Factors Influencing the Seawater Solubility of Aerosol Associated Trace Metals

ABSTRACT

Recent recognition of the importance of trace metals in oceanic biogeochemical cycling and of the significance of atmospheric trace metals inputs to marine waters, highlights the need to assess the dissolved trace metals inputs from atmospheric sources. Atmospheric inputs are important to the surface waters of the Eastern Mediterranean, due to the reduction of riverine inputs. High-volume aerosol samples were collected from Haifa, Israel and Erdemli, Turkey in 1996. These samples were characterised by air mass back trajectories, because contrasting aerosol sources (urban and crustal) are apparent in this region. Trace metal (Cu, Pb and Zn) seawater solubility studies were determined for selected samples, under carefully controlled conditions (seawater at pH 8.0 and 25.0 ± 1.0 °C; shaking rate 150 osc min⁻¹). The average seawater solubilities of Zn and Pb from the northern (predominantly European source) wind sector were statistically higher than the southern (mainly Saharan and Arabian desert source) wind sector. The total dry deposition fluxes of trace metals were estimated from the geometric air concentrations of both wind sectors, the wind sector weighting and assuming a deposition velocity of 0.1 cm s⁻¹. Trace metal seawater soluble fluxes were calculated using mean seawater solubilities of the aerosols from the northern and southern wind sectors. The soluble trace metal fluxes, by dry deposition, to the Eastern Mediterranean were compared with soluble wet deposition and riverine fluxes.

A novel experimental system was assembled and validated, in order to (i) enhance our knowledge of the physiochemical and biological factors that affect the seawater solubility of trace metals and (ii) to refine the soluble trace metal flux estimates. The experimental system was capable of monitoring trace metal desorption reactions at high temporal resolutions (> 45 s). It was initially applied to the measurement of the extent and rate of desorption of total dissolved and 'labile dissolved' Cu, Pb and Zn from Liverpool urban particulate material, then to the seawater solubility of trace metals associated with urban particulate standard reference material and Saharan dust. In order to increase our understanding of the fate of trace metals associated with aerosol particles after dry deposition into seawater, the effects of bacteria, proportional mixing of end member aerosols, particle concentrations, mixing rates, light and temperature on the desorption of aerosol associated trace metals were separately investigated. It was found that the presence of bacteria in seawater and seawater temperature enhanced the seawater solubility of Zn, Pb and Cu. In addition, natural light enhanced the solubility of Cu from Saharan dust. Conversely, increasing the particle concentrations and the mixing rate of the incubated seawater caused a decrease the observed seawater solubility of aerosol associated trace metals (the decrease was greater for Pb and Zn than Cd and Cu).
ACKNOWLEDGEMENTS

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Finally I would like to thank my husband, Roy, and my Mum for their continued support.
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 as a student at any other academic or research institution. This study was financed with the aid of a studentship from the University of Plymouth.

Training programmes attended

A programme of advanced study was undertaken, which included training in trace metal clean techniques at University of Plymouth; attendance of a training course: ‘Analytical methodologies for trace metal speciation in aquatic sampling with quality assurance’, at Porto, Portugal, 27th August 2000 and experience of collecting high-volume aerosol samples from Erdemli, Turkey in April 2001.

Publications


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Presentations and conferences attended

Attend meeting: 'Formation and fate of aerosols from road vehicles and gas turbines' at University College London. 18th September 2001.

Poster presentation: 'The application of an automated dissolved metal monitor for trace metal (Cu, Pb and Zn) particle/dissolved interactions in natural waters', at University of Wales (Bangor). 4th & 5th September 2001. Won best poster prize.


Oral presentation: 'The release of trace metals from atmospheric dust in seawater' at University of Southampton, UK, 9th May 2001.
Oral presentation: 'Factors influencing the seawater solubility of trace metals associated with the Eastern Mediterranean aerosol' at Institute of Marine Science, Middle East Technical University, Erdemli, Turkey, 27th April 2001.


Oral presentation: 'Factors that influence the seawater solubility of aerosol associated trace metals (Cu, Pb and Zn); Impact on their seawater speciation', at 7th FECS conference on Chemistry and the Environment, on 'Metal speciation in the aquatic environment', Porto, Portugal, August 28th-30th 2000.

Oral presentation: 'Factors influencing the seawater solubility of aerosol associated trace metals (Cu, Pb and Zn)', Department of Environmental Sciences, University of Plymouth, 5th May 2000.

Poster presentation: 'The seawater solubility of aerosol associated trace metals from the Eastern Mediterranean (Co, Cu, Ni, Pb and Zn)', Progress in Chemical Oceanography, University of Plymouth, 9th-10th September 1999.


Declaration

Dr Barak Herut (Israel Oceanographic and Limnological Research, National Institute of Oceanography) and Dr Nilgün Kubilay (Institute of Marine Sciences, Middle East Technical University) supplied high-volume aerosol samples collected in 1996 from Tel Shikmona (Haifa), Israel and Erdemli, Turkey respectively. NIO also supplied rainwater samples and Dr Malcolm Nimmo determined their trace metal concentrations (Cu, Pb and Zn). Dr Herut provided Al, Cu, Pb and Zn air concentration data for the Israeli samples, and Dr Kubilay also provided trace metal air concentration data (Al and Zn) for the Turkish samples, presented in Chapter 3.
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This thesis is dedicated to my darling husband,

my lovely daughter and my wonderful Mum
Chapter One

Introduction
1.1 Importance of atmospheric trace metals inputs to the ocean

It is important to quantify dissolved trace metal inputs to the euphotic zone of the oceanic system. The concentration of trace metals available to marine phytoplankton determines primary production in the ocean (Bruland et al., 1991; da Silva and Williams, 1991; Gledhill et al., 1997 and Sunda, 2000); and hence has an indirect impact on important global elemental cycles (e.g. C, S and N). In their lowest concentration range, trace metal nutrients limit primary production (for example see Bruland, 1989; Bruland et. al., 1991; Berger and Wefer, 1991; Martin et. al., 1991; Morel et al., 1994; and Fung et al., 2000); in the intermediate concentration range, optimum growth is obtained; and at higher concentrations, toxic effects are observed (Hunter et al., 1997).

Until the 1970s, riverine inputs were considered to be the only significant terrestrial source of trace metals to the global ocean. However, over the last three decades, the atmosphere has become increasingly recognised as an important source of trace metals for coastal and open ocean environments (for example, Lantzy and Mackenzie, 1979; Chester et al., 1993; Kobilay and Saydam, 1995; Jickells, 1995; Chester et al., 1997 and Herut et al., 2001). The modes of atmospheric and riverine trace metal inputs are distinctly different. Fluvial trace metal inputs are point sources, and supply a significant quantity of metals, primarily in the particulate phase (Table 1.1). However, a large fraction is subject to biogeochemical modifications and removal in estuarine and coastal systems (GESAMP, 1987 and Guieu et al., 1993). In contrast, atmospheric deposition occurs directly onto the surface of the entire ocean.

Most atmospheric trace metals are associated with aerosols, which are fine particulate matter suspended in the atmosphere (Prospero et al., 1983). The atmosphere is an effective transport medium for the transfer of terrestrial particles to the marine environment, as aerosol particles occur throughout the global atmosphere in a ‘dust veil’ (e.g. Blank et al.,
1985 and Guerzoni et al., 1997). Concentrations of aerosols are highly variable both temporally and spatially. Aerosol concentrations may vary from about $10^3 \mu g \ m^{-3}$ in air off arid regions to approximately $10^3 \mu g \ m^{-3}$ in remote oceanic regions (Chester, 2003).

Table 1.1 Deposition of trace metals to the global ocean ($10^9 \ g \ yr^{-1}$)

*Source: Duce et al. (1991)*

<table>
<thead>
<tr>
<th></th>
<th>Atmospheric input</th>
<th>Riverine input</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dissolved</td>
<td>Particulate</td>
</tr>
<tr>
<td>Cd</td>
<td>2.6</td>
<td>0.55</td>
</tr>
<tr>
<td>Cu</td>
<td>29.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Fe</td>
<td>$3.2 \times 10^3$</td>
<td>$29 \times 10^3$</td>
</tr>
<tr>
<td>Ni</td>
<td>9.5</td>
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<td>10</td>
</tr>
<tr>
<td>Zn</td>
<td>102</td>
<td>35.5</td>
</tr>
</tbody>
</table>

Using average trace metal concentrations in air over the surface of the global ocean, Duce et al. (1991) estimated the dissolved and particulate fluxes of trace metals (Cd, Cu, Fe, Ni, Pb and Zn) to the ocean, by wet and dry deposition (Table 1.1). It is clear from their estimates that atmospheric dissolved inputs for trace metals to the global ocean are of the same or a greater order of magnitude than fluvial dissolved inputs (for example Cd, Cu, Fe, Pb and Zn are a factor of 3 – 40 times higher from the atmosphere).

The extent and rate to which trace metals associated with aerosols desorb in seawater are of crucial importance to understanding the biogeochemistry of trace metals in the ocean. Duce et al. (1991) used trace metal seawater solubilities reported by numerous workers (including Hodge et al., 1978; Crecelius, 1980; Statham and Chester, 1988 and Maring and
Duce, 1989) to estimate soluble trace metal fluxes by aerosol dry deposition, to the sea
surface.

1.2 Aims and objectives of the current study

The overall objective of the current study is to define the seawater solubilities of trace
metals (Cu, Pb and Zn) associated with the marine aerosol, with a range of specified
experimental conditions (under controlled seawater pH, temperature, bacteria
concentrations, light, aerosol particle concentrations and stirring rate). The principle aims
are to: (i) assemble and validate an experimental system, which is capable of determining
the extent and rate of desorption of total and ‘labile’ dissolved trace metals at a high
temporal resolution (40 – 120 s) in seawater, under carefully controlled experimental
conditions, (ii) investigate the effect of a range of environmental factors (proportional
mixing of urban and crustal aerosols, presence of seawater bacteria, seawater temperature,
sunlight, mixing rate and particle concentrations) on the seawater solubility of aerosol
associated trace metals, (iii) determine the seawater solubility of environmental aerosols
collected from the Eastern Mediterranean, and (iv) estimate the soluble trace metal fluxes,
by dry deposition, to the Eastern Mediterranean.

1.3 Outline of the thesis

Chapter 2 examines the sources, transport and fate of trace metals associated with the
marine aerosol. Chapter 3 reports on novel work to define the seawater solubility of trace
metals associated with the Eastern Mediterranean aerosol. The impact of sampling
location, aerosol source, seasons and particle concentrations on the seawater solubility of
aerosol associated trace metals from this region was investigated. From this understanding,
dry deposition fluxes of total and soluble trace metals to the Eastern Mediterranean were
calculated.
The study of atmospheric aerosols collected from the Eastern Mediterranean was chosen because atmospheric inputs have become increasingly important, due to the reduction of riverine inputs since the 1960s (Azov, 1991). Furthermore, the region is of interest as it receives contrasting aerosol populations, from crustal sources (from Saharan and Arabian deserts) and urban sources (from local and European sources).

Chapter 4 sets out to describe a novel dissolved metal monitoring system, using stripping voltammetry, to determine the desorption kinetics of trace metals from aerosol particles. This system was optimised, validated and then applied to the measurement of the rate and extent of total and labile dissolved trace metal (Cu, Pb and Zn) release from Liverpool urban particulate material (LUPM). The effect of bacteria on the seawater solubility of trace metals associated with the marine aerosol has not been previously reported. In Chapter 5 the effect of the presence of bacteria is presented and together with an effective, trace metal clean protocol for removing the bacterial contamination.

The effect of temperature, sunlight, particle concentrations, stirring rate and the proportional mixing of urban and crustal aerosols are investigated in Chapter 6. The experiments were undertaken with controlled experimental conditions (constant salinity (S = 33 - 35), pH (8.0 - 8.2), mixing, light / dark conditions, temperature), using the dissolved metal monitoring system described in Chapter 4. The conclusions in Chapter 7 will reassess the soluble ‘dry deposition’ trace metal flux estimates to the Eastern Mediterranean, and highlight future work.
Chapter Two

Sources, transport and fate of trace metals associated with marine aerosols
2.1 Sources of trace elements associated with the marine aerosol

Atmospheric aerosols are chemically and physically heterogeneous, due to a number of factors that include (i) source type (ii) emission strength, (iii) modification reactions during transport, and (iv) removal processes (for example see Injuk et al., 1993; Kubilay and Saydam, 1995; Ganor and Foner, 1996; Gorbunov et al., 1998 and Spokes et al., 2001). These factors may affect the seawater solubility of trace metals associated with aerosol particles in seawater, and hence their fate in the oceanic system (Chester et al., 1993; Spokes and Jickells, 1996; Nimmo et al., 1998 and Guerzoni et al., 1999).

Figure 2.1 Sources of global particle emissions ($x \times 10^6$ tonnes) to the atmosphere per annum (Sources: Prospero et al., 1983 and Nriagu 1979)

The majority of global atmospheric particle emissions are from primary natural sources. Primary sources represent particles that are formed directly from terrestrial or oceanic sources (Murphy et al., 1998). The largest natural source is from sea-salt production; where $500 - 1000 \times 10^6$ tonnes of particles are emitted into the atmosphere each year (Figure 2.1). Sea salt injections are from bubbles bursting at the sea surface, which lead to enhanced concentrations of Na, K, Ca and Mg in the marine aerosol (Arimoto and Duce, 1986, Bergametti et al., 1989, Despiau et al., 1996 and Asher et al., 1996). Trace metals associated with sea-salt particles are largely recycled in the marine environment (Arimoto
et al., 1985 and Migon and Nicolas, 1998a), such that relatively small quantities of trace metals are emitted with sea-salts into the global atmosphere (for example 0.7 % Cd, 5.7 % Cu, 0.4 % Pb and 0.2 % Zn of the total contribution to the worldwide marine aerosol; Nriagu, 1989 and Nriagu and Pacyna, 1988).

Crustal weathering may represent 250 – 500 x 10^6 tonnes of the global particulate emissions per year (Figure 2.1). The Saharan desert is an important source of the terrestrial crustal aerosol; it may generate between 270 – 330 x 10^6 tonnes of particles per year according to Ganor and Mamane (1982). The disparity between the lower estimates of the emission of Saharan dust and the total global emission of crustal particles highlights the uncertainties of estimating source strength of natural particles. Once emitted into the atmosphere, Saharan dust may undergo long-range transport over the tropical North Atlantic, as far as the Caribbean, and southern and eastern parts of the United States, and may also extend over the entire Eastern and Western Mediterranean Basins (for example see Jickells, 1999; Prospero, 1996; Prospero, 1999; Ratmeyer et al., 1999; Herut et al., 2001; Kubilay and Saydam, 1995 and Guerzoni et al., 1995).

During intense desert dust events, the atmospheric aerosol concentrations of Al, Co, Fe and Mn are greatly enhanced (Chester et al., 1996; Jickells, 1999; Kubilay et al., 2000 and Koçak et al., 2004). For example, during periods when the North Atlantic trade winds carry desert dust plumes from the Saharan desert across the Atlantic, the atmospheric Al and Co concentrations may be 2 – 4 orders of magnitude higher than that observed in the typical remote marine aerosol (Table 2.1). Similarly it has been noted that during the spring, considerable dust clouds are transported over the Pacific Ocean from the Gobi and Maklan deserts in Asia (Blank et al., 1985 and Husar et al., 2001). Despite the dramatic desert dust inputs to the global atmosphere, the crustal contribution of Cd, Cu, Pb and Zn
to the global aerosol is only ca. 2, 13, 1 and 11 % respectively (Nriagu, 1979 and Nriagu and Pacyna, 1988).

Table 2.1 Geometric mean trace metal concentrations of atmospheric aerosol populations  
(Source: \textsuperscript{a}Murphy, 1985; \textsuperscript{b}Chester and Bradshaw, 1991; \textsuperscript{c}Fones, 1996; \textsuperscript{d}Duce et al., 1983 \textsuperscript{e}and \textsuperscript{f}Arimoto et al., 1987)

<table>
<thead>
<tr>
<th></th>
<th>Crustal aerosol</th>
<th>N. European aerosol</th>
<th>Remote marine aerosol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N. Atlantic NE trades\textsuperscript{a}</td>
<td>North Sea\textsuperscript{b}</td>
<td>Irish Sea\textsuperscript{c}</td>
</tr>
<tr>
<td>Al, ng m\textsuperscript{-3}</td>
<td>5925</td>
<td>219</td>
<td>210</td>
</tr>
<tr>
<td>Cd, ng m\textsuperscript{-3}</td>
<td>0.12</td>
<td>0.23</td>
<td>0.19</td>
</tr>
<tr>
<td>Co, pg m\textsuperscript{-3}</td>
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<tr>
<td>Zn, ng m\textsuperscript{-3}</td>
<td>16</td>
<td>26</td>
<td>26</td>
</tr>
</tbody>
</table>

An additional, important natural source of aerosols to the marine environment is from secondary aerosol production; which contributes nearly a quarter of the total global marine aerosol (Figure 2.1). Secondary aerosols are formed indirectly, within the atmosphere, through the condensation and chemical reactions of gases and vapours. One example is the production of non sea-salt sulphate. The predominant precursor is dimethyl sulphide (DMS), formed during marine biological production (Andreae, 1990 and Turner et al., 1996). Other primary natural sources of atmospheric particles include volcanic emissions, smoke from burning wood and biotic emissions (for example pollen, lipids and organic
acids; Gogou et al., 1996); which represents approximately 5% of the global annual particulate emissions (Figure 2.1).

Due to increasing industrialisation during the past two centuries, there has been an increased input of anthropogenic trace metals into the atmosphere, primarily from high-temperature processes. These trace metal emissions originate mainly from the northern hemisphere (Volkening and Heumann, 1990 and Duce et al., 1991). The main sources include fossil fuel combustion, chemical production, agricultural activity, kiln operations from cement plants, waste incineration and the processing of mineral ores (Nriagu and Pacyna, 1988 and Pirrone et al., 1999). Therefore, as a result of these anthropogenic sources, several metals are likely to be enriched in the marine aerosol; they include Sb, As, Cd, Cu, Hg, Ni, V and Zn; and it is thought that anthropogenic sources contribute ca. 56 - 84% of these metals to the global aerosol (Nriagu, 1979 and Nriagu and Pacyna, 1988). An example of such enhancement is presented in Table 2.1, where it is apparent that Irish Sea and North Sea aerosol trace metal concentrations (Cd, Co, Cu, Pb and Zn) are 1 – 2 orders of magnitude greater than those typically observed in remote marine aerosol in the Pacific. This is owing to the proximity of these two locations to European industrial regions.

The increased mobilisation of trace metals into the atmosphere since the industrial revolution was observed in Greenland snow and ice cores (Boutron et al., 1991 and Lobinski et al., 1994). For example, records of Pb inputs from leaded fuel consumption during the 20th century were observed from these cores. Figure 2.2 illustrates that has been an increase in Pb aerosol concentrations with time, particularly in the 1950s. In the 1980s anthropogenic sources contributed 97% global atmospheric Pb emissions (Nriagu, 1979 and Nriagu and Pacyna, 1988). However, since then the emissions of Pb to the atmosphere have declined rapidly in Western Europe and North America (Migon et al., 1993; Migon et
al., 1994; Migon and Nicolas, 1998b and Pirrone et al., 1999) mainly owing to a greater usage of unleaded petrol. From 1970 – 1990 Pb concentrations in Greenland snow have decreased by a factor of 7.5. Similarly, Cd and Zn concentrations have diminished by a factor of 2.5 over the same period of time (Boutron et al., 1991).

*Figure 2.2 Changes in Pb concentrations in Greenland ice and snow from 5,500 BP to present (Source: Boutron et al., 1991)*

![Graph showing changes in Pb concentrations in Greenland ice and snow from 5,500 BP to present.](image)

2.2 Methods used to identify marine aerosol elemental sources

2.2.1 Particle size distributions

It is evident that there are several contrasting sources, both natural and anthropogenic, to marine aerosol populations. It is therefore important to determine the sources of individual marine aerosol populations, in order to understand how they may influence the quantity of trace metals released into seawater. The particle size distribution of the marine aerosol is a possible source indicator (Prospero et al., 1983 and Despiau et al., 1996). It is governed by...
aerosol formation and subsequent modification in the atmosphere, ultimately determining their transport pathway in the atmosphere and their fate in the marine environment.

Figure 2.3 Distribution of aerosol particles based on particle size and particle formation processes (Source: Whitby, 1977)

Whitby (1977) illustrated that the particle size distribution of the global aerosol has a multi-modal distribution (Figure 2.3). 'Fine' particles (< 2 μm diameter) were generally associated with high temperature, anthropogenic sources, whilst 'coarse' particles (> 2 μm diameter) were usually related to low temperature, natural sources. The bimodal maxima in the 'fine' particle population (Figure 2.3) represent the 'Aitken nuclei' range (< 0.1 μm diameter) and the 'accumulation range' (0.1 – 2 μm diameter) (Prospero et al., 1983). Aitken nuclei are removed from the vapour phase via condensation reactions and gas-to-particle reactions, where vapour is adsorbed to other larger particles (Whitby, 1977). Thus,
many of the elements released during natural and anthropogenic high-temperature processes become associated with the accumulation range. It is to be expected that anthropogenic metals such as Zn, Pb, Cu and Cd are associated with the accumulation range (Arimoto and Duce, 1986; de Bock et al., 1994; Chester et al., 1999 and Morawska et al., 1999).

‘Coarse’ particles (> 2 µm diameter) are mainly the result of low-temperature, mechanical processes such as crustal weathering and bubbles bursting from the sea surface, causing sea spray. Coarse particles are also the result of incomplete combustion processes (Wadge et al., 1986), and from the re-suspension of particles from the land (Nicholson, 1988). Such particles have a shorter residence time in the atmosphere than ‘fine’ particles, due to their larger size and therefore greater settling velocities (Arimoto and Duce, 1986 and Chester et al., 1999). Typical elements associated with crust-derived particles are Al, Fe, Sc, Cr, and Co, and have median mass diameters (MMDs) between 2 – 3 µm. Whereas sea-salt aerosol particles include Na, Ca, Mg and K and the MMDs are between ~ 3 – 7 µm (Arimoto and Duce, 1986; de Bock et al., 1994 and Chester et al., 1999).

Close to the source, the composition and particle size distribution of the aerosol population will be strongly related to the parent material (Spokes and Jickells, 1995). During transport, the physical and chemical character of the aerosol may change due to ‘ageing’ (Andreae and Crutzen, 1997; Gorbunov and Hamilton, 1997; Song and Carmichael, 1999 and Ellison et al., 1999). For example, in the remote marine atmosphere, silicate and sea salt aerosols have a similar size distribution. Andreae et al. (1986) suggested that aerosol cycling within clouds causes an internal mixing of the aerosol particles. Subsequently the size of remote marine aerosol particles is typically uniform because of preferential removal of larger particles from the atmosphere. Therefore, the particle size distribution of an aerosol population is not always an ideal indicator of the original source.
2.2.2 Enrichment factors (EF)

The marine aerosol is composed of material from various sources, each with different chemical and physical characteristics that may influence the rate and extent of the release of trace metals from aerosol particles in seawater. The observed atmospheric aerosol trace metal concentrations are not always a good indicator of the elemental aerosol source because source emission strengths may vary, and because of the removal processes that occur prior to the aerosol population reaching the sampling site. The source of an aerosol population is more commonly determined by applying an enrichment factor (Chester et al., 1993; Migon and Nicolas, 1998a; Guieu et al., 1997 and Chester et al., 1999):

\[
\text{EF} = \left( \frac{E}{X} \right)_{\text{air}} / \left( \frac{E}{X} \right)_{\text{source}}
\]

where \( E \) is the element of interest and \( X \) is the elemental source indicator. A marine indicator such as Na is not generally used because \( \left( \frac{E}{Na} \right)_{\text{source}} \) will represent the sea surface microlayer, rather than bulk seawater. The problem with the sea surface microlayer is that its elemental composition is poorly defined; therefore, the calculations of \( \text{EF}_{\text{sea}} \) would be in doubt. There is no element that typifies global anthropogenic emissions; therefore, a terrestrial source indicator is more commonly used enabling the calculations of the crustal enrichment factors (\( \text{EF}_{\text{crust}} \)).

The \( \text{EF}_{\text{crust}} \) may be used to assess the degree to which a trace metal in an aerosol population is enriched relative to the crustal source. Aluminium is normally used as the crustal source indicator element (for example, Kubilay and Saydam, 1995; Ridame et al., 1999; Chester et al., 2000a and Herut et al., 2001). The crustal enrichment factor is calculated as follows:

\[
\text{EF}_{\text{crust}} = \left( \frac{E}{Al} \right)_{\text{air}} / \left( \frac{E}{Al} \right)_{\text{crust}}
\]
where, \((E/Al)_{air}\) are the concentrations of the element of interest and Al in the aerosol, and \((E/Al)_{crust}\) are the elemental concentrations in average crustal rocks (Taylor, 1964 and Taylor and McLennon, 1985). By convention an element in an aerosol with \(EF_{crust} < 10\) is largely crustal in origin and is termed a non-enriched element (NEE). Whereas if the \(EF_{crust} > 10\) the element is mainly of anthropogenic origin, and is referred to as an anomalously enriched element (AEE). Although the \(EF_{crust}\) is a useful method for comparing aerosol populations, it should be interpreted cautiously as it does not take into account regional variations in the mineralogy of the crustal precursor material and physical fractionation during dust generation (Guieu et al., 2002).

Noting the caution, the proportion to which an AEE is enriched within contrasting aerosol populations varies greatly (Table 2.2), depending upon the relative contribution of the different source types to aerosol populations. In some aerosol populations, where crustal material is the dominant source, those elements that normally behave as AEEs may exhibit NEE behaviour. Murphy (1985) demonstrated that this occurred for Cu, Pb and Zn in the North Atlantic northeast trade winds (calculated \(EF_{crust}\) values were 1.1, 7.7 and 3.2 respectively; \(Al = 5925 \text{ ng m}^{-3}\)). In contrast, the remote marine aerosol typically contains trace metals that are anomalously enriched (for example in the remote South Pacific calculated \(EF_{crust}\) for Cu, Pb and Zn were 27, 146 and 114 respectively; Arimoto et al., 1987). However, the observed trace metal atmospheric concentrations are lower than those normally observed in a coastal zone (for example 0.04, 0.12 and 0.17 ng m\(^{-3}\) of Cu, Pb and Zn in the South Pacific aerosol, Arimoto et al., 1987). This would indicate that the small, anthropogenically derived particles have a comparatively longer residence time in the atmosphere, compared with larger Al-rich crustal aerosol particles, leading to a differentiation in removal during their atmospheric transport.
Table 2.2 Elemental crustal enrichment factors of Cd, Co, Cu, Ni, Pb and Zn, and Al aerosol concentrations (ng m\(^{-3}\)) in contrasting atmospheric aerosol populations

(Sources: \(^a\) Murphy, 1985; \(^b\) Chester and Bradshaw, 1991; \(^c\) Fones, 1996; \(^d\) Wells, 1999; \(^e\) Chester et al., 1999; \(^f\) Kubilay and Saydam, 1995; \(^g\) Herut et al., 2001; \(^h\) Duce et al., 1983 and \(^i\) Arimoto et al., 1987)

<table>
<thead>
<tr>
<th></th>
<th>Crustal rich aerosol</th>
<th>European and Mediterranean aerosol</th>
<th>Remote marine aerosol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N. Atlantic NE trades(^a)</td>
<td>North Sea(^b)</td>
<td>Irish Sea(^c)</td>
</tr>
<tr>
<td>Al</td>
<td>5925</td>
<td>219</td>
<td>210</td>
</tr>
<tr>
<td>Cd</td>
<td>8.3</td>
<td>436</td>
<td>368</td>
</tr>
<tr>
<td>Co</td>
<td>1.2</td>
<td>2.7</td>
<td>2.1</td>
</tr>
<tr>
<td>Cu</td>
<td>1.1</td>
<td>30</td>
<td>33</td>
</tr>
<tr>
<td>Ni</td>
<td>1.2</td>
<td>13</td>
<td>19</td>
</tr>
<tr>
<td>Pb</td>
<td>7.7</td>
<td>601</td>
<td>468</td>
</tr>
<tr>
<td>Zn</td>
<td>3.2</td>
<td>139</td>
<td>139</td>
</tr>
</tbody>
</table>
Rahn et al. (1979) calculated the geometric mean $EF_{crust}$ from >100 samples from the global aerosol. It was found that nearly half of the considered elements were AEEs. These elements included Cu and Ni (~10—100), Zn (~100—1000), and Pb and Cd (~1000-10,000). These broad enrichment factor trends have been further highlighted and confirmed by a range of recent studies in coastal systems in NW Europe and the Mediterranean (see Table 2.2), whereby $EF_{crust}$ Co < Cu, Ni < Cd, Pb and Zn. The more recent $EF_{crust}$ values for Zn (~30 - ~140), Cd (~200 - ~450) and Pb (~40 - ~600) are approximately one order of magnitude less than that found in Rahn et al. (1979). This further illustrates abatement in the emission in anthropogenic trace metals (Cd, Pb and Zn) to the atmosphere in Europe since 1970's.

2.2.3 Air mass back trajectories

Most aerosols in the atmosphere are introduced initially into the troposphere; which then forms their primary transport route. The tropospheric boundary layer is typically 1 km above ground level, but may vary from 20 m to several km in height (Barry and Chorley, 1998). The movement of air masses within the troposphere varies, and is dependent on the surface conditions and the overlying synoptic systems. Aerosols can be transported for tens to hundreds of kilometres within the boundary layer (Prospero, 1981). Above the boundary layer, the wind speeds are greater; therefore, aerosols may be transported over longer distances.

The knowledge of the origin of aerosol samples collected at a specific location can be obtained with the use of air mass back trajectories. Back trajectories are calculated from wind vectors observed at different locations, and then from the application of a mathematical model (for example the ECMWF model from the Meteorological Office). The trajectories are typically calculated at different arrival heights (for example 700, 850,
950 and 1000 hPa) above the sampling location. Collected aerosol samples can then be
categorised into different wind sectors.

The accuracy of back trajectory models is dependent on the spatial resolution of the
observed meteorological data. A further drawback is that air mass back trajectories do not
provide information on precipitation during the transport of an air mass, which might
explain the variance in the atmospheric concentrations of the considered trace metals.
However, this approach has been successfully adopted by a number of recent studies on
understanding the impact of air mass source on atmospheric trace metal concentrations and
EF\textsubscript{crust} values (e.g. Kubilay, 1996; Wells, 1999; Chester et al., 2000a, Herut et al., 2001 and
Spokes et al., 2001).

2.3 Modes of deposition of the marine aerosol

The quantitative evaluation of trace metal fluxes and their fate is essential to understanding
marine biogeochemical cycles. The flux of aerosol associated trace metals to the sea
surface is controlled by 'dry' and 'wet' deposition. Wet deposition accounts for
approximately 80 % of the atmospheric removal of anthropogenically influenced elements
such as Pb, Zn, Cd, Cu, and Ni to the global ocean. For crustally derived elements (Fe and
Al), wet deposition contributes about 60 % of the atmospheric removal (Duce et al., 1991).
The relative importance of wet and dry deposition depends on the rainfall intensity at a
particular time and location.

Wet deposition involves scavenging aerosols from the atmosphere by cloud droplets and
precipitation. This mode is a sporadic process, controlled by rain events. In the dry
deposition mode, aerosols are delivered directly to the sea surface. This mode is an almost
continuous process, influenced by wind speed and humidity, as well as aerosol size (and
hence settling velocity; Buat-Menard, 1986 and Slinn, 1982).
2.4 Fate of aerosol associated trace in the oceanic system

It is now clear that the atmospheric cycles of some trace metals (especially Pb, Cu, Cd, Ni and Zn) are strongly perturbed by human activities (see previous sections). How such a geochemical perturbation in the atmosphere interacts with the oceanic cycles of anthropogenic elements is of crucial interest since most of these elements are micro-nutrients, and are potentially toxic at higher concentrations. In this section, the impact of trace metal dissolution upon vertical dissolved metal distributions and on metal biogeochemical cycles is considered.

The impact of atmospheric trace metal inputs on marine biogeochemical cycles is strongly dependent upon the physical and chemical forms in which the metals enter the marine system. Typical concentrations of particles in seawater are 20 – 50 µg l⁻¹ (Turner, 1995), some of which will be from atmospheric sources. Particulate associated trace metals are unlikely to have a significant impact on biological activity, except in the case of a few marine organisms (for example filter feeders, Allison et al., 1998). Soluble trace metal inputs, in contrast, are more easily taken up by biota (Spokes and Jickells, 1995, Jickells, 1999 and Sunda and Huntsman, 2000).

The wet and dry deposition modes may have different geochemical fates in the marine environment. Trace metal solubility from the wet deposition mode is initially controlled by the particle - rainwater reactivity. Several rainwater studies have shown that trace metal solubilities are primarily a function of aerosol type, particle size distribution and pH history of the aerosol in the atmosphere (Statham and Chester 1988; Losno et al., 1993; Spokes et al., 1994; Lim et al., 1994; Chester et al., 1997; Chester et al., 2000b and Desboeufs et al., 2001). In the dry deposition mode, the aerosols are delivered directly to the sea surface, therefore the rate and extent of the trace metal seawater solubility is
constrained by particle - seawater reactivity (Chester et al., 1993 and Chester et al., 1994). Trace metal seawater solubility is defined as:

Equation 2.3 \[ \% \text{ soluble} = \frac{D}{P} \times 100 \% \]

where D is dissolved concentration of the metal and P is the total metal concentration originally present with the aerosol material, in the particulate form.

It is important to evaluate the kinetics of the dissolution of aerosol associated trace metals, in order to understand the impact atmospheric deposition on biological productivity in the upper layer of the sea surface. Some studies have investigated the time taken for the release of trace metals from aerosol material to reach equilibrium in seawater (Mn: Statham and Chester, 1988 and Guieu et al., 1994; Ni, Co, Cu, Pb and Cd: Nimmo et al., 1998). From the kinetic profiles of these studies, it is clear that most trace metal dissolution occurs within the first 30 min. It appears that particle - dissolved equilibrium is attained within 1 h for Cd, Co, Cu, Ni and Pb (however the lifetime of the experiments by Nimmo et al., 1998 was only 1 h), and 2 h for Mn (Figure 2.4). Therefore, the dissolution of trace metals from aerosol particles may have a significant impact on biogeochemistry of the upper layer of the sea surface. However, rate constants and initial rates of reaction could not be determined from these studies, because of the low temporal resolution of the dissolved trace metal measurements. (For discussion on the time taken to reach particle-dissolved equilibrium, in the context of residence times in the seawater surface, see section 6.3.8).
Figure 2.4 Release of trace metals from Saharan dust (100 mg l⁻¹ dust for Ni, Co, Cu, Pb and Cd; 5 mg l⁻¹ for Mn) into seawater (Sources: Nimmo et al., 1998 and Statham and Chester 1988). For Mn kinetic profile: ○ = light experiment and ● = dark experiment.
The evaluation of trace metal dissolution kinetics may also be important when considering the uptake rate of trace metals by marine microorganisms. Several trace metal elements play a key role in a range of metabolic processes (Butler, 1998 and Morel et al., 1991), as micronutrients; for example in protein structures (Zn; Berg and Shi, 1996), as electron carriers in the photosynthetic cycle (Cu and Fe; Coale and Bruland, 1988), and as constituents in enzymes (for example Zn and Cd in carbonic anhydrase; Lee and Morel, 1995).

Surface dissolved concentrations of bioactive trace metals (Cd, Cu, Fe, Ni and Zn) in the ocean are often lower than those at depth due to enhanced uptake of these metals by phytoplankton (Boyle et al., 1976, Bruland et al., 1978, Bruland, 1980, Bruland et al., 1991, Yeats et al., 1995 and Butler, 1998). However, in non-steady state conditions, enhanced atmospheric dust inputs may lead to changes in the rate of primary production and to changes in the structure of algal communities (Brand et al., 1983; Brand, 1991; Di Tullio et al., 1993; Gonzalez-Davila, 1995; Subba Rao and Al-Yamani, 1999 and Sunda, 2000).

Atmospheric aerosol deposition may also control the concentration and distribution of scavenged-type metals, best exemplified by Al, Mn and Pb (Stumm and Morgan, 1996). These elements can show surface maximum concentrations, due to atmospheric dust deposition (Maring and Duce, 1990; Guieu et al., 1992; Jickells et al., 1994; Morley et al., 1997 and Measures and Vink, 2000). Furthermore, in the case of Pb and Al, they are not under active uptake by microorganisms because they are non-essential metals, and are potentially toxic (Hunter et al., 1997).

Dissolved concentrations of scavenged metals decrease with depth, due to particle scavenging. The typical ocean residence time of dissolved scavenged elements is \( \ll 10^3 \)
years. In contrast, for dissolved micronutrients the residence time is $10^3 - 10^5$ years, because they are recycled in the euphotic zone. Additionally, the particles with which they are initially incorporated are redissolved below the euphotic zone due to microbial activity (Whitfield and Turner, 1987).

2.5 Seawater solubility of aerosol associated trace metals

Various studies have been undertaken to evaluate the solubility of trace metals from aerosols equilibrated in seawater (Table 2.3). The results from these studies demonstrate a large degree of variability in the seawater solubility of aerosol associated trace metals. The observed variability may be influenced by abiotic factors such as (i) the chemical composition of aerosol populations, (ii) their particle concentration in seawater, (iii) solid-state speciation of the aerosol associated trace metals, (iv) seawater temperature, (v) photochemical processes and, (vi) the effects of organic ligands derived from both seawater and from the aerosol population itself. The variability may be also affected by the presence of microorganisms.

2.5.1 Effect of the aerosol source

Studies have been undertaken to investigate the influence of the aerosol source on the seawater solubility of aerosol associated trace metals (Chester et al., 1993; Guieu et al., 1994; Nimmo et al., 1998; Wells, 1999 and Guerzoni et al., 1999). It is evident from Table 2.3 that crustal aerosol populations (Saharan dust) have proportionally lower trace metal seawater solubility values and a lower range compared with urban aerosols. Chester et al. (1993) showed that trace metals could be categorised into a number of general types, which may be related to their solid-state speciation signatures, and hence explain their seawater solubility trends.
Table 2.3 Percentage seawater solubility of trace metals in the global marine atmospheric aerosol

<table>
<thead>
<tr>
<th>Aerosol source / sampling location</th>
<th>Aerosol type</th>
<th>Type 1</th>
<th>Type 2</th>
<th>Type 3</th>
<th>Type 4</th>
<th>Reference</th>
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<td>&lt; 1</td>
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<td>1</td>
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<td></td>
<td></td>
<td>Guieu et al., 1994</td>
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<td>&lt; 0.013</td>
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<td>Spokes and Jickells, 1996</td>
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<td>9</td>
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<td>34</td>
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</tr>
<tr>
<td>Arabian Sea</td>
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<td>&lt; 1</td>
<td>25</td>
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<td>4</td>
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<td>39</td>
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<td>55</td>
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<td>51</td>
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<td>5</td>
<td>&lt; 1</td>
<td>45</td>
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<tr>
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<td>55</td>
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<td></td>
<td></td>
<td>Zhuang et al., 1990</td>
</tr>
<tr>
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<td>Remote</td>
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<td></td>
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<td>Marian and Duce 1989</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Marian and Duce 1990</td>
</tr>
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</table>
The trace metal association with aerosol particles, is often categorised using three operationally-defined stages: (i) the exchangeable fraction that is released by 1 M ammonium acetate, (ii) the carbonate / oxide fraction dissolved by 1 M hydroxylamine hydrochloride and 25 % v/v acetic acid and (iii) the refractory stage that is released by nitric and hydrofluoric acids (Chester et al., 1989; Chester et al., 1993; Chester et al., 1994 and Chester et al., 1995). A statistically significant positive correlation exists between the trace metal seawater solubility and exchangeable fraction (Chester et al. 1993).

Figure 2.5 Solid-state speciation signatures in (A) a crustal, Saharan aerosol and (B) an urban aerosol (Liverpool urban material). (Source: Chester et al., 1993)

According to Chester et al. (1993), Type 1 elements are crust-controlled (Al, Si and Fe) and generally have very low seawater solubilities (< 10 %) from both crustal and urban aerosol populations. The solid-state speciation signatures in non-remote aerosols typically have < 5 % of Al and Fe in the exchangeable fraction (Figure 2.5). Similarly, Type 2 elements (Cr, Co and Mn) are crust-controlled (i.e. are NEEs), but have intermediate
seawater solubility values (~10 - ~50 %) from both crustal and urban aerosol populations. This may be explained in relation to the solid-state speciation signature: for example, even in the crustal aerosol population, an average of 38 % of Mn is associated with the exchangeable host (Figure 2.5).

Type 3 elements (Ni, Cu, Pb and Zn,) have higher $\text{EF}_{\text{crust}}$ and seawater solubilities in the urban than in the crustal aerosol populations. Urban aerosols from the UK, USA and the western Mediterranean, had a wide range of seawater solubility values (Cu 28 - 58 %, Ni 23 - 50 %, Pb 20 - 88 % and Zn 58 - 75 %; Hodge et al., 1978; Kersten et al., 1991; Chester et al., 1994; Fones, 1996; Nimmo et al., 1998 and Guerzoni et al., 1999). Whilst the seawater solubilities of Type 3 elements associated with Saharan dust were much lower (Cu 1 - 9 %, Ni 7 %, Pb < 1 - 9 % and Zn < 1 %; Chester et al, 1993, Nimmo et al., 1998 and Guerzoni et al., 1999).

Chester et al. (1993) showed that there was proportionally less Cu, Pb and Zn associated with crustal aerosols in the exchangeable fraction, in comparison with urban aerosols (Figure 2.5). Since the crustal aerosols are primarily formed through crustal weathering, the incorporated trace metals are chiefly within the aluminosilicate lattice. In contrast, high-temperature processes predominantly form urban aerosols. At high temperatures, some metals may undergo volatilisation, which may subsequently form loosely held, surface-associated trace metals via condensation, or adsorption onto the surfaces of ambient particles (Chester et al., 1989). Thus, a greater fraction of the trace metals associated with the particles is more readily exchangeable in solution.

Similar to the urban aerosol, the seawater solubility of Cu and Pb from the remote marine aerosol (Equatorial N Pacific) were relatively high compared to the crustal aerosol populations (74 - 99 % and 17 - 92 % respectively; Maring and Duce, 1989 and Maring
and Duce, 1990). Copper, Pb and Zn often behave as AEEs in the urban and remote marine aerosol, rather than as NEEs, and have a potentially different solid-state speciation signature (Chester et al, 1989). They hence could exhibit a different geochemical behaviour once deposited in seawater, than crustal aerosol populations.

Relatively high seawater solubility values for Cd in both anthropogenic (61 – 95 %) and crustal (19 – 57 %) aerosols were observed (Table 2.3). This element is classified as ‘Type 4’ because it was found to be largely located in exchangeable fractions in both aerosol types, even in the crustal aerosol, where the exchangeable fraction was 60 % (Chester et al., 1993). Even the Saharan aerosol may be subject to a small extent to some anthropogenic sources, thus Cd from high-temperature processes might be incorporated into the aerosol population.

2.5.2 Effect of seawater particle concentrations

A few studies have reported a decrease in the solubility of aerosol associated trace metals with increasing particle concentrations. For example Guerzoni et al., (1999) observed an inverse relationship between the particulate load of different filter-collected samples from Sardinia and the solubilities of Al, Fe and Pb. However, samples with the highest particulate loadings were Saharan, crustal aerosols, and the lowest particle loadings were associated with urban aerosol samples. Urban aerosols can be expected to have higher seawater solubilities than the Saharan aerosol, because they generally have higher proportions of trace metals in ‘exchangeable’ associations (Chester et al., 1993). Systematic studies of the effect of particle concentrations on the seawater solubility of trace metals from crustal and urban aerosols are required to further elucidate and decouple these conflicting impacts.
Spokes and Jickells (1996) also observed an inverse relationship between the solubility of Fe and the particle load in acidified Milli-Q water (pH 2), for a Saharan aerosol. At aerosol loadings < 0.5 mg l\(^{-1}\), up to 7% of the Fe present in the aerosol underwent dissolution, with this value decreasing rapidly to ~1.4% at particle concentrations > 120 mg l\(^{-1}\). Similarly, Zhuang et al., (1990) showed that increasing the total Fe concentrations in seawater significantly decreased the soluble Fe fraction. At total Fe concentrations below 2 nM, 50% of the aerosol associated Fe underwent dissolution, with this value decreasing to 7% at total Fe concentrations between 40 – 90 nM. At high particulate loadings, net readsorption may occur onto aerosol particles and colloids, resulting in the net removal of dissolved metals from seawater. Also, increased particle aggregation may occur with increased particle loadings, leading to a net decrease in trace metal desorption sites, leading to lower trace metal seawater solubilities (Spokes and Jickells, 1996).

The study into the trace metal seawater solubilities of fly ash by Crecelius (1980) may illustrate an extreme case of the particle concentration effect. Very high particle concentrations (1 g l\(^{-1}\)) were applied in this study. The trace metal seawater solubility values observed were surprisingly low (< 1% for Co and Zn) for an urban aerosol. This may be due to the presence of these metals as insoluble oxides in the glassy matrix of the fly ash particles. However, this may have also been partly due to the particle concentrations, which were far from environmentally realistic. As a result of such high concentrations, there might have been extensive readsorption of dissolved Zn and Co onto the aerosol particles or particle aggregation.

The wide use of filter-collected aerosol samples to determine trace metal seawater solubilities has meant that the particle concentrations in most seawater solubility studies were not specified. It is not known whether a ‘particle concentration effect’ was induced in these studies. However, most of these studies used a small volume of seawater (25 ml for
Chester et al., 1993 and Chester et al., 1994; Maring and Duce 1989 and 1990; 75 ml for Fones 1996 and Wells 1999; 100 ml for Hodge et al., 1978; Crecelius 1980 and Guerzoni et al., 1999). This would indicate that high particle concentrations may have been employed and that the seawater solubility of trace metals in the marine environment may have been underestimated, for some of these studies. Not enough information was given to provide even a rough approximation of the particle concentrations. In addition, there are potential problems of the presence of filter substrates in the incubated seawater volume, because they can act as sources or sinks of trace metals (see section 3.2.8).

2.5.3 Effect of seawater temperature

Sea surface temperature varies seasonally and spatially; it may vary from ~ 28 °C in the equatorial regions to ~ -2 °C in polar seas (Chester, 2003). The extent and rate of the trace metal desorption from aerosol particles may be affected by seawater temperature. No previous trace metal seawater solubility studies have investigated the impact of temperature on solubility. Few studies have noted or controlled the temperature during the dissolution experiments (Crecelius, 1980, 19 – 20 °C; Kersten et al., 1991, 20 – 25 °C and Zhuang et al., 1990, 20 ± 0.5 °C).

2.5.4 Effect of photochemical processes

No previous studies have investigated the effect of sunlight on the seawater solubility of aerosol associated trace metals, apart from Mn (Statham and Chester, 1988). From the data, an enhanced dissolution of Mn under light (~ 3000 lux) relative to dark conditions, using Saharan dust (Figure 2.4) might be observed. Similarly, Spokes and Jickells (1996) conducted photochemical reaction studies with Saharan dust and an urban aerosol in Milli-Q water (pH 2.2). They obtained results using both natural sunlight and a solar simulator. They found that the solubility of Fe was enhanced by sunlight. For the Saharan aerosol, soluble Fe (II) comprised 0.9 % in the light and 0.25 % in the dark in terms of total Fe.
Similarly, the urban aerosol comprised 8.4% of the total Fe in the light and 2.1% in the dark.

It is evident from the experiments that it is important to state the light intensity at which the seawater solubility experiments are carried out. No other studies presented in literature have done so except Guieu et al. (1994). The presence / absence of light might be an experimental artefact in these studies, contributing to some of the observed variability in seawater solubility results. (Mechanisms of photochemical effects are discussed later in section 6.3.4). Clearly there is a need to investigate the impact of sunlight on surface seawater during trace metal seawater solubility experiments.

2.5.5 Effect of dissolved organic material and bacteria

The studies by Maring and Duce (1989 and 1990) have shown that the presence of enhanced concentrations of dissolved organic carbon (DOC) in seawater increased the seawater solubility of Cu and Pb. In 'high' DOC seawater (389 μmole C kg⁻¹) most of the Cu (99%) and Pb (92%) associated with the remote marine aerosol had dissolved. In contrast, in seawater that had been UV irradiated prior to the dissolution experiments, to destroy most of the DOC (33 μmole C kg⁻¹), the seawater solubility of Cu was reduced to 74% and Pb only 17% (most of these seawater solubility values are higher than others found in the literature because they are the percentage nonaluminosilicate Cu or Pb in the sample).

The dissolved organic matter in the seawater may have complexed the soluble Pb and Cu. Organic complexation may stabilise the dissolved phase of the metals when aerosol particles are equilibrated in seawater. Thus, readsorption of dissolved trace metals is prevented; subsequently the extent of the dissolution of trace metals from the aerosol particles is enhanced.
From several studies, there is evidence that trace metals are organically complexed in natural seawater. For Cu, most (90 to > 99%) of this metal in all marine waters studied is strongly complexed by organic ligands (Coale and Bruland, 1990; Bruland et al., 1991; Donat et al., 1994 and Kozelka and Bruland, 1998). Similarly, 92 to 99% of Zn is organically complexed in surface water of the ocean (Bruland, 1989; Donat and Bruland, 1990; and Ellwood and van den Berg, 2000). In addition, Kozelka and Bruland (1998) found that for dissolved Pb and Cd organic chelates were the dominant form of these metals (67 – 94% and 73 – 83% respectively) in Narragansett Bay, USA. In contrast, in the northern parts of the Baltic Sea, the average fraction of complexed Cu is 45%. Lead and cadmium also showed considerable weaker tendency to form complexes, with corresponding fractions of 30 and 10% (Bordin et al., 1988).

The majority of other seawater solubility studies had not removed the DOC prior to the seawater solubility experiments (except Nimmo et al., 1998 and Wells, 1999) and had not specified the DOC concentration (except Chester et al., 1993 and Chester et al., 1994). The experiments with DOC present in the seawater may have produced enhanced trace metal seawater solubility values, compared to other studies that used UV irradiated seawater (for example Wells, 1999 and Fones, 1996). Therefore, clearly there is a need to state experimental conditions, and in particular, the concentration of DOC, if it was not removed prior to the seawater solubility experiments.

Bacteria are ubiquitous in the marine environment, but until recently, their impact on oceanic biogeochemistry was undervalued (Azam, 1998). It is now known that an average of 50% of oceanic primary production is channelled via bacteria into the microbial loop (Azam, 1998). Bacteria may also have an important role in the oceanic cycling of trace metals. For example, Gordon et al. (2000) observed that autotrophic and heterotrophic marine bacteria could produce strong copper-complexing ligands in chemostat cultures.
with estuarine water. However, no previous published studies have specified the bacterial concentrations in the seawater, during trace metal seawater solubility experiments with aerosol material. Bacteria may have been present in seawater solubility studies reported in Table 2.3, depending upon the seawater treatment and storage prior to the solubility studies.

A few investigators have evaluated the effect of bacteria on metal sorption onto estuarine particles. For example, Duursma and Bosch (1970) reported that with presence of an antibiotic there was a decrease in the adsorption of Zn and Mn to particles. Similarly, Jannasch et al. (1988) found that the presence of bacteria enhanced the fraction of Sc associated with the solid phase. More recently, Herzl and Roevros (1998) have reported that the presence of bacteria in estuarine water enhanced the adsorption of dissolved Mn onto the particulate phase. They also used antibiotics to terminate the bacterial activity in the control samples. It is apparent that bacteria adsorb trace metals from the aqueous media. Therefore, in the seawater solubility studies discussed above their presence may have enhanced the release of trace metals from atmospheric particles by subsequent bacterial uptake.

2.5.6 Effect of ionic strength and pH

Some studies investigating the solubility of trace metals from atmospheric aerosol particles have used deionised water as the leaching media (Lindberg and Harriss, 1983 and Guerzoni et al., 1999). Generated data from such studies may not be directly comparable to that generated from studies using seawater, which has a high ionic strength (0.7 mol kg⁻¹). The seawater media may enhance the solubility of trace metals from aerosols due to the subsequent complexation by inorganic anions (for example the formation of chloro complexes for Cd and Mn; the carbonate complex formation for Cu and Pb and the sulphate complexation for Mn) of the released metals. In addition, there may be enhanced
desorption of aerosol associated trace metals, due to cationic competition by the major seawater cations for adsorption sites on particle surfaces (Turner et al., 1981; Millward, 1995 and Spokes and Jickells, 1996). Also, changes in seawater pH and acid cycling may affect the seawater solubility of aerosol associated trace metals (see section 3.2.9 and p 159; and Spokes and Jickells, 1996). Previous seawater solubility studies had not assessed the effect of aerosol material on the final pH of the seawater.

2.6 Conclusions

Several studies have been undertaken to define the seawater solubility of trace metals associated with the marine aerosol, after dry deposition (for example Hodge et al., 1978; Maring and Duce, 1989; Chester et al., 1993 Spokes and Jickells, 1996 and Nimmo et al., 1998). However, different workers have used a range of experimental conditions (Table 2.4), therefore many of their studies may not be directly comparable. These studies had different: (i) particle concentrations, (ii) seawater temperatures, (iii) light intensities, and (v) seawater bacteria and dissolved organic carbon concentrations present. These conditions were not normally specified in previous studies (Table 2.4), and may explain some of the variability in the trace metal seawater solubility data. Furthermore, differences in the stirring rate, equilibration time and the operationally defined 'dissolved' trace metal fraction may also influence the extent of observed dissolution of trace metals.

This problem was counteracted in the current study by maintaining a consistent methodology and well defined series of criteria. The main objective of this study was to systematically investigate factors that may influence the extent and rate of the release of trace metals into seawater from aerosol particles. Most trace metal measurements were of Cu, Pb and Zn because they have ecotoxicological importance to marine phytoplankton, and they can be measured simultaneously by the analytical method employed (anodic stripping voltammetry).
<table>
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<th>Seawater volume, ml</th>
<th>Reaction vessel</th>
<th>Aerosol sample type</th>
<th>Particle concentration, mg l⁻¹</th>
<th>Temperature, °C</th>
<th>Stirring/shaking speed</th>
<th>Light intensity</th>
<th>Equilibration time, hours</th>
<th>Dissolved-particle separation</th>
<th>Analytical method</th>
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<td>N.S.</td>
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<td>Dark and 3000 lux</td>
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<td>N.S.</td>
<td>None</td>
<td>N.S.</td>
<td>upto 6</td>
<td>None</td>
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<td>274</td>
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<td>GFAAS</td>
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<td>N.S.</td>
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<td>2</td>
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<td>Bulk</td>
<td>32</td>
<td>N.S.</td>
<td>Constant illumination</td>
<td>upto 30</td>
<td>None</td>
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<td>Bulk</td>
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<td>N.S.</td>
<td>N.S.</td>
<td>upto 24</td>
<td>0.45 μm filter</td>
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<td>Teflon</td>
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<td>0.2 μm filter</td>
<td>FAAS/AAS- ETA</td>
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<td>1</td>
<td>0.45 μm filter</td>
<td>ACSV &amp; fluorimetry</td>
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</table>

Key: N.S. = not specified; FAAS = flame atomic absorption spectroscopy; GFAAS = graphite furnace atomic absorption spectroscopy; AAS-ETA = atomic absorption spectroscopy – electrothermal atomisation; ACSV = adsorptive cathodic stripping voltammetry; SE = solvent extraction; INAA = instrumental neutron activation analysis.
Chapter Three

Seawater solubility of trace metals associated with the Eastern Mediterranean aerosol
3.1 Introduction

The Mediterranean Sea is considered one of the most oligotrophic seas in the world (Krom et al., 1991; Kress and Herut, 1998 and Herut, 2002). The Mediterranean is a semi-enclosed sea, with an opening to the Atlantic Ocean at the Straits of Gibraltar, where the nutrient-depleted Atlantic surface water enters, and deeper Mediterranean water exits. Currents transport the Atlantic surface water through the Mediterranean, with increasing nutrient depletion being apparent as it moves eastward (Bethoux, 1980; Saydam et al., 1992 and Achterberg and van den Berg, 1997). Low productivity in the Eastern Basin is also caused by a lack of significant water mass upwelling regions, which can elevate nutrient-rich seawater to the surface (Azov, 1991). In the current study, soluble dry deposition will be highlighted as an important pathway for potentially bioavailable trace metals to reach the Eastern Mediterranean (EM) Sea.

Adjacent to the Mediterranean coast are large population centres. The Northern boundary of the Mediterranean consists of nations with different economies ranging from industrial to agricultural. In contrast, to the south and east are extensive desert belts (Sahara, Saudi Arabian and Syrian Deserts). Thus, the Mediterranean is an example of a marine region influenced by contrasting aerosol sources, principally urban or crustal in origin (Kubilay and Saydam, 1995; Al-Momani et al., 1998; Chester et al., 1999; Özsoy and Saydam, 2002 and Herut et al., 2001). Other sources such as volcanic activity, sea-salt recycling and biomass burning make only a negligible contribution to the trace metal concentrations in the Mediterranean aerosol (Chester et al., 1996).

In the Western Mediterranean (WM), anthropogenic aerosol production from Europe forms a continuous ‘background’ source of trace metals (Chester et al., 1996 and Chester et al., 1997). The atmospheric input of particulate material to the WM ranges from 10 – 27 t km$^{-2}$ yr$^{-1}$. Approximately 90 % to the atmospheric input comprises of Saharan dust, transported
by intense, sporadic 'pulses' (Martin et al., 1989; Guerzoni et al., 1997; Hamonou et al., 1999; Kubilay et al., 2000 and Ganor and Foner, 2001). Thus, significant inputs of trace metals to the WM Sea are from atmospheric sources. Atmospheric inputs contribute the largest share of terrestrial dissolved trace metal (Cu, Pb and Zn) inputs to the north-western Mediterranean (Cu, 55 - 65 %; Zn 65 - 100 % and Pb 97 - 99 %; Guieu et al., 1997). In this part of the Mediterranean, dry deposition fluxes of Cu, Pb and Zn exceed wet deposition fluxes (73, 81 and 52 % dry deposition respectively; Migon et al., 1997).

It is important to determine the soluble fraction of the Mediterranean aerosol because: (i) elements in the dissolved phase will undergo geochemical cycling more readily via adsorption / desorption reactions and precipitation / dissolution reactions, and (ii) it is generally postulated that typically only dissolved forms of trace metals are available for uptake by marine phytoplankton (Sunda, 1991 and 2000).

An investigation into the seawater solubility of trace metals associated with the EM aerosol has not been previously undertaken; hence, it is not known how closely the EM aerosol trace metal seawater solubility characteristics resembles those of the WM aerosol. Atmospheric inputs of trace metals to the EM Sea have become increasingly important in comparison to riverine inputs, mainly due to the damming of the River Nile in 1965 (Azov, 1991). Other riverine inputs to the Eastern Basin have also been reduced further owing to a number of Turkish rivers (Seyhan, Ceyhan and Manavgat) now being used as fresh water supplies for the Middle Eastern states (Kubilay et al., 1997).

Previous work indicates that there are wide variations in the atmospheric loadings across the EM. For example, Kubilay et al. (2000) stated that the annual total dust deposition rate at the Erdemli station is approximately 13 t km$^{-2}$ yr$^{-1}$. However to the south and east, (e.g.
Israel), this deposition rate is much greater and may vary from 40 – 210 t km$^{-2}$ yr$^{-1}$ from North to South (includes both local sources and dust episodes; Ganor and Foner, 2001). Clearly, the dust deposition across the EM region is not uniform. As Israel is in much closer proximity to the mineral aerosol generating regions than Turkey (for example the Arabian desert, Negev desert and Saharan desert), it is not surprising that there are greater dust deposition rates. Sporadic Saharan dust pulses average 19 dust storms per year (Ganor and Foner, 1996).

From Table 3.1 it is clear that atmospheric trace metal concentrations measured across the Mediterranean are not spatially constant. In particular, Al concentrations (an indicator of mineral dust, see section 2.2.2) in the EM are higher than the WM. Atmospheric trace metal aerosol concentrations are influenced by many factors including the proximity of aerosol sources, and their source strength; the type of aerosol source; the extent of wet and dry deposition during transportation; and dispersion within the layers of the atmosphere (Prospero et al., 1983, Chester et al., 1996 and Formenti et al., 2001). Furthermore, the results presented in Table 3.1 represent sampling undertaken in different years, therefore are not directly comparable.

For the current study, trace metal aerosol solubilities were defined for a series of selected high-volume aerosol samples, in Israel (Haifa) and Turkey (Erdemli) during 1996 (Figure 3.1). Aerosol samples from two EM coastal sampling sites were used, allowing spatial variations to be defined. Samples from the same year were used for better comparability. Hence, the aims of the current study were to: (i) develop, validate and utilise experimental and analytical (stripping voltammetric techniques) systems to evaluate the seawater solubility of trace metals (Cu, Pb, and Zn) associated with the EM aerosol, under carefully controlled experimental conditions (constant temperature, shaking rate and pH); (ii) assess whether there are any significant effects on the trace metal seawater solubilities from the
Figure 3.1 High-volume aerosol sampling sites in the Mediterranean

Sources: aMigon (1993); bGuerzoni et al. (1997); cBergametti et al. (1989); dGullu et al. (1998); eKoçak et al. (2004) and fFormenti et al. (2001).

Table 3.1 Geometric mean trace metal aerosol concentrations at Mediterranean sampling sites (ng m⁻³)

<table>
<thead>
<tr>
<th>Site</th>
<th>Al</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cap Ferrat</td>
<td>4.6</td>
<td>34.2</td>
<td>26.4</td>
<td></td>
</tr>
<tr>
<td>Corsica</td>
<td>168</td>
<td>2.1</td>
<td>15.9</td>
<td>19.1</td>
</tr>
<tr>
<td>Sardinia</td>
<td>164</td>
<td>9.8</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>Antalya</td>
<td>300</td>
<td>13.0</td>
<td>11.3</td>
<td></td>
</tr>
<tr>
<td>Erdemli</td>
<td>567</td>
<td>8.9</td>
<td>21.5</td>
<td>15.9</td>
</tr>
<tr>
<td>Haifa</td>
<td>952</td>
<td>5.9</td>
<td>24.9</td>
<td>24.4</td>
</tr>
<tr>
<td>Sde Boker</td>
<td>1880</td>
<td>10</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>
aerosol source, sample location, seasonality and dust concentration in seawater; (iii) use well defined crustal, urban and spatial trace metal aerosol concentrations, to calculate the atmospheric dry deposition fluxes, and (iv) compare soluble trace metal inputs to the EM Sea from dry deposition, with wet deposition and riverine inputs.

3.2 Methodology

3.2.1 Site description

Haifa is one of the locations (32° 49’ 34” N and 34° 57’ 24” E, Figure 3.1) where high-volume filter samples were collected and utilised for the trace metal seawater solubility determinations in the current study. Haifa is the largest city in northern Israel, with a population of a quarter of a million people. The commercial / industrial region is in the lower part of the city; it contains an oil-fired power station, oil refineries, a petrochemical complex, a cement plant and a fertilizer production plant, together with many smaller industries (Ganor et al., 1998).

The other high-volume filter sampling location used in the current seawater solubility study was at Erdemli, Turkey (36° 33’ 54” N and 34° 15’ 18” E, Figure 3.1). Like the sampling tower at Haifa, the samples at Erdemli were collected near to the shore of the Mediterranean Sea. The immediate surroundings of this sampling tower contain fewer urban and industrial dwellings than that at Haifa. The landward side of the sampling tower being covered mainly in semi-arid agricultural land, lemon trees and greenhouses. The nearest town and city are situated to the east of the tower at Erdemli (7 km away with 55,000 inhabitants) and Mersin (45 km away with 500,000 people). A petroleum refinery, soda, chromium and fertiliser industries are located around Mersin. Approximately 45 km to the west of the sample collection site, there exists pulp and paper industries.
3.2.2 Collection and storage of samples

Several devices have been used to collect aerosols; these include nylon meshes, cascade impactors, filter collectors, electrostatic precipitators, and surrogate collectors (Hochrainer, 1978). Of these methods, filter collectors (usually with Whatman 41, fibrous filters), combined with a high volume pumping system, are most commonly used (for example Chester et al., 1981; Murphy, 1985; Bradshaw, 1992; Guerzoni et al., 1995; Fones, 1996 and Kubilay et al. 2000). This sampling approach was adopted for the current study. Other samplers available normally have low sample yields leading to insufficient collected material for trace metal analysis after a 24 h collection time (Murphy, 1985), particularly for sample collection at coastal and remote sampling sites.

A series of high volume aerosol samples (n = 46, Appendix A) were collected at Haifa, Israel by researchers at the National Institute of Oceanography (NIO), from March to December 1996. In the laboratory, prior to sampling, a filter was placed in a polypropylene filter cassette (6" x 10", Sierra Andersen), using acid washed plastic tweezers, with the operator wearing a clean pair of disposable polythene gloves. The filter cassette was acid washed for > 24 h in 10% HCl (AnalaR, BDH) and rinsed with double distilled water, followed by drying in a Class 100 atmosphere. The filter cassette was placed in a resealable plastic bag before transit.

At the sampling site, the filter cassette was attached to a sampling head. Aerosol samples were collected using “in house” built high volume samplers. Each sampling period was between 24 and 72 h, to ensure an adequate quantity of aerosol material had been collected on the filter. Filter papers deployed were alternately Whatman 41 (Whatman Int. Ltd, U.K.) and glass microfibre filters (Whatman Int. Ltd, U.K.). The use of glass fibre filters (quartz filters) may result in higher trace metal filter blanks (Berg et al., 1993 and Herut, 1997). Furthermore, these filters are fragile and need careful handling. However, unlike
Whatman 41 filters, glass fibre filters are not hygroscopic and can be used to determine total suspended aerosol material.

After the sampling period, the filter cassette was taken back to the laboratory in a clean resealable plastic bag. Using acid washed plastic tweezers; the filter was removed, and folded in half with the collection surfaces facing inside. The folded sample was carefully placed in a labelled, clean plastic resealable bag, and then placed in a second protective plastic bag. The start and end of sampling, and the flow rate during the sampling period was noted on a log sheet (typical rate 1 m$^3$ min$^{-1}$, measured with a gas flow meter). During rain events, the sampling was stopped. The samples were stored at room temperature in their original plastic resealable bags.

The second high-volume aerosol-sampling site was situated at the Institute of Marine Sciences, Middle East Technical University (IMS-METU), Erdemli (Appendix A). The high-volume sampler was on top of a 21 m high sampling tower, constructed on a harbour jetty. The high-volume sampler was a GMWL-2000 model (General Works Inc., OH), with a high-speed motor and flow meter, mounted within a reinforced shelter constructed from 0.08" anodised aluminium (Kubilay, 1996). The flow rate of the air through the sampler was an average 1.2 ± 0.5 m$^3$ min$^{-1}$.

The aerosol material was collected on Whatman 41 filters. The filter was changed every 24 – 72 h by technical staff at IMS-METU (sampling periods given in Appendix A). Clean filters were carried to the sampling tower in their original storage box. A filter was mounted on an anodised aluminium filter holder, using Teflon coated tweezers. After sampling, the filter was folded in half, with the exposed side facing inside. The filter was then placed in a clean polyethylene bag. The bag was labelled with the sampling period. For 3 weeks in April 2001, the author obtained experience of the high-volume sampling
system at this site. Unfortunately, during this period, the high-speed motor on the sampler was not functioning; therefore, samples were not collected for this study.

3.2.3 Classification of high-volume samples into wind sectors

Back trajectories describe the prevailing pathways of dust and the approximate location of source areas. The air mass sources for the Haifa high-volume filter samples were determined with meteorological data, by ‘Trajplot’ computer-modelling software supplied by the Air Quality Research Branch of the Canadian Atmospheric Environment Service (AES; Herut et al., 2001 and Kahl et al., 1989). The air mass sources for the Erdemli high-volume collected samples were determined by trajectory data provided by the European Centre for Medium Range Weather forecasting (Kubilay, 1996). In the current study, 3 day back trajectories arriving at the 900 hPa and the 700 hPa pressure levels were calculated for each sampling day commencing at 1200 UT.

The EM basin was divided into 4 wind sectors (Figure 3.2). The dividing lines between the sectors were 34.5 °N and 34.5 °E. The time back trajectories paths were present in each sector were noted for each sample. If back trajectory paths were in a sector for > 20 % of the time, then the samples were assigned to that sector. With this type of categorisation, individual aerosol samples may belong to more than one sector. The direction of the vertical motion of the air masses during the 3-day trajectories was also noted (see Appendix A).

The two trajectory models (ECMRW and Trajplot) were compared, by classifying the air mass sources of Haifa high-volume samples using both models. There was complete agreement as to whether the aerosol samples originated from the northern zone (sectors A and D) or the southern zone (sectors B and C) for trajectories arriving at the 900 hPa pressure level. None of the Erdemli samples used in the seawater solubility studies came
Figure 3.2 Classification of the Eastern Mediterranean basin into different air mass sectors
solely from the southern zone. Four samples were classified in the "southern zone" that had Al concentrations > 1500 ng m\(^{-3}\) and came from a combination of sectors A and B.

### 3.2.4 Selection and division of the aerosol samples

Filter samples and blanks for HF total digest and seawater solubility studies were subdivided. A filter sample was removed from the storage polythene bag using acid washed (10% HCl, overnight) Teflon plastic tweezers (Lerloy) and placed onto the clean cling film in a Class 100 laminar flow cabinet (Model 56, Bass Aire). With an acid washed ruler wrapped in cling film, a 6 x 8 cm piece of filter paper was carefully torn, using the ruler as a straight edge (the filter unexposed edges were carefully torn off and discarded). Minimum amount of contact with the filter paper was ensured. The sub-sample was folded once with the collection surfaces facing inwards and placed into separate, new resealable plastic bags.

Selected high-volume Haifa samples (17 Whatman filter samples) from different wind sectors were chosen for the seawater solubility studies. Quartz filter samples were not used for the trace metal seawater solubility studies, because they adsorb trace metals (see section 3.2.8). Erdemli high-volume samples that were collected during the same sampling period as the Haifa samples were selected for seawater solubility studies. There were 9 periods in Year 1996 when high-volume aerosol samples in Haifa (n = 9) were collected at the same time as samples from Erdemli (n = 18). A further 11 Erdemli seawater solubility samples were selected from the library of Year 1996 samples for the seawater solubility studies (so that there were nearly equal number of samples representing the wet season (October – April) and the dry season (May – September)); together with two samples from Year 1998 that represent extreme desert dust events samples.
3.2.5 Collection and pre-treatment of seawater

Seawater used for all the aerosol trace metal seawater solubility studies was collected during the flood tide (salinity = 33.0 - 34.5), from the coast near Wembury, South Devon, UK (50° 18' 50" N and 4° 5' 18" W). The seawater was collected with an acid washed 2 l HDPE bottle (cleaned overnight in Decon, then 1 week in 6 M HCl; Aristar, Merck), then 1 week in 2 M HNO₃ (Aristar, Merck), thoroughly rinsed after each stage with Milli-Q water). Care was taken to avoid sampling the seawater surface microlayer (which may have enhanced concentrations of trace metals and organic matter), and to avoid atmospheric contamination, by opening the container below the sea surface. The seawater was immediately transferred to an acid washed 10 l carboy.

Natural seawater particulate matter and dissolved organic carbon may impact on the seawater solubility of aerosol associated trace metals in the natural environment (Maring and Duce, 1989 and Maring and Duce, 1990). However, they were removed from the seawater in the current study, to ensure well-defined seawater conditions, and to allow comparison with future work. The seawater was therefore filtered in the laminar flow hood with an acid washed polysulphonate filtration unit (Sartorius), containing a 0.45 μm cellulose acetate filter (Whatman), using a hand-held pump (Nalgene). The filtration unit was cleaned overnight in Decon, then for 3 h in 1.2 M HCl (Aristar, Merck) and thoroughly rinsed with Milli-Q water. The filter papers were acid-washed in 0.1 M HCl (Aristar, Merck) for 3 h, prior to being rinsed with Milli-Q water.

The seawater was UV irradiated on-line using a 400 W medium pressure mercury vapour lamp (Photochemical Reactors Ltd). The quartz coil was acid-washed on-line with 25 ml 1.2 M HCl, then with 25 ml Milli-Q water. A pumping speed of 1 ml min⁻¹ was used for the removal of dissolved organic material (Achterberg and van den Berg, 1994a). The treated seawater was stored in a 10 l HDPE carboy. After UV irradiation, total dissolved
trace metal concentrations were measured. Average Zn concentrations were $13.3 \pm 2.3$ nM and Cu concentrations were $5.60 \pm 0.67$ nM (Pb was below the limit of detection).

Prior to the seawater solubility experiments with the Erdemli high-volume aerosol samples, the seawater was sterilised by microwave treatment, after the UV digestion process (more detail in section 5.2.1). This was done because bacterial contamination may enhance the seawater solubility of aerosol associated trace metals (Chapter 5). This was not known at the time when the seawater solubility experiments with the Haifa high-volume aerosol samples were undertaken.

### 3.2.6 Laboratory protocols

Meticulous protocols were adopted throughout the study to minimise trace metal contamination of the samples and reagents (Howard and Statham, 1993). Manipulations of samples and reagents were carried out within a Class 100 laminar flow cabinet (Model 56, Bass Aire). During all the experimental work and preparation of reagents, the operator wore a clean pair of disposable plastic gloves to minimise trace metal contamination.

Prior to each seawater solubility experiment, the Teflon® reaction vessel was filled with hot $2 \% \, v/v$ Decon 90 (Decon Laboratories) for 1 h to remove organic surfactants, rinsed with Milli-Q water and then acid washed. Unless otherwise stated, laboratory equipment was cleaned overnight in $10 \% \, v/v$ HCl (Aristar, BDH) and then thoroughly rinsed with Milli-Q water.

### 3.2.7 Seawater solubility experimental protocol

The samples were equilibrated in organic and particulate free seawater at constant pH (8.0). The equilibration time of the samples in seawater was fixed at 3 h. Other studies have found that a significant fraction of Cu, Pb and Zn present in marine aerosols in
seawater was released within the first hour (Kersten et al., 1991; Fones, 1996; Hamilton-Taylor et al., 1993 and Nimmo et al., 1998). The constant temperature of 25.0 ± 1.0 °C during the equilibration study represented the mid values of the typical range of surface seawater temperatures (16 – 28 °C) of EM shallow coastal water (Kress and Herut, 1998).

The seawater solubility studies were undertaken in acid washed (fluorinated ethylene propylene, FEP) Teflon containers. The screw-topped Teflon bottles (n = 3, 500 ml, Nalgene) were soaked overnight in Decon, then 24 h in 10 % HCl (Aristar). A 500 ml polysulphonate filtration unit (Sartorius) was also kept overnight in Decon, placed into 10 % HCl for 1 h, then for 24 h in 1 % HCl. Between each stage, the vessels were thoroughly rinsed with Milli-Q water. Teflon tweezers and cellulose acetate filters (Millipore Type HV 0.45 μm diameter) were acid washed in 1 % HCl for 3 h, then rinsed with Milli-Q.

The Teflon vessels and the filtration unit were conditioned with UV irradiated seawater for 15 min, to minimise the amount of trace metal adsorption from the sample. Aliquots of UV irradiated seawater were then transferred from an acid washed glass volumetric flask (100 ml) to the Teflon vessels. Each aliquot of seawater was spiked with 5 μM borate (pH 8.0). Each Teflon vessel was sealed inside two resealable plastic bags and equilibrated for at least 40 min in a constant temperature room (25.0 ± 1.0 °C), to reach a stable temperature. The filter samples were divided into two and placed into the seawater. The Teflon vessels were returned to the constant temperature room and shaken (150 osc min⁻¹) for 3 h with a mechanical shaker (Stuart Scientific SF1 Flask Shaker). The contents of the Teflon vessels were then filtered, with a 0.45 μm pore size membrane filter (see section 3.2.5). The filtrate was acidified to pH 2 with HCl (Aristar, BDH) and stored in a refrigerator at 4 °C.

The filtrate was UV irradiated before analysis. The procedure involved acid washing the quartz tubes (30 ml) and high density Teflon caps in 10 % HCl (Aristar) acid baths for 2
days, followed by thorough rinsing in Milli-Q water. The samples were UV irradiated for 4 h, in a 400 W medium pressure mercury arc lamp (Photochemical Reactors Ltd.), in the quartz tubes. The digestion of dissolved organic material was complete within 4 h (Table 3.2). UV irradiation of seawater for 8 h did not increase the total dissolved trace metal concentrations in seawater by more than 8 %, therefore there was little more release of organically complexed trace metals.

Table 3.2 Effects of UV irradiation on the detection of dissolved trace metals in coastal seawater. For each element n = 3. Errors represent one standard deviation.

(nd = not detectable)

<table>
<thead>
<tr>
<th>Element</th>
<th>4 h Digestion (nM)</th>
<th>8 h Digestion (nM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>9.8 ± 0.2</td>
<td>10.6 ± 0.4</td>
</tr>
<tr>
<td>Pb</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Zn</td>
<td>15.1 ± 0.3</td>
<td>15.6 ± 0.5</td>
</tr>
</tbody>
</table>

3.2.8 Experimental characterisation

A series of controlled experiments (25 °C, pH 8.0) was undertaken to assess whether there is any contamination or adsorption of trace metals (Cu, Pb and Zn) with the Whatman and quartz filter samples. Portions of Whatman and quartz blank filters (n = 3, 6 x 8 cm) were separately equilibrated in UV irradiated seawater for 3 h. The contamination from quartz filters for Cu and Pb was generally similar to that of Whatman filters (Table 3.3). However, Zn contamination from Whatman filters was relatively high; although the contamination was < 10 % of the mean sample concentration and was felt to be acceptable.
The extent of contamination was subtracted from the observed total dissolved trace metal concentrations of seawater after equilibration of the aerosol samples.

Table 3.3 Total dissolved trace metal concentrations (nM) after equilibration of Whatman and quartz filters in seawater (nd = not detectable)

<table>
<thead>
<tr>
<th></th>
<th>Whatman filters</th>
<th>Quartz filters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
</tr>
<tr>
<td>Cu</td>
<td>6.3</td>
<td>7.7</td>
</tr>
<tr>
<td>Zn</td>
<td>14</td>
<td>67</td>
</tr>
<tr>
<td>Pb</td>
<td>nd</td>
<td>nd</td>
</tr>
</tbody>
</table>

An additional error in the experimental system is the potential adsorption of trace metals onto the filter media post-dissolution from the aerosol material. To assess the adsorption of trace metals by the blank filters, portions of quartz and Whatman filters were equilibrated in aliquots of UV irradiated seawater (n = 3) spiked with dissolved trace metals. The Whatman filters did not appear to significantly adsorb trace metals from the seawater. However, it was observed that quartz filters adsorbed approximately half of the dissolved Cu and Zn and a third of Pb (Table 3.4).

In spiked seawater with higher concentrations of dissolved trace metals (Table 3.4), quartz filters adsorbed even more Pb, Cu and Zn, although proportionally less than that observed in the lower metal spike experiments. The higher metal concentrations used were representative of those that would be released from equilibrated aerosol material. Owing to these potential errors, the quartz filter aerosol samples could not be used in the seawater solubility studies.
Table 3.4 Total dissolved trace metal concentrations (nM) after equilibration of Whatman and quartz filters in trace metal spiked, UV irradiated seawater

<table>
<thead>
<tr>
<th></th>
<th>Whatman filters</th>
<th></th>
<th>Quartz filters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
<td>Difference</td>
<td>Before</td>
</tr>
<tr>
<td>Cu</td>
<td>10.8</td>
<td>12.6</td>
<td>1.8</td>
<td>12.1</td>
</tr>
<tr>
<td>Zn</td>
<td>118</td>
<td>178</td>
<td>60</td>
<td>118</td>
</tr>
<tr>
<td>Pb</td>
<td>15.2</td>
<td>16</td>
<td>0.8</td>
<td>15.2</td>
</tr>
<tr>
<td>Cu</td>
<td>85.7</td>
<td>61.3</td>
<td>-24.4</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>2000</td>
<td>1660</td>
<td>-340</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>219</td>
<td>99</td>
<td>-120</td>
<td></td>
</tr>
</tbody>
</table>

3.2.9 Change of seawater pH

Any potential decrease in the experimental seawater pH owing to the release of acidic species would potentially influence the rate and extent of metal released from the aerosol material, with the likely result of the enhancement of metal dissolution. Decreases in seawater pH might be due to the presence of sulphuric, nitric or hydrochloric acids associated with urban aerosol particles (Prospero, 1983). Therefore, to assess if additions of filter aerosol samples changed the seawater pH, a portion of a sample originated from the northerly sector, collected in Haifa (21 - 23 May 1996, 1 x 1 cm) was equilibrated in seawater (10 ml) for 1 h. It was observed that there was a decrease of pH from 8.00 to 5.52. To raise the pH back, 5 µM of borate buffer was required. However, the addition of borate to the seawater, may affect the dissolution characteristics of the aerosol associated trace metals. Hence, to evaluate this impact a filter sample (21 - 23 May 1996, 10.2 x 10.2) was divided into two. One half was equilibrated in seawater with a spiked borate concentration of 5 µM borate, the other with 10 µM borate. The total dissolved
concentrations displayed in Table 3.5 shows that the borate concentration had no significant effect on the solubility of trace metals.

Table 3.5 Effect of added borate on the seawater solubility of trace metals associated with a sample from the northerly air mass. (Collected in Haifa on 21 - 23 May 1996; errors represent one standard deviation of 3 aliquots)

<table>
<thead>
<tr>
<th></th>
<th>5 μM</th>
<th>10 μM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>28.0 ± 2.7</td>
<td>31.3 ± 1.0</td>
</tr>
<tr>
<td>Zn</td>
<td>904 ± 75</td>
<td>904 ± 53</td>
</tr>
<tr>
<td>Pb</td>
<td>155 ± 13</td>
<td>162 ± 2</td>
</tr>
</tbody>
</table>

3.2.10 Optimisation and use of stripping voltammetry

Trace metal concentrations (Cu, Pb, and Zn) in the seawater samples were determined batchwise, using stripping voltammetry in the square wave mode. (The advantages of stripping voltammetry over other analytical techniques are discussed in section 4.4.1). The analysis was performed with a static mercury drop electrode (Metrohm 663 VA Stand electrode), with an electrochemical analyser (μAutolab, Eco Chemie). The system was controlled by GPES3 computer software (Eco Chemie).

The electrochemical parameters of the instrumentation (deposition potential, stripping frequency, step potential and amplitude) were optimised consecutively to gain adequate trace metal detection reproducibility and sensitivity (Table 3.6).
Table 3.6 Optimised instrumental parameters used during the determination of Cu by ACSV and, Pb and Zn by ASV, in UV irradiated seawater

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Frequency (Hz)</th>
<th>Step potential (mV)</th>
<th>Amplitude (mV)</th>
<th>Deposition potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>7.7</td>
<td>50</td>
<td>4.88</td>
<td>50</td>
<td>-0.15</td>
</tr>
<tr>
<td>Pb and Zn</td>
<td>2.0</td>
<td>50</td>
<td>4.88</td>
<td>25</td>
<td>-1.25</td>
</tr>
</tbody>
</table>

Prior to the analysis of each sample, a pipette with a clean tip (Finnipippette) was used to transfer 10 ml of the sample into the glass electrochemical cell. The sample was then purged with ultra-pure N₂ (BOC) for 3 min. The deposition time prior to each scan was 15 s. At least three replicate ASV (anodic stripping voltammetry) or ACSV (adsorptive cathodic stripping voltammetry) scans were performed on each sample, with the instrumental parameters given in Table 3.6, until the percentage relative standard deviation was < 5 %. The internal standards were made from Spectrosol (Merck) metal stock solutions (1000 mg l⁻¹). Similar measurements with two successive dissolved trace metal internal standard additions were determined in the same aliquot. At least two aliquots of each sample were determined. If the percentage relative standard deviation of the concentration was < 5 when two standard additions had been made on the first aliquot and one on the second, then the analysis was complete.

Between the analysis of each aliquot, the electrodes and quartz cell was thoroughly rinsed with Milli-Q. Trace metal “carry-over” was then assessed with a Milli-Q blank, determined with approximately the same deposition time as the next aliquot by ASV or ACSV. The risk of trace metal contamination was potentially significant, as relatively high concentrations of dissolved trace metals could be released in the equilibrated seawater. If a
peak was detectable, then the cell and electrodes were rinsed again and another Milli-Q aliquot was determined.

Typically after measuring the concentrations of Zn and Pb by ASV in the acidified sample, Cu was measured in the same aliquot (10 ml). The pH of the sample was raised to 7.6 by adding 22.5 μl of redistilled ammonia. Copper was then determined using ACSV with 25 μM salicylaldoxime (SA) and 0.01 M HEPES. Degradation products of SA interfered with the determination of Cu; therefore, a fresh solution (0.1 M) was made up daily, from a stock 0.5 M SA solution, which was stored in a refrigerator. The analysis of Cu was undertaken at least 24 h after UV irradiation of the samples to avoid interference from hypochlorite ions (Achterberg and van den Berg 1994a).

### 3.2.11 Trace metal contamination, accuracy and limits of detection

Contamination from the ASV and ACSV reagents was quantified in Milli-Q (n = 3). Contamination of Pb and Zn from 0.05 % of concentrated HCl could not be detected after 5 min deposition time. The contamination from SA and HEPES was 0.09 nM Cu (< 0.2 % for Cu of the mean sample concentration). The accuracy of the ASV (Pb and Zn) and ACSV (Cu) techniques were evaluated using UV irradiated seawater certified reference material (CASS-3, National Research Council, Canada). The concentration of Pb in the certified reference material was below the limit of detection. The recovery of Pb was therefore evaluated with MESS-1. This is an estuarine sediment certified reference material. It underwent HF / HNO₃ digest (see section 5.2.3.1), then UV irradiation for 12 h in quartz tubes with 400 W medium pressure lamp. The recovery of Pb measured by ASV was 104 %.
Table 3.7 Accuracy of ASV (Pb and Zn) and ACSV (Cu) techniques, and their analytical detection limits, with CASS-3 (nd = not detectable). Errors represent two standard deviations.

<table>
<thead>
<tr>
<th></th>
<th>Observed value (nM)</th>
<th>Certified value (nM)</th>
<th>Recovery (%)</th>
<th>Detection limits (nM)</th>
<th>% Detection limits of mean sample concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>8.70 ± 1.82</td>
<td>8.14 ± 0.98</td>
<td>107</td>
<td>2.7</td>
<td>7.9</td>
</tr>
<tr>
<td>Zn</td>
<td>20.8 ± 2.8</td>
<td>18.97 ± 3.82</td>
<td>110</td>
<td>4.2</td>
<td>0.7</td>
</tr>
<tr>
<td>Pb</td>
<td>nd</td>
<td>0.058</td>
<td></td>
<td>2.3</td>
<td>1.3</td>
</tr>
</tbody>
</table>

The analytical detection limits in Table 3.7 were defined as 3 times the standard deviation of 4 aliquots of CASS-3. They were well below the total dissolved concentrations determined in seawater after equilibration of the aerosol filter samples. The ASV Pb detection limits were assessed with aliquots of UV irradiated seawater (n = 4) spiked with 10 nM Pb.

3.2.12 Total digestion (HNO₃ / HF) of aerosol material

It was necessary to determine the total concentrations of trace metals on the high-volume aerosol samples, in order to calculate the seawater solubilities, and to determine the atmospheric trace metal concentrations and crustal enrichment factors. Prior to trace metal analysis, it was necessary to dissolve the entire sample in acid solution. In order to dissolve the alumino-silicate material, which is the most refractory component of aerosol material (Chester et al., 1989), both HNO₃ and HF was used.

NIO provided atmospheric trace metal concentration data for the high-volume samples collected at Haifa. Analyses of Pb, Cu, Zn, and Al in these aerosol samples were performed after total digestion of one eighth of the filter samples with HF / HNO₃ (Jeffrey, 55
with atomic absorption spectrometry (AAS, Perkin Elmer 1100B) and graphite furnace atomic absorption spectrometry (GFAAS; Herut, 1997). The trace metal concentrations measured for the aerosol filter samples were corrected with filter blanks. NIO assessed the accuracy of these measurements with Estuarine Sediment 1646 (NIST), MESS-2 Sediment (NRCC) and Coal Fly Ash. Recoveries of Al, Cu, Pb and Zn ranged from 91 – 104%.

Koçak (2001) performed HF / HNO₃ digest on a quarter of the high-volume Erdemli filter samples, using the methodology presented in Kubilay (1996). Aluminium and zinc were analysed by Koçak (2001) with flame atomic absorption spectroscopy (FAAS). The trace metal concentrations in the aerosol samples were corrected with filter blanks. These were filters processed in the same way as the aerosol filter samples, except that no air was passed through them. There were good elemental recoveries with the digested standard reference materials (CRM-142, Community Bureau of Reference and BCSS-1, National Research Council of Canada). In the current study, selected Erdemli high-volume samples underwent HF / HNO₃ total digest and further total trace metal concentrations (Cu and Pb) were analysed by ICP-MS (methodology and details on accuracy in section 5.2.3). The Cu data for the Erdemli samples was not used because there appeared to be a possible source of contamination arising from the high volume sampler valve. The average crustal enrichment factors for these samples were two orders of magnitude higher than the typical WM aerosol.

3.2.13 Repeatability of trace metal concentrations on a filter sample

To assess whether the distribution of trace metals associated with aerosols were evenly distributed (with consistent aerosol population chemical characteristics) on a high-volume aerosol sample, four portions (6 x 8 cm) of the same Haifa aerosol filter sample (collected 5 September 1996) were HF / HNO₃ digested. Trace metal concentrations from the digest
solutions were measured by ICP-MS. All the elements have a relative standard deviation of < 6 %. It was not therefore necessary to determine metal concentrations of the particulate phase after the equilibration of the filter aerosol samples in seawater.

Table 3.8 Repeatability of total metal concentrations on different sections of a high-volume filter sample collected at Haifa (n = 4). Errors represent one standard deviation.

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosol</td>
<td>4.3 ± 0.05</td>
<td>713 ± 41</td>
<td>24 ± 1</td>
<td>40 ± 2</td>
<td>89 ± 4</td>
</tr>
<tr>
<td>concentrations</td>
<td>(ng m⁻³)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% RSD</td>
<td>1.2</td>
<td>5.7</td>
<td>4.2</td>
<td>5.7</td>
<td>4.8</td>
</tr>
</tbody>
</table>

3.2.14 Rainwater sampling and trace metal analysis

Rainwater samples were collected at Haifa by the NIO from March 1996 to December 1996 (n = 13), on an event basis. An event was defined as > 5 mm precipitation. If there was a cessation for more than 8 h, a new event was defined. Rainwater samples were taken using plastic funnels (25 cm diameter) and bottle type collectors (100 cm height) corresponding to recommendations by UNEP (1985). The samples were retrieved soon after the rain event and measured for pH. The total amount of rain was measured for each event and was filtered through 0.45 μm cellulose acetate membrane filter (Whatman), and acidified with HCl (Aristar, BDH) to pH 2, then stored in a refrigerator at 4 °C. Most samples had been analysed for nutrient and major element concentrations, but not for dissolved trace metals (Herut, 1997). In the current study, analysis was carried out for Cu, Pb and Zn with ASV for the series of rainwater samples which had been previously UV irradiated for 4 h (see section 3.2.5), yielding the total dissolved trace metal concentrations (Appendix B).
3.3 Results and discussion

3.3.1 Impact of sampling location on trace metal seawater solubilities

The average seawater solubilities of Cu, Pb and Zn associated with aerosols collected from two sites in the EM (Haifa, Israel and Erdemli, Turkey (no Cu data)) are presented in Table 3.9. There were wide ranges of seawater solubility values from individual high-volume filter samples (e.g. seawater solubility of Cu associated with Haifa samples 14 – 69 %). The trend for the arithmetic mean % seawater solubility values in Table 3.9 was in the order Zn = Pb > Cu; in a similar trend, the average crustal enrichment factors for Pb (204) and Zn (171) were greater than those Cu (26) for the Haifa aerosol filter samples. However there was no correlation between the crustal enrichment factors and the seawater solubility values for individual aerosol filter samples, for each trace metal (Cu, Pb and Zn).

Table 3.9 Percentage trace metal seawater solubilities of the EM aerosol

<table>
<thead>
<tr>
<th>Source: aThis study, bWells, 1999 and cChester et al. 1993. Errors represent one standard deviation.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>EM aerosol</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Cu</td>
</tr>
<tr>
<td>Pb</td>
</tr>
<tr>
<td>Zn</td>
</tr>
</tbody>
</table>

It is likely that the trace metal aerosol solid-state speciation, reflected by the air mass source, partly controls the extent to which trace metals desorb from the aerosol samples in seawater (Chester et al., 1993; see section 2.5.1). Other factors that may affect the seawater
solubility of aerosol associated trace metals may include seasonal changes and aerosol particle concentrations in seawater; these will be discussed later (sections 3.3.6 and 3.3.7).

The average seawater solubilities of Zn and Pb associated with the Haifa samples were significantly higher than the Erdemli samples, with an unpaired two-tailed t test (p-values 0.00004 and 0.003 respectively). The Erdemli high-volume filter samples were equilibrated in sterile seawater, whereas the Haifa samples were equilibrated in non-sterile seawater. Chapter 5 highlights that the seawater solubility of aerosol associated trace metals is enhanced in non-sterile seawater. Correction factors of 0.68, 0.83 and 0.83 for Cu, Pb and Zn respectively, for Haifa high-volume filter samples could be applied (assuming that there are proportionally the same differences between the trace metal seawater solubilities with the Liverpool urban aerosol population used in Chapter 5 with the EM aerosols in the current study, in sterile and non-sterile seawater). After the application of the bacteria correction factors, the seawater solubilities of Pb and Zn were 45.1 ± 15.3 and 45.6 ± 16.1 % respectively for the Haifa filter samples; and there is no significant difference between the mean Pb seawater solubilities associated with aerosols from the two sampling sites (p-value = 0.103), but there is still a significant difference for Zn (p-value = 0.007).

The average seawater solubility of Zn associated with the Haifa high-volume filter samples (54.9 ± 19.4 %, in non-sterile seawater) were similar to that observed for aerosol samples from the WM (~ 63 %), which are polluted by European sources (Chester et al., 1993). The Zn atmospheric aerosol concentrations in Haifa in 1996 were statistically greater than Erdemli (unpaired t-test, p-value < 0.0001), due to enhanced pollution from local and / or regional sources (whereas for Pb there is no significant difference, p-value = 0.38). The source of Zn enrichment at Haifa is not clear (Herut, 2001). A major source of Zn might be the abrasion of car tyres (Foner and Ganor, 1992). It is also likely to emanate from the
local industrial complex, domestic heating, and long-range sources (Levin and Lindberg, 1979). Hence, the seawater solubility of Zn associated with aerosols collected at Haifa was higher than at Erdemli. The aerosol particles on the filter samples collected from Haifa may have had more Zn is associated in the ‘exchangeable phase’, than the Erdemli filter samples, thus a higher seawater solubility (Chester et al., 1989).

3.3.2 Defining contrasting air mass sources to the EM Sea

The impact of the aerosol source on the trace metal seawater solubilities of the EM aerosol was investigated by separating samples according to air mass source. Aerosol filter samples were classified into four wind sectors (A-D, see section 3.2.3). Sector A represents air mass sources that flow over the Commonwealth of Independent States and Eastern Turkey to the north and over the Syrian Desert to the east. Similarly, Sector D represents relatively local sources from the western side of Turkey, and long-range air masses from Eastern and Western Europe. In contrast, Sectors B and C are to the south, and represent relatively arid regions. Local sources of aerosols from sector B include the Lebanon, Jordan and Israel. This sector also includes the Negev and Arabian Deserts. Sector C represents North Africa, where the Saharan desert dust belt is situated.

The prevailing air mass source to the EM region is from Europe and western Turkey (sector D). Kubilay (1996) recorded that 47 % of air mass trajectories arriving at the 900 hPa pressure level in Erdemli, Turkey were from the NW. From this wind direction, air mass movements to this region are predominantly anticyclonic; therefore, air masses are sinking towards ground level during transit. Air masses that are transported over the European continent towards EM are typically within the upper troposphere (Kubilay, 1996 and this study). Hence, the EM might not be subjected to the same extent to the polluted ‘European background’ described for the WM (for example Chester et al., 1990, Chester et al., 1996 and Chester et al, 1997).
The average duration of individual desert dust episodes in the EM region is only an
average of 1.3 days (Ganor and Foner, 1996). There are two main synoptic types of
meteorological conditions cause dust storms; Type 1: a low-pressure system coming from
North Africa (sector C) or Type 2 from sector B, resulting from a low-pressure system
from the Arabian desert (Güllü et al., 1996 and Ganor et al., 1991). Most of the desert dust
to the EM comes from Type 1 synoptic conditions. Desert dust from Type 1 conditions
most commonly arrives from the Ahaggar Massif region (Algeria), Tibesti Mountains
(Chad), or the Libyan Desert (Yaalon and Ganor, 1979; Dayan et al., 1991 and Ganor and
Foner, 1996).

Type 1 synoptic conditions are meteorological depressions (Sharav cyclones) that develop
south of the Atlas Mountains due to the strong thermal contrast between the cold marine
waters and warm continent. These cyclones move eastward along the thermal gradient, just
south of the North African coast. They then normally cross the Mediterranean between
Libya and Egypt (Moulin et al., 1998). Ganor et al. (1991) described the chemical
composition of 23 severe dust intrusions to the EM, but only one of them was Type 2, from
the Arabian Peninsula. Type 2 dust storms may also come from the Sinai (Egypt) and
Negev (Israel) deserts.

In the current study, aerosol filter samples were categorised into northern and southern
zones rather into one of the four wind sectors because most of the samples collected in
Haifa and Erdemli belonged to more than one sector (see Appendix A). Six samples from
Erdemli in the current study were solely from sector A, and fourteen from sector D. Using
a t-test it was found that there was no statistical difference in the average trace metal
atmospheric concentrations, crustal enrichment factors or percentage seawater solubility
values for Pb and Zn for these two sectors (there were insufficient samples to make a
comparison of sectors B and C).
3.3.3 Impact of aerosol source on atmospheric trace metal concentrations

As background information, before assessing the impact of contrasting air masses have on the seawater solubility of trace metals in EM aerosols, the atmospheric trace metal concentrations of these contrasting air masses were defined and considered. Table 3.10 gives the geometric mean atmospheric aerosol trace metal concentrations and crustal enrichment factors (for Cu, Pb and Zn) for the northerly and southerly aerosol populations in Erdemli and Haifa.

It is evident from Table 3.10 that the atmospheric Al concentrations from crustal aerosol populations over both the EM and the WM are consistently higher than the urban aerosol populations, due to Al being predominantly associated with mineral aerosols (Chester et al., 1984; Ganor et al., 1991; Chester et al., 1996 and Kubilay, 1996). Similarly, the southerly aerosol populations in Haifa and Erdemli have statistically higher atmospheric Al concentrations than the northerly aerosol populations (p-value < 0.0001 for both sampling sites, with unpaired t-tests). The atmospheric concentration of Al has often been used as an indicator of the atmospheric dust load (Bergametti et al., Chester and Bradshaw, 1991, Dulac et al., 1987, and Kubilay et al., 2000). Typical Al concentrations associated with the southerly aerosol range from ca. 1500 – 4500 ng m\(^{-3}\), whereas concentrations in the northerly aerosol range from ca. 100 – 800 ng m\(^{-3}\).

At all sampling sites presented in Table 3.10 the atmospheric Cu, Pb and Zn concentrations were typically the same order of magnitude for the crustal aerosol population as the urban aerosol population. At Haifa and Erdemli, there were no statistical significant differences in the atmospheric Cu, Pb and Zn concentrations between the southerly and northerly aerosol populations. This suggests there is a continuous ‘background’ of urban aerosols from the European continent and / or local sources, punctuated with intermittent pulses of desert dust, which is indicated by elevated the atmospheric Al concentrations. Thus, the
Table 3.10 Geometric mean atmospheric trace metal concentrations (ng m\(^{-3}\)) in northerly and southerly aerosol populations from the Mediterranean

(Sources: \(^a\)This study, \(^b\)Güllü et al., 1996, \(^c\)Guerzoni et al., 1999, \(^d\)Chester et al., 1990 and \(^e\)Chester et al., 1996)

Elemental crustal enrichment factors in italics

<table>
<thead>
<tr>
<th></th>
<th>EASTERN MEDITERRANEAN</th>
<th></th>
<th>WESTERN MEDITERRANEAN</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Haifa, Israel(^a)</td>
<td>Erdemli, Turkey(^a)</td>
<td>Antalya, Turkey(^b)</td>
<td>Sardinia(^c)</td>
</tr>
<tr>
<td></td>
<td>Southerly Northerly</td>
<td>Major dust Incursion</td>
<td>Southerly Northerly</td>
<td>Crustal Urban</td>
</tr>
<tr>
<td>Al</td>
<td>1530</td>
<td>47300</td>
<td>2200</td>
<td>660</td>
</tr>
<tr>
<td>Cu</td>
<td>7.0</td>
<td>5.3</td>
<td>15</td>
<td>32</td>
</tr>
<tr>
<td>Pb</td>
<td>56.8</td>
<td>86.6</td>
<td>36.2</td>
<td>28.8</td>
</tr>
<tr>
<td></td>
<td>149</td>
<td>7.4</td>
<td>66</td>
<td>175</td>
</tr>
<tr>
<td>Zn</td>
<td>74.4</td>
<td>103</td>
<td>19.4</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>2.5</td>
<td>10</td>
<td>38</td>
</tr>
</tbody>
</table>
southerly aerosol populations at Haifa and Erdemli were not labelled as “crustal aerosol populations” because they were influenced by anthropogenic aerosol emissions. The crustal enrichment factors for Cu, Pb and Zn are typically an order of magnitude lower in the southerly aerosol populations because of the enhanced atmospheric Al concentrations. In the northerly and southerly aerosol populations, the crustal enrichment factors for Cu, Pb and Zn are > 10, therefore these elements are more predominantly derived from anthropogenic sources.

The average atmospheric Pb concentrations encountered in the EM region were similar to Cap Ferrat, a coastal site in the WM (Table 3.10). However, these concentrations were higher than those found in remote regions of the WM (Sardinia and the Tyrrhenian Sea, Table 3.10). This suggests that atmospheric Pb sampled at these EM sites were contaminated with local and / or regional pollution sources. Haifa is situated in the northern part of Israel, which is a densely populated country within a narrow strip of land along the Mediterranean coast. The atmospheric aerosol Pb concentrations in the southerly aerosol population of samples collected from Haifa were approximately twice as high as the northerly aerosol population. This might be due to the position of Haifa; most local urban centres are within the southern zone. Pollution, particularly from motor vehicle exhaust might have enhanced the atmospheric Pb concentrations found in the southerly aerosol population. In 1996 approximately 50% of the petrol used in Israel was leaded. In addition, Haifa may be subject to pollutant transfer from the South, for example from Egypt (Erel et al., 2002).

From the study of Pb isotopes, Erel et al. (2002) found that atmospheric Pb in Jerusalem was not only of local origin, but also emitted from other countries, principally from Egypt, Turkey and Israel. They found that the average concentration of foreign atmospheric Pb (23 ± 17 ng m$^{-3}$) in Jerusalem in 1996 / 1997 was similar to the local atmospheric Pb
concentrations (21 ± 18 ng m\(^{-3}\)). These concentrations are lower than the average concentrations found in Haifa (35 ng m\(^{-3}\)), Erdemli (31 ng m\(^{-3}\)) and Maagan Michael (49 ng m\(^{-3}\), on the Israeli coast, Herut et al., 2001). These sites might have been more polluted with local sources of Pb than the sampling site at Jerusalem, because the Pb atmospheric concentrations are greater. However, the more recent mean concentrations of atmospheric Pb in Haifa and Erdemli (1999-2001) have decreased to 25 and 22 ng m\(^{-3}\) respectively (Koçak et al., 2004), due to the decrease in the use of leaded petrol (Pirrone et al., 1999).

There was also a dramatic decrease in atmospheric Zn concentrations in Haifa between 1996 and 2001 from an average of 105 ng m\(^{-3}\) to 24 ng m\(^{-3}\) (Koçak et al., 2004). A smaller decline was also measured at Erdemli from an average of 23 ng m\(^{-3}\) to 16 ng m\(^{-3}\). There was no change in the atmospheric Cu concentrations in Haifa (5.7 ng m\(^{-3}\) average between 1999 and 2001). Consequently, the total and soluble fluxes of Pb and Zn to the EM Sea in 1996 are likely to be higher than those occurring during 2001.

### 3.3.4 Impact of aerosol source on trace metal seawater solubilities

For the selected aerosol filters from the Haifa and Erdemli sampling sites that underwent seawater solubility studies, the average trace metal solubilities for the southerly and northerly aerosol populations are presented in Table 3.11 (the data in Table 3.11 and the data presented in the remainder of the chapter have not been corrected for bacterial effects). The table excluded data from the Erdemli extreme desert dust event 27 - 30 March 1998, which will be discussed in the next section. The seawater solubilities of trace metals (Pb and Zn) associated with the southerly Erdemli aerosol population were significantly less than the northerly Erdemli population (p-values < 0.01, for an unpaired t-test). This is consistent with some previous seawater solubility studies. For example, the seawater solubility of Pb associated with the southerly aerosol population (this study) and associated
Table 3.11 Percentage seawater solubilities of trace metals associated with crustal and urban aerosols collected from Israel and Turkey; also comparison with literature data (Sources: aThis study, bChester et al., 1993, cNimmo et al., 1998, dGuerzoni et al., 1999 and eNimmo, unpublished).

Errors represent one standard deviation.

<table>
<thead>
<tr>
<th></th>
<th>Haifa, Israela</th>
<th>Erdemli, Turkeyb</th>
<th>Saharan Liverpoolb</th>
<th>Saharan Liverpoolb</th>
<th>Sardinia d</th>
<th>Cap Ferrat, Francec</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Southerly</td>
<td>Northerly</td>
<td>Crustal</td>
<td>Urban</td>
<td>Crustal</td>
<td>Urban</td>
</tr>
<tr>
<td>Cu</td>
<td>26.6 ± 10.2</td>
<td>30.4 ± 14.8</td>
<td>-</td>
<td>1</td>
<td>34</td>
<td>9</td>
</tr>
<tr>
<td>Pb</td>
<td>43.7 ± 5.5</td>
<td>60.1 ± 20.7</td>
<td>4.6 ± 1.5</td>
<td>&lt; 1</td>
<td>53</td>
<td>9</td>
</tr>
<tr>
<td>Zn</td>
<td>36.9 ± 8.3</td>
<td>64.7 ± 16.3</td>
<td>14.6 ± 1.3</td>
<td>&lt; 1</td>
<td>72</td>
<td>2</td>
</tr>
</tbody>
</table>

Southerly Northerly

Crustal Urban

"Saharan" "Pollutant"

29.8 ± 23.4 59.7 ± 14.5

51.0 ± 12.5 59.2 ± 13.3

76.3 ± 10.7 84.0 ± 3.2
with the Saharan aerosol populations in previous studies is < 10 % (Chester et al., 1993; Nimmo et al., 1998 and Guerzoni et al., 1999).

For the Haifa aerosol, there was no statistical significant difference in the trace metal seawater solubilities between the two designated aerosol populations, except for Zn (p-value < 0.01, for an unpaired t-test). It appears that local anthropogenic sources may have caused an enhancement in the solubility of Cu, Pb and Zn in the southerly aerosol population. These solubility values are much higher than those observed for Saharan dust (Chester et al., 1993, Nimmo et al., 1998 and Guerzoni et al., 1999; see Table 3.11). Similarly, anthropogenically derived aerosol material enhanced the seawater solubilities of Cu, Pb and Zn associated with “Saharan aerosols” collected at Cap Ferrat during 1989-1990 (Nimmo, unpublished). Since the seawater solubility of trace metals associated with the southerly aerosol collected from the Erdemli site is significantly lower than from the southerly Haifa aerosol, this would indicate that the Erdemli site may be more representative of the general EM aerosol, because it is less affected by anthropogenic inputs.

3.3.5 Impact of extreme events on trace metal seawater solubilities

Air mass back trajectories were used to define specific sources of aerosols that may lead to extreme trace metal seawater solubility values. The highest trace metal seawater solubility values (Cu 46 %, Pb 98 % and Zn 71 %) from the Haifa dataset were detected in the sample collected during 27 - 28 March 1996. The seawater solubilities of trace metals associated with the Erdemli aerosol collected during the same sampling period were also higher than the average for this sampling site (Pb 49 % and Zn 51 %), although much lower than those observed in aerosol samples collected at Haifa. Such high solubilities may be partly due to an enhancement of Pb and Zn associated with the aerosol “exchangeable”
Figure 3.3 Contrasting air mass sources of atmospheric aerosols to the Eastern Mediterranean from a) European sources and b) desert sources

Blue line = 900 hPa; Red line = 700 hPa pressure level

a) 27-28 March 1996

b) 27-30 March 1998
fraction from polluted aerosols from local sources and/or from long-range transportation from Europe (Chester et al., 1989).

At both Haifa and Erdemli, the long-range air mass trajectories were from continental Europe (Figure 3.3). For the sample collected at Haifa, isobaric trajectories (i.e. air masses have maintained the same pressure level throughout their transport) originating from Western (700 hPa) and Eastern Europe (900 hPa), suggest that air masses have incorporated the European urban aerosol (Figure 3.3). The air mass back trajectories for the Erdemli aerosol sample, were mainly over the Mediterranean Sea, therefore were likely to have transported less European pollution (Figure 3.3). Atmospheric Pb concentrations were 3 times higher in Haifa (42 ng m\(^{-3}\)) than in Erdemli (16 ng m\(^{-3}\)) during 27 – 28 March 1996, whilst Zn concentrations were 25 times greater (Erdemli, 6 ng m\(^{-3}\); Haifa, 149 ng m\(^{-3}\)).

Between 27 – 30 March 1998 there was a extreme desert dust incursion in Erdemli, Turkey where the mean atmospheric Al concentrations were > 47,000 ng m\(^{-3}\). The lowest trace metal seawater solubility values (Pb < 0.9 % and Zn 1.3 %) recorded in the current study were from this sample. The air mass back trajectories in the lower troposphere (arriving at 900 hPa) originated from the Syrian Desert, and the trajectories from the upper troposphere (arriving at 700 hPa) transported dust from a long track of the Saharan Desert (Figure 3.3).

### 3.3.6 Impact of seasonal changes to aerosol populations

In addition to considering the influence of the aerosol source and the sampling site on the elemental seawater solubility, the impact of seasonal changes was also considered. Weather patterns in the EM follow seasonal trends, with a wet season in winter and dry season in summer. In 1996 the wet season (> 40 mm per month) was from January to April, then from October to December, and the dry season (< 20 mm per month) was from
May to September (Özsoy and Saydam, 2002). Kubilay (1996) observed that the atmospheric concentrations of elements measured at Erdemli were related to the occurrence of precipitation. During the winter, precipitation scavenging decreases the atmospheric concentrations to their minimum values, whereas during the summer months the lack of precipitation results in the accumulation of aerosols in the atmosphere (Koçak et al., 2004). Between the wet and dry seasons, there are transitional periods where there is precipitation and also sporadic inputs of desert dust. Ganor (1994) and Kubilay (1996) found that most dust episodes in Israel and Turkey occurred in March and April and to a lesser extent in May, September, October and November.

Figure 3.4 illustrates the variations in atmospheric loadings during 1996, via the atmospheric aerosol Al concentrations. It shows that in summer, atmospheric Al concentrations in Erdemli regularly exceed 1000 ng m\(^{-3}\). For the WM, this threshold represents Saharan dust incursions (Chester et al., 1996). However, air mass back trajectories show that the source of the atmospheric dust is from the northern zone, not the more arid southern zone (Appendix A and Kubilay, 1996). The prevailing atmospheric conditions in the EM in summer are a dry, stable anticyclonic system (Alpert et al., 1992). In contrast, in winter there is a greater daily variation in the atmospheric loading depending on the frequency of precipitation events (Kubilay, 1996 and Figure 3.4).

Preferential scavenging of coarse particles during rain events may enhance the crustal enrichment factors of anomalously enriched elements (Chester et al, 1997). This process may enhance the trace metal crustal enrichment of the aerosol populations that undergo dry deposition after the wet deposition event. Thus, the trace metal seawater solubilities of an aerosol population may be enhanced (Chester et al., 1999). Furthermore, evaporation / condensation cycles, which create low pH micro-surfaces on aerosol material may also cause an enhancement in the solubility (Spokes et al., 1994). To investigate this, the trace
Figure 3.4 Variation in atmospheric Al concentrations during 1996 in Erdemli (Kubilay and Kocak, unpublished) and Haifa (Tel Shikmona, Herut et al., 2001)
metal seawater solubility data for Erdemli and Haifa were categorised into the wet and dry seasons. The southerly aerosol samples were excluded because they had significantly different seawater solubility values to the northerly samples.

It is noticeable from Table 3.12 that preferential scavenging had no effect on the seawater solubility of the samples considered. In fact, there was no statistical difference in the solubilities between both seasons (using unpaired t-test). For the samples collected in Erdemli, the atmospheric Al concentrations were significantly lower (p-value < 0.001 with unpaired t-test) in the wet season than the dry season, with corresponding higher trace metal enrichment in the aerosol population. This would indicate that (i) preferential scavenging of coarser material was occurring during transport to the sampling site at Erdemli, during the wet season, that was not having an impact on the overall aerosol population trace metal seawater solubilities over the seasonal timeframe or, (ii) there was less crustal dust production during the wet season.

3.3.7 Effect of particle concentrations

The relationship between particle concentrations of aerosol material in seawater and the seawater solubility of aerosol associated trace metals (Cu, Pb and Zn) were investigated. In the current study the filter samples used for the seawater solubility experiments were Whatman filters. They are hygroscopic; therefore the particulate load of aerosol material on each filter, and during the seawater solubility experiments cannot be directly measured, and calculated. Instead, the aerosol particle concentrations for individual seawater solubility experiments were estimated from the percentage Al content of individual aerosol samples and the concentration of aerosol associated Al (mg l⁻¹) in the incubated seawater for each experiment.
Table 3.12 Seasonal effect on Al atmospheric aerosol concentrations, trace metal crustal enrichment factors and trace metal seawater solubilities on the Eastern Mediterranean aerosol. Errors represent one standard deviation.

<table>
<thead>
<tr>
<th></th>
<th>HAIFA, ISRAEL</th>
<th>ERDEMLI, TURKEY</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wet season</td>
<td>Dry season</td>
</tr>
<tr>
<td></td>
<td>Atmospheric</td>
<td>Atmospheric</td>
</tr>
<tr>
<td></td>
<td>concentration</td>
<td>concentration</td>
</tr>
<tr>
<td></td>
<td>ng m$^{-3}$</td>
<td>ng m$^{-3}$</td>
</tr>
<tr>
<td>Al</td>
<td>520</td>
<td>530</td>
</tr>
<tr>
<td>Cu</td>
<td>5.9 37 33.3 ± 18.2</td>
<td>5.3 32 23.5 ± 1.7</td>
</tr>
<tr>
<td>Pb</td>
<td>36 291 65.4 ± 24.3</td>
<td>30 231 52.1 ± 8.2</td>
</tr>
<tr>
<td>Zn</td>
<td>123 298 65.4 ± 17.6</td>
<td>119 267 69.3 ± 14.4</td>
</tr>
</tbody>
</table>
The typical composition of Al in the upper crust is ca. 8.0 % (Taylor and McLennon, 1985). However, the mean composition of Al in dust storms in Israel is only 4.2 % (Ganor and Foner, 1996 and Herut et al., 2001). The Al content is ‘diluted’ because calcium carbonate is a dominant mineral in the Negev desert region (Ganor and Mamane, 1982; Luria et al., 1996). The quartz aerosol filter samples (not hygroscopic) were used to estimate the Al content of aerosol populations collected with the Whatman filters. It was found that there was a positive correlation between atmospheric Al concentration and percentage Al content of aerosols associated with each quartz filter sample (Figure 3.5). Hence, the northerly aerosol filter samples had a lower Al content than the southerly samples. Formenti et al. (2001) found in samples collected from the Negev desert, that crustal aerosols contained 70 % mineral dust (alumino-silicates and carbonates) by weight; meanwhile urban dust had only 20 % mineral dust. Instead, the urban-rich aerosol population had a much higher content of non sea-salt sulphate (53 %) than the crustal aerosols (5 %).

From the line equation in Figure 3.5, the percentage Al content in each Haifa Whatman sample used in the seawater solubility experiments was estimated. The particle concentrations in each seawater solubility experiment were estimated from the percentage Al content in the dust sample, the volume of air sampled and the exact size of each filter sample used in each experiment. The particle concentrations of the Erdemli Whatman samples were not calculated, because the Al content in the crustal-rich and urban-rich aerosols might be different from the Haifa samples.

In Figure 3.6 the trace metal seawater solubilities were plotted against aerosol particle concentrations. In this study, there was no clear relationship between the aerosol load in seawater and the seawater solubility of Pb. However, there appears to be a weak exponential inverse relationship for Zn and Cu. In a similar study, Guerzoni et al. (1999)
Figure 3.5 Relationship between atmospheric Al at Haifa, Israel and the Al content within each aerosol population

\[ y = 0.00060x + 0.548 \]
\[ R^2 = 0.948 \]

Figure 3.6 Relationship between the aerosol concentration within an incubated volume of seawater and the seawater solubility of aerosol associated trace metals
noted a particle concentration effect, where an increase in the particle concentration from 40 to 100 mg l⁻¹ decreased the solubility of Pb associated with the WM aerosol in Milli-Q water from 40 % to 5 %.

It is unclear from the present study whether it was the particle concentrations that had influenced the seawater solubility of Cu and Zn or whether it was the prevalence of urban aerosols (that generally have higher trace metal seawater solubilities) at the lower particle concentration range. The weakness in the current study and the work by Guerzoni et al. (1999) is that a range of mixtures of crustal and urban aerosols was used to investigate the particle concentration effect. There is a need to find whether a particle concentration effect exists for Cu, Pb and Zn in separate crustal and urban end member aerosols (see section 6.3.5).

3.3.8 Estimation of dry deposition fluxes of trace metals to the EM

Soluble and total (soluble and particulate) trace metal fluxes by dry deposition were estimated for the EM. The dry deposition flux comprises of several processes including gravitational settling, impaction and diffusion of particles to the sea surface (Slinn, 1982 and Buat-Menard, 1986). The dry deposition flux to the EM can be estimated by the following equation:

Equation 3.1  

\[ F_d = C_d \times V_d \times 31.5 \]

where \( F_d \) is the dry deposition flux (ng cm⁻² yr⁻¹), \( C_d \) is the geometric mean air concentration (ng m⁻³) and \( V_d \) (cm s⁻¹) is the deposition velocity (the number 31.5 is for the conversion of time and surface area units). The deposition velocity is dependent on a number of variables, including wind speed, particle size, relative humidity, air viscosity and sea surface roughness (Duce et al., 1991). A modelling approach by Slinn (1982)
showed that submicrometer (urban) aerosol particles have a deposition velocity of 0.1 cm s⁻¹ ± factor of 3, and for supermicrometer (crustal) particles a velocity of 1 cm s⁻¹ ± factor of 3. The adopted deposition velocity for Cu, Pb and Zn in the current study was 0.1 cm s⁻¹ because they were anomalously enriched elements ($EF_{\text{crust}} > 10$).

In this study, the annual flux of trace metals from southerly and northerly aerosol populations were calculated, because these two sources sometimes have distinctly different atmospheric aerosol trace metal concentrations. However, there was a limited dataset for the Southern zone at Erdemli ($n = 4$), therefore, more data was required on the atmospheric trace metal concentrations. Kubilay (1996) has produced this data for high-volume samples collected in 1992, and she had classified these samples into 4 wind sectors. These back trajectory data were reclassified into northern ($n = 141$) and southern zones ($n = 94$). The geometric mean concentrations for the two zones were evaluated (Northern zone: Al 577, Pb 26.0 and Zn 18.4 ng m⁻³; Southern zone: Al 1198, Pb 36.8 and Zn 19.3 ng m⁻³). For the evaluation of atmospheric trace metal concentrations from the two major air mass sources in Haifa, data from the Year 1996 samples were used (Northern zone: $n = 34$; Southern zone $n = 12$; resultant atmospheric trace metal concentrations are presented in Table 3.10).

One concern of using the Year 1992 dataset to calculate Erdemli Pb soluble flux was that the current mean Pb concentrations might have declined since that period (due to tightening restrictions on the use of leaded petrol; Migon et al., 1994). The average Pb concentrations in the Year 1992 dataset were 26 ng m⁻³ for the southerly aerosol and 37 ng m⁻³ for the northerly aerosol. This corresponds well with the Year 1996 samples used for the seawater solubility experiments: the mean atmospheric Pb concentrations for the southerly and northerly aerosol populations were 33 and 36 ng m⁻³ respectively.
In order to find the overall annual flux of trace metals by dry deposition a weighted mean on the air masses arriving from the Northern and Southern zones must be applied. Dayan (1986) showed that approximately 27% of the air mass trajectories arriving in Israel at the 850 hPa pressure level were from the southern sector. Similarly, Küblay (1996) found that 31% of trajectory pathways to the Erdemli sampling point at the 900 hPa pressure level were from the South. Koçak (2001) also found that 29% of trajectories at the 900 and 850 hPa pressure levels originated in the south. With this consensus, the air mass trajectory weighting for the total flux estimates (Table 3.13), between the Southern and Northern aerosol populations was 29:71.

The soluble flux estimates were calculated by multiplying the mean soluble fraction (given in Table 3.11) of the considered trace metal in the northerly or southerly aerosol population by the total flux of that aerosol population. In Table 3.13, it is apparent that overall total fluxes of Pb were similar in Haifa and Erdemli. However, the soluble Pb flux is nearly twice as high in Haifa because the seawater solubility was much higher in the Haifa southerly aerosol population than the Erdemli southerly aerosol population. Similarly, due to local Zn contamination in Haifa, the Zn atmospheric aerosol concentration and its seawater solubility was higher than the Erdemli aerosol population, therefore the calculated total and soluble fluxes of Zn were much greater in Haifa. The Haifa Cu total and soluble fluxes were an order of magnitude lower than fluxes calculated for WM. This indicates that the atmosphere over the Eastern Basin was less contaminated with Cu than the Western Basin.

The calculated fluxes of trace metals in Haifa represents an upper estimate of soluble trace metal fluxes to the Eastern Mediterranean, because of higher atmospheric trace metal concentrations and enhanced trace metal seawater solubilities than Erdemli (partly due to enhanced concentrations of bacteria in the incubated seawater used in the experiments).
Table 3.13 Total and soluble fluxes (ng cm\(^{-2}\) yr\(^{-1}\)) of trace metals by dry deposition to Haifa, Israel; Erdemli, Turkey and comparison with literature for the Western Mediterranean (Source: \(^{a}\)This study, \(^{b}\)Chester et al., 1999, \(^{c}\)Nejjar and Azami, 1992)

<table>
<thead>
<tr>
<th></th>
<th>EASTERN MEDITERRANEAN</th>
<th>WESTERN MEDITERRANEAN</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Haifa, Israel(^a)</td>
<td>Erdemli, Turkey(^a)</td>
<td>Cap Ferrat, France(^b)</td>
</tr>
<tr>
<td></td>
<td>Overall Flux</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Northerly Southerly</td>
<td>Overall Flux</td>
<td>Northerly Southerly</td>
</tr>
<tr>
<td>Cu</td>
<td>Total</td>
<td>11.9</td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td>Soluble</td>
<td>3.6</td>
<td>5.3</td>
</tr>
<tr>
<td>Pb</td>
<td>Total</td>
<td>67.1</td>
<td>119</td>
</tr>
<tr>
<td></td>
<td>Soluble</td>
<td>41.3</td>
<td>64</td>
</tr>
<tr>
<td>Zn</td>
<td>Total</td>
<td>226</td>
<td>294</td>
</tr>
<tr>
<td></td>
<td>Soluble</td>
<td>177</td>
<td>202</td>
</tr>
</tbody>
</table>
3.3.9 Calculation of wet deposition fluxes

The dissolved trace metal concentrations in rainwater collected at Haifa, Israel were generally within concentration ranges in rainwater sampled from other parts of the Mediterranean coast (Table 3.14). From these concentrations, the wet deposition fluxes for Haifa were calculated. The trace metal wet deposition fluxes \( F_w, \) ng cm\(^{-2}\) yr\(^{-1}\) can either be calculated from all individual rain events (Equation 3.2) or estimated from the annual amount of precipitation \( P \) at the sampling sites and the mean concentration \( C \) of the trace metal of interest (Equation 3.3). For the current study, not all the rain events at Haifa were sampled (only 50 to 89% of the total amount), therefore the geometric mean and the annual amount of precipitation were used for calculating the wet fluxes of dissolved trace metals to the EM. The mean concentration \( C \) applied to Equation 3.3 was the rainwater weighted mean (R.W.M., Equation 3.4). The R.W.M. is a volume weighted mean, where \( R \) is the amount of rainfall (mm).

Table 3.14 Mean trace metal concentrations (\( \mu g \, l^{-1} \)) in Mediterranean rainwater (Sources: \textsuperscript{a}This study; \textsuperscript{b}Al-Momani, 2003; \textsuperscript{c}Al-Momani et al., 1998 and \textsuperscript{d}Gueiu et al., 1997)

<table>
<thead>
<tr>
<th></th>
<th>Haifa, Israel\textsuperscript{a}</th>
<th>Northern Jordan\textsuperscript{b}</th>
<th>Coastal Turkey\textsuperscript{c}</th>
<th>Tour du Valet, France\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1.3 (nd - 4.4)</td>
<td>3.1 ± 1.6</td>
<td>3.1 ± 6.0</td>
<td>20 ± 20</td>
</tr>
<tr>
<td>Pb</td>
<td>3.1 (nd - 16.0)</td>
<td>2.6 ± 2.3</td>
<td>6.4 ± 13.6</td>
<td>11 ± 14</td>
</tr>
<tr>
<td>Zn</td>
<td>48.8 (1.7 - 226)</td>
<td>6.5 ± 7.8</td>
<td>124 ± 470</td>
<td>110 ± 132</td>
</tr>
</tbody>
</table>

Equation 3.2 \[ F_{wi} = \sum C_i \times P_i \]

Equation 3.3 \[ F_w = C \times P \]

Equation 3.4 \[ \text{R.W.M.} = \frac{\sum R_i C_i}{\sum R_i} \]
The dissolved wet fluxes of Cu and Zn at Haifa were similar to those for Cap Ferrat, in France, although the Pb fluxes for Haifa were approximately double (Table 3.15). However, it has to be remembered that the number of rainwater samples used to calculate the wet deposition fluxes at Haifa were low (n = 13), therefore the rainwater concentrations used may not be wholly representative of the true weighted mean. It is clear that further work is required in this area.

Table 3.15 Dissolved wet deposition fluxes (ng cm\(^{-2}\) yr\(^{-1}\)) of trace metals to the EM (Haifa, Israel, this study) and WM (Cap Ferrat, France, Migon et al., 1997)

<table>
<thead>
<tr>
<th></th>
<th>Haifa</th>
<th>Cap Ferrat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>52</td>
<td>58</td>
</tr>
<tr>
<td>Pb</td>
<td>126</td>
<td>58</td>
</tr>
<tr>
<td>Zn</td>
<td>2000</td>
<td>3870</td>
</tr>
</tbody>
</table>

3.3.10 Comparison of different trace metal fluxes to the EM

In this section the magnitude of the deposition of soluble trace metals from dry deposition, wet deposition and riverine inputs are compared for the EM Sea. Assuming that the surface area of the EM is 530,000 km\(^2\) (Azov, 1991), the annual mass input by dry and wet deposition of each considered dissolved trace metal (Cu, Pb and Zn) was estimated (Table 3.16). The total flux of soluble Cu from dry deposition to the EM appears to be of the same order of magnitude as the riverine source, which is the Nile River. According to the Erdemli data, the soluble Zn dry deposition flux is about twice that of the riverine flux, while the soluble Pb dry deposition flux is ca. 250 times greater. This highlights the importance of dry deposition of trace metals to the EM.
Table 3.16 Soluble inputs of trace metals (t yr\(^{-1}\)) to the Eastern Mediterranean from atmospheric and riverine sources

(Sources: \(^a\)This study and \(^b\)Dorten et al., 1991)

<table>
<thead>
<tr>
<th></th>
<th>Atmospheric</th>
<th>Riverine(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry deposition(^a)</td>
<td>Wet deposition(^a)</td>
</tr>
<tr>
<td></td>
<td>Erdemli</td>
<td>Haifa</td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>129</td>
<td>339</td>
</tr>
<tr>
<td>Zn</td>
<td>92</td>
<td>1070</td>
</tr>
</tbody>
</table>
It must be noted that there is a large uncertainty in the settling velocities of the considered trace metals associated with urban and crustal particles in the EM. The estimated settling velocity has a strong influence on the calculated soluble inputs of trace metals into the EM by dry deposition. Migon et al. (1997) for example observed that the settling velocities of aerosol associated Cu, Pb and Zn were 1.2, 0.2 and 4.4 cm s\(^{-1}\) respectively at Cap Ferrat, on the French Ligurian coast. These velocities were much higher than the designated 0.1 cm s\(^{-1}\) used in this study, and would have increased the calculated soluble inputs by dry deposition to 336, 678 and 47,100 t yr\(^{-1}\) of Cu, Pb and Zn respectively, to the EM Sea. If the settling velocities found at Cap Ferrat are adopted, then the soluble Cu and Pb inputs by dry deposition are similar to wet deposition inputs, and Zn inputs would be ca. 4 times greater.

3.4 Conclusions

This was the first study to estimate soluble inputs of trace metals (Cu, Pb, and Zn) to the EM by dry deposition. A rigorous methodology was developed to assess the seawater solubility of trace metals associated with the EM aerosol, under carefully controlled experimental conditions (constant temperature, shaking and pH), using protocols to minimise trace metal contamination. The analytical technique used to measure the dissolved trace metal concentrations in seawater was stripping voltammetry; which was suitably sensitive and accurate. Selected aerosol samples that were collected from two sampling sites in the EM underwent seawater solubility studies. It was found that the seawater solubility of trace metals (Pb and Zn) associated with aerosol samples from Haifa, Israel were higher than from Erdemli, Turkey.

With the use of air mass back trajectory calculations (arriving at the 900 hPa pressure level), each aerosol sample was classified into two contrasting sources: the urban-rich Northern zone and the crustal-rich Southern zone. It was found that the origin of the air
mass source had a significant impact on the seawater solubility of aerosol associated trace metals. Particularly in Erdemli, the seawater solubility of trace metals associated with the southerly aerosol population was significantly lower than the northerly aerosol population.

There was no evidence of there being seasonal differences in the seawater solubility of aerosol associated trace metals. There was a weak negative exponential relationship between particle concentrations and the seawater solubility of Zn and Cu associated with the Haifa high-volume aerosol filter samples. These two factors were not considered in the trace metal atmospheric flux estimates to the Eastern Mediterranean.

Using flux data from the Erdemli aerosol samples, it is evident that the particulate and soluble dry deposition fluxes of Pb and Zn from the EM are less than that of the WM. The reason might be the further distance from the European urban aerosol source. Within the EM, several processes might be affecting the extent and rate to which trace metals associated with aerosol particles dissolve in seawater. These aspects might include the relative proportions of crustal and urban aerosol present, dust concentrations in seawater and the presence of sunlight (which will affect temperature and may cause photochemical reactions) and microorganisms. To increase our knowledge of trace metal fluxes to the EM and other seas, a systematic approach is required to investigate factors that might influence them.
Chapter Four

Analytical development of an on-line dissolved trace metal detection system
4.1 Introduction

From the study presented in Chapter 3, it is clear there was a requirement for an experimental system that would enable a systematic investigation of the impact of environmental factors on the seawater solubility of aerosol associated trace metals. Thus the aim of the current study was to construct, optimise and validate an automated dissolved metal monitor, which later would allow various factors to be investigated (see Chapters 5 and 6). The monitor was used to define both the rate and extent of trace metal (Cu, Pb and Zn) desorption in seawater. The following criteria were established for the development of the monitor:

i. To be able to measure, in seawater, dissolved trace metal concentrations in the nM range, at a high temporal resolution (typically measuring once every 1 - 2 min), with both good accuracy and precision.

ii. Integration of flow and detection (electroanalytical) systems.

iii. The inclusion of an operationally defined on-line physical separation method between the dissolved and particulate phases.

iv. The ability to measure operationally defined trace metal chemical speciation concentrations (i.e. labile and non-labile fractions; see section 4.1.2).

4.1.1 “State of the art” dissolved metal monitors using stripping voltammetry

Several analytical methods are unsuitable for seawater trace metal analysis, without trace metal preconcentration and seawater matrix removal procedures (for example using solvent extraction or chelation columns prior to Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS), Chemiluminescence or Graphite Furnace Atomic Absorption Spectroscopy). For example without seawater matrix removal, atomic absorption spectroscopy suffers from instrumental spectral interferences and potential blockages of the nebuliser caused by
the high salt content of seawater (Johnson et al., 1992). With discrete sample pretreatment, all these methods are time-consuming and have a greater risk of sample contamination compared to those methods that are able to determine trace metals directly in seawater. Although recently flow injection solid phase extraction for the determination of trace metals in seawater has been combined with ICP-MS and chemiluminescence to reduce these problems (for example Bloxham et al., 1994 and Beck et al., 2002).

Therefore stripping voltammetry (anodic and adsorptive cathodic) was the adopted analytical technique for the current study as it is suitably sensitive (typical detection limits being sub nM), allowing the direct determination of trace metals in seawater (van den Berg, 1986; van den Berg, 1988; Achterberg et al., 1994b; Achterberg and van den Berg 1997 and Nimmo et al., 1998). The purchase and running costs of equipment required for stripping voltammetry are much lower than those for GFAAS and ICP-MS. In contrast to FI-Cl, stripping voltammetry has the capability of measuring more than one dissolved metal simultaneously. In this study, anodic stripping voltammetry (ASV) was used to measure dissolved Zn, Pb and Cu simultaneously. The geochemical importance of these trace metals has already been highlighted in section 2.4. One further advantage of this technique is that it is suitable for chemical speciation studies (see section 4.1.2).

During anodic stripping voltammetry (ASV), a deposition step is carried out whereby metal ions from the seawater sample are preconcentrated onto a hanging Hg drop electrode by reduction, followed by amalgamation with the Hg drop (Equation 4.1). The deposition step is maintained for a specific period, dependent on the seawater metal concentrations. This step is then followed by a voltammetric scan towards more positive potentials, and the amalgamated metals are oxidised. Associated with the oxidation is an oxidation current ($i_o$) occurring at a defined potential specific to the metal being oxidised. The peak height of the resultant current is proportional to the dissolved analyte concentration. For further details
For adsorptive cathodic stripping voltammetry (ACSV), a specific organic ligand (L) is added to the water sample, which forms a complex with the trace metals (M) under investigation (Equation 4.2). During an applied potential (more positive than the metal-ligand reduction potential), the metal-ligand complex (ML\textsuperscript{n+}) is adsorbed onto the Hg drop (Equation 4.3), using a fixed collection period (typically 1 min). After which a negative potential scan is applied. The resulting current from the reduced metal-ligand complex (Equation 4.4) is recorded. This is the analytical signal and is proportional to the dissolved metal concentration in the sample (see for example van den Berg, 1991 and Achterberg et al., 2000).

Equation 4.2
\[ \text{M}^{n+} + zL \rightarrow \text{ML}^{n+} \]

Equation 4.3
\[ \text{ML}^{n+} \rightarrow \text{ML}^{n+} \text{(adsorbed)} \]

Equation 4.4
\[ \text{ML}^{n+} \text{(adsorbed)} + e^- \rightarrow \text{M}^{(n-1)+} + zL \]

4.1.2 Operationally defined trace metal speciation by stripping voltammetry

The knowledge of total dissolved trace metal concentrations does not provide sufficient information about the toxicity, biological availability and geochemical behaviour of metals in seawater. The presence of organic ligands reduces the free metal ion concentration, hence the biological availability of metals. The uptake of a metal ion in an aqueous
medium by microorganisms is proportional to the concentration of the free metal ion (da Silva and Williams, 1991 and Sunda, 2000). The free aquo ion is not the only chemical species taken up by marine phytoplankton, but represents the chemical reactivity of the dissolved metal. In contrast, natural seawater metal-organic complexes are normally large, hydrophilic molecules, which are generally unable to diffuse across the cell membrane of microorganisms (Buffle, 1988).

The ion-selective electrode allows us to measure the free-metal ion concentration if it were sufficiently sensitive. However, due to the very low metal concentrations in seawater this is not possible (Skoog and Leary, 1992). In stripping voltammetric methods, the electrochemically 'labile' concentration can be measured. The labile metal ion concentration includes the free metal ion concentration, inorganic and weak organic complexes (van den Berg, 1988 and Donat and Bruland, 1990). Labile and total dissolved trace metal concentrations can be determined before and after UV irradiation respectively in seawater aliquots to assess the operationally defined chemical lability of the dissolved trace metals (Bordin et al., 1988; and Nimmo and Chester, 1993).

In ASV, the labile dissolved metal represents the fraction that can be deposited at the electrode under controlled conditions (forced convection, deposition potential and pH). The labile fraction includes inorganic metals and the reversible metal-organic complexed fraction, which dissociates at the applied deposition potential (weak organic complexes). The non-labile fraction consists of strong complexes, formed between the metal and organic ligands which are electrochemically inert i.e. complexes that do not dissociate at the working electrode (Florence, 1992).

Dissociation of the trace metal-organic complexes is dependent on the residence time of a chemical species on the surface of the electrode and the dissociation rate constants of the
metal complexes. The residence time is reliant on the thickness of the diffusion layer at working electrode (Kozelka and Bruland, 1998 and Mota and dos Santos, 1995). In ASV-speciation studies it is important to define the pH and deposition potential because the former defines which metal species are ASV-labile, whilst the latter influences the chemical equilibrium of the samples (van den Berg, 1991).

In this study, the ASV technique was used to simultaneously measure labile Pb and Zn, but the Hg peak potential obscured the Cu oxidation peak, owing to the high pH used (8.0). Labile Cu was determined using the ACSV ligand salicylaldoxime (SA). The use of SA had the analytical advantage of high sensitivity (3-4 fold higher than 8-hydroxyquinoline or tropolone) and selectivity for Cu (Campos and van den Berg 1994). In ACSV, the distributions of trace metals are determined by the concentrations and the $\alpha$-coefficients of the added ligand (AL) and the natural organic (ML) and inorganic ($m_{i}$) complexing ligands. The $\alpha$-coefficients are a measure of the degree of complexation of the metal with a particular ligand; they represent the ratio of the complexed metal to the free metal concentration. The amount of trace metal (M) complexed with the AL after equilibration represents the labile metal fraction hence $[MAL] = [M_{labile}]$ (van den Berg, 1988). The ACSV metal fraction may be defined as:

$$[M_{labile}] = [M^{n+}] (\alpha_{m_{i}} + \alpha_{MAL})$$

where $\alpha_{m_{i}}$ is the inorganic complexation coefficient and $\alpha_{MAL}$ the $\alpha$-coefficient for the added ligand. The ACSV labile metal fraction ($M_{labile}$) may also include metal that is present as weak organic complexes, which have $\alpha$-coefficients $< \alpha_{MAL}$. The $\alpha_{m_{i}}$ value may be calculated from:

$$\alpha_{m_{i}} = 1 + \sum \beta_{ML_i} [L_i]^j$$
\( \beta_{\text{MLi}} \) are the inorganic stepwise conditional constants determined by Turner et al. (1981), adjusted for seawater ionic strength. \([\text{L}]^i \) are the inorganic ligand concentrations. The \( \log_{10} \alpha_m \) for Cu at pH 7.8 is 0.65 (Nimmo et al., 1998).

\( \alpha_{\text{MAL}} \) is calculated from:

\[ \alpha_{\text{MAL}} = (\beta^{\text{M(AL)i}}_{\text{CALi}}) \]

\( \beta^{\text{M(AL)i}}_{\text{CALi}} \) is the conditional stability constant for the complex of metal M with i added ligands AL, and CAH are the added ligand concentrations (Nimmo et al., 1998). The \( \log_{10} \alpha_{\text{MAL}} \) for SA is 5.83 in seawater, at a concentration of 25 \( \mu \)M (Campos and van den Berg, 1994). The stability of the complexes of SA with Cu is intermediate to that of other organic ligands such as tropolone (\( \log_{10} \alpha_{\text{MAL}} \) 2.5 \(-4.0 \)) and 8-hydroxyquinoline (\( \log_{10} \alpha_{\text{MAL}} \) 6.4 \(-9.0 \)), which are commonly used ligands for the determination of labile Cu (for example Braungardt, 2000 and Nimmo et al., 1998).

### 4.1.3 Interfacing the dissolved metal monitor with incubated seawater

The manner in which stripping voltammetry is integrated into a reaction system with incubated seawater, to measure aerosol associated desorption in seawater needs careful consideration. The conventional method for monitoring trace metal desorption / adsorption kinetics is by batch experiments, where aliquots of seawater suspension are withdrawn from the reaction vessel, at predetermined intervals (Statham and Chester, 1988; Hamilton-Taylor et al., 1993; Guieu et al., 1994; Liu, 1996 and Nimmo et al., 1998). This step is followed by filtration, which terminates the particle-water reaction. The filtrate is then analysed for the metal(s) of interest. For example, batch experiments investigating Liverpool urban dust in seawater clearly indicated that the dissolved-particulate equilibrium of the trace metals (Cu, Pb, Cd, Ni and Co) was attained within an hour.
However the experiment produced too few data points to give mechanistic information during the initial desorption stage (Nimmo et al., 1998). The discrete sampling approach followed by dissolved trace metal analysis involves a number of sample-handling operations, which increases the potential for sample contamination. Furthermore this approach may result in considerable changes in the total volume of the incubated seawater, which may induce the 'particle concentration effect', where enhanced concentrations of particles may re-adsorb dissolved trace metals (Guerzoni et al., 1999 and Spokes and Jickells, 1996), and hence gives erroneous datasets.

To minimise these problems, Hamilton-Taylor et al. (1993) and Davison et al. (1994) carried out dissolution experiments on filter-collected aerosols in freshwater, directly in an electrochemical cell, with ASV. Automated direct measurement of the released labile Cu, Pb and Zn in the experimental vessel was performed at 1 min intervals. There was no loss of the incubation volume, but the experiment could not be continuously stirred, as the solution had to rest prior to each stripping voltammetric measurement, which would have yielded changes in the rate of metal desorption.

There were other disadvantages of this in situ technique such as: (i) the presence of the aerosol filter sample in the electrochemical cell would have affected the hydrodynamics of the voltammetric cell, impacting upon the reproducibility of each measurement, as the sensitivity of this technique would be affected by the amount of forced convection, (ii) the application of a voltammetric potential within the incubation solution may have impacted upon the extent and rate of desorption of metals and (iii) no distinction could be made in the chemical speciation of the dissolved trace metals in the incubated sample. However, an on-line system could make this distinction, whilst possessing the benefits of reduced contamination due minimal sample handling, and minimal changes in the chemical
speciation of the dissolved trace metal measurements. An on-line system also allows the continuous stirring of a solution whilst the analysis is performed.

Achterberg and van den Berg (1994a) developed an on-line automated monitor for the shipboard determination of dissolved trace metals in seawater, using ACSV. Discrete samples were transferred from a sample changer to an on-line voltammetric system where each sample was analysed within a conventional voltammetric cell. The rate of dissolved trace metal determinations was approximately 7 samples per hour, without calibration. They applied the monitor to the measurement of Cr speciation and Cu complexing capacities in Mediterranean seawater.

This system was further developed for fully automated sampling and analysis with continuous surface water collection. Samples were continuously filtered and UV irradiated on-line for total dissolved trace metal measurements. This system was applied to the automated monitoring of trace metals (Ni, Cu and Zn) in the Irish Sea (Achterberg and van den Berg, 1994b), a mine-polluted bay in South-west Spain (Braungardt et al., 1998), tidal cycles in the Tamar estuary, UK (Whitworth et al., 1998) and, Cu and Co in the western North Sea (Achterberg et al., 2003).

The on-line systems described above require approximately 20 ml of sample (the first 10 ml is allowed to flush through the sample loop). For the current application (high-resolution kinetic experiments) this technique is inappropriate because there would have been significant incubation volume loss. In contrast, a flow cell approach with a wall-jet system requires less sample volume and allows the frequency of measurements to be increased. Daniel et al. (1997) developed a low volume flow cell. The system was applied to the measurement of ACSV-labile Co in seawater, whereby approximately 60 measurements were made per hour.
Similar voltammetric flow systems have been applied to the determination of metals (Cu, Cd, Pb and Zn) in algal samples (Fernandez-Bobes et al, 1998), total dissolved Co measurements in seawater (Colombo et al., 1997) and measurement of trace metals (Cu, Pb, Zn and Ni) in soil extracts (Colombo and van den Berg, 1998). However, to date, an on-line stripping voltammetric system has not been applied to the determination of the desorption of trace metals from particles in seawater.

In the current study, a novel on-line system using stripping voltammetry was utilised whereby the sample was withdrawn continuously from an aerosol particle / seawater reaction system. The sample treatment was performed on-line and a commercially available wall-jet flow cell system was employed for trace metal analysis of dissolved total (with UV irradiation) and labile (without UV treatment) Cu, Pb and Zn. The analytical performance (including the instrumental limits of detection, linear range, accuracy; and the efficiency of UV irradiation to destroy organic material), and potential trace metal adsorption and contamination from the experimental system were assessed. The results and implications of these studies are presented in the following sections.

Initially, the system was applied to the determination of the extent and rate of the dissolution of Cu, Pb and Zn associated with Liverpool urban particulate material (LUPM), under controlled experimental conditions (constant temperature, stirring, pH, under dark conditions). LUPM was used in the initial kinetic studies, as it was a single, bulk sample representing an urban end member, which was available in sufficient quantities to carry out analytical optimisation studies. Similar material has been used in previous studies (Chester et al., 1993, Chester et al., 1989 and Nimmo et al., 1998). This chapter demonstrates that reproducible, high-resolution kinetic data were produced from the assembled analytical system.
4.2 Experimental methodology

4.2.1 Reagents

Ultra-clean water (Milli-Q water) was produced by reverse osmosis (Milli-RO, Millipore) followed by ion-exchange (Milli-Q, Millipore). The product had a resistivity of 18.2 mΩ cm⁻¹. Hydrochloric acid (Aristar grade, Merck) was purified in a sub-boiling quartz still. HEPES stock solution (1 M) was prepared from n-2-hydroxyethylpiperazine-N'-2-ethanesulphonic acid (Aldrich, analytical grade) in Milli-Q water. Its pH was adjusted to 7.70 with isothermally distilled ammonia. The stock solution of 0.5 M SA was prepared from salicylaldoxime (Aldrich, analytical grade) in Milli-Q water and acidified to pH 0.5 with HCl. Separate standard solutions of Cu, Pb and Zn (10⁻⁴ and 10⁻⁵ M) were prepared from Spectrosol standard solutions (Merck, 1000 mg l⁻¹) in HCl (0.01 M). All reagents and samples in this study were prepared using calibrated auto-pipettes (Finnpipette). All manipulations were carried out within the confines of a laminar flow cabinet (Class 100). When not in use, reagents and standards were stored in a refrigerator at 4 °C, to prevent evaporation and degradation of the solutions.

4.2.2 Design and construction of the analytical system

The adopted experimental system for the determination of the total seawater solubility of aerosol associated trace metals (Cu, Pb and Zn) is presented in Figure 4.1, as both a photograph and diagram, where the main components are highlighted. The chosen reaction vessel was an acid cleaned 1 l wide neck, low-density Teflon® (fluorinated ethylene propylene) vessel (Nalgene). The cap was loosely fitted, with a piece of polyethylene film on top. The entire vessel was placed inside a clean resealable plastic bag. An opaque cover was placed on top of the reaction vessel to prevent photochemical reactions occurring within the seawater. The seawater solution was continuously stirred with an acid cleaned
Figure 4.1 Diagram and photograph of the experimental system for the determination of total dissolved trace metals by ASV for particulate / dissolved kinetic experiments
Teflon® coated stirrer bar (15 mm length, Hanna Instruments) using a magnetic stirrer (Hanna instruments, HI190M model).

During each experimental run, the seawater temperature inside the reaction vessel was held constant at 25.2 ± 0.1 °C, using a close fitting temperature controlled water jacket. The water jacket consisted of a coil of rubber tubing (1 cm in diameter, i.d.), encased in a polystyrene housing. The temperature of the reaction vessel was maintained by pumping water through the jacket from a water bath containing a heater-thermostat (Techne Tempette TE-8A) and dip cooler (Grant, type CI9). The temperature between the reaction vessel and water jacket was constantly monitored using a temperature probe (Squirrel meter / logger). Figure 4.2 illustrates that the water temperature in the reaction vessel reached equilibrium within 10 h, after an initial temperature of 12 °C.

*Figure 4.2 Seawater temperature measured in 1 l Teflon® vessel over 40 h period, with temperature control setting of 25 °C*

All tubing used for sample transfer was manufactured from polytetrafluoroethylene (PTFE, 0.79 mm i.d., Altec). The tubing was connected to the different components of the experimental system with barbed PTFE tubing connectors (Altec) and 1 cm strips of Tygon® tubing (1 cc / m, Elkay). Prior to each experimental run, the tubing connections were checked for leaks and for the presence of air bubbles. Air bubbles may destabilise the
hanging Hg drop or cover it during analysis; reducing the reproducibility of the trace metal measurements.

On-line filtration was carried out using a 25 mm diameter Swinex filtration unit, containing a 0.45 μm pore size cellulose acetate membrane filter (Whatman). Prior to the analysis of total dissolved trace metal concentrations, the samples were subjected to on-line UV digestion using a 400 W medium pressure Hg vapour lamp (Photochemical Reactors) and a quartz coil (Achterberg et al., 1994a and Achterberg et al., 2001a). The length of the quartz coil was about 3.5 m with 1.0 mm i.d.; therefore the approximate volume inside was 2.75 ml. The lamp and quartz coil were housed in an aluminium case. A fan cooled the UV system to approximately 70 °C. The sample was further cooled to approximately room temperature during its transit to the flow cell.

The sample was continuously transferred from the reaction vessel, through the filtration unit, mixed with the reagent, and then through the UV lamp with a peristaltic pump (Watson-Marlow 501), fitted with Tygon tubing (Elkay). To allow the release of backpressure, a polystyrene vial (< 300 µl) was included between the first and a second pump (Minipulse 3, Gilson). The second pump was TTL controlled via port DIO 1 of the µAutolab voltammeter (Eco Chemie).

The amount of tubing connecting the different components in the experimental system was kept to a minimum, to reduce dispersion of the sample within the on-line system (the sample loop). The tubing was positioned at the same horizontal level to reduce the amount of backpressure, which may cause pulsing of the sample at the flow cell, and hence a decrease in the reproducibility of the trace metal measurements. Without these measures to prevent backpressure, the relative standard deviation of repetitive measurements of total dissolved Zn and Pb by the experimental apparatus was 15 – 20 % (Figure 4.3).
The electrochemical system used was a static mercury drop electrode (SMDE, EG & G PARC Model 303) with a Perspex flow cell (EG & G PARC Model 420), which fitted around the base of the working electrode. The entire assembly was immersed in a glass cell (approximately 50 ml volume, constructed "in house") which contained a solution that had the same solution matrix as the sample / reagent mixture inside the sample loop. The sample solution flowed past the hanging Hg drop, into the cell, which contained a Pt counter electrode and a reference electrode (Ag / AgCl). The solution inside the cell was continuously de-oxygenated with ultra-pure nitrogen (BOC). The nitrogen gas was pre-cleaned by bubbling it through Milli-Q water.

The analysis was fully automated, with the potentiostat and peristaltic pump controlled by an IBM-compatible computer, with an adapted version of the software EAS 1.0 (Eco Chemie). During each voltammetric measurement cycle, the pump was automatically switched off for 15.1 s to allow for the equilibration of the sample and during the voltammetric scan, and prior to next electrochemical measurement cycle.
4.3 Analytical optimisation

4.3.1 Voltammetric optimisation

Optimisation of the dissolved trace metal (Zn, Pb and Cu) analysis in seawater with stripping voltammetry, using the wall-jet electrode was undertaken in order to enhance the reproducibility and sensitivity of the system. The ASV scanning frequency, step potential, modulation amplitude and collection potential parameters were all altered sequentially until optimisation. These parameters were optimised in acidified (pH 2.2 with HCl), UV irradiated seawater spiked with 100 nM Zn, Pb and Cu, and measured with a 60 s deposition time, at a sample flow rate of 1 ml min⁻¹. The reproducibility was deemed acceptable when the relative standard deviation of six repetitive measurements was < 5 %.

Table 4.1 Adopted analytical parameters for the determination of Cu, Pb and Zn in UV irradiated seawater

<table>
<thead>
<tr>
<th></th>
<th>Frequency (Hz)</th>
<th>Step potential (mV)</th>
<th>Modulation amplitude (mV)</th>
<th>Collection potential (V):</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASV (Zn, Pb and Cu)</td>
<td>200</td>
<td>4.88</td>
<td>50</td>
<td>-1.4</td>
</tr>
<tr>
<td>ACSV (Cu)</td>
<td></td>
<td></td>
<td></td>
<td>-0.15</td>
</tr>
<tr>
<td>Final potential (V):</td>
<td></td>
<td></td>
<td></td>
<td>-0.15</td>
</tr>
<tr>
<td>ASV (Zn, Pb and Cu)</td>
<td></td>
<td></td>
<td></td>
<td>-0.55</td>
</tr>
<tr>
<td>ACSV (Cu)</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Equilibration time (s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak potential (V):</td>
<td></td>
<td></td>
<td></td>
<td>Zn</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pb</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cu</td>
</tr>
</tbody>
</table>

Table 4.1 shows the adopted optimised collection potentials and scanning parameters, for the total dissolved trace metal experiments for Cu, Pb and Zn with ASV; the labile dissolved experiments for Pb and Zn with ASV; and the labile dissolved experiments for Cu with ACSV, with the added ligand SA. Square wave stripping voltammetry was
selected because it is a sensitive technique that requires less than 1 s to perform each scan, which is ideal for high temporal resolution kinetic studies. Furthermore by using a fast scanning wave-form (200 Hz), it was possible to discriminate against the oxidation / reduction current of oxygen, which can interfere with the trace metal measurements (van den Berg, 1988).

During the ASV analysis, the applied collection potential was 0.25 V more negative than the Zn oxidation potential. In contrast, the adsorption potential during the analysis of Cu with the ACSV technique was 0.15 V more positive than the reduction potential of the metal-ligand complex. During the ASV voltammetric scan, the potential scan commenced at −1.4 V and finished at −0.15 V, whereas during the ACSV voltammetric scan spanned from −0.15 V to −0.55 V.

The overall sensitivity of the ASV technique could have been improved by using a mercury film electrode (MFE) rather than a SMDE. The MFE is a commonly used working electrode; it has a high surface area to volume ratio, hence it has excellent analyte limits of detection (Coale and Bruland, 1988; Donat and Bruland, 1990; Donat et al, 1994; Mota and dos Santos, 1995, Kozelka and Bruland, 1998). However, the MFE would require frequent cleaning (by stripping off the Hg film) because it may be more subject to fouling by surfactants than the SMDE. This type of working electrode would be unsuitable because the sensitivity of trace metal detection may decline during continuous analysis for the kinetic experiments.

The advantage of a SMDE compared to the MFE is that a new surface is reproduced prior to each measurement cycle. During each measurement cycle, the SMDE dispensed 4 drops to remove trace metal contamination from inside the tip of the working electrode and then it retained the last drop. A “medium” drop size was selected as a “large” drop size tended
to block the flow cell. Prior to each voltammetric scan, the sample was equilibrated for 10 s, whereby the pump was stopped, to allow the solution surrounding the Hg drop to acquiesce.

4.3.2 Flow rate of the sample

The effect on the sensitivity of the flow rate of the sample was evaluated in UV irradiated acidified seawater (pH 2.2 with HCl), spiked with 100 nM Cu, Pb and Zn, using the experimental system presented in Figure 4.1. The deposition time of the ASV measurements was 60 s. It is apparent from Figure 4.4 that the oxidative current of the anodic stripping voltammetric measurements for Cu, Pb and Zn linearly increased with the sample up to a flow rate of 3.25 ml min$^{-1}$. However, at a flow rate of $> 4$ ml min$^{-1}$, analysis is not possible owing to Hg drop dislodgement from the working electrode. Therefore the technique’s sensitivity is limited to that defined by a flow rate $< 4$ ml min$^{-1}$.

*Figure 4.4 Effect of flow rate on the ASV determination of dissolved Cu, Pb and Zn (100 nM) in UV irradiated seawater

*Error bars represent one standard deviation of triplicate measurements*

In order to gain a balance between adequate sensitivity for the measurement of dissolved Cu, Pb and Zn from LUPM, and the conservation of the incubation volume within the
reaction vessel during the life time of the experiment, a sample flow rate of $0.88 \pm 0.06 \text{ ml min}^{-1}$ was chosen (total flow rate to the wall-jet electrode $1.00 \pm 0.10 \text{ ml min}^{-1}$, with the reagent). A low pumping rate was chosen in order to decrease the amount of sample dispersion within the sample loop (Ruzicka and Hansen, 1988), and to minimise the loss of sample volume. With the chosen sample flow rate, there was $\sim 15\%$ loss of 1 l of sample after a 3 h kinetic experiment. The total and labile dissolved kinetic experiments were performed separately to prevent $>16\%$ loss of the original incubation volume.

4.3.3 Effect of tubing volume

To minimise sample dispersion within the tubing of the sample loop, the length of the tubing was kept to a minimum. Dispersion caused by the flow in an open narrow tube increases with the square root of the tubing length (Ruzicka and Hansen, 1988). The total dissolved experimental system had a greater fluid volume (9.46 ml) within the sample loop than the labile dissolved system (3.54 ml). The 3.54 ml labile dissolved experimental system had a much lower tubing volume because it did not require the silica coil within the UV lamp or the backpressure system, furthermore it required only one peristaltic pump (Minipulse 3, Gilson).

The difference in the desorption rate of labile Zn from LUPM was assessed with the two different tubing volumes (3.46 and 9.46 ml, using the total and labile dissolved experimental set-up respectively). ASV measured labile dissolved Zn by the on-line system previously described (after the addition of 0.01 M HEPES on-line), during the addition of 50 mg l$^{-1}$ of LUPM to 1 l of seawater (equilibrated at $25.2 \pm 0.1 ^\circ \text{C}$), in separate experiments for the contrasting tubing volumes. The sample flow rate to the flow cell was 1.0 ml min$^{-1}$ in both experimental runs.

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Figure 4.5 shows that a dissolved labile experimental system with a low volume (3.54 ml) produced a greater apparent initial Zn desorption rate (69.9 ± 6.3 nM min⁻¹) than a system with the same volume (9.46 ml) as the total dissolved experimental system (51.8 ± 4.2 nM min⁻¹). The initial rate of desorption was calculated with the line of best fit between the labile Zn concentrations and time, for the first 5 min of the kinetic experiment. There was no effect on the observed labile Zn concentrations at dissolved / particulate Zn equilibrium (after 15 min). These results confirm that the tubing volume enhances the amount of sample dispersion, therefore reduces the observed rate of desorption. This is an inherent limitation of this assembled experimental set-up. In future studies using this type of system, the volume of the sample loop between the reaction vessel and the flow cell needs to be clearly specified. Ideally, to prevent sample dispersion, the dissolved metal monitor should be in situ, however it may cause experimental problems highlighted in section 4.1.3.

Figure 4.5 Effect of the tubing volume on the dissolved labile Zn experimental system

(Error bars represent one standard deviation of two separate experimental runs)

The tubing volume of the labile dissolved experimental system for subsequent kinetic experiments was made the same as that used for the total dissolved experimental system, to allow comparability between the results (9.46 ml). Therefore the labile dissolved system
was assembled in the same way as the total dissolved experimental system (including the backpressure system). The UV coil in the total dissolved experimental system was replaced by 85 cm of PTFE tubing (Altec) with a 0.16 cm bore size in the labile experimental set-up.

There was an additional reason for adopting the high tubing volume (9.46 ml) rather than the low tubing volume for the ACSV analysis of labile Cu during the kinetic experiments. For the kinetic experiments measuring labile dissolved Cu, the ligand SA was allowed to react with the dissolved Cu for 7.5 min prior to analysis of seawater equilibrated with 50 mg l⁻¹ LUPM, within the on-line system. It was observed that the analytical signal did not increase if the sample was left in the sample loop for longer (15 min), which indicated that the Cu complexation formation was complete. However if the low tubing volume (3.54 ml) had been adopted for the kinetic experiments, SA would have had only 45 s to complex with Cu within the sample, before it reached the flow-cell. This would not have given sufficient time for the ligand-metal complex to reach equilibrium; the analytical signal after ACSV was only 74 % of the signal acquired with > 7.5 min equilibration time.

4.3.4 Efficiency of on-line UV irradiation

On-line UV digestion is an approach commonly used for the destruction of dissolved organic matter in seawater prior to voltammetric analysis (for example Achterberg and van den Berg 1994a; Nimmo and Fones, 1994; Whitworth et al., 1998 and Achterberg et al., 2001a). For the total dissolved experimental system, this technique was used to distinguish between total dissolved and labile dissolved metal fractions for the aerosol / seawater kinetic studies and to avoid analytical interferences from dissolved organic material. These interferences may be due to (i) competition for the dissolved trace metals by strong metal complexing ligands in the sample, causing a reduced voltammetric signal; (ii) organic compounds that may produce a reduction / oxidation current peak the stripping
step, which may overlap with the trace metal reduction / oxidation potentials; (iii) at high concentrations, surface-active compounds may present a physical barrier to the adsorption of the trace metals onto the Hg drop (van den Berg, 1991; Achterberg and van den Berg, 1994a and Mota and dos Santos, 1995).

The effectiveness of on-line UV irradiation of seawater for the total dissolved kinetic experiments was assessed (Table 4.2). During these experiments, the residence time of the sample in the quartz coil was $3.1 \pm 0.2$ min. To investigate whether this residence time was sufficient to release all of the dissolved trace metals (Cu, Pb and Zn) from the organic material, 50 mg l$^{-1}$ of LUPM was equilibrated with 1 l of seawater, then acidified (with HCl to final pH 2.2), filtered and UV irradiated on-line. The filtrate was then UV irradiated a second and third time ($6.2 \pm 0.4$ and $9.3 \pm 0.6$ min total residence time respectively) through the silica coil at the same flow rate as the first time ($0.9$ ml min$^{-1}$). The trace metal concentrations (Cu, Pb and Zn) from the filtrate from each UV irradiation cycle were then analysed on-line by ASV. The concentrations were calibrated with seawater spiked with 70 nM Cu, 20 nM Pb and 600 nM Zn. This entire procedure was done in triplicate.

<table>
<thead>
<tr>
<th>Metal (nM)</th>
<th>Residence time (min)</th>
<th>3.1</th>
<th>6.2</th>
<th>9.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td></td>
<td>62.2 ± 1.2</td>
<td>66.9 ± 1.5</td>
<td>65.8 ± 1.7</td>
</tr>
<tr>
<td>Pb</td>
<td></td>
<td>19.6 ± 0.3</td>
<td>20.1 ± 0.6</td>
<td>20.3 ± 0.5</td>
</tr>
<tr>
<td>Zn</td>
<td></td>
<td>544 ± 11</td>
<td>580 ± 5</td>
<td>578 ± 8</td>
</tr>
</tbody>
</table>

Assuming that all the trace metal organic complexes and surfactants were destroyed after 9.3 min, 94.5 % Cu, 96.6 % Pb and 94.1 % Zn were released in the first 3.1 min. It
therefore appears that the majority of the dissolved trace metals were released by the UV irradiation technique during the kinetic experiments with LUPM. Similarly, Achterberg et al. (2001a) found that with Tamar Estuary water, over 90% of ACSV labile Cu was released within 3 min of on-line UV irradiation.

4.4 Analytical performance

4.4.1 Linearity of voltammetric system

To ensure trace metal saturation did not occur on the Hg drop (which would lead to an underestimation of the trace metal concentrations) during the voltammetric measurements for the kinetic studies, the linear ranges of Cu, Pb and Zn were investigated. For the assessment of the linear range of the ASV technique, seawater was acidified with 6 mM of HCl and spiked with metal standards (up to 400 nM of Cu and Pb, and 2000 nM Zn). Three repetitive measurements were taken of each aliquot (Figure 4.6a) after a 2 min deposition time and a sample flow rate of 1 ml min⁻¹. Similarly, the linear range of ACSV Cu was determined (with 25 μM of the added ligand SA and 0.01 M HEPES, with 30 s deposition time; Figure 4.6b).

Figure 4.6a Linear ranges of total dissolved Cu, Pb and Zn in seawater at a deposition time of 2 min, and flow rate of 1 ml min⁻¹, determined by ASV

(Error bars represent one standard deviation of triplicate measurements)
Figure 4.6b Linear range of the ACSV Cu determination with 30 s deposition time and 1 ml min\(^{-1}\) flow rate

The concentrations of trace metals released by 50 mg l\(^{-1}\) of LUPM were well within the linear range of these techniques. Typical dissolved trace metal concentrations released during the kinetic experiments were 60 – 70 nM Cu, 19 – 21 nM Pb and 540 – 560 nM Zn at equilibrium. The measurements of Cu and Pb were still linear even at 400 nM (by ASV and ACSV) and Zn at 2000 nM (by ASV).

4.4.2 Limits of detection of the dissolved metal monitor

The limits of detection were calculated from 3 standard deviations of 5 replicate on-line total and labile dissolved trace metal measurements (Cu, Pb and Zn) of seawater equilibrated with 50 mg l\(^{-1}\) LUPM (filtered through 0.45 μm membrane filter and UV irradiated on-line). The measurements were performed at a flow rate of 1.0 ml min\(^{-1}\) and a deposition time of 60 s (Table 4.3). For ASV analysis of total dissolved Cu, Pb and Zn (Cd could not be detected in the LUPM), the sample was acidified with 6 mM HCl on-line. The detection limit for total dissolved Zn was only 14 % of the typical concentration observed in the kinetic studies with 50 mg l\(^{-1}\) LUPM. In the kinetic experiments, the total dissolved Zn was therefore measured every 75 s (60 s deposition time), to obtain a high temporal resolution.
Table 4.3 Detection limits (nM) of the total and labile dissolved experimental systems

<table>
<thead>
<tr>
<th></th>
<th>Cu (nM)</th>
<th>Pb (nM)</th>
<th>Zn (nM)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total dissolved</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(~2 min after UV irradiation)</td>
<td>105</td>
<td>40</td>
<td>64.2</td>
</tr>
<tr>
<td>on-line ASV</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(24 h after UV irradiation)</td>
<td>28.2</td>
<td>4.4</td>
<td>62.5</td>
</tr>
<tr>
<td>off-line ASV</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Labile dissolved</strong></td>
<td>1</td>
<td>5.1</td>
<td>74.5</td>
</tr>
<tr>
<td>on-line ACSV</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reproducible total dissolved Cu and Pb measurements could not be undertaken with ASV, in the seawater sample, which had been UV irradiated within a few minutes prior to analysis. Hence the limits of detection of Cu and Pb were nearly twice that of the concentrations encountered in seawater equilibrated with 50 mg l⁻¹ of LUPM. There was a broad interfering oxidation peak, between −0.5 V and −0.3 V, which caused an irreproducible baseline between the Pb and Cu peaks. This might have been caused by hypochlorite ions. Achterberg et al. (1994a) found that this ion, present in UV irradiated acidified seawater caused an interfering peak at −0.4 V, during the determination of Cu with ACSV. This interference was found to disappear after 18 h (Achterberg et al., 1994a).

For the current kinetic study, samples were withdrawn, filtered and UV irradiated on-line and were analysed over 24 h later, by ASV with a 2 min deposition time. With this deposition time, the limits of detection of Cu and Pb were 25 % and 12 % of the total dissolved concentrations found in seawater equilibrated with 50 mg l⁻¹ of LUPM, respectively.
The limits of detection for ASV labile Pb and Zn, measured on-line with 0.01 M HEPES buffer, were lower than the observed concentrations of Pb and Zn during the kinetic experiments. At the chosen deposition time of 120 s for the measurement of dissolved labile Pb and Zn, the limits of detection were 16 % and 8 % of the Pb and Zn concentrations from 50 mg l⁻¹ LUPM respectively. The deposition time selected for ACSV labile Cu (with 25 µM SA and 0.01 M HEPES) determinations was 30 s and the limit of detection (2.0 nM) was well below the measured dissolved labile Cu concentration from the LUPM kinetic experiments (16 – 18 nM). The duration of the Cu measurement cycle by ACSV was 45 s.

4.4.3 Accuracy of trace metal determinations by on-line stripping voltammetry

The accuracy of the Cu, Pb and Zn measurements using the on-line method were determined using standard reference materials. The accuracy of the Cu and Zn measurements were evaluated using 3 aliquots of seawater certified reference material (CASS-3, National Research Council, Canada), with ASV (5 min deposition time). Prior to analysis, the samples were UV irradiated for 6 h in acid cleaned quartz tubes with a 400 W medium pressure Hg vapour lamp (Photochemical Reactors). Each aliquot was measured in triplicate. Standard additions of Cu and Zn were added to three separate aliquots of the reference material. Table 4.4 illustrates that the observed recoveries for Zn and Cu were 107 and 110 % respectively.

Dissolved Pb in the CASS-3 was not detected by the ASV method. The accuracy of Pb ASV measurements by the on-line system was therefore evaluated using urban particulate reference material (NIST 1648). Three portions (ca. 100 mg) of reference material were HF / HNO₃ digested (see section 5.2.3) and UV irradiated for 15 h in acid cleaned quartz tubes with a 400 W medium pressure Hg vapour lamp. Prior to analysis, the samples were
diluted by a factor of 10 with Milli-Q water, and were approximately pH 2. The Pb recovery was found to be 93 % (Table 4.4).

Table 4.4 Accuracy of the on-line stripping voltammetric methods.

*Errors represent two standard deviations.*

<table>
<thead>
<tr>
<th>Reference Material</th>
<th>Method</th>
<th>Observed Value</th>
<th>Certified Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>CASS-3</td>
<td>8.95 ± 1.46 nM</td>
<td>8.14 ± 0.98 nM</td>
</tr>
<tr>
<td>Pb</td>
<td>NIST 1648</td>
<td>0.609 ± 0.094 % (m/m)</td>
<td>0.655 ± 0.008 % (m/m)</td>
</tr>
<tr>
<td>Zn</td>
<td>CASS-3</td>
<td>20.3 ± 3.0 nM</td>
<td>19.0 ± 3.8 nM</td>
</tr>
</tbody>
</table>

4.4.4 Assessment of the trace metal contamination from reagents

Trace metal contamination from the added reagents used in ASV (HCl or HEPES) and ACSV (SA and HEPES) was quantified in Milli-Q water in triplicate 10 ml aliquots, via a batch method. The deposition time was 5 min, prior to the voltammetric scan that had a frequency of 10 Hz. Each measurement was done in triplicate. The trace metal concentrations were measured with internal standard additions.

The Cu concentrations derived from the added ligand (SA) were determined in aliquots with the normal added concentration of SA (25 μM SA, 0.01 M HEPES), then with 5 times this concentration (125 μM SA, 0.01 M HEPES). From these measurements, 0.09 nM of Cu contamination from 25 μM SA was calculated. The contamination from the added ligand for the determination of Cu was 0.1 % of the mean sample concentration from 50 mg l⁻¹ equilibrated in seawater, therefore the contamination was deemed to be negligible.
There was no detectable difference between the Cu concentrations in 0.01 M and 0.05 M HEPES (with 25 µM SA). The contamination of Zn in 0.01 M HEPES was calculated to be 0.06 nM (0.01 % of mean sample concentration), after measuring the Zn concentrations in aliquots of Milli-Q water with 0.01 M and 0.05 M HEPES. Lead contamination was not detectable from the buffer. Contamination of Pb and Zn from 6 mM HCl was not detected after a 5 min deposition time, with ASV.

4.4.5 Assessment of trace metal contamination from the experimental system

Prior to each experimental run, all the tubing and the filtration unit were cleaned on-line with 20 ml of 6 mM HCl (Aristar, BDH quartz redistilled), then with 20 ml Milli-Q water at a flow rate of 1 ml min⁻¹. Then checks for trace metal contamination were made with Milli-Q water, and the reagent added on-line (either 6 mM HCl for total dissolved Cu, Pb and Zn with ASV, or 0.01 M HEPES for labile dissolved Pb and Zn with ASV, or 0.01 M HEPES and 25 µM SA for labile dissolved Cu with ACSV). If trace metal contamination was detected after 2 min deposition time, further 20 ml aliquots of HCl and Milli-Q water were pumped through the system until the trace metal contamination was not detectable.

4.4.6 Assessment of trace metal adsorption onto the experimental system

4.4.6.1 Sample loop

When acidified, adsorption sites within the sample loop are protonated, and become ion exchange sites with dissolved trace metals. Adsorption was observed when the sample loop was acidified to a high degree. When the sample loop was cleaned overnight with 60 mM HCl rather than for 20 min with 6 mM HCl, noticeable adsorption of total dissolved Zn occurred within the system during the initial desorption stages (Figure 4.7), during two comparable kinetic studies under controlled conditions (50 mg ⁻¹ LUPM, 1 ml min⁻¹
sample flow rate, 25.2 ± 0.1 °C, 6 mM HCl reagent, in the dark). When the sample loop was cleaned with 60 mM overnight the trace metal (Zn) concentration was initially suppressed, due to adsorption of Zn onto the tubing and/or quartz coil.

The possible advantage of ASV analysis of total dissolved Zn, Pb and Cu over labile dissolved trace metals (either by ASV or ACSV) is the use of on-line sample acidification. Acidification reduces the potential loss of dissolved trace metals to the walls of the quartz coil and tubing (van den Berg, 1988). It was therefore important to assess whether adsorption of Cu, Pb or Zn occurred onto the sample loop of the labile dissolved experimental system after cleaning the on-line system with 6 mM HCl (see section 4.4.5). To investigate this issue, unacidified seawater (pH 8.0) was spiked with dissolved Zn, Pb and Cu (100 nM), and was pumped at a flow rate of 1 ml min⁻¹ through the labile experimental system assembly after acid-cleaning. The dissolved trace metal concentrations (Cu, Pb and Zn) were measured by ASV, with the added reagent HEPES (0.01 M). There was no temporal change in dissolved trace metal concentrations over a 2 h period. This indicated that no adsorption of these metals onto the experimental system had occurred.
4.4.6.2 Reaction vessel

The adsorption of trace metals onto Teflon® reaction vessel walls was also assessed. Coastal seawater from the Plymouth area was collected in November 1999. The seawater was filtered through a 0.45 μm cellulose acetate membrane filter, then spiked with trace metals (Table 4.5), to simulate dissolved metals associated with aerosol material in seawater. One hundred ml aliquots of seawater were added to three acid cleaned Teflon® vessels (Nalgene, 500 ml) and were constantly shaken for 24 h at 25 °C. The rest of the spiked seawater was immediately acidified to pH 2 with HCl, and UV irradiated in acid cleaned quartz tubes for 8 h in a 400 W medium pressure Hg vapour lamp (Photochemical Reactors Ltd). The seawater samples in the Teflon vessels were decanted into quartz tubes after 24 h, and then acidified and UV irradiated in the same manner.

Table 4.5 Assessment of the effect of adding spiked, filtered seawater to Teflon® vessels

(n=3). Total dissolved concentrations (nM)

<table>
<thead>
<tr>
<th></th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>63.9 ± 4.2</td>
<td>60.5 ± 2.3</td>
</tr>
<tr>
<td>Pb</td>
<td>88.8 ± 8.0</td>
<td>95.6 ± 5.7</td>
</tr>
<tr>
<td>Zn</td>
<td>277 ± 32</td>
<td>288 ± 19</td>
</tr>
</tbody>
</table>

Total dissolved concentrations of Cu, Pb and Zn were determined in samples before and after equilibration of the seawater in the Teflon® vessels, by ASV. From the results (Table 4.5), it is apparent that the Teflon® vessels did not adsorb dissolved trace metals onto their walls. Hamilton-Taylor et al. (1993), in contrast, used 150 ml incubation volume in a glass voltammetric cell and their mean trace metal losses were large (29 % Pb and 22 % Zn, with lake water at pH 7.6, spiked with unspecified concentrations of dissolved Pb and Zn).
4.5 Application of the dissolved trace metal monitor

4.5.1 Protocol for the kinetic experiments

The following section describes how the aerosol trace metal seawater dissolution kinetic experiments were conducted and interfaced with the developed metal monitor. Prior to each experiment, the Teflon® reaction vessel was filled with hot 2 % v / v Decon 90 (Decon Laboratories) for 1 h to remove organic surfactants, rinsed with Milli-Q water and then acid-washed overnight in 10 % v / v HCl (Aristar, BDH), before being thoroughly rinsed with Milli-Q water. One litre of filtered (through 0.45 μm cellulose acetate membrane filter, Whatman), UV irradiated seawater was equilibrated overnight in the Teflon® reaction vessel at 25.2 ± 0.1 °C (collection and pre-treatment of the seawater is described in section 3.2.5). This time allowed for the removal of hydrogen peroxide, produced by UV irradiation as it may affect the extent or rate of the desorption of trace metals associated with LUPM (Donat pers. comm., 2000).

Prior to each experimental run, the flow rate of the on-line system was measured and the time lag of fluid movement from the reaction vessel to the flow cell was calculated (10.8 ± 0.8 min). Before the addition of the LUPM to the seawater, 20 ml of seawater was pumped through the sample loop to condition the walls of the tubing. Then five on-line voltammetric measurements of the incubated seawater sample were made. Throughout the experiments, the stirring rate was 750 rpm (Harden, pers. comm., 2001).

For each seawater solubility experiment, approximately 50.0 ± 5.0 mg of LUPM was accurately weighed. (Details of the collection and the physical properties of LUPM are in section 6.2.1). Typical particle concentrations in natural surface seawater may be ~ 10 - ~ 1000 μg l⁻¹ (Appendix C). A much higher dust concentration was used in the initial experiments, to validate and optimise the experimental system. If typical natural concentrations of dust were added to the seawater, difficulties in accurately weighing and
transferring the dust to the seawater would have occurred. It also would have been analytically difficult to measure rapid kinetics of the dissolution of trace metals, because of the lower dissolved trace metal, which would have been present. Longer collection times on the working electrode would have been required owing to the required lower analytical detection limits.

The rapid introduction of dust to the reaction vessel was challenging owing to the hydrophobic nature of the dust. When the dust was initially mixed with 10 ml seawater in a 30 ml polystyrene vial, then injected into the reaction vessel with a micropipette, most of the dust would remain in the vial or adhere to the pipette tip. Instead, for the kinetic experiments, the dust was weighed in an acid cleaned Petri dish (Greiner), and then rinsed into the reaction vessel with seawater (10 ml) from a wash bottle. There was no change in pH of the seawater after the addition of 50.0 mg l⁻¹ of LUPM.

For the determination of total dissolved trace metals (Cu, Pb and Zn), the sample was acidified on-line with HCl prior to UV irradiation (Aristar, BDH, quartz redistilled), to a final pH of 2.2. The acid reagent (50 ml, 0.072 M HCl) was made up in an acid cleaned 125 ml Teflon® vessel (Nalgene) and stored in resealable plastic bag. For the analysis of dissolved labile Zn and Pb, the sample was buffered on-line with HEPES. The final concentration of the buffer at the flow cell was 0.01 M. The pH buffer was used to control the pH of the sample, as the formation of the metal-ACSV ligand is pH dependent (van den Berg, 1988).

For the determination of labile dissolved Cu, the final concentration of SA and HEPES transported at the flow cell was 25 μM and 0.01 M respectively. It was noticed in the initial optimisation studies that degradation product(s) of SA interfered with the determination of Cu. They produced a broad reduction peak at the same reduction potential as Cu (at – 0.3
V vs Ag / AgCl) on the voltammogram. A fresh reagent solution was therefore made up daily, from the stock solution (0.5 M).

Throughout the experiments the reduction / oxidation peaks of the metals were automatically measured and recorded, together with the time of the analysis. All the scans were stored on the hard disk of the PC, and were individually checked and verified later. The duration of each kinetic experimental run was 2 – 3 h, as previous studies have shown that the equilibrium of the trace metals associated with the atmospheric aerosol was reached within 1 – 2 h (Crecelius, 1980; Statham and Chester, 1988; Hamilton-Taylor et al., 1993; and Nimmo et al., 1998).

In order to calibrate the dissolved trace metal measurements after the experimental run, 20 ml of the incubated seawater was filtered on-line (and also acidified and UV irradiated, in the case of the total dissolved experiments) and collected into polystyrene vials (30 ml, Patterson Scientific). Two 10 ml aliquots of the collected sample was spiked with Cu (50 nM), Pb (20 nM) and Zn (500 nM) and analysed by ASV or ACSV. For the labile dissolved experiments, the sample was equilibrated with the added metal standards for at least 20 min. The pH buffer (and for the determination of labile Cu, also the ligand SA) was added on-line prior voltammetric analysis. In order to calculate the dissolved metal concentrations released from the aerosol in seawater, the initial dissolved trace metal concentrations prior to the addition of LUPM were subtracted from the observed dissolved concentrations determined during the kinetic experiments.

In addition to the automated trace metal measurements, samples were collected at 5 min intervals for total dissolved Pb and Cu determinations with the experimental system assembly. These samples were on-line filtered and acidified to pH 2.2 with HCl (Aristar, BDH, quartz redistilled), and then collected into 30 ml polystyrene vials (Patterson
Scientific). The vials were stored in clean, resealable polythene bags and the samples were analysed after 24 h. Each sample was analysed off-line, by ASV, with 2 min deposition time.

4.5.2 Sensitivity of the labile dissolved experimental systems

The sensitivity of the analytical measurement of dissolved labile metals during the kinetic desorption experiments was monitored. The presence of dissolved organic material associated with LUPM may form strong metal complexing ligands in the sample, causing a reduced voltammetric signal; also surface-active compounds may form a physical barrier to the adsorption of the trace metals onto the Hg drop (van den Berg, 1991).

Figure 4.8 Change in the stripping voltammetric sensitivity of dissolved labile Cu, Pb and Zn during the equilibration of LUPM in seawater

(Error bars represent one standard deviation of duplicate experimental runs for labile Zn)

During experimental runs where 50 mg l⁻¹ LUPM was added to seawater under controlled conditions (in the dark, 25.2 ± 0.1 °C) samples were collected and filtered on-line every 5 min (15 min for labile Cu), at a flow rate of 2.2 ml min⁻¹. Sub-samples (5 ml) were spiked with trace metals (either 600 nM Zn or 60 nM Pb or 60 nM Cu) and equilibrated for >1 h. The labile dissolved Zn, Pb and Cu concentrations in the original and spiked samples were
measured with the on-line system. The sensitivity of the measurement of Cu, Pb and Zn during the experimental runs was calculated by subtracting the trace metal peak height in the spiked sample by the original unspiked sample. There was no change in the sensitivity of the labile Cu and Pb determinations (Figure 4.8), but the Zn sensitivity decreased by 15% during the first 25 min of the kinetic experiment. The labile Zn concentrations in the subsequent seawater solubility experiments were corrected for this change in sensitivity, using the line of best plotted though the data points (Figure 4.8). The change in sensitivity for labile Zn during the desorption experiments for LUPM may be different for other aerosol populations. They may contribute different concentrations of dissolved organic material to seawater; this may lead to analytical interferences previously discussed in section 4.3.4.

4.5.3 Evaluation of the repeatability of the experimental set-up

The repeatability of measurements by the dissolved metal monitor after the addition of 50 mg L⁻¹ LUPM into seawater, were assessed. Duplicate experimental runs were made for total dissolved (Pb and Cu; triplicate for Zn) and labile metals (Cu, Pb and Zn). The repeatability of the kinetic experiments is important to define because it reflects the rigour of the experimental procedures. There are numerous factors that could affect the repeatability of the trace metal desorption kinetic measurements, including (i) the effectiveness of the transfer of the dust to the seawater sample, (ii) errors in the calibration, (iii) variation in the hanging Hg drop surface area during the life-time of the experiment, (iv) contamination or adsorptive losses of trace metals in the experimental system, and (v) the introduction of air bubbles into the sample loop, that can then reduce the effective surface area of the hanging Hg drop, hence the analytical signal.

The temporal progress of the desorption of Cu, Pb and Zn from LUPM into seawater is presented in Figure 4.9. The results between the triplicate total dissolved Zn experimental
Figure 4.9 Repeatability of the determination of total and labile dissolved Cu, Pb and Zn after the addition of 50 mg l\(^{-1}\) LUPM to seawater (Key: red circles, triangles (and diamonds for Zn) total dissolved; blue squares and crosses, labile dissolved)
runs had a mean relative standard deviation (RSD) of 4.5 %. The relative standard deviation was calculated by dividing the standard deviation of trace metal concentrations determined at a specific time in the kinetic experiments by their mean at the same specific time. The mean RSD was calculated for the entire kinetic experiments.

The mean RSD for ASV-labile Zn and total dissolved Pb was < 5 % for duplicate experimental runs. ACSV-labile Cu and ASV-labile Pb had a mean RSD < 10 %. The poorest reproducibility was for total dissolved Cu (mean RSD 13 %). The reproducibility of these data are a significant improvement on the duplicated aerosol dissolution experiments made by Hamilton-Taylor et al. (1993), where the mean RSDs of ASV-labile Cu, Pb and Zn were 26, 15 and 10 % respectively. The reproducibility and accuracy of the trace metal measurements carried out in their study may have been hampered sample filter paper adsorbing onto the working electrode.

4.5.4 Temporal progress of trace metal desorption from LUPM equilibrated in seawater

For Cu, Pb and Zn, desorption into seawater reached equilibrium within the lifetime of the experiments (up to 3 h). There was rapid desorption of Zn for 15 min after the addition of LUPM to seawater, and the equilibrium of Zn between the dissolved and particulate phase appeared to be reached within 1 h (Figure 4.9). Meanwhile the desorption kinetics for Cu was slower; the equilibrium was attained within 2 h. Maring and Duce (1989) also observed comparatively slower Cu desorption kinetics. In their study, after 40 min the seawater solubility of Cu was 20 %, after 6 h it had reached 99 % from a remote marine aerosol. These results indicate that the Cu seawater solubility data from other studies that only used 1 h equilibration time might be an underestimate (for example Chester et al., 1993; Fones, 1996; and Wells, 1999).
After 40 min equilibration of LUPM in seawater, readsorption of Pb onto the particles was observed (Figure 4.9). The Pb possibly readsorbed onto a different fraction of the aerosol material, possibly the carbonate and oxide phases of the LUPM (Chester et al., 1995). Kersten et al. (1991), in a multi-chamber experiment, also observed that after 100 h aerosol material had readsorbed Pb. Kinetic modelling and further interpretation of the kinetic profiles are presented in section 5.3.

4.5.5 Trace metal lability in the LUPM – seawater incubation experiments

From Figure 4.9 it is apparent that the ASV-labile Zn and Pb, and ACSV-labile Cu fractions followed similar kinetic profiles to the total dissolved fractions of the respective trace metals. A comparison was made of the total dissolved and labile concentrations of Cu, Pb and Zn observed 90 min after the addition of LUPM to the seawater. To test whether there was a statistical difference between these two fractions, paired two-tailed t-tests was conducted for each trace metal, using the mean concentrations measured at the same specific time periods > 90 min after the addition of LUPM into seawater.

It was found that there was no significant difference between the total dissolved and ASV-labile fraction of Pb. Therefore all the detectable dissolved Pb released from LUPM was electrochemically labile within the operational constraints of the analytical technique. In a similar study by Nimmo et al. (1998) the ACSV-labile Pb released from a Liverpool urban aerosol population was only 45 % of the total dissolved concentration. In contrast, only a low proportion of Cu was in the ACSV-labile fraction (39 % of the total dissolved concentration after 90 min) in the current study, whereas Nimmo et al. (1998) found that the ACSV-labile fraction from a Liverpool urban aerosol was 74 % of the total concentration at equilibrium. However, their study was not directly comparable with the
current results as they used a different electrochemical technique, i.e. ACSV and 8-hydroxyquinoline as the added ligand.

There was a significant difference at the 95% confidence level in the total and labile concentrations of Cu and Zn 90 min after the addition of LUPM to the seawater. Although the ASV-labile content of Zn released from LUPM was 94%. It can be postulated that Cu and Zn undergo some complexation with strong organic complexes, and form a non-labile fraction within the operational constraints of techniques. The sources of organic metal complexing material in seawater may include the aerosol material, microorganisms, and their exudates and decomposed remains (Nimmo et al., 1998 and Gordon et al., 2000).

4.6 Conclusions

The novel automated metal monitor presented in this chapter was constructed, optimised and validated for high temporal resolution (every 45 s – 5 min) measurements of dissolved Cu, Pb and Zn (filtrate < 0.45 μm) by ASV (for the determination of labile dissolved Cu, ACSV was used instead, with the added ligand SA). The system was adapted to enable the determination of both total (with UV irradiation) or labile (without UV irradiation) dissolved trace metal concentrations (although the total dissolved Cu and Pb measurements could not be measured real-time on-line).

The system was applied to the investigation of the desorption of trace metals from an urban aerosol end member (LUPM, 50 mg l⁻¹) in seawater. Carefully controlled experimental conditions were implemented (seawater previously filtered through 0.45 μm membrane filter and UV irradiated; equilibrated at 25.2 ± 0.1 °C, in the dark, stirring speed 750 rpm; sample loop volume 9.46 ml; sample flow rate 1.0 ml min⁻¹). The voltammetric system had appropriate limits of detection and linear range. There was negligible contamination or adsorption of trace metals from the experimental system. The efficiency of UV irradiation
to destroy organic compounds was assessed; it was found that > 90 % of the dissolved trace metals (Cu, Pb and Zn) appeared to be released from aerosol metal-organic complexes. Separate experimental runs measuring the desorption of the dissolved trace metals from the aerosol sample were repeatable (for labile determinations mean RSD < 5 % for Zn; < 10 % for Cu and Pb).

There were several advantages of the current experimental set-up and protocol over kinetic experiments that required discrete (batch-wise) removal of seawater suspension; (i) after the addition of the dust to the seawater, the reaction vessel was covered for the duration of the experiment, to prevent sample contamination, (ii) the on-line system minimised sample handling, therefore further potential for sample contamination, (iii) fine temporal resolution can be achieved (as low as 45 s for labile Cu), and (iv) there was minimal incubated seawater loss (< 16 % of the original volume) during the life-time of the kinetic experiment (up to 3 h). Furthermore, the experimental assembly described in this chapter has advantages over an in situ working electrode, for example the voltammetric technique has no impact on the particle-dissolved trace metal partitioning. Also, the on-line system allows the continuous stirring of a solution whilst the analysis is performed, unlike an in situ assembly.

The fully automated dissolved metal monitor described could be adapted for the measurement of other trace metals, such as Fe, Ni, Co, Cd, Mo, Sb, Sn, Ti, U, V and Cr (total and operationally defined labile concentrations). This could be achieved by changing the added reagents and voltammetric conditions (see summary of different methods in van den Berg, 1991, also Gledhill and van den Berg, 1994; Achterberg and van den Berg, 1997 and Khodari, 1998). The experimental set-up could also be applied to other environmental studies such as trace metal particle / dissolved interactions in rainwater, estuarine and wastewaters; and enable the evaluation of the impact of environmental factors including...
particle concentrations, temperature, types of particles, effect of microorganisms or light, on these interactions (Chapter 5 and 6).
Chapter Five

Effect of bacteria on the seawater solubility of aerosol associated trace metals
5.1 Introduction

Although bacteria are ubiquitous in the environment, their effect on the dissolution of trace metals from aerosols in seawater has not been documented before. This study showed that bacteria were present in seawater, which had previously been filtered and UV irradiated. Therefore, an effective protocol was firstly developed to sterilise seawater, without introducing trace metal contamination or changing the inorganic constituents of seawater, using microwave sterilisation. Previous seawater solubility studies (e.g. Maring and Duce, 1990; Chester et al., 1993 and Fones, 1996) did not carry out deliberate sterilisation procedures, therefore the desorption of trace metals may have been affected by the presence of microorganisms.

To gain an understanding of the influence of bacteria on the fate of aerosol associated trace metals in seawater, the extent (% seawater solubility) and rate of the desorption of Pb, Cu and Zn was assessed. LUPM was added to seawater with high and low bacterial concentrations, and the dissolved trace metal concentrations were measured using the automated dissolved metal monitor and the experimental protocol outlined in Chapter 4. Total and labile dissolved Cu, Pb and Zn were determined during the kinetic experiments, to elucidate any changes in their chemical speciation, and the effects of the presence of bacteria.

In addition, separate desorption experiments with LUPM were undertaken with 0.2 and 0.45 μm membrane filters. The effect of the presence of bacteria, on the operationally defined “dissolved” (< 0.2 or < 0.45 μm diameter) concentrations of Cu, Pb and Zn, were measured. Most colloidal organic matter and bacteria can pass through a 0.45 μm filter and is thus included in the dissolved fraction with a corresponding high molecular weight (Guo and Santschi et al., 1997 and Makarov et al., 2001). The “colloids” include microparticles and macromolecules defined by sizes of 1nm to 1μm (Guo and Santschi et al., 1997;
Stumm and Morgan, 1996 and Buffle and Leppard, 1995). In this study colloidal material was operationally defined as particles with a diameter 0.2 – 0.45 μm. Furthermore, most bacteria are larger than 0.2 μm, therefore cannot pass through a 0.2 μm filter (Makarov et al., 2001). The contrasting desorption profiles of < 0.2 μm and < 0.45 μm “dissolved” Cu, Pb and Zn fractions will be compared.

5.2 Methodology

5.2.1 Enumeration and elimination of bacteria from seawater

Bacterial concentrations were assessed in (i) untreated seawater, (ii) seawater filtered through 0.45 μm cellulose acetate membrane filter (Whatman), (iii) filtered, on-line UV irradiated seawater (the procedures are outlined in section 3.2.5), (iv) microwave sterilised seawater (previously filtered and UV irradiated) and (v) sterilised seawater with 50 mg l⁻¹ LUPM added. The samples were kept in 30 ml polystyrene vials (Patterson Scientific) and were refrigerated at 4 °C. The bacterial populations were enumerated within 24 h after treatment. Aliquots of each sample (100 μl, n = 3) were spread onto seawater agar plates (Greiner, pH adjusted to 7.3) and incubated at 20 °C for 3 days. The colonies of bacteria on each plate were then counted. It was assumed that each colony of bacteria originated from one bacterium (Bloomfield et al., 1998 and Zaccone et al., 2002).

The seawater samples were also analysed for the presence of bacteria using a FACSort flow cytometer (Becton Dickinson, at Plymouth Marine Laboratories), equipped with a laser exciting at 488 nm, to gain enumeration of the bacterial cells. This is a rapid technique whereby >10³ cells can be measured per second. Cells were stained with SYBR Green (Molecular Probes) and were counted using green (530 ± 15 nm) fluorescence and side scatter. The fluorochrome stain targets nucleic acid in bacterial cells (Marie et al., 1997). Each sample was analysed for 3 min at a flow rate of ca. 30 μl min⁻¹.
Table 5.1 Bacterial counts (total or culturable bacterial cells per ml) in seawater determined by agar plating and flow cytometry (Sources: \textsuperscript{a}This study; \textsuperscript{b}Steward et al., 1996 and \textsuperscript{c}Zaccone et al., 2002). Errors represent one standard deviation of 3 separate aliquots.

\textit{nd} = not detectable

<table>
<thead>
<tr>
<th>Seawater treatment</th>
<th>Culturable bacteria</th>
<th>Total bacteria counts (x 10\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Agar plating\textsuperscript{a}</td>
<td>Flow cell cytometry\textsuperscript{a} Coulter counting\textsuperscript{b} Coulter counting\textsuperscript{c}</td>
</tr>
<tr>
<td>Untreated</td>
<td>3000 ± 650</td>
<td>1660 ± 170 200 - 2000 50 - 1900</td>
</tr>
<tr>
<td>Filtered</td>
<td>400 ± 85</td>
<td>339 ± 38</td>
</tr>
<tr>
<td>Filtered and UV irradiated</td>
<td>7800 ± 5800</td>
<td>215 ± 34</td>
</tr>
<tr>
<td>Microwave sterilised (previously filtered and UV irradiated)</td>
<td>nd</td>
<td>85.1 ± 7.1</td>
</tr>
<tr>
<td>Microwave sterilised with 50 mg L\textsuperscript{-1} LUPM</td>
<td>300 ± 165</td>
<td>85.7 ± 7.3</td>
</tr>
</tbody>
</table>

The bacterial counts with the agar plating method were 2 - 3 orders of magnitude lower than those measured by flow cytometry (Table 5.1). However, these two methods are not directly comparable, because different batches of seawater were used, collected four months apart. Other studies have also found that agar cultures can only detect a small proportion (0.01 – 22 %) of the natural bacterial population present in seawater (Edwards, 1999 and Zaccone et al., 2002). Agar plating will only show bacteria that are able to grow on the culture media; in contrast flow cytometry provides a total bacterial cell count. Bloomfield et al. (1998) suggested that the failure to recover bacterial cells by agar plating is due to the transfer of cells that are adapted to survive nutrient limitation, to rich culture media. Oxidation of substrates in the culture media by the bacterial cells may lead to the overproduction of superoxide and free radicals, thus many of the cells are killed as they have high-affinity substrate uptake pathways.
Bacterial concentrations found in the untreated seawater, by flow cytometry were of the same order of magnitude as reported in other seawater samples in previous studies (Steward et al., 1996 and Zaccone et al., 2002). It was found that filtration through the 0.45 μm membrane filter removed approximately 80% of the bacterial cells. The total bacterial concentrations in the filtered and UV irradiated seawater were of the same order of magnitude as that observed in filtered seawater (Table 5.1). The 10 l carboy that was used to store the UV irradiated seawater was not sterilised therefore may have contaminated the seawater with bacteria.

Bacterial contaminants from seawater were removed by microwave treatment, in a 900 W oven (Saisho MW400), adapted from the method provided by Keller et al. (1988). This type of treatment can eliminate bacteria (including their spores), algae, fungal cells and viruses (Keller et al., 1988). Unlike autoclaving, microwave treatment is a suitable means of removing bacteria from seawater without introducing trace metal contamination. The steam from autoclaves has been implicated as a source of trace metal contamination (Keller et al., 1988). Furthermore, high temperatures would induce the loss of CO₂, leading to a rise in pH and possible precipitation of inorganic constituents of the seawater.

For the microwave digestion procedure of seawater, aliquots (250 ml) of filtered, UV irradiated seawater were treated for 2 min in an acid washed 500 ml Teflon vessel, covered with cling film. The solution was gently shaken after 1 min of the treatment, since the microwave field strength is non-uniform. The final temperature of the seawater was 58°C. No precipitates were formed and the pH of the water before treatment and after cooling did not change (pH 8.0), therefore this sterilisation procedure did not appear to change the chemical character of the seawater. The sterilised seawater was transferred to the acid
washed, microwave sterilised 1 l Teflon reaction vessel, within a Class 100 laminar flow cabinet (Model 56, Bass Aire).

After microwave treatment, the total bacterial cell count was 85100 ± 7100 cells per ml (from flow cell cytometry measurements); therefore 60 % of bacteria had been removed. However, no bacteria from the microwaved seawater grew on the agar plates (zero colony counts), therefore it appears that they were non-viable. The flow cytometry method employed could not differentiate between viable and non-viable cells. Hence microwave treatment was a reasonably efficient method of removing the impact of bacterial activity. The cells may have been lysed during the microwave treatment, or the DNA may have cross-linked, preventing the cells from replicating (Smerdon pers. comm., 2000).

With the addition of 50 mg l⁻¹ of LUPM to microwave treated seawater, there was no net flux of bacteria (total bacterial cell count was 85700 ± 7300 cells per ml) from the dust particles to the seawater. However, agar plating revealed that there were some viable cells present (300 ± 165 cells per ml), which were likely to have originated from the dust sample. Bacteria associated with atmospheric dust have recently been cited in the literature (for example see Yee et al., 2000 and Griffin et al., 2001).

Therefore during the current study, trace metal desorption experiments were carried out in ‘high bacteria’ (HB) and ‘low bacteria’ (LB) seawater. The HB seawater was the filtered, UV irradiated seawater stored in a 10 l carbuoy (total bacterial cell count: ca. 215,000 cells ml⁻¹). The LB seawater contained no viable bacterial cells, due to microwave sterilization after filtration and UV irradiation. However, this seawater could not be considered ‘bacteria free’ because there were non-viable cells present (ca. 86,000 cells ml⁻¹) after sterilization, in addition to viable cells associated with the aerosol material (culturable cell count: ca. 300 cells ml⁻¹).
5.2.2 Seawater solubility experimental protocol

Trace metal (Cu, Pb and Zn) desorption (labile and total dissolved) from 50 mg L\(^{-1}\) LUPM was measured in both LB and HB seawater, under controlled experimental conditions (750 rpm stirring speed, 25.2 ± 0.1 °C, in the dark, 0.45 μm membrane filter, 1 ml min\(^{-1}\) sample flow rate). The experimental procedure is described in Chapter 4. During these kinetic desorption experiments, Cd was not detectable by the ASV method (even after 10 min deposition time).

Prior to LB dissolution experiments, the tubing in contact with the reaction suspension was microwave sterilised in an acid washed Teflon vessel, containing 100 ml Milli-Q water for 1 min. The tubing was then stored in a clean, resealable plastic bag. The stirrer bar was cleaned by storage overnight in sterilised Milli-Q water, in an acid washed Teflon bottle.

The HB seawater experiments, with filtration through 0.45 μm filter were those presented in Chapter 4 (these experiments were in duplicate, except total dissolved Zn determinations that were in triplicate). Total dissolved and labile dissolved Cu, Pb and Zn desorption experiments in LB seawater, with 0.45 μm filtration, were performed in duplicate. Total dissolved Cu, Pb and Zn were also measured in LB and HB seawater after 0.2 μm filtration. These were single experiments because there was insufficient dust to perform duplicate experiments.

5.2.3 Determination of total trace metal content of LUPM

5.2.3.1 Total digestion (HF / HNO\(_3\)) of aerosol particles

The total digestion of LUPM was achieved using a HF / HNO\(_3\) acid digestion procedure. This was necessary to calculate the seawater solubility of aerosol associated trace metals. About 100 mg of a certified reference material (National Institute of Standards and
Technology, USA, Urban Particulate Material, No. 1648) and LUPM were accurately weighed in 30 ml acid washed PTFE beakers. Concentrated nitric acid (18 ml, Aristar, BDH) was added to 30 ml Teflon beakers. The lids were tightly secured, and then the contents of the beakers were left to reflux at 90 °C on a hotplate (Bibby Sterilin Limited, B290), for approximately 24 h. Concentrated hydrofluoric acid (5 ml, Aristar, BDH) was added. The lids were screwed tightly again, and the mixture was allowed to reflux for a further 48 h at 100 – 120 °C to dissolve any remaining material. Once the solution became clear, the lids were removed and the mixture was allowed to evaporate to near dryness.

Concentrated nitric acid (2 ml, Aristar, BDH) was then added with a disposable acid washed Pasteur pipette, followed by evaporation to near dryness. This was repeated twice more to remove residual volatile fluorides. After the final evaporation, 5 ml of 0.1 M nitric acid (Aristar) was added. The lids were then replaced and the beakers transported to the laminar flow cabinet where the samples were made up to volume with 0.1 M nitric acid using acid washed 25 ml Teflon volumetric flasks (Nalgene). The samples were then transferred to polystyrene vials (Patterson Scientific) for storage. Reagent blanks (n = 3) were carried out alongside the samples during every batch to assess potential elemental contamination.

5.2.3.2 Trace metal analysis of the total digest solutions by ICP-MS

A Plasma Quad PQ2+Turbo (VG Elemental, Winsford, Cheshire) was used for the particulate metal analysis. The instrumentation was equipped with an Ebdon nebuliser and electron photomultiplier. A Fassel torch, linked to a quadrupole spectrometer produced positively charged metal ions (Ebdon et al., 1998). The sample uptake was 1 ml min⁻¹ and the dwell time in the quadrupole was 1024 μs. The carrier gas was argon. The multi-element software was in peak jump mode. Multi-element standards were made up in 0.1 M
HNO₃ (Aristar, BDH) from separate metal stock standards (1000 mg l⁻¹, Spectrosol, Merck).

An internal standard (100 µg l⁻¹ of In, BDH) was added to each sample, standard and blank to allow instrumental drift correction. After every 10 samples a 250 µg l⁻¹ multi-element standard was analysed to check for instrumental drift. During the measurements of the standards and samples, the integrals (counts per second) of three repeat measurements were automatically calculated and printed out.

The mean and standard deviation of each sample and standard were calculated. Values with relative standard deviation > 10 % were re-analysed. The samples and standards were then normalised against the In mean value of the first measured aliquot (the standard blank). The blank corrected integrals were calculated by subtracting the mean blank integral from the In corrected mean standard and sample integrals for each element. Mean integrals of each sample were converted into concentrations (µg l⁻¹) using the gradient of each elemental calibration curve. The R-squared for calibration lines were always > 99.85 %. The standard checks varied by > 5 % from the initial value, therefore a drift correction was applied, using the gradient between two adjacent checks.

5.2.3.3 Validation of the total digest procedure

The limit of detection by ICP-MS for the trace metals (blank + 3σ) was calculated from the reagent blank (0.1 M HNO₃). The metal (Cd, Cu, Pb and Zn) concentrations of the blank and the limits of detection were much smaller (< 0.02 %) than the mean trace metal concentrations in the LUPM HF / HNO₃ digest samples (Table 5.2).
Table 5.2 Calculated limits of detection and reagent trace metal blank concentrations by ICP-MS

<table>
<thead>
<tr>
<th>Blank (μg l⁻¹)</th>
<th>% blank contribution to trace metal concentrations from LUPM digest</th>
<th>Limit of detection (μg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>Cu</td>
<td>0.41</td>
<td>0.76</td>
</tr>
<tr>
<td>Pb</td>
<td>0.05</td>
<td>0.08</td>
</tr>
<tr>
<td>Zn</td>
<td>2.3</td>
<td>2.7</td>
</tr>
</tbody>
</table>

The elemental accuracies for the four replica NIST 1648 digests are presented in Table 5.3. During the analysis, good recoveries (88 - 103 %) for Zn, Cd, Pb and Cu were obtained. The recoveries indicate that the certified material underwent complete digestion during the HF / HNO₃ digest procedure.

Table 5.3 Accuracy of the determination of total trace metals (Cd, Cu, Pb and Zn) by ICP-MS in NIST 1648 (n = 4). Errors represent two standard deviations.

<table>
<thead>
<tr>
<th>Observed concentration (ppm)</th>
<th>Certified concentration (ppm)</th>
<th>Percentage recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd 71 ± 12</td>
<td>75 ± 7</td>
<td>95</td>
</tr>
<tr>
<td>Cu 594 ± 92</td>
<td>609 ± 27</td>
<td>98</td>
</tr>
<tr>
<td>Pb 5770 ± 770</td>
<td>6550 ± 80</td>
<td>88</td>
</tr>
<tr>
<td>Zn 4885 ± 660</td>
<td>4760 ± 140</td>
<td>103</td>
</tr>
</tbody>
</table>
5.3 Results and discussion

5.3.1 Desorption of Cu, Pb and Zn in LB and HB seawater

The time-dependent release of dissolved (< 0.45 μm) Cu, Pb and Zn from LUPM in LB and HB seawater is shown in Figure 5.1. Each trace metal displayed distinctively different kinetic profiles. However, the shapes of the total and labile dissolved profiles for each trace metal (Cu, Pb and Zn) were similar in both the LB and HB systems. Dissolved Pb and Zn showed an initial rapid increase in concentration during the first 15 min of the incubation. In contrast, dissolved Cu was released more slowly than Pb and Zn; total and labile dissolved fractions did not reach a plateau until at least 2 h after the addition of LUPM to LB and HB seawater (Figure 5.1a). The labile dissolved Zn fraction reached a plateau after only 45 min, followed by the plateau of the total dissolved fraction after 60 min (Figure 5.1b). Unlike Cu and Zn, the Pb concentrations reached a peak after 30 min, then decreased to equilibrium values after 150 min (Figure 5.1c). In the following sections the kinetic rates of these reaction profiles will be quantified, and the effect of bacteria on the rate and extent of the desorption of Cu, Pb and Zn from LUPM will be discussed.

5.3.2 Mechanism and kinetics of desorption processes

The time-dependent desorption data for the experiments, performed in LB and HB seawater, were interpreted using the assumption of two consecutive, first-order reversible reactions (Equation 5.1) to describe the transfer of the trace metals (Cu, Pb and Zn) between the dissolved and particulate phases (Millward et al., 1992 and Millward and Liu, 2003). Initially, the metals desorb from exchangeable sites of low binding energy, S-M^{1+}, into solution, M^{2+}, with forward (adsorption) and backward (desorption) rate constants k_1 and k_1 (Millward and Liu, 2003). As time progresses during the kinetic experiments, metals on stronger binding sites, S'-M^{(z-1)+}, within the particle matrix become involved in the partitioning process (with forward and backward rate constants k_2 and k_2):
Figure 5.1 Seawater solubility of labile and total dissolved (<0.45 μm) Cu, Pb and Zn associated with 50 mg l⁻¹ LUPM in high bacteria (HB) and low bacteria (LB) seawater during kinetic experiments

(a) Cu

(b) Zn

(c) Pb
The first stage of the mechanism in Equation 5.1 was quantified using an integrated form of the rate equation (see for example Moore, 1972; Hamilton-Taylor et al., 1993; Comber et al., 1996 and Millward and Liu, 2003):

Equation 5.2

\[
[M^{z+}]_t = [M^{z+}]_e \times \left\{ 1 - \exp\left(-\left(k_1 + k_{-1}\right) \cdot t\right) \right\}
\]

where \([M^{z+}]_t\) is the dissolved metal concentration at time \(t\), and \([M^{z+}]_e\) is the dissolved concentration at equilibrium. Equation 5.2 can be arranged to give \(k_1\) and \(k_{-1}\):

Equation 5.3

\[
(k_1 + k_{-1}) \cdot t = \ln\left(\frac{[M^{z+}]_e}{[M^{z+}]_e - [M^{z+}]_t}\right)
\]

Plotting the right hand side of Equation 5.3 against time gives a straight line, the slope of which is the sum of the rate constants \(k_1\) and \(k_{-1}\). Figure 5.2 shows a representative plot to illustrate the method of estimating the rate constants, for total dissolved Zn concentrations (from 0.45 μm filtration of LB seawater, Replicate 1). The backward rate constant \(k_{-1}\) was calculated with Equation 5.4, as follows:

Equation 5.4

\[
k_{-1} = \frac{[M^{z+}]_e \times (k_1 + k_{-1})}{[S-M^{(z-1)+}]_0}
\]

where \([S-M^{(z-1)+}]_0\) the initial exchangeable metal concentration. The derivations for the above Equations 5.3 and 5.4 are given in Appendix D. The particulate concentrations obtained from Stages 1 and 2 (1 M ammonium acetate, 1 M hydroxylamine hydrochloride...
and 25 % v/v acetic acid) of the three-stage sequential leach of trace metals associated with aerosols, described in Chester et al., (1989), was assumed to represent trace metals that are "weakly bound" to adsorption sites on the aerosol particles (Spokes and Jickells, 1996; Herzl et al., 2003 (acetic acid only) and Millward and Liu, 2003). Thus, this fraction was assumed as representative of the initial exchangeable particulate trace metal content. In the current study, the initial exchangeable Cu, Pb and Zn concentrations were 268, 138 and 1119 nM respectively, with 50 mg L\(^{-1}\) LUPM in 1 L seawater (Orif, 2003). For the calculation of \(k_2\) and \(k_{-2}\), it is assumed that the strong binding sites (S\(^{\cdot}\)-M\((^{\infty}\))\(^{+}\)) are the third stage of the three stage sequential leach scheme i.e. the refractory fraction (see Chester et al., 1989).

**Figure 5.2 Plot of the right hand side of Equation 5.3 versus time for total dissolved Zn concentrations (from 0.45 \(\mu\)m filtration of LB seawater, Replicate 1). The solid line is the linear regression analysis \((R^2 = 0.98, n = 22)\). The slope gives \(k_1 + k_{-1} = 0.115 \text{ min}^{-1}\).**

The characteristic chemical response time \((\tau_{\text{resp}})\) is a commonly used approach to assess the state of equilibrium (Honeyman and Santschi, 1988; Millward et al., 1992; Liu et al., 1998; Whitworth et al., 1999; Herzl et al., 2003 and Millward and Liu, 2003). It is defined as the
time required to attain 63% of the new equilibrium between the dissolved and particulate metals (Stumm and Morgan, 1996), is given by:

\[ T_{\text{resp}} = \frac{1}{k_i + k_1} \]

The desorption of trace metals from LUPM was simulated by simultaneous integration of the differential equations resulting from the reaction mechanism in Equation 5.1. A Runge-Kutta integration routine was used to carry out the calculations within a software-modelling package (ModelMaker 4). Thus the software package was used to (i) validate the \( k_1 / k_1 \) calculations and (ii) to calculate \( k_2 / k_2 \). The adsorption process may not be accurately described as the reversible reaction of desorption, therefore detailed attention is not paid to the \( k_1 \) values in the current study.

The Cu and Zn reaction curves in Figure 5.1, were modelled using only the first stage of the reaction mechanism (Equation 5.1, i.e. only \( k_1 \) and \( k_{-1} \)). Other aerosol – trace metal kinetic studies have also shown rapid desorption Cd, Co, Cu, Ni, Pb and Zn, followed by equilibrium within 30 min (Hamilton-Taylor et al., 1993 and Nimmo et al., 1998). However, these studies had lower temporal resolution (< 10 data points in 60 min; in comparison to 12 – 78 data points in the current study) and did not investigate the effect of bacteria.

In contrast to Cu and Zn, double exponential curves arose with the desorption of Pb (Figure 5.1) in the current study. Thus, it was necessary to consider the second stage of Equation 5.1. It appears that there was rapid equilibrium between dissolved Pb in the bulk solution and weak binding sites on the surfaces of the aerosol particles. The following decrease in dissolved Pb concentrations were either due to (i) the migration of Pb on the
particle surface to higher energy binding sites (Millward et al., 1990 and Millward and Liu, 2003) and/or (ii) the readesorption of trace metals onto different mineral phases (Kersten et al., 1991 and Chester et al., 1995). Evidence for readesorption of Pb onto the particles is found in Figure 5.1c, which illustrates the removal of non-labile Pb, in both the LB and HB systems (between 30 and 180 min after the addition of LUPM).

Millward and Liu (2003) observed similar behaviour during desorption experiments investigating the released Zn associated with riverine sediments (1.34 g l$^{-1}$) in seawater. The desorption of Zn was characterised by maximum dissolved concentrations after several min, followed by readesorption onto the suspended sediment. Similarly, in a multichamber leaching experiment with an urban aerosol (274 mg l$^{-1}$) after initial desorption of Zn and Pb in seawater in 1 h, these trace metals were scavenged by Fe / Mn oxide and by the aerosol particles within 100 h (Kersten et al., 1991). More recently (Chester et al., 1995), a study investigated the solid-state speciation of Pb before and after solubility experiments of Liverpool urban dust in seawater. It was clear that above pH 5.3 there was re-scavenging of Pb released by the dust onto carbonate and oxide phases.

5.3.3 Effect of bacteria on trace metal sorption rates

The desorption rates for Zn ($k_1 = 0.045 - 0.058$ min$^{-1}$) and Pb ($k_1 = 0.027 - 0.052$ min$^{-1}$) were much more rapid than those calculated for Cu ($k_1 = 0.003 - 0.015$ min$^{-1}$; Table 5.4). Thus, the chemical response times for Pb (5.6 – 7.8 min) and Zn (6.6 – 11.0 min) were shorter than for Cu (17.9 – 50.0 min). The particulate Cu may have been more associated with particulate organic material than Pb and Zn (Murphy, 1985, observed that 28 % of Cu was associated with this fraction in a Liverpool urban aerosol, whereas this fraction only accounted for 17 % of Pb and 7 % of Zn). Thus, the slow Cu desorption kinetics might be due to the slow dissociation of Cu-organic material on the particle surface prior to desorption into seawater (Millward and Liu, 2003). Furthermore, less Cu was associated
Table 5.4 Rate constants and chemical response times for the desorption of labile and total dissolved (< 0.45 μm) Cu, Pb and Zn from LUPM in LB and HB seawater; comparison of the current study with that in the literature (nd = not detectable).

<table>
<thead>
<tr>
<th></th>
<th>Total dissolved trace metals</th>
<th>Labile dissolved trace metals</th>
<th>Hamilton-Taylor et al. (1993)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$</td>
<td>$k_2$</td>
<td>$t_{resp}$</td>
</tr>
<tr>
<td></td>
<td>(min$^{-1}$)</td>
<td>(min$^{-1}$)</td>
<td>(min)</td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HB</td>
<td>0.041</td>
<td>0.015</td>
<td>17.9</td>
</tr>
<tr>
<td></td>
<td>± 0.016</td>
<td>± 0.005</td>
<td>± 7.6</td>
</tr>
<tr>
<td>LB</td>
<td>0.016</td>
<td>0.004</td>
<td>50.0</td>
</tr>
<tr>
<td></td>
<td>± 0.001</td>
<td>± 0.001</td>
<td>± 4.0</td>
</tr>
<tr>
<td>Pb</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HB</td>
<td>0.082</td>
<td>0.052</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td>± 0.050</td>
<td>± 0.020</td>
<td>± 1.3</td>
</tr>
<tr>
<td>LB</td>
<td>0.132</td>
<td>0.048</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>± 0.058</td>
<td>± 0.022</td>
<td>± 0.3</td>
</tr>
<tr>
<td>Zn</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HB</td>
<td>0.042</td>
<td>0.049</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>± 0.004</td>
<td>± 0.001</td>
<td>± 1.3</td>
</tr>
<tr>
<td>LB</td>
<td>0.062</td>
<td>0.045</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td>± 0.006</td>
<td>± 0.005</td>
<td>± 1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.11</td>
<td>0.26</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>± 0.058</td>
<td>± 0.22</td>
<td>(1.6 - 10.0)</td>
</tr>
</tbody>
</table>
with the exchangeable particulate phase (28 %), than Pb and Zn (57 and 79 % respectively; Orif, 2003). The exchangeable phase is associated with rapid ionic exchange (Chester et al., 1989).

Although the labile and total Cu desorption rate was the same in LB seawater (0.003 - 0.004 min⁻¹), in HB seawater the total Cu desorption rate was much greater than the labile Cu desorption rate (0.015 and 0.005 min⁻¹ respectively). This suggests that in HB seawater, non-labile Cu desorbs more rapidly than labile dissolved Cu from LUPM, and / or that the complex formation of dissolved non-labile Cu, in the aqueous phase or on the bacterial particles, occurs more rapidly than the formation of labile Cu organic complexes and inorganic species. The non-labile Cu fraction after desorption may be (i) strongly complexed by dissolved organic ligands produced by LUPM and / or (ii) by bacteria; and / or (iii) associated with bacterial surfaces. Both (ii) and (iii) may enhance the rate of desorption in the HB system, thus forcing equilibrium to “dissolved” complexed species / bacterial associations.

The desorption rates in LB and HB seawater were similar, for both Pb and Zn (given the errors shown in Table 5.4). Hence, the presence of bacteria were not causing a detectable difference on the desorption rates of Pb and Zn. Bacterial surfaces and / or bacterial organic complexing ligands may have lower conditional stability constants for Pb and Zn, than Cu. Unlike Cu, the desorption rates of labile and total dissolved Pb and Zn in the HB system are the same. Therefore, bacteria have a minimal impact on the desorption rates of Pb and Zn from LUPM. In previous studies it has been highlighted that the strength of Cu humic complexes is greater than Zn humic complexes (Millward, 1995) and that more Cu is strongly complexed in natural waters than Pb (90 - > 99 % and 67 - 94 % respectively; Kozelka and Bruland, 1998).
The desorption rates \( (k_1) \) in this study were lower than those observed by Hamilton-Taylor et al. (1993). The study consisted of in situ experiments with trace metals (Cu, Pb and Zn) associated with a rural aerosol in lake water (e.g. in Hamilton-Taylor et al. (1993), Zn \( k_1 \) = 0.22 min\(^{-1}\), in the current study Zn \( k_1 \) = 0.045 – 0.058 min\(^{-1}\)). However, a direct comparison may not be appropriate, as their study was undertaken in freshwater and did not define the particle concentration, temperature or characteristics of the aerosol population (e.g. the trace metal crustal enrichment factors or particle size distribution). All these factors may have affected the kinetics of desorption of trace metals from the aerosol particles (see Chapter 6).

The \( k_2 \) and \( k_{-2} \) rate constants for Pb (shown in Table 5.4) were much lower than the corresponding \( k_1 \) and \( k_{-1} \) rate constants. Thus the migration of Pb from the weak to the strong binding sites on the LUPM particles, together with the readsorption of Pb onto different mineral phases from the aqueous phase occurred more slowly than the desorption of Pb from the LUPM particles.

### 5.3.4 Effect of bacteria on the seawater solubility of trace metals (< 0.45 \( \mu m \))

Although the kinetic profiles of the desorption of (< 0.45 \( \mu m \)) Cu, Pb and Zn from LUPM are similar in both LB and HB seawater, it is apparent that the extent of desorption after 2 – 3 h, is greater in HB seawater, than in LB seawater (Figure 5.1 and Table 5.5). To test the null hypothesis that there was no significant difference between the mean seawater solubilities of each trace metal in LB and HB seawater, paired two-tailed \( t \)-tests on the kinetic profiles were performed. These tests revealed that there were statistically significant higher percentage seawater solubilities of Cu, Pb and Zn in both the total and labile fractions, at the 95 % confidence level in the HB seawater, than the LB seawater. In the LB system, the seawater solubility of Cu after 2 h was only 68 % of the HB system;
and the seawater solubility of Pb and Zn was 83 % of the HB system. Thus the presence of bacteria enhanced the desorption of Cu to a greater extent than Pb and Zn.

*Table 5.5 Percentage seawater solubilities of Cu, Pb and Zn of LUPM in HB and LB seawater after 2 h incubation. Errors represent one standard deviation of duplicate experimental runs.*

<table>
<thead>
<tr>
<th>Trace metal species</th>
<th>&lt; 0.45 μm fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low bacteria</td>
</tr>
<tr>
<td>Cu Total</td>
<td>13.8 ± 0.8</td>
</tr>
<tr>
<td>Cu Labile</td>
<td>5.1 ± 0.5</td>
</tr>
<tr>
<td>Cu Non-labile</td>
<td>8.7 ± 0.9</td>
</tr>
<tr>
<td>Pb Total</td>
<td>12.0 ± 0.6</td>
</tr>
<tr>
<td>Pb Labile</td>
<td>10.7 ± 0.4</td>
</tr>
<tr>
<td>Pb Non-labile</td>
<td>1.3 ± 0.7</td>
</tr>
<tr>
<td>Zn Total</td>
<td>39.6 ± 0.8</td>
</tr>
<tr>
<td>Zn Labile</td>
<td>34.9 ± 0.1</td>
</tr>
<tr>
<td>Zn Non-labile</td>
<td>4.7 ± 0.8</td>
</tr>
</tbody>
</table>

The non-labile dissolved seawater solubilities presented in Table 5.5 were calculated by subtracting the labile dissolved concentrations from the total dissolved concentrations. The presence of bacteria in HB seawater enhanced the seawater solubility of non-labile Cu from ca. 8.7 to 13.0 % after 2 h incubation. Bacteria may have contributed strong Cu-complexing organic ligands to seawater, which in turn had enhanced the presence of non-labile Cu in seawater. Gordon et al. (2000) demonstrated that autotrophic (*Synechococcus*) and heterotrophic (*Vibrio*) bacteria have the potential to contribute to the pool of strong copper-complexing ligands in chemostat cultures of estuarine water (using ASV and
ACSV). The enhanced Cu solubilities in HB seawater may be explained by the shift of
equilibrium to the dissolved phase owing to the presence of bacterial surfaces and/or
organic complexing ligands.

In contrast to Cu, it is apparent that the presence of bacteria in HB seawater had not
increased the seawater solubilities of non-labile Pb and Zn, after 2 h incubation (Table
5.5). Therefore, it would appear that the bacterial surfaces, and organic ligands that had
been released from bacteria, had low complex formation stability constants for Pb and Zn
(i.e. these complexes would have dissociated during the ASV-labile analyses). The non-
labile fraction of Pb and Zn in LB and HB seawater was likely to have been derived from
metal-organic complexes directly from the aerosol material or from subsequent
complexation of aerosol originated organic material, post desorption (Nimmo and Fones,
1997 and Nimmo et al., 1998).

There was a slight increase in the seawater solubility of labile Cu, Pb and Zn in HB
seawater, either due to weak associations of these trace metals with bacterial organic
complexing ligands and/or bacterial surfaces. Bacteria have the largest surface area to
volume ratio of any life form; therefore, trace metal adsorption may occur rapidly
(Schultze-Lam et al., 1996). For example, Fein et al. (1997) found that Cd adsorption
equilibrium was obtained within 30 to 45 min with *Bacillus subtilis*. Bacteria can adsorb
dissolved metal cations because they have a net negative charge; bacteria contain a variety
of surface organic functional groups, including amino, carboxylic, hydroxyl and phosphate
sites (Fein et al., 1997 and Fowle and Fein, 2000). Other studies have found that bacteria
are efficient scavengers of dilute trace metals and can concentrate them from the
surrounding aqueous environment (Southam, 2000 and Schultze-Lam et al., 1996). They
can react with soluble metals by binding and precipitating these metal ions on their
surfaces, producing hydrous, amorphous aggregates (Hutchins et al., 1986). In addition,
phytoplankton and possibly bacteria have a rapid uptake mechanism for lipophilic trace metal complexes (Croot et al., 1999).

5.3.5 Effect of bacteria on the seawater solubility of trace metals (< 0.2 \mu m)

The desorption rates \((k_{-1})\) of < 0.2 \mu m Cu, Pb and Zn from LUPM were similar in LB and HB seawater \((Cu k_{-1} = 0.003 - 0.004 \text{ min}^{-1}; Pb k_{-1} = 0.021 - 0.028 \text{ min}^{-1} \text{ and Zn } k_{-1} = 0.045 - 0.049 \text{ min}^{-1};\) see Table 5.6). Furthermore, the kinetic profiles of these trace metals, illustrated in Figure 5.3, are very similar between the two different types of seawater treatments. Paired t-tests found that there was no statistically significant difference in the observed seawater solubilities of Cu, Pb and Zn in the HB and LB seawater, during the lifetime of the experimental runs (up to 165 min). Thus after 165 min the percentage seawater solubilities of < 0.2 \mu m Cu, Pb and Zn were 4.5, 12 and 35 % respectively in both HB and LB seawater.

The presence of bacteria increased the seawater solubility of LUPM associated Cu, Pb and Zn in the “colloidal” fraction \((0.2 \mu m - 0.45 \mu m)\), but not in the < 0.2 \mu m dissolved fraction. The trace metal seawater solubilities were higher in the 0.45 \mu m filter studies than the 0.2 \mu m filter studies due to trace metals associated with the colloidal fraction, which had partly originated from the atmospheric aerosol population, and also partly due to trace metals associated with bacterial cells that can pass through the 0.45 \mu m membrane filter.

The lack of difference in the trace metal seawater solubilities, in HB and LB seawater, during the 0.2 \mu m filter experiments implies that the enhanced desorption of metals is not due to dissolved organic complexation. Dissolved organic complexes would pass through a 0.2 \mu m filter and be detected by ACSV / ASV. Therefore, it is more likely that the
Figure 5.3 Observed seawater solubilities of total dissolved Cu, Pb and Zn released from 50 mg l⁻¹ LUPM after filtration through 0.2 μm membrane filter.

Table 5.6 Rate constants and system response times for desorption of < 0.2 μm fraction of Cu, Pb and Zn released from LUPM in low bacteria (LB) and high bacteria (HB) seawater.

<table>
<thead>
<tr>
<th></th>
<th>k₁ (min⁻¹)</th>
<th>k₋₁ (min⁻¹)</th>
<th>tₑ₂₀ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LB</td>
<td>0.049</td>
<td>0.003</td>
<td>19.2</td>
</tr>
<tr>
<td>HB</td>
<td>0.055</td>
<td>0.004</td>
<td>16.9</td>
</tr>
<tr>
<td>Pb</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LB</td>
<td>0.13</td>
<td>0.028</td>
<td>6.3</td>
</tr>
<tr>
<td>HB</td>
<td>0.092</td>
<td>0.021</td>
<td>8.8</td>
</tr>
<tr>
<td>Zn</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LB</td>
<td>0.069</td>
<td>0.045</td>
<td>8.8</td>
</tr>
<tr>
<td>HB</td>
<td>0.072</td>
<td>0.049</td>
<td>8.3</td>
</tr>
</tbody>
</table>
bacterial cells sequestered metals, as metals associated with bacteria are retained on a 0.2 
\( \mu \text{m} \) filter. The 0.45 \( \mu \text{m} \) filter will allow bacteria to pass through, thus metals associated 
with the bacteria could be defined as "dissolved" and subsequently measured by ASV / 
ACSV. Hence, trace metals associated with bacteria were included in the colloidal fraction 
and the percentage seawater solubilities of Cu, Pb and Zn (in the 0.45 \( \mu \text{m} \) fraction) were 
higher in HB seawater than LB seawater.

5.4 Conclusions

The rate and extent of desorption of Cu, Pb and Zn from LUPM was measured in HB 
seawater (contaminated with bacteria, after UV irradiation) and LB seawater (sterilised by 
microwave digestion). The study presented in this chapter is novel because the temporal 
resolution of the trace metal measurements, during the desorption reactions from natural 
particles, is enhanced compared with previous studies (e.g. Statham and Chester, 1988; 
Hamilton-Taylor et al., 1993; Nimmo et al., 1998 and Millward and Liu, 2003). The results 
from this study are also unique because previous seawater solubility studies have not 
investigated the effects of bacteria on the extent and the rate of the desorption of trace 
metals. Via high temporal resolution, trace metal speciation measurements (labile and total 
dissolved; < 0.2 \( \mu \text{m} \) and < 0.45 \( \mu \text{m} \) "dissolved" fractions), the effect of bacteria on the fate 
of aerosol associated trace metals (Cu, Pb and Zn) in seawater was investigated (see 
summary in Figure 5.4).

Another major factor that may determine the extent to which trace metals desorb is the pre-
deposition solid partitioning of trace metals associated with aerosol particles (Chester et 
al., 1989 and Chester et al., 1993). The novel experiments in the current study indicate that 
trace metals with a large fraction in the exchangeable phase (Pb and Zn) undergo more 
rapid desorption than trace metals with significant associations in the organic phase (Cu). 
Unlike Cu or Zn, there was net readsorption of Pb onto LUPM particles, due to (i)
Figure 5.4 Proposed conceptual model for the effect of bacteria on the desorption of trace metals (Cu, Pb and Zn) from an urban aerosol (LUPM)

Aqueous phase
1) Strong organic complexes with LUPM associated ligands (non-labile)
2) Weak organic complexes with LUPM associated ligands (labile)
3) Inorganic complexes (labile)

Bacterial cells
Non-labile and labile associations:
1) surface complexation and precipitation
2) lipophilic interactions with plasma membrane

Filtration
0.2 μm filtration
Bacteria (and particulate and colloidal LUPM) retained on filter, therefore no difference in trace metal concentration in HB and LB seawater

0.45 μm filtration
Bacteria can pass through the membrane filter, thus labile Cu, Pb and Zn, and non-labile Cu concentrations are enhanced in HB seawater
migration of Pb onto higher energy sites on the LUPM particles, and / or (ii) the readsorption of Pb from the aqueous phase onto different mineral phase(s) on the aerosol particles.

The presence of bacteria in HB seawater significantly increased the seawater solubility of aerosol associated colloidal, labile Cu, Pb and Zn, and colloidal, non-labile Cu. The processes leading to this observed enhancement may be (i) the adsorption of trace metals onto the surface of bacterial cell walls, and / or (ii) bacterial production of strong trace metal complexing ligands. Both of these may cause a shift of equilibrium to the dissolved phase. The 0.2 μm filter experiments (which retain bacteria on the filter) eliminated the possibility of (ii), because the seawater solubilities of total dissolved Cu, Pb and Zn were the same in both HB and LB seawater.

The solubility experiments had one order of magnitude fewer bacteria in HB seawater than would be expected in natural seawater, therefore the effect of marine bacteria on the desorption of trace metals from aerosol particles may be even greater in the real environment. However, marine bacteria are difficult to culture (Smerdon, pers. comm., 2000), therefore it would be challenging to assess their effect on the solubility of aerosol associated trace metals, if they were inoculated into filtered, UV irradiated seawater. Furthermore, the effect of marine viruses and fungi on the seawater solubility of aerosol associated trace metals is still unknown (Fuhrman, 1999). Therefore, this study has important implications for other laboratory particulate-trace metal sorption studies. The wide range of seawater solubility values in the literature may partly reflect the effect of contrasting bacterial concentrations in seawater, as no previous attempts have been made to use sterile conditions. It is recommended that future particulate-trace metal sorption studies will require quantification of bacteria in the aqueous phase, before and after the addition of particle material.
Chapter Six

Effect of factors on the seawater solubility of aerosol associated trace metals
6.1 Introduction

It is evident from the literature review presented in Chapter 2 that previous seawater solubility studies (e.g. Hodge et al., 1978; Crecelius, 1980; Maring and Duce, 1989; Chester et al., 1993 and Nimmo et al., 1998) applied a range of experimental conditions (i.e. different aerosol, bacteria and dissolved organic carbon concentrations; seawater temperatures, light intensities, seawater pH, stirring rates, equilibration times and different methods of separating the dissolved and particulate metal phases). Therefore, it is questionable whether these studies are comparable.

Under carefully controlled conditions (UV irradiated seawater at pH 8.0 and 25.0 ± 1.0 °C; shaking rate 150 osc min⁻¹) the seawater solubilities of trace metals (Cu, Pb and Zn) associated with the Eastern Mediterranean aerosol were defined (Chapter 3). The study highlighted that the origin of the air masses, had an impact on the seawater solubility of Pb and Zn. In addition, a weak exponential inverse relationship was found between the seawater solubility of Zn and Cu and the aerosol particle concentrations. However, it was not clear whether this was due to the presence of crustal aerosols (that have lower solubility associated metal solubilities than urban aerosols, Chester et al., 1993) at the higher end of the particle concentration range, or a particle concentration effect.

In the current study, several experimental factors that may have an effect on the rate and extent of the desorption of total dissolved trace metals from aerosol particles were investigated. These were:

(i) Proportional mixing of crustal, Saharan dust (West African Saharan Dust (WASD) or Turkish Saharan Dust (TSD)), with urban aerosols (National Institute of Standards and Technology, urban particulate matter (NIST) or Liverpool Urban Particulate Material (LUPM)).

(ii) Seawater temperature at 10.8 °C and 25.2 °C.
These experiments were performed under carefully defined experimental conditions, applying the experimental system described in Chapter 4. These results will aid our understanding of the factors impacting on the post-depositional fate of trace metals associated with crustal and urban aerosol material.

In this study, the arbitrary ‘cut-off’ point between the particulate and dissolved trace metal fractions was 0.45 μm. It does not allow for distinguishing between ‘truly’ dissolved trace metals and those associated with the colloidal phase, which had not been retained on the filter (Buffle et al., 1992 and Horowitz et al., 1996). However, the fraction < 0.45 μm is thought to include trace metals that are available to algae (Gledhill et al., 1997), and it allows comparison with the results from the Eastern Mediterranean aerosol seawater solubility study.

Before commencing these seawater solubility studies, most of the seawater dissolved organic carbon and bacteria were destroyed. Although these two components occur naturally in the marine environment, they may cause poor reproducibility in the observed seawater solubilities of aerosol associated trace metals. Hence they may obscure the effect of individual environmental factors investigated.

6.2 Methodology

6.2.1 Collection of end member aerosols

The urban particulate reference material (NIST 1648) was purchased from the National Institute of Standards and Technology. The material was collected over a 12-month period (1977 – 78) from St. Louis, Missouri, using a specifically built baghouse system. The
material was removed from the filter bags, sieved through a fine mesh and thoroughly homogenised. It was then packaged into sequentially numbered glass bottles. The urban reference material was adopted for this study to enable future comparisons to be made.

A single, bulk aerosol sample of LUPM was obtained from filters of an air purification system on the campus of the University of Liverpool, in 1995, by staff from the Oceanography Laboratories. This material has been used previously in trace metal aerosol characterisation studies. For example, Chester et al. (1993) carried out trace metal re-scavenging experiments with LUPM (collected before 1995) and a crustal end-member (West African Saharan dust). Similar material ("Liverpool urban aerosol population") collected using a high-volume sampler, was used in trace metal solid-state speciation studies (Chester et al., 1989 and Chester et al., 1995) and trace metal seawater solubility studies (Chester et al., 1993; Fones, 1996 and Nimmo et al., 1998).

West African Saharan dust (WASD) was mesh collected, during a desert dust intrusion. Murphy (1985) collected the sample off the West African coast (04° 43' N 28° 55' W), on R.R.S Shackleton on 1st April 1981. The sample used in the current study is sample No. 176 in Chester et al. (1986), where it was used in trace metal solid-state speciation studies. Similar material, collected from the same region, has been used in previous trace metal seawater solubility and solid-state speciation studies (Chester and Murphy, 1986; Statham and Chester, 1988; Chester et al., 1989; Chester et al., 1993 and Nimmo et al., 1998).

Turkish Saharan dust (TSD) was collected on 11th April 2000, with a 1 m² nylon mesh tied to the top of the 21 m sampling tower in Erdemli. The dust originated from the central Saharan desert (Kubilay, pers. comm. 2003). The dust was shaken into a 30 ml polystyrene vial. Each dust sample was stored in a refrigerator at 4 °C.
6.2.2 Particle characterisation of end member aerosols

The morphology and the particle size distribution of NIST, LUPM, WASD and TSD were recorded to allow comparison with other end member aerosol populations in both previous and future studies. The particle size distributions of LUPM, WASD and TSD were determined using laser sizer apparatus (Mastersizer X long bed Ver 2.18, Malvern Instruments Ltd.), with a 45 mm lens. Ten replicate measurements were taken after the dust was dispersed in water, sonicated, then pumped through the flow cell system. The manufacturers verify the accuracy and the reproducibility of the system each year with standard glass beads (Ballotini 350/400, Phase Separations). The supplier of NIST provided particle size distribution data (MacDonald, pers. comm. 2001).

Scanning electron microscopy (SEM) is able to examine the surface structure of particles under a wide range of magnifications, with high resolution (Lavoie, 1992 and Gill, 1997). The four different dust samples were fixed onto separate sticky carbon stubs. The stubs were then gold-coated. The dust particles were observed using a JSM 6100 Scanning Microscope, and images were recorded. Particular attention was paid to select and examine representative particles from the samples.

Energy Dispersive X-ray analysis (EDAX) was used to provide useful qualitative information on the elemental composition of end member aerosol particles (Lavoie, 1992 and Gill, 1997). Each aerosol sample was carbon coated on a carbon-mounted stub. The instrumental conditions for the X-ray analyses were a scanning time of 50 s, a counting rate of 2500 - 3500 counts per second, and a detection range of 0 - 20 kV. The X-ray analyses were performed over an area of 600 $\mu$m$^2$. Furthermore to gain qualitative information on the spatial distribution of elements from an atomic weight of 6 – 20 g mole$^{-1}$ (C – Ca), “Cameo” software (Oxford Instruments) was utilised in conjunction with the EDAX data. It assigned minerals to different colours in the visual light spectrum.
6.2.3 Experimental protocol for the seawater solubility experiments

The seawater used in the seawater solubility experiments described below, was collected, filtered, UV irradiated and sterilised (see sections 3.2.5 and 5.2.1). Some of the following seawater solubility experiments \( n = 15 \) were 'kinetic' experiments i.e. were experiments that measured the extent and rate of desorption of trace metals real-time on-line from aerosol particles. A summary of all the experiments performed in the current study is in Appendix E and in section 6.2.5. The experimental system described in section 4.2.2 was used, and together with the same analytical parameters presented in Table 4.1 for the ASV analysis of total dissolved trace metals. The protocol for the kinetic experiments was the same as that described in section 4.5.1, except these experiments were of \( 5 - 6 \) h duration. Under these conditions, the sample flow rate was halved to \( 0.41 \pm 0.03 \text{ ml min}^{-1} \) (total flow rate of sample and reagent was \( 0.50 \pm 0.03 \text{ ml min}^{-1} \)). The hanging mercury drop electrode was an EG & G PARC Model 303A.

Other experiments were 'batchwise' experiments \( n = 59 \) in which aerosol samples were equilibrated in 100 ml seawater for a set time (6 or 144 h). These experiments augmented the kinetic experiments (a summary of these experiments are presented in Appendix E and in section 6.2.5). The advantage of batchwise experiment is that there is less preparation time; only 1.7 h is required to UV irradiate seawater prior a seawater solubility experiment, rather than 17 h. The protocol for these experiments was the same as those in section 3.2.6; except: (i) the incubated volume was normally stirred at 750 rpm (unless otherwise stated), and (ii) pre-weighed dust was added from a Petri dish (Greiner). The Petri dish was then weighed again to determine the final weight of the dust added to the seawater.

The batchwise samples were UV irradiated in quartz tubes for 4 h (see method in section 3.2.6). After at least 24 h, the total dissolved trace metals concentrations were measured using the on-line metal monitor. At least five replicate on-line ASV measurements were
taken of each sample (the relative standard deviations of the measurements were < 5 %),
and then internal standard additions were applied to each sample and measured.

6.2.4 Analytical performance

The limits of detection of total dissolved Cd, Cu, Pb and Zn with the on-line ASV method
(Table 6.1) were defined in the same way as described in section 4.4.2, except that 51.4 mg
l⁻¹ NIST was used, with 0.5 ml min⁻¹ sample flow rate and an EG & G PARC Model 303A
HMDE. The new limits of detection (after 60 s deposition time) were the same order of
magnitude as those presented in Table 4.3. The limit of detection for Pb immediately after
UV irradiation in Table 6.1 were approximately a quarter of the detection limit in Table
4.3, however the limit of detection for Cu were about 3 times higher (308 nM).
Immediately after UV irradiation, the Cu oxidation potential was observed on a steep
oxidation wave, which was partly the Hg oxidation potential. However, when the sample
was analysed 24 h after on-line UV irradiation, the Cu limit of detection was only 19 nM.
Consequently, dissolved Cu concentrations after every seawater solubility experiment were
measured batchwise, 24 h after UV irradiation. Unlike the LUPM samples in Chapter 4,
dissolved Pb and Cd concentrations associated with NIST were sufficiently high enough to
be measured on-line immediately after UV irradiation.

The limits of detection for Cd, Cu, Pb and Zn were also determined after 10 min deposition
time, with the on-line ASV system. They were measured in acidified (pH 2.2), UV
irradiated seawater spiked with 10 nM of Cu, Cd, Pb and Zn. After 10 min deposition time,
the limits of detection were sufficiently low enough to measure the extent of Cu and Zn
associated with 52 mg l⁻¹ TSD, but not low enough to measure dissolved Cd or Pb in the
seawater before or after the addition of TSD or WASD, at a seawater stirring rate of 750
rpm. Average trace metal concentrations in seawater were 10.5 ± 5.1 nM for Zn and 1.2 ±
0.4 nM for Cu. The standard deviations were high because they represent seawater
collected on different days. Dissolved Cd and Pb concentrations in the seawater prior to the addition of dust were below the limits of detection (after 10 min collection time).

Table 6.1 Detection limits (nM) of the on-line experimental system and dissolved trace metals concentrations associated with NIST and TSD from seawater solubility experiments, with 750 rpm. (nd = not detectable).

<table>
<thead>
<tr>
<th>Analysis time after UV irradiation</th>
<th>Limits of detection</th>
<th>Dissolved concentrations (nM) from:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>51 mg l(^{-1}) NIST</td>
</tr>
<tr>
<td></td>
<td>1 min deposition</td>
<td>10 min deposition</td>
</tr>
<tr>
<td><strong>Cd</strong></td>
<td>~ 5 min after</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>(on-line)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24 h after</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>(off-line)</td>
<td>2.7</td>
</tr>
<tr>
<td><strong>Cu</strong></td>
<td>~ 5 min after</td>
<td>308</td>
</tr>
<tr>
<td></td>
<td>(on-line)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24 h after</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>(off-line)</td>
<td>0.7</td>
</tr>
<tr>
<td><strong>Pb</strong></td>
<td>~ 5 min after</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td>(on-line)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24 h after</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>(off-line)</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>Zn</strong></td>
<td>~ 5 min after</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>(on-line)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24 h after</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>(off-line)</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Generally the ASV deposition times were 75 s for the batch experiments, but it depended on the metal concentrations in the samples. The deposition times were as short as 10 s for the determination of trace metals from NIST > 600 mg l\(^{-1}\), and as long as 10 min for the measurement of trace metals desorbed from TSD and WASD, when the seawater was stirred at 750 rpm.
The linear ranges of dissolved Cu, Pb and Zn measured by the ASV technique had to be re-determined as the concentrations of these trace metals are higher in NIST than those observed in LUPM. If Cu, Pb and Zn were fully desorbed from 314 mg l⁻¹ NIST (the highest concentration used for the kinetic experiments), then there would be approximately 21.8 μM Zn, 2.98 μM Cu and 9.5 μM Pb in solution (but only 210 nM Cd). It appears that the linear range would not be exceeded for these trace metal concentrations in acidified, UV irradiated seawater, given 25 s deposition time and 0.50 ml min⁻¹ sample flow rate (Figure 6.1).

The addition of 0.01 M borate was required to prevent pH change with NIST in seawater. Without an added buffer, the pH of seawater decreased to 4.79 after the addition of 300 mg l⁻¹ NIST; however with 0.01 M added borate, the pH returned to 8.00. The effect of the added borate (0.01 M) on the release of Cd, Cu, Pb and Zn from NIST into seawater was investigated. Two identical kinetic experiments were conducted (750 rpm stirring speed, no light, 25.2 ± 0.1 ºC seawater temperature, 51.4 – 54.4 mg l⁻¹ NIST, pH 8.0, in 1 l of 0.45 μm filtered, UV irradiated and sterilised seawater), except they had different added
concentrations of borate (0.01 M and 0.02 M). The ionic strength of the seawater increases by approximately 1.4 % with 0.01 M borate, and by 2.9 % with 0.02 M borate.

Figure 6.2 illustrates that there was no apparent effect of borate on the seawater solubility of Cd, Pb and Zn over the lifetime of the experiment (nearly 6 h). Similarly there appeared to be no difference in the seawater solubility of Cu, with 0.01 M (24.0 ± 1.5 %) and 0.02 M borate (24.4 ± 1.8 %). There was good reproducibility of the two experimental runs; the mean relative standard deviations of the 0.01 M and 0.02 M borate experiments were for Cd, Pb and Zn were low at 5.1, 1.3, and 4.1 % respectively. To all the seawater solubility experiments involving NIST, 0.01 M borate was added to the seawater.

Details of the accuracy of on-line ASV determination of total dissolved Cu, Pb and Zn are in section 4.4.3. Dissolved Cd could not be measured in CASS-3 by the ASV method. Therefore the accuracy of the on-line determination of Cd was measured using UV irradiated NIST (see details in section 4.4.3). The certified concentration of Cd in NIST is 75 ± 7 mg kg⁻¹, and the measured concentration in the current study was 66 ± 6 mg kg⁻¹; therefore the recovery amounted to 88 % of the total concentration.

6.2.5 Seawater solubility experiments

6.2.5.1 Proportional mixing of end members

Saharan (TSD and WASD) and urban (NIST and LUPM) aerosols were proportionally mixed to simulate ‘mixed’ aerosol populations (0:100, 25:75, 50:50, 75:25 and 100:0 % mixtures). Other factors were carefully controlled; particle concentrations in these experiments were 320 ± 20 mg l⁻¹; the seawater in each experiment was equilibrated at 25.2 ± 0.1 °C for the kinetic experiments or 25.0 ± 1.0 °C for the batchwise experiments, in the dark, and stirred at 750 rpm. Kinetic experiments, to assess the rate and extent of Cd, (Cu), Pb and Zn desorption, were undertaken on the WASD-NIST mixed aerosol populations. In
Figure 6.2 Effect of borate (0.01 or 0.02 M) on the seawater solubility of Cd, Zn and Pb released from NIST
addition, batchwise seawater leaches (for 6 h) were performed on proportionally mixed TSD-NIST and TSD-LUPM.

### 6.2.5.2 Particle concentrations and stirring speed

NIST, WASD and TSD were used separately, to examine the effects of aerosol particle concentrations and seawater mixing speed on the seawater solubility of aerosol associated trace metals. Batchwise seawater solubility experiments were performed on NIST, at mixing rates of 50 osc min^{-1} \((n = 6, 60 - 768 \text{ mg l}^{-1})\), 150 osc min^{-1} \((n = 5, 33 - 310 \text{ mg l}^{-1})\) and kinetic experiments with seawater stirred at 750 rpm \((n = 6, 14 - 314 \text{ mg l}^{-1})\). Similarly, the seawater solubility of trace metals associated with TSD was investigated at the three different mixing speeds, with particle concentrations ranging from \(-30 - 300 \text{ mg l}^{-1}\). For WASD, changes in the seawater solubility of trace metals were investigated at particle concentrations ranging from \(47 - 1056 \text{ mg l}^{-1}\), with a seawater agitation speed of 50 osc min^{-1}. There was not enough WASD particle material to investigate the particle concentration effect at mixing rate of 150 osc min^{-1}. There was only enough material to produce duplicate experiments with \(\sim 300 \text{ mg l}^{-1}\) WASD, at 750 rpm stirring speed.

If a stirring rate of 375 rpm (half the usual stirring rate) was applied to seawater, then material from NIST and LUPM would float on top, therefore a low stirring speed was avoided. However this did not happen when NIST-seawater suspension was shaken at either 50 \((\sim 0.35 \text{ m s}^{-1})\) or 150 osc min^{-1} \((\sim 1.05 \text{ m s}^{-1})\). The stirring rate of 750 rpm equated to an average flow rate of 2.10 m s^{-1} in the cylindrical 1 l Teflon reaction vessel.

### 6.2.5.3 Temperature

Kinetic desorption experiments with 50 mg l^{-1} NIST were undertaken at 10.8 ± 0.1 °C and 25.2 ± 0.1 °C. To gain the lower temperature, the seawater in the 1 l Teflon vessel had to be equilibrated for 3 days in the temperature-controlled water jacket as described in section
4.2.2. Measurements of dissolved trace metals were terminated after 9 min in the second 10.8 °C kinetic experiment, because of an air leak in the tubing. The seawater solubility of Cd, Cu, Pb and Zn in this experiment was determined after 6 h equilibration.

6.2.5.4 Light

To assess the effect of sunlight on the seawater solubility of aerosol associated trace metals, NIST and WASD were equilibrated in seawater, in light and dark conditions, under identical experimental conditions (50 osc min⁻¹ shaking rate, air temperature 24.5 – 27.2 °C). Acid washed quartz tubes containing either NIST (n = 3) or WASD (n = 3), in 25 ml seawater (UV irradiated), were equilibrated outside, in natural sunlight for 6 h. Concentrations of NIST were 669 ± 137 mg l⁻¹ and WASD 864 ± 112 mg l⁻¹ in seawater. To create dark conditions, identical samples (NIST, n = 3 or WASD, n = 3) were wrapped in Al foil. Each tube was secured with an acid washed Teflon cap. Additional ‘dark experiments’ with WASD (n = 3) and NIST (n = 3) under identical conditions were performed in 100 ml Teflon vessels, to achieve lower particle concentrations (47 – 298 mg l⁻¹). Samples were filtered and UV irradiated batchwise (see section 3.2.5). Total dissolved trace metals concentrations were analysed on-line.

Controls, containing only UV irradiated seawater, were also equilibrated. Dissolved trace metal concentrations in the seawater were measured before and after equilibration. The results in Table 6.2 reveals that there was no net trace metal contamination or adsorption in the quartz tubes.
Table 6.2 Total dissolved trace metal concentrations (nM) in UV irradiated seawater controls before and after sunlight experiment (nd = not detectable). Errors represent one standard deviation of three aliquots.

<table>
<thead>
<tr>
<th></th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Cu</td>
<td>53.0 ± 1.8</td>
<td>56.3 ± 4.0</td>
</tr>
<tr>
<td>Pb</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Zn</td>
<td>12.5 ± 1.3</td>
<td>12.4 ± 0.1</td>
</tr>
</tbody>
</table>

6.2.5.5 Long-term experiments

Not only were the seawater solubilities of trace metals determined 5 – 6 h after the addition of dust to seawater, but also after 144 h in separate batchwise experiments for NIST (52 – 298 mg l⁻¹ at 750 rpm stirring rate, (n = 6); and ~60 mg l⁻¹ at 50 osc min⁻¹ shaking rate (n = 2). WASD and TSD were also equilibrated in seawater for 144 h (duplicate experiments with ~300 mg l⁻¹, at 50 osc min⁻¹ and 750 rpm mixing rates).

Changes in the seawater solubility of trace metals associated with LUPM, 6 to 144 h after the addition of dust to seawater were assessed with a 1 l incubated volume of seawater, equilibrated with 51.4 mg l⁻¹ LUPM. Total dissolved metal concentrations were measured on-line after 6, 16, 32, 64 and 144 h. There was approximately 150 ml loss of seawater after 144 h.

6.2.6 Total digestion (HF / HNO₃) of end member aerosols

In addition to the determination of the total trace metal content of LUPM and NIST, TSD and WASD also underwent HF / HNO₃ digest, followed by trace metal analysis by ICP-MS (see method and its validation in section 5.2.3).
6.3 Results and discussion

6.3.1 Physiochemical properties of the end member aerosols

The particle morphology, particle size distribution, presence of major minerals and solid state speciation of trace metals associated with each aerosol population (NIST, LUPM, TSD and WASD) used in the current study was assessed. These properties may be source indicators (see sections 2.2.1 and 2.5.1), and hence provide information to help assess whether the aerosol populations are appropriate 'end members'. Here, end members ideally should be pure, unmixed aerosol sources, i.e. NIST and LUPM represent urban aerosol populations and WASD and TSD represent crustal aerosol populations. No previous seawater solubility studies in the literature have noted details of the particle size distribution or morphology (except Guieu et al., 1994), which may reveal the representative nature of the adopted 'end members'. However, some studies had given information on trace metal solid-state speciation (Kersten et al., 1991; Chester et al., 1993 and Chester et al., 1994).

SEM and EDAX is commonly used to classify marine particles into different chemical / mineral groups (for example see Andreae et al., 1986; Lim et al., 1991; Xhoffer et al., 1991; Injuk et al., 1993; Lim et al., 1994; Guieu et al., 1994; Falkovich et al., 2001; Kaegi and Holzer, 2003 and Sciare et al., 2003). Here, Cameo software was used to identify mineral and other substances in the aerosol populations (for example aluminosilicates, silicates, NaCl, CaSO₄, NaCO₃ and organic matter). It is evident from images in Appendix F that each of the four aerosol populations were heterogeneous i.e. there was chemical diversity of particles within each aerosol population, due to different aerosol production mechanisms (Xhoffer et al., 1991). Non-remote marine aerosol populations are frequently heterogeneous (for example see, Xhoffer et al., 1991; Injuk et al., 1993 and Mouri et al., 1999).
6.3.1.1 Particle morphology and particle size distribution

Nearly all the particles in each end member aerosol appeared to be 'coarse' particles (> 2 \( \mu m \)), even in the urban aerosols (LUPM and NIST). Typical urban aerosols are 'fine' particles (< 2 \( \mu m \); Whitfield, 1977 and Prospero, 1983, see section 2.2.1). Coarse particles are usually from low temperature, natural sources, although they can be the result of incomplete combustion or resuspension of particles from the land (Wadge et al., 1986 and Nicholson, 1988). The typical modal diameter of coarse particles in the urban atmosphere according to Morawska et al. (1999) is only approximately 4 \( \mu m \). The average particle diameter of NIST and LUPM were ca. 10 \( \mu m \) and 22.7 ± 16.9 \( \mu m \), respectively, and therefore were higher than would be expected for urban aerosols.

On inspection, scanning electron microscopic images revealed that LUPM and NIST are predominantly aggregated particles (see Appendix F (i-iv)). In the LUPM aerosol population, there were two main particle types; aggregated particles, typically ~ 20 \( \mu m \) in diameter, consisting mainly of aluminosilicates, sodium chloride, Ca-rich particles and silicates (Table 6.3), and to a lesser extent sodium carbonate and organic material. In addition, “giant particles” (up to 100 \( \mu m \)) were observed, consisting primarily of aluminosilicates, which also appeared to be agglomerates.

In the NIST aerosol population, most of the particles also appeared to be agglomerates, containing primarily calcium sulphate and silicates, and also organic material, aluminosilicates and sodium chloride (Table 6.3). Occasionally, fly-ash particles (5 – 40 \( \mu m \)) were observed in the NIST aerosol population. These were spherical aluminosilicate particles, indicative of anthropogenic high temperature processes (Xhoffer et al., 1991; Injuk et al., 1993; de Bock et al., 1994 and Guieu et al., 1994).
Table 6.3 Presence of the most abundant elements in the four 'end members' used in the current seawater solubility study.

Ticks in bold represent the most common elemental groupings; larger ticks represent the three most abundant minerals for each aerosol population.

(Elements in brackets were 5 - 20% of the total X-ray counts; examples of X-ray spectrograms in Appendix D).

<table>
<thead>
<tr>
<th>Cameo colour</th>
<th>Detected elements</th>
<th>Proposed minerals / substance</th>
<th>Observed in aerosol populations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 - 3.8 keV</td>
<td></td>
<td>NIST</td>
</tr>
<tr>
<td>Red</td>
<td>O, Na, C</td>
<td>Sodium carbonate</td>
<td>×</td>
</tr>
<tr>
<td>Orange</td>
<td>Si, Al, O (Ca)</td>
<td>Aluminosilicates with calcium</td>
<td>√</td>
</tr>
<tr>
<td>Yellow</td>
<td>Si, Al, O (Ca, S)</td>
<td>Aluminosilicates with calcium sulphate</td>
<td>√</td>
</tr>
<tr>
<td>Light green</td>
<td>Cl, Na</td>
<td>Sodium chloride</td>
<td>√</td>
</tr>
<tr>
<td>Dark green</td>
<td>S, O, (Si, Ca)</td>
<td>Calcium sulphate and silicates</td>
<td>√</td>
</tr>
<tr>
<td>Blue</td>
<td>Ca, Si, O</td>
<td>Calcium and silicates</td>
<td>√</td>
</tr>
<tr>
<td>Brown</td>
<td>Si, O, Al</td>
<td>Aluminosilicates</td>
<td>√</td>
</tr>
<tr>
<td>Black</td>
<td>C, O</td>
<td>Organic material</td>
<td>√</td>
</tr>
</tbody>
</table>
The aggregation of particles may have occurred during the formation of the particles and/or during transport in the atmosphere. Kaegi and Holzer (2003) and Sciare et al. (2003) also observed urban aerosols consisting of irregular-shaped aggregates. These were composed of soot particles, a few microns in diameter (Sciare et al., 2003; 2 – 8 μm in diameter). Alternatively, the agglomeration of aerosol particles may have occurred during sampling or storage of the LUPM and NIST dust populations. To find whether these particles might disaggregate during seawater solubility studies, LUPM (~300 mg l⁻¹) was equilibrated in seawater for one week (with shaking speed of 50 osc min⁻¹). The particle diameters did not decrease (21.5 ± 17.7 μm), therefore there was no disaggregation of these coarse particles in seawater.

The average diameter of TSD particles (26.7 ± 29.7 μm) were ~ 5 times larger than WASD particles (5.2 ± 4.7 μm). Mineral particles collected over Israel (0.4 – 8 μm diameter) and from Asian dust storm events over China (1.0 – 8.0 μm diameter) had similar particle size distributions to WASD (Falkovich et al., 2001 and Zhang et al., 2003). During a Saharan dust event over Sardinia, the particle size distribution of the aerosol population had a bimodal structure (Guerzoni et al., 1997). The modes were 2 – 4 μm and 15 – 30 μm. The smaller mode was similar to that observed for WASD and the larger modal diameter was comparable to that observed for TSD.

The TSD particles might be larger than those of WASD because of the shorter distance travelled from the source to the mesh collector (Erdemli, Turkey). The sampling site for the TSD is 600 km from the Syrian Desert and 1400 km from the Libyan Desert, whereas WASD was sampled much further away from the Saharan desert (3000 km). Thus there might have been preferential settling of more of the larger crustal particles prior to the sampling of WASD than TSD. Furthermore, in the TSD aerosol population, there were soot-like particles present, which were up to 200 μm in diameter, which may have caused
an enhancement of the observed particle size distribution. This organic material may have originated from biomass burning or from wind-blown plant debris, either from local or distant sources.

WASD was more homogeneous than the other aerosol populations; it primarily consisted of aluminosilicates, with Ca and S, which was possibly calcium sulphate. TSD appeared to have contained a higher proportion of Ca-bearing silicates than WASD, probably reflecting the mineralogy of the desert dust source region (Ganor and Mamane, 1982 and Luria et al., 1996). Similar to WASD, the TSD aerosol population contained aluminosilicates, calcium sulphate, sodium chloride and organic material.

Calcium sulphate has been observed in other marine aerosol populations, for example the North Sea aerosol (Xhofer et al., 1991 and de Bock et al., 1994). There are three main sources of calcium sulphate to the marine aerosol: (i) from the fractional crystallisation of sea-salt, (ii) from the aerosol interaction between airborne CaCO₃ with SO₂ or H₂SO₄ within clouds, (iii) from the weathering of gypsum from crustal material or (iv) from anthropogenic combustion sources, for example flue gas desulphurisation processes (Xhofer et al., 1991 and de Bock et al., 1994). The EDAX / Cameo study highlighted that the main distinction in the mineralogy of the urban (NIST and LUPM) and the crustal (WASD and TSD) aerosol populations, are the presence of a mineral(s) containing S, Si and Ca in the urban aerosol populations, which are absent in the crustal aerosol populations (Table 6.3). These compounds might be clay and gypsum aggregates (Falkovich et al., 2001).

The irregularly shaped aluminosilicates that occurred in the four aerosol populations in the current study can be derived from soil dust, and silicates can be produced from the combustion of coal (Xhofer et al., 1991). Sodium chloride, also observed in all four
aerosol populations, can be attributed to sea-salt particles (Xhoffer et al., 1991). Sodium and chloride contributed about 0.88 % mass to the NIST aerosol population, but the source of this substance in the NIST aerosol population is unknown, as St Louis is 1100 km from the Atlantic Ocean. Sodium carbonate, observed in LUPM, in the Cameo image (Appendix F), might be derived from the reaction between the clay mineral calcium carbonate with sodium ions to form sodium carbonate (Song and Carmichael, 1999).

6.3.1.2 Total metal concentration and solid-state speciation

The concentrations of trace metals (Cu, Cd, Pb and Zn) in the aerosol populations were too low for EDAX to provide details on the distribution of trace metals between the different mineral substances (limits of detection with EDAX are up to 2 %; Gill, 1997). Solid-state speciation data can provide insight into the partitioning between different operationally defined fractions: (i) "exchangeable" phase, (ii) "oxide / carbonate" layer and (iii) "refractory" phase. The operationally defined solid-state speciation of trace metals associated with the aerosol samples used in the current study, were reported in the literature by other workers (NIST in Lum et al., 1982; WASD in Chester et al., 1986; and LUPM in Orif, 2003). The full method of the three stage sequential leach is presented in Chester et al. (1989).

For WASD, Cd and Pb are largely in the oxide / carbonate layer (89 and 72 %), whilst Cu and Zn are mostly in the refractory phase. In contrast, at least 25 % of the trace metals considered are in the exchangeable phase in the urban aerosol end members (LUPM and NIST). The proportions of Cu, Pb and Zn in each operationally-defined solid phase is similar for both the LUPM and NIST aerosol populations; trace metals are present in all three fractions (Figure 6.3). For example, the exchangeable fraction of Zn associated with LUPM and NIST, are 78 and 67 % respectively. However, all the Cd in the NIST aerosol
Figure 6.3 Solid state speciation of Cd, Cu, Pb and Zn in the end member aerosols used in the current seawater solubility studies.
population is exchangeable (Lum et al., 1982), whereas only 25 % are exchangeable in the LUPM aerosol population. There is a much higher Cd content in NIST (75.0 mg kg\(^{-1}\)) than in LUPM, TSD or WASD (up to 2.1 mg kg\(^{-1}\), Table 6.4). High temperature processes probably formed the minerals that contain Cd in the NIST aerosol population; this is why Cd is present in the loosely held, surface associations (Chester et al., 1989).

Table 6.4 Comparison of total trace metal concentrations (mg kg\(^{-1}\)) in the average upper continental crust, and in aerosol populations used in the current trace metal seawater solubility experiments

(Source: \(^{a}\)National Institute of Standards and Technology, 1998; \(^{b}\)This study; \(^{c}\)Taylor and McLennan, 1985).

<table>
<thead>
<tr>
<th></th>
<th>NIST(^a)</th>
<th>LUPM(^b)</th>
<th>TSD(^b)</th>
<th>WASD(^b)</th>
<th>Upper Continental Crust(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>75</td>
<td>2.1</td>
<td>0.78</td>
<td>0.70</td>
<td>0.098</td>
</tr>
<tr>
<td>Cu</td>
<td>609</td>
<td>505</td>
<td>59</td>
<td>51</td>
<td>25</td>
</tr>
<tr>
<td>Pb</td>
<td>6550</td>
<td>663</td>
<td>35</td>
<td>58</td>
<td>20</td>
</tr>
<tr>
<td>Zn</td>
<td>4760</td>
<td>1600</td>
<td>547</td>
<td>103</td>
<td>71</td>
</tr>
</tbody>
</table>

The concentrations of Cu, Pb and Zn in NIST are also comparatively higher than LUPM (Table 6.4). Therefore it appears that NIST is more influenced by anthropogenic activities than LUPM. Very large population centres, in the eastern side of the United States (e.g Chicago, Cincinnati, Indianapolis, Louisville and Memphis), surround the NIST sampling site. Whereas Liverpool is a coastal region where the cleaner marine aerosol will to a certain extent dilute anthropogenic aerosols generated in the surrounding urban areas (Chester et al., 2000a). However both the urban end member aerosols (NIST and LUPM) are distinctly different from crustal end member aerosols (WASD and TSD); and trace
metal (Cd, Cu, Pb and Zn) concentrations in the urban end member aerosol populations are at least one order of magnitude higher (Table 6.4).

6.3.2 Effect of proportional mixing of crustal and urban aerosols

Generally, trace metals associated with crustal aerosols have lower seawater solubilities than urban aerosols (Hodge et al., 1978; Chester et al., 1993 and Nimmo et al., 1998 and see section 2.5.1). Therefore, if there were increasing proportions of urban aerosol particles to crustal aerosols, in ‘mixed’ aerosol populations, then increases in the seawater solubility of the aerosol associated trace metals might be expected. This occurred for Cu (1.4, 8.2, 13.0, 14.0 and 17.6 % seawater solubility) when the content of NIST in NIST-WASD ‘mixed’ aerosol populations increased (0, 25.2, 51.2, 75.2 and 100 % NIST respectively).

However, Cd, Pb and Zn did not follow this trend (Figure 6.4). There was no change in the seawater solubility of Cd (range 57.5 – 63.1 %); when the NIST content was increased from 25.2 to 100 %. In contrast, the seawater solubility of Pb and Zn decreased slightly (from 7.3 to 4.6 % and from 6.8 to 4.0 % respectively, when the NIST content was increased from 25.2 to 100 %). Given that the relative standard deviations of dissolved Pb and Zn between duplicate experimental runs were 1.3 and 4.1 % respectively (see section 6.2.4), the seawater solubilities of Pb and Zn are significantly different for seawater equilibrated with 25.2, 51.2, 75.2 and 100 % NIST. Paradoxically, total dissolved Pb concentrations from seawater equilibrated with either WASD or TSD (with no added NIST) were not detectable (the seawater solubility of Pb was < 2 %). Furthermore, during the 6 h equilibration of WASD in seawater, there was adsorption of dissolved Zn from the seawater (2.3 nM), to a concentration below the limit of detection (< 0.8 nM).

In Figure 6.5, the relationships between the initial seawater concentrations of trace metals associated with the aerosol particles ($C_p$) are presented (for proportionally mixed NIST-
Figure 6.4 Influence of proportional mixing of an urban aerosol population (NIST 1648) with a crustal aerosol population (WASD) on the seawater solubility of Cd, Pb and Zn from the combined populations.
WASD, NIST-TSD and LUPM-TSD) and the dissolved trace metal concentrations after 6 h equilibration of the ‘mixed’ aerosol populations in seawater ($C_d$). The $C_p$ concentrations increased with increasing urban content in the ‘mixed’ aerosol population. For Cd and Cu there was a positive, linear correlation. However, for Pb and Zn, the increase was non-linear. Thus, in a ‘mixed’ aerosol population with enhanced initial trace metal particulate concentrations, the extent of the desorption of Pb and Zn was less than expected.

The physiochemical mechanism that explains the decrease in the seawater solubility of Pb and Zn, with increasing urban dust in the aerosol population, is unclear. It might be due to the presence of dissolved organic ligands from Saharan dust. Maring and Duce (1989 and 1990) observed that dissolved organic carbon enhanced the dissolution of Pb and Cu from remote marine aerosols in seawater. Dissolved organic ligands from Saharan dust may have enhanced the Pb and Zn desorption more than the dissolved organic ligands from urban dust. However, this explanation is unlikely, because: (i) dissolved organic carbon from Saharan dust would have been expected to have enhanced the desorption of Cd and Cu as well, (ii) the presence of dissolved organic ligands did not prevent the adsorption of Zn from the seawater onto WASD particles and, (iii) Spokes and Jickells (1996) observed that there was typically 3 – 10 times more organic material in urban particles than in crustal particles.

An alternative explanation for the non-linear relationship between $C_d$ and $C_p$ for Pb and Zn is enhanced readsorption of these trace metals at higher $C_p$ concentrations. Lead and Zn are generally more particle reactive than Cd and Cu (Balistrieri et al., 1981; Nyffeler et al., 1984; Comans, 1987; Jannasch et al., 1988; Chester et al., 1993; Turner et al., 1993; Benoit et al., 1994; Millward et al., 1992; Benoit, 1995; Millward 1995; Comber et al., 1996; Pan and Liss, 1998a and Trivedi and Ave, 2000). Thus the trend in seawater solubilities of trace
Figure 6.5 Influence of the particulate trace metal content in aerosol particles on the release of dissolved trace metals into seawater (at $t = 6$ h)

**Cd**

$y = 0.569x - 0.88$

$R^2 = 0.949$

**Cu**

$y = 0.173x - 39.1$

$R^2 = 0.954$

**Pb**

$y = -3.27E-06x^2 + 0.0777x - 11.3$

$R^2 = 0.979$

**Zn**

$y = -1.51E-06x^2 + 0.0783x - 47.0$

$R^2 = 0.968$
metals associated with NIST (Cd > Cu > Zn > Pb) confirms the order of dissolved trace metal – particle reactivity.

When more geochemically available Pb and Zn are present at the beginning of the experiment, then more Pb and Zn desorption occurs into seawater. Dissolved Pb and Zn may thus undergo enhanced readsorption at higher C_p concentrations due to a greater probability of collisions of the dissolved metals with the aerosols particles. This is illustrated in the kinetic profiles (Figure 6.4), where double exponential curves have arisen for Pb and Zn. There is a greater probability of irreversible adsorption at enhanced C_p concentrations, possibly due to the migration of Pb and Zn into the internal pore structure of aerosol particles (Millward et al., 1990). Irreversible adsorption would lead to decreased C_d concentrations at equilibrium.

Using the line equations in Figure 6.5 for Cd, Cu, Pb and Zn, the seawater solubilities of these trace metals were predicted for the NIST-TSD, NIST-WASD and LUPM-TSD systems (Figure 6.6), with varying urban aerosol content ("100 % urban aerosol content" being NIST or LUPM only; whilst "0 % urban aerosol content" is WASD or TSD only). The model correctly predicted the slight decrease in the seawater solubilities of Pb and Zn with the increasing urban aerosol content for the NIST-Saharan aerosol system (Figure 6.6).

The seawater solubility of Cd could not be determined with ~320 mg l^-1 WASD, TSD or LUPM, because the dissolved Cd concentrations after equilibration were below the limits of detection. The model in Figure 6.6 predicted that the seawater solubilities of Cd in these aerosol populations were 9, 17 and 42 % respectively. These values are similar to literature data: 19 % for a Saharan aerosol and 61 % for a Liverpool urban aerosol (Nimmo et al., 1998).
For TSD, the model presented in Figure 6.5 correctly predicted the net desorption of Zn into seawater and the adsorption of Zn from the seawater onto WASD particles (see Figure 6.6). The $C_p$ value for TSD (ca. 2700 nM) is greater than the intercept on the x-axis (600 nM), hence desorption was predicted. In contrast, the $C_p$ concentration for WASD (ca. 500 nM) is 5 times less than TSD, and is lower than the $C_p$ value at the intercept. Thus, adsorption was predicted. The model also predicted that there was net readsorption of Pb onto the WASD and TSD particles, because the $C_p$ values of these aerosol populations were less than the $C_p$ concentration found at the intercept. This cannot be verified because dissolved Pb concentrations in the incubated seawater were below the limit of detection before and after equilibration with Saharan dust, under the given experimental conditions.

These seawater solubility experiments demonstrated that Saharan dust may act as a "sink" for Pb and Zn i.e. in the presence of Saharan dust, readsorption of Pb and Zn may exceed the desorption of these trace metals. In contrast, WASD and TSD are a "source" of Cu and Cd (Figure 6.6). Chester et al. (1993) also observed that Saharan dust may re-scavenge Pb and Zn from seawater, but does not remove dissolved Cd. Following experiments where 400 mg l$^{-1}$ of Saharan dust was exposed to trace metals leached from 20 g l$^{-1}$ of a Liverpool urban aerosol in seawater, it was found that 16 % of the total dissolved Zn, and 43 % of total dissolved Pb, was re-scavenged by the Saharan dust. Aston et al. (1972) also demonstrated that after dry deposition, crustal aerosols might act as re-scavenging substrates for Co from seawater.

The kinetic profiles in Figure 6.4 reveal that urban aerosols may be simultaneously both sources and sinks of trace metals in seawater. Therefore the seawater solubility of trace metals is not only dependent on the exchangeable trace metal fraction in an aerosol population (Chester et al., 1993), but also on the extent of readsorption. Readsorption of
Figure 6.6 Observed and predicted seawater solubilities of Cd, Cu, Pb and Zn from proportionally mixed urban and crustal aerosol populations.
trace metals is dependent upon the occurrence of collisions of dissolved trace metals with aerosol particles and particle reactivity (Pb > Zn > Cu > Cd).

6.3.3 Effect of temperature

No investigation into the effect of temperature on the seawater solubility of aerosol associated trace metals has been undertaken before. Very few previous seawater solubility studies have even specified the temperature (Crecelius, 1980; Zhuang et al., 1990 and Kersten et al., 1991). In the current study, there was an observed increase in the seawater solubility of Cu, Cd, Pb and Zn (associated with 52.9 ± 1.9 mg l⁻¹ NIST) with the 14.4 °C increase in temperature (the percentage increase was 19 % for Cd, 23 % for Cu, 28 % for Pb and 30 % for Zn, Table 6.5).

Table 6.5 Effect of temperature on the seawater solubility of trace metals associated with NIST. Errors represent one standard deviation of two separate experimental runs.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>% Seawater solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd</td>
</tr>
<tr>
<td>10.8 ± 0.1</td>
<td>61.1 ± 1.5</td>
</tr>
<tr>
<td>25.2 ± 0.1</td>
<td>72.5 ± 0.2</td>
</tr>
</tbody>
</table>

Figure 6.7 and Table 6.6 show that with increasing temperature, the rates of the desorption (kₐ) and adsorption (kᵢ) of Pb and Zn associated with NIST increased. With a seawater temperature of 10.8 °C, the Zn desorption equilibrium was reached within 150 min (kᵢ = 0.023 min⁻¹), however at 25.2 °C, the equilibrium was reached after only 45 min (kᵢ = 0.043 min⁻¹). Similarly, the Pb desorption equilibrium was reached within 25 min when the seawater temperature was 25.2 °C (kᵢ = 0.065 min⁻¹), but it took approximately three times longer at 10.8 °C (kᵢ = 0.034 min⁻¹). Furthermore, with a seawater temperature of 25.2 °C,
Figure 6.7 Effect of temperature on the seawater solubility of

(i) Pb and (ii) Zn associated with ~ 50 mg l$^{-1}$ NIST

(Error bars represent duplicate experimental runs)

(i) Pb

(ii) Zn
net readsorption of Pb began after only 30 min, whilst at 10.8 °C net readsorption commenced after 150 min.

Reactions occur if reactants collide with a certain minimum kinetic energy. The probability that reactants have sufficient energy to equal or exceed the activation energy increases with temperature, thus the rates of reaction increase with temperature (Atkins, 1992; see Table 6.6). The activation energy was calculated according to the method in Atkins (1992). The activation energy for the desorption of Pb and Zn from weakly bound sites on the NIST particles exceeds that of adsorption, thus $k_1 > k_i$.

**Table 6.6 Effect of seawater temperature on the kinetics of desorption and adsorption of Pb and Zn from 52.9 ± 2.3 mg l$^{-1}$ NIST (Errors represent one standard deviation of duplicate experiments)**

<table>
<thead>
<tr>
<th></th>
<th>Pb</th>
<th></th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ (min$^{-1}$)</td>
<td>$k_i$ (min$^{-1}$)</td>
<td>$t_{resp}$ (min)</td>
</tr>
<tr>
<td>10.8 °C</td>
<td>0.095 ± 0.001</td>
<td>0.034 ± 0.002</td>
<td>7.8 ± 0.2</td>
</tr>
<tr>
<td>25.2 °C</td>
<td>0.128 ± 0.006</td>
<td>0.065 ± 0.001</td>
<td>5.2 ± 0.2</td>
</tr>
<tr>
<td>$E_a$, kJ mol$^{-1}$</td>
<td>15600</td>
<td>35300</td>
<td>21300</td>
</tr>
</tbody>
</table>

**6.3.4 Effect of solar radiation**

The amount of sunlight available to the sea surface, thus the magnitude of photochemical reactions in seawater is subject to spatial, diurnal and seasonal variations. From Figure 6.8 it is apparent that natural sunlight did not affect the seawater solubility of Cu, Cd, Pb and
Figure 6.8 Effect of light on the seawater solubility of trace metals associated with (i) NIST and (ii) WASD.
Zn associated with the NIST aerosol population. Similarly, for the crustal end member aerosol, WASD, the dissolution of Pb and Zn was not affected by light. In contrast, the seawater solubility of Cu was enhanced by sunlight. Thus with 830 mg l⁻¹ WASD, the seawater solubility of Cu in the presence of sunlight was 20.8 %, compared to 17.8 % in the dark (constitutes 17 % increase in net Cu desorption).

The reason for the enhanced seawater solubility of Cu in the presence of sunlight is unclear. There are two possible explanations. Firstly, Cu might undergo photoreduction in a similar manner to Mn and Fe in seawater. Fe (III) and Mn (IV) occur as relatively insoluble hydrous oxides, while Fe (II) and Mn (II) are more soluble (Siefert and Sulzberger, 1989 and Duce and Tindale, 1991). The photochemically induced reduction of Mn (IV) to Mn (II) and Fe (III) to Fe (II) occurs through the mediation of dissolved organic material, such as humic acids, fulvic acids and siderophores (Graedal et al., 1985; Zuo and Hoigne, 1992; Spokes and Liss, 1995 and Barbeau et al., 2001). Not only does the presence of organic matter in aerosols have the potential to increase the rate of Fe (III) and Mn (IV) photoreduction, but also slow the rate of reoxidation (Zhu et al., 1993 and Spokes and Liss, 1995). The most common oxidation states of Cu are Cu (I) and Cu (II), apart from Cu⁰. Unlike Fe (III) and Mn (IV), they are both soluble in seawater, therefore the photochemical reduction of Cu (II) to Cu (I) is unlikely to increase the seawater solubility of Cu associated with Saharan dust.

The second possible reason for the enhanced seawater solubility of Cu in the presence of sunlight is that if Cu was largely associated with the Fe and Mn rich minerals in the Saharan aerosol population, then the photoreduction of Fe and Mn may also enhance the Cu solubility. According to solid-state speciation stages, ca. 20 % of Cu associated with WASD is in ‘Stage 2’. This stage includes ‘new’ oxides and oxyhydroxides of manganese and amorphous iron oxides and ‘aged’ manganese oxides and crystalline iron oxides
(Chester et al., 1994). Thus, the extra 3 – 6 % soluble fraction, in the presence of sunlight, might have emanated from the ‘Stage 2’ phase.

Extra release of Zn and Pb from WASD, during solar radiation, would also have been expected, because ca. 20 and 70 % of these trace metals are also associated with the ‘Stage 2’ solid phase. However, there is the possibility after release of Cu, Pb and Zn in the presence of sunlight as a result of Fe(III) reduction, Pb and Zn may undergo readsorption. In future studies, kinetic studies measuring dissolved Fe(II), Cu, Pb and Zn would be recommended.

In addition, the increase in seawater solubility of Cu (20.8 – 24.1 %) with decreasing WASD concentrations (from 836 to 736 mg l⁻¹) might be due to a decrease in the scattering of light by the dust particles. The WASD seawater suspensions were translucent. However, with > 400 mg l⁻¹ NIST, the seawater suspensions were nearly opaque. In future studies, seawater solubility studies with 1 l reaction vessel, rather than using 25 ml seawater in quartz tubes are recommended, to reduce the aerosol particle concentrations.

### 6.3.5 Effect of particle concentrations

A study was undertaken to investigate the effect of NIST particle concentrations on the seawater solubility of aerosol associated trace metals. During the study, other variables were kept constant (pH 8.0, no light, 750 rpm stirring speed and 25.2 ± 0.1 °C seawater temperature). From Figures 6.9 and 6.10, it is apparent that the seawater solubility of Cd, Cu, Pb and Zn decreased with increasing particle concentrations (14 – 314 mg l⁻¹). The seawater solubility of Cd decreased from 76 – 67 % and Cu from 27 – 18 %. More dramatically, the seawater solubility of Pb decreased from 34 – 5 % and Zn from 27 – 4 %. These results again suggest that Pb and Zn are more particle-reactive than Cd and Cu, and are undergoing readsorption onto the aerosol particulate phases.
Figure 6.9 Effect of particle concentration (mg l$^{-1}$) on the rate and extent of the release of Cd, Pb and Zn into seawater from NIST

**Cd**

- Percentage seawater solubility over time (minutes)
-Particles concentrations: 52.9 ± 2.1, 118, 209, 314

**Pb**

- Percentage seawater solubility over time (minutes)
-Particles concentrations: 13.7, 28.0, 52.9 ± 2.1, 118, 209, 314

**Zn**

- Percentage seawater solubility over time (minutes)
-Particles concentrations: 13.7, 28.0, 52.9 ± 2.1, 118, 209, 314
In Figure 6.9, the shape of the Cd kinetic profiles did not change with different particle concentrations. Therefore there was no trend in the desorption ($k_1$) and adsorption rate constants ($k_i$) with NIST particle concentrations ($k_1 = 0.061 \pm 0.016 \text{ min}^{-1}$ and $k_i = 0.098 \pm 0.011 \text{ min}^{-1}$). However at particle concentrations $\geq 118 \text{ mg l}^{-1}$, the adsorption rate to weakly bound sites for Pb ($k_i = 0.321 \pm 0.075 \text{ min}^{-1}$) and Zn ($k_i = 0.253 \pm 0.020 \text{ min}^{-1}$) were greater than at low particle concentrations ($< 118 \text{ mg l}^{-1}$; see Table 6.7).

Furthermore, with increasing particle concentrations net readsorption of Pb and Zn became more pronounced during the lifetime of the experiments (5 – 6 h) and commenced more quickly (Figure 6.9). For example, net readsorption of Pb began after 80 min with 28 mg l$^{-1}$ NIST. However, with 314 mg l$^{-1}$ net readsorption occurred after only 10 min. Several other studies have also observed a particle concentration effect, whereby particle concentrations have enhanced the extent of adsorption of trace metals or reduced the amount of desorption (for example Ni and Co with montmorillonite, Di Toro et al., 1986; Pb, Ag, Cu and Zn with estuarine particles, Benoit, 1995; and Fe (although not Mn or Al) from Saharan dust, Spokes and Jickells, 1996).
Table 6.7 Effect of NIST particle concentrations on the kinetic parameters relating to the desorption of Cd, Pb and Zn from NIST (nd = not detectable)

(Errors represent one standard deviation of separate duplicate experimental runs).

<table>
<thead>
<tr>
<th>NIST (mg l⁻¹)</th>
<th>Cd</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k₁</td>
<td>k₂</td>
<td>tₚₑₛₚ</td>
</tr>
<tr>
<td>13.7</td>
<td>0.070</td>
<td>0.043</td>
<td>12.4</td>
</tr>
<tr>
<td>28.0</td>
<td>0.092</td>
<td>0.052</td>
<td>6.9</td>
</tr>
<tr>
<td>52.9 ± 2.1</td>
<td>0.124</td>
<td>0.064</td>
<td>5.3</td>
</tr>
<tr>
<td>117.6</td>
<td>0.395</td>
<td>0.094</td>
<td>2.0</td>
</tr>
<tr>
<td>208.5</td>
<td>0.335</td>
<td>0.040</td>
<td>2.7</td>
</tr>
<tr>
<td>313.7</td>
<td>0.325</td>
<td>0.039</td>
<td>2.7</td>
</tr>
</tbody>
</table>
A possible reason for the observed particle concentration effect in the current study is increased particle aggregation, leading to a net decrease in the number of desorption sites. However, this should have lead to a substantial decrease in the solubility of Cu and Cd as well as Pb and Zn. Furthermore, there was no evidence of further aggregation of LUPM particles after they were equilibrated in seawater for one week (see section 6.3.1.1).

More likely is that as the particulate concentration increases, the number of collisions of dissolved trace metals with the aerosol particles also increases. The rate of redsorption is dependent on the frequency of collisions between the dissolved trace metals and the aerosol particles, and the efficiency of contact (Spokes and Jickells, 1996). Hence, the particle concentration effect may be caused by trace metals that are irreversibly adsorbed onto the particles, due to migration of trace metals into the internal pore structure of particles (Pan and Liss, 1998b and Millward and Liu, 2003).

6.3.6 Environmentally realistic particle concentrations

In the current study, the lowest particle concentration used was 13.8 mg l⁻¹ NIST. However, an environmentally realistic dust concentration in the euphotic zone of the Sargasso Sea might be only ~ 12 μg l⁻¹ (see Appendix C for the calculation). Applying a truly environmentally realistic dust concentration in open seawater would be fraught with problems. Measuring small quantities of dust (μg) would very difficult to accurately weigh and transfer to seawater. In addition, the resulting trace metal concentrations would be analytically challenging to measure. If there was complete dissolution of trace metals associated with 12 μg l⁻¹ of NIST, there would be only 0.87 nM Zn, 0.38 nM Pb and 0.12 nM Cu. Concentrations from a crustal-rich aerosol (WASD) would be at least one order of magnitude lower (19 pM Zn, 3 pM Pb and 9 pM Cu).
6.3.7 Effect of mixing rate

The shaking or stirring rate of seawater / aerosols suspensions may have an effect on the seawater solubility of aerosol associated trace metals. Figure 6.11 illustrates that over a range of different particle concentrations, the mixing rate of seawater can have a dramatic impact on the seawater solubility of trace metals, particularly for Pb. It is apparent from Figure 6.11a and b that increasing the mixing rate of the seawater-aerosol suspension, decreases the seawater solubility of Cd, Cu, Pb and Zn, 6 h after the addition of NIST, TSD and WASD to seawater. For example, when the seawater mixing rate was increased from 0.35 m s\(^{-1}\) (50 osc min\(^{-1}\)) to 2.10 m s\(^{-1}\) (750 rpm), then the seawater solubility (with 300 mg l\(^{-1}\) NIST concentrations) of Pb, Zn, Cu and Cd decreased from 62 - 4 %, 27 - 4 %, 37 - 17 % and 70 - 60 % respectively.

The stirring or shaking rate determines the kinetic energy of the suspension, by laminar or turbulent fluid shear (Morel and Hering, 1993). Thus, increasing the seawater mixing rate may increase the frequency of collisions of dissolved trace metals with the aerosol particles, hence the extent of readsorption is increased and the apparent seawater solubility of trace metals is reduced. Of the four trace metals studied, Pb is the most particle reactive, and Cd is the least, therefore they are the most and least affected by mixing rate respectively (see sections 6.3.2, 6.3.5 and Figures 6.11a and 6.11b).

6.3.8 Long-term post-depositional behaviour of trace metals associated with aerosols

When atmospheric particles are deposited on the sea surface, the first point of contact is with the sea surface microlayer. This microlayer has a patchy distribution on the surface film, but is typically 50 μm thick (Armstrong and Elzerman, 1982 and Wangersky, 1986). Residence times of atmospheric particles in surface microlayers may vary from a few seconds to ~35 min, depending on surface wind conditions (Armstrong and Elzerman,
Figure 6.11a Effect of stirring/shaking rate (m s$^{-1}$) on the seawater solubility of trace metals associated with NIST

**Zn**

- $(0.35 \text{ m/s}) y = 33.0e^{-0.000378} R^2 = 0.92$
- $(1.05 \text{ m/s}) y = 29.0e^{-0.00214} R^2 = 0.98$
- $(2.10 \text{ m/s}) y = 30.5e^{-0.00668} R^2 = 0.99$

**Pb**

- $(0.35 \text{ m/s}) y = 70.4e^{-0.00169} R^2 = 0.88$
- $(1.05 \text{ m/s}) y = 53.4e^{-0.00162} R^2 = 0.93$
- $(2.10 \text{ m/s}) y = 32.7e^{-0.00671} R^2 = 0.96$

**Cu**

- $(0.35 \text{ m/s}) y = 42.9e^{-0.000588} R^2 = 0.99$
- $(1.05 \text{ m/s}) y = 32.8e^{-0.000729} R^2 = 0.88$
- $(2.10 \text{ m/s}) y = 26.4e^{-0.00432} R^2 = 0.93$

**Cd**

- $(0.35 \text{ m/s}) y = 79.5e^{-0.000428} R^2 = 0.90$
- $(1.05 \text{ m/s}) y = 77.9e^{-0.000751} R^2 = 0.94$
- $(2.10 \text{ m/s}) y = 74.9e^{-0.000640} R^2 = 0.90$
Figure 6.11b Effect of stirring/shaking rate (m s$^{-1}$) on the seawater solubility of trace metals associated with TSD and WASD

**Zn**

\[
y = 19.6e^{0.00071x} R^2 = 0.99
\]

\[
y = 7.453e^{0.0011x} R^2 = 0.92
\]

**Pb**

\[
y = 19.2e^{0.00071x} R^2 = 0.98
\]

\[
y = 23.1e^{0.0012x} R^2 = 0.89
\]

**Cu**

\[
y = 35.6e^{0.00099x} R^2 = 1.0
\]

\[
y = 4.00e^{0.0011x} R^2 = 0.98
\]

\[
y = 20.2e^{0.0012x} R^2 = 0.84
\]

\[
y = 1.86e^{0.00088x} R^2 = 1.00
\]
The extent and rate of the desorption of trace metals from aerosol particles might be enhanced in the sea surface microlayer because of higher concentrations of microorganisms, and higher organic content, light intensity, and temperature (Hardy and Apts, 1984). The current study did not include an investigation of the sea surface microlayer, because sampling this environment is challenging, due the varying thickness of the microlayer (Armstrong and Elzerman, 1982).

If it assumed that the residence time of aerosol particles is 0.67 years in the euphotic zone (upper 100 m of the water column; Jickells, 1999), and that the particles sink at a constant rate, then 15 min after deposition onto the sea surface, the particle would be 4 mm below the sea surface. After 6 h, they would be a further 10 cm below; after 144 h, they would be a total of 2.4 m below the sea surface. The indicates that the current seawater solubility study represents trace metal behaviour, associated with aerosol particles, in the upper part of the euphotic zone, where biological productivity is generally at its maximum (Hardy and Apts, 1984; Sunda, 1991; Bruland et al., 1991 and Butler, 1998).

Crecelius (1980) found no apparent differences in the seawater solubilities for different metals from filter-collected aerosols after leaching times of 1 and 24 h. Therefore in several subsequent trace metal seawater solubility studies (Zhuang et al. (1990); Chester et al. (1993); Chester et al. (1994); Fones (1996); Nimmo et al. (1998) and Wells (1999)) aerosol-seawater leaching times of 1 h were applied, assuming equilibrium had been attained. It is apparent from Figure 6.12 that the desorption of Zn from LUPM had reached equilibrium within an hour, however this was not the case for Cu. Maring and Duce (1989) also observed slow Cu desorption kinetics. In their study, after 40 min the seawater solubility of Cu was only 20 %, however after 6 h it was 99 %, from a remote marine aerosol. This may indicate that the Cu seawater solubility data in previous studies may be underestimated. In addition, the seawater solubility of Cd from NIST and Zn from TSD...
Figure 6.12 Seawater solubility of trace metals from urban and crustal end member aerosols over 6 days, with 750 rpm stirring rate.

NIST 1648 (53 ± 2 mg l⁻¹)

LUPM (50.9 ± 1.2 mg l⁻¹)

WASD (300 ± 8 mg l⁻¹)

TSD (311 ± 16 mg l⁻¹)
had not reached equilibrium after 1 h in the current study, when there was 750 rpm stirring rate.

Furthermore, after 1 h equilibration time with LUPM and NIST there was readsoption of Pb onto the particles (Figure 6.12). Kersten et al. (1991) also observed this process in a multi-chamber leaching experiment with a Liverpool urban aerosol. After 100 h, half of the readsobered Pb and Zn fraction was rescavenged by the aerosol particles (the other half by model phases including algae, goethite, MnO₂ and illite). Therefore, the seawater solubility values in previous studies, with a 1 h equilibration time, may not represent the trace metal particle-dissolved equilibrium. The 144 h seawater solubility experiments in the current study reveal that even after 6 h, the equilibrium is not necessarily achieved (Figure 6.12). Therefore, the aerosol-seawater leaching time is an operationally defined period (Chester et al., 1993).

Figure 6.13 Change in seawater solubility of Cd, Cu, Pb and Zn from NIST, between 6 and 144 h, at a range of different particle concentrations (~50 – 300 mg l⁻¹, 750 rpm stirring rate).

Comparison studies between 6 and 144 h equilibration time for NIST at different particle concentrations in seawater were also conducted. Figure 6.13 illustrates the resulting trace
metal seawater solubilities for Cd, Cu, Pb and Zn, when the seawater stirring rate was 750 rpm. After 144 h, the seawater solubilities of Cd, Pb and Zn were less than at 6 h, therefore there appears to be adsorption of trace metals 6 - 144 h after the addition of NIST to seawater. During this time frame, there is desorption and net re-adsorption of trace metals by separate minerals in the NIST aerosol population (Chester et al., 1993). At the highest particle concentrations (300 mg l⁻¹), the seawater solubilities of Cd, Pb and Zn were less affected by time, than at lower particle concentrations. Therefore, after 6 h the re-adsorbed trace metals were likely to have occupied nearly all the available adsorption sites, at particle concentrations > 300 mg l⁻¹. With particle concentrations < 300 mg l⁻¹, there were fewer collisions between the metals in the dissolved phase and the dust particles, hence the observed seawater solubilities were enhanced, particularly after 144 h. For Cu there was little change in its seawater solubility between 6 and 144 h, throughout the range of NIST particle concentrations (50 – 300 mg l⁻¹).

When the mixing rate of seawater remains high (~ 2.10 m s⁻¹), there is re-adsorption of trace metals onto the aerosol particles between 6 and 144 h after the addition of dust to seawater, (Table 6.8). For example, between 6 and 144 h, the seawater solubility of Pb from ~ 50 mg l⁻¹ NIST and LUPM decreased by 46 % and 81 % respectively. Similarly, the seawater solubility of Cu, Cd and Zn decreased by 6, 22 and 57 % respectively, with ~ 50 mg l⁻¹ NIST. In contrast, with the solubility experiments conducted at the 50 osc min⁻¹ (~ 0.35 m s⁻¹) shaking rate, there was continuing desorption of Cd, Cu, Pb and Zn between 6 h and 144 h after the addition of urban and Saharan aerosols into the seawater (Table 6.8). Therefore, after 144 h, there were large differences in the trace metal seawater solubilities between the high and low speed mixing experiments. For example, the seawater solubility of Pb in the 0.35 m s⁻¹ experiment was 81.4 % after 144 h, whilst for the 2.10 m s⁻¹ experiment; the seawater solubility was only 12.3 %.
Table 6.8 Changes in the percentage seawater solubility of Cd, Cu, Pb and Zn released from urban (NIST) and crustal (TSD and WASD) aerosol populations after 6 hours and 6 days, with 50 osc min\(^{-1}\) shaking rate or 750 rpm stirring rate (standard deviation represents duplicate experiments)

<table>
<thead>
<tr>
<th>Dust type</th>
<th>Duration</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>50 osc</td>
<td>750</td>
<td>50 osc</td>
<td>750</td>
</tr>
<tr>
<td>NIST</td>
<td>6 h</td>
<td>76.6 ± 1.0</td>
<td>72.5 ± 0.2</td>
<td>42.0 ± 0.1</td>
<td>24.2 ± 0.3</td>
</tr>
<tr>
<td>58 ± 5 mg L(^{-1})</td>
<td>144 h</td>
<td>86.6 ± 4.4</td>
<td>56.2</td>
<td>42.9 ± 3.1</td>
<td>22.8</td>
</tr>
<tr>
<td>LUPM</td>
<td>6 h</td>
<td>/</td>
<td>nd</td>
<td>/</td>
<td>15.5 ± 0.9</td>
</tr>
<tr>
<td>50 ± 1 mg L(^{-1})</td>
<td>144 h</td>
<td>/</td>
<td>nd</td>
<td>/</td>
<td>15.3 ± 0.07</td>
</tr>
<tr>
<td>WASD</td>
<td>6 h</td>
<td>nd</td>
<td>nd</td>
<td>19.0 ± 1.1</td>
<td>1.6 ± 0.3</td>
</tr>
<tr>
<td>302 ± 5 mg L(^{-1})</td>
<td>144 h</td>
<td>nd</td>
<td>nd</td>
<td>19.7 ± 0.5</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>TSD</td>
<td>6 h</td>
<td>nd</td>
<td>nd</td>
<td>28.9 ± 0.1</td>
<td>2.2</td>
</tr>
<tr>
<td>306 ± 12 mg L(^{-1})</td>
<td>144 h</td>
<td>nd</td>
<td>nd</td>
<td>29.2 ± 0.8</td>
<td>2.4 ± 0.1</td>
</tr>
</tbody>
</table>
These results have environmental importance and important consequences to adsorption / desorption experimental protocols. No previous seawater solubilities have evaluated the impact of the mixing speed on the seawater solubility of trace metals or have noted the exact stirring or shaking speed of the incubated seawater. However, the current study has clearly shown that the shaking or stirring speed is a potential experimental artefact.

6.3.9 Comparison of the seawater solubility data with the literature

Comparison between trace metal seawater solubilities of the urban and crustal aerosol population in the current study are presented in Tables 6.9 and 6.10. The particle concentrations (except Kersten et al., 1991 and Nimmo et al., 1998) and temperature in previous studies were not specified (except Kersten et al., 1991). None of these experiments had specified the light intensity, the shaking or stirring rate, or the bacterial concentrations present in the seawater. Furthermore, Hodge et al. (1978) and Chester (1993 and 1994) separated the dissolved and particulate phase by centrifugation. It is not known from their work what the particle size 'cut-off' is between the two phases, impairing comparison with other seawater solubility studies. Therefore, a definitive comparison between the current study and previous work is not possible.

The seawater solubility of trace metals associated with the urban aerosol, NIST (equilibrated 5 – 6 h) are presented in Table 6.9. Due to various experimental conditions employed there was a very wide range in observed seawater solubility values (for example, Cd: 29 – 77 %). The highest being observed were for a dust concentration of 60 mg l⁻¹ NIST, and applying 50 osc min⁻¹ shaking rate; whilst the lowest values were detected using 314 mg l⁻¹ NIST and a stirring rate of 750 rpm.

The seawater solubilities of trace metals associated with LUPM for the current study are in Table 6.9 (from the ‘low bacteria’ seawater experiments, after 2 – 3 h aerosol equilibration
Table 6.9 Seawater solubility of trace metals associated with urban end member aerosol populations

(nd = not detectable; NA = not analysed)

<table>
<thead>
<tr>
<th></th>
<th>St Louis, US&lt;sup&gt;a&lt;/sup&gt;</th>
<th>California, US&lt;sup&gt;b&lt;/sup&gt;</th>
<th>North Sea&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Liverpool&lt;sup&gt;d&lt;/sup&gt;</th>
<th>North Sea&lt;sup&gt;e&lt;/sup&gt;</th>
<th>Celtic Sea&lt;sup&gt;f&lt;/sup&gt;</th>
<th>Liverpool&lt;sup&gt;g&lt;/sup&gt;</th>
<th>Liverpool&lt;sup&gt;h&lt;/sup&gt; (Northerly sector)</th>
<th>Erdemli&lt;sup&gt;i&lt;/sup&gt; (Northerly sector)</th>
<th>Haifa&lt;sup&gt;j&lt;/sup&gt; (Northerly sector)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>29 - 77</td>
<td>84</td>
<td>95</td>
<td>NA</td>
<td>NA</td>
<td>ND</td>
<td>61</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Cu</td>
<td>10 - 42</td>
<td>28</td>
<td>41</td>
<td>34</td>
<td>36</td>
<td>71</td>
<td>49</td>
<td>NA</td>
<td>30.4 ± 14.8</td>
<td>60.1 ± 20.7</td>
</tr>
<tr>
<td>Pb</td>
<td>5 - 69</td>
<td>39</td>
<td>40</td>
<td>53</td>
<td>51</td>
<td>54</td>
<td>88</td>
<td>40.0 ± 18.5</td>
<td>60.1 ± 20.7</td>
<td>64.7 ± 16.3</td>
</tr>
<tr>
<td>Zn</td>
<td>4 - 31</td>
<td>68</td>
<td>58</td>
<td>72</td>
<td>75</td>
<td>NA</td>
<td>7 - 39</td>
<td>NA</td>
<td>36.6 ± 10.9</td>
<td>64.7 ± 16.3</td>
</tr>
</tbody>
</table>

Sources: <sup>a</sup>This study; <sup>b</sup>Hodge et al., 1978; <sup>c</sup>Kersten et al. (1991); <sup>d</sup>Chester et al. (1993); <sup>e</sup>Chester et al. (1994); <sup>f</sup>Wells (1999) and <sup>j</sup>Nimmo et al. (1998)
time). Comparison with the literature values clearly indicates lower trace metal seawater solubilities observed for LUPM. In the 'high bacteria' experiments, the seawater solubilities of Cu, Pb and Zn were 17, 14 and 48 % respectively. Therefore, the use of sterilised seawater is not enough to explain the comparatively lower trace metal seawater solubilities. Another possible explanation is the high stirring rate employed in LUPM seawater solubility experiments, which may have caused enhanced readsorption of trace metals onto the aerosol particles.

There was also a wide range in the seawater solubilities of trace metals observed for the Saharan aerosol populations in the current study, attributed to contrasting experimental conditions (for example, for Cu associated with TSD, the seawater solubilities ranged from 1.0 – 34.3 %). The observed solubilities however were comparable to those reported in previous studies (Table 6.10).

Table 6.10 Percentage seawater solubility of trace metals associated with 300 mg TSD and WASD (6 h equilibration time); comparison with the literature (1 h equilibration time). NA = not analysed; nd = not detectable; Ads = adsorption

Sources: a This study; b Nimmo et al. (1998) and c Chester et al. (1993)

<table>
<thead>
<tr>
<th></th>
<th>TSDa</th>
<th>WASDa</th>
<th>Erdemli (Southerly sector)</th>
<th>Saharan Dust 1b</th>
<th>Saharan Dust 2c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>19</td>
<td>NA</td>
</tr>
<tr>
<td>Cu</td>
<td>1.0–34.3</td>
<td>1.4–20.6</td>
<td>NA</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;0.7–18.4</td>
<td>&lt;0.2–24.2</td>
<td>3.4±2.6</td>
<td>2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Zn</td>
<td>3.7–18.9</td>
<td>Ads–6.5</td>
<td>11.2±6.7</td>
<td>NA</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>
6.4 Conclusions

Contrasting trace metal seawater solubility behaviour between urban (NIST and LUPM) and crustal (TSD and WASD) aerosols was observed. There were distinctive physiochemical differences between the urban and crustal end member aerosols. The urban end member aerosols had much larger trace metal exchangeable fractions (25 – 100 %) than the crustal end member aerosol populations (< 1 %). Only the urban end member aerosol populations had calcium sulphate and silicates present together. Combined they are indicative of high-temperature anthropogenic processes (Xhoffer et al., 1991). Trace metal (Cd, Cu, Pb and Zn) concentrations in the NIST and LUPM are at least one order of magnitude higher than in TSD and WASD.

It is difficult to define ‘typical’ urban and crustal end member aerosol, because atmospheric aerosol populations are heterogeneous. The end member aerosol populations, in the current study, each contained several minerals and other substances, including aluminosilicates, sodium chloride and organic material. These aerosol population components probably came from a variety of different sources, including natural and anthropogenic combustion processes, sea-salt spray and wind-blown soil. In the current study the particle size distribution, particle morphology and presence of major minerals were examined; so that these characteristics can be compared with crustal and urban end members used in future seawater solubility studies.

The following conclusions from the trace metal seawater solubility experiments were found (see summary in Figure 6.14):

- In the presence of natural sunlight, there was an enhancement of the seawater solubility of Cu associated with a Saharan aerosol (17 - 34 % increase in net Cu desorption).

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Figure 6.14 Summary of results from the seawater solubility experiments in the current study

Mixing rate
Seawater solubility (Cd, Cu, Pb and Zn) decreases with increasing mixing rate (TSD, WASD, and NIST).

Particle concentration
Seawater solubility (Cd, Cu, Pb and Zn) decreases with increasing particle concentration (TSD, WASD, LUPM and NIST).

Factors impacting upon the seawater solubility of aerosol associated trace metals

End member aerosols
Urban aerosols (NIST and LUPM) > crustal aerosols (WASD and TSD)
Cd, Cu, Pb and Zn

Sunlight
Light > Dark for Cu from WASD

Temperature
25.2 °C > 10.8 °C
for Cd, Cu, Pb and Zn from NIST
• In addition, there was an enhancement in the seawater solubility of Cd, Cu, Pb and Zn associated with NIST when the temperature increased by 14.4 °C (the increase was 19, 23, 28 and 30 % respectively), after 6 h equilibration.

• The probability of collisions of dissolved trace metals with aerosol particles (and hence readsoption) also affects the observed seawater solubility of trace metals. The frequency of collisions is partly controlled by the dissolved metal concentrations, the aerosol particle concentrations and the mixing rate of the incubated seawater.

The results from the current study have important implications to the experimental design of future seawater solubility studies. It is evident from these experiments that it is important to state the light intensity, temperature, mixing rate and aerosol particle concentrations at which the seawater solubility experiments are carried out, as well as, trace metal solid-state speciation, particle size distribution and particle morphology. These factors might be experimental artefacts, contributing to some of the observed variability in seawater solubility results in previous studies.
Chapter Seven

Conclusions and future work
7.1 Seawater solubility of the Eastern Mediterranean aerosol

The current study was the first to evaluate the trace metal seawater solubility (Cu, Pb and Zn) of the Eastern Mediterranean aerosol, applying a rigorous protocol. The following conclusions can be cited:

- Seawater solubilities of Pb and Zn associated with aerosols from Haifa, Israel (54 ± 19 and 55 ± 19 %) were higher than from Erdemli, Turkey (35 ± 21 and 33 ± 14 % respectively).
- Seawater solubilities of Pb and Zn associated with the Erdemli aerosol from the crustal-rich Southern zone were only 4.6 ± 1.5 and 15 ± 1 %; in contrast the seawater solubility of these metals from the urban-rich Northern zone were 39 ± 19 and 36 ± 11 % respectively.
- Precipitation scavenging and the seawater aerosol concentrations had no clear effect on the seawater solubility of trace metals associated with the Eastern Mediterranean aerosol.

7.2 Analytical development and application of a dissolved metal monitor

A novel dissolved metal monitor, validated in Chapter 4, enabled the systematic investigation of the impact of physicochemical factors on the seawater solubility of aerosol associated trace metals (see Chapters 5 and 6). There were several advantages to this experimental system:

- The on-line approach minimises sample handling, thus reduces the risk of sample trace metal contamination.
- Throughout the lifetime of the kinetic experiments, there was minimal sample loss (< 16 % of the original incubated seawater volume).
- The experimental system could be adapted to determine the trace metal speciation (operationally defined, total and labile dissolved concentrations).
Although the laboratory seawater solubility experiments in Chapter 6, did not completely mimic conditions in natural surface seawater (particularly natural bacterial concentrations, and the presence of phytoplankton and dissolved organic ligands), the effects of (i) seawater bacteria, (ii) seawater temperature, (iii) sunlight, (iv) aerosol particle concentrations, and (v) seawater mixing rates were systematically investigated. These experiments were conducted under carefully controlled experimental conditions (0.45 μm filtered, UV irradiated, sterile seawater at pH 8.0; specified seawater temperature, light or dark conditions, aerosol particle concentrations and mixing rates).

7.3 Critical evaluation of EM trace metal seawater solubility studies, considering laboratory model studies

The dissolved metal monitor was applied to the study of the effect of seawater bacteria on the seawater solubility of trace metals (Cu, Pb and Zn) associated with an urban end member (LUPM). It was found that an increase of total bacteria concentrations from 8.5 x 10^4 cells per ml (low bacteria seawater) to 2.2 x 10^5 cells per ml (high bacteria seawater) caused a factor increase of 1.12, 1.25 and 1.24 in the seawater solubility of Cu, Pb and Zn respectively. In natural surface seawater, the bacterial concentrations are typically much higher (ca. 2 x 10^6 cells per ml: This study; Steward et al., 1996 and Zaccone et al., 2002), therefore the extent of desorption of trace metals from aerosol particles might be enhanced further. Hence the estimated soluble trace metal fluxes to the Eastern Mediterranean, by dry deposition, might be under-estimated.

It was observed that sunlight enhanced the seawater solubility of Cu associated with Saharan dust, by a factor of 1.17 – 1.34 (WASD, 736 – 836 mg l^-1). Further experiments are recommended, to find the seawater solubility of trace metals with much lower aerosol particle concentrations. The Eastern Mediterranean aerosols were equilibrated with
seawater in the dark, therefore the Cu soluble fluxes to the Eastern Mediterranean might be further underestimated.

The current study found that the seawater temperature increased the seawater solubility of trace metals (Cd, Cu, Pb and Zn) associated with an urban end member (NIST) by a factor between 1.19 - 1.30 with a 14.4 °C rise, after a 6 h equilibration time. During the Eastern Mediterranean seawater solubility study, the aerosol samples were equilibrated in seawater at 25.0 ± 1.0 °C; this represents the mid-range of temperatures found in surface seawater of the Eastern Mediterranean in the summer. However, in the wintertime, minimum temperatures are ca. 17 °C (Kress and Herut, 1998), thus the seawater solubilities of Cd, Cu, Pb and Zn, and the soluble fluxes by dry deposition, during this season might decrease by a factor of 0.88 - 0.92 (assuming that NIST represents the response of an Eastern Mediterranean aerosol).

Most of the Erdemli and Haifa high-volume aerosol samples that had originated from the northern wind sector exhibited Cu and Pb seawater solubilities within the range observed for NIST (Table 6.9). However, the average seawater solubilities for Zn of the Eastern Mediterranean aerosol were higher than NIST (NIST up to 31 %; 37 % for Erdemli northerly aerosols; 52 % for the Haifa aerosol population, with an applied bacteria correction factor). The reason for this is unclear; possibly a higher proportion of Zn in the Eastern Mediterranean northerly aerosol is in the exchangeable phase than the NIST aerosol (67 %; Lum et al., 1982). The particle size distributions of the Eastern Mediterranean aerosol samples were unknown because they were embedded in Whatman filter papers. However, if the Eastern Mediterranean particles were smaller than NIST (average ca. 10 μm), the seawater solubility might have been expected to be greater, because there would have been a greater surface area for dissolved-particle reactions to occur.
The aerosol particle concentrations in the Eastern Mediterranean seawater solubility experiments (115 ± 44 mg l⁻¹) were higher than would be encountered in the natural environment (~0.13 - 1.3 mg l⁻¹; see Appendix C). From the seawater solubility experiments with a range of particle concentrations with crustal (TSD and WASD) and urban (NIST) end member aerosol populations, it was estimated that the seawater solubility and the estimated soluble trace metal fluxes in the natural environment might be a factor of 1.08 - 1.29 higher for Cu, Pb and Zn.

Increasing the mixing rate of seawater from 0.35 to 2.10 m s⁻¹ decreased the seawater solubility of trace metals (Pb > Zn > Cu > Cd). In the Mediterranean Sea, the maximum current velocity (> 0.8 m s⁻¹; Obaton et al., 2000) is within the range of the experimental conditions. The mixing rate (shaking or stirring speed) determines the extent of turbulent or laminar fluid shear, which in turn controls the frequency of collisions between dissolved trace metals with the aerosol particles. In the natural environment, the extent of amount of fluid shear depends on the sea-state. Hence, in calm conditions, the seawater solubility of trace metals will be greater than in stormy conditions; which would have a greater probability of dissolved trace metal readsoption onto particles. Thus, the estimates of soluble fluxes to the Eastern Mediterranean are operationally defined by the mixing rate, light intensity, seawater bacterial concentrations, temperature, equilibration time and aerosol particle concentrations. Therefore, these factors need to be controlled and specified in future seawater solubility experiments.

7.4 Recommended future work

The extensive investigation into the effect of factors affecting the seawater solubility of aerosol associated trace metals was not exhaustive. In future studies, other factors that affect the seawater solubility of trace metals should to be investigated. These factors should include the role of the sea surface microlayer, the seasonal effect of phytoplankton,
viruses and dissolved organic ligands, the impact of aerosol modification in the atmosphere, via freeze-thaw action, pH cycling and initial trace metal concentrations in seawater. In addition, adsorption studies should be undertaken on crustal and urban aerosol particles, after they have desorbed trace metals, to simulate processes that may occur down-column.

Finally, the fully automated dissolved metal monitor described could be adapted for the measurement of the sorption behaviour of other trace metals (including Fe, Ni, Co, Cd, Mo, Sb, Sn, Ti, U, V and Cr; see for example van den Berg, 1991; Gledhill, 1995 and Khodari, 1998). In future studies on factors influencing the seawater solubility of aerosol associated Fe is recommended. There has been considerable interest in the role of Fe on the limitation of primary productivity in the oceanic regions, where surface seawater is relatively rich in N and P (see for example Berger and Wefer, 1991; Martin et al., 1991; Zhu et al., 1992; Coale et al., 1998; Kuma et al., 1998; Achterberg et al., 2001b; Jickells and Spokes, 2001; Bowie et al., 2002 and Baker et al., 2003). The novel metal monitor could also be applied to other trace metal sorption studies, such as in rain-estuarine- and wastewaters. From such exciting simulation studies a better understanding and more accurate modelling of trace metal dissolved / particle interactions within the aquatic environment would be possible.


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Donat, J.R. (2000) Personal communication, Old Dominion University, VA.


Kubilay, N.N. (2003) Personal Communication, Middle East Technical University, Erdemli, Turkey.


Appendices
Appendix A. Details of the Eastern Mediterranean high-volume filter samples

Source: This study, Koçak and Kubilay pers. comm., Herut pers. comm.

Filter type key: W = Whatman 41 filters; Q = quartz (glass fibre) filters
Vertical motion key: a = anticyclonic (downward); c = cyclonic (upward); n = neither

### Erdemli southerly samples

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<td>11/3/96 13/3/96 Q C/D a C/D n</td>
<td>165 6.5 41 61</td>
<td>126 998 419</td>
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<tr>
<td>13/3/96 14/3/96 Q A/C a C a</td>
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<td>85 1007 865</td>
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<tr>
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<td>66 575 582</td>
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<tr>
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<td>41 214 348</td>
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<td>23 148 276</td>
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<td>34 619 162</td>
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<td>38 205 911</td>
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<tr>
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<tr>
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<tr>
<td>15/8/96 18/8/96 Q A/D a B/C c</td>
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<td>460 2 20 43</td>
<td>12 177 106</td>
<td>20 195 139</td>
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Haifa northerly samples cond.

<table>
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<tr>
<th>Dates of sample collection</th>
<th>Filter type</th>
<th>Back trajectory classifications</th>
<th>Percentage seawater solubility</th>
<th>Atmospheric trace metal concentrations</th>
<th>Crustal enrichment factors</th>
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<td>700 hPa Sector</td>
<td>Vertical motion</td>
<td>Vertical motion</td>
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<td>C/D a</td>
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<td>C/D a</td>
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<td>C/D a</td>
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<td>C/D a</td>
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<td>C/D a</td>
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<td>D a</td>
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<td></td>
</tr>
<tr>
<td>10/10/96 - 13/10/96</td>
<td>Q</td>
<td>C/D a</td>
<td>C n</td>
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Appendix B. Dissolved concentrations of trace metals from rainwater collected from Haifa, Israel in 1996

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Sample date</th>
<th>pH</th>
<th>Rainfall (ml)</th>
<th>Dissolved trace metal concentrations (µg l⁻¹)</th>
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<td>Start</td>
<td>Finish</td>
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<td>Cu</td>
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<td>24/3/1996</td>
<td>24/3/1996</td>
<td>5.77</td>
<td>1.63</td>
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<tr>
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<td>24/3/1996</td>
<td>24/3/1996</td>
<td>5.82</td>
<td>0.46</td>
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<td>26/3/1996</td>
<td>27/3/1996</td>
<td>5.51</td>
<td>2.01</td>
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<td>23/10/1996</td>
<td>23/10/1996</td>
<td>4.95</td>
<td>3.1</td>
</tr>
<tr>
<td>8</td>
<td>24/10/1996</td>
<td>27/10/1996</td>
<td>5.36</td>
<td>0.18</td>
</tr>
<tr>
<td>9</td>
<td>29/10/1996</td>
<td>29/10/1996</td>
<td>5.92</td>
<td>2.0</td>
</tr>
<tr>
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<td>29/10/1996</td>
<td>30/10/1996</td>
<td>5.14</td>
<td>4.38</td>
</tr>
<tr>
<td>11</td>
<td>4/11/1996</td>
<td>5/11/1996</td>
<td>5.5</td>
<td>3.3</td>
</tr>
<tr>
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<td>4/12/1996</td>
<td>5/12/1996</td>
<td>6.65</td>
<td>0.08</td>
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<td>13</td>
<td>5/12/1996</td>
<td>8/12/1996</td>
<td>5.86</td>
<td>2.57</td>
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</table>
Appendix C. Calculation of dust particle concentrations in (i) the Sargasso Sea and (ii) the Eastern Mediterranean

(i) Sargasso Sea

Total Al input = 14.6 $\mu$mol m$^{-2}$ day$^{-1}$ (Jickells, 1999)

\[ = 0.14 \text{ g m}^{-2} \text{ yr}^{-1} \]

Assuming Al content in dust = 8.0 % (Taylor and McLennan, 1985):

Dust input \[ = 1.8 \text{ g m}^{-2} \text{ yr}^{-1} \]

Assuming residence time of dust in 100 m water column (100,000 litres with 1 m$^2$ sea surface) is 0.67 years (Jickells, 1999):

Dust concentration in seawater = 12 $\mu$g l$^{-1}$

(ii) Eastern Mediterranean

Part A – Urban-rich aerosol population

If geometric mean atmospheric Al concentration = 535 ng m$^{-3}$ and assuming a deposition velocity of 1 cm s$^{-1}$, then:

Total flux of Al = 0.17 g m$^{-2}$ yr$^{-1}$

Assuming the % Al content of the urban-rich aerosol population is 0.86 % (estimated from the equation in Figure 3.7), then:

Dust input \[ = 20 \text{ g m}^{-2} \text{ yr}^{-1} \]
Assuming residence time of dust in 100 m water column (100,000 l) is 0.67 years:

Dust concentration in seawater = 130 µg l⁻¹

Part B – Crustal-rich aerosol population

Given the same assumptions as Part A, except that the Al content of the atmospheric aerosol is 2.1 %, and given that the geometric mean atmospheric Al concentration = 1530 ng m⁻³, then:

Total flux of Al = 0.48 g m⁻² yr⁻¹
Dust input = 23 g m⁻² yr⁻¹
Dust concentration in seawater = 160 µg l⁻¹

Part C – After an extreme desert dust episode

The 27 – 29 March 1998 aerosol sample was used as an example of an extreme desert dust episode. With the same assumptions as in Part A, except that the mean atmospheric Al concentration = 47305 ng m⁻³ and the % Al content of the atmospheric aerosol population is 8.0 % (Taylor and McLennan, 1985) then:

Total flux of Al = 14.9 g m⁻² yr⁻¹
Dust input = 186 g m⁻² yr⁻¹
Dust concentration in seawater = 1.25 mg l⁻¹
Appendix D. Derivation of the forward and backward rate constants

The following are derivations of Equations 5.3 and 5.4:

The reaction is as follows:

\[
S^- + M^{z+} \quad \leftrightarrow \quad \text{S-M}^{(z-1)+}
\]

\[
\begin{align*}
[M_D] & \quad [M_P] \\
\end{align*}
\]

At Equilibrium:-

\[
k_1[M_D] = k_i[M_P] \\
\]

therefore, \( [M_P] = \frac{k_1[M_D]}{k_i} \) \hspace{1cm} - (1)

Mass Balance:-

\[
[M_D] + [M_P] = [M_D]_i + [M_P]_i \\
[M_P]_i = [M_D] + [M_P] - [M_D]_i \
\]

- (2)

Put (1) in (2):-

\[
[M_P]_i = [M_D] + k_1[M_D] - [M_D]_i \\
\]

- (3)

Differential Equation for above reaction:

\[
\frac{d[M_P]}{dt} = k_i[M_P] - k_1[M_D]_i \\
\]

- (4)

Substitute (3) in (4):

\[
\frac{d[M_P]}{dt} = [M_D](k_1 + k_i) - k_1[M_D] - k_1[M_D]_i \\
\]

\[
\frac{d[M_P]}{dt} = [M_D](k_1 + k_i) - [M_D](k_1 + k_i) \\
\]

237
\[
\frac{d[M_D]}{dt} = ([M_D]_e - [M_D]_t) (k_{-1} + k_t)
\]

\[
\int \frac{d[M_D]}{([M_D]_e - [M_D]_t)} = \int (k_{-1} + k_t) dt
\]

[c.f. \( \int \frac{dx}{(b-x)} = a dt \)]

Integrate:

\[-\log_e ([M_D]_e - [M_D]_t) = (k_{-1} + k_t)t + C \]

or

\[\log_e ([M_D]_e - [M_D]_t) = -(k_{-1} + k_t)t + C \]

Solve for integration constant C

when \( t = 0; [M_D]_t = 0 \)

therefore \( C = \log_e [M_D]_e \)

\[\log_e ([M_D]_e - [M_D]_t) = -(k_{-1} + k_t)t + \log_e [M_D]_e \]

\[\log_e ([M_D]_e - [M_D]_t) - \log_e [M_D]_e = -(k_{-1} + k_t)t \]

\[\log_e \frac{[M_D]_e - [M_D]_t}{[M_D]_e} = -(k_{-1} + k_t)t \]

(5)

Antilog:

\[\frac{([M_D]_e - [M_D]_t)}{[M_D]_e} = e^{(k_{-1} + k_t)t} \]

\([M_D]_e - [M_D]_t) = [M_D]_t e^{(k_{-1} + k_t)t} \]
\[ [M_D] = [M_D]_e - [M_D]_e e^{(k_1 + k_1)t} \]

\[ [M_D] = [M_D]_e (1 - e^{(k_1 + k_1)t}) \]

Taking Equation (5):

\[ \log_e \left( \frac{[M_D]_e - [M_D]_t}{[M_D]_e} \right) = -(k_1 + k_1)t \]

\[ y = mx \]

The slope of the line \( m = -(k_1 + k_1) \) gives the sum of the rate constants

At equilibrium:

\[ [M]_{\text{Total}} = [M_P]_e + [M_D]_e \]

Using equation (1)

\[ [M]_{\text{Total}} = \frac{k_1 [M_D]_e}{k_{-1}} + [M_D]_e \]

\[ [M]_{\text{Total}} = [M_D]_e \left( \frac{k_1 + k_{-1}}{k_{-1}} \right) \]

\[ k_{-1} = \frac{[M_D]_e}{[M]_{\text{Total}}} (k_1 + k_{-1}) \]

where \([M]_{\text{Total}} = [S-M]^{(n-1)+}\) = initial concentration of exchangeable metal
Appendix E. Summary of seawater solubility experiments conducted for Chapter 6

(i) Urban aerosol population - NIST

<table>
<thead>
<tr>
<th>Dust type</th>
<th>Concentration, mg l⁻¹</th>
<th>Experiment type</th>
<th>Added borate, M</th>
<th>Temperature, °C</th>
<th>Shaking speed</th>
<th>Light/dark</th>
<th>Duration, h</th>
<th>% seawater solubility</th>
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<td>batch</td>
<td>0.01</td>
<td>25.0 ± 1.0</td>
<td>50 osc min⁻¹</td>
<td>Dark</td>
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<td>42.1</td>
<td>77.3 69.2 31.3</td>
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<td>26.5 ± 1.0</td>
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<td>31.0</td>
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<td>32.7</td>
<td>77.0 53.1 28.2</td>
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<td>29.8</td>
<td>66.2 39.7 19.5</td>
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<td>Dark</td>
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<td>26.3</td>
<td>63.0 33.4 14.9</td>
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### Experimental conditions

<table>
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<th>Dust type</th>
<th>Concentration, mg L⁻¹</th>
<th>Experiment type</th>
<th>Added borate, M</th>
<th>Temperature, °C</th>
<th>Stirring speed</th>
<th>Light / dark</th>
<th>Duration, h</th>
<th>% seawater solubility</th>
</tr>
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<td>kinetic</td>
<td>0.01</td>
<td>10.8 ± 0.1</td>
<td>750 rpm</td>
<td>Dark</td>
<td>6.0</td>
<td>Cu 20.9, Cd 60.0, Pb 18.1, Zn 17.7</td>
</tr>
<tr>
<td>NIST 54.5</td>
<td></td>
<td>kinetic</td>
<td>0.01</td>
<td>10.8 ± 0.1</td>
<td>750 rpm</td>
<td>Dark</td>
<td>5.9</td>
<td>Cu 18.4, Cd 62.1, Pb 17.5, Zn 17.0</td>
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<td>Dark</td>
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## (ii) Crustal aerosol population - WASD

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<th>Added borate, M</th>
<th>Temperature, °C</th>
<th>Stirring / shaking speed</th>
<th>Light / dark</th>
<th>Duration, h</th>
<th>% seawater solubility</th>
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<th>Cd</th>
<th>Pb</th>
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### (iii) Crustal aerosol population - TSD

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<th>Temperature, °C</th>
<th>Stirring / shaking speed</th>
<th>Light / dark</th>
<th>Duration, h</th>
<th>% seawater solubility</th>
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(iv) Urban aerosol population - LUPM

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<th>Light/</th>
<th>Duration, h</th>
<th>% seawater solubility</th>
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(v) 'Mixed' aerosol populations

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<th>Stirring/shaking speed</th>
<th>Light/dark</th>
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Appendix F. SEM images, EDAX spectrums and elemental distributions of end member aerosol populations used in seawater solubility experiments

A: Urban particulate reference material (NIST 1648) - SEM images
B. Urban particulate reference material – EDAX spectrum and Cameo images

Cameo colour legend

- Green: S, O, (Si, Ca)
- Orange: Si, Al, O (Ca)
- Blue: Ca, Si, O
- Yellow: Si, Al, O (Ca, S)
- Light green: Si, O, Al
- Cyan: Cl, Na
- Black: C, O

Density (kg/m³)

Energy (keV)

Cps = counts per second
C. Liverpool urban particulate material – SEM images
D. Liverpool urban particulate material – EDAX spectrum and Cameo images

cps = counts per second

Cameo colour legend
- O, Na, C
- S, O, (Si, Ca)
- Ca, Si, O
- Si, Al, O (Ca, S)
- Si, O, Al
- Cl, Na
- C, O
E. West African Saharan dust – SEM image
F. West African Saharan Dust – EDAX spectrum and Cameo images

cps = counts per second

Cameo colour legend

- Si, Al, O (Ca)
- Ca, Si, O
- Si, Al, O (Ca, S)
- Si, O, Al
- Cl, Na
- C, O
G. Turkish Saharan Dust – SEM image
H. Turkish Saharan Dust – EDAX spectrum and Cameo images

cps = counts per second

Cameo colour legend
- Si, Al, O (Ca)
- Ca, Si, O
- Si, Al, O (Ca, S)
- Si, O, Al
- Cl, Na
- C, O
Appendix G. Published papers


Dry atmospheric inputs of trace metals at the Mediterranean coast of Israel (SE Mediterranean): sources and fluxes

Barak Herut*a, Malcolm Nimmoa, Angela Medwayb, Roy Chesterc, Michael D. Kromd

aIsrael Oceanographic and Limnological Research, National Institute of Oceanography, P.O. Box 8030, Haifa 31080, Israel
bDepartment of Environmental Sciences, University of Plymouth, Plymouth PL4 8AA, UK
cOceanography Laboratories, Department of Earth Sciences, Liverpool University, Liverpool L69 3BX, UK
dDepartment of Earth Sciences, Leeds University, Leeds LS2 9JT, UK

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Abstract

This study presents the first detailed data on aerosol concentrations of trace metals (Cd, Pb, Cu, Zn, Cr, Mn, Fe and Al) at the SE Mediterranean coast of Israel, and assesses their sources and fluxes. Aerosol samples were collected at two sampling stations (Tel-Shikmona and Maagan Michael) along the coast between 1994 and 1997. Two broad categories of aerosol trace metal sources were defined; anthropogenic (Cd, Cu, Pb and Zn) and naturally derived elements (Al, Fe, Mn and Cr). The extent of the anthropogenic contribution was estimated by the degree of enrichment of these elements compared to the average crustal composition (EFcrust). High values (median > 100) were calculated for Cd, Pb and Zn, minor values for Cu and relatively low values ( < 10) for Fe, Mn and Cr. The crustal-derived elements exhibited a statistically significant seasonal pattern of higher concentrations during spring and autumn (e.g. Al concentrations in some cases during these periods were observed to be in excess of 1500 ng m⁻³). In the eastern Mediterranean basin crustal-dominated elements are enriched by 2-3 times while others (Cd and Pb) are comparable to the northwestern Mediterranean. The Pb: Cd ratios of ~ 150 are higher than in coastal European sites (60-116) or emission materials (~ 50). It is speculated that these differences are attributed mainly to the mixing of crustal material with local and European emissions. At present, it is impossible to quantify the latter two fractions. Back trajectory analysis and the subsequent categorization of two main aerosol populations, 'European' and 'North Africa-Arabian', exhibited a significantly different geochemical imprint on the aerosol chemical composition. 'European'-derived air masses indicated significantly higher EFcrust values for Cd and Pb due to the greater anthropogenic character of the aerosol population, with a dilution by crustal material of this population leading to comparatively lower EFcrust values associated with the North African-Arabian air masses. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Trace metals; Aerosol; Atmosphere; Fluxes; Mediterranean; Pollution; Sahara

1. Introduction

Recent studies (e.g. Duce et al., 1991; Jickells, 1995) have considered the quantitative inputs of natural and anthropogenic trace elements to the world's oceans. In the Western Mediterranean Sea mass balance calculations revealed that the atmospheric fluxes of certain elements (e.g. Pb and Cd) exceed the river inputs and dominate the total external inputs (Martin et al., 1989; Güleu et al., 1997; Guerzoni et al., 1999). The potential impact of the atmospheric input is likely to be enhanced in the eastern Mediterranean, which is bordered to the north and northwest by industrialized European countries and to the south by the North African (Sahara) and Arabian Desert belts. In this basin, most of the freshwater...
is intercepted for use by man, reducing the riverine inputs and enhancing the significance of atmospheric inputs and their influence on oceanic biogeochemical processes.

Assessment of the inputs of pollutants into the Mediterranean Sea including the atmospheric contribution has long been recognized as an important component of the overall Mediterranean environmental protection strategy. This was recently reaffirmed in the revision of the Barcelona Convention. The principal available data on atmospheric inputs into the Mediterranean have been reviewed by GESAMP (1989) and recently by Guerzoni et al. (1999). Most of these data refer to the western area (Dulac et al., 1987; Bergametti et al., 1989; Martin et al., 1989; Chester et al., 1996; Guerzoni et al., 1997, 1999; Guieu et al., 1997; Migon et al., 1997). Little information is available on the eastern basin (Kubilay and Saydam, 1995; Kubilay et al., 1997; Gullu et al., 1998). In order to accurately assess inputs it is essential to define the temporal and spatial variability in the trace elemental aerosol concentrations and to identify and quantify as far as possible the dominant geochemical processes. Such processes will include a combination of (i) meteorological conditions; air mass movement and the frequency and intensity of rain events (leading to aerosol removal via in-cloud and below-cloud wet deposition), (ii) aerosol source type and emission strengths and (iii) modification of the chemical nature of the aerosol during transport from emission source to sampling location.

Dayan (1986) investigated the climatology of back trajectories from Israel. Air masses reach Israel from three major directions: (a) WNW to NNW representing a long fetch of maritime air masses from northwest Europe crossing the Mediterranean Sea, (b) N to NE mostly inland flows from eastern Europe crossing Turkey and (c) SW to SE air flows from inland North Africa and Arabian continents. The first two air mass back trajectories represent air masses with higher contributions of the aerosol populations from European and marine sources whilst the third is likely to have aerosol populations strongly influenced by mineral components from the deserts of North Africa (Sahara), Sinai and Arabian Peninsula. These major sources have been shown previously to influence the chemical composition of rainwater over Israel (Herut and Krom, 1996; Herut et al., 1993, 1995, 1999).

This current study represents the first concerted effort to obtain information on aerosol concentrations of trace elements in the Israeli Mediterranean coastline (SE Mediterranean). Long-term measurements of particulate atmospheric trace metals (Pb, Cd, Cu, Zn, Cr, Mn, Fe and Al) were carried out at two coastal sites in order to estimate the fluxes to the coast and to identify their sources. As emphasized in previous studies, such calculated fluxes will have large associated uncertainties mainly being due to: (a) the fact that the atmospheric material fluxes were calculated on the basis of atmospheric concentrations data, which have a large natural variability in space and time (daily, seasonal and annual) and (b) poor characterization of the individual elemental dry deposition velocities and scavenging ratios (e.g. Guerzoni et al., 1999).

2. Methods

2.1. Sampling

Total suspended particles (TSP) in air were collected by high-volume samplers located on the roof of the National Institute of Oceanography (NIO) at Tel-Shikmona (TS, Fig. 1) (located on the shore, 22 m above sea level) and at Maagan Michael (MM, about 900 m from shore, 13 m above sea level). Sampling was carried out predominantly at weekends for about 60 h (mostly on days without rain). In addition, sampling was also carried out on four occasions during special meteorological conditions of 'Hamsins' characterized by the influence of air masses from the southern deserts. Two selected dust event samples (on 6 February and 15 November 1996) were collected at Ashdod (ASH, about 2.5 km from shore, 30 m above sea level) and were used as reference samples representing crustal-dominated aerosol populations. Additionally, dry deposited material was collected from a plastic surrogate collector at Eilat (Gulf of Aqaba), Israel on 28 May 1998, and from the top of a solar panel at Beit Yannay, Israel, following a dust storm.

TSP were collected at TS from October 1994 to December 1997 and at MM from March 1996 to December 1997 following the UNEP/WMO (1992) recommendations. At TS, a total of 61 samples were collected on Whatman QM-A quartz microfibre and 35 on Whatman...
samples were collected on Whatman QM-A quartz microfibre filters (both 20.3 x 25.4 cm²) and at MM a total of 66 samples were collected on Whatman QM-A quartz microfibre. The filters were stored in a desiccator for 24 h and weighed before sampling. After collection the filters were dried in a desiccator for 72 h before being re-weighted. The Whatman #41 filter weights were inaccurate owing to their tendency to immediately adsorb humidity. Approximately, 1/8 of each filter was used for the trace metals analysis. Other sub-samples of the same filters were used to determine nutrient content (Herut et al., 1999).

Surface (1000 mb) air mass back trajectories (3-5 d) for 50 samples from TS and MM, collected during 1996, were calculated using the software Trajplot (Canadian Atmospheric Environmental Agency).

2.2. Chemical analysis and intercalibration

Analyses of Cd, Pb, Cu, Zn, Cr, Mn, Fe, Al, Ca and Na in TSP were carried out after total digestion with HF following the procedure of ASTM (1983). The digested samples were diluted to volume by double-distilled water. The concentrations were measured on a Perkin-Elmer 1100B atomic absorption spectrometer (AAS) and graphite furnace (GFAAS). The filter blanks were usually less than 10% of the total concentrations (except for Na in Whatman QM-A filters). The analytical precision was estimated to be within ± 4% of the values reported, increasing towards ± 8% for Zn and Cd. The accuracy of the methods was evaluated on the basis of analyses of International Standard Reference Materials: Estuarine Sediment 1646 (NIST), MESS-2 Sediment (NRCC) and Coal Fly Ash. All elemental results were within 5% of the certified values.

To further validate the analysis an inter-laboratory study was carried out between IOLR (Israel) and Plymouth University (UK). Eleven Whatman 41 filter samples from TS were selected to represent a range of particulate metal concentrations. For all elements, on applying a paired t-test to the aerosol concentrations determined by the two laboratories there were no significant differences at the 95% confidence interval, between the two datasets. This further validates the observed concentrations. Replicate analyses of portions of Whatman 41 filter yielded precision < 5% for all elements except Cd, which was 8%. This illustrates that the collected aerosol material is evenly distributed across the filter media.

The comparison between the trace metal chemical composition of aerosols with different air mass origin was made using the Mann–Whitney test.

2.3. Estimate of fluxes

The dry atmospheric deposition fluxes (F_d) were calculated by multiplying the geometric mean particulate concentration in air of the element of interest (i) by the elemental dry settling velocity (V_d):

\[ F_d = C_i \times V_d. \]

The term V_d varies with particle size (from gravitational settling of large particles to impaction) and is dependent on climatological and physical conditions in the troposphere, especially in coastal environments. The values used here follow the mean values used by Dulac et al. (1991). For Cd, Pb, Zn, Cu and Cr which are found primarily associated with submicrometer particles a mean value of 0.1 cm s⁻¹ was applied, and for Al, Fe and Mn which are present primarily in the coarse fraction a mean value of 2 cm s⁻¹ was adopted. These values fall close to the V_d range given in other studies (Rojas et al., 1993; Migon et al., 1997 and references therein). It should be emphasized, however, that the flux calculations might vary by approximately an order of magnitude due to the uncertainties in V_d.

3. Results and discussion

3.1. Total suspended particles in air

TSP concentrations in air were calculated for the QMA filter samples. TSP concentrations at TS ranged from 22 to 191 µg m⁻³ with a mean ± SD value of 71 ± 33 µg m⁻³ and at MM from 30 to 183 µg m⁻³ with a mean value of 70 ± 35 µg m⁻³. It should be noted that the TSP contained recycled sea salts. Assuming that all the Na is marine in origin and using its composition in seawater (Na constitutes 31% of the Mediterranean seawater salts; Herut et al., 1990), the amount of sea salts contribution to the aerosol population may be estimated. The Na concentrations in the blank QMA filters were too high to allow them to be used to calculate the sea salt fraction. Therefore, we used the average Na concentration measured on representative Whatman 41 samples at TS and MM. Based on the average Na concentration at TS and MM (11482 ± 3173 and 385 ± 281 ng m⁻³, respectively) the TSP contain 3.7 and 1.2 µg m⁻³ of sea salt, approximately 5 and < 2% of the TSP, respectively. Thus, the influence of sea salt on the TSP concentrations was estimated as minor. It is assumed that for the trace metals considered in this study it is even more insignificant. The concentration of these trace metals in the non-sea salt fraction (mainly mineral dust) is three to four orders of magnitude higher than in the sea salt fraction (sea spray) and therefore sea salt contribution of these trace metals is negligible (Weisel et al., 1984). Such a minor sea salt contribution was also found in the western Mediterranean Sea for some of the trace elements (Dulac et al., 1987).
To estimate mineral dust concentrations in air the concentration of Al may be used assuming that this element represents, on average, a known % by weight of the mineral aerosol. Such an approach was used by Duce et al. (1991) using the Al concentration in average crust material (8.04 wt%, Taylor and McLennan, 1985). The scatter plot of Ca vs. Al concentrations in air in the present study indicates that the Ca/Al ratios (as a proxy of carbonates/alumino-silicates ratio) vary from 0.3 to 50 probably due to differential local soil/rock contribution (Fig. 2). It is, therefore, likely that the use of Al concentration alone in dust events of Saharan origin (> 4.5 wt%) will underestimate the mineral dust concentration at this region because of the presence of variable amounts of carbonate. Indeed, the calculated average Ca concentration in dust collected at TS is 7.4 ± 2.9wt%, higher than the average concentration in crustal material (4.15wt%, Taylor and McLennan, 1985).

3.2. Particulate trace metals in air

The statistical summary of the particulate trace metal concentrations in air at TS and MM is presented in Table 1. At TS similar trace aerosol elemental concentrations were found for both Whatman 41 and Quartz filters although they represent different sampling dates. Similar concentrations of crustal-derived metals (Al, Fe, Mn and most Cr) and of Cd and Cu were observed at both MM and TS. The somewhat higher Zn concentrations at TS (although not having statistically significant difference from that observed at MM) may represent the influence...
of local unidentified anthropogenic sources. The higher Pb concentrations at MM may also reflect local source contributions to the collected aerosols during sampling in 1996. This is clearly shown by contemporaneous samples from TS and MM (Fig. 3) which are somewhat enriched by Pb at MM during 1996 while other metals had similar concentrations (only Al is shown). These enriched Pb data are excluded from the general baseline in Table 1.

A comparison of the aerosol trace metal concentrations from the present study with those observed at another Eastern Mediterranean coastal site (Edemli, Turkey), Table 2 (Kubilay and Saydam, 1995), would indicate generally slightly elevated concentrations of Al and Fe aerosol concentrations and comparable concentration values for Pb and Cd, whereas Zn is enriched, especially at TS, in comparison with the Edemli sampling site. The source of Zn enrichment along the Israeli coast is not clear and might be related to local traffic sources. The relatively high Cr concentrations in Erdemli were attributed to contamination by local ophiolitic rocks (Kubilay and Saydam, 1995). Comparing trace metal aerosol concentrations with typical values quoted in the literature for coastal sites at the western basin (Table 2; Chester et al., 1993; Guieu et al., 1997), it is evident that the crustal elements are enriched (2-3 times) in the Eastern Mediterranean aerosol population. This is not surprising owing to the greater dominance and proximity of surrounding arid regions to the Eastern Basin. Considering the predominantly anthropogenically derived trace elements, comparable concentrations were detected at TS and MM compared to those quoted for the western Mediterranean basin (Table 2; Chester et al., 1993; Migon et al., 1997), but their anthropogenic fraction is higher at the European coastal sites (see further below).

### Table 2

<table>
<thead>
<tr>
<th>Element</th>
<th>Northern Israel (TS)</th>
<th>Turkey Erdemli</th>
<th>European coastal sites</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(ng m⁻²)</td>
<td>EF</td>
<td>(ng m⁻²)</td>
</tr>
<tr>
<td>Al</td>
<td>865</td>
<td>1</td>
<td>685</td>
</tr>
<tr>
<td>Fe</td>
<td>787</td>
<td>2.3</td>
<td>685</td>
</tr>
<tr>
<td>Mn</td>
<td>15.7</td>
<td>2.4</td>
<td>12.6</td>
</tr>
<tr>
<td>Cr</td>
<td>2.4</td>
<td>6.4</td>
<td>8.5</td>
</tr>
<tr>
<td>Cu</td>
<td>5.7</td>
<td>2.4</td>
<td>n.a.</td>
</tr>
<tr>
<td>Zn</td>
<td>89</td>
<td>117</td>
<td>19</td>
</tr>
<tr>
<td>Pb</td>
<td>34.2</td>
<td>159</td>
<td>30</td>
</tr>
<tr>
<td>Cd</td>
<td>0.24</td>
<td>228</td>
<td>0.19</td>
</tr>
<tr>
<td>Pb: Cd</td>
<td>143</td>
<td>158</td>
<td>57 (80°, 116°)</td>
</tr>
<tr>
<td>Zn: Cd</td>
<td>371</td>
<td>100</td>
<td>59 (~ 100°)*</td>
</tr>
<tr>
<td>Zn: Pb</td>
<td>2.6</td>
<td>0.63</td>
<td>1 (1.3°, 0.8°)</td>
</tr>
</tbody>
</table>

*Present study (see Table 1).
*Chester et al. (1993) and Guieu et al. (1997).
*n.a. = not analyzed.
*Possible contamination problem.
*Migon et al. (1997).
*Sandroni and Migon (1997).
Common factors influencing the variations between aerosol trace metal concentrations at both collection stations (TS + MM) were examined by principal component analysis (PCA and SAS software). The application of PCA on the present dataset may facilitate (a) an understanding of inter-relationships between elements in the aerosols (Fones, 1996) and hence indicate common transport/removal mechanisms and/or emission source identification (e.g. Massart et al., 1988; Schaug et al., 1990). Datasets are reduced to a small number of representative vectors or principal components (PCs), which represent the entire variability in the dataset. Each PC is composed of a loading weight for each variable. Three main PCs (eigenvalues with eigenvalues > 1) were responsible for about 70% of the variance in the current trace metal aerosol dataset variability. PC1 (describes 32% of the variance) depicts similar loading to all elements while PC2 (describes 23% of the variance) depicts opposite loading of anthropogenically derived (Cd, Cu, Pb and Zn) vs. naturally derived elements (Al, Fe, Mn and Cr) (see further below in the discussion on EFcrust values), elucidating the different behavior and origin of these two groups of elements (Fig. 4).

Fe, Mn and Al concentrations had similar seasonal variability at both sampling sites attributed to their crustal origin. In contrast, smaller concentration variability and sometimes-different temporal variability were observed for Pb, Cd and Zn, attributed to their dominant anthropogenic origin. The seasonality was tested statistically using Duncan's Multiple Range Test (SAS software) and was found to be significant (p < 0.05) for the crustal-derived elements. Higher concentrations were recorded during spring and autumn as compared to those of summer and winter (e.g. mean Fe concentrations in TS + MM during spring and autumn were 1117 and 1502, respectively, whereas in winter and summer they amounted to 639 and 729 ng m⁻³). Similar seasonal patterns of desert dust pulses elevating the concentrations of crustally derived elements such as Al and Fe in the aerosol have been regularly observed at sampling sites in the Western Mediterranean (e.g. Guieu et al., 1997). The high concentrations peaks (> 1500 ng m⁻³) were attributed to dust storms ('pulses') moving from N African and surrounding desert regions as previously documented (Ganor and Mamane, 1982). Seasonal variability in crustal elemental aerosol concentrations, with enhanced concentrations (by 2-3 times) in the summer period has also been noted at collection sites located on the Turkish Mediterranean coast (Gullu et al., 1998). The enhancement was attributed to greater resuspension of soil particles during the dry summer months and minimum aerosol generation from damp soil surfaces in the winter. In addition, Gullu et al. (1998) stressed the importance of Saharan dust transport episodes occurring in May and April as well as September and October. Both these periods fall in their defined 'summer' period.

Defining the aerosol trace metal concentrations into different air mass groupings may provide preliminary information on elemental source regions. This approach has been adopted by a number of studies (e.g. Kubilay and Saydam, 1995; Gullu et al., 1998). For the current study the characteristics of contrasting air masses and hence aerosol sources were examined by calculating surface (1000mb) air mass back trajectories (3–5d) for 50 samples collected during 1996 at TS and MM. We classified the air masses into two geographical categories: (a) West–East European (EAM) and (b) North Africa and Saudi Peninsular (ASAM). This classification is based on Dayan's (1986) categorization, but combines his two European sources (see the Introduction) into one category (EAM). Using this categorization and then calculating the associated mean aerosol trace metal concentration, significantly higher concentrations of Al and Fe were observed in ASAM (median ≈ 1100 ng m⁻³) compared to EAM (median ≈ 500 ng m⁻³). There were small differences between the concentrations of the other considered anthropogenic trace metals between the two defined air mass categories (mean concentrations of Cd and Pb were 0.24 and 59 ng m⁻³, respectively, in ASAM and 0.29 and 62 ng m⁻³ in EAM), which would indicate the importance of regional sources rather than solely long-range transported material.

The mass of trace elements in a given volume of air derived from crustal and oceanic sources can be estimated from reference elements such as Al (or Fe) and Na (after correcting for crustal contribution), respectively (Chester et al., 1993; Weisel et al., 1984). Al was used here to estimate the enrichment factors relative to crustal composition according to the equation

\[ \text{EF}_{\text{crust}} = \frac{(\text{Tr}/\text{Al})_{\text{air}}}{(\text{Tr}/\text{Al})_{\text{crust}}} \]  

where \((\text{Tr}/\text{Al})_{\text{air}}\) is the concentration ratio of the trace element to Al in the air suspended particles and
Table 3
Trace element concentrations (µg g⁻¹ dry wt.; Al and Fe in %) and EFₐᵣₑᵣₚ values for samples of regional dust event and loess deposits from the Negev desert

<table>
<thead>
<tr>
<th>Site/sample</th>
<th>Parameter</th>
<th>Cd</th>
<th>Pb</th>
<th>Zn</th>
<th>Cu</th>
<th>Cr</th>
<th>Mn</th>
<th>Al</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eliat Dust 28 May 1997</td>
<td>Concentration</td>
<td>1.4</td>
<td>21.5</td>
<td>n.a.*</td>
<td>n.a.</td>
<td>n.a.</td>
<td>711</td>
<td>4.25</td>
<td>3.45</td>
</tr>
<tr>
<td></td>
<td>EFₐᵣₑᵣₚ</td>
<td>27</td>
<td>2</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>530</td>
<td>5.00</td>
<td>3.17</td>
</tr>
<tr>
<td>BY Dust March 1996</td>
<td>Concentration</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>2</td>
<td>1</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>EFₐᵣₑᵣₚ</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>2</td>
<td>1</td>
<td>1.6</td>
</tr>
<tr>
<td>Netivot loess</td>
<td>Concentration</td>
<td>0.12</td>
<td>8.7</td>
<td>65</td>
<td>23</td>
<td>70</td>
<td>595</td>
<td>4.50</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>EFₐᵣₑᵣₚ</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1.6</td>
<td>3.6</td>
<td>2</td>
<td>1</td>
<td>1.6</td>
</tr>
<tr>
<td>Ashdod 2nd Feb. 1996</td>
<td>Concentration</td>
<td>1.1</td>
<td>227</td>
<td>270</td>
<td>n.a.</td>
<td>91</td>
<td>617</td>
<td>4.75</td>
<td>3.56</td>
</tr>
<tr>
<td></td>
<td>EFₐᵣₑᵣₚ</td>
<td>20</td>
<td>19</td>
<td>6</td>
<td>—</td>
<td>4</td>
<td>1.7</td>
<td>1</td>
<td>1.7</td>
</tr>
<tr>
<td>Ashdod 11th Nov. 1996</td>
<td>Concentration</td>
<td>1.0</td>
<td>86</td>
<td>128</td>
<td>243</td>
<td>54</td>
<td>517</td>
<td>4.13</td>
<td>3.07</td>
</tr>
<tr>
<td></td>
<td>EFₐᵣₑᵣₚ</td>
<td>19</td>
<td>8</td>
<td>4</td>
<td>19</td>
<td>3</td>
<td>1.7</td>
<td>1</td>
<td>1.7</td>
</tr>
<tr>
<td>Upper crust</td>
<td>Concentration</td>
<td>0.098</td>
<td>20</td>
<td>71</td>
<td>25</td>
<td>35</td>
<td>600</td>
<td>8.04</td>
<td>3.2</td>
</tr>
</tbody>
</table>

*EFₐᵣₑᵣₚ is the ratio in average crustal material. EFₐᵣₑᵣₚ values (Table 2) is perhaps the most reliable ratio as the aerosol concentrations were evaluated after the significant decline with time of Pb emissions during the late 1980s and the early 1990s, especially in western Europe and to a lesser degree of Cd. The differences between the Pb : Cd ratios for the east and northwest Mediterranean sites are probably attributed to the combination of the following processes: (a) comparatively different regional rates of emissions of contaminants to the eastern basin, (b) differential settling between Cd and Pb during their passage from Europe to the Eastern Mediterranean, and (c) eastward enrichment of crustal material with Pb : Cd ratios of ~ 200. This eastward crustal enrichment is also reflected by higher Zn : Cd ratios of > 190 at the Israeli coast and in crustal material (~ 720) as compared to the European sites (~ 100) or the western and eastern European emissions (26-34, Pacyna et al., 1984). Similarly, the Zn : Pb ratios at the Israeli coast and crustal material (~ 1.3) are higher than at the European sites (~ 1) or the western and eastern European emissions (0.54-0.65, Pacyna et al., 1984).

Desert-type events (ASAM, category b) classified by air mass back trajectories contain significantly (p < 0.05) lower EFₐᵣₑᵣₚ values for Cd and Pb as compared to air masses from Europe (EAM) (Fig. 5). The geometric mean EFₐᵣₑᵣₚ values of Cd and Pb of EAM (category a) events (453 and 280, respectively) were significantly (p < 0.01) higher than in ASAM events (110 and 133, respectively). This general difference is likely to be attributed to the degree to which the anthropogenic aerosol components are 'diluted' with local and long-range transported crustal material, as there was no significant difference in the concentrations of the anthropogenically derived trace elements between air mass sectors. Individual events showed differences in EFₐᵣₑᵣₚ values attributed to different sources.
3.3. Mixing of anthropogenic and crustal aerosol end-members

The total mass of a certain particulate AEE in a given volume of air ($T_{\text{总}}$) is composed of

$$T_{\text{总}} = T_{\text{Crust}} + T_{\text{Anth}}$$

(3)

where the subscripts crust and anth designate its crustal (natural) and anthropogenic fractions. Assuming all the AEE in the air is of crustal origin,

$$A_{\text{total}} = A_{\text{Crust}}$$

(4)

then the mass of $T_{\text{Crust}}$ in aerosol population is given by

$$T_{\text{Crust}} = A_{\text{Crust}} \times (T_{\text{Total}}/A_{\text{total}})$$

(5)

Substituting Eqs. (4) and (5) into Eq. (3) we obtain

$$T_{\text{Total}}/A_{\text{total}} = (T_{\text{Crust}}/A_{\text{Crust}}) + T_{\text{Anth}}/A_{\text{total}}$$

(6)
Table 4
Estimates of trace element dry fluxes (μg m⁻² yr⁻¹; Fe, Mn and Al in mg m⁻² yr⁻¹) to the Israeli Mediterranean coast and to the southern coast of France (Migon et al., 1997)

<table>
<thead>
<tr>
<th>Station</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Cr⁺⁺</th>
<th>Mn</th>
<th>Fe</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maagan Michael</td>
<td>7</td>
<td>226</td>
<td>1542</td>
<td>1979</td>
<td>127</td>
<td>11</td>
<td>432</td>
<td>497</td>
</tr>
<tr>
<td>Tel Shikmona</td>
<td>8</td>
<td>178</td>
<td>1080</td>
<td>2806</td>
<td>75</td>
<td>10</td>
<td>496</td>
<td>545</td>
</tr>
<tr>
<td>Cap Ferrat (France)</td>
<td>33</td>
<td>1606</td>
<td>2555</td>
<td>41610</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

*Probably underestimated due to association with large crustal particles.

Substituting Eq. (2) into Eq. (6) we obtain

\[ \text{EF}_{\text{crust}} = 1 + \frac{\text{Tr}_{\text{anth}}}{\text{Al}_{\text{air}}} \times \frac{\text{Al}}{\text{Tr}} \]  

Eq. (7) describes a linear mixing between two possible end-members: (a) 'clean' crustal-derived particles characterized by \( \text{EF}_{\text{crust}} = 1 \) and (b) anthropogenic-derived particles. Within the \( \text{EF}_{\text{crust}} \) vs. \( 1/\text{Al}_{\text{air}} \) relationship (Fig. 6), the slope of the line represents the term \( \text{Tr}_{\text{anth}} \times \frac{\text{Al}}{\text{Tr}} \) from which \( \text{Tr}_{\text{anth}} \) can be estimated, similar to composite enrichment factor diagrams presented by Rahn (1976) and Chester et al. (1993). Thus, polluted samples will exhibit higher slopes than relatively clean samples. The dilution of clean crustal material in air is represented by the horizontal line along \( \text{EF} = 1 \) (\( \text{Tr}_{\text{anth}} \rightarrow 0 \)) or as defined here when \( \text{EF} < 10 \). This behavior was clearly exhibited by Fe (Fig. 6). Contamination by anthropogenic trace elements will shift the data upwards as shown by Pb and Cd (Fig. 6). The data fall in-between various mixing lines between crustal particles and anthropogenic Pb or Cd concentrations of about 10-250 ng m⁻³ of air. In general, TS samples showed somewhat lower Pb_{anth} concentrations as compared to samples from MM. The latter is attributed to contamination of Pb from local traffic and the nearby power plant during 1996.

The anthropogenic end-member is probably derived from two main sources, local and European emissions. At present (as given above), it is impossible to quantify the variations of these two fractions. An average composition of European coastal sites, representing the European 'background' composition, contains a similar fraction of anthropogenic Pb and Cd compared to the samples at the Israeli coast (Fig. 6). The EF of the European 'background' is relatively high, lying at the top edge of the Israeli sample distribution (Fig. 6), which is more 'diluted' by crustal material, exhibited by the 45° downwards distribution of most of the data.

3.4. Estimation of dry fluxes

The estimation of dry deposition fluxes of each trace element is problematic due to the use of different sampling methodologies, poor knowledge of the elemental mass-size distribution and other influencing factors (Guerzoni et al., 1999). Nevertheless, a large amount of data was published mainly for the western and central Mediterranean (Guieu et al., 1997). The average mineral flux into the coastal zone was estimated using Eq. (1). The calculated mean flux was 21 g m⁻² yr⁻¹ for TS and MM. Our estimate is quite similar to dust sedimentation rates of 20-40 g m⁻² yr⁻¹ calculated for the East Mediterranean by Ganor and Mamane (1982) or 30-60 g m⁻² yr⁻¹ estimated by Ganor and Foner (1996). These calculated fluxes are higher by almost an order of magnitude than those estimated over the northern Hemisphere Oceans (Duce et al., 1991).

The estimated dry fluxes of the trace elements are presented in Table 4. The Fe and Al fluxes are higher (by a factor of > 2) than fluxes to the Atlantic and Pacific Oceans (Duce et al., 1991). The fluxes of AEEs are significantly lower than those estimated for the North Sea (Rojas et al., 1993) or the central and western Mediterranean (Guieu et al., 1997, Migon et al., 1997, Table 4), but higher than those estimated for the Atlantic and Pacific Oceans (Duce et al., 1991).

4. Conclusions

1. Two main associations of particulate anthropogenic (Cd, Cu, Pb and Zn) and natural elements (Al, Fe, Mn and Cr) were detected (using principal component analysis). The composition of Pb, Cd, Zn and Cu in air indicated their dominant anthropogenic origin, exhibited by their high EF_{crust} values (>10).
2. A statistically significant seasonal pattern of higher concentrations of crustal-derived elements (Fe, Al, Mn and partly Cr) during spring and autumn as compared to summer and winter was observed.
3. Higher concentrations (by a factor of 2-3) of crustal-derived elements (AEE) and comparable concentrations of anthropogenic elements (AEE, e.g. Pb and Cd) were detected at the Israeli coast and the eastern Mediterranean Basin compared to the northwestern Mediterranean.
4. Distinct ratios of Pb: Cd and Zn: Cd were calculated at the Israeli coast compared to northwestern Mediterranean sites. It is speculated that these differences
are attributed to the mixing of crustal material with local and European emissions. At present, it is impossible to quantify the latter two fractions.

5. The use of back trajectory analysis and the subsequent categorization of aerosol populations enabled differences in the trace metal aerosol characteristics to be evaluated. The two main populations, European and North Africa–Arabian, exhibited a significantly different geochemical imprint on the aerosol composition. European-born air masses contained significantly higher EFcrust values for Cd and Pb due to the greater anthropogenic character of the aerosol population, with a dilution by crustal material leading to comparatively lower EFcrust values associated with the North African–Arabian air masses.

Acknowledgements

The authors would like to express their gratitude to the collaboration of Hadera Association of Towns for Environmental Protection and Ashdod-Yavneh Regional Association for Environmental Protection. The authors wish to thank Y. Gertner and G. Fainstein for their technical assistance in the dust filters analyses and sample collection. This study was supported in part by the Israeli Ministry of Environment, UNEP/WMO (Medpol Program, projects 8.072 and 5.116), the Israeli Ministry of Infrastructure and by UK NERC grant no: GRJ/10016.

References


An automated monitor to determine trace metal particle/dissolved interactions in natural waters

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Abstract

A novel automated metal monitor was optimised and validated for high temporal resolution (every 45 s to 5 min) measurements of dissolved Cu by adsorptive cathodic stripping voltammetry (AdCSV), Pb and Zn by anodic stripping voltammetry (ASV). The system was designed to allow the determination of both total (with UV digestion) and labile (without UV digestion) dissolved trace metal concentrations in seawater equilibrated with aerosol particles. There was negligible contamination or adsorption of trace metals from the experimental system and reaction vessel. Observed recoveries from certified reference materials for Cu, Pb and Zn were within the certified values; detection limits for total Cu, Pb and Zn were 28.4 and 63 nM, respectively.

The system was applied to the investigation of the desorption of trace metals from an urban aerosol end-member (Liverpool Urban Particulate Material; LUPM, 50 mg l⁻¹) in seawater. Carefully controlled and optimised experimental conditions were implemented. The analytical limits of detection of Cu, Pb and Zn were <25% of the mean desorbed metal concentrations from LUPM. Contamination from reagents were <0.1% of the mean sample concentration. Separate experimental runs measuring the desorption of the dissolved trace metals from the aerosol sample had good repeatability (e.g. for labile determinations mean R.S.D. <5% for Zn; <10% for Cu and Pb).

The high temporal resolution datasets generated by the metal monitor were used to calculate model desorption rate constants. The following range of constants were calculated 0.0047-0.015 min⁻¹ (Cu); 0.049-0.056 min⁻¹ (Zn) and 0.039-0.052 min⁻¹ (Pb).

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Keywords: Anodic stripping voltammetry; Adsorptive cathodic stripping voltammetry; Cu; Pb; Zn; Aerosols; Seawater

1. Introduction

Traditionally, budgets and residence time estimates for trace metals in the oceans have been based on fluvial inputs [1]. However, over the last 20 years, it has been increasingly recognised that the atmosphere is also an important route by which trace metals are transported to the sea surface in both the open ocean and coastal regions [2–6]. Most atmospheric metals are associated with aerosols, which are fine, particulate matter. In the dry deposition mode, aerosols are nearly continuously delivered directly to the sea surface. The rate and extent of the trace metal dissolution from aerosol material, from dry deposition, is constrained by particle–seawater reactivity [2,7].

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The conventional method for monitoring trace metal desorption kinetics is by batch experiments, where aliquots of seawater suspension are withdrawn from the reaction vessel, at pre-determined intervals [8–13]. This step is followed by filtration, which terminates the particle–water reaction. The filtrate is then analysed for the metal(s) of interest. However this type of experimental approach produces too few data points to give mechanistic detailed information during the initial desorption stage, and also involves a number of sample handling operations, which increases the potential for sample contamination.

To minimise these problems, in previous work, dissolution experiments on filter-collected aerosols in freshwater were carried out, directly in an electrochemical cell, with ASV [9,14]. Automated direct measurement of the released labile Cu, Pb and Zn in the experimental vessel was performed at 1 min intervals. There was no loss of the incubation volume, but the experiment could not be continuously stirred, as the
solution had to rest prior to each stripping voltammetric measurement, which would have yielded changes in the rate of metal desorption.

In recent work, an on-line automated monitor for the shipboard determination of dissolved trace metals in seawater was developed, using AdCSV [15]. Discrete samples were transferred from a sample changer to an on-line system where each sample was analysed within a conventional voltammetric cell. This system was further developed for fully automated sampling and analysis and applied to the Irish Sea [15]; polluted estuarine systems [16] and the Tamar Estuary [17]. Samples were continuously filtered and UV digested on-line for total dissolved trace metal measurements.

The on-line systems described above require approximately 20 ml of sample (the first 10 ml is allowed to flush through the sample loop). For the current application (high-resolution kinetic experiments) this technique is inappropriate because there would be significant incubation volume loss. In contrast, a flow cell approach with a wall-jet system can require less sample volume and allows the frequency of measurements to increase [18,19].

Similar voltammetric flow systems have been applied to the determination of metals (Cu, Cd, Pb and Zn) in algal samples [20], total dissolved Co measurements in seawater [21] and measurement of trace metals (Cu, Pb, Zn and Ni) in soil extracts [22]. However, to date, an on-line stripping voltammetric system has not been applied to the determination of the desorption kinetics of trace metals from particles in natural waters.

Therefore we report the construction, development, validation and application of a novel system, whereby seawater samples can be withdrawn continuously from an aerosol particle/seawater reaction system analysed near real time. The criteria established in the development of the detection system was: (i) to determine dissolved trace metal concentrations (in the nM range) in seawater, at a high temporal resolution (measuring every 45 s to 5 min), with both good accuracy and precision; (ii) to interface the electro-analytical system to a flow system which does not significantly reduce the reacting seawater sample (~15% of the total volume), for the duration of the experiment (up to 3 h); (iii) enable operationally defined trace metal chemical speciation measurements.

2. Description of experimental procedures

2.1. Description of novel analytical system

Separate on-line monitoring systems were assembled for the determination of total and electro-analytically 'labile' dissolved trace metals. The main components of the total dissolved on-line monitoring system are illustrated in Fig. 1. All tubing used for sample transfer was manufactured from PTFE (0.79 mm i.d., Altec). The amount of tubing connecting the different components in the experimental system was kept to a minimum, to reduce sample dispersion and positioned at the same horizontal level to further reduce backpressure. On-line filtration was carried out using a 25 mm diameter Swinex (Nalgene) filtration unit, containing a 0.45 μm pore size cellulose acetate membrane filter (Whatman). The UV lamp incorporated a silica coil (3 m length, 1 mm i.d.) and a fan cooled 400 W medium pressure Hg vapour lamp (Photochemical Reactors), housed in an aluminium case.

Samples analysed for total dissolved trace metal concentrations, underwent on-line UV digestion. The same equipment was used for the 'labile' dissolved system, without UV digestion of the non-acidified sample. To prevent backpressure, and therefore pulsing of fluid through the flow cell, which potentially would lead to a decrease in the analytical reproducibility (typically around 15–20%), two
peristaltic pumps were included with a break in the tubing. A polystyrene vial (Sterilin), with an overflow, collected the solution (<300 μl). The first pump (Wasion-Marlow 501) was switched on continuously. The second pump (Minipulse 3, Gilson) was switched off during the equilibration of the sample, prior to the voltammetric scan, and switched on at all other times. In both systems, dissolved trace metals were deposited onto the working electrode, SMDE (static mercury drop electrode, EG & G PARC Model 303), using a Perspex flow cell (EG & G PARC Model 420). The analysis was fully automated, with the potentiostat solution (<300 μl). The first pump (Wasion-Marlow 501) solution of Cu, Pb and Zn associated with Liverpool urban particulate material (LUPM) was immersed in a glass vessel, which contained a solution that had the same solution matrix as the sample/reagent mixture inside the sample loop. The solution inside the cell was continuously de-oxygenated with ultra-pure nitrogen (BOC, UK).

2.2. Experimental protocol for the aerosol metal/seawater dissolution experiments

The following description is the experimental protocol allowing the determination of the rate and extent of the dissolution of Cu, Pb and Zn associated with Liverpool urban particulate material (LUPM). LUPM was used, as it was a single, bulk sample representing an urban end-member, which was available in quantities sufficient to carry out analytical optimisation studies. Similar material has been used previously [2,12,23]. LUPM was obtained from filters of an air purification system on the campus of the University of Liverpool by staff from the Oceanography Laboratories.

Prior to each experiment, the Teflon® reaction vessel (1 L, Nalgene) was filled with hot 2% (v/v) Decon 90 (Decon Laboratories) for 1 h to remove organic surfactants, rinsed with ultra-high purity water (UHP, Milli-Q, Millipore) and then acid-soaked overnight in 10% (v/v) HCl (Aristar, BDH), before being thoroughly rinsed with UHP water. One litre of filtered, UV digested seawater was equilibrated overnight in the Teflon® reaction vessel at 25.2 ± 0.1°C. Before the addition of the LUPM to the seawater, 20 ml of seawater was pumped through the sample loop to condition the walls of the tubing. Then five on-line voltammetric measurements of the incubated seawater sample were made.

For each seawater solubility experiment, approximately 50.0 ± 5.0 mg of LUPM was accurately weighed into an acid washed Petri dish (Greiner) then rinsed into the reaction vessel with seawater (10 ml) from a wash bottle. For the ASV determination of total dissolved trace metals (Cu, Pb and Zn), the sample was acidified on-line with HCl (quartz redistilled) prior to UV digestion, to a final pH of 2.2. The acid reagent (50 ml, 0.072 M HCl) was made up in an acid washed 125 ml Teflon® vessel (Nalgene) and stored in resealable plastic bag. For the ASV analysis of dissolved labile Zn and Pb, the sample was buffered on-line with 1 M HEPES (N-2-hydroxyethylpiperazine-N'2-ethanesulphonic acid; Aldrich, analytical grade). The final concentration of the buffer at the flow cell was 0.01 M. The pH buffer was used to control the pH of the sample, as the formation of the metal-AdCSV ligand is pH dependent [24]. For the determination of labile dissolved Cu, the final concentration of SA (salicylaldoxime; Aldrich, analytical grade) and HEPES transported at the flow cell was 25 μM and 0.01 M, respectively.

Throughout the experiments the reduction/oxidation peaks of the metals were automatically measured and recorded, together with the time of the analysis. The duration of each kinetic experimental run was 2–3 h, as previous studies have shown that the equilibrium of the trace metals associated with the atmospheric aerosol was reached within 1–2 h [8,9,12,25]. Calibration of the system was achieved by measurement of samples spiked with metal additions.

3. Evaluation and validation of the experimental system

3.1. Analytical optimisation

The ASV and AdCSV scanning frequency, step potential, modulation amplitude and collection potential parameters were all changed systematically for system optimisation. Table 1 highlights the adopted optimised collection potentials and scanning parameters, for the determination of (i) total dissolved Cu, Pb and Zn by ASV; (ii) labile Pb and Zn by ASV; (iii) labile Cu by AdCSV, using the added ligand SA. The reproducibility was deemed acceptable when the relative standard deviation of six repetitive measurements of Cu, Pb and Zn were <5%.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Adopted analytical parameters for the determination of Cu, Pb and Zn in UV irradiated seawater (potentials are all vs. Ag/AgCl electrode)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency (Hz)</td>
<td>200</td>
</tr>
<tr>
<td>Step potential (mV)</td>
<td>4.88</td>
</tr>
<tr>
<td>Modulation amplitude (mV)</td>
<td>50</td>
</tr>
<tr>
<td>Collection potential (V)</td>
<td></td>
</tr>
<tr>
<td>ASV (Zn, Pb and Cu)</td>
<td>-1.4</td>
</tr>
<tr>
<td>AdCSV (Cu)</td>
<td>-0.15</td>
</tr>
<tr>
<td>Final potential (V)</td>
<td></td>
</tr>
<tr>
<td>ASV (Zn, Pb and Cu)</td>
<td>-0.15</td>
</tr>
<tr>
<td>AdCSV (Cu)</td>
<td>-0.55</td>
</tr>
<tr>
<td>Equilibration time (s)</td>
<td>10</td>
</tr>
<tr>
<td>Peak potential (V)</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>-1.15</td>
</tr>
<tr>
<td>Pb</td>
<td>-0.55</td>
</tr>
<tr>
<td>Cu (ASV)</td>
<td>-0.30 (±0.15)</td>
</tr>
</tbody>
</table>

These parameters were optimised in acidified (pH 2.2 with HCl), UV digested seawater spiked with 100 μM Zn, Pb and Cu, and measured with a 60 s deposition time, at a sample flow rate of 1 ml min⁻¹.
2.2 with HCI), spiked with 100 mM Cu, Pb and Zn. Using the experimental system presented in Fig. 1. The deposition time of the ASV measurements was 60 s. It was apparent that the oxidative current of the ASV measurements for Cu, Pb and Zn linearly increased with the sample up to a flow rate of 3.25 ml min⁻¹ (Fig. 2). However, at a flow rate of >4 ml min⁻¹, analysis was not possible owing to Hg drop dislodgement from the working electrode. Therefore, the technique's sensitivity is limited to that defined by a flow rate <4 ml min⁻¹.

3.2. Flow rate of the sample through the experimental system

The effect on the sensitivity of the flow rate of the sample was evaluated in UV digested acidified seawater (pH 2.2 with HCl), spiked with 100 mM Cu, Pb and Zn, using the experimental system presented in Fig. 1. The deposition time of the ASV measurements was 60 s. It was apparent that the oxidative current of the ASV measurements for Cu, Pb and Zn linearly increased with the sample up to a flow rate of 3.25 ml min⁻¹ (Fig. 2). However, at a flow rate of >4 ml min⁻¹, analysis was not possible owing to Hg drop dislodgement from the working electrode. Therefore, the technique's sensitivity is limited to that defined by a flow rate <4 ml min⁻¹.

In order to gain a balance between adequate sensitivity for the measurement of dissolved Cu, Pb and Zn from LUPM, and the conservation of the incubation volume within the reaction vessel during the lifetime of the desorption experiment, a sample flow rate of 0.88 ± 0.06 ml min⁻¹ was chosen resulting in a total flow rate to the wall-jet electrode of 1.00 ± 0.10 ml min⁻¹, including the reagent. A low pumping rate was also chosen to decrease the sample dispersion within the sample loop [26]. With the chosen sample flow rate, there was ~15% loss of the 11 incubation volume of sample after a 3 h kinetic experiment.

3.3. Assessment of the trace metal contamination from reagents and adsorptive artefacts

Trace metal contamination from the added reagents used in ASV (HCl or HEPES) and AdCSV (SA and HEPES) was quantified in Milli-Q water in triplicate 10 ml aliquots, via the standard ASV and AdCSV batch method, using a deposition time of 5 min. There was 0.09 nM of Cu contamination from 25 µM SA, representing 0.1% of the mean concentration in a seawater dust concentration of 50 mg l⁻¹. There was no detectable contamination from HEPES (with 25 µM SA). The contamination of Zn in 0.01 M HEPES was calculated to be 0.06 nM (0.01% of mean equilibrated sample concentration). Contamination of Pb and Zn from 6 mM HCl was not detected after a 5 min deposition time, with ASV.

The adsorption of trace metals onto Teflon® reaction vessel walls was also shown to be negligible. This was verified by measuring the total dissolved concentrations of Cu, Pb and Zn in spiked seawater (filtered and UV digested) before and after equilibration of the seawater in the Teflon vessels after 24 h, by ASV. Hamilton-Taylor et al. [9], in contrast, used 150 ml incubation volume in a glass voltammetric cell and their mean trace metal losses were large (29% Pb and 22% Zn, with lake water at pH 7.6).

3.4. Effect of tubing volume

To minimise sample dispersion within the tubing of the sample loop, the length of the tubing in the system was kept to a minimum. Dispersion caused by the flow in an open narrow tube increases with the square root of the tubing length [26]. The total dissolved experimental system had a greater fluid volume (9.46 ml) within the sample loop than the labile dissolved system (3.54 ml), because of the inclusion of the silica coil within the UV lamp and the backpressure system.

The difference in the desorption rate of labile Zn from LUPM (50 mg l⁻¹; equilibrated at 25.2 ± 0.1°C) was assessed with the two different tubing volumes (3.46 and 9.46 ml, using the total and labile dissolved experimental set-up respectively). The sample flow rate to the flow cell was 1.0 ml min⁻¹ in both experimental runs. The dissolved labile experimental system with a low volume (3.54 ml) produced a greater apparent initial Zn desorption rate (69.9 ± 6.3 nM min⁻¹) than a system with the larger volume (9.46 ml) as the total dissolved experimental system (51.8 ± 4.2 nM min⁻¹) (see Fig. 3). There was no effect on the observed equilibration labile Zn concentrations (i.e. after 15 min). These results confirm that the tubing volume enhances the amount of sample dispersion, therefore reduces the observed rate of desorption. The tubing volume of the labile dissolved experimental system was therefore made the same as that used for the total dissolved experimental system (9.46 ml), to allow comparability between the results.

3.5. Efficiency of on-line UV digestion

On-line UV digestion is an approach commonly used for the removal of interfering surfactants and the breakdown of the organic matrix. Efficiency of on-line UV digestion was assessed by comparing the concentration of Zn in spiked seawater (filtered and UV digested) before and after UV digestion. The efficiency of on-line UV digestion was determined for seawater samples spiked with 25 µM Zn, using the total dissolved experimental system. The concentration of Zn in spiked seawater before UV digestion was 0.09 nM, while the concentration of Zn after UV digestion was 0.03 nM. This indicates that the efficiency of on-line UV digestion was 75%, which is considered to be satisfactory.
of metal complexing ligands in seawater prior to voltammetric analysis (for example, [15,17,27,28]). This approach was used to distinguish between total dissolved (with UV digestion) and labile dissolved (without UV digestion) metal fractions for the aerosol/seawater kinetic studies.

The effectiveness of on-line UV irradiation of seawater for the total dissolved kinetic experiments was assessed. To investigate whether the applied residence time of 3.1 ± 0.2 min was sufficient to release all the dissolved trace metals (Cu, Pb and Zn) from the organic material, 50 mg l⁻¹ of LUPM was equilibrated with 11 of seawater, then acidified (with HCl to final pH 2.2), filtered and UV digested on-line. The filtrate was then UV digested a second and third time (6.2±0.4 and 9.3±0.6 min total residence time, respectively) through the silica coil. The trace metal concentrations (Cu, Pb and Zn) from the filtrate from each UV digestion cycle were then analysed (n = 3) and the results are presented in Table 2. Assuming that all UV digestible trace metal organic complexes were destroyed after 9.3 min, 94.5% Cu, 96.6% Pb and 94.1% Zn were released in the first 3.1 min. Similarly, in a recent work it was found that with Tamar Estuary water, over 90% of AdCSV-labile Cu was released within 3 min of on-line UV digestion [28]. However it is noted that there may be a small refractory pool of organic material which may be resistant to UV digestion.

3.6. Analytical performance

To ensure trace metal saturation did not occur on the Hg drop during the voltammetric measurements for the kinetic studies, the linear ranges of Cu, Pb and Zn were investigated. Acidified seawater (pH 2.2) was spiked with metal standards (up to 400 nM of Cu and Pb, and 2000 nM Zn). Three repetitive measurements were taken of each aliquot after a 2 min deposition time and a sample flow rate of 1 ml min⁻¹. Similarly, the linear range of AdCSV Cu was determined. The measurements confirmed that Cu and Pb responses were still linear even at 400 nM (by ASV and AdCSV) and Zn at 2000 nM (by ASV). The concentrations of trace metals released by 50 mg l⁻¹ of LUPM were well within the linear range of these techniques. Typical dissolved trace metal concentrations released during the kinetic experiments were 60–70 nM Cu, 19–21 nM Pb and 540–560 nM Zn at equilibrium.

Table 2

Efficiency of UV irradiation, using the on-line system at a flow rate of 0.9 ml min⁻¹, with dissolved trace metals from 50 mg l⁻¹ of LUPM in seawater

<table>
<thead>
<tr>
<th>Metal (nM)</th>
<th>Residence time (min)</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.1</td>
<td>62.2 ± 1.2</td>
<td>19.6 ± 0.3</td>
<td>544 ± 11</td>
</tr>
<tr>
<td></td>
<td>6.2</td>
<td>66.9 ± 1.5</td>
<td>20.1 ± 0.6</td>
<td>580 ± 5</td>
</tr>
<tr>
<td></td>
<td>9.3</td>
<td>65.8 ± 1.7</td>
<td>20.3 ± 0.5</td>
<td>578 ± 8</td>
</tr>
</tbody>
</table>

Table 3

Detection limits (nM) of the total and labile dissolved Cu, Pb and Zn applying the metal experimental systems (applying a 60 s collection/plating period)

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total dissolved (~2 min after UV irradiation)</td>
<td>105.4</td>
<td>40.0</td>
<td>64.2</td>
</tr>
<tr>
<td>Total dissolved (24 h after UV irradiation)</td>
<td>28.2</td>
<td>4.4</td>
<td>62.5</td>
</tr>
<tr>
<td>Labile dissolved</td>
<td>1.0</td>
<td>5.1</td>
<td>74.3</td>
</tr>
</tbody>
</table>

The limits of detection were calculated from three standard deviations of five replicate on-line total and labile dissolved trace metal measurements (Cu, Pb and Zn) of seawater equilibrated with 50 mg l⁻¹ LUPM. The measurements were performed at a flow rate of 1.0 ml min⁻¹ and a deposition time of 60 s (Table 3).

Reproducible total dissolved Cu and Pb measurements could not be undertaken with ASV, in the seawater sample, which had been UV digested within a few minutes prior to analysis. Hence the limits of detection of Cu and Pb were nearly twice than that of the concentrations encountered in seawater equilibrated with 50 mg l⁻¹ of LUPM. There was a broad interfering oxidation peak, between −0.5 and −0.3 V, which was located near the Pb and Cu redox potentials. This might have been caused by hypochlorite ions. Achterberg and van den Berg [15] found that this ion, present in UV digestion acidified seawater caused an interfering peak at −0.4 V, during the determination of Cu with AdCSV. This interference was found to disappear after 18 h [15]. For the current kinetic study, samples were therefore withdrawn, filtered and UV digestion on-line during kinetic studies. These aliquots were stored for >24 h, after which they were analysed for total Pb and Cu, by ASV with a 2 min deposition time. With this treatment and deposition time, the limits of detection of Cu and Pb were 25 and 12% of the total dissolved concentrated found in seawater equilibrated with 50 mg l⁻¹ of LUPM, respectively.

At the chosen deposition time of 120 s for the measurement of dissolved labile Pb and Zn, the limits of detection were 16 and 8% of the Pb and Zn concentrations for 50 mg l⁻¹ LUPM, respectively. The deposition time selected for AdCSV-labile Cu determinations was 30 s, the limit of detection being <10% of the measured dissolved labile Cu concentration from the LUPM kinetic experiments.

The accuracy of the Cu, Pb and Zn measurements using the on-line method was determined using standard reference materials. The accuracy of the Cu and Zn measurements were evaluated using three aliquots of seawater certified reference material (CASS-3, National Research Council, Canada), with ASV. Prior to analysis, the samples were UV irradiated for 6 h in acid cleaned 30 ml quartz tubes with a 400 W medium pressure Hg vapour lamp (Photochemical Reactors). Each aliquot was measured in triplicate. Table 4 illustrates that the observed recoveries were within the certified values.
Table 4
Accuracy of the on-line stripping voltammetric methods

<table>
<thead>
<tr>
<th>Reference material</th>
<th>Method</th>
<th>Observed value</th>
<th>Certified value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>AdCSV</td>
<td>8.95 ± 0.73 nM</td>
<td>8.14 ± 0.98 nM</td>
</tr>
<tr>
<td>Pb NIST 1648</td>
<td>ASV</td>
<td>0.609 ± 0.047%</td>
<td>0.655 ± 0.008%</td>
</tr>
<tr>
<td>Zn CASS-3</td>
<td>ASV</td>
<td>20.3 ± 1.5 nM</td>
<td>19.0 ± 3.8 nM</td>
</tr>
</tbody>
</table>

In contrast the accuracy of Pb ASV measurements by the on-line system was within that for the urban particulate reference material (NIST 1648), after total acid digestion.

3.7. Evaluation of the repeatability of the experimental set-up

The temporal progress of the desorption of labile and total Cu, Pb and Zn from LUPM (50 mg l⁻¹) into seawater is presented in Fig. 4(a)-(c), respectively. The results between the replica total dissolved Zn, Pb and labile Zn experimental runs had a mean relative standard deviation (R.S.D.) of <5%. AdCSV-labile Cu and ASV-labile Pb had a mean R.S.D. <10%. The poorest reproducibility was for total dissolved Cu (mean R.S.D. 13%). The reproducibility of these data are a significant improvement on the duplicated aerosol dissolution experiments made by Hamilton-Taylor et al. [9], where the mean R.S.D. of ASV-labile Cu, Pb and Zn were 26, 15 and 10%, respectively. The reproducibility and accuracy of the trace metal measurements carried out in their study may have been hampered further by sample filter paper adsorbing onto the working electrode.

3.8. Temporal progress of trace metal desorption from LUPM equilibrated in seawater

For Cu, Pb and Zn, the particle-seawater desorption process reached equilibrium within the lifetime of the experiments (up to 3 h). There was rapid desorption of Zn for 15 min after the addition of LUPM to seawater, and the equilibrium of Zn between the dissolved and particulate phase appeared to be reached within 1 h (Fig. 4(c)). In contrast the desorption kinetics for Cu was slower (Fig. 4(a)); the equilibrium was attained within 2 h. After 40 min equilibration of LUPM in seawater, readsorption of Pb onto the particles was observed (Fig. 4(b)). Following desorption, the particle reactive element Pb was likely to be re-adsorbed onto a different solid phase fraction of the aerosol population, possibly the carbonate and oxide phases of the LUPM [29]. Kersten et al. [30], in a multi-chamber experiment, also observed that after 100 h aerosol material had re-adsorbed Pb.

The release of metals from the aerosol material into seawater may be modelled, assuming that the desorption process comprises of two possible consecutive, reversible first order reactions [31].

This is presented in equation (1):

\[ S^- + M^{z+} \rightarrow S-M^{(z-1)+} + k_1 \]
\[ k_2 \]

The metal desorb from exchangeable sites on the aerosol material (low binding energy) into solution. The forward and reverse reaction being represented by \( k_1 \) and \( k_2 \) respectively. Over a longer period of time, metals within the particle matrix, may become involved in the partitioning process (this was the case for Pb in the current study) with forward and reverse constants \( k_2 \) and \( k_1 \). The desorption of metals may be quantified using an integrated form of the rate constant:

\[ [M^{z+}]_i = [M^{z+}]_e (1 - \exp(-k_1 + k_1) \tau) \]

Plotting \( \log_e \left( \frac{[M^{z+}]_e}{[M^{z+}]_e - [M^{z+}]_0} \right) \) against time will yield a straight line the slope of which is equal to \( (k_1 + k_1) \) where

\[ k_1 = \frac{[M^{z+}]_e (k_1 + k_1)}{[S-M^{(z-1)+}]_0} \]

\([M^{z+}]_i\) is the dissolved metal concentrations at time \( \tau \), \([M^{z+}]_e\) is equivalent to the dissolved metal concentration at equilibrium and \([S-M^{(z-1)+}]_0\), the initial exchangeable
Table 5
Aerosol-seawater solubility rate constants and response time (t) for total and labile dissolved Cu, Zn and Pb [LUPM] = 50 mg l⁻¹; UV/SW 25.2 ± 0.4 °C; dark condition

<table>
<thead>
<tr>
<th>Metal</th>
<th>k₋₁ (min⁻¹)</th>
<th>k₁ (min⁻¹)</th>
<th>k₋₂ (min⁻¹)</th>
<th>k₂ (min⁻¹)</th>
<th>t.resp (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Cu</td>
<td>0.015 ± 0.005</td>
<td>0.041 ± 0.016</td>
<td>-</td>
<td>-</td>
<td>19.8 ± 7.6</td>
</tr>
<tr>
<td>Labile Cu</td>
<td>0.0047</td>
<td>0.049 ± 0.002</td>
<td>-</td>
<td>-</td>
<td>19.7 ± 1.1</td>
</tr>
<tr>
<td>Total Zn</td>
<td>0.049 ± 0.001</td>
<td>0.042 ± 0.004</td>
<td>-</td>
<td>-</td>
<td>10.9 ± 1.3</td>
</tr>
<tr>
<td>Labile Zn</td>
<td>0.056</td>
<td>0.06 ± 0.001</td>
<td>-</td>
<td>-</td>
<td>8.8 ± 0.1</td>
</tr>
<tr>
<td>Total Pb</td>
<td>0.052 ± 0.02</td>
<td>0.082 ± 0.05</td>
<td>0.006 ± 0.001</td>
<td>0.0023 ± 0.01</td>
<td>5.6 ± 1.3</td>
</tr>
<tr>
<td>Labile Pb</td>
<td>0.039 ± 0.002</td>
<td>0.114 ± 0.008</td>
<td>0.004 ± 0.001</td>
<td>0.0008 ± 0.002</td>
<td>6.6 ± 0.6</td>
</tr>
</tbody>
</table>

metal concentration (obtained by a combined 1 M ammonium acetate and 25% acetic acidic/1 M hydroxylamine hydrochloride leach, see [32] for more details). The chemical response time, t.resp, i.e. the time for the first stage of Eq. (1) to attain 63% of the new equilibrium [31] is given by

\[ t_{\text{resp}} = \frac{1}{k_1 + k_{-1}} \]  

(4)

The advantage with the current experimental approach over batch wise studies is that a finer temporal resolution of the initial metal desorption is acquired, enabling a more accurate calculation of the rate constants. A typical plot of the logₑ function against time is highlighted in Fig. 5 for labile Cu dissolution from LUPM (50 mg l⁻¹) in UV/SW.

The k₂ and k₋₂ rate constants (for Pb only) were calculated by applying a Runga-Kutta integration routine within the MODELMAKER 4 software modelling package. The tabulated rate constants are presented in Table 5. Considering the rate constants it is clear that the rate of metal desorption follows in the order of total Pb (0.052 min⁻¹) ≈ total Zn (0.049 min⁻¹) > total Cu (0.015 min⁻¹). These rates are also reflected in the response times which were 19.8, 10.9 and 5.0 min, respectively, for total dissolved Cu, Pb and Zn. This trend of lower rates of desorption for Cu is consistent with Cu being more strongly (and to a greater extent) associated with organic phases on the particle surface of the aerosol material. Up to 30% organic associations for Cu have been stated for LUPM [32], determined by a five stage sequential leach scheme. Whereas Zn and Pb had comparatively lower organic phase associations (5 and 15%, respectively). Prior to desorption, the Cu would have had to dissociate from the aerosol organic material. The relative importance of strong Cu-organic interactions on the organic phase of the aerosol may explain the slow kinetics of this element. Maring and Duce [33] also observed comparatively slower Cu desorption kinetics for a remote marine aerosol. In their study, after 40 min the seawater solubility of Cu was 20%, after 6 h it had reached 99%. These results indicate that the Cu seawater solubility data from other studies that only used 1 h equilibration time might be an underestimate [2, 27, 34]. The comparatively faster desorption rate constants for Pb/Zn may in addition be explained by the higher association with the "exchangeable" fraction of aerosol material (67 and 45%, respectively for Pb and Zn [32] compared to 35% for Cu).

Table 5 also illustrates the very low rate constants for the migration of Pb onto higher energy bonding sites, leading to the readsorption of Pb onto the aerosol material. These rate constants are an order of magnitude lower than those for Pb desorption, indicating the slow kinetics of this partitioning process. Further interpretation of trace metal desorption kinetic profiles are presented in [35].

4. Conclusions

A metal monitor for the determination of aerosol trace metal dissolved/particulate interactions was successfully constructed, validated and applied. There are several advantages of the current experimental set-up and protocol over kinetic experiments that required discrete (batch-wise) removal of seawater suspension: (i) after the addition of the dust to the seawater, the reaction vessel is covered for the duration of the experiment, to prevent sample contamination; (ii) the on-line system minimised sample handling, therefore further potential for sample contamination; (iii) fine temporal resolution can be achieved (as low as 45 s for labile Cu); (iv) there was minimal incubated seawater loss (~15% of the original volume) during the lifetime of the kinetic experiment (up to 3 h).

The fully automated dissolved metal monitor described can also be adapted for the measurement of other trace metals, such as Fe, Ni, Co, Cd, Mo, Sb, Sn, Ti, U, V and Cr (by AdCSV [30]). This could be achieved by changing the added reagents and voltammetric conditions. The experimental set-up could also be applied to other environmental studies such as trace metal particle/dissolved interactions in rainwater, estuarine and wastewaters; and enable the
evaluation of the impact of environmental factors including particle concentrations, temperature, types of particles, effect of micro-organisms or light, on these interactions. From such exciting simulation studies a better understanding and more accurate modelling of trace metal dissolved/particle interactions within the aquatic environment would be possible.

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References