OCEANIC SOURCES OF COPPER TO THE ATLANTIC AEROSOL*

R. CHESTER and K.J.T. MURPHY

Department of Oceanography, The University, Liverpool L69 3BX (United Kingdom)

(Received August 20th, 1985; accepted August 27th, 1985)

ABSTRACT

Copper has been determined in a series of aerosols collected on a north-south Atlantic Ocean transect and its distribution has been related to those of Na, the marine source indicator, and Al, the crustal source indicator. Average Cu \( EF_{sea} \) values for a number of sample groups, calculated with respect to ambient surface sea water, range from a maximum of \( 60 \times 10^3 \) for aerosols collected off the U.K. coast to a minimum of \( 3.2 \times 10^3 \) for those from the remote South Atlantic westerlies. However, Cu can undergo fractionation in the micro-layer at the air/sea interface leading to sea-salts having enhanced Cu concentrations relative to bulk sea water. From the relationship between the concentrations of Cu and Na in the complete Atlantic aerosol data set, a minimum Cu/Na ratio was identified which was equivalent to a Cu enrichment of \( \sim 1.9 \times 10^3 \), relative to bulk sea water. This enrichment is similar to those estimated by other workers from the BIMS experiments (\( \sim 0.8 \times 10^3 \)), and from cascade impactor size-fractionated data (\( \sim 1.4 \times 10^3 \)). Using the relative sea water enrichment factor of \( 1.9 \times 10^3 \), the oceanic contribution of Cu to the total Cu in the Atlantic aerosol was calculated and was compared with that having a crustal source and that from a third “excess” source, which was probably mainly pollutant. It was shown that in remote areas of the Atlantic, where the influence of continental sources is decreased, oceanic Cu can make up over half of the total Cu in the aerosol.

INTRODUCTION

Research carried out over the past two decades or so has shown that some elements, such as Cu, Pb and Cd, are enriched in the marine aerosol relative to the natural sources. Much of this enrichment can result from the introduction of anthropogenic material into the atmosphere (see, e.g., Lantzy and MacKenzie, 1979). However, in order to assess the extent to which anthropogenically-derived elements affect an aerosol, account must be taken of the input from natural sources. For the marine aerosol, the two most important natural processes for the direct, low-temperature generation of aerosol material are crustal weathering and sea-salt production.

In order to assess the enrichments of an element relative to crustal and marine sources the “excess” fractions are defined with respect to the equations:

\*Dedicated to Professor John P. Riley in honour of his contributions to the marine chemical sciences.

0048-9697/86/$03.50 © 1986 Elsevier Science Publishers B.V.
\[ EF_{\text{crust}} = \frac{(E/Al)_{\text{air}}}{(E/Al)_{\text{crust}}} \]

\[ EF_{\text{sea}} = \frac{(E/Na)_{\text{air}}}{(E/Na)_{\text{sea}}} \]

in which \((E/Al)_{\text{air}}\) and \((E/Na)_{\text{air}}\) are the concentrations of an element, and either Al or Na, in the aerosol, and \((E/Al)_{\text{crust}}\) and \((E/Na)_{\text{sea}}\) are their concentrations in average crustal material and bulk sea water, respectively. That is, Al is employed as a crustal indicator element and Na as a marine indicator element. One of the main problems in the use of these enrichment factors (EFs) involves selecting the correct composition for the source material. For the crustal source it is usual to take the average composition of crustal material, and to limit the assessment of the resulting EFs to the order of magnitude level. Thus, \(EF_{\text{crust}}\) values close to unity are taken as an indication that an element has a mainly crustal source, and those \(> 10\) are considered to indicate that a substantial portion of the element has a non-crustal origin. For the oceanic source, however, the selection of a baseline trace metal composition is much more difficult. One reason for this is that the distributions of many trace metals in surface sea water can vary over a large range from one marine region to another. To a large extent this can be overcome as reliable trace metal data is now being produced for a variety of marine environments, thus allowing the \((E/Na)_{\text{sea}}\) term to be adjusted on a regional basis. There is, however, a much more fundamental problem involved in the assessment of marine enrichment factors, and this arises from the nature of the processes involved in the generation of sea-salts.

According to Berg and Winchester (1978), the bursting of bubbles produced by the trapping of air in surface waters by breaking waves, or whitecaps, is the principal mechanism for the formation of sea-salts. During this bubble-bursting process part of the sea surface micro-layer can be skimmed off. This micro-layer can contain concentrations of many trace metals which are enhanced relative to bulk sea water (for a discussion of this topic see Buat-Menard, 1983). As a result, considerable fractionation of trace metals can take place during the formation of sea-salts and bulk sea water itself will not therefore be the constraining factor on the composition of sea surface-generated particles, even if the sea surface itself does act as a significant elemental source.

A number of attempts have been made to evaluate a more realistic source composition for material generated from the sea surface by relating it directly to the micro-layer. One of the most rewarding ways of making such an evaluation has been by the collection and analysis of bubble-produced sea-salts using a Bubble Interfacial Microlayer Sampler (BIMS) (see, e.g., Fasching et al., 1974; Piotrowicz et al., 1979). Until recently, the BIMS in situ studies of bubble-produced aerosols had been largely confined to estuarine and coastal environments. However, Weisel et al. (1984) have recently reported data obtained from BIMS experiments carried out in the western North Atlantic. These data show the degree to which trace metals can be fractionated during the production of sea-salts, and so offer a much more realistic baseline for the evaluation of the sea surface as a source of elements to the marine aerosol.
Copper is a trace metal which can be concentrated in the micro-layer up to $10^3-10^4$ times relative to bulk sea water (see, e.g., Szekielda et al., 1972; Cattel and Scott, 1978), and it is an important element from the point of view of sea surface fractionation because once it is delivered to the air/sea interface it can become involved in oceanic biogeochemical cycles. The distribution of Cu in the marine atmosphere can be affected by man-made perturbations and it is therefore necessary for our understanding of the marine chemistry of the element to know the extent to which the Cu deposited at the sea surface undergoes recycling back into the atmosphere. In the present paper an attempt is made to assess the influence of sea-salt-associated Cu on the distribution of total Cu in a series of aerosols collected on a north—south Atlantic Ocean transect extending from 55°N to 65°S. Chester et al. (1984) pointed out that in many ways this Atlantic transect is ideal for the study of variations in the concentrations of major aerosol components because it passes through a number of wind systems having different particle catchment regions. These wind systems include: the North Atlantic westerlies, with catchments in the European “pollution” belt; the north east trades, with catchments in the North African deserts; and the South Atlantic westerlies, which are relatively remote from the land masses. That is, the transect represents increasingly more pristine oceanic environments along a north—south axis.

METHODS OF COLLECTION AND ANALYSIS

The atmospheric samples were collected on board R.R.S. Shackleton during a number of cruises over the period 1980—1982, and the general sample locations are illustrated in Fig. 1. Particulate samples were taken using a high-volume filter system which incorporated Whatman 41 filters (165 mm exposed diameter). The system was based on a heavy-duty centrifugal pump connected to two clear plastic filter holders in such a manner that no metal parts were in contact with the sampled air prior to its passing through the filters. The filter rig was mounted ~6 m beyond the bows of the ship, and air flow rates (typically, 2 m$^3$ min$^{-1}$) were measured using an orifice-type flow meter. The filters, two of which were exposed during each collection, were sealed in plastic bags before and after exposure. None of the data reported in the present investigation were obtained under sampling conditions in which following winds occurred.

In the analytical procedure all sampling handling was carried out in a clean-air cabinet and the filters were dissolved in redistilled HNO$_3$ and Aristar HF in PTFE beakers. The digests were stored in polystyrene vials. A number of blank filters were taken through the shipboard handling procedures, without actual exposure to the atmosphere in the rig, and blanks from the same batch as those used for the collections were run through the analytical techniques. After appropriate correction was made for filter
blanks (signal-to-blank ratio was typically $> 10:1$), the elemental concentrations for each individual collection were calculated as the means of the two exposed filters; average agreement between Cu concentrations for filter pairs was better than 10% for the data set. Copper was determined by an atomic absorption technique using graphite furnace atomization; Al was determined by an atomic absorption technique employing the flame mode; Na was determined by flame photometry. Replicate determinations on subsamples of a mesh-collected atmospheric particulate, for which sufficient sample was available, showed that the analytical techniques had coefficients of variations of 1.9% for Cu, 2.4% for Al and 3.6% for Na.
TABLE 1
Cu, Al and Na DATA FOR THE ATLANTIC AEROSOL

<table>
<thead>
<tr>
<th>Oceanic region</th>
<th>Average concentrations (ng m(^{-3}) of air)(^a)</th>
<th>Cu (EF_{\text{crust}})(^b)</th>
<th>Cu (EF_{\text{sea}})(^b)</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu  Al  Na</td>
<td>Cu EF(_{\text{crust}})</td>
<td>Cu EF(_{\text{sea}})</td>
<td></td>
</tr>
<tr>
<td>North Atlantic; U.K. coastal area</td>
<td>1.9  187  1729</td>
<td>17</td>
<td>60 (\times 10^3)</td>
<td>16</td>
</tr>
<tr>
<td>North Atlantic; eastern margins,</td>
<td>1.0  48   3907</td>
<td>30</td>
<td>22 (\times 10^3)</td>
<td>7</td>
</tr>
<tr>
<td>westerlies</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>North Atlantic; eastern margin,</td>
<td>2.4  827  5444</td>
<td>8.2</td>
<td>37 (\times 10^3)</td>
<td>6</td>
</tr>
<tr>
<td>Straits of Gibraltar</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>North Atlantic; eastern margin,</td>
<td>4.5  5925 10486</td>
<td>1.2</td>
<td>36 (\times 10^3)</td>
<td>7</td>
</tr>
<tr>
<td>north east trades</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>South Atlantic; westerlies</td>
<td>0.31  23   5566</td>
<td>34</td>
<td>4.7 (\times 10^3)</td>
<td>6</td>
</tr>
<tr>
<td>South Atlantic; westerlies</td>
<td>0.29  2.7  7433</td>
<td>225</td>
<td>3.2 (\times 10^3)</td>
<td>5</td>
</tr>
</tbody>
</table>

For details of bulk sea water concentrations used in calculation, see text.

\(^a\) Geometric means.

\(^b\) Arithmetic means.

RESULTS AND DISCUSSION

The samples collected on the north–south Atlantic transect have been assigned to a number of groups, which have been defined mainly on the basis of geographical position and prevailing wind direction. The average atmospheric concentrations of Cu, Al and Na for each of the groups are given in Table 1, together with the average \(EF_{\text{crust}}\) and \(EF_{\text{sea}}\) values for Cu.

The average Cu \(EF_{\text{crust}}\) for the north east trades aerosol is close to unity, indicating that in this region the input of Saharan dust dominates the aerosol population. Aerosols from the other regions have higher Cu \(EF_{\text{crust}}\) values, which reach a maximum of 225 in the South Atlantic westerlies. It may be concluded, therefore, that it is only at low latitudes that the Cu in the Atlantic aerosol has a mainly crustal source.

The distribution of dissolved Cu in Atlantic surface sea waters varies with location. For example, work by Kremling (1983) showed that in surface coastal waters of the North Sea the concentrations of Cu (average \(~200\, \text{ng}\, \text{l}^{-1}\)) are about twice as high as those in the adjacent open ocean (average \(~100\, \text{ng}\, \text{l}^{-1}\)). Other variations will occur under different circulation
conditions; for example, generally low concentrations will be found in the surface gyres. However, none of the present aerosol samples were collected over the central gyres and according to the data given by Boyle and Edmonds (1975) and Boyle et al. (1981) a reasonable average Cu concentration for the Atlantic non-gyre and Antartic surface waters is probably around 130 ng l\(^{-1}\). Therefore, in order to make a first approximation for the \(EF_{\text{sea}}\) values for the Atlantic aerosol a bulk surface sea water dissolved Cu concentration of 130 ng l\(^{-1}\) was assumed for the North and South Atlantic samples, with those from the U.K. coast being assigned a value of 200 ng Cu l\(^{-1}\).

The highest \(EF_{\text{sea}}\) value for Cu is found for the aerosol from the U.K. coast, i.e. the location where the input of pollutants should be strongest. The most prominent trend in the Cu \(EF_{\text{sea}}\) data is the general decrease in the values southwards, reaching a minimum of \(3.2 \times 10^3\) in the South Atlantic westerlies aerosol. This is in contrast to the Cu \(EF_{\text{crust}}\) values, which were highest in the South Atlantic westerlies. Marine aerosol Cu \(EF_{\text{sea}}\) values given in the literature include \(60 \times 10^3\) for the western North Atlantic (Weisel et al., 1984), which is in the same range as those for the North Atlantic in the present paper, and \(3 \times 10^3\) for the remote North Pacific, which is similar to those for the remote South Atlantic.

In remote marine areas, therefore, Cu \(EF_{\text{sea}}\) values appear to indicate an aerosol enrichment of about 3000 over that of local bulk sea water. However, it was pointed out above that bulk sea water is not the source for those elements, such as Cu, which are fractionated at the micro-layer air/sea interface. The BIMS experiment was an attempt to assess the extent of this fractionation. During these experiments bubbles were artificially generated and the resultant sea-salt particles were collected on filters, but no attempt was made to differentiate between the bubble scavenging of particulate and dissolved forms of trace metals. The net concentration of a trace metal on the sea-salt particles was then used, together with a North Atlantic sea water concentration, to calculate a BIMS \(EF_{\text{sea}}\) value. For Cu, bubbles were generated at a depth of \(< 0.1\) m, and relative to a sea water concentration for the North Atlantic of 100 ng l\(^{-1}\), the geometric average BIMS Cu \(EF_{\text{sea}}\) value was \(0.8 \times 10^3\). That is, sea-salt particles generated from the sea surface are enhanced 800-fold with respect to bulk sea water. Weisel et al. (1984) made the assumption that the BIMS \(EF_{\text{sea}}\) values can be applied globally, and used them to develop the interesting concept of a relative oceanic enrichment factor \((RE_{\text{sea}})\) which is the aerosol \(EF_{\text{sea}}\) value (calculated with respect to ambient sea water) divided by the BIMS \(EF_{\text{sea}}\) value. Thus, the western North Atlantic aerosol, which has a Cu \(EF_{\text{sea}}\) of 60 000 (see above), has a Cu \(RE_{\text{sea}}\) of only 75.

It can be seen from the data in Table 1 that the lowest average Cu \(EF_{\text{sea}}\) value found in the present work is that for the South Atlantic westerlies aerosol. This is the most pristine of the marine environments studied and the Cu \(EF_{\text{sea}}\) value of \(3.2 \times 10^3\) approaches that of the BIMS Cu \(EF_{\text{sea}}\) within a factor of about four. This would suggest that in this region of the South
Atlantic the sea surface is a non-trivial source for Cu in the aerosol. However, this was based on the assumption that the BIMS $EF_{\text{sea}}$ enhancements can be applied globally, and in order to test this the Cu—Na relationship was evaluated for the complete Atlantic aerosol data set.

In the initial discussion, trends in the distribution of the Cu $EF_{\text{sea}}$ values in the Atlantic aerosol were established on the basis of group averages. This is a useful approach since, for the Atlantic, the aerosols in the individual groups have their predominant inputs from different particle sources. However, within these latitudinally-defined groups there are variations in the strengths of the inputs of the various aerosol components, e.g. crustal dust and anthropogenic material. In order to examine the overall relationship between Cu and the generation of sea-salts, Cu concentrations in individual aerosol samples were plotted against those of Na (the marine indicator element) in the same samples for the Atlantic data set. Although most of the Na in the marine aerosol has a sea surface origin, crust-derived Na can be significant in areas which receive relatively large injections of continental dust. In order, therefore, to facilitate the interpretation of the Cu vs Na data plot in terms of a marine source, the crustal component of both elements was subtracted from the total aerosol concentrations on the basis of the $EF_{\text{crust}}$ values. The resulting Cu vs Na aerosol plot is illustrated in Fig. 2.

It can be seen from Fig. 2 that an interesting trend in the distribution of Cu in the Atlantic aerosol emerges when the data is displayed in the form of a Cu vs Na plot. This trend indicates that there is a tendency towards a minimum Cu/Na ratio in the Atlantic aerosol, and on the plot the relationship can be displayed in the form of a minimum $EF_{\text{sea}}$ line. The samples falling close to the $EF_{\text{sea}}$ minimum line are from a number of aerosol populations, and the line appears to be a real feature of the plot. Such a feature would be expected if a specific Na concentration was associated with a specific Cu concentration, and if for some samples the Na, i.e. the sea-salt component, became the principal contributor to the aerosol Cu. For other aerosol samples, Cu from non-oceanic sources will cause deviations from the $EF_{\text{sea}}$ minimum line. This will produce a “shotgun” type of plot as the non-oceanic Cu, e.g. that from pollutant sources, gives rise to relatively high Cu/Na ratios in the aerosols.

The BIMS $EF_{\text{sea}}$ data for Cu indicates an enrichment of $\sim 0.8 \times 10^3$ relative to bulk sea water, and this allows “BIMS lines” to be drawn on the Cu vs Na plot for a variety of surface sea water concentrations, and two of these lines have been drawn on Fig. 2. It can be seen that at the surface water Cu concentration used in the present work, the BIMS line plots reasonably close to that of the Cu $EF_{\text{sea}}$ minimum line derived from the Cu vs Na Atlantic aerosol relationship. For this Cu $EF_{\text{sea}}$ minimum line, the Cu enrichment relative to bulk sea water is $\sim 1.9 \times 10^3$, which is within a factor of $< 2.5$ of the BIMS enrichment value ($0.8 \times 10^3$). This is a surprisingly good agreement considering all the uncertainties in making such estimates.
Fig. 2. Cu vs Na plot in the Atlantic aerosol. Concentrations are on a non-crustal basis for high-volume collected samples. The broken 45° line is an approximation of the minimum Cu/Na ratio in the Atlantic aerosol. The sample having a Na concentration of \( \sim 8 \times 10^4 \, \text{ng m}^{-3} \) of air is included in the plot, although it has probably suffered from bow spray contamination. Two BIMS lines are drawn on the figure, using the BIMS sea-salt enrichment factor of \( 0.8 \times 10^3 \) relative to ambient sea water. B1 is for the Atlantic, at a surface water Cu concentration of 130 ng l\(^{-1}\); B2 is for the North Pacific central gyre, at a surface water Cu concentration of 30 ng l\(^{-1}\). Aerosol groups are identified by the following symbols. (●) U.K. coastal. (+) North Atlantic westerlies. (*) Straits of Gibraltar. (X) North east trades. (□) South east trades. (●) South Atlantic westerlies. The symbol (○) identifies an additional sub-set of samples; these were collected on the eastern margins of the Atlantic between \( \sim 30 \) and \( \sim 10^\circ N \), but were not included in the text discussion because the winds at the time of collection were too variable to allow the samples to be allocated to a specific group.
Further evidence for the magnitude of the enrichment of Cu in sea-salts has been provided from the study of the size distribution of elements in the marine aerosol. The sources of elements in the marine aerosol are often reflected in their mass size distributions. For example, cascade impactor data reported by Duce et al. (1983) for the aerosol collected at Enewetak (North Pacific) showed that ~75% of the total mass of the crustal elements Al, Fe and Mn was found on particles with diameters in the range ~0.92 to ~3.0 μm. The sea-salt elements Na, Mg, K and Cl were also associated with large particles, with >75% of their mass being on particles in the range ~3.0 to ~7.2 μm. In contrast, those elements which are enriched in the atmosphere, e.g. Cu, Pb and Zn, tend to be concentrated on small, sub-micrometer, particles. However, during the wet season at Enewetak, Cu and Zn were also highly enriched on larger particles with diameters of ~7.2 μm. According to Duce et al. (1983) this suggested that Cu and Zn were enriched on large sea-salt particles. Although these large particles were mainly composed of sea-salt during the wet season, some mineral aerosol was also collected on the same cascade impactor stage. Arimoto et al. (1985) made a correction for this crustal aerosol and calculated an adjusted large particle Cu enrichment of 1.4 × 10^3 relative to ambient sea water. This is very close to the Atlantic Cu $EF_{sea}$ minimum of 1.9 × 10^3 reported in the present work.

It should be pointed out, however, that extreme caution must be exercised when attempting to interpret the enrichment of trace metals on sea-salts. The formation of these salts by bubble production can involve the scavenging of both dissolved and particulate elements from the underlying sea water and from the surface micro-layer itself. Particles can be deposited at the sea surface by wet and dry deposition and some of them may be recycled back into the atmosphere during sea-salt production, thus making the trace element enrichment processes difficult to unravel. Some of the complexities involved in the transfer of material across the air/sea interface have been highlighted in terms of Pb by the very detailed and careful work reported by Settle and Patterson (1982). The general picture which emerged from their study, carried out at Enewetak (North Pacific), can be summarized as follows. The isotope composition of Pb in dry deposition showed that is must have originated from only a fraction of the Pb in the atmosphere, and the authors suggested that most of the Pb in dry deposition was associated with sea-salts. They were also able to demonstrate that the Pb isotope composition of precipitation (wet deposition) at the site was markedly different from that in sea water. Some of the Pb in the precipitation was contained in discrete, sub-micron-sized, particles and it was suggested that these Pb-rich particles could become trapped in organic films in the micro-layer. As a result, much of the Pb in the sea-salt aerosol may have originated from these Pb-rich particles which are recycled from the micro-layer. Further evidence to support this was provided by the fact that the isotope composition of Pb in the sea salts was similar to that in the precipitation.

It is clear, therefore, that a knowledge of the forms in which the elements
are present in sea-salts is critical before the nature of their association with oceanic recycling can be fully understood. However, evidence from both the BIMS experiments and the cascade impactor size-fractionated measurements have indicated that there appears to be a sea surface enrichment for Cu of around 1–2 × 10³ during the formation of sea-salts, and this has been confirmed using a different approach in the present work. Weisel et al. (1984) used their BIMS $EF_{sea}$ data to estimate the oceanic production rates of atmospheric trace metals, and concluded that on a global scale only a few percent of the atmospheric burden of Cu can be accounted for by an oceanic source. However, they pointed out that direct comparisons of the magnitudes of the source strengths for any element is not straightforward because some sources, such as anthropogenic emissions, are localized, whereas others, such as the ocean surface, cover large regions of the globe. As a consequence, they concluded that in the remote marine atmosphere, where the influence of continental sources is minimal, the ocean is a potentially important source for Cu, and a number of other elements, on particles having diameters greater than ~3 μm. This type of enrichment is apparent from the data given in the present paper, which shows the existence of a minimum $EF_{sea}$ value for Cu which is reached when sea-salt components dominate the aerosol. This can happen under a variety of conditions, and the Cu $EF_{sea}$ minimum value leads to a Cu enrichment, relative to ambient bulk sea water, of ~ 1.9 × 10³ which is similar to that of the BIMS and cascade impactor measurements.

If the Cu enrichment of 1.9 × 10³ is assumed to apply over the whole Atlantic, a relative oceanic enrichment factor ($RE_{sea}$) can be calculated following Weisel et al. (1984), but using the new value; i.e. $RE_{sea}$ is obtained by dividing the $EF_{sea}$ (calculated with respect to ambient sea water) by 1.9 × 10³. The $RE_{sea}$ values obtained in this way are given in Table 2, from which it can be seen that relative to sea surface fractionation, Cu is enhanced in sea-salts by a factor which ranges from ~32 in the U.K. coastal aerosol to ~1.7 in that collected from the South Atlantic westerlies.

The marine aerosol is made up of elements from a variety of sources. The contributions from the crustal source can be estimated from the Al concentrations if the ratio of an element to Al is assumed to be the same in the crust and the crustal component of an aerosol. The estimation of the contribution from the oceanic source is more difficult because for those elements which undergo fractionation at the sea surface it cannot be assumed that the ratio of an element to Na is the same in the aerosol as in bulk sea water. However, a first approximation estimate of the contribution made to an oceanic source can be obtained from the $RE_{sea}$ value. Using the present data set, therefore, the crustal and oceanic contributions made to the total Cu in the aerosols from each of the various groups was calculated. The remaining Cu, i.e. that not having either a crustal or an oceanic source, is designated “excess” Cu. The results are given in Table 3.

It can be seen from the data in Table 3 that the highest crustal contribution of Cu is found for the north east trades aerosol, for which
TABLE 2
RELATIVE OCEANIC ENRICHMENTS OF Cu IN THE ATLANTIC AEROSOL

<table>
<thead>
<tr>
<th>Oceanic region</th>
<th>Cu REsea a</th>
</tr>
</thead>
<tbody>
<tr>
<td>North Atlantic; U.K. coastal area</td>
<td>32</td>
</tr>
<tr>
<td>North Atlantic; eastern margin, westerlies</td>
<td>12</td>
</tr>
<tr>
<td>North Atlantic; eastern margin, Straits of Gibraltar</td>
<td>20</td>
</tr>
<tr>
<td>North Atlantic; eastern margin, north east trades</td>
<td>19</td>
</tr>
<tr>
<td>South Atlantic; south east trades</td>
<td>2.5</td>
</tr>
<tr>
<td>South Atlantic; westerlies</td>
<td>1.7</td>
</tr>
</tbody>
</table>

aFor method of calculation, see text.

TABLE 3
SOURCES OF Cu FOR THE ATLANTIC AEROSOL

<table>
<thead>
<tr>
<th>Oceanic region</th>
<th>Sources (expressed as a % of total Cu)a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oceanic Cu</td>
</tr>
<tr>
<td>North Atlantic; U.K. coastal area</td>
<td>3.2</td>
</tr>
<tr>
<td>North Atlantic; eastern margin, westerlies</td>
<td>9.0</td>
</tr>
<tr>
<td>North Atlantic; eastern margin, Straits of Gibraltar</td>
<td>5.2</td>
</tr>
<tr>
<td>North Atlantic; eastern margin north east trades</td>
<td>5.3</td>
</tr>
<tr>
<td>South Atlantic; south east trades</td>
<td>41.3</td>
</tr>
<tr>
<td>South Atlantic; westerlies</td>
<td>59.0</td>
</tr>
</tbody>
</table>

aFor details of source calculations, see text.
crust-derived Cu makes up \( \sim 90\% \) of the total Cu. For the aerosol from the Straits of Gibraltar, which is influenced by material originating in the North African deserts, crust-derived Cu makes up \( \sim 25\% \) of the total. However, over the rest of the Atlantic, crust-derived Cu makes up only between \( \sim 1 \) and \( \sim 10\% \) of the total aerosol Cu.

When the \( RE_{\text{sea}} \) value is used to estimate Cu derived from the sea surface, it is apparent that there are large variations in the contributions made to the total aerosol Cu from this source. However, unlike crustal material, variations in the concentrations of sea-salt are not due to massive fluctuations in the source strength, such as those found for the crustal source at low latitudes in pulses of Saharan dust transport. Sea-salt concentrations do vary, dependent on variables such as wind speed and height above the sea surface, but the reservoir is present at all latitudes and the concentrations do not vary to the same degree as those of crustal material. As a result, the sea-salt may be regarded as a background and the proportions in which it is present in the marine aerosol are largely dependent on the extent to which it is diluted by other components, e.g. crustal dust and anthropogenic material. Because of this, elements associated with sea-salts will make their highest contributions in regions in which other element-contributing components are present in only small amounts. This can be seen clearly in the present data set. Over the North Atlantic eastern margins ocean-derived Cu makes up \( <10\% \) of the total Cu, but in the remote South Atlantic westerlies this rises to an average of \( \sim 59\% \) of the total Cu. In remote regions like this, therefore, the present work confirms the suggestion made by Weisel et al. (1984) that sea-salt (i.e. large particle) Cu is an important aerosol component. The amount of Cu contributed from sea-salts will vary from one marine region to another. For example, a BIMS line is drawn on Fig. 2 for the North Pacific central gyre. Here, the surface sea water Cu concentration is only \( \sim 30 \text{ng} l^{-1} \) (Bruland, 1980), and as a consequence the oceanic Cu background associated with sea-salt will make a smaller contribution to the marine aerosol than in non-gyre regions, assuming a constant sea-salt production rate.

The “excess” Cu in the Atlantic aerosol can have a variety of sources which include volcanic activity, rock volatilization, release from plant surfaces, forest fires and anthropogenic emissions. According to the Cu source strength estimates made by Weisel et al. (1984) anthropogenic inputs exceed those from volcanoes and vegetation by at least an order of magnitude, and since the highest contributions of “excess” Cu are found in aerosols from the European latitudes it is likely that much of it has an anthropogenic source. For these aerosols “excess” Cu makes up almost 90% of the total Cu. In contrast, “excess” Cu contributes only about 40–50% of the total Cu in the South Atlantic aerosol.
CONCLUSIONS

Cu $EF_{sea}$ values for the Atlantic aerosol, calculated with respect to ambient bulk sea water, range from a maximum of $60 \times 10^3$ for those collected off the U.K. coast to a minimum of $3.2 \times 10^3$ for those from the South Atlantic westerlies. However, Cu can undergo fractionation in the sea surface micro-layer leading to sea-salts having enhanced concentrations relative to bulk sea water. From the relationship between the concentrations of Cu and Na in the Atlantic aerosol a minimum Cu/Na ratio was identified which was equivalent to a Cu enrichment of $\sim 1.9 \times 10^3$ relative to bulk sea water. This enrichment was reasonably similar to those estimated from the BIMS experiments ($\sim 0.8 \times 10^3$) and from cascade impactor, size-fractionated, data ($\sim 1.4 \times 10^3$).

Using the relative sea water enrichment factor of $1.9 \times 10^3$ the oceanic contribution of Cu to the total Cu in the Atlantic aerosol was calculated. It was shown that in remote marine areas, where the influence of continental sources is decreased, oceanic Cu can make up over half of the total Cu in the aerosol.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the kind assistance given to them during the project by the following: the Master, officers and crew of the R.R.S. Shackleton; R.V.S. (Barry) for help with the design and fitting of the shipboard collection systems; the Natural Environment Research Council (London) for financial support for the project; Dr P.F. Barker, Dr P. Hughes and Dr S.R. Ferguson, Chief Scientists during a number of cruises.

REFERENCES


