Trace elements in the atmosphere over the North Atlantic

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Abstract. The concentrations of trace elements in aerosol particles from the atmosphere over the North Atlantic Ocean were determined as part of a program designed to characterize the chemical climatology of the region. For these studies, which were part of the Atmosphere-Ocean Chemistry Experiment (AEROCE), 2 years of samples were collected at Tudor Hill, Bermuda (BTT), and at Ragged Point, Barbados (BAT); and 1 year of samples was collected at Mace Head, Ireland (MHT) and at the Izaña Observatory, Tenerife, Canary Islands (IZT). One major component of the aerosol was atmospheric dust, and the ranking for the median mineral dust concentrations as represented by aluminum was BAT > IZT > BTT > MHT. The Al concentrations at BAT, IZT, and BTT ranged over 4 orders of magnitude, i.e., from 0.001 to 10 \( \mu g m^{-3} \). At MHT the maximum dust concentrations were about a factor of 10 lower than at the other sites, but the lower end of the range in dust concentrations was similar at all sites. The mineral dust concentrations generally were highest in summer, and the flux of atmospheric dust was dominated by sources in North Africa. The elements showing clear enrichments over the concentrations expected from sea salt or crustal sources were I, Sb, Se, V, and Zn. At Izaña, which is in the free troposphere (elevation ~2360 m), the concentrations of Se and I were much lower than at the boundary layer sites; this difference between sites most likely results from the marine emissions of these elements. The impact of pollution sources on trace element concentrations was evident at all sites but varied with season and location. The concentrations of elements originating from pollution sources generally were low at Barbados. Analyses of trace element ratios indicate that there are large-scale differences in the pollution emissions from North America versus those from Europe and Africa. Emissions from pyrometallurgical industries, steel and iron manufacturing, and possibly biomass burning are more evident in the atmospheric samples influenced by transport from Europe and Africa.

1. Introduction

The Atmosphere-Ocean Chemistry Experiment (AEROCE) is a multidisciplinary program focusing on the atmospheric and marine chemistry of the North Atlantic Ocean region. The trace element studies described here were conducted for AEROCE in part as a result of concerns over perturbations to biogeochemical cycles caused by human activities. In addition, the chemistry and transport of mineral aerosol is considered in some detail because the magnitude of the dust flux from Africa to the North Atlantic is important from a geochemical standpoint [e.g., Duce et al., 1991]. In this paper we present results from the four AEROCE stations (Figure 1): Ragged Point, Barbados (BAT, 13.18°N, 59.43°W); Tudor Hill, Bermuda (BTT, 32.24°N, 64.87°W); Mace Head, Ireland (MHT, 53.43°N, 9.73°W); and the Izaña Observatory, Tenerife (IZT, 28.30°N, 16.48°W).

AEROCE is providing a unique record of long-term trends and climatological average concentrations of a variety of trace substances in the atmosphere over the North Atlantic. A major focus of our program is to characterize the chemical climatology of trace elements in aerosol particles over the North Atlantic Ocean. More specifically, our studies are designed to (1) characterize the geographical and temporal variability in the concentrations of mineral aerosol, sea salt, and selected enriched trace elements in the atmosphere; (2) assess how this variability in concentrations is related to physical, chemical, and biological processes occurring in the atmosphere and the oceans; and (3) investigate the mechanisms involved in the air-sea exchange of trace elements and improve estimates of the fluxes of trace elements across the air-sea interface.

Studies of the trace element fluxes related to the third objective will be reported elsewhere. Our studies of the climatology of trace elements also make it possible to delineate trends in concentrations, and they bring to light some of the potential impacts of changing sources and source distributions for trace elements in the atmosphere.

2. Experiment

2.1. Sampling and Sample Handling

Aerosol particle samples were collected for 2 years from Bermuda and Barbados starting in June and August 1988, respectively. One year of data are available from the Izaña Observatory, Tenerife (Canary Islands), and from Mace Head, Ireland, where sampling commenced in late April 1989 and August 1989, respectively. At BTT, BAT, and MHT, samples...
are collected from aluminum, walk-up type, sampling towers (≈ 20 m tall), while at IZT, sampling is conducted from the roof of a Spanish Meteorological Observatory. The Izana Observatory is the only AEROCE site not on a coast, and it is located at an elevation of ≈ 2360 m. At IZT the samplers only operate during the night when downslope conditions enable us to collect samples from the free troposphere.

At the AEROCE primary sites of Bermuda and Mace Head, custom-made computer-based systems are used to control the aerosol particle sampling with respect to wind direction, wind speed, condensation nuclei (CN) counts, relative humidity, and the occurrence of rain. This system, based on a design by Schwartz et al. (1988), was developed to minimize the contamination of samples from local sources. A simpler system was used at the secondary stations of Barbados and Izana; at those sites, CN counts, humidity, and rain were not used as control parameters. The wind sectors chosen for sample collection at the various sites were based on the location of the sampling platform, the local topography, etc. The wind sectors, expressed as degrees true, were as follows: BAT = 335° to 130°, BTT = 180° to 330°, MHT = 180° to 300°, IZT = 270° to 45°.

Bulk aerosol particles were collected with high-volume samplers operating at approximately 45 m³ h⁻¹. The samplers are made of noncontaminating materials, and to the greatest extent possible, standardized aerosol sample handling protocols were implemented at each of the stations. Samples were collected on single, unwashed, 8 in x 10 in Whatman 41® filters (Whatman International Limited, Maidstone, England). For each of the stations the volumes of air sampled were calculated from flow tubes with calibrated orifice plates. Errors in the volumes of air sampled are estimated to be 5 to 10%. The cutoff characteristics of the samplers are such that particles smaller than 10 μm are captured efficiently (J. M. Prospero, University of Miami, personal communication, 1989), and therefore the samplers' collection characteristics should not significantly bias the results.

One sample and one field blank are collected each day from the primary stations, but at Mace Head, inclement weather occasionally made it impossible to change samples on a daily basis. At the secondary stations, samples are collected every day and blanks are collected every third day. The daily sampling interval was used to facilitate comparisons among all of the aerosol species studied for AEROCE, i.e., sulfate, methanesulfonate, nitrate, ²¹⁰Pb, and ³¹Be. The sampling interval was not optimal for all elements, but it was suitable for sea salt and mineral dust which are two components of major interest. The sampling interval also was selected to make it possible to interpret our data using air mass trajectories.

The aerosol samples are sealed in plastic bags, and each week they are mailed to the University of Miami and then to our laboratory at the University of Rhode Island (URI). For the trace element studies, the aerosol particle samples are selected for analysis based on the volume of air pumped, i.e., all of the samples with volumes greater than 100 m³ are analyzed. This volume of air is required to obtain a sufficient and representative mass of the key trace species, and it is equivalent to a minimum pumping time of ≈ 10% per day.

Differences in the volumes of air sampled at the different sites introduce possible biases in the data; this is a potential problem not only when comparing the data among the sites but also with previous studies. The potential problem with experimental design is more than offset, however, by the ability to intercompare the AEROCE aerosol and precipitation data sets from different groups. This is made possible by employing a daily sampling interval for all of the studies. Furthermore, the ability to use air mass trajectories in interpreting the daily aerosol data, which is also made possible by the daily sampling protocol, is a decided advantage. The arithmetic mean volumes (± standard deviation) of the air sampled were BAT = 956 ± 240 (number of samples, n = 344) and 1016 ± 215 (n = 347) for the first and second years of sampling, respectively; BTT = 682 ± 452 (n = 183) and 853 ± 547 (n = 196) for the first and second year; IZT = 365 ± 170 (n = 173); and MHT = 1182 ± 1425 (n = 143).

For the URI trace element studies, the aerosol-laden filters and blank filters are prepared for chemical analysis in a class 100 clean room. The filters are cut using clean custom-made plastic scissors and plastic forceps. All manipulations of the filters are done by persons wearing clean room garb, including jumpsuits, face masks, hats, and shoulder-length plastic gloves. Quarters of the sample and blank filters are individually pressed into pellets at a pressure of ≈ 150 to 200 kg cm⁻² using a stainless steel press with titanium end-caps and a plastic liner. Separate aliquots of the filters are used for the two irradiation schemes described below, and the remainder is frozen and stored in a sample archive.

### 2.2. Chemical Analyses

The AEROCE samples are analyzed by instrumental neutron activation analysis (INAA) using the 2 MW research reactor (neutron flux = 4 × 10¹² neutrons cm⁻² s⁻¹) operated by the Rhode Island Nuclear Science Center [Duce et al., 1983]. These methods are nondestructive and provide data for up to 26 elements through two independent analytical procedures. A "short" (1 to 2 min) irradiation scheme is used for the determination of Al, Br, Ca, Cl, Cu, I, Mg, Mn, Na, and V. A "long" (≈ 28 hours) INAA procedure is used for the determination of Ba, Co, Cr, Cs, Cu, Fe, Hf, Pb, Rh, Sh, Sc, Se, Ta, Tb, Th, Yb, and Zn.

The concentrations of the trace elements were determined through the use of flux monitors (short INAA) or flux monitors...
and internal standards (long INAA). Peak searches and peak analyses initially were performed using a Prime 550 minicomputer, but more recently a VAX/VMS-based GENIE workstation multichannel analyzer system (Canberra Nuclear, Meriden, Connecticut) was used for this purpose. The uncertainties in the concentrations of most elements are estimated to be ~10%, mainly due to the uncertainties in the flow measurement system and to blank corrections. For Cu, Mn, Sb, and Zn the uncertainties are higher, 10 to 50% owing to the lower relative sensitivity of INAA for these elements as well as larger blank corrections. Blank corrections are made by subtracting the concentrations of the elements in the field blanks from those in the samples. Nine different Ge(Li) detectors were used for the sample analysis, and the operational detection limits were based on counting statistics, with a lower limit nominally set at 100 counts per element per sample.

Quality control and quality assurance (QC/QA) for the chemical analyses are documented and maintained through interlaboratory calibrations, including the U.S. EPA QC/QA program and through the analysis of standard reference materials. The reference materials routinely analyzed for QC/QA include National Institute of Standards and Technology standard reference materials such as coal fly ash (SRM 1633 or 1633a), urban particulate matter (SRM 1648), and ashless blank filter (SRM 2681).

3. Results and Discussion

A set of summary statistics for the trace element concentrations at each of the AEROCE sites is not included here but is available from the American Geophysical Union on microfiche.1 Included in the summary table are 2 years of data for BAT and BTT and one year of data for IZT and MHT. The different periods of coverage reflect the times when the stations first became operational. The raw data also can be obtained by contacting the authors.

In the discussion that follows, the trace elements are classified into groups on the basis of their presumptive sources: these are mineral aerosol, atmospheric sea salt, and a group of enriched elements (EEs). Sources for the trace elements are then assessed through analyses of interelemental relationships and through a consideration of transport pathways and temporal variability in the concentrations.

Multivariate statistical techniques have become widely used for assessing the sources for trace substances in the atmosphere, but after extensive discussions with our AEROCE colleagues, we opted not to use this approach for several reasons. First, the number of EEs is small given the number of sources that are potentially important. Second, in a substantial number of samples the concentration of one or more of the EEs was below detection limits, and these missing values complicate the analyses. Third, some of the anthropogenic source emissions are not well characterized and in other cases are not distinctive. Furthermore, as shown below, the pollution sources vary in importance with respect to source region, and their impacts are strongly influenced by seasonal changes in transport pathways. Finally, and perhaps most important, the multiple-colinearity imposed on the chemical data by meteorological processes tends to obscure the information that can be discerned relative to sources and source regions.

3.1. Mineral Aerosol

The long-range transport of mineral dust and its flux across the air-sea interface links the biogeochemical cycles of the continents, atmosphere, and oceans. Dust over the North Atlantic has been the subject of scientific reports dating from the late 1700s [e.g., Dobson, 1781], and the occurrence of dust storms has long been of interest to mariners and navigators [e.g., Darwin, 1846]. An African source for the mineral dust over the tropical North Atlantic is well established. For example, geochemical studies indicate that dust from the Sahara is the parent material for soils found on various islands in the Caribbean and in the western Atlantic [Muhs et al., 1990]. The quantity of mineral matter involved is considerable. Junge [1979] estimated that 60 to 200 Tg of Saharan dust are generated each year. More recently the atmospheric input of mineral dust to the North Atlantic has been estimated to be ~220 Tg yr⁻¹ [Duce et al., 1991].

A connection between the mineralogy of eolian particles and deep-sea sediments has been recognized for decades [e.g., Rex and Goldberg, 1958; Griffin and Goldberg, 1968; Chester et al., 1972; Windom, 1975]. These and more recent studies [e.g., Blank et al., 1985] demonstrate that the long-range atmospheric transport of weathered crustal material from the continents supplies a major portion of the nonbiogenic sediments that accumulate on the sea floor. The importance of information concerning the fluxes of mineral aerosol is further enhanced by the application of such information to studies of paleoclimate and to analyses of geographical patterns in the composition of deep-sea sediments [e.g., Rea et al., 1985; Sarine et al., 1982; Sirocko and Sarine, 1989].

Oceanographic studies have shown that the dissolution of certain trace metals, such as Fe and Al, following the air-to-sea transfer of mineral aerosol is an important and sometimes dominant source for these elements in surface waters of the open ocean [Duce, 1986; Orians and Bruland, 1986; Maring and Duce, 1987; Prospero et al., 1987; Martin and Fitzwater, 1988; Zhuang et al., 1990; Duce and Tindale, 1991]. Much of the recent attention has focused on Fe because phytoplankton production apparently can be limited by the supply of eolian iron [Martin and Fitzwater, 1988].

The results concerning mineral aerosol presented here address (1) the elemental composition of atmospheric dust and (2) the temporal and spatial variability in dust concentrations, particularly in relation to atmospheric transport pathways over the North Atlantic. The elemental composition of mineral dust from Barbados, Bermuda, and Izaña was investigated by focusing on the ratios of the trace elements relative to aluminum, which is often used as a representative crustal element and makes up ~8% of the upper continental crust [e.g., Uematsu et al., 1983; Duce et al., 1983]. Elemental ratios relative to Al were calculated for samples collected under high-dust conditions, i.e., mineral aerosol concentrations of > 2 μg m⁻³ for BAT and BTT and > 5 μg m⁻³ at IZT. The elemental ratios were calculated by a linear fitting procedure known as reduced major axis (RMA) regression analyses (also known as the calculation of lines of organic
correlation), as described by Hirsch and Gilroy [1984]. These authors concluded that RMA is preferred over ordinary least squares because it more accurately reflects the relationships between variables such as the trace element concentrations presented here.

The ratios of eighteen elements (Ba, Ca, Co, Cr, Cs, Eu, Fe, Hf, Mg, Mn, Na, Nb, Pb, Sc, Ta, Tb, Th, V, Yb) calculated relative to Al for the high-dust events are similar in the Barbados, Bermuda, and Izaña data sets (Table 1). The observed element to Al ratios for the high-dust samples also are comparable to those of the upper continental crust based on the compilation of Taylor and McLennan [1985]. This similarity is further evidence that many of the trace elements we study originate from a crustal source. During the high-dust events at BAT, BTT, and IZT, mineral aerosol is by far the dominant inorganic aerosol constituent on a mass per unit volume basis. In contrast, at Mace Head, the maximum dust concentrations were never so high that the pollutant contributions to the trace elements could be ignored. Under high-dust conditions at BAT, BTT, and IZT, some elements such as Ca and Mg whose concentrations are more commonly controlled by sea salt can be dominated by atmospheric dust (Table 1). Similarly, the concentration of Sb was at times strongly influenced by dust, but in general, Sb was substantially enriched. For example, Ellis et al. [1993] concluded that at Bermuda, only 6% of the Sb was crustal.

The short-term variability of the dust concentrations is clearly linked to synoptic meteorology, and during sporadic events, which generally last 2 to 4 days, the atmospheric dust concentrations at BAT, BTT, and IZT can exceed 100 \( \mu g \) m\(^{-3}\). Isentropic air trajectories indicate that the dust flux is dominated by sources in North Africa [Arimoto et al., 1992], and this is fully consistent with previous studies of dust over the North Atlantic [e.g., Prospero and Carlson, 1972; Lepple, 1975; Schütz et al., 1981; Morales, 1986]. For example, Prospero et al. [1970] traced the origin of a dust event at Barbados to West Africa, with a transport time of ~5 days. Related studies by Carlson and Prospero [1972] showed that the mineral aerosol from Africa is transported at altitudes of 1.5 to 4.5 km in large anti-cyclonic eddies.

Dust transport from Africa occurs throughout the year, but the source regions and main transport pathways change in concert with movements of the Inter-Tropical Convergence Zone (ITCZ) [see D'Almeida, 1986]. A pronounced seasonal cycle in mineral aerosol concentrations is evident at each of the four stations (Figure 2), presumably due to shifts in the major wind fields and the resultant changes in transport pathways [see Schütz, 1980]. The dust fluxes to the North Atlantic during the summer generally are higher than those in winter. It is noteworthy, however, that the single highest dust concentration observed in 2 years of sampling at Barbados occurred during the winter of 1988-1989.

Bergametti et al. [1989] used elemental ratios (Si/Al and Fe/Al) to distinguish between Sahelian versus Moroccan source regions for dust particles collected over the Canary Islands. These authors found that the Si/Al and Fe/Al ratios both were higher in dust originating from a Sahelian source compared with dust from the vicinity of Morocco. More than 20 years earlier, Delany et al. [1967] observed seasonal variations in the magnetic properties of dust collected at Barbados. Based on analyses of weather maps, these authors concluded that desert soils from Morocco were a likely source for the dust during the summer, while more southerly influences, i.e., vegetated regions to the south of Dakar, were implicated in the winter. Similarly, meteorological analyses by Morales [1986] indicate a seasonal north-to-south shift in dust storm activity in Africa from summer to winter. A three-dimensional analysis of the atmospheric cycling of dust particles by Joussaume [1990] also suggested seasonal changes in the African origins of mineral aerosol.

Silicon is not determined by our methods, but we were able to evaluate possible changes in source regions by considering the Fe/Al ratios for 2 years of data from Barbados. Based on the studies of Bergametti et al. [1989] and Delany et al., [1967], one would expect higher Fe/Al ratios in the winter owing to more southerly source regions with a higher magnetic content. We tested this hypothesis by considering the samples from Barbados with the 5% highest and the 5% lowest Fe/Al ratios. The median Fe/Al ratio for the complete sample set from Barbados was 0.58; this is comparable to a crustal average of 0.44 [Taylor and McLennan, 1985]. The median Fe/Al ratio for the uppermost 5% of the samples was 2.2, while the average ratio for the lowest 5% of the samples was 0.31.

Many of the samples (18 of 29 = 62%) exhibiting the highest Fe/Al ratios were collected from November to January, while most (66%) of the samples with lowest 5% Fe/Al ratios were collected between August and November. The Fe/Al ratios are highly variable from day to day, however, and both high and low Fe/Al ratios can occur within a given month. While semiquantitative at best, these results support the hypothesized seasonal differences in the African source regions for dust over the North Atlantic.

The geographical variability in the dust concentrations over the North Atlantic is pronounced, with the median concentrations of dust as represented by Al as follows:

### Table 1. Mass Ratios of Crustal Elements to Aluminum for High-Dust Events at Barbados, Bermuda, and Izaña

| Element | Barbados (BAT) | Bermuda (BTT) | Izaña (IZT) | Average Crustal Rock
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Ba</td>
<td>(6.2 \times 10^3)</td>
<td>(1.2 \times 10^2)</td>
<td>(9.8 \times 10^3)</td>
<td>(6.8 \times 10^3)</td>
</tr>
<tr>
<td>Ca</td>
<td>(2.9 \times 10^1)</td>
<td>(3.3 \times 10^1)</td>
<td>(3.6 \times 10^1)</td>
<td>(3.7 \times 10^1)</td>
</tr>
<tr>
<td>Co</td>
<td>(2.4 \times 10^4)</td>
<td>(2.4 \times 10^4)</td>
<td>(3.0 \times 10^4)</td>
<td>(1.2 \times 10^4)</td>
</tr>
<tr>
<td>Cr</td>
<td>(1.1 \times 10^3)</td>
<td>(1.9 \times 10^3)</td>
<td>(1.5 \times 10^3)</td>
<td>(4.4 \times 10^4)</td>
</tr>
<tr>
<td>Cs</td>
<td>(4.7 \times 10^5)</td>
<td>(6.2 \times 10^3)</td>
<td>(7.1 \times 10^3)</td>
<td>(4.6 \times 10^5)</td>
</tr>
<tr>
<td>Eu</td>
<td>(2.2 \times 10^5)</td>
<td>(2.3 \times 10^5)</td>
<td>(2.9 \times 10^5)</td>
<td>(1.1 \times 10^5)</td>
</tr>
<tr>
<td>Fe</td>
<td>(5.1 \times 10^4)</td>
<td>(6.1 \times 10^4)</td>
<td>(7.0 \times 10^4)</td>
<td>(4.4 \times 10^4)</td>
</tr>
<tr>
<td>Hf</td>
<td>(5.2 \times 10^5)</td>
<td>(5.8 \times 10^5)</td>
<td>(8.1 \times 10^3)</td>
<td>(7.2 \times 10^3)</td>
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<tr>
<td>Mg</td>
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<td>(3.2 \times 10^1)</td>
<td>(3.0 \times 10^1)</td>
<td>(1.6 \times 10^1)</td>
</tr>
<tr>
<td>Mn</td>
<td>(1.1 \times 10^2)</td>
<td>(9.5 \times 10^5)</td>
<td>(1.2 \times 10^4)</td>
<td>(7.5 \times 10^3)</td>
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<tr>
<td>Na</td>
<td>(1.1 \times 10^6)</td>
<td>(3.3 \times 10^7)</td>
<td>(1.1 \times 10^4)</td>
<td>(3.6 \times 10^4)</td>
</tr>
<tr>
<td>Nb</td>
<td>(1.1 \times 10^3)</td>
<td>(1.7 \times 10^3)</td>
<td>(1.6 \times 10^3)</td>
<td>(1.4 \times 10^3)</td>
</tr>
<tr>
<td>Nb</td>
<td>(1.2 \times 10^5)</td>
<td>(1.3 \times 10^5)</td>
<td>(1.4 \times 10^5)</td>
<td>(2.5 \times 10^6)</td>
</tr>
<tr>
<td>Sc</td>
<td>(1.7 \times 10^4)</td>
<td>(2.0 \times 10^4)</td>
<td>(2.3 \times 10^4)</td>
<td>(1.4 \times 10^4)</td>
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<tr>
<td>Ta</td>
<td>(2.1 \times 10^5)</td>
<td>(2.1 \times 10^5)</td>
<td>(2.8 \times 10^5)</td>
<td>(2.7 \times 10^5)</td>
</tr>
<tr>
<td>Tb</td>
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<td>(1.5 \times 10^5)</td>
<td>(1.9 \times 10^5)</td>
<td>(8.0 \times 10^5)</td>
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<tr>
<td>Th</td>
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<td>(2.0 \times 10^4)</td>
<td>(1.3 \times 10^4)</td>
</tr>
<tr>
<td>V</td>
<td>(1.5 \times 10^3)</td>
<td>(3.5 \times 10^5)</td>
<td>(1.6 \times 10^3)</td>
<td>(7.5 \times 10^4)</td>
</tr>
<tr>
<td>Yb</td>
<td>(4.2 \times 10^5)</td>
<td>(5.0 \times 10^5)</td>
<td>(5.2 \times 10^3)</td>
<td>(2.7 \times 10^3)</td>
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\(^{a}\text{Taylor and McLennan, 1985.}\)
Figure 2. Seasonal cycles in the concentrations of aluminum (mineral aerosol, open boxes) and sodium (sea salt, shaded boxes): (a) Barbados, (b) Bermuda, (c) Izaña, and (d) Mace Head. The horizontal line in the center of each box denotes the median, the bottom and top edges of the boxes mark the interquartile ranges, and the whiskers mark the tenth and ninetieth percentiles. All observations above the tenth and below the ninetieth percentiles individually plotted.
representative of mineral aerosol, at Barbados (BAT), Bermuda (BTT), Izafia (IZT), and Mace Head (MHT). Y1 stands for year 1 and Y2 stands for year 2.

Figure 3. Atmospheric aluminum concentrations, which are representative of mineral aerosol, at Barbados (BAT), Bermuda (BTT), Izafia (IZT), and Mace Head (MHT). Y1 stands for year 1 and Y2 stands for year 2.
concentrations. However, salt concentrations over the North Atlantic are much less variable than mineral dust. For example, at Barbados, the concentration of sea-salt Na in the atmosphere ranged over 2 orders of magnitude, i.e., from 0.30 to 17 µg m⁻³, while the corresponding dust concentrations ranged over 4 orders of magnitude.

In general, the annual median atmospheric sea-salt concentrations can be ranked as follows: BAT > MHT > BTT >> IZT. The median atmospheric Na concentrations at Barbados (4.9 and 4.8 µg m⁻³ for the first and second years of sampling, respectively) were slightly higher than that at Mace Head (4.1 µg m⁻³). The sea-salt sodium concentrations at both of these sites typically are higher than those at Bermuda (medians = 3.0 and 3.3 µg m⁻³, respectively, for Y1 and Y2). At the Izaña Observatory on Tenerife, sea-salt Na is essentially negligible (median = 0.03 µg m⁻³) owing to its location well above the marine boundary layer. In contrast, at Mace Head, sea-salt accounts for most of the mass of inorganic particulate matter in the atmosphere owing to the storminess of the region and its location far to the north of the main transport pathways for Saharan dust.

Previously Duce et al. [1976] reported that the sea-salt concentrations at Bermuda (based on Na) ranged from 0.65 to 40.3 µg m⁻³, with a seasonal (June to September) geometric mean salt concentration of 5.9 µg m⁻³. This is comparable to the geometric mean salt concentration we calculated for Bermuda for the same months in 1989 (8.3 µg m⁻³) even though the samples were collected from two different locations on the island. The sea-salt concentrations we observed at Barbados (annual geometric means of 15.0 and 15.1 µg m⁻³) were similar to those reported by Savoie and Prospero [1977] who reported a geometric mean salt concentration of 18.8 µg m⁻³ for 78 days of sampling during the summer at Barbados.

The production of atmospheric sea salt is driven by winds over the ocean [e.g., Blanchard, 1985], but at Bermuda the observed salt concentrations were not correlated with the sample-averaged wind speed recorded at the sampling tower (coefficient of determination, r² = 0.0006). This lack of correlation may be in part a result of the anemometer being located ~50 m above mean sea level, which is well above the reference height of 15 m that has been used to model the wind speed–sea salt relationship. In addition, the variance in the wind field influences the production of sea salt [Erickson et al., 1986], but this was not taken into account in our analysis. From a broader perspective, one can see that the seasonal changes in the sea-salt concentrations at BTT generally were consistent with the climatology of winds in the study region. An analysis by Oort [1983] revealed a slight strengthening of the tropical easterlies over the North Atlantic during the winter compared with a general steadiness of the trade winds at other times of the year. In the vicinity of Bermuda the eastward component of the wind is somewhat stronger in the summer than in the winter. More dramatic is the shift in the meridional component of the wind from equatorward in the winter to poleward in the summer. The ensemble of these effects, which presumably control the atmospheric sea-salt concentrations, are largely a result of the circulation associated with the Bermuda-Azores high-pressure system.

Each of the halogens we determine by INAA exhibits a unique behavior in the marine aerosol: Cl and Br often are depleted in varying degrees in aerosol particles [Duce et al., 1967; Okada, 1978; Keene et al., 1990; Mouri and Okada, 1993], while I is strongly enriched [Seto and Duce, 1972; Moyers and Duce, 1972]. The concentrations of the halogens in bulk aerosol samples are influenced by a variety of chemical reactions, possibly including artifacts on the filters [see Keene et al., 1990], and a detailed discussion of Cl and Br is beyond the scope of this paper. However, a comparison of the data for iodine shows that the median I concentrations follow an unusual pattern: BAT > BTT, MHT >> IZT (Figure 4). This pattern is unlike that of sea salt or mineral dust, and it is also unlike that for pollution-derived elements such as xs(V) and Sb. The relationships among I, other trace elements, and the transport pathways are discussed below.

### 3.3. Enriched Elements

In addition to the trace elements associated with atmospheric sea salt and dust, several enriched elements (EEs) are studied for AEROCE. Although the concentrations of the EEs are low in the absolute sense, they are higher than what can be accounted for by atmospheric sea salt or mineral aerosol; hence the term enriched. On the basis of the global anthropogenic emission estimates one would expect many of these EEs to be significantly affected by pollution sources. In our discussion of the sources for trace elements, we make extensive use of the emission estimates of Nriagu and Pacyna [1988] and Nriagu [1989]. It is important to acknowledge that the uncertainties in the estimated trace element emissions were an order of magnitude or greater for many sources. In our analyses we have opted to use the median values from the two reports.

Noncrustal manganese and especially noncrustal vanadium (xs(Mn) and xs(V), respectively) were evident in many of the aerosol particle samples from the AEROCE sites. Both of these elements are enriched over crustal concentrations as a result of anthropogenic emissions, V from the combustion of heavy fuel oil [Zoller et al., 1973; Rahn and Lowenthal, 1984; Nriagu and Pacyna, 1988] and Mn from a variety of pollution sources, including nonferrous metal production, iron and steel manufacturing, and possibly automobiles [Nriagu, 1988; Rahn, 1981]. We determine the amounts of noncrustal or pollution-derived Mn and V in the samples by assuming that the mineral particles are the only significant source for Al and by taking into account the empirically derived Mn/Al and V/Al ratios for mineral dust (Table 1).

Chen and Duce [1983] observed that when the air masses sampled at Bermuda had passed over North America, the concentrations of xs(V) and non-sea-salt sulfate were 2 to 3 times higher than when transport was from the eastern Atlantic. The V concentration at BTT in 1974 (arithmetic mean, \( \bar{X} = 1.2 \text{ ng m}^{-3} \)) [Chen and Duce, 1983] is similar to the AEROCE data for the same months in 1989 (\( \bar{X} = 1.3 \text{ ng m}^{-3} \)), suggesting that the amount of atmospheric V, much of which is pollution derived, has changed little over the past two decades. This similarity is in marked contrast to Pb, which over roughly the same time has decreased significantly in the North Atlantic due to the phaseout of leaded gasoline in the United States [Shen and Boyle, 1987].

The xs(V) data indicate that pollution emissions from heavy fuel oil are more evident at Bermuda and Mace Head than at Barbados or Izaña. The xs(V) concentrations at Barbados and Izaña were comparable, with annual median concentrations of xs(V) as follows: BAT, Y1 = 0.090 ng m⁻³, BAT, Y2 = 0.097 ng m⁻³, IZT = 0.080 ng m⁻³. The annual median
Figure 4. Concentrations of enriched trace elements at Barbados (BAT), Bermuda (BTT), Izaña (IZT), and Mace Head (MHT). Y1 and Y2, year 1 and year 2, respectively.

xs(V) concentrations at Bermuda and Mace Head were much higher than those at Barbados or Izaña: BTT.Y1 = 0.48 ng m\(^{-3}\), BTT.Y2 = 0.54 ng m\(^{-3}\), MHT = 0.47 ng m\(^{-3}\).

The INAA scheme we use is not optimized for the determination of Mn, and the xs(Mn) data are further limited in that the correction for the crustal component often was greater than 50%. The seasonally adjusted total Mn concentrations for the present AEROCE and the earlier Chen and Duce [1983] data sets differed by a factor of 2 (\(\bar{X}\) for 1974 = 3.5, \(\bar{X}\) for 1989 = 7.7), but the magnitude of the correction for crustal Mn precludes any assessment of the changes in the xs(Mn) concentrations over time. The relative contributions of crustal versus noncrustal sources to atmospheric Mn are potentially significant for marine systems because laboratory studies have shown that the solubility of Mn is different for aerosols from different sources [Guieu et al., 1994].

The anthropogenic emissions of copper are comparable to those from natural sources [Nriagu and Pacyna, 1988], and there is some indication that Cu is at times enriched relative to crustal and sea-salt sources at the AEROCE sites. The neutron activation methods we used are not optimal for Cu, however, and many samples had Cu concentrations near or below their detection limits. Therefore the limited data for Cu are not considered to be representative and do not warrant a detailed discussion.

Zinc is readily analyzed by INAA, but contamination can be a serious problem for this element. Even so, the trends in Zn concentrations are in several ways consistent with those of other enriched elements. For example, the median Zn concentrations at the AEROCE stations show a pattern similar to that of antimony, which is discussed below: IZT > BTT > BAT > MHT. In addition, at BAT and BTT the Zn concentrations covaried with those of Sb and Se, and contamination generally is not a problem for either of these two elements. The relationships between Zn and enriched elements at Barbados and Bermuda are discussed in more detail below.

Both Se and I exhibit much higher concentrations at BAT, BTT, and MHT compared with IZT, and because Izaña is the only site not in the marine boundary layer, the concentration differences probably reflect a marine source for these elements. Marine biogenic emissions of both elements are well documented: iodine, probably as methyl iodide, is released into the marine atmosphere, and thus I becomes enriched in atmospheric sea salt as a result of biological processes in the oceans [Lovelock et al., 1973; Rasmussen et al., 1982]. Selenium in the marine atmosphere can be substantially affected by anthropogenic activities, but Se too is enriched in marine aerosol particles as a result of emissions from the oceans [Mosher and Duce, 1983; Ross, 1985; Mosher et al., 1987; Ellis et al., 1993].

Even though the mass of selenium in marine aerosol particles is small relative to that of sulfur, information concerning the biogeochemical cycling of Se may be relevant for evaluating the role of sulfate aerosol particles in terms of the Earth's radiation balance and hence climate. Similarities
in chemical reactions, including biomethylation, provide links in the cycles of Se and S. The atmospheric Se data for Bermuda and Barbados have been discussed by Arimoto et al. [1992] and in detail by Ellis et al. [1993], and only a brief summary will be given here. Emissions from North America are the major source for Se at Bermuda; this was determined by examining the relationships among Se and other trace atmospheric constituents and through consideration of transport pathways as revealed by isentropic trajectory analysis. Ellis et al. [1993] showed that the concentrations of Se covaried with methanesulfonate (an oxidation product of dimethyl sulfide produced by marine biota) at Barbados but only during the summer, indicating a seasonal marine-biogenic signal for Se in the subtropical North Atlantic. This natural source accounted for 60% to 75% of the Se at Barbados during the summer; it was relatively less important (~45%) at Bermuda.

As was hypothesized for Se, the low iodine concentrations observed at Izaña compared with the other sites is probably due to the fact that ocean-derived I is not sampled at IZT. Vertical distributions of atmospheric I have been modeled by Chatfield and Crutzen [1990] in their assessment of interactions of the iodine and sulfur cycles in marine air. Of their two models, the “no interaction model” predicted a tenfold decrease in concentration of particulate I at ~2400 m compared with surface values. A second model, involving the formation of a reservoir species, HOI, predicted a smaller change in particulate I with height, approximately a factor of 2. The differences we observed in the arithmetic mean I concentration at IZT versus the three boundary layer sites were a factor of 3 to 6, and therefore the observations made for AEROCE appear to be intermediate between the two models of Chatfield and Crutzen [1990].

Antimony has been used in combination with data for aerosol nitrate and 210Pb to evaluate the anthropogenic contributions to non-sea-salt sulfate to the boundary layer over the remote North Atlantic Ocean (D. L. Savoie, et al., Oceanic and anthropogenic contributions to non-sea-salt sulphate in the marine boundary layer over the North Atlantic, submitted to the Journal of Geophysical Research, 1994 (hereinafter D. L. S. et al., 1994)). In that study, Sb and nitrate, i.e., two anthropogenic indicators, were used together with methanesulfonate, a biogenic indicator, to assess the relative contributions of anthropogenic versus marine biogenic sources to nss SO4 at three of the AEROCE sites. The emission estimates of Nriagu and Pacyna [1988] indicate that 42% of the global flux of Sb into the atmosphere is from natural sources; of these, soil, volcanoes, and sea salt each contribute about 10% of the global total. The major anthropogenic emissions of Sb are from nonferrous metal production (mostly Cu and Ni production); this source accounts for ~25% of the global anthropogenic emissions of Sb. Coal combustion and refuse incinerators amount to ~22% and ~11%, respectively, of the global anthropogenic emissions of Sb.

We considered only the Bermuda and Barbados data sets for the more detailed assessments of the trace element relationships that follow. The data sets for Mace Head and Izaña covered only one year, and the number of samples was considered to be too small for detailed analysis. Further analysis of trace element concentrations and sources at Mace Head and Izaña will be conducted as more data from those sites become available.

3.4. Trace Elements at Bermuda

North America is the dominant source for many of the atmospheric pollutants at Bermuda, while the mineral aerosol at that site originates mainly in North Africa [Duce et al., 1976; Chen and Duce, 1983; Talbot et al., 1986; Moody and Galloway, 1988; Arimoto et al., 1992; Ellis et al., 1993]. We investigated the effects of transport on natural and pollution-derived trace element concentrations using the simple airmass trajectory stratification scheme of Ellis et al. [1993]. Briefly, isentropic trajectories terminating at Bermuda and calculated backward in time were assigned to either of two groups based on the likelihood of influence from North America. Trajectories that spent more than half a day over or near North America were assigned to the North American sector. All others were categorized as trajectories whose main impact was likely to be from the east of Bermuda.

The relationships between transport pathways and trace element concentrations at Bermuda were evaluated by stratifying the 2 years of data for Al (mineral aerosol), Na (sea salt), and five EEs on the basis of air mass trajectories matched to the samples. An unpaired t test indicated that the Al concentrations in the two subsets were significantly different (probability for chance occurrence, p < 0.0001, Table 2). In agreement with earlier studies of dust transport, higher concentrations of Al occurred when transport was from the east. The difference in sodium concentrations stratified by sector was marginally significant at p = 0.04.

The concentrations of the pollution-derived EEs (Sb, Se, and xs(V)) all were higher in the samples from the North American sector while I was lower, suggesting large-scale geographical differences in the sources for these enriched elements. The observed differences in arithmetic mean I, Sb, Se, and xs(V) concentrations for the sector-stratified data were highly significant (t tests, p ≤ 0.01). The Zn concentrations in the samples from North America also were higher than when transport was from the east, but this difference was only marginally significant (p = 0.046, Table 2).

The relationships among five enriched elements (I, Sb, Se, Zn, and xs(V)) for the first year of data from Bermuda are presented as a scatterplot matrix in Figure 5. Scatterplot matrices of this type are particularly useful for examining large amounts of data for trends: more detailed analyses of the Bermuda data follow. The data are not transformed for the scatterplot matrix, and because the matrix is symmetrical, only the bottom-left half of it is shown. Several points are evident in the scatterplot matrix of the Bermuda data (Figure 5). First, Sb, Se, and Zn clearly covaried, indicating a coherency in the sources for these EEs. These elements also showed some similarities to xs(V). On the other hand, iodine was not correlated with any of the other enriched elements in the full year data set; the highest correlation was r = 0.14 (p > 0.05).

The trace element composition of continental materials transported to Bermuda from Europe and Africa apparently differs from that associated with North American emissions. The effects of transport pathways on the relationships among the EEs at Bermuda were investigated through RMA regression analysis of the data stratified by air mass trajectory. This analysis was based on the same trajectory-sectoring scheme as described above in which the trace element concentrations in samples influenced by North America were compared with those associated with airmass trajectories from the east.
The Zn/Sb ratios in the sector-stratified data subsets from Bermuda differed by more than a factor of 3, while the xs(V)/Sb and Se/Sb ratios for the two data subsets differed by less than 20% and were not significantly different (Table 3). Comparisons of the slopes of the Zn versus Sb regressions using the method of Miller and Kahn, [1962] showed that the differences in the Zn/Sb ratios in the samples from the two sectors were highly significant (Z score = 6.3, p < 0.001). The slope of the Zn versus Sb regression for the samples associated with trajectories from the east was 120 (standard error (SE) is equal to 14), while the slope for the subset of samples influenced by North America was 36 (SE = 1.9). In general, the Zn/Sb ratios for the Bermuda atmospheric samples are higher than those from natural emissions: the natural sources considered by Nriagu [1989] all have Zn/Sb ratios \(< 36\). Forest fires have a Zn/Sb ratio of 36, and while this is similar to the ratios observed for samples associated with transport from North America, forest fires are unlikely to be important for Bermuda because they amount to only \(~4\%\) of the global Zn and Sb emissions into the atmosphere and because the fires are seasonal.

The preceding analyses demonstrate that there are not only differences in the mean trace element concentrations associated with the main transport pathways but also differences in the relative proportions of the various elements. At least two processes could contribute to the observed differences: (1) large-scale geographical differences in sources and (2) differences in the transport and removal processes. In the first case, one might expect differences in both the quantities and the composition of pollution-derived materials as a result of the differences in the industrial makeup of North America versus Europe and Africa. In fact, further insight into the sources for trace elements at Bermuda is provided by the data from Barbados that is discussed below. A second consideration is that the vertical distributions of the trace elements, the lengths of the transport pathways, the strengths of the transporting winds, the size distributions of the elements, and hence the efficiencies of removal processes all could affect the relative concentrations of the EEs under different flow regimes.

Correlations among naturally occurring and pollution-derived substances have been attributed to mixing and dispersion as aerosol particles are advected westward from Europe and Africa to the tropical North Atlantic [Savoie and Prospero, 1989]. This meteorological explanation may explain another major difference in the subsets of the sector data, i.e., that the correlation between I and Sb at Bermuda was significant (r = 0.61) only in the samples associated with easterly flow. Furthermore unlike the other EEs, the concentration of I at Bermuda was higher under easterly flow (Table 2).

One possible explanation for the difference between the data subsets is that I in the east sector samples from Bermuda...
Table 3. Relationships Among Enriched Elements for Aerosol Particle Samples From Bermuda

<table>
<thead>
<tr>
<th>Elements</th>
<th>Trajectories From the East</th>
<th>Trajectories From North America</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>r</td>
</tr>
<tr>
<td>I versus Sb</td>
<td>40</td>
<td>0.61</td>
</tr>
<tr>
<td>xs(V) versus Sb</td>
<td>39</td>
<td>0.62</td>
</tr>
<tr>
<td>Se versus Sb</td>
<td>43</td>
<td>0.63</td>
</tr>
<tr>
<td>Zn versus Sb</td>
<td>30</td>
<td>0.79</td>
</tr>
</tbody>
</table>

All data in micrograms per cubic meter. Samples grouped by air mass trajectory.

Table 4. Trace Element Concentrations in Samples From Barbados Grouped by Season

<table>
<thead>
<tr>
<th>Element</th>
<th>July to October</th>
<th>November to February</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>X ± s.d.</td>
</tr>
<tr>
<td>Aluminum</td>
<td>209</td>
<td>1.50 ± 1.54</td>
</tr>
<tr>
<td>Sodium</td>
<td>211</td>
<td>4.94 ± 4.14</td>
</tr>
<tr>
<td>Iodine</td>
<td>198</td>
<td>4.4 ± 2.5</td>
</tr>
<tr>
<td>xs(Vanadium)</td>
<td>206</td>
<td>0.15 ± 0.30</td>
</tr>
<tr>
<td>Antimony</td>
<td>146</td>
<td>0.044 ± 0.029</td>
</tr>
<tr>
<td>Selenium</td>
<td>209</td>
<td>0.29 ± 0.15</td>
</tr>
<tr>
<td>Zinc</td>
<td>158</td>
<td>3.0 ± 2.5</td>
</tr>
</tbody>
</table>

Concentrations of aluminum and sodium in microgram per cubic meter. All others in nanogram per cubic meter.

Table 4. Trace Element Concentrations in Samples From Barbados Grouped by Season

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I, xs(V), Sb, and Zn all were higher in the July-October samples. Sodium was lower in the July-October samples, probably reflecting the lower wind speeds in summer.

The relationships among certain EEs differed in the seasonally grouped data from Barbados (see Table 5 and the discussion of elemental ratios in section 3.6, below). For example, both Se and Zn showed a stronger correlation with Sb in the November-February samples compared with the July-October samples. Iodine was strongly correlated with Sb in the November-February data set, and although the relationship between I and Sb was weaker in the July-October samples, it was still highly significant (\( p < 0.0001 \)). As was true for each of the two full-year data sets, xs(V) was at most weakly correlated with Sb in either the July-October or the November-February samples.

Prior analyses of seasonally stratified data from Barbados have shown that the concentrations of trace elements and major aerosol ions exhibit some important similarities in their temporal trends [Arimoto et al., 1992; Ellis et al., 1993; D. L. S. et al., 1994]. The seasonal trends in aerosol data from Barbados are used below to help interpret some of the findings from Bermuda and to further assess the impacts of continental sources on aerosol particles over the North Atlantic Ocean.

### 3.6. Trace Elements as Indicators of Sources and Source Regions

Typically, the concentrations of pollution-derived elements, including Sb and Zn, are higher at Bermuda than at Barbados (Figure 4), and this trend reflects the transport of North American emissions to Bermuda. In addition, the elemental composition of the aerosols over a broad region of the North Atlantic varies as a function of transport pathway. For example, the Zn/Sb ratios for the Bermuda samples stratified by trajectory differed significantly, but more revealing is the fact that the relatively high Zn/Sb ratio of 120 for the Bermuda East Sector samples was similar to the ratios calculated for the two subsets of samples from Barbados (July to October samples Zn/Sb = 150; November to February samples Zn/Sb = 110; Table 5). This pattern in the Zn/Sb ratios in the various subsets of AEROCE data provides evidence for large-scale differences in the trace elements emitted from the continents bordering the North Atlantic.

Inspection of the Nriagu and Pacyna [1988] emission estimates suggests that ferrous and nonferrous metal production are probable sources for the high Zn/Sb ratios observed in the samples that were influenced by emissions from Europe and Africa. These two anthropogenic sources not only have high Zn/Sb ratios but also account for significant amounts of the Zn and Sb injected into the atmosphere. According to Nriagu and Pacyna, the Zn/Sb ratio associated with Zn-Cd production is 930 while that for steel and iron manufacturing is 3600. To approach the values observed at BTT and BAT, the emissions from these sources would have to be mixed with material with lower Zn/Sb ratios. In fact, all of the other anthropogenic sources considered and all of the natural sources listed in the Nriagu and Pacyna paper either had Zn/Sb ratios less than those observed or were not likely to be a significant source for these elements.

Our conclusions relative to pollution emissions of Sb and Zn are of course sensitive to the degree to which the elemental ratios in the work of Nriagu and Pacyna [1988] and Nriagu [1989] are representative of emissions from the source regions surrounding the North Atlantic. Nevertheless this simple analysis of Zn/Sb ratios suggests that differences in the industrial makeup of North American versus Europe and Africa are evident in the trace elements that are emitted and transported to the atmosphere over the North Atlantic.

The iodine concentrations were generally low and uncorrelated with Sb or any of the other EEs when the air mass trajectories to Bermuda were from North America, suggesting that the flux of anthropogenic I from North America is relatively weak. In contrast, the correlation between I and Sb was substantial in the Bermuda samples that had easterly trajectories (r = 0.61, Table 3) and in both subsets of samples from Barbados (Table 5). While the oceans are a major source for atmospheric I [Cicerone, 1981], the oceanic emissions of Sb are small compared with those from continental sources [Nriagu, 1989]. Industrial uses for iodine include color photography and dyes, but these are not significant sources for Sb or other EEs.

One possible source for the I and Sb is biomass burning. Recently enrichments of I, Sb, and other elements including K, Ca, Mn, Zn, Mg, P, Sr, Cl, Cu, Br, Rb, and Pb have been observed in aerosols collected from a fire plume [Maenhaut et al., 1993]. Our analyses indicate that Bermuda and Barbados generally exhibited similar I/Sb ratios during the summer which is when the highest percentage of easterly trajectories to Bermuda occurs [Ellis et al., 1993]. Furthermore, the difference in I/Sb ratios in the Bermuda (East) samples and the

### Table 5. Relationships Among Enriched Elements for Aerosol Particle Samples From Barbados Grouped by Season

<table>
<thead>
<tr>
<th>Elements</th>
<th>July to October</th>
<th>November to February</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n*</td>
<td>r*</td>
</tr>
<tr>
<td>I versus Sb</td>
<td>134</td>
<td>0.41</td>
</tr>
<tr>
<td>xs(V) versus Sb</td>
<td>143</td>
<td>0.19</td>
</tr>
<tr>
<td>Se versus Sb</td>
<td>151</td>
<td>0.56</td>
</tr>
<tr>
<td>Zn versus Sb</td>
<td>128</td>
<td>0.51</td>
</tr>
</tbody>
</table>

All data in micrograms per cubic meter.

* n, number of samples.
* r, correlation coefficient.
* SE, standard error.
Both BTT data subsets, the xs(V) intercepts were only -10% of correlated in both trajectory-stratified subsets of samples from that Sb is more variable than I. July to October samples or the Bermuda easterly trajectory data sets from Barbados; however, the two elements were and Sb were not correlated in either of the seasonally grouped samples. A comparison of the arithmetic mean concentrations for the seasonally split data from Barbados (Table 5) suggests that Sb is more variable than I.

Oil combustion accounts for more than half of the global anthropogenic emissions of V [Nriagu and Pacyna, 1988], but this is a negligible source for Sb. The concentrations of xs(V) and Sb were not correlated in either of the seasonally grouped data sets from Barbados; however, the two elements were correlated in both trajectory-stratified subsets of samples from Bermuda. The slopes of the RMA regressions for xs(V) versus Sb for the Bermuda samples stratified by trajectory were not significantly different, with values of 9.3 (SE = 1.2) for the samples associated with easterly flow versus 7.9 (SE = 0.43) for the samples with trajectories from North America. For both BTT data subsets, the xs(V) intercepts were only ~10% of the arithmetic mean values, indicating that the relationship was not superimposed on a high background concentration of either element.

What is not clear is why the correlation between xs(V) and Sb is ~0.6 for the Bermuda (East) samples but not significant for either subset of the Barbados samples. One possible explanation is that anticyclonic flow can bring pollutants emitted from North America back to Bermuda from the east while such transport to Barbados is unlikely. A second possibility is that because xs(V) is a derived variable, the corrections based on the V/A1 relationship do not accurately account for the crustal component. A third possibility is that emissions from Bermuda itself are responsible for the observed correlation. A separate set of samples collected at Bermuda indicated that local sources can contribute significantly to xs(V) concentrations when winds blow across the island (R. Arimoto, unpublished data, 1991). Similarly, ships occasionally passing upwind of the tower may have affected the concentrations of xs(V) in some of the BTT samples.

4. Conclusions

In the atmosphere over the North Atlantic, the concentrations of the trace elements originating from both natural and anthropogenic sources change with season and vary strongly as a function of transport pathway. Mineral aerosol from sources in North Africa could be detected at all of the AEROCE sites, even at Mace Head, Ireland. The atmospheric dust concentrations exhibited pronounced variability on a daily basis and on seasonal scales even though the year-to-year differences during our study were small. Seasonal differences in the Fe/A1 ratio at Barbados are consistent with north-south shifts in the source regions for the mineral dust.

Pollution emissions from the United States are a particularly strong influence on the atmosphere over Bermuda, the AEROCE site in the western North Atlantic, but the strength of this influence varies with season and is stronger in the winter. At Barbados, emissions from Africa and Europe are dominant. Furthermore, continental emissions transported to the North Atlantic from Europe and Africa apparently are chemically different from those originating from North America. For example, the Zn/Sb ratio for a subset of samples from Bermuda likely to have been influenced by North America was a factor of 3 lower compared with the Bermuda samples associated with air from the east or with two subsets of samples from Barbados. Based on global emission estimates of Nriagu and Pacyna [1988], we expect that Zn-Cd production and steel and iron manufacturing contribute to the higher Zn/Sb values associated with transport from Europe and North Africa.

Additional evidence for large-scale differences in trace element concentrations associated with different flow regimes was obtained from analysis of I/Sb relationships, in this case possibly reflecting emissions from biomass burning. At Bermuda these two elements were correlated only in samples with easterly trajectories. Moreover, the I/Sb ratio calculated for the Bermuda east sector samples was comparable to that for the Barbados samples from the summer, which is when the trade winds bring material from Africa and Europe to both islands. Further studies will be required to identify the source for the iodine more definitively, and these efforts will involve the use of other tracers of biomass burning such as black carbon or soluble potassium.

The concentrations of both I and Se were much lower at Izaña compared with the other three AEROCE sites. While we tentatively attribute this observation to the location of Izaña above the marine boundary layer, additional research is clearly in order on the marine emissions of these and other compounds. Furthermore this observation indicates that comparisons of data from Izaña with the data from the boundary layer AEROCE sites may be particularly useful for assessing the impact of oceanic versus distant sources on the trace substances in the marine atmosphere.

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