Lead, Mercury, Cadmium and Arsenic in the Environment
Edited by T. C. Hutchinson and K. M. Meema

CHAPTER 11

Metal Transfer Across the Air–Sea Interface: Myths and Mysteries

PATRICK BUAT-MÉNARD

Centre des Faibles Radioactivites,
Laboratoire Mixte CNRS-CEA, PB 1,
91190, Gif sur Yvette, France

and

ROBERT A. DUCE

Center for Atmospheric Chemistry Studies,
Graduate School of Oceanography,
University of Rhode Island, Kingston,
RI 02881, USA

ABSTRACT

Our increasing awareness of the global atmospheric mobilization of heavy metals such as As, Cd, Hg and Pb by human activities has raised the question of the perturbation of the oceanic cycles of these elements. Such a perturbation is now evident for Pb and probably for Sn, and the level of perturbation appears closely related to the atmospheric input rate for these metals. However, there is growing evidence of significant spatial and temporal variability of atmospheric concentrations of heavy metals and their fluxes to the ocean. This variability is a major obstacle to obtaining representative field data.

A number of misconceptions, or 'myths', have developed over the years concerning heavy metals in the atmosphere and their exchange with the oceans. Several of these are evaluated critically in this chapter. For example, the concept of constant background concentrations of metals in air, rain, and dry deposition is certainly erroneous, and recent investigations indicate clearly that collection of precipitation in remote regions for trace metal analysis is not a routine task. Problems include sample contamination during collection and the representativeness of the rain samples collected. Problems with the use of scavenging ratios for estimating wet deposition and pitfalls in field studies of heavy metal dry deposition are also discussed.

Due to the recycling of metals from the ocean into the atmosphere, problems with determining net air/sea exchange rates arise, even if accurate total deposition measurements in remote marine areas can be made.

Several 'mysteries' still prevent us from attaining a comprehensive understanding of air/sea metal exchange, and several of these are discussed as well. For example, are there significant unknown natural or anthropogenic sources for atmospheric metals? What are the physical and chemical forms of metals in the marine atmosphere? What is the fate of atmospheric metals when they enter the ocean?

INTRODUCTION

Over the last 15 years there has been an increasing concern about the levels of toxic metals such as lead (Pb), cadmium (Cd), mercury (Hg) and arsenic (As) in remote marine air and rain. There is more and more evidence that, at least in the northern hemisphere, the atmospheric cycles of such elements are now strongly perturbed by human activities, primarily high-temperature combustion processes (Andreae *et al.*, 1984). How such a geochemical perturbation in the atmosphere interacts with the oceanic cycles of these elements is a matter of crucial interest, since many trace metals are both essential for the development of marine life and potentially toxic for marine life above certain concentration levels. The assessment of the human factor in the present cycling of metals through the atmosphere and oceans is, however, a very difficult exercise since natural sources are still poorly known. Nevertheless, recent years have seen a tremendous increase in our knowledge of the global atmospheric chemistry of trace metals. The use of improved sampling and analytical techniques has enabled us to document reasonably well latitudinal and longitudinal distributions of the atmospheric concentrations of trace metals. The combined use of geochemical and meteorological tracers has enabled considerable insight to be made into the relative contributions of the various natural and man-made sources (Buat-Ménard, 1983).

One major conclusion which now emerges is that the magnitude of the anthropogenic input of metals from the atmosphere to the ocean exhibits a strong spatial and temporal variability. This is primarily because of (a) meteorological factors (air mass circulation patterns) and (b) the fact that, with the exception of mercury, trace metals are found primarily associated with atmospheric particulate matter and, as a consequence, have very short atmospheric residence times (~ one week). Such regional variability is also a characteristic of the oceanic cycle of some of these elements. Elements such as manganese (Mn) and lead have a mean oceanic residence time of the order of 100 years (Bruland, 1983), much shorter than the mixing time of the ocean (1000 years). Thus any reliable assessment of the impact of the atmospheric deposition of trace metals on oceanic chemistry cannot be obtained simply by a consideration of global mass balance. Together with the obvious requirement for data on the chemical speciation of metals in the marine atmosphere (which addresses the problem of their biological availability once they enter the ocean), the need for accurate data on net air-to-sea fluxes is evident for any oceanic region. These data are extremely difficult to obtain because of theoretical, and especially experimental, difficulties.

The theoretical aspects of dry and wet deposition of aerosol particles to the ocean surface will not be reviewed here since this topic has already been treated extensively (e.g. Slinn, 1983). In principle, knowledge of aerosol particle deposition processes combined with the use of atmospheric transport models should allow an evaluation to be made of anthropogenic air-to-sea fluxes to a given oceanic region, provided accurate source-emission inventory data are available. At the present time such an approach is not possible for trace metals and we must rely on experimental field measurements for such an assessment.

In this chapter we will evaluate some of the commonly held myths relative to air-sea exchange of metals, for both wet and dry deposition, and outline some of the current mysteries which make the accurate quantitative determination of air/sea fluxes so difficult.

MYTHS

There are 'Background Concentrations' for Metals in Air, Rain and Dry Deposition

Ten to fifteen years ago it became fashionable to discuss a fairly uniform 'background aerosol', a particle population that was believed to have a rather uniform chemical composition and size distribution and that was relatively constant in space and time in the free troposphere. This led to the concept of background air and rain concentrations for those substances found primarily on particles in the atmosphere. During the last few years a number of rather intensive studies of the chemical composition and size distribution of aerosol particles in the remote marine atmosphere have given us a much more accurate description of the geographical and temporal variability of trace substances in the global troposphere. They have shown clearly that the background marine atmosphere is anything but constant relative to its trace element, and particularly metal, content. For example, over the North Pacific mean weekly differences in the aluminosilicate aerosol concentration can range up to a factor of 100 or more (Uematsu *et al.*, 1983), with similar differences in the rain concentrations. These differences are much larger than the variability due to analytical precision and/or accuracy of the chemical analysis of aerosol particles for trace metals over the ocean. Analytical variability ranges from 10 to perhaps 50%, depending on the metal. Geographical differences in the atmospheric concentration distribution of the metals of interest in this workshop can also span several orders of magnitude over the world's oceans, as is shown for lead in Table 11.1. While there have been relatively few careful studies of the metal content of precipitation over the ocean, the few data that are available (see Table 11.2) confirm that there is no 'background' concentration of metals in rain.

Table 11.1 Lead in rain carefully collected from islands and ships

Location	Pb conc. (ng/kg)	Reference
North Atlantic		
Tower–Florida Keys, 25° N, 81° W	770–960	Settle *et al.*, 1982
Ship's bow 34° N, 66° W	550	Settle *et al.*, 1982
North Pacific trades		
Tower–Enewetak, 11° N, 162° E	6–63	Settle *et al.*, 1982
Ship's bow, 11° N, 155° W	43	Settle and Patterson, 1982
South Pacific trades		
Tower–Samoa, 14° S, 170° W	7	Settle *et al.*, 1982
Ship's bow, 15° S, 150° W	9	Settle *et al.*, 1982
South Pacific westerlies		
Tower–New Zealand, 34° S, 173° E	17	Patterson and Settle, unpublished data
Ship's bow, 35° S, 161° E	41	Patterson and Settle, unpublished data

Table 11.2 Metal concentrations in marine rains (μg/kg)

Metal	Shetland Islands	Bay of Bengal	Bermuda	Enewetak	Samoa
Pb	11	—	0.77	0.023	0.007
Cd	—	—	0.06	0.0041	~0.002
Hg	—	—	—	0.002	—
As*	<8	—	—	—	—
Cu	15	—	0.66	0.03	~0.01
Zn	29	100	1.2	0.15	~0.1
V	1.8	—	—	0.03	—
Fe	170	30	4.8	1.5	~0.4
Mn	6	—	0.27	0.08	~0.01

* Hawaii: 0.019; California coast: 0.019 (Andreae, 1980).
Sources: Shetland Is. from Cambray *et al.*, 1975; Bay of Bengal from Mahadevan *et al.*, 1982; Bermuda from Jickells *et al.*, 1984; Enewetak from Arimoto *et al.*, 1985; Fitzgerald *et al.*, 1983; Settle *et al.*, 1982; Samoa from Duce *et al.*, unpub. data; Settle *et al.*, 1982.

Concentrations of metals in air and rain are, of course, related to the source strengths for the metals and the wind flow patterns over the ocean. For metals in aerosol particles derived primarily from pollution sources, we would expect the highest concentrations to be observed over the North Atlantic, downwind of industrial and population centers of North America. Lower concentrations would be expected over the North Pacific and northern Indian Oceans, while the lowest concentrations would be expected over the South Pacific and South Atlantic. The data in Table 11.3 confirm this

Table 11.3 Typical atmospheric metal aerosol concentrations in marine regions (ng/m^3)

Location	Pb	Cd	As particulate	As vapor	Hg particulate	Hg vapor	Reference
Shetland Islands	30	<9	1.3	–	<0.05	–	Peirson *et al.*, 1974
Western Mediterranean	50	0.5	1.8	–	0.17	–	Arnold *et al.*, 1982
Bermuda area	3	0.2	0.16	–	0.0007	1.6	Duce *et al.*, 1976; Fitzgerald *et al.*, 1983; Walsh *et al.*, 1979a
North Atlantic	10	–	–	–	<0.07	1.6	Buat-Ménard and Chesselet, 1979; Slemr *et al.*, 1981
Hawaii	2	0.02	0.06	–	–	–	Hoffman *et al.*, 1972; Walsh *et al.*, 1979a
Enewetak	0.12	0.003	–	–	0.0006	1.6	Duce *et al.*, 1983; Fitzgerald *et al.*, 1983; Settle and Patterson, 1982
South Atlantic	–	–	–	–	–	1.05*	Slemr *et al.*, 1981
Samoa Area	~0.02	<0.005	0.017	0.002	–	1.05*	Walsh *et al.*, 1979a; Fitzgerald *et al.*, 1983; Duce, unpub. data; Patterson unpub. data

* 10°–20° S.

general picture. For metals such as mercury, which may have significant natural sources, such as marine and terrestrial biological activity and volcanoes as well as pollution sources, the distribution pattern might not be expected to be so variable. Indeed, a significant marine biological source for atmospheric Hg has been suggested by Fitzgerald *et al.* (1984) on the basis of measurements during a crossing of the productive equatorial upwelling region in the Pacific Ocean.

There are very few data for arsenic in marine rain. Andreae (1980) has provided the most extensive data set (Table 11.2), but samples have only been analyzed from the west coast of the United States and Hawaii. In both locations the As concentration in rain is approximately the same. Walsh *et al.* (1979b) have calculated, and Andreae (1980) concurs, that approximately 75% of the global emissions of As to the atmosphere each year are from pollution sources. Measurements of particulate As (generally less than 10% of the As in the marine atmosphere is in vapor form) confirm that concentrations decrease from the North Atlantic to the North Pacific to the South Pacific (Walsh *et al.*, 1979a—see Table 10.3), supporting the importance of anthropogenic sources for As in the northern hemisphere.

Collection of Precipitation for Metal Analysis is Simple

Obviously the first step toward evaluation of the wet deposition of heavy metals to the surface of the ocean is collection of precipitation samples. This would appear to be a most trivial task, but it is perhaps here that most research studies of metal wet deposition in remote marine (or even continental) regions run aground. We will restrict the discussion to the collection of rain, where a number of problems quickly arise—some unique to rain collection over the sea and some applicable to rain collection anywhere. We will also consider only true wet deposition measured by continuously open collectors.

Representativeness of Rain Samples

All rain and rain samples are not the same. Rain over the ocean is associated with a variety of precipitation systems, ranging from simple trade wind showers, with a typical horizontal cross-section of 500 to 1000 meters and vertical extent of as little as 1500 to 2000 meters, to mesoscale storm systems in mid-latitudes, with horizontal dimensions of 1000 to 1500 km or more and a vertical extent up to or through the tropopause. The chemical composition of rain from these precipitation systems may be quite dissimilar. This can arise from several factors, ranging from differences in the vertical distribution of the rain-forming portions of the cloud systems to differences in duration, intensity, and droplet size of the precipitation.

As an example, over the North Pacific region most of the mineral aerosol particles are derived from Asian deserts. Particle production in these desert regions is very seasonally dependent, dropping by over an order of magnitude from the windy high dust period in the late winter and spring to the very low dust period in the late summer and fall (Duce *et al.*, 1980; Uematsu *et al.*, 1983; Parrington *et al.*, 1983; Parrington and Zoller 1984). In addition, upper level wind patterns (700 mb and above) result in strong transport to the east over the North Pacific during the late winter and spring, with weaker and more variable winds during the rest of the year. The temporal changes in the atmospheric mineral aerosol concentration are reflected in the rain concentrations. Measurements of metals derived from Asia in rain over the North Pacific during only October, for example, could give very misleading information relative to the annual flux of these metals to the North Pacific.

Mineral particles and associated metals from Asia enter the marine boundary layer from above as a result of gravitational settling, turbulent mixing, and/or precipitation, and thus are relatively uniformly distributed vertically. On the other hand, most metals whose source in the marine atmosphere is the ocean are found concentrated in the marine boundary layer, generally in the lower 1–2 km. In addition, metals present on the smallest particles (e.g. $< 1 \mu m$), whether derived from continents or the ocean, have longer atmospheric residence times and are more uniformly distributed vertically in the atmosphere. Obviously rain from mesoscale storm systems, with their greater vertical extent, would more effectively remove the metals transported in the upper troposphere and those on smaller size particles than the more vertically limited trade wind showers.

While there are essentially no data on the metals of interest here as a function of altitude over the ocean, and really not even sufficient data to distinguish concentration differences among different precipitation system types, we can illustrate the vertical variability in concentration using mineral aerosol and sea salt. For example, in Table 11.4 the mean and range of the aluminum (Al) concentration (an indicator of mineral aerosol from continental regions) and the sodium (Na) concentration (an indicator of sea salt) are presented for near sea level on Oahu and 3400 m on Hawaii, approximately 300 km apart horizontally. Note the very different Al concentrations during the high dust and clean periods at both sites. The standard deviation of the mean Al concentration during these two time periods is rather high because the dust storm activity in Asia results in pulses of dust being transported over the North Pacific. The analytical uncertainty in measurement of the Al and Na concentrations is 10% or less. Note also that there is relatively little difference in the mean Al concentrations at the two altitudes during the individual time periods, while the Na (or sea salt) concentration decreases from 2 to 3 orders of magnitude from sea level to 3400 m.

Table 11.4 Atmospheric concentrations at sea level and 3400 m in Hawaii* (ng/m^3)

Location	Aluminum		Sodium	
	Dust season	Clean season	Dust season	Clean Season
Oahu, 15 m (1981–84)				
Mean	95 ± 82	17 ± 20	4300 ± 1400	4300 ± 2200
Range	12 – 390	1.2 – 120	2400 – 6600	400 – 11,400
No. of samples	66	47	67	54
Hawaii, 3400 m (1979–82)				
Mean	71 ± 51	6.7 ± 2.3	25 ± 13	11 ± 9
No. of samples	88	89	88	89

* From Uematsu *et al.*, 1983; Parrington *et al.*, 1983; Uematsu (personal communication).

Contamination of Rain Samples

Contamination of rain samples collected in remote open ocean and continental regions is a fundamental problem that is often given relatively little attention. Contamination can occur as a result of (1) unsatisfactory collection of material, (2) inadequate cleaning of the collection system, (3) improper storage of the system between rain events, and (4) collection of locally produced material in the sampling system which is not representative of the marine rain being investigated.

The collection system must be constructed of material which will not itself contaminate the sample, for example, through leaching processes, etc. For most heavy metals, one of the cleanest collection materials is conventional (low density) polyethylene, which should be cleaned carefully and regularly with ultra-pure acid and water (see Settle *et al.*, 1982). The collector must be carefully covered between rain events and washed anew before each collection. Clean room techniques are required during the actual collection and processing of the precipitation samples.

Collection of a rain sample representative of rain falling to the ocean surface, rather than locally derived material in the air, is particularly difficult over the ocean. Collection of rain samples on land away from the coast is useless for obtaining information on metal transport from the atmosphere to the ocean. Collection along windward coastlines and/or from ships is necessary. In both cases, however, the sampling is fraught with pitfalls! To avoid local contamination from sea spray, sand and soil along a coastline, it is preferable to collect the rain from a tower several meters above ground level. Care must be taken to sample only when the wind is off the ocean and has been for some time. This is particularly difficult in convective rains, when the wind circulation in and around the shower itself is quite complex and unpredictable.

As an example, consider rain collected from an 18 meter high tower on the eastern tip of the island of Tutuila, American Samoa, as part of the Sea/Air Exchange (SEAREX) Program. Table 11.5 presents data on the atmospheric particulate concentration of lead and cadmium collected when the wind was coming directly off the ocean (O) and off the land (L). Note that even at this very remote and windward location on this relatively uninhabited island, the atmospheric lead concentrations were approximately an order of magnitude higher when the air flow was off the island, with the difference for Cd being somewhat less. The opportunity for contamination of rain with locally derived Pb and Cd during the passage of a tradewind shower is obvious.

Table 11.5 Atmospheric lead and cadmium in Samoa, 1981* (pg/m^3)

Sample no.	Pb	Cd
1-O†	25±5	2±1
1-L‡	120±20	10±3
2-O	22±5	4±2
2-L	130±20	14±4
3-O	1.5±0.8	8±2
3-L	210±40	8±2
4-O	5±2	<1
4-L	290±50	33±8

† Collected only when the air flow was off the ocean and condensation nuclei counts were <600/cm^3.

‡ Collected only when the air flow was off the island or the CN counts were >600/cm^3.

* Duce, unpublished data.

Collection of precipitation samples from ships also provides ample opportunity for contamination as a result of eddying of the wind around ship structures. However, the maneuverability of a ship often provides the opportunity to avoid these problems. The collection of uncontaminated rain samples at sea requires close coordination between the bridge and scientific teams. Rain areas should be carefully tracked by radar to establish the development, direction of movement, and speed of the rain system relative to the ship. If the rain system appears suitable for sampling, the ship should intercept the rainstorm from a direction that will cause the ship's exhaust plume to be carried downwind of the bow. When these precautions are taken and small towers, platforms, or poles are used for collection on the bow, clean rain samples can be obtained. Table 11.1 presents data for Pb in rains collected in a very careful and contamination-free manner in several open ocean regions from both island coastal towers and on the bows of ships. Similar concentrations of lead were observed from the different collection platforms in the individual regions, indicating that both types of rain collection can be made satisfactorily with proper care and planning.

Washout Factors are a Panacea for Estimating Rain Fluxes

Washout factors, or scavenging ratios, are often used to relate atmospheric concentrations of trace metals to their concentrations in rain. Washout factors have been defined in several ways, but all involve a ratio of the rain concentration to the atmospheric concentration of the substance of interest. A detailed review of washout factors and precipitation scavenging is presented by Slinn (1983) and Scott (1981), and these processes will not be discussed in depth here. We will define the washout factor, W, for any metal, M, as $(W)_{\mathrm{M}}$, given by:

$$(W)_{\mathrm{M}} = [(C)_{\mathrm{M,rain}} \times \rho]/(C)_{\mathrm{M,air}} \tag{1}$$

where $(C)_{\mathrm{M,rain}}$ is the concentration of metal M in rain in gm/kg, $(C)_{\mathrm{M,air}}$ is the concentration of metal M in the air in gm/m^3, and ρ is the density of air (1.20 kg/m^3) at standard conditions.

In this form washout factors are dimensionless,* but the density term is not used by all authors. Once the relationship between metal concentration in the air and in the rain has been established, one can utilize atmospheric metal concentrations to predict the concentrations in rain.

The use of washout factors to calculate metal deposition rates implicitly assumes that the concentrations of the metals in rain and air are linearly related. However, it is very difficult, if not impossible, to rigorously test the

---

* Washout is usually defined as

$$W = \frac{C(M, \mathrm{rain})}{C(M, \mathrm{air})}$$

with dimensions

$$\frac{\text{gm metal/kg rain}}{\text{gm metal/m}^3\text{ air}}$$

leading to m^3 air washed per kg rain. The Buat-Ménard and Duce definitions above lead to the dimensions

$$\frac{\text{gm metal/kg rain}}{\text{gm metal/m}^3\text{ air}} \times \frac{\text{kg air}}{\text{m}^3\text{ air}} = \frac{\text{kg air}}{\text{kg rain}} = \text{amount of air cleaned of all its metal by 1 kg rain}$$

significance of this relationship. Problems arise because of possible differences in the removal efficiency of particles as a function of chemical composition and rain droplet size. Rain concentrations represent an integrated removal throughout the atmospheric column through which the rain is falling, while the air concentration is determined only at the surface. Thus, metals with different vertical concentration profiles but similar surface air concentrations might have very different washout factors. An additional problem faced in truly remote marine regions is that it may take many hours, occasionally even days, to collect aerosol particle samples large enough to analyze, whereas rain samples may be collected over a period of minutes to hours. Thus, the true atmospheric concentration, even at the surface, appropriate to the washout factor calculation may not really be known. Scott (1981) also points out that smaller washout ratios would be expected in 'cold' clouds, that is, those where a much greater fraction of the precipitation occurs as a result of vapor growth rather than droplet coalescence processes. The latter apparently dominated in 'warm' rains, that is, those not containing ice particles or super-cooled droplets. Typical washout ratios for material present on particles in cold rains might be ~ 100, while in warm rains they might be ~ 1000.

One apparent advance in attempting to understand some of the factors leading to the variability in washout factors was the discovery that in urban or near-continental marine areas there was a relationship between the washout factor and the mass median diameter (MMD) of the particles containing the metals. For example, Scott (1981) has shown the relationship between $(W)_{\mathrm{M}}$ and the MMD for metals collected in St Louis (Gatz, 1975) and Chilton, UK (Cawse, 1974) (Figure 11.1), and Duce *et al.* (1979) have found similar results in the Florida Keys ($r = 0.76$, significant at $p = 0.01$) (Figure 11.2). In general, the washout factor increased with increasing particle size at all three locations. Scott (1981) and Slinn (1983) suggest that these results can be explained by the lower collection efficiency of the raindrops for the smaller particles (down to perhaps a few tenths of a micrometer radius), with the chemical composition, particularly solubility, of the different size particles also playing a role. The latter would be particularly important in marine areas for the sea salt aerosol particles, the major source for such metals as Na, K, Mg and Ca. However, for rains collected at Enewetak Atoll, over 5000 km from the nearest continent, there is strong evidence that there is no relationship between washout factor and particle size, as can be seen in Figure 11.3 ($r = 0.39$, not significant at $p = 0.1$). Corroboration of this result was obtained at Enewetak by Buat-Ménard *et al.* (1983). They measured the size distribution of aluminosilicate particles in the atmosphere and filtered from rain samples and were thus able to calculate washout factors for the various size particles. The results, presented in Table 11.6, show no statistical difference (1σ) in the values for $(W)_{\text{mineral aerosol}}$ for the different size

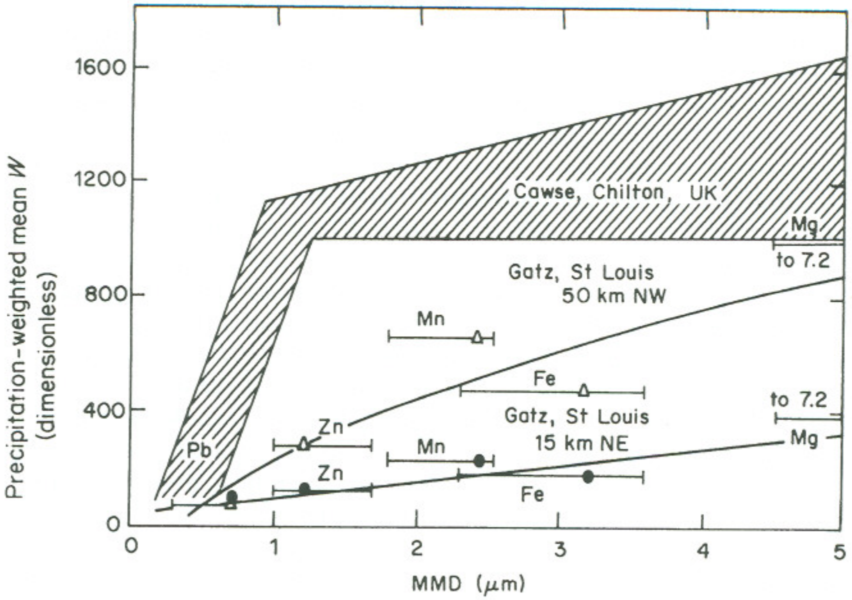

Figure 11.1 Variation of washout factor or scavenging ratio, *W*, as a function of particle size for various trace elements in urban areas (from Scott, 1981)

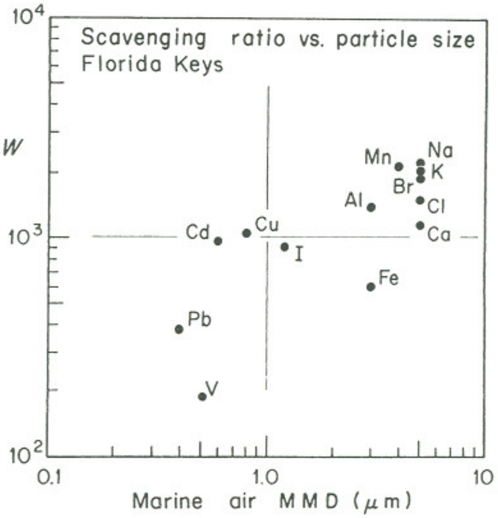

Figure 11.2 Variation of washout factor or scavenging ratio, *W*, as a function of particle size for various trace elements in the Florida Keys (from Duce *et al.*, 1979)

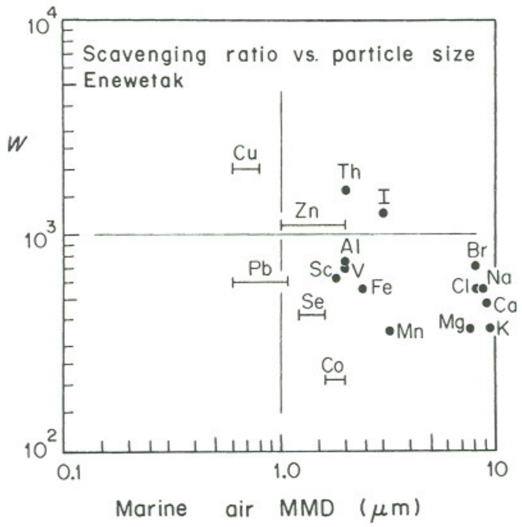

Figure 11.3 Variation of washout factor or scavenging ratio, *W*, as a function of particle size for various trace elements at Enewetak Atoll

Table 11.6 Washout factors for mineral aerosols, Enewetak*

Particle diameter (μm)	$(W)_{\text{mineral aerosol}}$†
<0.5	940 ± 1100
0.5–1	800 ± 620
1.0–1.5	500‡
1.5–3	310 ± 250
3.0–6	270 ± 170
>6	320 ± 120

* From Buat-Ménard *et al.*, 1983.

† One standard deviation, based on five air samples and three rain samples.

‡ Assumed value.

fractions. The cause of these differences between continental and remote marine regions is uncertain, although Slinn (1983) has suggested that in truly remote marine regions, where there are very few cloud condensation nuclei, essentially all particles are activated regardless of size and chemical composition. It is clear that any relationships developed between washout factors and particle size distribution in urban or continental regions may not apply over open ocean regions far from land.

A Field Approach to Dry Deposition Measurements is Straightforward

The dry deposition of aerosol particles to the ocean surface refers to all deposition processes except precipitation. It is often estimated by utilizing the deposition velocity, v_d, given by:

$$v_d = F/M \tag{2}$$

where v_d is the deposition velocity in cm/sec, F is the flux of particles to the surface in gm/cm^2 sec, and M is the atmospheric concentration in gm/cm^3.

Direct measurements of the dry deposition of trace elements to the ocean surface are not technically feasible at present. One method for obtaining reasonably accurate estimates of dry deposition is the use of available dry deposition models to a water surface as a function of particle size (Slinn and Slinn, 1980, 1981; Williams, 1982; Slinn, 1983). However, the use of such models requires an accurate measurement of the mass-size distribution of the trace metals. In addition, deposition velocities depend markedly upon particle size, relative humidity and wind speed, as shown for sea-salt deposition to the ocean in Figure 11.4.

Model calculations of dry deposition have been rather successful for sea-salt aerosol particles, provided extreme care was taken to obtain air samples that represent the true sea-salt particle mass and size distribution (McDonald *et al.*, 1982). Acceptably accurate size distribution for sea-salt aerosol particles can be deduced from the use of high-volume cascade impactors, when proper corrections are made for particle loss in the largest size range. However, the use of such sampling devices may cause serious problems for other types of aerosol particles to which trace metals may often be attached. For example, it appears that particle 'bounce' effects, especially for dry particles such as aluminosilicate minerals, can result in an apparent shift of the size distribution to smaller sizes (Buat-Ménard *et al.*, 1983). The situation is even worse for trace elements such as Pb, As and Cd because a major fraction of the mass of these elements occurs on particles less than $\simeq 0.25$ μm radius, and cascade impactors currently in use do not separate particles below that size range.

Since direct measurements of dry deposition of metals such as lead, cadmium and arsenic to the ocean are not possible, and model calculations suffer numerous pitfalls as well, most presently published dry deposition data are based on the use of surrogate surfaces, such as open vessels, plates or filters, for deposition measurements. The use of such surfaces has been seriously criticized because they do not accurately mimic the characteristics (microstructure, roughness, etc.) of natural water surfaces (Hicks *et al.*, 1980). Moreover, such measurements must be performed 10 to 20 m above

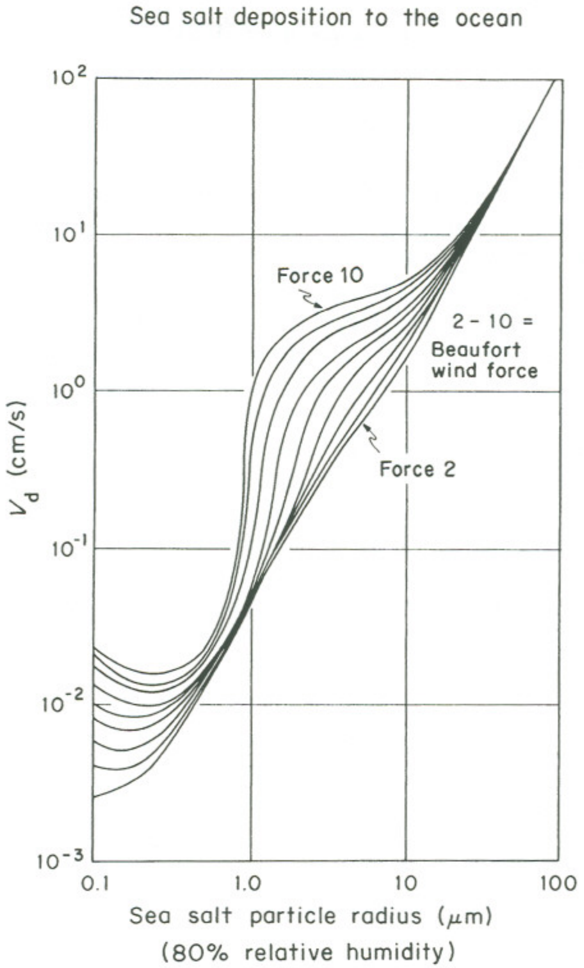

Figure 11.4 Atmospheric sea salt particle deposition velocity to the ocean surface as a function of wind speed and particle size, as derived from the theoretical considerations of Slinn and Slinn (1980)

sea-level (ships, islands), where the relative humidity, which influences the size of certain types of particles, is quite different from that close to the sea surface.

However, although the biases introduced by the use of a surrogate surface are real, model calculations appear to indicate that dry deposition of aerosol particles to the sea surface and to a surrogate surface such as a rimless plastic plate should agree to within a factor of two to three over a broad range of wind speeds and relative humidities. This has been shown for sea-salt aerosol particles and mineral aerosol particles collected over the tropical North Pacific (Arimoto *et al.*, 1985). Provided that such agreement holds for sub-micrometer aerosol particles, the correct magnitude of total dry deposition of some trace metals may be inferred through the use of such sampling devices.

In any event, we stress that such measurements must be performed in parallel with determinations of the mass-size distribution of the elements of interest. Although only a small percentage of the mass of Pb, Cd, and As in the marine atmosphere is present on large aerosol particles, that fraction may dominate the total dry deposition of these elements. The large particle fraction, in most cases, has a different origin than the sub-micrometer fraction. For example, anthropogenic lead is primarily associated with the sub-micrometer fraction whereas Pb of crustal origin or associated with sea-salt is present on much larger particles.

As an example, if the measured lead concentration as a function of particle size is applied to the theoretical deposition velocity as a function of particle size relationship (Slinn and Slinn, 1980), the small percentage of Pb on the largest particles (which may simply represent recycled Pb from the sea surface) controls the total Pb deposition, as shown in Figure 11.5 from Duce (1982). Therefore, a knowledge of the mass-size function of Pb

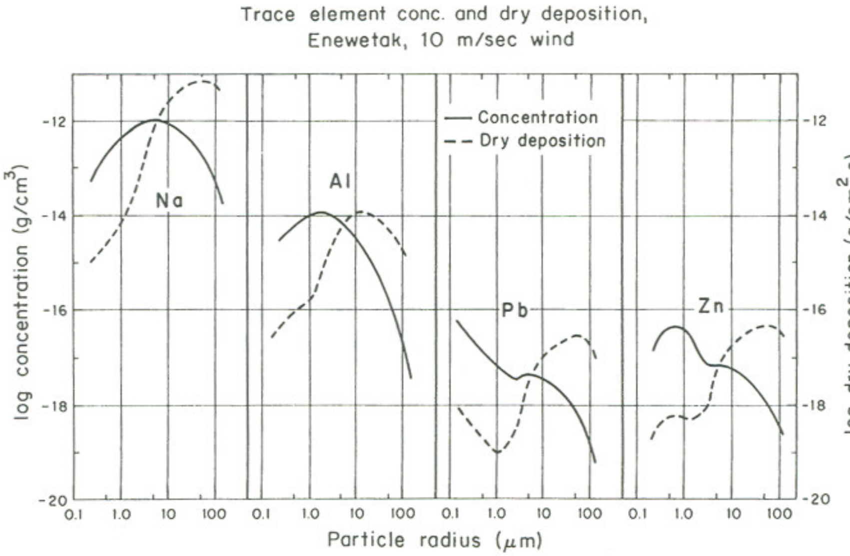

Figure 11.5 Atmospheric concentration and modeled dry deposition of trace elements at Enewetak Atoll as a function of particle size (from Duce, 1982)

is necessary to assess the relative contributions of the various Pb sources to the total dry deposition of this element.

Moreover, the atmospheric concentrations of particles derived from different sources vary temporally, so the relative contributions of the different sources to the total dry deposition will also vary temporally. Sampling must be undertaken at various times of the year to obtain representative annual dry deposition data at a given location. However, individual dry deposition samples should be collected over short enough time intervals to indicate the natural temporal variability in the deposition.

We have only considered the case of metals attached to aerosol particles. More than 90% of atmospheric mercury is present as gaseous elemental mercury. Fitzgerald *et al.* (1983) estimated the gas phase transfer of elemental Hg from the atmosphere to the ocean using the exchange model of Liss and Slater (1974) and assuming that the diffusivity of gaseous Hg is similar to radon and the sea surface is a perfect sink. Clearly, for metallic vapor phase compounds in the atmosphere, a completely different approach to that described here is needed to assess the significance of their dry deposition to the ocean (e.g. see Liss, 1983).

Accurate Deposition Measurements Guarantee Accurate Net Air/Sea Exchange Rates

While an accurate measurement of the concentration of metals in rain and dry deposition is a necessary first step in evaluating fluxes of these substances to the ocean, it is not sufficient in itself. The total amount of rainfall in the period of interest, per year for example, must be known. Potential problems arise concerning variability of rainfall amount and intensity with season and how this will affect the metal concentrations, as well as how seasonal changes in wind flow patterns or particle production processes will affect atmospheric metal concentrations at the marine location. Even taking these factors into consideration, significant problems remain. In the marine environment the gross deposition of a metal to the ocean is composed of a net input as well as a component associated with recycled sea spray. The importance of the atmosphere as a transport path for material from the continents to the ocean can only be assessed accurately if the relative contributions of the net and recycled components can be distinguished (Settle and Patterson, 1982; Jickells *et al.*, 1984; Arimoto *et al.*, 1985). There is strong evidence that atmospheric sea salt particles produced by bubbles bursting at the sea surface contain many metals in concentrations considerably higher than would be expected on the basis of the metal-to-sodium ratio of near-surface water. It is apparent that some fraction of these metals is associated with surface active organic material and is scavenged by the rising bubbles and concentrated on the sea-salt particles produced from a very thin layer of the air/sea interface when the bubbles burst (Weisel *et al.*, 1984). If this fractionation is not taken into account, the calculated net deposition to the ocean will be anomalously high.

As one approach to this problem, Arimoto *et al.* (1985) determined the metal/Na ratio on the largest atmospheric particles at Enewetak Atoll in the Marshall Islands, using only particles collected on the first stage of a cascade impactor. This represented, in general, particles with radii greater than about 3.5 μm. Most particles in this size range are sea salt, so this size range gave a good estimate of the metal/Na ratio in particles produced by bursting bubbles. These ratios also agreed well with direct measurements of the metal/Na ratios on sea-salt particles produced and collected artificially using the Bubble Interfacial Microlayer Sampler in the North Atlantic by Weisel *et al.* (1984) (see also Buat-Ménard, 1983 for an extensive discussion of this problem). The recycled component for any metal in the rain was calculated by

$$(\mathrm{M})_{\mathrm{recycled}} = (\mathrm{M/Na})_{\mathrm{Stage\ 1}} \times (\mathrm{Na})_{\mathrm{rain}} \tag{3}$$

where $(\mathrm{M})_{\mathrm{recycled}}$ is the concentration of metal M recycled from the sea in gm/kg, $(\mathrm{M/Na})_{\mathrm{Stage\ 1}}$ is the metal/Na ratio on stage 1 of the impactor and $(\mathrm{Na})_{\mathrm{rain}}$ is the sodium concentration in rain in gm/kg.

Recycled components calculated in this way for several metals ranged from 15% to about 50%, as shown in Table 11.7, and are comparable with the recycled fraction calculated using a similar approach by Jickells et al. (1984) at Bermuda. For Pb, ~30% was recycled in Enewetak rain according to Arimoto *et al.* (1985), compared with 10% at Enewetak calculated by Settle and Patterson (1982) and 17% at Bermuda determined by Jickells *et al.* (1984).

Table 11.7 Recycled metals in marine rains

Metal	Rain location	Percent metal Recycled	Reference
Pb	Bermuda	17	Jickells *et al.*, 1984
	Enewetak	30	Arimoto *et al.*, 1985
	Enewetak	10	Settle and Patterson, 1982
Cu	Bermuda	4	Jickells *et al.*, 1984
	Enewetak	48	Arimoto *et al.*, 1985
Zn	Bermuda	11	Jickells *et al.*, 1984
	Enewetak	15	Arimoto *et al.*, 1985
Fe	Bermuda	21	Jickells *et al.*, 1984
V	Enewetak	33	Arimoto *et al.*, 1985

Recycled components calculated in the same way for dry deposition measurements to a surrogate surface are shown in Table 11.8. They range from 12 to 100%. For lead, the percentage recycled varied considerably between samples. In two of the samples, approximately 50 to 60% of the gross Pb deposition was due to recycled material, but in a third sample, essentially all of the Pb could be attributed to sea spray.

Table 11.8 Dry deposition (gm/cm^{2}s) of lead, zinc and copper to a plastic plate[*]

Element	DD[†]	Total measured deposition	Deposition due to recycled sea salt	Net deposition		Percent recycled
				from crustal weathering	from other source(s)	
Pb	1	2.6×10^{-16}	1.4×10^{-16}	2.9×10^{-18}	1.2×10^{-16}	54
Pb	2[‡]	1.9×10^{-16}	2.1×10^{-17}	1.2×10^{-17}	0	100
Pb	3	$<8.5 \times 10^{-16}$	2.1×10^{-16}	3.6×10^{-18}	$<6.4 \times 10^{-16}$	>25
Pb	4[‡]	1.3×10^{-16}	7.4×10^{-17}	1.1×10^{-19}	5.6×10^{-17}	57
Zn	2	1.9×10^{-15}	2.3×10^{-16}	6.8×10^{-17}	1.6×10^{-15}	12
Cu	1	$\sim 5 \times 10^{-16}$	1.8×10^{-16}	1.3×10^{-17}	3.1×10^{-16}	~36
Cu	3	$\sim 3 \times 10^{-16}$	2.7×10^{-16}	1.6×10^{-17}	1.4×10^{-17}	~90
Cu	4	$\sim 2 \times 10^{-16}$	1.1×10^{-16}	4.9×10^{-19}	$\sim 9 \times 10^{-17}$	~55

[*] From Arimoto *et al.* (1985).
[†] Dry deposition sample number.
[‡] Pb dry deposition data from Settle and Patterson (1982).

These examples give an indication of the state of the art in this area. Clearly, more sophisticated techniques for accurately evaluating this recycled fraction must be developed. Future work should focus in two areas (a) the use of adequate tracers (stable or radioactive) during field measurements, and (b) an improvement of our knowledge of metal/Na ratios as a function of sea-salt particle size through carefully designed *in situ* or laboratory experiments.

MYSTERIES

Are there Significant Unknown Natural or Anthropogenic Sources for Atmospheric Metals?

One of the major mysteries in this field of research is our lack of knowledge of all the sources for metals in the atmosphere. As emphasized in other chapters of this book, a number of anthropogenic sources are still not well documented. Among these are waste incineration and other high temperature sources. Of particular concern is the need for accurate emission inventory data for these metals, especially for Third World countries. However, even less is known about natural sources. In recent years some information has emerged on the importance of volcanic activity, and we now have approximate values for the global volcanic source strength, especially for rather volatile metals such as Cd, Hg, Pb and As (Arnold *et al.*, 1981; Settle and Patterson, 1982; Fitzgerald *et al.*, 1983; Zoller, 1984). On the other hand, there is a dearth of data for such sources as crustal degassing and the terrestrial biosphere. Metal release from plants during their growth has been suggested as a source of zinc in the atmosphere (Beauford *et al.*, 1977). The importance of terrestrial biological sources for trace elements has yet to be established on a global basis. Little is known about mobilization of trace elements by forest fires or other land-burning practices. Also, the role of the oceans in the atmospheric chemistry of metals cannot be simply restricted to the ejection of sea-salt particles and their associated trace metals into the atmosphere. Micro-organisms in the marine environment can produce methylated forms of As, Hg, Se, Sn and other metals which may be released into the air. Evidence for this has been shown for Hg by Fitzgerald *et al.* (1984) and for Se by Mosher and Duce (1983).

What are the Physical and Chemical Forms of Metals in the Marine Atmosphere?

Before accurate estimates of the air-to-sea flux of metals can be made, we must have better information on the physical and chemical forms of the metals. For the metals of interest here, there is no evidence to date of any vapor phase for cadmium in the atmosphere—it is apparently all present on particles, although a careful search for a vapor phase has yet to be made. In the case of lead, there is some evidence that a small fraction is present in the vapor phase, at least in urban areas, very likely as tetraalkyl lead compounds (Harrison and Perry, 1977; Harrison and Laxen, 1978; Rohbock *et al.*, 1980), although there is no evidence for this as yet in the remote marine atmosphere. Evidence suggests that ~10% or less of the arsenic in the marine atmosphere is present either in the gas phase or on particles considerably smaller than 0.2 μm (Walsh *et al.*, 1979b). The chemical form of the vapor phase As is unknown.

In the case of mercury, well over 99% is in the vapor phase in the atmosphere, with only a very small fraction present on particles (Table 11.3) (Fitzgerald *et al.*, 1983). For Hg particularly, it is critical to know the physical and chemical form to evaluate the wet and dry deposition. From Hg measurements at Enewetak Atoll, Fitzgerald *et al.* (1983) have pointed out that all the Hg in rain can be accounted for by the very small particulate Hg concentration if the washout factor for particulate Hg is about 1200, a reasonable figure. It thus appears that only a small fraction of the wet deposition of Hg to the ocean results from removal of the primary physical form of Hg in the atmosphere, gaseous Hg, while removal of the 0.1% particulate Hg may account for essentially all the Hg wet deposition. This conclusion is complicated, however, by the fact that relatively little is known about the chemical species in the vapor phase. Fitzgerald *et al.* (1983) have found that from 27 to 82% of the gaseous Hg over coastal Long Island Sound is organically associated and suggested that dimethyl mercury and/or methyl chloride are possible species. However, Slemr *et al.* (1981) found that <10% of the gaseous Hg over the open North and South Atlantic was dimethyl mercury while Fitzgerald *et al.* (1983) found <20% of the gaseous mercury was methylated at Enewetak. Thus, it appears that the primary gaseous form is elemental Hg, although considerable additional research is needed in this area. Removal of gaseous forms of Hg by precipitation will be very species dependent, and adequate modelling of the wet deposition of Hg to the ocean cannot be undertaken until the chemical forms of Hg can be accurately quantified and their geographical and temporal variability determined.

What is the Fate of Atmospheric Metals when they Enter the Ocean?

We know virtually nothing about what happens to metals in air and rain after they enter the ocean. To date there is virtually no information from remote marine regions on the fraction of metals in rain which are in the particulate or dissolved form. We know nothing yet about reactions that occur during the mixing of rain and sea water. Solubilization, sorption, or flocculation processes involving metals may occur, and such processes would change the physical and chemical forms of the metals in the ocean and may have a significant impact on the cycling of the metals in surface waters. Similar concerns are obvious relative to dry deposition of aerosol particles containing metals. Reactions of these kinds would affect the residence times of the metals in the ocean and their interactions with biological systems.

It is now well established that the atmosphere is the primary transport path for lead found in the surface waters of the North Atlantic and North Pacific (Schaule and Patterson, 1983). Figure 11.6 shows the vertical profile of dissolved Pb at open ocean sites in both oceans. The strong concentration gradient near the surface identifies the atmospheric source for this Pb, and indicates that a considerable fraction of the atmospheric Pb entering the surface waters is soluble. Note that similar seawater profiles and conclusions relative to atmospheric input have been made for Sn by Byrd and Andreae (1982).

Walsh and Duce (1976) showed that a major fraction of the anthropogenically derived vanadium present on coastal North Atlantic aerosol particles is soluble in seawater. Similar results were found for several metals

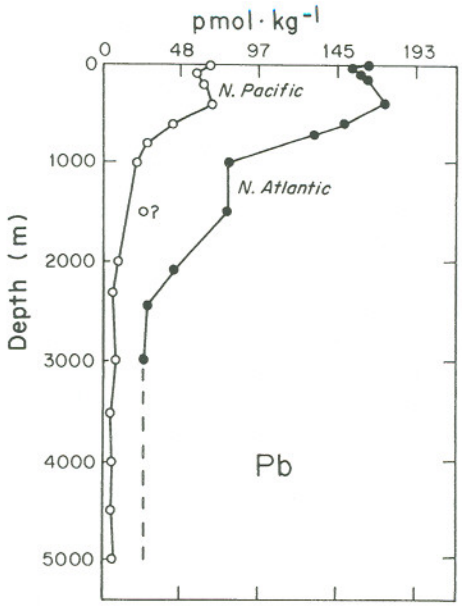

Figure 11.6 Depth profile of lead in the North Atlantic and North Pacific Oceans (from Schaule and Patterson, 1983)

during aerosol particle studies along the southern California coast (Hodge *et al.*, 1978), coastal Washington (Crecelius, 1980), and the southeastern US (Mullins, 1978). Results of some of these seawater solubility studies are presented in Table 11.9.

To determine whether particulate material atmospherically supplied to the ocean surface may be significantly leached, not only by direct interaction with sea water but also as a result of zooplankton grazing, Moore *et al.* (1984) have leached samples of atmospheric dust at pH values between 5.4 and 8.0. The elements Cu, As and V showed significant increases in the proportion leached as the pH was lowered. Approximately 10% of the iron was leached, independent of pH. An estimate of the atmospheric flux of iron in a leachable form supports the idea that this source may be the primary contributor to the Fe requirements of the biota. Since the efficiencies with which phytoplankton can grow at low Fe concentrations vary among species, it follows that the meteorological factors that govern the rate of transport of atmospheric dust to ocean areas could affect plankton ecology and productivity.

Indeed, numerous studies, based principally on the behavior of natural and artificial radionuclides, now support the conclusion that scavenging by sinking biogenic particles is the major removal process for many trace

Table 11.9 Seawater soluble fraction of metals on coastal aerosols

Metal	Percent soluble	Metal	Percent soluble
Quillayute, WA (1 hr)*		La Jolla, CA (3 hr)†	
As	50	Pb	39
Zn	65	Cd	84
		Zn	68
Quillayute, WA (24 hr)*		Ensenada, Mexico (3 hr)†	
As	49	Pb	13
Zn	72	Cd	80
		Zn	24
Narragansett, RI (1 hr)‡			
Excess V	72		

* Crecelius, 1980;
† Hodge *et al.*, 1978;
‡ Walsh and Duce, 1976.

elements from surface waters reservoir to deep waters. The short residence times of many trace elements (particulate and dissolved) in surface waters imply that relatively fast (of the order of a few months to a few years) geochemical coupling exists between the atmospheric input of trace metals (and other reactive substances) and their transport to the deep ocean (Buat-Ménard, 1984). This rapid particulate transport 'short-circuits' water mixing processes and has major geochemical implications which are of great importance to the health of the oceans. Induced chemical changes in the deep water column will be first observed in the particulate flux.

Using a steady state approach and indirect flux estimates, it has been calculated that atmospheric deposition is a significant source for some particulate trace metals in North Atlantic deep waters (Buat-Ménard and Chesselet, 1979). Such a source appears dominant in the case of lead, for which it can be inferred that the particulate flux in the ocean is, at present, primarily anthropogenic. For other trace elements anomalously enriched in marine aerosols possibly because of an anthropogenic component (Cu, Zn, Cd), the present anthropogenic air-sea flux still appears to be small relative to natural fluxes in the ocean. However, one can speculate that if the atmospheric input was to be one order of magnitude higher than at present over the North Atlantic for some metals, the detectable effect would be recorded in oceanic suspended matter and would alter the oceanic cycle of such elements. Such effects are extremely difficult to predict at present. Indeed, changes in the rate of input from the atmosphere will be biologically cycled at the same rate only if such changes do not affect the biological cycle itself. For example, increased levels of some trace metals in surface waters could either reduce or enhance the biogeochemical cycling.

CONCLUSION

Clearly much more work is needed before we can properly evaluate the impact of atmospheric input on the biogeochemical cycling of metals in the ocean. There is a need for carefully coordinated field programs to estimate more accurately net atmospheric fluxes to the ocean, as well as vertical particulate fluxes in the ocean at the mesoscale (coastal regions, enclosed seas) and at the global scale. Data from the southern hemisphere, where the atmospheric flux, both natural and anthropogenic, is a minimum, should be obtained with high priority to assess natural processes and fluxes in the ocean. Also, the observed temporal variabilities for both the atmospheric flux and the biogenic particulate flux clearly indicate that steady-state approaches are not valid on time scales of the order of one month, or when we consider gradually increasing inputs of pollutants. Sampling programs over several years are probably needed at a given location. Together with atmospheric flux assessments, the sampling strategy in the water column should consider concurrent sampling with sediment traps, large volume water in situ filtration units and conventional, small-volume water sampling. Finally, continued intercalibration of collection and analytical methods for trace elements in the marine atmosphere and ocean is mandatory.

REFERENCES

Andreae, M. O. (1980). Arsenic in rain and the atmospheric mass balance of arsenic. *J. Geophys. Res.*, **85**, 4512–4518.

Andreae, M. O., Asami, T., Bertine, K. K., Buat-Ménard, P. E., Duce, R. A., Filip, Z., Forstner, U., Goldberg, E. D., Heinrichs, H., Jernelov, A. B., Pacyna, J. M., Thornton, I., Tobschall, H. J., and Zoller, W. H., BUA(1984). Changing Biogeochemical Cycles. In Nriagu, J. O., (Ed.), *Changing Metal Cycles and Human Health*, pp. 359–374, Dahlem Konferenzen, Berlin, Springer-Verlag.

Arimoto, R., Duce, R. A., Ray, B. J., and Unni, C. K. (1985). Atmospheric trace elements at Enewetak Atoll: 2. Transport to the ocean by wet and dry deposition. *J. Geophys. Res.*, **90**, 7391–2408.

Arnold, M., Buat-Ménard, P., and Chesselet, R. (1981). *An Estimate of the Input of Trace Metals to the Global Atmosphere by Volcanic Activity*, IAMAP Third Scientific Assembly, Hamburg, FRG (abstract)

Arnold, M. A., Seghaier, D., Martin, D., Buat-Ménard, P. and Chesselet, R. (1982). *Geochimie de l'aerosol marin au-dessus de la Mediterranée Occidentale*, VI, Journées Etud. Pollutions, Cannes, CIESM, 27–37.

Beauford, W. T., Barber, T., and Barringer, A. R. (1977). Release of particles containing metals from vegetation to the atmosphere. *Science*, **195**, 571–573.

Bruland, K. W. (1983). Trace elements in sea water. In Riley, J. P., and Chester, R. (Eds.), *Chemical Oceanography*, pp. 157–220. Vol 8, Academic Press, New York.

Buat-Ménard, P. (1983). Particle geochemistry in the atmosphere and oceans. In Liss, P. S. and Slinn, W. G. N. (Eds), *Air–Sea Exchange of Gases and Particles*. pp. 455–532, Reidel, Dordrecht.

Buat-Ménard, P. (1984). Fluxes of metals through the atmosphere and oceans. In Nriagu, J. O. (Ed.)., *Changing Metal Cycles and Human Health*, pp. 43–69, Dahlem Konferenzen, Springer-Verlag, Berlin.

Buat-Ménard, P. and Chesselet, R. (1979). Variable influence of the atmospheric flux on the trace metal chemistry of oceanic suspended matter. *Earth Planet. Sci. Lett.*, **42**, 399–411.

Buat-Ménard, P., Ezat, U. and Gaudichet, A. (1983). Size distribution and mineralogy of aluminosilicate dust particles in tropical Pacific air and rain. In *Precipitation Scavenging, Dry Deposition, and Resuspension*, Proc. of the Fourth Intern. Conf., Santa Monica, California, Vol. 2, pp. 1259–1270, Elsevier, New York.

Byrd, J. T. and Andreae, M. O. (1982). Tin and methyltin species in seawater: concentrations and fluxes. *Science*, **218**, 565–569.

Cambray, R. S., Jeffries, D. F., and Topping, G. (1975). *An Estimate of the Input of Atmospheric Trace Elements into the North Sea and the Clyde Sea.* (1972–73), AERE-R7733, United Kingdom Atomic Energy Authority, AERE Harwell, HMSO, London, 30 pages.

Cawse, P. A. (1974). A survey of atmospheric trace elements in the United Kingdom. AERE Harwell Report R7669, UKAEA, HMSO, London.

Crecelius, E. (1980). The solubility of coal fly ash and marine aerosols in water, *Mar. Chem.*, **8**, 245-250.

Duce, R. A. (1982). Sea salt and trace element transfer across the sea/air interface. Presented at the Session on Ocean/Atmosphere Material Exchange, Joint Oceanographic Assembly, Halifax, Nova Scotia, Canada, 4 August.

Duce, R. A., Hoffman, G. L., Ray, B. J., Fletcher, I. S., Walsh, P. R., Fasching, J. L., Piotrowicz, S. R., Hoffman, E. J., Miller, J. M., and Heffter, J. L. (1976). Trace metals in the marine atmosphere: sources and fluxes. In Windam, H. L. and Duce, R. A. (Eds), *Marine Pollutant Transfer*, pp. 77–119. D. C. Heath and Co., Lexington, MA.

Duce, R. A., Unni, C. K., Harder, P. J., Ray, B. J., Patterson, C. C., Settle, D. M. and Fitzgerald, W. F., (1979). *Wet and Dry Deposition of Trace Metals and Halogens in the Marine Environment.* Presented at the IAMAP/CACGP Symposium on the Budget and Cycles of Trace Gases and Aerosols in the Atmosphere, University of Colorado, Boulder, CO, 12–18 August.

Duce, R. A., Unni, C. K., Ray, B. J., Prospero, J. M., and Merrill, J. T. (1980). Long-range atmospheric transport of soil dust from Asia to the tropical North Pacific: temporal variability. *Science*, **209**, 1522–1524.

Duce, R. A., Arimoto, R., Ray, B. J., Unni, C. K., and Harder, P. J. (1983). Atmospheric trace elements at Enewetak Atoll: 1. Concentrations, sources, and temporal variability. *J. Geophys. Res.*, **88**, 5321–5342.

Fitzgerald, W. F., Gill, G. A., and Hewitt, A. D. (1983). Air–sea exchange of mercury. In Wong, C. S., Boyle, E., Bruland, K. W., Burton, J. D. and Goldberg, E. D. (Eds.). *Trace Metals in Sea Water*, pp. 297–315, Plenum Press, New York.

Fitzgerald, W. F., Gill, G. A., and Kim, J. P., (1984). An equatorial Pacific Ocean source of atmospheric mercury. *Science*, **224**, 597–599.

Gatz, D. F. (1975). Scavenging ratio measurements in Metromex. In Beadle, R. W. and Semonin, R. G. (Eds.), *Precipitation Scavenging—1974*, pp. 71–87, ERDA Symposium Series, CONF-741014.

Harrison, R. M. and Perry, R. (1977). The analysis of tetraalkyl lead components and their significance as urban air pollutants. *Atmos. Environ.*, **11**, 847–852.

Harrison, R. M. and Laxen, D. H. P. (1978). Sink processes for tetraalkyl lead compounds in the atmosphere. *Environ. Sci. and Technol.*, **12**, 1384–1392.

Hicks, B. B., Wesely, M. L., and Durham, J. L., (1980). *Critique of Methods to Measure Dry Deposition.* Workshop Summary, EPA 1600.9-80-050, 70 pages.

Hodge, V., Johnson, S. R., and Goldberg, E. D., (1978). Influence of atmospherically transported aerosols on surface ocean water composition. *Geochem. J.*, **12**, 7–20.

Hoffman, G. L., Duce, R. A., and Hoffman, E. J., (1972). Trace metals in the Hawaiian marine atmosphere. *J. Geophys Res.*, **77**, 5322–5329.

Jickells, T. D., Knap, A. H., and Church, T. M. (1984). Trace metals in Bermuda rainwater. *J. Geophys. Res.*, **89**, 1423–1428.

Liss, P. S. (1983). Gas transfer: experiments and geochemical implications. In Liss, P. S. and Slinn, W. G. N. (Eds), *Air–Sea Exchange of Gases and Particles*, pp. 261–298, Reidel, Dordrecht.

Liss, P. S., and Slater, P. G. (1974). Fluxes of gases across the air-sea interface. *Nature*, **247**, 181–186.

McDonald, R. L., Unni, C. K., and Duce, R. A. (1982). Estimation of atmospheric sea salt dry deposition: wind speed and particle size dependence. *J. Geophys. Res.*, **87**, 1246–1250.

Mahadevan, T. N., Sadasivan, S., and Mishra, U. C. (1982). Chemical composition of precipitation in tropical marine atmosphere around Indian subcontinent. *Science of the Total Environment*, **24**, 275–285.

Moore, R. M., Milley, J. E. and Chatt, A. (1984). The potential for biological mobilization of trace elements from aeolian dust in the ocean and its importance in the case of iron. *Oceanol. Acta*, **7**, 221–228.

Mosher, B. W., and Duce, R. A., (1983). Vapor-phase and particulate selenium in the marine atmosphere. *J. Geophys. Res.*, **88**, 6761–6768.

Mullins, B. M. (1978). Geochemical aspects of atmospherically transported trace metals over the Georgia Bight. MS Thesis, Georgia Institute of Technology, Atlanta, GA, 36 pages.

Parrington, J. R., Zoller, W. H., and Aras, N. K. (1983). Asian dust: seasonal transport to the Hawaiian Islands. *Science*, **220**, 195–197.

Parrington, J. R. and Zoller, W. H. (1984). Diurnal and longer-term temporal changes in the composition of atmospheric particles at Mauna Loa, Hawaii. *J. Geophys. Res.*, **89**, 2522–2534.

Peirson, D. H., Cawse, P. A., and Cambray, R. S. (1974). Chemical uniformity of airborne particulate material and a maritime effect. *Nature*, **251**, 675–679.

Rohbock, E., Georgii, H. W., and Muller, J. (1980). Measurements of gaseous lead alkyls in polluted atmospheres. *Atmos. Environ.*, **14**, 89–98.

Schaule, B. K., and Patterson, C. C. (1983). Perturbations of the natural lead depth profile in the Sargasso Sea by industrial lead. In Wong, C. S., Boyle, E., Bruland, K. W., Burton, J. D. and Goldberg, E. D. (Eds), *Trace Metals in Sea Water*, pp. 487–503, Plenum Press, New York.

Scott, B. C., (1981). Modeling of atmospheric wet deposition. In Eisenreich, S. J. (Ed.), *Atmospheric Pollutants in Natural Waters*, pp.3–21, Ann Arbor Science, Ann Arbor, MI.

Settle, D. M., and Patterson, C. C. (1982). Magnitudes and sources of precipitation and dry deposition fluxes of industrial and natural leads to the North Pacific at Enewetak. *J. Geophys. Res.*, **87**, 8857–8869.

Settle, D. M., Patterson, C. C., Turekian, K. K., and Cochran, J. K. (1982). Lead precipitation fluxes at tropical oceanic sites determined from ^{210}Pb measurements. *J. Geophys. Res.*, **87**, 1239–1245.

Slemr, F., Seiler, W., and Schuster, G. (1981). Latitudinal distribution of mercury over the Atlantic Ocean. *J. Geophys. Res.*, **86**, 1159–1166.

Slinn, W. G. N. (1983). Air-to-sea transfer of particles. In Liss, P. S. and Slinn, W. G. N., (Eds), *Air–Sea Exchange of Gases and Particles.* pp. 299–405, Reidel, Dordrecht.

Slinn, S. A., and Slinn, W. G. N. (1980). Predictions for particle deposition on natural waters. *Atmos. Environ.*, **14**, 1013–1016.

Slinn, S. A., and Slinn, W. G. N. (1981). Modeling of atmospheric particulate deposition to natural waters. In Eisenreich, S. J. (Ed.), *Atmospheric Pollutants in Natural Waters*, pp. 23–53. Ann Arbor Science, Michigan.

Uematsu, M., Duce R. A., Prospero, J. M., Chen, L., Merrill, J. T., and McDonald, R. L. (1983). Transport of mineral aerosol from Asia over the North Pacific Ocean. *J. Geophys. Res.*, **88**, 5343–5352.

Walsh, P. R., and Duce, R. A. (1976). The solubilization of anthropogenic atmospheric vanadium in sea water. *Geophys. Res. Lett.*, **3**, 375–378.

Walsh, P. R., Duce, R. A., and Fasching, J. L. (1979a). Tropospheric arsenic over marine and continental regions. *J. Geophys. Res.* **84**, 1710–1718.

Walsh, P. R., Duce, R. A., and Fasching, J. L. (1979b). Considerations of the enrichment, sources, and flux of arsenic in the troposphere. *J. Geophys. Res.*, **84**, 1719–1726.

Weisel, C. P., Duce, R. A., Fasching, J. L., and Heaton, R. W. (1984). Estimates of the transport of trace metals from the ocean to the atmosphere. *J. Geophys. Res.*, **89**, 11,607–11,618.

Williams, W. M. (1982). A model for the dry deposition of particles to natural water surfaces. *Atmos. Environ.*, **16**, 1933–1938.

Zoller, W. H. (1984). Anthropogenic perturbation of metal fluxes into the atmosphere. In Nriagu, J. O. (Ed.). *Changing Metal Cycles and Human Health*, pp. 27–41. Dahlem Konferenzen, Springer-Verlag, Berlin.