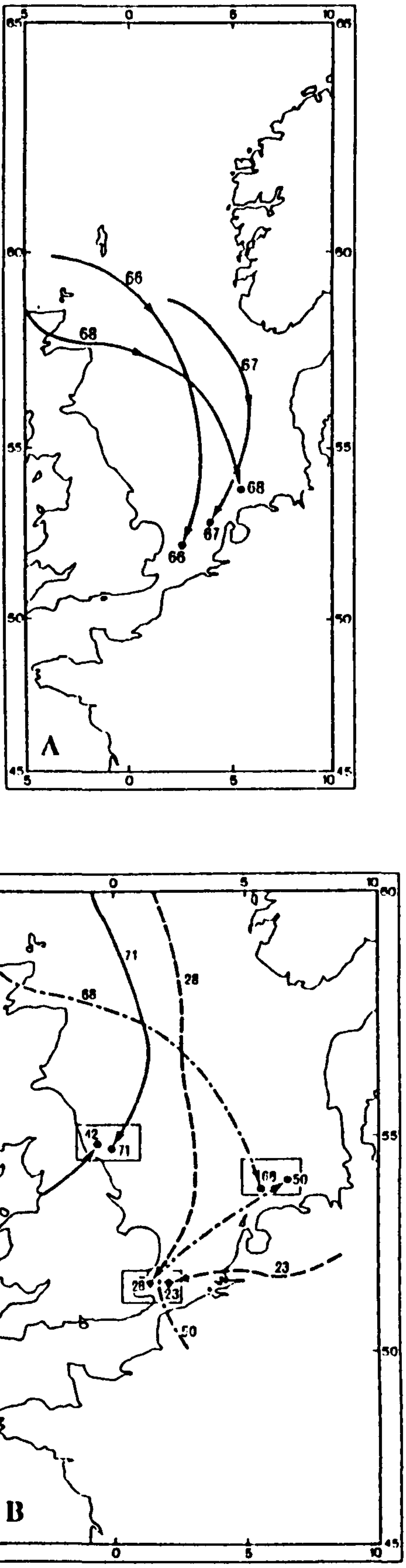

Figure 6.4 Air mass transport to the North Sea.Trajectories are averaged over the entire sampling runs; the numbers indicate individual samples, and the sample locations are placed at the mid-point of each sampling run. 4A Samples collected at different locations from air masses having the same general source. 4B Samples collected at the same location from air masses having different sources.

Table 6.7 Data on the atmospheric particulate trace element concentrations at different locations in the North Sea associated with air masses from a single source (conc. units ng m^{-3} of air).

Element	Sample 66	Sample 67	Sample 68
Al	108	37	185
Fe	205	82	173
Mn	3.7	2.6	4
Ni	0.46	0.31	0.42
Cd	0.05	0.01	0.02
Co	0.05	0.01	0.02
Cr	1.5	1.2	1.6
Cu	1.3	0.9	1.1
Zn	6.3	10.5	9
Pb	6.8	4.7	7.3
Na	31470	1820	63435

(2) Samples that have been collected over various regions of the North Sea can also be used to illustrate that it is the origin of the air masses, and not the location at which the sample is collected which constrains the trace element concentrations of the NSA. Examples in which different trace element concentrations are associated with air masses of different origins are illustrated in Figure 6.4b, and the associated trace element concentrations are listed in Table 6.8. From the table it can be seen that the concentrations of trace elements at similar locations over the NSA can vary depending on the origin of the air mass.

6.2.2.1.2 Conclusions.

There is a South to North decreasing gradient in the emissions of trace elements from the land masses that surround the North Sea. The emission strength in a source region will therefore impose a control on the concentrations of trace elements that are released into the air, and this can influence the concentration of trace elements that are transported to the North Sea atmosphere. However, it has been shown in Section 6.2.2 that air masses from a variety of source regions can be transported to any part of the North Sea. As a result, it is the origin of the air masses themselves and not the location at which an aerosol sample is collected that determines the atmospheric concentration of particulate trace elements in the atmosphere over the North Sea. However, this relationship can be perturbed by precipitation scavenging. Thus, the

Table 6.8 Data on the atmospheric particulate trace element concentrations at similar locations in the North Sea associated with air masses from different sources (conc. units ng m^{-3} of air).

Element	Sample pair*		Sample pair*		Sample pair*	
	28	23	42	71	68	50
Al	33	838	520	30	185	276
Fe	141	1241	298	32	173	495
Mn	5.4	57	13	2.6	4	18.5
Ni	2.9	13	5.5	0.04	0.22	7.9
Cd	0.08	1.7	0.49	0.01	0.25	1.74
Co	0.12	0.29	0.38	0.31	0.02	0.45
Cr	0.1	25	5.3	1.1	0.06	3.5
Cu	1.5	20	7.8	0.4	0.22	0.79
Zn	6.5	150	38	2.9	9	91.5
Pb	3.6	166	60	0.8	7.3	114
Na	7690	20870	1230	1820	63435	1990

effect of a heavy rain event prior to collection of the aerosol can effectively 'scrub' the atmosphere clean of particles, which will result in low atmospheric concentrations of trace elements regardless of the origin of the air mass.

Three principal conclusions regarding the concentrations of particulate trace elements in the North Sea atmosphere can therefore be drawn from the present study.

(1) The origin of an air mass is the primary influence which determines the concentrations of particulate trace elements over the North Sea, providing the air mass has not suffered from a rain event prior to the collection of aerosol samples.

(2) There will only be a south to north decreasing gradient in particulate trace element concentrations in the North Sea atmosphere if the wind regime is such that the air masses have passed over the continental regions immediately adjacent to the sea areas. On these continental regions there is a south to north decrease in the elemental source strengths. However, if the air masses reaching, for example, the southern North Sea, have crossed northern Europe and open sea regions the south to north decreasing trace element concentration can be overturned.

(3) Concentrations of the 'pollutant' trace elements, e.g. Cu, Zn, Pb, Cd, are considerably higher in the European than in the UK aerosols. However, data from the present study indicates that the atmospheric input of trace

elements into the North Sea atmosphere is dominated by the UK end-member aerosol. The reason for this is that during the survey period westerly wind systems generally dominated the air flow over the North Sea, with the result that the UK aerosols were the most common type in the atmosphere.

6.3 Inter-element Relationships in the NSA.

6.3.1 Elemental Tracers.

In the previous section air mass back trajectories have been applied to the NSA to gain information on the origin of particulate atmospheric trace elements over the North Sea. In addition, inter-element relationships in the NSA can provide information on the sources of elements themselves.

The main contributors of trace elements to the North Sea atmosphere are mineral dust (the crustal source), sea salts (the oceanic source) and anthropogenic emissions (the anthropogenic, or pollutant, source). In order to evaluate the relative contribution of each source to the NSA, use can be made of indicator elements; either in the form of enrichment factors or elemental tracers. Enrichment factors are considered in Section 6.4, and in the present section attention is confined to elemental tracers.

Elemental tracers have been developed by Rahn and his co-workers (see e.g.; Rahn and Lowenthal, 1984), in an attempt to identify source regions for some anthropogenic trace elements in the marine aerosol. The technique essentially utilizes the distinctive emission patterns of the atmospheric trace elements from different source regions, and assumes that this distinction is maintained during transportation of the aerosols. On the basis of this assumption, inter-element ratios in the aerosols can be related to those of the source emissions to identify the sources themselves. In this context, Schneider (1987) and Yaaqub et al., (1991) have calculated the ratios of some trace elements in the NSA using Zn as being characteristic of an anthropogenic element. The trace element to Zn ratios for Mn, Cr, Cd, Cu, and Pb from the current data set are presented in Table 6.9 together with those reported by Schneider (1987), and Yaaqub et al., (1991).

A degree of caution must be introduced when attempting to interpret the statistics resulting from the present data set. The primary reason for this being the different sample numbers for the aerosol populations. However, from the present data set in Table 6.9, there does appear to be a significant difference between the Pb/Zn ratios of the UK and Eu sample populations. The reasons for this are discussed below.

The UK end-member aerosol is enriched in Pb relative to Zn to a greater extent than the EU end-member; i.e. an aerosol from the UK has a higher proportion of Pb, relative to Zn, than an aerosol from continental Europe. This pattern of Pb enrichment in the UK end-member, or depletion in the EU end-member aerosol has also been reported by Yaaqub et al., (1991), who suggested it was broadly consistent with the source emission inventories for Pb and

Table 6.9 Selected elemental ratios by air mass sector, a comparison with other workers.

Element	Schneider (1987).	Yaaqub et al., (1991).				Present data.			
		UK	European*	North (O.Sea)	ú(UK+EU+OS)	UK	European	O.Sea	ú.pop.
Cr/Zn	0.034	-	-	-	-	0.32	0.34	0.11	0.23
MN/Zn	0.13	-	-	-	-	0.67	0.33	0.53	0.53
Cu/Zn	0.12	-	-	-	-	0.27	0.16	0.19	0.24
Pb/Zn	0.75	0.94	0.62	0.71	0.72	1.1	0.81	0.63	0.94
Cd/Zn	-	0.032	0.018	0.027	0.026	0.019	0.008	0.008	0.014

* = data is averaged from West and East Europe, for original data see Yaaqub et at., (1991).
- = no data.
ú = arithmetic mean data.

Zn given by Pacyna (1987) for 1985. Further, Yaaqub et al., (1991), suggested that trace element ratio comparisons, e.g. taken from Schneider (1987) and Lannefors et al., (1983), can be used to indicate differences in the emission rates of Pb relative to Zn over a time period. For example there is an increase in the Pb/Zn ratios from 0.75 (Schneider, 1987) to a value of 0.94 for the whole NSA sample population (present data set), and this could reflect the gradual decline in use of Pb in petrol throughout Europe in recent years (see also; Yaaqub et al., 1991).

In addition to elemental ratios, rank correlations can be used as a method of assessing the relative associations of trace elements in an aerosol, and these are discussed in the following section.

6.3.2. Rank Spearman Correlation Coefficients for the NSA.

Harrison and Williams (1982) pointed out that the use of parametric analysis is a popular method for the interpretation of atmospheric pollutant data (see also: Moyers et al., 1977; M^{c}Donald and Duncan, 1978; Turner, 1979). However, a correlation between a pair of variables is only valid statistically provided each variable is distributed normally (Bailey, 1959); otherwise, the significance of a correlation coefficient will be indeterminate. This has been illustrated by Till (1974), who demonstrated that one extreme value in a data set can easily produce a falsely significant value if the product moment correlation coefficient is used to interpret information.

In the present work there are some sets of data that contain extreme values, and are therefore not suitable for parametric correlation analysis. It was decided, therefore to use an analogous non-parametric test, the Spearman Rank Correlation Coefficient (r_s). The Spearman Rank Correlation Coefficient technique can be used for any distribution of data, and gives values between -1 and +1, whose significance can be tested. A positive correlation implies that large values of x are associated with large values of y, and small values of x are associated with small values of y. Generally, a statistically significant correlation between two variables will indicate that the variables are related. However, it is important when interpreting values of r_s, to remember that the results obtained must not be treated as an absolute indication of the correlation between two variables (Owen and Jones, 1990). Despite this the authors have pointed out that the correlation of variables can give an added weight to a relationship previously suggested by theory. In terms of the present work it is suggested that a significant positive correlation between trace elements in the NSA can be taken to indicate that the trace elements; (1) share the same source, and (2) retain the same ratios following transportation from the source.

Values of r_s have been calculated for the whole NSA population, and for the three end-member populations within it. The data for the Spearman Correlation Coefficients are given in Tables 6.10a - 6.10d, which also give the significance levels for the correlations. A number of conclusions can be drawn from the data in these tables, and these are summarised below.

<u>The whole sample population (n=98; Table 6.10a).</u> In this sample population there are significant correlations at the 0.1% level between all the trace elements; however, Na is not significantly correlated with any of the trace elements at <20% level. The strongest correlations are found between the following trace element pairs; all values at the 0.1% significance level. Al and Fe (0.73), Fe and Mn (0.84), Fe and Zn (0.79), Cd and Pb (0.76), Cu and Pb (0.73), Cu and Zn (0.73) and Pb and Zn (0.79).

<u>The UK end-member (n=36; Table 6.10b).</u> In this sample population there are significant correlations at the 0.1% level between all the trace elements; however, the major trace element Na is not significantly correlated with any of the trace elements. The strongest correlations are found between the following trace element pairs; all values at the 0.1% significance level. Al and Fe (0.73), Fe and Mn (0.73), Fe and Zn (0.80), Cd and Cr (0.77), Cd and Pb (0.85), Cu and Pb (0.82), Cu and Zn (0.72) and Pb and Zn (0.73).

<u>The EU end-member (n=13 Table 6.10c).</u> In this sample population there are significant correlations at the 0.1%

Table 6.10a The North Sea whole population Non-parametric Spearman rank correlation matrix (values of r_s) n=98.

	Al	Fe	Mn	Cd	Co	Cr	Cu	Ni	Pb	Zn
Fe	0.73									
Mn	0.64	0.84								
Cd	0.49	0.64	0.64							
Co	0.43	0.42	0.44	0.39						
Cr	0.54	0.58	0.59	0.41	0.40					
Cu	0.64	0.67	0.69	0.64	0.51	0.58				
Ni	0.45	0.56	0.50	0.57	0.33	0.37	0.58			
Pb	0.54	0.67	0.68	0.76	0.39	0.49	0.73	0.69		
Zn	0.62	0.79	0.69	0.69	0.48	0.56	0.73	0.59	0.79	
Na	-0.01*	0.01*	0.05*	-0.08*	-0.03*	-0.09*	0.09*	0.16*	-0.08*	-0.08*

* All correlations are significant at 0.1% level except for Na.

Table 6.10b The UK end-member Non-parametric Spearman correlation matrix (values of r_s) n=36.

	Al	Fe	Mn	Cd	Co	Cr	Cu	Ni	Pb	Zn
Fe	0.73									
Mn	0.59	0.73								
Cd	0.38	0.44	0.37							
Co	0.44	0.37	0.35	0.26						
Cr	0.35	0.57	0.65	0.36	0.40					
Cu	0.65	0.59	0.65	0.77	0.44	0.47				
Ni	0.44	0.56	0.52	0.57	0.50	0.24	0.62			
Pb	0.48	0.53	0.50	0.85	0.24	0.31	0.82	0.64		
Zn	0.59	0.80	0.57	0.69	0.33	0.45	0.72	0.61	0.73	
Na	-0.21*	-0.15*	-0.12*	-0.24*	-0.42*	-0.19*	-0.15*	-0.25*	-0.19*	-0.185*

* Correlations significant at < 20% level.
All other correlations significant at 0.1% level.

Table 6.10c The European end-member sample population Non-parametric Spearman rank correlation matrix (values of r_s) n=13.

	Al	Fe	Mn	Cd	Co	Cr	Cu	Ni	Pb	Zn
Fe	0.64*									
Mn	0.63*	0.94*								
Cd	0.49	0.79*	0.69*							
Co	-0.18	0.32	0.19	0.21						
Cr	0.64*	0.81*	0.83*	0.62*	0.11					
Cu	0.56*	0.86*	0.72*	0.76*	0.32	0.87*				
Ni	0.26	0.26	0.28	0.52	-0.15	0.19	0.24			
Pb	0.44	0.93*	0.93*	0.73*	0.30	0.68*	0.71*	0.37		
Zn	0.57*	0.94*	0.94*	0.81*	0.25	0.78*	0.76*	0.34	0.94*	
Na	0.07	0.43	0.45	0.12*	0.61*	0.29	0.24	-0.13	0.41	0.29

* = Significant at 0.1% level.
All others significant at < 20% level.

Table 6.10d The Open Sea end-member sample population Non-parametric Spearman rank correlation matrix (values of r_s) n=6.

	Al	Fe	Mn	Cd	Co	Cr	Cu	Ni	Pb	Zn
Fe	0.43									
Mn	0.66	0.68								
Cd	0.21	0.41	0.25							
Co	0.93[3]	0.37	0.81[1]	0.06						
Cr	0.64	0.36	0.43	-0.19	0.65					
Cu	0.97[3]	0.39	0.72	0.29	0.94	0.48				
Ni	-0.11	0.31	0.61	0.32	0.13	-0.33	0.05			
Pb	0.65	0.61	0.65	0.12	0.67	0.92	0.53	-0.02		
Zn	0.94[3]	0.28	0.90	0.32	0.89[2]	0.66	0.92	-0.11	0.69[1]	
Na	-0.03	0.61	0.47	-0.38	0.13	0.35	-0.09	0.32	0.41	-0.22

[1] Significant at 10% level.

[2] Significant at 5% level.

[3] Significant at 1% level.

All other correlations are significant at < 50% level.

level between all the trace elements; however, the major trace element Na is not significantly correlated with any of the trace elements. The strongest correlations are found between the following trace element pairs; all values at the 0.1% significance level. Fe and Mn (0.94), Fe and Cd (0.79), Fe and Cr (0.83), Mn and Cu (0.72), Mn and Pb (0.93), Mn and Zn (0.94), Cd and Cu (0.76), Cd and Pb (0.73), Cd and Zn (0.81), Cu and Pb (0.71), Cu and Zn (0.76) and Pb and Zn (0.94).

The OS end-member (n=6; Table 6.10d). In this population the samples are generally less well correlated than the other two NSA end-members, and the inter-element correlations range in significance over 1% - <50% range; however, the poor correlations may reflect the small number of samples in this population, i.e. 6. The strongest correlations are found between the following trace element pairs; all values at the 1% significance level Al and Co (0.93), Al and Cu (0.97,) and Al and Zn (0.94,).

In the whole NSA there are significant correlations at the 0.1% level between all of the trace elements, with the exception of Na. This suggests that the trace elements vary in the same way, and supports the suggestion made by Cawse (1974) that airborne particles sampled at sites distant from the immediate pollution sources have a generally uniform chemical nature. Thus, although the particulate concentrations of the aerosol vary with location and time, the ratios of many of them remain the same. This implies that overall the time averaged NSA is a well mixed population. Further, the strong correlations between some element pairs suggests that they may have the same general type of source. However, a better way of assessing the sources of trace elements in an aerosol population is by using indicator elements for a specific source in an enrichment factor, and this is considered in the next section.

6.4 Enrichment Factors in the NSA.

The principal primary sources of trace elements to the marine aerosol are the Earth's crust (crustal source), anthropogenic activity (pollutant source), with the sea surface (oceanic source) being a secondary or recycled, source. Trace element contributions from the crustal and the oceanic sources can be estimated using enrichment factors (EFs), and these are considered below.

6.4.1 EF_{crust} Values.

EF_{crust} values can be calculated using Equation 5.3. For this equation it is necessary to define a composition for the crustal source term. The most commonly used source term for this purpose is the average composition of the Earth's crust. However, because the average composition of crustal rocks does not necessarily reflect the composition of local source rocks, EF_{crust} values should be regarded only as order of magnitude estimates of crustal sources. Thus, values close to unity are taken as an indication that an element has a mainly crustal origin, and those > 10 are considered to indicate that a substantial portion of the element has a mainly non crustal origin. Rahn (1976), and Rahn et al., (1979), tabulated the EF_{crust} values for various elements in over a hundred samples taken from the World Aerosol, and an indication of the geometric means for these trace elements is presented in Figure 6.5. From the figure it can be seen that Cd, Pb, Zn, Cu, Ni and Cr have EF_{crust} values in the range 10 to ~5 x 10^3. These are referred to as the AEE. The elements Al, Fe, Mn and Co have EF_{crust} values in the World Aerosol of between 1 and 10, and these are termed the NEE, and are present in an aerosol in roughly crustal proportions.

The NEE will almost always be enriched relative to crustal materioal in all aerosols. However, it is important to stress that the degree to which an AEE is actually enriched can vary considerably. Variations can be caused by the mixing of aerosols from different sources which contain crustal and anthropogenic-associated trace elements in differing proportions. This can be illustrated by referring to the data in Table 1.9, which lists the EF_{crust} values of a series of trace elements from a variety of marine locations. These data show that the EF_{crust} values of the AEE Cu, Zn and Pb can vary between < 10 and > 100; thus showing that under certain conditions; following the injection of crustal dust into the atmosphere, the EF_{crust} values of some of the AEE can be found in crustal proportions.

The arithmetic mean, range, standard deviation and geometric mean EF_{crust} data are given for the whole NSA sample population and the three end-member aerosols in

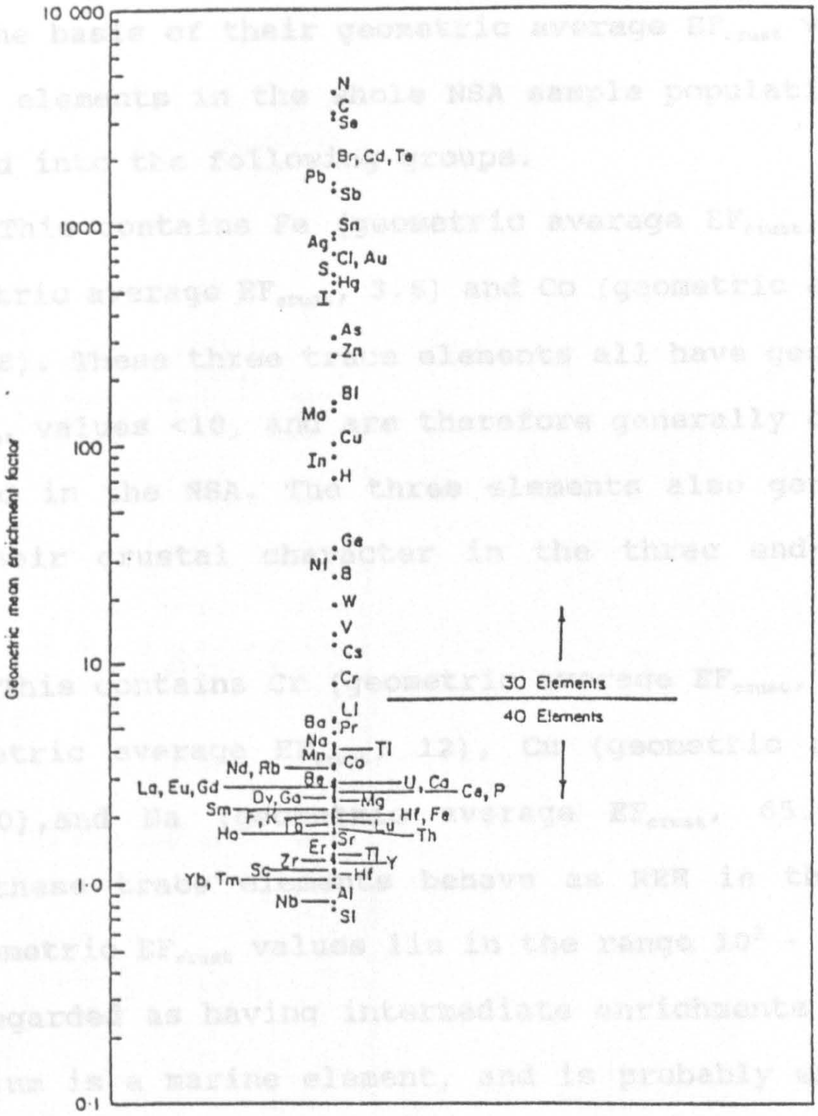

Figure 6.5 Geometric mean EF_{crust} values for elements in the world aerosol (from Rahn et al., 1979).

Tables 6.11a and b, respectively. The data values are discussed below in terms of the geometric average EF_{crust} values.

The whole sample population (Table 6.11a).

On the basis of their geometric average EF_{crust} values, the trace elements in the whole NSA sample population can be divided into the following groups.

Group 1. This contains Fe (geometric average EF_{crust}, 1.5), Mn (geometric average EF_{crust}, 3.6) and Co (geometric average EF_{crust}, 2.8). These three trace elements all have geometric mean EF_{crust} values <10, and are therefore generally crustal controlled in the NSA. The three elements also generally retain their crustal character in the three end-member aerosols.

Group 2. This contains Cr (geometric average EF_{crust}, 11.5), Ni (geometric average EF_{crust}, 12), Cu (geometric average EF_{crust}, 30),and Na (geometric average EF_{crust}, 65.5). On average these trace elements behave as NEE in the NSA. Their geometric EF_{crust} values lie in the range 10^1 - 10^2 and may be regarded as having intermediate enrichments in the NSA. Sodium is a marine element, and is probably enriched in the NSA from sea surface generation of sea salts. In contrast Ni, Cr and Cu are likely to be enriched in the NSA as a result of their generation from anthropogenic sources. These three trace elements retain their intermediate enriched character in the UK and the EU end-member aerosols. In the OS end-member, however, Ni, Cr and Cu have geometric EF_{crust} values which indicate that they are crust-

Table 6.11a Data on the atmospheric trace element EF_{crust} values from the NSA.

Element	Arithmetic mean EF_{crust}	Range	σ	Geometric mean EF_{crust}
Al	1	- - -	-	-
Fe	2.0	0.60 - 10.5	1.8	1.5
Mn	5.3	0.56 - 55.5	6.9	3.6
Cd	730	22.8 - 6058.5	910.2	436.5
Co	3.9	0.28 - 34	4.1	2.8
Cr	16	0.85 - 80.5	14.5	11.5
Cu	40	8.9 - 299.5	40.3	30
Ni	20	0.44 - 151	21.8	12
Pb	866	42 - 3290	716.2	605
Zn	192	7.8 - 657.5	148.4	141.5
Na	196	3.8 - 2626.9	401.9	65.5

σ = standard deviation.

Table 6.11b The arithmetic mean, range, standard deviation and geometric mean EF_{crust} values of atmospheric particulates taken from the three North Sea end-members (present study).

Element	UK (n=36)			Europe (n=13)			Open Sea (n=6)		
	Arithmetic mean / σ	Range	Geo. mean	Arithmetic mean / σ	Range	Geo. mean	Arithmetic mean / σ	Range	Geo. mean
Fe	1.5 ± 1.1	0.5 - 6.2	1.3	2.3 ± 1.3	0.6 - 5.5	2	2.7 ± 0.3	1.1 - 6.2	1.9
Mn	4.2 ± 4.6	0.7 - 22	3.1	5.4 ± 3.1	2 - 12.9	4.7	6.1 ± 4.7	1.9 - 14	4.3
Ni	17.2 ± 12.7	1.3 - 55	13	14.5 ± 13.5	3.9 - 52	11	21.5 ± 40	2.1 - 99	6.2
Co	3.2 ± 1.9	0.3 - 11	2.7	3.4 ± 2.5	0.03 - 8.7	2	4.7 ± 4	0.9 - 12	2.9
Cd	599 ± 474	23 - 2117	398	683 ± 663	129 - 2587	487.5	475 ± 471	26 - 1112	274
Cr	13 ± 13	3.2 - 65	9.6	19.5 ± 11.5	6.5 - 47	16.5	12 ± 8	2.5 - 27	7.7
Cu	31 ± 37	11 - 228	24	41 ± 21	13.5 - 82.5	36	39.5 ± 21	15 - 68	28
Zn	137 ± 104.5	7.8 - 417	103.5	237.5 ± 65.5	74.5 - 550	197	151 ± 109.5	50 - 333.5	132
Pb	705 ± 535	42 - 2145.5	517	1091 ± 697	245 - 2308	871.5	500 ± 254	114 - 836	426.5
Na	144 ± 309.5	8.2 - 1756	56.5	64.5 ± 61.5	3.8 - 216	65.5	502 ± 375	21 - 1015	300

σ = standard deviation.

dominated although it must be pointed out that the EF_{crust} values have large standard deviations in all three end-member aerosols so that it is difficult to assign them with a source with certainty.

Group 3. This contains Zn (geometric average EF_{crust}, 141.5), Cd (geometric average EF_{crust}, 436.5) and Pb (geometric average EF_{crust}, 605). Their geometric EF_{crust} values lie in the range 10^2 - 10^3 and may be regarded as being enriched in the NSA. The 'excess' Zn, Cd and Pb in the NSA probably has a anthropogenic source. The three trace elements are all enriched in the end-member aerosols. However the geometric average EF_{crust} values for Zn, Cd and Pb decrease in the order EU > UK > OS, indicating that the EU aerosol is more strongly enriched in these trace elements than the other two end-member aerosols.

With the exception of Na, the trace elements in the NSA which are present in excess of their crustal sources have probably been derived from anthropogenic sources in the NSA. However, before this can be established it is necessary to consider the sea surface as a source for trace elements in marine aerosols such as the NSA, and this is considered below.

6.4.2 EF_{sea} values.

In order to gain a first assessment of the importance of the sea surface as a secondary, or recycled source, of trace elements to the NSA, a simple EF_{sea} calculation has been applied to the current data set. For this purpose, Na was used as the marine indicator element, and the precursor source composition was assumed to be that of bulk sea water. Table 6.12 lists the arithmetic mean salinity and the trace element concentrations (in n mol l^{-1}) of Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn for North Sea water collected on the following surveys; CH33, CH43, CH51 and CH61. From the data in Table 6.12 the average salinity and trace element concentrations for the four survey cruises were calculated, and these values were then substituted into equation 5.4, and the corresponding EF_{sea} values for the NSA are presented in Table 5.7.

A selection of EF_{sea} values for aerosols from a number of marine regions is given in Table 1.4. In this table the regions have been ranked on the basis of their distance from the major continental trace element sources, and as a result represent increasingly more pristine marine environments with respect to particulate trace elements in the atmosphere. The trace elements EF_{sea} values given in Table 1.4 can be divided into three general groups, and these are summarised as follows.

Group 1; containing K and Mg. For these elements there does not appear to be any difference in the EF_{sea} values (approximately unity) between the marine regions, and this indicates that the sea is a predominant source of these trace elements to the marine aerosol from all regions.

Group 2; containing Mo. This trace element has EF_{sea} values ranging from ~1 in the South Atlantic Westerlies (remote aerosol) to >100 in the UK coastal aerosol. This indicates

Table 6.12 The sea water concentrations ($\mu g\ l^{-1}$) and associated salinitys (ppt) for a number of trace elements in the North Sea.

Survey	CH33	CH43	CH51	CH61
Salinity				
Mean	33.700	34.044	34.093	34.147
Range	30.810 - 34.934	29.165 - 35.048	31.211 - 35.142	31.884 - 35.084
σ	1.130	1.135	0.913	0.744
Cadmium				
Mean	0.18	0.21	0.33	0.19
Range	0.06 - 0.33	0.09 - 0.56	0.12 - 0.72	0.11 - 0.57
σ	0.05	0.08	0.14	0.07
Cobalt				
Mean	0.42	0.29	0.44	0.38
Range	0.05 - 1.12	0.04 - 1.17	0.17 - 2.76	0.07 - 1.53
σ	0.21	0.20	0.28	0.23
Copper				
Mean	4.91	5.62	5.26	6.65
Range	1.64 - 9.76	1.00 - 27.2	1.5 - 16.5	2.18 - 156
σ	2.05	3.7	2.43	14
Iron				
Mean	-	12.7	7.65	6.66
Range	-	0.95 - 246	1.74 - 36.4	1.42 - 29.9
σ	-	35.2	6.2	5.74

Manganese				
Mean	23.5	9.9	16.4	17.2
Range	3.11 - 98	1.33 - 344	0.86 - 92.2	1.04 - 127
σ	17.7	33	14.8	22.8
Nickel				
Mean	5.76	8.03	5.73	5.86
Range	2.52 - 12.2	2.52 - 27.2	1.07 - 25.3	3.29 - 12.3
σ	2.2	5.09	2.93	2.06
Lead				
Mean	0.2	0.15	0.19	0.13
Range	0.05 - 1.64	0.03 - 1.29	0.07 - 0.5	0.03 - 0.47
σ	0.18	0.17	0.09	0.07
Zinc				
Mean	10.7	11.3	17.8	6.52
Range	1.82 - 35	1.8 - 39.6	2.87 - 124	1.29 - 27.6
σ	6.8	8.8	14.4	3.9

- = no data.
σ = standard deviation.
Data from Statham (1991), personal communication.

that in remote areas bulk sea water can act as a significant source of this trace element to the marine aerosol.

Group 3; containing Al, Fe, Mn, Co, V, Cu, Pb and Zn. For these trace elements there is a significant decrease of the EF_{sea} values in the order, coastal aerosol to pristine marine aerosol. However, even at remote sites the trace elements are significantly enriched by factors ranging up to $6x10^5$, relative to bulk sea water.

The EF_{sea} values presented in Table 5.7, are summarised in Table 6.13 which contains the EF_{sea} arithmetic means, range, standard deviation and geometric means of the EF_{sea} values in the NSA for those trace elements for which sea water data are available.

From the data in Table 6.13 it can be seen that the EF_{sea} geometric means for the trace elements are Fe $3.8x10^6$, Pb $4.9x10^6$, Zn $2.9x10^5$, Cd $7.7x10^4$, Co $6.7x10^4$, Cu $10.3x10^4$, Mn 8.1 $x10^4$ and Ni $4.9x10^4$. Since an EF_{sea} value of ~1 indicates that the sea surface is the predominant source of a trace element. It may be concluded that none of the trace elements listed above have a significant oceanic source in the NSA.

It was pointed out in Section 1.5.2.1.2, that the calculation of EF_{sea} values present a number of problems. The major problem involves the selection of an accurate composition for the oceanic precursor material, and this is further complicated by the difficulties which arise from attempting to take account of the processes involved in the

Table 6.13 EF$_{sea}$ values for a number of elements in the NSA.

Element	N	Arthimetic mean x 10^3	Range x 10^3	σ	Geometric mean x 10^3
Fe	94	11317	62 - 192057	26408	3835
Mn	95	210	1.4 - 2298	386.5	81
Cd	95	237	1.2 - 3154	467	77
Co	95	131	0.5 - 595	130	67
Cu	95	223	1.7 - 2679	351	103
Ni	95	131	0.3 - 893	175	49
Pb	95	14382	32 - 197506	26312	4872
Zn	95	793	1 - 11944	1555	287

σ = standard deviation.

generation of sea salts. The fractionation of sea salts has been described in Section 1.5.2.1.2, where it was shown that it is the sea surface microlayer and, not bulk sea water, that is the immediate source of trace elements to the marine aerosol. A number of attempts have been made to identify a more realistic source composition for material generated from the sea surface by relating the material directly to the microlayer itself. One of these is the use of BIMS (see Section 1.5.2.1.2) data, in which the net concentrations of the trace elements on artificially bubble generated sea salts are combined with the concentrations of the trace elements in the parent sea water, and these concentrations are used to calculate a BIMS EF_{sea} value (see also Fasching et al., 1974; Piotrowicz et al., 1979). The geometric mean BIMS EF_{sea} values for some trace elements have been presented in Table 1.5, and from this data the trace elements can be divided into two broad groups.

Group 1; containing K and Mg. These trace elements have average BIMS EF_{sea} values of unity and together with Na, retain their original bulk sea water ratios on the bubble generated salts.

Group 2; containing Al, Fe, Mn, Co, V, Cu, Zn, Pb and Sc. These trace elements have relatively high BIMS EF_{sea} values, ranging from 10^1 for Sc to $2x10^4$ for Zn, and apparently undergo fractionation at the sea surface. Despite difficulties in producing accurate BIMS EF_{sea} values, these data do provide at least a first order of approximation of the degree of fractionation that has taken place at the sea surface.

In addition to using BIMS EF_{sea} data, Wiesel et al., (1984) proposed an important concept, that of a relative oceanic enrichment factor REF_{sea} (see Section 1.5.2.1.2). This is the EF_{sea} value divided by the BIMS EF_{sea} value, and therefore directly relates the enrichment of a trace element in the marine aerosol to the fractionation that occurs at the sea surface. The REF_{sea} value should therefore offer a more realistic assessment of the ocean as a source of trace elements to the marine aerosol. Hence, the REF_{sea} values will approach unity if the sea surface is a significant source of a trace element to the marine aerosol, and this has been evaluated with respect to a number of marine aerosol populations in Table 1.6. Average REF_{sea} values for the present data set have been calculated using the BIMS EF_{sea} values taken from Table 1.5, and these data are presented in Table 6.14. By comparing the data given in Table 1.6 and the REF_{sea} values from the present work (Table 6.14), the following general conclusions concerning the sea as a source of trace elements to the NSA can be summarised as follows.

(1). The mean REF_{sea} values of trace elements from the present work are; Fe 3.8×10^3, Pb 1.2×10^3, Co 1.1×10^2, Cu 1.3×10^2, Mn 8.1×10^2 and Zn 1.5×10^1.

(2) From comparing the REF_{sea} values of Cu and Co, for the present work with those from Table 1.6, it is apparent that

Table 6.14 Sea surface sources of trace elements in the NSA.

Trace Element	BIMS EF_{sea} as a % of aerosol EF_{sea}	REF_{sea}
Co	0.89	1.1×10^2
Cu	0.78	1.3×10^2
Fe	0.26	3.8×10^3
Mn	1.2	8.1×10^2
Pb	0.08	1.2×10^3
Zn	6.9	1.5×10^1

they are very similar to those reported for the North Atlantic.

(3) The mean Pb REF_{sea} value for the present work is ~7.5 times higher than the REF_{sea} value given for the North Atlantic.

On the basis of the REF_{sea} values for the samples in the present work it may be concluded that sea water is not a significant source for Co, Cu, Fe, Mn, Zn or Pb to the NSA. On the basis of their geometric average EF_{crust} values it was shown in Section 6.4.1 that Cr, Ni, Cu, Zn, Pb and Na were enriched in the NSA relative to crustal sources. Na is a major constituent of sea salt and has a significant oceanic source. However, it is apparent from the data presented in the present section that the sea surface is not a significant source for Co, Cu, Pb and Zn, and probably Cd and Ni (see Table 6.13) in the NSA. It may be concluded, therefore, that for these trace elements the anthropogenic source dominates their input to the North Sea atmosphere, and is responsible for, relatively high EF_{crust}, EF_{sea} and REF_{sea} values in the NSA.

The importance of the three major sources, i.e. crustal, oceanic and anthropogenic, of trace elements to the NSA is considered further in the following section in terms of size-fractionation of the elements.

6.5 Particle Sizes of Trace Elements in the NSA.

The particle size of trace elements in aerosols can provide information on their sources. Particle size data is usually expressed in terms of the particle mass median diameter (MMD). The MMD is the particle size for which 50% of the mass occurs on the larger particles and 50% on the smaller particles (Salomons and Forstner, 1984). According to the data summarised by Chester (1991) the following general trace element/particle size relationships are found in the marine aerosol.

(1) Sea salt associated trace elements have most of their mass on particles with MMDs in the range ~3 μm to > 7μm.

(2) Crust controlled trace elements have most of their total mass on particles with MMDs in the range ~1 μm to ~3μm.

(3) Trace elements associated with high temperature processes, mostly anthropogenic but including volcanic emissions, have most of their mass on particles with MMDs <~0.5μm.

In an attempt to establish the size distribution patterns of trace elements in the NSA two cascade impactor (CI) samples were taken on two cruises. However, a number of problems were experienced with the CI collection and these were as follows.

(a) It was not possible to accurately monitor the volume of air passing through the collectors. For this reason, attention in this section will concentrate on the <u>relative</u> size distributions of the trace elements and no attempt will be made to compare the CI loadings to those obtained using the hi-vol filtration system for total aerosol samples taken during the CI runs.

(b) Contamination was suspected for the CI back up filter, and data for this will not be presented here.

(c) Cu contamination was suspected for all the CI filter stages, and data for this trace element will not be presented here.

Because of the various problems encountered with the CI collections, the data will only be treated in a general way, and the following discussion will be confined to making an overall assessment of the trace element particle size relationship in the two CI samples.

6.5.1 General Trace Element Particle Size Relations in the Two CI Samples of the NSA.

The CI samples were taken on Cruises 39 (CH39) and 53 (CH53). The aerosols sampled on these two cruises represent two contrasting types of the NSA. These are.

(1) The CI samples taken on CH39 were collected over a period of ~12 days. Hi-vol samples were also collected over this period and their end-member classifications are as follows; Sample 28 (OS), Sample 29 (EU) and samples 30-35 (mixtures of OS, UK and EU). These samples were therefore collected from air masses which had passed over the UK and European continental regions in addition to the open sea.

(2) The CI samples taken on CH53 were collected over a period of ~12 days, and the corresponding hi-vol samples were as follows; Samples 66, 67 and 69 (OS), Samples 67, 70, 71 and 72 which were taken from air masses which had spent considerable times over the open North Sea. These

samples were therefore collected from air masses which had been mainly confined to the open sea.

A summary of the trace element size distribution data for the CI samples is given in Table 5.3a (CH39) and Table 5.3b (CH53), and the findings are discussed below in terms of the individual trace elements. Bayens and Dedeurwarder (1991) reported data on the size fractionation of a series of trace elements in the NSA sampled at West Hinder using a similar CI technique to that employed in the present work, and because an accurate estimation of the volume of air through each CI from the current work was not possible, for the purpose of the current work the particle size cut off diameters reported by these authors are used. These are as follows: $D_{p\ 50}$ (μm); Stage 1 (>9.3), Stage 2 (3.9 - 9.3), Stage 3 (1.97 - 3.9), Stage 4 (1.28 - 1.97), Stage 5 (0.67 - 1.28) and Stage 6 (<0.67). Further, their findings are referred to below were appropriate.

Al. For CH39 ~57% of the total Al (ΣAL) is found on particles in the 3.9 - > 9.3 μm size range, and ~21% on particles in the 1.28 - 3.9 μm size range. For this sample, therefore, the Al is fractionated on particles with larger MMDs than those usually associated with crustal material; i.e. in the ~1.28 - ~3 μm range; however, this may reflect the fact that the samples were taken relatively close to the surrounding land masses so that large sized particles could reach this marine region. In this context, Bayens and Dedeurwarder (1991) also found Al in the large sized, i.e. 3.9 - > 9.3 μm, material in CI samples from West Hinder, but the ΣAl associated with this size fraction was smaller by ~16%, than that found in the present work.

For CH53 ~33% of the ΣAL is associated with particles in the 3.9 - > 9.3 μm size range, and ~35% on particles in the 1.28 - 3.9 μm size range. During the collection of the CH53 samples the air masses had crossed the open sea and had a much smaller 'land influence' than the air masses associated with CH39. It is probable, therefore, that the greater fractionation of Al into the 1.28 - 3.9 μm size range of CH53 CI, compared to CH39 CI, arises because the material collected on the CH53 CI had not come directly from land areas. In addition to the size fraction of Al among the larger particle sizes there is also another difference between the two CI samples, and this is the relatively large fraction (~22%) of the ΣAl which is associated with the < 0.67 μm sized materials in CH53 CI; however, the reason for this is not known, because even in remote marine aerosols only a few percent of the ΣAl is usually found on the smallest sized particles (see e.g. Duce et al., 1983).

Fe In CH39, the size fractionation of Fe generally follows that of Al, with ~56% of the ΣFe being associated with particles in the 3.9 - > 9.3 μm size range, again suggesting that large sized land-derived material is found in the NSA. In CH53, however, size fractionation of Fe differs from that of Al in that ~50% of the ΣFe is found in the 1.28 - 2 μm size range. In both CI samples, the Fe EF_{crust} values of all the size fractions are ~1 or even considerably <1, indicating a crustal origin for Fe in the NSA.

Mn. For CH39, ~31% of the ΣMn is found on particles in the 3.9 - > 9.3 μm size range, indicating that it is associated with relatively large sized crustal components which contain Al. Most of the remainder of the Mn (~58% of the ΣMn) is found on small sized particles in the < 0.67 - 1.28 μm size range. This would suggest that a substantial fraction of the Mn in CH39 has an anthropogenic origin, and this is confirmed by the EF_{crust} value of 14.5 for the < 0.67 μm size class, compared to 1.9 in the > 9.3 μm sized material. In CH53, ~34% of the ΣMn is found on particles in the size range < 0.67 - 1.28; this is only about half of that associated with the same sized particles in the CH39, and the Mn EF_{crust} value for the < 0.67 μm size fraction in CH53 is only 0.6 compared to 14.5 in the same size fraction in CH39. It may be concluded, therefore, that aerosols transported to the North Sea in association with air masses that have passed the UK and Europe, e.g. CH39, can contain Mn which has an anthropogenic origin.

Cr. For CH39, the highest concentrations of Cr, i.e. ~49% of ΣCr is found on particles in the < 0.67 - 1.28 μm size range, indicating an anthropogenic source; this is confirmed by the Cr EF_{crust} values, which are between 17 and 21.5 for particles in this size range compared to values of <10 in the larger sized particles. In CH53, in contrast, only ~8% of the ΣCr is associated with particles in the < 0.67 - 1.3 μm size range, and for these the Cr EF_{crust} values lie between 2.9 and 5.3. The highest concentration of Cr in CH53, i.e. ~62% of the ΣCr is found on particles in the size range 1.28 - 3.9 μm. This would suggest that the Cr in the CH53 is largely crustal in origin. However, the Cr EF_{crust} value for this material is 47, and it may be that it is contaminated with respect to Cr.

Ni. For CH39 ~53% of the ΣNi is found on particles in the < 0.67 - 1.28 μm size range, indicating an anthropogenic source; this is confirmed by the Ni EF_{crust} values, which are between 36.5 and 121.5 for particles in this size range compared to values lying between 11 and 30 for the larger sized particles. In contrast, the highest concentrations of Ni in CH53 are found on particles in the 1.28 - 2 μm size range, which account for ~56% of the ΣNi in the sample. The Ni in this size class has an EF_{crust} value of 14.5; this is considerably smaller than the EF_{crust} values associated with the anthropogenic Ni in CH39 (36.5 - 123.5) but is still the highest value for any of the size fractions in CH53, suggesting that this sized material contains Ni from both crustal and anthropogenic sources. Overall, however, the particle size spectrum of Ni in the two CI samples, suggests that anthropogenic sources, i.e. those associated with small-sized particles, are far more important in CH39 than in CH53, CI's.

Zn. In CH39 ~77% of the ΣZn is associated with particles in the size range <0.67 - 1.28μm, indicating an anthropogenic source for most of the Zn in this sample; this is confirmed by the relatively very high Zn EF_{crust} values (1970 - 2408) in the small sized material. It must also be pointed out that even in the particles characteristic of crustal sources Zn is still considerably enriched; e.g. the Zn EF_{crust} value in the 1.28 - 9.3 μm sized particles ranges between 96 and 228. Clearly, therefore, anthropogenic sources affect the distribution of Zn over all particle sizes in the CH39 CI. Bayens and Dedeurwarder (1991) reported that ~71% of the ΣZn in the NSA at West Hinder was associated with particles in the size range < 0.67 - 1.28 μm. In CH53, Zn is also concentrated in the small-sized material, with ~74% of the ΣZn being associated with particles < 0.67 μm in size. However, the Zn EF_{crust} value for this small sized material is only 267, compared to 2408 in the same size class for CH39.

Pb. In CH39 ~80% of the ΣPb is associated with particles in the size range < 0.67 - 1.28μm, indicating an anthropogenic source; this is confirmed by the Pb EF_{crust} values (3125 - 6610). It is also apparent from the Pb EF_{crust} values that, as for Zn, particles in all size ranges in the CI have been influenced by Pb from anthropogenic sources. Bayens and Dedeurwarder (1991) reported that ~60% of the ΣPb in the NSA at West Hinder was associated with particles in the size range < 0.67 - 1.28 μm. In comparison with CH39, a smaller percentage (41%) of the ΣPb in the CH53 is found on particles in the < 0.67 - 1.28 μm size range, and the Pb EF_{crust} values (44 - 67.5) are lower than in the same fraction in CH39.

Cd. In CH39 ~83% of the ΣCd is associated with particles in the size range < 0.67 - 1.28 μm, indicating an anthropogenic source; this is confirmed by the Cd EF_{crust} values (774 - 11243) in the small sized material. It is also apparent from the Cd EF_{crust} values that, as for Zn and Pb, particles in all size ranges in the CI have been influenced by Cd from anthropogenic sources. Bayens and Dedeurwarder (1991) reported that ~60% of the ΣCd in the NSA at West Hinder was associated with particles in the size range < 0.67 - 1.28 μm. In CH53 CI, compared to CH39, a smaller percentage (32%) of the ΣCd is found on the particles in the size range < 0.67 - 1.28 μm, and the Cd EF_{crust} values (135 - 139) are lower than those in the same size fraction in CH39.

In general, the three trace elements Zn, Pb and Cd have similar particle size distributions in both the CI samples, and it may be concluded that although the Zn, Pb and Cd in both samples is predominantly anthropogenic in origin, CH39 has suffered a greater degree of pollution than CH53.

Na. The overall size distribution pattern of Na in both CI samples is similar, with most of ΣNa (~71% in CH39, and ~83% in CH53) being associated with particles in the size range 3.9 - > 9.3 μm. This is entirely consistent with an oceanic, i.e. sea salt, origin for Na in the NSA, and this is confirmed by the relatively high Na EF_{crust} factors, which range between ~60 and ~100 in the larger sized material from the two CI samples. Bayens and Dedeurwarder (1991) reported that ~61% of the ΣNa in the NSA at West Hinder was associated with particles in the size range 3.9 - 9.3 μm.

It is apparent from the discussion above that the data obtained from the two CI samples of the NSA differs from that for other marine aerosols in some respects. Overall, however, the NSA CI data confirms the general particle size trends found for trace elements in marine aerosols, and the important conclusions drawn for the data may be summarised as follows.

(1) There are a number of differences between the trace element/particle size relationships in the two contrasting CI samples. The most significant being that for CI CH39, for which the air masses sampled had a strong continental influence, shows a higher degree of anthropogenic influence than for CI CH53, for which the air masses sampled had a high degree of open sea influence.

(2) In CI CH39, and to a lesser extent in CI CH53, crustal material is associated with larger particle sizes than normally found in marine aerosols, and this probably reflects the fact that the North Sea is relatively close to continental sources of crustal material.

(3) In both CI samples Na is strongly associated with materials having a particle size characteristic of sea salts.

(4) Of the trace elements that behave as AEE in the NSA (i.e. Cr, Ni, Pb, Zn and Cd), Zn, Pb and Cd have their highest concentrations, and their highest EF_{crust} values, in the small sized (<0.61 - 1.28 μm) material in both CI

samples, indicating an anthropogenic origin from high-temperature generation processes. However, the degree of pollution is higher in CI CH39 than in CI CH53, which is consistent with origins of the air masses from which they were sampled. Both Cr and Ni also show a strong anthropogenic character, with respect to their particle size distribution, in CI CH39, i.e. both their concentrations and EF_{crust} values are highest on the smaller sized particles. However, in CI CH53 both trace elements are more crustal in character, and generally have EF_{crust} values which are <10 in most size fractions.

(5) In both CI CH39 and CH53, there is evidence from the EF_{crust} values that although anthropogenic sources affect Zn, Pb and Cd most strongly in the small sized material, an anthropogenic effect is found in all size fractions. For example, the EF_{crust} values for Pb range between 121 and 6610 in the size fractions of CI CH39, and between 16 and 80 in CI CH53.

(6) The particle size data confirms the conclusions drawn from the EF_{crust} and EF_{sea} data, that the enrichments of Cr, Ni, Zn, Pb and Cd in the NSA are the results of inputs from anthropogenic sources.

6.6 The Application of Rainfall Patterns Associated with Air mass Back Trajectories to the North Sea End-Member Aerosols.

Wet deposition is an important process for the removal of particulate trace elements from the atmosphere. This process is particularly important in the mid-latitude regions (Chester 1991). In an crude attempt to gain a estimate of the degree of rainfall the NSA had undergone prior to collection, modeled rainfall data in the form of a Fine Mesh Rainfall Model (FMRM) was provided by the UK Meterological Office (MO). For the purposes of the current work these data were kindly supplied by R. Procter and R. Lowry (personal communication) NERC, Bidston.

A brief description of the FMRM, and a discussion of some of its more important limitations are given in the following section.

6.6.1 Description of the FMRM.

6.6.1.1 The Model Observations.

The FMRM covers an area extending over ~44.3°W - 64.5°N and ~20.6°W - 25.4°N, and within this modelled rainfall patterns for selected NSA hi-vol samples, are presented in Appendix B. For the purpose of the model observations 6 hour convective rainfall accumulations were used.

6.6.1.2 The FMRM Forecasts.

The FMRM forecasts consist of 6-hourly accumulations of convective rainfall over the modelled area for the forecast periods ending T+6, T+12, T+18, T+24, T+30 and T+36 (where; T=time in hours, and the integers are real numbers). These amounts were stored twice a day at 0000Z and 1200Z respectively, along with the sum total of rainfall for each grid point.

6.6.1.3 Verification of the FMRM.

In order to verify the forecasts of the FMRM, observations were selected in such a way that there is one observed value to verify against a single model grid point. A station closest to each model grid point was selected by the MO as long as it reported rainfall on a regular basis. There were 53 stations from the UK, out of a total of 780 stations over the modelled area (station list not available). The MO applied some quality control to the observations, in so much as individual observations were rejected if they predicted > 99mm of rainfall, or if they were inconsistent in any way with the past weather report (for further information, contact R.A Bromley, UK MO).

The forecast precipitation at each grid point, and the observed precipitation at each corresponding station (or grid box averaged observation), were assigned to one of the rainfall categories given in Table 6.15. The rainfall category limits presented in Table 6.15 represent the approximate upper and lower limits expected from 6 hours of Light, Moderate and Heavy rainfall. Trace precipitation, i.e. defined as less than 0.05mm, was treated as zero rain. A lower limit of 0.1mm predicted rainfall as selected by the MO because the model was unable to accurately predict values of precipitation below this value. The rainfall data supplied by the MO was on the basis of the rainfall categories given in Table 6.15. These predicted rainfall data were compared with true rainfall, and by comparing the real with predicted rainfall, the MO were able to get an

Table 6.15 A Frequency table showing the rainfall verification scheme catorgories for the MO FMRM.

Category	Precipitation ammount, P(mm)
O	0.0 < P < 0.1
L	0.1 < P < 2.0
M	2.0 < P < 10.0
H	10.0 < P

O = no rainfall; L = light rainfall; M = moderate rainfall
H = heavy rainfall.
(Data supplied by UK MO).

idea of the %age accuracy of the model. The %age accuracy is reflected in Figures 6.7 (a-e). These figures represent the % occurrence for which there reasonable agreement between the FMRM predicted rainfall and observed rainfall over the time period indicated. From Figures 6.7 (a-e), it is apparent that the accuracy of the Model predictions falls into two distinct categories.

(1) Model predictions which are ~60 - 90% correct. This category includes the sampling period October - December 1988, and July - December 1989.

(2) Model predictions which are ~30 - 80% correct. This category includes the sampling period January - June 1989.

It is evident therefore that there is a large error in the model predictions for the sampling period January - June, 1989.

Before investigating the effects of modelled rainfall on NSA trace element concentrations it is important to consider the limitations of the model, and these are discussed in the subsequent section.

6.6.1.4 Limitations of the FMRM.

When investigating the effects of modelled rainfall on the atmospheric concentrations of particulate material, it is useful to look at the occurrence and quantity of rainfall at a particular site. However, precipitation processes are some of the most complicated in the whole of meterological modelling, and should be therefore be treated with extreme caution. From the data made available by the

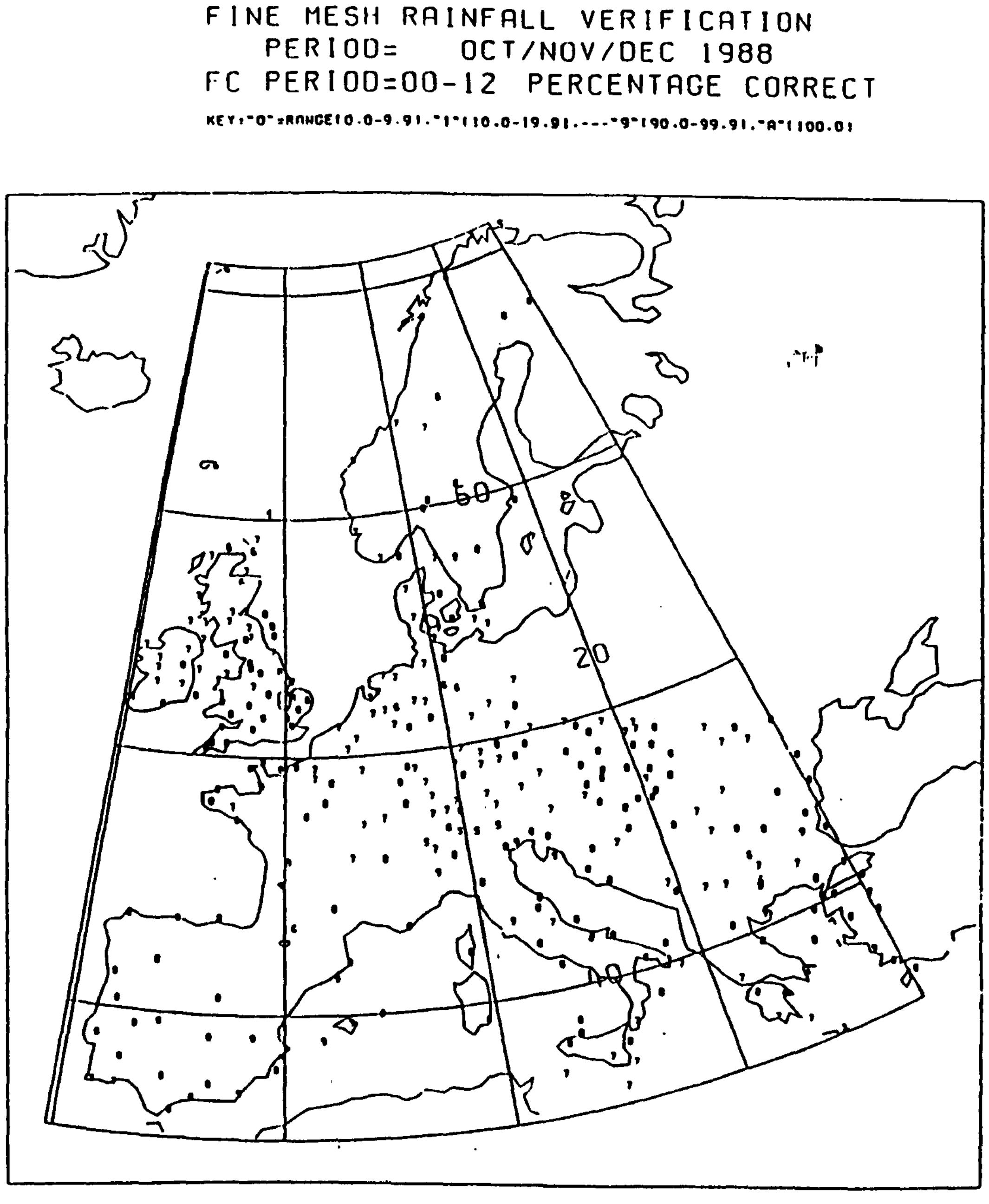
FINE MESH RAINFALL VERIFICATION
PERIOD= OCT/NOV/DEC 1988
FC PERIOD=00-12 PERCENTAGE CORRECT
KEY:"0"=RANGE(0.0-9.9),"1"(10.0-19.9),---"9"(90.0-99.9),"A"(100.0)
60
20
40

Figure 6.7a

FINE MESH RAINFALL VERIFICATION
PERIOD= JAN/FEB/MAR 1989
FC PERIOD=00-12 PERCENTAGE CORRECT

KEY:"0"=RANGE(0.0-9.9),"1"(10.0-19.9),---"9"(90.0-99.9),"A"(100.0)

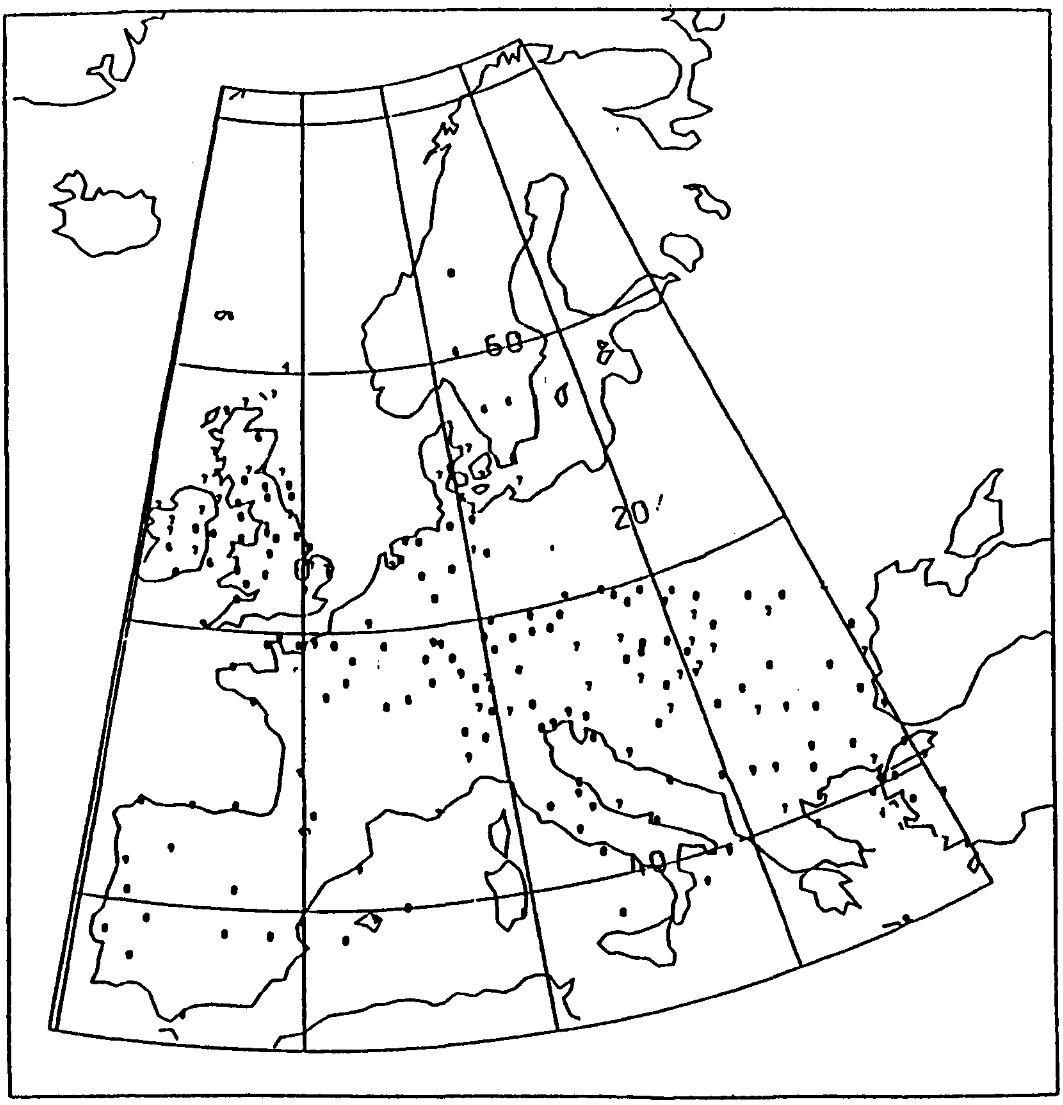

Figure 6.7b

FINE MESH RAINFALL VERIFICATION
PERIOD= APR/MAY/JUN 1989
FC PERIOD=00-12 PERCENTAGE CORRECT

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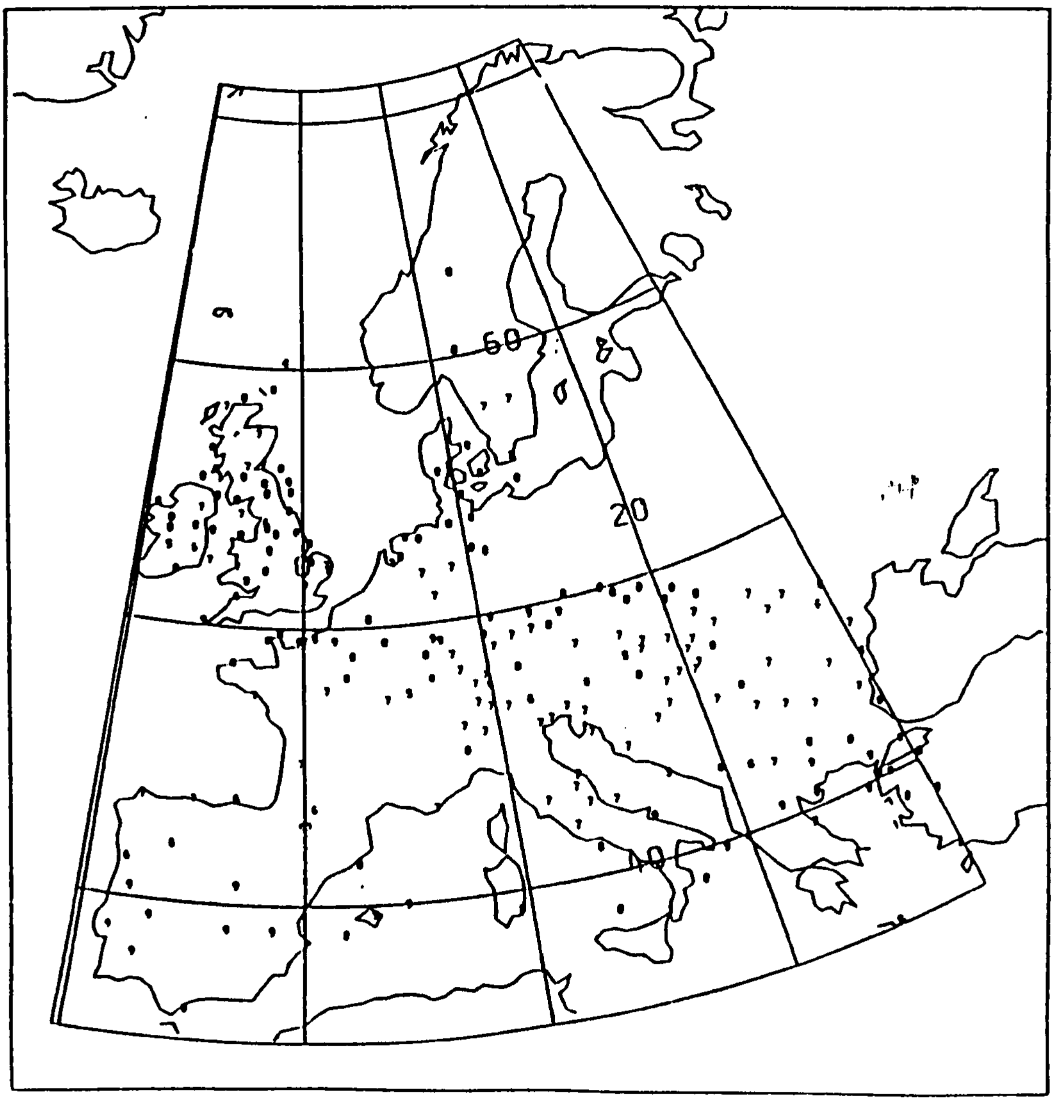

Figure 6.7c

FINE MESH RAINFALL VERIFICATION
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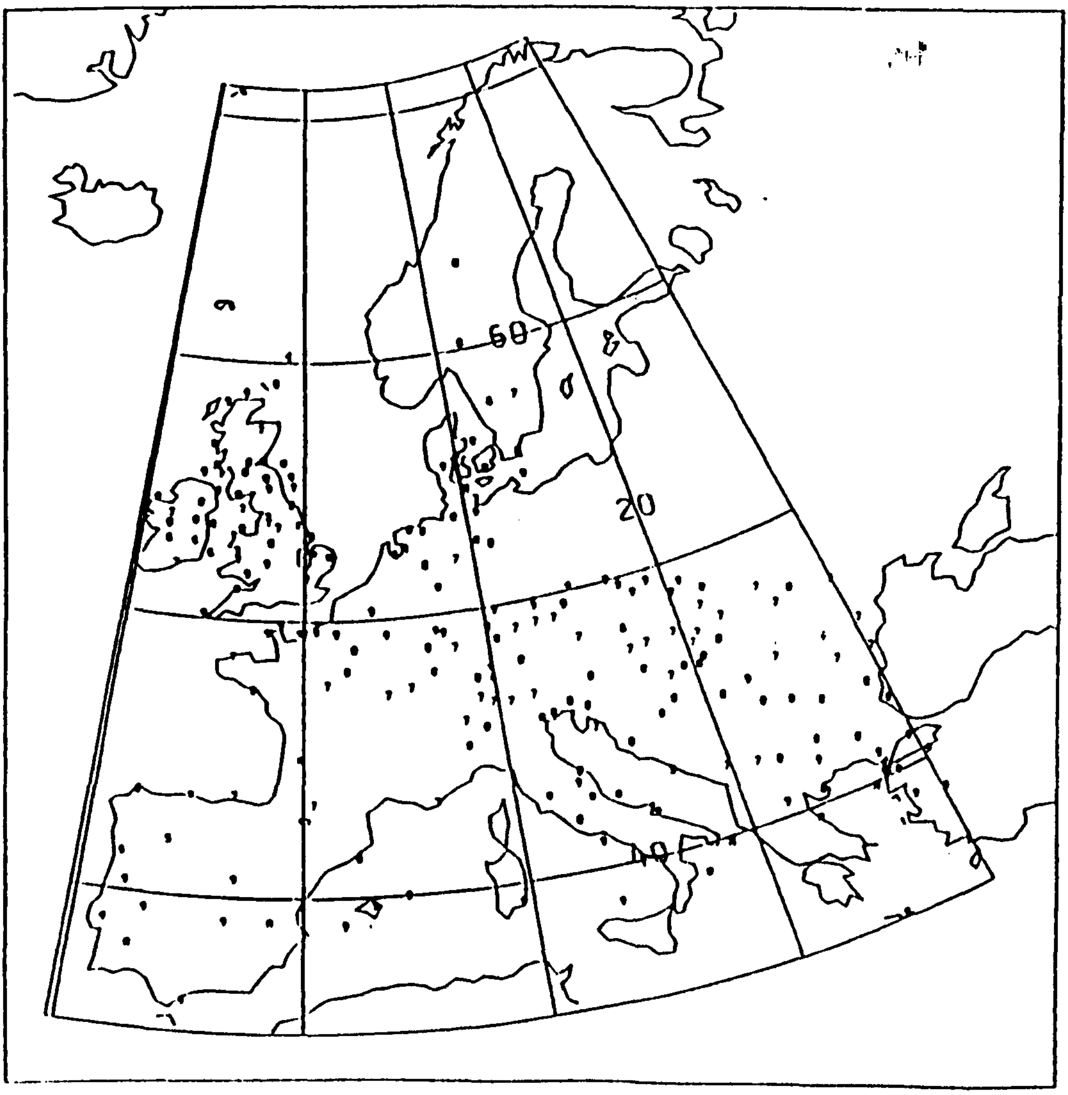


Figure 6.7d

FINE MESH RAINFALL VERIFICATION
PERIOD= OCT/NOV/DEC 1989
FC PERIOD=00-12 PERCENTAGE CORRECT

KEY:"0"=RANGE(0.0-9.9)."1"(10.0-19.9).---"9"(90.0-99.9)."A"(100.0)

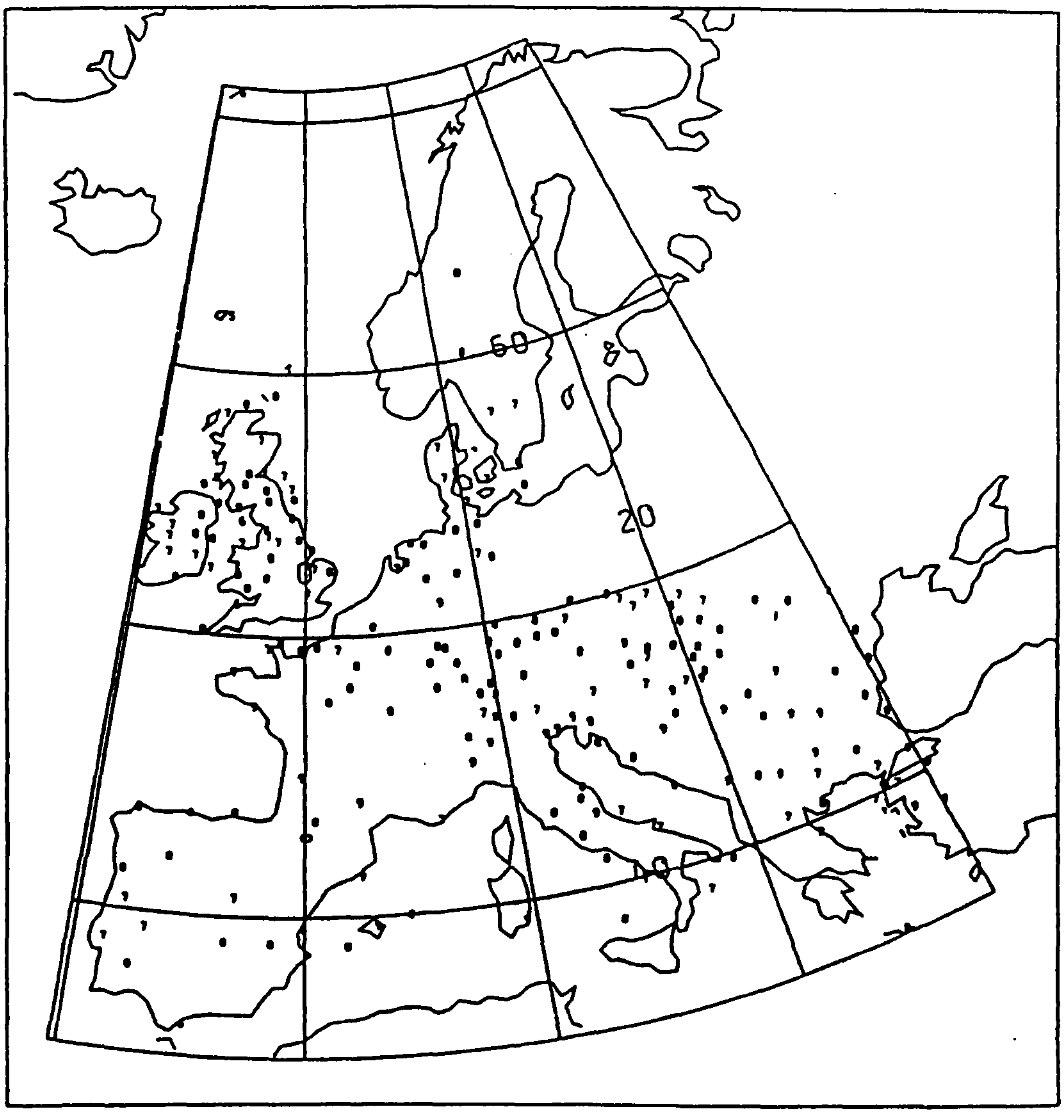


Figure 6.7e

MO there are three real limitations of the FMRM which must be taken into consideration.

(a) From the data presented in Table 6.15, it is clear that the four categories taken from the rainfall model i.e. O (zero rainfall), L (light), M (moderate) and H (heavy) have very wide rainfall ranges. It is suggested that the effects of real rainfall on atmospheric particulate concentrations cannot be simply attributed to these four categories. This point can be further investigated if the distinction between categories L (light rainfall), and M (medium rainfall) are considered as follows.

(1) Accumulative rainfall with a real value of 0.1mm will, according to Table 6.15, be categorised as being in group L, and can have any predicted value, with an equal confidence, between 0.1 - 2mm of rainfall. However, the effect of 2mm of rainfall in washing the atmosphere clean of particulates will probably be very much greater than for 0.1mm.

(2) Accumulative rainfall with a real value of 2.1 mm will be categorised as being in group M, and can have any predicted value with equal confidence of between 2.1 - 10.0mm of rainfall. It is probable that real rainfall with a value of 10.0mm will have a much greater effect of washing the atmosphere clean of particulates than 2.1mm of rainfall.

According to the rainfall categories listed in Table 6.15, an accurate distinction between the relative amounts of precipitation that are necessary to; (1) Dramatically reduce aerosol particulate concentrations (i.e. a heavy rainfall event, e.g. 10.0mm and higher), and (2) Partially reduce the aerosol particulate concentration (i.e. a light rainfall event e.g. 0.1mm), are not well enough defined. The relative magnitude of the precipitation events are therefore both wide ranging and not accurately defined.

(b) Verification statistics supplied for the FMRM over the sampling period have been calculated by comparing theoretical calculations produced from the model and real rainfall events as measured by the fixed sampling stations from the UK and European landmasses surrounding the North Sea. Subsequently, there are no verification statistics for the effectiveness of model calculations for predicted rainfall over the North Sea where the samples were collected. It is apparent, therefore, that rainfall in North Sea atmosphere, as predicted in the model can only be regarded as approximate estimates within the initial framework of accuracy (see figures 6.7 a-e). For the purpose of the present work, it is assumed that due to the relatively small distances involved between land stations on the UK mainland and Continental Europe, the accuracy of the FMRM over land will be approximated for the North Sea atmosphere (Leach, H.; personal communication).

(c) The modelled rainfall is for a total of 36 hours, however, FMRM justification statistics are available for the first 6 hours only. For the purposes of the present work, it will be assumed that the prediction of the rainfall by the model for the remaining 30 hours duration will be the same as those predicted during the first 6 hours.

The points (a - c) have been selected in order to give the reader an indication of some of the real limitations of the FMRM. It is suggested therefore that in any subsequent discussions the FMRM data are treated with a high degree of caution.

6.6.1.5 The FMRM Predictions Applied to the NSA.

The FMRM rainfall plots are in the form of contour-type diagrams and indicate the rainfall as generated by the FMRM distributed over the North Sea and the surrounding landmasses during the sample collection period.

In Section 6.2.2.1, the NSA hi-vol samples were classified into UK (n=36), Eu (n=13) and OS (n=6) end-members; or were shown to be mixed types based on air mass back trajectories. In order to assess the effects of rainfall on trace element concentrations in the NSA the following approach was used.

(a) Precipitation scavenging will wash out particulates from the atmosphere, with the result that the concentrations of particulate trace elements following a rain event will be lower than in the absence of rain. The concentrations of trace elements in aerosols which have sources in the UK and continental Europe vary with location; the source strengths being generally stronger in the south of both land regions (see Section 6.2.2.1.2). However, for this **first look** at the effect of rainfall on the trace element concentrations in the NSA, it was assumed that if rainfall was predicted to have occurred by the FMRM during the history of an air mass transporting an aerosol sample, then the trace element concentration of that sample would be considerably lower than that of the average for the end-member type to which it has been assigned.

(b) There are difficulties in assessing the extent to which precipitation scavenging removes aerosols from the atmosphere, and rainfall does not completely clean the atmosphere of particulates. For example, Chester et al., (1991) gave data on the effects of rain events on the concentrations of Pb in aerosols collected at Cap Ferrat (Southern France). In the study the authors calculated that the average concentrations of Pb fell from 144 to 38 ng m^{-3} of air following the rain events. Thus, the concentration of Pb fell to ~26% of the pre-rain average concentration. The extent to which precipitation scavenging removes aerosols from air will vary with location, the amount of rain falling, and the time over which it falls. However, for this **first look**, it will be assumed that if the air mass has been subjected to rainfall, the Pb concentrations should have fallen to < ~25% of their average concentrations in the end-member aerosols.

(c) Samples from the end-member populations were only considered if there was a rainfall contour plot available; This gave; 21 samples (no's 13 - 16, 21 26 31 34 39 47 51 58 60 61 62 83 84 88 90 92 95 and 96) from the UK end-member, 7 samples from the Eu end-member (no's 19 20 23 24

27 80 and 93), and 2 samples from the OS (no's 67 and 69) end-member. However, as a result of the small numbers of samples in the Eu (n=7) and OS (n=2) end-member populations, the following discussion will concentrate on the UK sample end-member population.

In Section 6.2 it was shown that there is a general south to north decrease in the atmospheric concentrations of some trace elements along the length of the North Sea. This general south to north trend for Pb is related to the UK and European emission rates (Van Aalst et al., 1983), and follows variations in the element source strengths on the surrounding land masses. Because such a distinct source/transport relationship was shown for Pb, this element will be used to make the **first look** assessment of the effects of rainfall on the trace elements on particulates from the North Sea atmosphere.

The **first look** assessment of the rainfall effects using Pb in the UK end-member samples is discussed in the following section.

6.6.1.5.1 The Application of the FMRM to the UK End-Member.

The UK end-member aerosol data were examined for apparent reduction in concentrations. It was found that six samples had atmospheric Pb concentrations which had fallen to 25%, or less of the arithmetic mean value for the UK end-member, i.e. 28 ng m^{-3} of air. These samples were as follows, Pb concentrations (ng m^{-3} of air) given in parenthesis; Sample 14 (3.7), Sample 17 (1.7), Sample 39

(6.3), Sample 75 (2.3), Sample 88 (2.0) and Sample 96 (3.3). It was possible to test the hypothesis that the relatively low Pb concentrations associated with these samples could have resulted from precipitation scavenging by superimposing the relevant FMRM contour plots onto the relevant air mass back trajectory plots, and this was done for samples 14, 39, 88 and 96; for samples 17 and 75 there was no FMRM data available. Each of the samples is considered individually below, and the relevant air mass back trajectory plots are illustrated in Appendix A (air mass back trajectory), and Appendix B (rainfall contour diagrams).

Sample 14, Pb 3.7 ng m^{-3}.

(a) The ship logbook. During the collection of this sample weather conditions were generally good, although there is mention of occasional spray. However, there was no mention of rainfall in the logbook during the whole collection period of this sample.

(b) FMRM prediction. Sample 14 was collected during Challenger survey number CH35 over a sampling period covering 04.09.88. Rain is predicted in the vicinity of the collection area of sample 14, although, not directly in the sample path and although the rain was not directly in the path of the air mass from which sample 14 was sampled, the relatively low concentration of Pb in this aerosol may have resulted from rainfall scavenging.

Sample 39, Pb 6.3 ng m^{-3}.

(a) The ship logbook. During the collection of this sample the sample conditions were ideal, and there was no mention of rainfall.

(b) FMRM prediction. Sample 39 was collected during Challenger survey number CH41 over a sampling period covering 08.12.88 to 09.12.88. Heavy rainfall is predicted in the vicinity of the collection area of sample 39, and could therefore account for the relatively low Pb concentration.

Sample 88, Pb 2.0 ng m^{-3}.

(a) The ship logbook. During the collection of this sample weather conditions were ideal and there was no mention of rainfall in the logbook during the whole collection period of this sample.

(b) FMRM prediction. Sample 88 was collected during Challenger survey number CH57 over a sampling period covering 03.08.89 to 04.08.89. Rain is not predicted between the source of atmospheric Pb and the sample collection point. Rainfall scavenging, as taken from the model cannot therefore account for the low Pb concentration of this sample.

Sample 96, Pb 3.7 ng m^{-3}.

(a) The ship logbook. During the collection of this sample heavy rain was noted in the logbook.

(b) FMRM prediction. Sample 96 was collected during Challenger survey number CH61 over a sampling period covering 24.09.89 to 25.09.89. Rainfall is predicted between the source of atmospheric Pb and the sample collection point, and the relatively low concentration of Pb in this aerosol may have resulted from rainfall scavenging. In summary; four UK end-member aerosols for which FMRM predictions are available, have their concentrations of Pb <25% of the UK arithmetic mean. Of these four samples, 3 (samples 14, 39 and 96) could have low Pb concentrations because of rain scavenging. However, this could not account for the relative low Pb concentration in sample 88, for which the FMRM did not predict rain.

Another way of assessing the rainfall trace element concentration relationship is to compare NSA samples which have high Pb concentrations and see if the FMRM predicts rainfall. This was done for sample 34, which had the highest Pb concentration from the UK end-member population.

Sample 34, Pb 126 ng m^{-3}..

(a) <u>The ship logbook.</u> During the collection of this sample rain was noted on the ships radar in the vicinity of the sample collection.

(b) <u>FMRM prediction.</u> Sample 34 was collected during Challenger survey number CH39 over a sampling period covering 12.11.88. Heavy rainfall is predicted by the model.

Clearly, therefore, on the basis of the heavy rainfall it would be predicted that sample 34 would have a relatively low Pb loading; however, it has the highest Pb loading from the UK end-member population and the FMRM predicted rainfall in the path of the air mass transporting the aerosol. The heaviest rainfall over the North sea was predicted by the FMRM at the time of collection of sample 47. It is therefore of interest to look at the Pb loading of this sample and compare the air mass back trajectory of this sample with the rainfall contour plot. The Pb loading is 37 ng m^{-3}, i.e. slightly above the mean (28 ng m^{-3}) for the UK end-member samples.

In summary samples 34 and 47 highlight the real difficulties involved in trying to interpret the FMRM in its present form, and to relate the predicted rainfall to the trace element concentrations in the NSA. For this reason no further attempts were made to correlate trace element loading and rainfall over the North Sea. However, as a result of the current rainfall study two very tentative conclusions can be drawn, and these are as follows.

(1) By studying the rainfall patterns in Appendix B, it s apparent that the input of atmospherically-transported material from the UK are associated with frontal wind systems, and as a result these inputs will be predominantly effected by rainout processes; although the magnitude of these processes will vary greatly. The overall effect of this will result in a significant fraction of UK aerosols entering the North Sea atmosphere with a reduced particulate concentration, and therefore these concentrations are not necessarily representative of the source area.

(2) The arithmetic mean concentrations of the trace elements from the UK end-member aerosol sample population (which includes samples which have had particulate concentrations reduced by rainfall) are therefore a true representation of the composition of an aerosol which has originated from the UK. Further, these average concentrations are a real estimate of the particle composition involved in the dry mode deposition to the North Sea from the UK.

In the current section data on the average composition of the aerosols transported from the UK to the North Sea atmosphere has been presented. In the following section an assessment is made of the fate of the trace elements following the deposition of the aerosols to the sea surface, In making this assessment the sea water solubility of the trace elements are related to the solid state speciation in the NSA.

6.7 The Sea Water Fates of Trace Elements Following the Deposition of the NSA; Speciation and Sea Water Solubilities.

6.7.1 Introduction.

So far, data have been given on the concentrations and distributions of trace elements in the NSA, and an attempt has been made to identify the factors which control these distributions in terms of air mass transport from their sources. The remaining sections concentrate on the fates of the trace elements. Once an atmospherically transported trace element has been deposited at the sea surface it becomes involved in the oceanic bio-geochemical cycles. According to Chester and Murphy (1990), the major constraint on the way an atmospherically transported trace element enters these cycles depends on the extent to which it is solubilised in sea water; i.e. whether it enters the dissolved or particulate mixed layer trace element pool. This is important since the physical state of the trace elements, i.e. whether they are in dissolved or particulate form, effects the way they enter the bio-geochemical cycles and their residence times in sea water. In turn, the solubility of a trace element from an aerosol depends on the manner in which it is partitioned between the host components in the parent aerosols; i.e. on its solid state speciation.

6.7.2 Solid State Speciation.

A number of studies on the solid state speciation of trace elements in aerosols, and on the relationship between this speciation and the sea water solubilities of trace elements have been reported in recent years. Two of the earliest studies on the solid state speciation of trace elements in aerosols were carried out by Lum et al., (1983) and Chester et al., (1986). Both these studies applied solid state speciation techniques originally designed for sediments to aerosol samples. The techniques used in both studies were essentially similar and involved a five-stage sequential leaching scheme. Lum et al., (1983) applied the scheme to an urban end-member aerosol and Chester et al., (1986) to a crustal end-member aerosol. The results showed that there were considerable differences in the way some trace elements were partitioned between the host components in the aerosols, especially for Cu, Zn, Pb and Cd, all of which were considerably less strongly held in the urban relative to the crustal aerosols. However, in both studies the sequential leaching technique was applied to separated aerosol samples, for which a considerable amount of material was available. Most aerosols collected over marine regions are sampled using some kind of filter technique. As a result relatively small amounts of material are available for analysis. Further, the aerosol samples are retained on the filter substrate. These two constraints, i.e small amounts of sample and filter substrate, mean that sequential leaching techniques designed initially for sediments cannot be applied to aerosols collected on filters. Because of this Chester et al., (1989) used a sequential leaching technique designed specifically for application to filter-collected aerosol samples. The technique involves a three-stage sequential leaching procedure and separates the following operationally-defined trace element associations, which were to cover the most important naturally binding fractions found in marine aerosols. The three stages; stage one (loosely-bound), stage two (oxide and carbonate associations), and stage three (refractory and organic associations) are described in Section 4.3.

Chester et al., (1989) applied their three stage leaching technique to two end-member marine aerosols; a crust rich end-member from the Atlantic north east trades, designated Saharan Crustal Aerosol Population (SCAP), and an urban-rich end-member from Liverpool designated Liverpool Urban Aerosol Population (LUAP). The average solid state speciation signatures of a series of trace elements in the SCAP and the LUAP aerosol end-members are illustrated in Figure 6.8a and 6.8b, respectively. The EF_{crust} values for the elements are also given in these figures and indicate that there are significant differences between the two aerosol populations. Thus, whereas all the elements in the SCAP are crustal in origin, Cu, Zn and Pb behave as AEEs in the LUAP.

On the basis of differences in their speciation signatures between the two aerosol end-members the trace elements may be classified into three general groups.

Group 1; Al and Fe. These two elements are predominantly crustal in origin in both aerosol populations, and are mainly held in stage 3 refractory and organic associations.

Group 2; Mn. In both aerosol end-members Mn is crust controlled, and the Mn is speciated between all three host associations. A larger fraction of the ΣMn is found in an exchangeable association in the LUAP (~44%) than in the SCAP (~23%), but Mn is unique among the elements studied in that it has > ~20% of its total concentration associated with exchangeable hosts in the crust-rich aerosols; the

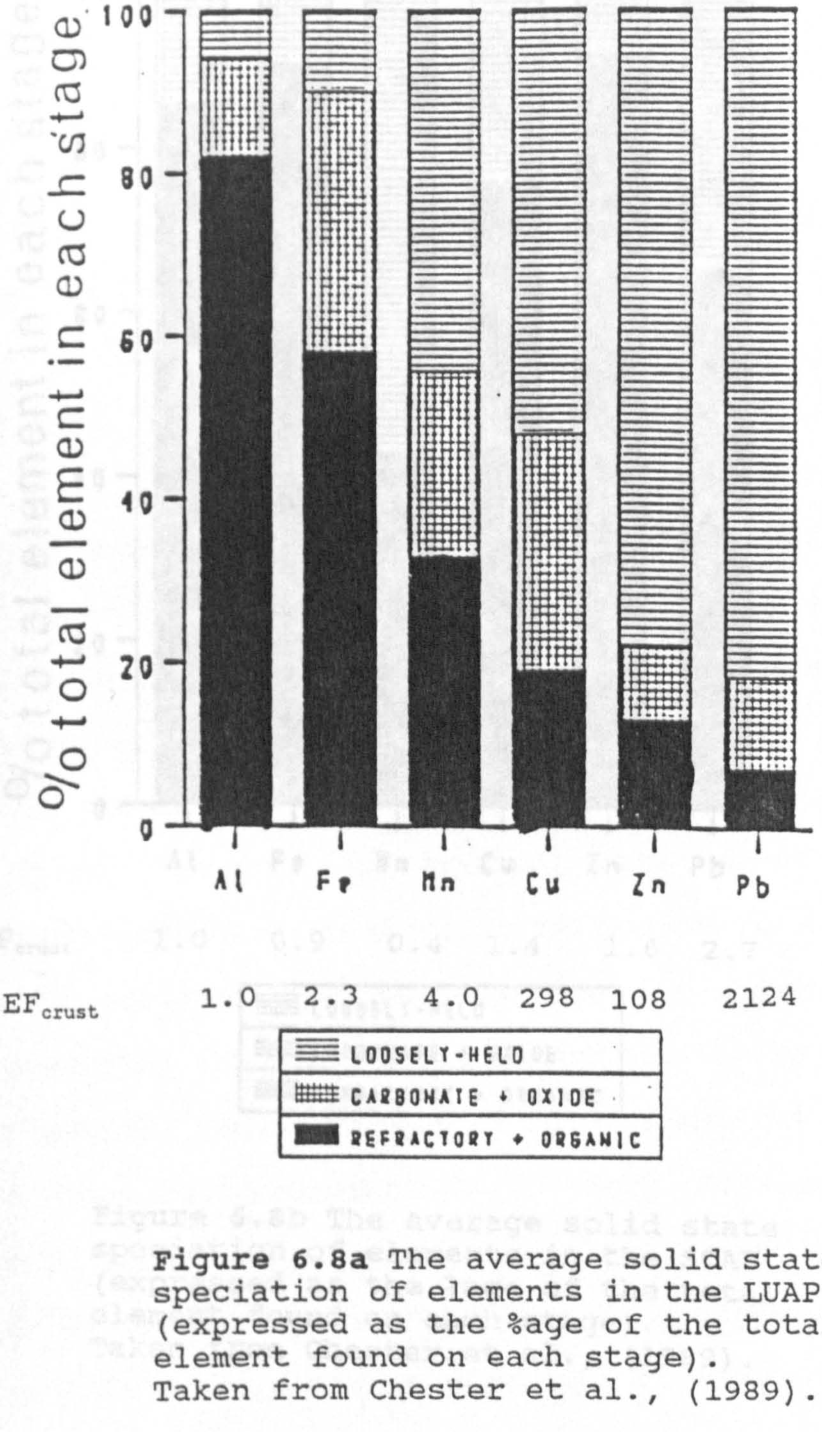


Figure 6.8a The average solid state speciation of elements in the LUAP (expressed as the %age of the total element found on each stage). Taken from Chester et al., (1989).

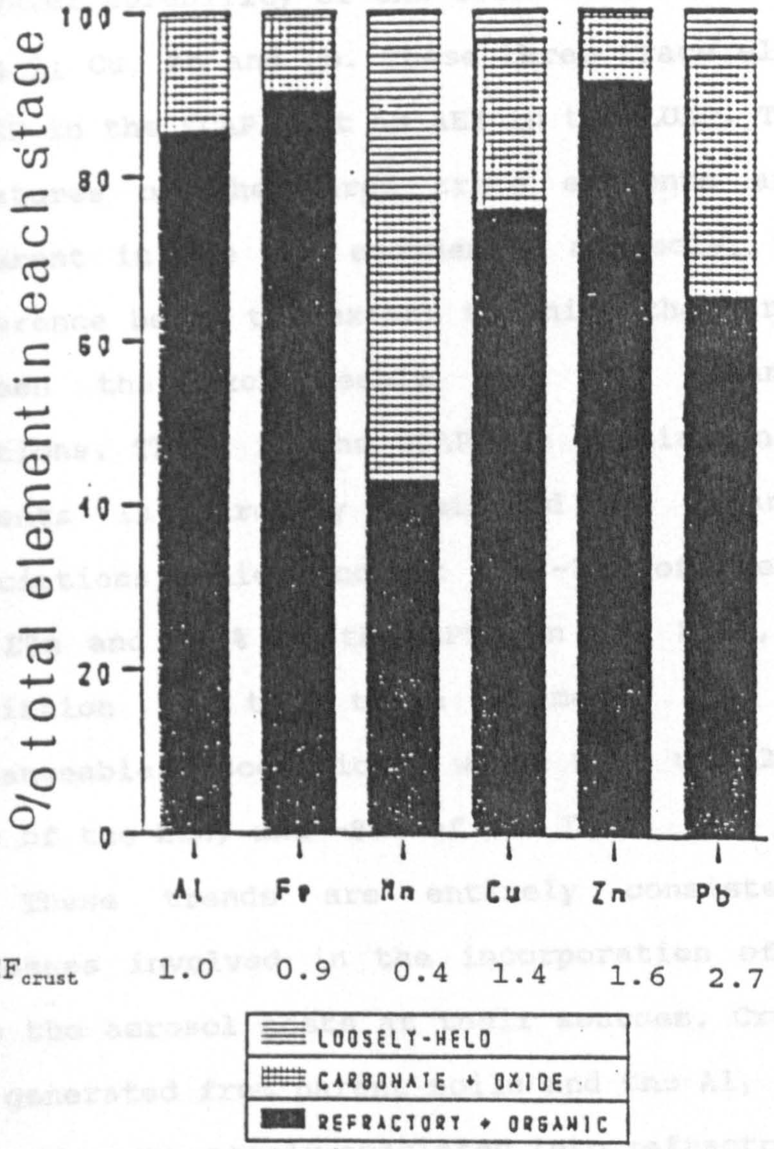


Figure 6.8b The average solid state speciation of elements in the SCAP (expressed as the %age of the total element found on each stage). Taken from Chester et al., (1989).

significance of this is discussed below in relation to the sea water solubility of the trace element from aerosols.

Group 3: Cu, Zn and Pb. These three trace elements behave as NEE in the SCAP, but as AEE in the LUAP. The speciation signatures of the three trace elements are also very different in the two end-member aerosols; the principal difference being the extent to which they are partitioned between the exchangeable and the organic/refractory fractions. Thus, in the SCAP the speciation of the three elements is strongly dominated by organic/refractory associations, which account for ~75% of the ΣCu, ~91% of the ΣZn and ~76% of the ΣPb. In the LUAP, however, the speciation of the three elements is dominated by exchangeable associations, which make up 52% of the ΣCu, ~78% of the ΣZn, and ~81% of the ΣPb.

These trends are entirely consistent with the processes involved in the incorporation of the elements into the aerosol hosts at their sources. Crustal aerosols are generated from parent soils and the Al, Fe, Cu, Zn and Pb in them are mainly speciated into refractory/organic and oxide/carbonate associations in soil forming minerals. However, in urban-dominated aerosols the speciation of Cu, Zn and Pb is dominated by exchangeable associations. This can be related to their release from anthropogenic sources during high temperature volatilisation processes (e.g. fossil fuel burning, waste incineration, ore smelting, production of chemicals), and either their subsequent association with particle surfaces (e.g. Cu and Zn), or their incorporation into individual compounds (e.g. the formation of Pb salts during the combustion of automobile fuels) some of which are leached in stage 1 of the sequential scheme).

The three stage sequential leaching scheme designed by Chester et al., (1989) provided data on the manner in which trace elements are speciated among the host phases of end-member aerosols; data which is not revealed by EF_{crust} values. The authors also showed that the speciation signatures of the trace elements in the aerosols could be related to their sources. Chester et al., (1989) then introduced the concept of a speciation related environmental mobility of a trace element in an aerosol, in which the exchangeable elements are the most mobile, and those associated with the refractory fraction are the least mobile.

The solid state speciation data provides information on both the sources and the environmental mobility of trace elements in marine aerosols. This environmental mobility can also be used to indicate the extent to which a trace element is soluble in sea water. In addition, the environmental mobility can be related to sea water solubility of the trace elements from the aerosols. Chester et al., (1986) first suggested that the solid state speciation of a trace element in an aerosol may control its sea water solubility. However, this was only a tentative conclusion because no techniques were then available to establish that the solid state speciation of an element in an aerosol may control its sea water solubility. In a later study Lin (1988) applied the three stage sequential leaching technique to the same urban aerosol used by Chester et al., (1990), and also determined the sea water solubility of a series of trace elements from the urban aerosols into sea water, and this relationship is indicated (see Figures 6.9 a-c). Chester et al., (1991) extended this investigation to include a range of marine aerosols, and showed that there is a well developed relationship between the extent to which Cu, Pb and Zn are associated with the exchangeable fraction of the aerosols and the extent to which they are soluble in sea water. The relationship for Cu, Pb and Zn from the present work is also illustrated in Figures 6.9 (a-c).

It may be concluded, therefore, that solid state speciation signatures of elements in marine aerosols provide information on; (a) the sources of the trace elements, and (b) their mobility in the environment. Further, the environmental mobility can be related to the solubility of the trace elements in sea water, and can be used to asses their fates following their deposition to the sea water, via the dry deposition mode. For the wet deposition mode, the environmental mobility is still a control on their oceanic fates, but here the solubilisation reactions are initiated in rain water; i.e. before they reach the sea surface.

In order to make a general assessment of the fate of trace elements following the deposition of the NSA to the

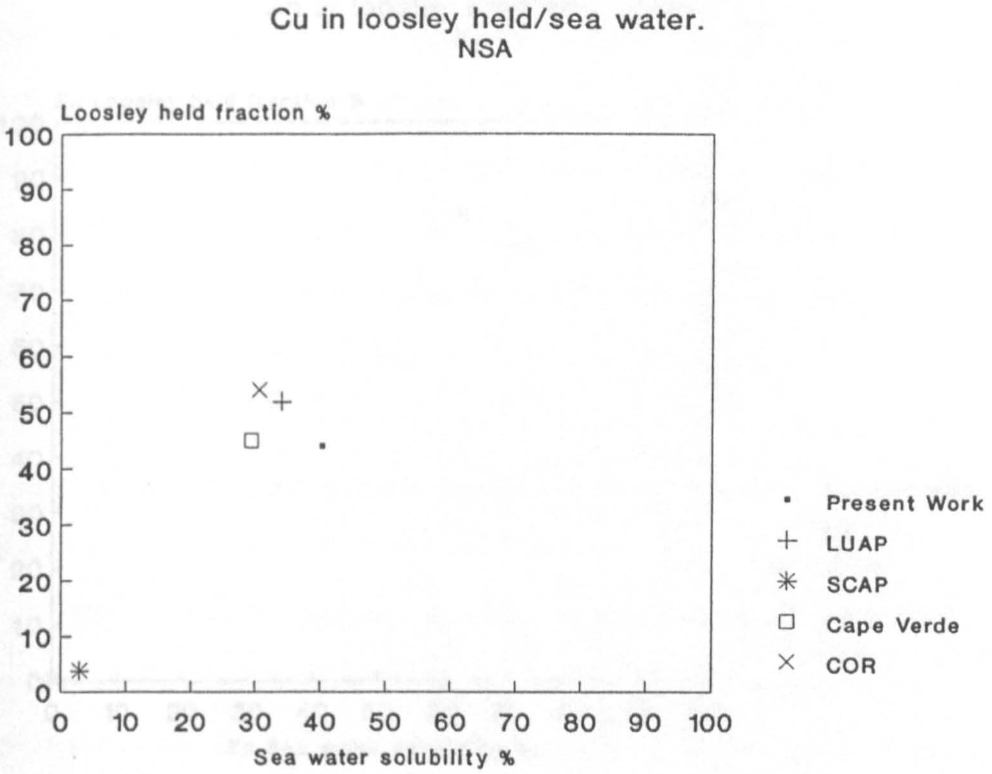


Figure 6.9a

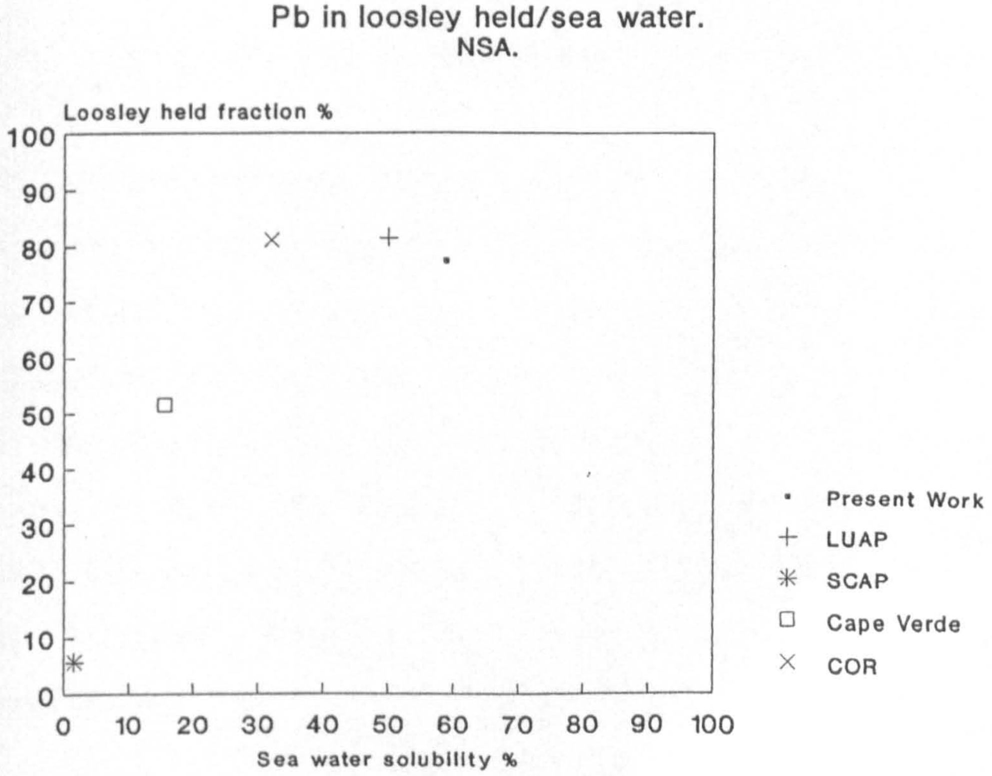


Figure 6.9b

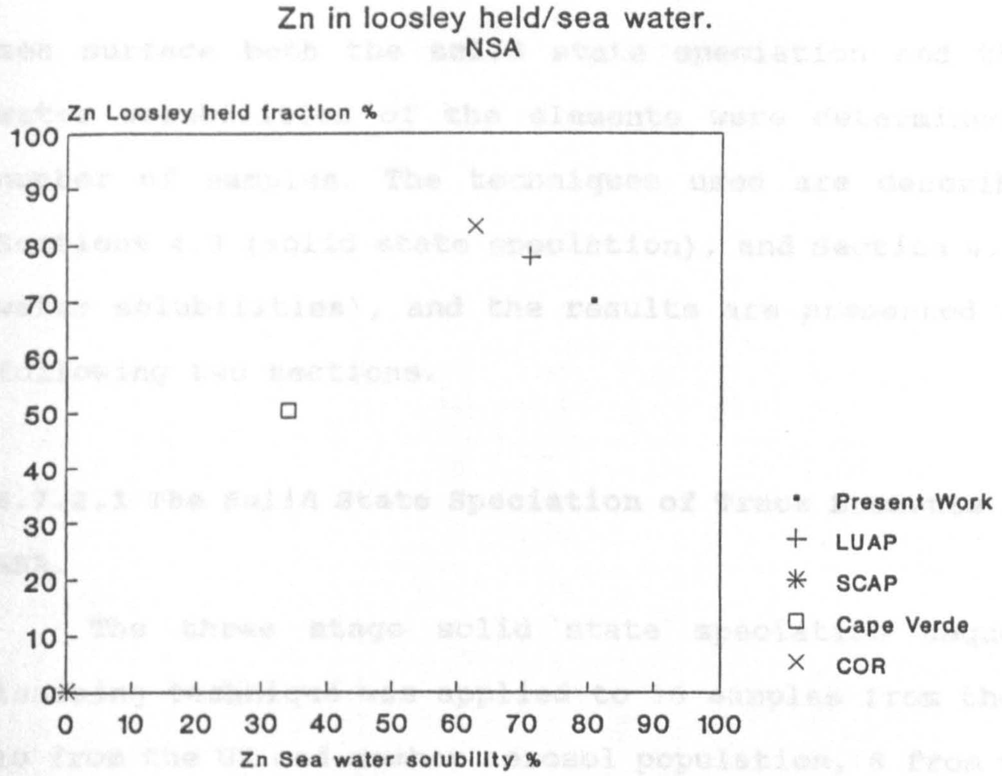

Zn in loosley held/sea water.
NSA
Zn Loosley held fraction %
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
100
Zn Sea water solubility %
• Present Work
+ LUAP
✳ SCAP
□ Cape Verde
× COR

Figure 6.9c

sea surface both the solid state speciation and the sea water solubilities of the elements were determined in a number of samples. The techniques used are described in Sections 4.3 (solid state speciation), and Section 4.4 (sea water solubilities), and the results are presented in the following two sections.

6.7.2.1 The Solid State Speciation of Trace Elements in the NSA.

The three stage solid state speciation sequential leaching technique was applied to 36 samples from the NSA; 10 from the UK end-member aerosol population, 8 from the EU aerosol population, 6 from the OS aerosol population and 12 from mixed aerosols. The arithmetic mean, range and standard deviations of the speciation signatures are given in Table 6.16 (a-d). These data are also plotted in Figures 6.10 (a-d), and from these several conclusions can be drawn as follows;

(a) Al and Fe have an average of > ~80% of there total concentrations in stage 3 hosts in all three end-member and the mixed aerosol groups. These elements are therefore refractory in character in the NSA.

(b) The speciation signature of Mn varies between the three sample groups. For example, the exchangeable (stage 1) Mn makes up, on average, between 49% and 68% of the total Mn, the highest value being found for the OS aerosol population.

Table 6.16a The average partitioning data of elements from the NSA, UK end-member population; data given as percentages of the of the total element concentration.

	n = 10	Stage 1	Stage 2	Stage 3
Al	mean	4.8	9.4	85.8
	range	0.6-15.8	2.6-20.6	62.7-94.6
Fe	mean	2.3	10.4	87.3
	range	0.1-9.9	0.1-31.1	68.3-98.8
Mn	mean	49.0	6.7	44.3
	range	14.8-81.3	1.2-20.1	16.7-76.8
Cd	mean	67.3	17.6	15.1
	range	19.2-95.8	1.3-45.7	1.0-35.1
Cu	mean	32.6	28.8	38.6
	range	19.6-42.7	17.1-40.9	30.9-51.2
Pb	mean	76.2	14.3	9.5
	range	63.2-91.6	0.1-26.8	2.5-14.6
Zn	mean	66.3	7.0	16.7
	range	62.1-83.0	4.5-10.5	63.2-91.6

Table 6.16b The average partitioning data of elements from the NSA, Eu end-member population; data given as percentages of the total element concentration.

	n = 8	Stage 1	Stage 2	Stage 3
Al	mean	4.3	14.2	92.1
	range	1.9-6.7	5.1-25.9	72.1-92.1
Fe	mean	3.1	17.7	79.2
	range	0.1-7.7	8.2-27.5	71.1-90.8
Mn	mean	57.2	4.3	38.5
	range	43.6-77.9	1.7-12.5	25.9-53.0
Cd	mean	59.6	34.1	6.3
	range	29.5-84.2	24.4-65.2	4.0-8.2
Cu	mean	41.4	32.1	26.5
	range	27.8-49.2	25.3-39.2	17.5-39.1
Pb	mean	70.7	22.9	6.4
	range	48.2-87.8	3.9-29.2	3.5-9.3
Zn	mean	80.8	8.2	11.0
	range	75.3-84.2	6.7-10.6	8.7- 14.3

Table 6.16c The average partitioning data of elements from the NSA, OS end-member population; data given as percentages of the total element concentration.

	n = 6	Stage 1	Stage 2	Stage 3
Al	mean	5.5	12.4	82.1
	range	1.0-16.6	5.5-21.1	71.3-92.1
Fe	mean	14.9	2.7	82.4
	range	0.1-22.8	0.1-6.6	73.4-94.2
Mn	mean	67.9	6.6	25.5
	range	41.8-95.0	2.6-13.8	0.1-51.7
Cd	mean	93.4	4.4	2.2
	range	82.2-99.8	0.1-12.8	0.1-12.8
Cu	mean	40.9	23.6	35.5
	range	30.2-62.6	22.4-28.7	36.0-41.4
Pb	mean	79.3	9.5	11.2
	range	72.9-84.7	1.6-17.4	8.1-18.8
Zn	mean	89.1	4.1	6.8
	range	80.1-97.1	0.1-15.2	2.3- 18.4

Table 6.16d The average partitioning data of elements form the NSA, Mixed populations; data given as percentages of the total element concentration.

	n = 12	Stage 1	Stage 2	Stage 3
Al	mean	5.7	11.6	82.7
	range	1.0-15.0	3.3-21.9	65.7-94.6
Fe	mean	7.2	7.9	84.9
	range	0.4-20.0	0.1-19.3	65.7-93.7
Mn	mean	60.7	6.8	32.5
	range	15.2-95.5	2.5-15.8	0.1-77.7
Cd	mean	73.9	16.2	9.9
	range	44.4-99.8	0.1-55.6	0.1-29.9
Cu	mean	54.2	23.1	22.7
	range	26.0-76.3	15.3-41.3	4.2-51.1
Pb	mean	79.3	13.6	7.1
	range	54.1-96.7	0.2-40.6	0.2-18.2
Zn	mean	64.7	16.6	18.7
	range	26.7-95.3	0.1-41.3	2.3- 50.4

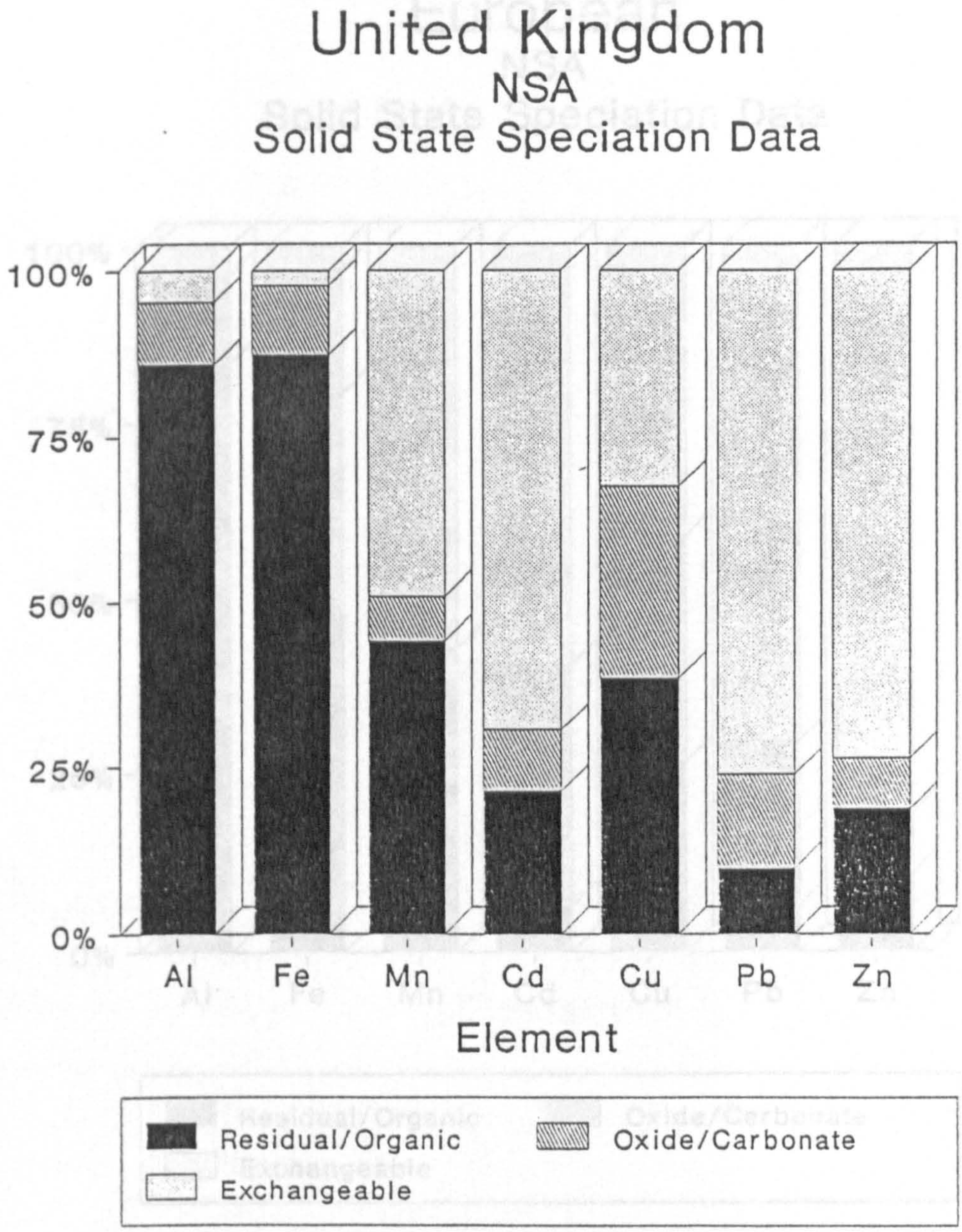

United Kingdom
NSA
Solid State Speciation Data
100%
75%
50%
25%
0%
Al
Fe
Mn
Cd
Cu
Pb
Zn
Element
Residual/Organic
Oxide/Carbonate
Exchangeable

Figure 6.10a

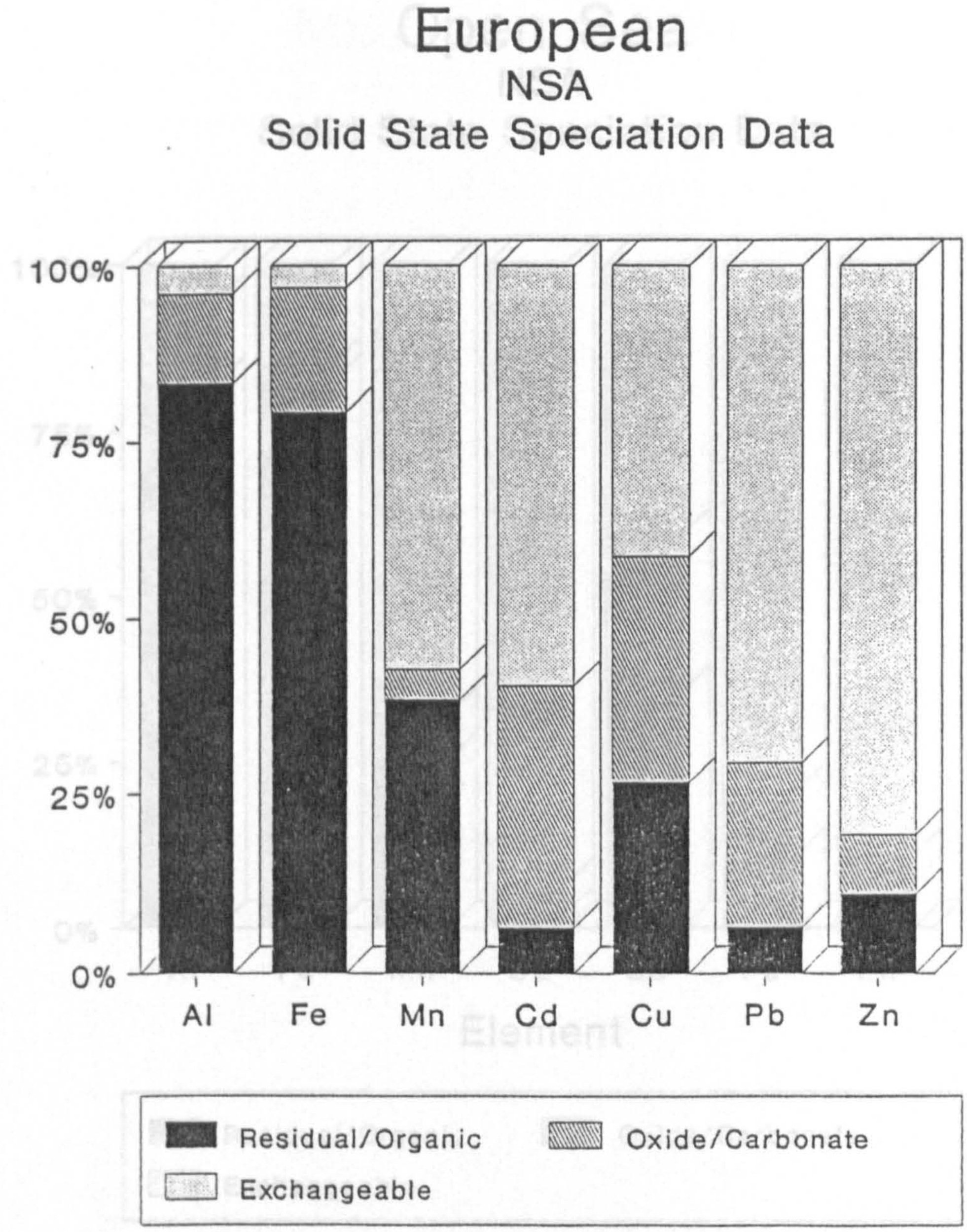

European
NSA
Solid State Speciation Data
100%
75%
50%
25%
0%
Al
Fe
Mn
Cd
Cu
Pb
Zn
Residual/Organic
Oxide/Carbonate
Exchangeable

Figure 6.10b

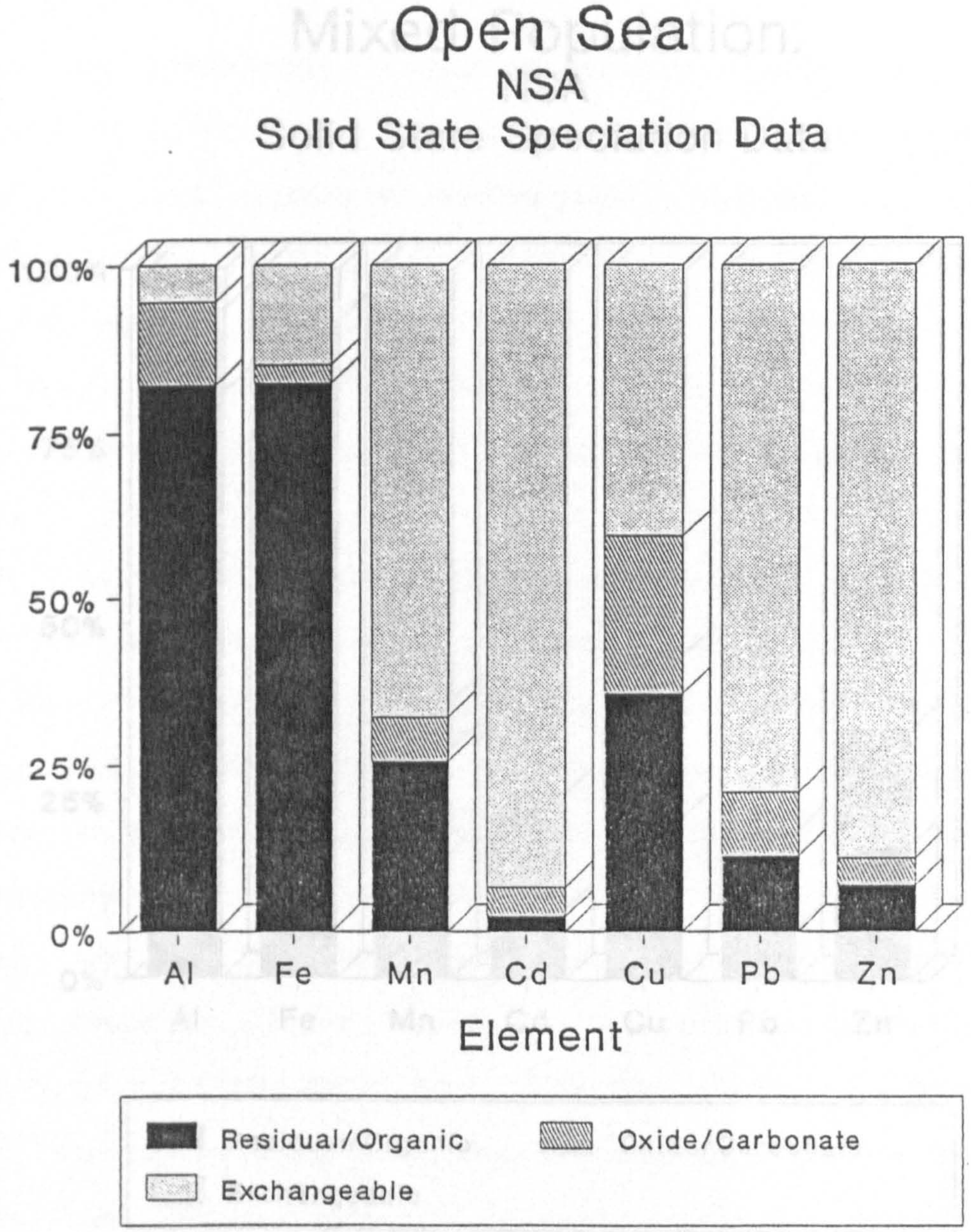

Open Sea
NSA
Solid State Speciation Data
100%
75%
50%
25%
0%
Al
Fe
Mn
Cd
Cu
Pb
Zn
Element
Residual/Organic
Oxide/Carbonate
Exchangeable

Figure 6.10c

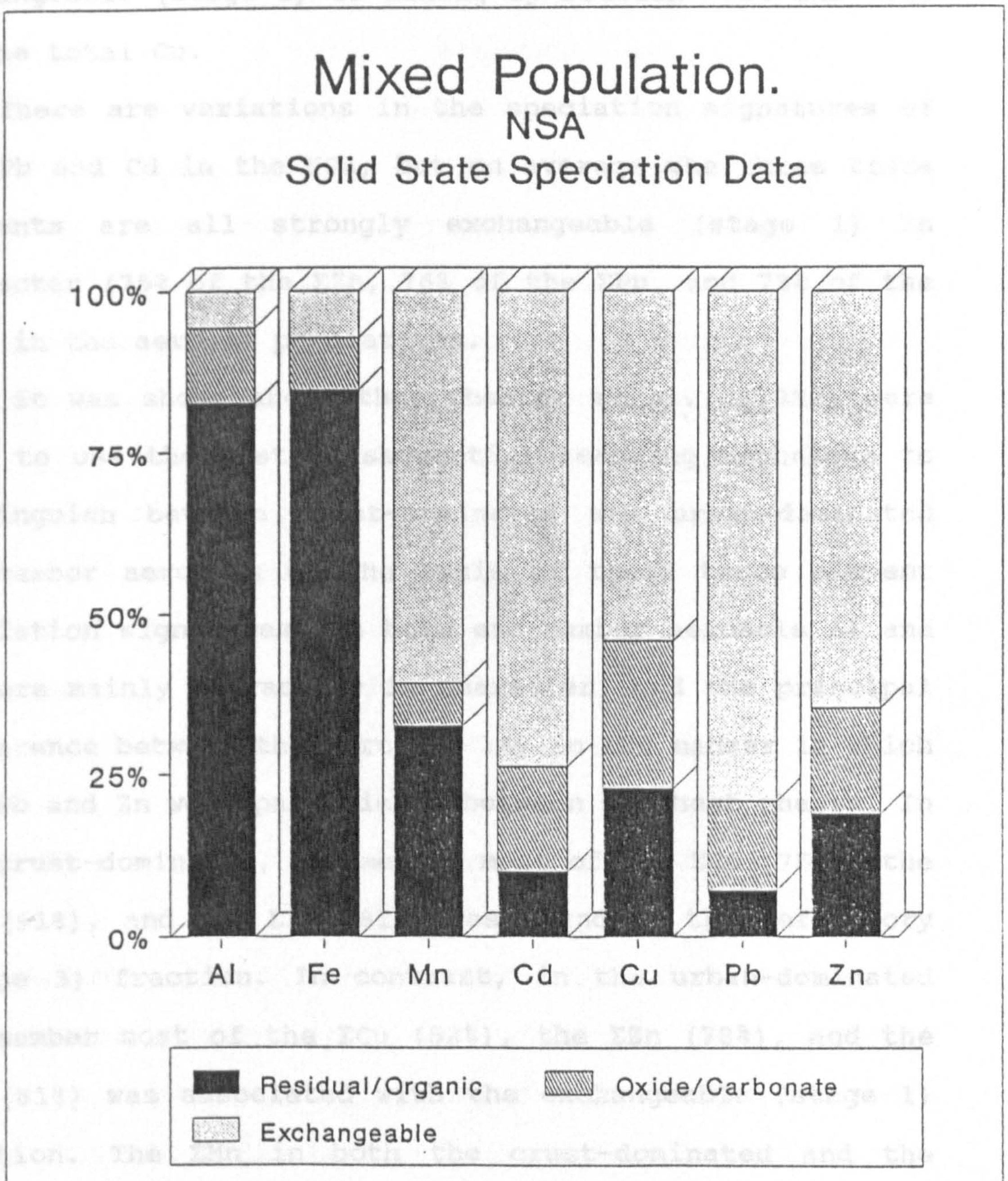

Mixed Population.
NSA
Solid State Speciation Data
100%
75%
50%
25%
0%
Al
Fe
Mn
Cd
Cu
Pb
Zn
Residual/Organic
Oxide/Carbonate
Exchangeable

Figure 6.10d

(c) On average, Cu is partitioned between the three host phases in all the aerosol sample groups, with the exchangeable (stage 1) Cu making up between ~33% and ~54% of the total Cu.

(d) There are variations in the speciation signatures of Zn, Pb and Cd in the NSA, but on average the three trace elements are all strongly exchangeable (stage 1) in character (75% of the ΣZn, 76% of the ΣPb, and 73% of the ΣCd) in the aerosol populations.

It was shown above that Chester et al., (1989) were able to use the 3-stage sequential leaching technique to distinguish between crust-dominated and urban-dominated end-member aerosols on the basis of their trace element speciation signatures. In both end-member aerosols Al and Fe were mainly refractory in character, and the principal difference between the aerosols lay in the manner in which Cu, Pb and Zn were partitioned between the host phases. In the crust-dominated, end-member most of the ΣCu (75%), the ΣZn (91%), and the ΣPb (81%) was found in the refractory (stage 3) fraction. In contrast, in the urban-dominated end-member most of the ΣCu (52%), the ΣZn (78%), and the ΣPb (81%) was associated with the exchangeable (stage 1) fraction. The ΣMn in both the crust-dominated and the urban-dominated aerosols was partitioned amongst the three host fractions, but the urban dominated end-member had a higher proportion of the ΣMn (~44%) associated with the exchangeable (stage 1) hosts than the crust-dominated end-member (~23%). In the NSA the highest proportion of Mn is also associated with exchangeable (stage 1) hosts.

It may be concluded, therefore, that the speciation signatures of the trace elements in the NSA are characteristic of those of an urban-generated aerosol, the most significant feature being the relatively large fractions of the ΣCu, ΣZn, ΣPb and ΣCd (not included in the trace elements investigated by Chester at al. (1989)), in exchangeable (stage 1) host associations. Thus, in the NSA considerable fractions of the total concentrations of Mn (average, ~35%), Cu (average, 31%), Zn (average ~75%), Pb (average, ~76%) and Cd (average ~73%) are present in potentially environmentally mobile (stage 1) associations. The extent to which this degree of environmentally is reflected in the sea water solubilities of the trace elements is considered in the next section.

6.7.3 The Sea Water Solubilities of Trace Elements from the NSA.

Several authors have carried out studies on the sea water solubilities of trace elements from aerosols deposited at the sea surface by the dry deposition mode; i.e. the solubilities have been determined directly in sea water, and not via a rain water precursor. The results of a number of these studies are summarised below.

Walsh and Duce (1976), simulated the dry deposition of aerosols to the sea surface, using filter collected aerosol samples, collected at Rhode Island. The authors estimated that ~70% of the V from the filter collected aerosols was rapidly solubilised, i.e. within < 2 minutes of exposure to sea water, and that the majority of this V was non crustal, i.e. anthropogenic in origin. This was based on the fact that during the sea water solubilization experiments the EF_{crust} values of the particulates fell from > 25 to ~ 10 after 1 - 2 minutes contact with sea water. The overall conclusions drawn by the authors, was that the manner in which an element is partitioned between crustal and non-crustal components of an aerosol, will exert a control on its fate in sea water.

Maring and Duce (1987) reported data that almost all the non-crustal Cu in marine aerosols collected at Enewetak North Pacific was soluble in sea water. It is, however, not only non-crustal elements which are soluble in sea water from aerosols. For example, Maring and Duce (1987) showed that between 3% and 6% of the Al, mainly a crustal element, is soluble in sea water from aerosols.

Creculuis (1980) carried out a major study on the solubilities of trace elements from aerosols in sea water, and divided the elements into a number of types as follows;
(1) Very soluble trace elements (>90% of the total trace element concentration soluble in sea water). The trace elements in this group include Na, Br and Cs, associated with the sea salt generated trace elements and are correspondingly very soluble in sea water.
(2) Relatively soluble trace elements (20-90% of the total trace concentration element soluble in sea water). The

trace elements in this group includes Cd, Zn, Se As, Se, Co, Sb, Cr, Ag, Mn, V and Pb. And the concentration of these trace elements entering the soluble fraction on contact with sea water will generally increase as the portion of the anthropogenic fraction the aerosol population increases. Cd and Mn are the exception to this, and the sea water solubilities of these trace elements appears to be largely independent of the aerosol source.

(3) Slightly soluble and insoluble trace elements (<10% of the total trace element concentration soluble in sea water). The trace elements in this group includes, Al, Fe, Sc, Ce, La, Hf, Yb, Pa and Lu. These trace elements are usually predominantly of crustal origin, and as a result will be relatively insoluble in sea water from all marine regions.

One of the most comprehensive studies on the solubilities of trace elements in sea water from aerosols was carried out by Hodge et al., (1978), (see also Section 1.8). This study is particularly interesting because it involved two different aerosol populations and it was possible to interpret the solubility data in terms of aerosol sources. These authors simulated the dry deposition of a series of elements to the sea surface from filter collected aerosols. The aerosols were from two contrasting populations; an anthropogenic rich, or urban rich, aerosol population from southern California, and a crust rich population from Baja, CA. The results of this study are summarised in Table 1.11.

From the data in Table 1.11 it can be seen that there are differences in the extent to which some trace elements are solubilised from the two aerosol populations. Further, there are strong indications that the solubilities of some trace elements from aerosols are related to their sources, as identified by their EF_{crust} values. For example Pb, Zn and Cu have higher crust values in, and are considerably more soluble in sea water from, urban-rich than the crust-rich aerosol populations. However, this is apparently not a universal trend as can be seen in the solubility data for examples of both enriched and non-enriched elements. Thus, although Cd (an AEE) is enriched in the urban-rich relative to the crust-rich aerosols, it is equally soluble in both. Further, although Mn is strongly crust controlled in both the crustal and the urban aerosols, it is still relatively soluble from both aerosol populations. Further, there appears to be no direct relationship between the extent to which an element is enriched in the parent aerosol and the extent to which it is soluble in sea water. For example, in the urban-rich population Pb has an EF_{crust} of 4148 but only 39% of the ΣPb is soluble in sea water, where as although the Zn EF_{crust} is only 116, 68% of the ΣZn undergoes dissolution in the sea water medium. It may be concluded, therefore, that for Pb, Cd and Mn, their sea water solubilities are not directly related to the degree to which they are enriched relative to crustal sources, in an aerosol. It is therefore necessary to identify a more fundamental control which constrains the sea water solubility of trace elements from an aerosol.

Lin (1988) suggested that this control on sea water solubility of a trace element from an aerosol may be related to the solid state speciation among the crustal components. This was further considered by Chester et al., (1991). These authors showed that the solubilities of a number of trace elements in marine aerosols were related to their partitioning i.e. exchangeable (stage 1 hosts - see Section 6.5). In addition, the authors showed that the reason why Mn and Cd were relatively soluble from urban and crustal aerosols was that significant amounts of the total concentration of the two elements were in exchangeable associations in both aerosols.

By considering all of the data available, Chester and Murphy (1988) have made rough estimates of the solubility of some trace elements from aerosols that have been deposited at the sea surface. These estimates are listed in Table 6.17. From the data in Table 6.17 it can be seen that the solubility of the trace elements is arranged in terms of three categories, characteristic of three different oceanic environments. These three environments have been selected in order to illustrate how the sea water solubility of trace elements from aerosols is dependant on its source. From the data summarised by the authors, there are three overall trace element solubility trends that can be identified. And these are as follows; (1) Very significant fractions of the AEE are soluble in sea water

Table 6.17 The seawater solubilities of trace elements from aerosols over various marine regions (% total element)[1]

Element	Coastal regions dominated by anthropogenic sources.	Coastal region dominated by crustal sources.	Open-ocean 'mixed-aerosol' sources.
Al	5	<5	5
Fe	7.5	<7.5	7.5
Mn	45	<20	35
Ni	50	<25	40
Co	25	<20	22.5
Cr	12.5	<10	10
V	30	<20	25
Cu	30	<5	30
Pb	50	<5	30
Zn	70	<5	45
Cd	85	-	80

[1] Data from various sources quoted in the text; values are rounded off first order estimates and are only approximate.
(Taken from Chester 1991).

from coastal regions where anthropogenic inputs are the highest.

(2) For coastal and open sea regions where desert-derived crustal dusts dominate the aerosol population, and in which the EF_{crust} values of the elements (including the AEE) are relatively low, considerably smaller amounts of the relatively soluble elements enter the dissolved phase. However, it must be stressed that in these areas, the atmospheric deposition fluxes of the elements are relatively high, and the resulting soluble fractions including those for relatively insoluble elements e.g. Al entering the sea water may be significant. This is especially relevant in those areas which receive the input of dust pulses, for example a Saharan dust pulse.

(3) Over the open ocean areas the extent to which components from the various aerosol sources, e.g. anthropogenic and crustal, are mixed together in the total particle population, will determine the overall solubility of elements from that aerosol population.

In order to establish the solubilities of a number of trace elements from the NSA, and to relate these to the elemental speciation signatures, a number of sea water solubility experiments were carried out. The experimental conditions are described below.

Sea water is complex medium which contains a variety of dissolved and particulate constituents, and according to Chester and Murphy (1990) many of these constituents have the potential to effect the extent to which trace elements are solubilised from aerosols. A number of major parameters must be considered in relation to the sea water used in aerosol solubility studies are discussed below.

(a) The concentration of suspended particulates. These are important because the particulates can scavenge trace elements initially released into sea water from aerosols, and so can apparently decrease the true aerosol solubility value. In the present study this was overcome by using filtered sea water.

(b) The concentrations of dissolved trace elements. Trace elements in a dissolved state in the original sea water must be taken into account when considering the equilibrium release of the elements from aerosols. This can create analytical difficulties and in the present study the sea water was passed through an ion exchange column to remove dissolved trace elements prior to the aerosol solubility experiments.

(c) The concentration of dissolved organics. Dissolved organic matter (DOM) is important in relation to the solubility of trace elements from aerosols for two principal reasons. (1) DOM can coat the aerosols with an organic film. Films of this type may trap the elements on the surface of the aerosols and so make them less soluble. The films can also act as substrate for the scavenging of some dissolved trace elements from sea water; e.g. according to Balisteri et al., (1981) trace element scavenging from sea water by particulate matter is controlled by organic coatings on the solids. (2) DOM can effect the speciation of some dissolved trace elements by forming complexes that keep them in a dissolved form and so prevent their re-scavenging by particulate matter.

(d) The volume of sea water used and the leaching times. In aerosol solubility studies reported in the literature various combinations of sea water volumes and leaching times have been employed. In their investigation Hodge et al., (1978) simulated the dry deposition of urban-generated and crust-dominated aerosols to sea water using a leaching time of 3 hours. Moore et al., (1978) studied the release of trace elements from filter-collected aerosols using 100ml of sea water and a leaching time of 2 hours. Maring and Duce (1987) reported data which showed that for the dry deposition mode there was a bimodal solubility of Al from aerosols, with ~5% - ~6% of the ΣAl being leached in < 6 hours, and a further ~3% - ~4% being released within 60 hours. However, Creculius (1980) found no apparent differences in the solubilities of a series of trace elements from filter collected aerosols after leaching times of 1 and 24 hours in 100mls of sea water.

One feature to emerge from these aerosol/sea water solubility studies is that some trace elements may be released fairly rapidly from the aerosols upon contact with sea water, whereas others may take longer to reach their maximum solubilities. It has been estimated that a particle deposited at the sea surface spends ~100hrs in the upper ~100m of the water column (Maring and Duce, 1987). However, their are difficulties in attempting to model aerosol/sea water solubilities in terms of this relatively long ~100hr residence time. For example, over a period of this length the aerosols may be taken into the gut of filter feeding organisms where the pH is much lower than that in the sea water, or they form aggregates with other particles. Chester and Murphy (1990) concluded, therefore, that it is unlikely that once they have been deposited at the sea surface that aerosols will retain their original characteristics over periods approaching ~100hrs. In view of this, the authors stressed that it is necessary to identify aerosol sea water solubilities obtained from laboratory simulations within strict operationally defined limits, in the same way as sequential leaching experiments are defined. The operationally defined limits for the sea water solubility determinations used in the present study are described in Section 4.4; together with the procedure used. The procedure was applied to 15 samples of the NSA, for which speciation signatures were known. The data are listed in Table 5.9, and are summarised in Table 6.18; and are discussed below. From the data listed in Table 6.18, it is apparent that the sea water solubilities vary considerably from one trace element to another. One way of validating the trace element solubility data obtained from the present investigation is by comparing them to those reported by other studies, and this is considered below in terms of individual elements.

Aluminium. The average solubility of Al from the NSA is 4.4%. The range is from 1.2 - 9.9%, but 66.6% of the sample

Table 6.18 The %age of the total concentration sea water solubility of the NSA.

	n = 15	Sea water shake	Residual material
Al	mean	4.4	95.6
	range	1.2 - 9.9	90.9 - 98.7
	σ	2.8	2.8
Fe	mean	8.1	91.9
	range	2.2 - 15.3	84.7 - 97.8
	σ	3.5	3.5
Cu	mean	40.2	59.8
	range	17.5 - 72.8	27.2 - 82.5
	σ	17.4	17.4
Pb	mean	58.9	41.1
	range	30.9 - 97.5	2.5 - 69.1
	σ	19.8	19.8
Zn	mean	80.6	19.4
	range	55.5 - 98.4	1.6 - 44.5
	σ	16.1	16.1

σ = Standard deviation.

have between 1.2 - 9.9% of their ΣAl, and 33.4% have between 4.6 - 9.1% of their ΣAl soluble in sea water. The average sea water solubility of Al from the NSA (4.4% of the ΣAl) is generally similar to the value of 6.8% reported by Lin (1988) for Liverpool urban aerosol (LUAP), and is agreement with the value <10% found by other workers (see e.g.: Maring and Duce, 1987; Hodge et al, 1978).

__Iron.__ The average solubility of Fe from the NSA is 8.1%. The range is from 2.2 - 15.3%, but 73% of the sample have between 2.2 - 8.9% of their ΣFe, and 27% have between 8.9 - 15.5% of their ΣFe soluble in sea water. The average sea water solubility of Fe from the NSA (8.1% of the ΣFe) is generally similar to the value of 5.1% reported by Lin (1988) for Liverpool urban aerosol (LUAP), and to those of ~1% - ~8% for urban aerosols found by Hodge et al., (1978) and Creceluis (1981).

__Copper.__ The average solubility of Fe from the NSA is 40.2%. The range is from 17.5 - 72.8%, but 47% of the samples have between 17.5 - 40% of their ΣCu, soluble in sea water. The average sea water solubility of Cu from the NSA (40.2% of the ΣCu) is considerably higher than that of ~1% reported by Lin (1988) for a crust dominated aerosol end-member, but is closer to that of 34% reported by the same author for an urban-dominated end-member. The average sea water solubility of Cu from the NSA is also generally similar to the average values reported for urban aerosols by Hardy and Creceluis (1981) (41%), but is far higher than the value of

28% found by Hodge et al., (1978) for an urban aerosol from Southern California.

__Zinc.__ The average solubility of Zn from the NSA is 80.6%. The range is from 55.5 - 98.4%, but 40% of the samples have between 70 - 98.4% of their ΣZn, soluble in sea water. The average sea water solubility of Zn from the NSA (80.6% of the ΣZn) is considerably higher than the <~1% reported by Lin (1988) for a crust dominated aerosol end-member, but is closer to that of 71% reported by the same author for an urban-dominated end-member. The average sea water solubility of Zn from the NSA is generally similar to the average values reported for urban aerosols by Hardy and Creceluis (1981) (66%), and by Hodge et al., (1978) (68%).

__Lead.__ The average solubility of Pb from the NSA is 58.9%. The range is from 30.9 - 97.5%, but 33% of the samples have between 30.9 - 97.5% of their ΣPb, and 67% have between 50 - 97.5% of their ΣPb soluble in sea water. The average sea water solubility of Pb from the NSA (58.9% of the ΣPb) is considerably higher than the <~1% reported by Lin (1988) for a crust dominated aerosol end-member, but is closer to that of 50% reported by the same author for an urban-dominated end-member. The average sea water solubility of Pb from the NSA is generally similar to the average values reported for urban aerosols by Hardy and Creceluis (1981) (54%), and by Hodge et al., (1978) (39%).

On the basis of the data discussed above it may be concluded that the sea water solubilities of trace elements from the NSA are characteristic of those transported to a coastal sea from predominantly urban sources. A similar conclusion was reached above with respect to the solid state speciation signatures of trace elements, and the relationship between the two parameters is discussed below.

It was pointed out in Section 6.7.2 that there is a well developed relationship between the extent to which Cu, Zn and Pb are associated with the exchangeable fractions of aerosols and the extent to which they are soluble in sea water (see Figures 6.9 a-c). It can be seen from these figures that the NSA confirms the general relationship between the extent to which Cu, Zn and Pb are held in exchangeable associations in aerosols and the extent to which they are soluble in sea water.

From the data obtained in this part of the study an estimate can be made about the extent to which a number of trace elements in the NSA are solubilised following their deposition to the sea surface. Thus, an average of ~5% of the ΣAl, ~8% of the ΣFe, 40% of the ΣCu, 80% of the ΣZn and 60% of the ΣPb are taken into solution from the NSA to enter the dissolved pool in the North Sea mixed layer. On the basis of these data, it will therefore be possible to partition the aerosol flux to the North Sea surface into a dissolved and a particulate phase.

The aerosol sea water solubility experiments in the present work were carried out by directly exposing the samples to sea water; i.e. a simulation of the dry deposition mode. During precipitation scavenging, however, the aerosols come into contact with an aqueous phase (rain water) before they reach the sea surface. There was insufficient time in the present investigation to carry out a detailed series of experiments designed to assess the effects of rain water on the solubilities of trace elements from the NSA. However, a preliminary experiment was carried out in which a series of 15 filter-collected samples of the NSA were leached in artificial rain water. The rain water was prepared as described in Statham and Chester (1988), and to simulate a North Sea rain event it was adjusted to a pH of 4 using 0.3M H_2SO_4.

The rain water leaching experiments are described in Section 4.5 and the results of the leaching experiments are presented in Table 5.10, in which the data are given as a percentage of the total concentrations of trace elements which are soluble in rain water at pH 4. The principal conclusions which can be drawn from these preliminary experiments are summarised below.

(1) An average of 40% of the ΣCu, 80% of the ΣZn and 74.5% of the ΣPb are soluble in the acid rain at pH 4. Losono et al., (1988) showed that in rainfall over the Western Mediterranean ~85 - 95% of the ΣZn was in a soluble form at pH value between ~4 - 6 which is similar to ~80% of the Zn soluble in the NSA at pH 4. Chester et al., (1990) presented data that indicated that ~85% of the ΣPb in rain waters from the same region was soluble in rain waters between pH ~3.5 - 4.5, which is also similar to the ~75% of the ΣPb soluble from the NSA at pH 4. Clearly therefore the rain water solubilities of Pb and Zn from the NSA are

consistent with the data given in the literature; however, no comparable data was available for the solubility of Cu from urban-type aerosols in rain water.

(2) Both Losono et al., (1988), for Zn, and Chester et al., (1990), for Pb, showed that the solubilities of the trace elements into rain waters was a pH dependant process, and the solubilities fell off to very low levels, <20% of their total concentrations, at pH values > ~5 - ~6. At pH values lower than this, such as pH 4 used in the present work, the percentage of the ΣZn ~80%, and the ΣPb ~60% are very much higher.

(a) Approximately the same amount of the ΣCu is soluble in both rain water (44%) and sea water (~40%), and

(b) Slightly less of the ΣZn is soluble in rain water (70.5%) than in sea water (60%).

However, overall, sea water appears to be generally as effective a leaching agent for trace elements from aerosols as rain water, with the result that Cu, Zn and Pb from aerosols will not be greatly affected by the mode, i.e. wet or dry, of deposition of an aerosol to the North Sea surface. It must be stressed, however, that this is a very tentative conclusion and considerably more data is required before it can be verified.

6.8 The Deposition Fluxes Atmospheric Particulates to the North Sea.

Although short term elemental concentrations of atmospheric particulates over the North Sea do exist, on a long term basis, the elemental aerosol concentrations are fairly homogeneous (Pierson et al., 1973; Deudeurwarder, 1988; Bayenes and Deudeurwarder 1990a). However, as a result of these short term variations in elemental concentrations, calculations of deposition fluxes to the North Sea may also show short term variations, rendering the quantification of the annual atmospheric input very difficult.

In its simplest form the equation for the calculation of the dry deposition flux to the North Sea may be expressed by an equation of the type;

$$F = C \cdot V_d \qquad \text{Equation 6.1}$$

Where; F = the dry deposition flux.

C = the particulate atmospheric concentration (ng m^{-3} of air).

V_d = the dry deposition velocity of the trace element (cm s^{-1}).

Buart-Menard and Chesselet (1979) used the equation;

$$F_1 = C_1 \cdot V_d \qquad \text{Equation 6.2}$$

to calculate the total deposition flux of trace elements from the atmosphere to the equatorial North Atlantic. To make the calculation the authors used the mean atmospheric concentration of the trace elements in the lower troposphere for the C_1 term in units of ng m^{-3} of air, and assigned a global deposition velocity of 1 cm s^{-1} for all the trace elements. The flux units were expressed as ng cm^2 yr^{-1}, and for this purpose Equation 6.2 became;

$$F_1 = C_1 \, . \, V_1 \, . \, 31.5 \qquad \text{Equation 6.3}$$

van Aalst et al., (1982) used a similar type of equation to calculate the dry deposition flux of elements to the sea surface. However, instead of giving the flux in terms of ng cm^{-2}, they used tons and adjusted the data in terms of the surface of the North Sea (525 000 Km^2). The equation thus became;

$$F = C \, . \, V_d . \, 165 \qquad \text{Equation 6.4}$$

where; F = the flux in ton yr^{-1}.

C = the concentration ng m^3 of air.

V_d = the deposition velocity in cm s^{-1}.

Unlike Buart-Menard and Chesselet (1979), van Aalst et al., (1979) used individual deposition velocities (V_d cm s^{-1}), obtained from the literature, for the various trace elements, and this approach was used in the present work. Dry deposition velocities are extremely difficult to estimate especially over the sea surface. Arimoto and Duce (1986) considered the problems involved and concluded that many models used to estimate the dry deposition of aerosols to the sea surface were inadequate because they did not include all the relevant physics, and because they could not be verified by field measurements. Problems arise in estimating dry deposition velocities because the velocities themselves are affected by a number of factors. These include; (a) differences in the transfer velocities from smooth to broken surfaces, (b) variations with wind speed, and (c) variations in the relative humidity.

Because of the difficulties involved in measuring the dry deposition velocities of atmospheric particles, a simple approach was used in the present work in which the dry deposition velocities reported by Cambray et al., (1975) were combined with the mean trace element content of the NSA and used in Equation 6.4 to give a first approximation of the dry deposition of trace elements to the North Sea surface. It must be pointed out, this approach takes no account of the presence of large particles in the NSA which may significantly affect the dry deposition velocities of some trace elements (see Ottley, 1991).

The dry deposition velocities and the mean trace element content of the NSA used in calculating the dry deposition velocities are given in Table 6.19, and the deposition fluxes are listed in Table 6.20. These preliminary deposition fluxes can be assessed under a number of headings;

(1) Comparison with other dry deposition fluxes to the North Sea.

A number of authors have given data on the dry deposition fluxes of trace elements to the North Sea, and a selection of these are given in Table 6.20. Most of the dry deposition fluxes listed in Table 6.20 have been derived from aerosol data collected on landmasses surrounding the North Sea, but they offer the only available data base to which fluxes obtained in the present study can be compared. From the data in Table 6.20 it is apparent that the dry deposition fluxes estimated in the present study for all the trace elements lie within the ranges found by the other workers, with the exception of the data obtained by Otten et al., (1989) which are considerably lower than any of the other values.

(2) Soluble and particulate fractions of the deposition flux.

The dry deposition flux to the North Sea obtained in the present study can be partitioned for some trace elements to yield a 'soluble' and a 'particulate' fraction on the basis of sea water solubility of trace element data taken from Section 6.7.2. Data for the trace element sea water solubility are given in Table 6.21, and may be summarised as follows. (a) for Al and Fe, the soluble fluxes are <10% of the total dry fluxes, (b) for Cu, the soluble fluxes are ~40% of the total dry flux, (c) for Pb, the soluble flux are ~59% of the total dry flux, and (d) for Zn, the soluble flux are ~81% of the total dry flux. Thus, following the dry deposition of the NSA to the sea surface Al and Fe remain mainly with the particulate phase.

Table 6.19 The dry deposition velocities V_d^* and the trace element concentrations used to calculate the Dry flux to the North Sea.

Element	Mean Conc.[1]	V_d cm s^{-1}
Al	294.5	1.7
Fe	353	1.3
Mn	14.5	0.56
Ni	3.8	2.1
Cr	4.7	0.54
Cu	6.3	1.19
Zn	41	0.56
Pb	34.5	0.41

* mean values taken from Cambray et al., (1975).

[1] mean values taken from Table 6.1.

Table 6.20 Dry deposition fluxes of trace elements to the North Sea; units, t yr^{-1} to the North Sea.

Trace Element	Present Study[1]	Van Aalst et al.(1982)[2]	Cawse (1972-1977)[3]	Otten et al.(1984)[4]
Al	82607	-	22050 - 220500	-
Fe	75748	-	24675 - 194250	5250
Mn	1340	-	578 - 7350	-
Ni	1317	16 - 800	<1600 - 2600	-
Cr	419	8 - 800	<42 - 1323	-
Cu	1247	<800 - 4000	<500 - 9000	284
Zn	3788	1600 - 16000	1500 - 35000	2415
Pb	2334	330 - 3300	<3000 - 9384	1155

[1] Dry deposition flux calculated from mean particulate trace element loadings over southern North Sea using Equation 6.4 (see text).

[2] Dry deposition flux calculated from various mean particulate trace element loading data sets around the North Sea using Equation 6.4 (see text).

[3] Dry deposition flux calculated from deposition to filter paper surface; data for stations at Styrrup, Leiston and Collafirth around the North Sea.

[4] Dry deposition flux calculated from data obtained from aeroplane collections using a dry deposition velocity of 0.2 cm s^{-1}; equation not specified.

However, Pb and Zn are both strongly partitioned in the soluble phases and so enter the dissolved trace element pool, although they may be subsequently removed onto particulate matter together with dissolved forms of the trace elements from other sources.

(3) Comparison between dry and total deposition fluxes to the North Sea.

Total deposition fluxes (i.e. wet + dry) for the North Sea have been estimated by a number of authors, and a summary of these data is given in Table 6.22. From the data in Table 6.22, it is apparent that there is a wide range of at least one order of magnitude, in the total deposition fluxes of all the trace elements which is similar to the ranges found for the dry deposition fluxes (see Table 6.20). Because of this wide range in the total fluxes of the trace elements it is difficult to assess the importance of the dry, relative, to the total fluxes. By comparing a number of estimates for dry and wet deposition, van Aalst et al, (1982) concluded that for Cr, Ni, Cu, Zn and Pb the dry fluxes were lower than the total fluxes; i.e. wet deposition make at least some contribution to the total fluxes of all these trace elements. Further, Cawse (1974) reported that the contribution made by the dry fluxes to the total fluxes for trace elements at Styrup and Leiston, two sites around the North Sea, were as follows (data given as %age dry of total flux); Al (5% - 35%), Fe(25% - 59%), Mn (17% - 33%), Ni (71% - 91%), Cr (12% - 56%), Cu (<20% - <56%), Zn (4.5% - 100%), and Pb (38% - 57%), Thus, the

Table 6.21 Partitioning of the dry deposition of trace elements to the North Sea with soluble and particulate fractions; units, t yr^{-1}.

Trace element	Total dry deposition flux[1]	% soluble in sea water from NSA[2]	Dry deposition soluble flux	Dry deposition particulate flux
Al	82,607	4.5	3717	78,890
Fe	75,748	8	6060	69,688
Cu	1,247	40	499	748
Zn	3788	81	3068	720
Pb	2334	59	1377	957

[1] Present study, data from Table 6.20
[2] Present study, data from Table 6.18

Table 6.22 Total dry deposition fluxes of trace elements to the North Sea; units, t yr^{-1}

Trace element	Total deposition flux[1]	Dry deposition flux[2]
Al	84000 - 4200000	82607
Fe	68250 - 761250	75748
Mn	3045 - 22050	1340
Ni	360 - 3600	1317
Cr	70 - 1400	419
Cu	1400 - 10000	1247
Zn	7200 - 58000	3788
Pb	3600 - 13000	2334

[1] Data range from various studies and computed by Van Aalst et al., (1982) for Ni, Cr, Cu, Zn and Pb. Data range from Cawse (1972) for Al and Fe.

[2] Present study, data from Table 6.20.

contribution to the total flux by the dry flux for the various trace elements, as reported by Cawse (1974) also show wide variations. In view of variations such as these, and because total fluxes were not determined as part of the present study, the only conclusion that can be drawn from the various data with any certainty is that for all the trace elements the dry deposition fluxes estimated from the present work are lower than the highest values given for the total deposition fluxes.

(4) Comparison between the atmospheric dry deposition and other fluxes to the North Sea.

The input of trace elements to the North Sea occurs via a number of routes, and according to van Aalst et al, (1982) the most important of these are atmospheric transport, fluvial run-off, dumping and various other discharges. The authors complied a data set on the magnitudes of these various fluxes for a series of trace elements, and this is given in Table 6.23. The mean dry atmospheric flux to the North Sea calculated in the present work is also listed in this table, together with contributions made by the dry atmospheric flux expressed as percentages of (a) the fluvial flux, and (b) the total non-atmospheric flux.

(a) For Ni and Pb, the dry atmospheric flux is almost equal to the fluvial flux, and for Cu it is 78% of the fluvial input. For Cr and Zn, however, the dry atmospheric flux is only ~20% of the fluvial flux.

Table 6.23 Comparison of the input fluxes of trace elements to the North Sea; units, t. yr^{-1}.

Trace element	Fluvial input[1]	Dumping[1]	Discharge[1]	Total; non-atmospheric fluxes[1]	Dry atmospheric flux[2]	Dry atmospheric flux as a %age of	
						fluvial input	tot. non atmos. inputs
Cr	1900	60	1800	3760	419	22	11
Ni	1430	10	560	2000	1317	92	65
Cu	1600	100	2300	4000	1247	78	31
Zn	16,500	900	5700	23,100	3788	23	16
Pb	2400	300	2200	4900	2334	97	48

[1] Data from van Aalst et al., (1982).

[2] Present study - data from Table 6.20

(b) For Ni (66%) and Pb (48%), the dry atmospheric flux is equal in magnitude to around half of the total non-atmospheric flux. However, for Cu the dry atmospheric flux is only ~30% of the total non-atmospheric flux, and for Cr and Zn it is < ~15%.

Despite the crude nature of these flux estimates it would appear that for Ni, Pb and Cu, the dry atmospheric fluxes alone are equivalent to > ~75% of their fluvial fluxes. This general conclusion is in broad agreement with the findings reached by other workers. For example, Cambray et al., (1975) estimated that the total atmospheric flux Ni, Cu, Zn and Pb to the North Sea exceeded the fluvial flux. In another study, Norton (1982) concluded that the total atmospheric fluxes of Cu and Pb to the North Sea exceeded the fluvial fluxes, and that for Ni the two fluxes were about the same. For Zn and Cr, however, Norton (1982) estimated that the total atmospheric flux was ~80% and ~48% of the fluvial flux, respectively.

(5) Geographical variations in flux inputs to the North Sea.

The fluxes discussed above have been assumed to be spread over the whole area of the North Sea, and there are two principal flaws in adopting this approach. These are described as follows;

(a) The dry atmospheric flux. It was shown in Section 6.2 that the geographical variations in the distributions of particulate trace elements over the North Sea, are constrained mainly by the aerosol source regions over which the winds transporting the particulates have passed. With respect to the strength of the source regions it was pointed out that there is a general south - north decrease in the surrounding land masses along the length of the North Sea. This trend can be perturbed however, since winds crossing any source sector can be transported to any region of the North Sea. Although, it may be that the overall south - north decrease in the 'source release' of particulate trace elements results in a time-averaged north > south decrease in the concentrations of particulate trace elements in the North Sea atmosphere. Even if this is not the case, the wind regime may result in individual areas of the North Sea receiving more air masses from one source region than from another. The overall result of these factors may mean that the time-averaged concentrations of particulate trace elements varies over different parts of the North Sea, so that the mean atmospheric fluxes cannot be applied to all the North Sea surface. At present, this forms part of an on-going study at Liverpool.

(b) The fluvial flux. Much of the particulate material transported by rivers is trapped in estuaries. Further, the particulate material that escapes, together with the dissolved components, enter a current system which in some places confines the river inputs. For example, inputs into the German Bight are generally contained within the area governed by the current regime. The fact that river inputs are not distributed evenly around the North Sea has been confirmed by a recent study on nutrients carried out as part of the NERC North Sea Programme. The nutrient maps produced by Hydes and Edmunds (1989) show several examples of the manner in which nutrients, including those from river inputs are confined largely to coastal regions of the North Sea. This type of contouring of river input with major effects being felt in coastal regions, means that in open-ocean areas the inputs of trace elements via atmospheric transport may be more important than would be suggested from an overall comparison of atmospheric and fluvial fluxes, in which it implicitly assumed that both fluxes are evenly distributed around the North Sea.

In the current chapter the results of the North Sea Project (aerosol studies) have been presented. In the next Chapter conclusions and suggestions for further work are presented.

Chapter 7

Conclusions and Suggestions for Further Work.

7.1 Conclusions.

(1) Aerosols were collected by a hi-vol sampling technique from the lower atmosphere of the southern North Sea over a period of ~15 months as part of the NERC North Sea Programme.

(2) Atomic adsorption analyses were carried out on the aerosols for Al, Fe, Mn, Ni, Cr, Cu, Zn, Pb and Cd, and these provided the first base-line data set for the concentrations of particulate atmospheric trace elements over the North Sea itself.

(3) On a time-averaged basis, a mean trace element concentration was established for the southern North Sea. This mean concentration agreed well with other recent estimates for the NSA obtained from collections on the surrounding land masses.

(4) On a day-to-day basis, there were considerable variations in the concentrations of the particulate trace elements in both space and time. Using air mass back trajectories it was shown that the major control on the trace element concentrations in the North Sea atmosphere is the source area form which the winds transporting the aerosols originate. On the basis of the air mass back trajectories, the aerosols over the North Sea were sub-

divided into those which had their principal trace element sources in; (a) the UK, (b) Continental Europe, and (c) the open-sea.

(5) Rainfall scavenging exerts a control on the concentrations of particulate trace elements in the atmosphere. To evaluate the importance of this control, the UK MO supplied a predictive rainfall model for the North Sea and surrounding land masses. However, when this was used in conjunction with the air mass back trajectories it did not provide useful data on the extent to which the particulate trace elements were affected by rainfall.

(6) Enrichment factors were employed to further characterise the sources of the trace elements in the NSA - i.e. NEEs and AEEs. It was shown that the AEEs did not have a significant sea surface source over the North Sea, and they were assumed to have an anthropogenic source.

(7) The trace element source relationships were confirmed using two other techniques, (a) size-fractionated aerosols were collected using a CI, and the data showed that the AEEs Cu, Zn, Pb and Cd had their highest concentrations on particles with MMDs of ~0.67 μm; this is characteristic of high temperature, urban-generated, trace elements, (b) Solid state speciation analysis demonstrated that the AEEs Cu, Zn Pb and Cd had > ~70% of their total concentrations associated with exchangeable hosts in the aerosols; this is typical of urban-derived aerosol populations.

(8) In order to assess the fates of the trace elements following the deposition of the aerosols to the sea

surface, a series of experiments were carried out to establish the solubilities of Al, Fe, Cu, Pb and Zn, in sea water and rain water. The data could be related to the solid state speciation of the trace elements and showed that under the 'dry' deposition mode; (a) Only relatively small percentages of the total Al and Fe are soluble in sea water, but that (b) ~40% of the ΣCu, ~81% of the ΣZn, and ~59% of the ΣPb are soluble in sea water and thus enter the dissolved trace element pool in the mixed layer, Preliminary data also showed that approximately similar percentages of the ΣCu, the ΣZn and the ΣPb were soluble in rain water having the pH expected for that over the North Sea.

(9) Very simple models were used to make a first approximation of the fluxes of the trace elements deposited to the surface of the North Sea via the dry deposition mode, and these were adjusted to evaluate the soluble fluxes; i.e. those entering the dissolved trace element pool.

7.2 Suggestions for Future Work.

During this study of the NSA an attempt was made to provide information on a wide range of trace element parameters. Because the study was designed to include a relatively large number of samples, some aspects of the trace element chemistry could only be treated in a preliminary manner. For future work, it is suggested that more attention should be paid to the following.

(1) The rainfall scavenging control on the concentrations of particulate trace elements over the North Sea. Rainfall data for the North Sea and surrounding regions should be made available in a more reliable form than that provided by the current rainfall model. This should then be related to air mass back trajectories to evaluate the effects of rainfall scavenging on the concentrations of trace elements transported into the North Sea.

(2) More detailed laboratory experiments should be carried out on the particulate/dissolved reactions which affect aerosol trace elements in rain water.

(3a) The collection of hi-vol aerosol samples should be taken simultaneously at fixed locations (1) over the North Sea, and (2) over the landmasses surrounding the North Sea. This would give a more accurate estimation of differences in trace element concentrations depending upon the location over the North Sea, i.e. samples taken from the same air mass at different locations over the North Sea could be compared. Further, these collections should also be 'partnered' with accurate meterological information on (1) rainfall quantity and direction, and (2) air mass direction. Therefore, when;

(a) Rainfall occurs between the source region of an aerosol and the collector, sampling can be stopped (This would give an indication of the concentrations of trace elements involved in the 'dry' deposition flux to the North Sea). Sampling for a short time immediately after the rainfall event and measuring the drop in atmospheric concentration of trace elements, and combining this with rainfall concentration data will give an idea of the 'wet' deposition flux.

(b) When a change of air mass direction occurs the sampling can be stopped and a fresh sample collected. This would give a grater quantity of samples in the UK, EU and OS categories.

(3b) The fluxes of particulate trace metals to the surface of the North Sea should be investigated in more detail (imposing the above controls 3a), and models should be devised to evaluate variations in the fluxes at different locations over the North Sea. Such a study is at present being carried out in the laboratories at Liverpool as an extension of the NERC North Sea Programme. As part of this study, air mass back trajectories are being used to establish the extent to which specific locations in the North Sea are subjected to winds which have crossed trace element source regions in the UK, continental EU and the OS. Aerosols from each of these source regions will then be assigned the average trace element concentrations found in the present study, and trace element fluxes to the North Sea will then be modelled on a regional basis.

(4) The data set from the present study should be combined with those obtained by other workers in the NERC North Sea Programme to make a more detailed assessment of the factors which control the sources, concentrations, fluxes and fates of trace elements in the North Sea atmosphere☺

BIBLIOGRAPHY

Adams, F. van Craen, M., van Espen, P. and Andreuzzi, D. (1980). The elemental composition of atmospheric aerosol particles at Chacaltaya, Bolivia. Atmos. Environ. V14, pp 879-893.

Arimoto, R. and Duce, R.A. (1986). Dry deposition models and the air/sea exchange of trace elements. J. Geophys. Res. V91(D2), pp 2787-2792.

Arimoto, R. and Duce, R.A. (1987). Air sea transfer of trace elements. Advances in Chemistry series, No 216, Sources and fates of aquatic pollutants. Editors R. A. Hits and S. J. Eisenreich. American Chem. Soc.1987.

Arimoto, R. and Duce, R.A., Ray, and Unni, C. K. (1985). Atmospheric trace elements at Enewetak Atoll: transport to the ocean by wet and dry deposition. J. Geophys. Res. V90, pp 2391-2408.

Arimoto, R. and Duce, R.A., Ray, B. J., Hewitt, A. D. and Williams, J. (1987). Trace elements in the atmosphere of American Samoa: concentrations and deposition to the South Pacific. J. Geophys. Res. V92, pp 8465-8479.

Bailey, N. T. J. (1959). Statistical methods in biology. English Universities Press, London.

Barbaray, B., Contour, J., Mouvier, G., Barde, R., Maffiolo, G. and Millancourt, B. (1979). Chemical heterogeneity of aerosol samples as revealed by atomic absorption spectrophotometry. *Environ. Sci. Technol. V13, pp1530-1532.*

Barry, R. G. and Chorley, R. J. (1982). *Atmosphere, weather and climate, fourth edition, Metheun, London.*

Bayens, W. and Dedeurwaerder, H. (1990). Particulate trace metals above the southern Bight of the North Sea; Origin and behaviour of the trace metals. *Atmos. Environ. V25A, pp1077-1092.*

Bayens, W. and Dedeurwaerder, H. (1991). Particulate trace metals above the southern Bight of the North Sea; Origin and behaviour of the trace metals. *Atmos. Environ. V25A, pp1077-1092.*

Berry, A. (1990). *Ph.D Thesis, University of Liverpool, UK.*

Berg, W. W. and Winchester, J. W. (1978). Aerosol chemistry of the atmosphere. *In Chemical Oceanography, Vol. 7, edited by J. P. Riley and R. Chester. Academic Press.*

Brimblecombe, P. (1986). Air composition and chemistry. *Cambridge Environmental Chemistry Series, edited by R. M.*

Harrison, G. R. Heltz and P. Liss. Published by Cambridge University Press.

Buart-Menard, P. (1983). Particle geochemistry in the atmosphere and oceans. In air-sea exchange of gases and particles, editors P. S. Liss and W. G. N. Slinn, pp 455-532. Dordrecht: Reidel.

Buart-Menard, P. and Chesselet, R. (1979). Variable influence of the atmospheric flux on the trace metal chemistry of the oceanic suspended matter. Earth Planet. Sci. Lett. V42, pp399-411.

Cambray, R. S., Jefferies, D. F. and Topping, G. (1975). An estimate of the input of atmospheric trace elements into the North Sea and the Clyde Sea (1972-1973). UK Atomic Energy Authority, Harwell, Rep. AERE-R7733.

Cawse, P. A. (1974). A survey of atmospheric trace elements in the UK. (1972-1973). AERE Harwell Report R7769, UKAEA, HMSO, London.

Chan, T. L. and Lawson, D. R. (1981). Characetristics of cascade impactors in size determination of diesel particles. Atmos. Envirom. V15, pp1237-1279.

Chester, R. (1990). Marine Geochemistry. Publi. Unwin and Hyman Ltd. London.

Chester, R. and Bradshaw, G. (1991). Source Control on the Distribution of Particulate Trace Metals in the North Sea Atmosphere. Marine Pollution Bulletin, V22, No1, pp30-36.

Chester, R. and Murphy, K.J.T. (1988). Metals in the marine atmosphere. In Heavy metals in the marine environment, editors R. Furness and P. Rainbow. Boca Raton, Florida: CRC Press.

Chester, R. and Murphy, K.J.T. (1990). Metals in the marine aerosol. In Heavy metals in the marine environment, edited by R. Furness and P. Rainbow. Boca Raton, Florida: CRC Press.

Chester, R., Lin, F. J. and Murphy, K.J.T. (1988). A scheme for the determination of elemental speciation in filter-collected aerosols. In press.

Chester, R., Lin, F. J. and Murphy, K. J. T. (1989). A three stage sequential leaching scheme for the characterisation of the sources and environmental mobility of trace metals in the marine aerosol. Environ. Tech. Lett. V10, pp887-900.

Chester, R., Murphy, K.J.T. Lin, F.J., Berry A.S. and Bradshaw G.F. (1991). Factors controlling the solubilities of trace metals from aerosols deposited to the sea surface by the 'dry' deposition mode. In Press.

Chester, R., Murphy, K.J.T. and Thomas, A. (1986). The partitioning of elements in crust dominated aerosols. Chem. Geol. V54, pp 1-15.

Crecelius, E. A. (1980). The solubility of coal fly ash and marine aerosols in sea water. Mar. Chem. V8, pp245-250.

Cushing, K. M., M^{c}Cain, J. D., and Smith, W. B. (1979). Experimental determinations of sizing parameters and wall loses of five source-test cascade impactors. Environ. Sci. Technol. V13, pp726-731.

Dams, R., Billiet, J., Black, C., Demuynck, M. and Janssens, M. (1975). Complete chemical analysis of airborne particles. Atmos. Environ. V9, pp1099-1106.

Davies, T.D. and Nicholson, K.W. (1982). Dry deposition velocities of aerosol sulphate in rural eastern England. In Dry deposition of atmospheric pollutants. Edited by H.W. Georgii and J. Pankrath. Reidel Publishing Co., Holand, pp31-42.

Davies, T. D., Farmer, G. and Barthelmie, R. J. (1990). Use of simple daily atmospheric circulation types for the interpretation of precipitation at a site (Eskdalemuir) in Scotland, 1978-1984. Atmos. Environ. V24A, pp63-72.

Davies, T. D., Kelly, P. M., Brimblecombe, P., Farmer, G. and Barthelmie, R. J. (1986). Acidity of scottish rainfall influenced by climate change. Nature V322, pp359-361.

Davidson, C. I. and Osborne, J. F. (1986). The sizes of airborne trace metal containing particles. Adv. Environ. Sci. Technol. V17, pp355-389.

Dedeurwaerder, H. L. (1988). Study of the dynamic transport of the fallout of some ecotoxicallogical heavy material in the troposphere of the southern bight of the North Sea. PhD thesis University of Brussels, 1988.

Dehairs, F. Deudeuwerder, H. Decadt, G. G. and Baeyens, W. (1983). Estimation of dry and wet deposition and resuspension fluxes of several trace metals in the southern bight of the North Sea. From Elsevier Science Publishing Co. Inc., Precipitation scavenging, dry deposition and resuspension. Pruppacher etd. Editors pp 119-1132.

Duce, R.A., Arimoto, R., Ray, B. J., Unni, C. K. and Harder, P. J. (1983). Atmospheric trace elements at Enewetak Atoll: 1, concentration, sources and temporal variability. J. Geophys. Res. V88, pp 5321-5342.

Duce, R.A., Unni, C. K., Ray, B. J., Prospero, J.M. and Merrill, T. T. (1980). Long range atmospheric transport of soil dust from Asia to the tropical North Pacific, temporal variability. Science V20, pp 1522-1524.

Duce, R. A., Ray, B. J., Hoffman, G. L. and Walsh, P. R. (1976a). Trace metal concentration as a function of particle size in marine aerosols from Bermuda. Geophys. Res. Lett. V3, pp339-342.

Dulac, F., Buart-Menard, P., Arnold, M., Ezat, U. and Martin, D. (1987). Atmospheric input of trace metals to the Western Mediterranean Sea; Factors controlling the variability of atmospheric concentrations. J. Geophys. Res. V92, pp8437-8453.

Dulac, F., Buart-Menard, P., Ezat, U., Melki, S. and Bergametti, G. (1989). Atmospheric input of trace metals to the western Meditarreanaen; uncertainties in modellind dry deposition from cascade impactor data. Tellus, V41B, pp362-378.

Duffus, J. H. (1980). Pollution Environmental Toxicology. Edward Arnold.

ERL. (1983). Acid rain, a review of the phenomenons in the EEC and Europe. A report prepared for the commission of the European Community. Environmental Resources Ltd., published by Grahmn and Trotman.

Fasching, J. l., Courant, R. A., Duce, R. A. and Piotrowiez, S. R. (1974). A new surface microlayer utilising the bubble microtome. J. Rech. Atmos. V8, 649-652.

Flanagan, F. J. (1973). 1972 values for international geochemical reference samples. Geochim. et Cosmochim. Acta, V37, pp1189-1200.

Goldberg, E. D. (1976) Rock volatility and aerosol composition. In Nature V260, pp128-129.

Greenberg, R. R., Zoller, W. H. and Gordon, G. E. (1978). Composition and size distributions of particles released in refuse incineration. Environ. Lett. V10, pp 129-158.

Hardy, J. T. and Crecelius, E. A. (1981). Is atmospheric particulate matter inhibiting marine primary productivity? Environ. Sci. Tech. V15, pp1103-1105.

Harrison, R. M. (1987). In correspondance. Atmos. Environ. V21, pp2734-2735.

Harrison and Perry (1986). Handbook of air pollution analysis. 2nd edition. Publishing Co. Chapman and Hall, London.

Harrison, R. M. and Williams, C. R. (1982). Airborne Cadmium, Lead and Zinc at rural and urban sites in North-West England. Atmos. Environ. V16, pp2669-2681.

Hasse, L. (1983). Introductory meteorology and fluid mechanics. In Air-sea exchange of gases and particles, editors P.S. Liss and W. G. N. Slinn, 1-51. Dordrecht: Reidel.

Hochrainer, D. (1978). Physical behavoiur and sampling of airborne particles. In Analysis of Airborne Particles by Physical Methods. Editor Mallisa, H, CRC, Press.

Hodge, V., Johnson, S. R. and Goldberg, E. D. (1978). Influence of atmospherically transported aerosols on surface ocean water composition. Geochem. J. V12, pp 7-20.

Höhn, R. On the climatology of the North Sea (1971). North Sea Science, NATO North Sea science conference Aviemore, Scotland, pp 15-20 November 1971. Editor Goldberg, E. D.

Hopke, W. Lanson, R. and Vietti, M. (1984). Aerosol size distribution at a site on the east coast of the United States. Atmos. Environ. V18 pp 1613-1621.

Hudrey, S. E. (1977). General sampling techniques. In Handbook of air pollution analysis, 2nd edition, Publishing Co. Chapman and Hall, London.

Hunt, C. B. (1972). Geology of soils: Their evolution, classification, and uses. Publ. W. H. Freeman and Co., San Francisco.

Hydes and Edmonds (1989). Qualitive assessment of nutrient measurements September 1988 - August 1989. IOS Deacon Laboratory UK. Report NO. 269 (1989).

ICES. International Council for the Exploration of the Sea, V39.

Junge, C. E. (1963). Air Chemistry and Radiactivity. Academic Press. New York.

Kitto, M. E. and Anderson, D. L. (1988). The use of Whatman 41 filters for particle collection. Corrospondance. Atmos. Environ. V22. pp2629-2630.

Lamb, H. H. (1950). Types and spells of weather around the year in the British Isles; annual trends, seasonal structure of the year, singularities. Q. JL R. Met. Soc. V59. pp393-438.

Lin, F. P. (1988). Ph.D Thesis. University of Liverpool, UK.

Liu, B. Y. H. and Pui, D. Y. H. (1981). Aerosol sampling inlets and inhalable particles. Atmos. Environ. V15, pp589-600.

Lodge, J.P., Waggoner, A.P., Klodt, D. T. and Crain, C. N. (1981). Non health effects of airborne particulate matter. Atmos. Environ. V15 pp 431-482.

Lowenthal, D. H. and Rahn, K. A. (1987). Further comments on the use of Whatman 41 filter papers for high-volume aerosol sampling. In corrospondence. In Atmos. Environ. V21, p2732-2733.

Lum, K. R., Betteridge, J. S. and McDonald (1982). The potential avaliability of P, Al, Cd, Co, Cr, Fe, Mn, Ni, Pb, and Zn in urban particulate matter. Environ. Tech. Lett. V3, pp 57-62.

McDonald, C. and Duncan, H. J. (1978). Variability of atmospheric levels of metals in an industrial environment. J. Envir. Sci. Hlth. A13 pp687-695.

McDonald, R.L., Uni, C. K. and Duce, R.A. (1982). Estimation of sea salt dry deposition; wind speed and particle size dependance. J. Geophys. Res., V87, pp1246-1250.

Marggrander, E. and Flothmann, D. (1982). Dry deposition of particles: A comparison of published and experimental results with model predictions. In Dry deposition of atmospheric pollutants. Edited by H.W. Georgii and J. Pankrath. Reidel Publishing Co., Holand.

Maring, H. B. and Duce, R. A. (1987). The impact of atmospheric aerosols on the trace metal chemistry in open ocean sea water. Earth Planet. Sci. Lett. V84, pp381-392.

Martinson, B. G., Hansson, H. and Lannefors, H. (1984). Southern Scandinavian aerosol composition and elemental size distribution Characteristic dependence on air-mass history. Atmos. Environ. V18 pp 2167-2182.

Miller, J. M. and Harris, J. M. (1985). The flow climatology to Bermuda and its implications for long-range transport. Atmos. Environ. V19, pp409-419.

Moore, R. M. (1983). The relationships between the distributions of dissolved Cd, Fe and Al and hydrography in the Central Artic Ocean. In Trace metals in sea water, C.S. Wong, E. Boyle, K. W. Bruland, J. D. Burton and E. D. Goldber (eds), 131-42, New York: Plenum.

Moyers, J. L., Ranweiler, L. E., Hopf, S. B. and Korte, N. E. (1977). Evaluation of particulate trace species in southwest desert atmosphere. Envir. Sci. Technol. V11, pp789-794.

Mosher, B. W., Duce, R. A., Prospero, R. M. and Savoie, D. L. (1987). Atmospheric selenium: geographical distribution and ocean to atmosphere flux in the Pacific. J. Geophys. Res. V92, pp 13277-13287.

Murphy, K.J.T. (1985). The trace metal chemistry of the atlantic aerosol. PhD thesis University of Liverpool, 1985.

Nicholson, K.W. (1985). The dry deposition of sulphur in rural East Anglia. PhD thesis University of East Anglia, 1985.

Nicholson, K.W. (1988b). A review of particle resuspension. Atmos. Environ. V22 pp 2639-2651.

Nicholson, K.W. (1988a). The dry deposition of small particles, a review of experimental measurements. Atmos. Environ. V22 pp 2651-2666.

Norton, R. L. (1982). Assesment of pollution loads to the North Sea. WRC, Medmenham, Malow, UK. Technical Report TR182.

Nriagu, J. O. (1979). Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. Nature V279, 409-411.

Noller, B. N., Bloom, H., and Arnold, A.P. (1981). Sampling and analysis of atmospheric particulates by graphite furnace atomic absorption spectrophotometry. In Prog. Analyt. Atm. Spectros. V4, pp 81-189.

Oblad, M. and Selin, E. (1986). Measurements of elemental composition in background aerosol on the west coast of Sweden. Atmos. Environ. V20 pp 1419-1432.

Ottley, C. (1991). Ph.D Thesis, University of Essex, UK.

Otten, Ph., Rojas, C., Wouters, L. and Van Grieken, R. (1989). Atmospheric deposition of heavy metals (Cd, Cu, Pb and Zn) into the North Sea, Report 2. University of Antwerp, Dept. of Chemistry, Micro and Trace Analysis Center.

Owen, F. and Jones, R. Statistics. 3rd edition, Pitman Publishing Co.

Pacyna, J. M. (1986b). Atmospheric trace elements from natural and anthropogenic sources. In Toxic Metals in the Atmosphere, edited by J. O. Niragu and C. I. Davidson, J. Wiley series, New York.

Pacyna, J. M. (1987). Long range transport of heavy metals-modelling and measurements. Proc. 16th International NATO technical meeting on air pollution modelling and its application. Lindau, F.R.G.

Pacyna, J. M., Semb, A. and Hanssen, J. E. (1984a). Emission and long range transport of trace elements in Europe. Tellus, 36B, V3, pp 163-178.

Patterson, C., Settle, D., Schaule, B. and Burnett, M. (1976). Transfer of pollutant lead to the oceans and within the ecosystems. In Marine Pollutant Transfer; editors H. L. Windom and R. A. Duce, Heath, Lexington, Massachusetts.

Pierson, D. H., Cawse, P. A. and Cambray, R. S. (1974). Chemical uniformity of airborne particulate material, and a maritime effect. Nature, V251, pp675-679.

Piotrowicz, S. R., Duce, R.A., Fasching, J.L. and Weisel, C.P. (1979). Bursting bubbles and their rffect on the sea-to-air transport of Fe, Cu and Zn. In Mar. Chem. V7 pp 307-324.

Prospero, J. M. (1979). Mineral and sea salt aerosol concentrations in various oceanic regions. J. Geophys. Res. V84, pp752-731.

Prospero, J. M. (1981). Eolian transport to the World Ocean. In The sea, editor C. Emiliani, V7, 801-874. New York: Interscience.

Prospero, J. M., Charlson, R. W., Mohnen, V., Jeanicke, R., Delaney, A. C., Moyers, C., Zoller, W. and Rahn, K. (1983). The atmospheric aerosol system: an overview. Rev. Geophys. Space Phys. V21, 1607-1629.

Rahn, K. A. (1976). The chemical composition of the atmospheric aerosol. Tech. Rep., Grad. School Oceanogr., Univ. Rhode Is., Kingston, RI.

Rahn, K. A., Borys, R. D., Shaw, G. E., Schultz, L. and Jaenicke, R. (1979). In Saharan dust, edited by C. Morales. (Scope 14). Wiley and Sons.

Rahn, K. A., Brosset, C. Ottar, B. and Patterson, E. (1982). Black and white episodes, the chemical evolution of Eurasian air masses and the long range transport of carbon to the Arctic. In Particulate Carbon: Atmospheric life cycle. Edited by G. T. Wolff and R. L. Klimisch, Plenum Publishing Coporation (1982).

Rahn, K. A. and Lowenthal, D. H. (1984). Elemental tracers of distant regional aerosols. Science V223, pp132-139.

Rantala, R. T. T. and Loring, D. H. (1975). Multi-element analysis of silicate rocks and marine sediments by atomic absorption spectrophotometry. A. A. News. V14, pp117-120.

Reiff, J., Forbes, G., Spieksma, F. and Reynders, J. J. (1986). African dust reaching north western Europe, a case study to verify trajectory calculation. J. Clim. App. Met. V25, pp 1543-1567.

Riley, J. P. and Chester, R. (1971). Introduction to Marine Chemistry. Academic press London.

Robinson, E. and Robbins, R. D. (1971). Emissions, concentrations and fates of particulate atmospheric pollutants. Publ. 4.67, Am. Petrol. Inst., Washington, DC.

Rohbock, E. (1982). Atmospheric removal of airborne metals by wet and dry deposition. In Dry deposition of atmospheric pollutants. Edited by H.W. Georgii and J. Pankrath. Reidel Publishing Co., Holand, pp 159-171.

Salomons, W. and Forstner, U. (1984). Trace metals in the hydrocycle. Berlin, Heidelberg, New York, Tokyo: Springer-Verlag. pp349.

Sanders, G. S. (1983). Metals in marine atmospheric particlates. Ph.D. Thesis, University of Liverpool, UK.

Savoie, D. L. and Prospero, J. M. (1977). Aerosol concentration statistics for the northern tropical Atlantic. J. Geophys. Res, V82, pp5954-5964.

Saydam, A. C. (1981). The elemental chemistry of the Eastern Mediterranean atmospheric particulates. Ph.D Thesis, University of Liverpool, UK.

Schneider, B. (1987). Source characterisation for atmospheric trace metals over the Kiel Bight. Atmos. Environ. V21 pp 1275-1283.

Settle, D. M. and Patterson, C. C. (1982). Magnitudes and sources of precipitation and dry deposition fluxes of industrial and natural leads to the North Pacific at Enewetak. J. Geophys. Res. V87, pp 8857-8869.

Slavin, M. (1978). Atomic Absorption Spectroscopy. Ed. John Wiley and Sons, New York.

Slinn, W.G. (1983). Air to sea transfer of particles. In air-sea exchange of gases and particles, edited by P. S. Liss and W. G. Slinn, NATO ASI series 108 Dodrecht, Holland, Reidel Publishing, pp299-407.

Statham, P. J. and Chester, R. (1988). Dissloution of Manganese from marine atmospheric particles into sea water and rain water. Geochim. Cosmochim. Acta. V52, pp2433-2437.

Suzuki, T. and Tsunogai, T. (1988). The daily variation of aerosols of marine and continental origin with the surface air over a small island. Okushiri in the Japan Sea. Tellus, V40B, pp 42-49.

Taylor, S. R. (1964). Abundance of chemical elements in the continental crust: a new table. Geochim. Cosmochim. Acta 28, pp 1273-1285.

Till, R. (1974). Statistical methods for the earth scientist. An introduction. M^{c}Millan, Lodon.

Turner, A. C. (1979). The midlands metal survey: concentrations of 15 elements in the air around factories in Birmingham and the Black Country-part 1. Report No. LR303 (AP), Warren Spring Laboratory, U. K. Department of Industry.

van Aalst, R.M., Duyzer, J. H. and Veldt, C. (1982). Atmospheric deposition of Pb and Cd, in the southern part of the North Sea; emissions and preliminary model calculations. TNO Report 83/222, Delft.

van den Berg, C.M.G. (1984). Organic and inorganic speciation of Cu in the Irish Sea. Mar. Chem. 16, pp121 - 30.

Van Jaarsveld, J. A., Van Aalst, R. M. and Onderlinden, D. (1986). Deposition of metals from the atmosphere into the North Sea: model calculations. RIVM Report 84015002.

Wadge, A. Hutton, M., and Patterson, P. J. (1986). The concentrationa and particle size relationships of selected trace elements in fly ashes from UK coal fired power plants and refuse incinerators. The Science of the Total Environment. V54, pp 13-27.

Walsh, P.R., Duce, R.A. and Fasching, J. L. (1979a). Tropospheric arsnic over marine and continental regions. J. Geophys. Res. V84, pp 1710-1718.

Walsh, P.R., Duce, R.A. and Fasching, J. L. (1978). Considerations of the enrichment, sources and fluxes of arsenic in the troposphere. J. Geophys. Res. V84, pp 1719-1726.

Walsh, P. R. and Duce, R. A. (1976). The solubilization of anthropogenic atmospheric vanadium in sea water. Geophys. Res. Lett. V3, pp375-378.

Watts. S.F., Yaqqub, R., and Davies, T.D. (1987a). The use of Whatman W41 filter paper for high volume aerosol sampling. Atmos. Environ. V21 pp 2731-2832.

Wedberg, G. H., Chan, K. C., Cohen, B. L. and Frohliger, J. O. (1974). X-ray flourescence study of atmospheric particulates in Pittsburgh. Environ. Sci. Technol. V8, pp1090-1093.

Wedding, J. B., M^{c}Farland, A. R. and Cermak, J. E. (1977). Large particle collection characteristics of ambient aerosol samplers. In Environ. Sci. Technol. V11, pp387-390.

Weisel, C. P., Duce, R.A., Fasching, J. L. and Heaton, R. W. (1984). Estimates of the transport of trace metals from the ocean to the atmosphere. J. Geophys. Res. V89, pp 11607-11618.

Whitby, K.T. (1977). The physical characterisation of aerosols. In National Bureau of Standards special publification 464, methods and standards for environmental measurements, Proceedings of the 8th IMR symposium, September 1976, Gathersburg md, pp 165-173.

Willeke, K. and Whitby, K. (1975). Atmospheric aerosol: size distribution interpretation. J. Air Pollut. Control. Assoc. V25, pp 529-534.

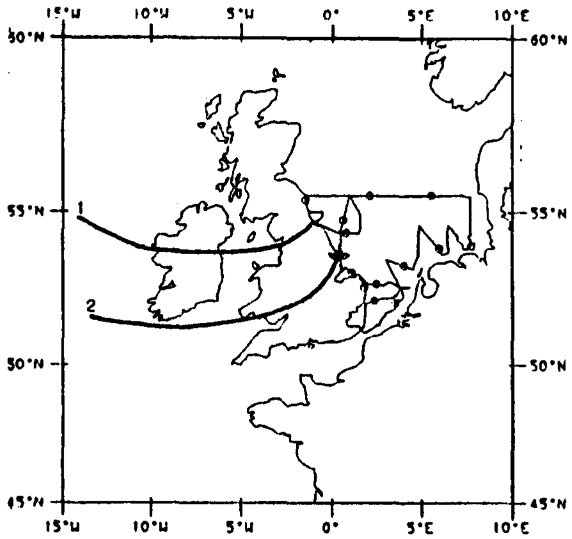
Yaqqub, R. (1989). Ph.D Thesis, University of East Anglia, Norwich, UK.

Yaqqub, R. R., Davies, T. D., Jickels, T. D. and Miller, J. M. (1991). Trace elements in daily collected aerosols at a site in southeast England. Atmos. Environ. V25A, pp985-996.

Appendix A

Air mass back trajectories for hi-vol samples over the North Sea and surrounding landmasses.

Sample 13



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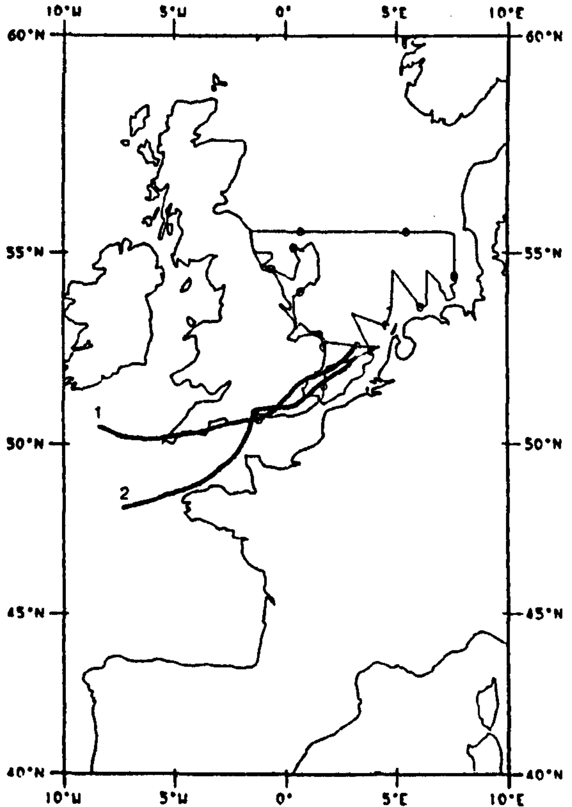
2 CR33 88 8 14 0000Z

Sample 14



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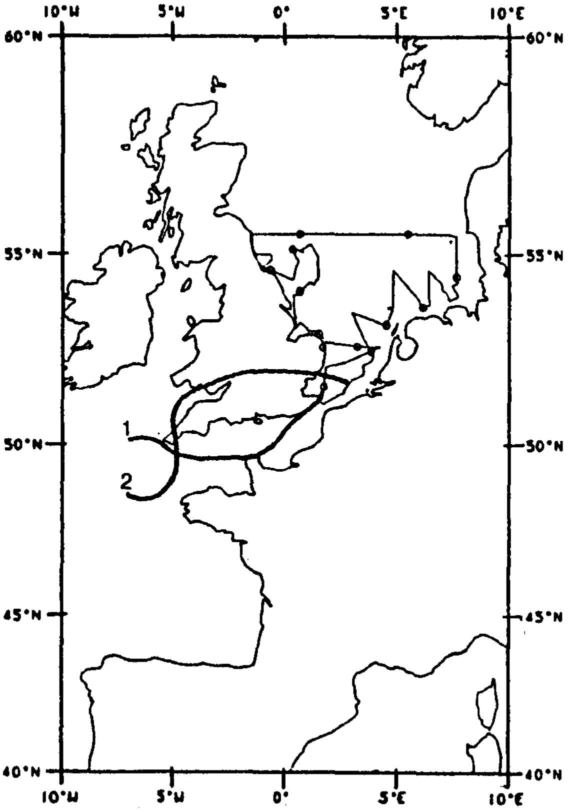
2 CR35 88 9 4 1200Z

Sample 15



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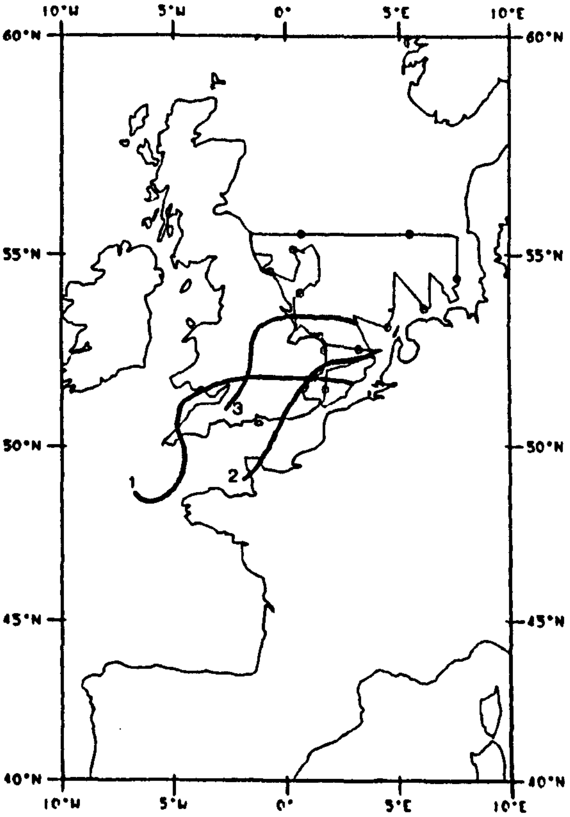
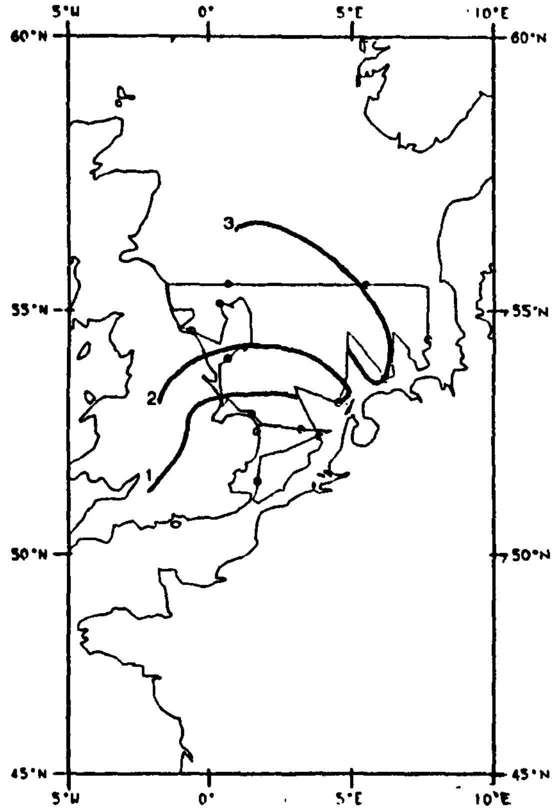
2 CR35 88 9 5 1200Z

Sample 16



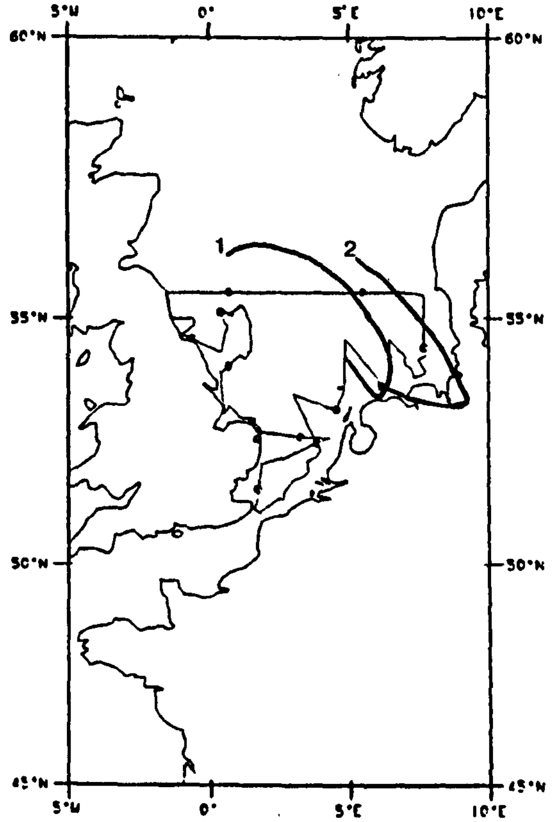
1 CR35 88 9 5 1200Z
2 CR35 88 9 6 0000Z
3 CR35 88 9 6 1200Z

Sample 17



1 CR35 88 9 6 1200Z
2 CR35 88 9 7 0000Z
3 CR35 88 9 7 1200Z

Sample 18



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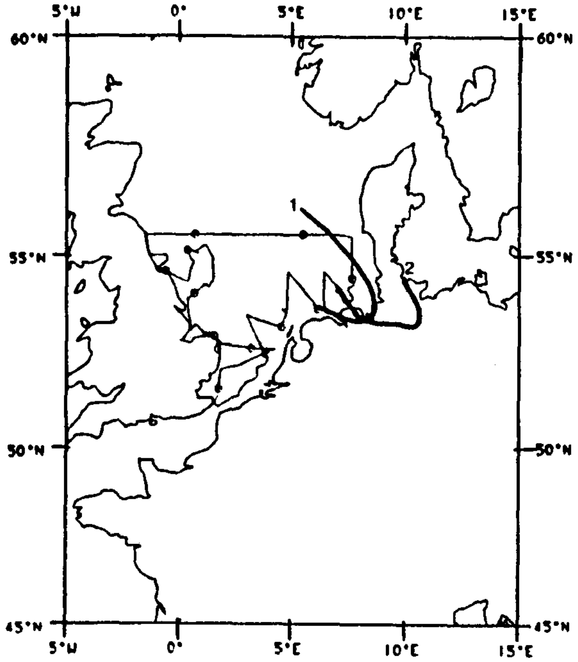
2 CR35 88 9 8 0000Z

Sample 19



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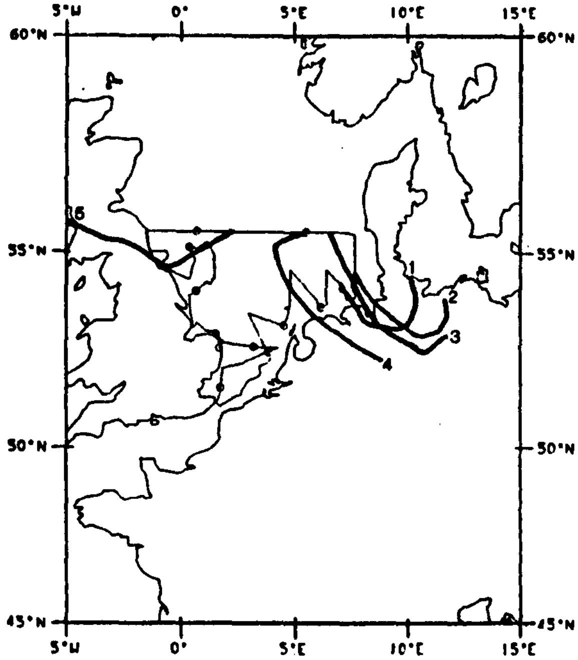
2 CR35 88 9 8 1200Z

Sample 20



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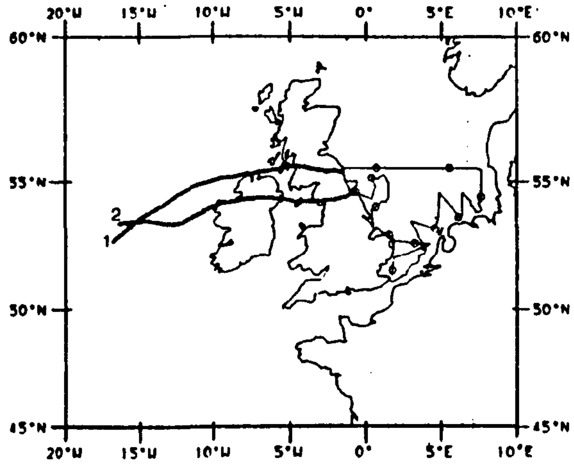
2 CR35 88 9 9 0000Z
3 CR35 88 9 9 1200Z
4 CR35 88 9 10 0000Z
5 CR35 88 9 10 1200Z

Sample 21



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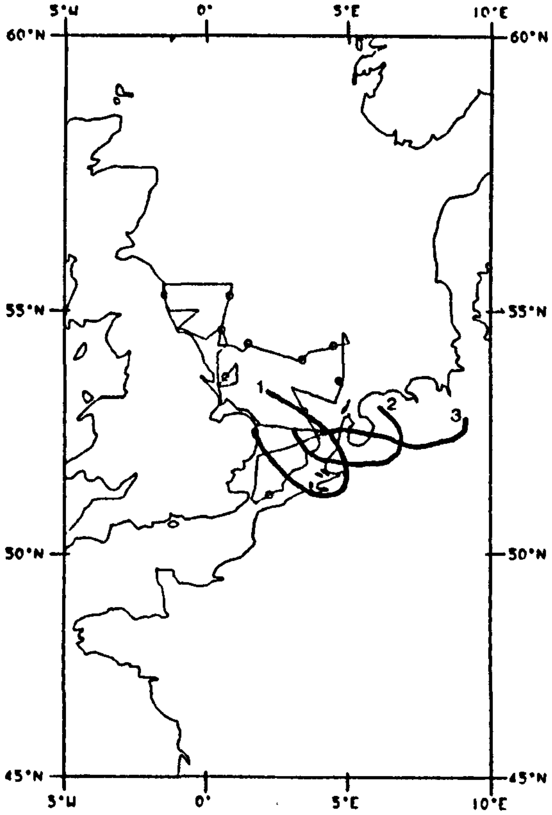
2 CR35 88 9 12 0000Z

Sample 22



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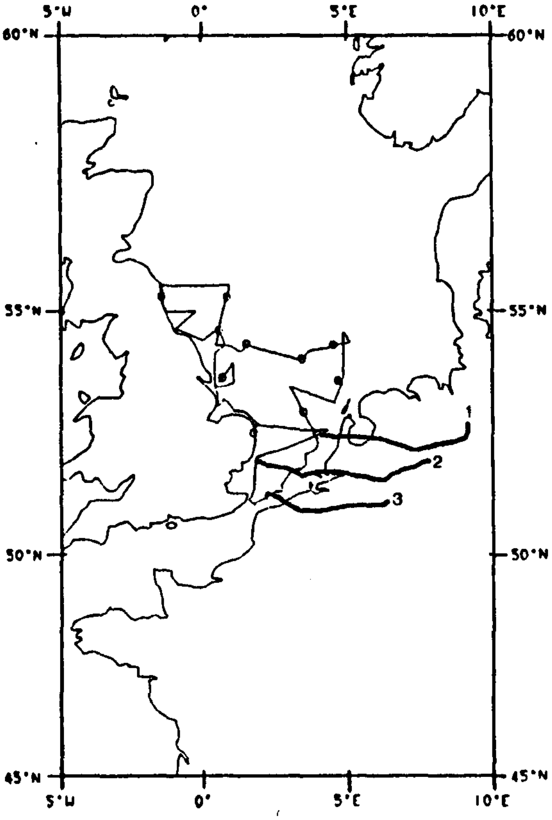
3 CR37 88 10 3 0000Z

Sample 23



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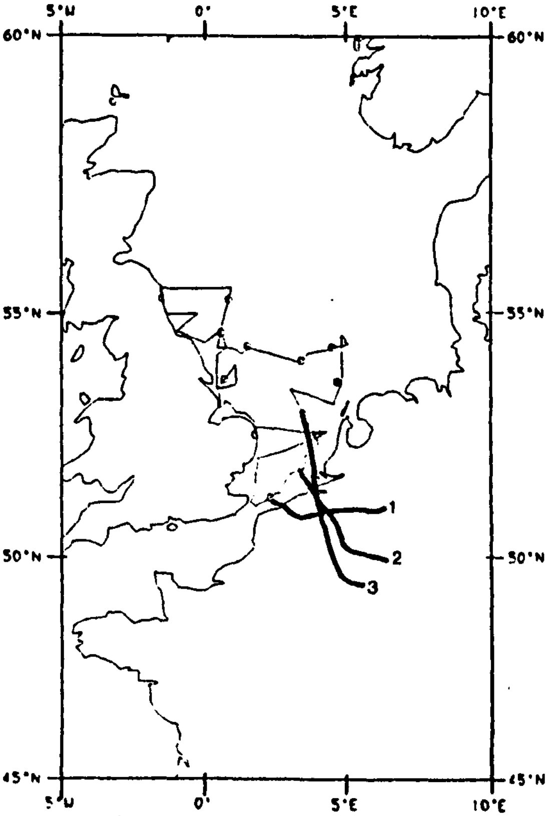
Sample 24



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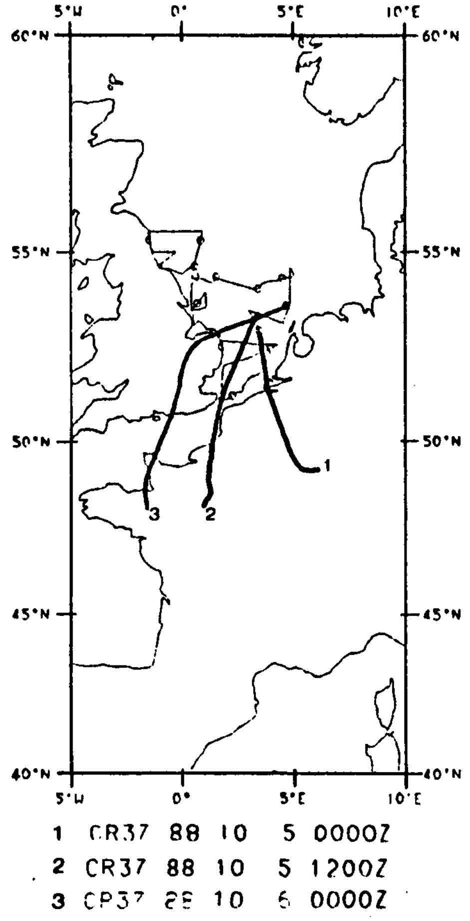
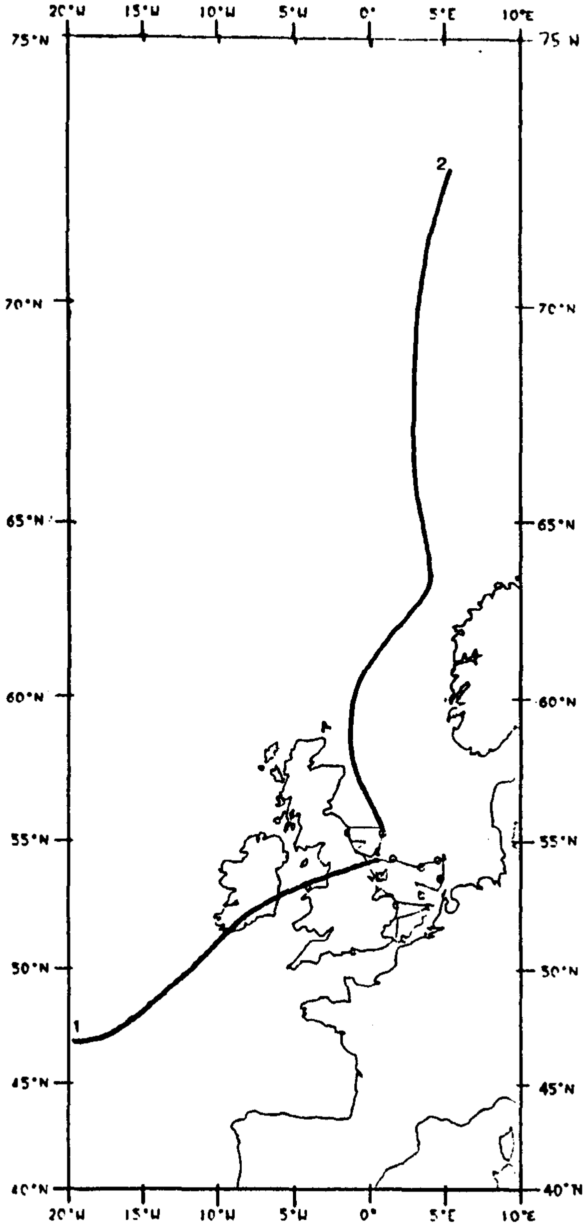
2 CR37 88 10 4 1200Z
3 CR37 88 10 5 0000Z

Sample 25


5°W
0°
5°E
10°E
60°N
55°N
50°N
45°N
40°N
1
2
3
1 CR37 88 10 5 0000Z
2 CR37 88 10 5 1200Z
3 CR37 88 10 6 0000Z

Sample 26



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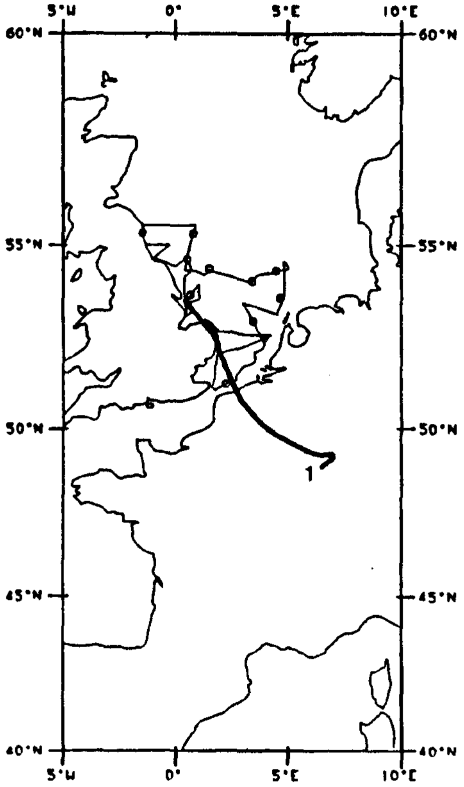
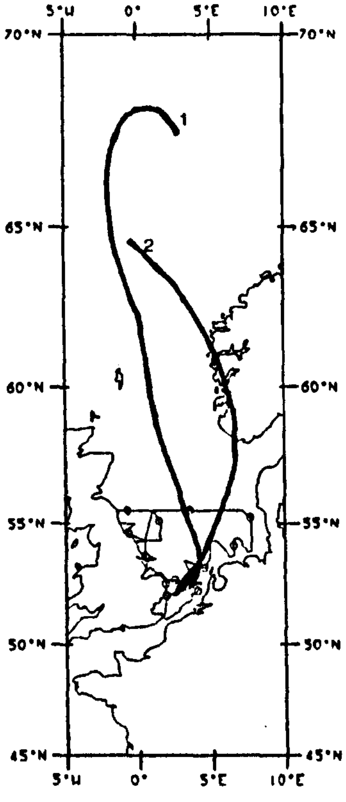
2 CR37 88 10 10 0000Z

Sample 27



1 CR37 88 10 12 1200Z

Sample 28



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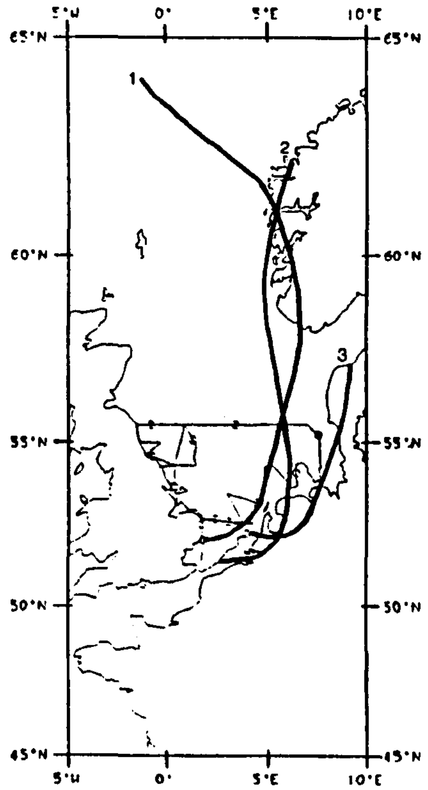
2 CR39 88 11 3 0000Z

Sample 29

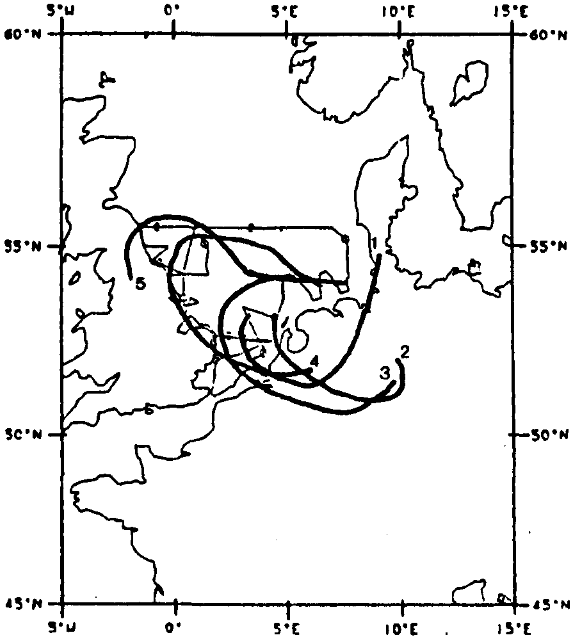


1 CR39 88 11 3 0000Z

2 CR39 88 11 3 1200Z

3 CR39 88 11 4 0000Z

Sample 30



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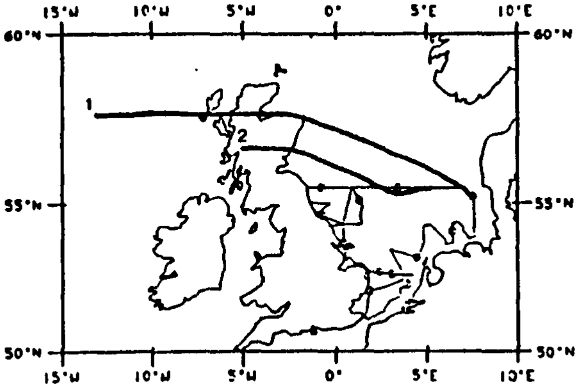
2 CR39 88 11 5 0000Z

3 CR39 88 11 5 1200Z

4 CR39 88 11 6 0000Z

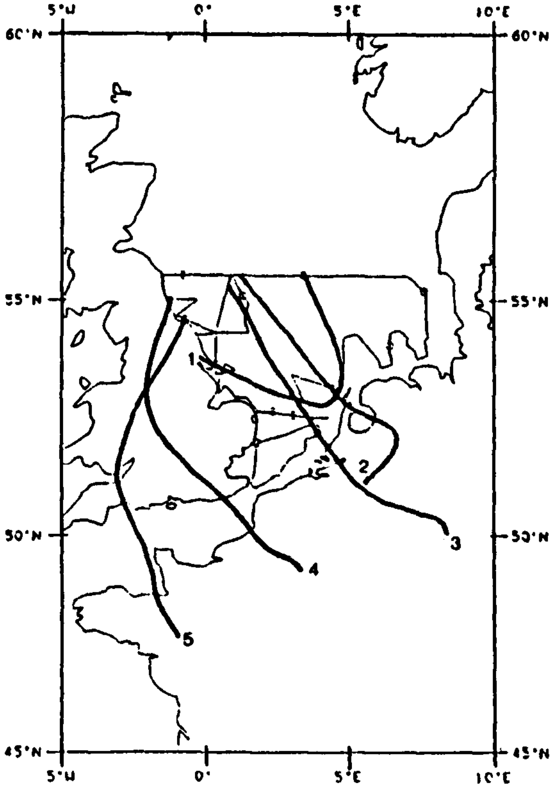
5 CR39 88 11 6 1200Z

Sample 31



1 CR39 88 11 7 0000Z
2 CR39 88 11 7 1200Z

Sample 32



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2 CR39 88 11 8 1200Z
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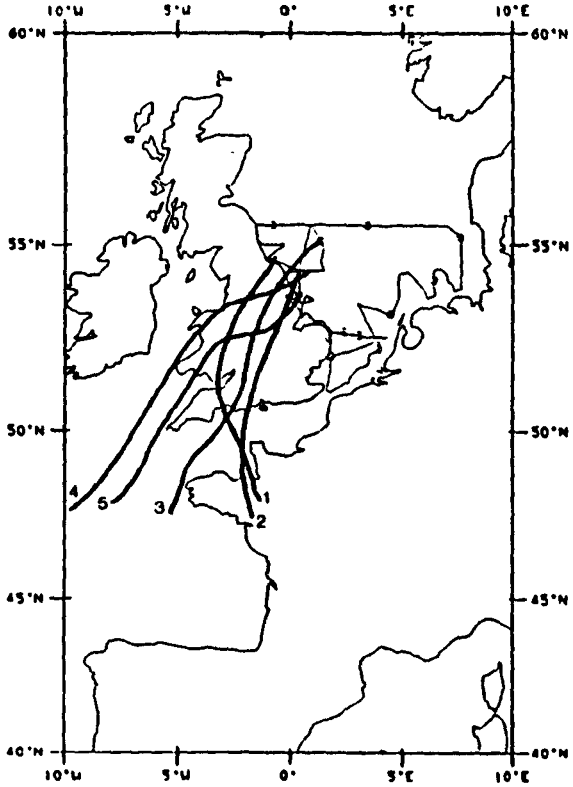
4 CR39 88 11 9 1200Z
5 CR39 88 11 10 0000Z

Sample 33



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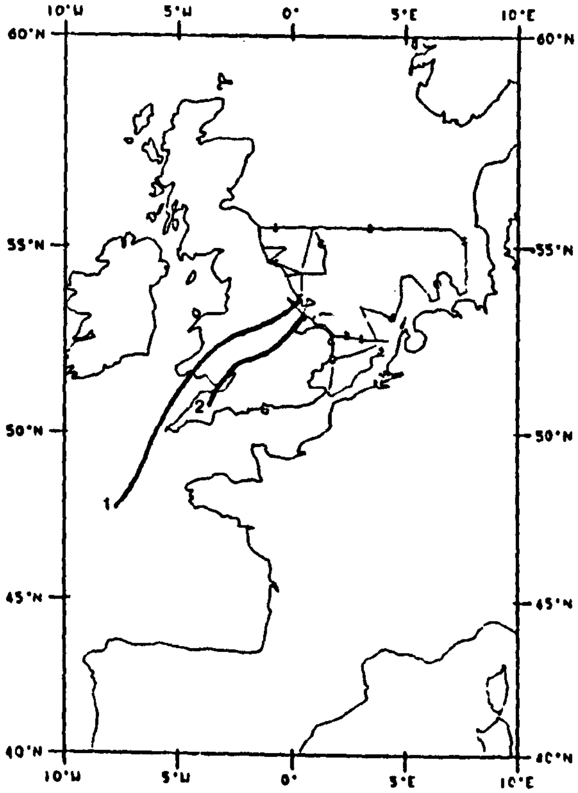
5 CR39 88 11 12 0000Z

Sample 34



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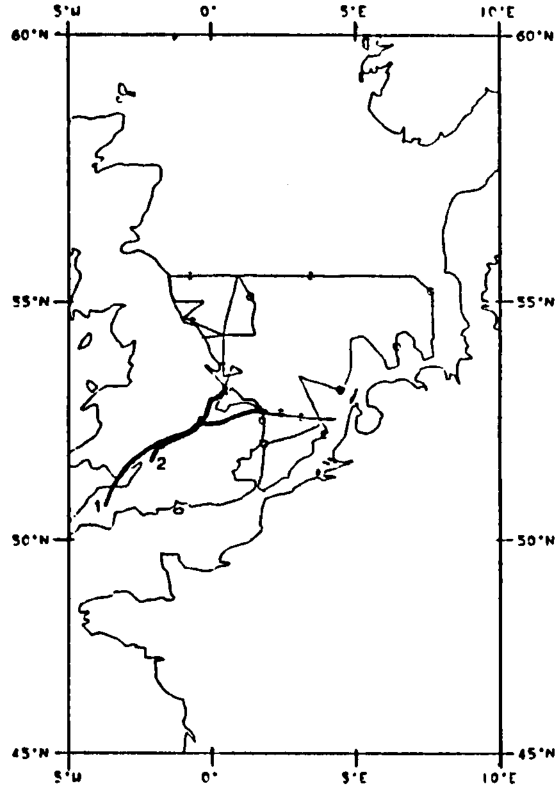
Sample 35



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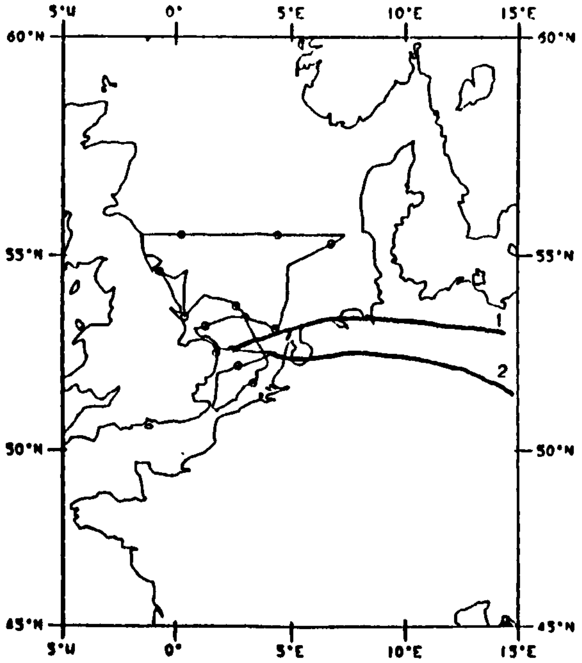
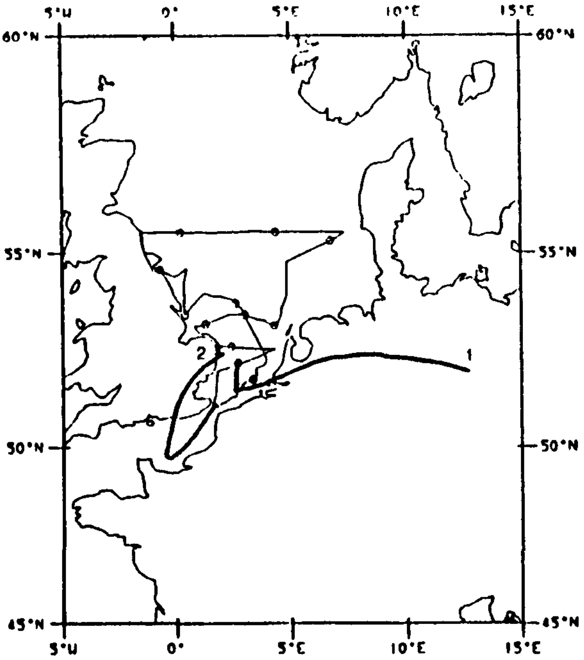
2 CR39 88 11 13 0000Z

Sample 36



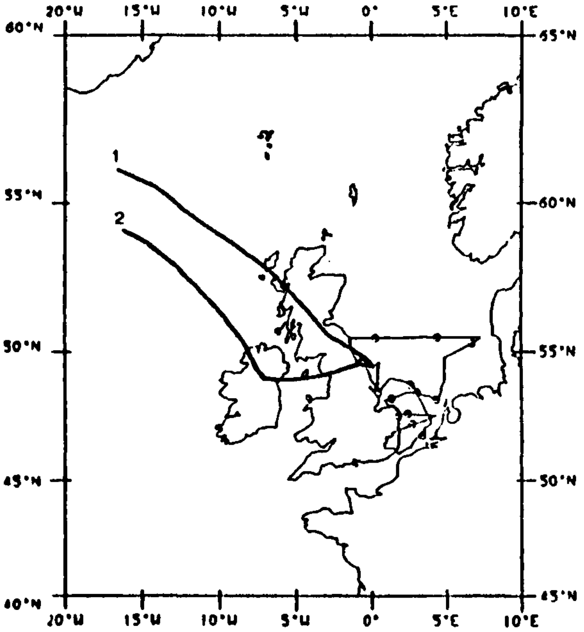
1 CR41 88 12 2 0000Z
2 CR41 88 12 2 1200Z

Sample 37



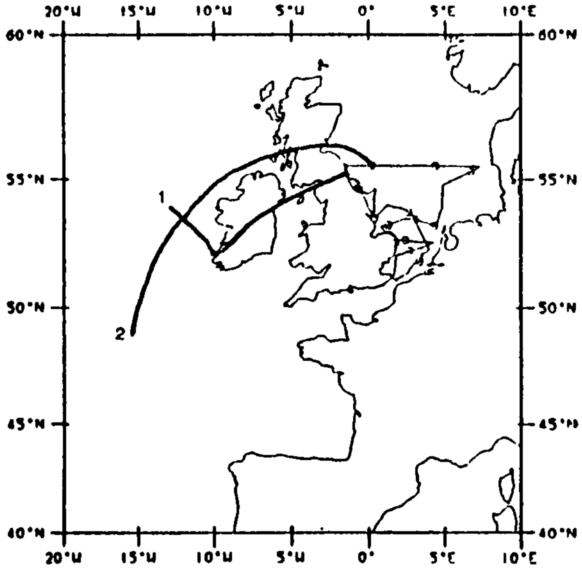
1 CR41 88 12 3 0000Z
2 CR41 88 12 3 1200Z

Sample 38



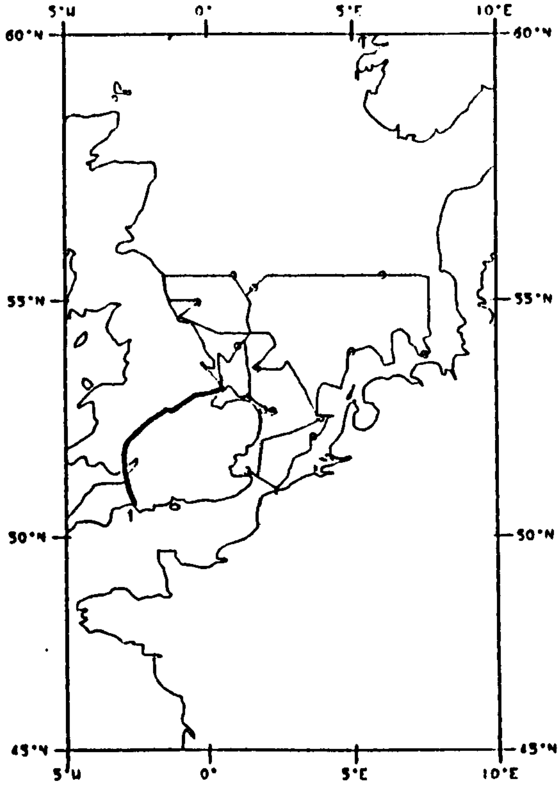
1 CR41 88 12 7 1200Z
2 CR41 88 12 8 0000Z

Sample 39



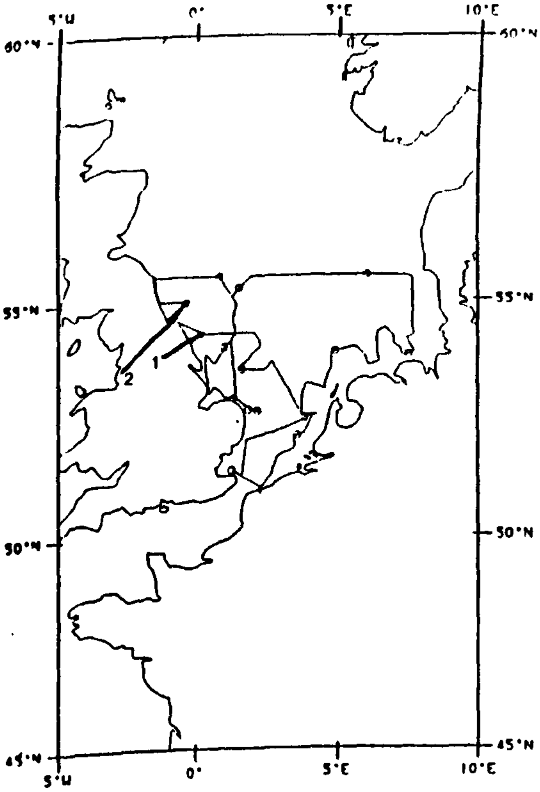
1 CR41 88 12 8 1200Z
2 CR41 88 12 9 0000Z

Sample 40



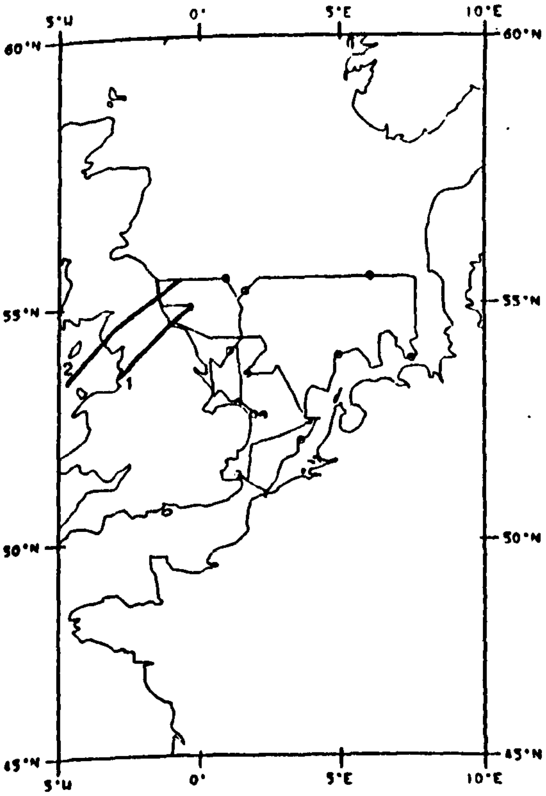
1 CR43 88 12 31 1200Z

Sample 41



1 CR43 89 1 1 1200Z
2 CR43 89 1 2 0000Z

Sample 42



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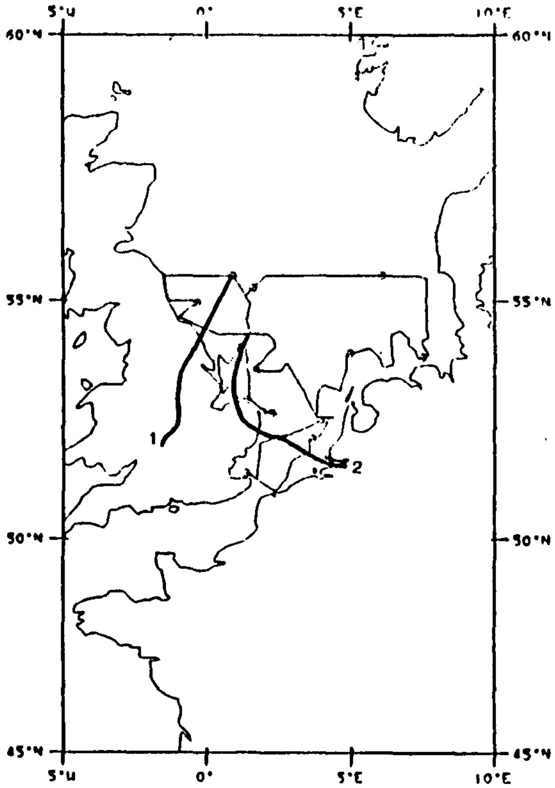
Sample 43



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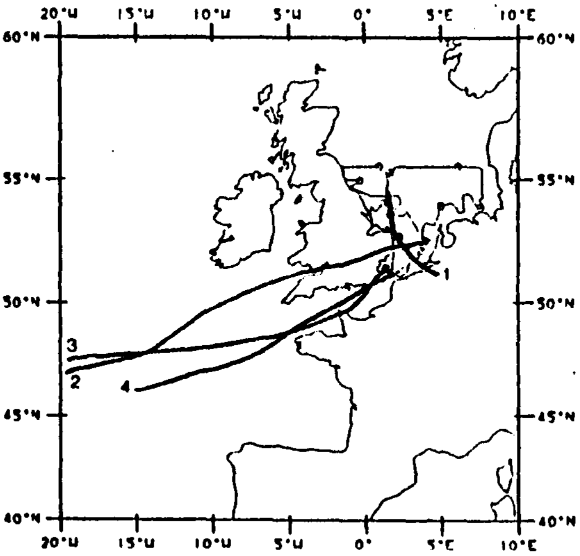
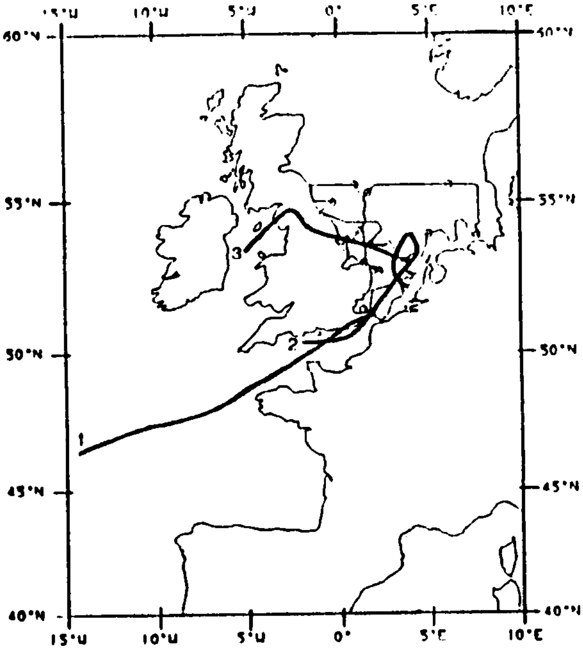
2 CR43 89 1 3 1200Z

Sample 44



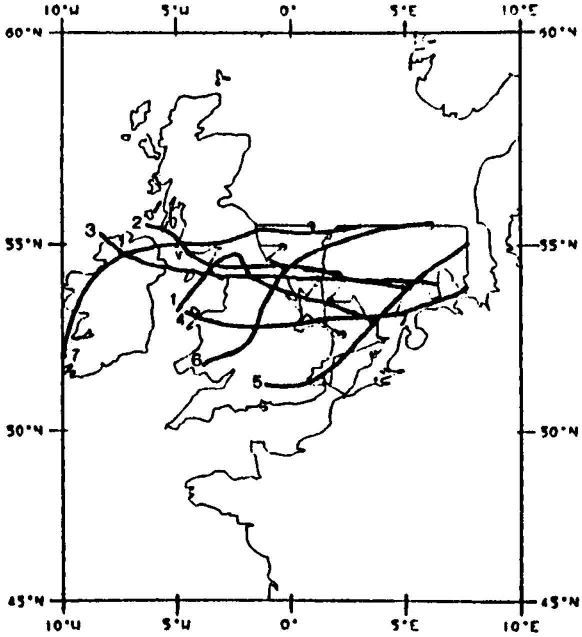
1 CR43 89 1 3 1200Z
2 CR43 89 1 5 1200Z
3 CR43 89 1 6 0000Z
4 CR43 89 1 6 1200Z

Sample 45



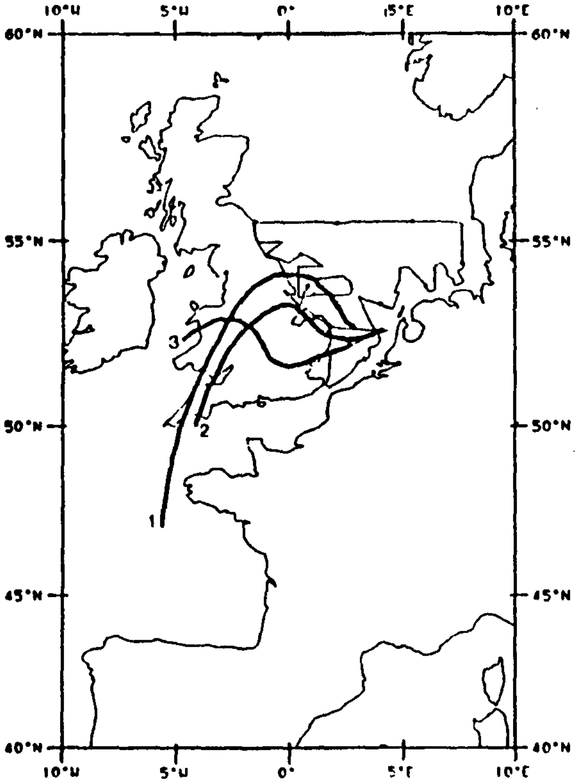
1 CR43 89 1 6 1200Z
2 CR43 89 1 7 0000Z
3 CR43 89 1 7 1200Z

Sample 46



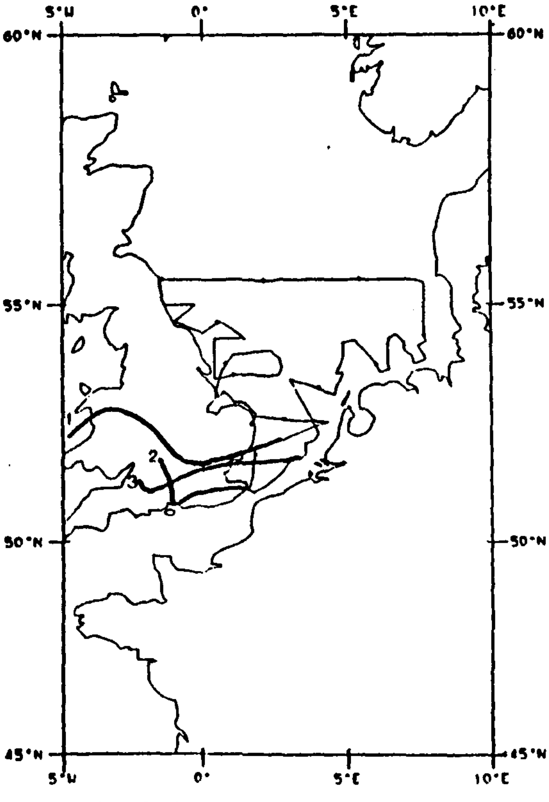
1 CR43 89 1 7 1200Z
2 CR43 89 1 8 0000Z
3 CR43 89 1 8 1200Z
4 CR43 89 1 9 0000Z
5 CR43 89 1 9 1200Z
6 CR43 89 1 10 0000Z
7 CR43 89 1 10 1200Z

Sample 47



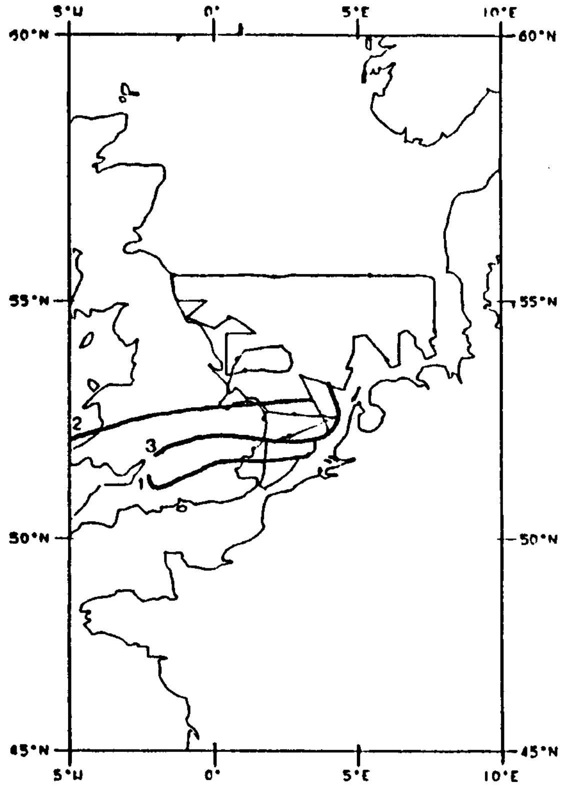
1 CR45 89 1 29 0000Z
2 CR45 89 1 29 1200Z
3 CR45 89 1 30 1200Z

Sample 48



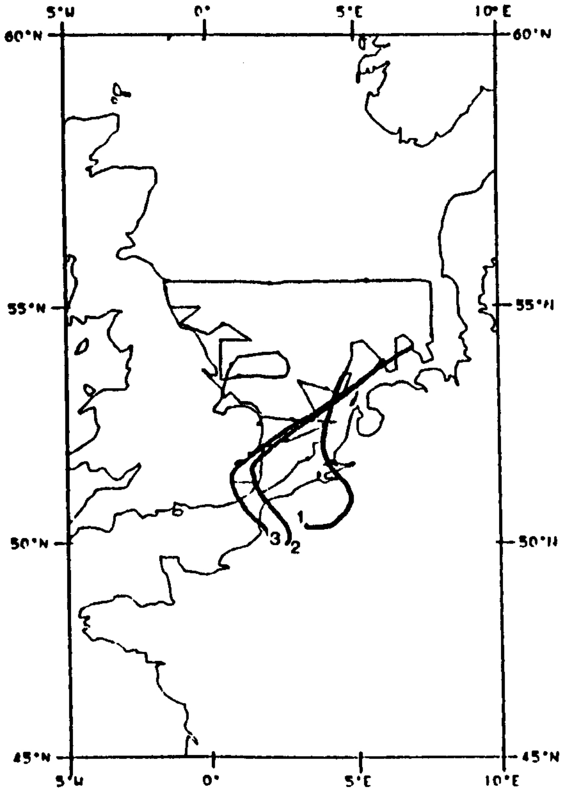
1 CR45 89 1 30 0000Z
2 CR45 89 1 30 1200Z
3 CR45 89 1 31 0000Z

Sample 49



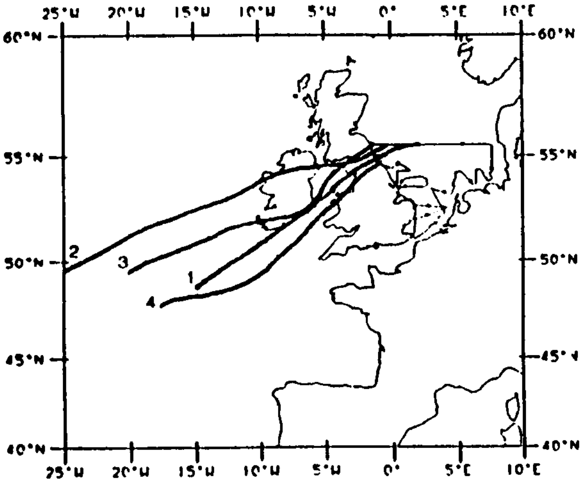
1 CR45 89 1 31 0000Z
2 CR45 89 1 31 1200Z
3 CR45 89 2 1 0000Z

Sample 50



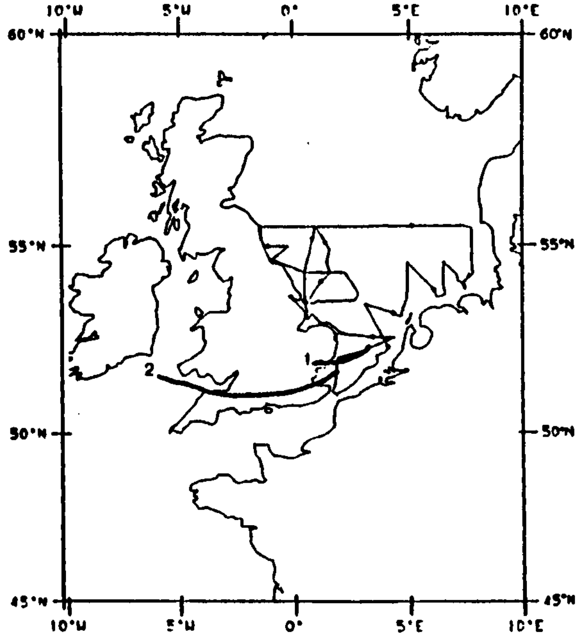
1 CR45 89 2 1 1200Z
2 CR45 89 2 2 0000Z
3 CR45 89 2 2 1200Z

Sample 51



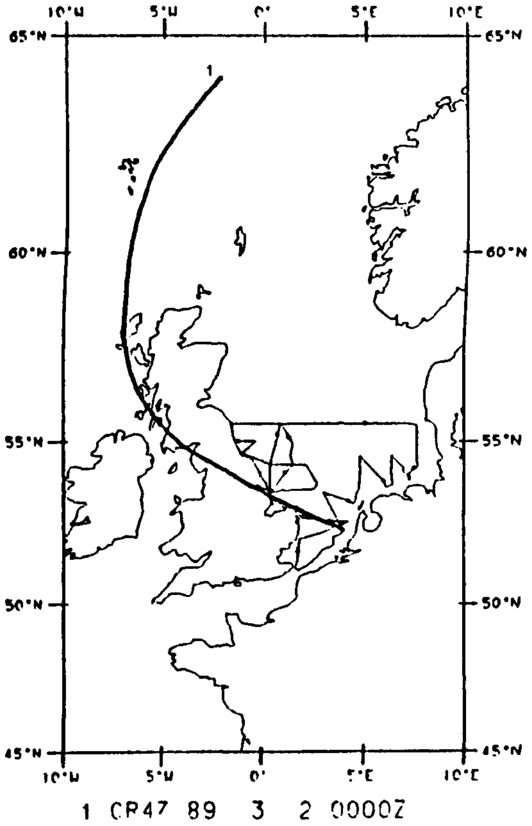
1 CR45 89 2 5 0000Z
2 CR45 89 2 5 1200Z
3 CR45 89 2 6 0000Z
4 CR45 89 2 6 1200Z

Sample 54

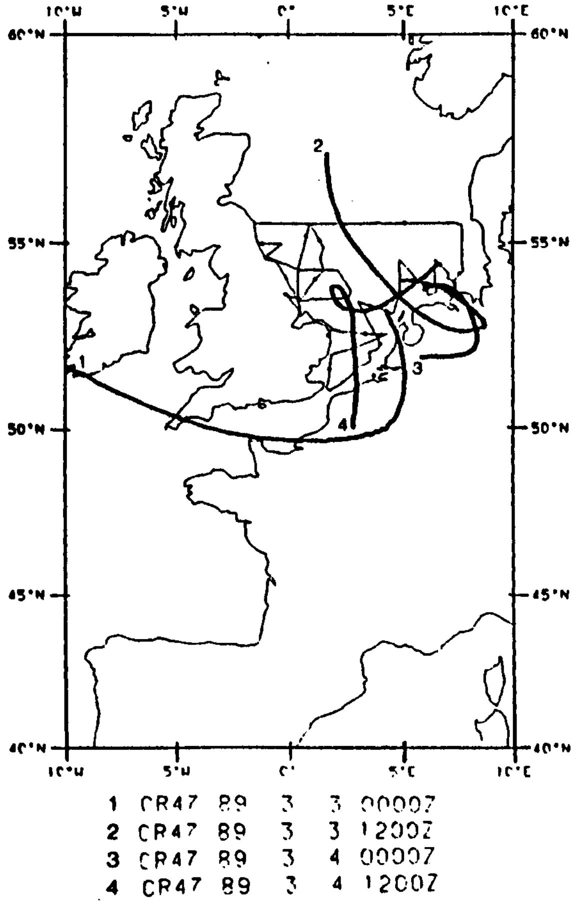


1 CR47 89 2 28 1200Z
2 CR47 89 3 1 0000Z

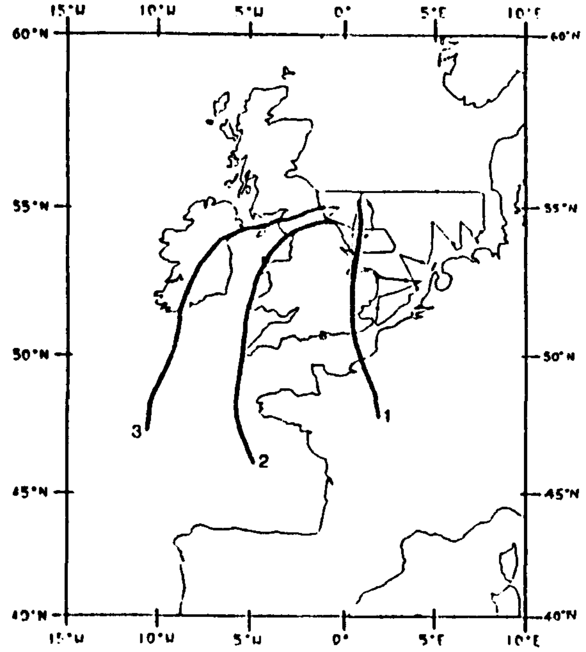
Sample 55



Sample 56

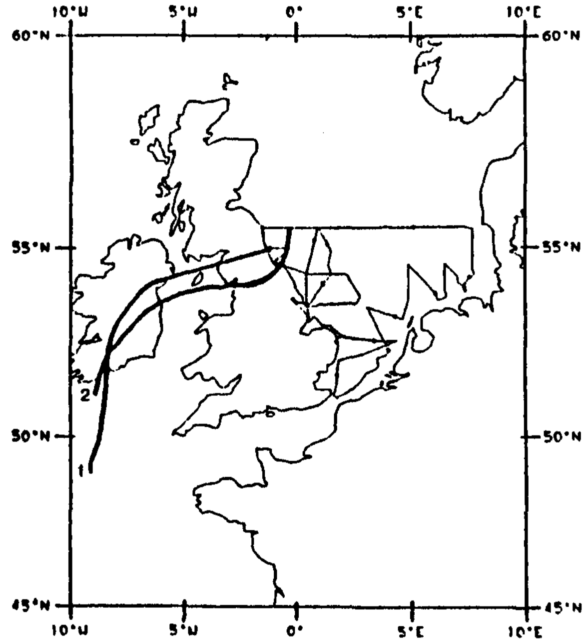


Sample 57



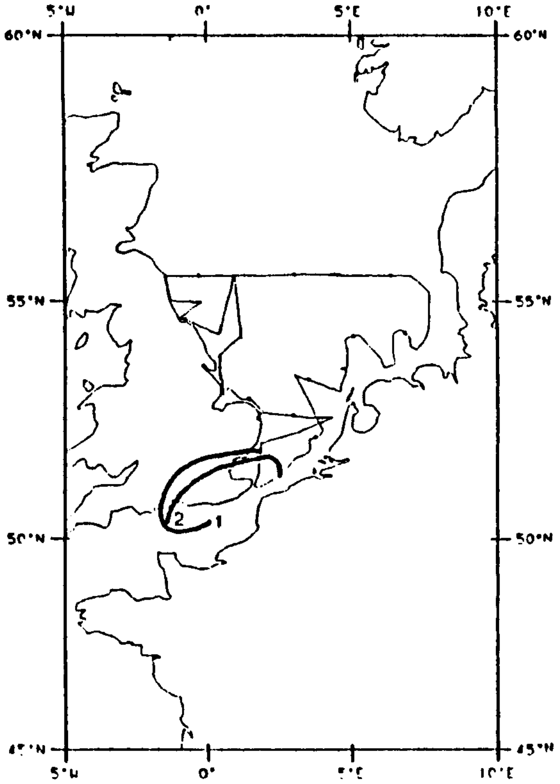
1 CR47 89 3 7 0000Z
2 CR47 89 3 7 1200Z
3 CR47 89 3 8 0000Z

Sample 58



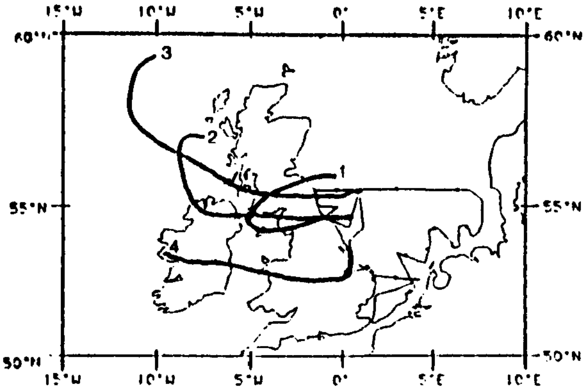
1 CR47 89 3 8 0000Z
2 CR47 89 3 8 1200Z

Sample 59



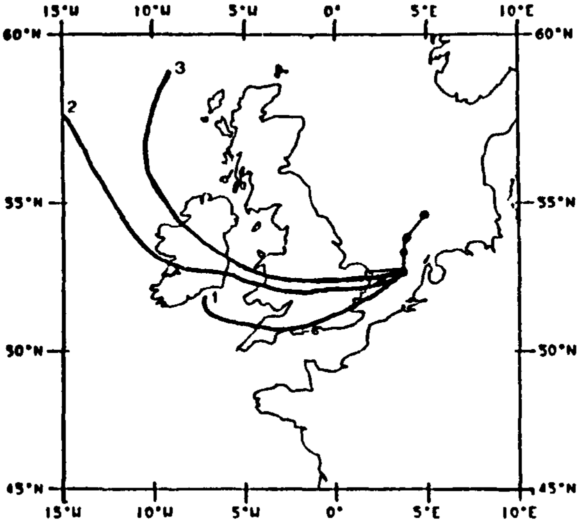
1 CR49 89 3 31 0000Z
2 CR49 89 3 31 1200Z

Sample 60



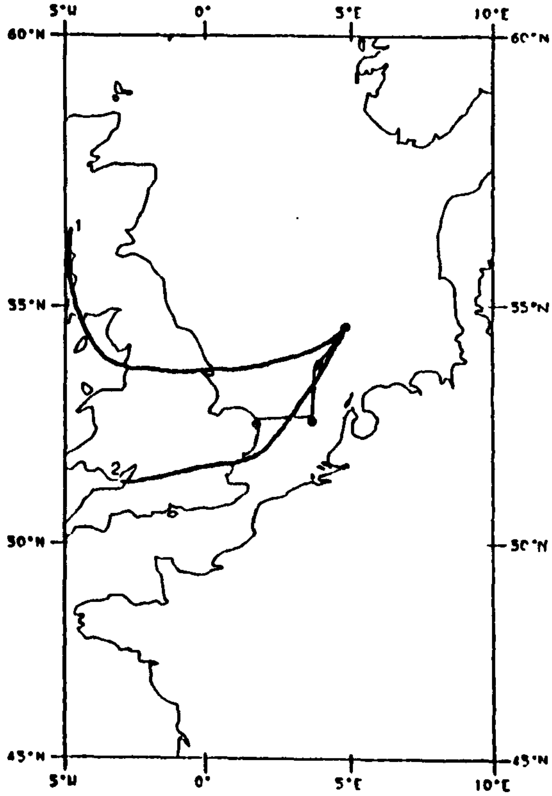
1 CR49 89 4 8 0000Z
2 CR49 89 4 8 1200Z
3 CR49 89 4 9 0000Z
4 CR49 89 4 9 1200Z

Sample 61



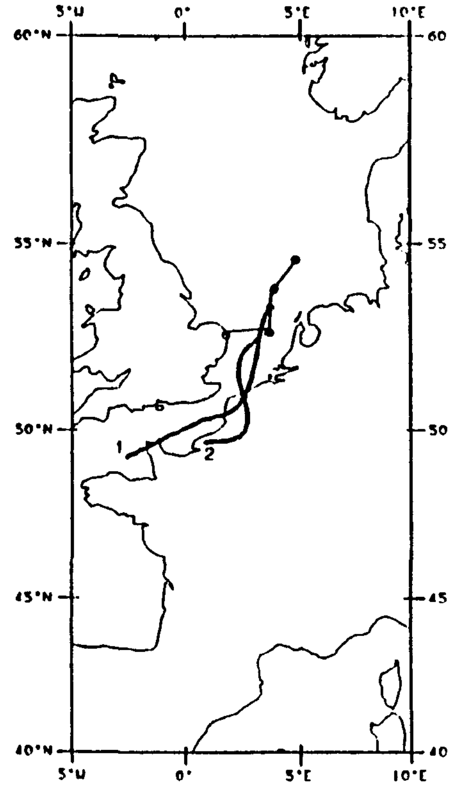
1 CR52 89 5 12 1200Z
2 CR52 89 5 13 0000Z
3 CR52 89 5 13 1200Z

Sample 62



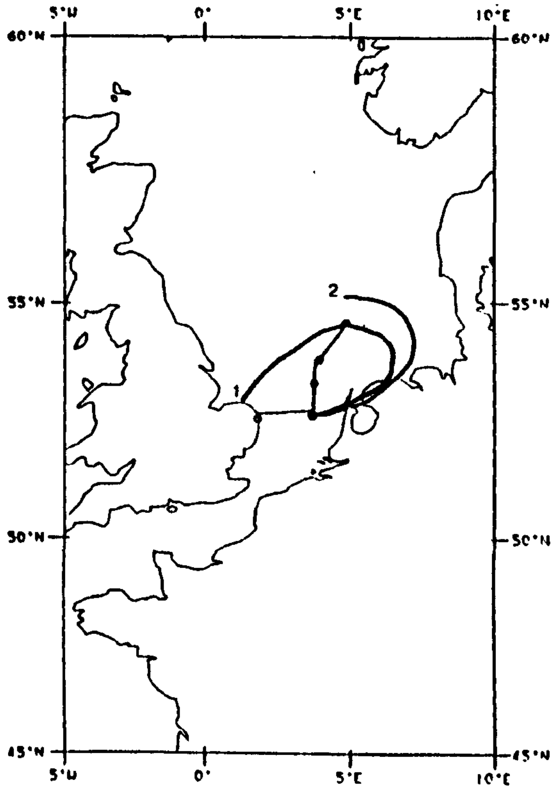
1 CR52 89 5 14 1200Z
2 CR52 89 5 15 0000Z

Sample 63



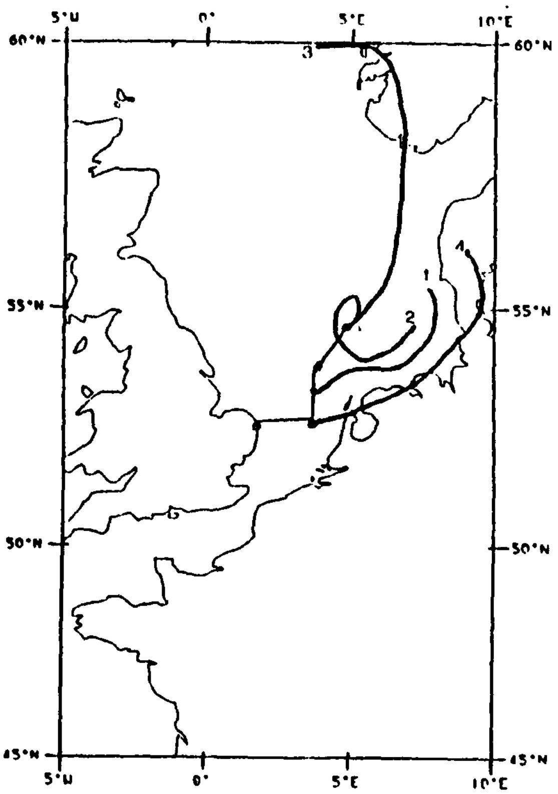
1 CR52 89 5 16 0000Z
2 CR52 89 5 16 1200Z

Sample 64



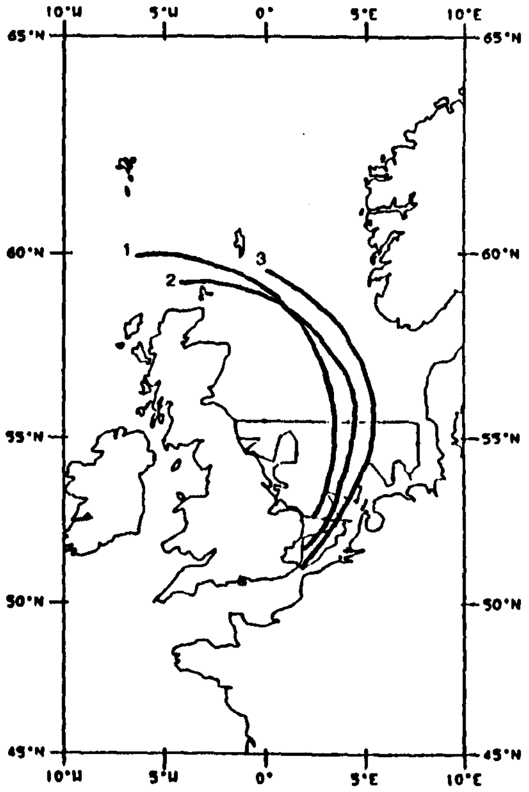
1 CR52 89 5 18 0000Z
2 CR52 89 5 18 1200Z

Sample 65



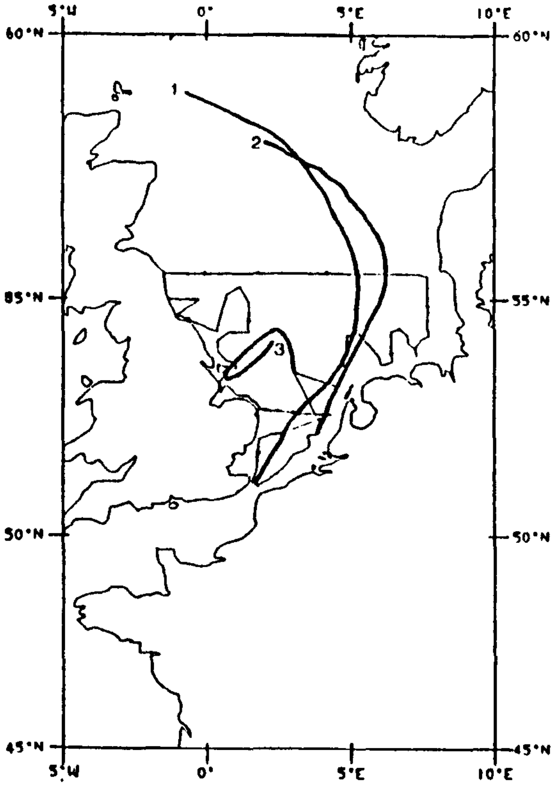
1 CR52 89 5 19 0000Z
2 CR52 89 5 19 1200Z
3 CR52 89 5 21 0000Z
4 CR52 89 5 21 1200Z

Sample 66



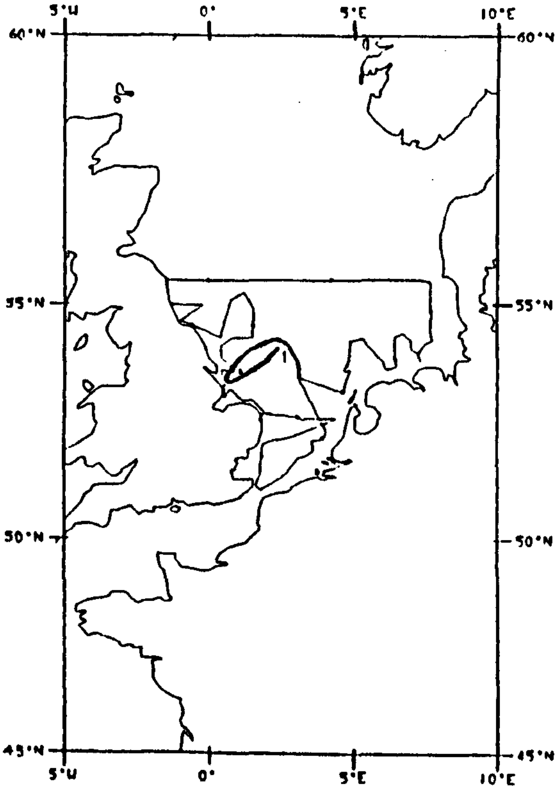
1 CR53 89 5 27 0000Z
2 CR53 89 5 28 0000Z
3 CR53 89 5 28 1200Z

Sample 67



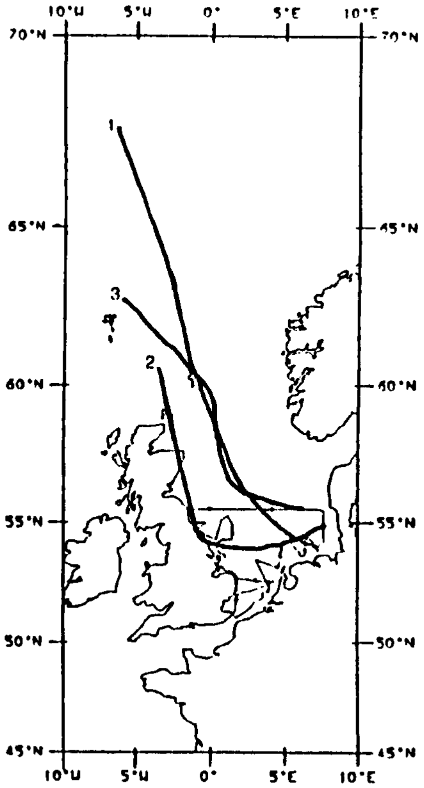
1 CR53 89 5 28 1200Z
2 CR53 89 5 29 0000Z
3 CR53 89 5 29 1200Z

Sample 68



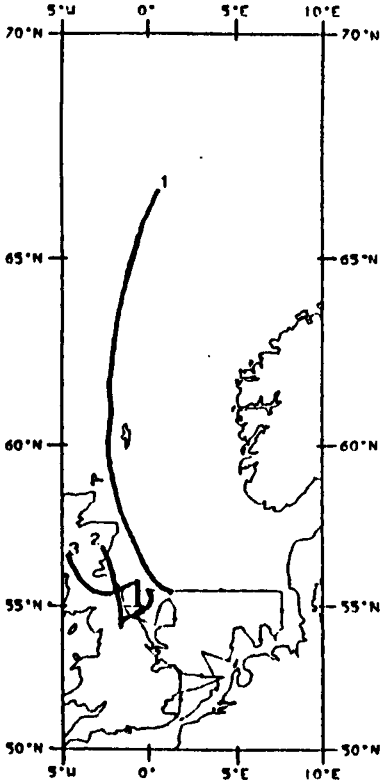
1 CR53 89 6 29 1200Z

Sample 69



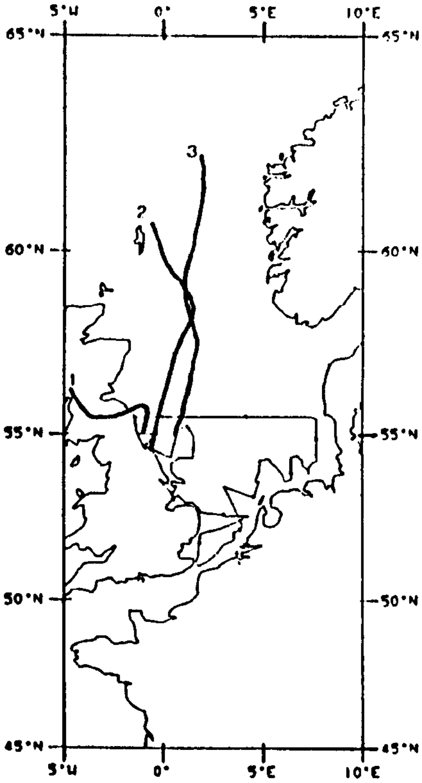
1 CR53 89 5 31 1200Z
2 CR53 89 6 1 0000Z
3 CR53 89 6 1 1200Z

Sample 70



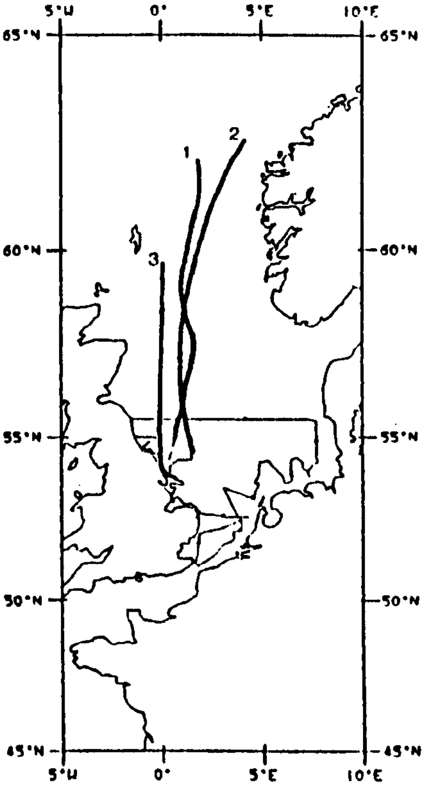
1 CR53 89 6 2 1200Z
2 CR53 89 6 3 0000Z
3 CR53 89 6 3 1200Z

Sample 71



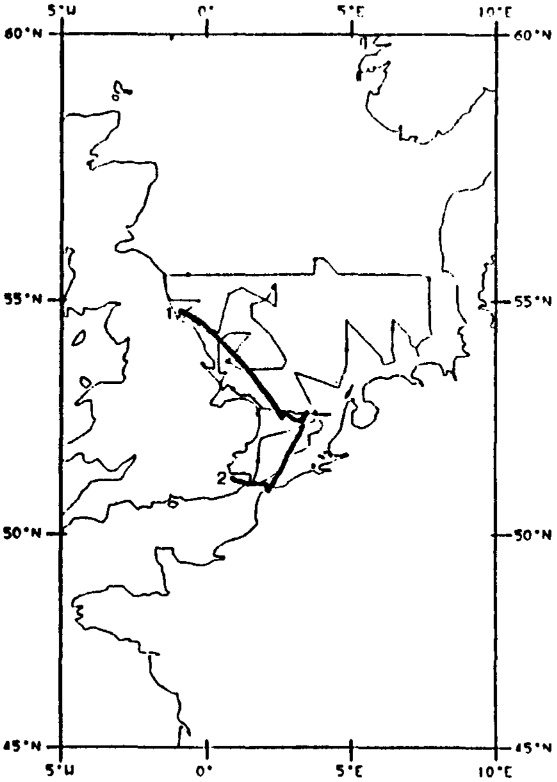
1 CR53 89 6 3 1200Z
2 CR53 89 6 4 0000Z
3 CR53 89 6 4 1200Z

Sample 72



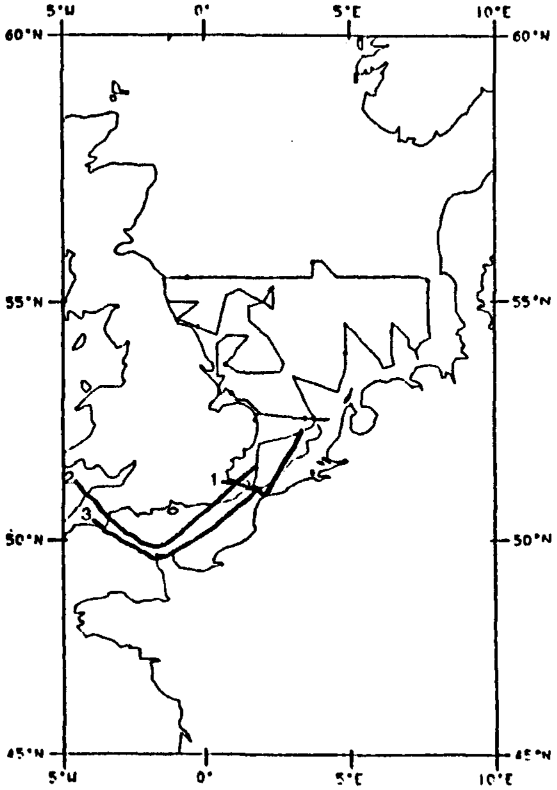
1 CR53 89 6 4 1200Z
2 CR53 89 6 5 0000Z
3 CR53 89 6 5 1200Z

Sample 73



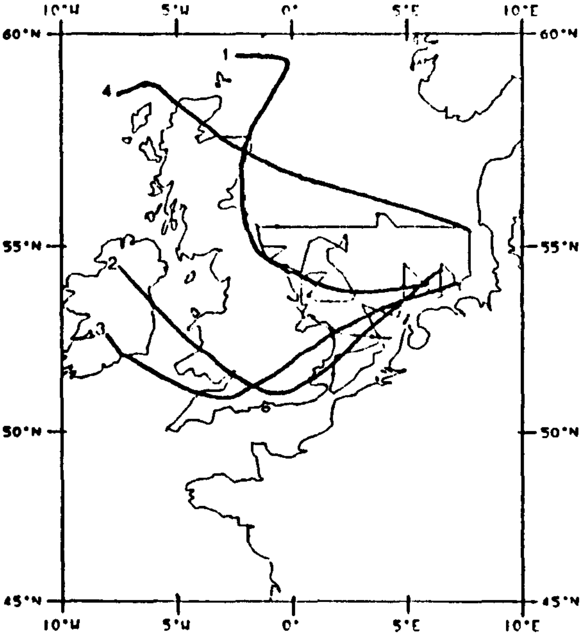
1 CR55 89 6 25 0000Z
2 CR55 89 6 25 1200Z

Sample 74



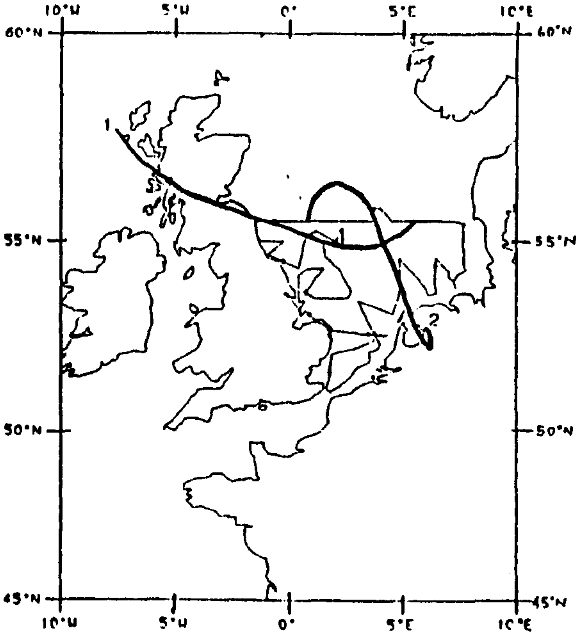
1 CR55 89 6 25 1200Z
2 CR55 89 6 26 0000Z
3 CR55 89 6 26 1200Z

Sample 75



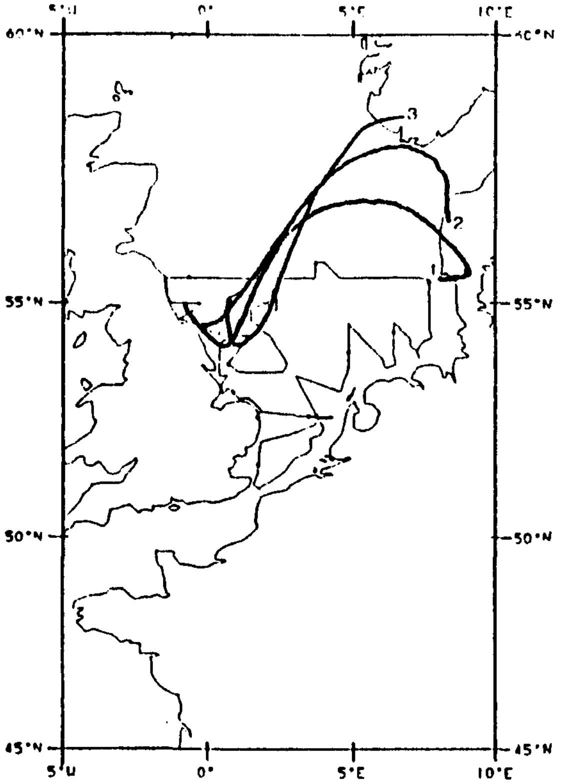
1 CR55 89 6 28 1200Z
2 CR55 89 6 29 0000Z
3 CR55 89 6 29 1200Z
4 CR55 89 6 30 0000Z

Sample 76



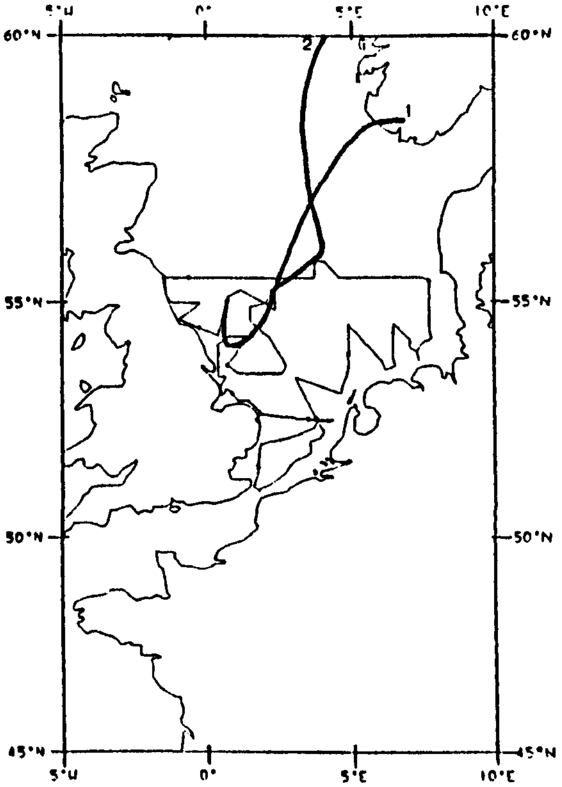
1 CR55 89 6 30 1200Z
2 CR55 89 7 2 0000Z

Sample 77



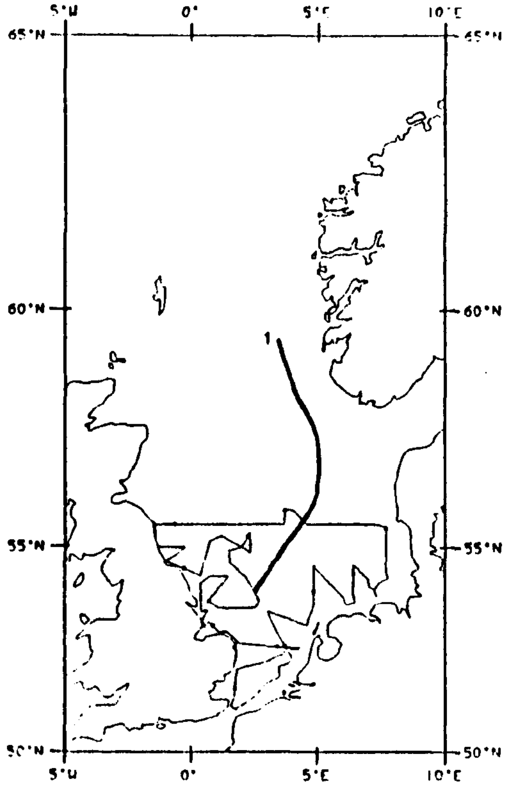
1 CR55 89 7 2 1200Z
2 CR55 89 7 3 0000Z
3 CR55 89 7 3 1200Z

Sample 78



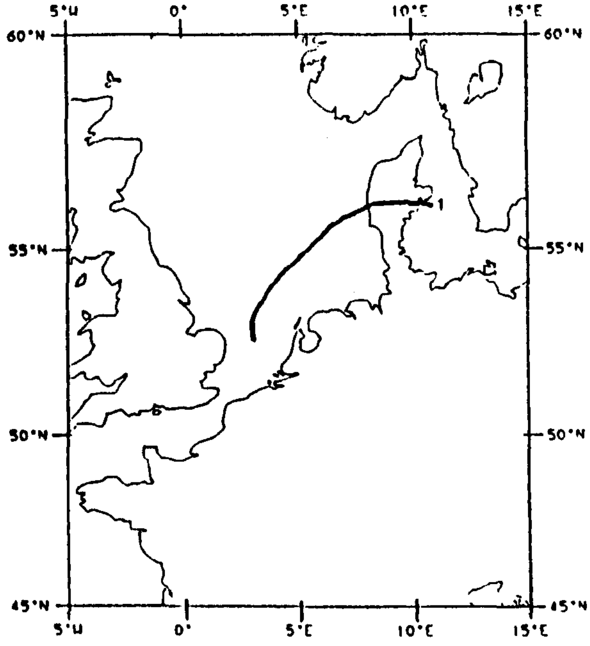
1 CR55 89 7 3 1200Z
2 CR55 89 7 4 0000Z

Sample 79



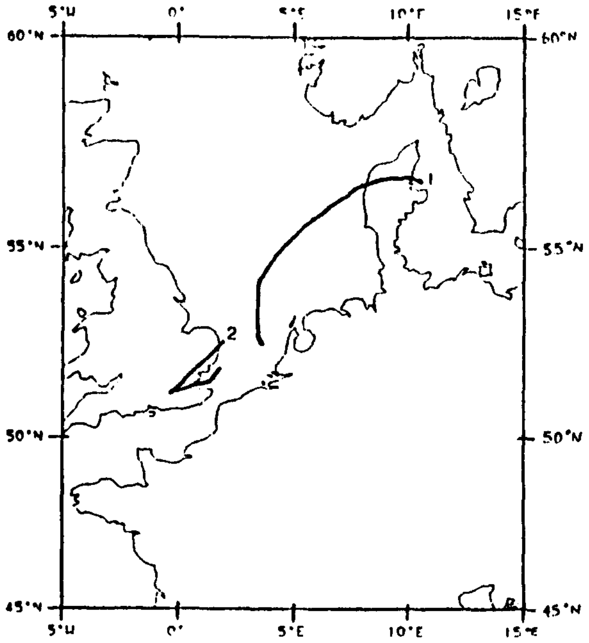
1 CR55 89 7 4 1200Z

Sample 80



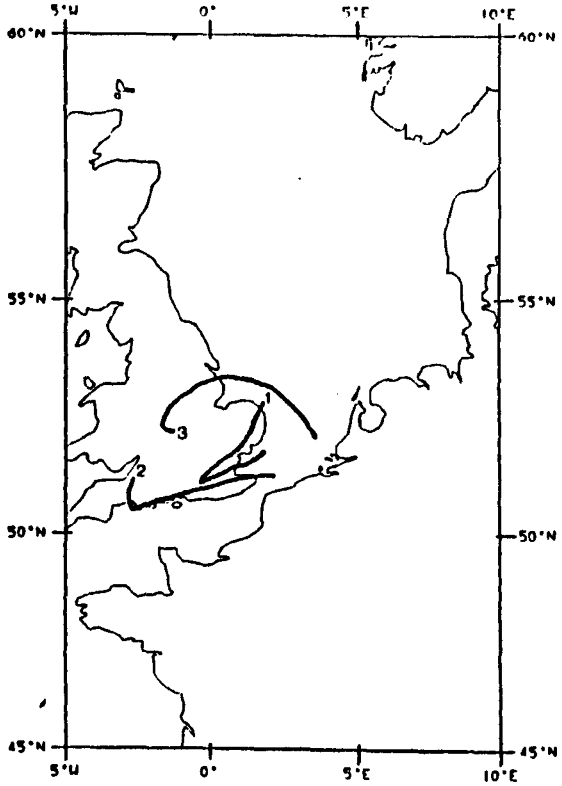
1 CR57 89 7 25 0000Z

Sample 81



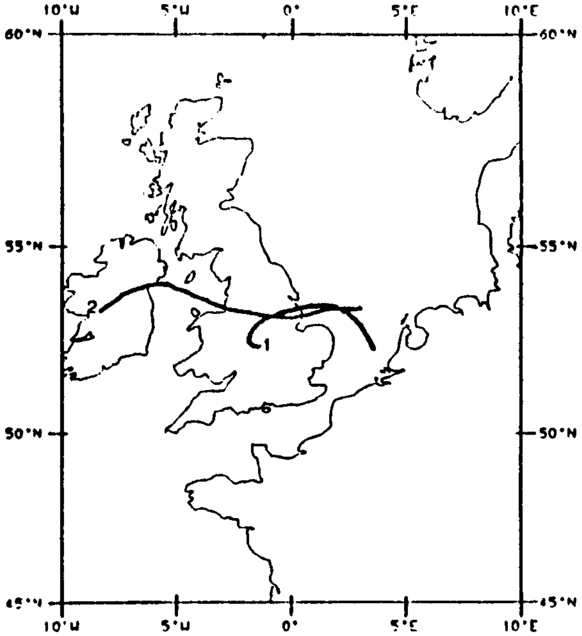
1 CR57 89 7 25 1200Z
2 CR57 89 7 26 0000Z

Sample 82



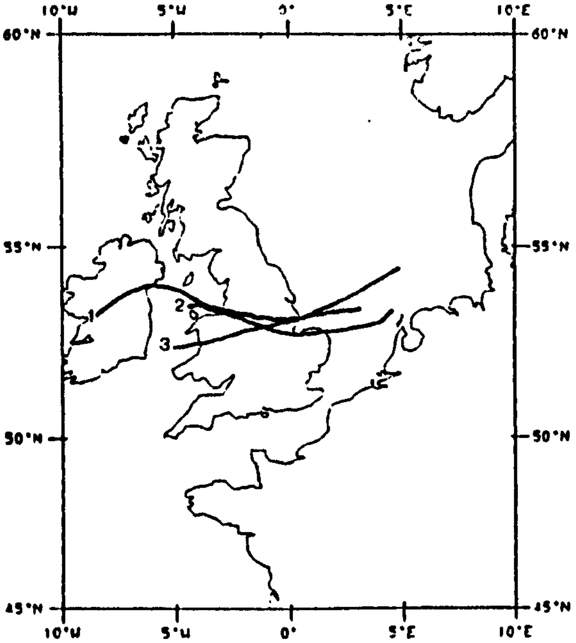
1 CR57 89 7 26 0000Z
2 CR57 89 7 26 1200Z
3 CR57 89 7 27 0000Z

Sample 83



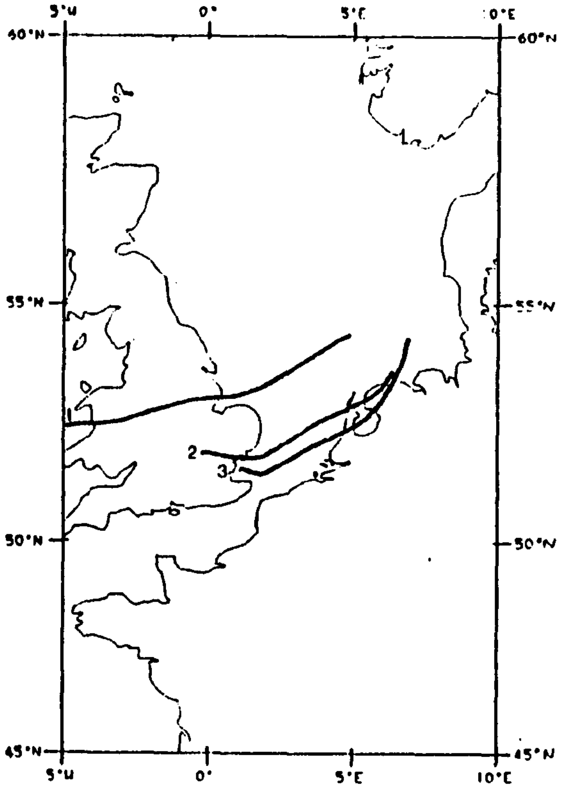
1 CR57 89 7 27 0000Z
2 CR57 89 7 27 1200Z

Sample 84



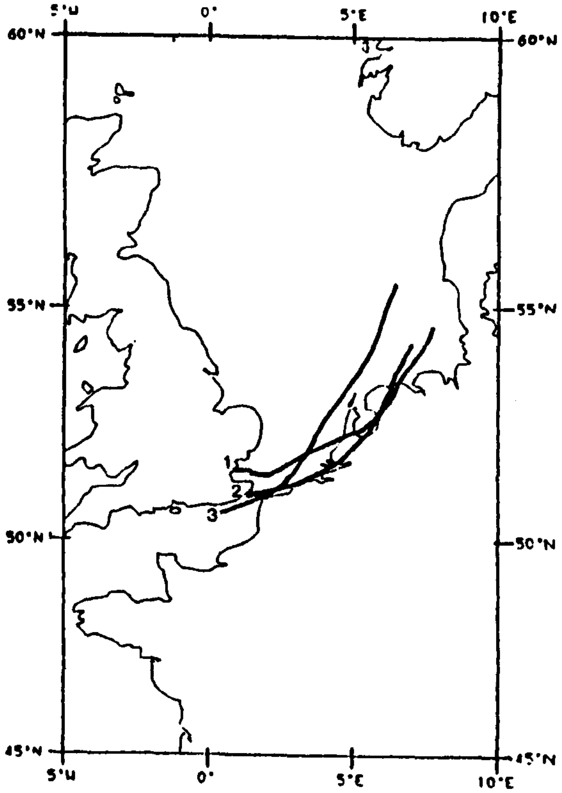
1 CR57 89 7 27 1200Z
2 CR57 89 7 28 0000Z
3 CR57 89 7 28 1200Z

Sample 85



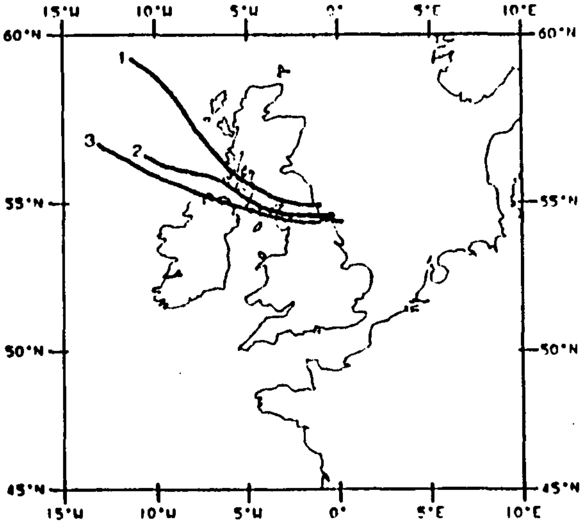
1 CR57 89 7 28 1200Z
2 CR57 89 7 29 0000Z
3 CR57 89 7 29 1200Z

Sample 86



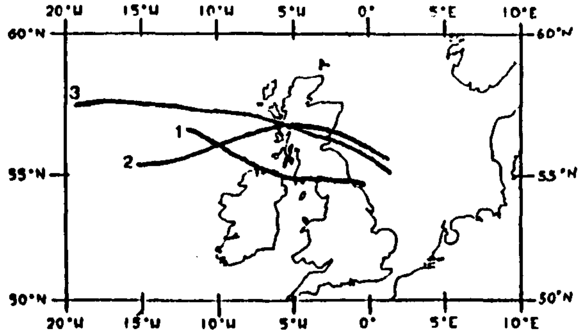
1 CR57 89 7 29 1200Z
2 CR57 89 7 30 0000Z
3 CR57 89 7 30 1200Z

Sample 87



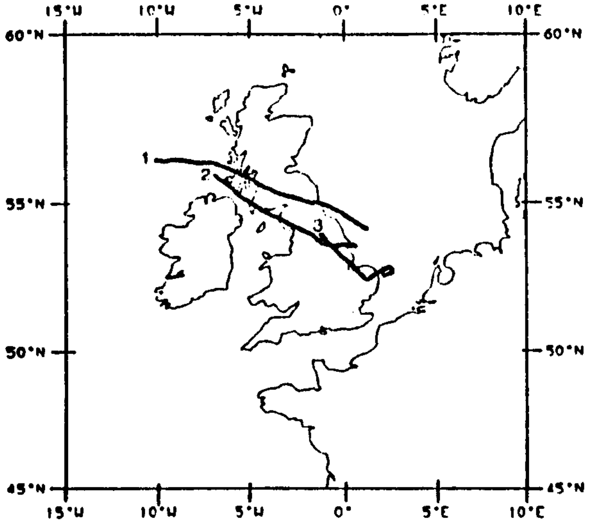
1 CR57 89 8 2 1200Z
2 CR57 89 8 3 0000Z
3 CR57 89 8 3 1200Z

Sample 88



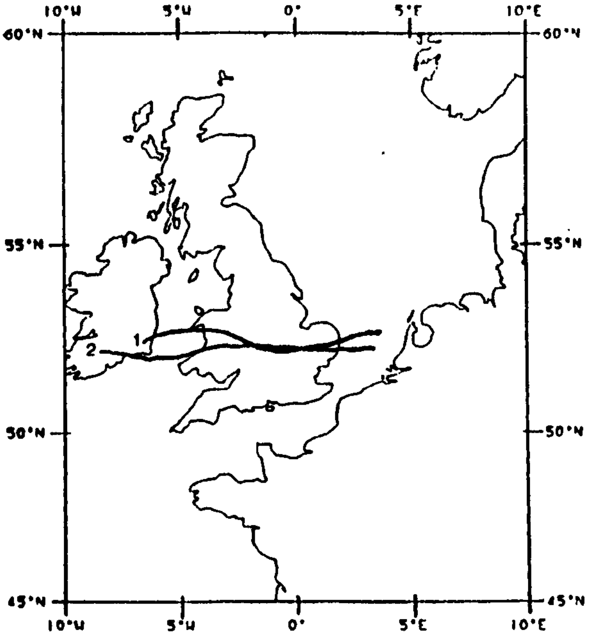
CR57 89 8 3 1200Z
CR57 89 8 4 0000Z
CR57 89 8 4 1200Z

Sample 89



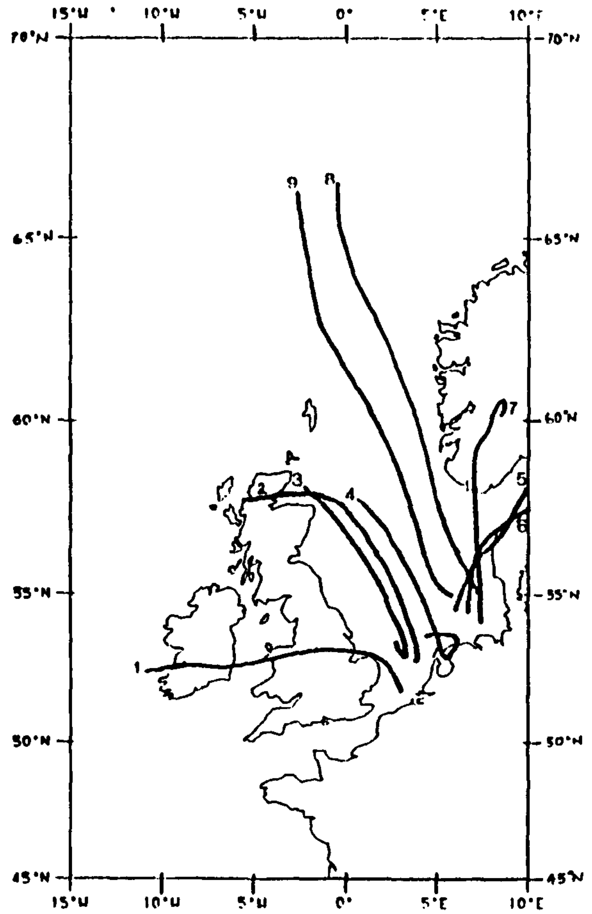
1 CR57 89 8 5 0000Z
2 CR57 89 8 5 1200Z
3 CR57 89 8 6 0000Z

Sample 90



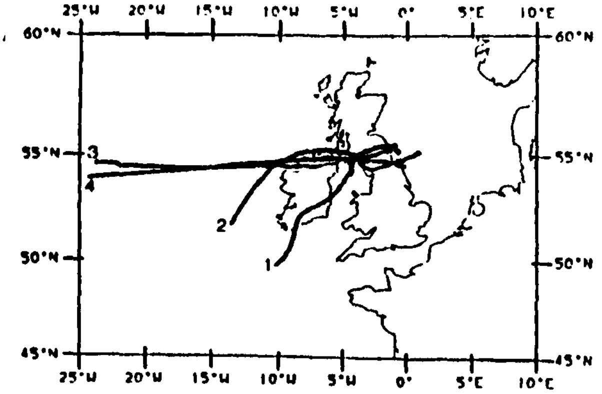
1 CR59 89 8 24 0000Z
2 CR59 89 8 24 1200Z

Sample 91



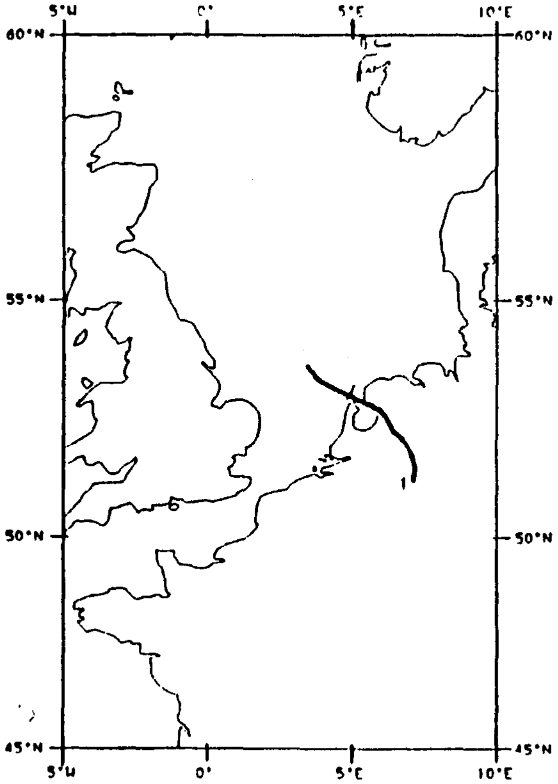
1	CR59	89	25	1200Z
2	CR59	89	26	0000Z
3	CR59	89	26	1200Z
4	CR59	89	27	0000Z
5	CR59	89	27	1200Z
6	CR59	89	28	0000Z
7	CR59	89	28	1200Z
8	CR59	89	29	0000Z
9	CR59	89	29	1200Z

Sample 92



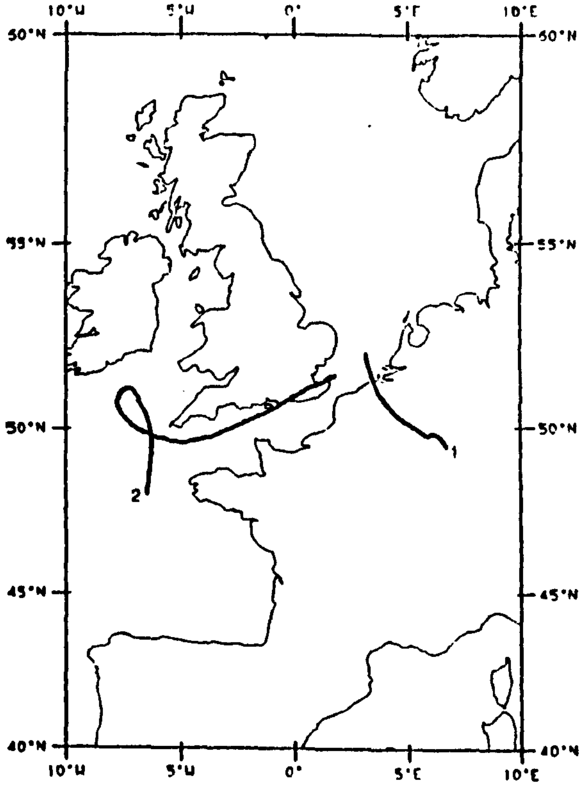
1	CR59	89	8	31	0000Z
2	CR59	89	8	31	1200Z
3	CR59	89	9	1	0000Z
4	CR59	89	9	1	1200Z

Sample 93



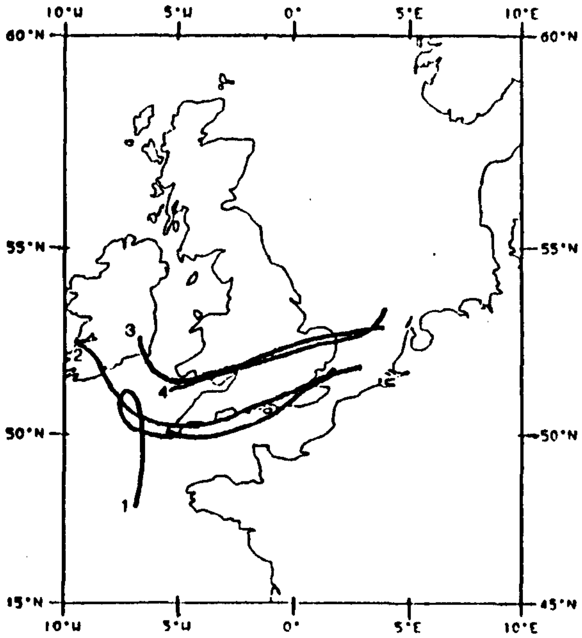
1 CR61 89 9 22 0000Z

Sample 94



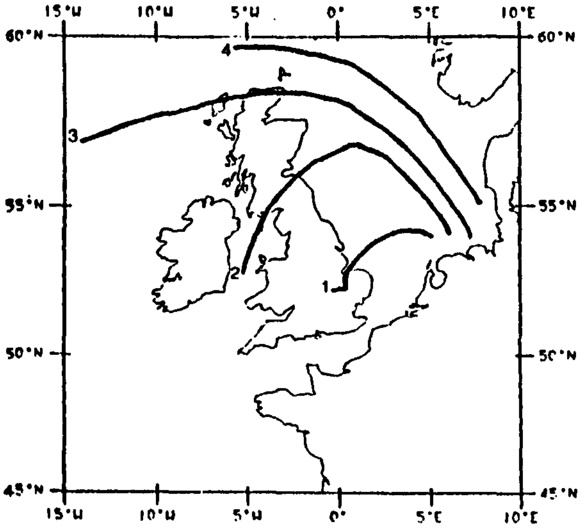
1 CR61 89 9 22 1200Z
2 CR61 89 9 23 0000Z

Sample 95



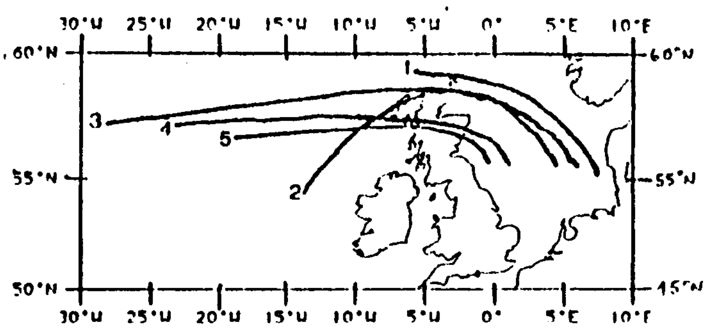
1 CR61 89 9 23 0000Z
2 CR61 89 9 23 1200Z
3 CR61 89 9 24 0000Z
4 CR61 89 9 24 1200Z

Sample 96



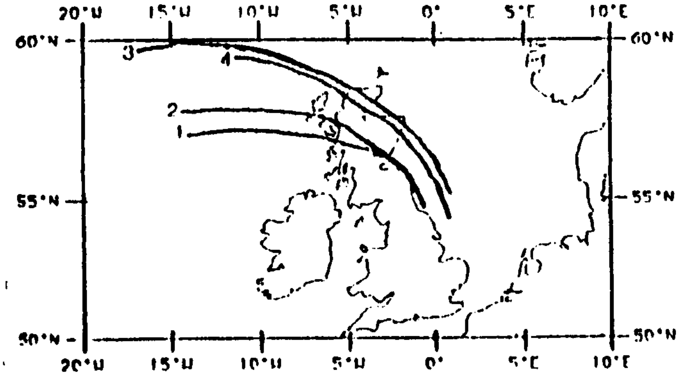
1 CR61 89 9 26 0000Z
2 CR61 89 9 26 1200Z
3 CR61 89 9 27 0000Z
4 CR61 89 9 27 1200Z

Sample 97



1 CR61 89 9 27 1200Z
2 CR61 89 9 28 0000Z
3 CR61 89 9 28 1200Z
4 CR61 89 9 29 0000Z
5 CR61 89 9 29 1200Z

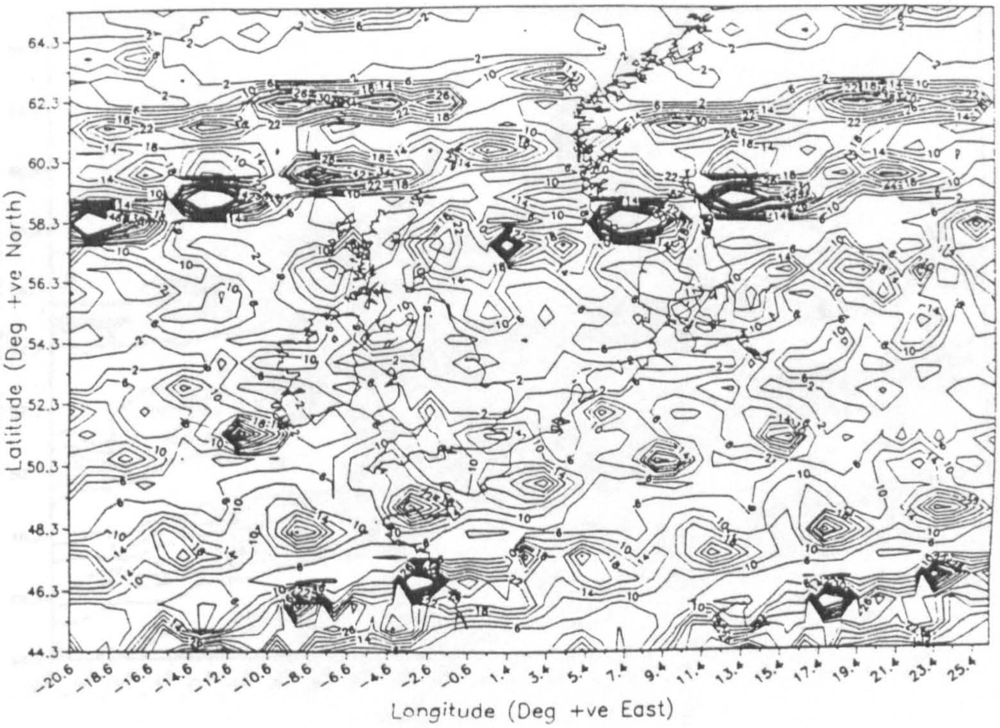
Sample 98



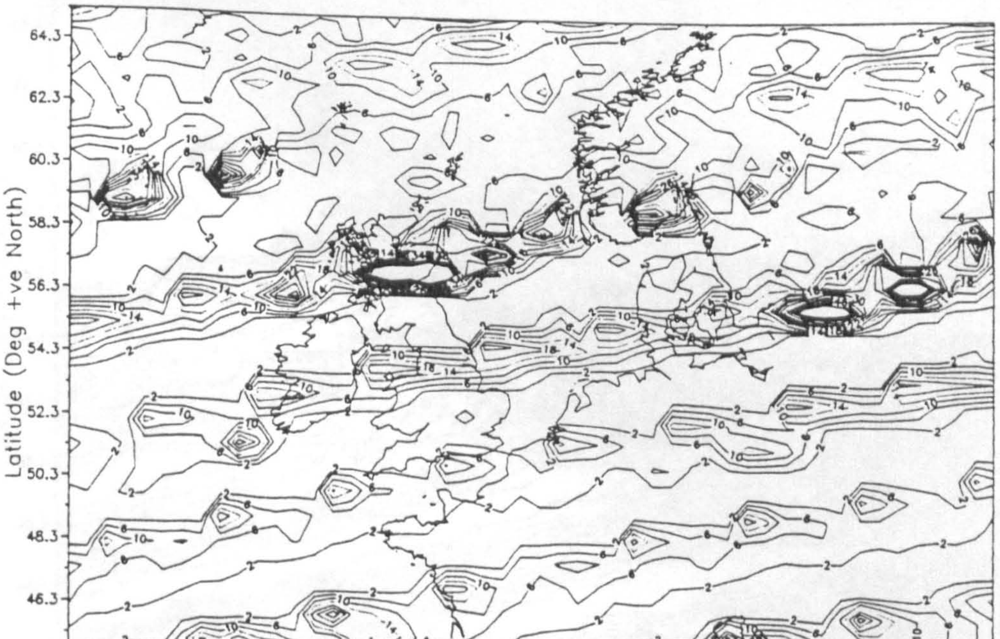
1 CR61 89 9 30 0000Z
2 CR61 89 9 30 1200Z
3 CR61 89 10 1 0000Z
4 CR61 89 10 1 1200Z

Appendix B

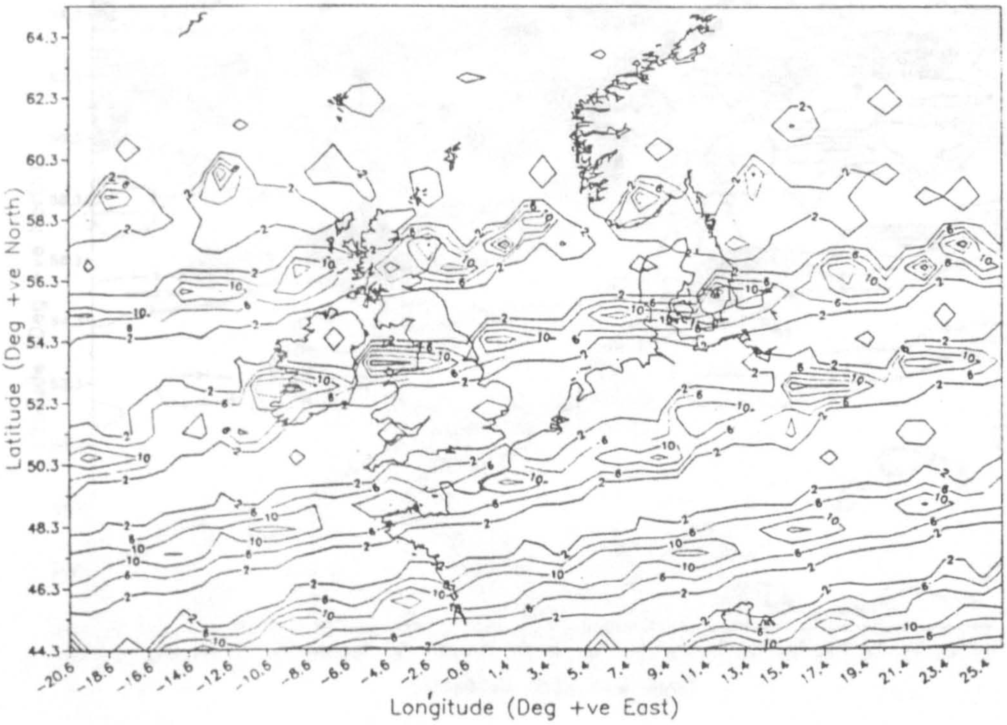
Fine Mesh Rainfall Modelled patterns over the North Sea and surrounding landmasses.



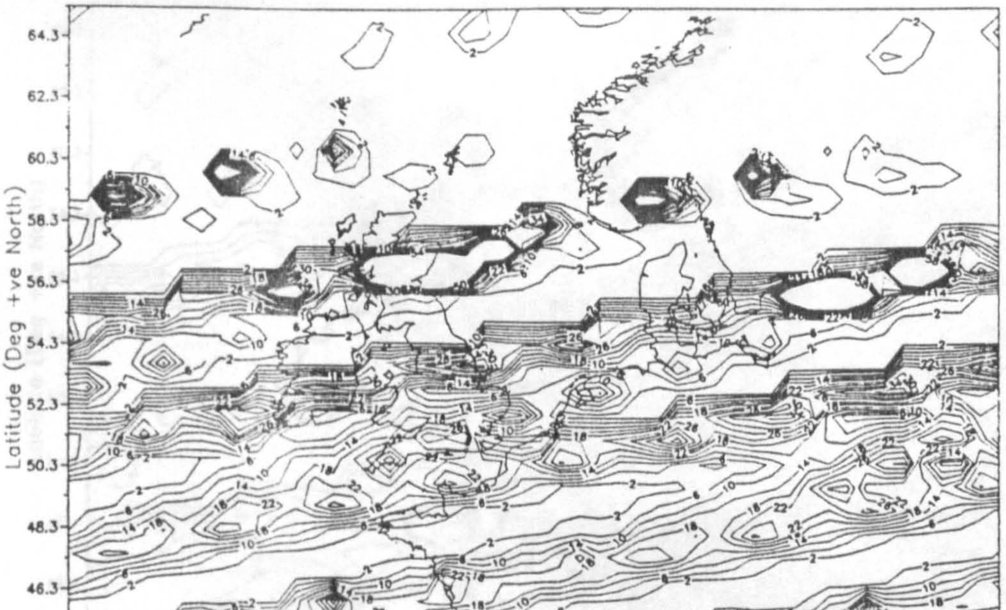
Sample 14: rainfall (0–58mm) for the time period 18:00 02/09/88 to 18:00 04/09/88.



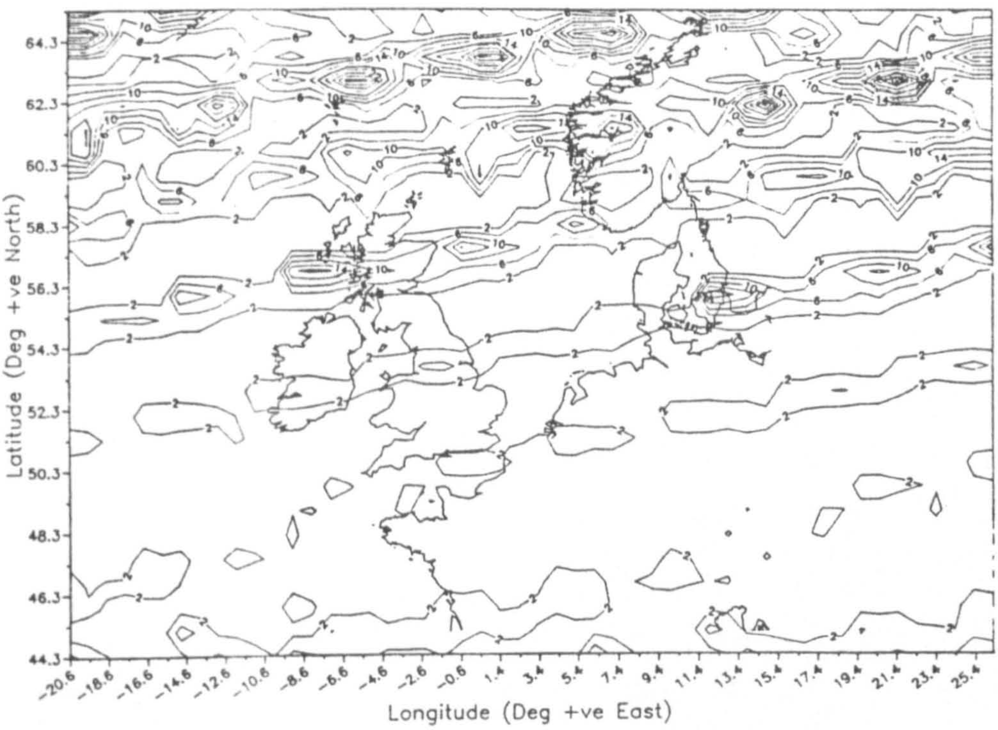
Sample 39: rainfall (0–58mm) for the time period 09:00 07/12/88 to 09:00 09/12/88.



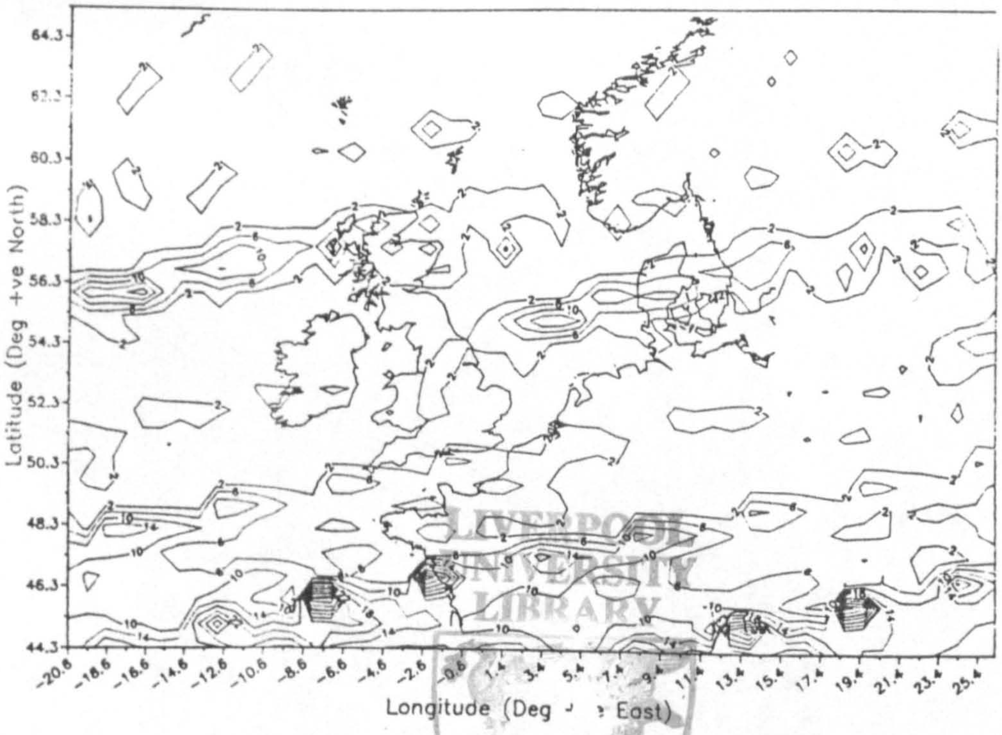
Sample 34: rainfall (0–58mm) for the time period 18:00 10/11/88 to 18:00 12/11/88.



Sample 47: rainfall (0–58mm) for the time period 06:00 28/01/89 to 06:00 30/01/89.



Sample 88: rainfall (0–58mm) for the time period
00:00 03/08/89 to 00:00 05/08/89.



Sample 96: rainfall (0–58mm) for the time period
00:00 23/09/89 to 00:00 25/09/89.

THE DISTRIBUTION, SEA WATER SOLUBILITY AND SOLID STATE SPECIATION OF SOME TRACE ELEMENTS FROM THE NORTH SEA ATMOSPHERE.

ABSTRACT. Data are presented on the concentrations of particulate atmospheric trace elements over the open regions of the southern North Sea. It is shown that there is a south to north decreasing gradient in the emission of trace elements from the land masses surrounding the North Sea. As a result it is the origin of the air masses themselves, and not the location at which they are sampled which constraints particulate trace element concentrations over the North Sea.

The sources of trace elements in the North Sea Aerosol (NSA) was investigated in terms of (a) EF_{values} using Al as a crustal indicator element. Results indicate that for the trace elements Al and Fe, crustal dust is the major source of these elements to the NSA. The trace elements Pb, Zn, Ni and Cd have a predominantly anthropogenic source, with Cr and Cu having a mixture of crustal and anthropogenic origin. (b) cascade impactor samples were used to asses the size fractionation of the NSA; results indicate that the trace elements Pb, Cd, Zn and Ni have a anthropogenic origin, while Al and Fe are of crustal origin and Cr had a mixture of crustal and anthropogenic origin.

A series of experiments were carried out on the NSA to assess (a) the solid state speciation of the trace elements Al, Fe, Cu, Cd, Zn and Pb. Preliminary results indicate that the trace elements Al and Fe have speciation signatures which are characteristic of crustal dusts, whereas the trace elements Cu, Cd, Zn and Pb show speciation signatures typical of urban generated anthropogenically produced particles. (b) the sea water solubility of Al, Fe, Cu, Zn and Pb in the NSA. Preliminary results indicate that there is a relationship between the amount of trace element from the NSA soluble in ammonium acetate and the sea water shake, and this is interpreted in terms of the environmental mobility of the trace elements. (c) artificial rain water solubilities pH ~4 were applied in order to assess the effects of rain water on NSA, and these solubilities were similar to those found for the solid state speciation and sea water solubility studies.

Modelled rainfall was applied to the UK end-member sample population. However, the results were indeterminate and no conclusions were drawn.

Finally the mean atmospheric concentrations of the trace elements Al, Fe, Cu, Pb and Zn are combined with the sea water solubility studies in order to assess (a) the fluxes of trace elements to the North Sea, and (b) the partitioning of these total fluxes into a soluble and a particulate flux.