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Metalloids in Wet Deposition on Bermuda: Concentrations, Sources, and Fluxes

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The concentrations of antimony, arsenic, and selenium were determined in wet deposition samples collected on a daily (event) basis from 1988 to 1990 on Bermuda as a part of the Atmosphere/Ocean Chemistry Experiment (AEROCE). Isentropic back trajectories were used to identify air masses that passed over North America (59% of the events), Europe or North Africa (8%), or were largely marine in origin (33% of the events). The North American trajectories had the highest volume-weighted average (VWA) concentrations and crustal enrichment factors for the three metalloids; the As/Se ratio and good correlations with acidity suggest inputs from fossil fuel combustion. The Euro-African trajectories had the lowest VWA concentrations and enrichment factors that approached crustal values, indicating mineral aerosol inputs; values for marine events fell between these two extremes. The atmospheric flux of metalloids to the western Atlantic Ocean represents a major source of these elements in surface waters (up to 100% for Sb and Se; up to 61% for As) and a corresponding sink in their global atmospheric budgets.

INTRODUCTION

The composition of the atmosphere over the ocean is affected not only by marine sources (e.g., sea-salt aerosols, biogenic sulfur emissions), but is also strongly influenced by terrestrial inputs (e.g., continental dusts, anthropogenic emissions). During atmospheric transport a variety of processes, including oxidation-reduction reactions, gas-to-particle conversions, and scavenging, alter the chemical composition of the atmosphere. In turn, many of these transformation processes control the long-range transport and deposition of materials to the ocean. Among the trace elements in the atmosphere, the metalloids, antimony, arsenic, and selenium, have unique sources, chemistries, and marine cycles that can influence their abundance and distribution in the marine atmosphere.

Metalloids may be introduced to the atmosphere naturally as biogenic gases, with mercury being the only other trace element that also has a natural gas phase source [Fitzgerald, 1989]. The emission of dimethyl selenide from the sea surface has been proposed as an important source for gas phase selenium in the marine atmosphere [Mosher and Duce, 1983]. Indeed, recent studies have detected picomolar concentrations of dimethyl selenide in surface waters of the Atlantic Ocean [Tanzer and Heumann, 1990]. Methylated forms of arsenic and antimony are also found in the surface ocean [Andreae, 1979; Andreae and Froelich, 1984], suggesting an equivalent pathway for these elements. While Walsh *et al.* [1979] presented data supporting the existence of gas phase arsenic species, other investigators have not reported further evidence for volatile trimethyl arsine in the marine atmosphere [e.g., Andreae, 1980; Scudlark and Church, 1988]. Metalloids can also be introduced to the atmosphere as components of mineral aerosols, but low surface water concentrations [Measures and Burton, 1980; Middelburg *et al.*, 1988] probably limit their input via sea-salt aerosols [e.g., Mosher and Duce, 1987]. The anthropogenic emissions of metalloids are numerous (see

review by Nriagu and Pacyna [1988]) and include coal combustion (As, Sb, Se), nonferrous smelting (As, Se), and municipal waste incineration (Sb). Thus metalloids have multiple natural and anthropogenic sources that can influence their concentrations and distributions in the marine atmosphere.

The importance of atmospheric transport in the global geochemical cycles of the metalloids has been invoked by many investigators [e.g., Andreae, 1980; Ross, 1985; Austin and Millward, 1986; Mosher and Duce, 1987]. Correspondingly, the atmospheric deposition of metalloids can significantly affect the biogeochemical cycles of these elements in oligotrophic surface waters [e.g., Buat-Menard and Chesselet, 1979; Cutter and Bruland, 1984; Measures *et al.*, 1984; Austin and Millward, 1986]. In terms of a mass balance for the central oceans, potential means of delivering metalloids to surface waters are vertical and horizontal advective/diffusive transport in the water column and atmospheric deposition. While water column input can be calculated using oceanographic data [e.g., Measures and Burton, 1980; Middelburg *et al.*, 1988], estimates of atmospheric deposition are limited.

Previous studies of atmospheric metalloids have largely been confined to the examination of one or two elements in aerosols. This paper will examine the sources and transport of three metalloid elements over the western North Atlantic Ocean using data for wet deposition collected at Bermuda as a part of the Atmosphere/Ocean Chemistry Experiment (AEROCE). Wet deposition was selected because metalloids are largely concentrated on submicrometer aerosols [Duce *et al.*, 1976b, 1983] that are efficiently removed during precipitation events [Arimoto *et al.*, 1989; Church *et al.*, 1990; Duce *et al.*, 1991]. In addition, precipitation sampling allows for the direct calculation of wet depositional fluxes that can then be compared with other inputs to surface waters.

METHODS

Sampling

Precipitation was sampled on a daily (event) basis at the AEROCE Tudor Hill site on Bermuda from July 1988 to September 1990. At this site, automated precipitation

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samplers (Aerochem Metrics, modified for the collection of trace metals) were placed atop a 23-m walk-up tower, and samples were recovered on a daily (if an event occurred) basis. The sample-handling protocol largely followed the methods described by *Tramontano et al.* [1987]. Briefly, acid-cleaned polyethylene buckets were used in the samplers and, after recovery, were returned to an on-site clean laboratory where the samples were adjusted to pH 1.5 with HCl, allowed to equilibrate for 24 hours, and then transferred to polyethylene storage bottles. Field blanks, consisting of ultrapure deionized water placed in a mounted bucket and then treated as a sample, were run bimonthly. Metalloid concentrations in these blanks did not exceed 0.01 nmol As/L, 0.001 nmol Sb/L, and 0.02 nmol Se/L (i.e., at or below the analytical detection limits).

Analytical Methods

Metalloids in precipitation samples were determined using selective hydride generation techniques. Total selenium was determined using the hydride generation/atomic absorption

methods described by *Cutter* [1978, 1983] and *Cutter and Bruland* [1984]. The detection limit is 0.02 nmol/L and precision is better than 4% relative standard deviation (RSD) at 0.40 nmol/L. Total inorganic arsenic and antimony were determined simultaneously using the method of *Cutter et al.* [1991], with detection limits of 3 pmol Sb/L and 10 pmol As/L and precision of better than 3% RSD at concentrations of 0.03 nmol As/L and 0.02 nmol Sb/L. All metalloid determinations were performed in triplicate to evaluate precision, and the standard additions method of calibration was used to assure accuracy.

The precipitation samples were not filtered, and some mineral aerosols are probably found in the samples. While it is possible that metalloids bound to these particles might not be detected using the above methods, this possibility is remote for several reasons. First, metalloids are typically adsorbed to clay minerals and iron oxides [*Wedepohl*, 1978], rather than being bound in the crystal lattice. Since the samples are stored at pH 1.5 for at least 1 month prior to analysis, the determinations would include any acid-leachable

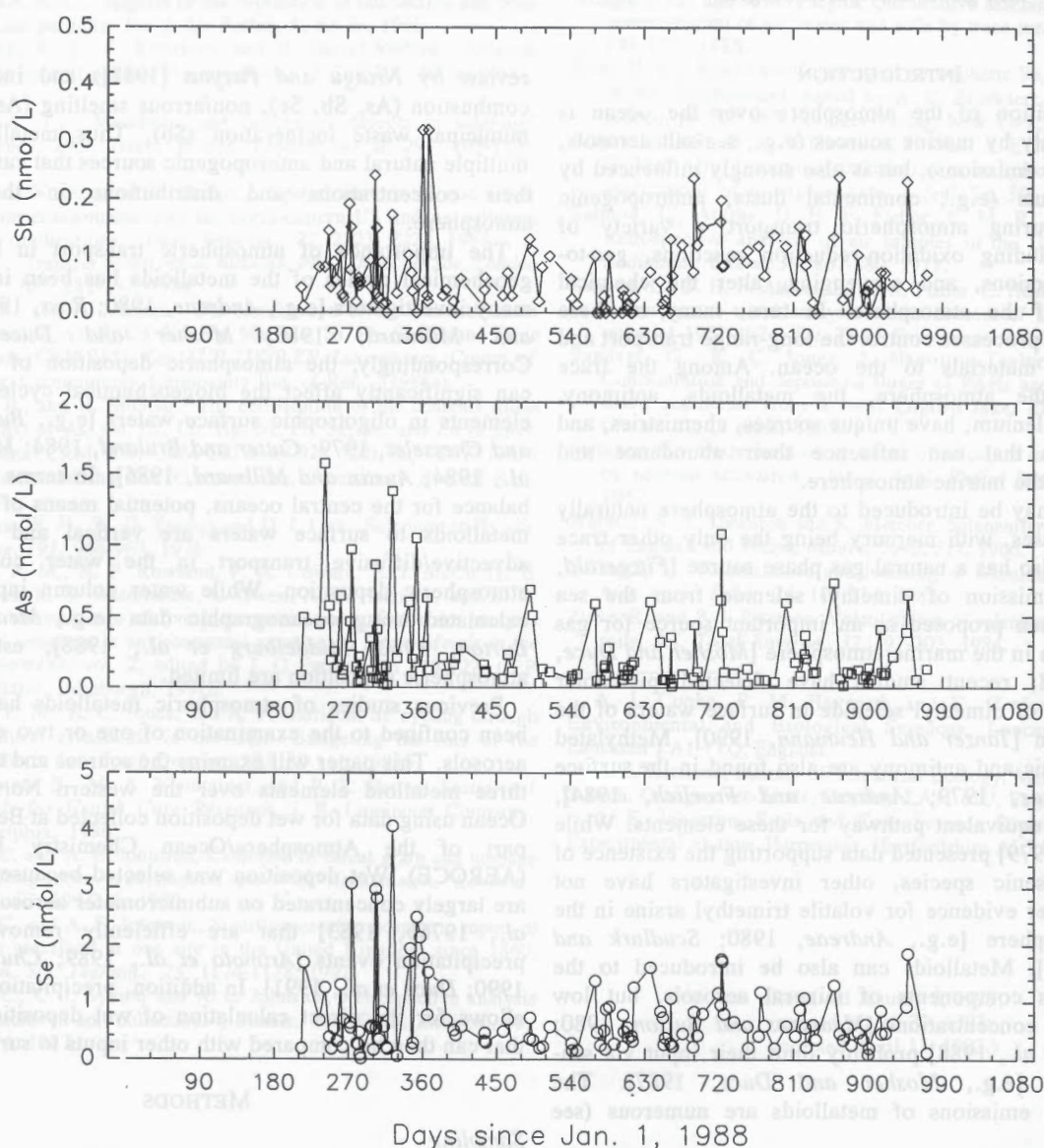


Fig. 1. Concentrations of antimony, arsenic, and selenium in precipitation collected on an event (daily) basis at the Atmosphere/Ocean Chemistry Experiment (AEROCE) site on Bermuda from July 1988 to September 1990. Antimony concentrations that were below the analytical detection limits of 0.001 nmol/L were assigned a value of 0.0 ($n=15$).

metalloids bound to aerosols. The determination of total selenium also includes a hydrochloric acid/persulfate digestion that should solubilize most mineral phases containing selenium. Finally, the filtration studies of *Heaton et al.* [1990] show that the fraction of antimony, arsenic, and selenium bound to particles in precipitation is small (80 - 100% of the totals are "dissolved"). Thus the sample storage and analytical methods employed in this study should be capable of determining total metalloid concentrations in precipitation.

RESULTS AND DISCUSSION

Time series data for arsenic, antimony, and selenium from Bermuda (Figure 1) exhibit considerable temporal variability. Amongst the three elements, concentrations of selenium and arsenic are the most highly correlated ($r = 0.72$; $n = 132$), followed by selenium and antimony ($r = 0.46$; $n = 132$), and then arsenic and antimony ($r = 0.42$; $n = 132$). These correlations suggest that the metalloids are not acting merely as a uniform group (i.e., only selenium and arsenic are well correlated), an observation consistent with their diverse sources (e.g., anthropogenic and marine biogenic emissions, mineral and sea-salt aerosols). To begin assessing the relative contributions of these metalloid sources to precipitation on Bermuda, elemental ratios such as those used to determine aerosol "signatures" [e.g., *Rahn and Lowenthal*, 1984; *Keeler and Sampson*, 1989] can be evaluated. A similar approach was used by *Heaton et al.* [1990, 1992] to examine regional sources of trace elements in precipitation from Rhode Island. An important assumption in using elemental ratios is that precipitation-scavenging processes do not differentially fractionate the trace elements during transport from their sources (i.e., change their ratios). In their study, *Heaton et al.* [1992] concluded that fractionation by particle size, by incorporation of an element with a gas phase, and by preferential nucleation is minor. Similarly, *Dutkiewicz et al.* [1987] found that fractionation of metalloids in aerosols is minimal over 300 to 1000 km, suggesting that removal during transport does not significantly affect elemental ratios.

Metalloid-metalloid plots for the Bermuda results are shown in Figure 2, and a regression of these data using the "organic correlation" method (slope = $s.d._y/s.d._x$ [*Hirsch and Gilroy*, 1984]) yields a slope that represents the elemental ratios. The organic correlation method to fit the data was selected over ordinary least squares because it is specifically designed to examine the relationship between two variables rather than estimating the value of y for a given x . Using the entire Bermuda precipitation data set (Figure 1), the resulting slope of the As/Se regression line is 0.41 ($r=0.71$), while that for Sb/Se is 0.10 ($r=0.46$) and the slope of the Sb/As regression is 0.24 ($r=0.42$). These precipitation ratios can be compared to those based on estimates of natural fluxes to the global atmosphere [*Nriagu*, 1989] as well as to existing aerosol and precipitation results (Table 1).

Of the three metalloid ratios calculated from the Bermuda precipitation data, only arsenic and selenium show a simple linear relationship. These precipitation results contrast with the highly linear correlation ($r=0.89$, organic correlation slope of 0.15) between antimony and selenium found in aerosols collected at the AEROCE Bermuda site [*Arimoto et al.*, 1992]. In comparison to the aerosol results the Sb/Se ratio in precipitation (0.10) indicates a slight depletion in antimony relative to selenium, while the low correlation

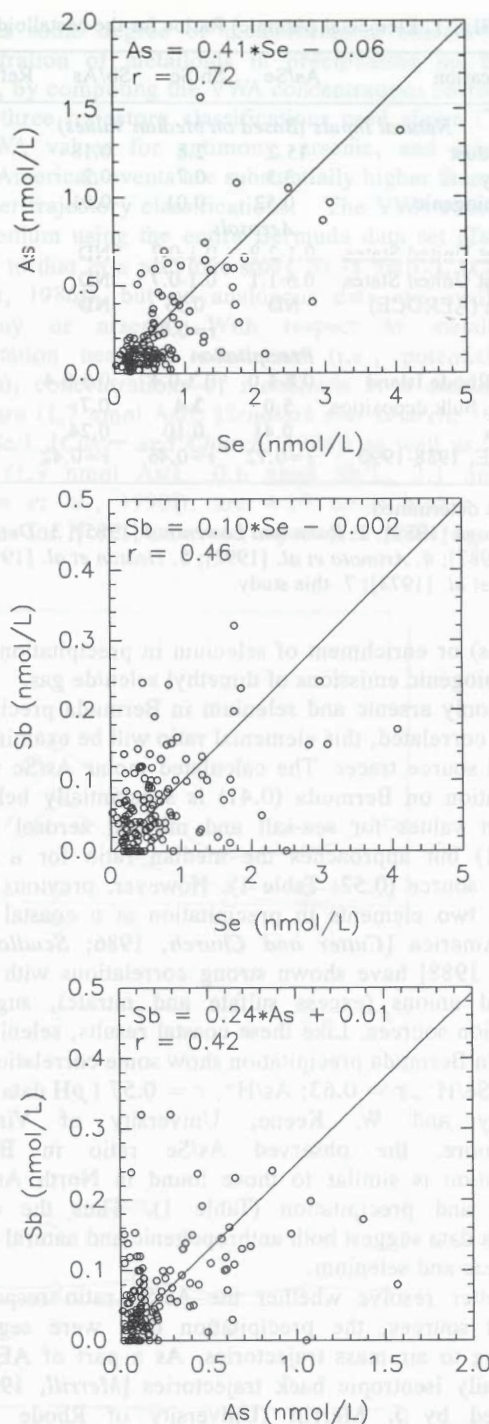


Fig. 2. Metalloid-metalloid plots for the entire 1988-1990 Bermuda data set. Regression lines were computed using the "organic correlation" method of *Hirsch and Gilroy* [1984]. Antimony values that were below the analytical detection limits of 0.001 nmol/L were assigned a value of 0.0 ($n=15$).

coefficient suggests a more complicated (i.e., nonlinear) relationship. It is not unprecedented for aerosol and precipitation results from the same site to diverge. Indeed, *Heaton et al.* [1992] noted that SO_4^{2-}/Se ratios in precipitation and aerosols in Rhode Island indicate the two are influenced by different sources. In the case of the Bermuda aerosol and precipitation results, differences could be due to sampling bias (i.e., ground based for aerosols, whereas the composition of precipitation is largely controlled by in-cloud

TABLE 1. Elemental (Atomic) Ratios for the Metalloids

Type/Location	As/Se	Sb/Se	Sb/As	Reference*
<i>Natural Inputs (Based on Median Values)</i>				
Mineral dust	15.2	2.8	0.18	1
Sea spray	3.3	0.7	0.2	1
Marine biogenic	0.52	0.01	0.01	1
<i>Aerosols</i>				
Northeast United States	0.1-2.9	0.1-0.7	ND	2
Northeast United States	0.6-1.1	0.1-0.7	ND	3
Bermuda (AEROCE)	ND	0.15	ND	4
<i>Precipitation</i>				
Coastal Rhode Island	0.8-1.0	0.3-0.4	0.3-0.4	5
England, bulk deposition	5.0	3.4	0.7	6
Bermuda	0.41	0.10	0.24	7
AEROCE, 1988-1990	r=0.72	r=0.46	r=0.42	

ND, not determined.

* 1. *Nriagu* [1989]; 2. *Rahn and Lowenthal* [1985]; 3. *Dutkiewicz et al.* [1987]; 4. *Arimoto et al.* [1992]; 5. *Heaton et al.* [1990]; 6. *Peirson et al.* [1973]; 7. this study.

processes) or enrichment of selenium in precipitation due to marine biogenic emissions of dimethyl selenide gas.

Since only arsenic and selenium in Bermuda precipitation are well correlated, this elemental ratio will be examined as a potential source tracer. The calculated molar As/Se ratio in precipitation on Bermuda (0.41) is substantially below the predicted values for sea-salt and mineral aerosol sources (Table 1) but approaches the median ratio for a marine biogenic source (0.52; Table 1). However, previous studies of these two elements in precipitation at a coastal site in North America [*Cutter and Church*, 1986; *Scudlark and Church*, 1988] have shown strong correlations with acidity and acid anions (excess sulfate and nitrate), suggesting combustion sources. Like these coastal results, selenium and arsenic in Bermuda precipitation show some correlations with acidity (Se/H^+ , $r = 0.63$; As/H^+ , $r = 0.57$ (pH data from *J. Galloway and W. Keene*, University of Virginia)). Furthermore, the observed As/Se ratio in Bermuda precipitation is similar to those found in North American aerosols and precipitation (Table 1). Thus the existing Bermuda data suggest both anthropogenic and natural sources for arsenic and selenium.

To better resolve whether the As/Se ratio responds to different sources, the precipitation data were segregated according to air mass trajectories. As a part of AEROCE, twice daily isentropic back trajectories [*Merrill*, 1989] are calculated by *J. Merrill* (University of Rhode Island). Anthropogenic emissions and mineral aerosols are derived from the continental regions surrounding the North Atlantic (North America, Europe, North Africa), while the ocean itself is a potential metalloid source (Table 1). Accordingly, isentropic trajectories were used to identify precipitation events when $\geq 20\%$ of the 5-day back trajectories were over North America ("North American" trajectories), Europe or North Africa ("Euro-African" trajectories), or did not pass over any continental or coastal regions ("marine/other" trajectories). Based on this conservative classification scheme, of the 132 events sampled for metalloids between 1988 and 1990, 59% were North American, 33% were marine/other, and 8% were Euro-African. The predominance of North American air masses is nearly identical to the 60% value reported by *Miller and Harris* [1985] for a 7-year period on Bermuda.

Using the trajectory assignments, the As/Se ratios were recomputed for the three trajectory types (Figure 3). Although few in number, the As/Se ratio for Euro-African trajectories (1.36) is substantially higher than that for the North American events (0.37), suggesting the increased importance of inputs from mineral aerosols (As/Se=15.2, Table 1) and sea-salt aerosols (As/Se=3.3, Table 1) for transport from the East; the As/Se ratio for marine/other events is only slightly higher than the North American ratio. Clearly more data are needed to explore the use of the As/Se ratio as a source indicator. However, the existing results do

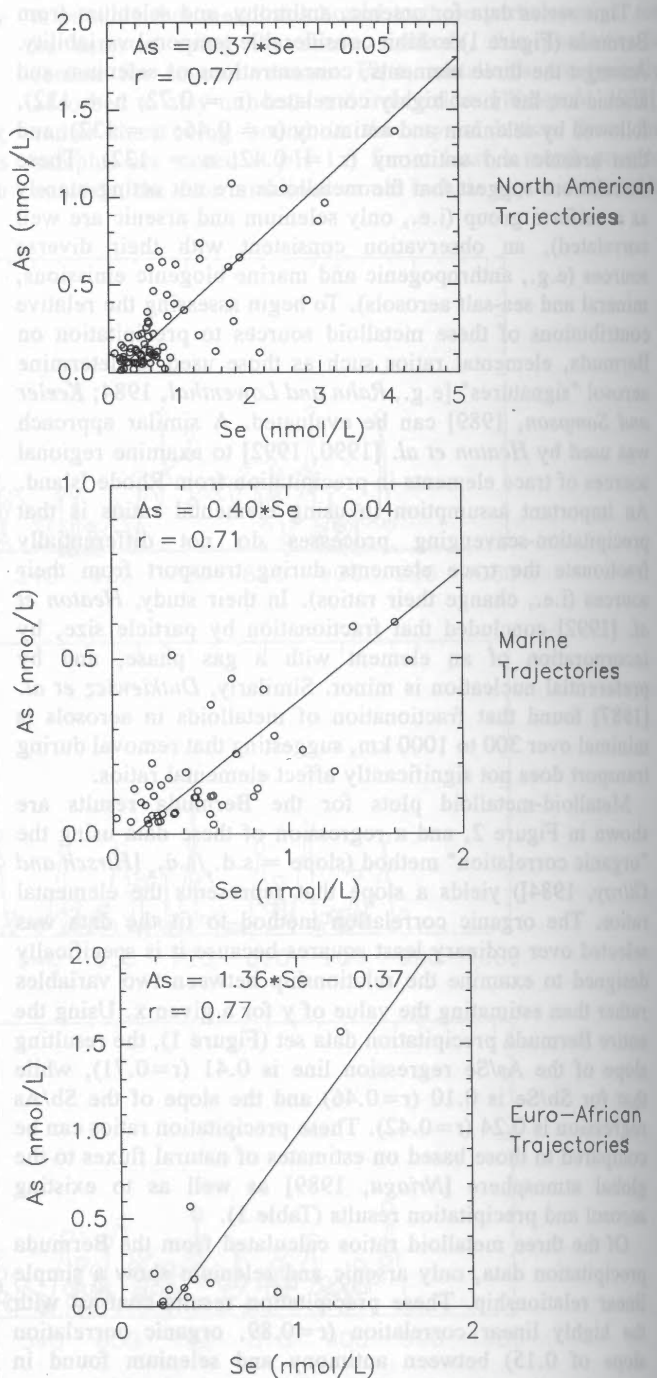


Fig. 3. Arsenic-selenium plots for the three trajectory classifications, North American ($n=78$), marine/other ($n=43$), and Euro-African ($n=11$). Regression lines were computed using the "organic correlation" method of *Hirsch and Gilroy* [1984].

suggest that the ratio on Bermuda is responding to a mixture of two very different signatures, anthropogenic emissions from North America with a low As/Se ratio (down to 0.1, Table 1) and natural inputs with a substantially higher As/Se ratios (up to 15.2, Table 1). Other methods for identifying the sources of metalloids in precipitation on Bermuda are explored below.

By computing monthly volume-weighted average (VWA) concentrations from the data in Figure 1, trends in the data and behaviors of the metalloids can be more easily observed (Figure 4). Concentrations follow the trend, $Se > As > Sb$, and considerable temporal variability is still evident for arsenic and selenium. In contrast, antimony, which has many of the same sources as arsenic and selenium, has relatively constant VWA concentrations. Two periods have regular occurrences of elevated VWA concentrations for metalloids (Figure 4), late summer (August and September) and early winter (December and January). This seasonal timing

suggests some degree of meteorological control over the concentration of metalloids in precipitation on Bermuda. Indeed, by computing the VWA concentrations corresponding to the three trajectory classifications used above (Table 2), the VWA values for antimony, arsenic, and selenium in North American events are substantially higher than those for the other trajectory classifications. The VWA concentration for selenium using the entire Bermuda data set (Table 2) is similar to that in a previous study (0.38 nmol/L [Cutter and Church, 1986]), but no analogous data are available for antimony or arsenic. With respect to metalloids in precipitation near the continents (i.e., potential source regions), concentrations of metalloids at a coastal site in Delaware (1.3 nmol As/L [Scudlark and Church, 1988], 2.2 nmol Se/L [Cutter and Church, 1986]) as well as in Rhode Island (1.9 nmol As/L, 0.6 nmol Sb/L, 2.1 nmol Se/L [Heaton et al., 1990]), are 4-10 times higher than the averages for North American trajectories on Bermuda (Table

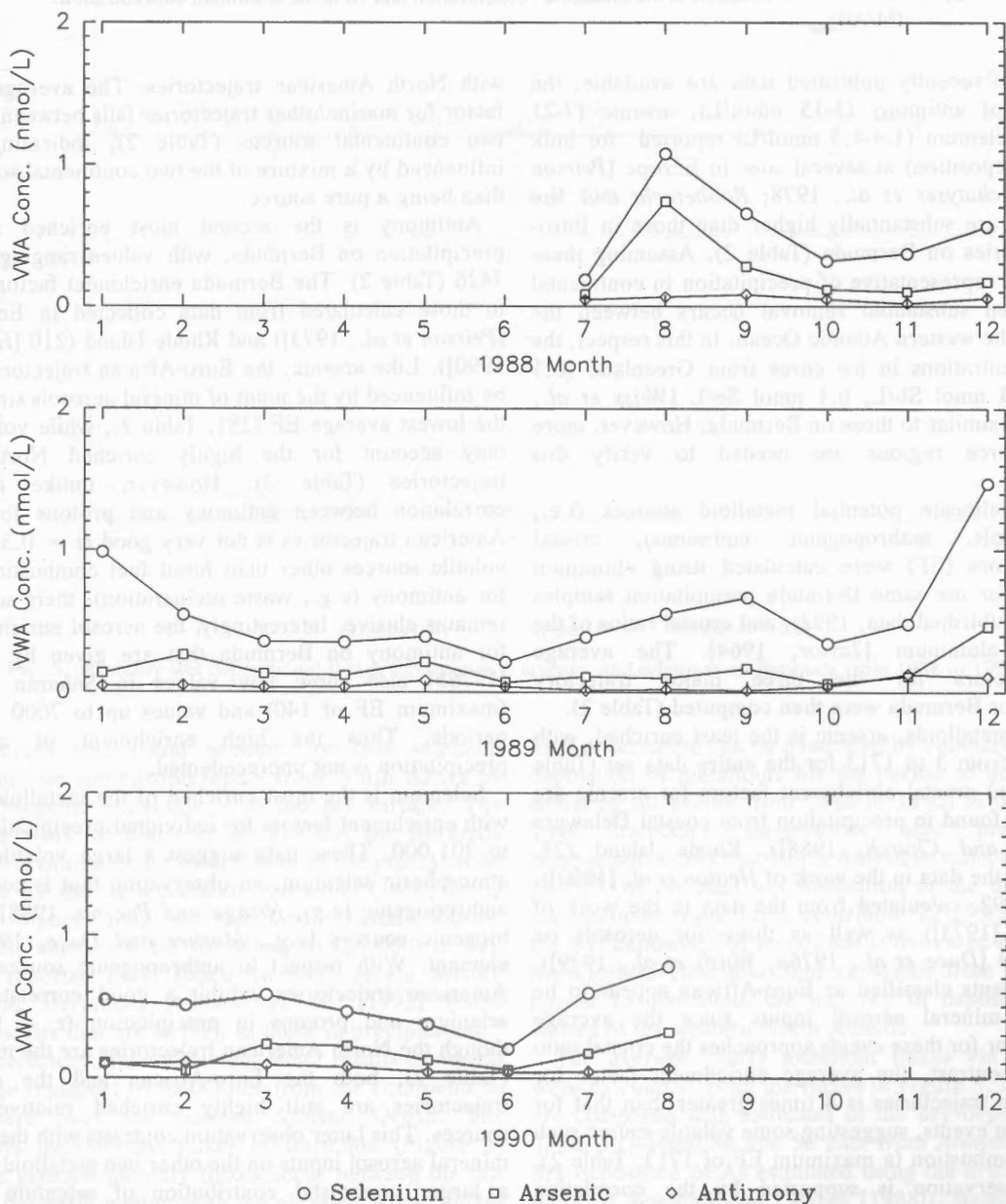


Fig. 4. Monthly volume-weighted average (VWA) concentrations of antimony, arsenic, and selenium in precipitation on Bermuda from 1988 to 1990.

TABLE 2. Volume-Weighted Average (VWA) Concentrations and Enrichment Factors (EF) for Metalloids in Precipitation on Bermuda, 1988 - 1990

Arsenic		Antimony		Selenium	
VWA, nmol/L, Range	Avg. EF* Range	VWA, nmol/L, Range	Avg. EF* Range	VWA, nmol/L, Range	Avg. EF* Range
<i>North American Trajectories (n = 78)</i>					
0.21 (0.02-1.38)	159 (3-1713)	0.07 (0-0.32)	1311 (11-7426)	0.66 (0.08-4.08)	31,324 (597-301,297)
<i>Euro-African Trajectories (n = 11)</i>					
0.07 (0.01-1.57)	40 (4-152)	0.02 (0-0.15)	281 (24-840)	0.33 (0.18-1.25)	10,181 (163-40,821)
<i>Marine/Other Trajectories (n = 43)</i>					
0.11 (0.03-0.60)	75 (6-506)	0.04 (0-0.14)	681 (19-3782)	0.37 (0.02-1.69)	17,369 (449-165,528)
<i>Entire Data Set (n=132)</i>					
0.16	118	0.05	1034	0.51	24,685

$$* EF = \frac{(M/Al)_{precip}}{(M/Al)_{crust}}, \text{ where } M \text{ is the metalloid concentration and } Al \text{ is the aluminum concentration.}$$

2). Although no recently published data are available, the concentrations of antimony (3-15 nmol/L), arsenic (7-21 nmol/L), and selenium (1.4-4.3 nmol/L) reported for bulk (wet plus dry deposition) at several sites in Europe [Peirson *et al.*, 1973; Schutysse *et al.*, 1978; Robberecht and Van Grieken, 1982] are substantially higher than those in Euro-African trajectories on Bermuda (Table 2). Assuming these limited data are representative of precipitation in continental air masses, then substantial removal occurs between the continents and the western Atlantic Ocean. In this respect, the metalloid concentrations in ice cores from Greenland (0.3 nmol As/L, 0.3 nmol Sb/L, 0.1 nmol Se/L [Weiss *et al.*, 1971, 1975]) are similar to those on Bermuda. However, more data from source regions are needed to verify this speculation.

To further delineate potential metalloid sources (i.e., mineral aerosols, anthropogenic emissions), crustal enrichment factors (EF) were calculated using aluminum concentrations for the same Bermuda precipitation samples (T. Church, unpublished data, 1992), and crustal ratios of the metalloids to aluminum [Taylor, 1964]. The average enrichment factors for the three major trajectory classifications for Bermuda were then computed (Table 2).

Of the three metalloids, arsenic is the least enriched, with values ranging from 3 to 1713 for the entire data set (Table 2). The observed crustal enrichment factors for arsenic are similar to those found in precipitation from coastal Delaware (25 [Scudlark and Church, 1988]), Rhode Island (28, calculated from the data in the work of Heaton *et al.* [1990]), and England (292, calculated from the data in the work of Peirson *et al.* [1973]) as well as those for aerosols on Bermuda (22-59 [Duce *et al.*, 1976a; Walsh *et al.*, 1979]). Precipitation events classified as Euro-African appear to be influenced by mineral aerosol inputs since the average enrichment factor for these events approaches the crustal ratio (Table 2). In contrast, the average enrichment factor for North American trajectories is 4 times greater than that for the Euro-African events, suggesting some volatile source such as fossil fuel combustion (a maximum EF of 1713, Table 2). This latter observation is supported by the correlation between arsenic and protons, which increases from $r = 0.57$ for the entire data set to $r = 0.71$ for precipitation events

with North American trajectories. The average enrichment factor for marine/other trajectories falls between those for the two continental sources (Table 2), indicating that it is influenced by a mixture of the two continental sources, rather than being a pure source.

Antimony is the second most enriched metalloid in precipitation on Bermuda, with values ranging from 11 to 7426 (Table 2). The Bermuda enrichment factors are similar to those calculated from data collected in England (4700 [Peirson *et al.*, 1973]) and Rhode Island (210 [Heaton *et al.*, 1990]). Like arsenic, the Euro-African trajectories appear to be influenced by the input of mineral aerosols since they have the lowest average EF (281, Table 2), while volatile sources may account for the highly enriched North American trajectories (Table 2). However, unlike arsenic, the correlation between antimony and protons for the North American trajectories is not very good ($r = 0.35$). Although volatile sources other than fossil fuel combustion may exist for antimony (e.g., waste incineration), their actual identity remains elusive. Interestingly, the aerosol enrichment factors for antimony on Bermuda that are given by Duce *et al.* [1976b] also show low values in Saharan dust events (maximum EF of 140) and values up to 7000 during other periods. Thus the high enrichment of antimony in precipitation is not unprecedented.

Selenium is the most enriched of the metalloids (Table 2), with enrichment factors for individual precipitation events up to 301,000. These data suggest a large volatile source for atmospheric selenium, an observation that is consistent with anthropogenic [e.g., Nriagu and Pacyna, 1988] and marine biogenic sources [e.g., Mosher and Duce, 1983] for this element. With respect to anthropogenic sources the North American trajectories exhibit a good correlation between selenium and protons in precipitation ($r = 0.68$). Even though the North American trajectories are the most enriched (Table 2), both the Euro-African and the marine/other trajectories are still highly enriched relative to crustal sources. This latter observation contrasts with the influence of mineral aerosol inputs on the other two metalloids, suggesting a larger noncrustal contribution of selenium in easterly trajectories (e.g., the ratio of the EFs for Euro-African to North American trajectories is 4.7 for Sb, 4.0 for As, and 3.1

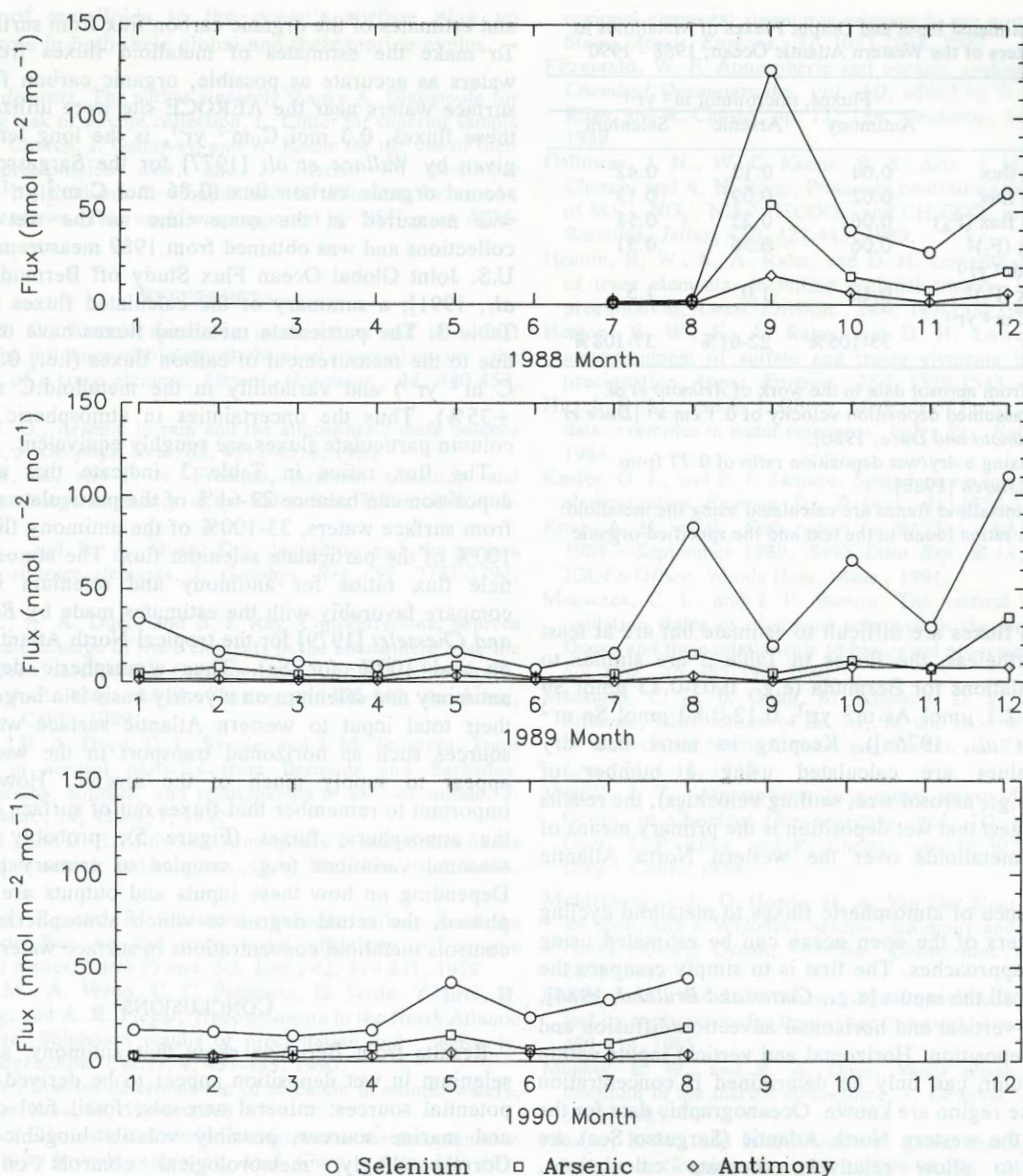


Fig. 5. Monthly wet depositional fluxes for antimony, arsenic, and selenium on Bermuda from 1988 to 1990.

for Se). Sources that could account for this selenium enrichment include combustion inputs from North Africa or Europe and biogenic emissions from the sea surface. The results in the work of *Duce et al.* [1976b] for Bermuda aerosols show a similar trend as that seen in the precipitation data, with the EF during a Saharan dust event (1400) being substantially higher than an assumed crustal source. However, their maximum EF for selenium (25,000) is well below those reported here. Based on more recent aerosol collections on Bermuda, *Arimoto et al.* [1992] found enrichment factors that are as high as those in precipitation.

The back trajectory and enrichment factor results document the long-range transport of metalloids from the continents to the atmosphere over the western Atlantic Ocean. The associated wet depositional fluxes at Bermuda (Figure 5) show that the greatest monthly fluxes occur between the late summer and the early winter, with the elevated winter fluxes corresponding to the months of primary transport from North America [*Miller and Harris, 1985; Galloway et al., 1989*].

This observation can be quantified by comparing the total wet deposition of metalloids for the period of observation (i.e., summing all events from 1988 to 1990) to those during the three trajectory assignments used previously. This comparison shows that North American trajectories contribute 68-70% of the total wet deposition of the three metalloids; marine/other trajectories contribute 22-25%; and 7-10% of the wet deposition of metalloids is delivered by Euro-African trajectories. Thus metalloid emissions from North America appear to contribute the majority of deposition to surface waters of the western North Atlantic.

The average yearly metalloid fluxes via wet deposition were calculated using the fluxes in Figure 5, and these values are compared with estimates of the dry depositional flux in Table 3 (aerosol Sb and Se data from *Arimoto et al.* [1992], dry deposition of As estimated using the dry/wet ratio in the work of *Scudlark and Church* [1988]). Based on the 2-year Bermuda record, the yearly wet fluxes of the metalloids have uncertainties of the order of $\pm 30\%$. The uncertainty of the

TABLE 3. Estimated Input and Output Fluxes of Metalloids in Surface Waters of the Western Atlantic Ocean, 1988 - 1990

Parameter	Fluxes, $\mu\text{mol m}^{-2} \text{yr}^{-1}$		
	Antimony	Arsenic	Selenium
Wet deposition flux	0.04	0.13	0.42
Dry deposition flux	0.02*	0.09†	0.13*
Σ Atmospheric flux (F_A)	0.06	0.22	0.55
Particulate flux (F_1)‡ at 0.3 mol C $\text{m}^{-2} \text{yr}^{-1}$	0.06	0.36	0.51
Particulate flux (F_2)‡ at 0.86 mol C $\text{m}^{-2} \text{yr}^{-1}$	0.18	1.0	1.5
F_A/F_2 or F_A/F_1	33-105%	22-61%	37-108%

* Calculated from aerosol data in the work of *Arimoto et al.* [1992] and an assumed deposition velocity of 0.1 cm s^{-1} [*Duce et al.*, 1976a; *Arimoto and Duce*, 1986].

† Estimated using a dry/wet deposition ratio of 0.77 from *Scudlark and Church* [1988].

‡ Particulate metalloid fluxes are calculated using the metalloid: organic carbon ratios found in the text and the specified organic carbon flux.

dry deposition fluxes are difficult to estimate but are at least $\pm 30\%$. Nevertheless, the fluxes in Table 3 are similar to previous calculations for Bermuda (e.g., $0.03\text{-}0.13 \mu\text{mol Sb m}^{-2} \text{yr}^{-1}$, $0.25\text{-}2.1 \mu\text{mol As m}^{-2} \text{yr}^{-1}$, $0.12\text{-}0.80 \mu\text{mol Se m}^{-2} \text{yr}^{-1}$ [*Duce et al.*, 1976a]). Keeping in mind that dry deposition values are calculated using a number of assumptions (e.g., aerosol size, settling velocities), the results in Table 3 suggest that wet deposition is the primary means of removal for metalloids over the western North Atlantic Ocean.

The importance of atmospheric fluxes to metalloid cycling in surface waters of the open ocean can be estimated using two different approaches. The first is to simply compare the magnitudes of all the inputs [e.g., *Cutter and Bruland*, 1984], which include vertical and horizontal advection/diffusion and atmospheric deposition. Horizontal and vertical inputs within the water column can only be determined if concentration gradients in the region are known. Oceanographic data for the metalloids in the western North Atlantic (Sargasso Sea) are too limited to allow relatively accurate calculations. However, existing data [*Measures et al.*, 1984; *Middelburg et al.*, 1988] do suggest that these inputs are probably minor, increasing the importance of atmospheric deposition.

The second approach to evaluating the role of atmospheric deposition in oceanic cycles was employed by *Buat-Menard and Chesselet* [1979] and uses a comparison of particulate fluxes of metalloids out of surface waters with atmospheric fluxes into them. Their approach assumes that the primary removal process in surface waters, incorporation into organic matter and downward transport, is balanced by atmospheric and water column inputs (i.e., steady state conditions). If there are other removal processes such as the production of volatile dimethyl selenide, then this approach can underestimate the overall importance of atmospheric deposition as a source of elements to surface waters. However, the simple comparison of fluxes allows a useful first-order examination of atmosphere-ocean coupling.

The particulate fluxes of metalloids from surface waters of the western North Atlantic were calculated using organic carbon:metalloid ratios for marine biogenic particles (molar C:As:Sb:Se = $1 : 1.2 \pm 0.4 \times 10^{-6} : 0.21 \pm 0.08 \times 10^{-6} : 1.7 \pm 0.5 \times 10^{-6}$ (G. Cutter, manuscript in preparation, 1993))

and estimates of the organic carbon flux from surface waters. To make the estimates of metalloid fluxes from surface waters as accurate as possible, organic carbon fluxes from surface waters near the AEROCE site were utilized. One of these fluxes, $0.3 \text{ mol C m}^{-2} \text{yr}^{-1}$, is the long term average given by *Wallace et al.* [1977] for the Sargasso Sea. The second organic carbon flux ($0.86 \text{ mol C m}^{-2} \text{yr}^{-1}$ at 150 m) was measured at the same time as the wet deposition collections and was obtained from 1989 measurements by the U.S. Joint Global Ocean Flux Study off Bermuda [*Knap et al.*, 1991]; a summary of the calculated fluxes is given in Table 3. The particulate metalloid fluxes have uncertainties due to the measurement of carbon fluxes (i.e., $0.3\text{-}0.86 \text{ mol C m}^{-2} \text{yr}^{-1}$) and variability in the metalloid:C ratios (i.e., $\pm 35\%$). Thus the uncertainties in atmospheric and water column particulate fluxes are roughly equivalent.

The flux ratios in Table 3 indicate that atmospheric deposition can balance 22-61% of the particulate arsenic flux from surface waters, 33-100% of the antimony flux, and 37-100% of the particulate selenium flux. The atmospheric/particulate flux ratios for antimony and selenium in Table 3 compare favorably with the estimates made by *Buat-Menard and Chesselet* [1979] for the tropical North Atlantic (31% for Sb and 100% for Se). Thus atmospheric deposition of antimony and selenium on a yearly basis is a large portion of their total input to western Atlantic surface waters; other sources such as horizontal transport in the water column appear to supply much of the arsenic. However, it is important to remember that fluxes out of surface waters, like the atmospheric fluxes (Figure 5), probably also show seasonal variations (e.g., coupled to primary production). Depending on how these inputs and outputs are temporally phased, the actual degree to which atmospheric deposition controls metalloid concentrations in surface waters will vary.

CONCLUSIONS

Results from Bermuda show that antimony, arsenic, and selenium in wet deposition appear to be derived from three potential sources: mineral aerosols, fossil fuel combustion, and marine sources, possibly volatile biogenic emissions. Correspondingly, meteorological controls on metalloid concentrations and enrichment factors are observed. The highest metalloid concentrations and enrichment factors in precipitation are found when air masses from North America are intercepted. In contrast, when air masses pass over North Africa metalloid concentrations are greatly reduced and enrichment factors approach crustal values. The resulting atmospheric fluxes of metalloids to the surface ocean can be substantial fractions of their total input, particularly for antimony and selenium. Furthermore, these air-sea fluxes represent an important sink in global metalloid budgets. As an example, the anthropogenic plus natural flux of selenium to the global atmosphere is estimated at $12 - 19 \times 10^9 \text{ g Se yr}^{-1}$ [*Mosher and Duce*, 1987]. If the atmospheric flux on Bermuda is extrapolated over the entire North Atlantic Ocean ($5.49 \times 10^{12} \text{ m}^2$), then $2.2 \times 10^9 \text{ g Se yr}^{-1}$, or 12-18% of the global emissions, are deposited in the North Atlantic. While extrapolating these Bermuda data to the entire North Atlantic basin is tenuous, this deposition value is probably a very conservative estimate since the Bermuda flux is lower than other regional estimates [e.g., *Ross*, 1985; *Duce et al.*, 1991]. Nevertheless, these deposition estimates and the flux ratios in Table 3 demonstrate that atmospheric transport and

deposition of metalloids to the ocean's surface play an important role in both their global and their marine cycles.

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