Atmospheric Trace Metals at Remote Northern and Southern Hemisphere Sites: Pollution or Natural?

Abstract. *The chemical composition of atmospheric particles collected near sea level over the North Atlantic indicates that Al, Sc, Mn, Fe, Co, Cr, Na, Mg, Ca, K, and Sr are derived from either crustal weathering or the ocean. The elements V, Zn, Cu, Cd, Pb, Sb, and Se are present in concentrations higher than expected from these sources. Although the V is probably derived from pollution sources on the North American continent, a comparison of enrichment factors relative to average crustal material for the remainder of these elements over the North Atlantic with enrichment factors for similar samples collected at the geographic South Pole suggests that the anomalously high enrichment factors may be due to natural rather than anthropogenic sources. A vapor phase for these metals may be involved at their source.*

Within the past several years there has been an increasing interest in the determination of the concentrations and sources of trace metals in the atmosphere in remote areas (*1, 2*). To a large extent, this interest has resulted from a concern that, as a result of technological advances, man may be affecting the distribution and composition of atmospheric particulates on a hemispheric, if not global, scale. We present here the results of the trace metal analysis of a series of atmospheric particulate samples collected north of 30°N over the Atlantic Ocean. In an attempt to determine whether natural or anthropogenic sources may be responsible for the trace metal concentrations observed, the relative quantities of these trace metals are compared to similar tropospheric samples collected at the geographic South Pole (*2*) (90°S, 2800 m above sea level).

Atmospheric samples have been collected over the past several years from a bow tower 8 m high on the University of Rhode Island's R.V. *Trident* over wide areas of the North Atlantic Ocean. Sampling has also been initiated recently from a tower 20 m high on the southeastern coast of Bermuda. Details of the collection and analytical procedures for samples collected from these platforms have been described elsewhere (*3*). Briefly, atmospheric particulate samples were collected on double (Whatman 41) or single (Delbag type 99/97 polystyrene) filters (20 by 25 cm) mounted in plastic filter holders. The typical sampling rate was 1 to 2 standard cubic meters (SCM) (298°K, 1 atm) per minute, and the sampling duration averaged approximately 24 hours. Both types of filters have collection efficiencies of better than 95 percent for particles with radii $\geqq 0.1$ μm at these flow rates. Sampling on the ship and at the Bermuda tower is controlled automatically by wind direction. On the *Trident* the collection pump operates only when the relative wind is ± 45° off the bow. At other times the pump is shut down, and a door closes automatically over the filter to protect it from shipboard contamination. A similar wind control system is used on the Bermuda tower to avoid local contamination. Since clean marine air contains approximately 200 to 400 condensation nuclei (CN) per cubic centimeter of air, CN counts significantly higher than this range suggest contamination from some local source. A recording CN counter is integrated into the wind control system on the Bermuda tower, and sampling is automatically terminated if the CN exceed approximately 500 cm^{-3} *or* if the wind is blowing off the land. By use of these automatic features, atmospheric particulate samples that are representative of the locally uncontaminated marine atmosphere can generally be collected from these sampling platforms.

Filters are processed both in the field and in the laboratory in laminar flow, clean benches to reduce contamination to a minimum. Filter blanks are taken at regular intervals at all locations. These filters are handled and processed in the same manner as the actual samples and are mounted in filter holders. The trace metals Na, Mg, K, Ca, Sr, Al, Fe, Se, V, Mn, Sc, Co, Cr, Zn, Cu, Sb, Pb, and Cd are determined by a combination of flame and flameless atomic absorption spectrophotometry and instrumental neutron activation analysis with the use of the Rhode Island Nuclear Science Center reactor ($\phi_{thermal} = 4 \times 10^{12}$ neutron cm^{-2} sec^{-1}).

Atmospheric particulate samples have been collected on 13 cruises of the *Trident* in the North Atlantic. Our discussion of samples from the Northern Hemisphere will be restricted to *Trident* samples collected north of 30°N over the North Atlantic (in the westerlies) during the period 1970 through 1972 and to several preliminary samples (for Zn and Cd only) collected from the Bermuda tower (32°15′N, 64°52′W). Most atmospheric samples collected over the North Atlantic between the equator and 30°N were dominated by large quantities of Sahara dust transported across the Atlantic Ocean by the northeast trades (*4*) and are not representative of the general atmospheric particle population over marine regions. Midpoint collection locations for the samples obtained from the *Trident* discussed in this report are shown in Fig. 1.

Obvious natural sources for atmospheric trace metals include the ocean and weathering of the earth's crust. Sodium is used as a reference element to estimate the contribution of the sea to any metal component of the marine aerosol. An enrichment factor, *EF*, for an element X in the atmospheric particles relative to bulk seawater, can be calculated as follows:

$$EF_{sea} = \frac{(X/Na)_{air}}{(X/Na)_{sea}}$$

where $(X/Na)_{air}$ and $(X/Na)_{sea}$ refer, respectively, to the ratio of the concentration of X to that of Na in the atmosphere and in bulk seawater; EF_{sea} values near unity for any element X would suggest the sea as a likely source for that element in the atmosphere. Calculation of EF_{sea} values for samples collected from the *Trident* and Bermuda indicate that the only atmospheric trace metals, aside from Na, which clearly originate predominantly from bulk seawater are K, Mg, Ca, and Sr (*5*).

In an attempt to determine the contribution of crustal weathering to any metal component of marine aerosols, Al, which comprises over 8 percent of the average crustal material, is used as a reference element. An enrichment factor, EF_{crust}, for any element X in the atmospheric particles relative to the crust, can be calculated as follows (*2*):

$$EF_{crust} = \frac{(X/Al)_{air}}{(X/Al)_{crust}}$$

where $(X/Al)_{air}$ and $(X/Al)_{crust}$ refer, respectively, to the ratio of the concentration of X to that of Al in the atmosphere and in the average crustal material; EF_{crust} values near unity for any element X suggest that crustal material is the probable source for that element in the atmosphere in remote areas. However, this approach will not distinguish between crustal material injected into the atmosphere by natural processes and that injected as a result of man's activities, for example, increased exposure of soil surfaces due to agriculture and other land-clearing operations; crushed stone, sand, and gravel operations; and soil particles suspended by vehicle traffic. Coal and even fly ash also have a relative concentration of many trace metals similar to that of average crustal material (*6*). In addition, mean crustal ratios can only be used as a crude approximation of the relative composition of crustal material aerosols, owing to differing types of crustal material and soils in various source areas and uncertainties concerning fractionation during weathering processes (*7*). Thus, EF_{crust} variations from unity up to an order of magnitude may still indicate a crustal material source for the elements. It is clear that enrichment factors must be used with caution in attempting to ascertain atmospheric trace metal sources.

Concentration ranges for the various trace metals collected over the North Atlantic are presented in Table 1. Since the collection sites were from several hundred to several thousand kilometers from major landmasses, the concentration range for any metal generally varied over approximately two orders of magnitude. Thus, mean concentrations for any metal have little significance for the sample set as a whole and are not reported. The EF_{crust} values for the various trace metals have a much smaller variation, however, and geometric mean EF_{crust} values are also presented in Table 1.

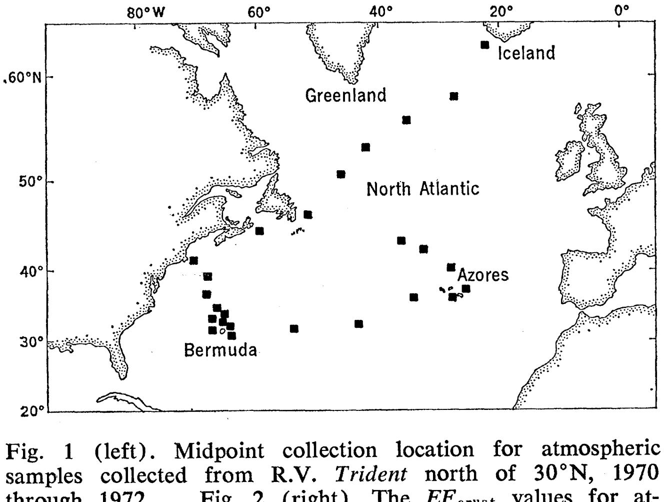
Table 1. Concentration range and mean EF_{crust} values for atmospheric trace metals collected over the Atlantic north of 30°N.

Element	Concentration range (ng/SCM)	Geometric mean* EF_{crust}
Al	8–370	1.0
Sc	0.0008–0.031	0.8
Fe	3.4–220	1.4
Co	0.006–0.09	2.4
Mn	0.05–5.4	2.6
Cr	0.07–1.1	11
V	0.06–14	17
Zn	0.3–27	110
Cu	0.12–10	120
Cd	0.003–0.62	730
Pb	0.10–64	2,200
Sb	0.05–0.64	2,300
Se	0.09–0.40	10,000

* Calculated on the basis of the mean crustal abundances of Taylor (*13*).

The elements Sc, Mn, Fe, Co, Al, and perhaps Cr appear to have a crustal source in these atmospheric samples. The elements V, Zn, Cu, Cd, Sb, Pb, and Se are apparently present in the atmospheric particulate matter in concentrations too high to be explained in terms of normal crustal weathering processes. The mean EF_{crust} values obtained for the North Atlantic samples are compared graphically with those for the South Pole samples (*2*) in Fig. 2. It is apparent, within the statistical variations presented, that the enrichment factors for all the elements determined in both locations are in very good agreement, with the exception of those for V. The significantly higher mean V enrichment factor found for samples collected in the North Atlantic westerlies [which is not apparent in samples collected in the North Atlantic northeasterly trades, where EF_{crust} is 1.4 (*8*)] is almost certainly due to the transport of pollution aerosols from the east coast of North America across the Atlantic on the prevailing westerlies. The source for V in these pollution aerosols is very likely the combustion of heavy fuel oils containing V-porphyrin complexes (*9*).

The general agreement between the EF_{crust} values for samples collected at the South Pole and over the North Atlantic is potentially significant relative to the source of these trace metals. With respect to the highly enriched elements at the South Pole, Zoller *et al.* have pointed out that these are also the more volatile elements and have suggested that the relatively high volatility of these elements and many of their compounds might well be associated with their high enrichment factors (*2*). Zoller *et al.* have also suggested that high-temperature processes, either natural or anthropogenic, could be responsible for the enrichment of these metals observed in Antarctica (*2*). Comparison of the North Atlantic results presented here with the South Pole data suggests that long-range transport of noncrustal anthropogenic pollution may not be the cause of the high enrichment factors observed in the



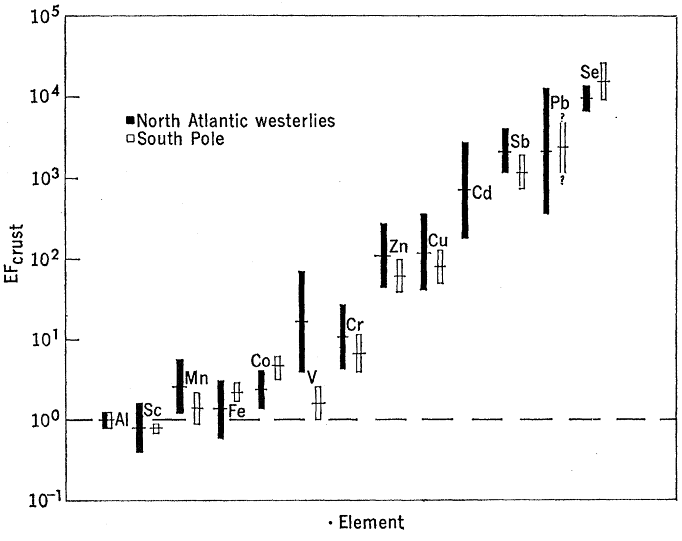


Fig. 1 (left). Midpoint collection location for atmospheric samples collected from R.V. *Trident* north of 30°N, 1970 through 1972. Fig. 2 (right). The EF_{crust} values for atmospheric trace metals collected in the North Atlantic westerlies and at the South Pole. The horizontal bars represent the geometric mean enrichment factors, and the vertical bars represent the geometric standard deviation of the mean enrichment factors. The EF_{crust} for Pb at the South Pole is based upon the lowest Pb concentration (0.2 ng/SCM) (*2*).

two locations. It has been estimated that approximately 90 percent of the particulate pollutants in the global troposphere are injected in the Northern Hemisphere (*10*). Interhemispheric mixing times in the troposphere are relatively long, on the order of 6 to 12 months (*11*), and the atmospheric residence time for particles in the troposphere is generally less than a week but certainly no longer than 3 to 4 weeks (*12*). Thus, there is not sufficient time for pollution source trace metals to be transported from their primary source area in the Northern Hemisphere to the Southern Hemisphere to give similar EF_{crust} values in both areas before the particles are removed from the atmosphere. This suggests that the anomalously high atmospheric concentrations of these trace metals may originate primarily from some natural source. Of course, alternative explanations are also possible. For example, the smaller land area in the Southern Hemisphere probably results in a lower natural production of atmospheric crustal material. This, combined with the lower pollution production in the Southern Hemisphere, could possibly account for the similarity in the ratios of pollution elements to Al in both hemispheres.

The chemical properties of the elements themselves suggest that a vapor phase, either from a high- or low-temperature source, probably plays an important role in the atmospheric chemistry of these elements. Possible natural processes which could be important for some of the metals include volcanism and biological mobilization (including methylation). Chemical fractionation of some of these trace elements during the production of atmospheric sea salt particles due to association of the trace elements with surface-active substances in the sea cannot be ruled out. All these potential natural sources for the enriched elements are presently under investigation.

The conclusions above may not apply to Pb, and the close agreement of the Pb enrichment values at the two locations may be coincidental. As described previously (*2*), in the calculation of the mean EF_{crust} value for Pb at the South Pole the lowest atmospheric Pb concentration observed was used because of concern that other samples may have been contaminated with this element. Recent measurements made with the improved collection techniques at the Bermuda tower described above suggest that background atmospheric Pb concentrations over North Atlantic areas may be significantly lower than those previously measured from the *Trident* by our group and by others as a result of contamination during sample collection. Improved collection techniques similar to those in use at the Bermuda tower have recently been instituted at the South Pole, and subsequent samples collected from both locations should make it possible to resolve the question of the magnitude and variation of the Pb enrichment.

We anticipate that additional samples will be obtained over the next several years from the sampling stations in Bermuda and Antarctica and from new stations in Hawaii and American Samoa. The samples collected at these sites (the improved collection techniques described above as well as particle size separation will be used at all these sites) will enable us to ascertain whether or not the similar enrichment factors observed to date at these two remote sites in the Northern Hemisphere and Southern Hemisphere are truly representative of the global background aerosol.

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Petroleum Pollutants in Surface and Groundwater as Indicated by the Carbon-14 Activity of Dissolved Organic Carbon

Abstract. *The ^{14}C activity of dissolved organic carbon (DOC) can be used to distinguish between the fossil organic carbon due to petrochemical effluents and modern organic carbon due to domestic wastes and natural decaying organic matter. Rivers polluted by petrochemical effluents show varying amounts of depression of the DOC ^{14}C activity, reflecting concentrations of ^{14}C-deficient fossil carbon of as much as about 40 percent of the total DOC.*

Variations in the carbon isotope ratios have proved useful in the study of many geochemical processes and can also serve as indicators of man's actions in cases where natural isotope ratios have been changed by the addition or removal of carbonaceous material with characteristic isotope ratios. This report describes a method in which the ^{14}C activity of nonvolatile dissolved organic carbon (DOC) (*1*) is used to measure concentrations of dissolved petrochemical pollutants in surface and groundwater.

Dissolved organic carbon consists of many complex organic compounds, such as humic and fulvic acids, herbicides, pesticides, synthetic detergents, phenols, and petroleum hydrocarbons. Once organic matter enters the aquatic