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ATMOSPHERIC TRACE METAL BIOGEOCHEMISTRY AND FLUXES TO SHELF SEAS

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WELLS, CHRISTINA LOUISE

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ATMOSPHERIC TRACE METAL BIOGEOCHEMISTRY AND FLUXES TO SHELF SEAS

by

CHRISTINA LOUISE WELLS

A thesis submitted to the University of Plymouth
in partial fulfilment for the degree of

DOCTOR OF PHILOSOPHY

Department of Environmental Sciences
Faculty of Science

June 1999

ABSTRACT

ATMOSPHERIC TRACE METAL BIOGEOCHEMISTRY AND FLUXES TO SHELF SEAS.

The total concentrations of particulate trace metals (Al, Cd, Co, Cu, Fe, Mn, Na, Ni, Pb, Zn) with analytical quality assurance, have been determined in atmospheric aerosols at two coastal sites, and during cruises in the Celtic Sea. Sampling at a site on the western English Channel covered 19 months and represents one of the most comprehensive time series of trace metals in atmospheric aerosols. Aerosol concentrations of Cd, Cu, Pb and Zn for the English Channel were lower than previously reported and Al, Co and Mn concentrations were similar to literature values. The elements were grouped according to behaviour such that Group 1 elements (Cd, Fe, Mn, Pb and Zn) displayed enhanced concentrations in autumn/winter 1994 and 1995, whereas Group 2 elements (Al, Co, Cu, Na and Ni) had enhanced concentrations during winter 1995 only. This was ascribed to source functions being dependant on wind direction with Group 1 elements being carried mainly by north easterly air masses, whereas Group 2 elements originated mainly with air masses from the south west. Dissolved trace metal (Al, Co, Cu, Ni, Pb) analyses were carried out on rain waters collected at the English Channel site. The rain water analyses showed that the soluble trace metal fraction was in the order Co = Cu > Ni >Pb > Na >> Al and wet and dry depositional fluxes accounted for the differential behaviour and the solubility of aerosol trace metals on contact with sea water. Aerosol concentrations are also reported for the north western Mediterranean and the Celtic Sea. In the former location, the aerosol trace metal concentrations were lower than those reported in literature and in the Celtic Sea there was a gradient in the trace metal composition of the aerosol from land to open sea. The solid state speciation of Cd and Pb gave an increasingly matrix-bound fraction in the order north western Mediterranean < western English Channel < Celtic Sea and the Celtic Sea aerosols had the greatest sea water solubilities of all elements, except Ni. Concentrations of Cu, Ni and Pb in English Channel aerosols, rain waters and the fraction partitioning from aerosols on contact with sea water, together with sea water concentrations from the literature, were used to devise a trace metal flux model for the English Channel. The model showed that of the total trace metal fluxes into the English Channel, the atmospheric fluxes were in the order of importance Pb > Cu > Ni. The overall budgets revealed discrepancies in the mass balances, which were identified as sediment-water exchange for Ni and Pb and adsorption onto particles for Cu. These budget calculations provide a basis for the development of more advanced modelling concepts involving coupled atmosphere-ocean interactions.

Acknowledgements.

Firstly, I would like to thank Prof Geoff Millward and Dr Malcolm Nimmo for their enthusiastic supervision throughout my research project. It was the best of times; it was the worst of times!

I am indebted to the following people, all of whom have aided the smooth running of this project: Keith Chell and all the staff of Slapton Ley Field Centre, particularly Karen, James, Louise and Lawrence; Department of Environmental Sciences Technical Staff particularly Andy; Brian Pateman and everyone in Technical Services (Mechanical); Department of Geology Technical Staff particularly Roger and Maggie; Dr Jeremy Clark; Dr Andy Fisher; Adrian Hopkins; Ann Kelly; Cristina Rivas; Dr Mark Williams; Dr Len Wood; Prof. Paul Worsfold; Paula Corcoran; and Gareth Johnston of the Environment Agency TAPS Centre. I would particularly like to thank Dr Peter Statham for allowing my participation on the cruise, Stan Smith and all the RVS personnel involved with deploying my sampling equipment. In addition I would like to thank Dr Scott Fowler and Dr Olivier Cotret of the International Atomic Energy Agency in Monaco for the collection of the north western Mediterranean aerosol samples, Prof. Roy Chester of the University of Liverpool for funding the sampling programme, and also Dr Eric Achterberg of the University of Plymouth for the collection of aerosol samples during the August - September 1995 OMEX research cruise. I would also like to thank Dr Gary Fones for his advice on many aspects of the research. My thanks also to everyone at West Lothian Council Environmental Health &Trading Standards for their support.

I would like to thank all my friends in the Department of Environmental Sciences, past and present, for making my time at the University of Plymouth such a memorable one, particularly Mark, Tonia, Yang Ping and Jo of the Marine Chemistry Group for their companionship over the past three years and for being great friends. The same goes for Dave, Andy and Bob for their continued support. Above all, my deepest gratitude goes to Marie and Carl for their love, support and friendship. Thank you. My thanks also to my Mum and Sister for their support throughout the last eight years and for always being there. I'm very proud of you both.

Finally, I would like to thank my husband, Ian, for putting up with the full range of emotions that have accompanied the production of this thesis. Without his support this thesis would not have been produced.

Author's Declaration.

At no time during the registration for the degree of Doctor of Philosophy has the author been registered for any other University award, nor registered as a candidate or enrolled student at any other academic or research institution. A programme of advanced study was undertaken, which included participation on a research cruise as part of the Ocean Margin Exchange Programme, and attendance on the Erasmus Eurocourse 'Frontiers in Analytical Chemistry: environmental trace analysis'. Relevant scientific seminars and conferences were regularly attended at which work was often presented.

Publications.

Hunt C.L., Nimmo M., Millward G.E., Fowler S.W., Cotret O. and Chester R., (1995) *Contrasting atmospheric trace metal geochemistries and fluxes to coastal systems.* Heavy Metals in the Environment 10, Vol. 1: 220-223.

Presentations and conferences attended.

Digestion and Analysis Procedures for the Standard Reference Material MESS-1 as a Precursor to Atmospheric Trace Metal Determination, Research and Development Topics in Analytical Chemistry (Royal Society of Chemistry - Analytical Division), July 10th -11th 1994, University of Hertfordshire, Watford.

Atmospheric Trace Metal Biogeochemistry and Fluxes to the Western English Channel, Slapton Research Seminar, November 26th 1994, Slapton Ley Field Centre, Slapton, Devon.

Atmospheric Trace Metal Inputs to Coastal Waters, Research Colloquium, 23rd March 1994, University of Plymouth.

Atmospheric Derived Dissolved Trace Metal Fluxes to the Western English Channel, Research and Development Topics in Analytical Chemistry (Royal Society of Chemistry - Analytical Division), July 10th -11th 1995, University of Hull, Hull.

Temporal Variations of Aerosol Trace Metals in the Western Mediterranean Sea, Progress In Chemical Oceanography, July 14th - 15th 1995, University of East Anglia, Norwich.

Contrasting Atmospheric Trace Metal Geochemistries and Fluxes to Coastal Systems, 10th International Conference on Heavy Metals in the Environment, September 18th - 22nd 1995, University of Hamburg, Hamburg, Germany.

Contrasting Atmospheric Trace Metal Geochemistries and Fluxes to Coastal Systems, Reasearch Colloquium, 18th October 1995, University of Plymouth.

Atmospheric Trace Metal Geochemistries of the Western English Channel, Slapton Research Seminar, November 25th 1995, Slapton Ley Field Centre, Slapton, Devon.

Contrasting Atmospheric Trace Metal Geochemistries of Selected Marine Environments, UK Oceanography '96, 2nd - 9th September 1996, University of Wales, Bangor, North Wales.

Signed Christina L Wells

Date 19th June 1999

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This thesis is dedicated to the memory of my Grandparents

Les and Iris Walker

'No door ever closed, but another one opened.'

-Gaelic Proverb.

Chapter 1.

Introduction.

Chapter 1.

Introduction.

1.1 The magnitude of the atmosphere as a source of trace metals to shelf seas.

Over the last two decades the atmosphere has been recognised as an important source of trace metals to the world's oceans (e.g. Martin *et al.*, 1989). This is particularly important in regions bordered by industrial nations where the atmospheric flux, for a number of elements, may exceed the fluvial flux. Martin *et al.* (1989) demonstrated that atmospheric inputs of anthropogenic derived trace metals (Cd, Cu, and Pb) to the north western Mediterranean Sea exceeded corresponding fluvial inputs by one to two orders of magnitude. Atmospheric inputs have been found to strongly influence coastal and open ocean spatial dissolved elemental distributions, most notably that of Pb, which has been attributed to vehicle particle emission deposition (Copin-Montegut *et al.*, 1986; Helmers *et al.*, 1991). Similarly, enhanced dissolved trace metal concentrations have been observed in the surface waters of the Atlantic Ocean (Jickells, 1995), the Pacific Ocean (Maring and Duce, 1990) and the Mediterranean Sea (Guieu *et al.*, 1992). Lead and Ni in the North Sea, have been found to have predominately atmospheric sources (Chester *et al.*, 1993a; Ottley and Harrison, 1993). It is therefore necessary to consider both fluvial and atmospheric sources when constructing trace metal budgets for the marine environment.

Atmospheric inputs have two components: dry deposition and wet deposition. Marine biogeochemistry may be influenced by the extent to which particle associated trace metals are solubilised in rain water (wet deposition input) and in sea water (dry deposition input) (Chester *et al.*, 1993a; Giusti *et al.*, 1993; Jickells, 1995). The solubilisation is largely influenced by the chemical characteristics, such as the solid state speciation or potential environmental mobility (Chester *et al.*, 1993a) of the particles and the particle source (crustal, marine or anthropogenic). Thus, the impact of atmospheric inputs on the trace metal biogeochemistry of marine systems is dependent upon the type and reactivity of particles transported atmospherically to the region.

Trace metal budgets for European shelf seas illustrate the lack of knowledge of the relative importance of atmospheric inputs. The western English Channel is an area where information is sparse. This coastal system has some data available on trace metal fluxes in the water column (e.g. Cabioch, 1996; James *et al.*, 1993; Prandle *et al.*, 1996; Reid *et al.*, 1993; Statham *et al.*, 1993), although the only documented atmospheric studies are those of Austin and Millward (1986), Losno *et* *al.* (1992) and Otten *et al.* (1994). Therefore, the current study addressed the deficiency of knowledge of atmospheric trace metal inputs to the western English Channel. The study of atmospheric fluxes was complemented by analyses of samples from the north western Mediterranean Sea which has been investigated by many workers over the past decade (e.g. Guieu *et al.*, 1992; Nimmo and Chester, 1993). This allowed inter-comparison of aerosols at two coastal sites, with differing meteorologies and aerosol source strengths and types. The north western Mediterranean is heavily influenced by anthropogenic emissions from northern Europe and seasonal pulses of crustal material from North Africa, whereas the western English Channel is influenced predominantly by marine Atlantic air masses. To assess the representative nature of the land based sampling site in the western English Channel, a study of the atmospheric inputs of trace metals to the north east Atlantic Ocean was carried out, through participation on two research cruises.

1.2 Aims of the study and thesis structure.

The aims were:

- to collect a time series of the trace metal (Al, Cd, Co, Cu, Fe, Mn, Na, Ni, Pb, Zn) content of atmospheric samples at a fixed site on the coast of the western English Channel, to facilitate a better understanding of the annual and seasonal impact of atmospheric deposition on trace metal cycling in sea water;
- to determine the trace metal content of atmospheric aerosols at a coastal site in the Mediterranean Sea, to provide contrasts with the mid-latitude site;
- to determine the trace metal content of atmospheric aerosols in a mid-latitude shelf sea environment for comparison with the land-based site;
- to enhance the understanding of trace metal geochemistry via a three stage sequential leach (Al, Cd, Fe, Mn, Pb) and model sea water solubility studies (Al, Co, Cu, Ni, Pb), to include the speciation of sea water soluble trace metals, and the speciation of trace metals in rain water samples using a Lumogallion/fluorescence technique for the analysis of Al, and Adsorptive Cathodic Stripping Voltammetry (ACSV) for all remaining metals;
- to provide a link between trace metal source, transport through the atmosphere, deposition mechanisms, and marine cycling, via the development of box models for selected trace metals (Cu, Ni and Pb).

From the outset, the aims were directed towards the English Channel, as only two previous studies had been conducted on this region, and also from a sampling point of view, it was readily accessible. This enabled one of the most comprehensive time series of trace metals in atmospheric aerosols that has been obtained to date for a coastal site. Therefore, a significant component of the results and discussion (Chapter 5) centres on the English Channel. However, during the first year of the project, aerosol samples, which were collected at a coastal site in Monaco during spring 1993, became available and it was felt that these samples could provide a valuable comparison with the English Channel aerosol samples (Chapter 6). In discussions with Dr Peter Statham in February 1995, the possibility of aerosol sampling on board RRS Charles Darwin arose, which would enable the collection of aerosol particles from the Celtic Sea. Such samples would represent marine aerosols and would interface with the land-based collection of the English Channel aerosols. The details are given in Chapter 7.

The three regions are reported separately to give a clear account of the individual trace metal characteristics. They are then compared and contrasted in Chapter 8 where fluxes, calculated from the three different data sets, are summarised and compared. The flux data from the English Channel also allows box models to be developed for selected elements (Cu, Ni and Pb) to demonstrate the relative importance of trace metal sources to the English Channel and potential movement within the system.

Chapter 2.

Trace metals in the marine atmosphere.

Chapter 2.

Trace metals in the marine atmosphere.

2.1 Trace metals in the marine environment.

Trace metals enter the marine environment via five distinct pathways: (i) riverine, (ii) atmospheric, (iii) glacial, (iv) hydrothermal, and (v) remobilisation from sediment (Chester, 1990) (Figure 2.1). Of these pathways, the riverine and atmospheric routes are probably the most important, particularly in coastal zones (Martin *et al.*, 1989). Both of these pathways receive trace metals through chemical and/or physical weathering, and human exploitation of geological reserves, with the latter becoming increasingly important over the past two centuries, due to increased industrialisation. Increased input of trace metals to the marine environment (particularly those of anthropogenic origin) can have a potential detrimental affect on water quality, particularly within semi-enclosed seas such as the Mediterranean Sea, which is subject to the influence of the heavily industrialised areas of Europe (Martin *et al.*, 1989).

2.2 Atmospheric inputs of trace metals to the marine environment.

The atmosphere is an effective transport mechanism for the transfer of aerosol particles to shelf seas and remote regions. For example, Delaney (1967) maintained that material in equatorial North Atlantic deep sea sediments, collected in the vicinity of the Mid Atlantic Ridge, were terrestrially derived, and transferred to that region entirely by atmospheric transport. Non-biogenic materials in deep sea sediments of the North Pacific have also been attributed to atmospheric origin (Blank *et al.*, 1985).

The transfer of Pb by atmospheric transport has been widely reported. Sturges *et al.* (1993) reported the discovery of Pb in the Alaskan Arctic aerosol that reportedly originated from the former Soviet Union, and eastern and western Europe. Evidence has also been found of anthropogenic Pb in Greenland snow (Lobinski *et al.*, 1994a;b), to the extent that a record of leaded fuel consumption over the past 70 years, was observed in snow and ice cores, according to the assumption that 'the Pb concentration in successive layers of precisely dated snow and ice is proportional to that existing in the polar troposphere at the time of precipitation.'

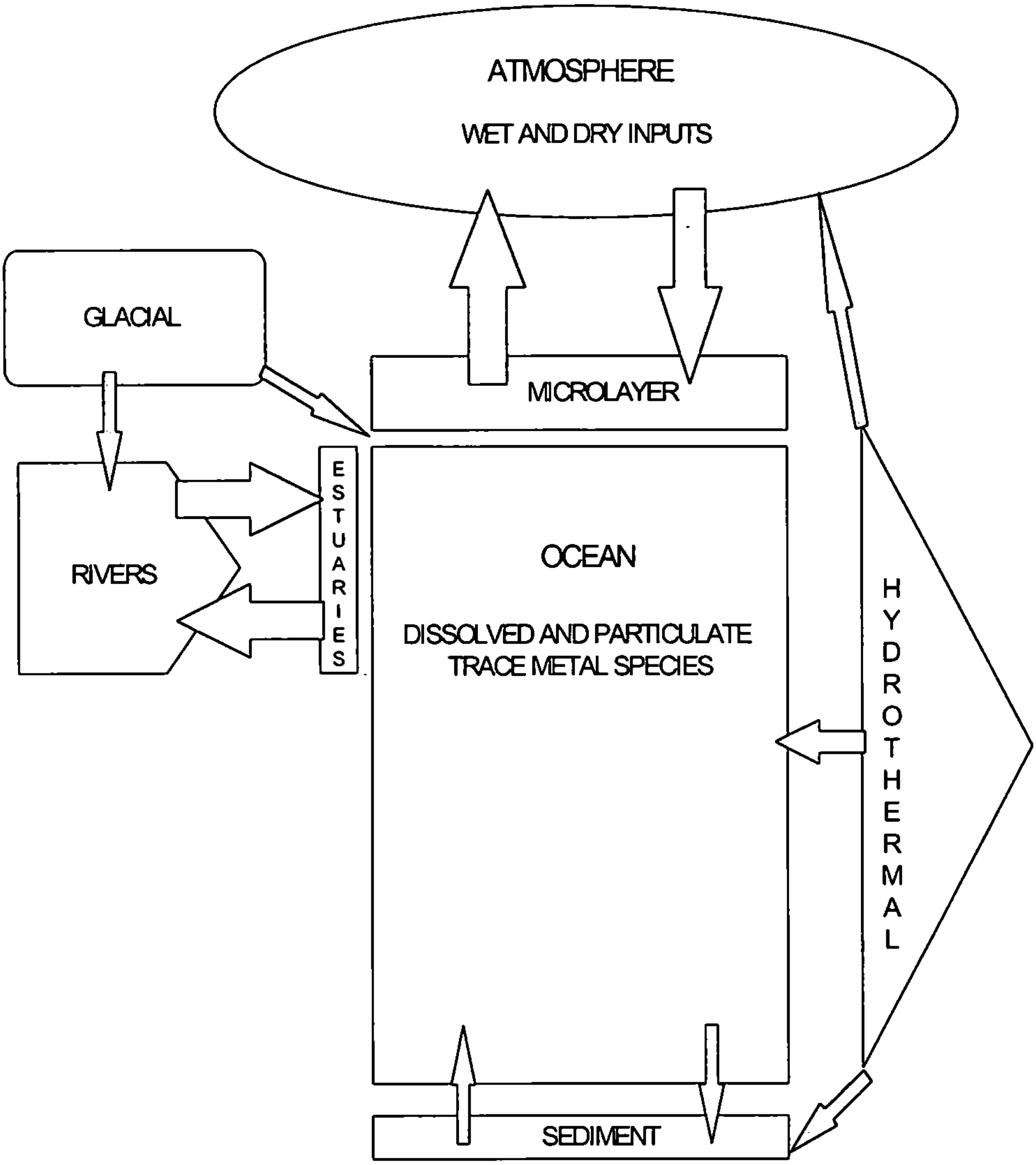

Figure 2.1: sources of trace metals to the marine system (based on Chester, 1990). There is no significance in the size of the boxes.

Martin *et al.* (1989) reported that the atmospheric flux of Pb (plus Cd and Cu) to the western Mediterranean Sea exceeded riverine inputs by one to two orders of magnitude, while Patterson and Settle (1974) estimated that 45 percent of the pollutant Pb input to a 12 000 km^2 area of the Southern Californian Bight originated from atmospheric input. Duce *et al.* (1975) estimated that ~ 13 percent of the pollutant Pb input to 1000 km^2 of the New York Bight originated from atmospheric input. It was also reported that atmospheric input accounted for ~ 5 percent of the Fe and ~ 2 percent of the Cd input to this area. More recently, Ottley and Harrison (1993) estimated that atmospheric transport was responsible for the input of 370 tonnes of Pb per year, plus 33 tonnes of Cd, 350 tonnes of Cu and

2640 tonnes of Zn to the North Sea. Indeed Pb, and other trace metals having a predominately anthropogenic source, have been used as markers of long range atmospheric transport of pollutant plumes (Mukai *et al.*, 1994) and of both crustal and anthropogenic material (Veron *et al.*, 1992). However, atmospheric and oceanic concentrations of anthropogenic Pb appear to be waning rapidly (Wu and Boyle, 1997) due to the diminished use of leaded petrol.

In order to assess and understand the importance of the atmosphere as a transport pathway of trace metals to the marine environment, the following key factors should be addressed:

(i) sources of trace metals to the marine atmosphere;
(ii) trace metal transport mechanisms within the marine atmosphere;
(iii) methods of trace metal removal from the marine atmosphere, through wet and dry deposition;
(iv) the magnitude of trace metal fluxes and inputs to the marine environment;
(v) post deposition biogeochemistry of trace metals within the marine environment.

2.3 The marine aerosol.

Aerosols can be defined as a suspension of solid or liquid particles in gaseous media, where the particles are comprised of a small, discrete mass of solid or liquid matter (Harrison and Perry, 1986), and have diameters in the range of 1 x 10^{-3} to 100 µm (Lodge *et al.*, 1981). Factors that influence particle concentration in the atmosphere include (i) particle sources, (ii) emission rates, (iii) chemical reactions, and (iv) efficiency of particle removal processes. Particle components of the world aerosol are formed via two processes: (i) direct formation of particles (through sea salt generation, crustal weathering and volcanic emissions), and (ii) indirect formation, within the atmosphere, through the condensation of gases and vapours, and chemical reactions (Chester, 1990). The size and shape of individual types of particle are determined by their method of formation and source, and are rarely uniform (Brimblecombe, 1986).

Studies undertaken by Whitby (1977) have presented a multi-modal distribution of aerosol particles (Figure 2.2), which are generally associated with particle formation processes, and particle size. Particles of diameter < 2 µm were termed the 'fine' particles and were generally associated with anthropogenic sources, whilst particles of diameter > 2 µm were termed the 'coarse' particles, and were generally associated with natural sources.

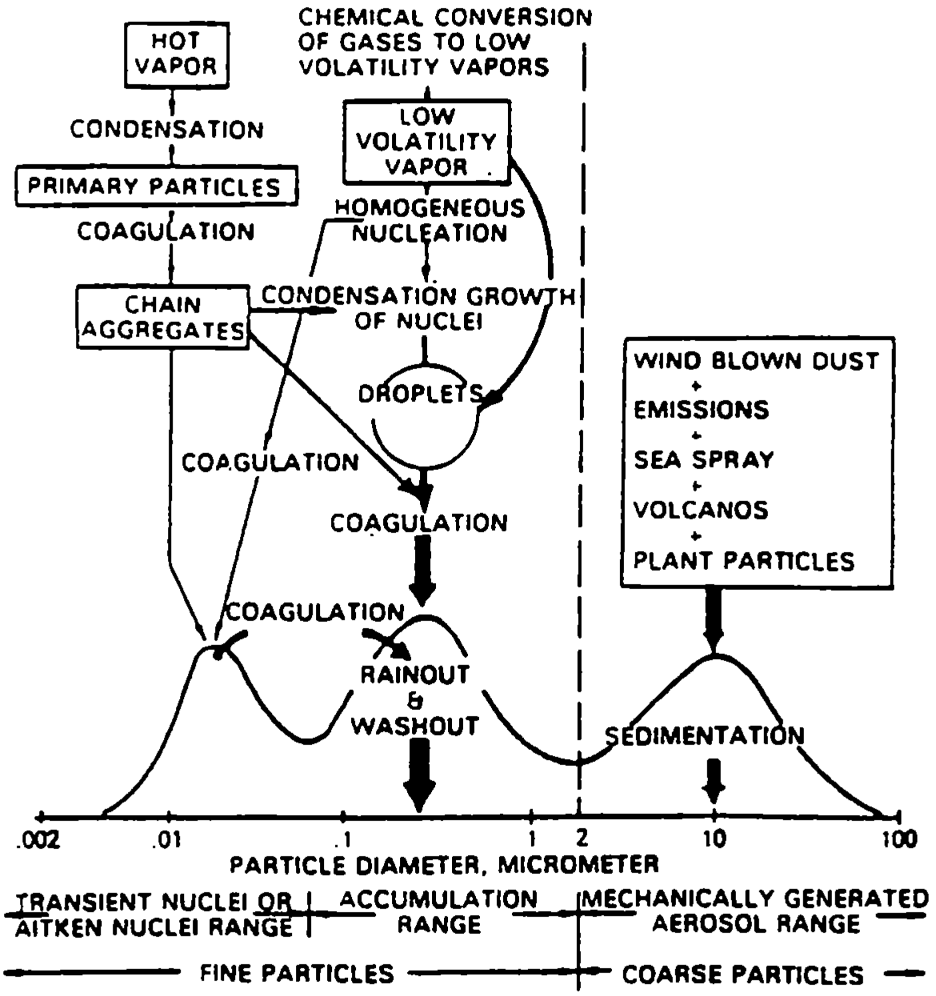

Figure 2.2: the distribution of aerosol particles based on particle size and particle formation processes (from Whitby, 1977).

The maxima associated with 'fine' particles represent two particle populations: (i) those with diameters < 0.1 μm which are in the 'Aitken nuclei' range and (ii) those with diameter of 0.1 - 2 μm which are in the accumulation range (Chester, 1990). Aitken nuclei originate from combustion processes, both anthropogenic and natural (e.g. from volcanic emissions and forest fires). They can also originate from some non-combustion processes. The coagulation of Aitken nuclei result in larger aggregated particles being formed - these comprise the accumulation range. The condensation of reaction products or water onto primary particles also results in the formation of particles in the accumulation range (Whitby, 1977). 'Coarse' particles originate primarily as a result of mechanical processes, such as crustal weathering and sea spray (Oblad and Selin, 1986), but also as a result of the incomplete combustion of other particles (Wadge *et al.*, 1986) and of the re-suspension of precipitated dust in the atmosphere (Nicholson, 1988). Such particles have a shorter residence time in the atmosphere (typically only a few days) compared with 'fine' particles, due to their larger size and hence greater settling velocities (Arimoto and Duce, 1986). However, their atmospheric residence time can be increased, during periods of unstable meteorological conditions, due to strong winds maintaining aerosols in suspension.

Junge (1972) classified the size of particles in the North Atlantic marine aerosol. Five classes were identified: (i) particles with diameters > 40 μm (biological material, cenospheres, giant sea spray particles), (ii) sea spray particles, (iii) mineral dust particles, (iv) tropospheric background particles, and (v) particles with diameters < 0.06 μm. Each component was similar in nature to its source when the aerosol was in the vicinity of the source. However, at distance from the source, the component had been chemically and physically modified. Therefore the character of the overall aerosol changed with increasing distance from component sources: components were dispersed resulting in lower component concentrations, the particle size distribution was altered (due to variations in particle settling velocity) and therefore the chemical composition of the aerosol became more uniform (Chester, 1990). The composition of the marine aerosol (both chemically and physically) is extremely temporally and spatially variable, being continually governed by processes which control the generation, modification, transport and removal of particles, thereby fulfilling the description of an aerosol, given by Prospero *et al.* (1983), as a 'dynamic aerosol continuum'.

2.3.1 Sources of trace metals to the marine aerosol.

When considering the sources of trace metals to the marine aerosol, it is necessary to consider the temperature at which the particles were formed. The temperature of particle formation is particularly important in application to metal speciation studies. The low temperature generation of particles includes natural processes such as aeolian weathering of crustal material (originally formed at high temperature), the mechanical generation of sea salts and the emission of particles and vapours from plant and soil surfaces, while anthropogenic examples include industrial processes such as mining, and agricultural utilisation. High temperature generation of particles include volcanic activity, the burning of vegetation, waste material incineration, fossil fuel combustion, chemical production and ore processing. Elements like Hg, As, Se and Sb may undergo volatilisation by physical processes (Goldberg, 1976) or by biomethylation (Austin and Millward, 1986). For trace metals, their enrichment factors in atmospheric aerosols are inversely related to the boiling points of the metal oxides (Duce *et al.*, 1976a).

The size of different sources has been estimated by several workers (e.g. Lantzy and Mackenzie, 1979; Nriagu, 1979; Prospero *et al.*, 1983). A summary of the magnitude of natural and anthropogenic emissions, divided into direct and particle conversion processes, is given in Table 2.1 and the general processes which supply metals to the atmosphere, are (Chester, 1990):

(i) those dominated by injection of crustal material to the atmosphere, such as Al, Co, Fe, Mn and Sc;

(ii) those dominated by the generation of sea salts e.g. K, Mg, Na;

(iii) those dominated by anthropogenic inputs, such as Ag, As, Cd, Cu, Hg, Mo, Ni, Pb, Sb, Se, Sn, V and Zn.

The influence of these inputs is more localised for some than others. The Earth's crust and the sea surface are more of a source of trace metals to the global atmosphere than anthropogenic inputs, as anthropogenic inputs originate from a number of localised industrial regions predominantly in the Northern Hemisphere.

2.3.1.1 Identification of trace metal sources.

Since the marine aerosol is composed of material from different sources, each with different chemical characteristics, the overall composition of the marine aerosol varies in response to the extent to which the various components are present. It has also been shown that the influence of specific sources can vary locally, and this is reflected in the concentration of individual components. For example, the estimated concentration range (ng m^{-3}) for Al and Fe is 1 - 10^4, 0.1 - 10^1 for Cu, and 0.1 - 10^2 for Mn, Pb and Zn (Chester, 1990). At a certain location, the aerosol trace metal concentrations are dependent on a number of factors and the extent to which the aerosol has been modified, which is related to its age.

Losno *et al.* (1992) utilised trace metal concentration variations to determine the origins of particles in aerosols over the North Sea, English Channel, and the North and South Atlantic Oceans, with respect to latitude. The areas were categorised into three classes each influenced by a different trace metal source. The North Sea and English Channel were grouped together and were deemed to be predominantly influenced by anthropogenic emissions. The tropical North Atlantic was the second classification, being strongly affected by dust pulses originating from the arid and semi-arid areas of Africa. The third class was the tropical South Atlantic, where the major source of trace metals to the atmosphere was through the burning of biomass. However, other methods of source identification

Table 2.1: estimates of global particle emissions to the atmosphere (10^{12} g yr^{-1}).

Source	Global Production#		
	1	2	3
Man made			
Direct particle production	30		
Particles formed from gases			
Converted sulphates	200		
Others	50		
Total man made	280		200
Natural			
Direct particle production			
Forest fires	5	36	
Volcanic emissions	25	10	
Vegetation		75	
Crustal weathering (mineral dust)	250	500	
Sea salt	500	1000	
Particles formed from gases			
Converted sulphates	335		
Others	135		
Total natural	1250		
Overall total	1530		

1. Prospero *et al.*, 1983; 2. Nriagu, 1979; 3. Lantzy and MacKenzie, 1979.

have been employed:

(i) particle size and shape (Arimoto and Duce, 1986);

(ii) elemental enrichment factors (Rahn *et al.*, 1979);

(iii) Pb isotopic ratios (Kersten *et al.*, 1992).

As has been previously mentioned, the marine aerosol is comprised of 'fine' and 'coarse' particles, and that the process of particle formation can be either classified as high temperature or low temperature. It has been generally noted that 'fine' particles are associated with high temperature, anthropogenic sources, while 'coarse' particles are derived from low temperature, natural sources. Within the 'coarse' fraction of the aerosol, there are two divisions, based on particle size: those particles of crustal origin, and those of marine origin. Crustal particles have an irregular shape, while marine derived particles are more geometrically regular (e.g. sea salt nuclei). It can therefore be demonstrated that an assessment of the size and shape of the particles with which the element associates can determine the source of an element. A number of studies have used this theory to demonstrate source attribution. For example, Arimoto and Duce (1986) determined the mass size distributions of ^{210}Pb, which can be approximated as an element having a mass predominantly associated with sub-micrometer particles, inherent to anthropogenic sources; Al, which is typically associated with crustal sources of particles; and Na which is typical of sea salt derived elements (Figure 2.3).

Chester (1990) concluded that:

- sea salt associated elements (Ca, K, Mg and Na) have most of their total mass on particles with median mass diameters (MMDs) in the range ~ 3 - 7 μm.
- crustally derived elements (e.g. Al, Ce, Co, Eu, Fe, Hf, Rb, Sc, Th and V) have most of their total mass on particles with MMDs in the range ~ 1 - 3 μm.
- elements associated with high temperature sources (mainly anthropogenic) (Cd, Cu, Pb, Sb and Zn) have most of their total mass on particles with MMDs 0.5 μm.

Chester *et al.* (1991) also used particle size distributions to determine trace metal sources over the Indian Ocean. Using a cascade impactor sampler, with sizes ranging from 16.7 μm to < 0.55 μm, they were able to attribute a dominant source to each element, even though they found that all elements were associated with particles of all sizes. They noted that Al, Fe and Mn were associated with particles of MMD >3.6 μm, Cd, Pb and Zn were associated with all sizes of particles, while Cu was associated with all, except small, particle sizes. Therefore Chester *et al.* (1991) were able to conclude that there were two end-member aerosols in the lower atmosphere over the Indian Ocean/Arabian Sea: one was a strong pollutant influenced end-member, and the other was a strong crustally influenced end-member. In remote areas it is also likely that a number of trace elements will be

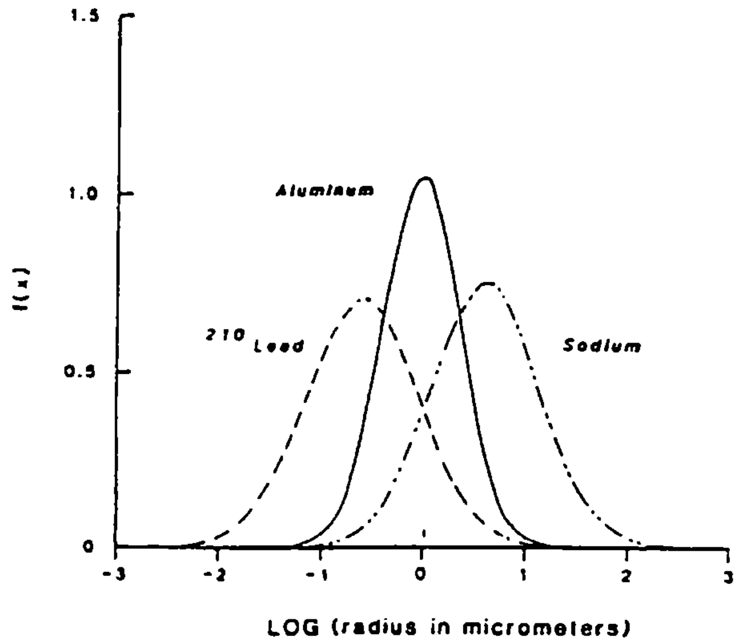

Figure 2.3: frequency (f) vs. radius (x) distribution of ^{210}Pb, Al and Na as markers of anthropogenic, crustal and marine sources (from Arimoto and Duce, 1986).

associated with particles having MMDs in the range of ~ 3 - 7 µm, indicative of a sea salt source (Duce *et al.*, 1983).

Elemental enrichment factors assess the relationship of an element in the aerosol to source composition using the equation:

$$EF_{Source} = (E/I)_{Air} / (E/I)_{Source} \qquad \text{(Eqn 2.1)}$$

where $(E/I)_{Air}$ is the ratio of the concentration of element E with the concentration of the source marker I in the aerosol, and $(E/I)_{Source}$ is the ratio of the concentration of element E to the concentration of source marker I in the source material.

The most commonly used enrichment factor is the crustal enrichment factor (EF_{Crust}), which uses Al as the source marker, although Fe has also been used (Yaaqub *et al.*, 1991). The largest error which can occur with this type of calculation is the use of inappropriate $(E/I)_{Source}$ data. The most commonly used data is that of average crustal rock (e.g. Taylor, 1964). Thus the equation employed for EF_{Crust} calculations is:

$$EF_{Crust} = (E/Al)_{Air} / (E/Al)_{Crust} \qquad \text{(Eqn 2.2)}$$

where $(E/Al)_{Air}$ is the ratio of the concentration of element E to the concentration of Al in the sampled aerosol, and $(E/Al)_{Crust}$ is the ratio of the concentration of element E to the concentration of Al in average crustal rocks. However, due to the use of average crustal ratios for $(E/Al)_{Crust}$, EF_{Crust} calculations should only be regarded as source indicators within an order of magnitude, and for this reason, $EF_{Crust} = 10$ is considered to be the 'boundary' between elements which are largely crustal in origin ($EF_{Crust} < 10$) and elements which are largely non-crustal in origin ($EF_{Crust} > 10$) (Chester *et al.*, 1993b).

Rahn *et al.* (1979) classified ~ 70 elements according to their EF_{Crust} in the world aerosol. The geometric mean EF_{Crust} are given in Table 2.2, which shows that in the world aerosol, the majority of the considered elements are largely crustal in origin, having an $EF_{Crust} < 10$. Such elements are known as crustal, or non-enriched elements (NEEs). Elements with $EF_{Crust} > 10$ are known as non-crustal or anomalously enriched elements (AEEs) (Chester, 1990). NEEs will almost always have $EF_{Crust} < 10$, indicating that they retain their crustal character in all aerosol types. Conversely, the EF_{Crust} of AEEs are greatly affected by the proportion of non-crustal material in the atmosphere. Murphy (1985) illustrated this by comparing Cd, Cu, Fe, Pb and Zn EF_{Crust} in North Atlantic westerly air masses, which are influenced by the industrial regions of northern Europe, with EF_{Crust} of the elements in North Atlantic North East Trade Winds, which are influenced by the North African desert regions. The AEEs (Cd, Cu, Pb, Zn) demonstrated $EF_{Crust} > 100$ in the North Atlantic westerlies, but $EF_{Crust} < 10$ in the North Atlantic North East Trade Winds. However, Fe displayed $EF_{Crust} \sim 1.0$ in each aerosol type. Thus, Murphy (1985) concluded that under particular conditions, such as when there is a predominant crustal influence on the aerosol, AEEs can behave as NEEs because the concentration of Al, the crustal marker, is considerably higher in concentration than anthropogenically derived elements.

Chester *et al.* (1993a) employed EF_{Crust} to define the trace metal chemical composition of the Mediterranean aerosol. They observed that anthropogenically dominated aerosols were supplied from northern Europe, which is the main centre of European industrial activity. In addition, they found that the Mediterranean aerosol was heavily influenced by seasonal crustally dominated aerosols, which originated from the Saharan region. It was therefore concluded that the trace metal composition of the

Table 2.2: geometric mean EF_{Crust} values for ~ 70 elements in the world aerosol (from Rahn *et al.*, 1979).

Source	EF_{Crust} range	Elements
Crustal / marine	~ 0 - 10^1	Al, Ba, Be, Ca, Ce, Co, Cr, Dy, Er, F, Fe, Ga, Gd, Hf, Ho, K, La, Li, Lu, Mg, Mn, Na, Nb, Nd, Pr, Pu, Rb, Sc, Si, Sm, Sr, Tb, Th, Ti, Tl, Tm, U, Y, Yb, Zr
Anthropogenic / marine	~ 10^1 - 10^2	B, Cu, Cs, Ge, H, In, Ni, V, W
	~ 10^2 - 10^3	Ag, As, Au, Bi, Cl, Hg, I, Mo, S, Sn, Zn
	~ 10^3 - 10^4	Br, C, Cd, N, Pb, Sb, Se, Te

Mediterranean aerosol was constrained as a result of the mixing of anthropogenic and crustal components.

The enrichment factor concept can be applied to marine sources. In such cases, Mg can be used as the marine indicator (Keene *et al.*, 1986) although Na is more commonly used. EF_{Sea} is calculated using the equation:

$$EF_{Sea} = (E/Na)_{Air} / (E/Na)_{Sea\ water} \qquad \text{(Eqn 2.3)}$$

where $(E/Na)_{Sea\ water}$ is the ratio of the concentration of element E to the concentration of Na in bulk sea water. The main problem associated with EF_{Sea} is the use of bulk sea water elemental ratios, as their use can lead to high EF_{Sea} values, which suggest that the sea surface is not a contributory source of trace metals to the atmosphere. This is largely due to the nature of sea salt formation. Sea salts are formed when droplets of sea water are injected into the atmosphere through bubble bursting at the sea surface. During this process, sea salts become encapsulated within the surface microlayer material, which is itself enriched with trace metals with respect to bulk sea water (up to 10^3 to 10^4 times greater than bulk sea water) (Chester, 1990). Therefore, the use of elemental ratios from bulk sea water is unrepresentative of the natural processes.

In order to better understand marine trace metal sources, attempts to quantify trace metal concentrations in the microlayer have been made. One method of fulfilling this aim was the collection and analysis of bubble produced sea salts using the Bubble Interfacial Microlayer Sampler (BIMS) (Piotrowicz *et al.*, 1979). BIMS EF_{Sea} allow for trace metal enrichment with respect to bulk sea water.

BIMS EF_{Sea} values for the North Atlantic (Table 2.3) reveal two groups of elements: group 1 contains K, Mg and Na; group 2 contains Al, Co, Cu, Fe, Mn, Pb, Sc, Zn. Group 1 elements have BIMS EF_{Sea} and bulk sea water EF_{Sea} close to unity, thus retaining their original bulk sea water ratios in bubble generated sea salts. Group 2 elements have BIMS EF_{Sea} ranging from 10 for Sc up to 20 000 for Zn (Chester, 1990), thus indicating that the marine environment is not a significant source of these elements to the atmosphere. It should however be noted that the BIMS EF_{Sea} are lower than those for EF_{Sea}, where $EF_{Sea\ water}$ were taken from bulk sea water, thus illustrating the trace metal enriched nature of the microlayer.

Table 2.3: a comparison of EF_{Sea} values for selected elements.

Element	EF_{Sea}[a]	BIMS EF_{Sea}[b]
Al	1×10^6	5×10^3
Cd	-	-
Co	8×10^3	6×10^2
Cu	6×10^4	8×10^2
Fe	4×10^7	1×10^4
K	1.3	1.00
Mg	0.9	1.00
Mn	4×10^5	1×10^3
Na	1	-
Pb	5×10^5	4×10^3
Zn	2×10^6	2×10^4

[a] Chester *et al.*, 1984; [b] Chester, 1990.

Anthropogenic trace metals (largely AEEs) in the marine atmosphere are generally associated with high temperature processes, which do not have a readily identifiable source indicator. It is therefore difficult to calculate $EF_{Anthropogenic}$. While their presence can be acknowledged using EF_{Crust} and EF_{Sea}, other approaches must be employed for identification purposes. Particle size and shape can be used, although analysis of Pb isotopic ratios had potential application in this context. Recent studies have demonstrated that anthropogenic pollution is widespread. For example, 25 m ice cores have been removed from Greenland, and analysed for organo-Pb compounds, which are emitted following the combustion of leaded fuels (Lobinski *et al.*, 1994b). Lead concentrations in the precisely dated snow and ice, were believed to be proportional to the concentration of the compounds in the polar aerosol, and were found to correlate with the distribution of organo-Pb species in fuel, and the consumption of leaded fuel in both Europe and the USA. Total Pb concentrations ranged from a background level of 1 pg g^{-1} for a few millenniums of Greenland ice, down to ~ 480 fg g^{-1} covering a period of 4 - 6 months, with the highest concentrations observed in the 1970s to 1980s. It was thus concluded that anthropogenic emissions of Pb, from Europe and the USA, were reaching remote regions in relatively large quantities. Similar studies have also been conducted (e.g. Lobinski *et al.*, 1994a; Mukai *et al.*, 1994).

Owing to its relative abundance, Pb has become a useful marker of anthropogenic pollution. The most common method of analysis is by Pb isotopic ratio analysis which has become popular since the advent of inductively coupled plasma-mass spectrometry (ICP-MS). Lead has four naturally occurring isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. Of the four isotopes only ^{204}Pb is non-radiogenic and has an average natural abundance of 1.4 percent. The remaining isotopes are radiogenic daughters of ^{238}U, ^{235}U and ^{232}Th, with average natural abundances of 24.1 percent, 22.1 percent and 52.4 percent respectively. Since three of the four naturally occurring isotopes are radiogenic, the ratios of the four isotopes to each other will vary depending on the age of the source rock. Thus, provided the Pb isotopic ratios in source rocks are known, the source of atmospheric Pb can be traced. In western Europe, Pb which is added to petrol originates from Canadian and Australian ores. These ores are older in geological age compared with natural European sources, and therefore have lower Pb isotopic ratios, which allows distinctions between anthropogenic (< 1.1 for $^{206/207}$Pb) and natural (> 1.2 for $^{206/207}$Pb) Pb to be made (Kersten *et al.*, 1992). The isotopic ratio of $^{206/207}$Pb has been used over the past three decades to assess the influence of fuel combustion emissions on the composition of Pb in aerosols (e.g. Hopper *et al.*, 1991; Kersten *et al*, 1992; Sturges *et al.*, 1993).

2.3.2 Transport of trace metals in the atmosphere.

Terrestrially-derived material is initially injected into the planetary boundary layer where it mixes with the global aerosol. The transfer of material beyond the planetary boundary layer can be inhibited due to the presence of an inversion, which defines the boundary limit (Prospero, 1981) (300 to 600 m over the sea, to 1000 to 1500 m over land (Hasse, 1983)). According to Prospero (1981) material reaches the sea surface, prior to sea surface deposition, through two mechanisms: (i) through the marine boundary layer within distances of hundreds of kilometres of continental land masses, and (ii) material is transported via the free troposphere and then deposited through the marine boundary layer at distances > hundreds of kilometres, i.e. in remote oceanic regions. Thus in remote regions, the efficiency with which material is transferred from the free troposphere to the marine boundary layer will influence the distance which a component is transported. It could also be said that the composition of the aerosol in the marine boundary layer (principally a marine aerosol) would be different in composition to that of the overlying tropospheric aerosol (Chester, 1990).

The primary method of particle transport in the troposphere is via the major global wind systems which are driven by seven pressure belts which cover the Earth's surface (Barry and Chorley, 1992). These zonal wind systems aid the dispersion of aerosol particles around the globe, although transfer between zones is usually inhibited by the pressure belts. Long range aerosol particle transport is also restricted by the short residence time of particles within the troposphere, usually not in excess of a few weeks, while inter-hemispheric transfer requires a time scale of between 3 to 12 months.

The concentration of trace metals in the marine aerosol exhibit order of magnitude variations according to geographical location. Such variations can be attributed to factors previously mentioned (see section 2.3), with the lowest concentrations observed at remote regions. In addition, the composition of the aerosol will depend on the extent to which components of the aerosol are mixed in the atmosphere. The variation of aerosol trace metal concentration has been the subject of many investigations, in a variety of regions. A compilation of data from marine locations, arranged in order of remoteness from primary trace metal sources (crustal and anthropogenic) is displayed in Table 2.4. From the data, four principal trends emerge:

1. the highest concentrations of AEEs are found over coastal seas which are adjacent to continental anthropogenic sources;
2. the highest concentrations of NEEs are found over marine regions which are close to desert/arid regions;
3. the concentrations of both AEEs and NEEs decrease with increasing remoteness from continental sources, and give the general order of coastal seas > North Atlantic > North Pacific > South Pacific;
4. EF_{Crust} are higher in coastal seas, although those for the Samoan aerosol were higher than those for the less remote Enewatak aerosol (Duce *et al.*, 1983). This indicates that small, anthropogenic particles, which contain high concentrations of AEEs, have a longer residence time in the atmosphere, compared with the larger, NEE containing crustally derived particles.

Radlein and Heumann (1992) assessed the distribution of trace metals in aerosols over the Atlantic Ocean from Antarctica to Europe. They observed that total Fe concentrations varied from 0.22 ngm^{-3}

Table 2.4: geometric mean trace metal concentrations (1) and EF_{Crust} (2) over marine regions.

Conc	Coastal seas - bordering industrial regions				Coastal seas and open ocean - bordering arid regions				Open ocean											
(m^{-3} of air)	North Sea[a]		Irish Sea[b]		W. Med.[c]		N. Atlantic NE Trades[d]		Tropical N. Atlantic[e]		N. Atlantic (Bermuda)[f]		N. Atlantic westerlies[d]		S. Atlantic westerlies[d]		N. Pacific (Enewetak)[g]		S. Pacific (Samoa)[h]	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Al ng	219	1.0	210	1.0	324	1.0	5925	1.0	160	1.0	140	1.0	48	1.0	2.7	1.0	21	1.0	0.72	1.0
Cd ng	0.23	436	0.19	368	1.9	2413	0.12	8.3	-	-	0.19	558	0.11	943	0.02	3048	0.01	78	-	-
Co pg	190	2.7	140	2.1	-	-	2100	1.2	80	1.6	-	-	50	3.4	10	12	8	1.3	0.37	1.7
Cu ng	4.4	30	4.57	33	-	-	4.5	1.1	0.79	7.4	0.9	10	1.0	31	0.29	161	0.04	3.2	0.01	27
Fe ng	230	1.5	159	1.0	-	-	3865	1.0	100	0.9	94	1.0	36	1.1	2.6	1.4	17	1.2	0.21	0.4
Mn ng	9.1	3.5	4.43	1.8	-	-	65	1.0	2.2	1.2	1.2	0.7	1.7	3.1	0.11	3.5	0.29	1.2	0.01	0.6
Ni ng	2.5	13	3.71	19	-	-	6.6	1.2	0.64	4.4	0.08	0.6	0.51	12	0.02	8.1	-	-	-	-
Pb ng	20	601	15.1	468	40	812	6.9	7.7	9.9	407	3.5	164	6.0	882	0.97	2364	0.12	38	0.02	146
Zn ng	26	139	25.3	141	-	-	16	3.2	4.4	32	3.2	27	7.5	184	1.8	784	0.17	9.5	0.07	114

[a]Chester and Bradshaw, 1991; [b]Fones, 1996; [c]Dulac *et al.*, 1987; [d]Murphy, 1985; [e]Buat-Menard and Chesselet, 1979; [f]Duce *et al.*, 1976b; [g]Duce *et al.*, 1983; [h]Arimoto *et al.*, 1987;

in the Antarctic to 36 200 ng m^{-3} between the equator and 20 °N, which is influenced by the North East Trade Winds from the Sahara Desert. Copper concentrations were highest in both this zone of maximum crustal influence, and close to the European continent, while maximum Cd, Pb and Zn concentrations were only found close to Europe, due to its industrial nature. Conversely, the lowest concentrations of Cd, Cu, Pb and Zn were found in the Antarctic aerosol. However, their EF_{Crust} were high due to the very low crustal influence. Radlein and Heumann (1992) proposed that these trace metals originated from either anthropogenic contamination in Antarctica, long range transport of anthropogenic particles in the atmosphere, or emission from the polar Antarctic Sea.

Studies have also been undertaken on regional seas, such as the North Sea (e.g. Chester *et al.*, 1993a; Ottley and Harrison, 1993). Chester *et al.* (1993a) reported a S-N decrease in trace metal emissions from land masses surrounding the area. Three major source regions were identified, each with its own end-member type aerosol: continental Europe, UK and the open sea. Ottley and Harrison (1993) established a correlation between elemental distribution and source region, which indicated that the highest trace metal concentrations were associated with air masses which had passed over northern Europe, while the lowest were observed in air masses from the North.

2.3.3 Fluxes and inputs of aerosol particles to the marine environment.

Slinn (1983) described dry deposition as a combination of gravitational settling, turbulent diffusion, Brownian diffusion, interception and impaction. The removal of particles prior to dry deposition is predominantly as a result of wind speed and particle size, and is a continuous process. For example dry deposition of sea salts was found, by McDonald *et al.* (1982), to be dominated by particles which had MMDs > 10 μm. This fraction accounted for ~ 70 percent of the total deposition although only 13 percent of the total mass. It can therefore be stated that dry deposition processes are particularly important for the removal of large particles from the atmosphere. The calculation of particle fluxes involves the use of settling velocities. Settling velocities encompass all of the processes pertaining to dry deposition, such as gravitational settling, impaction and particle diffusion to the sea surface. However, since all of these processes occur simultaneously and are dependent on a number of variables (e.g. wind speed, particle size, particle shape, particle density, relative humidity, air viscosity, sea surface conditions), it is difficult to accurately define the term 'settling velocity'.

Duce *et al.* (1991) used two models to assess the dry deposition of particles which were too small to be greatly influenced by gravitational settling:

1. the first model was from Slinn and Slinn (1980). The relative humidity was assumed to be 98 percent, which is the maximum which can occur in air which is in contact with sea water (except under non-equilibrium conditions). The predicted settling velocities ranged from < 0.01 to > 0.1 cm s^{-1} depending on the particle size;
2. the second model was from Hicks and Williams (1980). This approach yielded settling velocities ranging from 0.01 to > 0.3 cm s^{-1} depending on the wind speed.

Both models were also applied to particles which were influenced by gravitational settling, and yielded comparable results, which did not differ greatly from those obtained via field measurements. From these studies it was concluded that for sub-micrometer aerosol particles a settling velocity of 0.1 cms^{-1} ± a factor of 3 should be used; for super-micrometer crustal particles, excluding those associated with sea salts, a settling velocity of 1.0 cm s^{-1} ± a factor of 3 should be used; and for large sea salt particles, a settling velocity of 3.0 cm s^{-1} ± a factor of 2 should be used.

A variety of field studies have been undertaken to quantify settling velocities, but these have yielded large variations. This has been attributed to the inadequacies of the adopted techniques, but mostly to environmental and geographical influences (e.g. Nicholson, 1988). Ottley and Harrison (1993) used a cascade impactor sampler to efficiently collect size separated aerosol particles from the North Sea atmosphere. From this they were able to estimate mass-weighted settling velocities (cm s^{-1}) in the order of Al: 0.33; Cd: 0.24; Cu: 0.44; Fe: 0.30; Pb: 0.13; Zn: 0.30. These settling velocities corresponded well with the model results of Duce *et al.* (1991), and revealed that the aerosol population of the North Sea was largely sub-micrometer in size. Field measurements made by Arimoto *et al.* (1990) estimated the settling velocities (cm s^{-1}) of selected trace metals in the remote New Zealand aerosol to be Cu: 1.5; Fe: 2.0; Mn: 4.8; Pb: 2.1; Zn: 5.8. This demonstrates the difference in settling velocities of particles in remote aerosols, where the particles are either crustal and/or marine in origin.

2.3.4 Trace metal post-deposition marine biogeochemistry.

Inevitably particles reach the sea surface, where they are incorporated into the marine environment. However, the biogeochemical role which particle-associated trace metals undertake, largely depends on the particle source. Various methods of source attribution were discussed in section 2.3.1, however, none allowed the investigation of the actual geochemistry of the particle i.e. the solid state speciation of particle associated trace metals. This could be achieved by the application of a sequential leach.

2.3.4.1 The determination of the speciation of trace metals in particles.

A variety of sequential leaching schemes have been applied to aerosol samples in order to release metals from specific host associations in an attempt to distinguish between elements from different sources (e.g. Chester *et al.*, 1989). This information can also be used to assess the marine environmental mobility (i.e. solubility in sea water) of trace elements, which enter the marine environment from aerosols through dry deposition. The benefit of using sequential leach schemes to assess the solid state speciation of trace metals, with respect to assessing their potential sea water fate, is most clearly demonstrated by a comparison of two studies: Lum *et al.* (1982) and Chester *et al.* (1986). Lum *et al.* (1982) investigated the solid state speciation of trace metals in the pollution dominated (i.e. high temperature generated) urban aerosol of St Louis (USA). They used a five stage sequential leaching scheme, extracting trace metals from the following solid phases: (a) exchangeable (or loosely held); (b) surface oxide and carbonate; (c) oxide; (d) organic, and; (e) residual (or refractory). The results are displayed in Figure 2.4, and reveal high proportions of Cd, Cu, Mn, Ni, Pb and Zn in stage one, the exchangeable fraction, which is indicative of an anthropogenic source, while the proportions of the elements in the residual stage, indicative of crustal origin, are low.

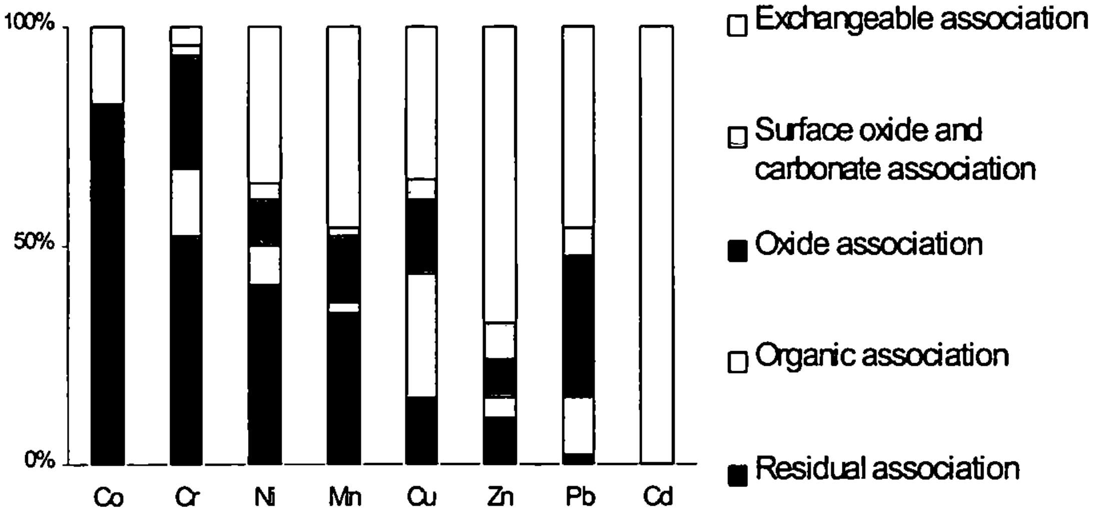

Figure 2.4: sequential extraction of trace metals in St. Louis (USA) aerosol particles: 1. Exchangeable association. 2. Surface oxide and carbonate association. 3. Oxide association. 4. Organic association. 5. Residual association. (Lum *et al.*, 1982)

Chester *et al.* (1986) investigated the solid state speciation of trace metals in soil-sized particles from the crustally dominated (low temperature generated) aerosol in the North East Atlantic Trade Winds off the coast of West Africa. Using the same sequential leaching scheme, they discovered that the majority of elements were located in the residual phase of the leach which is indicative of crustal influence (Figure 2.5). Even those elements generally accepted as having an anthropogenic origin

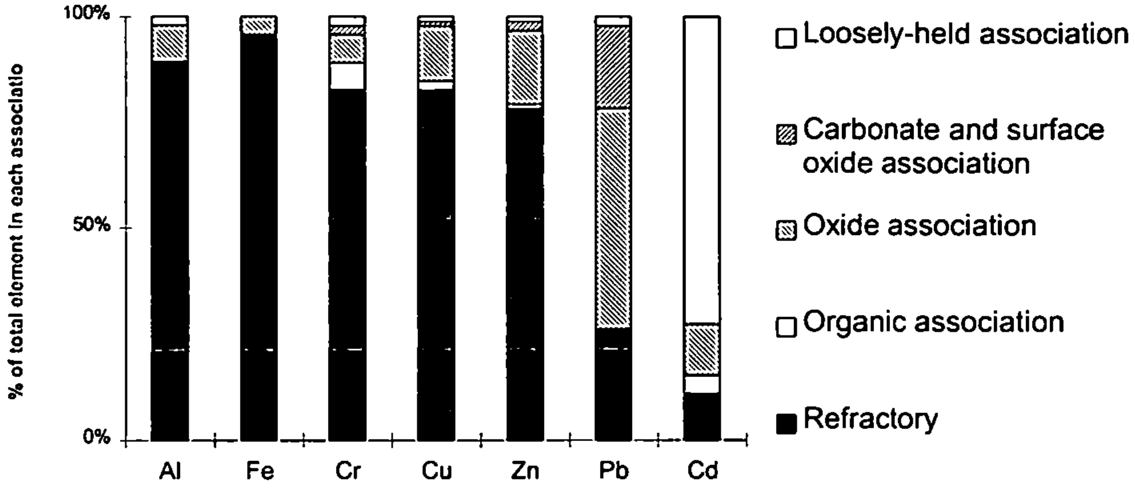

Figure 2.5: sequential extraction of trace metals in Atlantic North East Trade Wind aerosol particles (Chester *et al.*, 1986).

(Cd, Pb, Zn) had a comparatively higher residual fraction, indicative of a crustal origin or preferential release of easily exchangeable material during long range transport by for example washout processes. It can therefore be seen that aerosols which have been subject to different source influences contain particles which have unique trace metal solid state speciation signatures. According to Chester (1990), two trends emerge:

1. the refractory nature of some elements (e.g. Al and Fe) varies little between the two contrasting aerosol types assessed by Lum *et al.* (1982) and Chester *et al.* (1986). However, for other trace metals (e.g. Cd, Cu, Pb, Zn) the refractory portion is smaller in the urban dominated aerosol. For example the refractory portions of Cu and Zn in the crustally dominated aerosol are ~ 80 percent, but decline to ~ 15 percent in the urban aerosol;
2. similarly, the loosely-held portions of Al, Cr and Fe vary little between the two aerosol types, at < 5 percent for each, whereas the loosely-held portions of Cd, Cu, Pb and Zn are considerably higher in the urban dominated aerosol compared with the crustally dominated aerosol.

This clearly illustrates that elements which are potentially more volatile (e.g. Cd, Pb, Zn) have a greater affinity with the loosely-held fraction of the urban dominated aerosol with respect to the crustally dominated aerosol, indicative of high temperature, vapour phase emission, and subsequent adhesion to ambient particle surfaces.

Chester *et al.* (1989) illustrated the variation in the proportion of the loosely-held fraction at distance from pollution sources. They collected aerosol particles on filters along a N-S transect from the European coast to the North East Trade Winds off the coast of West Africa, and applied a three stage sequential leach to assess the solid state speciation of Cu, Pb and Zn. They observed that the loosely-held fraction of the trace metals decreased away from the European coast, towards the coast of West Africa. For example, the loosely-held fraction of Zn fell from ~ 80 percent in aerosols collected over Liverpool (representative of a European urban aerosol) to ~ 10 percent in aerosols collected in the Atlantic North East Trade Winds.

2.3.4.2 Trace metal sea water solubility and fate.

It has thus been demonstrated that aerosols which have been influenced by different sources will contain trace metals with distinctive solid state signatures. Chester *et al.* (1986) were the first to suggest that the solid state speciation of an element may influence its sea water solubility and hence, its fate. This was later investigated by Chester *et al.* (1993a) who demonstrated that the proportion of the loosely-held fractions of Cu, Pb and Zn was strongly related to the extent of their solubility in sea water.

Other authors who have investigated the impact of dry deposition in surface waters include: Fones, 1996; Guieu *et al.*, 1994; Statham and Chester, 1988 (Table 2.5). Their studies suggested that the solubility of aerosol associated trace metals is dependant on particle size, aerosol pH and on particle residence time in different pH environments during their transport through the atmosphere (Giusti *et al.*, 1993). However, it has been shown that the most soluble fractions of the dry deposited aerosol are those derived from marine and anthropogenic sources, while the solubility kinetics display a bimodal pattern, indicative of initial solubilisation (within a few minutes) of a fraction of the material, followed by the solubilisation of a further fraction after a longer period (hours/days) of sea water exposure (Giusti *et al.*, 1993).

Hodge *et al.* (1978) investigated the solubility of elements from two aerosols: one having a strong crustal influence, and the other having a significant anthropogenic influence. They reported that there were considerable differences between the sea water solubility of elements originating from the two contrasting aerosols, and that the difference was most marked for Cu, Pb and Zn. More of each of

Table 2.5: the sea water solubility of dry deposited trace metals.

Element	% solubility	References
Al	0.6 - 10	Hodge *et al.*, 1978; Maring and Duce, 1987
Cd	29 - 84	Fones, 1996; Hodge *et al.*, 1978
Co	14 - 44	Fones, 1996
Cu	15 - 86	Fones, 1996; Hodge *et al.*, 1978; Maring and Duce, 1989; Moore *et al.*, 1984
Fe	< 1 - 50	Crecelius, 1980; Hodge *et al.*, 1978; Moore *et al.*, 1984
Mn	25 - 49	Hodge *et al.*, 1978; Moore *et al.*, 1984; Statham and Chester, 1988
Ni	29 - 47	Fones, 1996; Hodge *et al.*, 1978
Pb	13 - 90	Fones, 1996; Hodge *et al.*, 1978; Maring and Duce, 1990
Zn	24 - 76	Crecelius, 1980; Hodge *et al.*, 1978

these elements dissolved from the anthropogenic aerosol, in which they had high EF_{Crust}, compared with the crustally dominated aerosol, in which they had lower EF_{Crust}.

Chester *et al.* (1993b) reported that elemental sea water solubility was not entirely connected to enrichment in the aerosol but instead to their solid state speciation. They attempted to explain elemental sea water solubility in terms of a 'potential environmental mobility' (PEM) framework. Their results demonstrated that a well defined relationship existed between the fraction of an element located within loosely-held particle associations in non-remote aerosols, and their sea water solubility. Copper, Pb and Zn displayed greater sea water solubility when they originated from anthropogenic aerosols compared with crustally dominated aerosols, due to their more loosely-held, exchangeable nature in anthropogenic material. However, Cd and Mn have relatively high solubility from both anthropogenic and crustal aerosols, as they were found to be largely located in loosely-held associations in both aerosol types.

The fate of trace metals dissolved from aerosols was investigated by Kersten *et al.* (1991). They investigated the partitioning of trace metals, which were released into coastal seas from a polluted marine aerosol, using a multi-chamber leaching experiment. They discovered that a significant fraction of the total aerosol elemental concentrations were released into the sea water within 1 hour (Cd - 81 percent; Cu - 41 percent; Pb - 74 percent; Zn - 58 percent), and when exposed to aerosol particles and suspended particulate matter (SPM) for a further 100 hours, a significant proportion of the dissolved metals (ranging from 10 to 60 percent) was re-adsorbed. Sixty-seven percent of the total scavenged Cu was bound to phytoplankton cell walls. This illustrates the considerable ecological impact of the polluted marine aerosol in coastal waters. Lead and Zn were mostly scavenged by Fe/Mn oxides or re-adsorbed by aerosol particles.

Hence it can be seen that anthropogenically influenced aerosols, following deposition to the sea surface, can act as sources for dissolved Cd, Mn, Pb and Zn in the mixed layer. Crustal aerosols provide dissolved sources of Cd and Mn, but can also act as sinks for dissolved Pb and Zn.

2.4 Trace metals in rain water over marine areas.

The formation of precipitation (water vapour, cloud droplets and ice crystals) is a complex and delicately balanced process (Shaw, 1983). Wash-out processes occur below clouds due to impaction and/or interception of aerosols by falling rain drops and snow flakes (Junge, 1963). Rain-out processes occur within clouds (Junge, 1963). Aerosol particles provide nuclei around which water vapour can condense. Such 'condensation' nuclei can be divided into two groups: (i) hygroscopic particles, which are mainly comprised of sea salts, have an affinity for water vapour, therefore condensation is possible prior to air saturation; (ii) non-hygroscopic particles, which are mainly crustal and anthropogenic in origin, require a degree of supersaturation before condensation will occur (depending on particle size). However, before precipitation will occur, moist air must be cooled close to its dew point, and once cloud droplets are formed, their growth will depend on hygroscopic and surface tension forces, the humidity of the air, the rate at which vapour is transferred to water droplets, and the release of the latent heat of condensation. When determining wet deposition to an area it is important to consider (i) the formation of rain clouds, and (ii) the areas where the rain is to be deposited. Cumulo-nimbus and nimbo-stratus clouds are the main rain-bearing clouds. Precipitation (as drizzle, snow, sleet or hail) often occurs as air masses are forced to rise (and therefore cool) over coastal or mountainous zones. This type of precipitation is known as 'orographic' rainfall, and is most common over the western coasts and mountainous regions of the UK. Such precipitation is prolonged and gradually intensifies when associated with warm fronts, but is heavy and short lived when associated with cold fronts.

The dissolved composition of precipitation consists mainly of H^+, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-} and a variety of trace metals. The specific composition of rain water can vary between locations and during the course of a rain event, with high elemental concentrations often observed at the start of a rain event relative to subsequent precipitation (Hansen *et al.*, 1994). The rain water scavenging of trace metals from aerosol particles is also variable.

2.4.1 Geographical variation of trace metals in marine influenced rain waters.

The composition of rain water has been investigated in a variety of regions, both coastal and open ocean, a selection of which is presented in Table 2.6. The data show a similar trend, in trace metal concentrations, compared with that observed in aerosol samples, particularly for AEEs, which are greater in concentration in rain waters collected in regions which are adjacent to continental sources of pollution (e.g. North Sea). The lower contamination of the westerly air mass is evident in rain waters collected over the Irish Sea.

Table 2.6: elemental concentrations in precipitation over selected marine regions (μg l^{-1})

Element	North Sea[a]	Irish Sea[b]	Bermuda[c]	North Pacific (Enewetak)[d]	South Pacific (Samoa)[e]
Al	105	43.5	-	2.1	16
Cd	-	0.06	0.06	0.0021	-
Co	0.017	0.06	-	-	-
Cu	15	2.4	0.66	0.013	0.021
Fe	84	-	4.8	1.0	0.42
Mn	< 12	-	0.27	0.012	0.02
Na	19 000	2708	3400	1100	2500
Pb	-	1.2	0.77	0.035	0.014
Zn	35	-	1.15	0.052	1.6

[a]Cambray *et al.*, 1975; [b]Fones, 1996; [c]Jickells *et al.*, 1984; [d]Arimoto *et al.*, 1985 ([e]1987)

Rain waters exhibit intra-regional concentration variations as well as regional variations. For example, a comprehensive study of rain waters in the North Sea was undertaken by Chester *et al.* (1993a). These workers collected samples from a coastal and an open sea site, and their results are shown in Table 2.7 compared with data from other studies. Owing to the high concentrations observed at the Belgian Coast site, it was suggested that a N-S gradient existed. However, the concentrations observed at the Scottish site did not substantiate this. Chester *et al.* (1993a) therefore concluded that the coastal and open sea concentrations agreed reasonably well, and that the concentrations observed at some coastal sites may be more representative of the local environment.

Table 2.7: North Sea rain water trace metal concentration observed ranges (μg l^{-1}).

Element	North Sea 'Challenger'[a]	East coast of England[a]	NE coast of Scotland[b]	Belgian coast[c]	North coast of Germany[d]
Al	21	56	-	-	-
Cd	0.08	0.25	0.68	3	0.48
Cu	0.98	4.0	2.3	39	1.7
Fe	31	17	88	159	18
Mn	3.6	2.7	3.8	9.5	4.2
Pb	3.5	4.1	4.0	13	6.4
Zn	7.6	2.9	13	194	25

[a] Chester *et al.*, 1993a; [b] Balls, 1989; [c] Deudeurwaerder *et al.*, 1983; [d] Stossel, 1987.

2.4.2 Trace metal partitioning in marine influenced rain waters.

Trace metals in rain water can be found in the dissolved and particle associated phases, with the partitioning dependent upon trace metal solubility. This is ultimately dependent upon the pH of the rain water and elemental aerosol solid state speciation (see section 2.3.4.1). Natural rain water pH values range between pH = 4.8 to 5.6 (Barry and Chorley, 1992), compared with sea water which is generally ~ pH = 8. This leads to enhanced rain water trace metal leaching from the surface of aerosol particles, compared with that occurring in sea water. Chester *et al.* (1990) studied the relationship between dissolved Cd, Cu and Pb, and rain water pH over the western Mediterranean Sea. They observed that the dissolved proportion of Pb, for example, was 80 percent of the total (dissolved and particle associated) Pb at pH = 4, which declined to < 10 percent at pH = 6 (Figure 2.6), thus illustrating a relationship between dissolved trace metal concentration and rain water pH.

This relationship can also be extended to include the solid state speciation of the trace metal, which is greatly influenced by the source region. Chester *et al.* (1990) observed two 'end member' aerosols over the western Mediterranean Sea, which produced two 'end member' rain waters. The first end member rain water was influenced by air masses which had passed over the European industrial regions, and had pHs ~ 4. The second end member rain water was associated with air masses which had passed over the arid regions of North Africa, and had pHs ~ 6 to 7. European aerosols contain more total Pb, and a greater proportion of Pb in the 'easily exchangeable' fraction, compared with North African aerosols. As a consequence, 'European' rain waters contain higher relative proportions

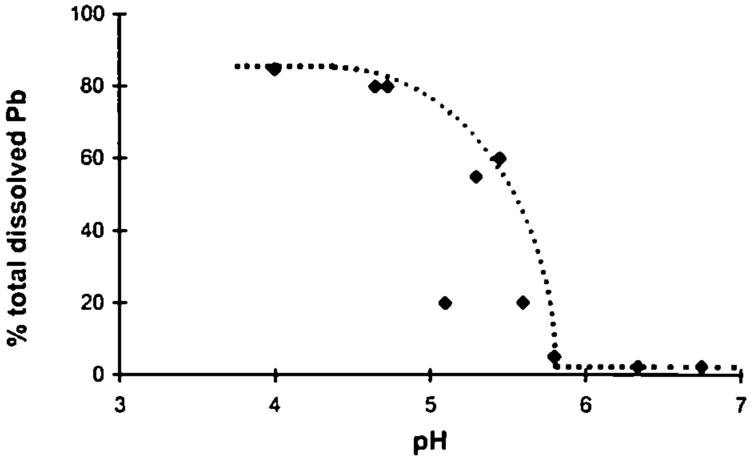

Figure 2.6: relationship between the dissolved portion of Pb and rain water pH (from Chester *et al.*, 1990).

of dissolved Pb compared with 'North African' rain waters. A similar trend was observed for other AEEs such as Cd and Cu. In contrast they observed higher concentrations of NEEs (i.e. Al and Fe) in 'North African' rain waters, with a lower proportion of the total element present in the dissolved phase (~ 10 percent).

Similar work has been undertaken at other sites: continental (Colin *et al.*, 1990), coastal (Guieu *et al.*, 1991) and the open ocean (Lim *et al.*, 1994). Lim *et al.* (1994) investigated the dissolved/particle partitioning of Al, Cu, Pb and Zn in open ocean precipitation. They observed a complex relationship between Al solubility and rain water pH, and suggested that dissolved Al was in thermodynamic equilibrium with insoluble Al salts present in the rain water. They also noted that the solubility of Al was controlled by different processes compared with Cu, Pb and Zn, and stressed that rain water pH was likely to be the major influence, although other factors including concentration and type of dissolved organic ligands were also likely to be important.

2.4.3 Dissolved trace metal speciation in marine influenced rain waters.

The speciation of dissolved trace metals in rain water (i.e. labile or organically complexed) will ultimately affect trace metal biogeochemical pathways (e.g. bioavailability, toxicity, adsorption/desorption relationships with SPM). Nimmo and Chester (1993) demonstrated the existence of metal-organic complexation in rain water. From their studies it was found that Ni and Co in Mediterranean rain waters were significantly complexed (25 and 44 percent respectively) with organic ligands. Nimmo and Fones (1996) further demonstrated the organic complexation of Ni (35 percent) and Co (33 percent) in rain waters collected at urban and coastal sites. Both sets of workers proposed that the atmosphere may be an important source of Ni and Co organic complexing ligands to the marine environment. The importance of the presence of dissolved organic material in rain water is illustrated by its ability to (i) either decrease or increase trace metal solubility in rain water, and (ii) reduce redox reactive metals such as Fe and Mn through photochemically induced reactions (Spokes and Jickells, 1995; Statham and Chester, 1988).

The nature of the metal-complexing dissolved organic material in rain water is largely unknown, although possibilities include porphyrins and their analogs (Ni and Co complexation) which may be introduced to the atmosphere via petrochemical emissions (van den Berg and Nimmo, 1987). Other possibilities include lignins, tannins, carboxylic acids, aldehydes and organic acids such as formic and acetic acids (Lickens *et al.*, 1983). Evidence also exists of the presence of humic acids which are thought to be derived from soil based aerosols (Mukai and Ambe, 1986).

Dissolved trace metals can also complex with inorganic anionic species, the most dominant of which is Cl^-, with SO_3^{2-}, SO_4^{2-} and OH^- also being present in significant amounts. Losno *et al.* (1993) demonstrated that > 90 percent of soluble Al in rain waters is present as the aquated free ion, Al^{3+} and as $Al(OH)^{+}_2$, and that this was essentially independent of pH between 3 and 7. Fluoride ion complexes were also found to be important, and, in more polluted rain waters, a small fraction of the soluble Al was predicted as $Al(SO_4)^+$.

2.5 Atmosphere-ocean trace metal fluxes.

Atmospheric trace metal fluxes (wet and dry) have been investigated by a number of workers in a variety of regions. Buat Ménard (1983) stated that wet deposition was the primary flux mechanism for the input of AEEs (small particle size) to the marine environment, while dry deposition was most significant for sea salt and crustal particles (large particle size). Duce *et al.* (1991) demonstrated that, for Pb, the wet deposition flux exceeded the dry deposition flux over the North and South Pacific, North and South Atlantic, and the North and South Indian Oceans, with a total global wet flux of 0.20×10^{-3} g m^{-2} yr^{-1}, and a total global dry flux of 0.04×10^{-3} g m^{-2} yr^{-1}.

However, it is possible for deposited trace metals to be recycled at the air-sea interface, during the generation of sea salts. Arimoto *et al.* (1985) estimated the percentage of wet deposited trace metals which were recycled in association with sea salts (Enewetak, North Pacific) to be 48 percent for Cu, 30 percent for V and 15 percent for Zn. When this was accounted for, it was observed that wet deposition exceeded dry deposition for Cd, Fe, Pb, Se and V but not for Cu and Zn. It can therefore be seen that trace metal recycling must be taken into account when estimates of net atmospheric deposition fluxes to the sea surface are considered.

Atmospheric trace metal fluxes to marine regions quoted in the literature are presented in Table 2.8. The data do not take into account sea surface recycling with the exception of the data for Enewetak and Samoa. Therefore, it can be considered that the AEE fluxes are over-estimated. However, it can be seen that the atmospheric trace metal fluxes decrease by orders of magnitude with increasing remoteness from continental aerosol sources. This is highlighted by Pb for which the atmospheric flux in the South Pacific westerlies is more than 50 times smaller than that observed in the North Atlantic westerlies.

The North Sea has been subject to considerable research regarding wet and dry atmospheric fluxes (e.g. Bradshaw, 1992; Ottley and Harrison, 1993; Rojas *et al.*, 1993). The atmosphere has been found to be a significant source of trace metals to the region, with Rojas *et al.* (1993) reporting that, in the Southern Bight, the atmosphere, principally wet deposition, was the dominant mode of input for Cd and Pb, while the riverine mode was more important for Cu and Zn.

2.6 Summary.

The investigation of atmospheric trace metal geochemistries, marine biogeochemistry, and the magnitude of the atmosphere as a source of trace metals to the marine environment is well established. However, little is known of the atmospheric trace metal geochemistry and inputs to the English Channel, with only two previous studies being conducted in the region, neither of which lasted in excess of a year.

Austin and Millward (1986) investigated the atmospheric input of As and Sb to the Atlantic Ocean and the English Channel. They established three sampling sites: in the North Atlantic Ocean on board an Ocean Weather Ship at Ocean Station Lima (57 °N; 20 °W); Plymouth (UK); and on board a Channel Lightvessel (49°54'N; 2°54'W); collecting aerosol samples on cellulose acetate filters (0.8 μm pore size). They observed that the atmospheric deposition of both elements was an order of magnitude higher in coastal regions (As: 0.83 ng m^{-3} and 1.70 ng m^{-3}; Sb: 0.45 ng m^{-3} and 0.80 ng m^{-3}; for Plymouth and the Channel Lightvessel respectively) compared with those encountered in the open ocean (As: 0.075 ng m^{-3}; Sb: 0.086 ng m^{-3}; for Ocean Station Lima), stating that mineralised land masses of the South West Peninsula was a probable source. They also challenged the conventional view that fluvial input of trace metals dominated in coastal waters, suggesting that in large industrial or

Table 2.8: atmospheric trace metal fluxes to marine regions (ng cm^{-2} yr^{-1}).

Element	North Sea[a]	Irish Sea[b]	W. Med.[c]	S. Atlantic Bight[d]	Bermuda[e]	N. Atlantic NE Trades[f]	Tropical N. Atlantic[g]	Tropical N. Pacific: total net deposition[h]	S. Pacific total net deposition[i]	N. Atlantic westerlies[j]	N. Pacific westerlies[j]	S. Pacific westerlies[j]
Al	3624	5873	5000	2900	3900	97 000	5000	1200	132-1800	-	-	-
Cd	17.7	6.2	13	9	4.5	-	5	0.35	-	-	-	-
Co	-	7.7	3.5	-	1.2	12	2.7	-	0.25	-	-	-
Cu	189	257	96	220	30	48	25	8.9	4.4-7.9	-	-	-
Fe	3784	-	5100	5900	3000	48 000	3200	560	47-337	-	-	-
Mn	-	-	-	60	45	570	70	9.0	3.6	-	-	-
Ni	-	148	-	390	3	67	20	-	-	-	-	-
Pb	285	162	1050	660	100	32	310	7.0	1.4-2.8	170	50	3
Zn	1505	-	1080	750	75	152	130	67	5.8-2.4	-	-	-

[a]Chester *et al.*, 1993a; [b]Fones, 1996; [c]Arnold *et al.*, 1982; [d]Windom, 1981; [e]Duce *et al.*, 1976b; [f]Chester *et al.*, 1979; [g]Buat-Menard and Chesselet, 1979; [h]Arimoto *et al.*, 1985; [i]Arimoto *et al.*, 1987; [j]Settle and Patterson, 1982.

urban areas, the dominant pollutant input may be derived from the atmosphere. Otten *et al.* (1994) undertook two campaigns in the English Channel, collecting aerosol material on 47 mm polycarbonate membrane - type filters (0.4 µm pore size). They observed an increasingly maritime influence as they sampled further south west along the Channel, with a corresponding decrease in aerosol (crustal and anthropogenic derived) elemental concentrations. For example, the increasing marine influence was reflected in the Cl concentration which ranged from < 600 ng m^{-3} off the Normandy coast up to 3560 ng m^{-3} off Land's End; in addition, the S concentration (representing anthropogenic emissions) fell from 1360 ng m^{-3} to 410 ng m^{-3}, and Fe concentration (representing crustal material) fell from 48 ng m^{-3} to 7.3 ng m^{-3}, in samples collected off the Kent coast and off Land's End respectively.

This work seeks to redress the balance by studying this area, in depth, over a period in excess of one year. This will allow (i) an understanding of the factors influencing the geochemistry of aerosol/rain water associated trace metals, (ii) the magnitude of trace metal fluxes, and (iii) an assessment of the marine fate of atmospherically derived trace metals. The atmospheric trace metal geochemistries of ten metals were investigated, representing all of the major sources of trace metals to the atmosphere of the South West Peninsular: crustal (Al, Co, Fe and Mn), marine (Na), anthropogenic (Cd, Pb and Zn), crustal / anthropogenic (Cu and Ni). The geochemistry of Ni also served as a regional crustal source marker due to the unusually high concentrations of Ni in the local rock (Webb, 1978). The western English Channel atmospheric trace metal geochemistries will be compared with two contrasting areas: the north western Mediterranean, where the aerosol has a strong seasonal crustal input and an anthropogenic background influence; and the more marine dominated Celtic Sea.

Chapter 3.

Development of applied sampling and analytical techniques.

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Development of applied sampling and analytical techniques.

3.1 Introduction.

This chapter reports on the development of sampling and analytical protocols employed within this study. The aims of the study were to:

(i) characterise sources of trace metals to the marine atmosphere (English Channel; NW Mediterranean Sea; NE Atlantic Ocean);
(ii) evaluate the variability of aerosol trace metal concentrations;
(iii) assess atmospheric trace metal inputs to the considered marine systems;
(iv) predict the impact of atmospheric trace metal inputs on the marine environment.

In order to achieve the aims of the study, a representative set of aerosol and rain water samples were collected in a selection of locations (English Channel; north west Mediterranean Sea (aerosols only); NE Atlantic Ocean (aerosol only)). In addition, the sample set from the English Channel was enhanced by collection of dry deposition samples onto a surrogate surface. Specialised equipment was designed and constructed to collect samples with minimum contamination. Specific equipment designs and protocols are discussed in sections 3.3 and 3.4.

Following collection, aerosol samples underwent a total acid digest (HNO_3/HF), with selected samples undergoing sequential leach (to assess the aerosol trace metal solid state speciation) and sea water solubility studies. Rain water particle and dry deposition samples also underwent a similar total digest. Figure 3.1 gives an overview of the experimental strategy for aerosols, and Figure 3.2 shows the approach for rain waters. Analysis of trace metals in the acid digests was by flame atomic absorption spectrophotometry (FAAS) or graphite furnace atomic absorption spectrophotometry (GFAAS), and inductively coupled plasma - mass spectrometry (ICP-MS) for Pb isotope determinations. Rain and equilibrated aerosol-sea water samples were analysed directly for Co, Cu, Ni and Pb, using the sensitive electrochemical technique Adsorptive Cathodic Stripping Voltammetry (ACSV) (as used by Fones, 1996; Nimmo and Chester, 1993). Dissolved Al in equilibrated sea water was analysed using an established Lumogallion/fluorescence technique (Hydes and Liss, 1976).

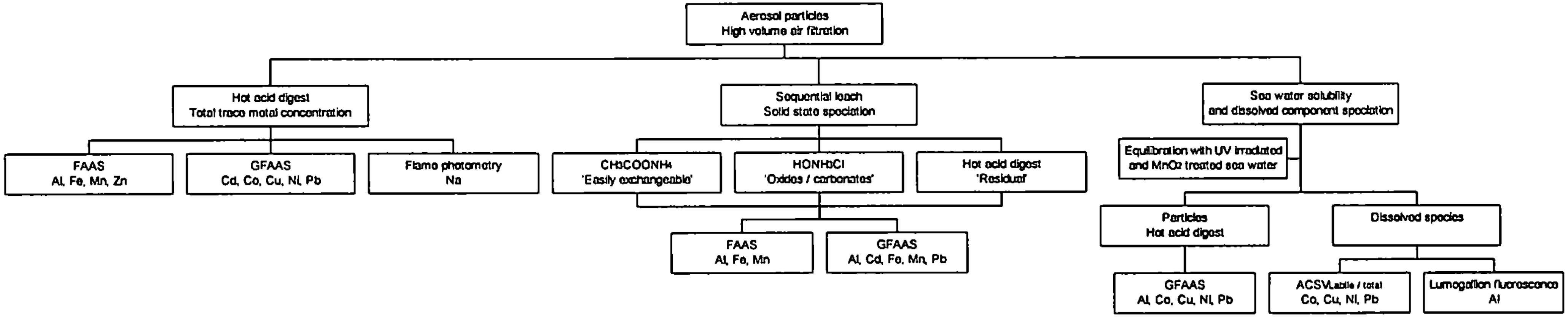

Figure 3.1: flow diagram of aerosol particle sample collection, pre-treatment and analysis.

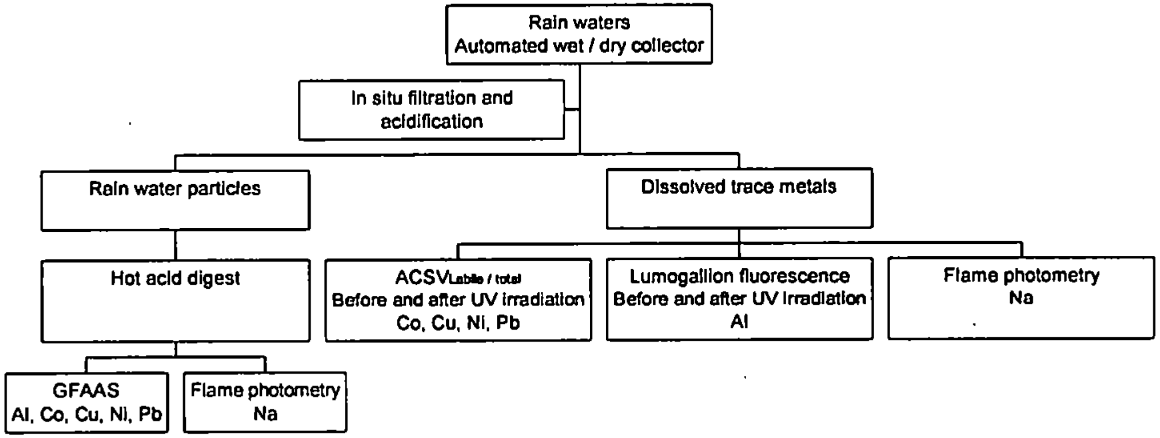

Figure 3.2: flow diagram of rain water sampling, pre-treatment and analysis.

3.2 Sampling locations.

In order to obtain a representative data set, the sampling location had to be carefully considered. The choice of the priority sampling location - the western English Channel - was largely based on meteorological, geographical and logistical factors. Important criteria considered included the following:

(i) the site should be representative of the study area;
(ii) the site should be operational 365 days per year;
(iii) the site should possess a power supply;
(iv) meteorological data should be collected contemporaneously at or close to the site.

The details of the sampling sites, sampling methodologies and number of samples collected are shown in Table 3.1.

3.3 Sampling the marine aerosol.

3.3.1 Methods of sampling.

Early methods of sampling the marine aerosol involved suspending nylon meshes or 'sails' on board ship. However, these were found to be inefficient in the collection of particles with diameters < 1 μm (Rahn *et al.*, 1979), thus eliminating anthropogenic material which has a typical diameter of 0.06 - 1 μm (Whitby, 1977). To enhance sampling efficiency, a variety of devices were introduced including impactors (e.g. cascade), filter collectors, electrostatic precipitators, centrifuges, and devices for gravitational settling (Hochrainer, 1978). A commonly used system involves impacting atmospheric particles onto a filter medium (typically Whatman 41) incorporating a high volume pumping system (e.g. Murphy, 1985).

3.3.2 Aerosol sampling equipment.

The samplers employed for the present studies were modified versions of the ones used by Bradshaw (1992), Fones (1996) and Murphy (1985). The main criteria influencing the design and construction of the samplers were:

Table 3.1: the sampling details for each investigated region.

Region	Location	Sample type	Sampling Method	Duration	Number collected
Western English Channel	Slapton Ley Field Centre Slapton, South Devon	• Aerosol particles	• High volume air filtration	• August 1994 - February 1996	• 68
		• Rain water (particles and dissolved species)	• Automated wet / dry deposition collector with in situ filter	• January 1995 - February 1996	• 35
		• Gravitational dry deposition	• Automated wet / dry deposition collector	• January - August 1995	• 15
North western Mediterranean Sea	Oceanographic Museum Monte Carlo, Monaco	• Aerosol particles	• High volume air filtration	• February - July 1993	• 27
Celtic Sea	• RRS Charles Darwin, CD94	• Aerosol particles	• High volume air filtration	• June 1995	• 7
	• RRS Discovery, D217	• Aerosol particles	• High volume air filtration	• August / September 1995	• 7

(i) the sampler should not be a source of contamination to the sample media;

(ii) the sampler should have a high volume sampling rate ensuring sufficient collection of particles to allow subsequent trace metal analyses;

(iii) the filter heads should be protected from wet deposition contamination, with the inclusion of sampler termination, at the onset of precipitation.

A pressure differential manometer was connected to the pump exhaust to enable air flow measurements to be made (Murphy, 1985):

$$Q = 1.579 * 10^{-4}\left(1.635*10^{6}(h_1 - h_2)\right)^{1/2} \qquad \text{(Eqn 3.1)}$$

where:

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

$h_1 - h_2$ = difference in manometer limb readings (cm)

Flow rate (Q) was calculated by inserting the heights (h_1 and h_2) of the water columns in the manometer at the start of the sampling period. However, as aerosol material impacted on the filter, the flow of air was reduced. Therefore Q was recalculated using the heights of the manometer water columns at the end of the sampling period. Assuming that the decline in flow rate was linear, the mean flow rate was calculated to cover the whole sampling period. The mean flow rate for the sampler was typically 0.70 $m^3\ min^{-1}$. The flow rate was multiplied by the number of minutes of the sampling period to give the volume of air which passed through the collection media.

3.3.3 Type of filter media.

The type of filter media for the collection of aerosol particles were selected according to the following criteria. It should:

(i) have a high retention efficiency for a wide range of particle sizes particularly < 1 μm;

(ii) cause minimal restriction to the air flow, allowing large volumes of air to be sampled;

(iii) dissolve completely in a mixture of concentrated HNO_3 and concentrated HF;

(iv) give low trace metal blank values;

(v) be relatively inexpensive and readily obtainable.

The use of filters such as glass fibre filters result in high elemental blank values (Berg *et al.*, 1993), particularly for Al, and are therefore largely used for major elemental and organic compound determinations. Teflon filters are generally cleaner (Berg *et al.*, 1993), but are prohibitively expensive for a long term, high temporal resolution study. Chester *et al.* (1985) describe using Whatman 41 filter papers as a collection media. They are fabricated from cellulose acetate and are fibrous in structure, generating low blank values, particularly after the filters have been acid washed. An additional benefit of Whatman 41 filters is their low cost. Whatman 41 filter papers are now widely used in the collection of atmospheric particles for trace metal determinations (e.g. Bradshaw, 1992; Fones, 1996; Murphy, 1985) allowing temporal and spatial comparisons between research programmes. They were also used during the international Sea-Air Exchange (SEAREX) programme (e.g. Arimoto *et al*, 1987) in the Pacific Ocean.

3.3.4 Aerosol sampling protocols.

Before sampling, the Whatman 41 filters were acid washed. The cleaning procedure involved placing the filter into an acid washed 1 litre plastic container, containing 5 percent 'Aristar' HCl (BDH) in Milli-Q water, and left to soak for 48 hours. The filters were then drained and thoroughly rinsed with fresh Milli-Q water, until the pH of the wash water was neutral. The filters were then placed on cling film, in a Class 100 laminar flow cupboard, and left to dry, after which they were placed in a clean polythene resealable storage bag.

Filter heads, nuts and bolts were regularly acid washed throughout the sampling period. They were placed in a 10 litre plastic tank (BDH) containing a solution of 2 percent Decon-90 (BDH) in distilled water for 24 hours, and then rinsed in copious quantities of distilled water. They were then placed in a similar tank containing a solution of 10 percent 'Analar' HCl (BDH) in Milli-Ro water and left for 48 hours. Upon removal from this tank, the filter heads and components were rinsed in copious quantities of Milli-Q water and dried on cling film in a Class 100 laminar flow cupboard. Once dry they were placed in a clean plastic resealable bag.

In order to minimise contamination all manipulations were conducted under clean conditions, using a Class 100 laminar flow cupboard where possible and disposable polythene gloves were worn by the operator at all times. The filters were frozen at -20 °C until required for trace metal analysis; the filter heads and components were acid washed before re-use.

3.3.5 Assessment of the accuracy and precision of the applied digestion techniques.

Prior to trace metal analysis, it was necessary to dissolve the sample in acid solution. This was achieved by subjecting the material to a mixture of concentrated 'Aristar' HNO_3 (BDH) and 'Aristar' HF (BDH). The latter is required to destroy alumino-silicate material present in the sample. The destruction of this material releases metals such as Al into solution. This is of particular importance, due to the use of EF_{Crust} (see section 2.3.1.1). The certified reference material (CRM) MESS-1 (an estuarine sediment) produced by the National Research Council Canada (NRCC), was used to validate the acid digestion techniques employed. It is relatively inexpensive, and has previously been used to assess acid digestion techniques (Fones, 1996). Seven protocols were assessed with the most accurate deemed to be the technique which resulted in the greatest number of highest elemental recoveries.

3.3.5.1 Preparation of reagents and equipment.

PTFE beakers of 30 ml capacity were used for initial digestion evaluation studies, after which 30 ml Teflon vials were used as they were safer to use and less prone to contamination. 'Aristar' reagents were used throughout. Trace metal standards were prepared from 1000 ppm stock solutions (BDH) and were made up in 10 ml volumetric flasks, using 0.1M HNO_3, to concentrations within the instrumental linear ranges.

3.3.5.2 Performance of the selected digestion techniques.

An electronic balance was used to accurately weigh sub-samples of CRM into the acid washed digestion vessels which were then transported to a HF classified fume cupboard for the digestion procedure. A summary of each of the assessed digestion techniques is displayed in Figure 3.3. After each digest, the acid extract was made up to 25 ml with 0.1M HNO_3 in an 'A' grade volumetric flask and stored in a universal container ready for analysis. Major variations between the digestion techniques were (i) variations in the volumes of reagents used, (ii) time allocated to various stages, and (iii) combination of reagents used.

Additions of o-H_3BO_3 (0.1 g) and $Zr(SO_4)_2$ (0.1 g) were made to separate aliquots of the acid digests derived from the second digestion technique. This was done in an attempt to release Al from any fluoride complexes formed during the digest procedure. Such complexes are insoluble and thermally stable. Borate and zirconium ions have higher complex stability constants with fluoride compared with Al and should, therefore, compete with Al for fluoride complexation.

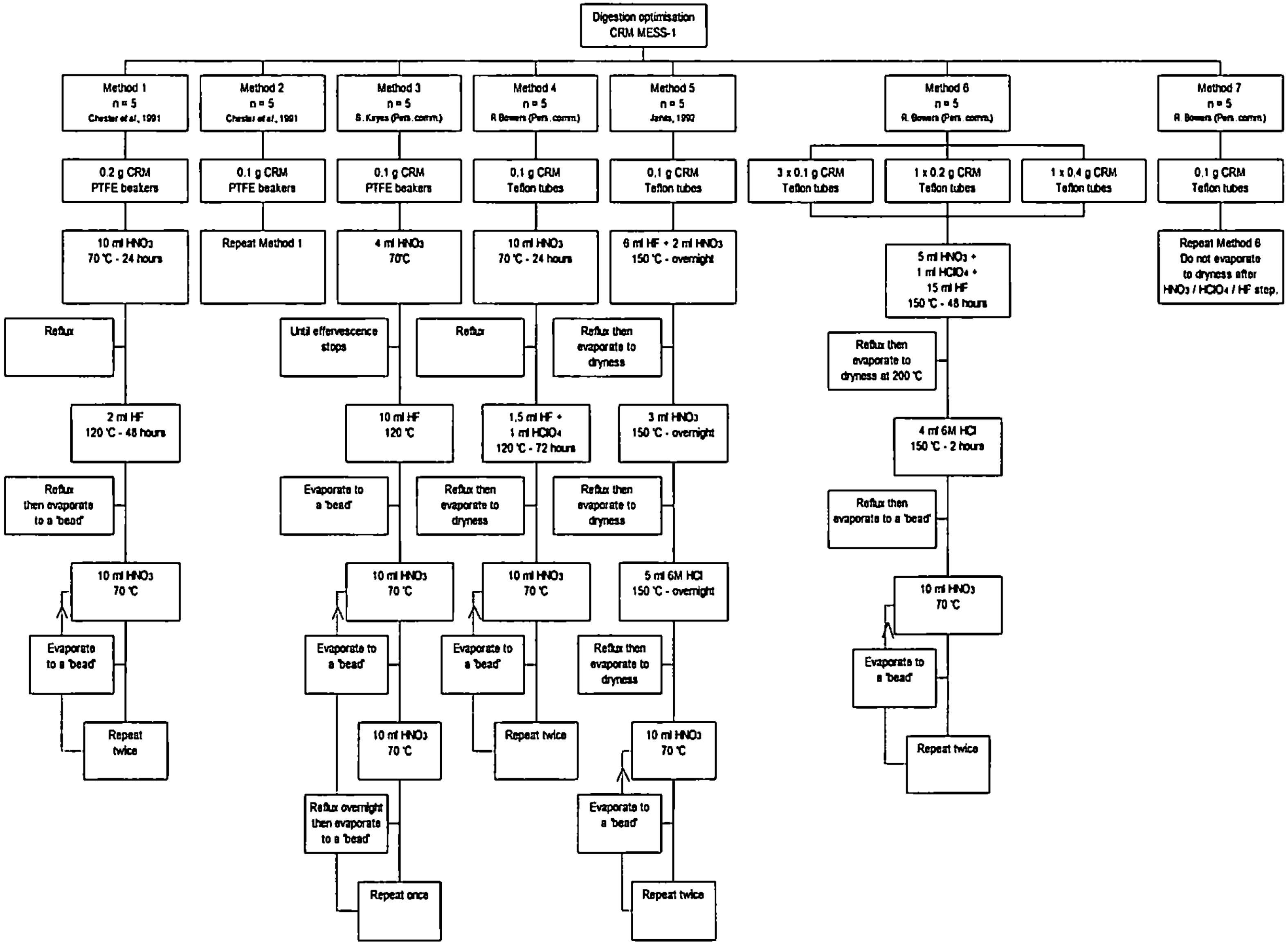

Figure 3.3: the seven employed digestion procedures.

3.3.5.3 CRM digest extract analysis and calculation.

Ten elements were targeted for analysis to represent all possible sources. The elements were: Al, Co, Fe and Mn (dominant crustal source); Cd, Pb and Zn (dominant anthropogenic source); Na (marine source); and Cu and Ni (crustal / anthropogenic source). Elemental standards were made from 1000 ppm stock standards (BDH) diluted in 0.1 M HNO_3, which were stored in universal containers. All CRM digests were analysed for Al, Fe, Mn and Zn by FAAS (GBC 902 for Al and Varian SpectrAA 400+ for Fe, Mn and Zn) and for Cd, Co, Cu, Ni and Pb by GFAAS (Perkin Elmer 4100ZL). The FAAS instruments were set up according to the instrumental manuals. The GFAAS was set up according to the elemental parameters in the instrument's software. They were then optimised by varying the temperature and hold time of the ashing stage (Step 3), and then the atomisation stage (Step 4) while monitoring the absorption of the highest calibration standard solution. In addition to developing an optimal temperature programme, a variety of modifiers were used for some elements. The peak shape and calculated characteristic mass were used to determine the optimum temperature programme and modifier. Appendix 1 contains details of the temperature programmes employed. Determinations of Na were by flame photometry. Instrumental detection limits, linear ranges and instrumental blanks, determined by the analysis of the digest extracts of the seven digestion techniques, are shown in Table 3.2. Digest solution trace metal concentrations were evaluated from five replicate analyses. Calibration graphs were calculated by the instrument, and their reliability assessed by their regression coefficients. Calibrations were acceptable where the R^2 value was greater than 0.995.

3.3.5.4 Efficiency of the digest techniques.

The results of the application of seven digestion techniques (Table 3.3) to the acid digestion of the CRM MESS-1 indicate that no single digestion technique resulted in 100 percent recoveries for all of the elements. However, it would appear that the second digestion technique proved to be the most effective technique for the dissolution of the majority of the metals. The addition of o-H_3BO_3 and $Zr(SO_4)_2$ to aliquots from the digest performed using the second digestion technique, did not improve the recovery of Al (4.3 percent in each case) and caused the FAAS aspirator tubes to block due to incomplete dissolution of the added compounds.

3.3.5.5 Modification of the selected digest technique.

The optimum digestion technique (Digest 2 - section 3.3.5.2) was additionally assessed by the digestion of an urban particle CRM (1648, NBS). However, a number of modifications were made. The Teflon tubes were regarded as being both safer to use, compared to the PTFE beakers which

Table 3.3: determined MESS-1 elemental concentrations and percentage recoveries (calculated as a percentage of the certified value) achieved by the selected digestion techniques (n = 5). All certified and determined values in $\mu g\ g^{-1}$ except for Al and Fe which are expressed as percent (LOD = limit of detection).

Element	Certified value	Method 1		Method 2		Method 3		Method 4		Method 5		Method 6		Method 7	
		Value	%	Value	%	Value	%	Value	%	Value	%	Value	%	Value	%
Al	5.84 ± 0.20	4.76 ± 0.31	81.5 ± 5.30	5.29 ± 0.17	90.6 ± 2.91	5.26 ± 0.53	90.1 ± 9.08	4.82 ± 0.44	82.5 ± 7.53	4.46 ± 0.89	76.4 ± 15.2	4.66 ± 0.66	79.8 ± 11.3	5.64 ± 0.33	96.6 ± 5.65
Cd	0.59 ± 0.10	0.28 ± 0.16	47.5 ± 27.1	0.86 ± 0.05	146 ± 8.47	0.64 ± 0.09	109 ± 15.3	0.59 ± 0.24	100 ± 40.7	0.73 ± 0.08	124 ± 13.6	0.51 ± 0.06	86.4 ± 10.2	0.68 ± 0.03	115 ± 5.08
Co	10.8 ± 1.90	9.48 ± 0.34	87.7 ± 3.15	13.5 ± 2.08	125 ± 19.3	10.4 ± 0.74	96.3 ± 6.85	10.5 ± 0.78	97.2 ± 7.22	8.85 ± 0.20	81.9 ± 1.85	8.78 ± 0.50	81.3 ± 4.63	9.72 ± 0.73	90.0 ± 6.76
Cu	25.1 ± 3.80	20.9 ± 1.91	83.3 ± 7.61	21.2 ± 1.97	84.5 ± 18.2	15.2 ± 1.14	60.6 ± 4.54	14.9 ± 1.67	59.4 ± 6.65	15.3 ± 1.38	61.0 ± 5.50	17.0 ± 1.04	67.7 ± 4.14	18.4 ± 1.63	73.3 ± 6.49
Fe	3.05 ± 0.17	2.98 ± 0.99	97.7 ± 32.5	3.08 ± 0.10	101 ± 3.28	2.02 ± 0.02	66.2 ± 0.66	2.26 ± 0.28	74.1 ± 9.18	2.20 ± 0.07	72.1 ± 2.30	2.22 ± 0.03	72.8 ± 0.98	2.23 ± 0.18	73.1 ± 5.90
Mn	513 ± 25.0	454 ± 20.1	88.5 ± 3.92	498 ± 10.7	97.1 ± 2.09	339 ± 9.27	66.1 ± 1.81	351 ± 40.9	68.4 ± 7.97	360 ± 28.3	70.2 ± 5.52	351 ± 12.5	68.4 ± 2.44	305 ± 45.6	59.5 ± 8.89
Ni	29.5 ± 2.70	44.9 ± 6.48	152 ± 22.0	24.7 ± 3.70	83.7 ± 12.5	19.6 ± 0.25	66.4 ± 0.85	21.3 ± 2.20	72.2 ± 7.46	21.5 ± 1.41	72.9 ± 4.78	22.0 ± 5.30	74.6 ± 18.0	25.8 ± 3.55	87.5 ± 12.0
Pb	34.0 ± 6.10	29.1± 16.1	85.6 ± 47.4	29.2 ± 2.18	85.9 ± 6.41	5.36 ± 0.75	15.8 ± 2.21	4.08 ± 0.59	12.0 ± 1.74	11.9 ± 2.81	35.0 ± 8.27	Below LOD	-	Below LOD	-
Zn	191 ± 17.0	102 ± 9.24	53.4 ± 4.84	147 ± 5.57	77.0 ± 2.92	162 ± 9.44	84.8 ± 4.94	151 ± 17.2	79.1 ± 9.00	162 ± 5.34	84.8 ± 2.80	156 ± 3.80	81.7 ± 1.99	175 ± 11.2	91.6 ± 5.86

Table 3.2: elemental detection limits, linear ranges and instrumental blanks obtained from CRM analysis (μg ml^{-1} FAAS and flame photometry / μg l^{-1} GFAAS) (n = 5).

Element	Instrumental technique	Detection Limit (Blank + 3)	Linear Range	Instrumental Blank
Al	FAAS	0.54	0 - 60.0	0.06 ± 0.16
Cd	GFAAS	0.36	0 - 10.0	0.21 ± 0.05
Co	GFAAS	6.87	0 - 50.0	1.71 ± 1.72
Cu	GFAAS	0.70	0 - 100	0.01 ± 0.23
Fe	FAAS	0.34	0 - 10.0	0.01 ± 0.11
Mn	FAAS	0.15	0 - 5.00	0.00 ± 0.05
Na	Flame photometry	0.10	0 - 10.0	0.07 ± 0.01
Ni	GFAAS	20.2	0 - 100	0.01 ± 6.73
Pb	GFAAS	2.39	0 - 100	1.22 ± 0.39
Zn	FAAS	0.07	0 - 3.00	0.01 ± 0.02

were used in the first three digestion experiments, and less susceptible to contamination and were therefore adopted for all subsequent digests. Additionally:

(i) the volume of HF used was increased to 6 ml;

(ii) following reflux with HF, samples were evaporated to just dryness;

(iii) following evaporation, concentrated HNO_3 was added and the lids replaced to allow the samples to reflux overnight.

The second modification required careful observation but removed all hazard associated with using HF. The third modification allowed complete dissolution of all material.

3.3.5.6 Efficiency of the optimum acid digest technique on the urban particle CRM.

The results of the application of the optimum acid digest technique on the urban particle CRM are shown in Table 3.4. Although the standard deviations were high for some elements (Cu, Fe, Mn, Pb and Zn), the digest technique appeared to be adequate for the digestion of urban particles, and should therefore be acceptable for application to urban end-member aerosols.

Table 3.4: determined urban particle elemental values obtained using the optimum acid digestion technique (* indicates uncertified value - for information only) (n = 10). All units are in µg g^{-1} except for Al, Fe, Pb and Zn which are expressed as percent.

Element	Certified Value	Determined value	% recovery
Al	3.42 ± 0.11	3.23 ± 0.21	94.4 ± 6.14
Cd	75 ± 7	52.6 ± 2.47	70.0 ± 3.29
Co*	18	14.3 ± 2.01	79.4 ± 11.2
Cu	609 ± 27	611 ± 130	100 ± 21.3
Fe	3.91 ± 0.10	2.41 ± 0.77	61.6 ± 19.7
Mn*	860	762 ± 136	88.6 ± 15.8
Na	0.425 ± 0.002	0.41 ± 0.02	96.5 ± 4.71
Ni	82 ± 3	78.6 ± 3.21	95.9 ± 3.91
Pb	0.655 ± 0.008	0.67 ± 0.22	102 ± 33.6
Zn	0.476 ± 0.014	0.39 ± 0.20	81.9 ± 42.0

3.3.6 Acid digestion of collected aerosol samples.

A variety of methods (incorporating both hot plate and microwave) exist for the digestion of atmospheric particles (e.g. Jarvis, 1992), although all include the use of concentrated HNO_3 and HF. Such strong acids are required to ensure dissolution of all trace metals in the sample, particularly those contained within crustally derived particles. Similarly, sample analysis is variable ranging from (i) non-destructive techniques such as neutron activation analysis (Demuynck *et al.*, 1976) and X-ray fluorescence spectrometry (Fifield, 1995), to (ii) techniques which require the sample to be dissolved prior to analysis (i.e. atomic absorption/emission spectrophotometry and inductively coupled plasma techniques). The latter category is more commonly used although direct solid determination of elements in atmospheric particles, by graphite furnace atomic absorption spectrophotometry has been attempted, with limited success (Migon *et al.*, 1993).

The acid digest technique described in section 3.3.5.5 was used to digest all collected aerosol samples with subsequent analysis as described in section 3.3.5.3. Table 3.5 displays the sample blank values obtained directly from the instrument, and the average concentrations observed in the digest extracts. The blank Whatman 41 trace metal concentrations are all below the limit of detection (except for Al and Na), and are therefore unlikely to affect the average concentrations observed in digest extracts. At the lowest Al concentrations, the Whatman 41 blank concentration is ~ 50 percent

Table 3.5: determined experimental aerosol blank values compared with average trace metal concentrations observed in acid digest extracts (µg ml^{-1} for FAAS and flame photometry / µg l^{-1}for GFAAS).

Element	Instrumental technique	Aerosol particle Whatman 41 filters	Average concentration observed in acid digest extract (n = 68)
Al	FAAS	0.56	4.05 ± 2.99
Cd	GFAAS	< 0.36	1.21 ± 1.78
Co	GFAAS	< 0.33	0.54 ± 0.08
Cu	GFAAS	< 0.70	32.7 ± 48.0
Fe	FAAS	< 0.34	1.08 ± 0.88
Mn	FAAS	< 0.05	0.10 ± 0.11
Na	Flame photometry	0.26	136 ± 113
Ni	GFAAS	< 20.2	463 ± 750
Pb	GFAAS	< 2.39	9.63 ± 20.9
Zn	FAAS	< 0.07	0.21 ± 0.14

of the concentration in the digest extract. The Whatman 41 blank value for Na is unlikely to adversely affect digest extract results.

3.3.6.1 Aerosol trace metal calculations.

Sample concentrations, fluxes and inputs were calculated according to equations 3.2, 3.3 and 3.4. Where appropriate, crustal enrichment factors (EF_{Crust}) were calculated using equation 2.2. The aerosol analyte concentrations, in ng m^{-3}, were calculated according to the equation:

$$C = \left(\frac{(C' * V)}{A}\right) \qquad \text{(Eqn 3.2)}$$

where:

C = analyte concentration in ambient air (ng m^{-3})

C ' = digest extract concentration (ng ml^{-1})

V = volume of the digest extract (ml)

A = volume of air which passed through the sampling device during the sampling period (m^{3})

The fluxes of aerosol associated trace metals to the sea surface were calculated using the following equation:

$$F = \left(C * V_{dep} * T\right) * 10^{-4} \quad \text{(Eqn 3.3)}$$

where:

F = dry deposition flux (ng cm^{-2} yr^{-1})

C = concentration of the trace metal in ambient air, derived from the total digest of an aerosol sample (ng m^{-3})

V_{dep} = deposition velocity (m s^{-1})

T = number of seconds per year (s)

Trace metal inputs were calculated according to equation 3.6:

$$I = (F * SA) * 10^{-5} \quad \text{(Eqn 3.4)}$$

where:

I = trace metal input (tonnes yr^{-1})

F = trace metal flux (ng cm^{-2} yr^{-1})

SA = surface area of the body of water (km^2)

3.3.7 Analysis for Pb isotopic ratios.

The concentration of Pb in the atmosphere has risen due to the use of leaded fuels. In addition, the Pb used in such European fuels is derived from Australian, American and Canadian reserves. Owing to the geological age of the reservoir ores, Pb in leaded fuels has a different isotopic composition compared with local Pb ores. This can subsequently be used to differentiate between Pb of natural and anthropogenic sources.

3.3.7.1 Accuracy of the Pb isotopic ratio analysis.

Analysis of aerosol samples was conducted by ICP-MS (FI Elemental Analysis VG Plasmaquad) for all four naturally occurring Pb isotopes. Two isotopes of Hg were also determined as ^{204}Hg is an interferent of ^{204}Pb. The presence of ^{202}Hg was used to calculate ^{204}Hg, using their natural abundances, so that it could be subtracted from ^{204}Pb counts. A common Pb isotopic standard, produced by the National Institute of Standards and Technology (NIST) was diluted to a concentration of 10 ng ml^{-1} in 0.1 M HNO_3, and was used to assess instrumental accuracy and precision during each period of analysis (Table 3.6); the dwell time of ^{204}Pb was increased, due to its low abundance (~1.4

Table 3.6: common Pb isotopic standard values and ratios determined by ICP-MS (n = 10).

Isotope/isotopic ratio	Certified value	Determined value	Precision % RSD
Pb^{204}	1.4255 % ± 0.00037	1.419 % ± 0.070	5.19
Pb^{206}	24.1442 % ± 0.0057	24.13 % ± 0.118	0.49
Pb^{207}	22.0833 % ± 0.0027	22.45 % ± 0.026	0.12
Pb^{208}	52.3470 % ± 0.0086	52.08 % ± 0.174	0.33
Pb^{204} / Pb^{206}	0.059042 ± 0.000037	0.056 ± 0.003	4.95
Pb^{207} / Pb^{206}	0.91464 ± 0.00033	0.931 ± 0.004	0.43
Pb^{208} / Pb^{206}	2.1681 ± 0.0008	2.159 ± 0.018	0.82

percent), to give better precision. Samples were diluted to a concentration of < 50 ng ml^{-1} to reduce the number of counts per second identified by the instrument, so as not to overload the mass spectrometer. An internal standard was not used as concentration was not determined by this instrument.

3.3.8 Sequential leaching of aerosol associated trace metals.

A sequential leach is applied to aerosol populations in an attempt to evaluate their trace metal solid state speciation. The aerosol material is exposed to a series of chemical reagents which sequentially extract trace metals from different solid phases. For the current study, the scheme developed by Chester *et al.* (1989) was adopted. This scheme involved (i) CH_3COONH_4 extracting 'easily exchangeable' trace metals, which are generally anthropogenic in their origin (Chester *et al.*, 1989), (ii) $HONH_3Cl$ containing 25 percent v/v CH_3COOH (Chester-Hughes reagent (Chester and Hughes, 1967)) which extracts metals associated with carbonates and oxide phases, and (iii) a total HNO_3/HF digest to dissolve the residual fraction. However, no certified reference material currently exists for this procedure, although a 'certified' method now exists for the sequential extraction of trace metals in sediments (Quevauviller *et al.*, 1994). During the current study, the adopted sequential leach scheme was applied to the urban particle CRM 1648 (NBS) to enable future workers to assess the efficiency of the current scheme with their adopted leach methodologies.

3.3.8.1 Preparation of equipment and reagents.

Ammonium acetate and the combined 'Chester-Hughes' reagent were prepared according to Chester *et al.* (1989) and Chester and Hughes (1967). Manganese dioxide suspension was prepared according to Fones, 1996 in order to purify the ammonium acetate reagent prior to use.

3.3.8.2 Purity assessment of the stage one reagent - CH_3COONH_4.

Chester *et al.* (1989) state that the $CH_{3.}COONH_4$ reagent should be cleaned by being passed through a chelating ion-exchange column, containing 'chelex 100' resin in the ammonium form prior to its use. Attempts were made to assess the necessity of this step by analysing CH_3COONH_4 which had been equilibrated with MnO_2 suspension. Ten ml of the CH_3COONH_4 reagent was pipetted into an acid washed HDPE bottle to which 1 ml of the MnO_2 suspension was added. The bottle was sealed, placed in a resealable plastic bag and shaken overnight on a mechanical shaker. The reagent was then filtered through an acid washed Sartorius 0.45 μm 47 mm diameter membrane filter, using a polycarbonate filtration system, and stored in a universal container. A second aliquot was cleaned using a 'chelex 100' column and stored in a universal container. A third aliquot received no treatment, and was stored in a universal container. Each aliquot was analysed by GFAAS using optimised temperature programmes (Appendix 1). The results are displayed in Table 3.7. The results clearly indicate that it is unnecessary to column clean or MnO_2 equilibrate CH_3COONH_4 prior to use, provided 'Aristar' reagents and high purity water (e.g. Milli-Q water) are used. Use of such protocols actually introduced metal contamination to the reagent.

Table 3.7: comparison of the effect of pre-treatments on the trace metal content of blank CH_3COONH_4 (n = 3).

Element	Untreated $ng\ ml^{-1}$	MnO_2 treated $ng\ ml^{-1}$	Column cleaned $ng\ ml^{-1}$
Al	0.13	0.32	0.19
Cd	< 0.36	< 0.36	< 0.36
Fe	< 0.34	< 0.34	< 0.34
Mn	0.02	1.33	0.04
Pb	< 2.39	< 2.39	< 2.39

3.3.8.3 Application of the three stage sequential leach protocol to an urban particle CRM.

Owing to the lack of an aerosol sequential leach CRM, the current protocol was applied to an urban particle CRM (1648, NBS) as a marker for future workers. Five aliquots of ~ 0.1 g of the CRM were deposited into separate universal containers and accurately weighed using an electronic balance. Twenty five ml of the first stage reagent, CH_3COONH_4, was added to each of the five universal containers plus another unused universal container which served as the procedural blank sample. The containers were shaken using a mechanical shaker for 15 minutes and then centrifuged for 3 minutes at 3000 rpm. The reagent was transferred into a second set of universal containers and weighed to ascertain the magnitude of 'carry over' i.e. the contamination of stage two leaches caused by the retention, in the universal container, of a portion of the CH_3COONH_4 reagent, and thus the leached trace metals. The transferred stage one reagent aliquots were weighed using an electronic balance, along with a similar universal container containing 25 ml of CH_3COONH_4. The volume of the reagent 'carried over' was calculated according to the equation:

$$V = \frac{W_T}{W_R} * 25\text{ml} \qquad \text{(Eqn 3.6)}$$

where:

V = volume 'carried over' (ml)

W_T = mass of the transferred reagent (g)

W_R = mass of 25 ml of reagent (g)

The potential trace metal contamination of the stage two aliquots was calculated by multiplying the volume 'carried over' (ml) (x = 9.83 percent) by the trace metal concentration in the aliquot (ng ml^{-1}). The leachates were then acidified to pH 2 with 1.6 ml of 1:1 HCl:Milli-Q water, placed in a resealable bag and frozen to await analysis. Twenty-five ml of the second stage reagent, the Chester-Hughes reagent, was then added to each of the sample containers, shaken overnight and centrifuged as described for the stage one reagent. The leachate was then transferred into separate universal containers, weighed to ascertain 'carry over' to stage three, placed in a resealable bag and frozen. 'Carry over' for stage two was typically 8.21 percent. The remaining filter residue then underwent a total digest. Analysis was as described in section 3.3.5.3 with the graphite furnace re-optimised for the stage one and stage two reagents (Appendix 1).

The results (Table 3.8) show that Al and Fe, the predominantly crustally derived elements, are most abundant in the residual (third) stage, whereas Cd, a largely anthropogenic element, was most abundant in the first stage relating to its 'easily exchangeable' anthropogenic nature. Lead was most abundant in stage two, followed by stage one. Manganese was equally abundant in all three stages.

Table 3.8: the percentage distribution of selected urban particle CRM trace metals in each of the stages of the three stage sequential leach (corrected for 'carry over') (n = 5).

Element	Stage One 'Easily exchangeable'	Stage Two Carbonates and oxides	Stage Three 'Residual material'
Al	2.02 ± 0.42	13.9 ± 1.28	84.1 ± 41.2
Cd	70.5 ± 11.4	24.3 ± 11.5	5.21 ± 7.57
Fe	0.58 ± 0.21	24.9 ± 2.86	74.6 ± 35.2
Mn	34.9 ± 5.81	31.9 ± 4.76	33.2 ± 17.1
Pb	36.5 ± 6.73	58.5 ± 6.96	4.98 ± 3.07

3.3.8.4 Application of the three stage sequential leach to aerosol samples.

A selected sample filter was separated, using acid washed tweezers, into 1 cm^2 pieces and placed in a clean universal container. The three stage sequential leach was then performed as described in section 3.3.8.3.

3.3.9 Sea water solubility of aerosol associated trace metals.

The solubility of particle associated trace metals in sea water, deposited by dry deposition, is important when considering the biogeochemical cycling and residence times of trace metals in the marine environment (e.g. Chester *et al.*, 1993b; Kersten *et al.* 1991). Researchers have used a variety of methods to ascertain trace metal sea water solubilities (e.g. Chester *et al.*, 1993b; Statham and Chester, 1988). This study has followed the method described by Fones (1996), using an electrochemical technique (ACSV) for the analysis of soluble Co, Cu, Ni and Pb, and a fluorimetric method for the determination of soluble Al (Hydes and Liss, 1976) in aerosol equilibrated sea water. Atomic absorption spectrophotometry is inferior to the employed techniques due to instrumental spectral interferences and potential blockages caused by the high salt content of sea water, and the high detection limits in comparison to the trace metal concentrations observed in these experiments (Donat and Bruland, 1995; Johnson *et al.*, 1992).

3.3.9.1 Preparation of equipment and reagents.

A 4M solution of sodium acetate was used to adjust the pH of equilibrated sea water to 5.0 for dissolved Al analysis. An ammonia solution was used to adjust the pH of equilibrated sea water samples for Co and Ni (pH 8.2 and Cu and Pb (pH 7.7) analysis. Lumogallion reagent (3-(2,4-

dihydroxyphenylazo)-2-hydroxy-5-chlorobenzenesulphonic acid (Pfaltz and Bauer)) was used as the complexing ligand in dissolved Al analysis.

3.3.9.2 Assessment of dissolved trace metal adsorption/desorption in the reaction vessel.

Prior to commencing aerosol sample sea water solubility studies, two experiments were conducted to assess the extent of dissolved trace metal adsorption and desorption onto the HDPE equilibration vessel and equilibrated filter material. Organic-free and trace metal-free sea water was prepared by subjecting filtered sea water to UV radiation (see section 3.4.4) for 4 hours, and then equilibrating with MnO_2 suspension as described in section 3.3.8.2. The cleaned sea water was stored in a 500 ml Teflon bottle. An acid washed Whatman 41 filter was separated into 1 cm^2 pieces, using acid washed tweezers, and placed in an acid washed HDPE 250 ml bottle. Seventy-five ml of clean sea water (pH = 7.5, salinity 34 ‰) was added to the HDPE sample bottle which was then shaken on a mechanical shaker for 1 hour. Previous studies have shown that the majority of available trace metals will dissolve in sea water within this period (Fones and Nimmo, 1995). The equilibrated sea water was separated from the filter material by passing through an acid washed 0.45 µm membrane filter held in a polycarbonate filtration system (Nalgene). The filtered equilibrated sea water was stored in universal containers. The sample and membrane filters for each sample were stored together in a clean petri dish, in a resealable bag and frozen to await total digestion followed by analyses for Al (FAAS), Co, Cu, Ni and Pb (GFAAS). Ten ml of the equilibrated sea water was pipetted into a separate universal container and frozen, to await Al $\text{Lumogallion}_{\text{Labile}}$ analysis. Twenty-five ml of the remaining sample underwent immediate analyses for dissolved $\text{ACSV}_{\text{Labile}}$ trace metal content (Co, Cu, Ni, Pb) (see section 3.4.3). The remaining sea water (~40 ml) was acidified to pH 2 using 1:1 HCl:Milli-Q water and then UV irradiated to allow total dissolved trace metal (Co, Cu, Ni, Pb) determinations. Following this, a further 10 ml of the sample was pipetted into a separate universal container for total Al analysis. A second experiment was conducted according to the above protocol. However, the sea water was first spiked with a known concentration of Al, Co, Cu, Ni and Pb metal standards. Analysis was conducted as described above. The results of these two experiments (Table 3.9 and Table 3.10) reveal that the reaction vessels were not a source of contamination during the experiments, nor receptors for trace metal adsorption. However, it is clear that organic complexing ligands were not completely removed from the sea water prior to use as demonstrated by the higher total concentrations, with respect to the labile concentrations, for all of the spiked samples (Table 3.10).

Table 3.9: results obtained before and after blank sea water solubility studies for Lumogallion/ACSV$_{Labile}$ and Lumogallion/ACSV$_{Total}$ trace metals (µg l^{-1}) (n = 3).

Element	Concentration at 0 minutes		Concentration after 60 minutes	
	Labile	Total	Labile	Total
Al	< 0.06	0.07	< 0.06	0.07
Co	0.03	0.03	0.02	0.03
Cu	0.04	0.21	0.05	0.20
Ni	0.02	0.03	0.02	0.03
Pb	0.05	0.07	0.05	0.07

Table 3.10: results obtained before and after spiked sea water solubility studies for Lumogallion/ACSV$_{Labile}$ and Lumogallion/ACSV$_{Total}$ trace metals (µg l^{-1}) (n = 3).

Element	Spike concentration	Concentration at 0 minutes		Concentration after 60 minutes	
		Labile	Total	Labile	Total
Al	0.36	0.14	0.36	0.14	0.36
Co	0.71	0.19	0.70	0.18	0.71
Cu	6.04	4.88	6.08	4.51	6.04
Ni	2.00	1.37	1.95	1.51	2.08
Pb	2.90	2.00	2.86	1.92	2.80

3.3.9.3 Performance of the aerosol particle solubility studies.

The experiments were model studies designed to imitate the sea water solubility of aerosol associated trace metals (Al, Co, Cu, Ni, Pb) deposited by the dry mode. Sample selection criteria are discussed in section 3.3.10. Sea water was cleaned as described in section 3.3.9.2. The appropriateportion of the aerosol filter (see sections 4.2.2, 5.2.2 and 6.2.2) was separated into 1 cm^2 pieces, using acid washed tweezers, and placed in an acid washed HDPE 250 ml bottle. Seventy-five ml of clean sea water (pH = 7.5, salinity = 38.0 ‰) was added to the HDPE sample bottle which was then shaken on a mechanical shaker for 1 hour. Storage and analysis was as described in section 3.3.9.2.

3.3.9.4 Determination of dissolved Al in sea water.

A Lumogallion/fluorescence technique, described by Hydes and Liss (1976), was used to determine both 'labile' and total Al concentrations (see section 3.4.3.3, Table 3.13 for determined values, precisions and detection limits for the applied technique obtained using CRMs CASS-2 and SLRS-2).

Analysis was undertaken at the Plymouth Marine Laboratory (PML) in collaboration with Mr Robin Howland. Each sample was prepared in duplicate, in preconditioned 20 ml plastic bottles, using 5 ml aliquots. Sixty-three μl of acetate buffer (BDH) was added to each aliquot to adjust the pH to 5.0. Where samples had been acidified (i.e. for total measurement), the pH was adjusted with the appropriate volume of 1:3 NH_3 solution:Milli-Q water. Lumogallion reagent (63 μl) was added, and the samples were left overnight. Sample fluorescence was measured at a wavelength of 555 nm, and calibrated against standard solutions (made to volume with clean sea water) of concentration between 0 and 50 ng ml^{-1}.

3.3.10 Modifications of the aerosol sampling protocols.

3.3.10.1 The western English Channel

The intake framework used for the current study, was suspended from an epoxy painted support (approximately 7 m above the ground) by a Kevlar rope and plastic pulley system. A polypropylene box was constructed in the University of Plymouth mechanical workshop, and fixed to a bracket on the support, above the intake framework, offering sample protection in the event of rain. The box was found to have no affect on the passage of air through the sampling device. Owing to the noise of the high volume pump, the sampling time was limited to 12 hours during day time and only one filter could be collected per sample. Subsequently only half of the filter was used for the total digest, with the other half being selectively used for either a sequential leach or sea water solubility study. A selection of samples, representing the range of aerosol populations influencing the sampling site with respect to wind direction, were chosen to undergo the three stage sequential leach. A similar sample set was selected which was subjected to model sea water solubility experiments to serve as a comparative study. In all cases, digest extracts were made up to a volume of 10 ml, the volume used of sequential leach stage one and two reagents was 10 ml and the minimum volume of sea water (75 ml) was used for the solubility study.

3.3.10.2 The north western Mediterranean Sea.

The employed sampling device was similar to the one described above although it was fixed horizontally in a frame similar to that described by Fones (1996). Three filters were collected simultaneously per sample, over a period ranging from three to seven days, between February and July 1993. All sampling operations, described in section 3.3.4, were conducted by Olivier Cotret of the International Atomic Energy Agency in Monaco, in association with the University of Liverpool. One third of each sample filter was separated using an 'Arnold Separator', a circle of perspex cut to the same diameter as the filters, with one third removed. The removed portion from each sample filter were digested together and made up to 25 ml prior to analysis. Several samples, which represented the entire data set with respect to wind direction, were selected to undergo sequential leach and sea water solubility experiments. One third of each of the sample filters was removed and subjected together to the sequential leach. Twenty-five ml of the stage one and two reagents were used, and the final digest was made up to 25 ml. The sea water solubility experiment was as described in section 3.3.9, using the remaining sample filter portions.

3.3.10.3 The Celtic Sea.

The high volume intake system used during the OMEX cruises, was constructed in the University of Plymouth mechanical workshop, and was identical to the one used during the western English Channel sampling programme, except that it consisted of two filter ports rather than three. During each cruise, the intake framework was suspended approximately 1 m beyond and 1 m above the bow of the ship from an epoxy-painted support. The pump was situated approximately 15 m behind the bow, on an upper deck, in an aluminium box, and permanently connected to the electricity supply. It was connected to the intake framework via a 25 m length of 2.5 cm i.d. flexi-hosing and using stainless steel jubilee clips. Samples were collected over a period of ~ 2 days and were comprised of 2 filters. Filters were stored in separate labelled plastic bags and frozen until required for analysis. Half of each sample filter underwent combined total acid digestion, with the digest extract made up to 10 ml. The remaining portions of samples from OMEX cruise 1 underwent a three stage sequential leach. Volumes of reagents and final digest volume were 10 ml in all cases. The remaining portions of OMEX cruise 2 aerosol samples underwent a sea water solubility experiment.

3.4 Sampling marine rain waters.

3.4.1 Introduction.

The relative importance of wet deposition has been illustrated by e.g. Church *et al.*, 1991, Fones, 1996, Nimmo and Chester, 1993. Rain water samples require strict collection protocols, to avoid contamination by dry deposition. Additionally, due to intra-rain event trace metal concentration variability, the sample must incorporate precipitation from the entire duration of the event to yield a representative sample (Hofmann *et al.*, 1991). This has resulted in a variety of sampling techniques, ranging from manual samplers (Lim *et al.*, 1991) to sophisticated automatic samplers (Fornaro *et al.*, 1993).

3.4.2 Sampling.

3.4.2.1 Design and construction of the automated collector.

Rain water was collected using an automated wet/dry sampler built in the University of Plymouth mechanical workshop (Figure 3.4 and Plate 3.1). It was based on a design created at the University of Liverpool and fulfilled the following criteria.

The collector:

(i) should present minimal risk of trace metal contamination to the collected samples;
(ii) must incorporate collection systems for both wet (precipitation) and dry deposition samples;
(iii) must automatically open at the onset of precipitation;
(iv) must allow protection against wet deposition contamination of dry deposition samples;
(v) must allow protection against dry deposition contamination of rain water samples;
(vi) must incorporate an automatic filtration system in the wet deposition collector to immediately separate dissolved and particle associated trace metal rain water phases.

Each collection system consisted of a polypropylene funnel (0.554 m^2 surface area-Orme), and a two litre high density polyethylene (HDPE) collection bottle (BDH). The funnel was slotted into a ring of plastic piping (South West Water Ltd.) situated above the respective compartments, and the collection bottle was slotted into a 'cup' within each compartment. This allowed stability and maintained the correct height between the bottle neck and funnel base. The wet collection system also contained an 'in-house' constructed filtration unit composed of a nylon block (5.1 x 5.1 x 6.35 cm) containing a Nalgene polysulphone open faced filtration unit, secured in the block using plastic screws. A tapered hole was drilled through the length of the nylon block allowing the funnel to fit securely.

3.4.2.2 Sampling protocol.

Rain water sample pre-treatment is an area of controversy. According to guidelines for the collection and analysis of trace metals in rain water (UNEP, 1988),

> 'pre-acidification is not recommended...(as)...the first rain collected will be subject to very acid conditions which may affect the particulates associated with the rain'.

This argument can be resolved by gravity filtering the sample *in situ*, thus removing rain water particles prior to acidification. A second argument states that acidification of the sample results in a change in

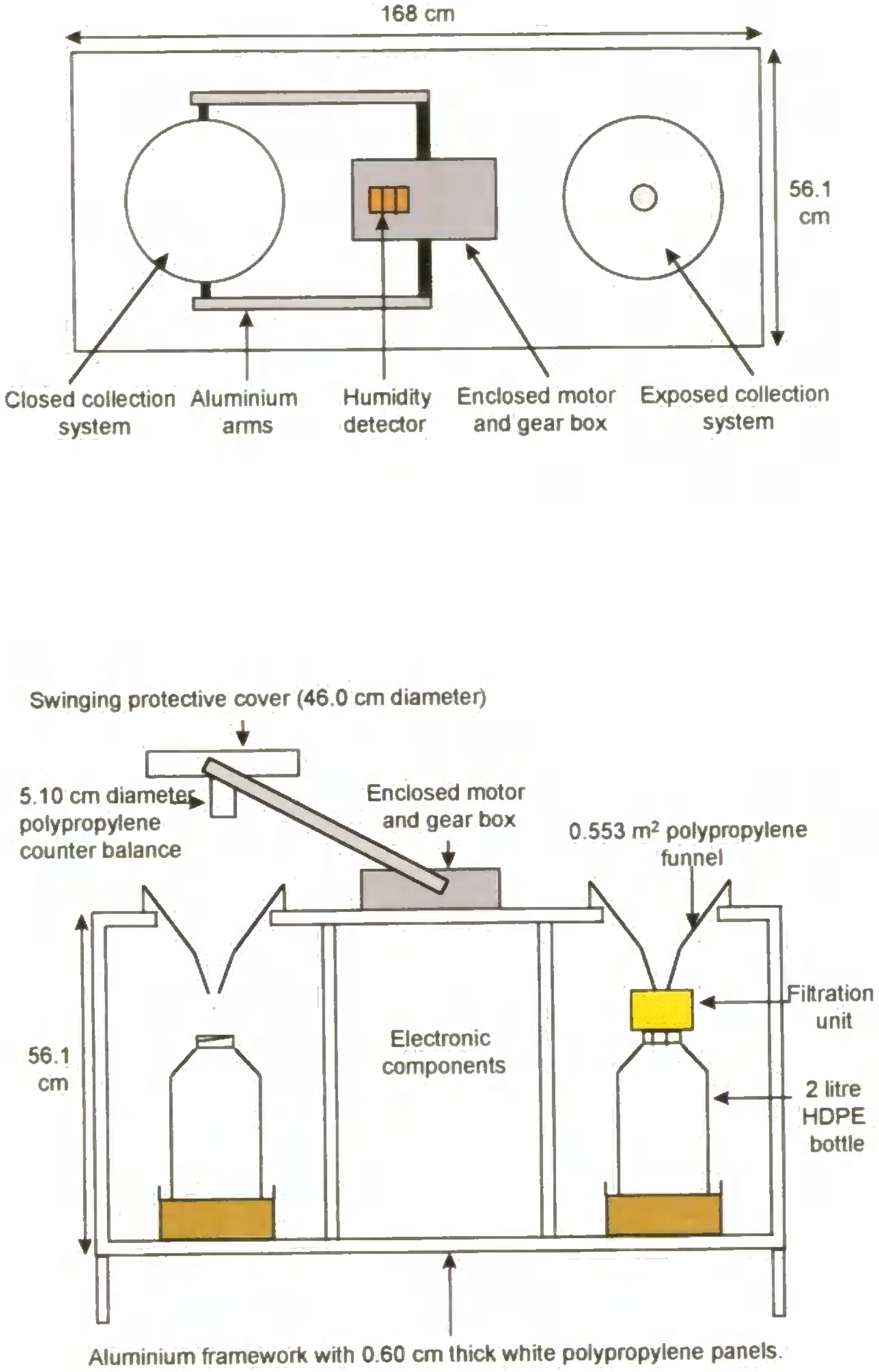

Figure 3.4: top and side views of the automated wet/dry collector.

Plate 3.1: the wet/dry deposition collector at the western English Channel sampling site.

the speciation of trace metals, thus invalidating 'labile' measurements. However, it must be remembered that (i) rain water is generally acidic with observed values as low as pH 3 (Muia *et al.*, 1991), (ii) most metal-ligand complexes are reversible and will revert to their original structure when the pH is raised for analysis, although the measured metal-organic complexation will be higher than that in the natural environment (Fones, 1996), (iii) the potential change in speciation is a compromise against the loss of analyte due to adsorption in unacidified samples (Hewitt and Allott, 1992), (iv) 'labile' determinations are often bound by constraints of the sampling and analytical protocols, thus data comparison is possible provided similar protocols are adhered to. Fones (1996) assessed the efficiency of two methods of rain water sample preservation with respect to the trace metal (Cd, Co, Cu, Ni, Pb) $ACSV_{Labile}$ fraction. The storage methods considered were: (i) acidification with cool storage (4 °C), and (ii) acidification with frozen storage (-20 °C). The results of $ACSV_{Labile}$ and total dissolved trace metal concentrations were in good agreement after storage for a period of a few weeks. However, after 6 months the $ACSV_{Labile}$ trace metal concentrations in selected rain water samples were higher in samples stored under cool conditions compared with frozen samples, although total dissolved trace metal concentrations remained the same for samples stored under both contrasting conditions. This suggested that trace metal organic complexing ligands degraded during long term storage unless samples were frozen. Therefore, samples in the present study were gravity filtered *in situ*, pre-acidified and frozen at -20 °C. All equipment and filters were acid washed prior to use, as described in section 3.3.4. All manipulations were conducted under clean conditions, using a Class 100 laminar flow cupboard where possible, and clean procedures were adopted. Disposable polythene gloves were worn by the operator at all times.

3.4.2.3 Assessment of the sample blank and potential contamination sources.

To ensure that the collection system was not a source of contamination, 2 litres of Milli-Q water were passed through the system once every two months. Trace metals in the filtrate were determined by the technique described in section 3.4.3 (Table 3.11). A further 2 litres of Milli-Q water were spiked to typical rain water trace metal concentrations, and passed through the system to assess potential adsorption of trace metals on the collection system (Table 3.12). The results show that contamination originating from the collection system was unlikely to contribute to the determined trace metal concentrations in the collected samples. It is also clear that the collection system was not a source of trace metal complexing ligands. The potential trace metal adsorption onto the surfaces of the collection system was also negligible.

Table 3.11: contamination results for the rain water collection system (µg l^{-1}) (n = 7).

Element	Concentration before filtration		Concentration after filtration	
	Labile	Total	Labile	Total
Al	< 0.06	< 0.06	< 0.06	< 0.06
Co	< 0.01	< 0.01	< 0.01	< 0.01
Cu	< 0.03	0.02 ± 0.004	< 0.03	0.02 ± 0.004
Ni	< 0.02	< 0.02	< 0.02	< 0.02
Pb	< 0.05	< 0.05	< 0.05	< 0.05

Table 3.12: adsorption results for the rain water collection system (µg l^{-1}) (n = 7).

Element	Spike	Concentration before filtration		Concentration after filtration	
	concentration	Labile	Total	Labile	Total
Al	0.68	0.63 ± 0.09	0.67 ± 0.06	0.64 ± 0.08	0.67 ± 0.06
Co	0.83	0.76 ± 0.23	0.81 ± 0.23	0.75 ± 0.23	0.80 ± 0.14
Cu	2.22	2.14 ± 0.10	2.29 ± 0.11	2.12 ± 0.11	2.27 ± 0.10
Ni	0.94	0.89 ± 0.08	0.99 ± 0.07	0.92 ± 0.16	0.96 ± 0.08
Pb	2.49	2.51 ± 0.87	2.53 ± 0.86	2.47 ± 0.83	2.59 ± 0.84

3.4.2.4 Storage of rain water particle samples.

After sample collection, the filtration system was returned to a Class 100 laminar flow cupboard (Bass Aire), and the funnel removed for acid washing. The membrane filter was removed from the filtration unit, using acid washed tweezers, and placed in a petri dish which was placed in a resealable bag and frozen to await further treatment. The rain water sample was weighed to ascertain its volume and then transferred to a 250 ml HDPE bottle, placed in a resealable bag and frozen to await analysis. This method of storage has been found to preserve the speciation of trace metals for up to 20 weeks (Fones, 1996).

3.4.3 Rain water analysis.

A variety of analytical techniques are available for the analysis of dissolved species in rain water, including Inductively Coupled Plasma Spectroscopy (Jickells et al., 1992), FAAS/GFAAS (Lim *et al.*, 1991) either by direct determination or with pre-concentration, or electrochemical techniques such as anodic and cathodic stripping voltammetry (ASV/CSV) (e.g. Marin *et al.*, 1993). In this study, dissolved trace metals in rain water samples were analysed using ACSV. The technique involves an *in situ* pre-concentration step onto a hanging mercury drop electrode (HMDE). This technique is very sensitive allowing direct determination of dissolved trace metals in rain waters. For a more comprehensive review of ACSV and its application, the reader is referred to van den Berg (1991). Aluminium concentrations in rain waters were determined as described in section 3.3.9.4.

3.4.3.1 Preparation of equipment and reagents.

A 1M solution of 'Aristar' boric acid (H_3BO_3) (BDH) was used as a buffer for the analysis of Co and Ni, and was cleaned with MnO_2 suspension prior to use; a 4 x 10^{-3} M solution of 'Aristar' dimethylglyoxime (DMG) (BDH) was prepared in a 7 x 10^{-3} M NaOH solution and was the corresponding ligand. A 1 M solution of N-2-Hydroxyethylpiperazine-N'-2-ethanesulphonic acid (HEPES) was prepared in a 1.25 x 10^{-2} M NaOH solution and was the buffer for the determination of Cu and Pb. The complexing ligand was a 4 x 10^{-3} M solution of 8-hydroxyquinoline (Oxine) which was prepared in dilute HCl. Ammonia and HCl solutions were used to adjust the pH of the solution. Metal standard solutions were prepared from 1000 ppm stock solutions (BDH).

3.4.3.2 Applied analytical protocols for the determination of dissolved trace metals (Co, Cu, Ni, Pb) in rain waters.

An EG & G PARC electrode (model 303) and a polarographic analyser (model 384) were employed for all ACSV analyses. Full instrumental parameters used in this work are reported in Appendix 3. Each analysis required 5 ml of rain water sample which was pipetted, using a Gilson 1-1000 µl Pipetteman automatic pipette, into a quartz electrochemical cell. Dissolved Ni and Co were determined in separate aliquots, using a technique first proposed by Pihlar *et al.* (1981), whereas Cu and Pb were determined in the same aliquot using a technique reported by van den Berg (1986). For all analyses, a duplicate aliquot was pipetted into a universal container. Buffer and ligand solutions were added to each duplicate. For the analysis of Ni and Co, 400 µl of 1 M o-H_3BO_3, yielding a concentration of 0.08 M, was added to buffer the solution and 10 µl of 4 x 10^{-3} M of the ligand DMG was then added, yielding a concentration of 8×10^{-6} M. For the analysis of Cu and Pb, 400 µl of the buffer HEPES (1 M) was added to give a final concentration of 0.08 M and 10 µl of the ligand oxine (0.01 M) was also added resulting in a final concentration of 2×10^{-5} M. The pH of the duplicate in the universal container was then adjusted to 8.2 for Co and Ni, and 7.7 for Cu and Pb using 1:3 NH_3:Milli-Q water solution. The required volume of 1:3 NH_3:Milli-Q water was then added to the aliquot in the quartz electrochemical cell. After the initial scan had been completed, according to the stated experimental parameters (Appendix 3), the analytical system for each sample was calibrated by two internal standard additions. Five µl of the 1.00 mg l^{-1} standard solutions were added as standard additions yielding sample solution spikes of 1.00 µg l^{-1}. Samples were analysed to obtain the $ACSV_{Labile}$ fraction of the trace metals in each sample, calculated as µg l^{-1} according to the equation:

$$C = \left(\frac{S_{ph}}{\overline{X}_{sph}}\right) * C_s \qquad \text{(Eqn 3.7)}$$

where:

C = concentration of the analyte (µg l^{-1})

S_{ph} = sample peak height (mV)

x_{sph} = mean increase in peak height due to spike addition calculated from calibration line of best fit (mV)

C_s = concentration of the spike (µg l^{-1})

Each sample was re-analysed, following UV irradiation, to determine the total dissolved trace metal content of the sample and thus enabling the determination of the 'organically complexed' trace metal fraction (µg l^{-1}). Using the whole rain water data set, volume weighted mean trace metal concentrations were calculated according to equation 3.8:

$$C_{VW} = \frac{\sum (C * V_{RW})}{\sum V_{RW}} \qquad \text{(Eqn 3.8)}$$

where:

C_{VW} = volume weighted concentration (µg l^{-1})

C = concentration of the analyte (µg l^{-1})

V_{RW} = volume of the rain water sample (l)

3.4.3.3 Assessment of the instrumental blanks and analytical detection limits.

Accuracy and precision, obtained from analyses of the CRM SLRS-2 (river water), and detection limits (blank + 3σ), obtained from 10 replicate analyses of Milli-Q water are given in Table 3.13. Comparable values for Al, determined by the Lumogallion/fluorescence technique (see section 3.3.9.4) are also presented. The results demonstrate good agreement between the certified and the experimentally obtained values for all investigated trace metals, although lower percentage RSDs for

Table 3.13: SLRS-2 determined values and precisions, and Milli-Q water detection limits obtained using ACSV (n = 10).

CRM	Element	Certified value µg l^{-1}	Determined value µg l^{-1}	Precision (% RSD)	Detection limit (Blank + 3σ) µg l^{-1}
SLRS-2	Al*	84.4 ± 3.4	78.6 ± 6.20	7.89	0.06
	Co	0.063 ± 0.012	0.06 ± 0.02	33.3	0.01
	Cu	2.76 ± 0.17	2.73 ± 0.33	12.0	0.03
	Ni	1.03 ± 0.10	1.04 ± 0.14	13.5	0.02
	Pb	0.129 ± 0.011	0.11 ± 0.06	54.6	0.05

* determined using the Lumogallion/fluorescence technique (section 3.3.9.4)

Co and Pb could have been obtained using longer collection times. The experimental value for Al was 78.6 ± 6.20 µg l^{-1} compared with a certified value of 84.4 ± 3.4 µg l^{-1}, although the percentage RSD was the lowest obtained during this assessment.

3.4.4 UV irradiation of rain water samples.

UV irradiation was used to oxidise natural dissolved organic complexes in samples enabling total metal analyses. The unit consisted of an aluminium box (71 x 31 x 31 cm) and a 0.4 kW mercury discharge lamp (Type PM 135, Applied Photophysics). The lid was designed to prevent UV light exposure and had an exhaust to allow O_3 venting. The system incorporated an automatic safety cut out switch which terminated power to the lamp if the lid was removed. Electrical power was supplied to the lamp using a DC transformer and start/stop switches. A Parvalux fan (flow rate 3.55 m^3 min^{-1}) was used to keep the lamp and samples cool as well as venting O_3 from the system. During operation, the unit was placed in a fume cupboard for safe removal of the O_3 produced. Sample UV irradiation was carried out in quartz tubes (volume ≅ 40 ml) which had loose quartz caps (fabricated in the University of Plymouth glass workshop). Thirty ml of the acidified samples were placed in the quartz tubes, four of which were inserted into brackets in the centre of each wall of the box, and irradiated for four hours. Prior to sample irradiation, a series of experiments were conducted to assess the efficiency of the technique at oxidising dissolved organic carbon (DOC) to CO_2. Initial studies used fluorescence to determine the DOC content of a sea water sample spiked with a humic acid solution to concentrations of 1, 5 and 10 mg l^{-1} prior to and during ~100 minutes of UV irradiation (Figure 3.5).

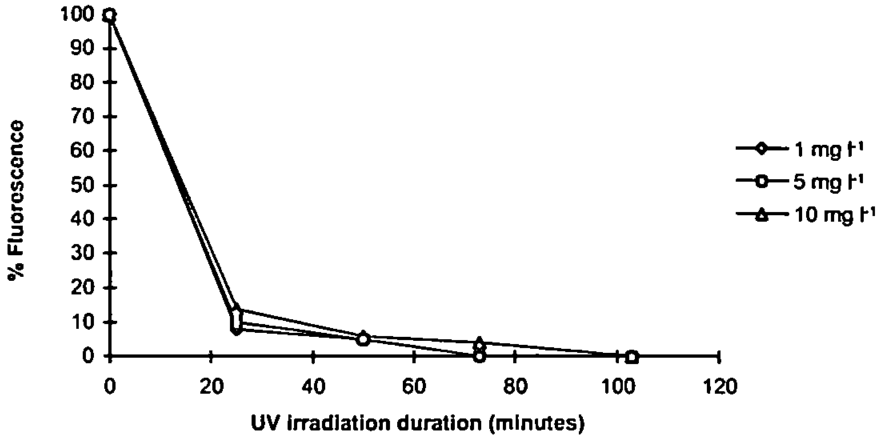

Figure 3.5: the effect of UV irradiation duration (minutes) on the DOC content of a series of sea water samples spiked with different concentrations of humic acid, expressed as a change in % fluorescence.

The effect of UV irradiation was also monitored in an unspiked sea water sample, by observing changes in fluorescence over a period of 103 minutes (Figure 3.6). The unspiked sea water samples were also analysed using High Temperature Catalytic Oxidation (HTCO) facilitated by a Shamadzu TOC 5000, by Dr Axel Miller (PML). The instrument housed a licor 6252 solid state photometric infrared detector, and calibration was achieved using potassium hydrogen phthalate (KHP) standards supplied with the TOC instrument. The results (Figure 3.7) show that the majority of the DOC was oxidised within one hour, although it took a further three hours of UV irradiation to reach a minimum of 26 μmol l^{-1} C. Based on these results, samples were UV irradiated for four hours and then allowed to cool. Once cool, the samples were transferred to clean universal containers and frozen to await analysis.

3.4.5 Digestion and analysis of rain water particle samples.

Rain water particle samples underwent total acid digestion as described in section 3.3.5.5, with analysis as described in section 3.3.5.3. Average blank values are displayed in Table 3.14 along with the average concentration determined in the digest extract. The results indicate that the blank filter concentrations do not adversely affect rain water particle digest concentrations. Volume weighted elemental concentrations of rain water particles C_{RW} were estimated using equation 3.8.

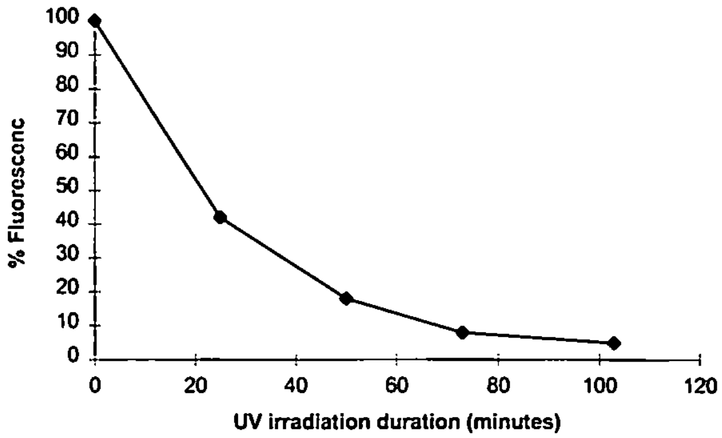

Figure 3.6: the effect of UV irradiation duration (minutes) on the DOC content of a sea water sample expressed as % fluorescence.

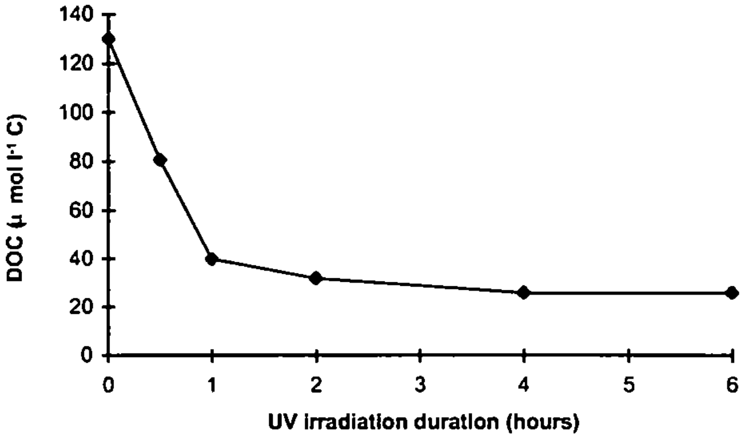

Figure 3.7: the effect of UV irradiation duration (hours) on the concentration of DOC.

Table 3.14: procedural rain water particle blank filter concentrations compared with average digest concentrations (FAAS and flame photometry in μg ml^{-1} / GFAAS in μg l^{-1}).

Element	Instrumental technique	Rain water particle Sartorius 0.45 μm membrane filters (n = 5)	Average concentration observed in the digest extracts (n = 35)
Al	FAAS	1.35	9.44 ± 19.3
Co	GFAAS	< 0.33	1.03 ± 1.06
Cu	GFAAS	< 0.70	33.9 ± 66.3
Na	Flame photometry	< 0.11	10.5 ± 11.2
Ni	GFAAS	1.35	6.88 ± 7.49
Pb	GFAAS	16.2	108 ± 350

3.4.6 Calculation of wet fluxes.

Wet fluxes were calculated according to equation 3.13:

$$F = C * R_A \qquad \text{(Eqn 3.9)}$$

where:

F = the wet deposition flux (ng cm^{-2} yr^{-1})

C = analyte concentration (ng l^{-1})

R_A = annual rainfall (cm yr^{-1})

Wet inputs to the investigated region were calculated according to equation 3.6.

3.5 Gravitational dry deposition.

3.5.1 Introduction.

Atmospheric trace metal fluxes to the sea surface are dependant on the concentration of the trace metal in the atmosphere and the settling velocity of the particle type. Such settling velocities are presented in the literature (e.g. Bradshaw, 1992; Guieu *et al.*, 1990; Ottley and Harrison, 1993). The collection of dry deposition, and corresponding aerosol concentrations, allows the calculation of settling velocities which are more applicable to the sampled aerosol.

3.5.2 Sampling.

3.5.2.1 Sampling protocol.

The collection funnel was placed on the support above the dry collection compartment of the automated wet/dry collector (Figure 3.4). The 2 litre acid washed HDPE bottle, which had been sealed in a resealable plastic bag, was placed on the stand within the compartment. The plastic bag was opened to expose the neck of the bottle for collection. The collection system was exposed for periods of ~ 14 days. All exposure times were corrected for rainfall periods.

After the collection of the first dry deposition sample, the collection bottle was removed and the collection funnel was rinsed with three separate 50 ml aliquots of 4M HNO_3 to release any adsorbed trace metal from the funnel surface. The rinses were collected in separate 2 litre HDPE bottles. Following each acid rinse, the funnel was further rinsed with a 50 ml aliquot of Milli-Q water thus transferring any remaining drops of acid to the collection bottle. Analysis of the sequentially collected aliquots revealed that the first wash efficiently removed Al, Cd, Co, Mn, Pb and Zn, while a second rinse was required for Ni. Copper, Fe and Na required three rinses to remove the majority of the adsorbed material (Table 3.15). At the end of each subsequent sampling period, the collection funnel was thoroughly rinsed with ~ 100 ml of 4 M HNO_3 and ~ 100 ml of Milli-Q water to remove any remaining material from the funnel surface. The rinse was collected in the collection bottle. The funnel was then removed for acid washing.

Table 3.15: the efficiency of adsorbed trace metal removal from the collection funnel surface, using 4M HNO_3 ($\mu g\ ml^{-1}$ FAAS and flame photometry/$\mu g\ l^{-1}$ GFAAS).

Element	Analytical technique	Wash 1	Wash 2	Wash3
Al	FAAS	< 0.54	< 0.54	< 0.54
Cd	GFAAS	< 0.36	< 0.36	< 0.36
Co	GFAAS	< 0.33	< 0.33	< 0.33
Cu	GFAAS	25.6	4.50	3.49
Fe	FAAS	0.10	0.01	0.02
Mn	FAAS	< 0.05	< 0.05	< 0.05
Na	Flame photometry	191	20.2	1.05
Ni	GFAAS	< 20.2	< 20.2	< 20.2
Pb	GFAAS	< 2.39	< 2.39	< 2.39
Zn	FAAS	0.30	< 0.07	< 0.07

3.5.3 Acid digestion of the dry deposition samples.

3.5.3.1 Digestion protocol.

Owing to the large dissolved volume of the dry deposition samples, ~ 25 ml of the sample was placed in a Teflon vial and evaporated at 70 °C. Upon evaporation of the acid solution, a further sample aliquot of ~ 25 ml was added, and evaporated. This procedure was repeated until the entire dissolved sample had evaporated. The collection bottle was rinsed three times with ~ 20 ml of concentrated HNO_3. Each rinse was added to the Teflon vial and evaporated. Once the last rinse had evaporated, the digestion procedure described in section 3.3.5.5 was followed with subsequent analysis as described in section 3.3.5.3.

3.5.3.2 Flux calculation.

The elemental dry deposition fluxes were calculated according to the formula:

$$F=\left(\frac{C'*V}{A*T}\right)*Y \qquad \text{(Eqn 3.10)}$$

where:

F = dry deposition flux (ng cm^{-2} yr^{-1})

C' = experimental concentration (ng ml^{-1})

V = made up volume of the digest extract (ml)

A = surface area of the collection orifice = 0.554 m^2 = 5540 cm^2

T = accumulated duration of the collection period (hrs)

Y = number of hours per year

3.6 Critical appraisal of the selected sampling sites, equipment, and applied protocols.

3.6.1 Sampling locations.

Ideally marine aerosols should be sampled at sea, but this was logistically difficult due to the length of the proposed sampling period, and the necessity to change sample collection devices regularly. It was also necessary to locate the western English Channel site at some distance from urban centres, particularly Plymouth, to limit potential contamination of the collected samples from local anthropogenic sources. This required that the selected site was occupied throughout the year, as the distance required to prevent contamination from urban sources, prevented daily travelling from Plymouth to the sampling site. The western English Channel site was therefore chosen due to its location and technical support. Estimation of the contamination caused by the location of the sampling site was facilitated by participation on two OMEX cruises, which centred on the Celtic Sea. Kane *et al.* (1994) have since reported that sampling on-shore does not invoke large errors when compared to sampling off-shore for trace metals.

3.6.2 Sampling equipment.

3.6.2.1 Aerosol sampling.

An inherent problem associated with aerosol collection on filter media, is that of isokinetic sampling (Pio, 1986). Aerosol sampling is based on the assumption that a particle in an air stream will have inertia which is a product of its mass and velocity. Optimum aerosol sampling would be conducted isokinetically, that is, the rate of air passing through the sampling device is equal to the velocity of the ambient air stream. Without sophisticated sampling equipment, which can vary the air flow rate of the pump and move the filter unit to face the oncoming air stream, this is very difficult to achieve. Sampling which is conducted anisokinetically may result in the collection of an unrepresentative particle size (and therefore elemental concentration) distribution. However, Pio (1986) states that isokinetic sampling is less important when the sampled particle size is exclusively less than 3 to 5 μm in diameter, as smaller particles suffer insignificant inertial effects to cause significant sampling error. Isokinetic sampling is also less important when sampling low velocity air streams. All aerosol sampling carried out in the current study was performed anisokinetically.

A number of reports have been made concerning the inefficiency of Whatman 41 filter papers to collect fine particles (< 2 μm diameter (Whitby, 1977)). In reply Lowenthal and Rahn (1987) conducted a large - scale field study and found that, under the sampling conditions used, the Whatman 41 filter media had a collection efficiency of ~ 90 percent or better for 13 of the 14 elements, ranging from 'coarse' (e.g. Na and Al) to 'fine' (e.g. Zn and As) particles. Prospero (1989) also commented on the use of Whatman 41 for the collection of aerosol particles stating that they were no worse than any other filter media currently in use. Therefore the use of Whatman 41 filter papers are a compromise between efficiency, purity, availability and cost (Lowenthal and Rahn, 1987), and accepted as an appropriate filter medium for the collection of aerosol particles.

3.6.2.2 Rain water sampling.

The rain collector employed at the western English Channel site was automatic, designed to operate at the onset of a rain event, and closed once the rain event had terminated, thus collecting uncontaminated wet and dry deposition samples. The collector itself was constructed from materials specifically chosen to limit contamination and to be water tight. However, the box, rated to IP67, which was used to house the motor and gearbox, was adapted for mechanical purposes. On two occasions during the sampling period, rain entered the box and shorted several of the transformers. Owing to the action of the motor moving the protective cover between collection systems, the aluminium arms were vulnerable in strong winds. On one occasion it is believed that such winds caused enough resistance to the motor that it seized, requiring replacement. Whenever the collector ceased operating, an electrician from Plymouth was required to visit the sampling site, assess the problem, then return to Plymouth to arrange replacement parts. Once the parts had arrived, they had to be fitted on site, during dry weather. This procedure took up to three weeks, during which time no dry deposition samples were collected and rain water samples were potentially contaminated by dry deposition, although this was calculated to be negligible on the occasions when it occurred.

3.6.3 Critical appraisal of the adopted sampling protocols.

3.6.3.1 Aerosol sampling protocols.

Ideally samples would have been collected over a period of 24 hours or more, enabling use of higher detection limit (and therefore less expensive) instrumentation. However, proximity of the sampling site to a small residential area prevented this as the noise of the high volume pump during operation caused some irritation to local residents. After failure to adequately noise proof the pump, a compromise was established so that samples were only collected during the day time. Also samples should be collected during all dry periods in order to obtain a representative data set. However, the research assistants who collected the samples were occasionally absent thus preventing sample collection. Gaps in the data set have therefore arisen. Sample manipulation at the western English Channel sampling site was undertaken in a plastic tent, and not, as would have been preferable, in a laminar flow cupboard. Samples were also stored at room temperature, for ~ seven days, until transferred to the University where they were frozen until required.

3.6.3.2 Wet deposition sampling protocols.

To maintain chemical integrity, rain water samples should ideally have been analysed immediately and at their natural pH. However, due to the distance of the sampling site from the University, and adopted analytical methodology, a compromise had to be made. *In situ* filtration was used to separate particles from the dissolved rain water fraction, which was subsequently acidified to prevent adsorption onto the container walls during storage. At the field centre, the samples were stored at room temperature, for ~ seven days, but were frozen upon arrival at the University. This method is comparable with that used by Fones (1996) and Nimmo and Chester (1993).

3.6.4 Pre-treatment and analytical protocols.

3.6.4.1 Pre-treatment and analytical protocols relating to particle samples.

Efforts were made to obtain 100 percent dissolution of trace metals from particle samples (aerosol, rain water and dry deposition). A limited study was undertaken, and a method chosen based on overall efficiency. A sequential leach, containing three stages, was also employed as it had been used previously by other workers, on atmospheric particles, and it was thought that the quantity of collected material would not be sufficient to support a leach of additional stages. The solubility studies were designed to investigate the biogeochemistry of dry deposited atmospheric trace metals. It does not incorporate the effects of the microlayer, variable wind strengths, temperatures etc. due to the limited time scale of this project.

3.6.4.2 Analytical protocols relating to rain and sea water samples.

ACSV is an ideal tool for the investigation of the speciation of trace metals in rain and particularly sea water samples. However, it is subject to a small number of interferents which can largely be overcome by carefully adjusting the pH of the buffered sample. Acidification of solubility study sea water samples prior to UV irradiation was necessary to prevent adsorption onto the quartz tube walls, but required meticulous adjustment of the buffered sample pH prior to analysis for Al.

Chapter 4.

Description of the sampling sites.

Chapter 4.

Description of the sampling sites.

4.1 The western English Channel.

4.1.1 Physical characteristics of the English Channel.

The English Channel is a stretch of water connecting the North Sea to the Atlantic Ocean (Figure 4.1). It is bordered by 650 km of English and 1100 km of French coast, covering some 77 000 km^2 (Reid *et al.*, 1993). Residual current flow is dependent on the wind and the tide, and is greatest in the central Channel current velocities are generally low (Taylor *et al.*, 1981).

There are 31 estuaries along the UK coast of the English Channel, ranging from ria to bar estuary to coastal, with a total annual discharge of 25 km^3 of water, largely fed by chalk aquifers and agricultural land run-off. Mean river discharges range from < 0.3 m^3 s^{-1} to 35.8 m^3 s^{-1} and amount to a total of 327 m^3 s^{-1} (Reid *et al.*, 1993). There are 45 estuaries of various types along the French coast, with mean river discharges ranging from 2.4 m^3 s^{-1} for the Rance to 428 m^3 s^{-1} for the industrially influenced Seine, amounting to a total of 665 m^3 s^{-1}. Typical dissolved trace metal concentrations of rivers flowing into the English Channel are given in Table 4.1.

4.1.2 Anthropogenic factors influencing the English Channel.

The immediate coastline and estuarine fringes of the English Channel are occupied by ~ 8.84 million people. Forty-four percent live along the UK coastline, in densities ranging from 0.8 to 46.0 people per hectare (Reid *et al.*, 1993). The corresponding French region encloses ~ 3700 towns, only four of which have populations in excess of 100 000 inhabitants.

The major mode of transport to and from the UK coastline is by private car (82 percent) (Devon Tourist Statistics, 1995). Ease of access and the weather experienced (1204 sunshine hours, 19.6 °C average maximum temperature and 111 days without rain, between May and September 1995) resulted in considerable human mobility during the sampling period (Devon Tourist Statistics, 1995).

The UK Channel coast possesses a wide variety of industry which is largely concentrated around urban centres and ports such as Plymouth, Southampton, Portsmouth, Folkestone and Dover; naval activity is centred on Plymouth and Portsmouth. The hinterland of Southampton is arguably the most

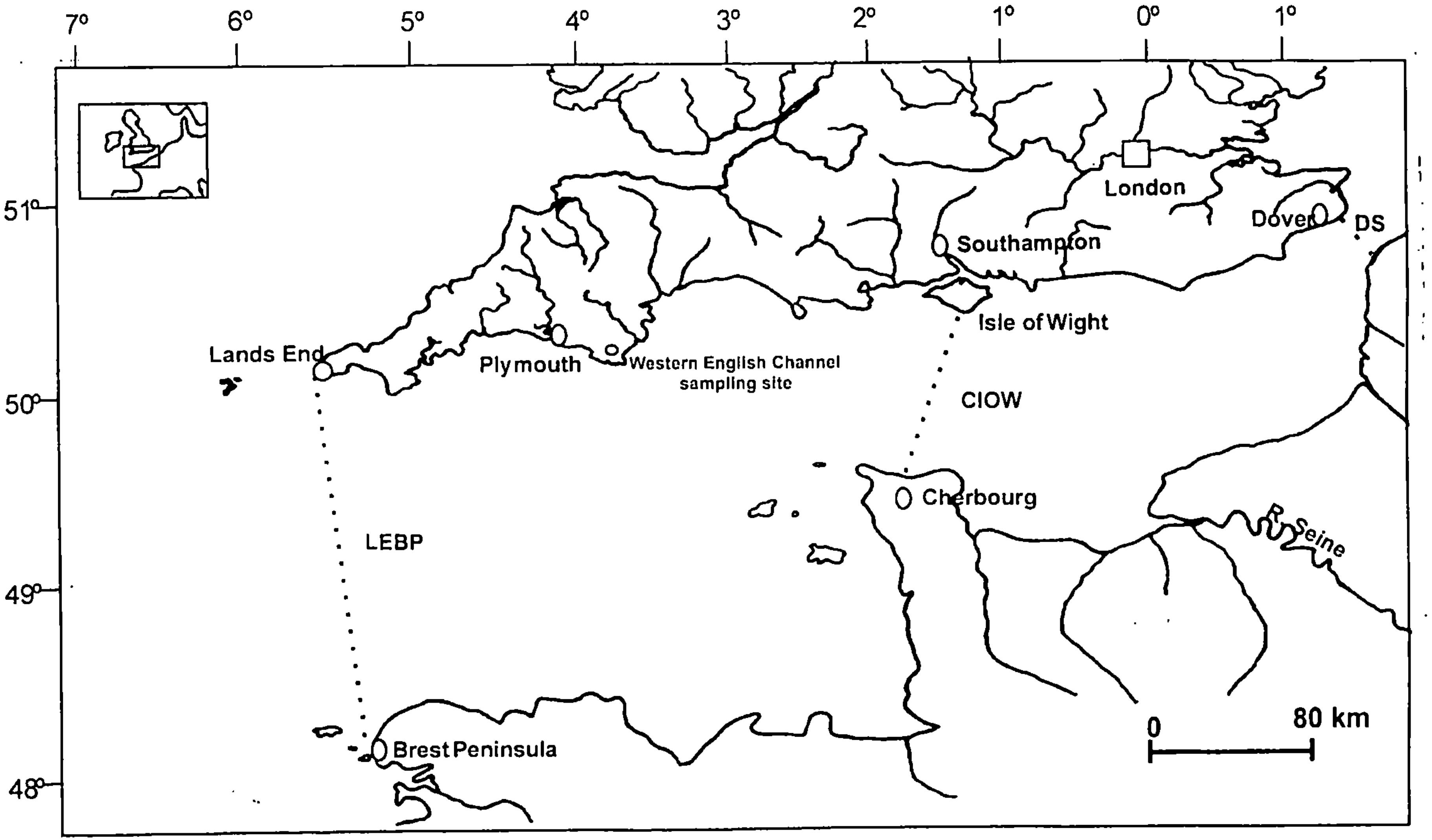

Figure 4.1: diagram of the English Channel displaying major cities and rivers, the Fluxmanche transects (see Chapter 8) and the western English Channel sampling site.

Table 4.1: typical dissolved trace metal concentrations in rivers discharging into the English Channel (SWA = Southern Water Authority).

Element	River	Concentration ($\mu g\ l^{-1}$)	Literature Source
Cd	Seine	0.1 - 0.2	Boust, 1981
	Itchen/Test	< 0.1 - 2.12	SWA (unpublished)
Cu	Seine	1.54 - 3.2	Boust, 1981
	Tamar	1.02 - 6.02	Ackroyd *et al.*, 1986
Mn	Seine	~ 7.7	Boust, 1981
	Tamar	99.0	Reid *et al.*, 1993
	Itchen/Test	< 10.0 - 165	SWA (unpublished)
Ni	Itchen/Test	< 1.0 - 39.7	SWA (unpublished)
	Tamar	1.0 - 2.01	Reid *et al.*, 1993
Pb	Seine	< 0.48 - 3.31	Boust, 1981
	Itchen/Test	0.95 - 5.69	SWA (unpublished)
Zn	Seine	~ 19.9 - 24.7	Boust, 1981
	Tamar	3.97 - 13.9	Ackroyd *et al.*, 1986
	Itchen/Test	0.98 - 43.8	SWA (unpublished)

industrial region along the southern UK coastline, with an oil refinery and an oil burning power station at Fawley, near Southampton, increasing atmospheric emissions (Reid *et al.*, 1993).

Until the latter half of this century, mineral mining was prevalent in the south west of England. This has left old mine workings, flooded with heavy metal contaminated water, which is discharged to coastal waters by the water course. The most significant incident of this kind was the flooding of the Wheal Jane tin mine in January 1992, which resulted in elevated heavy metal concentrations in Restronguet Creek and the Fal estuary (NRA, 1992). Mine spoil tips, enriched with elements such as As, Cu, Ni, Pb, Sb and Sn, are also present along the South West Peninsula (Scrivener, 1996). The discharge of raw/partially treated sewage, urban runoff and china clay waste, into south west England coastal waters are other sources of elevated metal and suspended particulate matter (SPM) concentrations (NRA, 1992).

The majority of the French industry in the region is focused on the Seine estuary and includes TiO_2 processing plants (discharging acid iron waste) and three phosphate manufacturing plants (discharging phosphogypsum) (Reid *et al.*, 1993). A major petrochemical complex is sited within the industrial region of Le Havre, and three nuclear power stations are in operation along the French Channel coast. A comparison of the direct discharges made along the UK Channel coast and from the Seine is displayed in Table 4.2.

Table 4.2: annual direct industrial discharges to the English Channel from the UK Channel coast and the Seine (Reid *et al.*, 1993).

Region	Cd t yr^{-1}	Cu t yr^{-1}	Pb t yr^{-1}	Zn t yr^{-1}
UK Channel	1.2 - 2.7	47 - 51	15 - 27	384
Seine (France)	7.4	166	236	676

4.1.3 Meteorological characteristics of the English Channel.

Daily meteorological charts for the UK, from 1873 to 1947, have been classified according to wind direction and isobaric pressure (Barry and Chorley, 1992). Two types of weather system were identified: low pressure cyclonic (C) depressions, and high pressure anticyclones (A); along with five directional sources: northerly (N), easterly (E), southerly (S), westerly (W) and north westerly (NW). Between December and January, westerly air masses account for 35 percent of the experienced air masses and 33 percent between July and September, reaching a minimum of 15 percent in May. During this month, air masses from the north and east reach their greatest frequency at around 10 percent each. Mid latitude depressions are most frequent in July and August (13-17 percent) and have a 10 percent frequency at all other times. Anticyclones are most frequent in June and September (20 percent), and have a frequency of 13 percent at all other times (Barry and Chorley, 1992).

Based on this, air masses influencing the UK can be divided into seven categories: tropical maritime (mT), warm polar maritime (mPw), polar maritime (mP), arctic maritime (mA), polar continental (cP), transitional polar continental, and tropical continental (cT) (Figure 4.2) (Barry and Chorley, 1992). The English Channel is characterised by a maritime climate, dominated by North Atlantic westerlies. The frequencies of mP and mPw air masses show clear predominance at 30 percent or more in all months except March, with mP air having a maximum frequency of 33 percent in July with a further 10 percent of mPw air (Barry and Chorley, 1992). These air masses induce cool, showery weather on western coasts, particularly over the Celtic Sea and the western English Channel. The passage of deep, westerly moving depressions and their associated winds, particularly when associated with spring tides, can generate large, travelling waves, ranging from 25 m in the western English Channel to 13 m

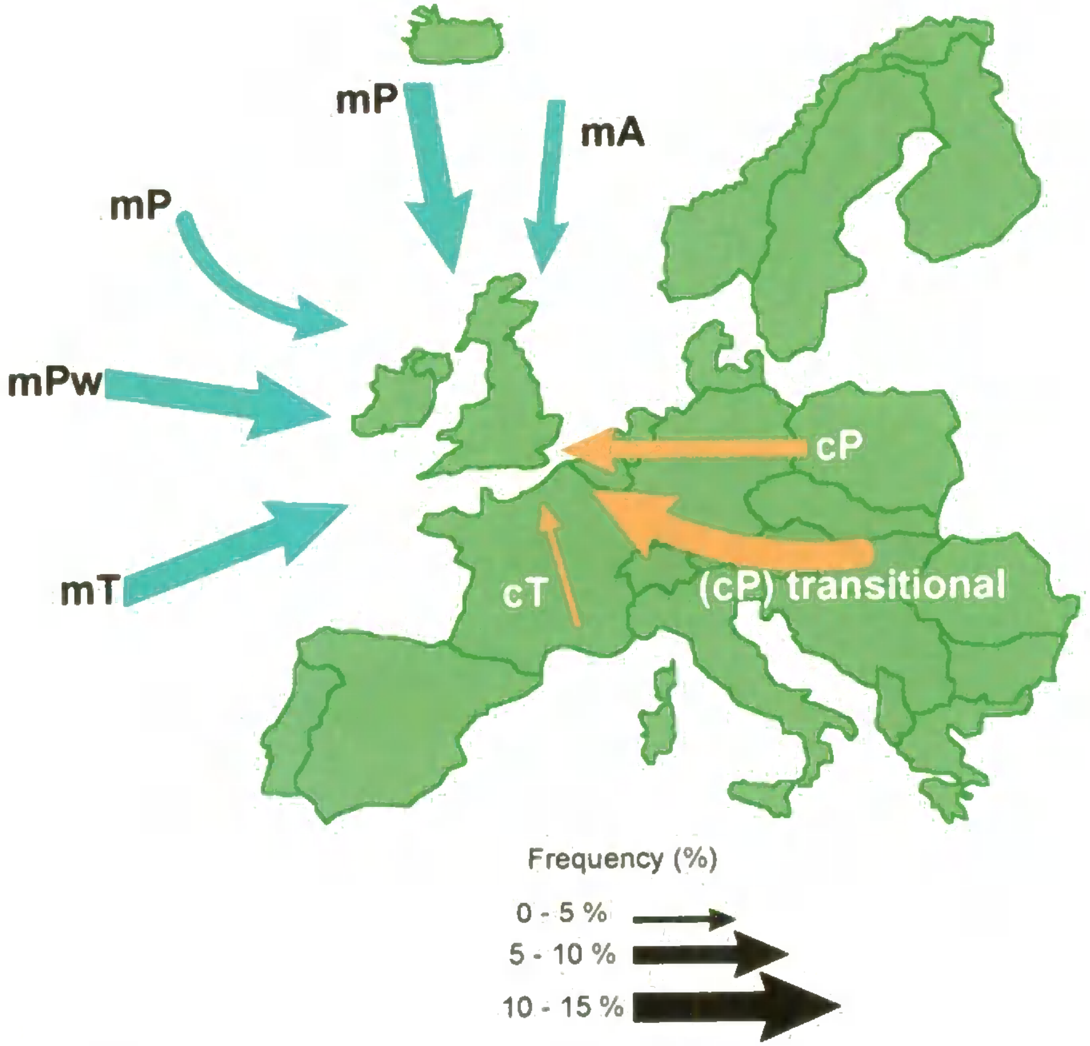

Figure 4.2: air masses influencing the UK, and their frequencies.

in the east (Reid *et al.*, 1993), thus re-suspending and transporting more material eastwards along the Channel than would normally be observed. Warm polar maritime air masses are an intermediate between mP and mT air masses which commonly form the air present as the warm sector of depressions, bringing mild, damp conditions in winter (Figure 4.2). Arctic maritime air masses bring cold, clear weather with few showers (Barry and Chorley, 1992). Cold, dry, stable cP air affects the UK infrequently between December and February, with the west UK coast least affected. Similarly, cT air affects the UK infrequently during the summer months. Such air masses approach from the south and east, and are generally hot and stable, although instability in upper layers often induce electrical storms. In winter, modified cT air masses bring fine, hazy, mild weather. Transitional cP air masses influence the UK throughout the year although less in summer, and bring dry, stable conditions.

The climate of the western English Channel can be summarised as an area of mild climate moderate rainfall (average of 1076 mm per year between 1991 and 1996) and little temperature variation (temperature range: 1.5 to 24.4 °C), with sporadic continental and weak arctic influences (Meteorological Office, 1998). However, despite the seemingly seasonal regularity of the weather patterns influencing the English Channel, there is much variability in wind direction and strength (wind experienced from all compass points and with mean strengths of 5 m s^{-1} in the winter and ~ 2.5 m s^{-1} in the summer) (Reid *et al.*, 1993). Over the decade between 1983 and 1993, a decrease in the number of westerlies influencing the UK was observed, from 130 to 90 days per annum.

4.1.4 The western English Channel sampling site.

The sampling site was situated at Slapton Ley Field Centre, in the village of Slapton, approximately one mile from the coast of Start Bay in South Devon. Start Bay is a barrier beach, behind which a fresh water lake exists - Slapton Ley. The barrier is believed to be comprised of flints, cherts, quartzite and igneous pebbles believed to be transported to the area by the rising sea level following the last glacial period (approximately 10 000 BP), and is thought to have been in place since 2000 B.P. (Job, 1994). The beach is lined with shingle and pebbles, with sand close to the low water mark: material from the beach is not easily re-suspended to the atmosphere. The sampling site is a grassed field and the field centre, a small farm and three houses are within a 200 m radius.

The meteorology of the site is dominated by Atlantic pressure systems and mid latitude depressions are a common occurrence. Prevailing south westerly winds pass over approximately 15 km of land prior to sampling although northerly air masses (passing over approximately 80 km of land before reaching the sampling site) are susceptible to terrestrial contamination. The only major potential sources of urban contamination are Plymouth, to the west north west, and Torbay and Exeter to the north. The sampling site is also potentially influenced by Dartmoor to the north west which has remnant mine waste heaps containing ores of As, Cu, Pb and Sn together with the influence of china clay extraction industries which extend along the South West Peninsula. Long range transport of material, from e.g. North Africa, USA, Western and Eastern Europe, may also contribute to the English Channel aerosol.

4.2 The north western Mediterranean Sea.

4.2.1 Physical characteristics of the Mediterranean Sea.

The Mediterranean Sea is a semi-enclosed sea which exchanges with the Atlantic Ocean through the Straits of Gibraltar (Figure 4.3). It is about 3900 km in length and up to 1600 km wide, and borders southern Europe to the north, the Levant to the east, and North Africa to the south. It has a surface area of 2 500 000 km^2, it has a maximum depth of 4400 km and highly variable bathymetry; it is highly influenced by the deposition of sediments close to the mouths of major rivers such as the Rhône, Axios and Nile. Bottom sediments consist mainly of clay-silt deposits, but also contain fine sands, small mollusc shells and coccoliths (Eisma, 1993).

One of the main features of the Mediterranean Sea is the small tidal range. This is partially caused by the Straits of Gibraltar which is the only inlet/outlet of the Mediterranean Sea to the open ocean. At its narrowest, the Straits are only 13 km wide, thus severely restricting water exchange with the Atlantic Ocean. This feature enables thermal intensification of the trapped sea water, making it a warmer body of water than oceanic seas (i.e. abyssal temperatures ~13 °C vs. 4 °C for oceans) (Millán *et al.*, 1991). The Mediterranean Sea can be separated into two basins: western and eastern geographically separated by the Sicily Strait (Copin-Montegut *et al.*, 1986). This is also an area of plate tectonics with two active volcanoes: Mt. Vesuvius, near Naples; Mt. Etna on Sicily, which last erupted in 1986.

4.2.2 Meteorological characteristics of the Mediterranean Sea.

The climate of the Mediterranean is characterised by hot, dry summers and mild, relatively wet winters. The climate is interposed between temperate maritime and arid subtropical desert regimes, and is controlled by westerly winds in the winter and subtropical anticyclones in the summer, due to the movement of the subtropical westerly jet stream (Barry and Chorley, 1992). There is much regional variation due to the topography of the area, which sustains local stagnation/re-circulation air flows. Such flows can last for between one and several days, covering an area of tens of km. This

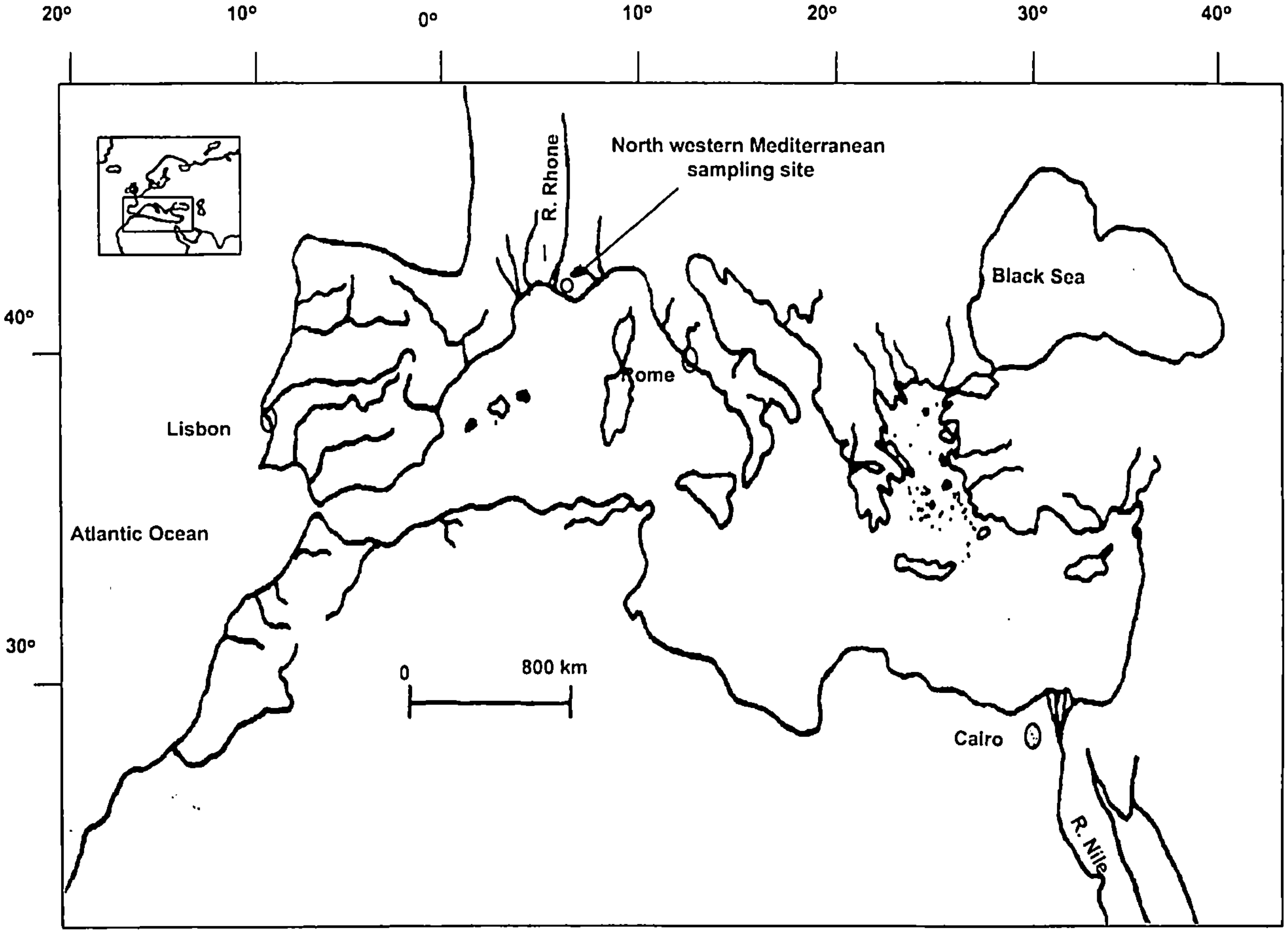

Figure 4.3: map of the Mediterranean Sea displaying the north western Mediterranean sampling site.

has considerable implications for air quality and atmospheric pollution (Millán *et al.*, 1987). In addition, marked diurnal and seasonal variations have been observed (Millán *et al.*, 1991).

Winter in the Mediterranean commences abruptly around 20th October with the collapse of the Azores high pressure cell, and is accompanied by an increase in the probability of rain (in any 5 days) from 50 - 70 percent in early October to 90 percent in late October (Barry and Chorley, 1992). Precipitation is largely associated with cold fronts due to cold air meeting warm surface sea waters (January sea temperatures are ~ 2 °C higher than the mean air temperature). This causes convective instability along the cold front which results in precipitation (Barry and Chorley, 1992). Rainfall can also be orographic, with different regions experiencing maximum precipitation at different times of the year (Figure 4.4).

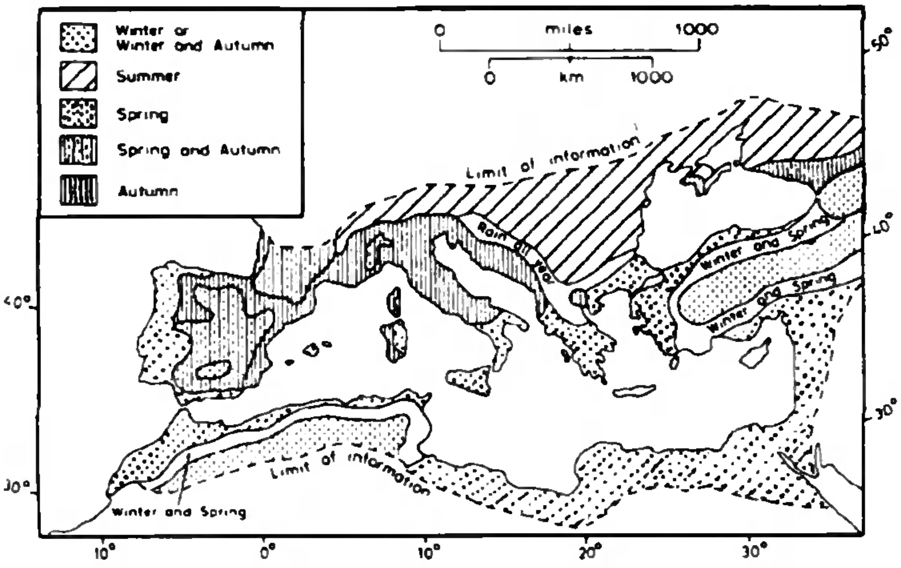

Figure 4.4: Mediterranean rainfall regimes (Barry and Chorley, 1992).

The occurrence of cA and mA air masses are infrequent at only 6 - 9 invasions each year. mP air masses are more frequent, and cause Mediterranean depressions. Such Atlantic derived depressions account for 9 percent of the depressions experienced over the Mediterranean; baroclinic waves or *Saharan depressions* account for 17 percent of the depressions experienced and are an important source of rainfall in the winter and spring; 74 percent of the depressions develop in the western Mediterranean, to the lee of mountain ranges such as the Alps and the Pyrénées and are known as *Genoa depressions* - they are characterised by intense precipitation along the warm front, and heavy showers and thunderstorm rainfall to the rear of the cold front (Barry and Chorley, 1992). Genoa depressions result in the warming of mP air which produces characteristic air termed *Mediterranean*. The boundary between this air mass and north eastwardly moving Saharan cT air is referred to as the *Mediterranean Front*. As these air masses move eastwards, a zone of low pressure is formed which draws warm, dust laden cT air northward ahead of the cold front. This northward flow is called the *Scirocco*, and is particularly important in spring and autumn (Barry and Chorley, 1992). Anticyclones are also important during winter. Between October and April, they are dominant over the Mediterranean for 25 percent of the time (48 percent over the western basin). This results in high mean pressure with few rainy days (up to 12 per month especially on windward peninsula slopes).

Hot, dry, stable summer weather moves into the Mediterranean from the south west between March and May, due to the northward and eastward extension of the Azores anticyclone, displacing depressions northward. By mid June, the Azores anticyclone dominates the western Mediterranean, while low pressure over the Sahara results in northerly winds. The *mistral* is a seasonal wind which is common between January and July. It occurs in association with northerly mP airflows, when a Genoa depression lies in the Gulf of Genoa, to the east of a high pressure ridge from the Azores anticyclone. This induces funnelling down the Rhône valley producing a cold, potentially pollutant-laden, northerly wind (Barry and Chorley, 1992).

Guerzoni *et al.* (1989) identified the prevailing wind directions experienced over the Mediterranean. They observed that over a 10 year period, 38 percent of air masses in the western basin originated from SW to NW, 28 percent from NW to NE, 13 percent from SW to SE and 1 percent from NE to SE. In the eastern basin, 39 percent of the air masses originated from NW to NE, 28 percent from W to NW, 17 percent from NE to SE and 16 percent from SE to W. The importance of northerly air masses can therefore be seen, while southerly air masses are amongst the most infrequent. However, a study undertaken on Sardinia, between October 1990 and December 1991, by Guerzoni *et al.* (1993) revealed strong southerly episodes between October and December 1990 and February and March 1991. This correlates with the autumn/spring occurrence of the *Scirocco* wind.

4.2.3 The western Mediterranean sampling site.

The aerosol sampling equipment was situated on the roof of the Oceanographic Museum, on the edge of the naturally formed harbour, in Monte Carlo, Monaco. Monaco, an independent principality in SE France, has an area of ~ 150 hectares, a population of ~ 30 000, and is a leading tourist resort, with major industries in shipping and perfume manufacture.

4.3 The Celtic Sea.

4.3.1 Characteristics of the Celtic Sea.

The Atlantic Ocean has a surface area of ~ 82 362 000 km^2 (Briggs, 1989) and reaches depths of up to 8530 m. The Celtic Sea is a portion of the Atlantic Ocean where the South West Approaches meet the English Channel and the Irish Sea. Its bathymetry is dominated by the continental shelf break where water depths rise from > 4500 m to < 200 m, with the most dominant feature being the Goban Spur.

The Celtic Sea is subject to similar meteorological conditions to the western English Channel, which is dominated by westerly air masses (4.1.3). Such air masses introduce marine air to the region, although long range pollutant transfer from the American continent is possible (Rahn *et al.*, 1979). Terrestrial contamination of Celtic Sea aerosols can occur close to the coastline, through off-shore breezes. The Celtic Sea atmosphere is periodically disrupted by the passage of tropical storms from the Gulf of Mexico and further north. Such storms have an annual frequency of 8.8 in the western North Atlantic, and occur mainly between August and October. They induce winds up to speeds of > 25 ms^{-1} and are transferred to the North East Atlantic by prevailing westerly winds (Barry and Chorley, 1992). Most rainfall is associated with the passage of weather system fronts. As for the western English Channel, very little is known of the atmospheric trace metal geochemistry over the Celtic Sea.

4.3.2 Sampling in the Celtic Sea.

Sample collection was carried out during two cruises during the Ocean Margin Exchange (OMEX) Programme. The first cruise took place between the 3rd and 20th of June 1995, on board RRS Charles Darwin. The ship's track passed down the west coast of Ireland before reaching the shelf break region of the Celtic Sea (Figure 4.5). Seven aerosol and three rain water samples were collected. The second OMEX cruise took place between the 26th of August and the 12th of September 1995, on board RRS Discovery. The ship sailed directly to the Celtic Sea shelf break region (Figure 4.6). The cruise was interrupted by the passage of the remains of Hurricane Iris, which caused gale force weather conditions over the North East Atlantic Ocean. Seven aerosol samples were collected during the cruise.

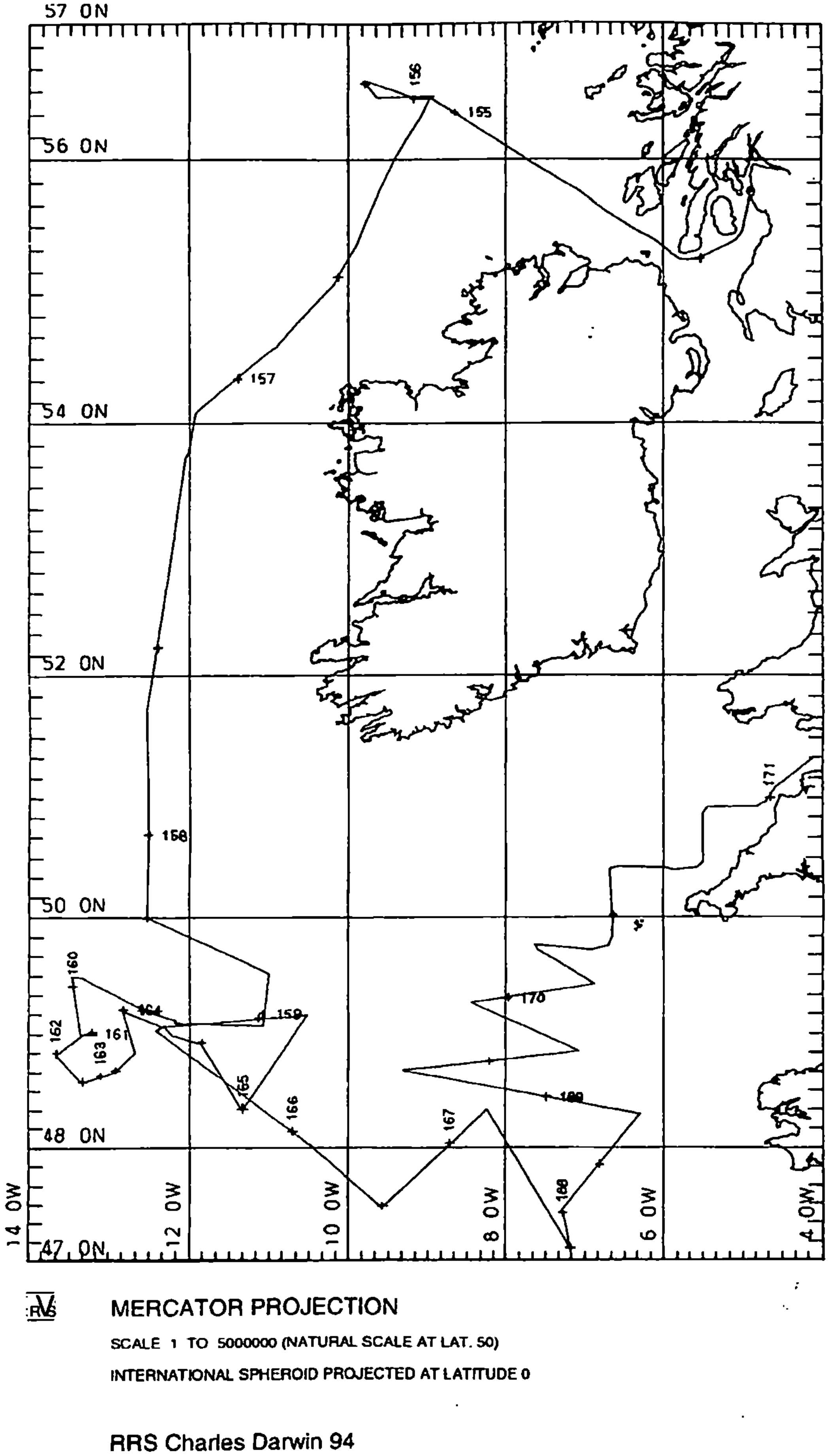

Figure 4.5: track of OMEX cruise 1 (3rd-20th June 1995).

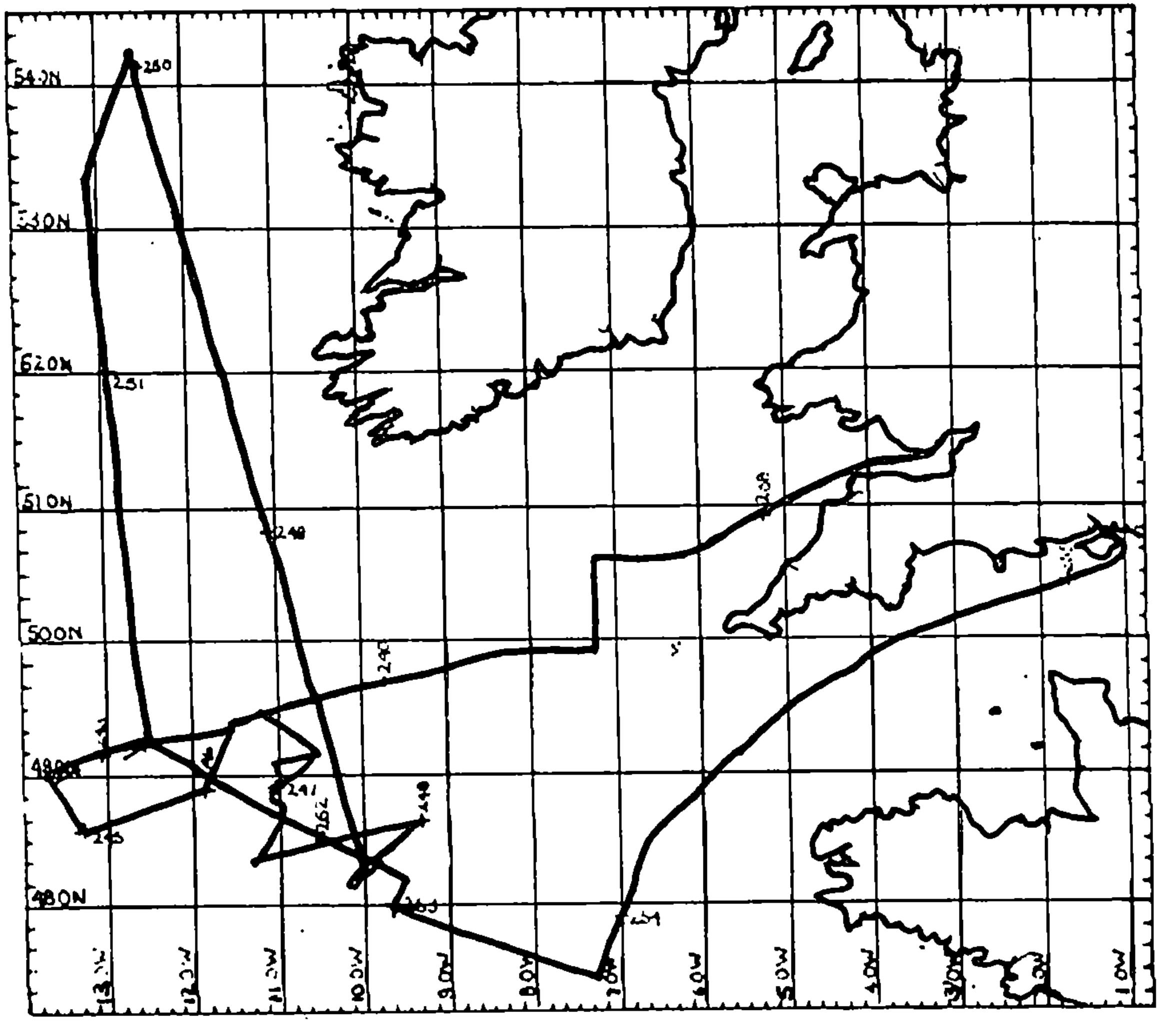

Figure 4.6: track of OMEX cruise 2 (Scale 1 to 4000000 (Natural scale at Lat. 50)).

Chapter 5.

Atmospheric trace metal characteristics of the western English Channel.

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Atmospheric trace metal characteristics of the western English Channel.

5.1 The concentrations and geochemistry of trace metals in the western English Channel aerosol.

The geometric mean aerosol trace metal concentrations for the English Channel atmosphere are compared with other European coastal regions in Table 5.1. The geometric mean aerosol concentrations for Cd, Cu and Pb are the lowest reported for European coastal regions (Irish Sea: Fones, 1996; North Sea: Chester and Bradshaw, 1991; Western Mediterranean: Chester *et al.*, 1990), suggesting a minor anthropogenic component in the western English Channel aerosol. The Pb concentrations were particularly low (of the order 1.2 ng m^{-3}) compared to higher values for the Irish Sea (Fones, 1996), which could be associated with the introduction of unleaded petrol and a decline of Pb emissions to the atmosphere (Wu and Boyle, 1997). Decreases in aerosol Pb concentrations in the urban and coastal atmospheres in the UK have also recently been observed (Fones, 1996) and the impact of lower Pb atmospheric emissions has also been detected in surface North Atlantic waters (Wu and Boyle, 1997), with dissolved Pb concentrations showing a consistent decrease.

The aerosol concentrations for Al, Fe, Mn, and Zn were similar to those observed for the Irish Sea (Fones 1996). However, comparatively elevated aerosol concentrations were detected for Na and Ni. Higher Ni aerosol concentrations (up to 15.1 ng m^{-3}) may result from a contribution to atmospheric aerosols of re-suspended waste material from historical extraction activities (Hamilton-Jenkin, 1974) and/or soils from unworked mineralised regions (McGrath and Loveland, 1992). Since extraction techniques were inefficient, large quantities of metals were retained within spoil tips. Owing to the loose, uncompacted nature of the spoil, it could be susceptible to erosion by seasonally-active winds, which could give rise to a possible source of land-based Ni to the western English Channel aerosol (Scrivener, 1996). The significance of this source is discussed further in Section 5.1.2.

Aerosol concentrations of Cd, Cu, Fe, Mn and Pb were compared to those detected at sampling sites located in Cumbria and Oxfordshire. Higher concentrations were detected at these sites compared with those for the western English Channel, because of the prevalence of anthropogenic sources. There was little marine influence as indicated by the Na concentrations. Trace metal concentrations in the western Mediterranean aerosol were generally higher than those of the western English Channel aerosol. This will be discussed further in Chapter 6.

Table 5.1: geometric mean atmospheric trace metal concentrations (ng m^{-3}) over European regions.

Element	Western English Channel[a]	Irish Sea[b]	North Sea[c]	North Sea (Hemsby)[d]	Irish Sea[e]	Wraymires (Cumbria)[f]	Harwell (Oxfordshire)[f]	Western Mediterranean Sea[g]
Al	229	210	219	-	264	192	242	370
Cd	0.11	0.19	0.23	1.1	-	< 2	< 2	0.36
Co	0.12	0.14	0.19	-	-	0.2	0.3	-
Cu	2.34	4.57	4.4	-	2.4	17	19	6.2
Fe	115	159	230	216	226	242	285	320
Mn	7.94	4.42	9.1	10	6.5	10.9	14.9	11
Na	2570	1140	4100	-	-	992	818	-
Ni	15.1	3.71	2.5	2.7	-	4.6	6.6	2.8
Pb	1.20	15.1	20	34	31	68	124	58
Zn	20.9	25.3	26	41	15	59	99	41

[a]current study; [b]Fones, 1996; [c]Chester and Bradshaw, 1991; [d]Yaaqub *et al.*, 1991; [e]Murphy, 1985; [f]D.O.E., 1992; [g]Chester *et al.*, 1990.

The arithmetic and geometric means, range, arithmetic standard deviation and relative standard deviation of the aerosol trace metal concentrations, for the entire sampling period, are presented in Table 5.2. The presented relative standard deviations reveal that the concentrations for all elements under investigation vary considerably, and can be ranked in the following order : Cu (249 %) > Ni (246 %) > Na (223 %) > Cd (203 %) > Pb (196 %) > Co (185 %) > Zn (143 %) > Al (137 %) > Fe (125 %) > Mn (114 %). Large variations in aerosol trace metal concentrations have been previously reported at coastal locations (e.g. Fones, 1996; Bradshaw, 1992).

Figures 5.1 to 5.10 display the temporal variability in aerosol concentration temporal variation of the trace elements. The temporal trace metal aerosol concentrations clearly indicate pronounced seasonal variations. Generally all the elements were present at higher concentrations in the autumn-winter periods. The elements may, however, be further categorised into two groups:-

(i) Group 1 being defined as those elements (i.e. Cd, Fe, Mn, Pb, Zn) whose autumn-winter/spring-summer relative seasonal concentrations were enhanced over the whole sampling period;

(ii) Group 2 being classified as those elements (i.e. Al , Co, Cu, Na, Ni) whose autumn-winter / spring-summer relative seasonal concentrations were significantly enhanced during 1995/96 only.

The observed increase in trace metal concentrations during autumn/winter 1995 for Group 2 elements is illustrated by aluminium concentrations, which were generally <1000 ng m^{-3} throughout the sampling period, until autumn 1995, when the concentrations generally exceeded this threshold. Cadmium, Pb and Zn displayed concentration increases during autumn/winter 1994/1995 and autumn/winter 1995/1996. Such elements are likely to have been produced by high temperature anthropogenic processes with enhanced emissions of these elements during the winter periods. However, Pb and Zn displayed aerosol concentration increases (samples 23, 26, 28, 35 and 40) during the spring/summer 1995 period, which correspond with the temporal profiles of all elements (including the crustally derived elements, Al, Fe and Co) except for Cd and Na, which suggests a common terrestrial source, possibly from re-suspension of mineral waste and/or metal-rich soils. The effect of trace metal aerosol sources, wind direction and removal processes on the variability in trace metal concentrations will be discussed further in sections 5.1.1, 5.1.2 and 5.2.

Principal Components Analysis (PCA) is a method of multivariate data analysis and is suited to the analysis of large data sets, as it contributes to (a) an understanding of inter-relationships between

Table 5.2: atmospheric trace metal aerosol concentrations for the western English Channel (LOD = limit of detection).

Element	Arithmetic Mean (ng m^{-3})	Range (ng m^{-3})	Standard Deviation	RSD (%)	Geometric Mean (ng m^{-3})
Al	503	15.3 - 3500	688	137	229
Cd	0.60	Below LOD - 6.18	1.23	203	0.11
Co	0.35	Below LOD - 3.32	0.64	185	0.12
Cu	5.88	Below LOD - 89.2	14.6	249	2.34
Fe	222	Below LOD - 1100	278	125	115
Mn	15.4	0.67 - 92.3	17.6	114	7.94
Na	21 400	Below LOD - 278 000	47 600	223	2570
Ni	198	Below LOD - 2980	486	246	15.1
Pb	4.83	Below LOD - 44.2	9.49	196	1.20
Zn	48.7	4.98 - 413	69.5	143	20.9

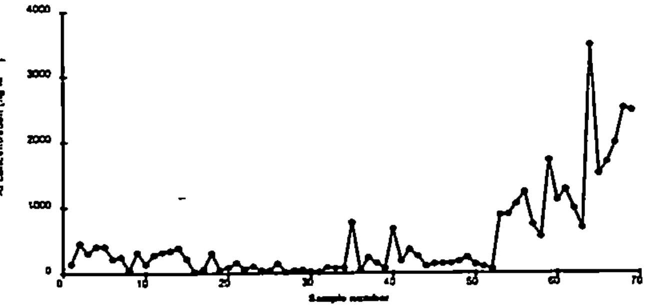


Figure 5.1: variation of Al concentration during the sampling period.

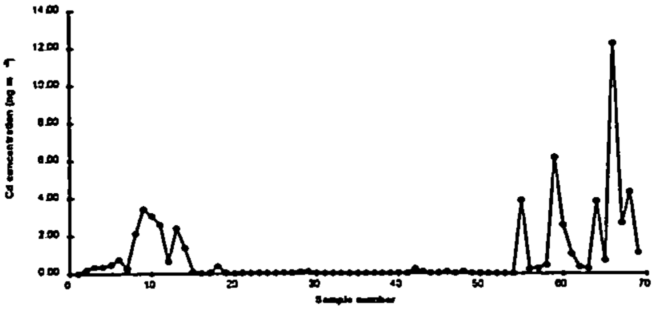


Figure 5.2: variation of Cd concentration during the sampling period.

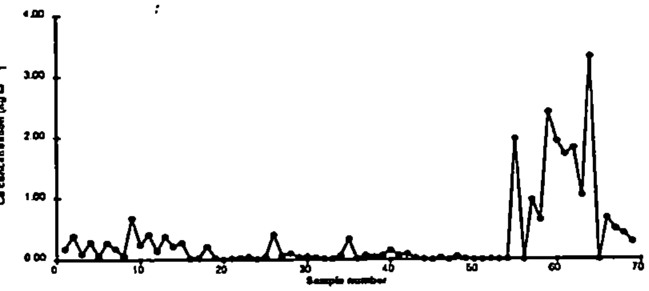


Figure 5.3: variation of Co concentration during the sampling period.

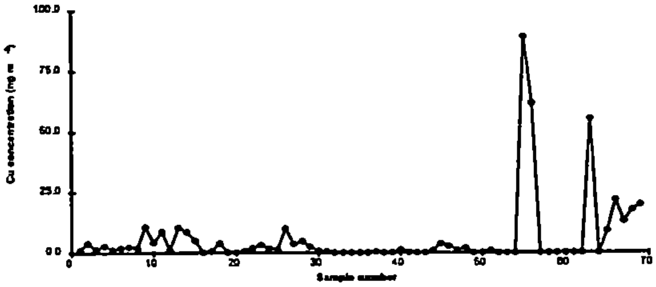


Figure 5.4: variation of Cu concentration during the sampling period.

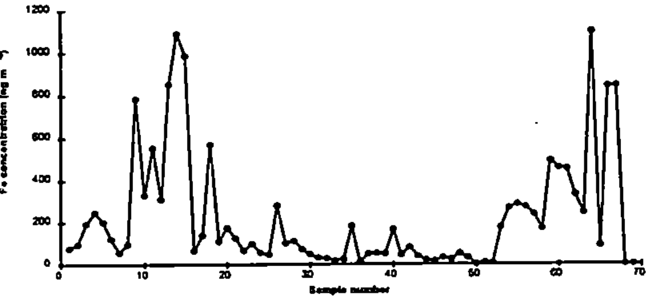


Figure 5.5: variation of Fe concentration during the sampling period.

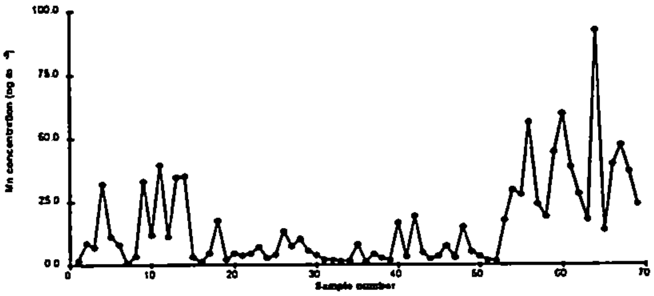


Figure 5.6: variation of Mn concentration during the sampling period.

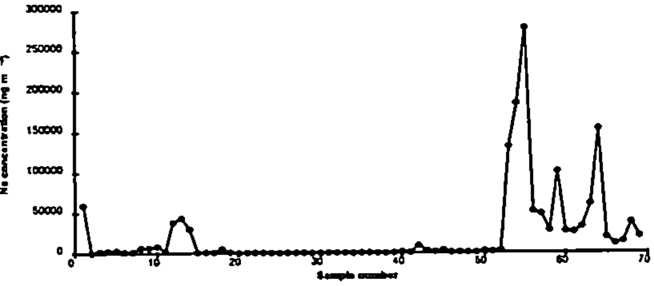


Figure 5.7: variation of Na concentration during the sampling period.

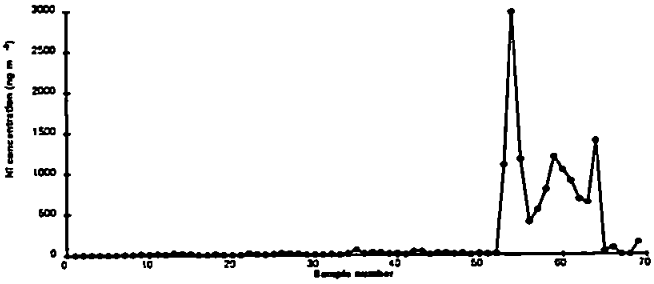


Figure 5.8: variation of Ni concentration during the sampling period.

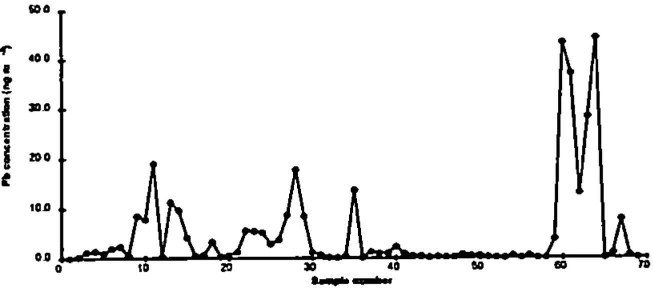


Figure 5.9: variation of Pb concentration during the sampling period.

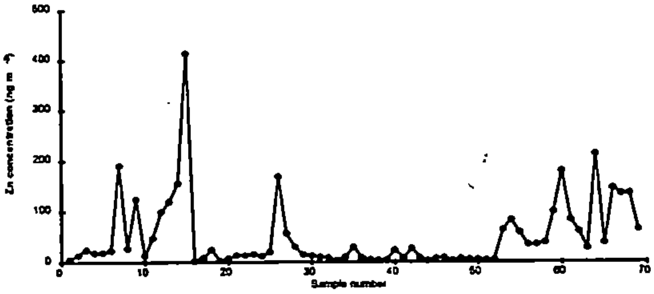
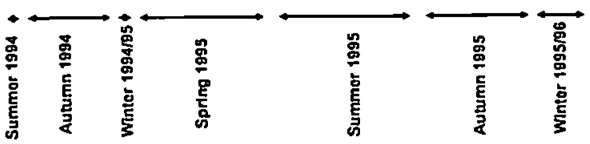
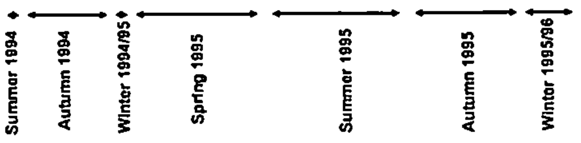


Figure 5.10: variation of Zn concentration during the sampling period.





elements in the aerosols (Bradshaw, 1992; Fones, 1996) and (b) source identification (e.g. Massart *et al.*, 1988; Schaug *et al.*, 1990). Akerjord and Christophersen (1996) have described the application of PCA to the identification of the end-members resulting from the mixing of air masses of different elemental composition. Data sets are reduced to a small number of representative vectors or Principal Components (PCs) which represent the entire variability in the data set. Each PC is comprised of a loading weight for each variable, i.e. the loading weight describes how much each variable has influenced that PC. PCs can be plotted against each other to produce scores plots, which display the relationships between objects. Usually, the two PCs explaining the highest percentage of the variation in the data set will be used to plot the scores of the objects. However, PCs can be used to assess the relationships between objects when influenced by a particular variable e.g. wind direction, by selecting at least one PC with a high loading weight for that particular variable. In the current study, the samples were variables, the elements were objects and the selected PCs explained the greatest percentage variation in the data set (Figures 5.11 and 5.12). The scores plot (Figure 5.13) revealed a cluster of elements with Ni, Zn, Fe, Al and Na located at increasing distances from the cluster; Na was separated from the main group of elements. This suggests that Ni, Zn, Fe, Al and Na display increasing temporal variability, while Cd, Co, Cu, Mn and Pb display relatively lower temporal variations. However it was apparent that PCA, using elemental aerosol concentrations, revealed very little regarding inter-elemental relationships and hence the factors influencing their geochemistries. Therefore PCA, as well as simple linear regression analysis is of limited use in analysis of elemental concentrations for the current data set.

5.1.1 Sources of trace metals to the western English Channel aerosol.

EF_{Crust} were calculated (Eqn 2.2) for all elements in the aerosol trace metal data set, using crustal ratios obtained from Taylor (1964). Aluminium was assumed to be predominantly of crustal origin and was used as the indicator element. The geometric mean EF_{Crust} obtained from the current study are compared with results from other regions in Table 5.3. The geometric mean EF_{Crust} for Cd (214) was the highest for any trace metal, observed in the western English Channel aerosol, although it was 2 to 20 times lower compared to other European coastal and rural sites. The geometric mean EF_{Crust} for Pb in the western English Channel aerosol was 10 to 100 lower than elsewhere (e.g. Rahn *et al.*, 1979), including the western Mediterranean Sea and the Celtic Sea. Since emissions of Pb to the European atmosphere have diminished (see section 5.1.1.1) this will have contributed to a decline in the aerosol EF_{Crust} in European aerosol populations. However, the western English Channel geometric mean EF_{Crust} for Ni was between 3 and 8 times higher than observed in any other region.

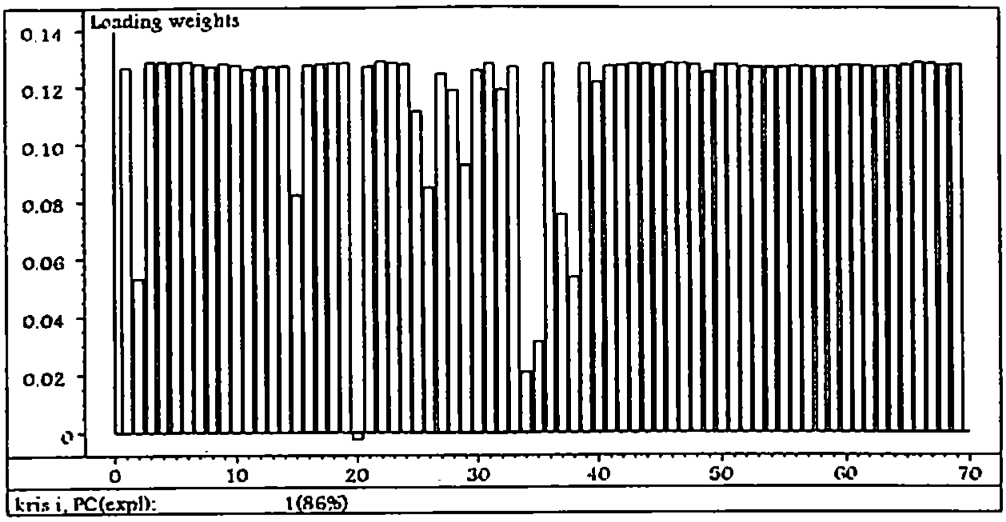


Figure 5.11: PC1 loading weights displaying dominance of almost all samples.

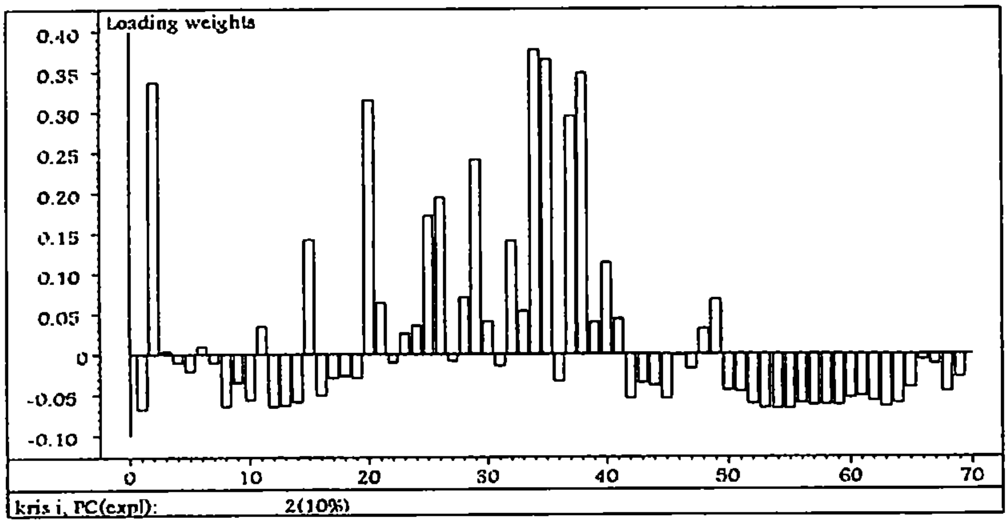


Figure 5.12: PC2 loading weights.

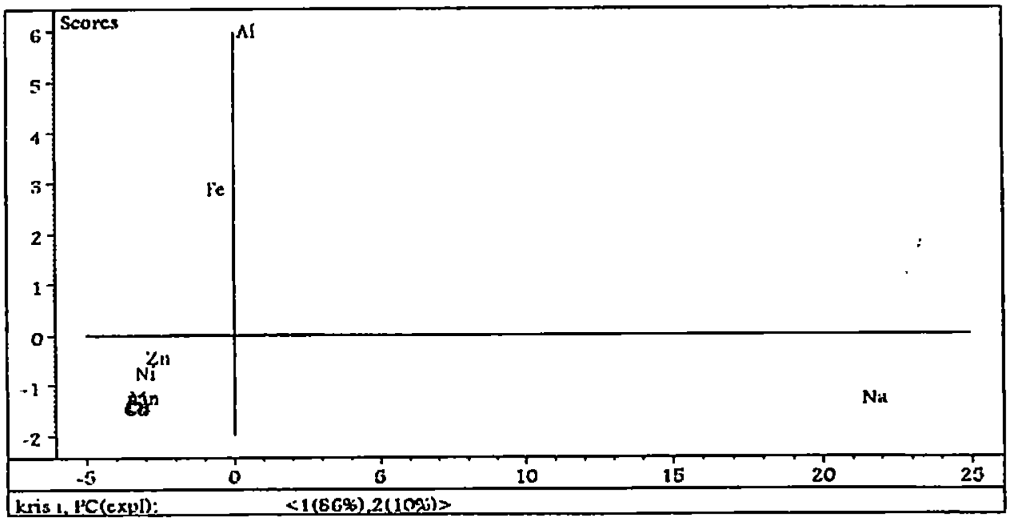


Figure 5.13: relationship of samples according to the variation of their concentration.

Table 5.3: trace metal geometric mean EF$_{Crust}$ values at other coastal/rural sites in Europe.

Element	Western English Channel[a]	Irish Sea[b]	North Sea[c]	North Sea[d] (Hemsby)*	North Sea[e] (Helgoland)	Irish Sea[f]	Wraymires[g] (Cumbria)	Harwell[g] (Oxfordshire)	Western Mediterranean Sea[h]
Cd	214	368	436	1436	2743	-	4286	3400	392
Co	2.09	2.1	2.7	-	3.5	-	3.2	3.8	-
Cu	19.5	33	30	-	27	14	132	117	24
Fe	0.79	1.0	1.5	1.0	1.4	1.3	1.8	1.7	1.2
Mn	3.02	1.8	3.5	3.2	2.9	2.1	4.7	5.1	2.6
Na	43.7	19	66	-	79	-	18	12	-
Ni	77.6	19	13	10	14	-	26	29	26
Pb	39.8	468	601	504	908	772	2331	3372	1024
Zn	107	141	139	118	184	67	361	481	128

([a]Current study; [b]Fones, 1996; [c]Chester and Bradshaw, 1991; d[c]Yaaqub *et al.*, 1991; [e]Kersten *et al.*, 1989; [f]Murphy, 1985; [g]D.O.E., 1992; [h]Chester *et al.*, 1990). * Yaaqub *et al.* geometric mean EF$_{Crust}$ values calculated using shale values using Fe as the indicator element.

This could be as a result of the re-suspension of local Ni-rich materials or enhanced sea salt generation and injection into the English Channel atmosphere (refer to section 5.1.2.).

The arithmetic and geometric means, range, arithmetic standard deviation and relative standard deviation for the aerosol data set are presented in Table 5.4. Aluminium, Co, Fe and Mn had geometric mean EF_{Crust} which were < 10 (Al having an EF_{Crust} value of 1). These values were consistent with those proposed by Rahn *et al.* (1979) for the world aerosol, and are termed the crustal or non-enriched elements (NEEs). The EF_{Crust} standard deviations for the NEEs were low despite the high variability observed for their aerosol concentrations (Table 5.2). This indicates that while atmospheric concentrations of such elements may vary considerably, their EF_{Crust} remain relatively constant. Copper, Na, Ni and Pb had geometric mean EF_{Crust} which were between 10 and 100 (20, 44, 78, and 40, respectively). This is indicative of elements comprised of a substantial portion of non-crustal material. This was expected for Ni, although, in the world aerosol, Cu and Pb have geometric mean EF_{Crust} > 100 and Na has a geometric mean EF_{Crust} < 10. Cadmium and Zn had geometric mean EF_{Crust} > 100 and are classified as anomalously enriched elements (AEEs).

For the AEEs, both aerosol concentrations and EF_{Crust} vary considerably, in contrast to the NEE's. The variability in the EF_{Crust} of AEE's is influenced by the degree to which crustal material mixes with anthropogenically derived material in the aerosol.

Figures 5.14 to 5.22 illustrate the temporal variability of the elemental EF_{Crust}. If the temporal variability of enriched Group 1 elements is considered (i.e. Cd, Pb and Zn), it can be clearly seen that greater enrichment occurs during the autumn/winter period 1994/95 with lower EF_{Crust} in the following autumn/winter period. Enrichment may be explained by the seasonally enhanced anthropogenic emissions of these elements from sources on the European continent. Such seasonal trends have also been detected by other workers (e.g. Fones, 1996; Bradshaw 1992). The lower enrichment of autumn/winter 1994/95 was probably as a result of greater proportion of injected crustal material within the aerosol population, as exemplified by the high Al concentrations in the aerosols during this period. Hence under such conditions the Group 1 EF_{Crust} for the enriched elements would be lowered. Common to the Group 1 enriched elements, Pb and Zn have very high EF_{Crust} in samples collected during May 95. This will be discussed further in section 5.1.2. All elements except Na and Ni displayed variable behaviour during spring 1995, which was largely absent from 4th July 1995 (sample 32) onwards; Na and Ni displayed similar EF_{Crust} peaks during autumn and early winter 1995.

Table 5.4: atmospheric trace metal aerosol EF_{Crust} for the western English Channel (LOD = limit of detection).

Element	Arithmetic Mean	Range	Standard Deviation	RSD (%)	Geometric Mean
Cd	882	Below LOD - 18 500	2630	298	214
Co	3.62	Below LOD - 22.9	4.51	125	2.09
Cu	28.3	Below LOD - 294	46.7	165	19.5
Fe	1.35	Below LOD - 7.69	1.58	117	0.79
Mn	4.44	0.23 - 33.4	4.99	112	3.02
Na	126	Below LOD - 1470	237	188	43.7
Ni	279	Below LOD - 3660	553	198	77.6
Pb	188	Below LOD - 2950	493	262	39.8
Zn	256	23.8 - 3500	522	204	107

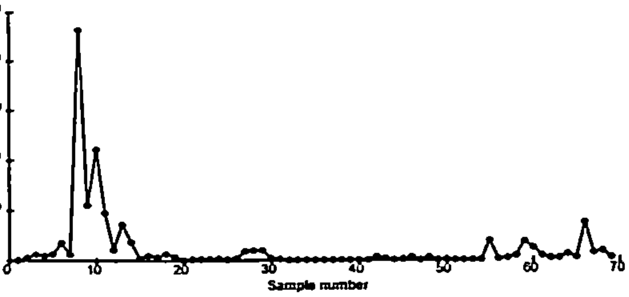


Figure 5.14: variation in Cd EF_{Crust}.

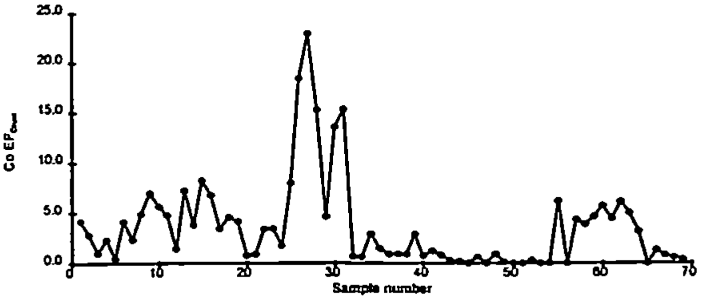


Figure 5.15: variation in Co EF_{Crust}.

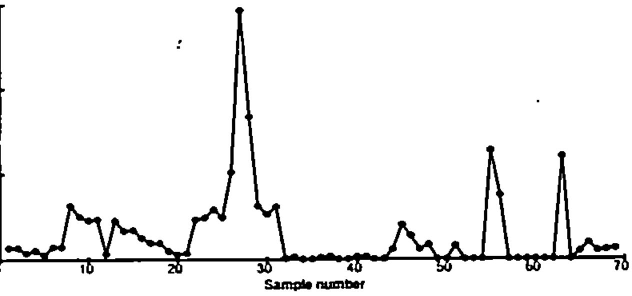


Figure 5.16: variation in Cu EF_{Crust}.

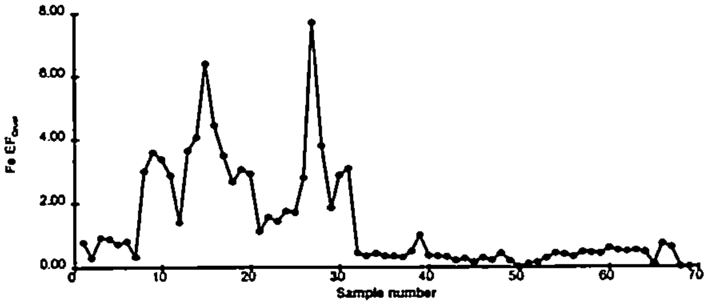


Figure 5.17: variation in Fe EF_{Crust}.

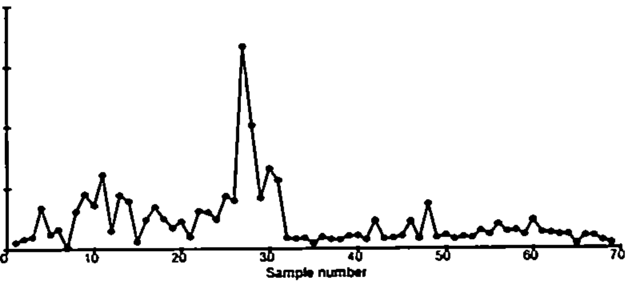


Figure 5.18: variation in Mn EF_{Crust}.

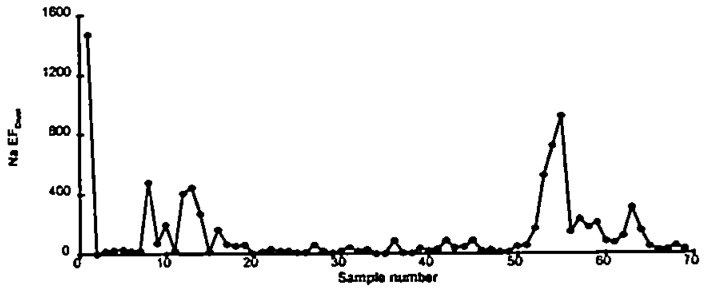


Figure 5.19: variation in Na EF_{Crust}.

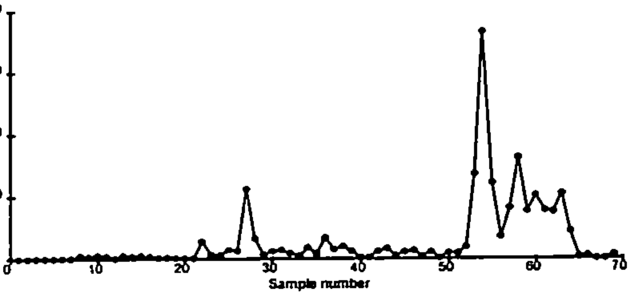


Figure 5.20: variation in Ni EF_{Crust}.

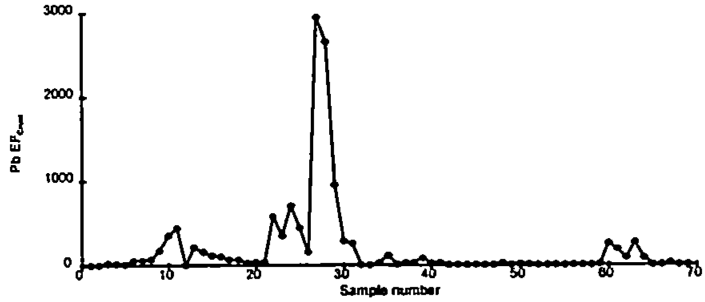
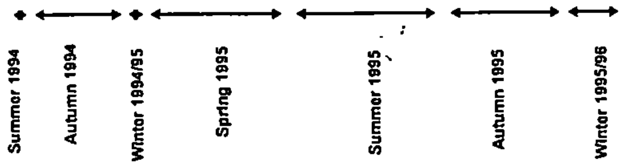


Figure 5.21: variation in Pb EF_{Crust}.



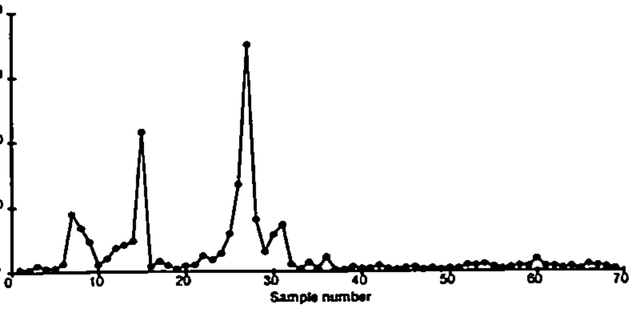
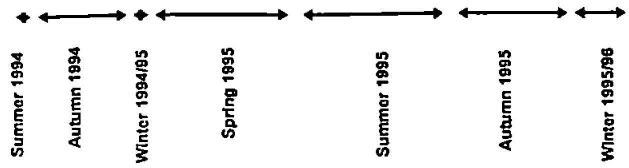


Figure 5.22: variation in Zn EF_{Crust}.



PCA analysis was carried out on elemental EF_{Crust} in a similar manner to that outlined in section 5.1. The scores of the two PCs describing the greatest portions of variation in the data set (Figures 5.23 and 5.24) were plotted to investigate the relationships between the elements in the western English Channel aerosol (Figure 5.25). Cobalt, Fe and Mn were tightly clustered indicating that, within the data set, their EF_{Crust} varied to similar extents, this being geochemically consistent due to their predominant crustal source with EF_{Crust} <10 The remaining elements can therefore be ranked, considering Figure 5.25, in order of decreasing crustal input: Cu > Pb > Na > Zn > Ni >> Cd. This is in agreement with the aerosol elemental EF_{Crust} trends depicted on Table 5.4. Therefore it is apparent that PCA may be useful for the identification and separation of elemental aerosol sources.

5.1.1.1 The application of Pb isotopic ratios to aerosol trace metal source attribution.

It was suggested in section 2.3.1.1 that Pb isotopic ratios may be used to evaluate sources of Pb in the aerosol population. Theoretically, the $^{206/207}$Pb isotopic ratio of an aerosol sample will be highest (about 1.20 to 1.24) when the EF_{Crust} is low, indicative of the greater presence of unmodified crustal material. In such material Pb is geologically younger than that used as a fuel additive, which has a Pb isotopic ratio of <1.10. This is due to the decay rates of ^{238}U and ^{235}U of which ^{206}Pb and ^{207}Pb are the respective daughter products. End member $^{206/207}$Pb isotopic ratios are also increasingly diluted at increasing distance from source. A comparison was made between the $^{206/207}$Pb isotopic ratios and the EF_{Crust} obtained from the western English Channel samples (Figure 5.26). A correlation coefficient of 0.05 was obtained indicating no statistical relationship. The samples were spread within $^{206/207}$Pb isotopic ratios of 1.08 and 1.16 which could encompass samples containing Pb of anthropogenic and natural origin.

The absence of a correlation between $^{206/207}$Pb isotopic ratio and EF_{Crust} suggests that the western English Channel aerosols are well mixed, with diffuse sources both anthropogenic and natural. This scenario was supported by lower Pb concentrations (Table 5.1) and the decline in geometric mean EF_{Crust} for Pb compared with other European sites (Table 5.3). Since vehicular emissions of Pb have been reduced by ~ 80 percent since 1975 (DOE, 1996), the mean $^{206/207}$Pb isotopic ratio of 1.11 may be due to a combination of natural background Pb and that from vehicular emissions.

The absence of a correlation between $^{206/207}$Pb isotopic ratio and EF_{Crust} may however be rationalised. Previously, Pb isotopic ratios have been used to attribute Pb sources in European aerosol populations

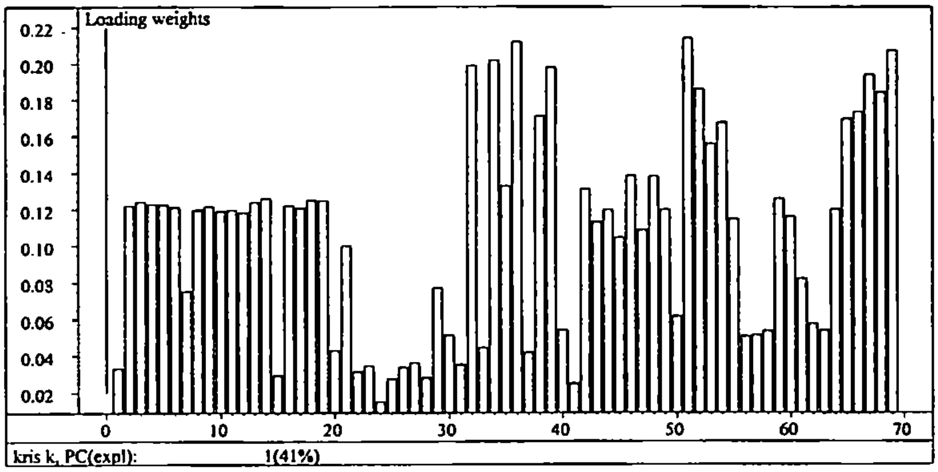


Figure 5.23: PC 1 loading weights.

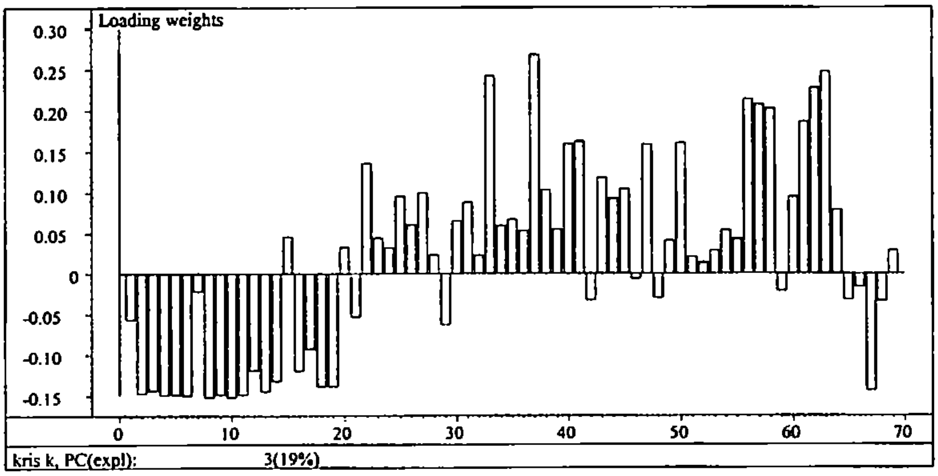


Figure 5.24: PC 3 loading weights.

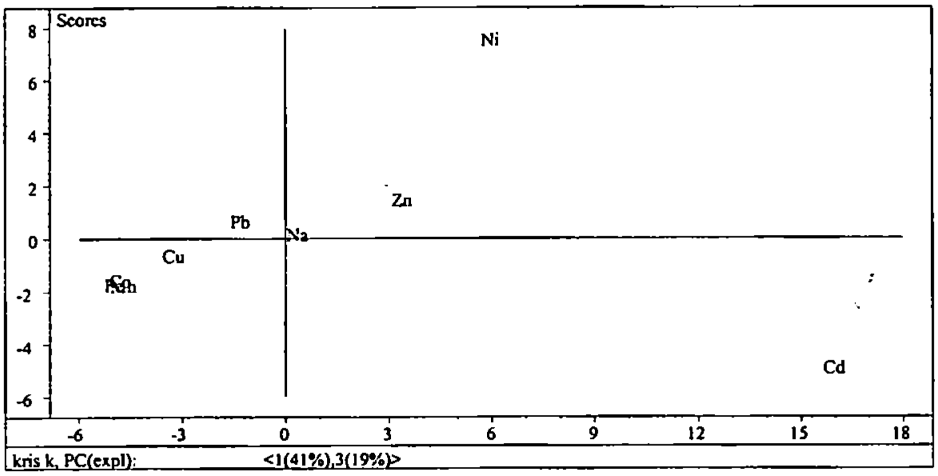


Figure 5.25: inter-elemental relationships revealed by PCA.

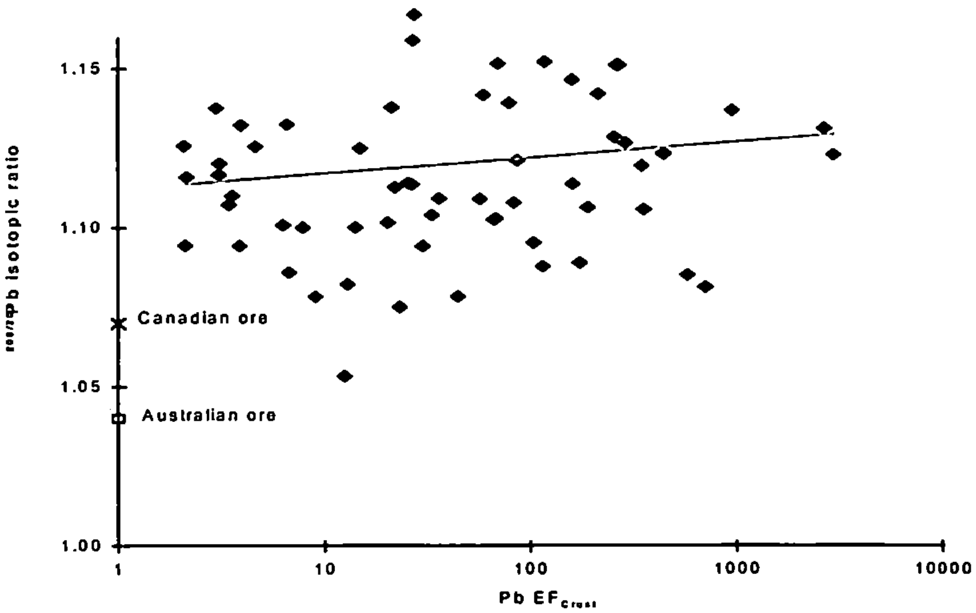


Figure 5.26: correlation of $^{208/207}$Pb isotopic ratio (x = 1.11; σ = 0.02; RSD = 2.07 percent) and EF$_{Crust}$ for the western English Channel aerosol, compared with the $^{208/207}$Pb isotopic ratios for two ores used in European fuels.

as (i) Pb was not derived from natural sources but was predominantly derived from western European anthropogenic emissions and (ii) naturally derived Pb and western European anthropogenically derived Pb (see for example Hopper *et al.*, 1991) isotopic ratios were significantly different. However now that Pb concentrations in the western European aerosol have diminished (see section 5.1), a higher proportion of Pb from anthropogenic sources is from emission from eastern Europe. Eastern European anthropogenically-derived Pb has an isotopic ratio similar to that of natural European background material. Therefore the current Pb isotopic ratio of the aerosol population will be dependent upon the relative proportions of the different anthropogenic signals (eastern and western European sources) as well as natural European background material. A significant relationship of Pb isotopic ratios with aerosol EF$_{Crust}$ is no longer a valid assumption. Enriched Pb in the aerosol populations may be derived from two anthropogenic sources each with different isotopic signals whereas in the past only one anthropogenic source dominated. Therefore a plot such as Figure 5.26 may yield high or low Pb isotopic ratios with enriched EF$_{Crust}$ depending upon the predominant source of the anthropogenic aerosol material.

5.1.2 Atmospheric transport of aerosol associated trace metals at the western English Channel site.

The daily variation in aerosol trace metal concentrations may be caused by (i) different air masses, which have different aerosol sources and (ii) removal processes during aerosol transport to the sampling site. The effect of air mass source on the trace metal aerosol geochemistry of the English

Channel atmosphere will be considered in this section. As discussed in section 4.1.3, the western English Channel is subject to a number of different air mass types dominated by Atlantic westerlies, although this dominance has been recently on the decline (Wu and Boyle, 1997). Westerly winds circulating over the Atlantic Ocean will have aerosols with a high sea salt concentration in the range 15 to 40 mg m^{-3} (Chester, 1990).

However, due to the relatively large area of land mass in the Northern Hemisphere, the troposphere has a high dust burden ($3.0 \pm 2 \times 10^{12}$ g), a large portion of which is derived from the Sahara Desert ($1.2 - 4.0 \times 10^{12}$ g). The Southern Hemisphere has a much lower dust burden ($1.0 \pm 2 \times 10^{12}$ g) due to less land surface area. The concentration of crustal material in the aerosol is likely to increase as the air mass moves over land (depending on the nature of the surface cover), since wind erosion is the primary method of crustal entrainment in the atmosphere. The concentration of anthropogenic trace metals is also likely to increase in relation to air mass exposure to industrial emissions.

Inspection of Table 5.5 shows that there are clear seasonal differences in the wind direction under which aerosol samples were collected (the wind direction for twelve samples could not be identified). It should also be noted that inter-annual variation is clear between the summer (June to August), autumn (September to November) and winter (December to February) periods (the spring period was not duplicated). A second important observation to note is that autumn 1995 was dominated by S/SW winds. Several episodes, with elevated wind velocities, were also observed during autumn 1995, primarily due to the aftermath of Hurricane Iris, which affected the western coast of the UK in September 1995. Wind speeds averaging 60 mph and gusting up 100 mph were recorded by local weather stations. Thus, strong winds could have caused re-suspension of local terrestrial material and augmented the production of sea salt particles; both processes contributing to high aerosol loads in the English Channel atmosphere.

The influence of the air mass on aerosol trace metal geochemistry was investigated initially by grouping each aerosol sample according to the predominant wind sector at the time of sampling. This approach has previously been adopted by a number of workers (e.g. Yaaqub *et al.*, 1991). Mean elemental concentrations were then calculated for each sector and plotted to attempt to identify the most influential wind direction for each trace metal (Table 5.6 and Figures 5.27 to 5.36). Group 1 (see section 5.1 for definition) enriched elements, Cd, Pb and Zn, display enhanced concentrations in the N to E wind sectors. These elements also display a repeatable seasonal enhancement (see section 5.1). The observed enhancement of these elements is likely to be due to long range transport of

Table 5.5: seasonal wind direction frequency over the aerosol sampling period.

Wind direction	Summer 1994	Autumn 1994	Winter 1994/95	Spring 1995	Summer 1995	Autumn 1995	Winter 1995/96
N	-	1	-	1	5	-	1
NNE	-	-	-	-	-	-	-
NE	-	-	-	-	3	-	-
ENE	-	-	-	-	1	-	-
E	-	2	-	-	-	-	1
ESE	-	4	1	6	2	-	-
SE	-	-	-	-	-	-	-
SSE	-	-	-	-	1	1	-
S	-	3	-	-	-	2	-
SSW	-	-	-	-	-	2	-
SW	-	-	-	-	-	2	-
WSW	-	-	-	-	-	-	-
W	2	-	-	-	-	2	-
WNW	-	-	-	-	3	-	-
NW	-	-	-	1	1	-	1
NNW	-	1	1	3	1	-	1

Table 5.6: mean elemental aerosol concentrations (ng m^{-3}) for each wind direction (± 22.5°).

Wind direction	Al	Cd	Co	Cu	Fe	Mn	Na	Ni	Pb	Zn
N	327 ± 480	0.14 ± 0.36	0.23 ± 0.60	1.15 ± 1.32	104 ± 151	9.01 ± 13.1	20 500 ± 45 900	256 ± 463	6.05 ± 12.7	24.7 ± 30.6
NE	267 ± 120	0.69 ± 1.15	0.13 ± 0.16	3.42 ± 4.90	268 ± 391	16.5 ± 13.8	14 000 ± 20 000	25.4 ± 16.9	4.25 ± 5.20	42.4 ± 51.6
E	217 ± 246	0.74 ± 0.93	0.16 ± 0.09	6.78 ± 2.65	602 ± 690	22.7 ± 17.7	14 900 ± 21 000	13.4 ± 0.75	13.6 ± 5.75	92.4 ± 88.7
SE	58.3	0.03	0.03	0.76	139	4.64	1050	1.02	0.59	7.79
S	371 ± 380	0.13 ± 0.22	0.20 ± 0.14	1.62 ± 2.09	267 ± 270	9.80 ± 7.13	1660 ± 2580	23.1 ± 32.0	5.95 ± 6.66	21.7 ± 8.88
SW	608 ± 640	1.95 ± 2.76	1.01 ± 1.37	44.6 ± 63.1	170 ± 165	15.2 ± 17.8	139 000 ±197 000	599 ± 807	0.40 ± 0.56	30.5 ± 38.9
W	520 ± 662	0.18 ± 0.21	0.93 ± 1.27	0.17 ± 0.24	220 ± 156	15.0 ± 18.4	16 700 ± 22 400	340 ± 479	6.60 ± 9.00	30.9 ± 41.1
NW	207 ± 243	0.01 ± 0.01	0.05 ± 0.06	0.90 ± 1.49	83.2 ± 76.4	6.44 ± 5.39	693 ± 748	9.40 ± 5.94	2.02 ± 3.29	17.6 ± 20.5

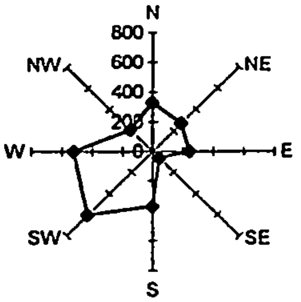


Figure 5.27: Al concentration vs. wind direction.

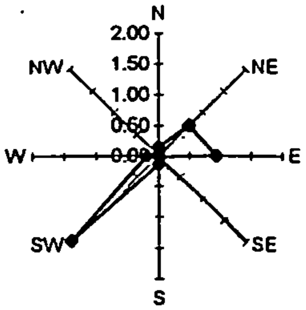


Figure 5.28: Cd concentration vs. wind direction.

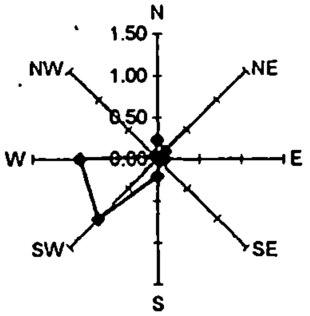


Figure 5.29: Co concentration vs. wind direction.

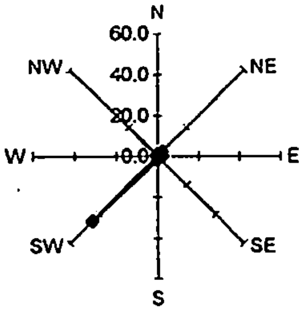


Figure 5.30: Cu concentration vs. wind direction.

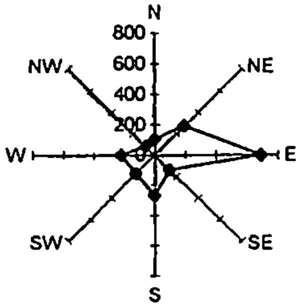


Figure 5.31: Fe concentration vs. wind direction.

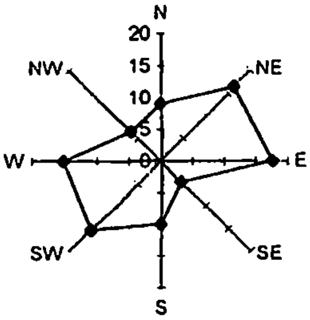


Figure 5.32: Mn concentration vs. wind direction.

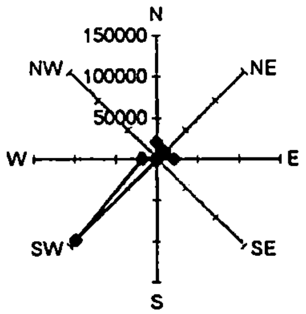


Figure 5.33: Na concentration vs. wind direction.

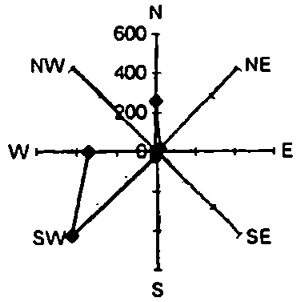


Figure 5.34: Ni concentration vs. wind direction.

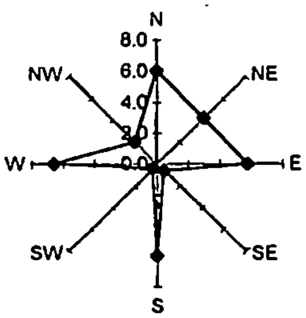


Figure 5.35: Pb concentration vs. wind direction.

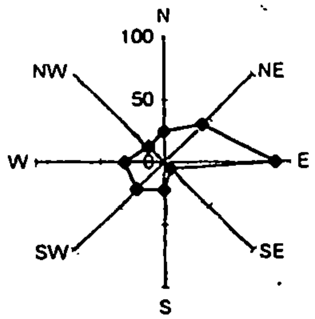


Figure 5.36: Zn concentration vs. wind direction.

anthropogenically derived aerosol material emitted from high temperature processes from a combination of western and eastern European sources, with additional contributions from UK sources. Enhanced aerosol concentrations for these elements have also been detected in European originated air masses sampled over the North Sea (e.g. Ottley and Harrison, 1993; Yaaqub *et al.*, 1991). The non-enriched Group 1 element, Fe, also indicated enhanced concentrations in the N-E wind sectors.

Group 2 elements, (Al, Co, Cu, Na & Ni) which exhibited relatively higher aerosol concentration in autumn/winter 1995/96 (see section 5.1), displayed enhanced concentrations in the SW wind sector (Pb also displayed high concentrations in the W and S wind sectors). For example the geometric mean concentrations for Al, Cu, Co and Ni were 608 ng m^{-3}, 45 ng m^{-3} , 1.01 ng m^{-3} and 599 ng m^{-3} respectively. These are higher than normally expected for a coastal sampling location (see Table 5.1). However it should be noted that only two samples were collected under the influence of the SW wind direction (collected 1st October & 17th November, 1995). However the enhanced concentrations detected for Group 2 elements, for example Ni, during autumn 1995 may be due to (i) the re-suspension of local terrestrial material whose input will be essentially controlled by the material availability and the ambient wind speeds and/or (ii) association with sea salt production enriched with trace metals originating from the sea surface microlayer. Intense injections of crustal and sea salt particles into the aerosol during these events is clearly indicated by the high Na and Al mean concentrations (139 µg m^{-3} and 608 ng m^{-3}). Contrasting concentrations of Ni were detected in the samples collected from the SW wind sector at different wind speeds (1st October = 13.7 m s^{-1}, Ni = 1170 ng m^{-3}; 17th November 5 m s^{-1}, Ni = 678 ng m^{-3}) further suggesting of a crustal and/or a marine source for this element. The local crustal material being more readily re-suspended in autumn 1995 due to a dry preceding spring and summer period (Meteorological Office, 1998).

The composition of soils to the west and south west of the western English Channel sampling site were considered as a source of aerosol elements. The Lizard Peninsular, in particular, represents a special case from the geochemical viewpoint, with deposits of serpentine. Soils deposited over serpentine rocks tend to have elevated concentrations of Co (upto 80 µg g^{-1}) and Ni (up to 160 µg g^{-1}), (Webb, 1978). The concentrations of other metals in soils from the Lizard are relatively low for example Mn (<600 µg g^{-1}), Pb (<28 µg g^{-1}) and Zn (~ 0 - 50 µg g^{-1}). Copper concentrations are relatively high up to 120 µg g^{-1} due to contamination of many areas by mining activities especially in west Cornwall (McGrath & Loveland, 1992). The concentrations of Fe are in the range 3 to 6 % and are concomitant with the general distribution of Fe concentrations throughout the region. The data gives the broad range of trace metal concentrations in soils for the region. It is not possible to delineate further what actual concentrations may exist either on the Lizard or at specific metal contaminated sites. Thus the data assembled above gives a general overview of the terrestrial sources which may contribute to trace metal concentrations in the English Channel aerosol. It would seem clear that the identification of Ni and Co as Group 2 elements may be related to a terrestrial source (i.e. serpentine on the Lizard) to the south west of the sampling site. In additional identification of Cu as a Group 2 element supports this hypothesis as it has relatively elevated concentrations in soils from west Cornwall. However Group 1 elements Mn, Pb and Zn have relatively low concentrations in soils from the SW of England. Thus, whether trace metals have either Group 1 or Group 2 behaviour, during south westerly winds, may be a function of their general abundance in the soils of the south west of England.

Further evaluation of the source was carried out using mean elemental EF_{Crust} for each wind direction (± 22.5^{o}) (see Table 5.7; Figures 5.37 to 5.45). All Group 1 trace metals had high EF_{Crust} for the E sector re-enforcing the argument of the long range transport anthropogenic aerosol. Bradshaw (1992) highlighted the anthropogenic influence on aerosol populations with a significantly higher EF_{Crust} for Cd, Pb and Zn in European air masses. This observation has also been noted for the Mediterranean Sea (e.g. Dulac *et al.*, 1987) and the Black Sea (Hacisalihoglu *et al.*, 1992). Copper, Na and Ni had high EF_{Crust} in SW air masses, which has been discussed earlier as being due to resuspended terrestrial material and/or associated with sea salt generation. To evaluate the potential contribution of the regional terrestrial material from the south west peninsular (i.e. the Lizard) the comparative EF_{Crust} of the precursor material was calculated using the global element: aluminium ratio from Taylor (1964) and that for the Lizard Peninsula precursor material using data presented in McGrath and Loveland, (1992). These values are presented on Table 5.7. Of the Group 2 elements considered (Co, Cu, and Ni), only Co has a similar EF_{Crust} (4.6) for the precursor crustal material and the element's corresponding aerosol EF_{Crust}. It is apparent or Ni the calculated EF_{Crust} (710) for the SW wind sector can not be explained entirely by the input of regional metal enriched crustal material, whose EF_{Crust} was calculated as being 3.5. An additional source is likely to make a contribution of Ni to the English Channel aerosol population. As maximum enrichment occurs in SW wind sectors and coincides with maximum concentrations of Na in the aerosol, it is possible that the Ni enrichment derives from the elements association with sea salt generation. This is further indicated by the significant relationship (defined by the Pearson's product moment correlation at the 1 percent level) between the EF_{Crust} values for Ni and Na (0.41) and their respective aerosol concentrations (0.80). It is possible that Ni might be concentrated within the sea surface microlayer via complexation with organic ligands. The

Table 5.7: mean elemental EF_{Crust} for each wind direction (± 22.5°).

Wind direction	Cd	Co	Cu	Fe	Mn	Na	Ni	Pb	Zn
N	95.0 ± 110	3.19 ± 5.19	27.9 ± 26.8	0.99 ± 1.06	3.99 ± 3.37	104 ± 170	362 ± 467	220 ± 281	200 ± 227
NE	852 ± 1360	2.91 ± 3.18	23.6 ± 27.2	1.40 ± 1.59	5.26 ± 3.00	146 ± 199	101 ± 51.9	143 ± 168	178 ± 164
E	1116 ± 494	9.52 ± 8.15	100 ± 95.2	3.92 ± 0.19	14.1 ± 8.82	140 ± 174	183 ± 205	1410 ± 1770	632 ± 235
SE	234	3.42	19.4	3.49	6.93	62.8	19.2	66.6	157
S	228 ± 264	6.51 ± 6.30	23.9 ± 26.6	1.96 ± 1.40	6.34 ± 6.25	24.7 ± 25.2	75.4 ± 48.3	157 ± 117	233 ± 288
SW	760 ± 1080	3.51 ± 3.73	63.3 ± 89.5	0.45 ± 0.07	1.88 ± 0.58	461 ± 647	710 ± 721	16.7 ± 23.6	43.6 ± 29.8
W	212 ± 104	5.11 ± 1.37	4.87 ± 6.88	1.78 ± 1.82	2.95 ± 0.69	87.0 ± 39.4	384 ± 522	56.4 ± 42.0	56.3 ± 21.2
NW	139 ± 289	4.56 ± 9.06	50.4 ± 119	1.93 ± 3.02	7.63 ± 12.7	22.5 ± 25.0	241 ± 436	509 ± 1200	639 ± 1400
Lizard	-	4.6	1.45	-	2.7	-	3.5	-	3.7

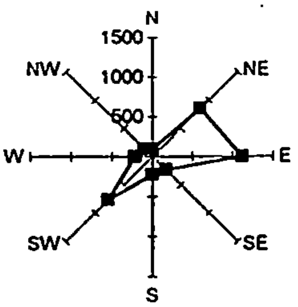


Figure 5.37: Cd EF_{Crust} vs wind direction.

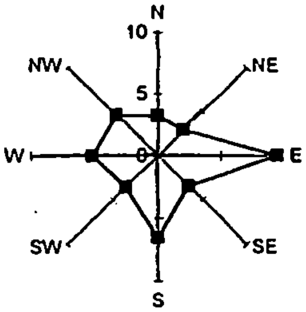


Figure 5.38: Co EF_{Crust} vs wind direction.

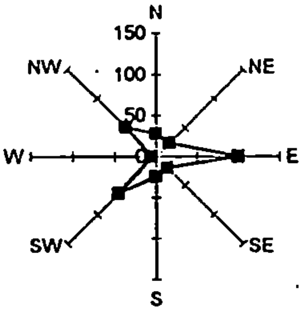


Figure 5.39: Cu EF_{Crust} vs wind direction.

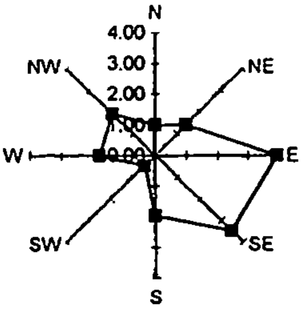


Figure 5.40: Fe EF_{Crust} vs wind direction.

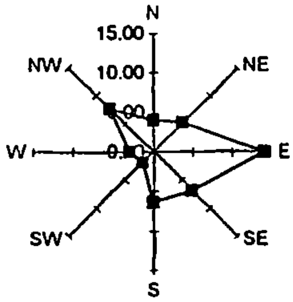


Figure 5.41: Mn EF_{Crust} vs wind direction.

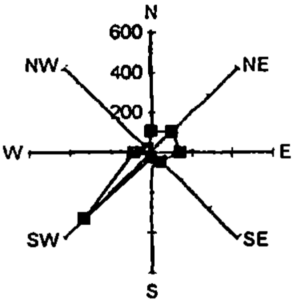


Figure 5.42: Na EF_{Crust} vs wind direction.

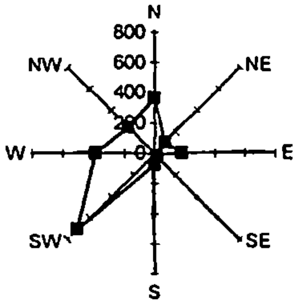


Figure 5.43: Ni EF_{Crust} vs wind direction.

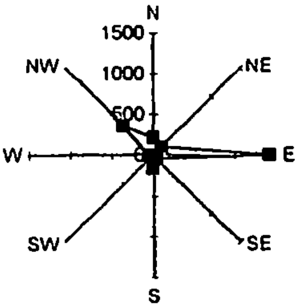


Figure 5.44: Pb EF_{Crust} vs wind direction.

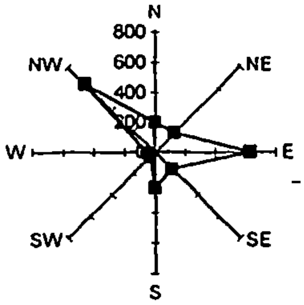


Figure 5.45: Zn EF_{Crust} vs wind direction.

organic complexation of Ni in sea water has previously been documented (Nimmo *et. al.*, (1989); van den Berg and Nimmo, 1987).

A number of aerosol samples (n = 28) which had been selected for further geochemical analysis (see section 5.1.4), underwent back trajectory analysis to obtain a more accurate assessment of the origin of the sampled air masses. The tracks of air masses prior to sampling were observed using three day back trajectory calculations (see Appendix 4, Figure 4.1). Of the selected samples, the most dominant wind directions were N (n = 8) and NW (n = 6), with 10 of the samples having a westerly influence and 18 of the samples having a northerly influence. To assess if the EF_{Crust} composition of a sample was influenced by wind direction, the EF_{Crust} for all of the investigated elements in the selected samples were modelled using PCA. The model also incorporated wind direction as a variable, which was converted into a bearing. The variation in the data set was explained by 10 PCs. PC 3 (10 %) and PC 4 (12 %) both contained high loading weights for wind direction, indicating that the variation in wind direction was the major influence on the PC (Figures 5.46 and 5.47). They could therefore be employed to assess the influence of wind direction on the EF_{Crust} composition of a sample (Figure 5.48a). Figure 5.48a shows that there does appear to be a relationship between wind direction and EF_{Crust} sample composition. However, some samples were not grouped together as might have been expected. For example, the two westerly derived samples, 27th March 1995 and 2nd May 1995, were not grouped together, possibly due to different air mass tracks prior to that calculated by the three day back trajectory. However, a simpler method of sample grouping revealed that samples could be grouped according to the primary wind direction (Figure 5.48b). Hence wind direction does appear to influence EF_{Crust} and therefore, the aerosol chemical composition.

5.1.3 Aerosol trace metal fluxes to the western English Channel.

The current study included the collection of gravitational dry deposition samples (see section 3.5). This allowed the calculation of trace metal settling velocities which were particular to the western English Channel, and therefore the calculation of more accurate dry deposition fluxes.

5.1.3.1 Dry deposition fluxes derived from western English Channel gravitational dry deposition samples.

Gravitational dry deposition samples were collected between February and July 1995 (n = 15). Table 5.8 displays the arithmetic mean, range, standard deviation, relative standard deviation and geometric mean for each trace metal. Sodium had the highest arithmetic (and geometric) mean, due to the close proximity of the sampling site to the coast, and hence indicating that the site was strongly influenced

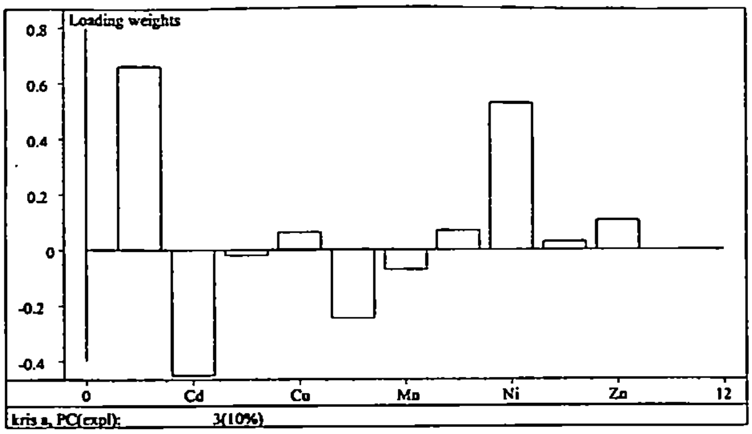


Figure 5.46: PC 3 loading weights displaying dominance of wind (Variable 1).

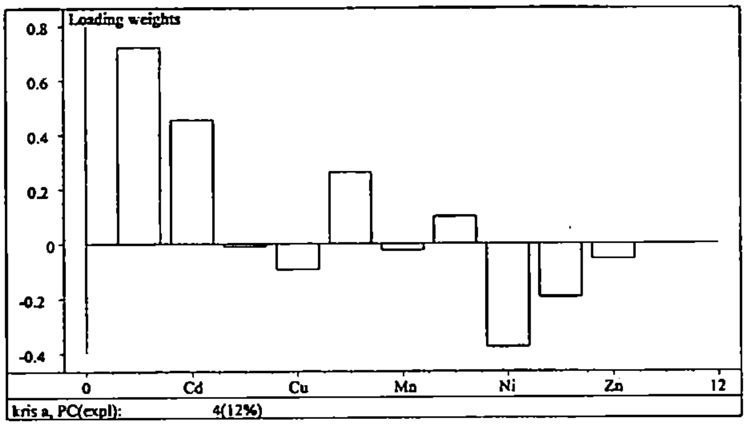


Figure 5.47: PC 4 loading weights displaying dominance of wind.

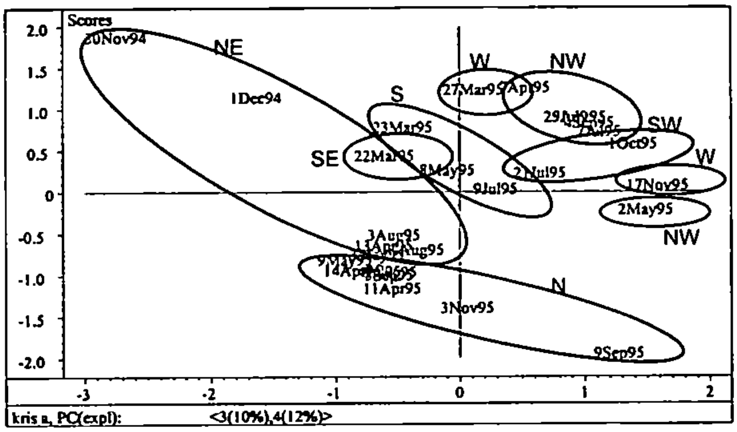


Figure 5.48a: relationship of samples according to wind direction.

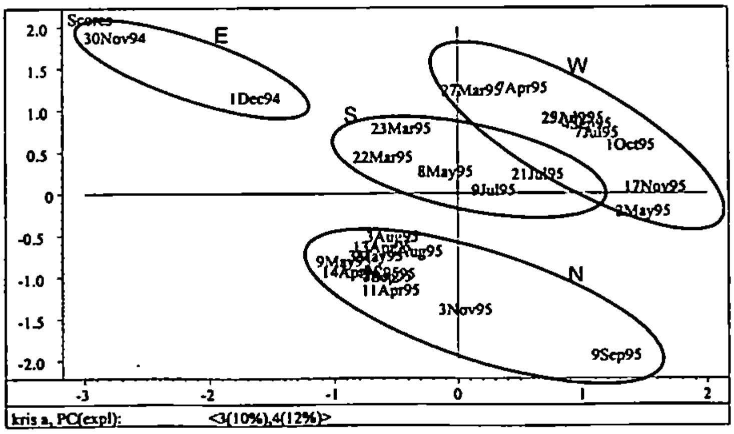


Figure 5.48b: simplified relationship of samples according to wind direction.

Table 5.8: trace metal arithmetic means, ranges, standard deviations, relative standard deviations and geometric means derived from western English Channel gravitational dry deposition samples (ng cm^{-2} yr^{-1}) (LOD = limit of detection).

Element	Arithmetic Mean	Range	Standard Deviation	RSD %	Geometric Mean
Al	3970	49.2 - 15 000	4120	104	1620
Cd	0.05	Below LOD - 0.39	0.10	179	0.03
Co	0.94	Below LOD - 2.93	0.93	99.0	0.74
Cu	23.8	0.60 - 117	35.8	151	9.55
Fe	281	34.6 - 797	258	92.0	182
Mn	110	0.46 - 303	115	104	35.5
Na	16 000	3700 - 59 600	13 000	81.0	12 900
Ni	22.2	Below LOD - 77.5	26.4	119	8.51
Pb	2.60	0.08 - 22.6	5.67	218	0.91
Zn	58.3	3.52 - 196	57.8	99.0	31.6

by marine aerosols. Aluminium provided the second highest arithmetic (and geometric) mean, with the remaining elemental concentration ranked in the order: Fe > Mn > Zn > Cu > Ni > Pb > Co > Cd. The arithmetic (and geometric) mean of Al was 14 times larger than that of Fe. Explanations for this might include (i) preferential Fe washout during aerosol transport prior to collection compared to that of Al, thus reducing the Fe loading in the aerosol, or (ii) the collection of Al containing, coarse particles, which are more susceptible to gravitational deposition due to their size and weight (Chester, 1990). Investigation of the geometric mean EF_{Crust} values (Table 5.9) revealed that all of the aerosol associated trace metals, with the exception of Na and Zn, have values < 10, indicative of crustal origin. This suggests that the particle population had a greater proportion of coarse particles having crustal and marine origins, (as indicated by the high arithmetic (and geometric) Al and Na fluxes).

5.1.3.2 Comparison of settling velocities with literature values.

The settling velocities derived from western English Channel gravitational dry deposition samples were compared with settling velocities obtained from the literature (Table 5.10). The western English Channel settling velocities for Co, Cu, Mn and Na are close to those reported in literature; the settling velocities of Cd, Fe, Ni, Pb and Zn were much lower than previously reported, indicating elemental associations with finer particles. Since Cd, Pb and Zn (Group 1 elements) are assumed to originate from long range transport from continental Europe, they would more likely be associated with "permanently suspended" aerosols. Such particles are less susceptible to deposition and have lower settling velocities. The largest settling velocities were observed for Al and Na.

The settling velocities for Al and Na are consistent with those quoted in the literature. This could be an sampling artefact, as this type of sampling results in the preferential collection of coarse particles (i.e. those of crustal and marine origin) which are more susceptible to deposition. Thus, the data could be biased towards the dominant elements within those particles (i.e. Al and Na). It should also be noted that settling velocities are affected by factors such as: (i) variations in wind speed, (ii) transfer velocities from smooth to broken surfaces, and (iii) variations in the relative humidity (Arimoto and Duce, 1986). Therefore, this data is only representative of the elemental settling velocities at thislocation and the time of sample collection. The means of the western English Channel settling velocities were therefore applied to the trace metal geometric means of the western English Channel aerosol samples in order to accurately assess the dry deposition flux.

Table 5.9: trace metal EF$_{Crust}$ arithmetic means, ranges, standard deviations, relative standard deviations and geometric means derived from the western English Channel gravitational dry deposition samples (units in ng cm^{2} yr^{-1}) (LOD = limit of detection).

Element	Arithmetic Mean	Range	Standard Deviation	RDS %	Geometric Mean
Cd	156	Below LOD - 2010	516	332	6.92
Co	1.15	Below LOD - 6.60	1.60	139	0.93
Cu	35.6	0.71 - 169	65.5	184	8.91
Fe	0.84	0.01 - 3.95	1.39	165	0.17
Mn	2.59	0.15 - 6.75	1.76	68.0	1.91
Na	256	1.69 - 617	552	216	28.2
Ni	9.91	Below LOD - 36.1	11.1	112	6.03
Pb	31.9	0.52 - 293	75.1	235	3.72
Zn	166	0.90 - 403	384	232	22.9

Table 5.10: comparison of the experimentally derived western English Channel settling velocities with those obtained from literature (in cm s^{-1}).

Element	English Channel[a]	North Sea[b]	India[c]	S. Holland[d]	Gulf of Lions[e]	W. Atlantic[f]
Al	1.08	0.46	-	-	-	-
Cd	0.04	0.38	-	0.36	-	-
Co	0.38	-	-	0.43	0.85	-
Cu	0.44	0.70	-	0.29	-	-
Fe	0.08	0.45	-	-	-	-
Mn	0.69	-	-	0.41	-	0.60
Na	0.94	1.52	0.91	-	-	-
Ni	0.07	-	-	0.52	-	0.60
Pb	0.02	0.17	-	0.21	-	-
Zn	0.09	0.52	-	0.24	-	-

[a]Current study; [b]Ottley and Harrison, 1993; [c]Prakasa Rao *et al.*, 1992; [d]van Daalen, 1991; [e]Guieu *et al.*, 1990; [f]Jickells *et al.*, 1985.

5.1.3.3 Western English Channel trace metal dry deposition fluxes.

Trace metals can be ranked in order of decreasing dry deposition flux as follows: Na > Al > Fe > Mn > Zn > Ni > Cu > Co > Pb > Cd (Table 5.11). As may be expected, those elements associated with larger particles (e.g. Na and Al) had the highest fluxes, whereas the smaller values were associated with those elements generally associated with smaller particles (e.g. Pb and Cd); Co is, perhaps, an exception to this rule.

The western English Channel flux for Na is comparable with that of the Irish Sea (Fones, 1996), being only 1.40 times larger than the Irish Sea flux (Table 5.11). However, the western English Channel flux for Al is more than double that of the Irish Sea flux (2.6 times larger) although the western English Channel geometric mean Al aerosol concentration was only 1.09 times larger than that for the Irish Sea. It was similar to dry Al fluxes observed over the western Mediterranean Sea. The greater Al flux calculated for the western English Channel was due to the application of a more appropriate settling velocity. The dry deposition fluxes of Cd, Co, Cu, Fe and Zn were smaller than those reported for the Irish Sea by 15, 2.6, 3.1, 7.6, 2.1 and 7.2 times respectively. A comparison of their geometric mean aerosol concentrations revealed that the western English Channel aerosol concentrations for Cd, Co, Fe and Zn were similar to those for the Irish Sea aerosol; Cu was lower by a factor of two and Ni was

Table 5.11: western English Channel trace metal dry deposition fluxes compared with other European regions (ng cm^{-2} yr^{-1}).

Element	English Channel[a]	Irish Sea[b]	North Sea[c]	W. Mediterranean Sea[d]	W. Mediterranean Sea[e]	W. Mediterranean Sea[f]	North Atlantic Westerlies[g]	North Sea[h]
Al	7830	3043	2854	-	9379	5000	-	30 000
Cd	0.15	2.27	14.9	-	4.9	13	-	43
Co	1.45	3.75	-	3.0	1.8	3.5	-	39
Cu	32.1	100	152	13	89.5	96	-	1300
Fe	296	2253	2608	8220	-	5100	-	25 500
Mn	172	77.9	-	145	156	-	-	920
Na	76 200	54 583	182 183	-	-	-	-	-
Ni	33.0	70.1	-	10	24	-	-	260
Pb	0.86	80.9	156	29	141	1050	170	2650
Zn	57.5	414	1221	-	-	1080	-	8950

[a] Current study; [b] Fones, 1996; [c] Ottley and Harrison, 1993; [d] Guieu *et al.*, 1991; [e] Chester *et al.*, 1990; [f] Arnold *et al.*, 1982; [g] Settle and Patterson, 1982; [h] Cambrey *et al.*, 1975.

four times larger. They were also lower than those reported elsewhere for European coastal zones. The western English Channel dry deposition flux for Pb was about ninety times smaller than that of the Irish Sea, while the western English Channel aerosol concentration was thirteen times lower than the Irish Sea concentration. Lead dry flux is also significantly lower than reported over other European regions (~ 2 to 3 orders of magnitude), which can be attributed to the settling velocities (dominated by fine particles) used for the western English Channel flux calculations.

5.1.4 Potential marine biogeochemistry of aerosol trace metals.

The marine biogeochemistry or 'potential environmental mobility' (PEM) (Chester *et al.*, 1994) of the western English Channel aerosol associated trace metals was investigated using a three stage sequential leach (see section 3.3.8) and model sea water solubility experiments (see section 3.3.9). The assessment of the trace metal aerosol solid state speciation may also indicate the predominant elemental sources to the sampled aerosol population. Chester *et al.*, (1986) clearly highlighted the difference in solid state speciation of the volatile elements Cd, Pb and Zn according to the predominant source to the aerosol population. In Liverpool urban aerosol the speciation of these elements was dominated by exchangeable associations whereas in Saharan crustal material the dominant speciation was the residual fractions.

5.1.4.1 Solid state speciation of aerosol associated trace metals (Al, Cd, Fe, Mn, Pb).

A three stage sequential leach (see section 3.3.8) was applied to 15 selected samples, representing the entire data set with respect to wind direction to assess the aerosol trace metal solid state speciation. This approach allows the estimation of trace metal sea water solubility arising from dry deposition (Chester *et al.*, 1994). Tables 5.12, 5.13 and 5.14, and Figure 5.49 display the proportion of trace metal in each of the three stages (1. easily exchangeable; 2. carbonate/oxide; 3. residual) Figure 5.49 and Table 5.14 clearly show that greater than 90 percent of Al and Fe were associated with stage 3 (i.e. the residual fraction) which is indicative of a predominant crustal origin. The degree to which Al is associated with the residual fraction (i.e. 95 percent) is comparable to those quoted in the literature for Urban/Saharan aerosol (e.g. Chester *et al.*, 1989) and for the North Sea aerosol (e.g. Bradshaw, 1992) (Table 5.15). Manganese did not display the same behaviour despite its crustal origin (see section 5.1.1). However, Chester (1990) states that the solubility of Mn appears to be independent of its source, and therefore does not necessarily display NEE behaviour, i.e. predominant residual phase associations. The proportion of Cd in stage 1 (82 %), which represents the easily exchangeable association is indicative of its anthropogenic origin, while this was not wholly true for

Table 5.12: western English Channel sequential leach stage 1 % trace metal solubility (LOD = limit of detection).

Element	Arithmetic Mean	Range	Standard Deviation	RSD %	Geometric Mean
Al	0.44	0.01 - 1.21	0.385	86.7	0.24
Cd	82.0	Below LOD - 100	26.7	32.6	63.1
Fe	Below LOD	-	-	-	Below LOD
Mn	69.4	46.3 - 98.7	15.4	22.1	67.6
Pb	54.5	17.9 - 95.2	31.2	57.1	50.1

Table 5.13: western English Channel sequential leach stage 2 % trace metal solubility (LOD = limit of detection).

Element	Arithmetic Mean	Range	Standard Deviation	RSD %	Geometric Mean
Al	4.00	0.50 - 30.1	7.80	192	1.71
Cd	11.0	Below LOD - 53.6	14.7	134	5.00
Fe	3.31	Below LOD - 17.8	5.82	177	3.21
Mn	15.5	0.61 - 27.8	9.62	61.7	11.0
Pb	19.4	1.82 - 60.7	15.8	81.6	12.6

Table 5.14: western English Channel sequential leach stage 3 % trace metal solubility (LOD = limit of detection).

Element	Arithmetic Mean	Range	Standard Deviation	RSD %	Geometric Mean
Al	95.5	69.8 - 99.2	7.63	8.21	95.2
Cd	0.30	Below LOD - 2.12	0.71	217	0.98
Fe	96.7	82.2 - 100	5.81	6.00	95.5
Mn	15.0	0.6 - 27.5	8.42	55.8	11.6
Pb	26.0	2.96 - 62.7	21.2	81.5	15.9

Table 5.15: comparison of the solid state speciation of aerosol populations (percent) (1 = easily exchangeable; 2 = oxide/carbonate association; 3 = residual).

Element	Western English Channel[a]			Liverpool, UK[b]			North Sea			North Sea			Sahara[b]		
							(UK end-member)[c]			(European end-member)[c]					
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Al	0.44	4.00	95.5	5.6	12.1	82.3	4.8	9.4	85.8	4.3	14.2	92.1	0.05	14.4	85.6
Cd	82.0	11.0	0.30	-	-	-	67.3	17.6	15.1	59.6	34.1	6.3	-	-	-
Fe	-	3.31	96.7	9.9	31.9	58.2	2.3	10.4	87.3	3.1	17.7	79.2	0.03	9.5	90.5
Mn	69.4	15.5	15.0	44.2	22.7	33.1	49.0	6.7	44.3	57.2	4.3	38.5	22.8	34.2	43
Pb	54.5	19.4	26.0	81.5	11.1	7.4	76.2	14.3	9.5	70.7	22.9	6.4	5.7	28.8	65.5

[a]Current study; [b]Chester *et al.*, 1989; [c]Bradshaw, 1992.

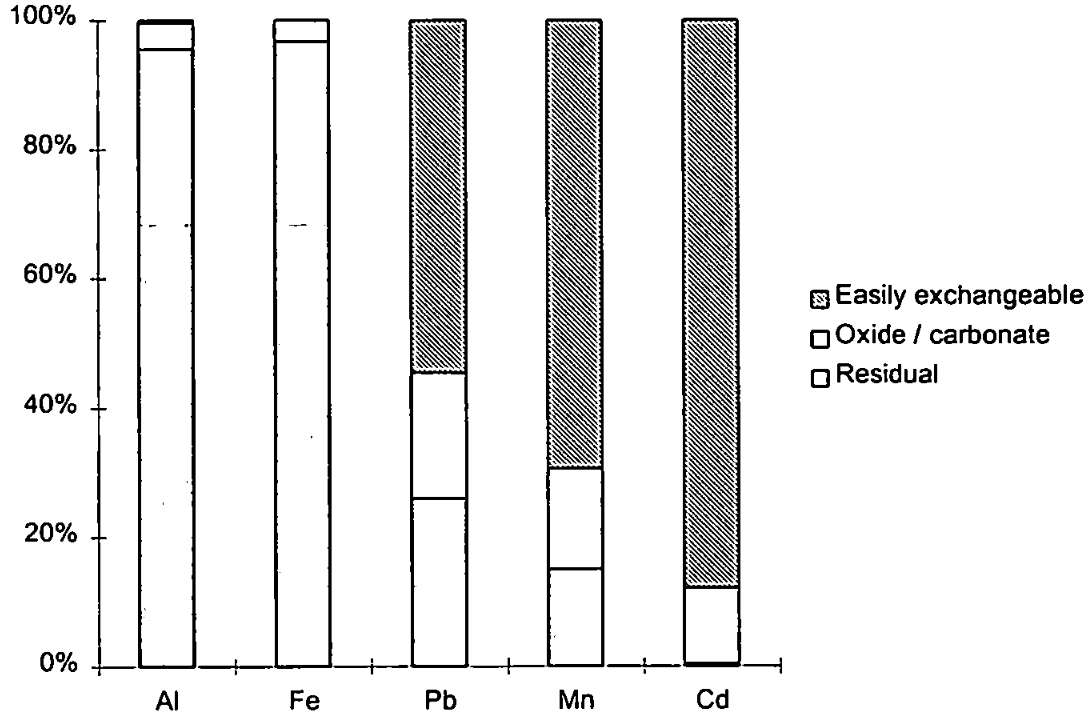


Figure 5.49: mean solid state speciation of trace metals in western English Channel aerosol particles (n = 15).

Pb. Although the greater proportion of Pb was found in stage 1 of the leach (55 %) the proportion was lower than observed for other urban dominated aerosols (typically ~ 80 %) but higher than that observed in stage 1 of crustally dominated aerosols, such as Saharan dusts (~ 6 %) (Chester *et al.*, 1989; 1993b). This is indicative of a well mixed aerosol which has undergone only minor anthropogenic modification, as suggested by the comparison of $^{206/207}$Pb with Pb EF$_{Crust}$ (see section 5.1.1.2). From these studies, it may be stated that Al and Fe will exhibit low percentage solubilities in sea water, while > 50 % of Cd, Mn and Pb will be soluble.

The results from selected samples were subjected to PCA to assess if wind direction influenced the proportions of trace metals located in the easily exchangeable (stage 1) leach. The PC 2 (Figure 5.50) and PC 4 (Figure 5.51) were typified by high variance due to wind direction, and each element significantly contributed to the variance in at least one of the PCs. The scores plot obtained from PC 2 vs PC 4 revealed a separation of samples according to air mass direction (Figure 5.52a) and was further simplified by grouping the samples according to the primary wind directions (Figure 5.52b). Thus, wind direction, and therefore source, does appear to influence the easily exchangeable proportion of trace metals in aerosols over the western English Channel.

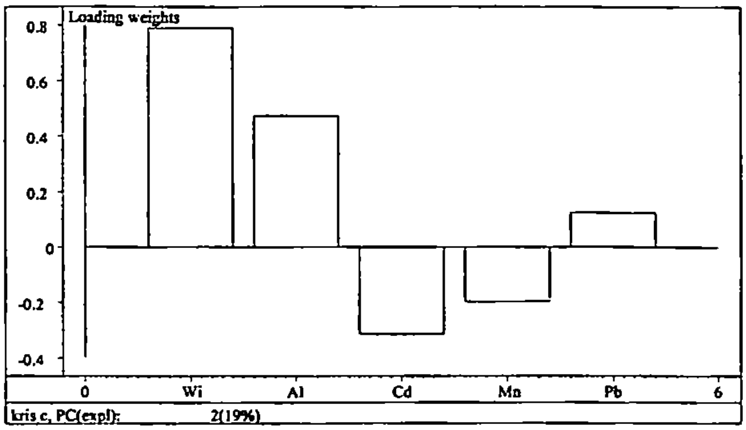


Figure 5.50: PC 2 loading weights displaying dominance of wind direction.

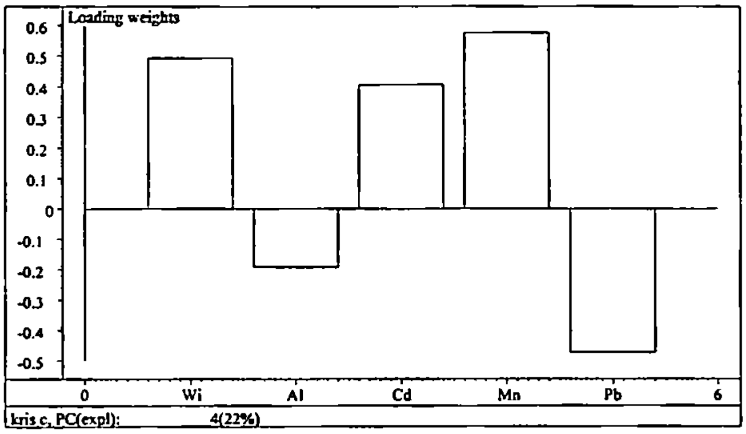


Figure 5.51: PC 4 loading weights displaying dominance of wind, Cd and Mn.

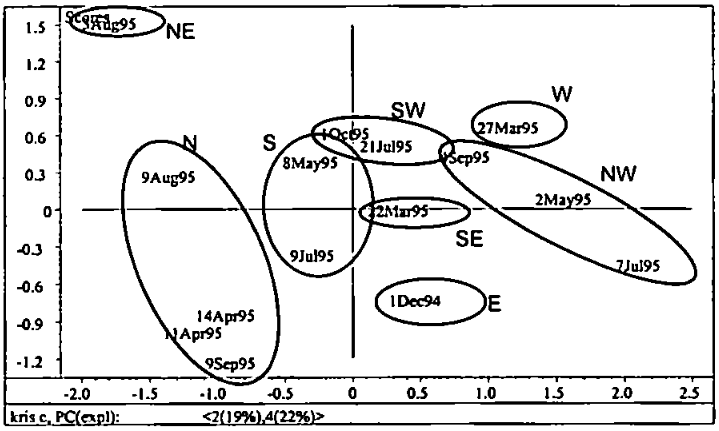


Figure 5.52a: relationship of samples according to wind direction.

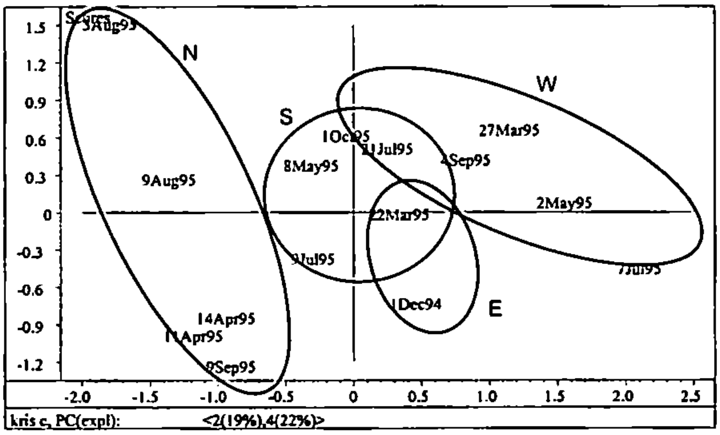


Figure 5.52b: simplified relationship of samples according to wind.

5.1.4.2 Solubility of aerosol associated trace metals in sea water.

Atmospheric aerosols may be an important source of trace metals to coastal waters and it is the extent to which aerosols dissolve in sea water which is important with regard to the potential impact that the metal input may have on biological systems. The sea water solubility of aerosol associated trace metals can determine their subsequent involvement in marine biogeochemical cycles, which will influence their spatial and temporal concentrations and ultimately their residence times in sea water. Arithmetic and geometric means, range, standard deviation and relative standard deviation for percentage aerosol trace metal sea water for selected samples (n = 13) are displayed in Table 5.16. Aluminium had a low solubility in sea water (2 %) while about 40 % of aerosol Pb solubilised. This was slightly lower than observed in stage 1 of the sequential leach and can be attributed to the relative strength of the stage 1 leach, ammonium acetate, as a leaching agent. Chester *et al.*, (1994) has also indicated that the exchangeable trace metal aerosol phase might, for some trace elements, represent an over estimation for its sea water solubility (see section 3.3.9). The mean percentage solubility of Ni was similar to that reported in literature (Chester, 1990), although those determined for Co and Cu were higher than previously reported (Table 5.17). They were also higher than those reported by Fones (1996) for the Irish Sea.

Table 5.17: comparison of aerosol associated trace metal solubility in sea water (percent).

Element	Western English Channel[a]	Irish Sea[b]	Southern California[c]	Baja, California[c]
Al	1.90	-	0.56	0.09
Co	67.6	32	25	20
Cu	83.9	58	28	14.5
Ni	50.3	38	47	28
Pb	48.8	37	39	13

[a]Current study; [b]Fones, 1996; [c]Hodge *et al.*, 1978.

The results of selected samples were subjected PCA to assess the influence of wind direction on percentage trace metal sea water solubility. Variation due to wind direction was most apparent in PC 3 which was also highly influenced by variation due to Co, Cu, Ni and Pb percentage solubility (Figure 5.53). The PC 6 was highly influenced by the percentage solubility variation due to Al, Ni and Pb (Figure 5.54), thus the two selected PCs represented the variation in the entire data set due to all six variables. The scores plot (Figure 5.55) revealed groupings of samples to which a wind direction could be attributed, but was less conclusive than for the sequential leach due to the dominance of northerly

Table 5.16: percentage solubilities for western English Channel aerosol associated trace metals (LOD = limit of detection).

Element	Arithmetic Mean	Range	Standard Deviation	RSD %	Geometric Mean
Al	1.90	0.90 - 7.38	1.71	89.5	1.58
Co	67.6	Below LOD - 100	30.8	45.6	67.0
Cu	83.9	43.9 - 107	16.8	20.0	82.0
Ni	50.3	17.0 - 82.4	21.6	43.0	45.2
Pb	48.8	0.66 - 100	32.6	74.1	24.9

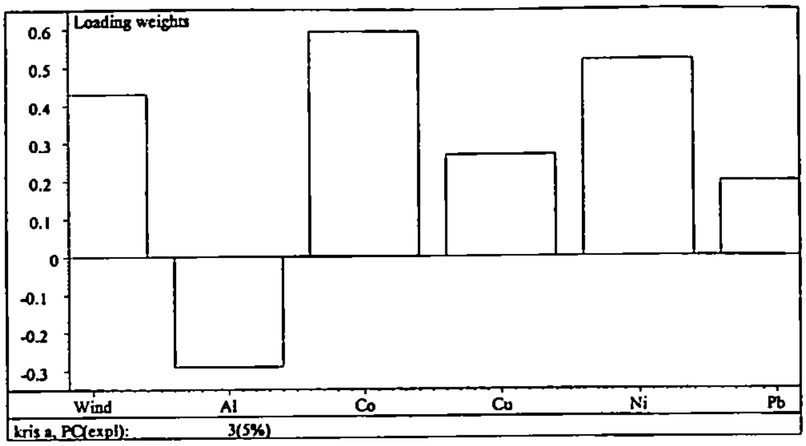


Figure 5.53: PC 3 loading weights displaying dominance of wind and Co, Cu, Ni and Pb % sea water solubilities.

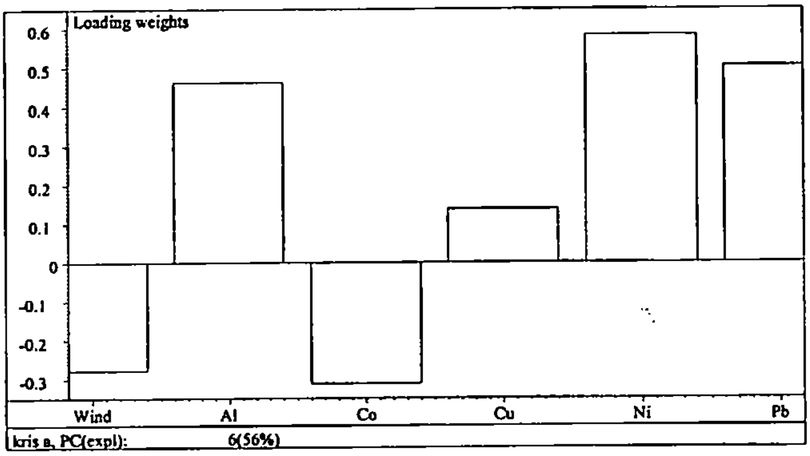


Figure 5.54: PC 6 loading weights displaying dominance of Al, Cu, Ni and Pb % sea water solubilities.

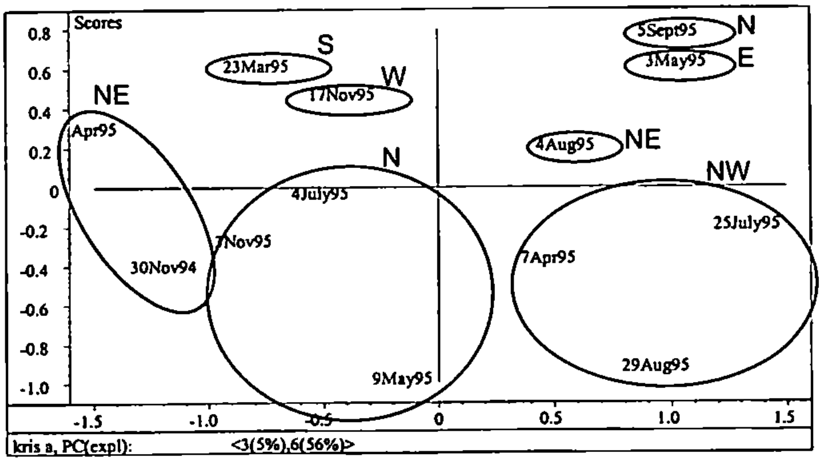


Figure 5.55: relationship between samples according to wind direction.

influenced samples in the set. However, it is suggested that wind direction does influence the percentage solubility of aerosol associated trace metals in sea water.

In addition to determining the percentage solubility of aerosol trace metals, the chemical speciation of the dissolved trace metals was investigated. The chemical speciation was represented by the percentage of the detectable $\text{Lumogallion}_{\text{Labile}}$ or $\text{ACSV}_{\text{Labile}}$ metal fraction (prior to sample UV irradiation) of the total dissolved metal fraction. Dissolved labile fractions were found to be: Al (69 %), Co (36 %), Cu (38 %), Ni (32 %) and Pb (14 %) (Table 5.18). The remaining proportion of dissolved metal fraction (i.e. $\text{Lumogallion}_{\text{Non-labile}}$ or $\text{ACSV}_{\text{Non-labile}}$,) was assumed to be organically complexed as this fraction was released after UV irradiation of the equilibrated seawater. However the $\text{Lumogallion}_{\text{Non-labile}}$ Al fraction may also be composed of inorganic colloids, which may be released into the dissolved phase after UV irradiation (and heating) of the sample. To investigate this, six samples were UV irradiated (see section 3.4.4) in duplicate - one duplicate was covered completely with polythene film, and then a layer of Al foil to block out all light; the second duplicate was left uncovered permitting oxidation of organic material present in the sample. Both samples were subsequently analysed for dissolved Al. The uncovered samples contained 41 ± 25 % more $\text{Lumogallion}_{\text{Total}}$ Al than that of the covered duplicates, were a significant component of the Al dissolved chemical species. Following UV irradiation, when > 80 % of the natural organic ligands had been decomposed, the source of organic complexing ligands was release from the aerosol particles themselves. Furthermore, if this mechanism applied to other trace metals, such complexing ligands may be more important for anthropogenically derived elements (e.g. Pb) than for crustally derived elements (e.g. Al), since Pb displayed a lower percentage labile portion than Al. Thus, it can be seen that dry deposited aerosol particles are not only sources of soluble trace metals but also organic complexing ligands which may subsequently influence the chemical speciation of dissolved trace elements in the sea surface, post aerosol deposition.

5.2 The geochemistry of trace metals in western English Channel rain waters.

Trace metals are present in rain water due to the scavenging of aerosol particles, followed by whole or partial dissolution. The extent to which aerosol material is scavenged (below cloud or in cloud) from the air mass is dependent upon (i) the aerosol concentration and (ii) the aerosol population size spectrum, both of which will vary considerably depending on the area in which the sample was collected, (iii) track of the sampled air mass and (iv) past and present rainfall (Granat, 1972). For example, aerosols of different particle sizes are scavenged at varying efficiencies by rain water, unless the particle concentration in the atmosphere is low (Arimoto *et al.*, 1985).

Table 5.18: percentage Lumogallion / $ACSV_{Labile}$ of the total dissolved fraction from western English Channel aerosols (LOD = limit of detection).

Element	Arithmetic Mean	Range	Standard Deviation	RSD %	Geometric Mean
Al	69.1	30.4 - 103	17.5	25.4	66.7
Co	35.6	Below LOD - 100	40.5	114	31.3
Cu	38.3	2.00 - 112	29.1	76.0	27.3
Ni	32.2	Below LOD - 83.5	30.2	93.6	30.1
Pb	13.7	Below LOD - 70.3	21.8	160	12.3

Rain water trace metal concentrations are known to vary within a rain event (Chester, 1990). Nguyen et al. (1979) observed a decrease in trace metal concentration in sequential rain water samples. This effect was also observed by Helmers and Scherms (1995). They noted washout effects for Cd, Cu and Zn in samples collected in the South West Atlantic. Concentrations were found to decrease by up to 75 percent in samples collected ninety minutes after the initial rain event. Trace metal concentrations in rain water are also influenced by the trace metal concentration in the aerosol and the efficiency of aerosol scavenging. For example, the lower efficiency of Pb rain water scavenging from the western Mediterranean aerosol has been attributed to the finer particles resisting scavenging, thus leading to longer transport and Pb residence times in the atmosphere (Chester *et al.*, 1997).

However, a knowledge of total (dissolved and particulate) trace metal rain water concentrations is inadequate when investigating the 'potential environmental mobility' (Chester *et al.*, 1993c) or toxicity of trace metals to biota following wet deposition to the marine environment. In order to assess the potential availability of trace metals to organisms within aquatic systems, it is essential to investigate the speciation of such metals (e.g. Losno *et al.*, 1993; Luoma, 1982). The speciation of trace metals (Al, Co, Cu, Ni, Pb) in western English Channel rain waters will be discussed in terms of (i) soluble trace metal percentage of the total rainwater concentration and (ii) percentage $\text{Lumogallion}_{\text{Labile}}$ or $\text{ACSV}_{\text{Labile}}$ of the total dissolved fraction.

5.2.1 Total (dissolved and particulate) rain water trace metal concentrations.

Thirty-five rain water samples were consecutively collected between January 1995 and February 1996. Table 5.19 summarises total trace metal (Al, Co, Cu, Na, Ni and Pb) rain water concentrations, where the mean values are volume weighted. All trace metals display considerable variation over the sampling period. The total trace metal volume weighted rain water concentrations were divided into seasons (winter: December - February; spring: March - May; summer: June - August; autumn: September - November) and the mean concentrations for each season were calculated. The seasonal means are presented in Table 5.20 along with the total rainfall for each equivalent season. It can be clearly seen that the highest mean concentrations for Al, Cu, Ni and Pb were observed in autumn 1995. The second highest total rainfall also occurred during this season, and the prevailing wind direction was from the S/SW (see Table 5.5). Since elevated rain water trace metal concentrations were not observed during winter 1994/95, when the highest rainfall was observed (Wood, 1998), it is likely that the prevailing wind characteristics, and hence particle source, are responsible for the elevated rain water concentrations. This hypothesis was further supported by the

Table 5.19: total (dissolved and particle associated) western English Channel rain water concentrations.

Element	Arithmetic mean ($\mu g\ l^{-1}$)	Range ($\mu g\ l^{-1}$)	Standard deviation ($\mu g\ l^{-1}$)	% RSD	Volume weighted mean ($\mu g\ l^{-1}$)
Al	102	2.41 - 860	169	166	94.4
Co	1.05	0.05 - 6.93	1.72	164	1.23
Cu	13.5	0.57 - 74.7	17.2	127	14.4
Na	168	5.15 - 1085	214	127	240
Ni	5.15	0.47 - 26.2	5.59	109	4.68
Pb	4.58	Below LOD - 54.7	10.2	222	4.41

Table 5.20: mean seasonal rain water concentrations and total rainfall for the rain water sampling period.

Season	Al (µg l^{-1})	Co (µg l^{-1})	Cu (µg l^{-1})	Na (µg l^{-1})	Ni (µg l^{-1})	Pb (µg l^{-1})	Rainfall (l)
Winter 1994/95	7.44	0.23	4.51	57.2	1.15	2.71	9.35
Spring 1995	25.6	1.65	9.28	105	3.13	1.43	5.53
Summer 1995	167	1.85	18.6	314	6.11	0.36	6.63
Autumn 1995	221	2.41	34.4	305	10.7	21.7	9.14
Winter 1995/96	115	0.51	13.8	528	5.12	0.73	4.70

absence of S/SW winds during winter 1994/95. It was suggested in section 5.1.2 that such winds, when combined with the speeds observed, resulted in elevated aerosol trace metal concentrations, probably as a result of the re-suspension of local terrestrial material and enhanced sea salt generation. Rain water scavenging of such particles probably resulted in the high Al, Cu, Ni and Pb total rain water concentrations.

The volume weighted mean concentrations in western English Channel rain waters are compared with those of other regions in Table 5.21. The concentrations observed in western English Channel rain waters exceed those observed in other European coastal regions, and approximate to those observed in western Mediterranean rain waters for Al and Pb. This demonstrates the importance of wet deposition as a source of trace metals to the English Channel during the sampling period. An exception to this is Na. If it is assumed that rain bearing air masses are derived from the Atlantic, it is probable that Na concentrations will decrease as precipitation develops in the air mass as it moves along the South West Peninsula. However, it may be that 1995 was an unrepresentative year due to (i) the difference between the total trace metal concentrations for winter 1994/95 and for winter 1995/96, and (ii) the impact of Hurricane Iris created somewhat anomalous meteorological conditions.

5.2.2 The partitioning of trace metals in rain water

Rain water is generally quantitatively the more dominant atmospheric source of dissolved trace metals to the sea surface (Galloway *et al.*, 1982), and is therefore of importance when considering marine biogeochemical cycles. The trace metal availability within marine biogeochemical cycles is highly dependent on their physico-chemical forms (e.g. Maring and Duce, 1987; Moore *et al*, 1984). The controls on the partitioning of trace metals between dissolved and particle associated phases in rain waters have been investigated by a number of workers (e.g. Lim *et al.*, 1994; Losno and Bergametti, 1988). Controls governing trace metal partitioning are:

(i) aerosol solid state speciation (Chester *et al.*, 1989; 1992). Trace metals derived from an anthropogenic source are more easily exchangeable (and therefore soluble) than trace metals which are crustal in origin (Lim, 1991), as elements which are crustally derived are locked within the mineral lattice of the scavenged particle (Jickells *et al.*, 1992);

(ii) the extent to which particles have undergone condensation/evaporation cycles within clouds (Pruppacher and Klett, 1980). Such cycles can alter particle surface characteristics due to large variations in acidity and ionic strength; rain water

Table 5.21: volume weighted total (dissolved and particle associated) trace metal rain water concentrations (μg l^{-1}) for coastal and open ocean regions.

Element	Western English Channel[a]	Irish Sea[b]	North Atlantic[c]	North Sea (Open sea)[d]	North Sea (Coastal)[d]	Western Mediterranean (Cap Ferrat)[e]	Bermuda[f]	Western Samoa[g]
Al	94.4	43.5	42	21	56	97.5	16	10
Co	1.23	0.06	-	-	-	0.06	-	-
Cu	14.4	2.4	0.5	0.98	4.0	2.75	0.27	0.04
Na	240	2708	-	-	-	-	-	2600
Ni	4.68	1.2	-	-	-	0.63	0.21	-
Pb	4.41	1.2	0.47	3.5	4.1	4.56	0.87	0.04

[a]Current study; [b]Fones, 1996; [c]Church *et al.* (1990); [d]Chester *et al.* (1993a); [e]Chester *et al.* (1990); [f]Church *et al.* (1984); [g]Arimoto *et al.* (1987).

characteristics, i.e. pH (Guieu *et al.*, 1991; Jickells *et al.*, 1992), ionic strength, ligand concentration and variety (Maring and Duce, 1990)).

To assess trace metal dissolved/particle partitioning, rain waters were filtered *in situ*, through 0.45 µm membrane filters, with subsequent treatment and analysis as described in sections 3.4.3 and 3.4.5. Dissolved and particle associated trace metal concentrations were calculated as volume weighted means (µg l^{-1}) according to equation 3.8. Table 5.22 displays the arithmetic and volume weighted mean, range, standard deviation and relative standard deviation for percentage soluble trace metal fractions. Greater than 50 % of Co, Cu and Ni concentrations were present in the dissolved fraction of the rain waters, indicating that for wet deposition, their primary mode of transport is in the dissolved phase. Forty seven percent of Pb was present in the dissolved fraction indicating that the particle associated phase was slightly more important, although the standard deviation indicates that this is highly variable. Aluminium exhibited a low dissolved fraction concentration; Al solubility has been previously reported to be as low as 0.2 - 0.1 percent (Losno *et al.*, 1993; Lim *et al.*, 1994).

Previous workers have demonstrated that the solubility of trace metals in rain water is highly variable, ranging from an average of ~ 20 % (Al) to > 90 % (Zn) (e.g. Colin *et al.*, 1990; Guieu *et al.*, 1990; Jickells, 1995; Lim *et al.*, 1994) (Table 5.23). Percentage dissolved Co and Cu fractions were higher than observed elsewhere. If the European aerosol is responsible for the elevated trace metal rain water solubilities, it is probable that the trace metals are far removed from their sources and have undergone enhanced weathering as a result. (Chester, 1990). In addition, contribution of the unique regional metal soils from the South West Peninsular may have led to enhanced trace metal solubilities.

The relative amount of Pb in the dissolved fraction of rain water is highly variable, ranging from 53 % to 90 % (Lim *et al.*, 1994), whereas for the western English Channel it was about 47 %. This could be due to (i) less anthropogenic influences within the air masses affecting the western English Channel compared with the other regions (ii) a land-based source of Pb, such as mineral extraction wastes or (iii) as a result of the decline in the use of leaded fuels.

Table 5.22: EF_{Crust} of total rain water concentrations for coastal and open ocean regions.

Element	Western English Channel[a]	Irish Sea[b]	North Atlantic[c]	North Sea (Open sea)[d]	North Sea (Coastal)[d]	Western Mediterranean (Cap Ferrat)[e]	Bermuda[f]	Western Samoa[g]
Co	147	4	-	-	-	2	-	-
Cu	877	82	18	70	107	42	25	6
Na	25.4	217	-	-	-	-	-	905
Ni	187	30	-	-	-	7	14	-
Pb	1640	182	74	1097	482	308	358	26

[a]Current study; [b]Fones, 1996; [c]Church *et al.* (1990); [d]Chester *et al.* (1993a); [e]Chester *et al.* (1990); [f]Church *et al.* (1984); [g]Arimoto *et al.* (1987).

Table 5.23: comparison of percentage dissolved trace metals in rain waters over selected regions.

Element	Western English Channel[a]	Irish Sea[b]	Bermuda, Atlantic Ocean[c]	Corsica, Mediterranean Sea[c]	Cap Ferrat, Mediterranean Sea[d]
Al	0.27	32	20	9	18
Cd	-	79	-	-	91
Co	92.3	70	-	-	61
Cu	92.3	82	84	48	82
Fe	-	-	-	-	-
Mn	-	-	-	-	60
Ni	58.1	69	-	-	54
Pb	46.5	63	90	53	65
Zn	-	-	96	72	-

[a] Current study; [b] Fones, 1996; [c] Lim *et al.*, 1994; [d] Chester *et al.*, 1990.

5.2.2.1 Speciation of dissolved trace metals.

Arithmetic and volume weighted percentage $\text{Lumogallion}_{\text{Labile}}$ / $\text{ACSV}_{\text{Labile}}$ means, range, standard deviation and relative standard deviation are presented in Table 5.24. All elements exhibited organic complexation to some extent, with Al displaying the greatest complexation (91 %) and Co the least (32 %). Cobalt, Cu and Ni displayed similar complexation behaviour (32, 47 and 36 %, respectively). Such organic complexation characteristics were dissimilar to those observed in the aerosol particle sea water solubility experiment (see section 5.1.4.2): all elements with the exception of Al displayed greater complexation in the rain waters. It is therefore possible that organic complexation depends on:

(i) kinetics of complexation (i.e. length of exposure to aerosol particles);
(ii) pH of the aquatic medium;
(iii) ligand concentration in the aquatic medium.

Since rain waters were acidified upon collection, it is possible that the extent of metal complexation may have been affected. These results suggest, however, that the atmosphere may be a significant source (primary/recycled) of trace metal organic complexing ligands to the marine environment. Similar experiments were carried out by Fones (1996) and his results, as percentage $\text{ACSV}_{\text{Non-labile}}$ trace metal concentrations in Irish Sea rain waters, are presented in Table 5.25. These values are

Table 5.24: percentage Lumogallion/ACSV$_{Labile}$ of the total dissolved fraction in western English Channel rain waters (LOD = limit of detection).

Element	Arithmetic Mean	Range	Standard Deviation	RSD %	Geometric Mean
Al	9.42	Below LOD - 97.4	27.2	289	1.64
Co	67.8	Below LOD - 100	27.4	40.4	64.7
Cu	52.8	0.42 - 97.3	32.5	61.6	38.0
Ni	64.3	Below LOD - 97.9	22.1	34.3	63.2
Pb	33.9	Below LOD - 98.1	33.5	99.1	13.2

compared to the western English Channel percentage $\text{ACSV}_{\text{Non-labile}}$. Cobalt and Ni compared reasonably well with the Irish Sea data, although Cu was 68 % more complexed in the western English Channel rain waters. Lead displayed the greatest difference having almost double the organically complexed fraction observed in the Irish Sea rain waters. This may be related to the higher Pb aerosol concentration observed over the Irish Sea, compared with the western English Channel. It may also be due to the particle type (i.e. source), or the degree of particle weathering.

Table 5.25: speciation of dissolved trace metals in western English Channel rain waters (n = 35), compared with complexed trace metal fractions in Irish Sea rain waters (n = 26).

Element	% Lumogallion/$\text{ACSV}_{\text{Non-labile}}$ Western English Channel	% $\text{ACSV}_{\text{Non-labile}}$ Irish Sea
Al	90.6 ± 24.9	-
Co	32.2 ± 27.3	38
Cu	47.2 ± 32.5	32
Ni	35.7 ± 22.1	35
Pb	66.1 ± 33.5	34

5.2.3 Wet deposition fluxes to the western English Channel.

Total wet deposition fluxes were calculated according to equation 3.9, where the total annual rainfall was estimated to be 680 mm (Meteorological Office, 1995). The figure for annual rainfall was similar to that estimated for the Irish Sea (650 mm - Fones, 1996). The elements can be ranked in order of decreasing wet deposition flux as follows: Na > Al > Cu > Ni > Pb > Co. Total wet deposition fluxes for the current study are compared with selected regions in Table 5.26. With the exception of Na, the total wet deposition fluxes observed over the western English Channel exceed those observed elsewhere. This highlights the importance of wet deposition as a source of trace metals to the area during the sampling period. The total wet deposition flux for Al was comparable with that for the western Mediterranean which is subject to seasonal crustal pulses from the Sahara Desert (Chester *et al.*, 1993d). Similarly the total wet deposition flux for Pb was comparable to this region. This is also surprising as the western Mediterranean is influenced by the European industrial regions (Chester *et al.*, 1993d), unlike the western English Channel. It appears likely that the high fluxes are due to the influence of the European aerosol, regional crustal material, which have been sufficiently weathered to aid trace metal rain water solubility, and the domination of orographic rainfall in south west England (Barry and Chorley, 1992).

Table 5.26: total wet deposition fluxes to selected regions (ng cm^{-2} yr^{-1}).

Element	W. English Channel[a]	Irish Sea[b]	Brittany Coast[c]	Dutch Coast[c]	UK East Anglia[c]	North Sea[d]	W. Mediterranean Sea[e]	Bermuda (Atlantic Ocean)[f]	Sargasso Sea[g]	Enewetak Atoll (Pacific Ocean)[h]
Al	6450	2830	-	-	-	770	5060	1400	2800	210
Co	83.8	3.9	-	-	-	-	3.3	-	-	-
Cu	986	157	41	178	106	37	171	26	48	4.4
Na	16 400	176 000	-	-	-	-	-	-	-	-
Ni	320	78	32	-	77	-	33	21	37	-
Pb	301	81	108	429	261	129	236	82	150	2.0

[a]Current study; [b]Fones, 1996; [c]Reid *et al.*, 1993; [d]Chester *et al.*, 1993a; [e]Chester *et al.*, 1990; [f]Jickells *et al.*, 1985; [g]Jickells *et al.*, 1987;[h]Arimoto *et al.*, 1985.

5.3 Trace metal inputs to the English Channel.

Dry deposition trace metal fluxes to the western English Channel were presented in section 5.1.3.3, although these experiments did not determine trace metal solubility in sea water, following dry deposition. Similarly, wet deposition fluxes, presented in section 5.2.3 did not differentiate between the non-soluble particle associated and soluble fractions. It was therefore necessary to ascertain dissolved dry deposition and relative dissolved/particle associated wet deposition trace metal fluxes in order to estimate:

(i) total particle associated trace metal fluxes (and inputs);
(ii) total dissolved trace metal fluxes (and inputs);
(iii) total trace metal fluxes (and inputs).

5.3.1 Total particle associated and dissolved trace metal fluxes.

Total particle associated trace metal fluxes were comprised of the proportion of aerosol associated trace metal which did not dissolve in sea water and the particle associated (i.e. insoluble) fraction of wet deposition (Table 5.27). Total wet deposition fluxes were comprised of the proportion of trace metal that would dissolve upon impact with the sea surface and the dissolved portion of the wet deposition flux (Table 5.28). The corrected fluxes clearly illustrate the importance of particle transport for Al. This is due to its low solubility in rain water (e.g. Lim *et al.*, 1994; Losno *et al.*, 1993) and its larger particle size, which results in greater settling velocities and hence increased dry deposition. Cobalt and Cu each display similar behaviour: <10 % of each element was transported in the particulate phase. The dominance of the dissolved wet flux for Co and Cu is possibly due to the enhanced weathering of local sources such as mineral waste, enriched crustal material or the long range transport of material in the European aerosol. Nickel and Pb display similar dependence on both dissolved and particulate transport. However, the $^{208/207}$Pb isotopic ratio study suggested that the aerosol was well mixed with respect to Pb; both natural and anthropogenic origins have been suggested as potential Pb sources, although, in reality, a combination of sources is most likely. This was sustained by the sequential leach and sea water solubility studies, which also included Ni in this scenario. Anthropogenic input was possible from N/NE/E wind directions.

5.3.2 Total particulate and dissolved trace metal inputs to the English Channel.

Annual inputs were calculated using dissolved and particle fluxes presented in section 5.3.1 to assess the impact of atmospheric particle and dissolved trace metal sources to the marine biogeochemical cycles of the English Channel. Atmospheric trace metal annual inputs (Table 5.29) were calculated

Table 5.27: mean total (dry and wet) particle associated flux to the western English Channel (ng cm^{-2} yr^{-1}).

Element	Dry deposition flux (ng cm^{-2} yr^{-1})	% sea water insoluble	Particulate dry deposition flux (ng cm^{-2} yr^{-1})	Wet deposition flux (ng cm^{-2} yr^{-1})	% rain water insoluble	Particulate wet deposition flux (ng cm^{-2} yr^{-1})	Total particulate flux (ng cm^{-2} yr^{-1})
Al	7830	98.1	7680	6450	99.7	6430	14 100
Co	1.45	32.4	0.47	83.8	5.50	4.61	5.08
Cu	32.1	16.1	5.17	986	6.80	67.1	72.3
Ni	33.0	47.6	15.7	320	42.7	137	153
Pb	0.86	51.2	0.44	301	54.1	163	163

Table 5.28: mean total (dry and wet) dissolved flux to the western English Channel (ng cm^{-2} yr^{-1}).

Element	Dry deposition flux (ng cm^{-2} yr^{-1})	% sea water soluble	Dissolved dry deposition flux (ng cm^{-2} yr^{-1})	Wet deposition flux (ng cm^{-2} yr^{-1})	% rain water soluble	Dissolved wet deposition flux (ng cm^{-2} yr^{-1})	Total dissolved flux (ng cm^{-2} yr^{-1})
Al	7830	1.91	150	6450	0.26	16.8	167
Co	1.45	67.6	0.98	83.8	94.5	79.2	80.2
Cu	32.1	83.9	26.9	986	93.2	919	946
Ni	33.0	52.4	17.3	320	57.3	183	200
Pb	0.86	48.8	0.42	301	45.9	138	138

according to equation 3.4 where the area of the English Channel was estimated as 77 000 km^2 (Reid *et al.*, 1993). Assuming trace metal concentrations were uniform over the English Channel, the data show that in excess of 100 t of Al, Cu, Ni and Pb enter the English Channel in a readily available form per annum. In addition, almost 11 000 t of particle associated Al enter the English Channel each year. This may have important implications for the marine geochemical cycling of surface active trace metal heavy metals such as Pb and Zn which have been shown to be scavenged by Al containing crustal particles, thus removing them from solution and hence reducing their potential bioavailability (Kersten et al., 1991) and hence impact.

Table 5.29: mean total particle and dissolved trace metal inputs to the English Channel (t yr^{-1}) (n = 28).

Element	Particulate Input (t yr^{-1})	Dissolved Input (t yr^{-1})
Al	10 900	129
Co	3.90	61.8
Cu	55.7	728
Ni	118	154
Pb	126	106

The wet input mode was dominant for Co, Cu and Ni. This agrees with studies undertaken by Chester *et al.*, 1990 who made similar observations in the western Mediterranean. Rojas *et al.* (1993) and Fones (1996) also observed ehanced wet deposition for Cu, in the Southern Bight of the North Sea and the Irish Sea respectively. However, these studies, accompanied by others in the North Sea (Chester *et al.*, 1993a; Ottley and Harrison, 1993) suggest that the dry deposition distribution of Pb is relatively more important. This may be attributed to its less anthropogenic and crustal origin to the English Channel aerosol population.

5.3.3 Total trace metal fluxes to the English Channel.

To assess the relative importance of atmospheric trace metal inputs, a comparison was made with land based (i.e. non-atmospheric) sources of trace metals to the English Channel. Draft data for 1995 on English land based sources of trace metals to the English Channel were supplied by the Environment Agency TAPS Centre, and were compared with atmospheric sources in Table 5.30. The data show that the atmosphere was a greater source of trace metals to the English Channel compared

Table 5.30: comparison of mean total atmospheric trace metal inputs with final draft total UK land based trace metal inputs to the English Channel and annual direct industrial discharge to the English Channel from the Seine (Table 4.2) (t yr^{-1}) (ND = not determined).

Element	Atmospheric input (t yr^{-1})	UK River Input (t yr^{-1})	Seine Input (t yr^{-1})
Al	11 000	ND	ND
Co	65.7	ND	ND
Cu	784	83	166
Ni	272	28	ND
Pb	232	19	236

with English land based sources being approximately an order of magnitude higher for all considered metals.

5.4 Summary of atmospheric trace metal characteristics over the western English Channel.

This chapter has reported on the atmospheric trace metal biogeochemistry of the western English Channel. The following is a summary of the observations:

Enriched trace metal (Cd, Cu, Pb, and Zn) aerosol geometric mean concentrations were lower than those previously reported in the literature for western European coastal sites (Fones, 1996; Chester and Bradshaw, 1991; Chester *et al.*, 1990). These elements also exhibited the lowest regional EF_{Crust} (highlighted by Cd and Pb), indicative of a diminished anthropogenic contribution to the English Channel aerosol population. The $^{206/207}Pb$ isotopic ratio comparison with Pb EF_{Crust} indicated that the aerosol population was well mixed with no dominant western European anthropogenic source. The decline in use of leaded fuel almost certainly contributed to the reduced aerosol Pb concentration. This effect has also been noted at other European sampling locations. Crustally derived trace metals (Al, Co, Mn) all exhibited comparable aerosol concentrations to literature values.

Pronounced seasonal variability In the trace metal aerosol concentrations was apparent. Group 1 elements being defined as those elements (i.e. Cd, Fe, Mn, Pb, Zn) which exhibited autumn - winter enhanced concentrations over the whole sampling period. Group 2 elements (i.e. Al , Co, Cu, Na, Ni) exhibited much greater autumn/winter concentration enhancement during 1995/96. The Group 1 elements Cd, Pb and Zn, typically demonstrated greater EF_{Crust} in sampled air masses from the N/E sectors indicating long range transport from western European anthropogenic sources. Group 2 elements illustrating enhanced concentration in SW wind sectors. This behaviour was particularly apparent for Ni. This is likely to be a result of (i) re-suspension of regional mineralised terrestrial material after an unusually dry season and or (ii) association with enhanced sea salt generation.

A three stage sequential leach was employed to assess the solid state speciation of trace metals in selected samples, to assess the potential impact of aerosol associated trace metals once deposited into the English Channel. Aluminium and Fe were found almost entirely in the residual stage (Stage 3), indicative of crustal origin; Cd was found mostly in the easily exchangeable stage (Stage 1), indicative of anthropogenic origin; Mn was also located mostly in the easily exchangeable stage although its solubility is reported by Chester (1990) to be largely independent of its source; 55 percent of Pb was located in the easily exchangeable stage which was lower than observed in anthropogenic dominated aerosols, but higher than for crustally dominated aerosols. This was thought to confirm the low anthropogenic influence, well mixed nature of the western English Channel aerosol. PCA revealed a strong aeolian influence on the proportion of easily exchangeable trace metals in selected samples.

Complementary aerosol trace metal (Al, Cd, Co, Cu, Ni, Pb) sea water studies were performed on a similar set of samples. Form these studies it was observed that Al exhibited a very low solubility in sea water inherent of its crustal origin; Pb had a solubility of ~ 50 % which was similar to that located within the easily exchangeable fraction of the sequential leach; Co, Cu and Ni had solubilities > 50 %. These solubilities were higher than those reported by other workers (e.g. Fones, 1996; Hodge *et al.*, 1978. The organic complexation of sea water soluble aerosol trace metals was found to be significant for all investigated trace metals. Aerosol particle deposition was thought to be an important source of organic complexing ligands to the marine environment. The fraction of the dissolved metal organically complexed could be ranked in the order: Al < Cu < Co < Ni < Pb. PCA analysis revealed aeolian influence on trace metal sea water solubility although not as clearly as for the sequential leach.

The volume weighted trace metal mean rain water concentrations were higher than those reported in the literature for a selection of coastal and open ocean regions. It is surprising that the rainwater concentrations are in excess to those previously reported for other European coastal locations considering that the aerosol trace metal concentrations for the English Channel were lower than any other reported region. The observed comparatively elevated rainwater concentrations may have arisen owing to the following factors (i) higher aerosol trace metal concentrations in autumn/winter 1995 (as a result of local re-suspended terrestrial material). The scavenging efficiency of the regional terrestrial derived material would also be greater during this period in comparison to long range transported material.

Dissolved trace metal organic complexation in rain waters was found to be important for all investigated trace metals and the extent of complexation could be ranked in the order: Al < Co < Ni < Cu < Pb. This complements the work by Nimmo and Chester (1993) who detected the presence of metal organic ligands in coastal rain waters (western Mediterranean and Irish Sea). Therefore it is apparent that atmospheric inputs may not only contribute to the marine trace metal pool, but may also influence changes in their chemical speciation which may impact upon their marine biogeochemical cycling.

Dry and wet deposition fluxes were calculated using particle settling velocities and annual rainfall figures specific to the western English Channel. Fluxes were corrected to account for particle sea water solubility, and the rain water particle associated phase, yielding total particle and total dissolved trace metal fluxes. Aluminium was observed to dominate in the particle associated phase, indicative of its crustal origin; Co and Cu were found to dominate to in the dissolved flux as a possible result of the influence of the European aerosol, resulting in the long range transport of elements from their emission source; Ni and Pb were found in almost equal proportions in both fluxes. This was likely to result from the variety of proposed sources for Ni and Pb: the European aerosol, the South West Peninsula, local anthropogenic emissions, sea salt generation. Annual trace metal inputs were found to be higher than land based inputs. The atmospheric metal input data set will be incorporated into a refined budget box model of the English Channel in Chapter 8. The model will also undergo sensitivity checks to assess the impact on the budget model of seasonal variability of the dry and wet atmospheric trace metal inputs.

Chapter 6.

Atmospheric trace metal characteristics of the north western Mediterranean Sea.

Chapter 6.

Atmospheric trace metal characteristics of the north western Mediterranean Sea.

6.1 Geochemistry of trace metals in the north western Mediterranean aerosol.

A comparison of the trace metal aerosol concentrations obtained in this work with those in the literature is presented in Table 6.1. All elemental concentrations in this study, except for Pb and Zn, were lower than those detected during previous Mediterranean studies. It is possible that the lower elemental concentrations were due to the considerable efforts made, during the current study, to minimise contamination and to better instrumental precision. Alternatively, inter-annual variability of meteorological conditions could be a factor, since there may be differences in the elemental removal rates (particularly wet deposition) and the type and strength of the aerosol source contributing to the aerosol between sampling periods.

Table 6.1: comparison of arithmetic mean aerosol associated trace metal concentrations (ng m^{-3}).

Element	Monaco[a]	Cap Ferrat[b]	Western Mediterranean[c]	Mediterranean Sea[d]	Tyrrhenian Sea[e] (Saharan influenced)
	(n = 27)	(n=75)	(n = 16)	(n = 21)	(n = 4)
Al	256	370	210 - 445	14 773	2000
Cd	0.11	0.36	1.6 - 2.2	0.27	0.31
Co	0.16	-	-	-	-
Cu	5.03	6.2	-	12	2.7
Fe	278	320	-	10 092	1249
Mn	7.38	11	-	160	18.5
Na	908	-	1900 - 2300	-	-
Ni	2.05	2.8	-	14	3.1
Pb	25.9	58	27 - 51	13.5	7.4
Zn	29.6	41	-	26	8.4

[a]Current study; [b]Chester *et al.*, 1990; [c]Dulac *et al.*, 1987; [d]Chester *et al.*, 1993d; [e]Chester *et al.*, 1984. All samples underwent a HNO_3/HF digest prior to analysis with the exception of Dulac *et al.*, 1987 where the samples underwent a HNO_3/HCl digest.

The relatively low concentrations for Pb and Zn in the earlier studies by Chester et al., (1984) and Chester et al., (1993d) may be explained by the strong influence, on the sampled aerosol population of Saharan dust which has a proportionally lower content of these elements compared to that in the 'background' European aerosol. The arithmetic and geometric means, range, arithmetic standard deviation and relative standard deviation of the aerosol associated trace metals are presented in Table 6.2. North western Mediterranean aerosol associated trace metals could be ranked according to their relative standard deviations in the following order: Al (109%) > Pb (97.6%) > Cd (89%) > Co (88 %) > Fe (81%)> Mn (79%) > Na (73%) > Zn (72%) > Ni (68%) > Cu (60%). The relative standard deviations of the north western Mediterranean aerosol trace metal concentrations were all <100 % with the exception of Al, which had the highest percentage RSD, followed by Pb. This implies the existence of different trace metal aerosol sources, possibly as a result of wind patterns, to the north western Mediterranean, which are characterised by either crustal or anthropogenic inputs. It is evident that both NEEs and AEEs are variable in the north western Mediterranean aerosol.

Figures 6.1 to 6.10 display the temporal variation in trace metal concentration during the sampling period. Pulses of high Al concentrations in the aerosols can be clearly seen (in excess of 1000 ngm^{-3}). This is indicative of episodic outbreaks coming from the south, which occur during the Mediterranean spring due to the *Scirocco* (Barry and Chorley, 1992; Guerzoni *et al.*, 1993; Chester et al.,1993d). The profile of Al is also duplicated by Co, Fe and Mn. In addition, Cu, Pb and Zn display concentration peaks which coincide with those of Al. It is possible that these elements are, in part, derived from crustal sources in North Africa, where such elements are mined. The profile of Cd displays a number of similar trends to that of Pb, which suggests that Pb still has a dominant anthropogenic source (see section 6.1.1.)

6.1.1 Sources of trace metals to the north western Mediterranean aerosol.

The following sources may contribute to the north western Mediterranean aerosol:

(i) crustal weathering;
(ii) sea salt formation;
(iii) anthropogenic emissions;
(iv) volcanic emissions.

Volcanic activity is sporadic and such inputs would be negligible for the period of the sampling campaign reported here. North western Mediterranean aerosol associated trace metal EF_{Crust} were calculated using precursor crustal elemental ratios, determined from aerosol data reported by Murphy (1985). Aerosol samples collected off the west coast of Africa, contained a high proportion of Al which

Table 6.2: atmospheric trace metal aerosol concentrations for the north western Mediterranean aerosol (n = 27) (LOD = limit of detection).

Element	Arithmetic Mean (ng m^{-3})	Range (ng m^{-3})	Standard Deviation	RSD (%)	Geometric Mean (ng m^{-3})
Al	256	7.00 - 1110	278	109	143
Cd	0.11	Below LOD - 0.38	0.10	89.0	0.01
Co	0.16	Below LOD - 0.62	0.14	88.0	0.11
Cu	5.03	0.30 - 11.7	3.04	60.4	3.64
Fe	278	Below LOD - 1050	225	81.0	175
Mn	7.38	Below LOD - 26.1	5.86	79.4	4.38
Na	908	79.0 - 3140	665	73.4	653
Ni	2.05	0.03 - 5.59	1.40	68.6	1.26
Pb	25.9	Below LOD - 126	25.2	97.6	15.9
Zn	29.6	Below LOD - 94.6	21.5	72.4	19.3

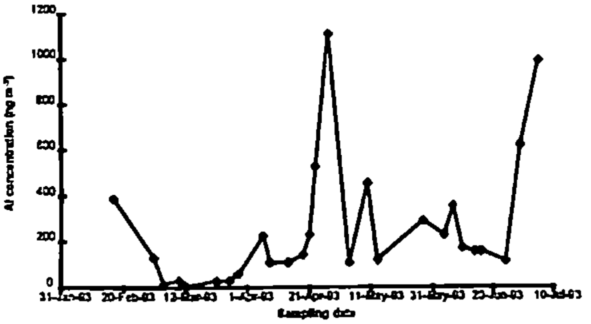


Figure 6.1: temporal variation of Al concentration.

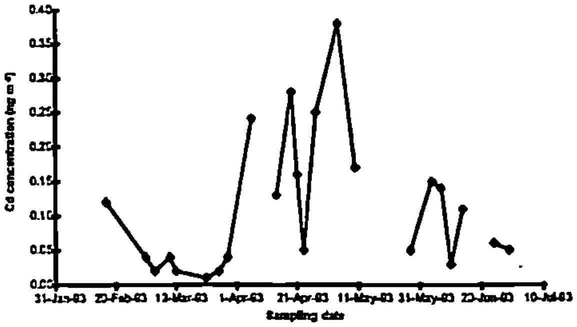


Figure 6.2: temporal variation of Cd concentration.

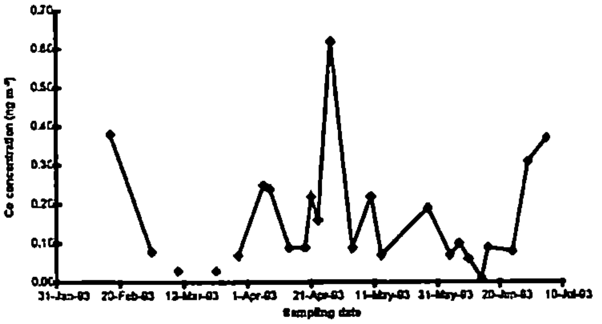


Figure 6.3: temporal variation of Co concentration.

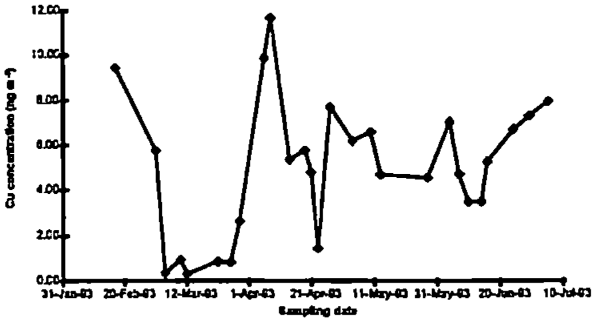


Figure 6.4: temporal variation of Cu concentration.

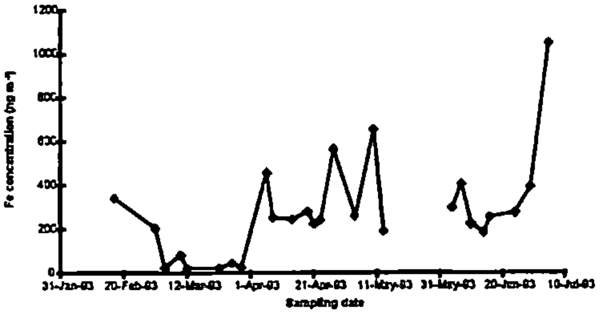


Figure 6.5: temporal variation of Fe concentration.

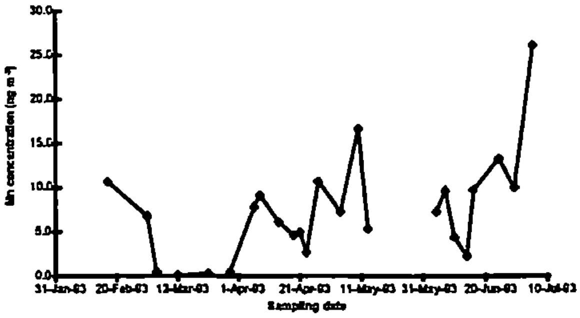


Figure 6.6: temporal variation of Mn concentration.

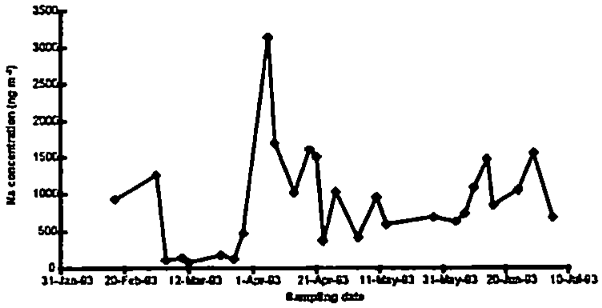


Figure 6.7: temporal variation of Na concentration.

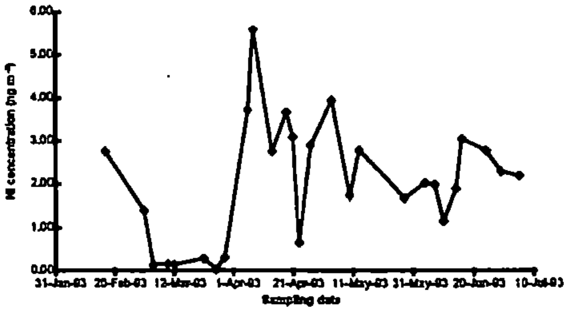


Figure 6.8: temporal variation of Ni concentration.

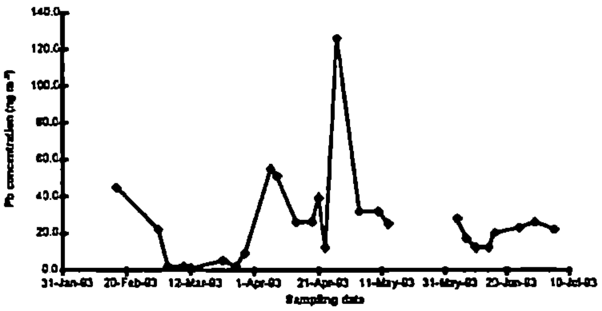


Figure 6.9: temporal variation of Pb concentration.

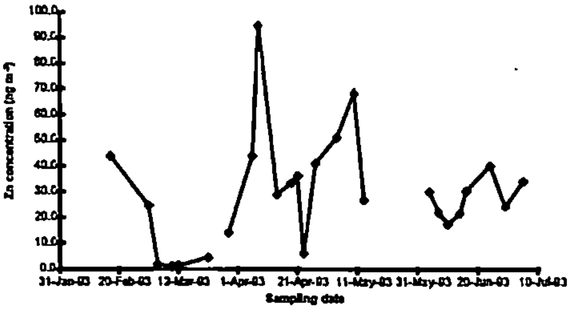


Figure 6.10: temporal variation of Zn concentration.

was believed to be derived from Saharan dust (Murphy, 1985). During the current sampling period, a high occurrence of the Saharan dust-laden *Scirocco*, was predicted. It is likely that the elemental crustal ratios, calculated from high Al west African aerosol samples, are more representative than the global elemental ratios presented by Taylor (1964). The two sets of elemental crustal ratios are presented in Appendix 2.

EF_{Crust} values were calculated (Equation 2.2) for all elements in the aerosol trace metal data set - arithmetic and geometric means, range, arithmetic standard deviation and relative standard deviation are presented in Table 6.3. Aluminium, Co, Fe, Mn and Na have EF_{Crust} values <10, which is indicative of crustal origin (i.e. NEEs). The observed low EF_{Crust} for Na may be a result of similar input sources, but is more likely due to the influence on the Na EF_{Crust} calculation of the corresponding high Al concentrations in the sampled aerosol as a result of Saharan dust transport. The high EF_{Crust} of Cd and Pb (72 and 99 respectively) demonstrate the importance of anthropogenically derived Cd and Pb in the north western Mediterranean aerosol, even though the period sampled is typified by high Al concentrations. Figures 6.11 to 6.19 demonstrate the temporal variation of elemental EF_{Crust} throughout the sampling period. All elements displayed a number of high peaks, the largest of which (except for Cd) occurred between 8 to 14 April 1993. The temporal concentration profile for Al (Figure 6.1) revealed that this sample was collected between two Al pulses. Sodium (Figure 6.15) displayed a number of EF_{Crust} peaks throughout the sampling period, although its EF_{Crust} was generally higher between February and mid April 1993. It is possible that stronger winds resulted in higher entrainment of Na in the sampled aerosols, resulting in a higher Na concentration with respect to Al. Another striking feature of the EF_{Crust} temporal profiles, is that Ni, Pb and Zn (Figures 6.17, 6.18 and 6.19 respectively) behave almost identically. This suggests that they are derived from the similar sources, which due to their high EF_{Crust}, are likely to be anthropogenic.

Principal Components Analysis was used to assess inter-elemental compatibilities within the entire north western Mediterranean EF_{Crust} data set. The variation in the data set was explained by 5 PCs, the most significant of which were PC 1 (71 % of the variance - Figure 6.20) and PC 2 (20 % of the variance - Figure 6.21). PC 1 demonstrated that the majority of the variance was due to the most non-crustal elements (Cd, Pb, Zn) - the NEEs had comparable scores. The variation in PC 2 was largely due to Cd, which indicated that its geochemistry was different to that of Pb and Zn. The scores of PC 1 were plotted against the scores of PC 2 to investigate the relationships between elements in the north western Mediterranean aerosol (Figure 6.22). A cluster of Co, Fe, Mn and Na was observed, implying that these elements are from the same source and subject to similar atmospheric

Table 6.3: atmospheric trace metal aerosol EF$_{Crust}$ for the north western Mediterranean (n = 27) (LOD = limit of detection).

Element	Arithmetic Mean	Range	Standard Deviation	RSD (%)	Geometric Mean
Cd	113	Below LOD - 449	116	102	72.2
Co	2.54	Below LOD - 8.10	1.62	63.9	2.08
Cu	37.6	3.2 - 125	24.9	66.2	29.8
Fe	2.12	Below LOD - 4.25	1.01	47.6	1.87
Mn	3.06	Below LOD - 9.80	2.21	72.1	2.40
Na	3.85	0.44 - 9.80	2.58	67.0	2.88
Ni	20.1	1.71 - 76.9	17.8	88.5	13.5
Pb	129	Below LOD - 413	87.3	67.9	99.8
Zn	74.7	Below LOD - 331	67.4	90.2	53.1

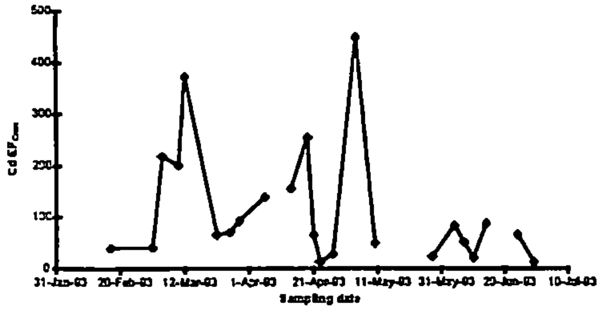


Figure 6.11: temporal variation of Cd EF$_{Crust}$.

Figure 6.12: temporal variation of Co EF$_{Crust}$.

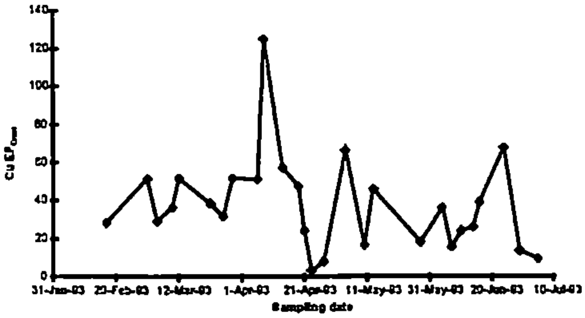


Figure 6.13: temporal variation of Cu EF$_{Crust}$.

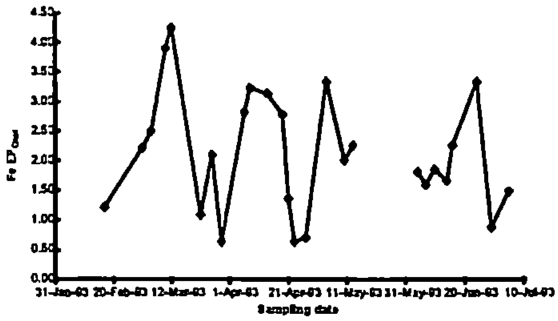


Figure 6.14: temporal variation of Fe EF$_{Crust}$.

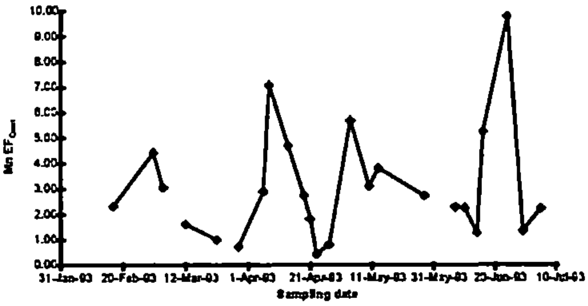


Figure 6.15: temporal variation of Mn EF$_{Crust}$.

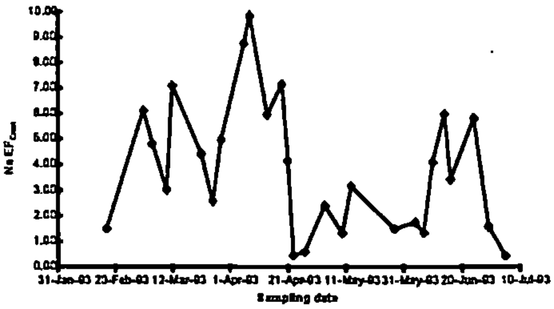


Figure 6.16: temporal variation of Na EF$_{Crust}$.

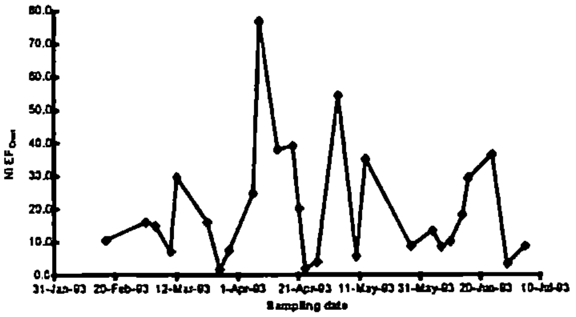


Figure 6.17: temporal variation of Ni EF$_{Crust}$.

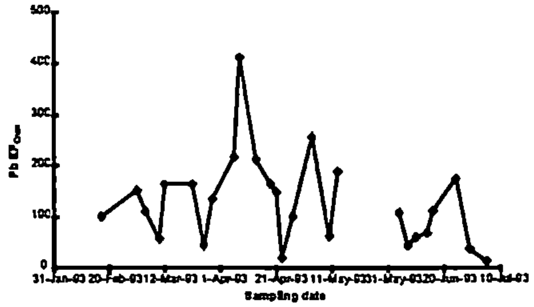


Figure 6.18: temporal variation of Pb EF$_{Crust}$.

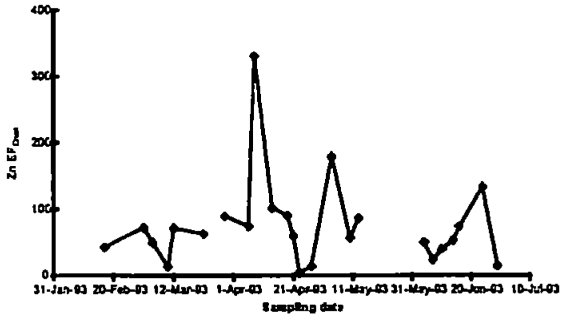


Figure 6.19: temporal variation of Zn EF$_{Crust}$.

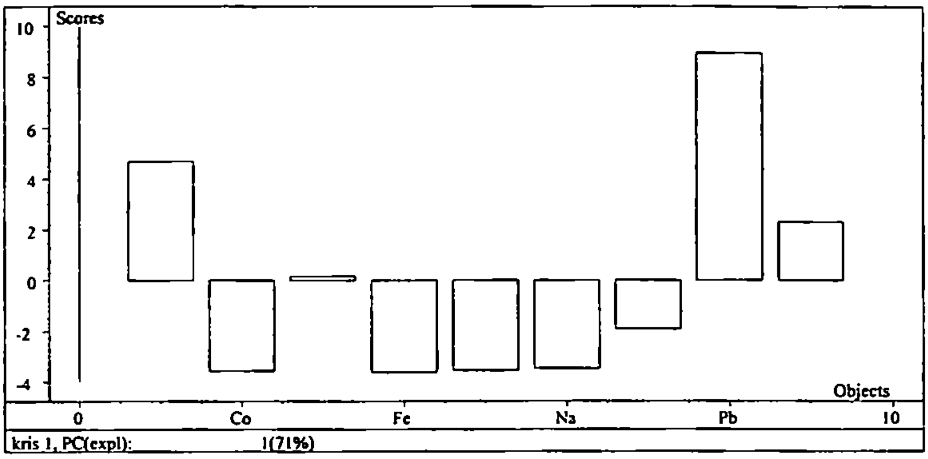


Figure 6.20: PC 1 loading weights displaying dominance of Al, Cu, Pb and Zn.

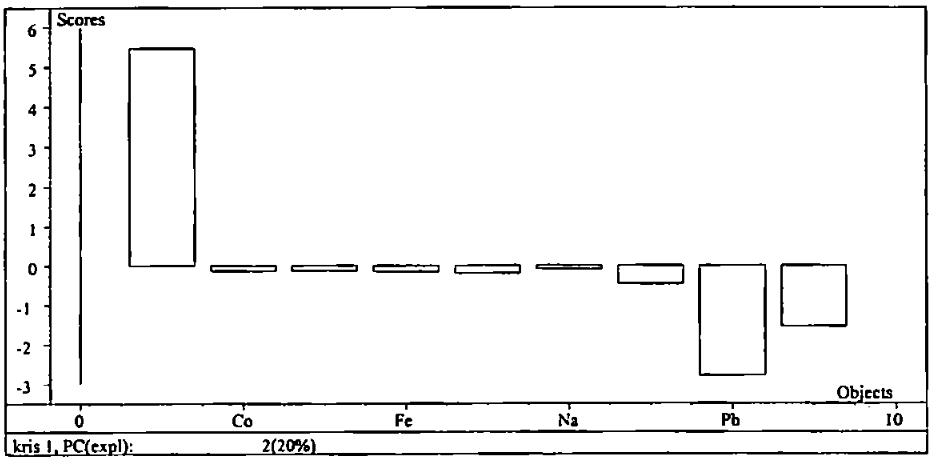


Figure 6.21: PC 2 loading weights displaying dominance of Al.

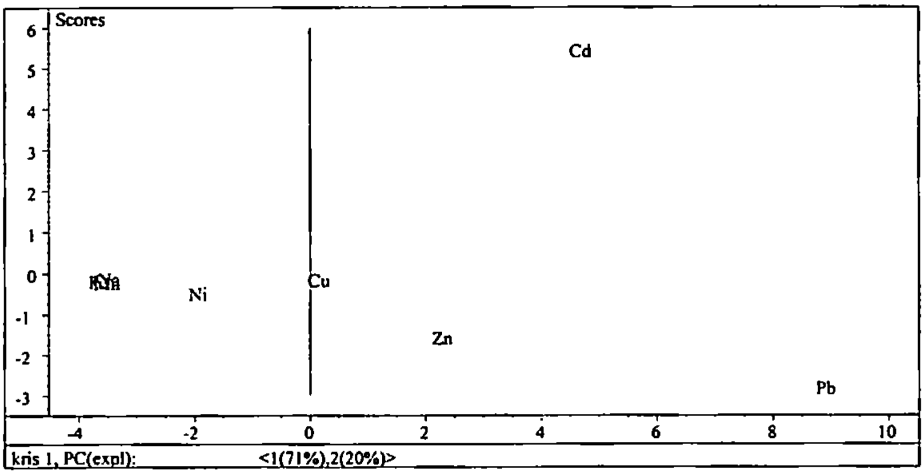


Figure 6.22: inter-elemental relationships revealed by PCA.

mechanisms. Copper, Ni and Zn appear to be subject to similar constraints, which are different to those of Co, Fe, Mn and Na; Cd and Pb were the most distinct. Although the relative standard deviation for Pb EF_{Crust} was low, its occurrence in the north western Mediterranean aerosol is controlled by different mechanisms compared with those for the crustally derived elements. Cadmium aerosol concentrations appeared to be controlled by mechanisms unique to Cd. Therefore, PCA has exposed further subtle differences between elements which may be indicative of elemental source rather than common removal processes. Such detail was not obtained by linear regression, and thus highlights the usefulness of PCA.

Arithmetic mean EF_{Crust} values obtained from the current study, are compared with values obtained from other studies in Table 6.4. The data reveals the variability, and inherent difficulty, in inter-annual comparisons of aerosol trace metal data. The most interesting observations are those for Cd (113) and Pb (129) which display lower EF_{Crust} values in the current study compared with reported values (approximately ten times lower for Pb and four times lower for Cd). This could be due to one or more of the following :

(i) natural inter-annual variation;

(ii) seasonal meteorological conditions favouring the injection and subsequent transport of a high quantity of crustally derived trace metals into the north western Mediterranean aerosol ;

(iii) in the case of Pb, a decline in anthropogenic emissions, e.g. from the combustion of leaded petrol (Hopper *et al.*, 1991; Krause *et al.*, 1993).

Natural inter-annual variation requires investigation over a period of decades to deduce if the information derived from the current study is anomalous. Meteorological conditions are likely to greatly influence aerosol trace metal concentrations, although whether they were responsible for high inputs of crustal material to the north western Mediterranean aerosol during the current study cannot be concluded from the data, since the EF_{Crust} of Fe and Mn are higher than observed for the Saharan influenced Tyrrhenian Sea aerosol (Chester *et al.*, 1984). However, it is possible that Fe and Mn concentrations in the north western Mediterranean aerosol have been enhanced by emissions from the steel industry such as that located to the east of the sampling site at Genoa (Huang *et al.*, 1994). The influence of the decline in Pb emissions (Wu and Boyle, 1997) are discussed in the context of $^{206/207}$Pb isotopic ratio observations.

Table 6.4: comparison of arithmetic mean aerosol associated trace metal EF_{Crust} values.

Element	Monaco[a] (n = 27)	Cap Ferrat[b]	Western Mediterranean[c] (Geometric mean) (n = 16)	Mediterranean Sea[d] (n = 21)	Tyrrhenian Sea[e] (Saharan influenced) (n = 4)
Al	1.00	1.0	1	1.0	1.0
Cd	113	392	2680	522	96
Co	2.54	-	-	-	-
Cu	37.6	24	-	14.5	5.6
Fe	2.12	1.2	-	1.1	0.92
Mn	3.06	2.6	-	2.5	0.84
Na	3.85	-	26.5	-	-
Ni	20.1	26	-	17	2.8
Pb	129	1024	595	487	46
Zn	74.7	128	-	86	5.6

[a]Current study; [b]Chester *et al.*, 1990; [c]Dulac *et al.*, 1987; [d]Chester *et al.*, 1993d; [e]Chester *et al.*, 1984. All samples underwent a HNO_3/HF digest prior to analysis with the exception of Dulac *et al.*, 1987 where the samples underwent a HNO_3/HCl digest.

The coastline of the Mediterranean Sea contains a number of major urban centres, with industry and tourism being major features. As a consequence, anthropogenic emissions are likely to be sources of trace metals to the Mediterranean aerosol population, particularly in the west of the region. Lead is a major component of such emissions, particularly from the combustion of leaded fuel.

The $^{206/207}Pb$ isotopic ratio was investigated in samples collected during the current study, and compared with Pb EF_{Crust} (Figure 6.23). Figure 6.23 revealed no statistically significant correlation between $^{206/207}Pb$ isotopic ratio and Pb EF_{Crust}.

Similar observations were made for the English Channel aerosol (section 5.1.1.1). The $^{206/207}Pb$ isotopic ratio appears to be relatively constant with a mean value of 1.14 which is close to that observed for natural European sources (Hopper et al., 1991) The diminished influence of western European anthropic emissions has led the comparatively enhanced importance of anthropogenic Eastern European inputs having a similar $^{206/207}Pb$ isotopic ratio than that for natural sources, explaining the lack of variability with Pb EF_{Crust}.

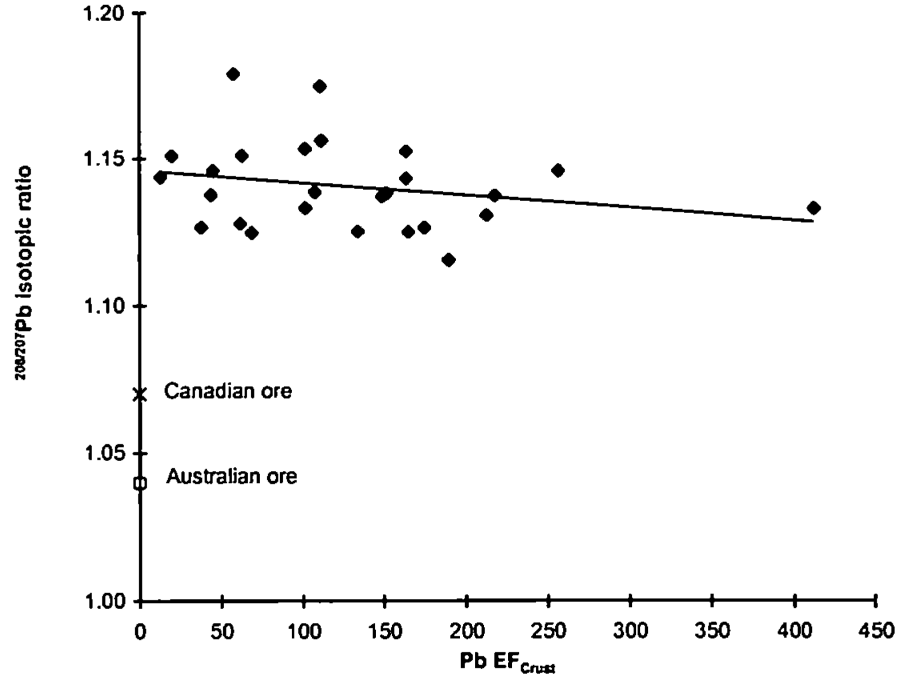


Figure 6.23: correlation of Pb EF$_{Crust}$ and $^{208/207}$Pb isotopic ratio (n = 27) (x = 1.14; σ = 0.02; RSD = 1.32 %) for the north western Mediterranean Sea aerosol, compared with the $^{208/207}$Pb isotope ratios for two Pb ores used in European fuels (Hopper *et al.*, 1991).

6.1.2 Transport of aerosol associated trace metals to the north western Mediterranean.

The north west Mediterranean aerosol is subject to stable meteorological conditions (see section 4.2.2) which are likely to have characteristic trace metal signatures. Initial wind directions, recorded at the start and end of the sampling period for each sample, indicated a strong southerly influence. Back trajectory analyses of selected samples which covered mainly W-NW-N air masses was carried out. Aerosol trace metal concentrations were plotted to assess the relative importance of each wind direction (± 22.5°) (Table 6.5 and Figures 6.24 to 6.33). Aluminium, Fe and Mn concentrations were highest in air masses originating from the N; Co concentration was greatest in W air masses; Na and Ni concentrations were greatest from the NW and NE; Pb concentrations were greatest from the NE, potentially from the industrial region of northern Italy; Cd, Cu and Zn displayed similar concentrations in each of the air mass directions, which suggests that they are mostly derived from central Europe, potentially the industrial regions.

A similar study was conducted using the EF$_{Crust}$ of the selected samples (Table 6.6 and Figures 6.34 to 6.42). All trace metals (except Co) displayed high EF$_{Crust}$ in air masses from a NW direction. This indicates that Al concentrations in NW air masses were low with respect to all other trace metals. ANOVA did not reveal any difference between wind directions for either the concentration, nor the EF$_{Crust}$ data sets. To investigate the influence of wind direction on trace metal sources, PCA of the

Table 6.5: mean trace metal concentration for each wind direction (ng m^{-3}) (± 22.5°).

Wind direction	Number of samples in each sector	Al	Cd	Co	Cu	Fe	Mn	Na	Ni	Pb	Zn
N	n = 3	542 ± 442	0.22 ± 0.23	0.21 ± 0.15	5.20 ± 3.36	518 ± 461	12.0 ± 12.4	497 ± 175	2.27 ± 1.65	22.0 ± 10.0	30.3 ± 22.7
NE	n = 1	230	0.16	0.22	4.8	224	5.00	1510	3.10	39.0	36.1
E	n = 0	-	-	-	-	-	-	-	-	-	-
SE	n = 0	-	-	-	-	-	-	-	-	-	-
S	n = 0	-	-	-	-	-	-	-	-	-	-
SW	n = 0	-	-	-	-	-	-	-	-	-	-
W	n = 2	226 ± 234	0.08 ± 0.06	0.23 ± 0.22	6.06 ± 4.82	184 ± 221	5.60 ± 7.21	705 ± 329	1.53 ± 1.74	27.0 ± 25.5	29.0 ± 21.2
NW	n = 2	126 ± 23.3	0.21 ± 0.11	0.09 ± 0.01	5.56 ± 0.30	263 ± 26.9	5.35 ± 1.06	1320 ± 410	3.22 ± 0.65	26.0 ± 0.05	31.2 ± 3.25

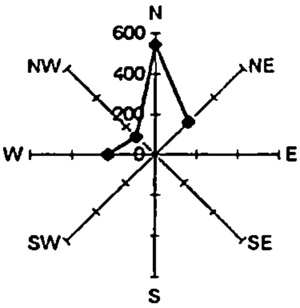


Figure 6.24: Al concentration vs. wind direction.

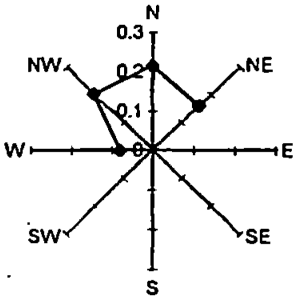


Figure 6.25: Cd concentration vs. wind direction.

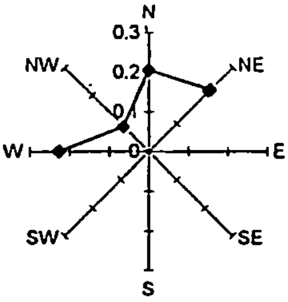


Figure 6.26: Co concentration vs. wind direction.

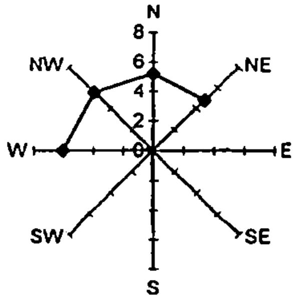


Figure 6.27: Cu concentration vs. wind direction.

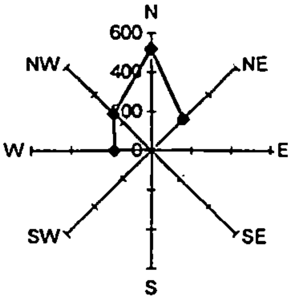


Figure 6.28: Fe concentration vs. wind direction.

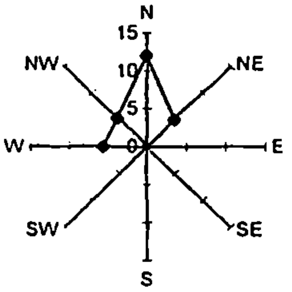


Figure 6.29: Mn concentration vs. wind direction.

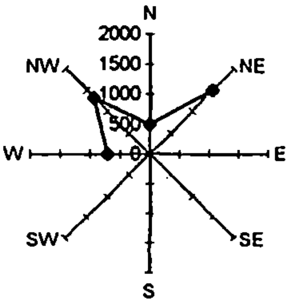


Figure 6.30: Na concentration vs. wind direction.

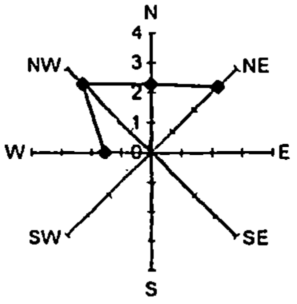


Figure 6.31: Ni concentration vs. wind direction.

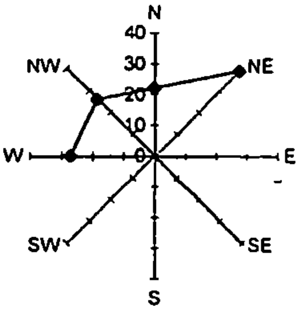


Figure 6.32: Pb concentration vs. wind direction.

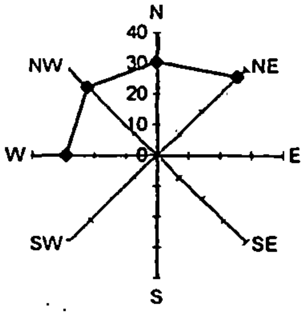


Figure 6.33: Zn concentration vs. wind direction.

Table 6.6: mean trace metal EF_{Crust} for each wind direction (± 22.5°).

Wind direction	Number of samples in each sector	Cd	Co	Cu	Fe	Mn	Na	Ni	Pb	Zn
N	n = 3	231 ± 308	1.83 ± 1.02	26.3 ± 34.7	1.82 ± 1.38	2.78 ± 2.66	1.10 ± 1.13	21.6 ± 28.5	96.7 ± 139	91.5 ± 123
NE	n = 1	65.0	3.47	24.3	1.36	1.83	4.13	20.2	149	60.0
E	n = 0	-	-	-	-	-	-	-	-	-
SE	n = 0	-	-	-	-	-	-	-	-	-
S	n = 0	-	-	-	-	-	-	-	-	-
SW	n = 0	-	-	-	-	-	-	-	-	-
W	n = 2	66.5 ± 37.5	3.95 ± 0.61	40.0 ± 16.6	0.93 ± 0.41	1.53 ± 1.12	3.23 ± 2.43	9.14 ± 2.12	118 ± 22.6	66.5 ± 33.2
NW	n = 2	205 ± 70.0	2.69 ± 0.55	52.5 ± 7.00	2.96 ± 0.25	3.74 ± 1.37	6.54 ± 0.84	38.6 ± 0.62	189 ± 33.9	96.4 ± 7.99

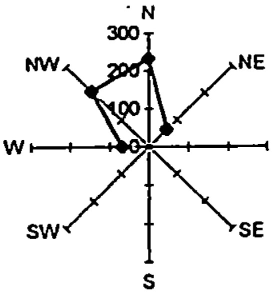


Figure 6.34: Cd EF_{Crust} vs. wind direction.

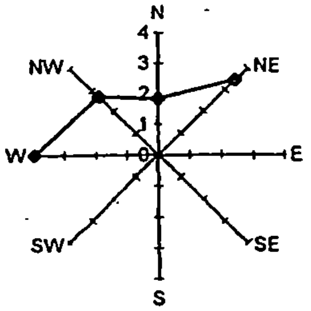


Figure 6.35: Co EF_{Crust} vs. wind direction.

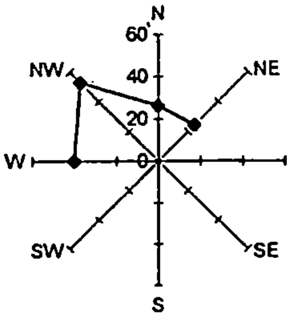


Figure 6.36: Cu EF_{Crust} vs. wind direction.

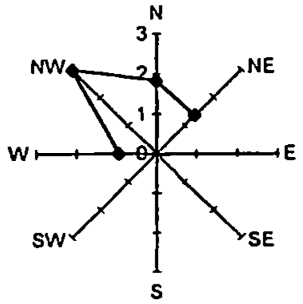


Figure 6.37: Fe EF_{Crust} vs. wind direction.

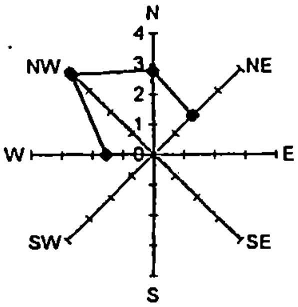


Figure 6.38: Mn EF_{Crust} vs. wind direction.

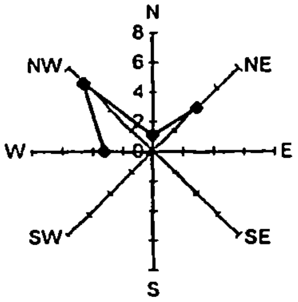


Figure 6.39: Na EF_{Crust} vs. wind direction.

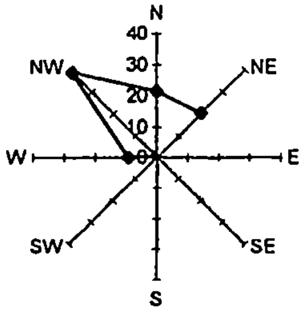


Figure 6.40: Ni EF_{Crust} vs. wind direction.

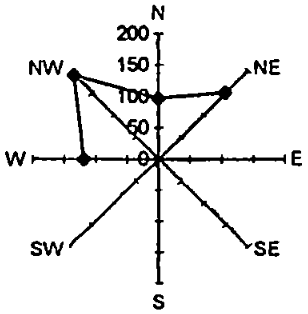


Figure 6.41: Pb EF_{Crust} vs. wind direction.

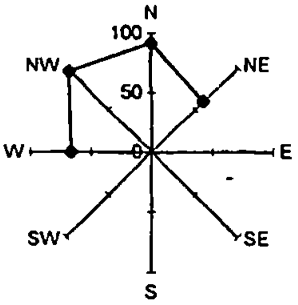


Figure 6.42: Zn EF_{Crust} vs. wind direction.

EF_{Crust} data set was undertaken. The total variance was described by 9 PCs. PC 1 represented the greatest sample variation at 62 % and was dominated by all variables (Figure 6.43). PC 2 accounted for 9 % of the variance which was largely attributable to variation in wind direction. The variation in the EF_{Crust} of Cd, Fe and Mn were also significant in this PC (Figure 6.44). The scores of PC 1 were plotted against the scores of PC 2 to assess the influence of wind direction on aerosol trace metal EF_{Crust} composition (Figure 6.45). The relationship between wind direction and EF_{Crust} in the north western Mediterranean aerosol was not easily defined. This is attributable to the period of collection of north western Mediterranean aerosol samples making it arduous to determine (i) whether the sample was collected under the influence of one air mass, and (ii) overall wind direction. The samples can, however, be regarded according to northerly, southerly and westerly derived groups. However, it is clear that southerly winds were important during the sampling period with influence from other wind directions in the order: W > N > E. This agrees with observations made by Guerzoni *et al.* (1989) who noted a dominance of wind in the western Mediterranean from SW to NW (38 %) and NW to NE (28 %). Guerzoni *et al.* (1993) also observed strong southerly episodes between February and March 1991.

PCA was used to investigate the relationship between wind direction and $^{206/207}Pb$ isotopic ratios. Two PCs described the variation in the data set: PC 1 represented 15 % of the variation, which was largely due to wind direction (Figure 6.46); PC 2 represented 85 % of the variation, which was largely attributable to variations in $^{206/207}Pb$ isotopic ratio (Figure 6.47). The scores of PC 1 were plotted against the scores of PC 2 (Figure 6.48). From this it was possible to group the samples according to wind direction, which indicated that the $^{206/207}Pb$ isotopic ratio did vary depending on the wind direction and hence the source. It can be seen that the N and NE air masses are distinctly different from NW air masses. This is probably due to the proximity to the Atlantic Ocean (and therefore marine sources) in a NW direction from the sampling site, while air masses travelling from a N/NE direction will have passed over central/eastern Europe prior to sampling, and will thus be terrestrially (crustally and anthropogenically) influenced.

6.1.3 Aerosol trace metal fluxes to the north western Mediterranean Sea.

Assuming that the trace metal settling velocities obtained for the western English Channel are applicable to other sampling sites, they can then be used to estimate the dry deposition fluxes to the north western Mediterranean Sea. The dry fluxes obtained in this study are compared with other western Mediterranean studies in Table 6.7.

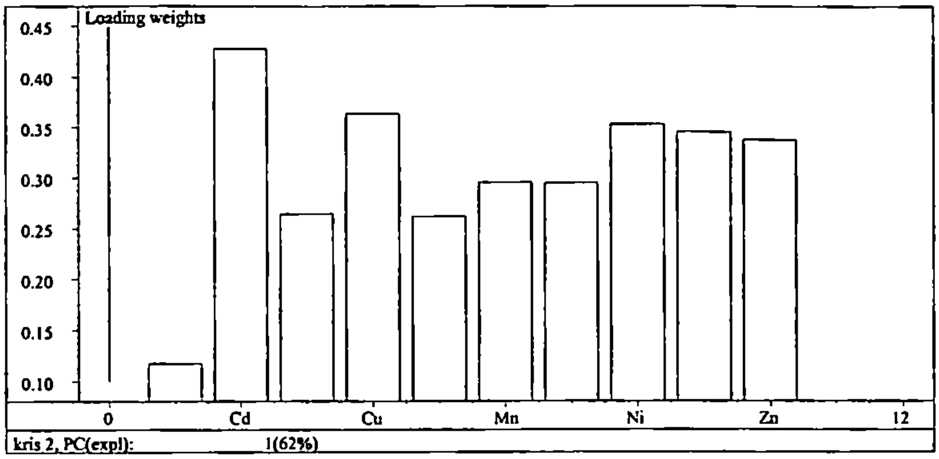


Figure 6.43: PC 1 loading weights displaying dominance of all trace metal EF_{Crust}.

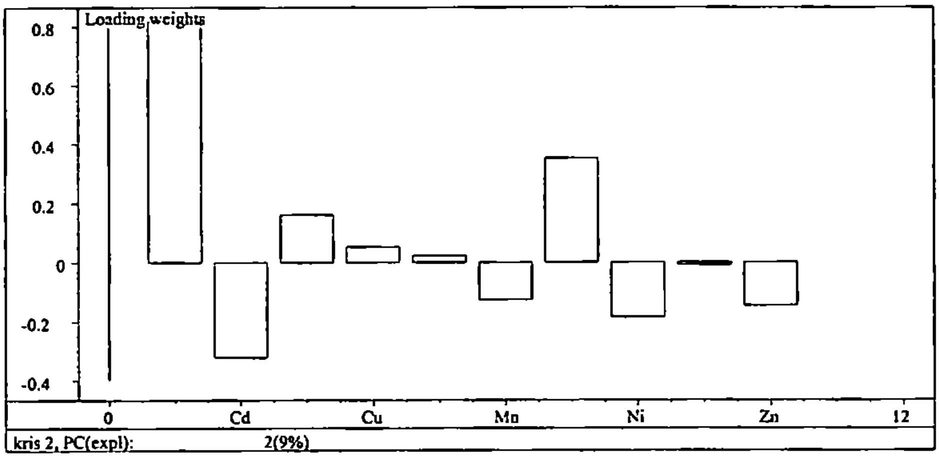


Figure 6.44: PC 2 loading weights displaying the dominance of wind direction, and Co, Cu, Fe and Na EF_{Crust}.

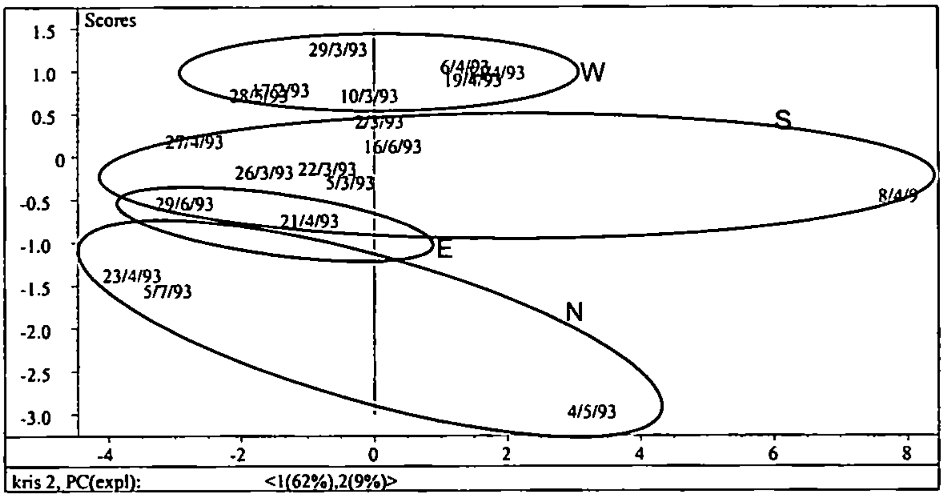


Figure 6.45: relationship of samples according to wind direction.

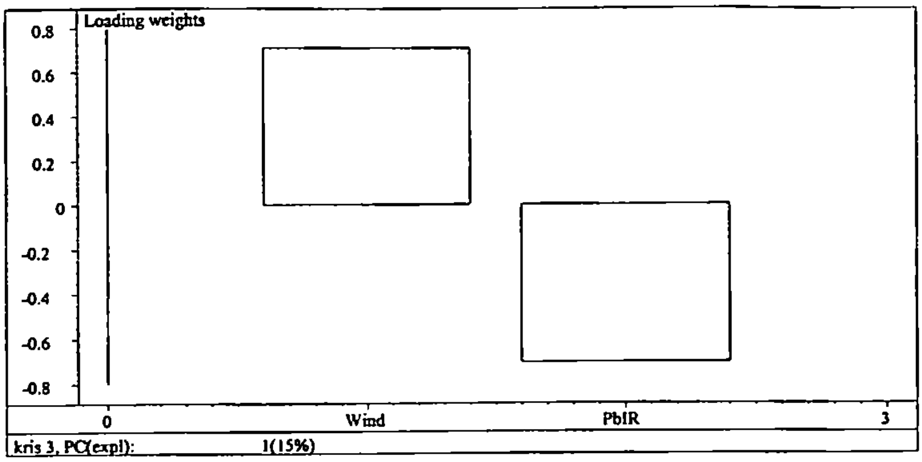


Figure 6.46: PC 1 loading weights displaying dominance of wind direction.

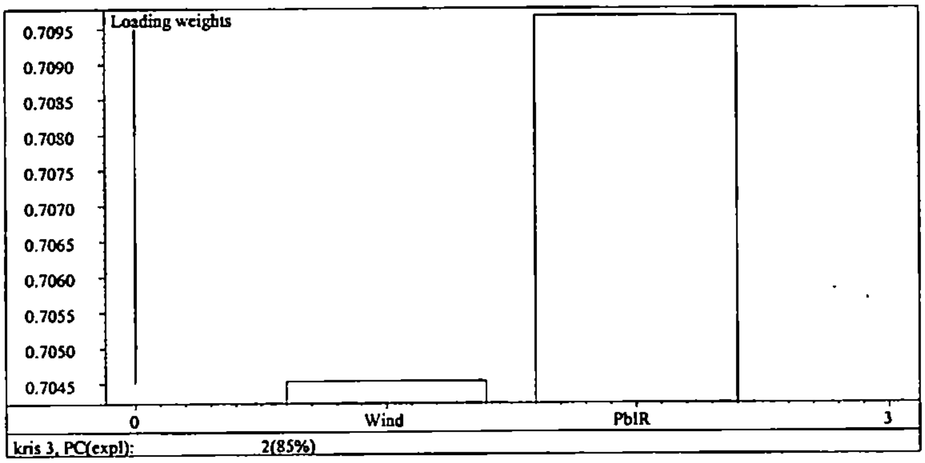


Figure 6.47: PC 2 loading weights displaying dominance of $^{206/207}$Pb isotopic ratios.

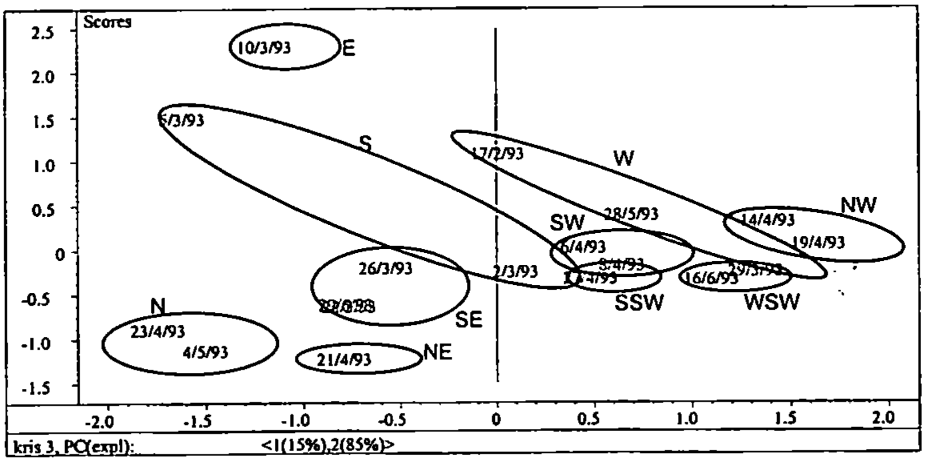


Figure 6.48: relationship of samples according to wind direction.

Table 6.7: comparison of gross dry deposition fluxes to the western Mediterranean Sea derived from four separate studies (ng cm^{-2} yr^{-1}).

Element	Current study	Arnold *et al.* (1982)	Chester *et al.* (1990)	Guieu *et al.* (1991)
Al	8710	5000	9379	-
Cd	0.15	13	4.9	-
Co	1.98	3.5	1.8	3.0
Cu	69.0	96	89.5	13
Fe	718	5100	-	8220
Mn	160	-	156	145
Na	26 900	-	-	-
Ni	4.45	-	24	10
Pb	18.8	1050	141	29
Zn	81.3	1080	-	-

Aluminium displayed a similar flux to that observed by Chester *et al.* (1990); Co and Mn dry fluxes were also similar to previous results. However, dry fluxes of Cd, Fe, Ni, Pb and Zn were lower than reported for the other studies. This may be a result of (i) the unrepresentative nature of the applied western English Channel settling velocities, (ii) seasonal and inter-annual variability of sampling conditions between the studies reported in Table 6.7 and (iii) reduced anthropogenic emissions, as a result of more stringent European air quality directives and the adoption of cleaner industrial technologies.

6.1.4 Potential aerosol associated trace metal marine biogeochemistry.

6.1.4.1 Sequential leaching of aerosol associated trace metals.

A three stage sequential leach was applied to a selection of samples (n = 8) to assess atmospheric trace metal solid state speciation, and potential marine biogeochemistry. Tables 6.8, 6.9 and 6.10, and Figure 6.49 display the proportion of trace metal in each of the three stages (1. easily exchangeable; 2. carbonate/oxide; 3. residual). The greatest concentrations of Al and Fe were located in stage three of the leach (approximately 80% of the total), indicative of their crustal origin, although 8% of Al and 5% of Fe were located in stage one of the leach.

Table 6.8: north western Mediterranean sequential leach stage 1 % trace metal solubility (n = 8) (LOD = limit of detection).

Element	Arithmetic Mean	Range	Standard Deviation	RSD %	Geometric Mean
Al	8.13	3.00 - 12.0	3.14	38.6	7.43
Cd	71.4	55.0 - 96.5	14.7	20.6	70.1
Fe	3.63	Below LOD - 17.0	5.61	155	2.07
Mn	38.5	23.0 - 53.0	11.2	29.0	37.0
Pb	73.9	50.0 - 93.2	13.7	18.5	72.7

Table 6.9: north western Mediterranean sequential leach stage 2 % trace metal solubility (n = 8) (LOD = limit of detection).

Element	Arithmetic Mean	Range	Standard Deviation	RSD %	Geometric Mean
Al	6.75	1.00 - 17.0	5.44	80.7	4.83
Cd	18.3	3.50 - 45.0	16.7	91.6	13.1
Fe	17.5	8.00 - 33.0	7.69	43.9	16.1
Mn	5.25	Below LOD - 11.0	4.65	88.6	16.1
Pb	24.9	5.94 - 48.0	13.5	54.1	21.3

Table 6.10: north western Mediterranean sequential leach stage 3 % trace metal solubility (n = 8) (LOD = limit of detection).

Element	Arithmetic Mean	Range	Standard Deviation	RSD %	Geometric Mean
Al	85.6	77.0 - 91.0	5.55	6.49	85.5
Cd	10.3	Below LOD - 30.6	11.6	113	5.20
Fe	79.0	50.0 - 92.0	13.0	16.5	77.9
Mn	56.3	35.0 - 77.0	15.2	27.1	54.3
Pb	1.26	0.59 - 2.00	0.62	49.2	1.14

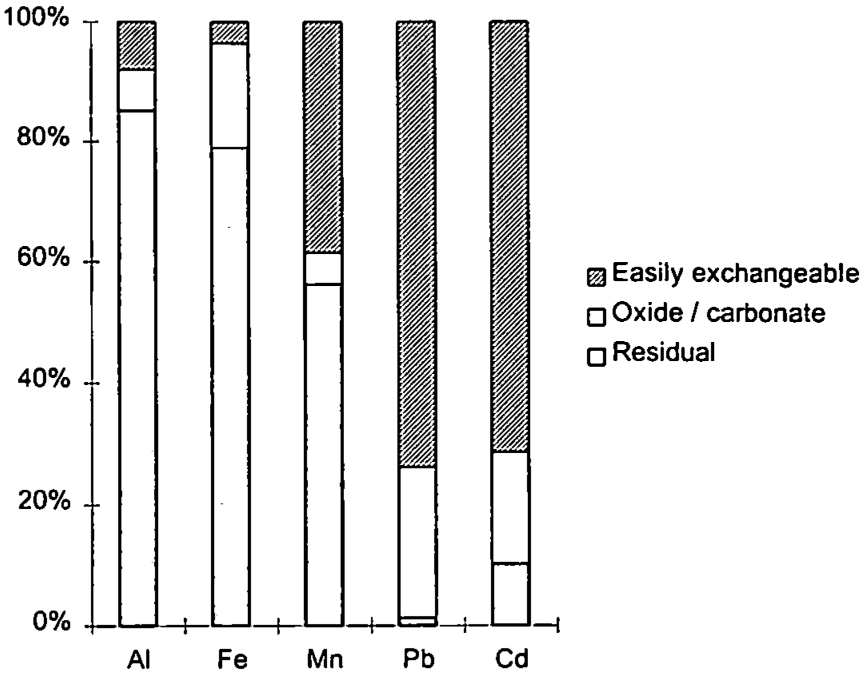


Figure 6.49: mean solid state speciation of trace metals in aerosol particles over the western Mediterranean Sea (n = 8).

PCA was used to investigate the relationship between wind direction and percent trace metal located in stage one (i.e. easily exchangeable association). The PC 2, which explained 12 % of the sample set variation, contained the highest loading weight for wind direction (Figure 6.50). The PC 3, which represented 17 % of the variation, contained high loading weights form Al and Pb, which were found to be the most variable trace metals in the sample set (Figure 6.51). The scores of the two PCs were plotted against each other (Figure 6.52). It was possible to group the samples according to wind direction, which suggested that wind direction, and hence trace metal source, influenced the easily exchangeable portion of trace metals, even though the variation in wind direction was limited.

6.1.4.2 Sea water solubility of aerosol associated trace metals.

As the dry deposition fluxes indicated the atmosphere is an important source of trace metals to the marine environment, with their subsequent involvement in marine biogeochemical cycles determined by their sea water solubility. Arithmetic and geometric means, range, standard deviation and relative standard deviation for percent aerosol associated trace metal sea water solubility of selected samples (n = 8) are displayed in Table 6.11. All percent trace metal solubilities were comparable with solubilities reported by other workers (e.g. Hodge *et al.*, 1978). Trace metal solubilities exceeded those reported for anthropogenic rich aerosols for Al, Co and Cu, yet were lower for Ni and Pb. All trace metal solubilities were higher than those reported for dust rich aerosols (Hodge *et al.*, 1978).

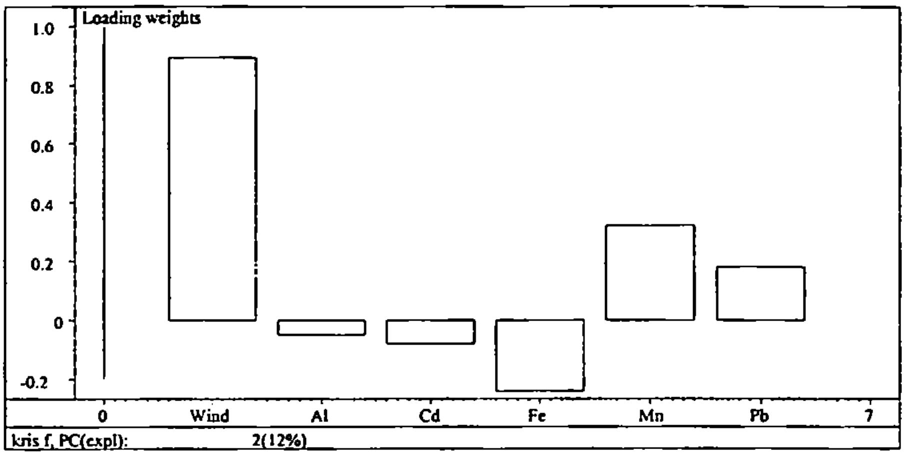


Figure 6.50: PC 2 loading weights displaying dominance of wind direction, and Mn and Pb % easily exchangeable trace metal.

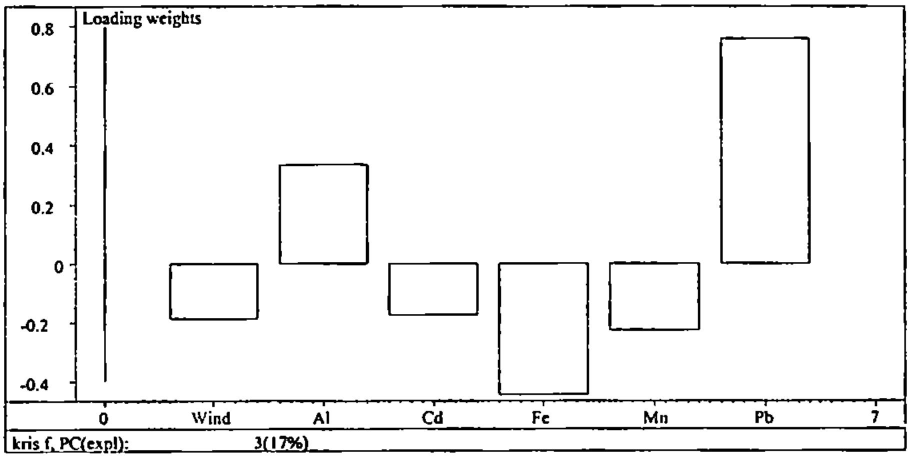


Figure 6.51: PC 3 loading weights displaying dominance of Al and Pb % easily exchangeable trace metal.

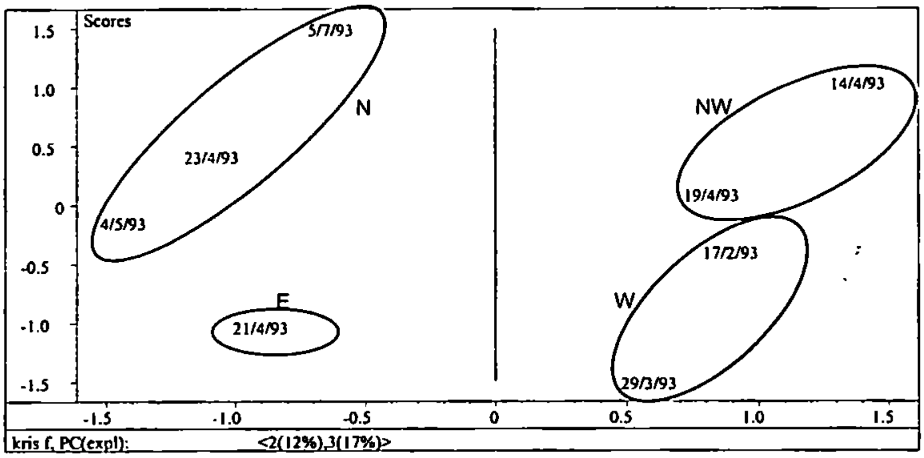


Figure 6.52: relationship of samples according to wind direction.

Table 6.11: percentage solubilities for north western Mediterranean aerosol associated trace metals (n = 8) (LOD = limit of detection).

Element	Arithmetic Mean	Range	Standard Deviation	RSD %	Geometric Mean
Al	0.93	0.13 - 5.88	1.99	208	0.35
Co	43.1	13.9 - 79.6	22.0	51.1	37.8
Cu	34.1	7.58 - 83.6	25.2	73.7	25.9
Ni	40.8	3.34 - 67.9	23.1	56.5	30.2
Pb	36.7	Below LOD - 100	37.5	102	13.7

EF_{Crust} revealed that the non-crustal portion of the trace metals dissolved in sea water, while the crustal portion did not.

Principal Components Analysis was applied to percent soluble fraction of each trace metal and sample wind direction to investigate their relationship. PC 1 described 31 % of variation, with wind direction, Al, Co and Cu percentage solubility being important (Figure 6.53). PC 2 represented 28 % of the variation which was due to the variation in trace metal percentage solubility (Figure 6.54). The scores of PC 1 were plotted against the scores of PC 2 (Figure 6.55). The grouping was evident, but not particularly clear for four samples. The NW and W samples were separated forming two groups, each containing a NW and a W derived sample. However, in each group, the NW sample was closer to the N group than the W sample. This is probably due to the inability to accurately ascertain the track of the dominant air mass sampled (see section 6.1.2), rather than the quality of the data, or any artefacts arising from the use of PCA on a limited data set.

The chemical speciation of the dissolved trace metals (represented as the percent $Lumogallion_{Non-labile}$/ $ACSV_{Non-labile}$ of the total soluble fraction) was found to be: Al (99%), Co (48%), Cu (45%), Ni (48%) and Pb (2 %) (Table 6.12). The degree of organic complexation may therefore be ranked in the following order (i.e. Al > Ni ~ Co ~ Cu > Pb). This data clearly highlights the importance of aerosol material as a potential source of seawater soluble organic complexing ligands. The significance this pool of complexing ligands to marine systems has been previously documented (see section 5.2.2.1 and Fones, 1996).

6.2 Trace metal inputs to the Mediterranean Sea.

In section 6.1 it was shown that consideration of trace metal sea water solubility must be included when determining the impact of dry inputs of trace metals to the marine environment. Table 6.13 shows dry fluxes (which were corrected to account for sea water solubility), aerosol derived dry annual inputs and dissolved dry inputs of aerosol associated trace metals to the Mediterranean Sea, which has a surface area ~2,500, 000 km^2.

Rainfall during the sampling period was low (~ 107 mm between 17 February and 9 July 1993), therefore, dry inputs were likely to have been the dominant atmospheric source of trace metals to the Mediterranean Sea, during this period. A large atmospheric-ocean input of crustal material may also have consequences for heavy metal transport within the marine environment, as aerosol heavy metals

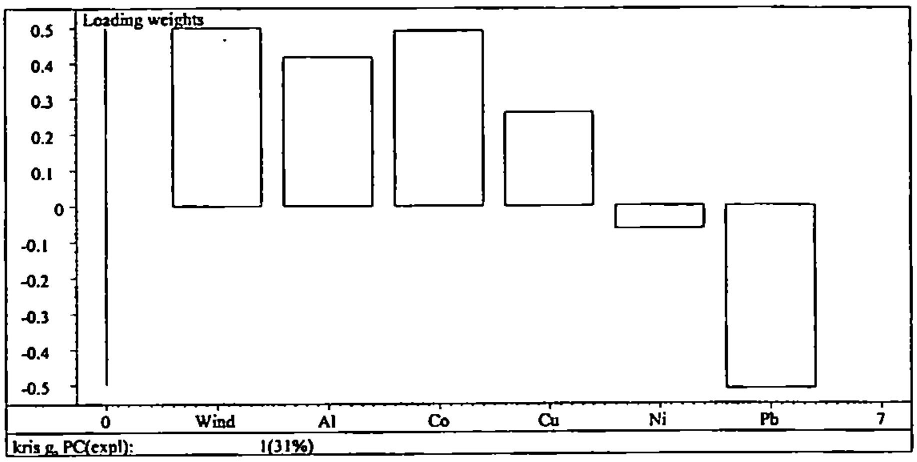


Figure 6.53: PC 1 loading weights displaying dominance of wind direction, and Al, Co and Cu % trace metal sea water solubilities.

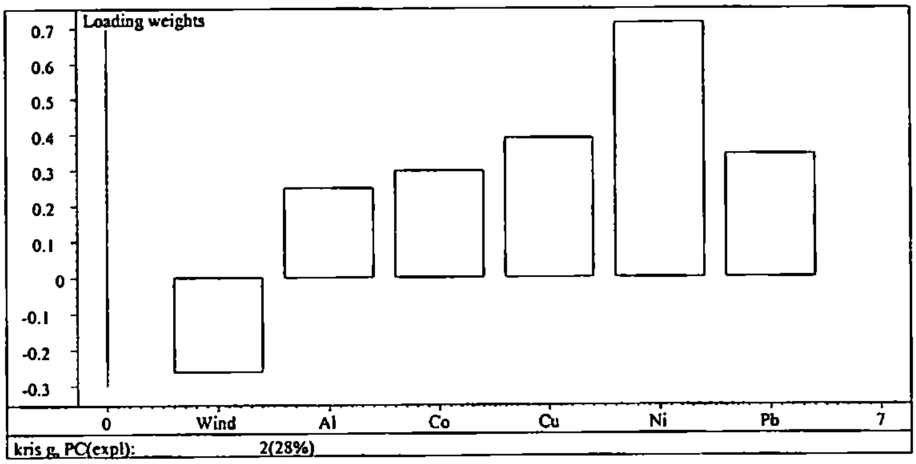


Figure 6.54: PC 2 loading weights displaying dominance of all trace metal % sea water solubilities.

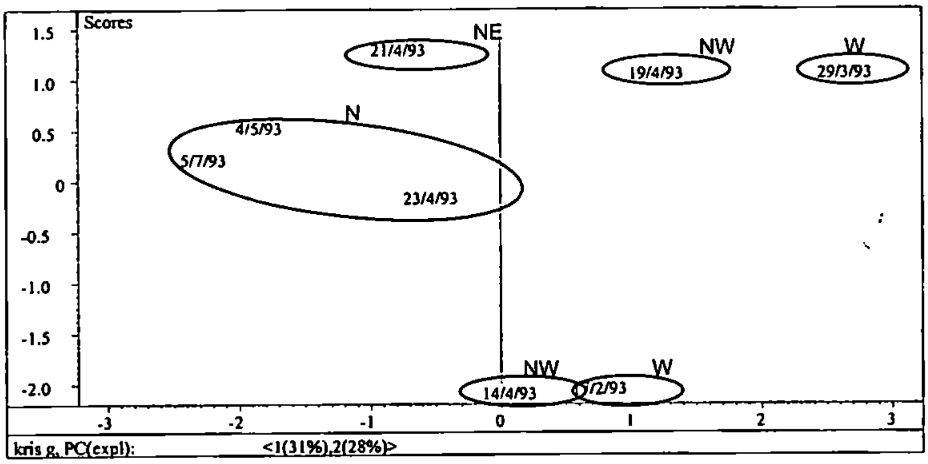


Figure 6.55: relationship between samples according to wind direction.

Table 6.12: percentage Lumogallion/ACSV$_{Labile}$ of the total dissolved fraction of trace metals from north western Mediterranean aerosols (n = 8) (LOD = limit of detection).

Element	Arithmetic Mean	Range	Standard Deviation	RSD %	Geometric Mean
Al	99.4	98.3 - 100	0.69	0.69	99.4
Co	48.1	17.2 - 80.8	24.5	51.0	41.9
Cu	44.6	3.10 - 88.2	31.6	70.8	29.5
Ni	48.4	13.2 - 94.1	27.2	56.3	40.5
Pb	1.80	Below LOD - 11.0	4.48	245	1.49

Table 6.13: corrected dry fluxes, dry inputs and dissolved dry inputs of aerosol associated trace metals to the Mediterranean Sea (n = 27).

Element	Gross dry flux ($ng\ cm^{-2}\ yr^{-1}$)	Sea water solubility (%)	Corrected dry flux ($ng\ cm^{-2}\ yr^{-1}$)	Corrected dry input ($t\ yr^{-1}$)	Dissolved dry input ($t\ yr^{-1}$)	Total dry input ($t\ yr^{-1}$)
Al	8710	0.9	8680	217 000	2000	218 000
Co	2.0	43	1.1	28	21	50
Cu	69	34	46	1140	590	1730
Ni	4.5	41	2.6	66	45	110
Pb	19	37	12	298	170	470

such as Pb and Zn may be scavenged by crustal particles, subsequent to them being solubilised from anthropogenically derived aerosol particles in contact with sea water (Kersten *et al.*, 1991). However, since this period of investigation was limited to only a few months, annual variations in meteorological conditions were not detected. Thus, it is probable that rainfall, occurring at times outside the sampling period, would lead to the greater importance of wet deposition of trace metals.

6.3 Summary of atmospheric trace metal characteristics over the north western Mediterranean Sea.

The concentration of trace metals in the north western Mediterranean aerosol were found to be comparatively invariable (RSD < 110 %), with the greatest variability demonstrated by Al and Pb. This implied a continuous trace metal supply which were perturbed by Al or Pb laden air masses. EF_{Crust} < 10 were obtained for Al, Co, Fe, Mn and Na, with PCA revealing a tight cluster between Co, Fe and Mn. The low EF_{Crust} for Na could be due to increased crustal concentrations with respect to Na. A comparison of EF_{Crust} with other European studies revealed comparable values for Co, Cu, Fe, Mn and Ni, although Cd, Pb and Zn were much lower than reported elsewhere. This could be due to increased crustal input, reduced anthropogenic emissions or natural inter-annual variation. $^{206/207}Pb$ isotopic ratios displayed a weak negative correlation with Pb EF_{Crust} in agreement with Kersten *et al.* (1992). However, $^{208/207}Pb$ isotopic ratio could not be used to determine a decline in the emission of Pb from the combustion of leaded fuels.

Aluminium and Fe displayed a significant proportion in the easily exchangeable stage (stage one) of the sequential leach. This suggested that the crustal material was weathered during long range transport, enabling enhanced leaching by the stage one reagent, or that a portion of the trace metal composition was anthropogenic in origin. Cadmium and Pb were largely contained within the easily exchangeable fraction, which is indicative of their anthropogenic nature. All aerosol trace metal percentage sea water solubilities were higher than those reported for dust rich aerosols. However, the percentage sea water solubilities of Al, Co and Cu exceeded those reported for anthropogenic rich aerosols. This may imply an anthropogenic origin for Al, Co and Cu, or it may be as a result of weathered crustal material, as indicated by the increased proportion of Al in stage one of the sequential leach.

The current study resulted in trace metal dry fluxes which were comparable with other western Mediterranean studies for Al, Co and Mn; all other trace metals displayed lower fluxes. This is possibly due to inter-annual variation in aerosol concentrations, or the use of non-representative settling velocities. Dry inputs were considered to be the dominant atmospheric source of trace metals due to the low volume of rainfall during the sampling period.

Chapter 7.

Atmospheric trace metal characteristics of the Celtic Sea.

Chapter 7.

Atmospheric trace metal characteristics of the Celtic Sea.

7.1 The concentrations and geochemistry of trace metals in the Celtic Sea aerosol.

A comparison of the aerosol concentrations of the Celtic Sea with other European regions (Table 5.1) revealed comparable concentrations of Al, Cd and Cu, relatively higher concentrations of Co, Fe, Mn, Na and Ni, and relatively lower concentrations of Pb and Zn. The concentrations support the general contention that the Celtic Sea aerosols were mainly marine and less anthropogenically influenced. However, enhanced concentrations of Co, Fe, Mn and Ni could have originated by long range transport from North America or from Europe or from regional sources in the South West Peninsula of the UK.

Arithmetic and geometric means, range, standard deviation and relative standard deviation of the aerosol trace metal concentrations are presented in Table 7.1. The trace metals can be ranked according to their relative standard deviations as follows: Cd (238%) > Cu (174%) > Pb (167%) > Co (162%) > Zn (150%) > Fe (137%) > Ni (126%) > Na (125%) > Mn (97%) > Al (63%). Figures 7.1 to 7.10 display the temporal variation of trace metal concentration, over 16 days, OMEX Cruise 1. All elements, except Al and Na, displayed similar profiles. This was higher concentrations at the start and end of the cruise (i.e. closer to the land) with lower concentrations observed during the middle of the cruise (i.e. at ~ 320 km from land). Aluminium (Figure 7.1) displayed two concentration peaks superimposed upon the basic profile: the first (between 5-10 June) was obtained from samples under the influence of a westerly air stream (see Appendix 6), so it is possible that the material had been transported from America, or the air mass had passed over Europe/North Africa prior to the air mass changing track to a westerly direction. In either scenario, the aerosols appeared not to have been anthropogenically-modified, due to the absence of Cd (Figure 7.2) and Pb (Figure 7.9) peaks. A second increase in Al concentrations (between 12-18 June) was obtained from samples which had been collected under the influence of a northerly air stream which had traversed Ireland prior to sampling. It is possible that the air mass entrained Al containing particles during its passage over Ireland, although was unlikely to have been anthropogenically influenced due to the absence of other trace metal peaks. Sodium concentrations (Figure 7.7) displayed a contrasting profile of low concentrations close to land, and high concentrations at a distance from land (11 June). This suggests that all the elements with the exception of Na have a terrestrial (crustal/anthropogenic) source (Austin and Millward, 1986), while Na was mainly marine generated.

Table 7.1: atmospheric trace metal aerosol concentrations for the Celtic Sea (n = 14) (LOD = limit of detection).

Element	Arithmetic Mean (ng m^{-3})	Range (ng m^{-3})	Standard Deviation	RSD (%)	Geometric Mean (ng m^{-3})
Al	300	61.0 - 697	188	62.7	244
Cd	0.37	Below LOD - 3.33	0.88	238	0.23
Co	1.14	Below LOD - 5.56	1.85	162	1.00
Cu	32.9	Below LOD - 183	57.4	174	3.00
Fe	564	62.5 - 2940	771	137	300
Mn	26.5	1.97 - 103	25.7	97.0	17.4
Na	550 000	119 000 - 2 050 000	686 000	125	33 100
Ni	76.0	8.34 - 372	95.8	126	46.8
Pb	4.95	Below LOD - 30.6	8.27	167	2.66
Zn	52.6	Below LOD - 226	79.0	150	13.6

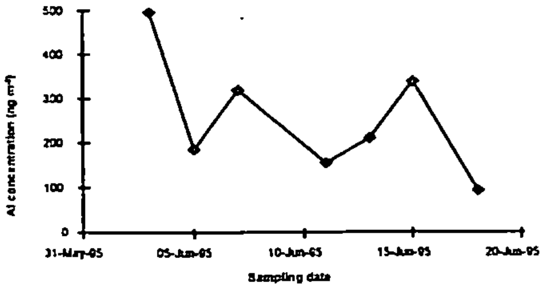


Figure 7.1: temporal variation in Al concentration during OMEX cruise 1.

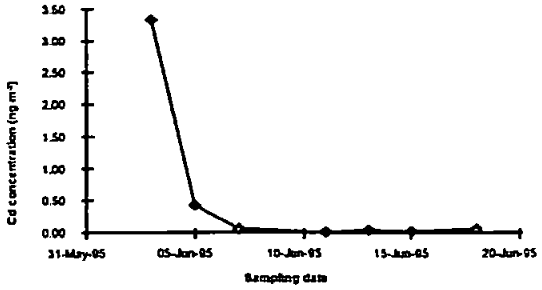


Figure 7.2: temporal variation in Cd concentration during OMEX cruise 1.

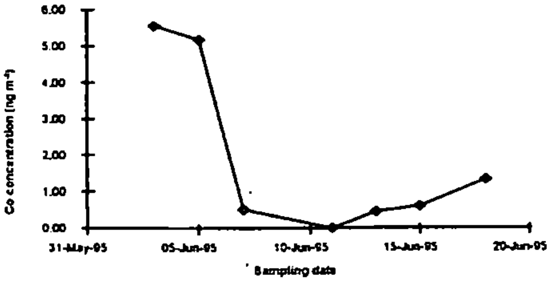


Figure 7.3: temporal variation in Co concentration during OMEX cruise 1.

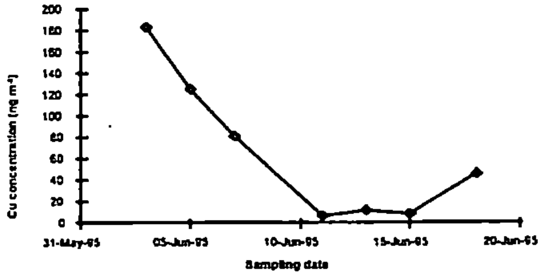


Figure 7.4: temporal variation in Cu concentration during OMEX cruise 1.

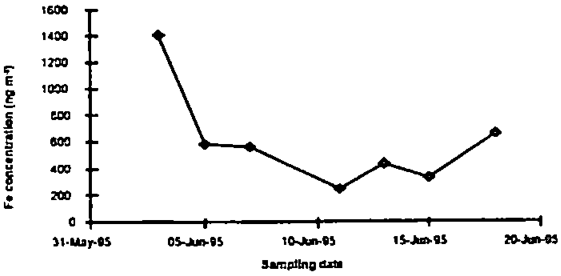


Figure 7.5: temporal variation in Fe concentration during OMEX cruise 1.

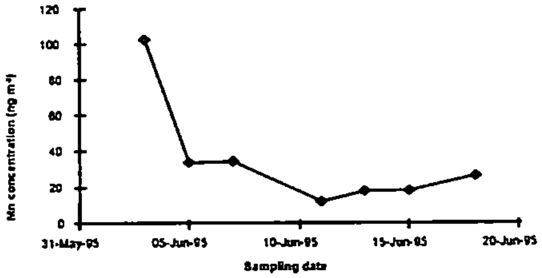


Figure 7.6: temporal variation in Mn concentration during OMEX cruise 1.

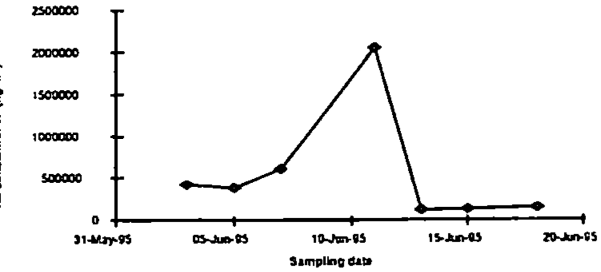


Figure 7.7: temporal variation in Na concentration during OMEX cruise 1.

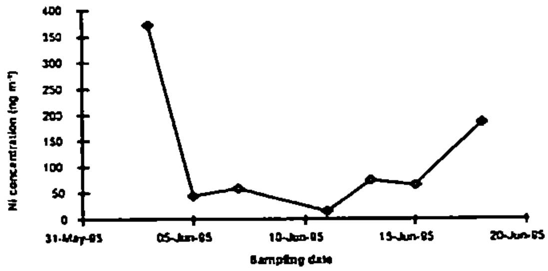


Figure 7.8: temporal variation in Ni concentration during OMEX cruise 1.

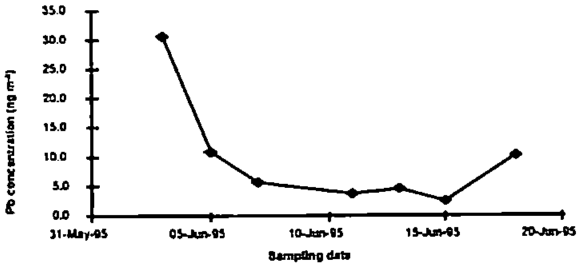


Figure 7.9: temporal variation in Pb concentration during OMEX cruise 1.

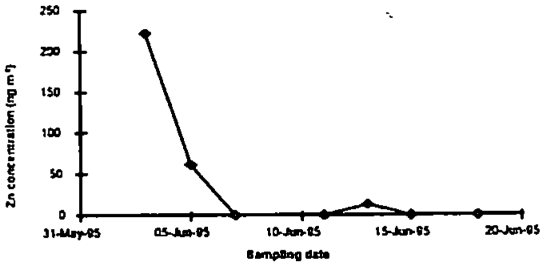


Figure 7.10: temporal variation in Zn concentration during OMEX cruise 1.

With the exception of Al and Zn, the trace metal concentrations observed during the autumn cruise (OMEX cruise 2) (Figures 7.11 to 7.16), were lower than observed during the summer cruise. Indeed, the concentrations of Cd, Co, Cu and Pb were often below the limit of detection (see Appendix 6), and therefore, temporal plots of these elements for the autumn period have not been presented. In addition, the profile observed for the majority of elements during the summer period was not reflected during the autumn period. Aluminium (Figure 7.11) again displayed two concentration peaks: the first peak was obtained from a sample which had been collected under the influence of a north westerly air stream which had passed over Ireland and South Wales prior to sampling. This sample also had elevated Fe (Figure 7.12), Mn (Figure 7.13) and Zn (Figure 7.16) concentrations. The second Al concentration peak (between 10-11September) was associated with a northerly air stream which had been influenced by the passage of the remains of Hurricane Iris (Meteorological Office, 1995). This tropical storm was large enough to cause considerable disturbance of the Atlantic atmosphere, and could have enhanced entrainment of crustal material into the aerosol. Such material may have been derived from the American continent or North Africa. It is also likely that the European aerosol was sufficiently disturbed as to mix with the Celtic Sea aerosol (usually beyond its limit - Pacyna et al., 1984) to have caused elevated levels of these elements. Increases in Fe, Mn, Ni and Zn concentrations were observed between the 7 and 9 of September. This sample was collected under the influence of a northerly air stream, which was also potentially modified by Hurricane Iris. It is possible that Fe, Mn and Zn were associated with a smaller particle size compared with Al, Cu and Ni, thus enabling them to be transported in suspension comapred to their larger counterparts. Such a distinction would only be evident following considerable particle removal, e.g. by the copious rainfall observed during the passage of the tropical storm. Iron, Mn and Zn displayed increased concentrations in the sample collected between 11 - 12 September, which was within the confines of the English Channel and was therefore likely to be anthropogenically influenced. Sodium (Figure 7.14) displayed a similar profile to that observed during the summer cruise.

Statistical analyses, using ANOVA, revealed significant differences (to 95 %) for Cu and Pb between the two periods. The lower autumn concentrations displayed by all of the elements (except Al and Zn) may be due to increased washout caused by prolific rainfall during the passage of the aftermath of Hurricane Iris.

7.1.1 Potential sources of trace metals to the Celtic Sea aerosol.

EF_{Crust} were calculated using Taylor (1964) crustal ratios (Appendix 2). Arithmetic and geometric means, range, standard deviation and relative standard deviation of the Celtic Sea trace metal EF_{Crust}

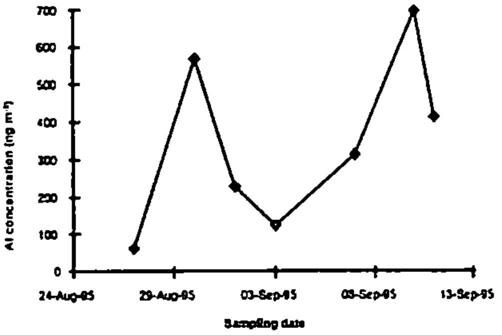


Figure 7.11: temporal variation in Al concentration during OMEX cruise 2.

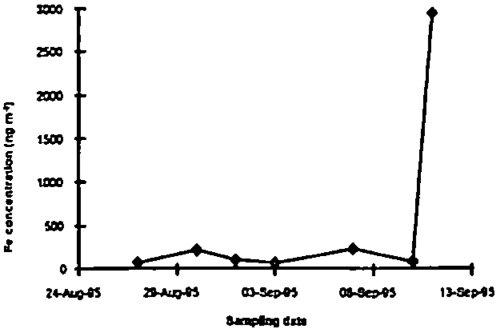


Figure 7.12: temporal variation in Fe concentration during OMEX cruise 2.

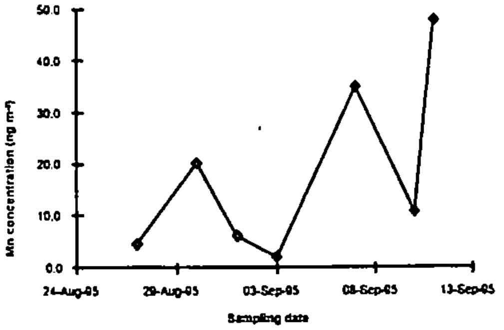


Figure 7.13: temporal variation in Mn concentration during OMEX cruise 2.

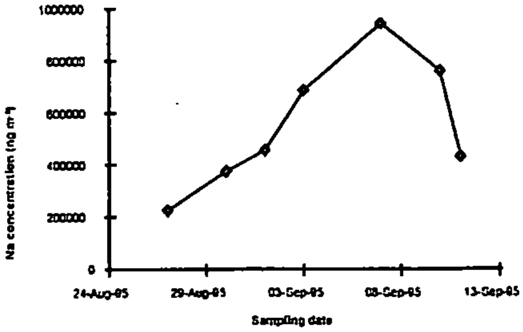


Figure 7.14: temporal variation in Na concentration during OMEX cruise 2.

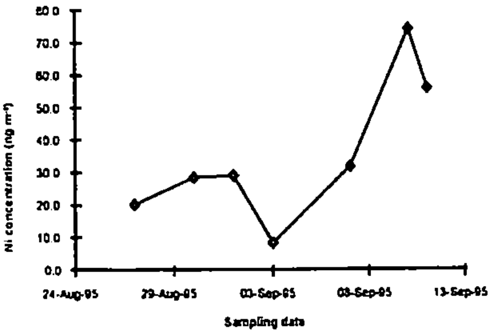


Figure 7.15: temporal variation in Ni concentration during OMEX cruise 2.

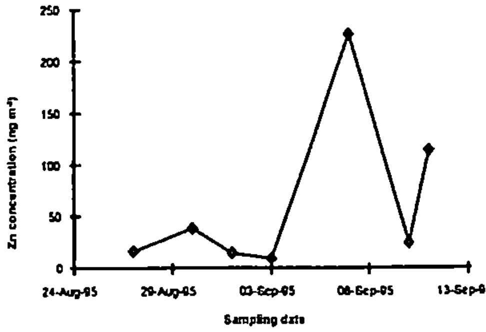


Figure 7.16: temporal variation in Zn concentration during OMEX cruise 2.

data set are presented in Table 7.2. Aluminium, Co, Fe and Mn had EF_{Crust} values which were < 10, which agreed with those reported by Rahn *et al.* (1979). The geometric mean EF_{Crust} for Cd, Cu, Pb and Zn were low reflecting a relatively pristine aerosol over the Celtic Sea. Only Na and Ni had geometric mean EF_{Crust} values > 100. It is possible that the higher Ni aerosol concentration and EF_{Crust} is due to specific sources within the mineralised region of the South West Peninsula. If this source is important (as suggested in Chapter 5), then it influences a wide area of the Celtic Sea and may contribute to enhanced concentrations of Ni in the surface microlayer of the Celtic Sea.

Figures 7.17 to 7.30 display the temporal variation of elemental EF_{Crust} during OMEX cruises 1 and 2. The trends in the EF_{Crust} temporal profiles for the summer period were similar to those for the concentration temporal plots. This indicated a gradient in crustal influence towards from the coast. However, Co and Cu displayed an increase in non-crustal behaviour from 6 - 8 June. The trends in the temporal EF_{Crust} plots for the autumn were also similar to the concentration temporal plots. The exceptions were where elemental and Al concentration peaks coincided, e.g. Mn from 30 August to 1 of September and Ni between 7 and 12 September. The EF_{Crust} for Ni from 27 - 30 August was high due to the higher Ni concentration with respect to Al. Statistical analyses using ANOVA revealed significant differences (to 95%) between the summer EF_{Crust} of Cu, Fe, Mn and Pb compared with the autumn. The elemental EF_{Crust} for the autumn period were generally lower than for the summer period, due to the lower observed concentrations with respect to Al. Principal components analysis was also applied to investigate relationships between trace metals in the combined data set. The PC 1 described 75% of the variation in the data set, which was attributable to all samples, particularly those collected during OMEX cruise 2 (Figure 7.31). The PC 2 described 12% of the variation which was largely attributable to one sample collected during OMEX cruise 2 with contributions from 6 samples collected during OMEX cruise 1 (Figure 7.32). The scores of PC 1 were plotted against the scores of PC 2 (Figure 7.33).

Cobalt, Cu, Fe, Mn, Ni, Pb and Zn were clustered together, suggesting that they were derived from similar sources. Cadmium was separated from the cluster suggesting that it had a different source. However, most importantly, both Cd and the cluster were separated from Na which suggested that none of the trace metals originated from the same source as Na, i.e. a marine source. Celtic Sea aerosol trace metal EF_{Crust} were compared with those of other European regions (Table 5.3). The NEEs (Co, Fe and Mn) had comparable EF_{Crust} values with other European regions. The EF_{Crust} of Na was higher than observed elsewhere, possibly due to sea salt accumulation during passage across the Atlantic Ocean.

Table 7.2: atmospheric trace metal aerosol EF_{Crust} for the Celtic Sea (LOD = limit of detection).

Element	Arithmetic Mean	Range	Standard Deviation	RSD (%)	Geometric Mean
Cd	336	Below LOD - 2760	739	220	37.2
Co	14.5	Below LOD - 91.5	26.5	182	4.13
Cu	204	Below LOD - 1010	332	163	12.0
Fe	2.57	0.08 - 4.16	2.82	110	1.27
Mn	7.40	0.66 - 18.0	7.25	98	4.39
Na	10 200	1320 - 46 200	16 000	157	5110
Ni	371	55.2 - 2190	560	151	211
Pb	142	Below LOD - 724	218	153	16.3
Zn	133	Below LOD - 525	179	135	27.9

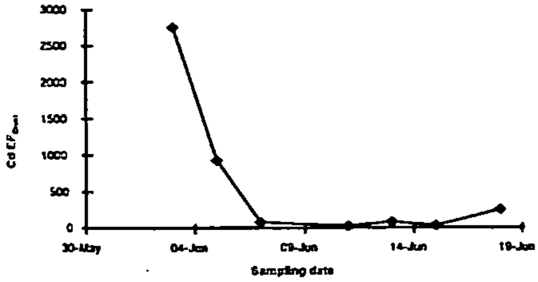


Figure 7.17: temporal variation in Cd EF$_{Crust}$ during OMEX cruise 1.

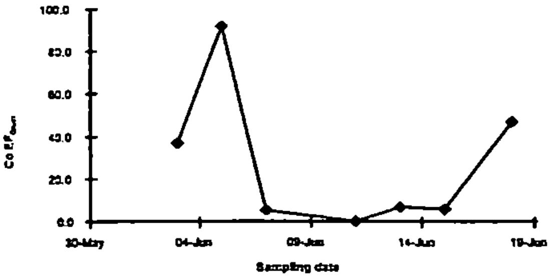


Figure 7.18: temporal variation in Co EF$_{Crust}$ during OMEX cruise 1.

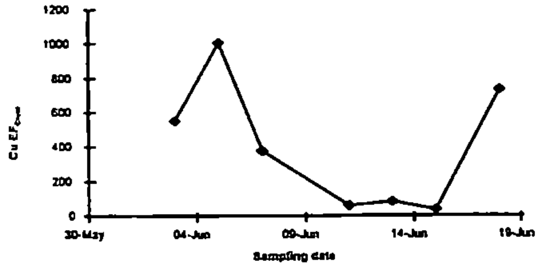


Figure 7.19: temporal variation in Cu EF$_{Crust}$ during OMEX cruise 1.

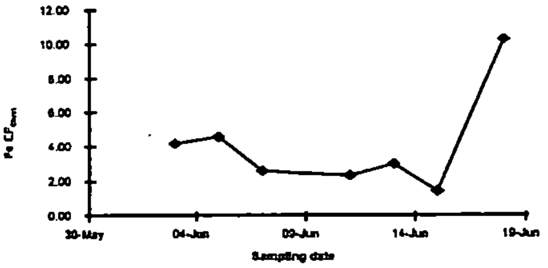


Figure 7.20: temporal variation in Fe EF$_{Crust}$ during OMEX cruise 1.

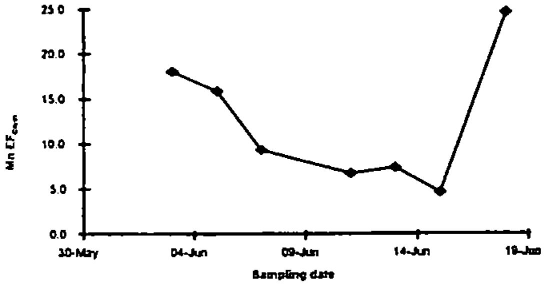


Figure 7.21: temporal variation in Mn EF$_{Crust}$ during OMEX cruise 1.

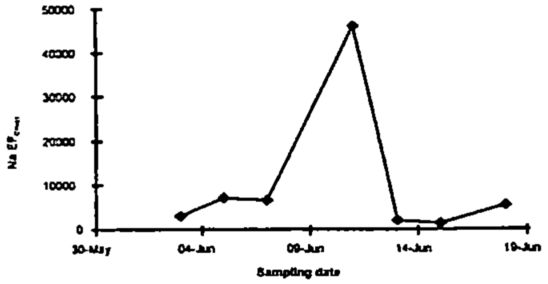


Figure 7.22: temporal variation in Na EF$_{Crust}$ during OMEX cruise 1.

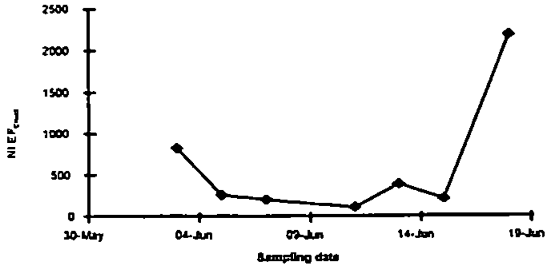


Figure 7.23: temporal variation in Ni EF$_{Crust}$ during OMEX cruise 1.

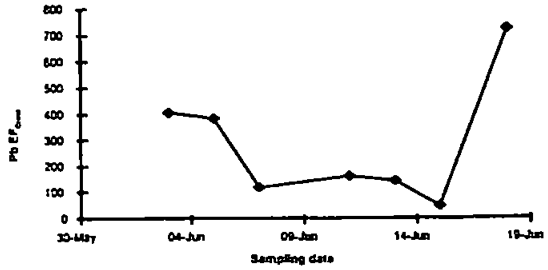


Figure 7.24: temporal variation in Pb EF$_{Crust}$ during OMEX cruise 1.

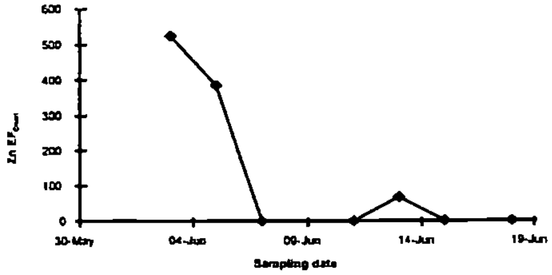


Figure 7.25: temporal variation in Zn EF$_{Crust}$ during OMEX cruise 1.

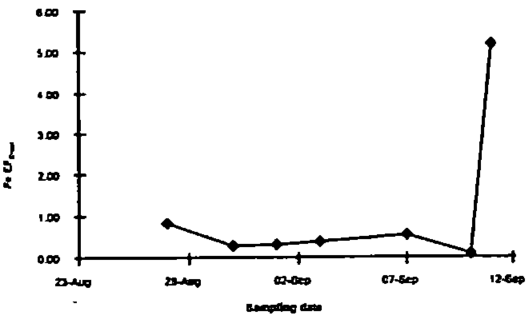


Figure 7.26: temporal variation in Fe EF$_{Crust}$ during OMEX cruise 2.

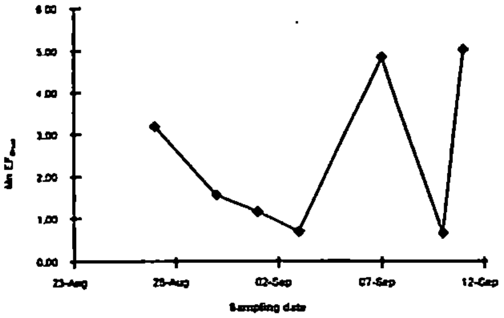


Figure 7.27: temporal variation in Mn EF$_{Crust}$ during OMEX cruise 2.

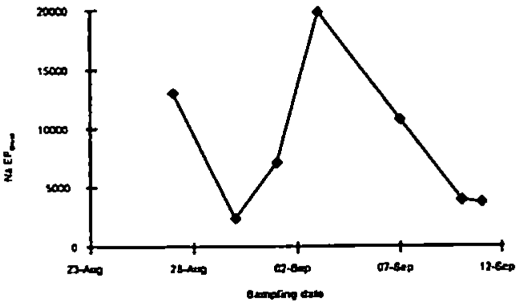


Figure 7.28: temporal variation in Na EF$_{Crust}$ during OMEX cruise 2.

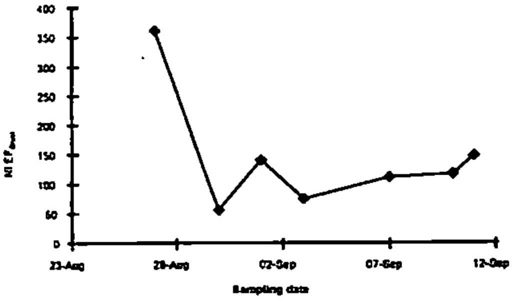


Figure 7.29: temporal variation in Ni EF$_{Crust}$ during OMEX cruise 2.

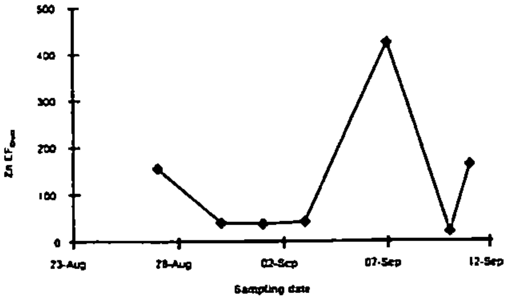


Figure 7.30: temporal variation in Zn EF$_{Crust}$ during OMEX cruise 2.

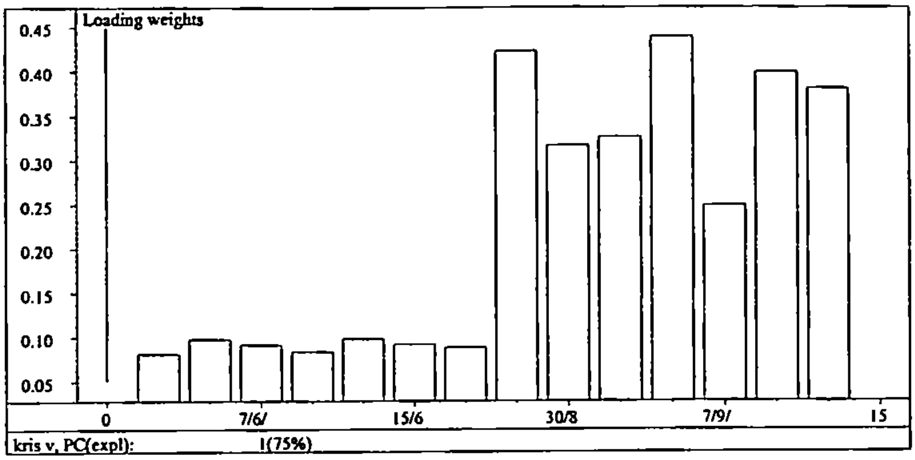


Figure 7.31: PC 1 displaying dominance of all samples particularly those of OMEX cruise 2.

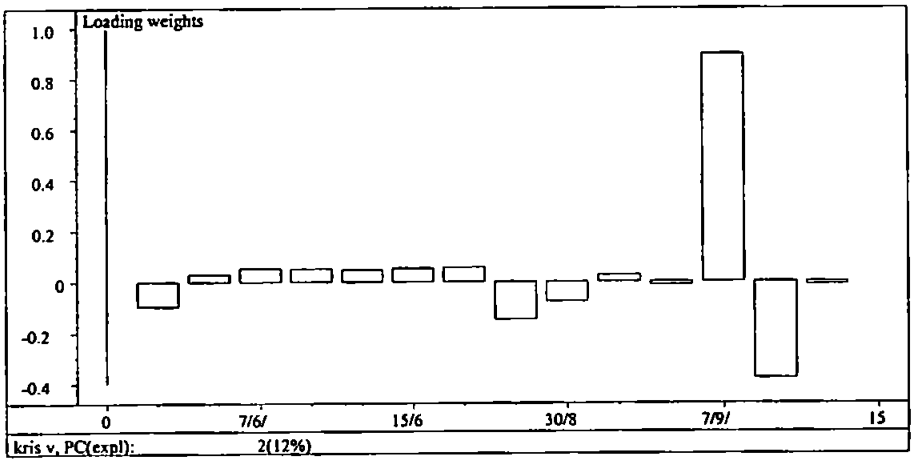


Figure 7.32: PC 2 displaying dominance of OMEX cruise 1 samples and the sample collected on 7th September 1995.

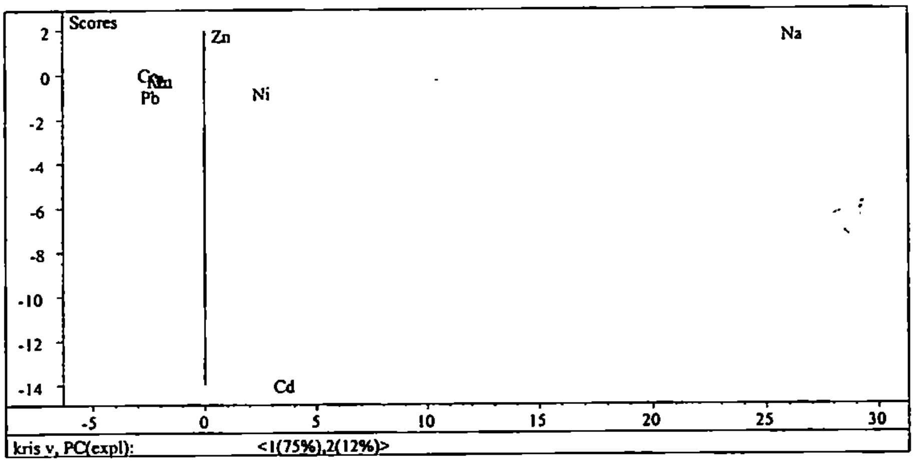


Figure 7.33: inter-elemental relationships revealed by PCA.

In Chapters 5 and 6, $^{206/207}$Pb isotopic ratios proved to be of limited use for distinguishing between Pb sources. Celtic Sea Pb EF$_{Crust}$ were compared with Celtic Sea $^{206/207}$Pb isotopic ratios to evaluate their relationship (Figure 7.34). A correlation coefficient of 0.70 was obtained (95 %; significance = 0.71) indicating a reasonable correlation between the two variables i.e. as Pb EF$_{Crust}$ increases, $^{206/207}$Pb isotopic ratio increases. This result suggests that anthropogenic Pb is associated with aerosols with a relatively low enrichment factors for Pb, whereas natural Pb is highly enriched in atmospheric aerosols over the Celtic Sea. This is a somewhat contradictory result (Hopper *et al.*, 1991; Kersten *et al.*,1992) and suggests that there may be a Pb-rich terrestrial source (such as remnant mining activity) which may be cobtributing to this observation. The wind direction (manly N, NW and W) was relatively constant Figure 7.35) during the two OMEX cruises, which potentially limits the number of terrestrial sources of Pb.

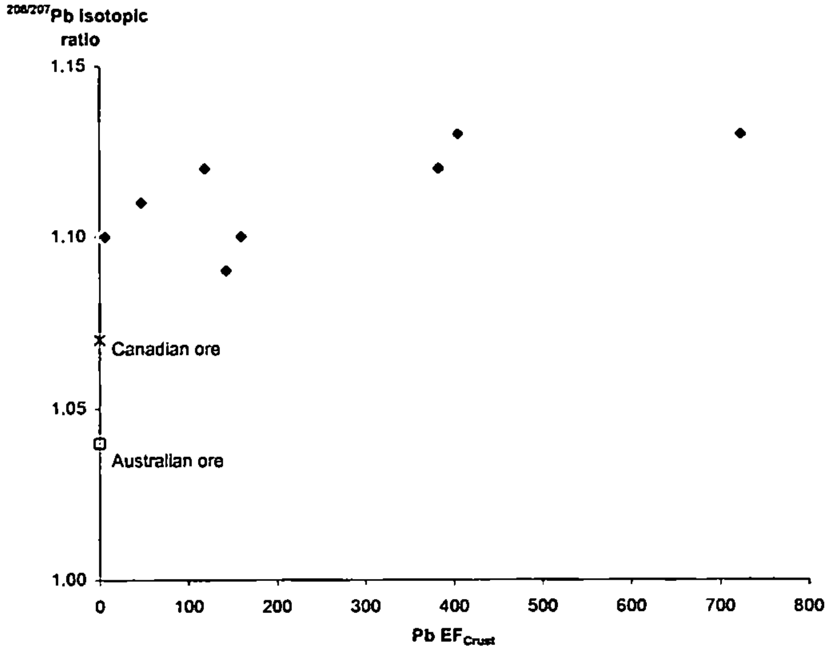


Figure 7.34: correlation of Pb EF$_{Crust}$ and $^{206/207}$Pb isotopic ratio (n = 8) (x = 1.11; σ = 0.02; RSD = 1.35 %) for the Celtic Sea aerosol, compared with ores used in European fuels (Hopper *et al.*, 1991).

7.1.2 Transport of aerosol associated trace metals to the Celtic Sea.

Little variability in wind direction was observed during the two cruises: all except one of the samples were collected under N, NW or W conditions (Figure 7.35). Table 7.3 displays the mean concentration for each wind direction - it should be noted that, due to the collection of only one sample, the concentrations observed from the E wind direction may not be representative. Aluminium concentration was almost equal from each of the experienced wind directions, which may indicate the presence of a crustal veil over the region. Iron concentrations were greater from the NW and W wind directions, Na concentration was greatest from the N, and Zn concentrations from N, NW and W wind directions exceeded those from the east. However, all elements, with the exception of Al and Na,

Table 7.3: mean trace metal concentration for each wind direction (± 22.5°).

Wind direction	Number of samples in each sector	Al	Cd	Co	Cu	Fe	Mn	Na	Ni	Pb	Zn
N	n = 5	343 ± 211	0.01 ± 0.02	0.43 ± 0.47	5.33 ± 5.12	263 ± 132	18.7 ± 9.70	801 000 ± 791 000	52.3 ± 27.2	2.15 ± 2.11	52.5 ± 97.7
NE	n = 0	-	-	-	-	-	-	-	-	-	-
E	n = 1	227	0.11	0.00	0.00	93.5	6.07	457 000	29.1	0.00	14.2
SE	n = 0	-	-	-	-	-	-	-	-	-	-
S	n = 0	-	-	-	-	-	-	-	-	-	-
SW	n = 0	-	-	-	-	-	-	-	-	-	-
W	n = 4	274 ± 175	0.97 ± 1.59	3.14 ± 2.60	109 ± 59.0	803 ± 407	49.3 35.8	388 000 ± 189 000	165 ± 152	14.3 ± 11.1	70.7 ± 105
NW	n = 4	291 ± 239	0.28 ± 0.33	0.32 ± 0.53	0.05 ± 0.07	820 ± 1420	18.6 ± 21.1	430 000 ± 194 000	28.2 ± 20.2	0.27 ± 0.54	44.2 ± 48.2

displayed considerable concentration increases from a W wind direction. This contradicts the traditionally held belief that W air streams bring pristine aerosols. It is quite likely that the elevated levels were caused by an extension of the European aerosol, or may even have originated from the American continent. The ANOVA treatment of the data did not reveal any difference between the wind directions.

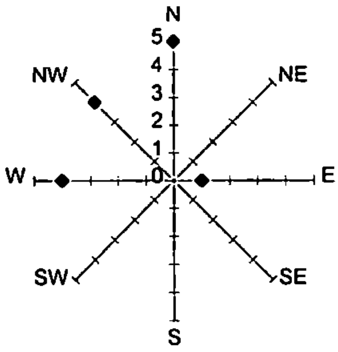


Figure 7.35: wind direction frequency during the two OMEX cruises in the Celtic Sea.

Similar analysis was applied to trace metal EF_{Crust} - the data are presented in Table 7.4. Again, with the exception of Na, the larger EF_{Crust} values were observed from a W wind direction. Principal Components Analysis was also applied to the EF_{Crust} and wind direction data set to investigate the relationship between samples. However, no significant geochemical information could be extracted. This further supports the scenario of a well mixed aerosol, with no particular relationship between source and wind direction.

7.1.3 Aerosol trace metal fluxes to the Celtic Sea.

The western English Channel settling velocities were employed for the calculation of Celtic Sea trace metal dry deposition fluxes. The trace metal fluxes could be ranked as follows: Na > Al > Fe > Mn > Ni > Cu > Zn > Co > Pb > Cd (Table 7.5). Sodium had the greatest dry flux, which might be anticipated due to the marine nature of the region, while Pb and Cd had the lowest dry fluxes, due to the less anthropogenic influence. All other elements had dry fluxes ranging from Al (8340 ng cm^{-2} yr^{-1}) to Co (12.1 ng cm^{-2} yr^{-1}).

Celtic Sea trace metal dry deposition fluxes were compared with those of other European regions (Table 5.11). The Celtic Sea dry fluxes of Cd, Cu, Fe, Pb and Zn, remained lower than observed in

Table 7.4: mean EF_{Crust} for each wind direction (± 22.5°).

Wind direction	Number of samples in each sector	Cd	Co	Cu	Fe	Mn	Na	Ni	Pb	Zn
N	n = 5	24.0 ± 31.0	3.68 ± 3.38	36.4 ± 36.8	1.47 ± 1.21	4.85 ± 2.61	12 800 ± 19 000	187 ± 120	69.9 ± 76.9	103 ± 183
NE	n = 0	-	-	-	-	-	-	-	-	-
E	n = 1	97.0	0.00	0.00	0.30	1.16	7000	140	0.00	36.6
SE	n = 0	-	-	-	-	-	-	-	-	-
S	n = 0	-	-	-	-	-	-	-	-	-
SW	n = 0	-	-	-	-	-	-	-	-	-
W	n = 4	1000 ± 1230	45.1 ± 35.7	668 ± 269	5.41 3.39	16.9 6.28	5530 1850	869 ± 924	408 ± 248	227 ± 269
NW	n = 4	119 ± 137	1.22 ± 2.13	0.29 ± 0.33	1.66 ± 2.36	2.62 ± 1.91	9590 ± 8140	160 ± 140	1.56 ± 3.12	99.4 67.9

Table 7.5: English Channel and Celtic Sea dry deposition fluxes (ng cm^{-2} yr^{-1}) calculated using western English Channel settling velocities.

Element	English Channel (n = 68)	Celtic Sea (n = 14)
Al	7830	8340
Cd	0.15	0.30
Co	1.45	12.1
Cu	32.1	41.1
Fe	290	771
Mn	172	376
Na	76 200	981 000
Ni	33.0	102
Pb	0.86	1.92
Zn	57.5	37.4

other European aerosols, indicative of the more pristine nature of the Celtic Sea atmosphere. In contrast the Celtic Sea dry fluxes of Al, Co, Mn, Na and Ni were higher than reported elsewhere, and implicates marine and terrestrial pools as important sources to the Celtic Sea aerosol

7.1.4 Potential aerosol associated trace metal marine biogeochemistry.

7.1.4.1 Sequential leaching of aerosol associated trace metals.

A three stage sequential leach was applied to OMEX cruise 1 samples (n = 7). Tables 7.6, 7.7 and 7.8, and Figure 7.36 display the portion of trace metal located in each stage of the leach.

Approximately 12 percent of Fe was located in stage one (easily exchangeable). It is possible that a secondary, potentially anthropogenic or heavily weathered, Fe source exists; this secondary source is unlikely to be the ship itself (in the form of rust) since Fe derived from rust would be located in the oxide/carbonate (stage 2) leach. Manganese was divided almost equally between stages 1 (easily exchangeable) and 3 (residual), while both Pb and Cd were comprised of considerable residual portions - both metals, however, were most abundant in the easily exchangeable phase.

Table 7.6: Celtic Sea sequential leach stage 1 % trace metal solubility (n = 7) (LOD = limit of detection).

Element	Arithmetic Mean	Range	Standard Deviation	RSD %	Geometric Mean
Al	0.78	0.29 - 1.14	0.27	34.4	0.73
Cd	74.1	3.50 - 89.4	31.4	42.4	54.3
Fe	12.1	Below LOD - 74.6	27.8	230	3.01
Mn	51.9	10.1 - 84.8	31.2	60.0	40.0
Pb	53.7	Below LOD - 71.3	24.5	45.6	62.4

Table 7.7: Celtic Sea sequential leach stage 2 % trace metal solubility (n = 7) (LOD = limit of detection).

Element	Arithmetic Mean	Range	Standard Deviation	RSD %	Geometric Mean
Al	4.10	0.03 - 10.0	4.06	99.1	0.87
Cd	3.10	Below LOD - 9.80	3.10	101	2.52
Fe	1.10	Below LOD - 3.30	1.40	131	1.56
Mn	2.20	1.99 - 2.32	0.20	8.00	2.15
Pb	10.2	3.86 - 13.8	3.34	32.6	9.58

Table 7.8: Celtic Sea sequential leach stage 3 % trace metal solubility (n = 7).

Element	Arithmetic Mean	Range	Standard Deviation	RSD %	Geometric Mean
Al	95.1	89.1 - 99.7	4.23	4.40	95.1
Cd	22.8	1.13 - 96.5	33.0	145	11.3
Fe	86.8	25.4 - 100	27.3	31.5	80.1
Mn	46.0	13.1 - 87.9	31.1	67.7	36.8
Pb	36.0	19.0 - 86.2	22.9	63.4	31.9

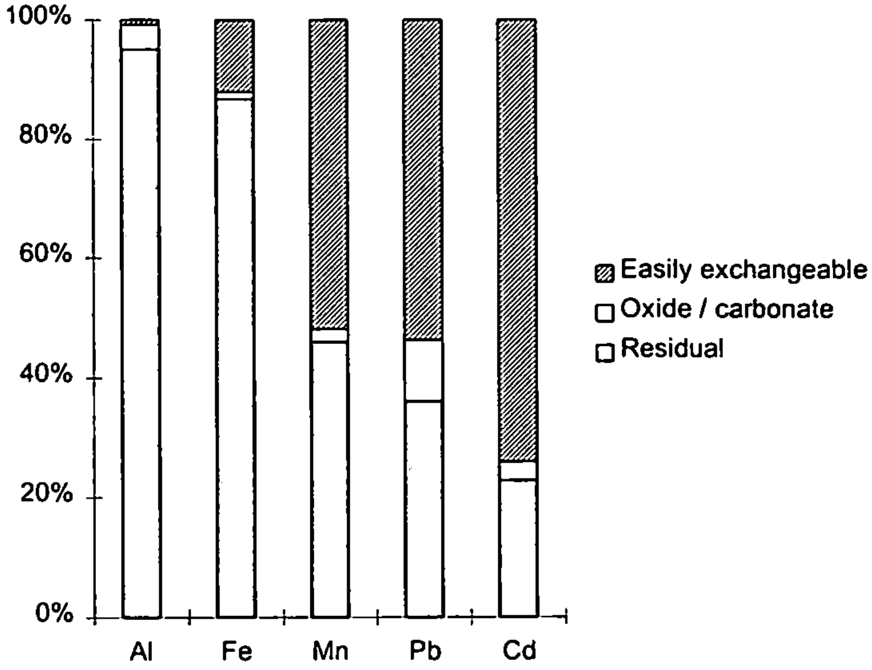


Figure 7.36: mean solid state speciation of trace metals in Celtic Sea aerosol particles (n = 7).

7.1.4.2 Solubility of aerosol associated trace metals in sea water.

The sea water solubility study was carried out on all samples collected during OMEX cruise 2 (n = 7). Arithmetic and geometric means, range, standard deviation and relative standard deviation of percentage trace metal solubility are presented in Table 7.9. Aluminium displayed the lowest percentage solubility although this was more than 10 times higher than that observed for anthropogenic rich aerosols (Hodge *et al.*, 1978). High Al solubilities may be derived from weathered material, such as that transported across the Atlantic Ocean or present in the tropospheric background aerosol (Maring and Duce, 1987). Similarly the solubility of Pb, at 54 %, was greater than that observed for anthropogenic rich aerosols. The mean percentage solubility of Ni (39 %) was similar to that reported by Fones (1996) for Irish Sea aerosols, and between the percentage solubilities obtained for anthropogenic rich (47 %) and dust rich (28 %) aerosols (Chester, 1990). For Co and Cu, the mean percentage solubilities were higher than reported elsewhere.

Arithmetic and geometric means, range, standard deviation and relative standard deviation of percentage Lumogallion / ACSV$_{\mathrm{Labile}}$ trace metals are presented in Table 7.10. Aluminium displayed the greatest degree of lability at 78%, while Pb was completely complexed. This suggests that Al and Pb have different sources and/or different geochemistries. Copper and Ni displayed a comparable degree of complexation behaviour, with ACSV$_{\mathrm{Labile}}$ being 62 % and 45 %, respectively. Cobalt was almost entirely complexed at 8 %

Table 7.9: percentage sea water solubilities for Celtic Sea aerosol associated trace metals (n = 7) (LOD = limit of detection).

Element	Arithmetic Mean	Range	Standard Deviation	RSD %	Geometric Mean
Al	6.26	3.01 - 14.5	3.97	63.3	5.47
Co	96.3	89.3 - 100	4.06	4.21	96.2
Cu	71.0	18.9 - 89.1	26.4	37.2	64.0
Ni	38.8	Below LOD - 86.0	25.5	65.9	24.8
Pb	54.2	12.1 - 90.3	28.5	52.6	45.8

Table 7.10: percentage Lumogallion/ACSV$_{\text{Labile}}$ of the total sea water dissolved fraction of trace metals from Celtic Sea aerosols (n = 7) (LOD = limit of detection).

Element	Arithmetic Mean	Range	Standard Deviation	RSD %	Geometric Mean
Al	77.8	57.4 - 97.5	17.7	22.7	79.4
Co	8.06	Below LOD - 48.1	17.9	222	2.72
Cu	62.0	Below LOD - 96.9	33.9	54.6	37.1
Ni	45.4	Below LOD - 75.2	33.5	73.9	31.0
Pb	0.00	-	-	-	-

7.2 Trace metal inputs to the Celtic Sea.

Total particle associated trace metal fluxes were corrected for the portion of sea water soluble aerosol trace metal; annual inputs were then calculated to assess the impact of particulate trace metal inputs to the Celtic Sea (Table 7.11), using equation 3.6. Owing to the absence of a well-defined value, the Celtic Sea was arbitrarily delimited between 6 and 14 °W, and 47 and 51 °N, resulting in a surface area of 22 000 km^2. Aluminium has the greatest flux to the Celtic Sea, which may be enhanced by its prevalence as a veil over the region and to the meteorological conditions experienced during the cruises. Estimates of seasonality in fluxes for the elements would be more precise had sampling been possible at least during winter and spring. However, it is clear that the atmosphere is a significant source of trace metals, in a region where fluvial inputs are unlikely to be influential.

Table 7.11: mean total particulate dry deposition fluxes and trace metal inputs to the Celtic Sea (n = 14).

Element	Dry deposition flux ($ng\ cm^{-2}\ yr^{-1}$)	% sea water insoluble	Particulate dry deposition flux ($ng\ cm^{-2}\ yr^{-1}$)	Total particulate input ($t\ yr^{-1}$)
Al	8340	94	7820	1720
Co	12	3.7	0.5	0.1
Cu	41	29	12	2.6
Ni	100	61	62	14
Pb	1.9	46	0.9	0.2

7.3 Summary of atmospheric trace metal characteristics over the Celtic Sea.

The coefficient of variation for aerosol trace metal concentrations were found to lie between 238 % for Cd to 63 % for Al. Sodium was one of the least variable at 125 % and it also displayed a different temporal profile during the two sampling periods compared with the remaining investigated elements: low coastal/high open ocean concentrations. This suggested a terrestrial (crustal/anthropogenic) for the remaining elements. Generally lower concentrations were observed during the second cruise, with the exception of Al, potentially as a result of meteorological conditions following the passage of the decaying Hurricane Iris. A positive correlation coefficient for Pb EF_{Crust} vs. $^{206/207}Pb$ isotopic ratio was observed.

The sampled air masses largely originated from N, NW and W directions. Generally the highest trace metal concentrations and EF_{Crust} were largely observed in westerly air masses. PCA identified relationships between wind direction and EF_{Crust}, $^{206/207}Pb$ isotopic ratio, percentage easily exchangeable trace metal, and percentage sea water solubility.

The sequential leach identified considerable residual portions of both Cd and Pb, although they were still most abundant in the easily exchangeable form. Twelve percent of Fe was located in the easily exchangeable stage. This may identify a secondary source for Fe, although it is unlikely to be contamination from rust, as this would be located in the oxide/carbonate phase. Aluminium displayed the lowest sea water solubility of the investigated trace metals, although this was more than 10 times higher than reported for anthropogenic enriched aerosols (Hodge *et al.*, 1978). Similarly the solubilities reported for Co, Cu and Pb were higher than reported for such aerosols. Nickel solubility was between that determined for anthropogenic and dust enriched aerosols (Hodge *et al.*, 1978). This may have been a result of enhanced weathering of the aerosol (see for example Spokes et al., 1995), possibly during transport to the Celtic.

Dry fluxes of Cd, Pb and Zn were lower than observed elsewhere in Europe, which is indicative of the reduced anthropogenic influence on the Celtic Sea. In the absence of significant riverine inputs and data to support trace metal inputs via sediment-water exchange, it is concluded that the atmospheric inputs are the most significant source of trace metals to the Celtic Sea.

Chapter 8.

Conclusions and further work.

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8.1 Inter-comparison of trace metal concentrations at the three sites.

Aerosol concentrations for each of the three regions displayed large variability (indicated by standard deviation), which can be attributed to (i) air mass source, (ii) seasonal effects, and (iii) washout. Concentrations of Al, Cd and Ni had the largest standard deviations over the western English Channel, while the standard deviation of Pb was highest in the north western Mediterranean aerosol. Other elements displayed high standard deviations in the Celtic Sea aerosol although this site was the least represented in terms of sample numbers (Figures 8.1 to 8.10). Investigation of seasonal variability in the composition of the north western Mediterranean Sea and Celtic Sea aerosols was limited by the retricted sampling periods, although trace metal concentrations in aerosols from the northern western Mediterranean covered a crucial period in spring and early summer when outbreaks of southerly winds were evident. For the Celtic Sea, it appears that the lower trace metal concentrations obtained for the August/September 1995 OMEX collections compared to those for the June 1995 OMEX collections may have been as a result of rainfall augmented by the passage of a decaying hurricane.

The collection and analysis of aerosols at the western English Channel site yielded a large, comprehensive time series of quality assured trace metal concentrations, against which seasonal and inter-annual variability may be assessed. Geometric mean aerosol concentrations for the western English Channel were generally lower than for other European regions (e.g. the Irish Sea and North Sea), particularly in the case of Pb, although Ni concentrations were often higher. The lower Pb concentrations may be related to a decline in the use of leaded fuels, while higher Ni concentrations could not attributed unambiguously to a particular source. The seasonal variability of the elemental aerosol concentrations suggested that there were two groups of elemental behaviour: Group 1 (Cd, Fe, Mn, Pb, Zn) which exhibited enhanced autumn/winter concentrations during the whole sampling period and Group 2 elements (Al, Co, Cu, Na, Ni) which exhibited enhancement of elemental concentrations during autumn/winter 1995/1996. Group 1 elements, particularly Cd, Pb and Zn, displayed higher concentrations in N/E wind sectors, which suggested long range transport of these elements from western European anthropogenic sources. Group 2 elements, particularly Ni, displayed elevated concentrations in S/W wind sectors. The high concentrations for Ni are especially interesting

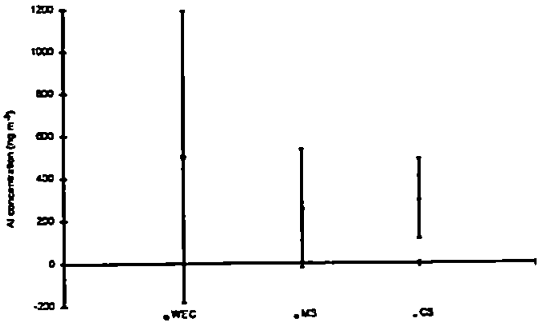

Figure 8.1: comparison of Al concentration.

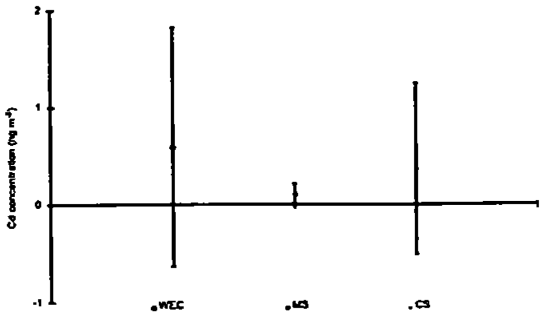

Figure 8.2: comparison of Cd concentration.

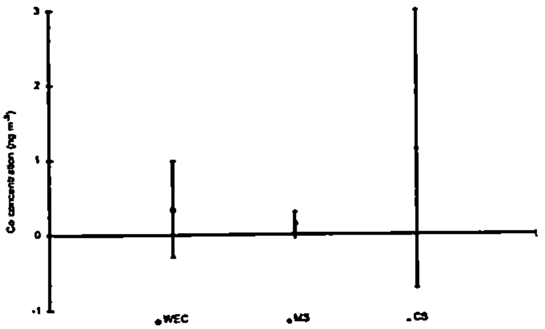

Figure 8.3: comparison of Co concentration.

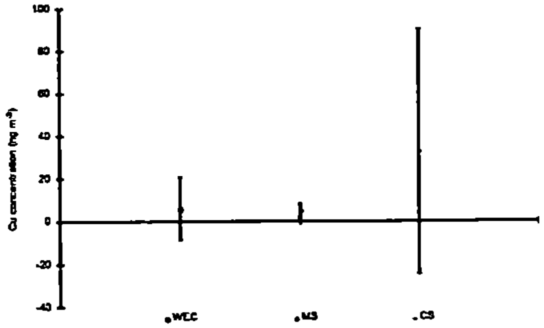

Figure 8.4: comparison of Cu concentration.

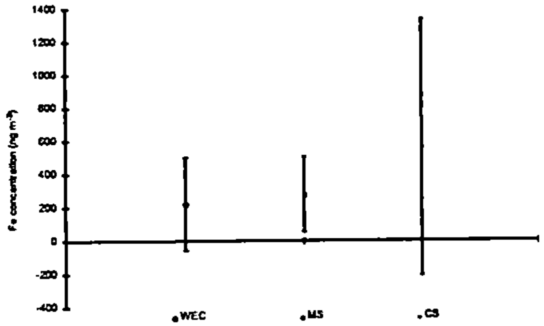

Figure 8.5: comparison of Fe concentration.

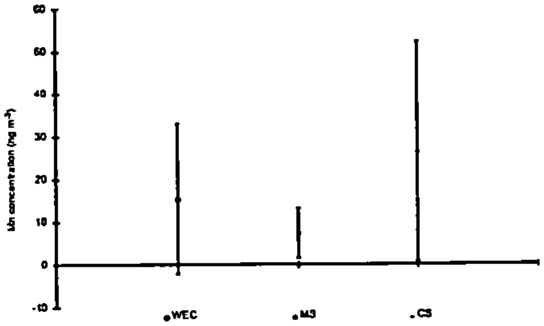

Figure 8.6: comparison of Mn concentration.

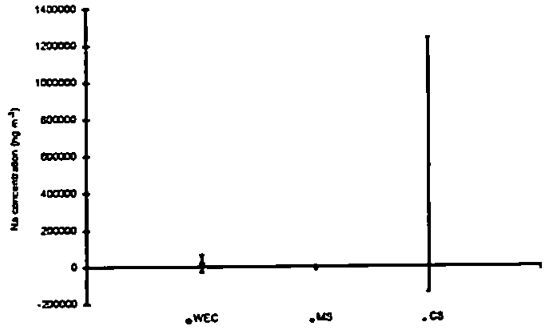

Figure 8.7: comparison of Na concentration.

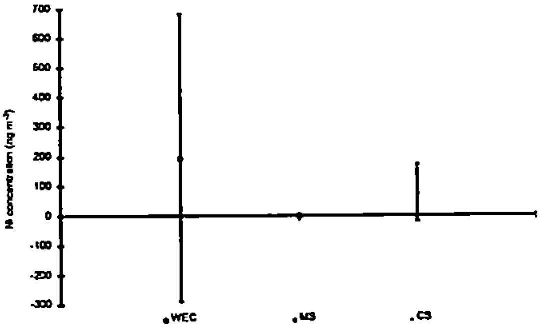

Figure 8.8: comparison of Ni concentration.

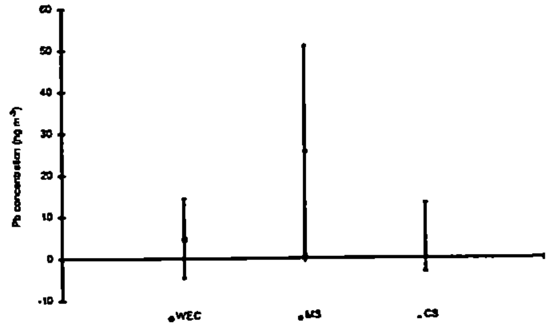

Figure 8.9: comparison of Pb concentration.

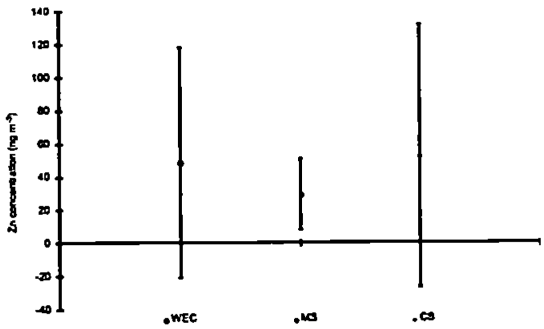

Figure 8.10: comparison of Zn concentration.

in that it is tempting to conclude that they originated from the re-suspension of relatively local terrestrial material, such as serpentine-rich soils from the Lizard Peninsula. However, an examination of the enrichment factors shows that even if the presence of these local materials in the aerosol is accounted for, the aerosols, particularly in SW airmasses, are still significantly enriched in Ni. This implies another source of Ni enriched aerosols. In the absence of a terrestrial source, in the SW direction, it is possible that the sea surface could be the source of the enriched Ni; an hypothesis supported by a strong correlation between Ni and Na. The question of the mechanism of enrichment remains unresolved but, since Ni is significantly complexed with DOM, it is possible that aerosol enrichment in Ni involves processes in the sea surface microlayer. Sea surface enrichment processes have been observed for Fe, Cu and Zn (Piotrowicz *et al.*, 1979) and these may be applicable to Ni. Furthermore, since the enrichment in aerosols studied here occurred during a period of the autumn phytoplankton bloom, there maybe a connection between aerosol enrichment and biological activity which has not yet been detected. This explanation of the Ni enrichment observed in this study is circumstantial but there is considerable scope for further work to substantiate this mechanism.

Geometric mean EF_{Crust} values of <10 were observed for Co, Fe and Mn in all aerosols at the three sites and these metals were considered not to be enriched. The EF_{Crust} for Pb decreased in the order north western Mediterranean > western English Channel > Celtic Sea. This illustrates the reduced influence of anthropogenic sources of trace metals on the Celtic Sea aerosol (Figures 8.11 to 8.19). No correlation was observed between western English Channel Pb EF_{Crust} and $^{206/207}Pb$ isotopic ratio. This highlighted the well mixed, less anthropogenic nature of the region. The low $^{206/207}Pb$ isotopic ratio observed is most likely to be as a result of the surrounding crustal material, than being indicative of anthropogenic origin.

Analyses of the metal concentration datasets for western English Channel and north western Mediterranean dataset, using principal component analysis, showed statistically significant inter-relationships between metal concentrations. All elements in the Celtic Sea aerosol, except Cd and Na, were clustered suggesting that they may have originated from similar sources, and that the source was not marine. Principle component analysis was also used to investigate the relationship between wind direction (i.e. air mass track) and EF_{Crust} for each aerosol data set. It was possible to group samples according to primary wind direction, with the Celtic Sea aerosol providing the best separation, and the north western Mediterranean aerosol the least; this was largely due to the inability to precisely

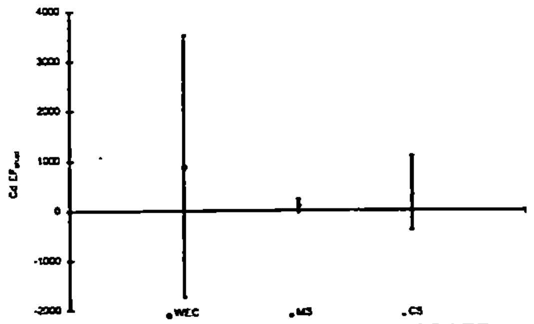

Figure 8.11: comparison of Cd EF_{Crust}.

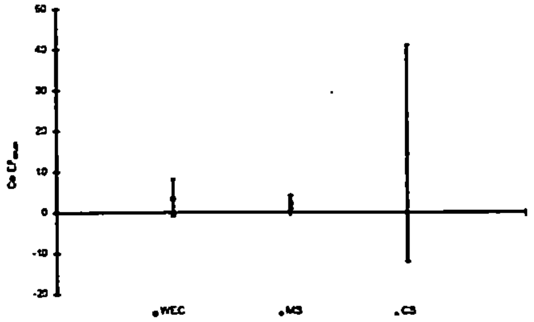

Figure 8.12: comparison of Co EF_{Crust}.

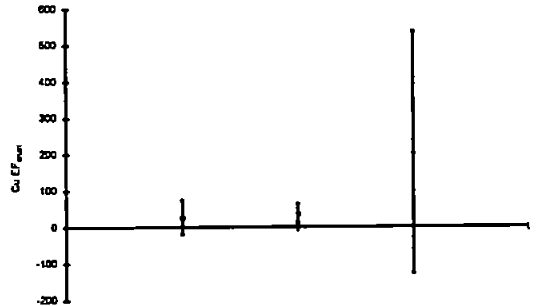

Figure 8.13: comparison of Cu EF_{Crust}.

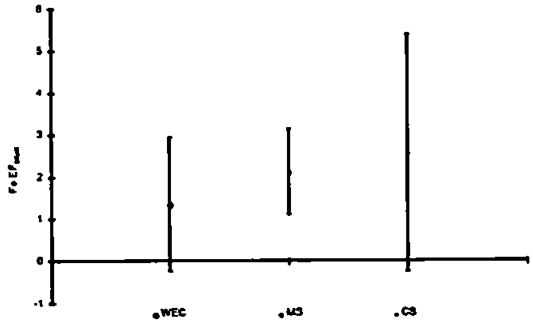

Figure 8.14: comparison of Fe EF_{Crust}.

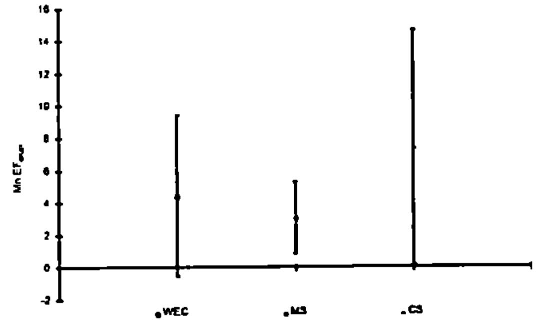

Figure 8.15: comparison of Mn EF_{Crust}.

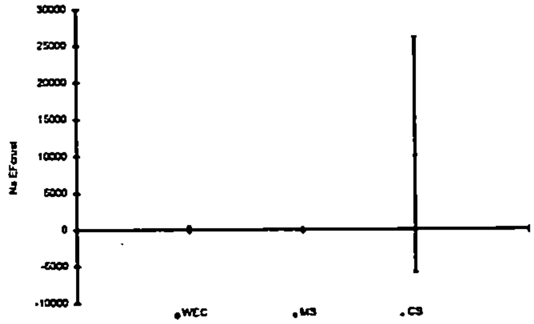

Figure 8.16: comparison of Na EF_{Crust}.

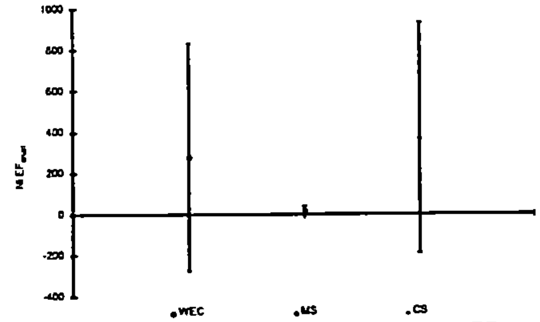

Figure 8.17: comparison of Ni EF_{Crust}.

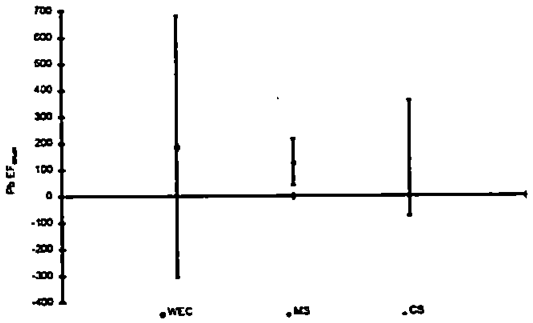

Figure 8.18: comparison of Pb EF_{Crust}.

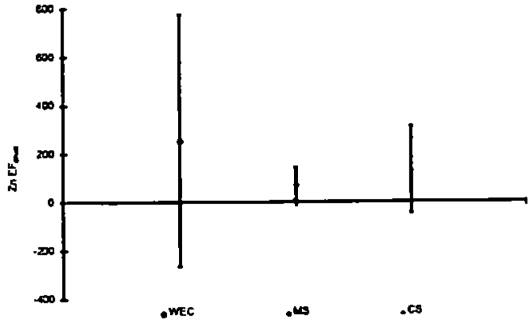

Figure 8.19: comparison of Zn EF_{Crust}.

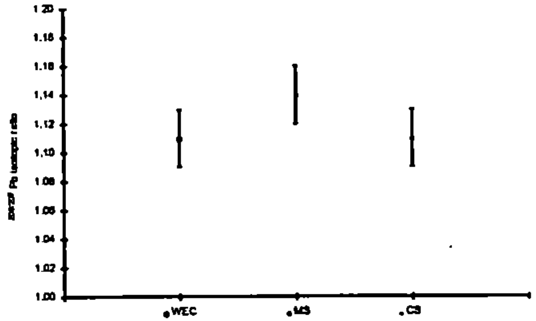

Figure 8.20: comparison of $^{206/207}Pb$ isotopic ratios.

determine the influence of wind direction on samples due to the duration of collection of north western Mediterranean samples (three to seven days).

8.1.1 Lead isotopic ratios.

Figure 8.20 compares the mean $^{206/207}$Pb isotopic ratio for the three sites. The western English Channel and the Celtic Sea have similar mean $^{206/207}$Pb isotopic ratios, while the north western Mediterranean atmosphere is higher. The higher mean for the western Mediterranean may be as a result of the mixing of crustal aerosols, unaffected by anthropogenic emissions and with relatively high isotopic ratios, with anthropogenic aerosols from eastern Europe. Figure 8.21 shows a relatively large scatter when the $^{206/207}$Pb isotopic ratio is plotted against the Pb EF_{Crust} for each of the regions. There is little coherence in the isotopic ratio data for the three regions despite the fact that, for many samples, Pb had EF_{Crust} in the range 100-1000. The large variability in all the values of $^{206/207}$Pb, covering 1.05 to 1.19 precluded any significant conclusions. Even within each data set it was difficult to find any trends, although many of the lowest $^{206/207}$Pb isotopic ratios were found for the western English Channel aerosols. Overall it may be concluded that the tracing of air masses using the $^{206/207}$Pb isotopic ratio has now run its course due to the reduction in the use of leaded fuel (Wu and Boyle, 1997).

8.1.2 Sequential leaches of atmospheric aerosols and sea water solubility studies.

Particulate trace metal speciation was investigated using a three stage sequential leach and sea water solubility studies. The sequential leach revealed that Al and Fe were found predominantly in the residual phase at all three sites, whereas for Cd the order was Celtic Sea > north western Mediterranean > western English Channel. The amounts of Pb in the residual phase followed the sequence Celtic Sea > western English Channel > north western Mediterranean. The solid state speciation of Pb strongly suggests a stronger anthropogenic influence on the north western Mediterranean aerosol, which was further confirmed by values of EF_{Crust} for Pb.

Solubilities of trace metals in seawater (expressed in % of total metal) for western English Channel aerosol associated trace metals were: Al = 2 %, Co = 68 %, Cu = 84 %, Ni = 50 % and Pb = 49 %. All north western Mediterranean aerosol trace metal solubilities were lower than for the western English Channel, possibly due to enhanced crustal particle concentrations within the aerosol and/or trace metals in anthropogenic particles residing in higher energy binding sites. However, the material was

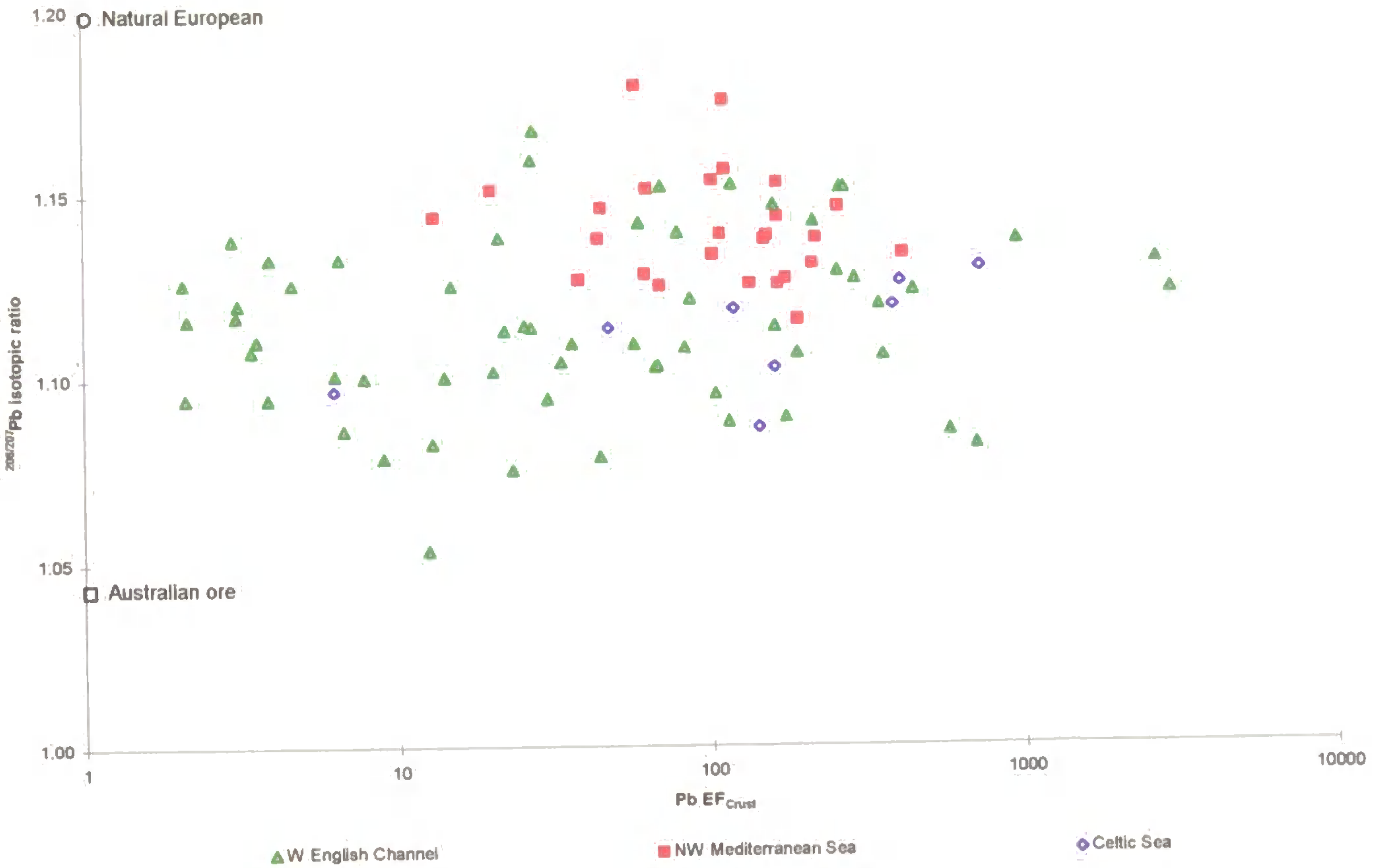

Figure 8.21: Pb EF$_{Crust}$ vs. $^{206/207}$Pb isotopic ratio for each of the investigated regions.

not exclusively crustal, as implied by the sequential leach, especially since the sea water solubilities were higher than those reported for crustally-dominated aerosols. Sea water solubilities for trace metals in Celtic Sea aerosols were higher for Al, Co and Pb compared with the western English Channel, possibly due to increased weathering of crustal source material rather than greater anthropogenic activity, which was inferred by the solid state speciation of the elements. Lower percentage solubility was observed for Cu and Ni, possibly due to their derivation from a less weathered source material such as mineral waste. The soluble fraction of aerosol trace metals was found to be related to wind direction.

Organic complexation of the aerosol seawater soluble trace metals (i.e. the non-labile fraction) appeared to be most important for Pb followed by Cu , Ni, Co and Al. It was most important for Al, Cu and Ni from western English Channel aerosols, and for Co and Pb in Celtic Sea aerosols, with complexation being least important for Al, Co and Ni from north western Mediterranean aerosols. This demonstrated the importance of atmospheric sources of trace metal complexing ligands and complements similar findings by Nimmo *et al.* (1998) for the Irish Sea marine aerosol.

8.1.3 Dry and wet trace metal fluxes.

Dry deposition fluxes to north western Mediterranean Sea of Al, Co, Cu, Fe, Pb and Zn were greater than the western English Channel (Figures 8.22 to 8.31), which is a reflection of different trace metal sources. For example, the dry deposition flux of Pb to the north western Mediterranean Sea was 22 times higher than that to the western English Channel. The lower Na dry flux arises from an aerosol dominated by terrestrial material and dissolution in rainwater during passage over the Pyrenees prior to reaching the sampling site. The comparatively reduced Ni dry flux to the north western Mediterranean Sea could reflect the importance of mineral waste sources to the western English Channel aerosol. However, the dry fluxes of Al, Co and Mn were similar to dry fluxes observed by other workers in the western Mediterranean (Table 5.11) although dry fluxes of Cd, Cu, Fe, Ni, Pb and Zn were lower than previously observed. This is possibly due to inter-annual variation or a decline in the emission of these metals through anthropogenic sources. It is also possible that the settling velocities used to estimate the dry fluxes were inapplicable to this area and is, therefore, a major uncertainty in the calculations.

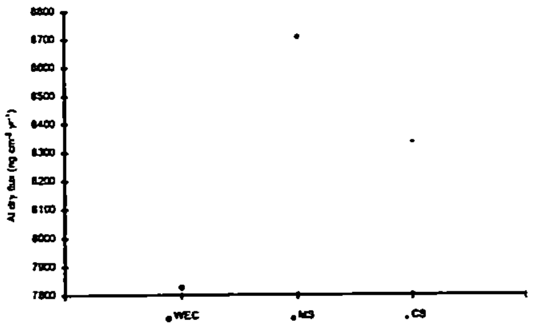

Figure 8.22: comparison of Al fluxes.

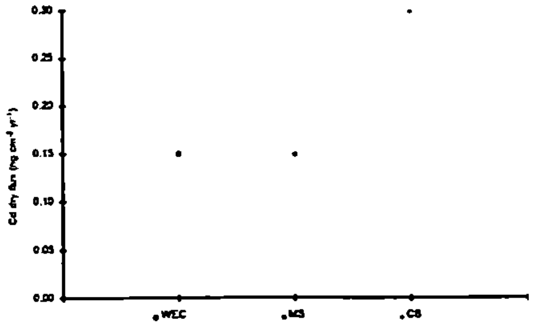

Figure 8.23: comparison of Cd fluxes.

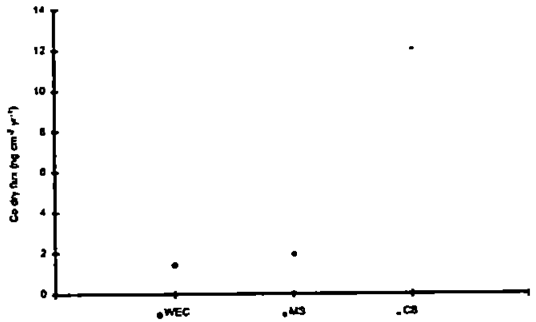

Figure 8.24: comparison of Co fluxes.

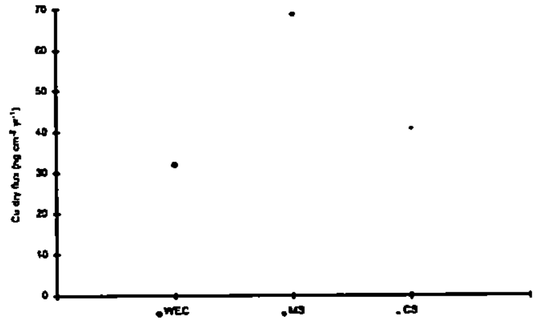

Figure 8.25: comparison of Cu fluxes.

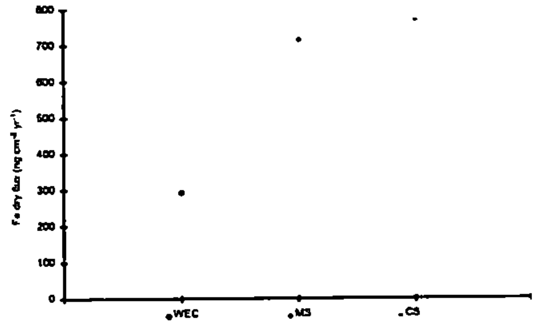

Figure 8.26: comparison of Fe fluxes.

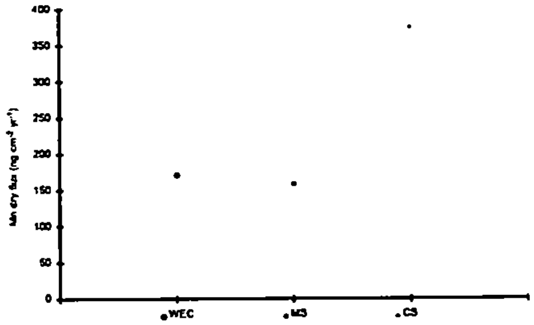

Figure 8.27: comparison of Mn fluxes.

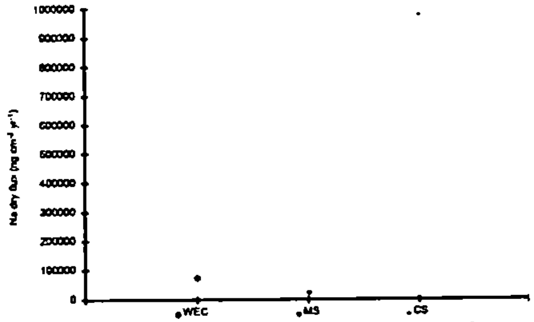

Figure 8.28: comparison of Na fluxes.

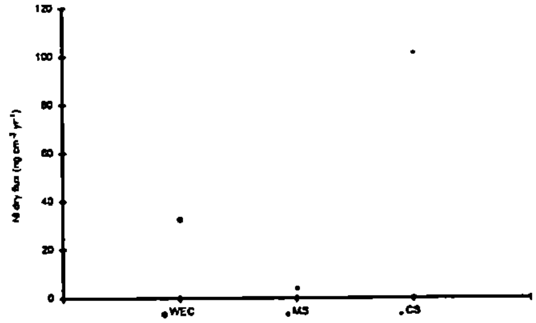

Figure 8.29: comparison of Ni fluxes.

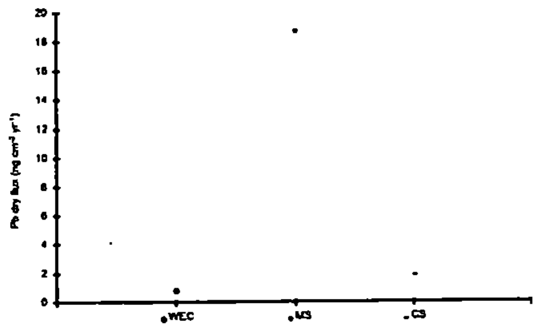

Figure 8.30: comparison of Pb fluxes.

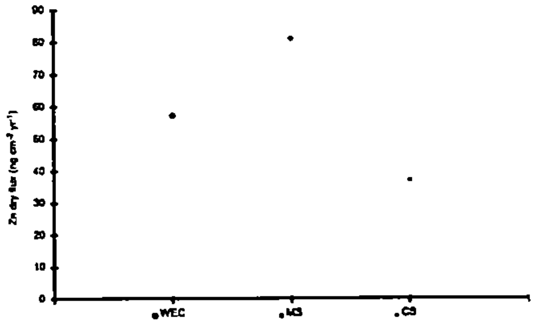

Figure 8.31: comparison of Zn fluxes.

All Celtic Sea trace metal dry fluxes exceeded those of the western English Channel except for Zn. This, correlated with the concentration data, suggested that either (i) land derived material was transported offshore prior to mixing with the Celtic Sea marine aerosol, (ii) a terrestrially derived trace metal veil exists over the Celtic Sea, (iii) the European aerosol had influenced the Celtic Sea and western English Channel aerosols, or (iv) orographic rainfall over the South West Peninsula resulted in the lowering of trace metal concentrations prior to sampling at the western English Channel site, or more likely a combination of these processes occurred. It should be remembered that the deposition fluxes to the Celtic Sea were determined on a limited number of aerosol samples, such that Celtic Sea fluxes are less representative than those fluxes calculated at the other sites.

8.2 Modelling trace metal fluxes in the English Channel.

8.2.1 Model set up and assumptions.

The comprehensive data base of aerosol trace metal concentrations obtained for the western English Channel allowed estimates of atmosphere-ocean trace metal fluxes to be made. The results of the solubility studies were used to assess the relative fluxes of dissolved and particle associated trace metals to the sea surface from the atmosphere. The data from this study were used, in combination with literature values of dissolved and particulate trace metal concentrations in the water column and in rivers, to develop a model of trace metal fluxes into and out of the English Channel. In order that the overall flux calculations for the English Channel could be made it was first necessary to establish the boundary conditions and to develop a set of basic assumptions. These approaches are explained below.

A box model for the English Channel (see Figure 4.1) is, of necessity, fairly basic because of a lack of extensive trace metal concentrations for the various compartments. However, the results of the FLUXMANCHE Programme (Statham *et al.*, 1993; Cabioch, 1996) and the Quality Status Report for sub-region 9 of the North Sea (Reid *et al.*, 1993) have important data-sets for model development. The quantification of water transport at the eastern end of the English Channel (i.e. the Dover Strait transect DS) were obtained by the Prandle model (Statham *et al.*, 1993; Prandle *et al.*, 1996) which estimated annual water fluxes across the transect to be:

from September 1990 to September 1991 - 2.94×10^{12} m^3 yr^{-1}

from September 1994 to September 1995 - 4.07×10^{12} m^3 yr^{-1}

Furthermore, the model also predicted the water flux across a western boundary between Cherbourg and the Isle of Wight (CIOW) which was:

from September 1994 to September 1995 - 4.27×10^{12} m^3 yr^{-1}

Thus, these calculations suggest that there is an approximate balance between water entering the English Channel across the CIOW transect and that leaving it across the DS transect (see Figure 4.1), which is in keeping with a residence time of about 1 year for the eastern English Channel (Reid *et al.*, 1993). Thus, for the purposes of the calculations the amount of water passing these transects is taken to be 4×10^{12} m^3 yr^{-1}. The advantage of using the CIOW transect as the western boundary of the English Channel is that dissolved and particulate trace metal concentrations have been obtained as part of the FLUXMANCHE Programme and these values have been converted into trace metal fluxes (Cabioch, 1996). However, a minor problem exists for the particulate trace metals fluxing across the CIOW transect in that for determinations Cu and Pb, hydrofluoric acid was used to obtain a total metal concentration but for Ni in SPM, only acetic acid available concentrations were reported. Riverine inputs of trace metals are available from the Quality Status Report (Reid *et al.*, 1993), although there is no discussion of the relative proportions of trace metals in either the dissolved or particulate phase. The River Seine has the largest trace metal input and some attempts have been made to quantify their fluxes in the dissolved and particulate phases (Chiffoleau *et al.*, 1994). Thus, in the budgets presented below, it has been assumed that the relative proportions of trace metals in the dissolved and particulate phase in other rivers entering the English Channel are the same those for the Seine. The atmospheric fluxes were estimated using the measured aerosol concentrations and the total sea surface area between the CIOW and the DS transects determined from Admiralty charts, which gave approximately 30×10^3 km^2.

However, the English Channel extends further west than the CIOW transect, which could be of significance for atmospheric inputs of trace metals since rivers make only a minor contribution in this region. Thus, a second westerly transect is taken as that between Lands End and the Brest Peninsular (LEBP) and assuming continuity exists throughout the English Channel, the amount of water passing across the transect annually is 4×10^{12} m^3 yr^{-1}. Thus, assuming that the extremes of the English Channel are the DS and LEBP transects, the total area is 77×10^3 km^2. The main difficulty with using the LEBP boundary is that there is relatively sparse data on dissolved and particulate trace metals in the adjacent oceanic water masses. The Quality Status Report (Reid *et al.*, 1993) includes some dissolved trace metal concentrations in the Celtic Sea but no particulate trace metal values are given.

Despite the absence of a comprehensive database, first order budgets have been developed using available data for both western transects, thereby allowing a comparison for different spatial extents of the English Channel. In compiling the trace metal data to establish the model it was found that there was only sufficient data, in each compartment, for the fluxes of Cu, Ni and Pb to be estimated with any confidence. The trace metal fluxes across the DS transect were originally estimated by Statham *et al.* (1993) but more recently Prandle *et al.* (1996) have re-examined the fluxes using more reliable data for the water transport. It was found that the trace metal fluxes estimated by Prandle *et al.* (1996) were similar to those obtained earlier. Thus, in the box models developed in this thesis the fluxes for the dissolved and total particulate trace metals were taken from Statham *et al.* (1993). The budgets presented below are Budget A, with LEBP as the westrn transect and Budget B, with CIOW as the western transect.

The budget for a particular trace metal is assumed to be in balance if the total inputs are within ± 20 % of the output. The ± 20 % threshold is arbitrary but could take account of some of the errors in the flux calculations. Thus, if the outflow exceeds the inputs by > 20 % then the English Channel is acting as a source of trace metals and if the inputs exceed the outflow by > 20 % then the Channel is a sink for trace metals.

8.2.2 Copper Budget.

The Quality Status Report (Reid *et al.*, 1993) gives a total riverine input of Cu of 218 t yr^{-1}, for 1990, using the upper range for the flux from the UK. Of this the Seine apparently contributes 166 t yr^{-1}, a flux which is an order of magnitude greater than the range 16-20 t a^{-1} estimated by Chiffoleau *et al.* (1994). These authors also showed that the dissolved Cu flux was a variable proportion of the total flux but was approximately 60 %. Thus, for Budget B the dissolved and particulate fluxes from the rivers have been apportioned 60:40, respectively. All fluxes in the fluxes given in the budget are in t yr^{-1}.

Budget A (LEBP data) Inputs -		Rivers	217
		LEBP transect	1600
		Atmosphere	784
	TOTAL		2601
	Outputs -	DS transect	1320
	Overall -		**+ 1281 Excess**

Budget B (CIOW data)		**Total**	**Dissolved**	**Particulate**
Inputs -	Rivers	217	130	87
	CIOW transect	919	653	266
	Atmosphere	305	256	49
	TOTAL	1442	1039	402
Outputs -	DS transect	1316	894	422
Overall		**+ 125 Balance**	**+ 145 Balance**	**- 20 Balance**

The mass balance for the LEBP transect shows that there is an excess of Cu entering the English Channel, which needs to be accounted for by a removal process. In contrast, the CIOW budget suggests that Cu is in approximate balance, with a slight excess, mainly in the dissolved phase. The large excess in the LEBP budget is likely, therefore, to be dominated by the dissolved phase. In order for the LEBP budget to be balanced, the dissolved Cu must have a sink, and uptake onto suspended particulate matter (SPM) and involvement with phytoplankton metabolic processes are possible mechanisms by which the excess dissolved Cu is removed. The flux from the atmosphere to the sea surface represents a contribution of about 20 % (CIOW transect) to 30 % (LEBP transect) of the total inputs to the English Channel. However, the wet deposition fluxes reported in this study for the LEBP transect (730 t yr^{-1}) are higher than those determined on the coast of Brittany (32 t yr^{-1}), which may be a function of different air masses and their frequencies at the sampling sites. The application of a lower value for the wet flux for the LEBP transect would tend to bring both the total and the dissolved budgets into balance. The dry deposition flux is determined using aerosol concentrations, which include the autumnal peak values, but even so, it only amounts to about 7 % of the total atmospheric flux. If the elevated autumnal concentrations are omitted then the dry deposition flux becomes about 4 t yr^{-1}, which means that dry deposition is a minor component of the atmospheric Cu flux and it makes a relatively small contribution to the overall trace metal budget for the English Channel.

8.2.3 Nickel budget.

There are no data for Ni riverine fluxes in the Quality Status Report. Thus, the total flux of Ni from the Seine, in the range 16-23 t yr^{-1} was used in the budget calculations. Given that for other elements the Seine is the largest contributor to the English Channel of dissolved and particulate trace metals, in the ratio 90:10, this is a reasonable approximation. All fluxes in the budgets below are in t yr^{-1}.

Budget A (LEBP data)	**Inputs -**	Rivers	23
		LEBP transect	1040
		Atmosphere	270
		TOTAL	1333
	Outputs -	DS transect	1143
	Overall		+ 190 **Balance**

Budget B (CIOW data)		**Total**	**Dissolved**	**Particulate**
Inputs -	Rivers	23	21	2
	CIOW transect	620	618	2
	Atmosphere	105	55	53
	TOTAL	748	694	57
Outputs -	DS transect	1143	1040	103
Overall		- 395 **Deficit**	- 346 **Deficit**	- 46 **Deficit**

For the LEBP budget, having a Seine input would serve to move the balanced budget into an excess, which would be small in any case. For the CIOW total budget, an additional river input of about 200 t yr^{-1} of Ni from the Seine (which is of the same order of magnitude for that of Cu) could bring the budget into approximate balance. Since the deficit for dissolved Ni is similar to that for the total, this suggests that any Ni fluxing from the Seine would be mainly in the dissolved form. If the deficits in the CIOW budgets are not accounted for by an input from the Seine, than an additional source of dissolved Ni could be from porewater infusions. It is notable that the dissolved phase plays an important role for Ni, which is probably to be expected due to its general lack of reactivity with particulate matter. The atmosphere plays a minor role in the overall Ni inputs to the Channel, contributing < 20 percent (LEBP and CIOW transects). The wet deposition of Ni found in this study is

150 t yr^{-1}, whereas the value obtained from using fluxes reported in the Quality Status Report (Reid *et al.*, 1993) is 25 t yr^{-1}. If the lower value was used for the calculations for the CIOW transect, then the total deficit would increase, as would the deficit for the dissolved phase. This may serve to enhance the suggestion that the additional source could be porewater infusions. The dry deposition Ni flux is determined using aerosol concentrations which include the autumn peak concentrations and it amounts to about 44 percent of the total atmospheric flux. If the elevated autumnal concentrations are omitted then the dry deposition flux becomes about 8 t yr^{-1}, which means that the dry deposition might be a minor component of the atmospheric Ni flux. Thus, using the lower value for the dry deposition flux brings the LEBP budget closer to the balanced condition. For the CIOW budget, the lower dry deposition Ni flux would increase the deficit slightly but would not significantly affect the conclusions as the overall budget is strongly regulated by the deficit in the dissolved Ni phase.

8.2.4 Lead budget.

The Quality Status report gives a riverine Pb flux, in 1990, of 263 t yr^{-1}, of which the Seine contributes 236 t yr^{-1}. Chiffoleau *et al.* (1994) estimated a total Pb flux from the Seine in the range 9-14 t yr^{-1}, with 80 percent of the transport being in the particulate phase.

Budget A (LEBP data)	**Inputs -**	Rivers	263
		LEBP transect	104
		Atmosphere	240
		TOTAL	607
	Outputs -	DS transect	1170
	Overall		- 563 **Deficit**

Budget B (CIOW data)		**Total**	**Dissolved**	**Particulate**
Inputs -	Rivers	263	53	210
	CIOW transect	216	139	77
	Atmosphere	94	47	47
	TOTAL	573	239	334
Outputs -	DS transect	1170	170	1000
Overall		- 597 **Deficit**	+ 69 **Excess**	- 666 **Deficit**

Both Pb budgets are significantly impacted by the flux of Pb from the Seine, representing about 45 % of the total input, with the atmosphere contributing an additional 40 % of the total Pb input. One can tentatively assign the relative proportions of dissolved and particulate Pb entering the English Channel via the Seine, since it has been shown that most of the Pb will be associated with SPM (Chiffoleau *et al.*, 1994). If this hypothesis is correct and the dissolved Pb in the Seine is transferred to the particle phase, then the amount of excess dissolved Pb in the CIOW budget will be reduced. Thus, dissolved Pb will come close to balance as would be predicted from its potential to react with particles. For the CIOW transect, the atmosphere contributes < 20 % of the total Pb input. The CIOW total budget suggests that there is more Pb leaving the English Channel than entering it (a fact also confirmed by the LEBP budget) and that most of the deficit is accounted for by particulate Pb. Thus, the additional source of Pb could be sediment re-suspension and/or pore water infusions followed by rapid adsorption onto SPM. The wet deposition at the Brittany coast site gave an overall value for the English Channel of 83 t yr^{-1}, which is in relatively good agreement with a wet deposition flux of 110 t yr^{-1} found in this study.

Thus, the box model shows that first order budgets can be made for some trace metals using the data obtained in this study combined with complimentary data in the literature. However, the difficulty of carrying out this type of calculation is illustrated by the large differences in the magnitudes of the wet deposition for Cu, Ni and Pb found in this study compared to those found on the Brittany coast, and some of the gross assumptions made in obtaining fluxes, particularly across the LEBP transect. Thus, the resulting net fluxes are not intended to be taken as absolute values, rather they are meant to be indicative of additional processes for which information is not currently available. The budgets therefore target areas of uncertainty and define potential processes for further investigation.

An interesting outcome of the calculations is that each element appears to behave differently. Thus the Cu budget is largely in balance for the CIOW transect but a large excess of dissolved Cu was predicted using the LEBP transect, which suggests that adsorption of dissolved Cu onto SPM may be occurring. On the other hand, Ni, which is not particle reactive, requires an additional source of dissolved Ni, such as sediment pore waters, in order to be balanced. For Pb, the deficit occurs in the particulate phase and sediment re-suspension may provide an additional source. There is little or no information on these processes, particularly sediment - water exchange processes which are apparently important for Ni and Pb. Thus attention should be paid to the trace metal content of sediments of the English Channel, which may contain a historical pollution load of importance to trace metal budgets. Furthermore, quantification of sediment - water fluxes would enable more accurate budgeting to be carried out. Taking into account differences in the dry deposition fluxes induced by the autumnal pulses in trace metal aerosol concentrations makes little difference to the overall budgets for Cu and Ni. Future determinations of the impact of atmospheric inputs of Cu and Ni into the English Channel could, therefore, be more specifically targeted towards a more accurate quantification of the wet deposition mode.

8.3 Summary.

The following conclusions can be drawn from this research:

- the European aerosol appears to influence both the western English Channel and Celtic Sea aerosols;
- the western English Channel and Celtic Sea aerosols also appears to be influenced by re-suspended terrestrial material from the South West Peninsula;
- trace metal concentrations are dependent on meteorological conditions particularly wind direction;
- the dissolved trace metal flux is clearly the dominant atmospheric deposition route for the western English Channel aerosol;
- atmospheric inputs play a minor part in the geochemical cycling of Cu, Ni and Pb within the English Channel.

8.4 Suggestions for further work.

1. Aerosol samples should be collected (i) over a period of years, and (ii) simultaneously at a number of locations around the western English Channel. This would enable more accurate flux calculations through better spatial resolution, and accountability for inter-annual variations.
2. Meteorology and geology should be integrated into the sampling strategy to enable better understanding of the climatic influences on the area, and the unique source regions of South West England. Rainfall is highly variable over the Peninsula, and this should be more closely monitored. Back trajectories could more accurately determine air mass tracks if calculated more regularly e.g.

every three or six hours. Closer examination of the region's geology would provide accurate crustal source ratios for more accurate EF_{Crust}.

3. Peninsula trace metal sources could also be identified by inclusion of characteristic elements to the investigated suite. Such elements could include As, Sn or U. Investigation of their isotopic ratios in Peninsula crustal source material would provide an accurate method of source fingerprinting unique to South West England.
4. The efficiency of rainfall leaching could be investigated by the collection of aerosol samples before and after rain events - sequential rain water sample collection would provide an insight into the rate of trace metal (and particle) washout.
5. It is clear that both sea and rain water dissolved trace metals undergo complexation, and that such complexation appears to vary according to regional aerosols. Characterisation of such complexing ligands would enable better understanding of aerosols as a source of such ligands to the marine environment, and of the marine biogeochemistry of dissolved trace metals.
6. Model sea water solubility studies could be enhanced by investigation of the affect of e.g. SPM, dissolved organic complexing ligands and microlayer-imitating humic acids, on the extent of trace metal dissolution.

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Appendices

Contents

All appendices are in the form of Microsoft Access databases (Windows 95)

Each database is comprised of tabulated data

Appendix 1: FAAS/GFAAS instrumental parameters – Disk 1

Appendix 2: enrichment factor crustal ratios – Disk 1

Appendix 3: ACSV instrumental parameters – Disk 1

Appendix 4: western English Channel data – Disk 2

Appendix 5: north western Mediterranean data – Disk 1

Appendix 6: Celtic Sea data – Disk 1

Figures 4.1, 5.1 and 6.1 are located on the following pages

Figure 4.1: western English Channel air mass back trajectories.

30 November 1994

27 March 1995

1 December 1994

7 April 1995

22 March 1995

11 April 1995

23 March 1995

13 April 1995

14 April 1995

9 May 1995

2 May 1995

4 July 1995

3 May 1995

7 July 1995

8 May 1995

9 July 1995

21 July 1995

25 July 1995

3 August 1995

4 August 1995

9 August 1995

29 August 1995

4 September 1995

5 September 1995

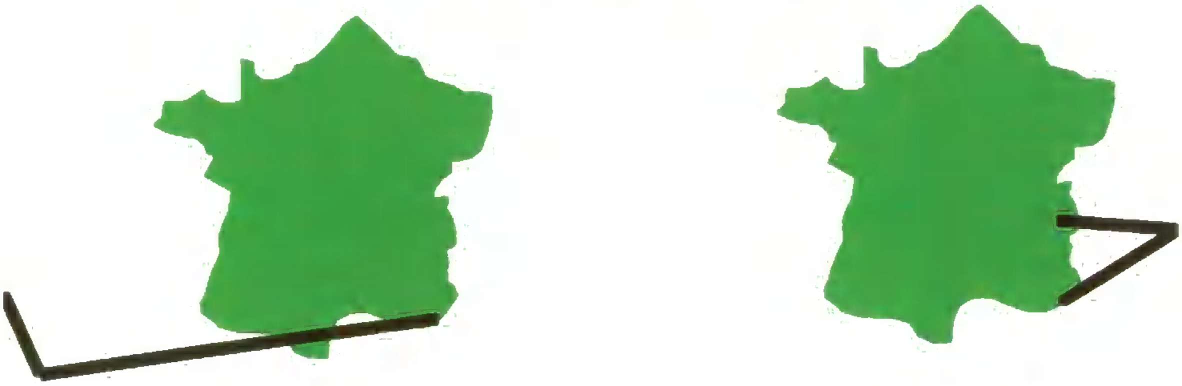
9 September 1995

3 November 1995

1 October 1995

17 November 1995

Figure 5.1: north western Mediterranean air mass back trajectories.

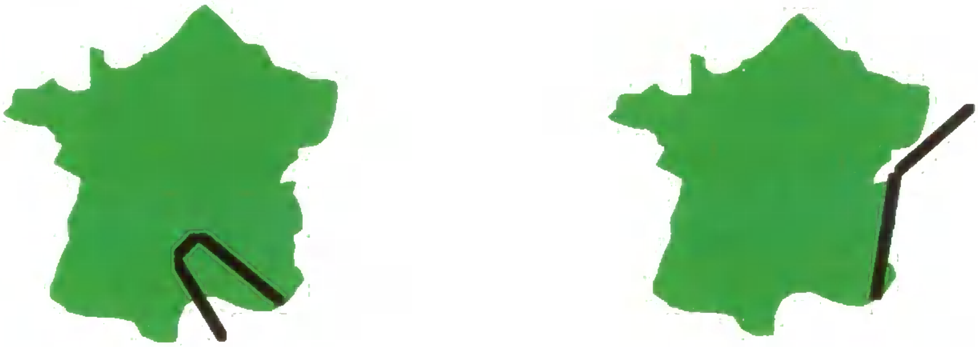


19 February 1993

22 April 1993

2 April 1993

25 April 1993



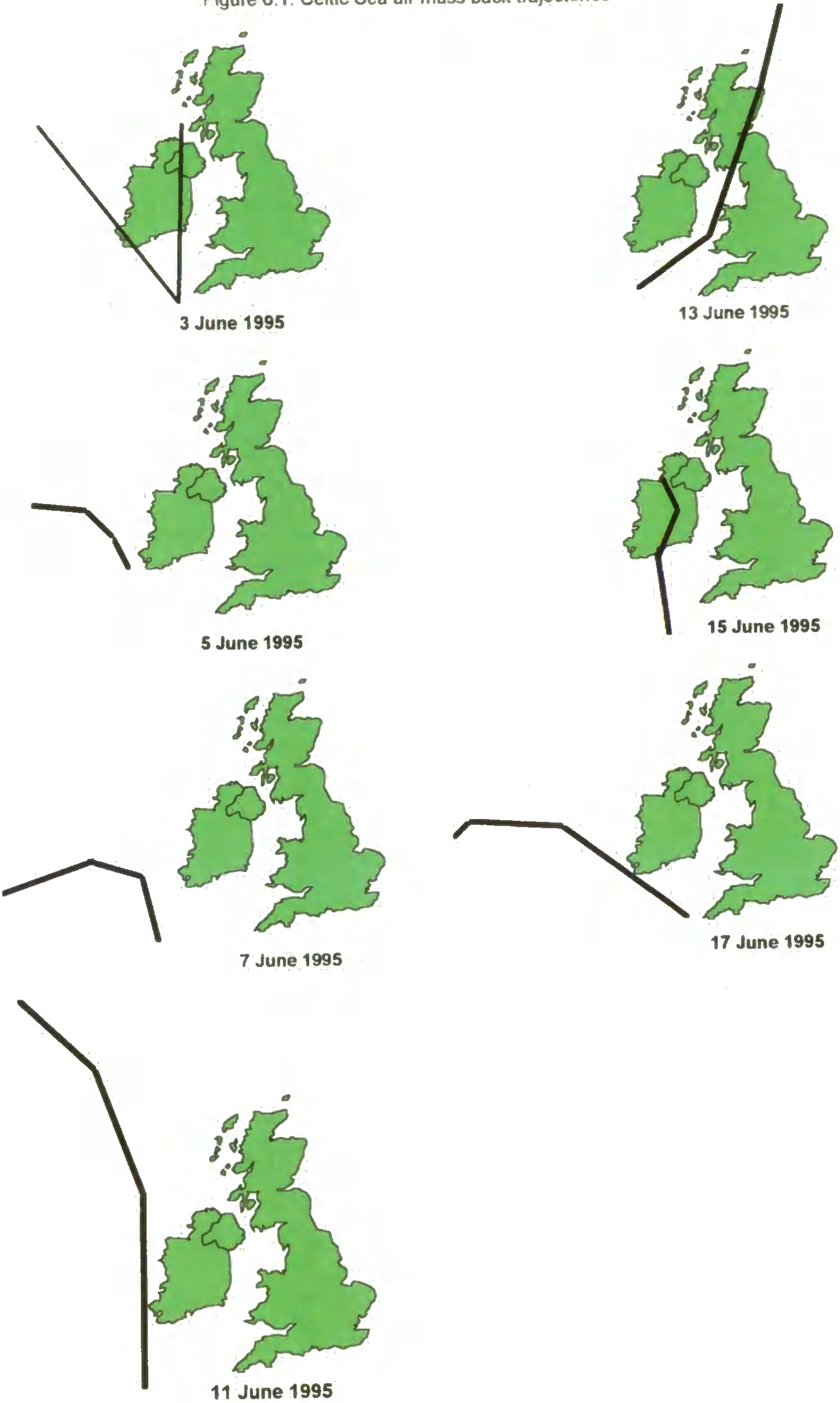
16 April 1993

7 May 1993

20 April 1993

7 July 1993

Figure 6.1: Celtic Sea air mass back trajectories



3 June 1995

13 June 1995

5 June 1995

15 June 1995

7 June 1995

17 June 1995

11 June 1995

27 August 1995

30 August 1995

1 September 1995

3 September 1995

7 September 1995

10 September 1995