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REGIONAL SEAS

GESAMP:

Atmospheric input of trace species to the world oceans

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Prepared in co-operation with

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UNEP 1990

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PREFACE

It is now recognized that the atmosphere is a significant pathway for the transport of many natural and pollutant materials from the continents to the ocean but only recently, due to the developments in monitoring trace species in air, aerosol and precipitation over the ocean, in understanding and quantifying atmospheric removal processes and in modelling the long-range atmospheric transport and deposition, it has become possible to quantitatively estimate the atmospheric fluxes of trace species to the marine environment.

The proposal to make such estimations on global and regional scales was originated in 1987 by the WMO-led GESAMP Working Group on the Interchange of Pollutants between the Atmosphere and the Oceans established in 1976 to provide advice to the WMO Members and the GESAMP sponsoring organizations on scientific aspects of air/sea exchange of pollutants.

Considering international concern about atmospheric transport of pollutants to the oceans and regional seas, the WMO Executive Council at its thirty-ninth session in 1987 supported the proposal to hold a meeting of the Working Group to assess recent progress and knowledge in this field and to compare pollutant inputs to the oceans from the atmosphere with those from rivers. This proposal was also endorsed by GESAMP at its eighteenth session in 1988.

To tackle this task, the Working Group convened a Workshop on Atmospheric Input of Trace Species to the World Ocean, held in October 1988, to determine the strategy for the report and to compile the various concentration data bases. Subsequent to this, the flux computations were carried out. A second meeting of the chairmen of the various workshop working panels was held in December 1988 to prepare the first draft of the report. In May 1989, GESAMP-XIX approved the report and recommended that it should be published in the GESAMP Reports and Studies series, taking into account the comments made by GESAMP. The present report, which is available in English only, was finalized in October 1989.

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EXECUTIVE SUMMARY

INTRODUCTION

In October, 1988 GESAMP Working Group 14 ('Interchange of Pollutants Between the Atmosphere and the Oceans' - INTERPOLL) convened, with financial support from WMO and UNEP, a Workshop on 'Atmospheric Input of Trace Species to the World Ocean.' The workshop was held at the University of Rhode Island (URI), U.S.A., and about 20 scientists from around the world took part. The meeting consisted of plenary sessions and 5 separate panels dealing with the topics of atmospheric transport, deposition processes, trace metals, nutrients, and synthetic organics. Following this, in December, 1988, a second meeting involving the workshop co-chairmen and the chairmen of the workshop panels was held, also at URI, and a draft report produced. This was submitted and approved by GESAMP at its 19th session in May, 1989. The present document, the final version of the report, incorporates comments made by GESAMP XIX, and was prepared, with input from the 5 panel chairmen, by the workshop co-chairmen at URI in June, 1989.

Chemicals, both natural and man-made, reach the oceans by a number of routes, including rivers, direct dumping, and via the atmosphere. The first two paths have been studied for several decades, but it is only relatively recently that it has become possible to estimate the amounts of material entering the oceans from the atmosphere. Further, as the calculations have become less crude, for some substances the atmospheric route seems to have gained in importance relative to the other paths. This improvement in quantifying atmospheric inputs has come about through better understanding of the transport and deposition mechanisms carrying material to the surface of the oceans, as well as the availability of a greatly improved data base of concentration measurements in the marine environment. The main objective of the present exercise is to use the best currently available information and data to calculate inputs of a variety of chemicals to the oceans on a global basis. These estimates are then compared to the amounts of the various materials which enter the oceans through river inflow.

Substances to be examined were selected on the basis of their impact (positive or negative) on marine organisms and/or their importance in the cycling of chemicals in the oceans. They are dealt with in the following three classes: Trace elements and mineral aerosol, nitrogen species, and synthetic organic compounds; each of these groups constituting a major part of the report.

Before these three sections is one on the way the deposition processes for gases, particles and rain are parameterized in the present calculation. Then comes a description of the climatology of the marine atmosphere, which concentrates on the primary transport paths and precipitation patterns which, respectively, move and remove atmospheric materials.

DEPOSITION PROCESSES

Although direct measurements of material fluxes from the atmosphere to the sea surface have been attempted, they have generally been unsuccessful or the meaning of the results open to significant doubt. An exception to this general statement is in the case of rain where, provided great care was taken in sample collection and analysis, meaningful results have been obtained. In view of the general lack of reliable directly measured fluxes, in the present exercise resort is made to indirect approaches to estimate air-to-sea fluxes.

In order to calculate deposition indirectly, use is made of the fundamental concept that the flux of matter to the sea surface is given by the product of a concentration term (which drives the flux) and a kinetic parameter, which controls the rate of mass transfer. This is then applied to deposition of gas molecules, 'dry' particles and rain, as appropriate for each particular substance. The concentration term has to be obtained from field measurements. In the case of gas exchange, concentrations need to be known in surface seawater and in the marine boundary layer. For particles and rain, concentrations have to be measured in size-fractionated atmospheric aerosols. In the latter case, aerosol concentrations are converted to concentrations in rain by use of a 'scavenging ratio,' which is obtained from paired field measurements of the ratio of concentrations in rain to those in atmospheric aerosol. The kinetic term for rain is just the rate at which it falls. For gases and particles, the kinetic parameter is obtained from a combination of theory, laboratory results, and field measurements.

ATMOSPHERIC TRANSPORT AND PRECIPITATION CLIMATOLOGY

There are two different approaches to the use of meteorological information as an aid in the calculations attempted here. The first is to construct a transport or General Circulation Model (GCM), and knowing the distribution and strength of the various sources of the substances of interest, to allow the model to predict the pattern of their deposition over the oceans. Although this is a fundamental and potentially very powerful approach, it was not deemed appropriate for the present task. A major reason is that for many of the substances emission inventories are not sufficiently well known. Also, it is difficult to use transport models iteratively with observed atmospheric concentrations or measured air-sea fluxes.

For these and other reasons we chose to adopt a climatological approach in which the known yearly average distributions of meteorological parameters such as precipitation are combined with the observed concentration field of the various chemicals on a grid point by grid point basis in order to derive the required fluxes. Meteorological information is also used to interpolate and extrapolate the concentration data to overcome the lack of observations in several marine areas.

To perform the calculation the oceans are divided into 10°x10° boxes. For each box the average yearly concentration is estimated for each substance, either from direct measurements or by extrapolation. In the case of dry deposition, the corresponding flux is calculated by multiplying the concentration in each box by a deposition/transfer velocity. For deposition in rain, the flux per box is obtained from the product of the climatological rainfall rate for the box, the air concentration of each substance in it, and an appropriate scavenging ratio.

As a cross-check on the calculated fluxes they are compared with directly measured fluxes, where such data are available. The global atmospheric inputs are also compared with riverine inflows to the oceans for the substances of interest. In addition, we have attempted to perform similar air-sea flux calculations for some of the better studied regional seas. Examples are the North, Baltic, and Mediterranean Seas in Europe, which are of particular interest in view of their proximity to major industrial, urban, and agricultural sources.

Splitting the oceans into 648 10°x10° boxes provides the ability to perform the deposition computation on any scale ranging from global down to the size of the individual boxes. This is an important advantage of the scheme adopted since it allows, for all the substances examined, inter-ocean, inter-hemispheric and regional comparisons to be made, as well as global assessment. Further, it permits the importance of the continents as sources for much of the material deposited onto the oceans from the atmosphere to be identified. The small grid size allows the deduction that for many substances this deposition is much larger close to continents, with potentially important implications for fishing and recreation in heavily populated coastal regions. Another advantage of the computational scheme adopted is the ease with which the fluxes can be recalculated as better data on both chemical concentrations and deposition rates become available in the future.

TRACE ELEMENTS AND MINERAL AEROSOL

The flux calculations for these substances show that wet deposition is more important than dry; for Pb and other trace metals (Cd, Cu, Ni, Zn) the ratio of wet to dry deposition is about 80:20; for mineral aerosol, which contains elements including Al, Fe, Si, and P, the corresponding ratio is approximately 60:40. Both classes of substance show much greater deposition in the northern (90%) than in the southern (10%) hemisphere.

Comparison of atmospheric and riverine inputs of these substances into the oceans in particulate form reveals that rivers are the dominant route, except for phosphorus. However, with respect to the open oceans the atmospheric path is likely to dominate since much of the riverine input of particles to the oceans is removed to the sediments in nearshore and coastal areas. For inputs in soluble form, which are likely to be more important for the 'health' of the oceans since they can have a more direct impact on biological systems, atmospheric inputs are approximately equal to those from rivers for Fe, P, Cu, Ni, and As. For Zn, Cd, and Pb the atmospheric path is the major source of these metals reaching the oceans.

There is quite a detailed data base of concentration measurements for trace metals and mineral aerosol over the European regional seas. Flux calculations have been carried out for the North, Baltic, and Mediterranean Seas, and it appears that of the total emission of these substances from Europe, between 1 and 15% is deposited on the North Sea, with 4-20% being deposited over the northwestern Mediterranean (the ranges in the estimates largely reflect inter-element differences). It is clear that when riverine inputs are added to those from the atmosphere, the seas of Europe, taken together, provide a sink for a significant fraction of human-derived emissions of trace metals from the region.

NITROGEN SPECIES

Dealing first with the oxidized forms of nitrogen (NO_3^{-}· HNO_3, NO_x), we find about 60% of the amount entering the oceans from the atmosphere is by wet deposition of nitrate and nitric acid. Deposition of NO_x can effectively be ignored since it is very small when compared to the other oxidized forms, even over the North Atlantic where dry deposition of NO_x is at a maximum. Of the total deposition of oxidized nitrogen, 70% occurs over the northern hemisphere oceans. Of this northern hemisphere deposition, it is estimated that 40-75% comes from anthropogenic sources on land. The highest air-to-sea flux of oxidized nitrogen (i.e., per unit area) is for the North Atlantic, reflecting the impact of anthropogenic sources in North America, Europe, and Africa. A somewhat surprising outcome of the calculation is that the second highest oxidized nitrogen fluxes are calculated for the North Indian Ocean. This arises in part from the relatively small area of this basin, with much of it surrounded by land masses. Further, the high rainfall rate leads to substantial removal by wet deposition.

Reduced forms of nitrogen (mostly NH_4^+ and NH_3) constitute about 40% of the total flux of N to the oceans from the atmosphere. However, this figure should be treated with caution since the data base of marine measurements of reduced nitrogen forms is poor relative to that for oxidized species. Further, there is a distinct possibility that much of the reduced nitrogen measured in the marine atmosphere is material recycled through the sea surface and thus not really net input.

Our calculated global deposition numbers fall within the range of previous estimates, although they are towards the upper end of the range of published values. The present analysis is, of course, considerably more thorough than previous attempts.

Comparing our values for atmospheric inputs with inflows of nitrogen to the oceans via rivers, it appears that in total (i.e., natural plus anthropogenic sources) the two flows are approximately equal. However, as with trace metals, much of the river-borne nitrogen never reaches the open ocean. A large fraction of it will be removed to coastal and shelf sediments by biological transfer as well as being lost to the atmosphere following denitrification. Thus, for the open oceans transfer via the atmosphere is almost certainly the prime route for entry of new nitrogen.

It is also instructive to compare the rate of input of nitrogen to the oceans with the rate at which it is buried in marine sediments. This comparison indicates that only a few percent of the total input appears in the sediments, implying very considerable recycling of nitrogen (as, for example, N_2O and NH_3) back to the atmosphere through the sea surface. However, current estimates of such emission fluxes are very uncertain. These apparent quantitative inconsistencies in the global nitrogen cycle indicate that major components of it are poorly understood at the present.

Although in coastal waters the importance of riverine inputs of nitrogen will increase relative to those from the atmosphere, such a comparison for the North and Mediterranean Seas shows that atmospheric inputs are about 40% of riverine inputs for the former, but that in the western part of the latter (Italy to Gibraltar) the two sources of nitrogen are approximately equal.

SYNTHETIC ORGANIC COMPOUNDS

The human-derived organic compounds considered in this section are PCBs, hexachlorocyclo-hexanes (HCHs), DDTs, chlordane and dieldrin, and chlorobenzenes. The deposition process for these compounds is more complex than for the groups considered above. Not only are they deposited in rain and by dry particle deposition, they also exist in the atmosphere as gases whose air-sea transfer must be quantified. The calculations presented show that even exchange of these substances in gaseous form is not simple, since they generally show both gas and liquid phase resistance to their interfacial transfer.

Our calculations confirm that the majority of the deposition of these compounds is to the North Pacific and North Atlantic Oceans, reflecting their major production and use in the northern hemisphere. However, differences between basins are apparent when particular groups of compounds are considered. For example, HCHs and DDT have the greatest deposition rates over the North Pacific, reflecting their major use on the Asian continent, whereas PCBs and dieldrin show greater deposition over the North Atlantic than the North Pacific, which appears to be related to the proximity of sources in Europe and North America.

Comparing the calculated atmospheric inputs of these compounds with the very crude estimates presently available of the amount coming into the oceans in rivers indicates that the atmospheric route is very dominant, constituting between 80% (for PCBs) and 99% (for HCHs) of the total input.

As before, we have extended the atmospheric deposition calculation to the regional seas of Europe. The results indicate that flux rates are higher over these coastal seas than over the open oceans by factors ranging from about 2 to 12, depending on the group of compounds considered. Comparing river and atmospheric inputs to these seas, the latter appears dominant for HCHs. For the other organo-chlorine compounds the riverine input may approach (PCBs) or even exceed (HCBs) deposition from the atmosphere.

RECOMMENDATIONS

In carrying out the calculations reported here, several important gaps in knowledge have become apparent. From these it is clear that much further work remains to be done. Rather than give a detailed list of recommendations for future research, we list below five areas which appear to be of special importance:

1. The best way to quantify atmospheric inputs to the oceans is by direct flux measurements. However, methods for measuring fluxes directly are lacking at the present, except for precipitation. The development of techniques to enable direct dry flux measurements to be made should be a top priority. In addition, the geographical coverage of rain sampling programmes should be expanded considerably.

2. In default of direct flux methods, we must resort to indirect approaches that use measured air concentrations. The presently available concentration data fields need to be improved both temporally and spatially. Areas for which concentration data are particularly lacking are the South Atlantic, South Pacific, Indian, and Arctic Oceans.

3. To convert concentrations to fluxes requires knowledge of the kinetic parameter (deposition/ transfer velocity) controlling the deposition rate. Better parameterisation of this term, which can come from better understanding of the controlling processes, is required for both particles and gases.

4. Scavenging ratios for particular substances vary substantially both temporally at a fixed site and between different locations. There are many reasons for the existence of these ranges. Part of the problem may be that scavenging ratios often have to be computed from rain and air concentrations measured on samples that were not collected contemporaneously. There is an urgent need for simultaneous collections and measurements, including vertical profiles, so that scavenging ratios can be obtained from truly paired rain and air samples.

5. An important uncertainty in flux calculations for synthetic organic compounds is the concentration of the 'free' (i.e., able to exchange across the air-sea interface) compounds in the surface oceans. Although technically difficult to address, such measurements should have a high priority in future studies.

INTRODUCTION

Transport of potentially harmful trace substances to the world oceans, whether it be by rivers, by bulk dumping, or via the atmosphere has recently become a major topic of both public and scientific discussion. However, though the polluting of the oceans is not a new phenomenon, it has generally thought to have accelerated in recent years. How important a role the atmosphere plays in transporting pollutants to the oceans is a critical unknown. A first attempt to address this question was published over a decade ago (NAS, 1978). Since that report a considerable amount of research and monitoring has gone on to document transport of both natural and man-made substances to the oceans via the atmosphere. SEAREX, WATOX, PHYCEMED, AEROCE, and others are examples of major research programmes including such studies. These programmes have produced a set of high quality atmospheric chemistry data that can be used in estimating the total deposition of many trace substances to the oceans and coastal areas. These studies showed that large quantities of continental materials are often carried great distances over the oceans. In some cases these are natural substances such as mineral dust and organic matter derived from plants. However, many substances transported over the oceans are derived from anthropogenic sources, for example: Pb from leaded gasoline, V from the combustion of fuel oils, pesticides from agricultural use, and halocarbons from a variety of industrial processes. It is likely that some of these substances have a significant impact on ocean processes when their deposition flux to the ocean surface is sufficiently large. For example, some metals and many chlorinated hydrocarbons could inhibit the growth of phytoplankton. On the other hand some trace metals (e.g., Fe) are essential to biological processes, and their absence could limit primary productivity. Similarly, atmospheric nitrogen species could provide vital plant nutrients. Knowledge about atmospheric inputs would be useful for other purposes as well. Some species (e.g., 210-Pb) are useful as tracers for ocean mixing processes and the dating of corals. The oceanic chemical cycles of a number of elements (e.g., Al, Pb, some rare earths) are known to be significantly impacted by the atmospheric inputs of these species. In many ocean regions, eolian mineral dust is the major non-biogenic component in deep-sea sediments; this dust is also the principal source of many trace elements mentioned above. Thus, atmospheric inputs can have both positive and negative impacts on the oceans. For these reasons, it is important to have a quantitative knowledge of the fluxes of these materials to the oceans and of their geographical distribution.

Because of recent research efforts, it is now possible for the first time to assess the atmospheric fluxes of many materials to the oceans. To this end, GESAMP instructed its Working Group No. 14 to assess the data at hand and to develop global scale estimates of the atmospheric inputs of trace species to the oceans. Finally these estimates will be compared to those fluxes entering the oceans from rivers.

SELECTION OF CHEMICAL SPECIES

The primary objectives of this paper are to assess the flux of those species that can have an impact on biological processes and on chemical cycling in the oceans. There are two types of biologically important species: those that are deleterious to organisms and those that are essential to growth. Certain metals such as Cd and Pb are known to be toxic to marine organisms, as are many synthetic organic species including the PCBs and a variety of pesticides. For example, Subramanian et al. (1986, 1987) have reported data that suggest a relationship between chlorinated hydrocarbon uptake and the decreasing concentration of reproductive hormones in marine mammals and birds. However, the growth of marine phytoplankton is also dependent on the availability of certain trace species. Nitrogen and phosphorus are two of the most critical nutrients. Organisms that build siliceous frustules also require silicon. Finally, certain metals are essential for various biological functions; for example, phytoplankton enzyme systems require trace amounts of iron, manganese, copper, zinc, cobalt and molybdenum.

In some regions, primary productivity is limited by the dearth or absence of one or more of the above nutrients. In such regions, the deposition of these elements from the atmosphere could play an important role in controlling productivity. For example, recent work (Martin et al., 1988; Martin and Gordon, 1988) suggests that phytoplankton growth is limited by the atmospheric input of Fe in some regions. Paerl (1985) showed that productivity increased sharply in coastal water samples when he added continental rain waters containing high concentrations of nitrate. Duce (1986) made a detailed assessment of the importance for primary productivity in oligotrophic waters of atmospheric deposition relative to oceanic sources of iron, nitrogen, and phosphorus. This study focused on two regions, the Sargasso Sea and the North Pacific Gyre. Duce estimated nutrient fluxes from atmospheric deposition to surface waters and from oceanic processes (vertical advection, eddy diffusion and nitrogen fixation). He concluded that: i) in these two regions the atmospheric deposition of Fe could have the greatest impact, ii) the atmospheric flux of nitrogen species can have a significant impact at times, and iii) the role of atmospheric phosphorus is negligible.

In this report we assess the global atmosphere-to-ocean deposition rates of species that might be significant as nutrients. These include oxidized and reduced nitrogen species, both gaseous and particulate, and various trace elements including Si, Fe, and P. We also consider potentially harmful species such as synthetic organics and such heavy metals as Pb, Cd, Zn, Ni, As, and Cu, which at high concentrations may have deleterious effects on marine organisms. Finally we assess Al, whose atmospheric input may have a significant impact on its chemical cycle in the oceans.

ORGANIZATION OF REPORT

The assessment of atmospheric fluxes to the global ocean is difficult for a number of reasons. First there are very few measurements of actual deposition rates. Furthermore, most deposition studies focus only on the wet-deposited component; there are very few measurements of dry deposition of either particles or gases. However, there are relatively more data on the atmospheric concentration of various aerosol and gaseous species. As a consequence, the strategy used in this assessment is to calculate deposition rates based on atmospheric concentration data. Deposition rates are calculated for ten degree by ten degree ocean areas using measured concentration data or concentration data extrapolated from actual concentration measurements. These concentration data are then combined with appropriate exchange coefficients for the various species. As a test, the computed fluxes for some species are compared to the more limited direct deposition measurements at certain sites. In order to carry out such computations it is necessary to have a knowledge of atmospheric transport processes, as well as removal mechanisms and physical and physico-chemical properties of aerosols and gases. Unfortunately, in many of these areas our knowledge is poor or inadequate. Consequently it is often necessary to make assumptions about one or more of these parameters.

The organization of the report derives from this strategy. In the Deposition Processes section we discuss the state of knowledge about air/sea exchange processes. These include gas exchange, dry deposition of particles, and the precipitation scavenging of both particles and gases. In that section a general description of the fundamental principles underlying the methods used to estimate the fluxes of particular classes of substances is provided. We also describe how the actual fluxes are calculated once the relevant atmospheric concentration data, exchange coefficients and precipitation scavenging ratios are available. In the next section Atmospheric Transport and Precipitation Climatology are discussed for the various ocean regions, with emphasis on the primary transport paths, and summaries of precipitation patterns and their temporal variability. The objective is to relate our knowledge of atmospheric transport paths to known atmospheric concentration distributions and to probable source areas on the continents. In this section the actual procedures used for computing the atmospheric fluxes are described in detail, and a specific example of such a computation is given.

In the succeeding sections the available atmospheric concentration data are assessed and the subsequent flux computations described. The deposition species are grouped into three categories:

Trace Elements and Mineral Aerosols, Nitrogen Species, and Synthetic Organic Compounds. This classification is largely based on the different physical and chemical characteristics of substances in these groups, their removal processes, and the availability of data sets. Finally, some recommendations for future research are given.

HISTORY OF THE GESAMP STUDY

The first meeting of the subgroup of GESAMP Working Group 14 - Interchange of Pollutants Between the Atmosphere and Oceans - was held at the Alton Jones Campus of the University of Rhode Island from October 10 to 14, 1988. At that meeting, the strategy for the report was determined and the various concentration data bases compiled. Subsequent to this, the flux computations were carried out. A second meeting of the chairmen of the various working panels was held at the same location from December 19-21, 1988. At this session the results of the flux computations were assessed and the first draft of the report put together. A rough draft of the report was submitted to WMO in late December, 1988. An intermediate draft was submitted to GESAMP in early March, 1989.

DEPOSITION PROCESSES

INTRODUCTION

The total deposition of chemicals to the ocean from the atmosphere is the sum of the amounts transferred in gas, liquid and solid phases. Materials transferred in gas and solid phases are referred to as 'dry' deposition. Liquid deposition, often referred to as 'wet' deposition, will comprise water and its dissolved gases and solutes, together with any insoluble particulate material contained therein. Net upward transport from the ocean is also possible for many species and is in some cases of overriding importance. However, here the emphasis will be on net deposition since we are principally interested in the atmosphere as a provider of material to the oceans.

DIRECT MEASUREMENT OF ATMOSPHERE-OCEAN MASS FLUXES

There are a number of direct measurements of inputs of chemicals into the oceans. Most of these are for deposition via rain since it is relatively easy to collect the samples. However, there are very real difficulties with this simple approach for determining wet deposition. Unsophisticated funnel-in-bottle precipitation samplers may collect dry deposition as well as rain. Even though it is possible to arrange for the collector to be exposed only when rain is falling, this increases the complexity of the apparatus. Another difficulty with direct measurements of wet deposition arises because of the natural variability of concentrations of trace substances in precipitation (see, for example, Jickells et al., 1984), which means that a large number of rain events must be sampled and analysed before meaningful average wet fluxes can be obtained. Also, great care has to be taken to ensure that the samples do not become contaminated prior to analysis; this is particularly critical for substances present in trace amounts.

Despite these complexities, direct measurements have revealed several important features of the mechanisms controlling wet deposition, most of which are consistent with the chemistry of the constituents. It is clear that the concentration of a substance in precipitation varies with its concentration (or the concentrations of its precursors) in the atmosphere and tends to be highest close to sources (Arimoto et al., 1985), although the relationship is not necessarily simple. For example, the presence of discrete layers of elevated particulate concentrations in the atmosphere can make direct comparisons of ground level aerosol concentrations and precipitation chemistry uncertain (Buat-Menard and Duce, 1986).

Soluble and reactive gaseous constituents (e.g., HNO_3 and SO_2) are readily removed from the atmosphere by rain, while relatively insoluble gaseous constituents (organochlorines and Hg vapour) are removed inefficiently by wet deposition (Slinn et al., 1978; Bidleman and Christensen, 1979; Fitzgerald et al., 1983). The small amounts of these largely insoluble gaseous constituents found in rain probably reflect scavenging of the small proportion of the substances associated with aerosol particles.

Particulate matter is removed in wet deposition by collision with and capture by falling precipitation, or via the particles themselves acting as condensation nuclei. Some aerosol particles will readily dissolve in precipitation (e.g., sea salt, ammonium sulphate), while the extent of dissolution of less soluble particles such as fly ash or clays probably varies with the pH and pE (redox potential) of the rain. Both dissolved and particulate forms of many constituents can be expected to be present in precipitation, and the different environmental effects of these forms needs to be considered (Lindberg and Harriss, 1983).

The efficiency of wet depositional air-sea transfer varies with the form of the precipitation (rain, snow, etc.) and the meteorology of the storm (Buat-Menard and Duce, 1986). The importance of large-scale convective storms which penetrate the lower stratosphere as a removal mechanism for bomb and cosmic ray-produced radionuclides has been described by Burchfield et al. (1983).

Direct measurement of dry particle fluxes has been attempted using flat plate collectors having a variety of surfaces. Apart from the problems of contamination and natural inhomogeneity mentioned above, a fundamental difficulty is in knowing how well the collector surface mimics the sea surface. This approach may be adequate only when gravitational settling of large particles is responsible for a major fraction of the dry deposition (e.g., sea-salt and soil-dust particles).

Similarly, direct measurements of air-sea gas fluxes are also fraught with difficulties. In this case a major problem with the use of chamber methods is that the enclosure clearly disrupts the normal aero- and hydro-dynamics of the interfacial transfer process. While micrometeorological methods can be applied, their use has so far been largely limited to the standard meteorological fluxes - heat, moisture, and momentum. For these reasons, it is our view that no reliable direct estimates of air-sea fluxes currently exist for gases, other than water vapour and ozone.

In view of the lack of direct measurements, indirect approaches are often used to estimate air-sea fluxes. This is particularly necessary here since the object of this exercise is to estimate inputs to the ocean globally; by their very nature direct measurements are local and refer only to the time and place at which the data were collected. The limited amount of directly measured deposition data is used in this paper as a cross-check on the indirect approaches used to estimate global fluxes of nitrogen and synthetic organics.

INDIRECT ESTIMATES OF ATMOSPHERE-OCEAN MASS FLUXES

Basically, in indirect approaches the air-water flux is calculated from the product of a concentration term (which drives the flux) and a kinetic parameter (which quantifies the rate of mass transfer). This concept is now discussed for exchange of gases, 'dry' particles and precipitation.

GASES

For gases, the flux (F_g) driving term is the concentration difference across the interface (ΔC, the sign of which determines the direction of F_g), and the rate expression (K) is variously known as an exchange constant/coefficient or a piston/transfer velocity (the lattermost term will be used here), and has the dimensions of a velocity. Then,

$$F_g = K \cdot \Delta C = K_w\,[Cg_a(H/RT)^{-1} - Cg_w] = K_a\,[Cg_a - Cg_w(H/RT)] \qquad (1)$$

K_w and K_a refer to whether the calculation is made with concentrations expressed on a liquid phase or a gas phase basis. Cg_a and Cg_w are the gas concentrations in air and water, respectively. H/RT (where R is the Gas Constant and T is temperature in degrees K) is the dimensionless Henry's law constant, expressed as the ratio of the concentration of the gas in the air to its concentration in un-ionised form in the water, at equilibrium.

It is often more convenient to think in terms of the reciprocal of K, which is a measure of the resistance (R) to gas exchange. On a liquid phase concentration basis the following equations show how R may be split into resistances in the air (r_a) and water (r_w),

$$1/K_w = 1/\alpha k_w + RT/Hk_a \qquad (2)$$

$$R_w = r_w + r_a \qquad (3)$$

In (2), k_a and k_w are the transfer velocities for chemically unreactive gases in the air and water, respectively. The factor α quantifies any enhancement in the value of k_w due to chemical reactivity of the gas in water. In the present context it is probably safe to ignore α since the compounds of interest do not react rapidly with water ($\alpha = 1.0$).

On a gas phase basis (2) would be:

$$1/K_a = 1/k_a + H/RT\alpha k_w \qquad (4)$$

and

$$R_a = r_a + r_w \qquad (5)$$

By substituting appropriate values in (2) - (5), it is possible to calculate r_w and r_a for particular gases and so to identify whether one of the resistances is dominant or whether both must be considered. When this substitution is done, many simple gases are found to fall into one of two distinct groups: i) those for which $r_a \gg r_w$ (H_2O, SO_2, NH_3) and ii) those for which $r_w \gg r_a$ (O_2, N_2, CO_2, CO, CH_4, CH_3I, DMS). Gases in group i) are those which tend to partition into the aqueous phase (low H) and/or have rapid water-phase chemistry; those in group ii) have high H values, tend to be unreactive in water, and partition into the gaseous phase. Some gases do not fit neatly into one or the other of these categories, and in their cases both r_a and r_w are of importance. Several of the high molecular weight organics of interest here appear to fall into this intermediate category (Mackay and Yuen, 1981; Atlas et al., 1982; and Table 32 of this paper).

In summary, in order to use (1) to calculate F_g, both ΔC and K must be known. The ΔC term has to be obtained by direct field measurements of gas concentrations in marine air and surface seawater. It will be dealt with in the sections of the paper considering specific types of trace substances, as appropriate. The value of H must be known for each of the gases of interest at the temperature and salinity of the water samples. H arises not only in the specification of ΔC, but also in the solution of (2) and (4). It can be obtained either from laboratory experimental determinations or from a knowledge of the vapour pressure and solubility of the individual compounds (Mackay and Shiu, 1984).

In order to specify K, (2) or (4) has to be solved. Apart from H (discussed above) and α (taken as 1.0), the only unknowns are k_a and k_w. In the following paragraphs a brief indication is given of how these individual phase transfer velocities may be formulated in terms of a widely available meteorological variable - wind speed.

The Air-Phase Transfer Velocity

The air phase transfer velocity, k_a, is the reciprocal of the air-phase transfer resistance, r_a, which is often treated in terms of two resistances in series. The first resistance corresponds to turbulent exchange in the upper part of the atmospheric boundary layer. In near neutral atmospheric stability this resistance can be approximated as,

$$r_{a(turb)} = u/u_*^2 \qquad (6)$$

where u is the wind speed and u_* is the friction velocity (defined in terms of the surface drag of the wind and the air density). For the case of the open ocean, we can approximate the friction velocity using a drag coefficient,

$$C_d = (u_*/u)^2 \qquad (7)$$

The drag coefficient is known to vary with wind speed, but the variation is small and, for present purposes, it will be assumed that C_d is constant and equal to 1.3×10^{-3}. Using this value, $r_{a(turb)}$ can be approximated from the wind speed data alone. In doing so, the role of aerodynamic stability is neglected; when the water is warmer than the air the atmosphere is dynamically unstable and $r_{a(turb)}$ will be lower than estimated above. When the water is colder than the air, $r_{a(turb)}$ will be greater than estimated here.

The second part of the atmospheric resistance is that which applies close to the sea surface, where transfer is assumed to be by diffusion. The resistance ($r_{a(diff)}$) associated with exchange across this boundary layer depends on both the diffusivity of the substance in air (D_a) and u_*. Many specialised formulae have been proposed to relate $r_{a(diff)}$ to u_* and D_a; for the present it is adequate to adapt a simplification involving the Schmidt number in air, $Sc_a = v_a/D_a$, where v_a is the air viscosity. Then,

$$r_{a(diff)} = (5/u_*) \cdot Sc_a^{2/3} \tag{8}$$

(after Hicks et al., 1986). Available information indicates that (8) is most applicable over solid surfaces; over water, somewhat different forms of the role Sc_a have been suggested but are not recommended here because of lack of data and the small differences that are likely to result.

It is useful to observe that Sc_a is related to the square root of the molecular weight (M.W.) of trace gases, and hence (5) - (8) can be combined to yield the following simple formula for r_a (in mks units):

$$r_a = (r_{a(turb)} + r_{a(diff)}) = (770 + 45(\text{M.W.})^{1/3})/u \tag{9}$$

The Water-Phase Transfer Velocity

The water phase transfer velocity, (k_w), and its formulation in terms of wind speed (u) are discussed by Liss and Merlivat (1986). They have used the results of various wind tunnel studies to try to specify the relationship between k_w and u. The situation is more complex than for k_a since a singular relationship is not possible. Wind tunnel results show that the relationship between k_w and u can be approximated to three linear portions, with different slopes. Up to $u \sim 3.6$ m s^{-1} the water surface is smooth; between $u = 3.6$ to 13 m s^{-1} the surface is covered with waves but they are generally not breaking, above $u = 13$ m s^{-1} wave breaking occurs. The slopes of the straight-line segments increase as the surface becomes rougher. A further complication is that in the regime above $u = 13$ m s^{-1}, bubbles produced by the breaking waves act as an additional gas exchange mechanism whose magnitude varies with gas solubility in the water. This means that at higher wind speeds there is a family of curves having different slopes, with the least soluble gases showing the greatest slopes.

In order to make these laboratory results applicable in the environment, they are 'tuned' using the field studies employing SF_6 as a tracer carried out by Wanninkhof et al. (1985) in a freshwater lake. Although the applicability of lake results to the oceans, with their much longer fetch, is open to question, it is the best that can be done at the present. Further, the predictions made using this approach are in reasonable agreement with those ocean results which do exist (see Figure l). The equations derived by Liss and Merlivat describing the three portions of the k_w / u relationship for the oceans are as follows:

$$k_w = 0.17\,u \qquad \text{for } u \leq 3.6 \text{ m s}^{-1} \tag{10}$$

$$k_w = 2.85\,u - 9.65 \qquad \text{for } 3.6 < u \leq 13 \text{ m s}^{-1} \tag{11}$$

$$k_w = 5.9\,u - 49.3 \qquad \text{for } u > 13 \text{ m s}^{-1} \tag{12}$$

where k_w is in cm h^{-1} and u is in m s^{-1} at a height of 10 m. Equations (10) - (12) apply to CO_2; for other gases corrections can be made through the water phase Schmidt number ($Sc_w = \nu_w/D_w$) as follows: for u (at 10 m) ≤ 3.6 m s^{-1}, $k_w \propto Sc_w^{-2/3}$; for u > 3.6 m s^{-1}, $k_w \propto Sc_w^{-1/2}$.

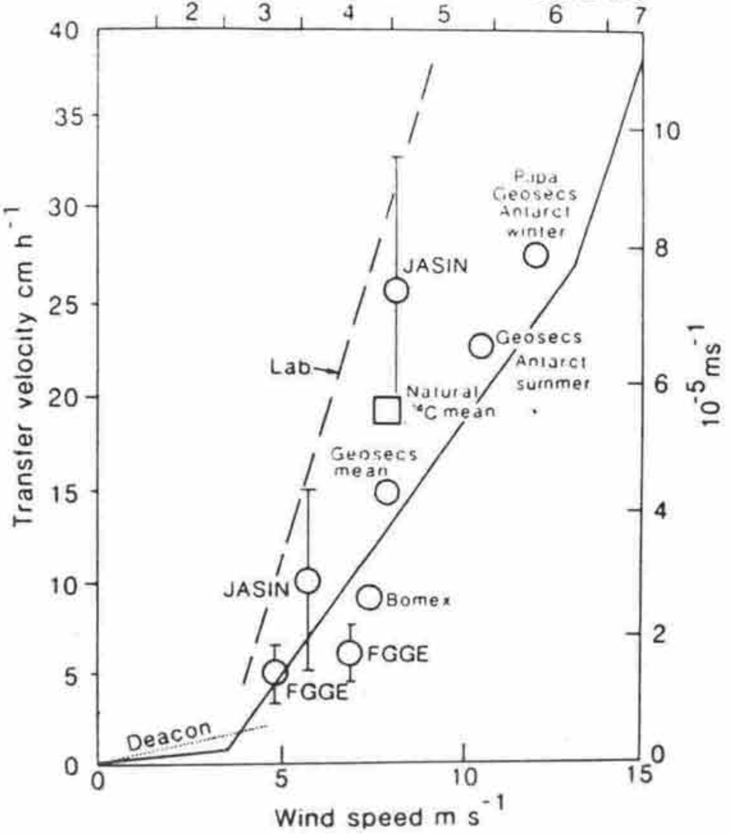

Figure 1. Oceanic measurements of k_w plotted as a function of wind speed measured at a height of 10m and the corresponding Beaufort scale number. The dotted line represents predictions based on the Deacon (1977) smooth surface model. The dashed line represents the results for intermediate wind speeds from laboratory wind tunnel studies. All data are converted to $Sc_w = 600$, corresponding to CO_2 at 20°C, by assuming that $k_w \propto Sc^{-1/2}$ (After Roether, 1986). The three full lines are plots of equations 10-12 (Liss and Merlivat, 1986).

PARTICLES

For deposition of particles the flux (F_p) is given by the product of the measured concentration of the particles in air (C_{pa}) and a deposition velocity (V_d),

$$F_p = V_d \cdot C_{pa} \qquad (13)$$

The term V_d comprises all the processes of deposition, such as gravitational settling, impaction and diffusion of particles to the water. It is very difficult to describe properly since each of these processes acts simultaneously and because each of them is dependent on a number of variables (i.e., wind speed, particle size, relative humidity, air viscosity, sea-surface roughness). The two-layer model outlined earlier for the prediction of the air transfer velocity for gaseous deposition (k_a) can be applied to particle deposition also, but only to those particles small enough that gravitational settling is not dominant. However, it is found that even for very small particles the Schmidt number term in (9) dominates the overall atmospheric resistance computed as outlined previously for k_a, yielding deposition velocity predictions that are unreasonably low. For small particles the simplification afforded by (8) is inadequate, and more detailed consideration of the roles of particle impaction and diffusion is then required. For present purposes, two models have been used to provide guidance on the deposition of particles too small to be strongly influenced by gravitational settling. First, the model of Slinn and Slinn (1980) has been used, with relative humidity assumed to be 98% (about the maximum that can occur in air contacting sea water, except under non-equilibrium conditions). The predictions range from less than 0.01 cm s^{-1} to more than 0.1 cm s^{-1}, depending on particle size (see Figure 2). The second model used is that of Hicks and Williams (1980), which yields deposition velocities ranging from 0.01 cm s^{-1} to more than 0.3 cms^{-1}, depending on wind speed.

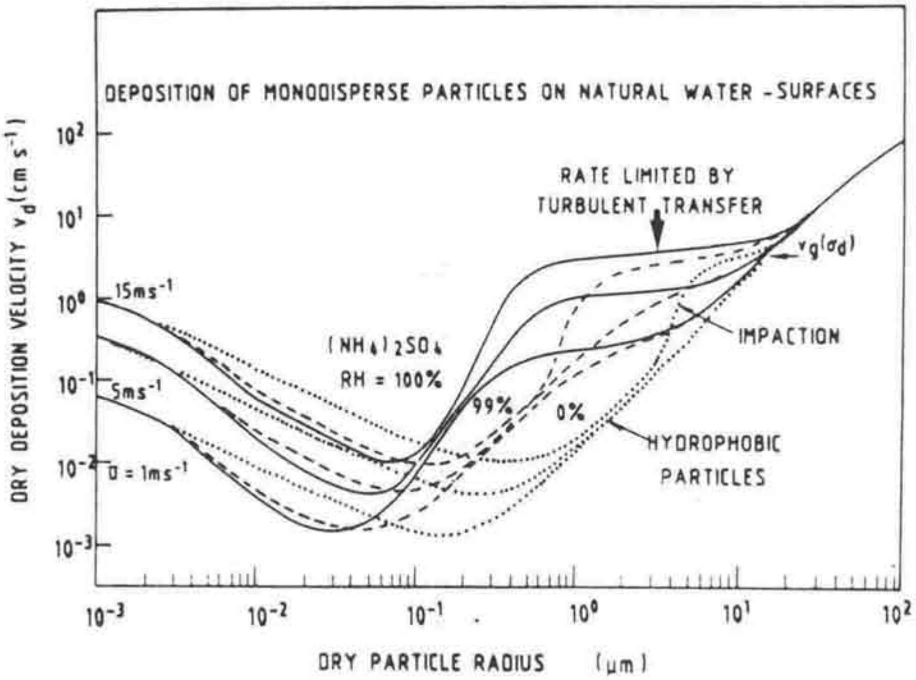

Figure 2. Dry deposition velocity of particles in a water surface as a functions of relative humidity and particle size. (After Slinn and Slinn, 1980).

For particles in the size range where gravitational settling is the controlling factor, both models agree and do not appear to differ greatly from values derived from direct field measurements. These various approaches indicate that the 'best' values for use in the present exercise are as follows:

Submicrometer aerosol particles:	0.1 cm s^{-1}, +/- a factor of three
Supermicrometer crustal particles, not associated with sea-salt	1.0 cm s^{-1}, +/- a factor of three
Large sea-salt particles and materials carried by them	3.0 cm s^{-1}, +/- a factor of two

Because V_d varies with particle size, application of (13) has to be through measurements of concentration (C_{pa}) on aerosols size-fractionated at least into the three size classes given above. It should also be noted that in some cases corrections may need to be made for any recycled sea-salt component, i.e., the measured C_{pa} may contain both new material entering the ocean for the first time (the net input) and 'old' material recycling in sea spray.

RAIN

The wet deposition flux (F_r) is formally expressed as the product of the precipitation rate (P, discussed in the next section of the paper) and the concentration (C_r) of the substance of interest in rain,

$$F_r = P \cdot C_r \tag{14}$$

Equation (14) is often expressed not in terms of C_r, which effectively implies making a direct flux measurement, but through a scavenging ratio (S) (also sometimes called a washout factor), which is the ratio C_r/C_{pa} , such that

$$F_r = P \cdot S \cdot C_{pa} \cdot \rho^{-1} \tag{15}$$

In (15), ρ (the density of air) appears in order to make particle concentrations, which are generally expressed as mass per unit volume of air (often $\mu g\ m^{-3}$), dimensionless. By analogy between (13) and (15), $P \cdot S$ is equivalent to a wet deposition velocity. The advantage of (15) over (14) is that provided S is known (see later), measurement of C_{pa} provides the concentration driving term for both equations and hence for estimation of deposition of 'dry' particles as well as of material in rain and other forms of 'wet' deposit. The scavenging ratio is a dimensionless quantity, which in this report is computed from concentrations expressed as mass of substance per unit mass of rain or air. As with (13), equations (14) and (15) yield only gross fluxes, and in some cases corrections have to be applied in order to obtain the net inputs.

Factors known to affect the scavenging ratio (S) include the size of the particles being scavenged, their physical and chemical form, and cloud properties including droplet size, temperature and cloud type. Because of the complexity implied by the large number of processes affecting scavenging, there is no satisfactory theoretical treatment available to predict values of S. In view of this, resort is made to indirect, empirical approaches. The most widely used one is to measure concentrations in collected rain and simultaneously measured air concentrations at ground level; the ratio giving S for the substance(s) examined. Uncertainty arises not only because this approach assumes equilibrium, or at least a constant degree of approach to equilibrium, but also there is no certainty that concentrations at the ground truly reflect conditions in the cloud where the rain acquires most of the scavenged material. In view of these substantial problems, available values of S have to be treated with considerable caution. For example, at a given measurement site S can vary by an order of magnitude for any particular substance, and different substances exhibit different values of S. The problem is exacerbated by the small number of measurements which exist from which S can be calculated. However, there does appear to be some consistency between substances which exist on particles of similar size. Further, if a large number of separate determinations of S are made representative average values can be obtained. The most reliable values for S appear to lie in the range 200 to 2000. The values used for individual substances and particular oceans are discussed in the relevant sections of the paper. Of special interest is the case in which some (or all) of the chemical species in falling rain are derived from gas-phase (rather than particulate) concentrations in air. The additional complexity of in-cloud chemical conversion must then be considered. However, expected values of S appear to be in the same general range as given earlier.

ATMOSPHERIC TRANSPORT AND PRECIPITATION CLIMATOLOGY

INTRODUCTION

To make the calculations in this paper, meteorological information concerning transport and deposition must be utilized. Two approaches are considered:

1 Use of climatological fields, such as those for precipitation, which can be combined with the chemical concentration data to calculate the deposition on a grid point by grid point basis.

2. Use of Lagrangian/Eulerian transport models and General Circulation Models (GCMs), which can be configured to calculate deposition of certain substances to the oceans and inland seas.

Before reviewing the two approaches above, it should be noted that long-range atmospheric transport of trace materials to the oceans has been the subject of a number of workshop reports since the first attempts to address this question were made over a decade ago (NAS, 1978). These include the chapters by Hasse (1983) and Merrill (1986), both of which are primarily pedagogical reviews, and those by Rodhe (1985) and Whelpdale and Moody (1989), which emphasize discussion of research results.

CLIMATOLOGICAL DATA OVER THE OCEANS

There are numerous atlases and other collections of data which contain information on the climatology of wind flow and other meteorological phenomena over the oceans, averaged by month, season or year. In some, the vast quantities of ship-of-opportunity data have been screened by rather subjective techniques, and the final analysis made by knowledgeable marine climatologists. Included among these are the atlases for each ocean basin prepared from data compiled for the U.S. Navy (Meserve, 1977). In others the emphasis is on a straightforward presentation of data from a limited period of time, with attention paid to making both the screening of suspect data and the analysis objective. Included among these are Oort (1983) and Slutz et al. (1985). While these contrasting approaches tend to be complementary, the limited use of climatological data for temperature fields and mean wind speeds required for the calculations made in this report is adequately covered by either type of climatological analysis. However, the actual transport path of a substance from its source to the point of ultimate removal is typically not given by the time-averaged wind fields; i.e., the mean transport is not given by the mean winds. For example, when a large-scale wave pattern extends over a source region (south of the mean streamline position, say) and over a region of high precipitation (north of the mean streamline position), there can be sporadic transport from the source area towards the precipitating area, where removal can take place by wet deposition. As the wave pattern migrates there may later be southward flow of about the same strength; however, this may not result in significant transport to the rainy area. The mean north-south wind will be close to zero, but the transport is non-zero. However, in most cases data on the temporal and spatial variations in source and removal rate are so limited that general air flow patterns must still be used.

Attempts have been made to describe the general flow patterns that are the major atmospheric paths for such phenonmena as the Saharan dust outbreaks or the transport of aerosols from the Chinese mainland. In a recent paper by Whelpdale and Moody (1989), the flow patterns and storm tracks over the six major oceans have been extensively reviewed. The authors concluded that long-range transport was indeed an important factor, especially eastward from North America, westward from Africa, eastward from southern South America, eastward from Asia, westward from northern South America and into the Polar regions. The authors made the following recomendations:

- The major source areas should be better characterized, including temporal behaviour, vertical distributions and other parameters.

- An intensive experimental and modeling study of the coastal zone, especially downwind of major source areas, should be made.

- The importance of mesoscale features such as the sea breeze should be studied, especially their role in transport across land-sea boundaries.

Compiling back-trajectory flow climatologies for ocean areas is another way of summarizing flow conditions. When used in conjunction with standard climatological data, back trajectories calculated over periods of five years or longer for a given station can give some idea of the month-to-month flow patterns and hence potential deposition of the substance of interest. Such calculations have been made for sites including: Hawaii, American Samoa, Amsterdam Island, Alaska, Bear Island, New Zealand, Enewetak Atoll, and Bermuda. These studies give a summary of the gross transport paths to the station of interest, and their use is discussed by Rodhe (1985), Miller (1987) and Merrill et al. (1989).

INLAND SEAS AND COASTAL AREAS

Over the last decade, there has been a vigorous effort to understand transport pathways of pollutants and other substances to inland seas such as the Mediterranean, Baltic, and North Seas in Europe, and the Great Lakes in North America. Some initial work has also been done in the Gulf of Mexico. Much of the emphasis has been on riverine inputs and dumping. However, it was realized that because these bodies of water are so close to atmospheric pollution sources, the air pathway may also be important as a contributor to the deposition of harmful substances. For example, in the Mediterranean region, ship expeditions (PHYCEMED) and ground station measurements made over the last decade have produced a set of data that can be used to estimate trace substance inputs. A number of recent publications have used meteorological parameters either to interpret these data or to establish flow climatologies for the region (Dayan, 1986; Dulac et al., 1987; Martin et al., 1987; Maring et al., 1987; Miller et al., 1987; inter alia). Similar work has been done for the Baltic and North Seas. In North America, along with the major effort to study the pollution input to the Great Lakes, transport studies to the Gulf of Mexico have begun (Parungo and Miller, 1988).

Coastal areas present a complex meteorological and chemical situation that makes it difficult to estimate deposition via the atmosphere quantitatively. For some substances in some areas the input from riverine outflow and local dumping totally mask the atmospheric contribution. The meteorological situation may be highly variable in space and time because of the land-sea breeze circulation, which exists owing to the temperature differential over the two surfaces. Even with these complications, atmospheric deposition can be estimated for some substances and may be substantial, as has been suggested for nitrate input into the Chesapeake Bay in the United States (Fisher et al., 1988).

LAGRANGIAN AND EULERIAN MODELS

Since the identification of possible environmental damage due to acid deposition, a considerable effort has gone into developing transport models that could be used calculate the deposition of acidic substances (Eliassen and Saltbones, 1983; Chang et al., 1988). One recent application of such models to large water bodies is that of the use of the EMEP model to estimate sulphur and nitrogen deposition to the Baltic and North Seas. For example, model calculations suggest that 138 x 10^9 g of NO_x-N and 634 x 10^9 g of S were deposited into the Baltic during 1985 (Eliassen et al., 1988). Further model results for trace metals are given in Petersen et al., 1988. However, these models are mainly regional in nature and have not yet been implemented at the global scale.

A global scale Lagrangian trace species model has been developed by the Lawrence Livermore National Laboratory in the United States (Walton et al., 1988). Source data are used to specify the initial concentrations distributed with latitude and longitude according to best estimates from the literature. Climate-model winds are used, and each mass of air is advected and deformed, allowing for continuous tracking of the concentration. Some of the preliminary results of long-range transport calculations for nitrogen were made available for discussion during the workshop. At this point, the model results must be considered as preliminary because further refinements are needed, including better treatment of physical processes, such as mixing and turbulent and convective exchange.

Another approach is to use an Eulerian Chemical Transport Model (CTM) to describe transport of a trace material. Levy and Moxim (1988 and 1989) have used the Geophysical Fluid Dynamics Laboratory general circulation transport model to simulate the global spread and deposition of nitrogen emitted by fossil fuel combustion. They have allowed the nitrogen species to be transported without explicit chemistry; chemical reactions are implicitly introduced through bulk coefficients for dry and wet removal. Calculated and measured deposition values in western Europe and over the North Pacific have been compared and agree within a factor of two. Further tests of this approach, in which natural sources of nitrogen species will be accounted for, are planned.

Though models provide a way of estimating deposition to the oceans of certain substances which is grounded in first principles, it was decided that, for the purposes of this study, the climatological approach was more appropriate. This is in part because CTM results cannot be used readily in an iterative comparison with observed concentrations or fluxes. Since the models account for many processes and multiple sources, the results at a given place or time cannot be adjusted independently. Simulation of global transport and deposition is a major computational task requiring weeks of effort. For many substances the source dependencies on meteorological and other factors are presently not well known. In the near future the CTM results should provide a useful point of comparision with other estimates. Eventually, as our knowledge of source behaviour and skill in parameterization increases, CTMs may become the models of choice. However, climatological techniques are more suited to the purposes of the present exercise.

FRAMEWORK FOR THE CALCULATION

THE METHOD

The deposition calculations made for this report have been done for 10°x10° areas of the ocean using microcomputers and spreadsheet software. Working maps were prepared in advance for each ocean basin, indicating the grid areas to be used. The first step in the calculation was the annotation of these working maps with chemical concentration values, scavenging ratios, dry deposition velocities and other data needed to make the deposition estimates. When the concentration values and other chemical data were agreed upon, they were entered into the spreadsheets. On the spreadsheet, each 10°x10° area was represented by a cell, i.e., the intersection of a row and a column.

We used a regular longitude/latitude coordinate system represented in the illustrations via a cylindrical equidistant map of the globe, with the upper left corner representing 90°N, 30°E. This modest spatial resolution was chosen largely because of the shortage of chemical data. Consequently, higher resolution is not justified. For the purposes of data exchange we agreed on the grid numbering scheme used in the Comprehensive Ocean/Atmosphere Data Sets (Slutz et al., 1985), in which each of the grid areas is assigned a number between 1 and 648. This system is similar to, but less cumbersome than, the Marsden Square grid system.

A means of previewing the results was developed. The 10°x10° resolution chemical data were printed directly from the microcomputer, one page for each ocean basin and for each chemical substance or class of substances. Overlay maps were prepared for orientation; the working arrays themselves provide no explicit indication of their location on the earth. This overlay procedure made possible interactive checking of the data fields (including possible data entry errors). It also allowed iterative modification of the parameters, given the estimated deposition results.

The deposition at any place or time depends more or less critically upon the ambient precipitation value. The precipitation fields used in the calculations are those of Jaeger (discussed in Jaeger, 1983). While the oceanic precipitation values are uncertain and need to be improved, they are not the main source of uncertainty in the discussion at hand, and can be taken to be representative. Nevertheless, a brief discussion of the known problems with these data is warranted. Gridded precipitation data were obtained by interpolation of values of precipitation frequency, multiplied by the precipitation depth estimates of Geiger (1965). The precipitation frequency data used are from the US Marine Climatic Atlas, the most recent edition of which is Meserve (1977). Jaeger then adjusted the oceanic values by increasing them uniformly by 6.2% to reach a global average precipitation depth of 1 m. The latter value was indicated by independent studies of the global water balance. Only the marine areas were adjusted because they are generally less certain than those over land. The Jaeger precipitation data are available at high spatial resolution (2.5°x5°) and for each month. For use in this study, seasonal total precipitation maps were prepared at the lower resolution chosen for the deposition calculations. However, only the annual total data were used in the calculations, again limited by the availability of chemical data.

Examples of the global precipitation rates contoured from these fields for the winter and summer seasons are shown in Figures 3 and 4 in millimeters of water per month. The December-January-February averages show values over 100 mm month^{-1} in the midlatitude North Pacific and North Atlantic areas, with much higher values confined to the equatorial zone and to the tropical areas between 120°E and the Dateline. The June-July-August averages have values higher than 100 mm month^{-1} over wide areas of the southern hemisphere oceans, and show increased equatorial precipitation, especially west of Africa. The variation from month to month is significant, but is suppressed in the calculations in this paper because annual average precipitation data have been used. It should be obvious that this can introduce significant errors.

The aerosol dry depositon calculation was made using the following formulation. A deposition velocity is specified for each substance or class of substances. The dry flux is then given by the concentration times the dry deposition velocity as described in the previous section, equation (13). Because the value of the deposition velocity is not uniform in space or time, the range of values outlined earlier has been used in the calculation.

Because the fluxes are calculated separately, a direct comparison of the relative importance of dry and wet deposition processes can be made from the calculated flux values. This is informative in those cases where separate dry and wet deposition estimates are available from field data or careful calculations.

As an example, consider a cell in the mineral aerosol calculation where the atmospheric particle concentration (Cp_a) is 2 μg m^{-3} and the dry deposition velocity of the particles (V_d) is 1.0 cm s^{-1}. Then the dry deposition flux (F_p) is given by,

$$F_p = Cp_a \cdot V_d = (2\ \mu\mathrm{g\ m}^{-3})\ (1.0\ \mathrm{cm\ s}^{-1})\ (10^{-6}\ \mathrm{g}\ \mu\mathrm{g}^{-1})\ (10^{-2}\ \mathrm{m\ cm}^{-1})\ (3.15 \cdot 10^{7}\ \mathrm{s\ yr}^{-1})$$

$$= 0.63\ \mathrm{g\ m}^{-2}\ \mathrm{yr}^{-1}$$

This can then be multiplied by the area of the 10°x10° box, which is

$$(10 \cdot 111.1 \cdot 10^{3}\ \mathrm{m})^{2} \cdot \cos(\phi)$$

where ϕ is the latitude at the middle of the box.

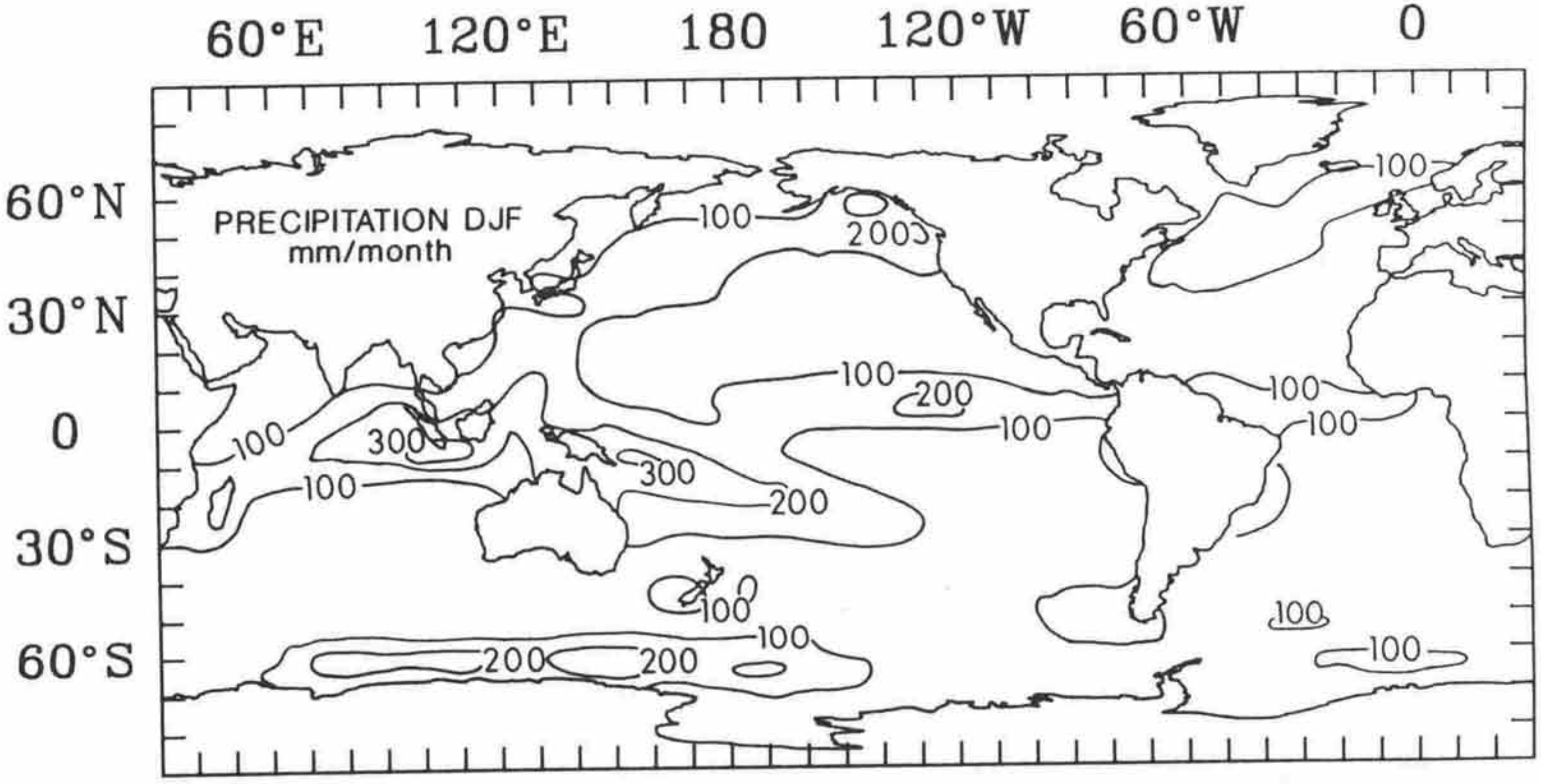

Figure 3. Global Precipitation Rates for Months of December, January, and February in mm per Month. (As discussed in the text, this figure is based on precipitation estimates of Jaeger (1983)).

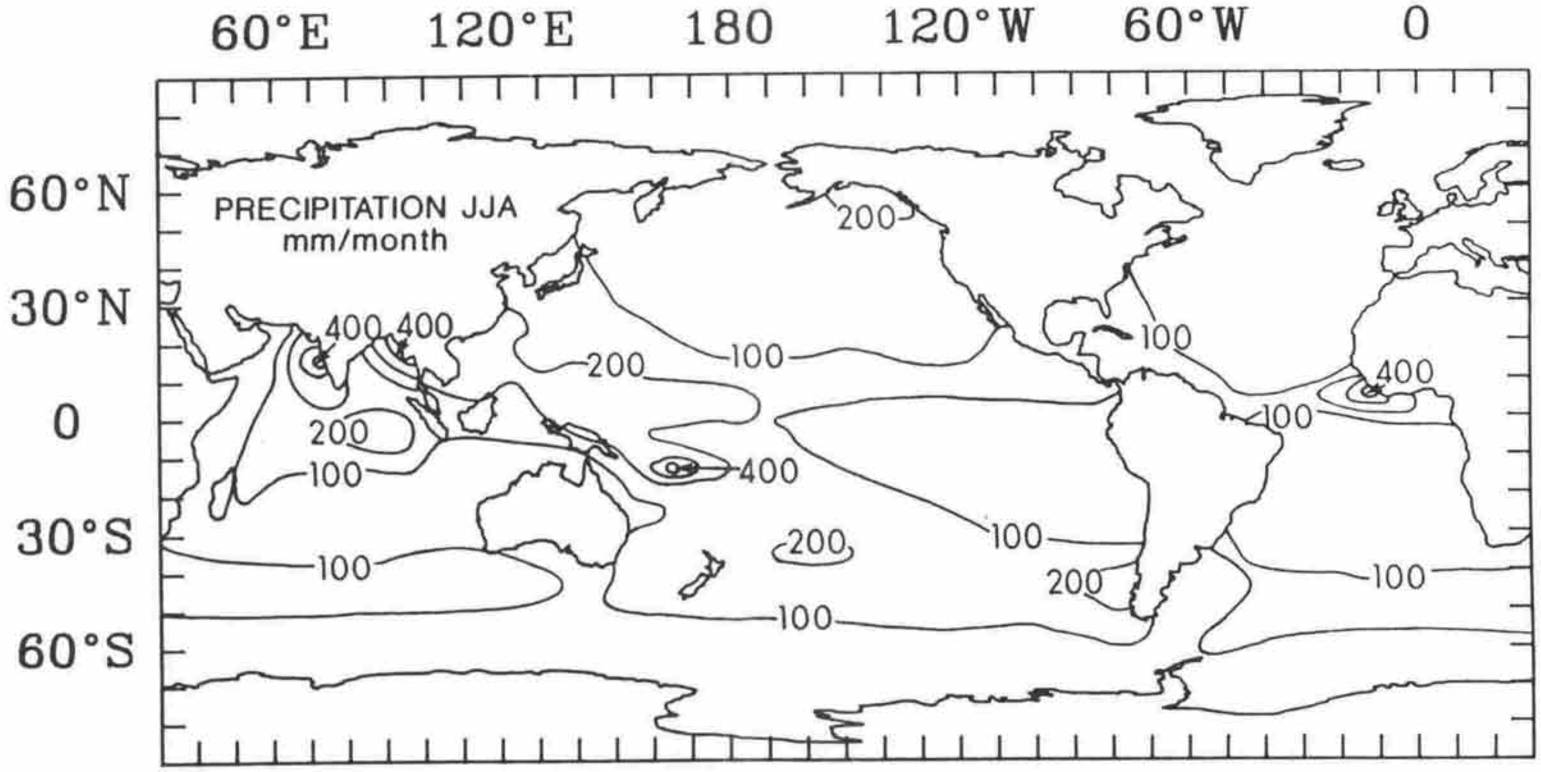

Figure 4. Global Precipitation Rates for Months of June, July, and August in mm per Month.
(As discussed in the text, this figure is based on precipitation estimates of Jaeger (1983)).

Assuming a scavenging ratio (S) of 1000, and a precipitation rate (P) of 462 mm yr^{-1}, the corresponding wet deposition flux (F_r) is given by equation (15), i.e.,

$$F_r = P \cdot S \cdot C_{pa} \cdot \rho^{-1}$$

$$= (462 \text{ mm yr}^{-1})(1000)(2\ \mu\text{g m}^{-3})(0.00083 \text{ m}^3\text{g}^{-1})(10^{-6}\text{g}\ \mu\text{g}^{-1})(10^3\text{g m}^{-2} \text{ mm}^{-1})$$

$$= 0.77 \text{ g m}^{-2}\text{yr}^{-1}$$

where P is the annual rainfall amount, and the conversion from rainfall depth to mass of water per unit area is made at standard temperature and pressure. The density of air (ρ) is taken as 1200 g m^{-3}, within 5% of the global average surface value. The resulting flux can similarly be multiplied by the area of the box before being added in the sum for the basin-wide or global flux estimates.

The deposition process for organic substances is more complex, and a more sophisticated approach is required. This is because many of the compounds may be present in significant amounts in particulate, aqueous, and gaseous phases. The way in which these complexities have been dealt with is discussed in detail in the section on deposition of organics compounds.

ESTIMATING CONCENTRATIONS USING OBSERVATIONS AND TRANSPORT PATTERNS

In the open ocean there are vast areas bereft of concentration or flux data. In cases where nearshore values are relatively well known, various techniques of extrapolation were used to estimate the concentrations further from the source. The extrapolation was subjective and involved consideration of the main transport paths and areas of removal, as well as the relevant residence time or decay distance of the concentration. Often there are also data at distant offshore points. Along the main lines of transport passing such sites, judicious interpolation was used to estimate the concentration values. The interpolation procedures are discussed in the sections dealing with the each particular species.

All of the calculations are based upon the 10°x10° area estimates. Basin-total deposition, and basin-average flux values are tabulated in the following sections. These are obtained by summing and by dividing the sum by the area of the summed boxes, respectively. The nominal basin areas for the boundaries used in the calculations are as follows (in units of 10^{12} m^2): North Pacific, 89.6; South Pacific, 110.2; North Atlantic, 54.9; South Atlantic, 51.2; North Indian, 14.4; South Indian, 53.7; Global Ocean, 374.1. These values differ somewhat from atlas values. First, we arbitrarily included the area south of Australia from 120°E to 150°E in the South Pacific rather than the Indian Ocean. Second, we have not taken account of the fraction of land area in the coastal boxes; rather, we assumed these are entirely oceanic. The discrepancies are generally less than 10%, and we did not choose to correct the area estimates.

SUMMARY

Although both climatological methods and model calculations are discussed above, only the grid square technique was applied to estimate the deposition of gases and aerosols to the world oceans. Spreadsheet calculations were used to estimate the aeolian fluxes to the ocean. A serious limitation is apparent in that only annual total fluxes are estimated. While the limited availability of chemical data for each season is responsible for this, the strong variation of the precipitation distribution from winter to summer illustrates the likely importance of determining the variation of concentrations (and thus fluxes) throughout the year. A significant benefit of the microcomputer-spreadsheet approach is that the calculations can be repeated easily with revised values of the various parameters. This allows for continuing use of the spreadsheets as new chemical and meteorological data become available.

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THE ATMOSPHERIC INPUT OF TRACE ELEMENTS AND MINERAL AEROSOL TO THE WORLD OCEAN

INTRODUCTION

The trace elements considered in this section are those whose distribution in oceanic systems appear to be influenced by atmospheric concentrations and fluxes. With the exception of Hg, which occurs predominantly (≈99%) in the gas phase (e.g., Fitzgerald, 1986), these elements are associated with aerosol particles that are produced both naturally and as a result of anthropogenic activities. The dry and wet deposition mechanisms responsible for the air-to-sea transfer of trace elements may be particle-size dependent, and we have therefore considered two categories of elements.

Elements of the first group are found primarily on particles in the accumulation (< 1 μm) mode. It is in this size fraction that most of the aerosols exist that result from the high temperature anthropogenic processes largely responsible for their release into the environment, (e.g., Rahn, 1976). We have considered here those elements for which there is evidence of a significant anthropogenic perturbation, at least in the northern hemisphere. These are among the so-called anomalously enriched elements (AEEs) because their atmospheric concentrations are far in excess of those expected from such natural sources as mineral aerosol and atmospheric sea salt. Furthermore, the elements considered here (Pb, Cd, Zn, Cu, Ni, As, Hg, and Sn) are those for which a reasonable data base exists.

Elements of the second group are those that are present mainly in the coarse mode (> 1μm), and comprises elements such as Al, Fe, Si, and P that are derived primarily from natural mineral aerosol of terrestrial origin. The major source regions of this atmospheric dust are the arid and semi-arid areas of the world (North Africa, Central Asia, Australia, and North and South America; Prospero, 1981 and 1989). The atmospheric deposition of mineral aerosol to the ocean represents an important source of non-biogenic material in deep sea sediments (e.g., Duce et al., 1980). Fractions of the elements associated with mineral aerosol are soluble in seawater, but these values are not at present well constrained. This is an important consideration because a variety of nutrients and micronutrients are associated with mineral dust, and input of this material to the oceans may affect chemical and biological processes in seawater.

To predict the atmospheric deposition rates of most of these trace elements, we normalized fluxes of the two groups of elements to Pb and the mineral aerosol data, respectively. The normalization to mineral aerosol for Fe, Si, P, and Al was made because a considerable body of data has shown that these elements are normally in crustal abundances in both continental and oceanic areas. The data base for Pb is larger and more reliable than for the other AEEs (with the possible exception of Hg), and the fluxes of the enriched elements were approximated by scaling the Pb flux by the ratio of the atmospheric concentration of the element of interest to that of Pb.

Some elements, such as Mn, V, and Cr, are significantly affected by both the natural and pollution sources we have considered. The fluxes of these elements could also be scaled according to their observed enrichments relative to mineral aerosol, but we have not done so here in view of their likely smaller effects in the oceans. Mercury and tin have been treated separately. This was necessary because Hg is predominantly in the gas phase, and thus gas transfer among the various environmental compartments is important. For Sn there are limited data, and these have been previously summarized (Byrd and Andreae, 1986); we have used this summary without modification.

For the five ocean basins considered, the mean atmospheric concentration fields of Pb and mineral aerosol have been generated from the available data with extrapolation for grids with missing data based on our knowledge of source regions and the dominant transport pathways (e.g., Whelpdale and Moody, 1989). The concentration fields of 210-Pb, which has been used as a tracer for continental emissions (Lambert et al., 1983), were also used in our extrapolations. The selection of the data bases and details regarding the approaches used are discussed further in the following section.

In addition to our calculations for the global ocean, three regional seas (North, Baltic, and Mediterranean) were considered separately because recent research has produced sufficient data for this more detailed analysis. The details of the regional seas assessments are discussed later.

The values used for the dry deposition velocities and scavenging ratios are given in Table 1. For dry deposition, the values are based on available knowledge of the particle-size distribution of the elements. For pollutant elements (e.g., Pb) we do not expect the dry deposition velocity to vary significantly over different oceanic regions and a mean global ocean value of 0.1 cm s^{-1} (Patterson and Settle, 1987) has been adapted. This is not possible for mineral aerosol since its size distribution varies strongly as a function of the distance from the source region. Based on available data over the Atlantic and the Pacific (Uematsu et al., 1985; Savoie, 1984), we have adopted a mean value of 0.4 cm s^{-1} for the remote open ocean (distance from the coast greater than 1000 km) and a mean value of 2 cm s^{-1} for coastal and near shore areas.

Based on available and reliable air and rain concentration data for lead over the North Atlantic and the Pacific Ocean (Duce et al., 1976; Duce et al., 1983; and Church et al., 1984; Arimoto et al., 1985, 1987; Settle et al., 1982; Settle and Patterson, 1982; Patterson and Settle, 1987; Jickells et al., 1987), most values for lead scavenging ratios range from 100 to 500. We have adopted a mean global value of 200 and have assumed that this value holds for other AEEs. This assumption seems justified on the basis of available data and the fact that pollutant elements considered here exhibit similar particle size distributions in remote marine air (Duce et al., 1976 and 1983) and should therefore exhibit similar precipitation scavenging efficiencies (Buat-Menard and Duce, 1986).

On the other hand, for mineral aerosol, the available data base suggests significant differences in mean scavenging ratios between the North Atlantic and Pacific Ocean. The data base for the North Atlantic (Savoie, 1984; Prospero et al., 1987; Duce et al., 1976; Church et al., 1984; Jickells et al., 1987) is limited to only two sites, Miami and Bermuda, and the data tend toward a value of 200, which has been adopted here for this basin only. The Pacific data of Uematsu et al. (1985) show little variability in the mean scavenging ratio from one site to another, and their mean value of 1000 has been used for this and all other ocean basins except the North Atlantic. The reasons for such differences are unclear. One possible explanation is that the scavenging ratio in the North Atlantic and especially at Bermuda is being calculated from temporally unmatched data sets, since the rain and air samples used to calculate the ratio were collected several years apart. Further, since scavenging ratio values are estimated from near-surface air concentrations, which can be quite different from those at the altitude of cloud scavenging, another possibility is that the vertical distribution of mineral aerosol is different between the North Atlantic and the Pacific Ocean. Yet again, differences in mean cloud properties and precipitation patterns between the two Atlantic sites and the Pacific sites, together with differences in mass-size distribution of mineral aerosol particles might also explain the observed differences in scavenging ratios (see earlier and Buat-Menard and Duce, 1986). Nevertheless, though we stress that a more extensive data base is urgently needed for the North Atlantic, we have assumed that the differences in mean scavenging ratios between the North Atlantic and the Pacific Ocean are real and should be taken into account in the calculation of global wet deposition fluxes of mineral aerosol.

Table 1. Parameterizations used for the Trace Metal Calculations

	Dry Deposition Velocity, cm s^{-1}		Scavenging Ratio	
Type of Particle	Range	Mean	Range	Mean
Pollutant Aerosol	0.03 - 0.3	0.1	100 - 500	200
Mineral Aerosol	0.3 - 3	see text	100 - 2000	see text

METHODOLOGY

LEAD

North Atlantic Ocean

The concentration of lead in the atmosphere over the North Atlantic has been reliably measured over the past fifteen years (see Table 2). Aerosol samples have been collected from islands over long periods and from ships over restricted periods. All these data reveal large gradients in aerosol lead with concentrations decreasing away from coastal margins. In addition, there is evidence of short-term temporal variability related to seasonal changes in trans-Atlantic atmospheric transport. Longer-term changes due to the removal of lead from gasoline, primarily in the United States, requires that measurements made in the early seventies be adjusted downward by roughly a factor two to reflect more accurately concentrations currently expected (Shen and Boyle, 1987).

Table 2. Lead Aerosol Concentrations over the Atlantic and Pacific Oceans
(Mean or Range)

Site	Concentration ng m^{-3}	Reference
ATLANTIC		
Bermuda	3.3 3.6	Duce et al., 1976 Wolff et al., 1986a
Pigeon Key, Florida	5	Settle et al., 1982
Weather Station "C"	0.6-4.4	Ryaboshapko et al., 1986
Faeroe Islands	6	Kemp, 1984
Western Atlantic	2.4	Patterson and Ng, unpub.
Northeastern Atlantic	1.4-17.7	Veron, 1988
North and South Atlantic	4.3-7 0.1-66	Chester et al., 1983 Volkening et al., 1988
PACIFIC		
Enewetak	0.088-0.26 0.12	Settle and Patterson, 1982 Duce et al., 1983
North Pacific	0.2-1 0.26	Maring et al., 1989 Patterson, 1988
Samoa	0.02-0.15 0.016	Patterson and Settle, 1987 Arimoto et al., 1987
New Zealand	0.019-1.0	Arimoto and Duce, unpub.

Lead was measured in aerosols at High Point, Bermuda (32°N; 62°W) from 1973 to 1974 in non-winter months (Duce et al., 1976). When transport was stratified into westerly, southeasterly, and easterly directions, it was found that the lead concentration in air masses coming from the west was twice that in air coming from the south or east of Bermuda. Wolff et al. (1986a) made further aerosol measurements some ten years later at ground level at the same location and obtained comparable values when corrected for decreases in leaded gasoline usage. Similar values were also obtained in the Florida easterlies in 1978 (Settle et al., 1982). Lead concentrations were determined for aerosol particles collected in the Canadian Arctic (Barrie et al., 1981). Concentrations of about 1 ng m^{-3} appear to be substantially greater than global background levels and are attributed to long-range transport of pollutants to the Arctic. The value of 1 ng m^{-3} is applied to all arctic latitudes from 70°-90°N.

Lead has also been measured in aerosols collected from ships in the North Atlantic. Veron (1988) measured aerosol lead from ships in the eastern North Atlantic. Using air-mass trajectory analysis he showed concentrations about an order of magnitude higher in those air masses coming from Europe relative to those coming from the central Atlantic. The areas to the west, near the center of the Azores high, are characterized by some of the cleanest air in the North Atlantic, reflecting aged marine air from which much of the lead has been scavenged. Ryaboshapko et al. (1986) have made lead aerosol measurements from a weather ship stationed in the central North Atlantic (52.7°N; 35.5°W) since 1976. They also stratified their data according to wind trajectory, and they estimate a relative increase of a factor two or more in air coming from North America. Lead was also measured in aerosols from ships on at least two occasions in conjunction with complete cruise transects from the North to South Atlantic. We used those data to extrapolate from the larger data sets mentioned above into other areas of the North Atlantic. Chester et al. (1983) measured lead over a large range of concentrations on a cruise from England to the South Atlantic. Measurements were also made recently by Volkening et al. (1988) on a cruise from Germany to the South Atlantic. Both cruises verified strong coastal gradients for lead aerosols, as well as a strong latitudinal gradient across the western and eastern sides of the Azores high. These gradients, which are typically a factor ten in magnitude, are attributed to transport from North America and Europe, respectively.

Extrapolating Aerosol Concentrations

The natural radionuclide 210-Pb, which is the product of the radioactive decay of its parent 222-Rn, provides a way of estimating stable lead aerosol concentrations. This assumes some knowledge of the emission or deposition ratio of the radioactive and stable forms of lead in the area. From 1985-86, Hartman (1987) measured both stable Pb and 210-Pb in bulk deposition at the eastern Atlantic coast near Lewes, Delaware, USA and at Bermuda. The deposition ratio of Pb/210-Pb at both locations was about 400 ng Pb/dpm 210-Pb, with a seasonal variation of nearly fifty percent at the coast. This supports a value of 390 for this ratio reported by Settle et al. (1982) for the Sargasso Sea. Using the 210-Pb aerosol measurements of Turekian et al. (1983), one is able to predict stable aerosol lead values near the northeast US coast of 10-15 ng Pb m^{-3}. Likewise, using the 210-Pb values of Lambert et al. (1983) across the North Atlantic one would predict values of approximately 4 ng Pb m^{-3} through most of the North American plume to Europe. Similarly the relatively high values observed for lead in the eastern Atlantic off Africa are supported by correspondingly high 210-Pb values.

North and South Pacific Ocean

Most of the atmospheric lead concentrations over the remote Pacific Ocean were obtained by Patterson and Settle and have been summarized in a recent review paper (Patterson and Settle, 1987). Some additional data for lead concentrations in the Pacific Ocean region have been reported by Maring et al. (1989), Duce et al. (1983), Arimoto et al. (1987), and Patterson (1988) as part of the SEAREX Program. These and the other available data are summarized in Table 2. The SEAREX data were obtained in the four major surface level wind fields over the Pacific Ocean: collections were made at Enewetak Atoll (11°N, 162°E, North Pacific trade winds), American Samoa (14°S, 170°W, South Pacific trade winds), the North Island of New Zealand (34°S, 172°W, South Pacific westerlies), and during two cruises in the North Pacific westerlies (20-50°N, 155-170°W). The lack of data in other regions of the Pacific made it necessary for us to extrapolate from the available data to the other grid boxes over the North and South Pacific.

These extrapolations were made using three sources of information. First, we used the global distribution of 210-Pb in the atmosphere as compiled by Lambert et al. (1983). Second, trajectory information compiled by Whelpdale and Moody (1989) was used as a guideline for delineating the major transport pathways. Finally, our subjective judgement regarding sources, transport, and removal was used to predict concentrations when no other data were available.

South Atlantic and Indian Oceans

Very few data are available for these oceanic regions. We have considered here lead concentrations as measured during various cruises by Chester et al. (1983) and by Volkening et al. (1988). For the high latitudes of the southern hemisphere, we have taken as a background lead concentration a value of 10 pg m^{-3} based on the work of Wagenbach et al. (1988) at a coastal station in Antarctica. As mentioned previously, extrapolation to the other grid boxes was made on the basis of the global distribution of 210-Pb (Lambert et al. , 1983).

MINERAL AEROSOL

North Atlantic Ocean

We have based our calculations on either total mineral aerosol data or extrapolations from Al concentrations by assuming that this element represents on average close to 8% by weight of mineral aerosol. Most of the data base has been obtained during several cruises and long time-series measurements at Bermuda and Barbados (Duce et al., 1976; Prospero, 1979 and 1981; Prospero et al., 1989; Savoie, 1984). The highest mineral aerosol concentrations are observed in the tropical North Atlantic and reflect the long-range transport of Saharan dust, with a strong east-west decrease in near-surface concentrations. As is the case for lead, extrapolations to some grid boxes have been based on the consideration of 210-Pb concentration fields.

The North and South Pacific Ocean

Most of the mineral aerosol concentrations and fluxes for a number of sites, both short-term and long-term (several years), in the Pacific Ocean region have been obtained as part of the SEAREX Program or related projects. Many of these data are summarized in Prospero (1979, 1981), Uematsu et al. (1983, 1985) and Prospero et al. (1989). In addition, Tsunogai and Kondo (1982) and Tsunogai et al. (1985) have reported data from a network of aerosol sampling stations in Japan. The data for mineral dust concentrations are far more comprehensive than those for lead, but extrapolations were still needed, and were made using available 210-Pb concentration fields, the trajectory information compiled by Whelpdale and Moody (1989), and our subjective judgement regarding sources, transport, and removal.

South Atlantic and Indian Oceans

We have considered here the data obtained or compiled by Prospero (1979), Savoie (1984), Chester et al. (1983), and Volkening et al. (1988). Also, a background value of 10 ng m^{-3} for mineral aerosol concentrations south of 50°S has been adopted based on the data of Wagenbach et al. (1988) at a coastal Antarctic station. Extrapolations of the existing data were made in the same way as for the Pacific Ocean.

EXTRAPOLATIONS TO OTHER ELEMENTS

In order to estimate the inputs of some of the AEEs considered here (Cd, Cu, Ni, Zn, and As), we based our calculations on elemental ratios relative to Pb. These ratios were determined for aerosol and precipitation samples from a wide range of environments. We considered only recent data which we thought would be representative of global patterns. These elemental ratios, which are presented in Table 3, are rather constant among sites even though the actual concentrations span more than three orders of magnitude. In our calculations we converted the Pb fluxes into fluxes of other elements based on these elemental ratios. This approach was undertaken based on our belief that the uncertainties arising from this normalization procedure would be no larger than those that would result from extrapolating from the small existing data sets for these elements to the global ocean, and would avoid bias in some areas arising from few and perhaps unrepresentative data. The calculations given here represent gross fluxes to the ocean.

However, in the marine environment the gross deposition of materials such as trace metals is composed of a net input as well as a component associated with recycled sea spray. 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 metal-to-sodium ratios of near-surface seawater (Settle and Patterson, 1982; Buat-Menard, 1986; Jickells et al., 1984; Arimoto et al., 1985; Weisel et al., 1984). Therefore our calculated net deposition fluxes to the ocean may be upper limits or biased high, especially for very remote areas where the contribution of the recycled component is likely to be the greatest.

There have been some attempts to evaluate the importance of the recycled flux of trace metals. In most cases the approach is based on a consideration of metal-to-sodium ratios of the largest atmospheric particles, which should represent the recycled component in air (Arimoto et al., 1985). These ratios have been determined from the analysis of particles collected on the first stage of a cascade impactor. They agree reasonably well with direct measurements of sea-salt particles artificially produced and collected in the North Atlantic (Weisel et al., 1984). Although the atmospheric concentrations of trace metals associated with large sea-salt particles represent only a minor fraction of the total atmospheric concentration of these elements, this fraction is likely to account for a significant, if not major, part of the gross dry deposition flux. This is because sea-salt particles have much higher dry deposition velocities than materials attached to small particles. For example, using this approach for lead and other metals, the recycled component of dry deposition to a surrogate surface was shown to range from 12 to 100% for samples collected over the Pacific (Arimoto et al., 1985). For some samples, essentially all the gross measured dry flux could be attributed to sea-spray.

However, it is unlikely that our calculations of dry deposition for lead represent only a recycled flux. First, they are based on total atmospheric concentration data so that the contribution of the recycled component is only a small percentage of the total concentration. Second, the dry deposition velocity used here, 0.1 cm s^{-1}, is essentially that of submicrometer aerosol particles which contain most of the atmospheric concentration of lead and other pollutant elements. Thus, our calculation procedure is designed to minimize the recycled component, which probably represents < 50% of the calculated gross dry flux.

Recycled components for trace metals in rain collected over the North Atlantic and Pacific Ocean (Jickells et al., 1984; Arimoto et al., 1985; Settle and Patterson, 1982) represent between 10 and 50% of the gross wet deposition. It can therefore be assumed that the gross wet lead fluxes calculated here may be high by similar factors for remote oceanic areas.

Overall we expect that these calculations do not overestimate the net input of lead to the ocean by more than 50%. For other elements the uncertainty may be somewhat larger since the mean elemental ratios relative to lead in Table 3 may not give an accurate indication of the relative amount of each metal entering from non-marine sources. We believe, however, that these ratios are probably representative of the net input to the ocean within a factor of two.

As a check on our assumptions we have used an alternative approach based on the ratio of the global anthropogenic and natural atmospheric sources of a trace metal to the global anthropogenic and natural sources of lead. Estimates of these global emission fluxes are presented in Table 4, and element-to-lead ratios calculated from the global emission data in Table 4 are given at the bottom of Table 3. Despite large uncertainties (as indicated by the ranges of values shown in Table 4), the ratios calculated using the two approaches generally agree to within a factor of 2-5. Both approaches are used to calculate the global atmospheric fluxes to the ocean of these metals.

To estimate the flux of elements predominantly associated with mineral aerosol particles (Al, Fe, Si, and P) we have used upper continental crustal abundances (Taylor and McLennan, 1985) so that the mineral aerosol contains 8.04% Al, 3.5% Fe, 30.8% Si, and 1050 ppm P.

Table 3. Mean Elemental Ratios by Weight for Aerosols (A) and Precipitation (P) from Various Locations

Location	Cd/Pb	Cu/Pb	Ni/Pb	Zn/Pb	As/Pb	Sn/Pb	Ref.
Faroe Island (A)	0.08	0.17		5.4		0.08	(1)
Ireland (P)	0.05	1.6	0.7	4.6			(2)
Bermuda (A)		1.6		3.0			(3)
Bermuda (P)	0.08	0.31	0.24	2.0			(4)
North Atlantic (P)		1.3		5.0			(5)
Lewes, Delaware(P)	0.06	0.22	0.26	2.1	0.03		(6)
Southern North Sea (A)	0.03	0.14	0.07	1.1	0.05	0.03	(7)
Baltic Sea (A)	0.015	0.12		0.9	0.05		(8)
Wet Enewetak (A)	0.03	0.55		1.6			(9)
Dry Enewetak (A)	0.03	0.15		1.3			(9)
Samoa (A)		0.81		4.0			(10)
Hawaii (A)	0.03						(11)
Mediterranean (A)	0.045	0.07		0.85	0.04		(12)
Mean Value	0.045	0.59	0.32	2.6	0.04	0.05	
Range	0.015 - 0.08	0.07 - 1.6	0.07 - 0.7	0.85 - 5.4	0.03 - 0.05	0.03 - 0.08	
From Global Atmospheric Emissions -- Table 4	0.026	0.18	0.25	0.51	0.09		
Range*	0.011 - 0.036	0.08 - .26	0.09 - 0.36	0.25-0.70	0.04 - 0.12		

(1) Kemp (1984); (2) Church (unpublished); (3) Wolff et al. (1986); (4) Jickells et al. (1987); (5) Church et al. (in press); (6) Church et al. (1984), Scudlark and Church (1988); (7) from Table 11; (8) from Table 14; (9) Duce et al. (1983); (10) Arimoto et al. (1987); (11) Patterson (1988); (12) from Table 15.

* Calculated from paired minimum and paired maximum values in Table 4.

Table 4. Global Atmospheric Emissions of Trace Metals (10^9 g yr^{-1}); Median value in bold type and range

	Global Anthropogenic Emissions (1)	Global Natural Emissions (2)
Pb	289 - **332** - 376	1 - **12** - 23
Cd	3.1 - **7.6** - 12.0	0.15 - **1.3** - 2.6
Cu	20 - **35** - 51	2.3 - **28** - 54
Ni	24 - **56** - 87	3 - **30** - 57
Zn	70 - **132** - 194	4 - **45** - 86
As	12 - **18** - 26	0.9 - **12** - 23

(1) Nriagu and Pacyna, 1988
(2) Nriagu, 1989

SOLUBILITY OF TRACE ELEMENTS IN SEAWATER

The solubility in seawater of trace elements present on atmospheric aerosols is important in determining their impact on oceanic biogeochemical cycles. The solubility of an element reflects its chemical partitioning in the aerosol and the environmental history of the particles. Crecelius (1980) and Chester et al. (1986) have demonstrated that the chemical partitioning of several elements is different in aerosols dominated by mineral dust or by anthropogenic components. Lindberg and Harriss (1983) have shown a particle-size dependence of solubility which is probably caused by the different sources of different sizes of aerosols. Several authors (e.g., Moore et al., 1984; Maring and Duce, 1987; Statham and Chester, 1988) have demonstrated that pH significantly affects the leaching of aerosols. The possibility of oxidation or uptake of acid gases on aerosol surfaces (Andreae et al., 1986; Berresheim and Jaeschke, 1986; Graedel et al., 1985) means that atmospheric particles may be subject to low pH regimes during atmospheric transport that may affect their subsequent dissolution.

Although it is not possible to give unambiguous values of solubilities, the ranges observed are presented in Table 5. These data demonstrate that elements predominantly associated with mineral aerosol (e.g., Al, Si, and Fe) are less soluble than those associated with accumulation mode aerosol (e.g., Zn, Cu, Pb, and As). For the purposes of the present calculations, it is assumed that 5% of the aluminum, 10% of the Fe, 5% of the Si, 33% of the P, and 90% of the Pb that enters the ocean from the atmosphere is soluble.

Table 5. Solubility in Seawater of Elements Attached to Aerosol Particles

Element	Solubility (%)	Reference
Al	0.6 - 10	1, 2
Si	5 - 10	3
P	21 - 51	4
Fe	<1 - 50	2, 5, 6, 9
Mn	25 - 49	2, 6, 7
V	31 - 85	2, 6, 8
As	48 - 78	5, 6
Cd	81 - 84	2
Cu	15 - 86	2, 6, 10
Ni	29 - 47	2
Pb	13 - 90	2, 11
Zn	24 - 76	2, 5

1- Maring and Duce, 1987; 2- Hodge, et al., 1978; 3- Wollast and Chou, 1986; 4- Graham and Duce, 1982; 5- Crecelius, 1980; 6- Moore, et al., 1984; 7- Statham and Chester, 1988; 8- Walsh and Duce, 1976; 9- Zhuang and Duce, 1988; 10- Maring and Duce, 1989; 11- Maring, 1985.

Very few data are available on the partitioning of trace elements in rainwater between soluble and insoluble forms. This is an important area for future research since most of the flux of the elements is associated with wet deposition. It seems that the solubility of the elements is highly variable depending on the pH of rainwater. For example, Losno et al. (1988) found that in Mediterranean rainwater the solubility of zinc ranged between 15 and 99% of the total zinc with the higher percentage observed for low pH (4) and the lower percentage for high pH (7). This solubility-pH relationship can be explained by an adsorption-desorption equilibrium. There is some evidence that a similar relationship exists for Pb, Cu, and Cd (Elbaz-Poulichet, 1988).

Prospero et al. (1987) found that the dissolved Al concentration in rainwater containing Saharan dust was highly variable; however, the mean solubility of 5% was similar to that measured for the seawater solubility of Al in mineral aerosols (Maring and Duce, 1987). Dissolution kinetics of Al and Si from feldspar minerals have also been investigated in the laboratory for a wide range of pH. Such kinetics are often be described in terms of surface-complex reactions (Wollast and Chou, 1986; Webb and Walther, 1989).

RESULTS

The global atmospheric fluxes for lead and for mineral aerosol as calculated from the concentration fields, dry deposition velocities, precipitation scavenging ratios and precipitation amounts for each grid are given in Tables 6 and 7 for each ocean basin. Global maps of the atmospheric fluxes of lead and mineral aerosol are presented in Figures 5 and 6.

Table 6. Atmospheric Flux of Lead to the Ocean

Ocean	Flux (10^{-3} g $m^{-2}yr^{-1}$) Wet	Dry	Total	Deposition (10^9 g yr^{-1}) Wet	Dry	Total
North Pacific	0.17	0.03	0.20	15.5	2.4	17.9
South Pacific	0.02	0.003	0.02	1.9	0.3	2.2
North Atlantic	0.85	0.18	1.03	46.9	9.6	56.5
South Atlantic	0.06	0.02	0.08	3.1	1.1	4.2
North Indian	0.27	0.06	0.33	3.9	0.9	4.8
South Indian	0.04	0.01	0.05	2.1	0.3	2.4
Global Total	0.20	0.04	0.24	73.4	14.6	88.0

Table 7. Atmospheric Flux of Mineral Aerosol to the Ocean

Ocean	Flux (g $m^{-2}yr^{-1}$) Wet	Dry	Total	Deposition (10^{12} g yr^{-1}) Wet	Dry	Total
North Pacific	3.76	1.52	5.28	337	136	473
South Pacific	0.23	0.13	0.35	25	14	39
North Atlantic	1.11	2.91	4.03	61	160	221
South Atlantic	0.27	0.20	0.47	14	10	24
North Indian	5.07	2.01	7.08	73	29	102
South Indian	0.60	0.22	0.82	32	12	44
Global Total	1.45	0.97	2.42	542	361	903

The range of deposition rates for the other AEEs presented in Table 8 represents the results from the calculations using the two approaches described earlier. This represents the total deposition of these metals to the ocean since it does not take into consideration the fraction of the metals that is soluble in the water. Note that for some elements, e.g., Cu and Zn, the flux range is roughly a factor of 4 to 5. These large differences may result from significant marine recycling and/or large errors in the estimation of the global anthropogenic or natural atmospheric emissions for these metals.

The global atmospheric depositions of Al, Fe, Si, and P to the ocean, as calculated from the mineral aerosol input to the ocean in Table 7 and the percent crustal abundances described above, is given in Table 9.

Table 8. Atmospheric Deposition to the Ocean of Primarily Anthropogenic Trace Metals (10^9 g yr^{-1})

The first number of each pair is obtained using element to lead ratios obtained from global atmospheric emissions; the second from such ratios measured in aerosol and rain samples (Table 3).

	Cd	Cu	Ni	Zn	As
North Pacific	0.47-0.81	3.2-10.6	4.5- 5.7	9.1- 46.5	1.6-0.7
South Pacific	0.06-0.10	0.4- 1.3	0.6- 0.7	1.1- 5.7	0.2-0.09
North Atlantic	1.47-2.54	10.2-33.3	14.1-18.1	28.6-147	5.1-2.3
South Atlantic	0.11-0.19	0.8- 2.5	1.1- 1.3	2.1- 10.9	0.4-0.17
North Indian	0.12-0.22	0.9- 2.8	1.2- 1.5	2.4- 12.5	0.4-0.2
South Indian	0.06-0.11	0.4- 1.4	0.6- 0.8	1.2- 6.2	0.2-0.1
Global Total	2.3 -4.0	16 - 52	22 - 28	44 -228	7.9-3.6

Table 9. Atmospheric Deposition to the Ocean of Trace Elements Derived from Mineral Aerosol

	Al (10^{12} g yr^{-1})	Fe (10^{12} g yr^{-1})	Si (10^{12} g yr^{-1})	P (10^9 g yr^{-1})
North Pacific	38.0	16.6	145.7	497
South Pacific	3.1	1.4	12.0	41
North Atlantic	17.8	7.7	68.1	232
South Atlantic	1.9	0.8	7.4	25
North Indian	8.2	3.6	31.4	107
South Indian	3.5	1.5	13.6	46
Global Total	72.5	31.6	278.2	948

In Tables 6-9 the depositions given are estimates of the amounts of material arriving at the sea surface. For some purposes, e.g., impact of such inputs on seawater biology, it may be more useful to know the proportion of the input which readily dissolves in the water. Such values may be obtained by multiplying the fluxes in Tables 6, 8, and 9 by the solubility factors discussed earlier (Table 5); our best estimates of the means of the solubility are given in Table 11. In order to convert from deposition to flux, the fluxes should be divided by the basin areas given on page 23.

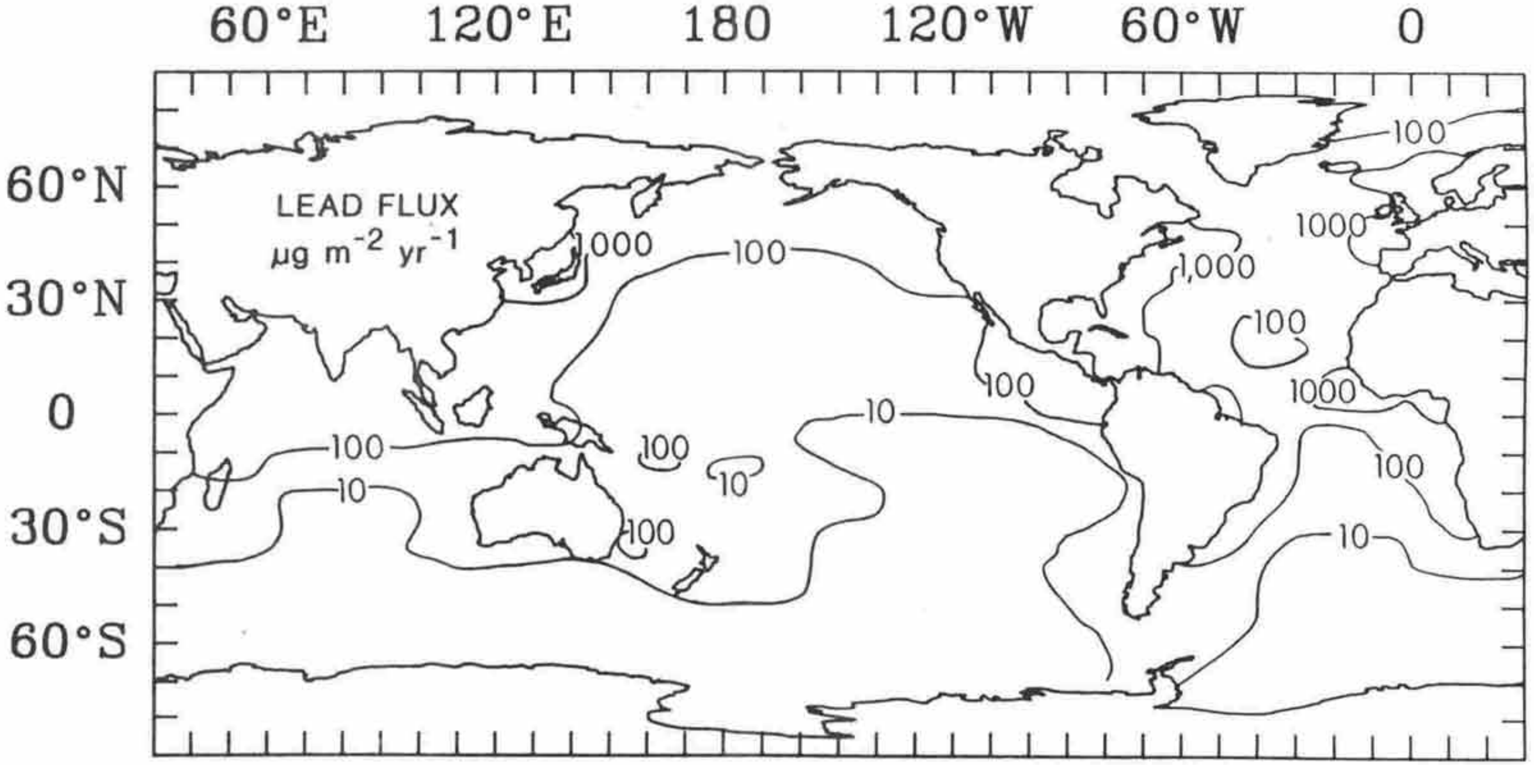

Figure 5. Global Fluxes of Lead to the Oceans in μg Pb m^{-2} yr^{-1}.

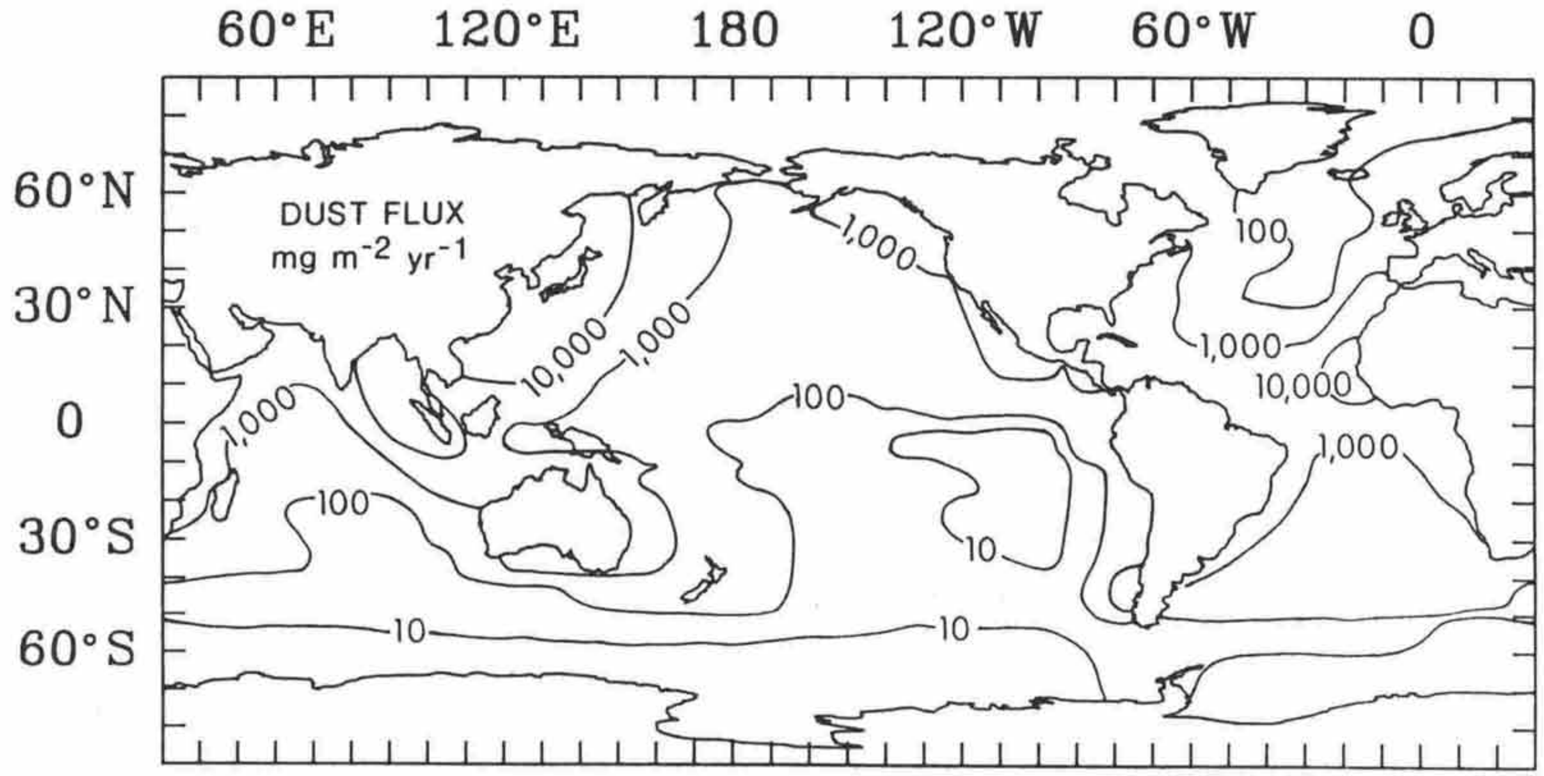

Figure 6. Global Fluxes of Mineral Aerosol to the Oceans in mg m^{-2} yr^{-1}.

Mercury and Tin

For both elements recent global budgets have been produced and we report these without modification.

Mercury

The recent compilations of Gill and Fitzgerald (1987) give inputs of mercury to world oceans as shown in Table 10. This estimate of deposition to the ocean appears consistent with the lower range of estimates by Lindquist (1985) of global deposition rates (i.e., including deposition to land) of 2-17 x 10^9 g yr^{-1}.

Table 10. Atmospheric Hg Deposition to Ocean Basins (10^9 g yr^{-1})

Region	North Atlantic	South Atlantic	North Pacific	South Pacific	North Indian	South Indian	Total
Hg deposition	0.42	0.09	0.58	0.33	0.07	0.2	1.7

Tin

Byrd and Andreae (1986) report results from the North Atlantic and South Pacific which they scale to estimate inputs to the Northern Hemisphere oceans of 0.3 x 10^9 g yr^{-1} and to Southern Hemisphere oceans of 0.023 x 10^9 g yr^{-1}. This leads to an estimated input to the world oceans of 0.32 x 10^9 g yr^{-1}.

COMPARISON BETWEEN GLOBAL ATMOSPHERIC AND RIVERINE INPUTS OF TRACE ELEMENTS

Global atmospheric and riverine inputs of trace elements in the dissolved and the particulate forms are presented in Table 11. It appears that rivers are generally the major source of particulate trace elements for the ocean, with the exception of phosphorus. However, it must be stressed that particulate riverine inputs are likely to be deposited in the ocean close to the source regions, whereas inputs via the atmosphere will certainly be transported to remote oceanic areas. For example, in the case of iron, if one assumes that the particulate input is essentially refractory, the atmospheric input is likely to be the major contributor to the non-biogenic sedimentation rate of iron in remote areas, as has been shown for the North Pacific (Arimoto et al., 1985).

Of more immediate concern for the "health" of the oceans is the soluble input which can have a direct impact on marine biological systems. Some elements (such as iron and phosphorus) are essential nutrients, and some pollutant elements enter the trophic food chain via active or passive uptake processes. From Table 11 it can be seen that atmospheric inputs of Fe and P are similar to those from rivers. Since most of these inputs are natural, the atmospheric source must be taken into account for an accurate understanding of the biogeochemical cycling of these elements in the ocean, especially in open ocean areas. As demonstrated by Duce (1986), atmospheric deposition plays a major role in the regulation of dissolved iron concentrations in the surface waters of oligotrophic marine regions, such as the Sargasso Sea and the tropical North Pacific.

For pollutant elements, the global atmospheric and riverine inputs are comparable for dissolved Cu, Ni, and As; for Zn and Cd, atmospheric inputs appear to dominate. It is likely that riverine inputs dominate in pericontinental areas, especially those close to the mouths of large rivers, whereas atmospheric inputs represent the dominant contribution in open ocean areas. For lead the data presented in Table 11 confirm that, at the present time, the major source of pollution lead to the coastal and open oceans is via atmospheric deposition. Currently about 75% of the atmospheric deposition of pollution Pb is due to automotive sources. Since lead is being phased out of use in gasoline in North America and Europe, atmospheric inputs of lead to the ocean may decrease by a factor of 3 within the next few decades. Nevertheless, even if this pollution source disappears, the deposition of Pb from the atmosphere to the ocean due to other pollution sources (Nriagu and Pacyna, 1988) will still dominate riverine inputs.

Table 11. Global Deposition of Metals to the Ocean (10^9 g yr^{-1})

	Pb	Cd	Cu	Ni	Zn	As	Fe	P
				Atmospheric Input#				
Assumed % Solubility##	90	83	86	38	76	63	10	33
Dissolved	79	1.9-3.3	14-45	8-11	33-173	2.3-5.0	3.2x10^3	315
Particulate	9	0.4-0.7	2- 7	14-17	11- 55	1.3-2.9	28 x10^3	630
				Riverine Input*				
Dissolved	2	0.3	10	11	6	10	1.1x10^3	300**
Particulate	1600	15	1500	1400	3900	80	110 x10^3	

\# Calculated using Tables 5, 6, 8 and 9

\#\# In selecting solubility factors results from experiments in which open-ocean aerosols were used have been preferred.

* GESAMP (1987)

** Total P input to marine sediment

REGIONAL SEAS

ATMOSPHERIC INPUT OF TRACE ELEMENTS TO THE NORTH SEA

A review of available data revealed several useful aerosol and precipitation data sets. These involved samples that were carefully collected and analyzed and that covered a relatively long time period. This latter criterion is necessary because all available data sets reveal temporal variability in concentrations of at least one order of magnitude. This variability can be related to the direction of air mass transport and to precipitation patterns. The aerosol results are presented in Tables 12A and B and are separated into stations around the Southern Bight of the North Sea and from more northerly areas. Despite variations in collection procedures for samples collected over a 16 year period, the agreement between the results is encouraging, with two caveats:

i) There is evidence of a decline in lead concentrations in this area presumably due to reduced emissions (e.g., Pattenden and Branson, 1987). The average values selected here have therefore been adjusted by excluding the results for lead in the southern North Sea from the 1970s and by reducing concentrations in the northern region by 50%.

ii) Results from the West Hinder Lightship located off the Belgian coast are higher than those for other stations, probably because this site is close to sources (Dedeuwaerder, 1988). The concentration gradient cannot be well defined, so all the southern North Sea Bight stations have been averaged and the northern stations treated separately. The southern North Sea is taken to be 30% of the total North Sea (area 5.3 x 10^5 km^2) as defined by Cambray et al. (1979).

Trace metal concentrations in precipitation collected from sites around the North Sea are shown in Table 13. They show much less consistency, undoubtedly because of the greater sampling and analytical problems associated with such measurements. These results have therefore not been used directly to calculate deposition fluxes but only for the purpose of comparison of measured and calculated rain composition.

In order to calculate fluxes, scavenging ratios of 200-1000 have been applied to elements believed to be associated with accumulation mode size particles (Cd, Cu, Ni, Zn, Mn, Pb, V, and As) and 500-2000 for elements associated with larger particles (Al, Fe). These ratios are higher than those applied to the open ocean regions because results from the Baltic (Schneider, 1988), southern North Sea (Dedeuwaerder, 1988), and Mediterranean (Bergametti, 1987) suggest that such high ratios are more appropriate for coastal seas. The values of Dedeuwaerder (1988) are higher than those used here, but this may reflect proximity to sources of the sampling site used in that study. Precipitation amounts over the North Sea are uncertain, but Van Aalst et al. (1982) suggests a value of 68 cm yr^{-1}. Estimates of dry deposition using deposition velocities of 0.1 cm s^{-1} for As, Cd, Cu, Ni, Pb, and Zn and 1.0 cm s^{-1} for Al, Fe, Mn, and V suggest dry deposition is <10% of the total deposition, and hence this process has not been taken into account. Comparison of observed rainwater concentrations in Table 13 with rainwater concentrations calculated from aerosol concentrations in Tables 12A and B using the above scavenging ratios indicates quite good agreement.

The fluxes to the North Sea reported in Table 14 are similar to those produced previously that are based on measured concentrations, but somewhat larger than those predicted from previous model calculations (Krell and Rockner, 1988; Petersen et al., 1988). This difference arises because of the assumption in earlier models of rapid decay of aerosol concentrations away from the coast. There is no experimental verification of such gradients currently available, and this represents another major area of uncertainty. As shown in Table 14, the fluxes calculated here for the North Sea represent 0.7-15% of the estimated European emissions of these trace elements (Pacyna et al., 1984).

Table 12A. Aerosol Concentration Data - Southern North Sea (ng m^{-3})

	1972-73 (1)	1980-85 (2)	1984-85 (3)	1987-88 (4)	Mean
Al	155-240	390	-	-	300
Cd	-	4	0.7	1.1	2
Cu	-	17	3	-	10
Fe	290-330	560	192	216	320
Mn	14-22	28	9	10	16
Ni	5-7	-	5	3	5
Pb	96-130	150	39	34	83
V	9-11	-	7	-	9
Zn	75-120	150	41	41	80
As	4-5	-	3	-	4
Sn	-	-	2	-	2

(1) Cambray et al. (1975); (2) Dedeuwaerder (1988); (3) Stoessel (1987); (4) Yaaqub (1989).

Table 12B. Aerosol Concentration Data - Northern North Sea (ng m^{-3})

	(1)	(2)	Mean
Al	44	71	60
Cd	-	0.3	0.3
Cu	-	7	7
Fe	60	-	60
Mn	4	5.4	5
Ni	3	-	3
Pb	27	19	23
V	1.8	3.1	2.5
Zn	24	-	24
As	1.0	1.0	1.0

(1) Cambray et al. (1975); (2) Pacyna et al. (1984)

Table 13. Trace Elements in Rainwater Over the North Sea (μg l^{-1})

	Southern North Sea			Northern North Sea		
	(1)	(2)	(3)	(4)	(5)	(6)
Al	210-530	340	-	100-1700		53
Cd		9.5	0.5		0.7	0.27
Cu	12-24	77	2.5	<10-41	2.3	
Fe	220-600	430	26	105-990	88	
Mn	11-30	45	6.3	<6-20	3.8	7.4
Ni	<6-6.6		1.8	<6-12		
Pb	<18-131	29	10		4.0	11
V	5.8-7.4		2.5	2-11		1.8
Zn	85-220	490	26	25-63	13	15
As	<4		1.0	<1-4		0.8
Sn			0.6			

(1) Total wet, 1974-1976 (Cambray, et al., 1979); (2) wet only, 1980-1985 (Dedeuwaerder, 1988); (3) wet only,1984-1985 (Stoessel, 1987); (4) total wet 1974-1976 (Cambray et al., 1979); (5) wet only, 1986-1987 (Balls, 1989); (6) weekly bulk (Pacyna et al., 1984).

Table 14 . Total Atmospheric Deposition and Fluxes of Trace Elements to the North Sea

	Calculated Total Flux mg m^{-2} yr^{-1}	Calculated Total Deposition 10^9 g yr^{-1}	Estimated European Anthropogenic Emissions* 10^9 g yr^{-1}	% of European Emissions Entering the North Sea
Al	38 - 150	20 - 81		
Cd	0.1 - 0.5	0.05 - 0.25	2.7	2 - 9
Cu	1 - 4.4	0.5 - 2.3	15.5	3 - 15
Fe	38 - 150	20 - 81		
Mn	1 - 5	0.5 - 2.7	17.6	3 - 15
Ni	0.4 - 2.1	0.23 - 1.1	16.0	1 - 7
Pb	4 - 23	2.3 - 12	123	2 - 10
V	0.4 - 2.1	0.23 - 1.1	34.5	0.7 - 3
Zn	5 - 23	2.7 - 12	80	3 - 15
As	0.2 - 1.1	0.13 - 0.58	6.5	2 - 9

* Pacyna et al. (1984).

ATMOSPHERIC INPUT OF TRACE ELEMENTS TO THE BALTIC SEA

For the Baltic Sea area, data for atmospheric trace metals are available from a monitoring network established by the Baltic Marine Environment Protection Commission (HELCOM). At five coastal stations around the Baltic Sea the concentrations of Pb, Cd, Zn, and Cu in bulk deposition since 1984 have been determined. These data have been used to estimate the mean fluxes and the total input of these elements to five different sub-basins (Schneider, 1988). Mercury concentrations in precipitation are reported from three sites along the Swedish and Danish coastline by Iverfeldt and Rodhe (1988). For the elements As, V, Cr, Mn, and Fe atmospheric concentrations have been determined in the southern part of the Baltic Sea (Oblad and Selin, 1986; Martinsson et al., 1984; Kemp, 1984; Schneider, 1987). To convert these data to dry deposition fluxes and concentrations in precipitation we used the parameterizations given earlier. Those elements which are significantly affected by crustal material are corrected for this contribution using Ti concentrations as a tracer for crustal material and the relative abundance of elements in the earth's crust (Mason, 1966).

For the determination of the wet deposition fluxes, precipitation data for the different sub-basins of the Baltic according to Rodhe et al. (1980) were used. For most of the elements, no information was available to document a possible deposition gradient between the coastline and the open sea. Hence, the deposition measured at the various coastal sites was considered to be representative for the corresponding sub-basins. However, in the case of Pb and Cd, model simulations of the long-range transport over Europe (EMEP Model, Petersen et al., 1988) have been performed. The resulting gradients for atmospheric Pb and Cd over the sub-basins were used to extrapolate the measured fluxes at the coastal sites to each of these sub-basins. The fluxes for As, V, Cr, Mn, and Fe could be determined only for a relatively small sub-basin. In order to relate values to the whole Baltic the corresponding relationship for Pb, Cd, Zn and Cu was calculated and applied to As, V, Cr, Mn, and Fe. In Table 15 the mean atmospheric fluxes and the annual total deposition to the Baltic are summarized. The calculation of the total deposition to the Baltic Sea is based on an area of 415,000 km^2.

Table 15. Total Atmospheric Deposition and Fluxes of Trace Elements to the Baltic Sea

	Total Flux mg m^{-2} yr^{-1}	Total Deposition 10^9 g yr^{-1}
Pb	2.4	1.0
Cd	0.14	0.06
Zn	11	4.7
Cu	2.9	1.2
As	0.46	0.19
V	1.1	0.44
Cr	0.53	0.22
Mn	2.4	1.0
Fe	87	36
Hg*	0.014	0.006

* Wet flux only.

Except for mercury, the data in Table 15 refer to the sum of wet and dry deposition. The contribution of dry deposition is estimated to range between about 5% and 30%. This wide range is due to the uncertain estimate of the dry deposition velocity for anthropogenic trace metals.

The uncertainties for the wet deposition are within a factor of 2 when the fluxes were calculated on the basis of atmospheric concentrations (As, V, Cr, Mn, and Fe). For the elements determined in deposition samples a range of +/- 50% is estimated.

ATMOSPHERIC INPUTS OF TRACE ELEMENTS INTO THE MEDITERRANEAN SEA

Most of the data presently available for the Mediterranean Sea are limited to the western area. Aerosol concentration data have been obtained from various oceanographic cruises between 1980 and 1983. These data suggest that the atmospheric transport of trace elements to the Mediterranean atmosphere from natural and anthropogenic land-based sources plays a significant role in the geochemistry of Mediterranean seawater (Arnold et al., 1982; GESAMP, 1985; Dulac et al., 1987; Chester et al., 1981, 1984). However, a quantitative assessment of such an influence is difficult because of the strong variability of atmospheric elemental concentrations. Concentration changes of two orders of magnitude have been shown to occur on a daily time scale, and these are due to changes in continental source strengths, airflow and precipitation patterns. Continuous sampling strategies have recently allowed more representative estimates to be made at two sites: one in south Corsica (total deposition flux of mineral aerosol; Loye-Pillot et al., 1986;) and one on the coast of northwestern Corsica, where continuous aerosol and total deposition flux measurements began in 1985 (Bergametti et al., 1989 and Bergametti, 1987). Tables 16 and 17 provide the best estimates of elemental concentrations and fluxes for that site as well as mean trace element concentrations obtained during various cruises. Over the western Mediterranean Sea, concentrations exhibit a seasonal pattern inversely related to the frequency and amount of rainfall, such that the highest concentrations are observed between May and October. Elements associated with mineral aerosol particles exhibit sporadic but intense concentration peaks that are superimposed on this general pattern and are associated with transport of mineral matter from Africa. Most of the input of pollutant elements, such as lead, are derived from sources to the north and west of the area.

Table 16. Mean Atmospheric Concentrations over the Western Mediterranean Sea

	Mean from Various Cruises (ng m^{-3})*	Capo Cavallo, Corsica (ng m^{-3})#
Al	324	350
Cd	1.9	0.86
Cu	2.5	3.2
Fe	182	261
Mn	8	7.3
P	-	13.7
Pb	39	22
Si	-	891
V	10	-
Zn	26	26
As	1.3	-

* Various cruises between 1980 and 1983 (Arnold, 1985; Dulac, 1986; Dulac et al., 1987).

\# Capo Cavallo, northwestern Corsica; daily aerosol sampling from March 1985 to April 1986 (Bergametti, 1987; Bergametti et al., 1989).

The temporal variability of deposition fluxes is not linearly related to that of atmospheric concentrations (Bergametti, 1987). Indeed, other factors such as precipitation frequency and, to a lesser extent, cloud types must be considered. For example, scavenging ratios are much higher in summer (during convective storms) than in winter (stratiform cloud systems), and they are on the average much higher than over the open ocean (range from 3000 to 5000). Because of the relatively low precipitation and the proximity of source regions, it is likely that dry deposition fluxes are more important than over the open ocean. Indeed, it is estimated that dry deposition represents 30-50% of the total deposition flux for the region.

The data presented in Table 17 suggest that total deposition fluxes of pollutant elements, per unit area, are of the same order of magnitude as those observed for the North Sea and significantly higher than over the North Atlantic. The total deposition obtained for the northwestern Corsican station have been extrapolated to the northwestern Mediterranean basin (5 x 10^5 km^2). Depending on the element, they represent between 4 and 20% of the total European anthropogenic emissions.

This extrapolation provides only an order of magnitude estimate of the elemental deposition for the basin. Indeed, although air flow climatology is not particularly variable within the area, precipitation patterns certainly affect the spatial variability of the deposited flux. It is likely that the atmospheric pollutant flux data for northwestern Corsica represent an overestimate for areas south of Corsica and an underestimate for areas to the north.

We have not attempted to extrapolate these data to the entire Mediterranean basin. The Adriatic represents a very special situation with unique climatology. It is also likely that over the eastern Mediterranean mineral aerosol fluxes are at least five times higher than over the western Mediterranean, whilst pollutant element fluxes are lower.

Table 17. Total Atmospheric Deposition Fluxes of Trace Elements to the North Western Mediterranean (Bergametti, 1987)

	Total Flux ($mg\ m^{-2}\ yr^{-1}$)	Total Deposition to the NW Mediterranean ($10^9\ g\ yr^{-1}$)	% of European Man-Made Emissions Entering the NW Mediterranean
Al	970	435	-
Cd*	1	0.5	19
Cu*	4.2	2.1	11
Fe**	720	360	-
Mn	22	11	-
P	32	16	-
Pb	29	14.5	12
Si	3070	1535	-
V*	25	12.5	4
Zn*	34	17	21
As*	1	0.5	7

* derived from aerosol concentration data and scaled to measured Pb flux;
** same approach but scaled to Al.

THE ATMOSPHERIC INPUT OF NITROGEN SPECIES TO THE WORLD OCEAN

INTRODUCTION

This section focuses on those nitrogen species that can be utilized as nutrients. These fall into two classes. Oxidized nitrogen species: aerosol nitrate and gas-phase oxides of nitrogen (NO, NO_2, HNO_3 and related species). Reduced nitrogen species: aerosol ammonium and gaseous NH_3 (and related organic nitrogen species).

There are a number of quantitative assessments of the global nitrogen cycle (Soderlund and Svensson, 1976; Anderson, 1983; Stedman and Shetter, 1983; Logan, 1983; Galloway, 1985; NAS, 1984). Of these, the most detailed analysis is that by Logan (1983) who considers both the sources for the principal nitrogen species and their eventual sinks. Logan obtains for the global source a range of 25-99 x 10^{12} g N yr^{-1} with a best estimate of about 50 x 10^{12} g N yr^{-1}. The largest single source of NO_x is fossil fuel combustion, 21 x 10^{12} g N yr^{-1}. A recent exhaustive evaluation of global fossil-fuel combustion sources (Hameed and Dignon, 1988) yields a similar value of 22 x 10^{12} g for 1980. Of all the sources, the anthropogenic one is probably the most accurately known.

The second largest source in Logan's assessment is biomass burning, 12 x 10^{12} g N yr^{-1}, although the range of uncertainty is rather large (4-24 x 10^{12} g N yr^{-1}). Biomass burning can be considered as both an anthropogenic and a natural activity, but the anthropogenic portion is considered to be dominant (Seiler and Crutzen, 1980; Logan et al., 1981).

The major natural atmospheric/marine sources of oxidized nitrogen are thought to be NO production by lightning and downmixing of NO from the stratosphere where it is produced by the photolysis of N_2O. The only established oceanic source is through the photolysis of nitrite in surface waters; however this source is generally considered to be minor (Zafiriou and McFarland, 1981). Another potential biological source is the oxidation of marine-derived organic nitrogen compounds, e.g., amino acids and proteinaceous material, which are highly enriched in marine aerosols and rain (Mopper and Zika, 1987). Duce (1983) estimated that the concentration of organic nitrogen is about three times greater than that of nitrate nitrogen in marine aerosols over pristine oceanic areas. How much, if any, of this organic nitrogen is actually oxidized to nitrate in the atmosphere remains to be determined. Another major source of NO_x is microbial activity in soils, estimated to be 8 x 10^{12} g yr^{-1} but with considerable uncertainty, 4-16 x 10^{12} g yr^{-1} (Logan, 1983).

Thus, of the total oxidized nitrogen budget, over 80% is derived from sources located on land. Consequently, the distribution and deposition of oxidized nitrogen over the oceans will be heavily influenced by the distribution of land masses in general and anthropogenic sources in particular. Moreover, an overwhelmingly large percentage of the anthropogenic sources are located in the Northern Hemisphere. Of the 22 x 10^{12} g N emitted from combustion sources to the global atmosphere, less than 2 x 10^{12} g is emitted in the southern hemisphere (Hameed and Dignon, 1988). Consequently, we might expect that the impact on ocean deposition would be greatest in the Northern Hemisphere.

OXIDIZED NITROGEN SPECIES

NITRATE AEROSOL

By far the largest body of data for the oxidized species is that for nitrate aerosol, which is the oxidative end member of the atmospheric nitrogen cycle. For this reason, we begin our discussion with this species. We follow with the discussion of the more limited data for the major precursor species.

Concentration Data

The nitrate aerosol concentration data are mainly from two sources. The first consists of a data set of about 1000 aerosol samples gathered during the Global Weather Experiment in 1979 (Savoie, 1984). The samples were collected aboard ships in the Atlantic, Pacific and Indian Oceans and also at a number of island stations in the North Atlantic. The data are summarized in Figure 7. In this figure Savoie also incorporates data from the literature up to the early 1980s. The 25 regions in Figure 7 are defined on the basis of concentration trends in the data sets and on assumptions about the controlling transport conditions. Savoie made no attempt to interpolate between the measured means for the various regions.

The second major data set is that obtained in the Pacific in the SEAREX network of aerosol sampling stations (Prospero et al., 1985; Savoie et al., 1989a,b). The network extends from Shemya in the Aleutians (52°44'N, 174°06'E) to Norfolk Island (29°05'S, 167°59'E). The network began operations in the North Pacific in 1981 and in the South Pacific in 1983. This set contains data from the analysis of a total of 2058 samples collected at 13 stations.

In assessing the data for the flux computations, we have interpolated between the coastal regions (where concentrations are usually relatively high) and the central ocean regions by assuming a half-decrease distance of 1000 km. This half-distance value is based on the concentration gradients observed for NO and NO_2 off the east coast of the United States, about 500 km (see below). Since the aerosol nitrate concentration will depend on both the nitrate originally present in the air parcel and that produced during transit from NO and NO_2, we assume a half decrease distance that is twice that of the precursors with the understanding that this is a crude approximation. The half decrease distance of 1000 km is equal to that observed for 210-Pb, a submicrometer aerosol species that is also generated during transit (from 222-Rn, half life 3.8 days). However, it should be understood that in the vast majority of cases, there are very little or no data in most ocean regions, especially along the coasts. Consequently, many of these values are little more than rough estimates based on reasonable assumptions. Nonetheless it is clear that remote ocean areas appear to be characterized by a rather uniform "background" nitrate concentration of about 0.025 $\mu g\ N\ m^{-3}$ (Savoie et al., 1989a). It is also apparent that the concentrations over the northern oceans are generally considerably higher than this background value (Prospero and Savoie, 1989).

Deposition Velocity

Nitrate aerosol over the oceans has a mass median diameter of several micrometers, the nitrate mass being distributed as the surface area of sea salt aerosol (Savoie and Prospero, 1982). This distribution appears to result from the sorption or reaction of oxidized nitrogen species with sea salt aerosol. In the absence of measured deposition rates, and as a consequence of the size distribution, we use a deposition velocity value for large particles, 1.0 cm sec^{-1}, as recommended earlier. This value is larger than that used in past studies. Logan (1983) and Liu et al. (1983) use 0.3 cm s^{-1} based on the nitrate aerosol size measurements of Savoie and Prospero (1982). We chose the higher value based on studies of nitrate deposition made by Pszenny (1987) who shows higher dry deposition fluxes which he attributes in part to the deposition of very large particles.

Scavenging Ratio

Studies made at American Samoa and Miami, Florida, yielded values for the scavenging ratio of 270 and 330, respectively (Savoie et al., 1987); on Bermuda, Wolff et al. (1986a) measured a value of 870 for total nitrate. These measurements constitute the primary data set for aerosol nitrate in ocean regions. However, these sites are located in the tropics and mid latitudes. Therefore we cannot be certain that these values are generally applicable to other ocean areas. For the scavenging ratio we use a value of 500. This value falls in the midrange of scavenging ratios determined for a variety of other species over the continents (see Jaffrezo and Colin, 1988).

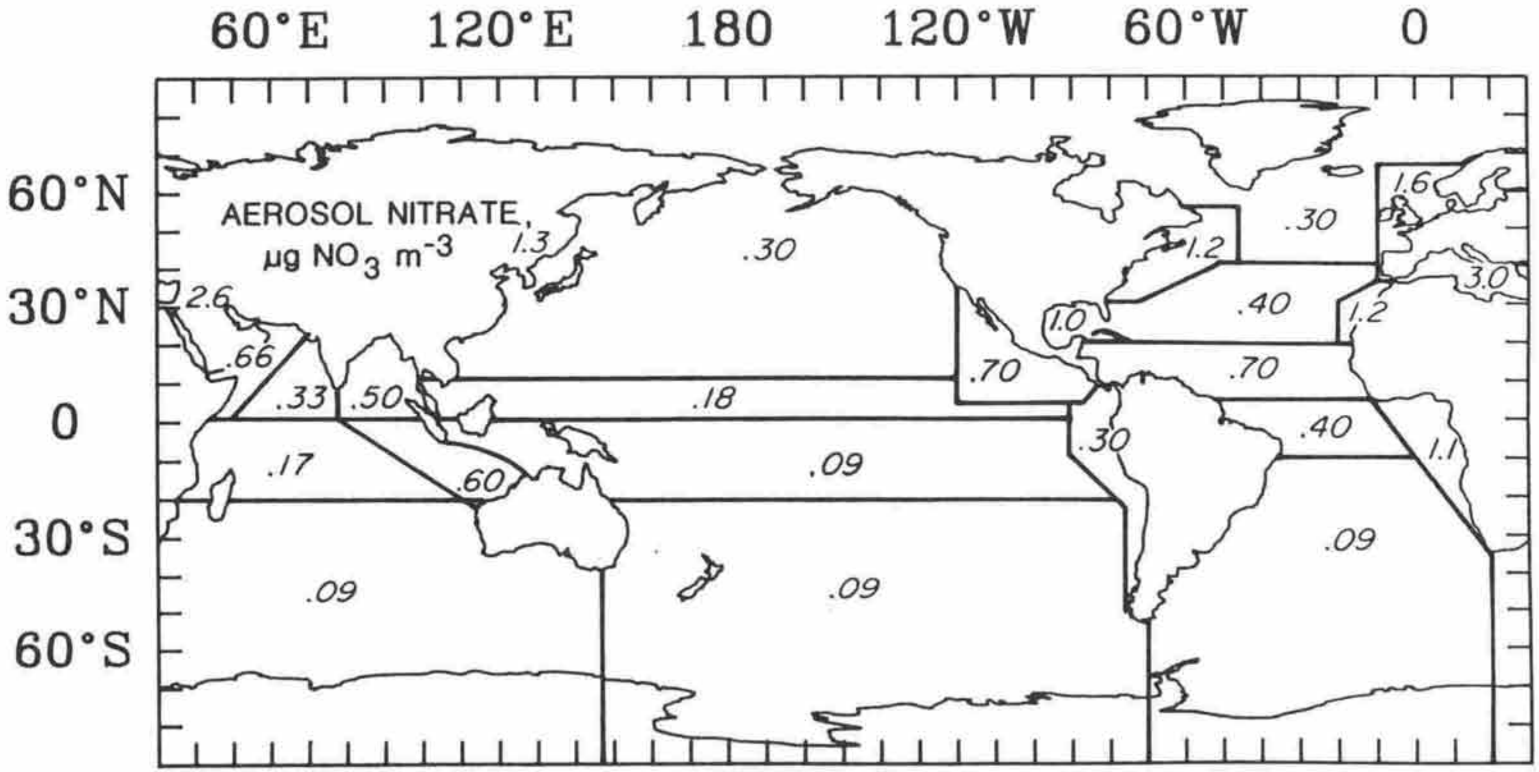

Figure 7. Aerosol Nitrate Concentrations over the Oceans in µg NO_3^- m^{-3}. (After Savoie, 1984).

NITROGEN OXIDE GASES

Concentration Data

The species of principal interest are NO and NO_2. It has proven to be very difficult to measure the atmospheric concentration of these species at ambient levels in marine regions where pollutant impacts are small. Only recently have techniques become available that yield consistently reliable values. Even so, the measurement is still one of the most difficult to make. The problem of interpreting the older literature is compounded by the fact that techniques were used that purported to simultaneously measure NO and NO_2, which are collectively referred to as NO_x. However, recent studies show that these instruments were sensitive to the presence of a variety of other oxidized nitrogen species including HNO_3 and peroxyacetyl nitrate (PAN). Consequently, the older data must be used with caution. Nonetheless, these data can be useful in showing the general levels of the concentrations of nitrogen oxides and to indicate trends in their areal distribution.

The most extensive remote ocean measurements of NO are those of Davis et al. (1987) and Ridley et al. (1987). These were made aboard aircraft flying over the eastern North Pacific between Hawaii and the west coast of North America. Davis obtains an average midday value of 4 pptv (0.0025 $\mu g\ N\ m^{-3}$) at altitudes less than 1.8 km. Ridley reports a mean of 1.7 pptv (0.0011 $\mu g\ N\ m^{-3}$) with a median 1 pptv (0.00064 $\mu g\ N\ m^{-3}$) for the region near Hawaii and 3.7 pptv (0.0023 $\mu g\ N\ m^{-3}$) with a median 1 pptv (0.00064 $\mu g\ N\ m^{-3}$) for the open ocean off the west coast.

For the purpose of this report we assume a mean NO value of 4 pptv (0.0025 $\mu g\ N\ m^{-3}$) for relatively remote ocean regions where no measurements have been made. We acknowledge that it might be more appropriate to use the median value of 1 pptv rather than the mean.

There are very few reliable measurements of NO_2 over the oceans. In Logan's review article on global nitrogen fluxes (Logan, 1983) a world average boundary layer NO_2 concentration of 0.06 $\mu g\ N\ m^{-3}$ is used. However recent measurements in the remote ocean boundary layer yield values of 30 pptv (0.019 $\mu g\ N\ m^{-3}$) (Warneck, 1988). In computing the global ocean fluxes we assume a background value of 0.02 $\mu g\ N\ m^{-3}$; this value is uniformly applied to the Pacific Ocean, the South Atlantic and the Indian Oceans. Higher values are found mostly over the North Atlantic; these values are used accordingly. (The selection of the lower value (0.02 vs 0.06 $\mu g\ N\ m^{-3}$) is not a critical issue because, as will be shown, the NO_2 deposition flux computed with either value is quite small and of minor significance, except for the coastal regions of some continents where pollution plays a dominant role.)

There are additional data for areas of the North Atlantic that are expected to be impacted by continental sources. For example, the concentrations of NO_x off the east coast of North America range from 0.2 $\mu g\ N\ m^{-3}$ to 7.6 $\mu g\ N\ m^{-3}$ (Table 18). Compared to the NO_x background values of 0.02 $\mu g\ N\ m^{-3}$ estimated above, these are large enrichments which will significantly increase the rate of deposition to the western North Atlantic Ocean. The extent of the continental impact will depend upon the rate of removal of NO_x. For the western North Atlantic Ocean, Hastie et al. (1987) and Wolff et al. (1986a,b) estimate that the decay distance is 500 km and 400 km respectively. Comparable decrease distances are obtained from the extensive data presented by Ryaboshapko et al. (1986) for the North Atlantic.

Although data are lacking for most other marine regions downwind of continents, it is anticipated that these enrichments of NO_x are not unique to the western North Atlantic Ocean.

In regions where more extensive measurements are available, we interpolate between the high concentration regions (which are normally close to the continents) to the mid-ocean regions by using a half-decrease distance of 500 km. The highest concentrations occur over the North and Baltic Seas (4.4 and 1.7 $\mu g\ N\ m^{-3}$ respectively), the Bay of Biscay (2.0 $\mu g\ N\ m^{-3}$), along the east coast of the United States (1.5 - 2.5 μg N m^{-3}), the Gulf of Mexico (2.0 μg N m^{-3}). In all other regions, the mean concentration is always less than 1.0 μg N m^{-3}.

Table 18. Concentrations (μg N m^{-3}) of Oxidized Nitrogen in the Atmosphere of Coastal North America and the Western North Atlantic Ocean

Location	$[NO_x]_g$	$[HNO_3]_g$	$[NO_3^-]_a$	$[NO_3]_{g+a}$	Ref.
		East Coast of North America			
Bay D'Espoir, Newfoundland, Canada	-	-	-	0.06	1
Kejimkujik, Nova Scotia, Canada	-	-	-	0.13	1
28-34°N	3.1	-	-	0.1	2
34-38°N	4.6	-	-	0.1	2
38-43°N	5.5	-	-	0.1	2
43-47°N	3.2	-	-	0.1	2
Lewes, Delaware	4.7	0.31	0.10	0.4	3
Lewes, Delaware	4.4	0.46	0.37	0.83	4
		Western North Atlantic Ocean			
43°W, 60°N	-	0.10	0.41	0.51	5
*50 km off east coast	7.6	0.18	0.20	0.38	4
*50 km off east coast	1.7	-	-	-	6
*300 km off east coast	0.7	-	-	-	7
WNAO, average	-	-	0.36	-	8
30-40°N, 70-80 W	0.24	-	-	-	9
30-40°N, 60-70 W	0.22	-	-	-	9
40-50°N, 60-70°W	0.33	-		-	9
Bermuda	0.37	0.04	0.10	0.14	10
Bermuda	-	0.042	0.20	0.24	4
Bermuda	-	-	0.14	-	8
Bermuda	-	-	0.30	-	11
*Bermuda	0.61	0.04	0.13	0.17	4

All concentrations are surface values, except for some measurements made in the boundary layer (marked with an asterisk).

g = gaseous; a = aerosol

1. A.Sirois, personal comm. (1987); 2. Galloway et al. [1984]; 3. Wolff et al. [1986b]; 4. Hastie et al. [1988]; 5. Church et al. (1989); 6. Misanchuk et al. [1987]; 7. Luke and Dickerson [1987]; 8. Savoie [1984]; 9. Ryaboshapko et al. [1986]; 10. Wolff et al. [1986]; 11. Savoie and Prospero [1983]

Deposition Fluxes

On the basis of their chemical properties (i.e., relatively insoluble (high H) gases with similar Sc) the oceanic deposition velocities of NO and NO_2 will be nearly identical. For the purpose of computing the deposition flux, we simply use a concentration value of 0.02 μg N m^{-3} for combined NO and NO_2 in remote ocean regions, with the exception of the North Atlantic, where actual values were used.

NITRIC ACID AND VOLATILE NITRATES

Concentration Data

There are very few data for nitric acid or volatile nitrate. Since most sampling techniques cannot distinguish between the various forms of volatile nitrate, the terms "HNO_3" and "volatile nitrate" are often used interchangeably. The term volatile nitrate includes low molecular weight organic species.

Volatile nitrate concentrations over the oceans are often referenced to particulate or total nitrate. Huebert (1980) reports a volatile nitrate/total nitrate ratio of about 0.5 for samples obtained aboard aircraft in the marine boundary layer of the Pacific. Huebert and Lazrus (1980a) obtain a ratio of 0.35 during a cruise in the equatorial Pacific. Savoie and Prospero (1982) find that the volatile nitrate concentration is 10% or less of the total nitrate in the tropical North Atlantic. Pszenny (1987) obtains essentially the same result from samples in the central and western South Pacific. During a recent cruise in the North Atlantic ratios between 10% to 20% were found in regions not impacted by pollutants (Pszenny, pers. comm.).

Given the paucity of HNO_3 and volatile nitrate data, we calculate fluxes by equating the HNO_3 to some fraction of the total nitrate. However, it is difficult to resolve the discrepancy between the reported values. Consequently, in preparing our distributions and flux estimates we use an intermediate value for volatile nitrate (HNO_3) and set it equal to 30% of the aerosol nitrate.

PAN is perhaps the most important volatile nitrate species after HNO_3. PAN could serve as a reservoir for nitrogen oxides over the oceans (Singh et al., 1986). However, very little is known about its distribution in marine air. The mean wintertime concentration in the boundary layer over the eastern North Pacific is 38 pptv (0.024 μg N m^{-3}) and in the South Pacific, 5 pptv (0.003 μg N m^{-3}; Singh et al., 1986). Thus, the concentration of PAN in the South Pacific is less than half that of HNO_3, assuming that the latter is present at 30% of the nitrate aerosol concentration. There are very few measurements of PAN in the free oceanic troposphere. Rudolph et al. (1987) found that concentrations were less than 10 pptv (0.006 μg N m^{-3}) in the free troposphere over the South Atlantic. Given the low concentrations and the lack of knowledge about the removal properties of PAN, we have ignored its possible role in the deposition flux of nitrogen to the oceans.

Scavenging Ratio

We cannot directly measure the concentration of nitric acid in rainwater. The concentration can be estimated on the basis of ion balances. However, these estimated values are very imprecise and cannot be used for estimating the scavenging ratio for nitric acid. In the absence of such information, we will simply use the same scavenging ratio as that used for aerosol nitrate, i.e., 500. If anything, this is likely to be an underestimate in view of the very strong partitioning of $HNO_{3(g)}$ into water implied by the Henry's Law constant for nitric acid reported by Clegg and Brimblecombe (1988).

Transfer Velocity

The transfer velocity is calculated under the assumption that nitric acid is extremely soluble, so that $r_a \gg r_w$ and equation (9) will give the appropriate value.

REDUCED NITROGEN SPECIES

The decomposition and volatilization of organic materials release a number of reduced nitrogen compounds (e.g., ammonia, amines, amino acids) to the atmosphere. In the atmosphere, these compounds can be hydrolyzed, oxidized or removed by deposition processes. Since the concentrations of these compounds can be similar to the oxidized nitrogen species, their contribution to the deposition of nitrogen to the oceans should be examined.

The principal inorganic reduced nitrogen compounds are gaseous NH_3 and aerosol NH_4^+. Since there is so little information on their concentrations, we choose not to create concentration maps as with the other species. Alternatively, we use the available data to estimate the coastal and open ocean concentrations.

It should be noted that in some regions the oceans may be a source of ammonia (Quinn et al., 1987, 1988). Because of the limited data on ammonia/ammonium, we cannot identify which areas are sources and which are sinks for NH_3. Therefore, the fluxes that we calculate may not be very meaningful from the standpoint of our objective to assess the impact of continental inputs on the oceans.

AMMONIUM

The estimates of the concentrations of ammonium aerosol over the open ocean range from 0.007 to about 0.1 $\mu g\ N\ m^{-3}$ (Table 19). We choose a value representing the central tendency, 0.08 $\mu g\ N\ m^{-3}$. The values near continents are larger, 0.3 to 1.2 $\mu g\ N\ m^{-3}$, in keeping with strong terrestrial sources of ammonia. For near-coastal areas we select an "average" value of 0.4 $\mu g\ N\ m^{-3}$.

For the calculation of a dry deposition flux, we use a deposition velocity of 0.1 $cm\ s^{-1}$, since most of the ammonium aerosol is in the accumulation mode. There are no direct measurements of ammonium scavenging ratios. We can estimate a scavenging ratio for ammonium by using aerosol ammonium data (Wolff et al., 1986a) collected at Bermuda coupled with ammonium data for rainfall (Galloway, 1985) which were not contemporaneous with the aerosol samples; these yield a ratio of about 100. By analogy, we might expect ammonium to have a scavenging ratio similar to that of sulfate which is also an accumulation mode aerosol. The only extensive data for the sulfate scavenging ratio is that obtained at American Samoa and Miami, 420 and 290, respectively (Savoie et al., 1987). For accumulation mode aerosols, we would normally use a scavenging ratio of 200. For the purpose of this report, we will calculate the wet deposition flux using scavenging ratio of 200, which is satisfactory from the standpoint of the limited experimental data.

AMMONIA

The data base on the concentration of ammonia is limited (Quinn et al., 1987). Data are summarized in Table 19. The values range from 0.014 to 0.6 $\mu g\ N\ m^{-3}$ with most of the concentrations being near 0.05 $\mu g\ N\ m^{-3}$. For the purpose of calculating ocean fluxes, we will use the value of 0.05 $\mu g\ N\ m^{-3}$.

There have been no measurements of the wet scavenging ratio for ammonia. As a result, we simply treat it as a highly soluble gas. For the scavenging ratio, we use 200, the same as that for ammonium aerosol.

Since it appears that in some regions the oceans may be a source of ammonia (Quinn et al., 1988), we do not choose to estimate a dry deposition flux.

Table 19. Concentrations of Reduced Nitrogen Species in the Marine Atmosphere

Location	Concentration ($\mu g\ N\ m^{-3}$)	Reference
NH_3		
Global Marine Estimate	0.06	Soderlund and Svensson, 1976
Global Marine Estimate	0.01	Georgii and Gravenhorst, 1977
Cape Grim	0.05	Ayers and Gras, 1980
Global Estimate	0.06 to 0.6	Taylor et al., 1983
Cape Grim	0.06	Ayers and Gras, 1983
NW Pacific Ocean	0.014	Quinn et al., 1988
NH_4^+, Open Ocean		
Global Marine Estimate	0.4	Soderlund and Svensson, 1976
Global Marine Estimate	0.01-0.19	Huebert and Lazrus, 1980b
Tropical Atlantic	0.1	Talbot et al., 1986
Pacific Ocean	0.007-0.21	Parungo et al., 1986
NW Pacific Ocean	0.084	Quinn et al., 1988
Central N. Atlantic	0.07	Church et al., 1989
NH_4^+, Coastal Ocean		
Lewes, DE, USA	1.2	Wolff et al., 1986b
W. North Atlantic	0.45	Whelpdale et al., 1987
W. North Atlantic	0.42	Church et al., 1989
E. North Atlantic	0.42	Church et al., 1989

OTHERS

In addition to the inorganic forms of reduced nitrogen, there are also organic species. Examples are the amines and amino acids. Although data on their atmospheric concentrations are sparse, some measurements have been made. Mopper and Zika (1987) reported concentrations of dissolved organic nitrogen (DON) in the form of dissolved free amino acids (DFAA) and aliphatic amines in precipitation samples collected in the north-western Atlantic Ocean and Gulf of Mexico. The DFAA concentrations ranged from 1.1 to 15.2 μM, with an average of about 6.5 μM. Aliphatic amines contributed between 0.08 and 1.36 μM DON. Van Neste et al. (1987) reported vapour phase concentrations of primary, secondary, and tertiary methylamines measured in Hawaii. Together, these three amines total an average of 134 pmol N m^{-3}. The same authors report rainwater concentrations of these amines to range from 0.024 to 0.057 μM in rain samples collected along the Rhode Island coast. Recent studies (Gorzelska pers. comm.) indicate that, in the summertime, dissolved free amino acids and aliphatic amines in precipitation collected over the North Atlantic contribute from 0.012 to 0.595 μM DON and from 0.006 to 0.132 μM DON, respectively. These compounds also add between 0.3 and 1614 pmol DON m^{-3} to the summertime North Atlantic aerosol. Both rain and aerosol concentrations seem to be subject to pronounced seasonal and spatial variations. Thus these initial data suggest that reduced organic nitrogen compounds might make a significant contribution to the fixed nitrogen content of the atmosphere at certain times and in particular regions of the oceans. However, there are so few data for these types of compounds that it is difficult to estimate any meaningful deposition rates.

SUMMARY AND DISCUSSION

COMPARISON OF CALCULATED FLUXES WITH MEASURED VALUES

Table 20 presents measured deposition fluxes of nitrate and ammonium in marine and coastal areas. Table 21 presents a comparison of the calculated deposition values with actual measured values. For this comparison, we chose data (from Table 20) for those stations that were located on islands or on the coasts of continents adjacent to major ocean areas. Some of the measured flux values were obtained with continuously open collectors. The latter collect dry deposition as well as wet, although the dry collection efficiency is difficult to quantify. Consequently we present both the calculated wet and total deposition values for comparison purposes. In Table 21 we also show the ratios of the calculated-wet to measured (CW/M) flux and the calculated-total to measured (CT/M) flux.

For some stations, the agreement between the calculated and measured values is quite good (e.g., Bermuda, Miami, Nova Scotia, Hawaii). However, for some stations there are large discrepancies between the calculated and measured values. Some of these differences can be rationalized. First, in many cases the computed values are based on mean atmospheric concentrations derived from data which were not usually concurrent with the precipitation data. Second, in some cases the data were extrapolated from other regions or even other oceans; for example, the atmospheric nitrate and NO_x data used for Amsterdam Island and Reunion were extrapolated from the South Pacific.

Finally, many of the parameters used in these calculations are based on a few measurements made in a limited number of regions. In the case of the scavenging ratio, we used a value of 500, which was based primarily on measurements made in Miami and American Samoa. There is no reason to expect that this ratio is universally applicable to all types of rain events (for example, to convective and frontal rains). Furthermore, the scavenging ratio is computed using aerosol and gas measurements made in surface level air. The vertical concentration profile (which is invariably unknown) is implicitly incorporated in the scavenging ratio when it is measured at the sea surface. However, the profile will undoubtedly vary from region to region and especially in ocean regions adjacent to the continents.

In making the comparisons, there is a problem in deciding which concentration values are applicable for those sites which are located in regions adjacent to major source areas. For example, in Table 21 we show two computed fluxes for Ireland. In both cases, the measured deposition rates were obtained from a site near the west coast near 10°W. The values computed for Ireland I are based on the relatively low measured concentrations for the ocean region west of 10°W; these fluxes are small compared to the measured values. A second set of fluxes (Ireland II) was computed using the higher concentration values obtained for the region that includes Ireland and British Isles; these results are much closer to the measured values. Similarly, the computed fluxes for the Faroe Islands are very low compared to the measured values. The Faroes are located at 61°N, just north of the British Isles square and, consequently, it might be more appropriate to compute fluxes using the higher concentrations of this region as was done for Ireland II. Indeed, the computed fluxes for the latter are in reasonable agreement with the measured Faroe values. Similarly, Reunion Island is located immediately adjacent to a block with considerably higher concentrations; these latter values were used to compute the fluxes for Reunion II in Table 21. In general, the agreement between the computed values and the measured values is reasonably good. In fact, the agreement is somewhat surprising when one considers the poor quality of the input data and the often crude assumptions that had to be made in computing the flux.

Table 20. Measured Deposition Fluxes of Nitrate and Ammonium in Marine and Coastal Locations

Location	Lat./Long.	Period	NO_3^- Flux $gN\ m^{-2}\ yr^{-1}$	NH_4^+ Flux $gN\ m^{-2}\ yr^{-1}$	Total N Flux $gN\ m^{-2}\ yr^{-1}$	Ref.	Note
		WESTERN NORTH ATLANTIC					
Bermuda	32°N, 65°W	4/80-5/84	0.086	0.055	0.141	(1)	
WNAO, ship		5/80-10/83	0.077	0.042	0.119	(1)	(a)
NAO, ship	57°N, 20°W	1/82-1/85	0.05	0.071	0.121	(2)	
Florida	26°N, 80°W	5/82-4/85	0.139	-	-	(3)	
Florida	24°N, 80°W	1984-1985	0.114	0.089	0.203	(4)	
Florida	30°N, 82°W	1984-1985	0.211	0.129	0.34	(4)	
Georgia	33°N, 82°W	1984-1985	0.178	0.123	0.301	(4)	
North Carolina	37°N, 77°W	1984-1985	0.218	0.132	0.35	(4)	
Delaware	39°N, 75°W	1979-1983	0.313	0.199	0.512	(5)	
New Jersey	40°N, 75°W	1984-1985	0.378	0.192	0.57	(4)	
New York	41°N, 73°W	1979-1983	0.303	0.168	0.471	(5)	
Massachusetts	42°N, 70°W	1984, 1985	0.258	0.129	0.387	(4)	
Massachusetts	42°N, 71°W	1984, 1985	0.285	0.107	0.392	(4)	
Nova Scotia	43°N, 65°W	1981-1982	0.235	-	-	(6)	
Nova Scotia	44°N, 65°W	1985-1986	0.217	0.122	0.339	(7)	
Maine	44°N, 68°w	1984-1985	0.252	0.123	0.375	(4)	
Nova Scotia	45°N, 63°W	1980-1983	0.201	-	-	(6)	
Nova Scotia	45°N, 64°W	1985-1986	0.206	0.111	0.317	(7)	
New Brunswick	45°N, 66°W	1980, 1982	0.413	-	-	(6)	
New Brunswick	46°N, 65°W	1985-1986	0.182	0.109	0.291	(7,8)	
New Brunswick	46°N, 66°W	1980-1983	0.248	-	-	(6)	
Maine	47°N, 68°W	1984-1985	0.167	0.1	0.267	(4)	
Newfoundland	48°N, 55°W	1985-1986	0.118	0.084	0.202	(7,8)	
New Brunswick	48°N, 68°W	1980-19982	0.177	-	-	(6)	
Newfoundland	49°N, 55°W	1981	0.084	-	-	(6)	
Newfoundland	49°N, 55°W	1985-1986	0.064	0.03	0.094	(7)	
Newfoundland	49°N, 59°W	1982	0.225	-	-	(6)	
Quebec	50°N, 67°W	1986	0.229	0.076	0.305	(8)	
		EASTERN NORTH ATLANTIC					
Ireland	52°N, 10°W	11/84-10/87	0.146	0.166	0.312	(9)	
Portugal	37°N, 8°W	1983-1985	0.043	0.036	0.079	(10)	
United Kingdom	50°N, 5°W	1983-1985	0.218	0.212	0.43	(10)	
Faroe Islands	61°N, 7°W	1983-1985	0.263	0.174	0.437	(10)	
Norway	63°N, 9°E	1983-1985	0.135	0.096	0.231	(10)	
Norway	66°N, 14°E	1983-1985	0.101	0.118	0.219	(10)	
Norway	69°N, 25°E	1983-1985	0.046	0.089	0.135	(10)	
Norway	74°N, 19°E	1983-1985	0.056	0.101	0.157	(10)	
			GREENLAND				
DYE 3	65°N, 43°W	recent snow		0.0049	0.0048	(11)	
North Central	75°N, 40°W	recent snow	0.0024	-	-	(12)	
Crete	71°N, 37°W	recent snow	0.0038	-	-	(13)	
Camp Century	77°N, 61°W	recent snow	0.0045	-	-	(12)	
DYE 3	65°N, 43°W	recent snow	0.0056	-	-	(12)	
			NORTH SEA				
United Kingdom	53°N, 0.5°E	1983-1985	0.321	0.528	0.849	(10)	
Netherlands	53°N, 7°E	1983-1985	0.459	0.852	1.311	(10)	
West Germany	55°N, 8°E	1983-1985	0.499	0.543	1.042	(10)	
Denmark	56°N, 10°E	1983-1985	0.384	0.532	0.916	(10)	
Norway	59°N, 7°E	1983-1985	0.516	0.577	1.093	(10)	

Table 20. (Continuted).

Location	Lat./Long.	Period	$N0_3^-$ Flux gN m^{-2} yr^{-1}	NH_4^+ Flux gN m^{-2} yr^{-1}	Total N Flux gN m^{-2} yr^{-1}-	Ref.	Note
BALTIC SEA							
Denmark	55°N, 11°E	1983-1985	0.378	0.384	0.762	(10)	
Sweden	57°N, 18°E	1983-1985	0.382	0.495	0.897	(10)	
Finland	60°N, 21°E	1983-1985	0.382	0.373	0.755	(10)	
Finland	60°N, 28°E	1983-1985	0.383	0.52	0.903	(10)	
USSR	58°N, 22°E	1984-1985	0.344	0.294	0.638	(10)	
USSR	55°N, 21°E	1984-1985	0.379	0.379	0.758	(10)	
INDIAN OCEAN							
Amsterdam Is.	38°S, 78°E	5/80-6/86	0.039	0.058	0.097	(19)	
Reunion Island	21°S, 56°E	9/79-8/80	0.043	0.162	0.205	(20)	
NORTH PACIFIC OCEAN							
Hawaii	19°N, 155°W	5/83-5/87	0.050	-	-	(9)	(b)
RV Korolev	1°N, 130°W		0.03	0.062	0.092	(14)	(c)
RV Discoverer	30°N, 170°W		0.05	0.06	0.11	(14)	(c)
SOUTH PACIFIC OCEAN							
Samoa	14°S, 171°W	1981	0.005	-	-	(15)	
Samoa	14°S, 171°W	1984, 1986	0.012	0.002	0.032	(16)	
New Zealand	35°S, 173°W	1983	0.008	-	-	(17)	
Tasman Sea	35°S, 167°E	1983	0.04	-	-	(17)	(c)
Chile		3/84-5/87	0.0004	0.0005	0.0009	(18)	

NOTES a. Samples collected from May to October only

b. Data are from Mauna Loa Observatory

c. The latitudes and longitudes are the midpoint of the cruise track.

REFERENCES

(1) Galloway et al., 1989; 2) Buijsman et al., 1985; (3) Savoie et al., 1987; (4) NADP, 1986; 1987; (5) Dana and Easter, 1987; (6) UDDBC, 1986; (7) Vet et al., 1986; (8) Vet, R.J., pers. comm., as cited in Galloway and Whelpdale, 1987; (9) Galloway, unpub. data; (10) Schaug et al., 1987; (11) Busenberg and Langway, 1979; (12) Herron, 1982; (13) Risbo et al., 1981; (14) Galloway, 1985; (15) Pszenny et al., 1982; (16) Miller, per. comm; (17) Pszenny and Duce, unpub. data; (18) Galloway, unpub. data; (19) Galloway and Gaudry, 1984; (20) Unreferenced data.

Table 21. Comparison of Computed and Measured Nitrate Deposition Fluxes (g NO_3^- N m^{-2} yr^{-1})

Location	Lat./Long.	Computed Wet	 Total	Measured Nitrate	Ratio+ CW/M	 CT/M	Notes
Bermuda	32°N,65°W	0.123	0.217	0.086	1.4		
Nova Scotia	44°N,65°W	O.161	0.279	0.217	0.74		
Ireland I	52°N,10°W	0.056	0.096	0.146	0.38		a)
Ireland II	53°N,10°W	0.143	0.327	0.146	0.98		a)
Faroe Islands	61°N,7°W	0.038	0.070	0.263		0.27	b)
Miami	26°N,80°W	0.158	0.245	0.139	1.1		
Amsterdam Is.	38°S,78°E	0.010	0.020	0.039	0.26		
Reunion Is. I	21°S,56°E	0.016	0.024	0.043		0.56	
Reunion Is. II	21°S,56°E	0.026	0.038	0.043		0.88	c)
Hawaii	19°N,155°W	0.035	0.059	0.050	0.70		d)
American Samoa	14°S,171°W	0.031	0.041	0.012	2.6		

\+ Ratio: CW/M, computed wet-to-measured; CT/M, computed total-to-measured. CW/M is shown for data from event rain collectors; CT/M is shown for total (wet + dry) deposition data.

a) The Ireland station is located at the 10°W longitude. The values for Ireland I were calculated using the concentrations for the 10° block located to the west; the Ireland II values were calculated with concentrations from the block to the east, which are much higher because of the impact of anthropogenic sources in England and Europe.

b) The calculations for Ireland II might also apply to the Faroe Islands because of their location immediately north of the British Isles block.

c) Reunion Is. II was calculated with concentration values for the block immediately to the north.

d) The measured values were obtained at Mauna Loa Observatory which lies well above the marine boundary layer. These values might not be representative of boundary layer conditions.

CALCULATED FLUXES TO THE GLOBAL OCEANS

The calculated fluxes of all N species are summarized in Table 22 for major ocean regions and for the oceans as a whole. Global maps of the atmospheric deposition of oxidized and reduced nitrogen are shown in Figures 8 and 9, respectively. The global total oxidized N deposition is ~28 x 10^{12} g yr^{-1}. Of this total, ~19 x 10^{12} g yr^{-1} (70%) is deposited to the Northern Oceans. Of the total oxidized N deposition, ~16 x 10^{12} g yr^{-1} (59%) is deposited by the wet removal of NO_3^- aerosol and HNO_3. As should be clear from the preceding discussion, the wet deposition aspects of the flux are much better understood and more accurately known than the dry flux.

The deposition rates of NO_x (i.e., NO and NO_2) are extremely small because of its very low solubility in precipitation and in sea water. Indeed, the wet removal rates are effectively zero in Table 22. Even in the North Atlantic, where the dry flux of NO_x to the ocean is greatest, it can be ignored in budget estimates.

Table 22. Estimated Atmospheric Input of Certain Nitrogen Species to the Oceans

Species	Deposition Type	North Atlantic	South Atlantic	North Pacific	South Pacific	North Indian	South Indian	Global
OXIDIZED NITROGEN: TOTAL DEPOSITION (10^9 g N yr^{-1})								
NO_3	Wet	4140	505	4090	2070	748	1240	12,800
NO_3	Dry	3690	627	2520	1360	452	718	9370
HNO_3	Wet	1140	151	1140	620	224	371	3650
HNO_3	Dry	641	153	589	332	86	187	1990
NO_x	Wet	0	0	0	0	0	0	0
NO_x	Dry	32	1	2	3	0	1	40
Subtotal		9640	1440	8340	4390	1510	2520	27,800
REDUCED NITROGEN: TOTAL DEPOSITION (10^9 g N yr^{-1})								
NH_4	Wet	2740	1220	4050	3790	1170	1940	14,900
NH_4	Dry	532	309	627	577	174	334	2550
NH_3	Wet	455	311	944	1040	152	471	3370
Subtotal		3730	1840	5620	5410	1500	2750	20,800
TOTAL NITROGEN DEPOSITION (10^9 g N yr^{-1})								
Total		13,400	3280	14,000	9800	3010	5270	48,600
FLUX (mg N m^{-2} yr^{-1})								
NO_3	Wet	75.4	9.9	45.6	18.8	51.9	23.1	34.2
NO_3	Dry	67.2	12.2	28.1	12.3	31.4	13.4	25.0
HNO_3	Wet	20.8	2.9	12.7	5.6	15.6	6.9	9.8
HNO_3	Dry	11.7	3.0	6.6	3.0	6.0	3.5	5.3
NO_x	Wet	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NO_x	Dry	0.6	0.0	0.0	0.0	0.0	0.0	0.1
NH_4	Wet	49.9	23.8	45.2	34.4	81.3	36.1	39.8
NH_4	Dry	9.7	6.0	7.0	5.2	12.1	6.2	6.8
NH^3	Wet	8.3	6.1	10.5	9.4	10.6	8.8	9.0
Total		244	64.0	155	88.7	209	98.0	130
TOTAL WET AND DRY DEPOSITION BY REGION (10^{12} g N yr^{-1})								
Nitrogen	Wet	8480	2190	10,200	7520	2290	4020	34,700
Nitrogen	Dry	4860	1090	3740	2270	712	1240	13,900
RATIO: WET TO TOTAL DEPOSITION								
Wet/Total		0.64	0.67	0.73	0.77	0.76	0.76	0.71

Table 22 also presents the estimates of the mean flux for the various oceans. The highest flux per unit area is obtained in the North Atlantic. As might be expected, this reflects the impact of anthropogenic sources in North America, Europe and Africa. The second highest deposition fluxes are obtained in the northern Indian Ocean. This is a consequence of several factors. First of all, this region is relatively small and much of it is bounded by land masses. Thus, the concentrations of the various species are relatively high. Secondly, rainfall rates tend to be relatively high leading to high wet removal fluxes. In contrast, the flux per unit area in the Southern Indian Ocean is relatively low. However, it should be noted that the computed rates might be too low in this region as evidenced by the large discrepancies between the computed fluxes (Table 21) for Reunion and Amsterdam and the values actually measured there (the latter being as much as four times greater than the computed).

The range of flux rates for the various regions is quite large, a factor of 3.8 between the largest (the North Atlantic) and the smallest (the South Atlantic). If we consider only the oxidized N species, the largest ratio is between the North and South Atlantic, 6.3. In contrast, the difference between the North and South Pacific is only 1.7. The computed flux per unit area for all northern oceans is 191 mg N m^{-2} yr^{-1} while that for all southern oceans is 85 mg N m^{-2} yr^{-1}, the ratio N/S being 2.2. If we consider only the oxidized N species, the fluxes for northern and southern oceans are 123 and 39 mg N m^{-2} yr^{-1}, respectively, and the N/S ratio is 3.2. Thus, all our estimates show quite clearly that the northern oceans are much more highly impacted by transport of N species from the continents. While a large fraction of these species have natural sources, we can assume that a substantial fraction is derived from anthropogenic sources.

Recently Prospero and Savoie (1989) estimated the impact of continental NO_3^- over the North Pacific based on the assumption that the NO_3^- values measured in the equatorial and central South Pacific (0.025 g N m^{-3}) are representative of the oceanic "background" and that these values are applicable to the central North Pacific. On this basis they estimate that about 40-70% of the NO_3^- over the central North Pacific appears to be derived from continental sources. Of course, impacts will be much greater closer to the continents.

The southern oceans do not appear to be substantially impacted by anthropogenic sources in general or by northern hemisphere sources in particular. The large difference between North and South Pacific NO_3^- concentrations (Prospero and Savoie, 1989) is taken as evidence that cross equatorial transport is sharply suppressed by the intertropical convergence zone (ITCZ). ITCZ precipitation processes efficiently remove aerosol NO_3^- and its gaseous precursors (Levy and Moxim, 1989). Northern hemisphere air parcels (as indicated by sharply increased concentrations of gaseous pollutants such as CO_2 and methylchloroform (Halter, 1984)) are often observed at American Samoa during March and April; however, nitrate concentrations at this time of year are actually at a minimum (Savoie et al., 1989a). Southern hemisphere combustion sources can only account for about 10% of the observed NO_3^- concentrations over the central South Pacific (Levy and Moxim, 1989).

In Table 22, the fluxes of NH_4^+ and NH_3 are shown to be quite large. For the global ocean, the reduced N flux is almost as large as that for oxidized N, 43% of the total flux. This estimate should be considered as very crude. There are few measurements of NH_4^+ in aerosols for many ocean regions, and there are many fewer still for NH_3. The dearth of NH_3 data is such that we have had to assume a fixed ratio of NH_3 to NH_4^+ in order to compute fluxes; this is a very questionable procedure.

Furthermore, the ocean may serve as a source of NH_3 in some regions. Consequently, much of our computed flux of NH_4^+ and NH_3 could consist of recycled oceanic material. Consequently the reduced N data should be used with caution. Nonetheless the wet deposition rate of NH_4^+ accounts for the largest flux of all the species in most ocean regions and it is the largest in the global flux inventory. Bearing in mind the uncertainty in the NH_4^+ data, they nontheless suggest that NH_4^+ could play an important role in the atmospheric flux of nutrients to the ocean.

The total wet and total dry depositions are also shown in Table 22 along with the ratio of the wet deposition to the total (i.e., both wet and dry). The wet/total ratio is lowest in the North Atlantic as a consequence of the relatively high concentration of the gas phase species. In other regions the ratio is about 70%, somewhat lower than the generally accepted value of 80-90%. This discrepancy could indicate that the dry deposition rate is over estimated.

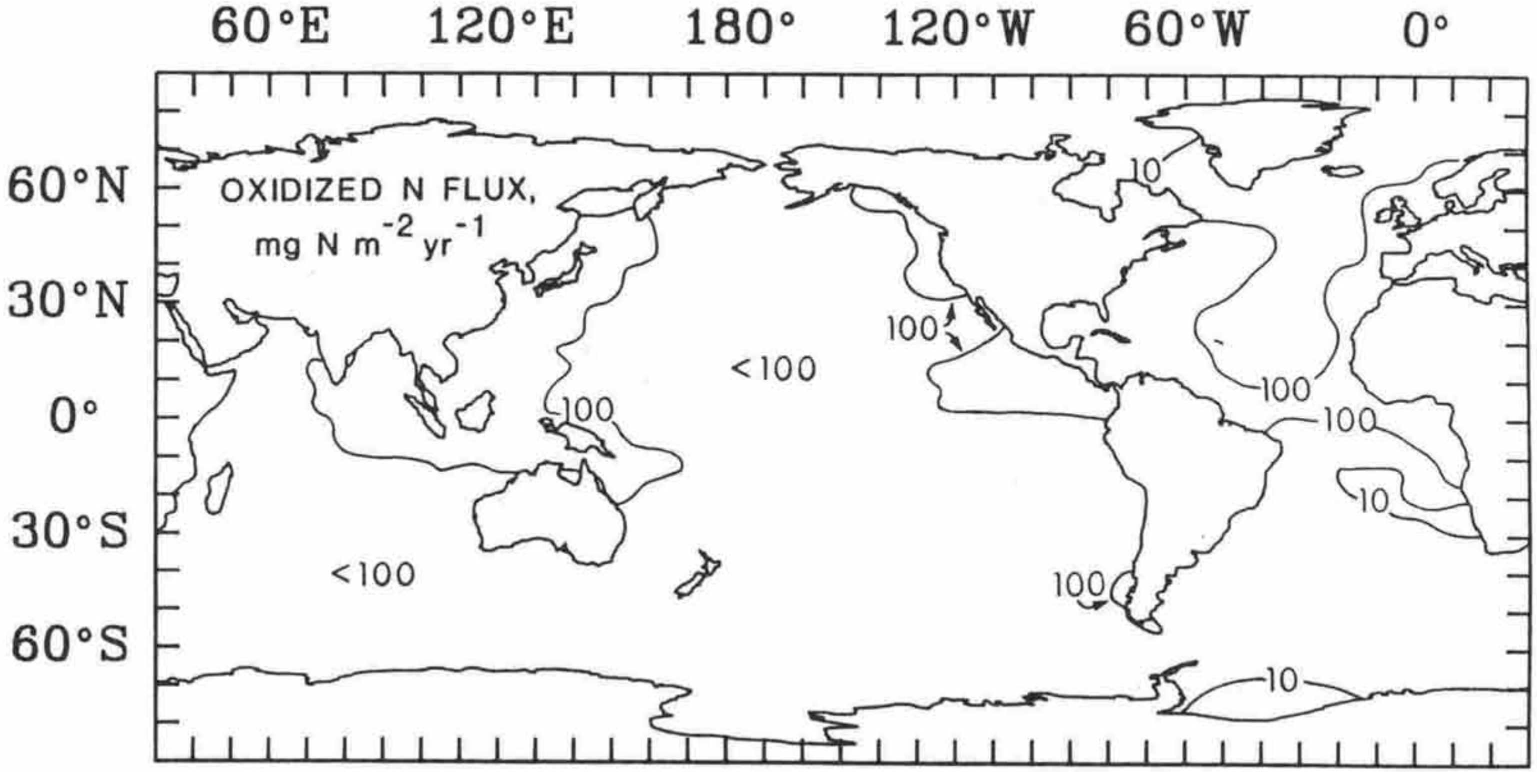

Figure 8. Global Fluxes of Oxidised Nitrogen to the Oceans in mg N m^{-2} yr^{-1}.

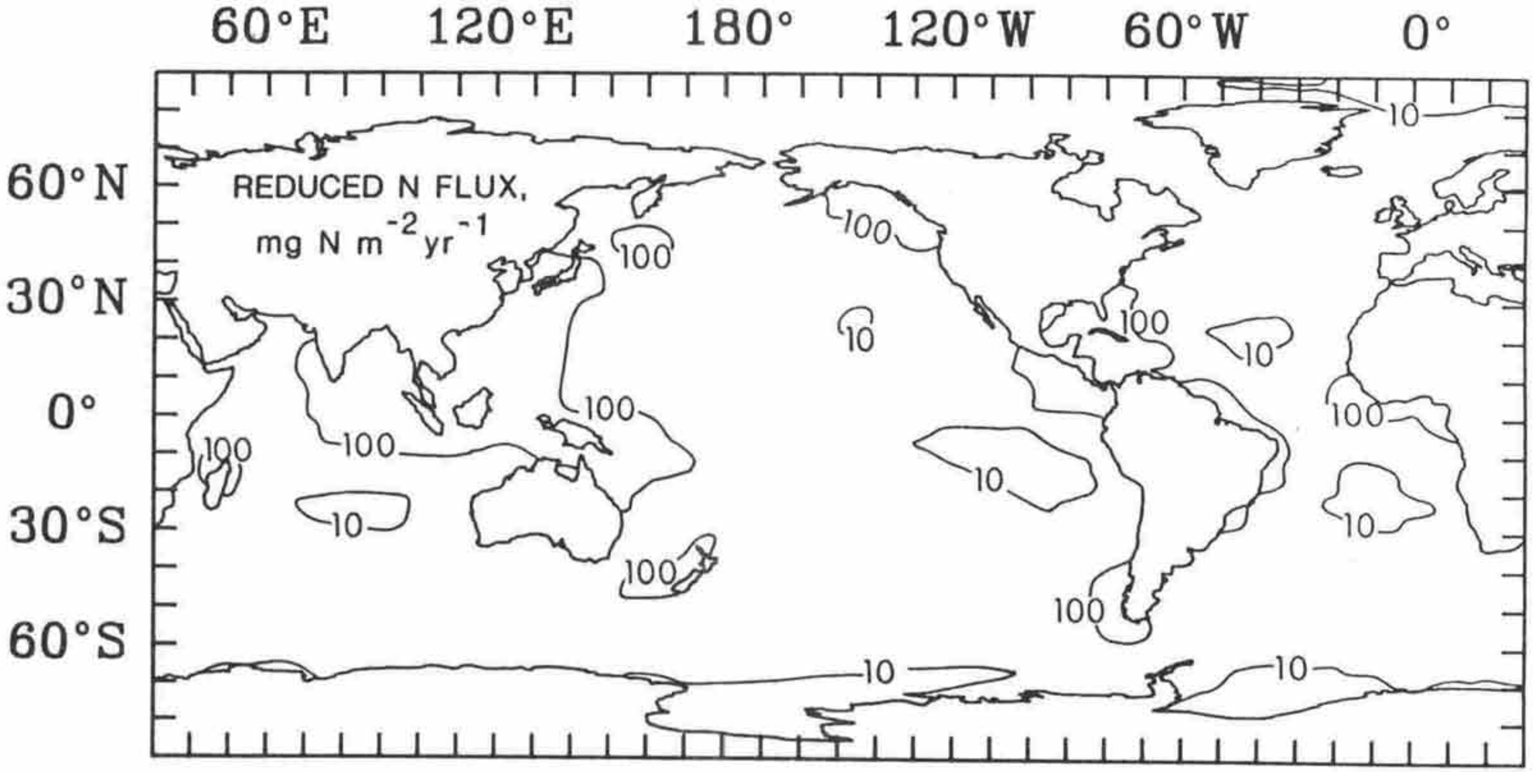

Figure 9. Global Fluxes of Reduced Nitrogen to the Oceans in mg N m^{-2} yr^{-1}.

COMPARISONS WITH OTHER ESTIMATES OF GLOBAL OCEAN FLUXES OF OXIDIZED NITROGEN

In Table 23 we summarize the previously published estimates of the deposition of oxidized N species to the ocean. Included in Table 23 are the figures obtained in this work. Our deposition numbers are within the range of the previous estimates but they tend to be toward high end of the published values. The reasons for these differences can be illustrated by comparing our values with Logan (1983). Logan's estimate of wet deposition to the oceans is 4-12 x 10^{12}g N yr^{-1}. This is considerably lower than our estimate. Her estimate is based on the very few measurements of NO_3^- in rainfall that were available at that time for remote regions, principally Samoa, Hawaii and Amsterdam Island. Logan uses a deposition flux range of 0.1-0.3 kg N ha^{-1} yr^{-1} (0.01-0.03 g N m^{-2} yr^{-1}). In contrast, our computed mean flux for the global oceans is 0.74 kg N ha^{-1} yr^{-1} (0.074 g N m^{-2} yr^{-1}).

Table 23. Summary of Published Estimates of Atmospheric Oxidized Nitrogen Deposition to the Global Ocean

Wet Deposition 10^{12} g N yr^{-1}	Dry Deposition 10^{12} g N yr^{-1}	Total 10^{12} g N yr^{-1}	Reference
18.2	4.2	22.4	Burns and Hardy (1975)
4.2 - 15.4	5.6 - 16.8	9.8 - 32.2	Soderlund and Svensson (1976)
5.6 - 15.4	2.0 - 13.0	7.6 - 28.4	Anderson (1983)
5.6 - 15.4	0.98 - 7.0	6.5 - 22.4	Stedman and Shetter (1983)
4.2 - 12.0	2.8 - 12.0	7.0 - 24.1	Logan (1983)
2.0 - 36.4 (9.8)*	5.6	7.6 - 42.0	Galloway (1985)
4.34 - 8.26	1.22 - 6.16	5.6 - 14.4	Pszenny (1987)
16.5	11.3	27.8	This Work

* Value in parentheses is Galloway's (1985) "best" estimate

For the dry deposition velocity of HNO_3 Logan simply uses a range of 0.6-1.2 cm s^{-1}. In contrast, ours are directly computed, as described previously; nonetheless, our effective deposition velocities fall in the range used by Logan. For NO_3^- aerosol, she uses a deposition velocity of 0.3 cm s^{-1}, referencing Liu et al. (1983) and Savoie and Prospero (1982) for NO_3^- aerosol size. In our calculations, we use 1 cm s^{-1} because of the fact that the NO_3^- aerosol is found primarily on sea-salt particles which have a size of several micrometers. As for the dry deposition velocity of NO_x over the oceans, Logan simply says that it should be small, less than 0.1-0.2 cm s^{-1}. As we have shown, this flux is indeed negligible.

Finally, we can compare our calculated depositions with pollution transport estimates. Recently, Levy and Moxim (1989) used a general circulation model to simulate the global transport and deposition of reactive N species emitted by fossil fuel combustion sources. Their estimates do not include biomass burning which could be about 25% of the emitted N oxides (i.e., 0.25 of 21.3 x 10^{12}g yr^{-1}, or 5.4 x 10^{12}g yr^{-1}) are transported to the oceans. If valid, 16% of the global oceanic deposition of NO_3^- is derived from anthropogenic combustion sources. Since most combustion sources are located in the northern hemisphere, the effects of the pollutant inputs will be greatest over the northern oceans. This is consistent with recent estimates that Asian emissions account for 40-70% of the deposition to the North Pacific (Prospero and Savoie, 1989) and that US/Canadian emissions account for 75% of the deposition to the North Atlantic.

SOURCES OF ERROR IN FLUX ESTIMATES

Some sources of error in the wet deposition estimates were discussed earlier in the section on comparisons with actual measurements. In particular, there is considerable uncertainty in the determination of the scavenging ratios used in this work. In effect, they are derived from measurements made at two locations, both of them in the tropical latitudes. However, our scavenging ratios are reasonably consistent with other studies carried out over land in various locations (Jaffrezo and Colin, 1988). Furthermore, our computed fluxes for specific sites agree reasonably well with actual field data, although such data are quite limited in number and scope.

A major source of uncertainty in these estimates is the dry deposition rate of the various oxidized N species. In this report we use a dry deposition velocity of 1 cm s^{-1} for NO_3^- aerosol based on experiments with a wide range of aerosol types. This value is several times larger than that used in earlier estimates. This choice was motivated in part by recent work by Pszenny (1987) who made a detailed study of NO_3^- wet and dry deposition at a number of sites in the Pacific. He obtained a ratio of the dry deposition to total deposition fluxes of 22% to 43%. Our computed ratio for the South Pacific is 38% while that for all oceans is 40%, which suggests that we may be overestimating the dry component. However, Pszenny's measured ratios were highly variable from event-to-event and the number of cases studied was not great. Thus, it is not clear if his values are representative.

The deposition fluxes obtained for HNO_3 are almost certainly an overestimate. First of all, in the absence of actual measurements, the HNO_3 concentration is obtained by defining it as 0.3 times the NO_3^- concentration. This procedure was applied to all regions except the North Atlantic. However, recent unpublished data suggests that, for the marine boundary layer, this ratio may really be about 0.1 to 0.2 (Huebert, pers. comm.). Secondly, most of the NO_3^- data were obtained with cellulose filters which will collect HNO_3 with high efficiency once the filters become coated with sea salt. On this basis alone, it is conceivable that the HNO_3 deposition flux might be overestimated by as much as a factor of two. Considering both the possible filter artifact and the uncertainty in the HNO_3/aerosol-NO_3^- ratio, the HNO_3 concentrations could be too high by about a factor of four to six. However, because the HNO_3 fluxes are relatively small to begin with, a reduction by a factor of four to six would reduce this flux to a minor component of the total.

Finally, as stated previously, the net flux of reduced nitrogen to the oceans could be considerably smaller than our computed value if the ocean itself is a significant source of ammonia.

COMPARISON OF ATMOSPHERIC AND RIVERINE INPUTS OF DISSOLVED NITROGEN

GLOBAL FLUXES

In this section we compare our computed deposition fluxes of the various N compounds to those estimated for rivers. For river fluxes we use the estimates of natural fluxes presented in GESAMP (1987), as summarized in Table 24. In the table we also include our estimates for the global ocean N deposition rates. The atmospheric input of NO_3^- is eight times greater than the riverine input while that for NH_4^+ is 35 times larger. Indeed, the atmospheric flux of N is three times that of the total riverine input (14 x 10^{12} g N yr^{-1}) for all natural N species including dissolved organic N.

However, there is also a substantial flux of pollutant N in rivers. Estimates (GESAMP, 1987) range from 7 to 35 x 10^{12} g N yr^{-1} (see Table 24). The total riverine flux (natural and anthropogenic) ranges from 21 to 49 x 10^{12} g N yr^{-1}. Thus the total river flux is essentially identical to the total atmospheric deposition.

Table 24. Gross River Fluxes of Dissolved Nitrogen and Estimated Global Atmospheric Deposition (10^{12} g N yr^{-1})

	NO_3^-	NO_2	NH_4^+	DIN	DON	TOTAL	AUTHOR
a: River Fluxes - Natural$^+$							
	7						Livingstone (1963)
				7	8	15	Van Bennekom and Salomons (1981)
	3.7	negligible	0.6	4.3	9.7	14	Meybeck (1982)
b: River Fluxes - Anthropogenic$^+$							
						18	Soderlund and Svensson (1976)
						35	Delwiche and Likens (1977)
						32	Van Bennekom and Salomons (1981)
						7	Meybeck (1982)
						21	Wollast (1983)
c: Atmospheric Deposition Fluxes							
	28	negligible	21	-	-	49	This Work

$^+$ From GESAMP (1987)

The river fluxes presented in Table 24 are gross fluxes. That is, they show the amount of N being delivered into the estuaries. However, very little of the river flux will ever reach the open ocean because these species are important nutrients that are extensively involved in the biological and chemical processes which occur in estuaries and coastal waters. As a result most of the dissolved nutrients are removed from the water column and deposited to the shelf sediments. A large fraction of the N may also be lost to the atmosphere by denitrification processes. Only a small fraction of the river input reaches the open ocean.

The assessment of net riverine fluxes to the ocean is made more difficult by the fact that coastal areas are often upwelling zones. These constitute another source of nutrient supply which greatly complicates mass balance calculations. Nonetheless, it is clear that only a small fraction of the river input reaches the open oceans. Thus, the relative importance of the atmospheric input is further enhanced.

It is interesting to compare the atmospheric deposition of N compounds to the burial rate of N in the sediments. The burial rate is estimated in GESAMP (1987) based on the rate of accumulation of organic C in pelagic sediments, 5.7 x 10^{12} g C yr^{-1} (Berner, 1982). Assuming a molar C/N ratio of 15 for organic matter preserved in those sediments (Wollast, 1981), the GESAMP authors obtain a rate of accumulation of organic N of 0.44 x 10^{12} g N yr^{-1}. This represents only 3% of the gross natural dissolved river input (of which, as was said, very little reaches the open ocean). Furthermore, the N burial rate is only 0.9% of the total atmospheric nitrogen deposition rate (1.6% of the total NO_3^- rate).

The large difference between the atmospheric input rate and the burial rate suggests that the N cycle in the ocean must be balanced by a very large recycling flux of N to the atmosphere. This flux is generally assumed to consist primarily of gaseous species (mainly N_2O and NH_3). However, the present estimates of these emitted fluxes are very uncertain. Much of the emission flux apparently takes place over the shelves and regions of upwelling. In contrast, the atmospheric deposition flux is relatively uniform (compared to the emission flux) over the oceans. Thus the open ocean emission fluxes appear to be too small to balance the cycle. These inconsistencies suggest that there are major components of the atmosphere/ocean N cycle that are very poorly understood.

REGIONAL SEAS

There is very little data that would allow an accurate estimate of fluxes to coastal waters. Thus far, only two regions have been studied well enough to enable an assessment, the North Sea and the Mediterranean.

FLUX OF NUTRIENTS TO THE NORTH SEA

Anon. (1987) gives the atmospheric input of nutrient N to the North Sea as 400×10^9 g yr^{-1}. This compares with 1000×10^9 g yr^{-1} for river input and 95×10^9 g yr^{-1} for direct discharge. Thus, the atmospheric flux constitutes a major fraction of the nutrient input to the region.

FLUX OF NUTRIENTS TO THE MEDITERRANEAN

Recently Martin et al. (1989) estimated the atmospheric flux of various nutrients (total inorganic N and P) to the western Mediterranean Sea, a region extending from the west coast of Italy to Gibraltar. For dissolved organic N they obtain a deposition flux of 4.1 g N m^{-2} yr^{-1}. This rate is about 17 times the mean rate computed by us for the whole North Atlantic (0.24 g N m^{-2} yr^{-1}, Table 22). The rate of 4.1 g N m^{-2} yr^{-1} yields a total flux of 350×10^9 g N yr^{-1}. In contrast, the rivers entering this region carry 227×10^9 g N yr^{-1}. Thus, the two fluxes are approximately equal.

The atmospheric input in this region corresponds to 10% of the average "new" production and up to 50% of the production during oligotrophic periods. This estimate is supported by studies during the summer of 1987 which showed sharp increases in chlorophyll production following heavy rains. However, the increased productivity could also be due, in part, to increased concentration of trace metals such as Fe and Co, which appear to play a critical role in phytoplankton productivity.

CONCLUSION

The gross fluxes computed in this study are generally consistent with those obtained in past studies, although they tend to lie toward the high end of previous estimates. Our results differ from those of earlier efforts in that they show quite clearly the very large regional differences that are due to the effects of transport from continental sources which are presumed to be predominantly anthropogenic. Thus, any impact that atmospheric fluxes might have on oceanic productivity could vary quite dramatically from region to region. In this regard, much higher fluxes are observed for northern hemisphere oceans compared to the southern oceans. Coastal regions are especially vulnerable to high deposition fluxes. This is most clearly demonstrated by the estimates of deposition rates to the North Sea and the western Mediterranean.

The comparisons with river inputs suggest that the impact of atmospheric deposition on open ocean chemistry will be much greater than that for rivers. Although the magnitude of the fluxes are comparable, the effects of the riverine inputs will be primarily limited to estuaries and coastal waters. However, even in coastal waters, the atmospheric input could be the major source of nutrients since in many regions the net river flux to coastal waters could be quite small or non-existent.

Finally, it must be emphasized that, while the estimates made here are based on reasonable assumptions, they are subject to considerable uncertainty. There is clearly an immense need for more and better data. This need is especially great for remote ocean regions and it is particularly critical for all southern oceans. At the very least, this assessment serves to emphasize the importance of obtaining such data.

THE ATMOSPHERIC INPUT OF SYNTHETIC ORGANIC COMPOUNDS TO THE WORLD OCEAN

INTRODUCTION

Synthetic organic chemicals have been observed in a variety of environmental systems from all areas of the earth. Accumulation of certain types of synthetic species, particularly the chlorinated hydrocarbons, has been shown to occur in Arctic ecosystems (Hargrave et al., 1987; Patton et al., 1989), in the Antarctic environment (Giam et al., 1974; Risebrough and Carmignani, 1972; Tanabe and Tatsukawa, 1983; Bacci et al., 1986), in deep-sea organisms (Barber and Warlen, 1979; Ballschmiter et al., 1981), and in a variety of other areas (Tanabe et al., 1983b and Tatsukawa and Tanabe, 1989). Even though the concentrations of synthetic chlorinated hydrocarbons are low in remote areas, there have been data that suggest a relationship between chlorinated hydrocarbon uptake and the decreasing concentration of reproductive hormones in marine mammals (Subramanian et al., 1987). Other experimental evidence on the relationship between synthetic organic species and various biological effects in marine ecosystems underscores the necessity to understand and predict the inputs of potentially harmful chemical species in broad areas of the world ocean.

Most evidence available now suggests that atmospheric transport and deposition of synthetic organic compounds are significant processes for carrying organic pollutant compounds to much of the ocean surface (Atlas, 1989; Atlas and Giam, 1981, 1986, 1989; Atlas et al., 1986; Knap et al., 1988; Bidleman et al., 1981; Harvey and Steinhauer, 1974). Some measurements, modelling efforts, and calculations have been performed to estimate inputs of organic species to certain specific ocean areas (Atlas et al., 1986; Burns et al., 1985; Tateya et al., 1989; Villeneuve and Cattini, 1986; Masclet et al., 1988) as well as to the Great Lakes (Eisenreich, 1981; Eisenreich et al., 1981; Rice et al; 1986; Swackhamer and Armstrong, 1986). This chapter attempts to synthesize the available data base of synthetic organic compounds in the atmosphere and to extrapolate measurements from the marine atmosphere to obtain basin scale and global scale estimates of synthetic organic deposition to surface ocean waters.

CHOICE OF COMPOUNDS

The compounds selected for this study have been restricted to synthetic organic species for which there is a reasonable data base. In practice, this limits the choice of compounds to several classes of chlorinated hydrocarbon pesticides or industrial compounds. The compounds to be considered are discussed below; their formulae are shown in Figure 10.

POLYCHLORINATED BIPHENYLS (PCBs)

The PCBs have been widely recognized and studied as ubiquitous environmental pollutants. They have been used in the past as dielectric compounds, paint additives, in carbonless copy paper, and in a variety of other applications. Their open use is now restricted or banned in most areas, but the fate of existing stocks of PCB makes their distribution and transport a concern for years to come (Tanabe, 1988; Tateya et al., 1989).

The composition of PCB is quite complex, consisting of a possible 209 individual congeners. However, a much lower number of congeners (<50) is found in significant concentration in the environment. Nonetheless, the chemistry of "total" PCB is determined by the combined behaviour of the individual congeners. Thus, a rigorous treatment of PCB deposition should consider the entire suite of congeners. Unfortunately, there are insufficient data on the environmental distribution and chemistry of the individual congeners to allow one to apply this treatment at present, and for the purposes of this report such a rigorous treatment is unwarranted. The data available in the literature are commonly reported in one of several ways: as total PCB, as Aroclor equivalents, or as "light" or "heavy" PCB. For this report, we have chosen to subdivide environmental PCB as equivalent to Aroclor 1242 or Aroclor 1254. Based on existing data from

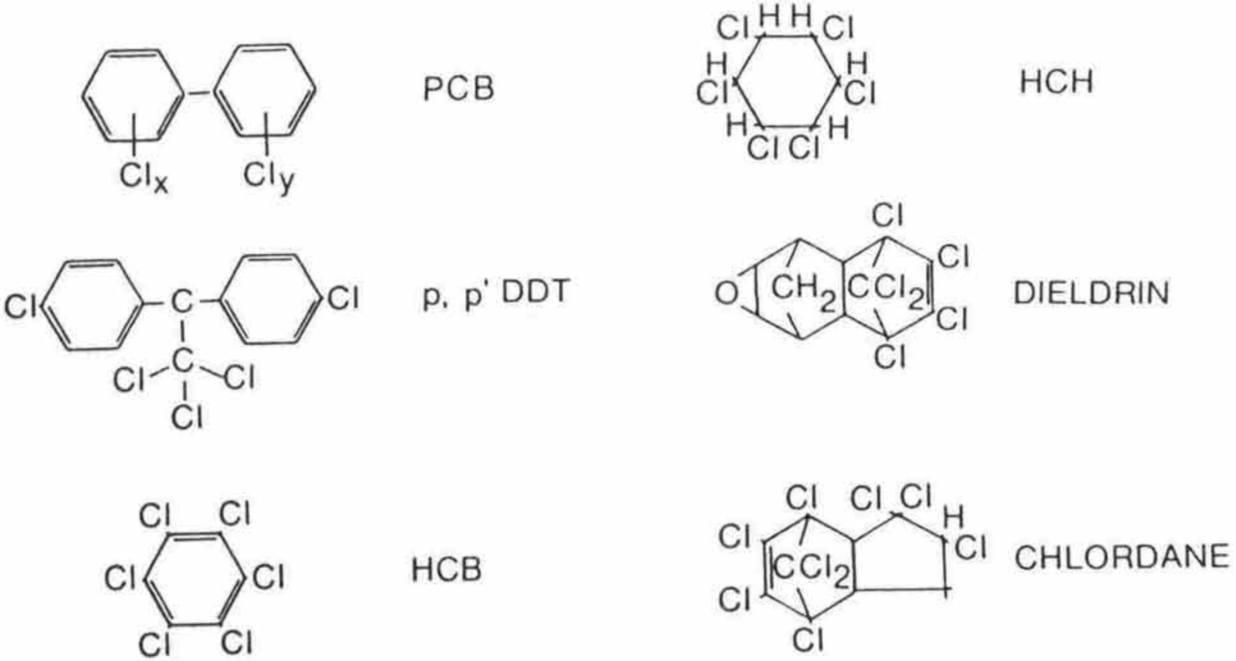

Figure 10. Structural Formulae of Synthetic Organic Organic Compounds Considered.

atmospheric samples (Atlas et al., 1986), we have uniformly partitioned total PCB into 60% Aroclor 1242 + 40% Aroclor 1254.

HEXACHLOROCYCLOHEXANES (HCHs)

The HCHs are a pesticide mixture, commonly referred to as BHC, which has been widely used in the past and which is still used in some parts of the world. Reports suggest that $>10^{11}$ g have been used and applied throughout Asia (FAO 1979; Colson, 1979; Tanabe et al., 1982b), and some estimates suggest that increased usage will be required in the future (Ray et al., 1985). Because of their intensive use, HCHs are typically the most abundant chlorinated hydrocarbon pesticide observed in marine atmospheres.

The technical HCH mixture contains several isomeric forms of hexachlorocyclohexane, as well as pentachloro- and heptachloro- components. Typically, the technical mixture is composed of 70% α-HCH, 7% β-HCH, 14% γ-HCH, and 10% other isomers. The γ isomer is the insecticidal component, lindane. In some areas, pure lindane or a mixture fortified with lindane is used in pesticidal applications. In this section, we will evaluate deposition of α-HCH and γ-HCH. These are the main HCH components reported in the marine atmosphere. Usually, data are given in terms of the individual species, and these data are used directly in our calculations. In some instances, total HCH is reported and an average partition between α- and γ-HCH is used for our calculations.

DDTs

The DDT group of pesticides and related metabolites (DDD and DDE) have been among the most intensively studied class of chlorinated hydrocarbons in the environment. Their use is banned in most areas of the world, but there is limited use in some areas. For example, Bidleman et al. (1988) compile data which indicate that 3×10^9 g of technical grade DDT was used in Mexico, Turkey, and India during 1982-1984. Ray et al. (1985) estimate that even larger quantities of DDT ($\sim 10^{10}$ g) may be required in India to meet food production targets. Also, traces of DDT compounds are still observed in marine, estuarine, and other organisms throughout the world (Tanabe et al., 1983; Subramanian et al., 1986; Wade et al., 1988; Sericano et al., 1989), though there is evidence of declining concentrations over the last decade (Addison and Zinck, 1986; Olsson and Reutergardh, 1986).

For this section, we will estimate the deposition of two major species most often reported in the atmosphere- p,p'-DDE and p,p'-DDT.

CHLORDANE AND DIELDRIN

Among the other chlorinated pesticides used throughout the world, the two compounds chlordane and dieldrin are most often reported in remote atmospheres (Atlas and Giam, 1981; Bidleman and Leonard, 1982; Bidleman et al., 1981). Past usage of these compounds is in the range of 10^9 to 10^{10} g yr^{-1}, though detailed information on the global pattern of usage is unavailable.

Technical grade chlordane used for pesticidal application contains several individual components, primarily cis- and trans- chlordane, and cis- and trans -nonachlor (Sovocool et al., 1977). Unless otherwise specified in the data base we have assumed chlordane reported is the sum of cis + trans chlordane, and we have treated this sum as a single compound. Data available on the chemistry of these two isomers suggests that this assumption will not introduce significant error in the deposition calculation. Nonachlor isomers are not included in the calculation.

CHLOROBENZENES

Chlorobenzenes containing 2-6 chlorine atoms per molecule have been measured in the atmosphere (Atlas and Giam, 1989). These compounds have a wide variety of uses, depending on the chlorine composition. Some chlorobenzenes are used in pigment synthesis and as intermediates in herbicide production (Guicherit and Schulting, 1985), while the more highly chlorinated benzenes are produced as fungicides but are also byproducts of solvent manufacture.

One of these chlorobenzenes, hexachlorobenzene (HCB), has been found to be one of the more abundant chlorinated hydrocarbons in the marine atmosphere. It is chemically stable in the atmosphere and it is widely distributed throughout the global troposphere. Only limited data are available on the concentration and distribution of the other chlorobenzenes. Thus, in this paper, we will consider only the deposition of HCB.

OTHER COMPOUNDS

There are other compounds and classes of organic chemicals whose deposition to the ocean is of interest, but which are not being considered in this chapter. These compounds include several chlorinated hydrocarbons, e.g., toxaphene, endosulfan, and halogenated dibenzodioxins and furans, as well as "soot" carbon and petroleum and polynuclear aromatic hydrocarbons. For the chlorinated hydrocarbons mentioned, we feel that there are insufficient data to estimate global or basin scale deposition rates. The same is true for polynuclear aromatic hydrocarbons (PAH) and soot carbon. There may be some relationship between >4 ring PAH (primarily found on particles), soot carbon, and "pollutant" aerosol (e.g., lead), at least in urban areas , but there are insufficient data to show that such a relationship is applicable to remote ocean areas. Degradation of PAH in the atmosphere may also confound such a relationship far from source areas. Furthermore, biomass burning can produce substantial quantities of PAH and soot carbon, but only negligible quantities of lead. No attention is paid here to low molecular weight (C_1 - C_3) organo-halogen compounds (e.g., chlorofluoromethanes, di- and per-chlorethenes, carbon tetrachloride) used as refrigerants, propellants and solvents.

There are somewhat more data available on high molecular weight alkanes in the marine atmosphere, but these data have already been evaluated by Duce and Gagosian (1982) to produce an estimate of atmospheric deposition of $>C_{10}$ alkanes to the global ocean. Further work, however, is necessary to evaluate inputs of the full range of petroleum-derived hydrocarbon compounds, but such an evaluation is beyond the scope of the present paper.

DATA SELECTION AND EXTRAPOLATION

We were struck by the paucity of data on which to base reasonable average concentrations of synthetic organic compounds over basin-wide scales and over time. To obtain the necessary spatial coverage, practically all data collected over the last decade were used (Table 25). This necessarily includes single measurements taken along cruise tracks as well as longer term measurements. Only in a few cases, e.g., at Bermuda, during SEAREX experiments, and at several Arctic sites, were there more than a few measurements taken over a season at a single location. This method of data utilization inevitably has problems. It is known, for example, that the source function for chlorinated hydrocarbons has varied in time and space over the last several decades due to restrictions on production and application. Also, analytical methodology has advanced so that more recent data may not be directly comparable to older data. In cases where more than one data set was available for a given location, the most recent data set was used for our calculation. Another problem associated with using all available data is that there are only a handful of research groups in the world making measurements of synthetic organic compounds in the remote atmosphere, and intercomparability of results between investigators has not been demonstrated. Thus, data from one group can skew the distribution of a particular compound over large ocean regions. Such a discrepancy was observed, for example, between the South Pacific and Indian Oceans for DDT compounds. In most cases, one data set has not been chosen over the other, but an attempt was made to smooth abrupt concentration gradients. In the case of DDT, calculations were also performed on a revised data set which was based on estimation of lower concentrations of DDTs in areas far from continental sources. This data set is referred to as DDT (rev). Certain other areas contained virtually no data (the South Atlantic was notably devoid of measurements), and best estimates for these areas are obtained by extrapolating or imposing data from adjacent ocean areas.

Table 25. Summary of Data Used to Construct Distribution of Chlorinated Hydrocarbons in the Marine Atmosphere. Data Listed Here are Average Concentrations. For Data Obtained on Cruises, Individual Measurements at Sample Mid-Points Were Used in the Grid

	Concentration ($pg\ m^{-3}$)						
Location	HCB	ΣHCH	ΣDDT	Chlordane	Dieldrin	PCBs	Ref
ATLANTIC/ARCTIC:							
North Atlantic	133	386	—	8*	8	–	1
North Atlantic	–	230	–	18	18	332	2
Barbados	150	390	4	9	5	57	3
Bermuda	111	240	26^^	10	8	–	2
Baltic Sea	291	553	–	–	–	–	4
North Sea	125	130	–	–	–	–	4
Gulf of Mexico	126	439	28	36	17	58**	5
South Atlantic	–	59	<105	–	–	<230	6
Brazilian Coast	–	<41	<15^	–	<7	<84	6
Arctic Ice Island	32	177	<1	<1.7	<6	<5	7
Norwegian Arctic	109	407	—	1.3*	–	–	8
Ellesmere Island	189	577	1.0	3.9	1.9	14	9
Ellesmere Island	147	385	5.2	6.3	0.6	17	9
Bear Island	40	390	—	–	–	17	10
Bear Island	111	237	—	1*	–	–	10
Canad. Arctic	–	–	—	3.9	–	–	11
Sweden	64	489	7.2	8.4	–	165	12
PACIFIC/INDIAN:							
Enewetak Atoll	100	260	<6	13	7.9	110	13
North Pacific (40N)	108	365	0.4^	6.8	1.9	32	13
Central N. Pacific	–	–	–	–	–	43	14
North Pacific	97	222	–	<4	<2	–	15
NW Pacific	–	424	257	–	–	<500	16
Bering Sea	–	1014	8	–	–	41	16,14
Southern Ocean	–	–	9	6	–	–	17
American Samoa	55	34	1.9	<1	1.1	11	13
Coastal Peru	63	11	2	1	4	12	13
New Zealand	61	26	<2.8	1.3	1.9	6	13
NW Pacific/Indian	–	1195	320	–	–	–	18
SW Pacific/Indian	–	320	262	–	–	–	18
Indian Ocean	–	–	60	18	–	–	17
Indian Ocean	–	350	–	–	–	–	19
Arabian Sea	–	–	75^^	7.8	3.9	–	19
E. Indian Ocean	–	–	–	–	–	150	14,18
W. Indian Ocean	–	–	–	–	–	160	20
Arabian Sea	–	3200	–	–	–	–	21
Red Sea	–	–	132^^	16	13	–	19
Antarctic	–	–	–	–	–	91	14,20
Antarctic(Showa Stn.)	–	80	20	–	–	61	14,20

* alpha chlordane only; **Aroclor 1254 only ; ^ p,p'-DDE only; ^^ p,p'-DDT only

Ref: 1) Atlas, unpublished data; 2) Knap, A.H., unpublished data; 3) Bidleman et al., 1981; 4) Reinhardt and Wodarg, 1988; 5) Chang et al., 1985; 6) Weber, R., unpublished data; 7)Hargrave et al., 1987; 8) Pacyna and Oehme, 1988; 9) Patton et al., 1989; 10) Oehme and Stray, 1982; 11) Hoff and Chan, 1986; 12) Bidleman et al., 1987; 13) Atlas and Giam, 1989; 14) Tanabe and Tatsukawa, 1986; 15) Kurtz and Atlas, unpublished data; 16) Tanabe and Tatsukawa, 1980; 17) Kawano et al., 1985; 18) Tanabe et al., 1982a; 19) Bidleman and Leonard, 1982; 20) Tanabe et al., 1983a

The data available suggested that, except near large sources, the concentrations of some compounds were relatively uniform within an ocean basin. Also, somewhat higher concentrations are observed along continental margins. This type of distribution is expected for the relatively long-lived, gas-phase chlorinated hydrocarbons examined in this report. Such an expected distribution allows reasonable extrapolation of concentrations over relatively large geographic areas.

Examples of data handling for specific compounds are:

HCHs

Most of the data were taken as reported and linearly interpolated. The concentration of HCHs over the Arctic Ocean was taken from recent measurements in the Canadian Arctic (Patton et al., 1989; Hargrave et al., 1987), and these were extrapolated into areas of the North Atlantic. The South Atlantic data were based on the South Pacific data of Atlas et al. (1986a) and Atlas and Giam (1989), and recent unpublished data from coastal Brazil (Weber, personal communication) suggests that this is a reasonable approximation. Reasonable coverage of the Indian Ocean and the central and western Pacific is obtained from cruise data of Tanabe et al., Bidleman and coworkers, and SEAREX experiments of Atlas et al. (See Table 25).

DDTs

Much of the data used for these compounds is based on collections in the late 1970s. There are only limited numbers of measurements obtained in the last few years, and these more recent measurements suggest lower concentrations of DDTs than observed earlier. Most of the DDT concentrations for the Western Pacific and Indian Oceans are based on reports of total DDT by Tanabe et al. (1982b). These authors suggest that of the total, 60% was p,p' DDT and 15% was p,p' DDE. This proportion was used to obtain individual species concentrations from the reported data. It is interesting to note that others have found higher DDE:DDT ratios in air samples away from sources of "fresh" DDT (Atlas et al., 1988). It is expected that as technical grade DDT degrades in the environment the volatilized pesticide will be more enriched in DDE (Rapaport et al., 1985). Thus it may be that the older observations of Tanabe et al. (1982b) reflected fresher sources of DDT to those ocean areas he was studying.

PCBs

The North Atlantic area had the best coverage for PCB concentrations. Most data were taken from Bidleman et al. (1981) and Knap (unpublished data). The South Atlantic contained only near coastal measurement of PCB. For the open ocean areas of the South Atlantic we used concentrations reported by Atlas and Giam (1989) for the South Pacific. Higher concentrations were used in grid boxes adjacent to a coastline. In the Pacific Ocean, data of Tanabe et al. (1982b) and Atlas et al. (1985) and Atlas and Giam (1989) were used to determine the concentration field.

HCB

Available measurements of HCB suggest that its concentration is relatively uniform within the northern or southern hemisphere. Even urban areas have concentrations of HCB that are within a factor of 2 - 3 of remote ocean regions. Thus, we felt comfortable in extrapolating HCB concentrations uniformly within ocean basins.

CHLORDANE AND DIELDRIN

The majority of data reported for chlordane and dieldrin applies to the North Atlantic and adjacent areas. Both compounds show the highest concentrations near the North American coast, and dieldrin concentrations are relatively high along the European coast. There are only a few reports of these compounds in the southern hemisphere (Atlas et al., 1986a; Atlas and

Giam, 1989). Concentrations from three South Pacific sites were fairly uniform, and these concentrations (1 pg m^{-3}) were extrapolated to other areas of the southern hemisphere.

DATA SOURCES - ATMOSPHERIC CONCENTRATIONS

Table 25 summarizes sources of data used for this report. Average concentrations are reported in the Table. However, when samples were collected along a cruise track, individual measurements were assigned to the appropriate data grid locations. Table 26 presents basin wide averages of organochlorine concentrations calculated from the measured and extrapolated data. The data used here are assumed to represent gas-phase concentrations of organochlorines, since most reports indicate that >95% of these compounds are measured as a gas in typical regions of the marine atmosphere.

Table 26. Mean Concentrations (pg m^{-3}) of Organic Compounds Calculated from Measured and Extrapolated Data Assigned to 10° x 10° Grids

	Atlantic		Pacific		Indian
Compound	North	South	North	South	
α - HCH	260	26	420	33	177
γ - HCH	53	3	126	18	71
HCB	126	60	102	60	60
Total PCB	290	33	96	33	117
Chlordane	14	1	9	1	3
Dieldrin	13	1	5	3	3
p, p' DDE	6	4	11	7	25
p, p' DDT	6	4	29	20	52
p, p' DDT (rev)	6	4	25	2	20

METHODS OF CALCULATION

Deposition processes for atmospheric organic compounds and their flux to the ocean have been discussed by Atlas et al. (1986b), Atlas and Giam (1986, 1989), Bidleman (1988), Bidleman et al. (1989), and Tateya et al. (1989). These studies emphasize the complexities and uncertainties involved in modelling the air-sea flux of synthetic organic species. Because the organic compounds discussed here have a particle and gas phase component in the atmosphere, an estimate of the air-sea flux necessarily incorporates all the uncertainties of dry and wet deposition of particles and gases. Still, it is useful to examine the specific deposition processes involved to determine the primary mechanisms of deposition and to estimate the magnitude of the air-sea flux. In a previous section, the theoretical background and equations necessary for computing air-sea exchange were discussed. The discussion that follows presents details of how the equations are applied to the specific compounds addressed here.

PARTICLE DEPOSITION PROCESSES

The first problem in assessing particle deposition of organic compounds is to estimate the fraction of each organic compound associated with particles and that fraction present as a gas in the ambient atmosphere. Even though the bulk of organochlorines are present as a gas, partitioning between gas and particle phases is critical in determining the mechanism and rate of deposition of an organic compound from the atmosphere. Recent reviews have discussed theoretical aspects of equilibrium partitioning of organic compounds onto atmospheric particles (Bidleman, 1988; Pankow, 1987). The theoretical partitioning has been described in terms of Langmuir adsorption isotherms or other parameterizations based on temperature, surface area, and/or total suspended matter. For present purposes, we have chosen to use the relationship proposed by Yamasaki et al. (1982) and Bidleman et al. (1986) which describe the relationship of adsorbed and gas-phase organic compounds based on field and laboratory observation. The equation is of the form:

$$\log [(Cg/Cp)(TSP)] = m/T + b \qquad (16)$$

where Cg = concentration of compound in the gas phase; Cp = concentration of compound in the particle phase; TSP = total suspended particle concentration; m and b = constants specific for each compound; and T = temperature (°K). The measured and extrapolated constants for each compound are given in Table 27. Even though the relationship has been developed during field experiments from different geographical locations, Bidleman (1988) cautions that (16) should only be considered valid for urban areas, until tests can demonstrate the applicability to clean continental or marine atmospheres. Pankow (1987), however, reformulates equation (16) in terms of vapour pressure, sorption sites on the aerosol, and the specific surface area of the aerosol particles. Thus, it appears that the relationship described by equation (16) may be useful for our calculation if differences in particle size (surface area) of an urban aerosol and the marine aerosol can be accommodated. In extending this relationship to other areas, we also recognize that we assume no specific or non-equilibrium partitioning between the chlorinated hydrocarbons and particular solid phases in the urban or marine aerosol.

Table 27. Slope and Intercept Values for Calculation of Gas/Particle Partitioning of Atmospheric Organic Compounds According to Equation 16 (from Bidleman et al., 1986)

Compound	Slope (m)	Intercept (b)
α - HCH	-2755	14.286
γ - HCH (Lindane)*	-2755	14.286
Chlordane	-4995	21.010
p, p' DDE	-5114	21.048
p, p' DDT	-5870	22.828
PCB (Aroclor 1254)	-4686	19.428
Dieldrin*	-5114	21.048
PCB (Aroclor 1242)*	assume = 0.2 x Φ_p calculated for PCB 1254	

* Values with asterisk are estimated based on comparison to suitable reference compound. Other values are reported based on observations in field and laboratory studies.

** The fraction of compound, Φ_p, associated with particulate matter is calculated from the equation:

$$\Phi_p = 1/\{1 + [10^{(m/T + b)}]/TSP\}$$

where: T = temperature in °K ; TSP = total suspended matter (or equivalent) in mg m^{-3}.

To do this calculation, we assume that the marine aerosol consists of three basic components: sea-salt aerosol, mineral aerosol, and "background" aerosol consisting mainly of small-particle sulphate aerosol from gas-particle conversion processes. Global distributions of sea-salt aerosol have been computed by Erickson et al. (1986), and mineral aerosol estimates have been generated in an earlier section of this paper. The background aerosol is assumed constant at 0.5 µg m^{-3} (Savoie, personal communication; Ayers et al., 1986). The estimated size and area distributions for these three particle groups are given in Table 28. Based on the particle characteristics given in this table, one can "normalize" the marine aerosol to obtain a total suspended particulate (TSP) concentration which can be applied to equation (16). The normalization is performed with the following equation:

$$\text{Corrected TSP}(\mu g\ m^{-3}) = [SO_4]\cdot 1.35 + [MA]\cdot 0.27 + [SS]\cdot 0.08 \qquad (17)$$

where SO_4 = background sulphate aerosol (non-sea salt), MA = mineral aerosol concentration, and SS = sea salt concentration. When this equation is applied to the model data grids, a distribution of aerosol concentrations is calculated which corresponds to aerosols with a uniform surface area of 11.2 $m^2\ g^{-1}$, equivalent to an average urban aerosol (Bidleman, 1988). The total concentrations of "corrected" TSP are in the range of 1 - 3 $\mu g\ m^{-3}$, compared to > 10 $\mu g\ m^{-3}$ for uncorrected TSP.

Table 28. Parameters Used to Normalize Marine Aerosol Distribution Based on Surface Area Characteristics*

Aerosol Type	Sulphate	Mineral	Seasalt
Median Diameter (μm)			
Mass	0.4	2.0	7.0
Surface	0.2	1.0	3.5
Number	0.05	0.25	0.87
Geometric Std. Dev.	2.3	2.3	2.3
Surface Area ($m^2\ g^{-1}$)	15.2	3.0	0.9
Correction Factor**	1.35	0.27	0.08

* Corrected total suspended matter (TSP') = 1.35 x $[SO_4]$ + 0.27 x [MA] + 0.08[SS]; $[SO_4] = 0.5\ \mu g\ m^{-3}$, mineral aerosol (MA) based on data grid in this report, sea salt (SS) concentration based on data calculated by Erickson et al. (1986).

** Correction factor based on average urban aerosol surface area of 11.2 $m^2\ g^{-1}$.

This calculation is strictly a practical method for obtaining a reasonable estimate of gas-particle partitioning over different conditions of temperature and particle loading over the marine atmosphere. More ideally, one would have directly measured particle-size information specifically related to organic pollutants. Given current technology and the trace concentrations of most species over the oceans, this type of data is not practically obtainable. However, some preliminary results from the Florida Keys (Atlas and Giam, unpublished) and data on particle size distribution of hydrocarbons (Ohta and Handa, 1985; Schneider et al., 1983; Sicre et al., 1987) suggest that most of the mass of the compounds will be associated with sub-micrometre particles.

The calculations of particle/gas partitioning were combined with the array of atmospheric concentration for each compound to obtain a concentration field of particle-bound organic species. These particles were then assumed to be scavenged by precipitation and deposited as dry deposition at rates equivalent to other compounds present on sub-micrometre particles (e.g., Pb). Actual data to evaluate particle scavenging and dry deposition are rare. Particle scavenging rates can vary depending on a number of meteorological and particle dependent processes. Data summarized by Bidleman (1988) for wet deposition of particle-bound organic compounds are given in Table 29.

In the Table the very low scavenging ratios of organic compounds in Portland (and probably Kiel) are likely related to a strong gradient in concentration between polluted surface-level air and air at rain-forming altitudes (Ligocki et al., 1985a and b). Other available data from rural or more remote areas suggest a reasonable range for particle scavenging of organic species may fall between 200 - 500. Once again, though, it needs to be emphasized that this scavenging ratio is a practical device to relate mean concentrations in rainfall to mean concentrations in surface level air. Any individual events or locations may show scavinging ratios far different from those described here. However, it is at least satisfying that the few measurements of particle scavenging of organic compounds are at least consistent with scavenging ratios of inorganic particulate species.

(Certainly, any large differences between organic and inorganic particles would need considerable explanation.)

Table 29. Measured Scavenging Ratios for Particle-Associated Organic Compounds

Compound Class	Location	Scavenging Ratio	References
n-Alkanes	College Station, TX	330 - 580	1
n-Alkanes	Portland, OR	13 - 22	2
n-Alkanes	Enewetak Atoll	>1000	3
n-Alkanes	Norfolk, VA	400 - 1600	4
PAH	Portland, OR	2 - 11	2
PAH	Isle Royale, MI	140 - 250	5
Phthalate Esters	Portland, OR	13 - 36	2
PCB	Kiel, FRG	30, 37	6
PCB, CHC	College Station, TX	500 (est'd)	1

Ref: 1) Atlas et al., 1988; 2) Ligocki et al., 1985b; 3) Zafiriou et al., 1985; 4) Farmer and Wade, 1986; 5) McVeety, 1988 ; 6) Duinker and Bouchertall, 1989.

There are fewer data available to evaluate dry deposition velocities of organochlorine compounds. Field measurements are often confounded by the potential for adsorption of gas-phase material, and there is the general difficulty of executing and interpreting measurements obtained in the field. Typical deposition velocities for a variety of semi-volatile organic compounds in continental areas range from 0.05 - 1 cm s^{-1} (Bidleman and Christensen, 1979; Bidleman, 1988), with a central tendency in the range of 0.1 - 0.2 cm s^{-1}. Data of Murphy et al. (1981) from Lakes Michigan and Huron suggest, though, that measurements of deposition velocities on the lake margin may be dominated by large-particle fluxes. Actual deposition rates in the center of the lake are smaller. Uncertainties in the actual size distribution of organic compounds adsorbed to the marine aerosol make extrapolation of particle dry deposition rates to open ocean areas just as problematical. Given the present state of knowledge, it seems reasonable to assume that the dry deposition rate of particle-associated organic matter in the marine atmosphere follows that of other "pollutant" aerosol (Pb). Since there may be some influence of larger mineral and sea-salt particles on the deposition of organic matter, and these larger particles have higher deposition rates, it is also reasonable to extend the possible range of deposition rates for organic particles up to 0.5 cm s^{-1}.

GAS-PHASE EXCHANGE PROCESSES

The basic equations which are applicable to modelling gas exchange processes were discussed earlier. It was shown that the flux of any gas is the product of the overall transfer velocity, K, and the disequilibrium between air and surface water concentrations. If a compound in the ocean is undersaturated with respect to the atmosphere, a net transfer of the gas-phase compound into the ocean will occur at a rate proportional to the degree of undersaturation. This simple relationship masks a highly complex phenomenon. For example, the transfer velocity for any particular compound is a function of its temperature-dependent Henry's Law Constant, Schmidt number, and water temperature. Wind-speed, wave formation, and bubble penetration are other factors affecting gas transfer in a complex way. To simplify the calculations here, the non-linear effects of wind speed on the exchange process have been eliminated. For all calculations in this section we assume a uniform wind speed over the ocean of 8 m s^{-1}. This assumption also allows one to use a uniform square root Schmidt number dependence for the liquid phase transfer velocity. Still, even with these simplifications, there are a number of uncertainties in the basic physical properties of the individual organic compounds and on their temperature dependent behaviour (see Table 30).

First we will examine the equations used to calculate the gas exchange flux and identify the assumptions and uncertainties in the different terms. Equation 2 is the one used to calculate the overall transfer velocity, that is,

$$1/K_w = 1/k_w + RT/H\,k_a \tag{2}$$

The overall transfer velocity (K) is calculated from the individual water and air transfer velocities (k_w and k_a), the Henry's Law Constant (H), the Gas Constant ($R=8.2 \times 10^{-5}$ m^3 atm deg^{-1} mol^{-1}), and the water temperature (T) in degrees K. The first term, k_w, is based on the exchange of CO_2 and needs to be corrected for temperature and diffusivity of the organic compound. This is done with the following relationship:

$$k_w\ (\text{organic}) = k_w(CO_2) \cdot [Sc(CO_2)/Sc(\text{organic})]^{0.5} \tag{18}$$

We have information on the temperature dependence of the Schmidt number for CO_2 (Liss and Merlivat, 1986) but not for the organic compounds of interest. Thus to make the calculation of k_w at any temperature, we assume that the ratio of the Schmidt numbers of CO_2 and the organic compound can be approximated as a constant which is equal to the ratio of their respective diffusivities in water. For the organic compounds here, the ratios of their diffusivity to that of CO_2 is approximately 0.2 (Atlas et al., 1982). To correct for temperature, we multiply k_w for CO_2 at 20°C and 8 m s^{-1} wind velocity (= 13.2 cm hr^{-1}, Sc=600) as follows:

$$k_w(T\,^\circ C) = k_w(20^\circ C) \cdot (600/Sc(T^\circ C))^{0.5} \tag{19}$$

Thus, the overall equation for calculating k_w of an organic compound at any temperature T is:

$$k_w\ (\text{organic}, T^\circ C) = k_w(CO_2, 20^\circ C) \cdot [D(\text{organic})/D(CO_2)]^{0.5} \cdot [600/Sc(T^\circ C)]^{0.5} \tag{20a}$$

$$= 13.2 \cdot (0.2)^{0.5} \cdot (600)^{0.5} \cdot (Sc(T^\circ C))^{-0.5} \tag{20b}$$

$$= 144.6 \cdot (Sc(T^\circ C))^{-0.5} \tag{20c}$$

The temperature dependence of the Schmidt number of CO_2 was estimated from a polynomial fit of the data given in Liss and Merlivat (1986, from the original data of Jahne, 1980). The Schmidt number of CO_2 from 0 - 40°C is given by:

$$Sc(T) = 1858 - 108.7 \cdot T\,(^\circ C) + 2.77 \cdot T(^\circ C)^2 - 0.026 \cdot T(^\circ C)^3 \tag{21}$$

The second term on the right-hand side of (2) represents the gas phase transfer resistance. The value for k_a was calculated according to equation (9). It should be noted that this equation produces less of a dependence on molecular weight than models of gas exchange reported elsewhere (Atlas et al., 1982; Smith et al., 1981). In effect, the equation used here shows that most of the resistance to gas transport is associated with turbulent exchange away from the air-water boundary layer rather than with diffusive exchange across the interfacial zone. In numerical terms, the typical k_a of an organic compound is only 10 - 20% less than that of water vapour. At 8 m s^{-1}, k_a of water molecules is 3200 cm hr^{-1} while that of an organic compound of molecular weight 300 is 2690 cm hr^{-1}. Earlier equations had suggested that k_a for high molecular weight organic compounds might be only 20 - 40% of the transfer velocity of water vapour.

More uncertainty is introduced into the calculation of transfer velocity through uncertainties in the Henry's Law Constant and its temperature dependence. Table 30 gives values of H adopted here, compared to reports in the literature relating to direct measurement of Henry's Law Constants and estimation of the constants based on vapour pressure and solubility determinations. In fact, this table represents only a fraction of the literature data judged to be the most representative. Reported or calculated values of Henry's Law Constants can range over orders of magnitude (e.g., see Callahan et al., 1979; or Suntio et al., 1987). In choosing values for H, we have preferred actual measurements over calculated constants. Otherwise, recommended constants or averages of Henry's Law Constants were used.

Table **30**. Summary of Physical Properties of Organic Compounds at 20-25°C*: Vapour Pressure (Solid, (p°S); Sub-Cooled Liquid, (p°L)), Solubility (S), and Henry's Law Constants (H) both reported in the literature and adopted here

Compound	p°S	p°L	S (ug l^{-1})	H (x 10^{-5} atm m^3 mol^{-1})	
	(10^{-3} pascals)			reported**	adopted
α - HCH	3.3	84	~2,000	0.85	0.46
γ - HCH	3.7	32	~6,500	0.12 - 0.23	0.23
HCB	1.5	186	5	7 - 81	81
trans-chlordane	0.52	3.9	56	5.9-8.9	7.5
cis-chlordane	0.40	2.9	---	---	---
p,p' DDE	0.35	1.7	1.2-120	7.8	7.8
p,p' DDT	0.021	0.17	<1 - 25	1.3-2.3	1.8
Aroclor 1254	10.2	1.9	45-70	28 - 70	28
Aroclor 1242	54	---	340-730	16 - 70	34
Dieldrin	0.40	---	195	1.1-3.2	2.0

* Literature references are from Fendinger and Glotfelty (1988), Suntio et al. (1987), Foreman and Bidleman (1987), Atlas et al. (1982, 1983), Callahan et al. (1979), Slater and Spedding, (1981), Murphy et al. (1987), and Bidleman (personal communication).

** Values listed as reported are based on actual measurements or those recommended by Suntio et al. (1987).

Given the relatively uncertain state of knowledge of Henry's Law Constants it is not surprising that even less information is available on the magnitude of the temperature dependence. Some measurements and theoretical calculations are available for PCB mixtures (Burkhard et al., 1985; Murphy et al., 1986; Tateya et al., 1988), but not for other organics considered here. Often, the temperature dependence of the Henry's Law Constant is given in the form:

$$\ln H = A + B/T \qquad (22)$$

The slope of this equation, B, defines the temperature dependence. Table 31 lists data on the temperature dependence of selected organic compounds. Based on these data, we have chosen to apply an average of B = -7750 (based on PCB) to other high molecular weight organic compounds. After these calculations were complete, new measurements and calculations became available on the temperature dependence of HCHs and several other high molecular weight organic compounds (Hinckley and Bidleman, personal communication). These data are shown in Table 31. From these data it appears that the temperature dependence of the Henry's Law Constant may be similar (within 25%) for several different classes of high molecular weight organic compounds, and the initial value chosen for these calculations may be appropriate for the compounds being considered here. However, more direct measurements of Henry's Law Constants for specific compounds over the temperature range from -2 ° to 40°C are still needed.

To calculate H(T) at any temperature, we applied the following equation:

$$H\,(T) = H(T_{ref}) \cdot e^{B(1/T\,-\,1/T_{ref})} \qquad (23)$$

where T is the temperature of interest, T_{ref} is the temperature at which the Henry's Law Constant, H, is determined (usually 293 or 298 °K), and B is the slope from Equation 22 (= -7750). Approximately a factor of 2 change in Henry's Law Constant occurs for a temperature change of 8°C.

Table 31. Temperature Dependences of Henry's Law Constants of Selected Organic Compounds Based on Equation (22)

COMPOUND	SLOPE (B)	REFERENCE
PCB	-7868	Tateya et al. (1988)
PCB 1242	-7346	Burkhard et al. (1985)
PCB 1254	-8060	Burkhard et al. (1985)
Biphenyl	- 6166	Hinckley and Bidleman (pers. comm.)
4-Chlorobiphenyl	-7517	Hinckley and Bidleman (pers. comm.)
2,2',4,5,5' PCB	-7308	Hinckley and Bidleman (pers. comm.)
2,2',3,3',5,5',6,6' PCB	-6122	Hinckley and Bidleman (pers. comm.)
Decachlorobiphenyl	-6629	Hinckley and Bidleman (pers. comm.)
α-HCH*	-7329	Hinckley and Bidleman (pers. comm.)
γ-HCH*	-7329	Hinckley and Bidleman (pers. comm.)
Naphthalene	-5947	Hinckley and Bidleman (pers. comm.)
Fluorene	-6664	Hinckley and Bidleman (pers. comm.)
Anthracene	-5770	Hinckley and Bidleman (pers. comm.)
Phenanthrene	-7242	Hinckley and Bidleman (pers. comm.)
Fluoranthene	-5378	Hinckley and Bidleman (pers. comm.)
Pyrene	-6701	Hinckley and Bidleman (pers. comm.)
C_2Cl_4	- 5119, -4622	Lincoff and Gossett(1984)
$CHCl_3$	-4180, -4322	Lincoff and Gossett(1984)
$CHCl_3$	-3649	Hunter-Smith et al. (1983)
CCl_4	-3230	Hunter-Smith et al. (1983)
Dimethyl Sulphide	-3547	Dacey et al. (1984)

Hinckley and Bidleman (pers. comm.) is a compilation by H. and B. of existing data and also includes their own experimental results.

*Measurements in seawater.

Henry's Law Constants also enter into the calculation of gas exchange processes in the determination of the saturation state of seawater. Thus the concentration in surface seawater in equilibrium with the atmosphere, C_{eq}, is calculated from:

$$C_{eq}(\text{seawater}) = C_g(\text{air}) \cdot [RT/H(T^\circ C)] \tag{24}$$

where C_g(air) is the concentration of gas phase organic in the atmosphere and the Henry's Law terms are defined as before. The same equation applies to calculating the equilibrium concentration of an organic compound in rainwater at temperature (T°C). To correct for the salting out effect of organic compounds in seawater, we decrease H determined in distilled water by 20%. This reduction in H is driven by a decreased solubility of organic compounds in seawater versus distilled water.

The factors which result from equations relating to gas exchange are summarized in Table 32. This table shows typical gas exchange constants for different compounds in the ocean basins and the estimated concentration of organic compounds in seawater at equilibrium with the atmosphere. In terms of gas or liquid phase control of exchange (equation 2), our calculations show that HCB is mostly liquid-phase controlled, HCHs are mostly gas-phase controlled, and all other compounds have signficant resistances to exchange in both gas and liquid phases, as shown in Table 32. It should be realized in evaluating the data in Tables 32 and 33 that the gas transfer velocities and the relative importances of gas and liquid phase resistances will be a function of temperature and wind speed.

Table 32. Contribution of Gas and Liquid Phase Resistances to Overall Transfer Velocity of Selected Organochlorine Compounds (at T = 20°C, wind speed = 8 m s^{-1})

COMPOUND	TRANSFER VELOCITY ($cm\ hr^{-1}$)	RESISTANCE % GAS	RESISTANCE % LIQUID
α-HCH	0.47	92	8
γ-HCH	0.25	96	4
HCB	5.54*	6	94
PCB 1254	4.97*	16	85
PCB 1242	5.11*	13	87
trans-Chlordane	3.47	41	59
Dieldrin	1.62	73	27
p,p'-DDE	3.52	40	60
p,p'-DDT	1.50	75	25

* at 25 °C

The final calculation of flux multiplies the overall transfer velocity (K_w) with the difference in concentration between actual seawater concentration and that in equilibrium with the atmosphere. This seemingly simple calculation brings another level of uncertainty to the estimate of gas flux. There are extraordinarily few data on the concentration of high molecular weight organochlorines in open ocean seawater which can be used to assess the saturation state of surface seawater. Some of the few data available are listed in Table 33. These data suggest that, on average, surface seawater may be near equilibrium with the atmosphere. However, there are really too few data on which to make this judgement. Also, interactions occurring between organic compounds and particulate or colloidal matter in seawater make the saturation state of seawater even more uncertain (Atlas and Giam, 1986; Caron et al., 1985; Whitehouse, 1985).

In spite of these difficulties, we will make several assumptions regarding gas exchange to allow a reasonable estimate of the magnitude of the deposition process. Given the fact that the organochlorines discussed in this report have been cycling in the environment for several decades (at least), it seems reasonable to assume that atmosphere-ocean interactions have reached some sort of quasi-steady state situation. If organochlorines behave as inert gases, such as chlorofluorocarbons, then certainly one would expect equilibrium with surface waters to be reached in a relatively short time. At a transfer velocity of 4 cm hr^{-1} (see Table 32), organochlorines dissolved in the upper 100m of the ocean equilibrate with the atmosphere approximately 3 times per year. Thus, the surface ocean is in a very dynamic equilibrium with the atmosphere. Transient conditions of atmospheric concentrations, temperatures, and ocean dynamics may result in local regions of gas phase disequilibrium. Under these transient conditions, the ocean may be a sink or a source of organochlorine compounds. However, when averaged over suitably long intervals (months to years), net gas deposition of organochlorines into the ocean is probably controlled by processes in the water column which remove the compounds to the deep ocean. These processes include sedimentation and mixing with undersaturated water deeper in the water column. To what extent these processes influence the magnitude of gas exchange can only be guessed now. Atlas et al. (1986) suggested that these processes might limit gas exchange to only 5% of the maximum rate. Studies based on transient tracer species, such as tritium, indicate mixing processes which might double this rate (Broecker and Peng, 1982). For the purposes of this report, we will use a "best" estimate of net gas deposition equal to 10% of the maximum rate. In other words, we are assuming that "average" seawater is 90% saturated with respect to organochlorines in the atmosphere. We acknowledge that there is little evidence on which to base this estimate, and we suggest that further measurement and modelling studies are required to elucidate the process.

Table 33. Calculated Gas Deposition Factors: K_w = Overall Gas Transfer Velocity ($cm\ hr^{-1}$) and Seawater Concentration in Equilibrium with the Atmosphere ($pg\ l^{-1}$)

Compound	Atlantic		Pacific		Indian	
	North	South	North	South		
k_w ($cm\ hr^{-1}$)						
α - HCH	0.32	0.31	0.47	0.35	0.46	
γ - HCH	0.17	0.16	0.25	0.18	0.24	
HCB	4.1	4.0	4.8	4.3	4.8	
PCB(1254)	3.3	3.2	4.0	3.5	4.0	
PCB(1242)	3.5	3.4	4.2	3.6	4.2	
Chlordane	2.4	2.3	3.1	2.5	3.0	
Dieldrin	1.1	1.1	1.5	1.2	1.5	
DDE	2.5	2.4	3.1	2.6	3.1	
DDT	1.0	0.98	1.4	1.1	1.4	
Sat'd Seawater ($pg\ l^{-1}$)						**(measured)***
α - HCH	1880	300	2600	310	520	300->2000
γ - HCH	1020	70	1400	430	561	20 - 600
HCB	9	6	6	6	4	6 - 100
PCB(1254)	48	9	12	8	16	--
PCB(1242)	40	7	10	7	13	--
Total PCB	88	16	22	15	29	<3 ->200
Chlordane	7	1	4	1	1	1 - 7
Dieldrin	23	4	5	7	5	<2 - 11
DDE	2	2	2	5	5	--
DDT	10	11	19	6	32	1 - 30

* Data from DeLappe et al., 1983; Burns et al., 1985; Tanabe et al., 1982a and b; Kurtz and Atlas, unpublished data; and Hargrave et al., 1987.

FLUX ESTIMATES

Calculations of deposition of organochlorine compounds were performed covering a range of conditions. Dry deposition of particles was assumed to range from 0.05 - 0.5 cm s^{-1}. A "best" estimate was 0.1 cm s^{-1}. Because of major uncertainties regarding particle size distribution and extent of gas-particle partitioning, no additional refinements to deposition velocity, e.g., in pericontinental areas, were added to the calculation. Dry deposition of gas was calculated using the Henry's Law Constants in Table 30 and the same temperature dependence for each compound was assumed. Annual average sea surface temperatures were used for the calculation in each grid box. Since wet deposition may be dependent on equilibration at rain-forming altitudes (Bidleman, 1988; Ligocki et al., 1985a), two different sets of assumptions were used. One assumed that rain equilibrated with particles and gases at an altitude that was 15°C cooler than sea surface temperature. Assuming a standard lapse rate, this corresponds to about 2 km altitude. At this altitude, the compound has a greater solubility in rain and also a greater fraction of the compound is adsorbed to particles. The second assumption was that rain equilibrated with organic compounds at the temperature of the sea surface. Scavenging ratios ranged from 200 to 1000. A "best" estimate of wet deposition used the cooler temperature with a scavenging ratio of 200.

RESULTS

In spite of all the caveats, assumptions, and uncertainties in our estimates, we think that the calculations performed here are a reasonable representation of the total deposition of organochlorines to the world ocean. Different observed features of the deposition of organochlorine compounds are reasonably simulated in our calculations. The calculations provided a "best" estimate of the deposition of each organochlorine compound in each ocean basin. Table 34 summarizes these calculations as total deposition (x 10^6 g yr^{-1}) and flux (μg m^{-2} yr^{-1}). The geographical mean flux distribution of the calculated fluxes of ΣHCH and ΣPCB are shown in Figures 11 and 12.

Table 34. Summary of Total Deposition (x 10^6 g yr^{-1}) and **Mean Flux (μg m^{-2} yr^{-1})** of Organochlorine Compounds to the Oceans

Compound	Atlantic		Pacific		Indian	Total Deposition
	North	South	North	South		**Mean Flux**
ΣHCH	851	97	2640	471	698	4754
	15.5	**1.9**	**29.5**	**4.3**	**10.3**	**12.7**
HCB	16.8	10	19.9	18.9	11.4	77.1
	0.31	**0.20**	**0.22**	**0.17**	**0.17**	**0.23**
Dieldrin	16.6	2.0	8.9	9.5	6.0	42.9
	0.30	**0.04**	**0.10**	**0.09**	**0.09**	**0.11**
ΣDDT	15.6	14.0	66.4	25.7	43.3	165
	0.28	**0.27**	**0.74**	**0.23**	**0.64**	**0.44**
Chlordane	8.7	1.0	8.3	1.9	2.4	22.1
	0.16	**0.02**	**0.09**	**0.02**	**0.04**	**0.06**
ΣPCB	99.7	13.8	35.5	29.1	52.1	239
	1.81	**0.27**	**0.40**	**0.26**	**0.77**	**0.64**

Since major sources of organochlorine compounds are in the Northern Hemisphere, it is not surprising that our calculations show that a majority of the deposition of these compunds is to the North Atlantic and North Pacific Oceans. Because of the different sources and transport of compounds over the ocean basins, different compounds predominate in different ocean basins. For example, HCH and DDT compounds have the greatest deposition rates in the North Pacific. This deposition is largely influenced by sources of these compounds on the Asian continent. PCBs and dieldrin have higher deposition rates in the North Atlantic than in the North Pacific. This difference appears to be related to proximity of sources of these compounds in Europe and North America. Chlordane and HCB have somewhat higher deposition rates over the North Atlantic,but total deposition of these two compounds is approximately the same in the North Atlantic and the North Pacific.

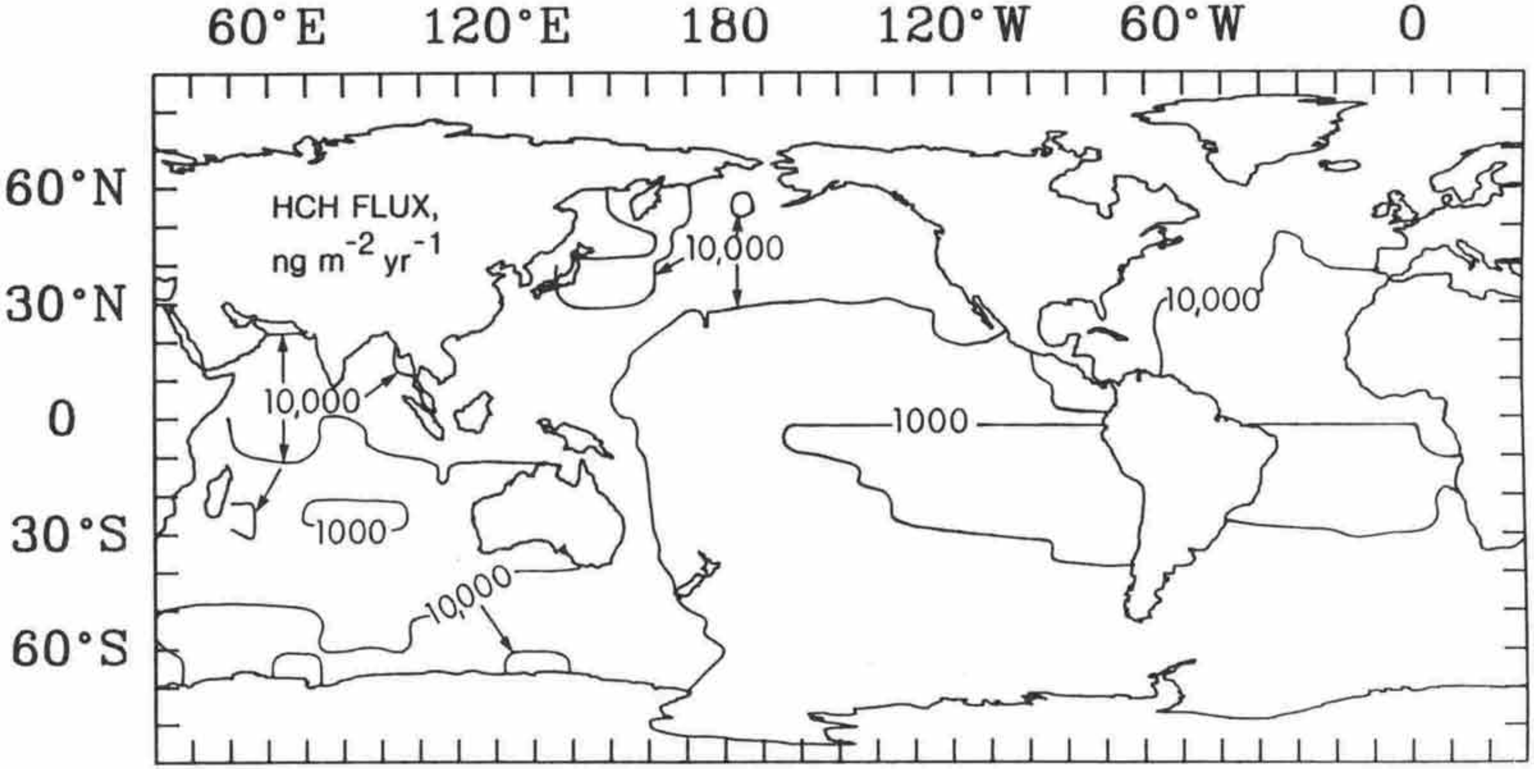

Figure 11. Global Fluxes of HCHs to the Oceans in ng m^{-2} yr^{-1}.

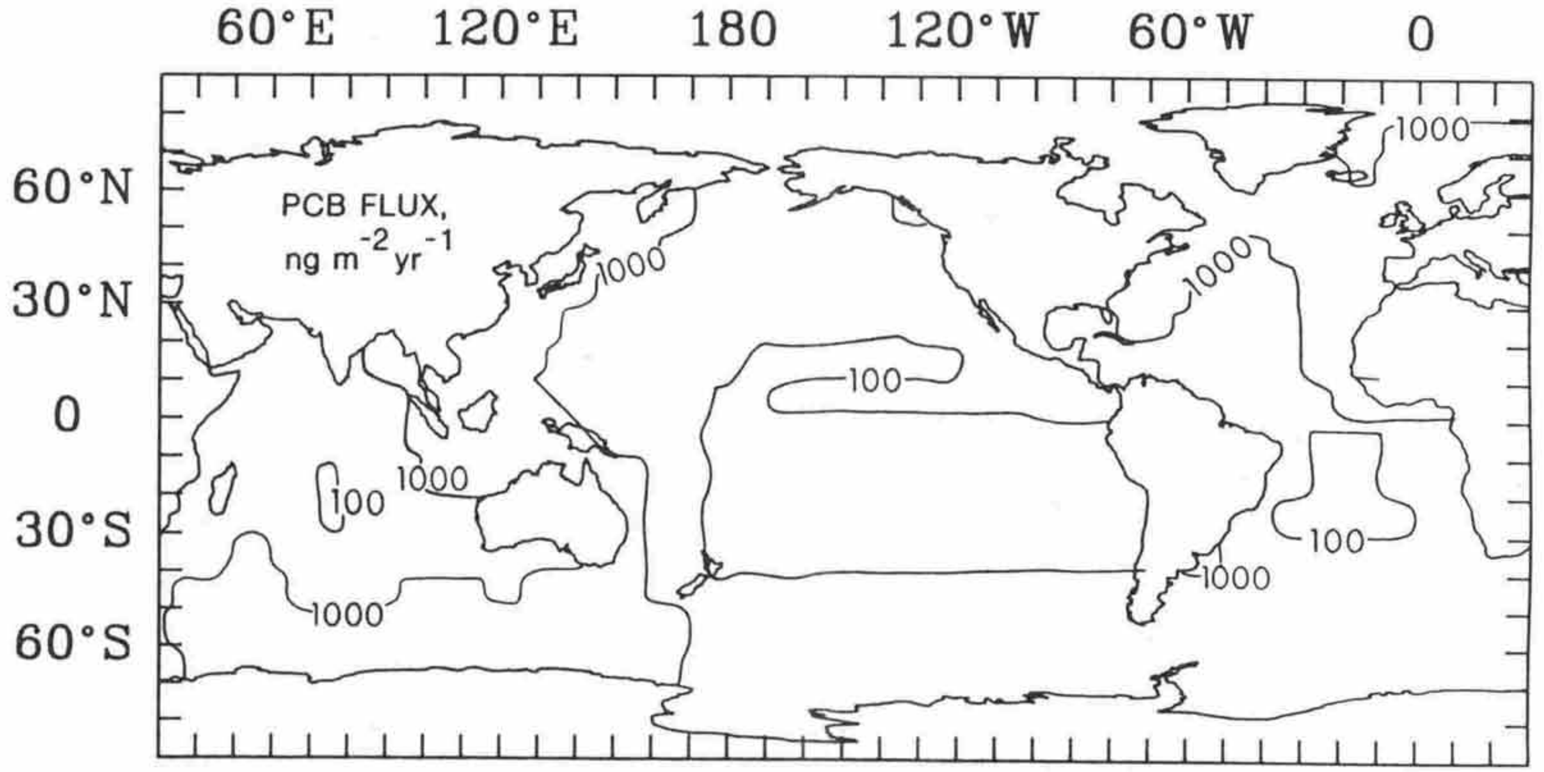

Figure 12. Global Fluxes of PCBs to the Oceans in ng m^{-2} yr^{-1}.

In this section, the Indian Ocean is treated as a single basin, and no distinction is made between the Northern Indian and Southern Indian Ocean. However, we note that high atmospheric concentrations and fluxes of HCHs, DDTs, and PCBs have been reported in the coastal region off India (Bidleman and Leonard, 1982; Tanabe and Tatsukawa, 1980; Tanabe et al., 1982a and b). Our calculations also indicate over an order of magnitude higher fluxes of organochlorine compounds in some areas adjacent to India compared to the interior of the Southern Indian Ocean. Further, there have been reports of high concentrations of organochlorine pesticides in the rivers of Southern India (Tanabe, pers. comm). Thus, in addition to atmospheric deposition, runoff and river drainage also may be an important route for pesticide inputs to the Northern Indian Ocean area.

Table 35. Estimates of Deposition Mechanisms of Organochlorines to the World Oceans (Expressed as % of Total Deposition)

	Particle		Gas	
Compound	Dry	Wet	Dry	Wet
α - HCH	<0.1	0.1	38.4	61.5
γ - HCH	<0.1	<0.1	22.8	77.1
HCB	0.1	2.2	85.1	12.6
Dieldrin	0.3	12.6	54.1	33.1
p, p' DDT(rev)	0.7	34.1	44.9	20.4
p, p' DDE	0.4	20.8	63.6	15.2
Chlordane	0.2	9.5	72.2	18.1
ΣPCB	0.6	22.8	65.3	11.3

Calculations also show that the mechanisms of exchange differ between individual organochlorine compounds, although there are some broad similarities (Table 35). In all cases, the magnitude of direct gas exchange across the sea surface is uncertain. However, given the assumptions described above, even a limited rate of gas exchange can provide an average of 25 - 85% of the total exchange for organochlorine compounds. Direct dry deposition of particle-bound organic material is a minor component of the deposition of all compounds considered here. There may be situations of high particle loading and low rainfall where particle dry deposition may be more important, but on average dry deposition is <5% of the total particle deposition. The primary differences in deposition mechanisms between compounds occurs in wet deposition. Particle scavenging by precipitation is most significant for PCB and DDT compounds; gas scavenging is the predominant mechanism removing HCH compounds in rain. Particle scavenging accounts for 15 - 30% of the wet deposition of the other organochlorines.

While these estimates provide a guideline for comparing compounds and obtaining total deposition rates, it should be remembered that the relative importance of mechanisms described here is dependent on the various assumptions used in the calculation. A factor of two error in the gas-particle partition coefficient or the Henry's Law Constant can change the relative importance of particle vs gas scavenging. Still, there are various checks we can make on our calculations to evaluate how appropriate they are for estimating deposition to the oceans.

To check the calculations of deposition rates, we can make several comparisons with existing data. The first check compares estimates of the predicted wet deposition with actual measurements of organochlorine compounds in rain water at specific sites in the model grid (Table 36). For this comparison we use only measurements of rain at remote marine locations. Thus, there are only a few sites available for comparison. These include the four SEAREX sites in the Pacific Ocean, one site at Bermuda, and an average of several samples taken during a research cruise in the Indian Ocean. With the exception of HCH, most organochlorine compounds are below detection in marine rain. The low levels of most organochlorines is consistent with model calculations. For the more abundant HCH, there is generally excellent agreement between observed and predicted concentrations in the Pacific and Indian Oceans. Our model calculation (based on a scavenging ratio of 200 and assuming equilibration at surface temperature minus 15°C) tends to overestimate HCH concentration in rainfall at Bermuda, but to underestimate the chlordane and dieldrin concentration there. Better agreement for HCH at Bermuda is obtained when we assume equilibration at sea surface temperature.

Table 36. Comparison of Measured Rainfall Concentration (pg l^{-1}) at Specific Locations **(bold type)** with Model Predictions (based on surface temperature minus 15°C and scavenging ratio = 200)

	NORTH PACIFIC		SOUTH PACIFIC		INDIAN	ATLANTIC
Compound	N. Pacific	Enewetak	Samoa	New Zlnd.	Indian Oc.	Bermuda
α - HCH	6400	2435	375	765	3800	4439
	6300	**3100**	**320**	**450**	**5000**	**854**
γ - HCH	1240	292	47	61	1300	1030
	1900	**510**	**30**	**--**	**1100**	**126**
HCB	23	9	7	19	6	24
		<30		**<30**		
Total PCB	47	66	7	13	64	468
		<600	**<200**			
Dieldrin	11	20	3	17	11	46
		<20				**158**
Chlordane	11	9	1	3	3	17
		<20	**<30**			**77**
DDE	2	2	1	6	4	11
		<20				
DDT (rev)	13	12	5	21	30	40
		<20		**<20**		**<310**

The second check we can make is to compare our estimates of deposition rates with other direct or indirect measurements of deposition to water bodies or other surfaces (Table 37). For most of the cases available for comparison, the measurement describes only net deposition rates. When applied to sedimentation, deposition rates describe only that fraction of the total deposition which becomes attached to sinking particles. Accumulation in peat bogs is probably best compared to wet deposition rates; gas exchange at peat forming layers in the bog may not be significant (Rapaport et al., 1988). Overall, the comparison between estimated deposition rates for the North Atlantic and deposition rates measured at other Northern Hemisphere sites is surprisingly good. There is a suggestion in the data that maximum flux rates, i.e., those assuming maximum gas exchange, will overestimate the net flux of organochlorines to the oceans. A more reasonable comparison is obtained using a limited rate of gas dry deposition.

Finally, a comparison is made between the magnitude of the atmospheric input of organochlorines to the oceans to the global amount from riverine input (Table 38). There is, however, a lack of data on organochlorine inputs to the world ocean from large river systems. The data situation for organochlorines in major rivers is much worse than for the marine atmosphere. A recent report (GESAMP, 1987) also noted the lack of data on anthropogenic organic compounds in rivers. River data in Table 38 were taken from Atlas and Giam (1986). They assumed that upper limits for "global average" riverine concentrations were 1 ng l^{-1} for PCB and HCH and

0.1 ng l^{-1} for other organochlorines. For these cases, atmospheric input is the dominant mechanism of deposition of organochlorine compounds to the world ocean. However, for the reasons already discussed, it is important to recognize that such a comparison is very crude.

Table 37. Comparison of Estimated and Measured Deposition of Chlorinated Hydrocarbons (μg m^{-2} yr^{-1}). Calculated Fluxes **(bold type)** in this Table Include the Maximum Range and "Best" Estimate (in brackets) of the Flux

Compound	Flux	Location	Reference
ΣPCB	0.1 - 4.0	N.E. US PEAT CORES	1
	0.8 - 3.1	RURAL WISCONSIN LAKES	2
	1.6	N. ATLANTIC SED. TRAP	3
	0.57-13.6 (1.8)	**N. ALANTIC, CALCULATED**	**this work**
HCB	0.03- 0.4	N.E. US PEAT CORES	1
	0.24	MEDIT. SEA RAIN	4
	0.04-2.8 (0.31)	**N. ATLANTIC, CALCULATED**	**this work**
ΣDDTS	0.4 - 1.5	N.E. US PEAT CORES	1
	0.33	CENTRAL MINNESOTA SNOW	5
	0.97	MEDIT. SEA SED. TRAP	6
	1.6	MEDIT. SEA - RAIN	4
	0.15-1.5 (0.28)	**N. ATLANTIC, CALCULATED**	**this work**
Chlordane	0.02	N. ATLANTIC SED. TRAP	3
	0.044-1.25 (0.16)	**N. ATLANTIC, CALCULATED**	**this work**
Dieldrin	0.04	N. ATLANTIC SED. TRAP	3
	0.14-1.9 (0.32)	**N. ATLANTIC, CALCULATED**	**this work**
Lindane	0.97	MEDIT.SEA SED. TRAP	6
	2.4	MEDIT. SEA- DRY DEPOSITION	4
	7.5	G. BRITAIN-N. SEA RAIN	7
	3.2-13.2 (4.2)	**N. ATLANTIC, CALCULATED**	**this work**

Ref: 1) Rapaport and Eisenreich, 1988; 2) Swackhamer and Armstrong, 1986; 3) Knap et al., 1986; 4) Villeneuve and Cattini, 1986; 5) Rapaport, 1985 (cited in [1]); 6) Burns et al.,1985; 7) Wells and Johnstone, 1978.

Table 38. Comparison of Atmospheric and Riverine Input Rates of Organochlorine Compounds to the World Oceans (x 10^{6} g yr^{-1})

Compound	Atmospheric	Estimated Riverine	% Atmospheric
ΣHCH	4754	40 - 80	99
HCB	77.1	4	95
Dieldrin	42.9	4	91
ΣDDT	165	4	98
Chlordane	22.1	4	85
ΣPCB	239	40 - 80	80

REGIONAL SEAS

In this section, we attempt to estimate the atmospheric input of high-molecular weight organic compounds into regional seas adjacent to the European continent, i.e., the North, Baltic, and Mediterranean Seas. As one might expect, there are numerous difficulties and uncertainties involved in such an estimation. The first problem is to estimate a reasonable concentration of pollutants in the atmosphere over each basin. This estimate is complicated by the scarcity of actual concentration measurements of organic pollutants and by the large variation of concentrations of individual chemical compounds near source areas (e.g., Duinker and Bouchertall, 1989; Guicherit and Schulting, 1985). Furthermore, the potential source areas of organic pollutants which can be deposited from the atmosphere include a radius of several 100s to 1000s of km around each basin (Van Aalst et al., 1982). The physical properties of organic pollutants may also be variable near source areas surrounding the basins. For example, the partitioning of compounds between gas phase and particle phase may be influenced by soot or other aerosol components, and the size range of particle-associated organic pollutants will change depending on source characteristics (Van Vaeck et al., 1979). These differences may cause large changes in deposition rates of organic pollutants. Unfortunately, there are few data available in appropriate geographical areas surrounding the regional seas to sufficiently estimate the temporal and geographical variability in all parameters necessary to calculate deposition (Van Aalst et al., 1982). Thus, there is a large uncertainty in the fluxes and depositions calculated here. Because the regional seas considered may receive inputs of organic pollutants from the same sources and because of the scarcity of data, we will use a common base of atmospheric concentrations to calculate fluxes to the different basins.

Data available on concentrations of organic pollutants in the European atmosphere are given in Table 39 (see Table 25 to compare with remote data). These data emphasize the degree of variation observed in organic pollutants throughout Europe. In particular, there appears to be a great deal of variation in the concentration of γ-HCH (lindane). Some sites indicate that lindane is the single most abundant organochlorine, while other regions, such as Sweden, show that α-HCH is the main HCH isomer in the atmosphere. The differences in HCH concentrations and composition presumably reflect proximity to regions where lindane is currently in use. The concentrations of organic compounds selected for purposes of calculation here are also given in Table 39. Comparing the range of concentrations measured on the coasts of the North and Baltic Seas with values for the open ocean and for an inland site (Ulm) shows that concentrations of pesticides measured at coastal stations at times approach levels measured on the open ocean, but are otherwise more indicative of air masses from land.

Table 39. Concentration of Organic Pollutants in Air Near Regional Seas - Mediterranean, Baltic, and North Seas. Concentrations given in pg m^{-3}

Compound LOCATION		α-HCH	γ-HCH	ΣHCH	ΣDDT	PCBs	Dieldrin	Chlordane	HCB	Ref.
North Sea:	(min.)				10					1
	(max.)				20					
Delft	(avg.)	250	360	610	148	960	73	–	100	2
	(max.)	1200	3400	4600	1060	3050	370	–	480	
Off Noordwijk	(min.)	20	20	40					20	3
	(avg.)	70	60	130					200	
	(max.)	250	7000	7250					450	
Baltic Sea:										
Kiel	(min)					300				4
	(avg.)					1940				
	(max.)					3310				
Off Kiel	(min.)	100	20	120					50	5
	(avg.)	236	317	553					290	
	(max.)	900	2000	2900					1000	
Sweden	(min.)	189	21	210	0.6	23		2.4	18	6
(Aspvreten)	(avg.)	690	207	897	15	341		11	67	
	(max.)	3250	660	3910	100	1190		15.2	165	
Open Baltic Sea				200	250					7
Mean, North and										
Baltic Seas	(min).	103	20	123	53	162		2.4	29	
	(avg.)	312	236	478	138	1080	73	11	164	
	(max.)	1400	3270	4670	395	2520	380	15.2	524	
For comparison:										
Ulm, FRG	(avg.)	570	2400	2970	25	830				8
	(max.)	1300	11000	12300	59	2600				
Mean North Atlantic (from Table 25)				362	11	74	8	9	115	
Estimated for for this report.		350	350	700	40*	750	75	10	250	

*p,p'-DDE + p,p'-DDT only.

Ref: 1) Dawson and Riley, 1977, 2) Guicherit and Schulting, 1985; 3) Reinhardt and Wodarg, 1988a, 4) Duinker and Bouchertall, 1989; 5) Reinhardt and Wodarg, 1988b, 6) Bidleman et al., 1987, 7) Korolev, 1984, 8) Wittlinger and Ballschmiter, 1987.

To estimate the flux of organic compounds to the regional seas we use the same calculation procedures described earlier for the global ocean. The appropriate parameters are given in Table 40.

Table 40. Parameters used to Calculate Flux of Organic Compounds to Regional Seas

	North Sea	Baltic Sea	Mediterranean Sea*
Sea surface temp. (°C)	10	10	20
"Corrected" TSP (μg m^{-3})	3.2	3.2	3.2
Rainfall (mm yr^{-1})	685	620	335
Area (x 10^5 km^2)	5.25	4.15	5.0
Scavenging Ratio	200	200	200
Particle Vd (cm s^{-1})	0.1	0.1	0.1

*Northwest Mediterranean only.

In Table 41 the total deposition fluxes we calculate are compared to actual measurements of atmospheric fluxes and to sedimentation rates of organic pollutants. The range of calculated fluxes is caused by the temperature dependence of precipitation scavenging processes and by differences in rainfall amounts between the seas. The higher calculated flux is typical of the North and Baltic Seas, while the lower flux is calculated for the Mediterranean. Even though the atmospheric concentrations are selected to be the same over all basins, the flux calculated for the northwestern Mediterranean is lower because of higher temperatures and lower total rainfall. Similar rainfall rates and low temperatures in the Baltic and the North Sea produce nearly identical fluxes which are higher than for the Mediterranean Sea. However, given normal variability and uncertainties in our calculations, we expect that the range of fluxes calculated here may apply to any of the basins rather than to a specific sea.

Our calculations indicate that direct gas exchange may contribute from 1/2 to 2/3 of the total deposition of organic pollutants to the regional seas. This calculation is based on an exchange rate which assumes that seawater is on average 90% saturated with respect to organochlorine compounds in the atmosphere. The few measurements of organochlorines in the regional seas suggest this assumption may be reasonable (Table 42). In fact, concentrations of PCB and DDT appear supersaturated in most waters measured. This apparent supersaturation may be caused by binding of PCB and DDT in an adsorbed or colloidal form in seawater which does not participate in gas exchange reactions (Atlas and Giam, 1986).

The estimates of gas exchange given here may overestimate the actual input of organic pollutants to the regional seas via this process, and one must consider the possibility that the regional seas may serve only as a temporary sink for organic pollutant compounds from the atmosphere. For bodies of water which are near equilibrium with the atmosphere, organic pollutant input may be regulated by the ability to remove pollutants from surface waters either by sedimentation or via mixing with undersaturated waters. In shallow areas the capacity to remove pollutants is limited. In a study of Lake Siwiskit, Swackhamer et al. (1988) used a mass balance approach to suggest that sedimentation removed only 40% of the wet and dry deposition of PCBs to the lake. The "excess" deposition was revolatilized to the atmosphere. They suggested a scenario in which episodic pulses of deposition of PCB to the lake occur in rain and snow. These episodes are followed by longer periods during which the PCBs are slowly removed from surface waters via mixing, sedimentation, and volatilization. A similar situation may be applicable to coastal areas of the Mediterranean Sea, and to the North and Baltic Seas. Indeed, from a comparison of coastal and rural DDE/DDT ratios, Rodhe et al. (1980) concluded that the Baltic Sea can act as a source of airborne organic compounds. Presumably, these areas are subject to intense pulses of deposition from polluted source regions. The ability of the water bodies to totally accommodate these inputs will depend on a number of factors including mixing rates, biological productivity, and sedimentation rates (Burns and Villeneuve, 1987).

Table 41. Comparison of Total Atmospheric Deposition Flux of Organic Pollutants to Measured Deposition using Rain Collectors and to Sedimentation Rates Measured in Regional Seas, all in units of $\mu g\ m^{-2}\ yr^{-1}$

Compound	α-HCH	γ-HCH	ΣHCH	ΣDDT	ΣPCB	Dieldrin	Chlordane	HCB	Ref.
MEASURED PRECIPITATION AND DRY DEPOSITION									
Medit. Sea (wet)	1.9	10.5	12.4	1.9	8.4	–	–	0.22	1
(dry)	2.4	2.4	4.8	7.3	14.6	–	–	0.08	1
(total)	4.3	12.8	16.2	9.2	23.0	–	–	0.30	1
North Sea (wet)			3.6	2.49	3.32	0.47	–	–	2
Brest (FR)(wet)	12.6	16.6	29.2	1.7	8.3	–	–	–	3
Sweden (wet+dry)	–	–	–	11.5 - 25	0.17-21	—	–	–	4
MEASURED SEDIMENTATION RATE									
Mediterranean Sea	–	48	–	0.8*	13-28	–	–	–	5
Hano Bight	–	–	–	–	58	–	–	–	6
CALCULATED (THIS REPORT)									
(wet only)	2.4-14	4.8-27	7.2-41	0.12-1.1	0.3-2.2	0.15-0.95	0-0.04	0.02-0.09	
(gas exchg. 10%)	6.1-6.3	5-27	11-33	0.5-0.6	3.0-4.6	1.0-1.1	0.08-0.11	0.3-0.8	
TOTAL	8.5-20	10-54	18-74	0.6-1.7	3.3-6.8	1.2-2.0	0.08-0.15	0.3-0.9	
OTHER ESTIMATES									
North Sea (total) (minimum)	7.6	11.4	19	4.95	19	2.3	–	3.8	7
Baltic Sea	12.8	10.3	23.1	44.1	--	--	--	--	8

* p,p'-DDE only

Ref: 1) Villeneuve and Cattini, 1986; 2) Wells and Johnstone, 1978; 3) Marchand et al., 1983; 4) Sodergren, 1972; 5) Burns and Villeneuve, 1987; Burns et al., 1985; 6) Larsson, 1984; 7) Van Aalst et al., 1982; 8) Korolev, 1984.

The total atmospheric inputs to each regional sea are given in Table 43. Where possible, these inputs are compared to previous estimates and to estimated riverine inputs. Again, it needs to be emphasized that the riverine fluxes of organic pollutants are poorly defined. Thus a direct comparison of atmospheric and riverine inputs into the regional seas is still highly uncertain. Also, the riverine flux may influence only the nearshore areas since much of the river load of organochlorines will be deposited near the mouth of the river. The atmospheric input, however, has a wider scope for impact over the regional seas. With these caveats in mind, we estimate that HCH is deposited into the regional seas mainly via atmospheric inputs. For other organochlorine compounds, the riverine input may approach or even exceed the atmospheric flux. Additional measurements of both riverine and atmospheric fluxes and concentrations over extended time periods are necessary to resolve this question.

Table 42. Concentrations of Organochlorine Compounds in Seawater (ng l^{-1}) in Regional Seas

Compound	α-HCH	γ-HCH	ΣHCH	ΣDDT	ΣPCB	Dieldrin	Chlordane	HCB	Ref.
OBSERVED									
Mediterranean Sea	–	0.13-1.1	–	–	0.4-16.9	–	–	–	1
Brest (FR)	–	–	–	1.5	4.3	–	–	–	2
Mediterranean Sea	–	–	–	–	2.0	–	–	–	2
Baltic Sea	–	–	–	0.4-2.6	1.1-7.2	–	–	–	2
North Sea	0.44-2.3	0.12-2.77	–	–	0.07-6.8	0.01-0.33	–	0.01-0.30	3
CALCULATED									
@ 10°C	3.6	7.2	10.8	0.07	0.4	0.2	0.01	0.02	
@ 20°C	1.5	2.9	4.4	0.03	0.14	0.1	<0.01	0.01	

Ref: 1) Burns and Villeneuve, 1987; 2) Marchand et al., 1983; 3) Von Aalst et al., 1982.

Table 43. Calculated Total Atmospheric Inputs (in 10^6 g yr^{-1}) of Organic Pollutants to the North Sea, the Baltic Sea, and the Mediterranean Sea

Compound	α-HCH	γ-HCH	ΣHCH	ΣDDT	ΣPCB	Dieldrin	Chlordane	HCB	Ref.
North Sea	10.4	17.6	28	0.9	3.7	1.1	0.1	0.5	-
Baltic	7.7	12.8	20.5	0.7	2.8	0.9	0.1	0.4	-
NW Mediterranean	4.3	5.6	9.9	0.3	1.7	0.6	0.05	0.2	-
OTHER ESTIMATES									
North Sea	4-40	6-60	10-100	1.2-12	10-160	1.2-12	–	2-17	1
Baltic Sea	5	4	9	14	–	–	–	–	2
Mediterranean	–	–	–	–	22	–	–	–	3
Wet Deposition:									
North Sea	–	–	2.1	1.4	1.9	0.27	–	–	4
Mediterranean	1.5	8.4	9.9	1.3	6.8	–	–	0.20	5
Riverine Input:									
Mediterranean	–	–	–	–	3.8	–	–	–	3
North Sea	1	1.5	2.5	–	–	–	–	4	1

Ref: 1) Von Aalst et al., 1982; 2) Korolev, 1984; 3) Burns and Villeneuve, 1987; 4) Wells and Johnstone, 1978; 5) Villeneuve and Cattini, 1986.

In general the comparison between the few measurements of deposition rates of organic pollutants and the model calculations reported here is surprisingly good, though we may be underestimating the flux of DDTs and PCBs. However, it should be kept in mind that the deposition measurements shown here are derived from a time span of over a decade. With environmental concentrations of a number of organochlorine compounds showing a decline over the last ten years, it is not surprising that the measurements and calculations are in modest disagreement. More importantly, these calculations show that there may be large seasonal differences in deposition fluxes of pollutants to the regional seas considered here. These differences may be caused by a combination of temperature effects on deposition processes, source strength variation, and different transport trajectories.

RECOMMENDATIONS

In carrying out the calculations reported here, several important gaps in knowledge have become apparent. From these it is clear that much further work remains to be done. Rather than give a detailed list of recommendations for future research, we list below five areas which appear to be of special importance:

1. The best way to quantify atmospheric inputs to the oceans is by direct flux measurements. However, methods for measuring fluxes directly are lacking at the present, except for precipitation. The development of techniques to enable direct dry flux measurements to be made should be a top priority. In addition, the geographical coverage of rain sampling programmes should be expanded considerably.

2. In default of direct flux methods, we must resort to indirect approaches that use measured air concentrations. The presently available concentration data fields need to be improved both temporally and spatially. Areas for which concentration data are particularly lacking are the South Atlantic, South Pacific, Indian, and Arctic Oceans.

3. To convert concentrations to fluxes requires knowledge of the kinetic parameter (deposition/ transfer velocity) controlling the deposition rate. Better parameterisation of this term, which can come from better understanding of the controlling processes, is required for both particles and gases.

4. Scavenging ratios for particular substances vary substantially both temporally at a fixed site and between different locations. There are many reasons for the existence of these ranges. Part of the problem may be that scavenging ratios often have to be computed from rain and air concentrations measured on samples that were not collected contemporaneously. There is an urgent need for simultaneous collections and measurements, including vertical profiles, so that scavenging ratios can be obtained from truly paired rain and air samples.

5. An important uncertainty in flux calculations for synthetic organic compounds is the concentration of the 'free' (i.e., able to exchange across the air-sea interface) compounds in the surface oceans. Although technically difficult to address, such measurements should have a high priority in future studies.

REFERENCES

Addison, R.F. and M.E. Zinck. (1986). PCB's have declined more than DDT-group residues in Arctic ringed seals (Phoca hispida) between 1972 and 1981. Environ. Sci. Technol., 20: 253 - 256.

Anderson, L.G. (1983). Fate of nitrogen oxides in urban atmospheres, In: Advances in Environmental Science and Technology, 12. S. E. Schwartz, Ed. John Wiley, New York, 371 - 409.

Andreae, M.O., R.J. Charlson, F. Bruynseels, H. Storms, R. Van Grieken, and W. Maenhaut. (1986). Internal mixture of sea-salt, silicates, and excess sulfate in marine aerosols. Science, 232: 1620 - 1623.

Anon. (1987). Quality status of the North Sea. Second International Conference on the Protection of the North Sea. London, 88 pp.

Arimoto, R., R.A. Duce, B.J. Ray, and C.K. Unni. (1985). Atmospheric trace elements at Enewetak Atoll: 2. Transport to the ocean by wet and dry deposition. J. Geophys. Res., 90: 2391 - 2408.

Arimoto, R., R.A. Duce, B.J. Ray, A.D. Hewitt, and J. Williams. (1987). Trace elements in the atmosphere of American Samoa: concentrations and deposition to the tropical South Pacific. J. Geophys. Res., 92: 8465 - 8479.

Arnold, M. (1985). Géochimie et transport des aérosols métalliques au-dessus de la Méditérranée Occidentale. Ph.D. Thesis, University of Paris 7, France.

Arnold, M., A. Seghaier, D. Martin, P. Buat-Menard and R. Chesselet. (1982). Geochemie de l'aerosol marin au-dessus de la Mediterranee occidentale. Workshop on Pollution of the Mediterranean. Cannes, December 2-4, CIESM, 27-37.

Atlas, E. (1989). Long-Range Transport of Organic Compounds. In: Long-Range Transport of Natural and Contaminant Substances. T. Knap, Ed. Reidel, Dordrecht. In press.

Atlas, E., R. Foster, and C.S. Giam. (1982). Air-sea exchange of high molecular weight organic pollutants: laboratory studies. Environ. Sci. Technol., 16: 283 - 286.

Atlas, E.L. and C.S. Giam. (1981). Global transport of organic pollutants; ambient concentrations in the remote marine atmosphere. Science, 211: 163 - 165.

Atlas, E.L. and C.S. Giam. (1986). Sea-Air Exchange of High Molecular Weight Synthetic Organic Compounds. In: The Role of Air-Sea Exchange in Geochemical Cycling. P. Buat-Menard, Ed. Reidel, Dordecht, 295 - 330.

Atlas, E.L. and C.S. Giam. (1989). Sea-Air Exchange of High Molecular Weight Synthetic Organic Compounds - Results from the SEAREX Program. In: Chemical Oceanography, Vol 10. J. P. Riley, R. Chester, and R.A. Duce, Eds. Academic Press, London, In press.

Atlas, E.L., A. Velasco, K. Sullivan, and C.S. Giam. (1983). A Radio-Tracer Study of Air-Water Exchange of Synthetic Organic Compounds. Chemosphere, 12: 1251 - 1258.

Atlas, E.L., M. Madero, and C.S. Giam. (1988). Synthetic organic compounds in rural air and rainfall. Water, Air, and, Soil Pollution, 38: 19 - 36.

Atlas, E.L., R. Foster, and C.S. Giam. (1982). Air-sea exchange of high molecular weight organic pollutants: laboratory studies. Environ. Sci. Technol., 16: 283 - 286.

Atlas, E.L., T. Bidleman, and C.S. Giam. (1986). Atmospheric transport of PCB to the oceans. In: PCB's and the Environment Volume I. J.S. Waid, Ed. CRC Press Inc., Boca Raton, Florida, 79 - 100.

Ayers, G.P. and J.L. Gras. (1980). Ammonia gas concentrations over the Southern Ocean. Nature, 284: 539 - 540.

Ayers, G.P. and J.L. Gras. (1983). The concentration of ammonia in southern ocean air. J. Geophys. Res., 88: 10655 - 10659.

Ayers, G.P., J.P. Ivey, and H.S. Goodman. (1986). Sulfate and methanesulfonate in the maritime aerosol at Cape Grim, Tasmania. J. Atmos. Chem., 4: 173 - 185.

Bacci, E., D. Calamari, C. Gaggi, R. Fanelli, S. Focarki, and M. Morosini. (1986). Chlorinated hydrocarbons in lichen and moss samples from the Antarctic Peninsula. Chemosphere, 15: 747 - 754.

Balls, P.W. (1989). Trace metal and major ion composition of precipitation at a North Sea coastal site. Atmos. Environ. In press.

Ballschmiter, K., H. Buchert, S. Bihler, and M. Zell. (1981). Baseline studies of global pollution: IV. The pattern of pollution by organochlorine compounds in the North Atlantic as accumulated by fish. Fresnius Z. Anal. Chem., 306: 323 - 339.

Barber, R.T. and S.M. Warlen. (1979). Organochlorine insecticide residues in deep sea fish from 2500 m in the Atlantic Ocean. Environ. Sci. Technol. 13: 1146 - 1148.

Barrie, L.A., R.M. Hoff, and S.M. Daggupathy. (1981). The influence of mid-latitude pollution sources on haze in the Canadian Arctic. Atmos. Environ., 15: 1407 - 1419.

Bergametti, G. (1987). Apports de matière par voie atmosphérique à la Méditerranée Occidentale: Aspects géochimiques et météorologiques. Ph.D. Thesis, University of Paris 7, France.

Bergametti, G., A.L. Dutot, P. Buat-Ménard, R. Losno, and E. Remoudaki. (1989). Seasonal variability of the elemental composition of atmospheric aerosol particles over the northwestern Mediterranean. Tellus, 41B: 353 - 361.

Berner, R.A. (1982). Burial of organic carbon and pyrite sulfur in the modern ocean. Am. J. Sci., 282: 451 - 473.

Berresheim, H. and W. Jaeschke. (1986). Study of metal aerosol system as a sink for atmospheric SO_2. J. Atmos. Chem., 4: 311 - 334.

Bidleman, T.F. (1988). Atmospheric processes. Environ. Sci. Technol. 22: 361 - 367.

Bidleman, T.F. and R. Leonard. (1982). Aerial transport of pesticides over the Northern Indian Ocean and adjacent seas. Atmos. Environ. 16: 1099 - 1107.

Bidleman, T.F., E.J. Christensen, W.N. Billings, and R. Leonard. (1981). Atmospheric transport of organochlorines in the North Atlantic gyre. J. Mar. Res., 39: 443 - 464.

Bidleman, T.F., R. Atkinson, E. Atlas, B. Bonsang, K. Burns, W. Keene, J. Miller, J. Rudolf, and S.Tanabe. (1989). Transport of Organic Compounds in the Atmosphere: Review and Recommendations. In: Long-Range Transport of Natural and Contaminant Substances, T. Knap, Ed. Reidel, Dordrecht. In press.

Bidleman, T.F., U. Wideqvist, B. Jansson, and R. Soderlund. (1987). Organochlorine pesticides and polychlorinated biphenyls in the atmosphere of southern Sweden. Atmos. Environ., 21: 641 - 654.

Bidleman, T.F., W.N. Billings, and W.T. Foreman. (1986). Vapor-particle partitioning of semivolatile organic compounds: Estimates from field collections. Environ. Sci. Technol, 20: 1038 - 1043.

Broecker, W.S. and T.-H. Peng. (1987). Tracers in the Sea. Lamont-Doherty Geological Observatory, Columbia University, Palisades, NY., 690 pp.

Buat-Menard, P. (1986). The ocean as a sink for atmospheric particles. In:The role of air-sea exchange in geochemical cycling. P. Buat-Menard, Ed. Reidel, Dordrecht, pp. 165 - 183.

Buat-Menard, P. and R.A. Duce. (1986). Precipitation scavenging of aerosol particles over remote marine regions. Nature, 321: 508 - 510.

Buijsman, E., W.A.H. Asman, T.B. Ridder, A.J. Frantzen, and R.Adolphs. (1985). Chemical Composition of Precipitation Collected on a Weather Ship in the North Atlantic. Report R-85-5, Institute for Meteorology and Oceanography, University of Utrecht, The Netherlands.

Burchfield, L.A., J.D. Akridge, and P.K. Kuroda. (1983). Temporal distributions of radio-strontium isotopes and radon daughters in rainwater during a thunderstorm. J. Geophys. Res., 88: 8579 - 8584.

Burkhard, L.P., D.E. Armstrong, and A.W. Andren. (1985). Henry's Law Constants for the polychlorinated biphenyls. Environ. Sci. Technol., 19: 590 - 596.

Burns, K.A. and J.P. Villeneuve. (1987). Chlorinated hydrocarbons in the open Mediterranean ecosystem and implications for mass balance calculations. Marine Chem., 20: 337 - 359.

Burns, K.A., J.P. Villeneuve, and S.W. Fowler. (1985). Fluxes and residence times of hydrocarbons in the coastal Mediterranean: How important are the biota? Est. and Coastal Shelf Sci., 20: 313 - 330.

Burns, R.S. and R.W.F. Hardy. (1975). Nitrogen Fixation in Bacteria and Higher Plants, 189 pp., Springer-Verlag, Berlin.

Busenberg, E., and C.C. Langway, Jr. (1979). Levels of ammonium, sulfate, chloride, calcium, and sodium in snow and ice from southern Greenland. J. Geophys. Res., 84: 1705 - 1709.

Byrd, J.T. and M.O. Andreae, (1986). Concentrations and fluxes of tin in aerosols and rain. Atmos. Environ., 20: 931 - 939.

Callahan, M.A., M.W. Slimak, N.W. Gabel, I.P. May, C.W. Fowler, J.R. Freed, P. Jennings, R. L. Durfee, F. C. Whitmore, B. Maestri, W. B. Mabey, B. R.Holt, and C. Gould. (1979). Water-related environmental fate of 129 priority pollutants. Vol. I and II. EPA-440/4-79-029a.

Cambray, R.S., D.F. Jefferies, and G. Topping. (1975). An estimate of the input of atmospheric trace elements into the North Sea and Clyde (1972-1973). AERE Rep R7733, 30 pp.

Cambray, R.S., D.F. Jefferies, and G. Topping. (1979). The atmospheric input of trace elements to the North Sea. Mar. Sci. Comm., 5: 175 - 194.

Caron, G., I.H. Suffet, and T. Belton. (1985). Effect of dissolved organic carbon on the environmental distribution of nonpolar organic compounds. Chemosphere, 14: 993 - 1000.

Chang, J.S., R.A. Brost, I.S.A. Iseksen, S. Madronich, P. Middleton, W.R. Stockwell, and C.J. Walcek. (1988). A three dimensional Eulerian acid deposition model: Physical concepts and formulation. J. Geophys. Res., 92: 14681 - 14700.

Chang. L.W., E.L. Atlas, and C.S. Giam. (1985). Chromatographic separation and analysis of chlorinated hydrocarbons and phthalate esters from ambient air samples. J. Intern. Environ. Anal. Chem., 19: 145.

Chester, R., A.C. Saydam, and E.J. Sharples. (1981). An approach to the assessment of local trace metal pollution in the Mediterranean atmosphere. Mar. Poll. Bull., 12: 426 - 431.

Chester, R., E. Joanna, K. Murphy, A.C. Saydam, and G.B. Sanders. (1983). The atmospheric distribution of lead over a number of marine regions. Mar. Chem., 13: 57 - 72.

Chester, R., E.J. Sharples, G.S. Sanders, and A.C. Saydam. (1984). Saharan dust incursion over the Tyrrhenian Sea. Atmos. Environ., 18: 929 - 935.

Chester, R., K.J.T. Murphy, J. Townsend, and A. Thomas. (1986). The partitioning of elements in crust dominated marine aerosols. Chem. Geol., 54: 1 - 15.

Church, T.M., J. Tramontano, D.M. Whelpdale, M.O. Andreae, J.N. Galloway, W.C. Keene, J. Tokos. (1989). Atmospheric and precipitation chemistry over the North Atlantic; Shipboard results, April - May 1984. J. Geophys. Res. In press.

Church, T.M., J.M. Tramontano, J.R. Scudlark, T.D. Jickells, J.J. Tokos, Jr., and A.H. Knap. (1984). The wet deposition of trace metals to the western Atlantic ocean at the mid-Atlantic coast and on Bermuda. Atmos. Environ., 18: 2657 - 2664.

Clegg, S.L. and P. Brimblecombe. (1988). Equilibrium partial pressures of strong acids over concentrated saline solutions - I. HNO_3. Atmos. Environ., 22: 91 - 100.

Colson, J.G. (1979). Benzene hexachloride. In: Encyclopedia of Chemical Technology. R.E. Kirk and D.F. Othmer, Eds. Wiley-Interscience, New York, pp. 808 - 818.

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

Dacey, J.W.H., S.G. Wakeham, and B.L. Howes. (1984). Henry's Law Constants for dimethylsulfide in freshwater and seawater. Geophys. Res. Lett., 11: 991 - 998.

Dana, M.T. and R.C. Easter. (1987). Statistical summary and analyses of event precipitation chemistry from the MAP 3S Network, 1976-1983. Atmos. Environ., 21: 113 - 128.

Davis, D. D., J. D. Bradshaw, M. O. Rodgers, S. T. Sandholm, and S. Kesheng. (1987). Free tropospheric and boundary layer measurements of NO over the central and eastern North Pacific Ocean. J. Geophys. Res., 92: 2049 - 2070.

Dawson, R. and J.P. Riley. (1977). Chlorine-containing pesticides and PCB in British coastal waters. Estuarine and Coastal Marine Science, 4: 55 - 69.

Dayan, U. (1986). Climatology of back trajectories from Israel based on synoptic analysis. J. Clim. Appl. Meteorol., 25: 591 - 595.

de Lappe, B.W., R.W. Risebrough, and W. Walker II. (1983). A large-volume sampling assembly for the determination of synthetic organic and petroleum compounds in the dissolved and particulate phases of seawater. Can. J. Fish. Aquat. Sci., 40(Suppl. 2): 322 - 336.

Deacon, E.L. (1977). Gas transfer to and across an air-water interface. Tellus, 29: 363 - 374.

Dedeuwaerder, H. (1988). Study of the dynamic transport and of the fallout of some ecotoxicological heavy metals in the troposphere of the southern Bight of the North Sea. Ph.D. Thesis, Vrije University, Brussels, Belgium.

Delwiche, C.C., and G.E. Likens. (1977). Biogeochemical response to fossil fuel combustion products. In: Global Cycles and Their Alteration by Man, W. Stumm, Ed. Dahlem conf., Berlin, 73-88.

Duce, R.A. (1983). Biogeochemical cycles and the air-sea exchange of aerosols. In: SCOPE 21, The Major Biogeochemical Cycles and Their Interactions. B. Bolin and R.B. Cook, Ed., 427 - 459, Wiley, Chichester, U.K.

Duce, R.A. (1986). The impact of atmospheric nitrogen, phosphorus, and iron species on marine biological productivity. In:The Role of Air-Sea Exchange in Geochemical Cycling. P. Buat-Menard, Ed. Reidel, Dordrecht, pp. 497 - 529.

Duce, R.A. and R.B. Gagosian. (1982). The input of atmospheric n-C_{10} to n-C_{30} alkanes to the ocean. J. Geophys. Res., 87: 7192 - 7200.

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

Duce, R.A., G.L. Hoffman, B.J. Ray, I.S. Fletcher, G.T. Wallace, J.L. Fasching, S.R. Piotrowicz, P.R. Walsh, E.J. Hoffman, J.M. Miller, and J.L. Heffter. (1976). Trace metals in the marine atmosphere: sources and fluxes. In: Marine Pollutant Transfer. H.L. Windom and R.A. Duce, Eds. Lexington Books, Lexington, MA., pp. 77 - 119.

Duce, R.A., R. Arimoto, B.J. Ray, C.K. Unni, and P.J. Harder. (1983). Atmospheric trace elements at Enewetak Atoll. J. Geophys. Res., 88: 5321 - 5342.

Duinker, J. C. and F. Bouchertall. (1989). On the distribution of atmospheric PCB congeners between vapour phase, aerosols, and rain. Environ. Sci. and Technol., 23: 57 - 62.

Dulac, F. (1986). Dynamique du transport et des retombées d'aérosols métalliques en Méditerranée occidentale. Ph.D. Thesis, University of Paris 7, France.

Dulac, F., P. Buat-Menard, M. Arnold, and U. Ezat. (1987). Atmospheric input of trace metals to the Western Mediterranean Sea: 1. Factors controlling the variability of atmospheric concentrations. J. Geophys. Res., 92: 8437 - 8453.

Eisenreich, S. (1981). Atmospheric Pollutants in Natural Waters. S. Eisenreich, Ed. Ann Arbor Science, Ann Arbor, MI, 512 pp.

Eisenreich, S., B.B. Looney, and J.D. Thornton. (1981). Airborne organic contaminants in the Great Lakes ecosystem. Environ. Sci. Technol., 15: 30 - 38.

Elbaz-Poulichet, F. (1988). Transferts de plomb de cadmium et de cuivre des continents aux oceans par les fleuves et l'atmosphère. Ph.D. Thesis, University Pierre et Marie Curie, Paris, France.

Eliassen, A. and J. Saltbones. (1983). Modeling of long-range transport of sulfur over Europe: A two-year model run and some model experiements. Atmos. Environ., 17: 1457 - 1473.

Eliassen, A., O. Hov, T. Iverson, J. Saltbones, and D. Simpson. (1988). Estimates of airborne transboundary transport of sulfur and nitrogen over Europe. EMEP/MSC-W 1/88, 79 pp.

Erickson, D.J., J.T. Merrill, and R.A. Duce. (1986). Seasonal estimates of global atmospheric sea-salt distributions. J. Geophys. Res., 91: 1067 - 1072.

FAO. (1979). FAO Production Year Book, Food and Agriculture Organization, 245, Rome.

Farmer, C.T. and T.L. Wade. (1986). Relationship of ambient atmospheric hydrocarbon (C_{12}-C_{32}) concentrations to deposition. Water, Air, and Soil Poll., 29: 439 - 452.

Fendinger, N.J. and D.E. Glotfelty. (1988). A laboratory method for the experimental determination of air-water Henry's Law Constants for several pesticides. Environ. Sci. Technol., 22: 1289 - 1293.

Fisher, D., J. Ceraso, T. Mathew, and M. Oppenheimer. (1988). Polluted coastal waters: The role of acid rain. Environmental Defense Fund Report, 101 pp.

Fitzgerald, W.F. (1986). Cycling of mercury between the atmosphere and oceans. The Role of Air-Sea Exchange in Geochemical Cycling. P. Buat-Menard, ed., Reidel, Dordrecht, 363 - 408.

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

Foreman, W.T. and T.F. Bidleman. (1987). An experimental system for investigating vapor-particle partitioning of trace organic pollutants. Environ. Sci. Technol. 21: 869 - 875.

Galloway, J.N. (1985). The deposition of sulfur and nitrogen from the remote atmosphere: background paper. In: Biogeochemical Cycling of Sulfur and Nitrogen in the Remote Atmosphere. J.N.Galloway, R.J. Charlson, M.O. Andreae and H. Rhode, Ed. Reidel, Dordrecht, Holland, 143 - 173.

Galloway, J.N. and A. Gaudry. (1984). The composition of precipitation on Amsterdam Island, Indian Ocean. Atmos. Environ., 18: 2649 - 2656.

Galloway, J.N. and D.M. Whelpdale. (1987). WATOX-86 overview and western North Atlantic Ocean S and N budgets. Global Biogeochemical Cycles, 1: 261 - 281.

Galloway, J.N., D.M. Whelpdale, and G.T. Wolff. (1984). The flux of S and N eastward from North America. Atmos. Environ. 12: 2595 - 2607.

Galloway, J.N., W.C. Keene, R.S. Artz, J.M. Miller, T.M. Church, and A.H. Knap. (1989). Processes controlling the concentrations of $SO_4^=$, NO_3^-, NH_4^+, H^+, $HCOO_T$ and CH_3COO_T in precipitation on Bermuda. Tellus, 41B: 427 - 433.

Geiger, R. (1965). World Maps 1 : 30,000,000: The Earth's Atmosphere Nr. 5, Mean Annual Precipitation. Darmstadt, Justus Perthes.

Georgii, H.W. and G. Gravenhorst. (1977). The ocean as a source or sink of reactive trace gases. Pageoph, 115: 503 - 511.

GESAMP. (1985). Atmospheric transport of contaminants into the Mediterranean region. Reports and studies GESAMP No. 26.

GESAMP. (1987). Land/sea boundary flux of contaminants: contributions from rivers. Reports and studies GESAMP No. 32.

Giam, C.S., R.L. Richardson, M.K. Wong, and W.M. Sackett. (1974). Polychlorinated biphenyls in Antarctic biota. Antarctic J. U.S., 8: 303 - 305.

Gill, G.A. and W.F. Fitzgerald. (1987). Mercury in surface waters of the open ocean. Global Biogeochemical Cycles, 1: 199 - 212.

Graedel, T.E., C.J. Weschler, and M.L. Mandich. (1985). Influence of transition metal complexes on atmospheric droplet acidity. Nature, 317: 240 - 242.

Graham, W.F. and R.A. Duce. (1982). The atmospheric transport of phosphorus to the western North Atlantic. Atmos. Environ., 16: 1089 - 1097.

Guicherit, R. and F.L. Schulting. (1985). The occurrence of organic chemicals in the atmosphere of the Netherlands. The Science of the Total Environment, 43: 193 - 195.

Halter, B.C. (1984). Carbon dioxide and meteorology at Samoa. In: Geophysical Monitoring for Climatic Change, Volume 12, Summary Report 1983. J. M. Harris and E. J. Nickerson, Ed., 88-92. NOAA Air Resources Laboratory, Boulder, Colorado.

Hameed, S., and J. Dignon. (1988). Changes in the geographical distributions of global emissions of NOx and SOx from fossil-fuel combustion between 1966 and 1980, Atmos. Environ., 22: 441 - 449.

Hargrave, B.T., W.P. Vas, P.E. Erickson, and B.R. Fowler. (1987). Supply of Atmospheric Organochlorines to Food-Webs in the Arctic Ocean. Sixth Int. Symp. of the Commission on Atmospheric Chemistry and Global Pollution on Global Atmospheric Chemistry, Peterborough, Canada, 23-29 August.

Hartman, M.C. (1987). The total deposition of Pb, Cd, Zn, 210-Pb and atmospheric transport to the western Atlantic using 222-Rn and air mass trajectory analysis. M.S. Thesis, Univ. Delaware, USA, 123 pp.

Harvey, G.R. and W.G. Steinhauer. (1974). Atmospheric transport of polychlorobiphenyls to the North Atlantic. Atmos. Environ., 8: 777 - 782.

Hasse, L. (1983). Introductory meteorology and fluid dynamics, In: Air-sea Exchange of Gases and Particles. P.S. Liss and W.G.N. Slinn, Eds. Reidel, Dordrecht, pp. 1-52.

Hastie, D.R., H.I. Schiff, D.M. Whelpdale, R.E. Peterson, W.H. Zoller, and D.L. Anderson. (1988). Nitrogen and sulphur over the western Atlantic Ocean. Atmos. Environ., 22: 2381 - 2391.

Herron, M.M. (1982). Impurity sources of F^-, Cl^-, NO_3^-, and $SO_4^=$ in Greenland and Antarctic precipitation. J. Geophys. Res., 87: 3052 - 3060.

Hicks, B.B. and R.M. Williams. (1980). Transfer and deposition of particles to water surfaces. In: Atmospheric Sulfur Deposition. D.S. Shriner, C.R. Richmond, and S.E. Lindberg, Eds. Ann Arbor Science, Ann Arbor, pp. 237 - 244.

Hicks, B.B., M.L. Wesely, S.E. Lindberg, and S.M. Bromberg, Eds. (1986). Proceedings of the NAPAP Workshop on Dry Deposition, 25-27 March, 1986, Harpers Ferry, WV., 77pp.

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

Hoff, R.M. and K.W. Chan. (1986). Atmospheric concentrations of chlordane at Mould Bay, N.W.T., Canada. Chemosphere 15: 449 - 452.

Huebert, B.J. (1980). Nitric acid and aerosol nitrate measurements in the equatorial Pacific region. Geophys. Res. Lett., 7: 325 - 328.

Huebert, B.J., and A.L. Lazrus. (1980a). Tropospheric gas-phase and particulate nitrate measure-ments. J. Geophys. Res., 85: 7322 - 7328.

Huebert, B.J. and A.L. Lazrus. (1980b). Bulk composition of aerosols in the remote troposphere. J. Geophys. Res., 84: 7337 - 7344.

Hunter-Smith, R.J., P.W. Balls, and P.S. Liss. (1983). Henry's Law Constants and the air-sea exchange of various low molecular weight halocarbon gases. Tellus, 35B: 170 - 176.

Iverfeldt, A. and H. Rodhe. (1988). Atmospheric transport and deposition of mercury in the Nordic countries. Progress report prepared for the Nordic Council of Ministers.

Jaeger, L. (1983). Monthly and areal patterns of mean global precipitation, In: Variations in the Global Water Budget. A. Street-Perrot, M. Beran, and R. Ratcliffe, Eds. Reidel, Dordrecht, pp. 129 - 140.

Jaffrezo, J.-L. and J.-L. Colin. (1988). Rain-aerosol coupling in urban area: scavenging ratio measurement and identification of some transfer processes. Atmos. Environ., 22: 929 - 935.

Jahne, B. (1980). Zur parameterisierung des Gasaustausches mit Hilfe Von Laborexperimenten. Ph.D. Thesis, University of Heidelberg, F.R.G.

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

Jickells, T.D., T.M. Church, and W.G. Deuser. (1987). A comparison of atmospheric inputs and deep-ocean particle fluxes for the Sargasso Sea. Global Biogechemical Cycles, 1: 117 - 130.

Kawano, M., S. Tanabe, T. Inoue, and R. Tatsukawa. (1985). Chlordane compounds found in the marine atmosphere from the southern hemisphere. Transactions of the Tokyo University of Fisheries, 6:, 59 - 66.

Kemp, K. (1984). Multivariate analysis of elements and SO2 measured at Danish EMEP stations. Tech. Report of Air Pollution Laboratory, Danish National Agency of Environmental Protection (MST LUFT - A88).

Knap, A.H., K. Binkley, and R. Artz. (1988). The occurrence and distribution of trace organic compounds in Bermuda precipitation. Atmos. Environ., 22: 1411 - 1423.

Knap, A.H., K. Binkley, and W. Deuser. (1986). The flux of synthetic organic chemicals to the deep Sargasso Sea. Nature, 319: 572.

Korolev, S.M. (1984). Input of organochlorine pesticides from the atmosphere into the Baltic Sea water area. Baltic Marine Environment Protection Committee, Meeting 18-21 September 1984, Stockholm, Sweden.

Krell, U. and E. Rockner. (1988). Model simulations of the atmospheric input of lead and cadmium into the North Sea. Atmos. Environ., 22: 375 - 381.

Lambert, G., G. Polian, J. Sanok, B. Ardouin, A. Buisson, A. Jegou, and J.C. LeRoulley. (1983). Cycle du radon et de ses descendants: application a l'etude des echanges troposphere -stratosphere. Ann. Geophys., 38: 477 - 531.

Larsson, P. (1984). Sedimentation of polychlorinated biphenyls (PCBs) in limnic and marine environments. Water Res., 18: 1389 - 1394.

Levy, H. and W.J. Moxim. (1988). Examining the global impact of local/regional air pollution: The role of global transport chemistry models. Presentation at the 17th NATO/CCMS meeting on Air Pollution Modeling, 15 pp.

Levy, H. and W.J. Moxim. (1989). Simulated global distribution and deposition of reactive nitrogen emitted by fossil fuel combustion. Tellus, 41B: 256 - 271.

Ligocki, M.P., C. Leuenberger, and J.F. Pankow. (1985a). Trace organic compounds in rain - II. Gas scavenging of neutral organic compounds. Atmos. Environ., 19: 1609 - 1617.

Ligocki, M.P., C.L. Lewenberger, and J.F. Pankow. (1985b). Trace organic compounds in rain--III. Particle scavenging of neutral organic compounds. Atmos. Environ., 19: 1619 - 1626.

Lincoff, A.H. and J.M. Gossett. (1984). The determination of Henry's constant for volatile organics by equilibrium partitioning in closed systems. In: Gas Transfer at Water Surfaces. W. Brutsaert and G. Jirka, Eds. D. Reidel Publishing, Dordrecht, pp. 17 - 26.

Lindberg, S.E. and R.C. Harriss. (1983). Water and acid soluble trace metals in atmospheric particles. J. Geophys. Res., 88: 5091 - 5100.

Lindquist, O. (1985). Atmospheric mercury - a review. Tellus, 37B: 136 - 159.

Liss, P.S. and L. Merlivat. (1986). Air-sea exchange rates: introduction and synthesis. In: The Role of Air-Sea Exchange in Geochemical Cycling. P. Buat-Menard, Ed. Reidel, Dordrecht, pp. 113 - 127.

Liu, S.C., M. McFarland, D. Kley, O. Zafiriou, and B. Huebert. (1983). Tropospheric NO_x and O_3 budgets in the equatorial Pacific. J.Geophys. Res., 88: 1360 - 1368.

Livingston, D.A. (1963). Chemical composition of rivers and lakes, In: Data of Geochemistry, M. Fleischer, Ed. Sixth Edition, Geological Survey Professional Paper 440-G, United States Printing Office,Washington D.C., 61 pp.

Logan, J.A. (1983). Nitrogen oxides in the troposphere: Global and regional budgets. J. Geophys. Res., 88: 10,785 - 10,807.

Logan, J.A., M.J. Prather, S.C. Wofsy and M.B. McElroy. (1981). Tropospheric chemistry: a global perspective. J. Geophys. Res., 86: 7210 - 7254.

Losno, R., G. Bergametti, and P. Buat-Menard. (1988). The partitioning of zinc in Mediterranean rainwater. Geophys. Res. Lett., 15: 1389 - 1392.

Loye-Pillot, M.D., J.M. Martin, and J. Morelli. (1986). Saharan dust: influence on the rain acidity and significance for atmospheric input to Mediterranean. Nature, 321: 427 - 428.

Luke, W.T. and R.R. Dickerson. (1987). The flux of reactive nitrogen compounds from eastern North America to the western Atlantic Ocean. Global Biogeochemical Cycles, 1: 329 - 343.

Mackay, D. and A.T.K. Yuen. (1981). Transfer rates of gaseous pollutants between the atmosphere and natural waters. In: Atmospheric Pollutants in Natural Waters. S.J. Eisenreich, Ed. Ann Arbor Science, Ann Arbor, pp. 55 - 65.

Mackay, D. and W.Y. Shiu. (1984). Physical-chemical phenomena and molecular properties. In: Gas Transfer at Water Surfaces. S.J. Brutsaert, and G.H. Jirka, eds. Reidel, Dordrecht, pp. 3 - 16.

Marchand, M., J.-C. Caprais, M.A. Cosson-Mannevy, and P. Moriniere. (1983). Apports et distribution des residus organochlores a haut poids moleculaire dans la rade de Brest (milieu marin semi-ferme). Oceanologica Acta, 6: 269 - 282.

Maring, H., C. Patterson, and D. Settle. (1989). Atmospheric input fluxes of industrial and natural Pb from the Westerlies to the mid-North Pacific. In: Chemical Oceanography, 10. J.P. Riley, R. Chester, and R.A. Duce, Eds. Academic Press, London. In press.

Maring, H., D.M. Settle, P. Buat-Menard, F. Dulac, and C.C. Patterson. (1987). Stable lead isotope tracers of air mass trajectories in the Mediterranean region. Nature, 330: 154 - 156.

Maring, H.B. (1985). Impact of atmospheric aerosols on trace metal chemistry in open ocean surface seawater. Ph.D. Thesis, University of Rhode Island, Kingston, U.S.A.

Maring, H.B. and R.A. Duce. (1987). The impact of atmospheric aerosols on trace metal chemistry in open ocean surface seawater. I. Aluminum. Earth Planet. Sci. Lett., 84: 381 - 392.

Maring, H.B. and R.A. Duce. (1989). The impact of atmospheric aerosols on trace metal chemistry in open ocean surface seawater. II. Copper. J. Geophys. Res., 94: 1039 - 1045.

Martin, D., C. Mithieux, and B. Strauss. (1987). On the use of the synoptic vertical wind component in a transport trajectory model. Atmos. Environ., 21: 45 - 52.

Martin, J.-M., F. Elbaz-Poulichet, C. Guieu, M.-D. Loye-Pilot, and G. Han. (1989). River versus atmospheric input of material to the Mediterranean Sea: an overview. Marine Chemistry. In press.

Martin, J.H. and R.M. Gordon. (1988). Northeast Pacific iron distributions in relation to phytoplankton productivity. Deep-Sea Res., 35: 177 - 196.

Martin, J.H., M. Gordon, and S. Fitzwater. (1988). Oceanic iron distributions in relation to phytoplankton productivity. AGU National Meeting, San Francisco, December.

Martinsson, B.G., H.-C. Hansson, and H.O. Lannefors. (1984). Southern Scandinavian aerosol composition and elemental size distribution characteristics dependence on air-mass history. Atmos. Environ., 18: 2167 - 2182.

Masclet, P., P. Pistikopoulos, S. Beyne, and G. Mouvier. (1988). Long-range transport and gas/particle distribution of polycyclic aromatic hydrocarbons at a remote site in the Mediterranean Sea. Atmos. Environ., 22: 639 - 650.

Mason, B. (1966). Principles of Geochemistry. John Wiley, New York, 3rd edition, p. 329.

Maybeck, M. (1982). Carbon, nitrogen and phosphorous transport by world rivers. Am. J. Sci., 282: 401 - 450.

McVeety, B.D. and R.A. Hites. (1988). Atmospheric deposition of polycyclic aromatic hydrocarbons to water surfaces: a mass balance approach. Atmos. Environ., 22: 511 - 536.

Merrill, J.T. (1986). Atmospheric pathways to the oceans. In: The Role of Air-Sea Exchange in Geochemical Cycling. P.Buat-Menard, Ed. Reidel, Dordrecht, pp. 35 - 63.

Merrill, J.T., R. Bleck, and M. Uematsu. (1989). Meteorological analysis of long range transport of mineral aerosols over the Pacific. J. Geophys. Res., 94: 8584 - 8598.

Meserve, J.M. (1977). The U.S. Navy Marine Climatic Atlas of the World. Naval Weather Service Detachment and National Climatic Center, Asheville, NC.

Miller, J.M. (1987). The use of back air trajectories in interpreting atmospheric chemistry data: A review and bibliography. NOAA Technical Memorandum ERL ARL-155, 28 pp.

Miller, J.M., D. Martin, and B. Strauss. (1987). A comparison of results from two trajectory models used to produce flow climatologies to the western Mediterranean. NOAA Technical Memorandum ERL ARL-151, 11 pp.

Misanchuk, B.A., D.R. Hastie, and H.I. Schiff. (1987). The distribution of nitrogen oxides off the east coast of North America. Global Biogeochemical Cycles, 1: 345 - 355.

Moore, R.M., J.E. Milley, and A. Chatt. (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.

Mopper, K. and R.G. Zika. (1987). Free amino acids in marine rains: evidence for oxidation and potential role in nitrogen cycling. Nature, 325: 246 - 249.

Murphy, T. J., M. D. Mullin, and J. A. Meyer. (1987). Equilibration of polychlorinated biphenyls and toxaphene with air and water. Environ. Sci. Technol., 21: 155 - 162.

Murphy, T.J., A. Schinsky, G. Paolucci, and G. Rzeszutko. (1981). Inputs of polychlorinated biphenyls from the atmosphere to lakes Huron and Michigan. In: Atmospheric Pollutants in Natural Waters. S.J. Eisenreich, Ed. Ann Arbor Science, Ann Arbor, MI, 445 - 458.

National Atmospheric Deposition Program (NADP). (1986). NADP/National Network Trends (NTN) annual data summary: Precipitation chemistry in the United States for 1984. NADP/NTN Coord. Off., Natl. Resour. Ecol. Lab., Colo. State Univ., Fort Collins.

NADP. (1987). NADP/NTN Coord. Off., Natl. Resour. Ecol. Lab., Colo. State Univ., Fort Collins.

NAS. (1978). The Tropospheric Transport of Pollutants and Other Substances to the Oceans. National Academy of Sciences Press, Washington, D.C., 243 pp.

NAS. (1984). Global Tropospheric Chemistry: A Plan for Action. National Academy of Sciences Press, Washington, D.C., 194 pp.

Nriagu, J.O. (1989). Natural sources of trace metals in the atmosphere: global assessment. Nature, 338: 47 - 49.

Nriagu, J.O. and J.M. Pacyna. (1988). Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature, 333: 134 - 139.

Oblad, M. and E. Selin. (1986). Measurements of elemental composition in background aerosol on the west coast of Sweden. Atmos. Environ., 20: 1419 - 1432.

Oehme, M. and H. Stray. (1982). Quantitative determination of ultra-traces of chlorinated compounds in high-volume air samples from the Arctic using polyurethane foam as collection medium. Fresenius Z. Anal. Chem., 311: 665 - 673.

Ohta, K. and N. Handa. (1985). Organic components in size-separated aerosols from the Western North Pacific. J. of the Oceanographical Soc. of Japan, 41: 25 - 32.

Olsson, M. and L. Reutergardh. (1986). DDT and PCB pollution trends in the Swedish aquatic environment. Ambio, 15: 101-107.

Oort, A.H. (1983). Global Atmospheric Circulation Statistics, 1958-1973. NOAA Professional Paper 14, Washington, D.C.

Pacyna, J.M. and M. Oehme. (1988). Long-range transport of some organic compounds to the Norwegian arctic. Atmos. Environ., 22: 243 - 257.

Pacyna, J.M., A. Semb, and J.E. Hanssen. (1984). Emission and long-range transport of trace elements in Europe. Tellus, 36B: 163 - 174.

Paerl, H.W. (1985). Enhancement of marine primary production by nitrogen-enriched rain. Nature, 315: 747 - 749.

Pankow, J.F. (1987). Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere. Atmos. Environ., 21: 2275 - 2283.

Parungo, F. and J. Miller. (1988). Air chemistry studies over the Gulf of Mexico. NOAA Technical Memorandum ERL ESG-29, 254 pp.

Parungo, F.P., C.T. Nagamoto, J. Rosinski and P.L. Haagenson. (1986). A study of marine aerosols over the Pacific Ocean. J. Atmos.Chem., 4: 199 - 226.

Pattenden, N.J. and J.R. Branson. (1987). Relation between lead in air and in petrol in two urban areas of Britain. Atmos. Environ. 21: 2481 - 2483.

Patterson, C.C. and D.M. Settle. (1987). Review of data on eolian fluxes of industrial and natural lead to the lands and seas in remote regions on a global scale. Marine Chemistry, 22: 137 - 162.

Patterson, T.L. (1988). Ph.D. Thesis, University of Rhode Island, Kingston, U.S.A.

Patton, G.W., D.A. Hinckley, M.D. Walla, T.F. Bidleman, and B.T. Hargrave. (1989). Airborne organochlorines in the Canadian high arctic. Tellus, 41B: 243 - 255.

Petersen, G., H. Weber, and H. Grassl. (1988). Modeling the atmospheric transport of trace metals from Europe to the North Sea and Baltic Sea. NATO Workshop on Control and Fate of Atmospheric Heavy Metals, Oslo, Norway, 12-16 September, 1988.

Prospero, J. M. and D. L. Savoie. (1989). Effect of continental sources on nitrate concentrations over the Pacific Ocean. Nature, 339: 687 - 689.

Prospero, J.M., D.L. Savoie, R.T. Nees, R.A. Duce, and J. Merrill. (1985). Particulate sulfate and nitrate in the boundary layer over the North Pacific Ocean. J. Geophys. Res., 90: 10586 - 10596.

Prospero, J.M. (1979). Mineral and sea salt aerosol concentration in various ocean regions. J. Geophys. Res., 84: 725 - 731.

Prospero, J.M. (1981). Aeolian transport to the world ocean, In: The Sea, Vol. 7, The Oceanic Lithosphere. C. Emiliani, Ed. Wiley Interscience, New York, 801 - 874.

Prospero, J.M. (1989). Mineral aerosol transport to the North Atlantic and North Pacific: the impact of African and Asian sources. In: The Large Scale Atmospheric Transport of Natural and Contaminant Substances. A. Knap, Ed., Reidel, Dordrecht. In press.

Prospero, J.M., M. Uematsu, and D.L. Savoie. (1989). Mineral aerosol transport to the Pacific Ocean. In: Chemical Oceanography, 10. J.P. Riley, R. Chester, and R.A. Duce, Eds. Academic Press, London. In press.

Prospero, J.M., R.T. Nees, and M. Uematsu. (1987). Deposition rate of particulate and dissolved aluminum derived from Saharan dust in precipitation at Miami, Florida. J. Geophys. Res., 92: 14,723 - 14,731.

Pszenny, A.A.P. (1987). Atmospheric deposition of nitrate to the ocean surface. Ph.D. Thesis, University of Rhode Island, Kingston, U.S.A.

Pszenny, A.A.P., F. MacIntyre, and R.A. Duce. (1982). Sea-salt and the acidity of marine rain on the windward coast of Samoa. Geophys. Res. Lett., 9: 751 - 754.

Quinn, P.K., R.J. Charlson, and T.S. Bates. (1988). Simultaneous observations of ammonia in the atmosphere and ocean. Nature, 335: 336 - 338.

Quinn, P.K., R.J. Charlson, and W.H. Zoller. (1987). Ammonia, the dominant base in the remote marine troposphere: a review. Tellus, 39B: 413 - 425.

Rahn, K. (1976). The Chemical Composition of the Atmospheric Aerosol. Technical Report. Graduate School of Oceanography, University of Rhode Island, Kingston.

Rapaport, R.A. and S.J. Eisenreich. (1988). Historical atmospheric inputs of high molecular weight chlorinated hydrocarbons to eastern North America. Environmental Science and Technology 22: 931 - 941.

Rapaport, R.A., N.R. Urban, P.D. Capel, J.E. Baker, B.B. Looney, S.J. Eisenreich, and E. Gorham. (1985). "New" DDT inputs to North America: Atmospheric deposition. Chemosphere, 14: 1167 - 1173.

Ray, P.K., A.K. Prasad, and R. Nandan. (1985). Pesticides - Major environmental problem. Science and Culture, 51: 363 - 371.

Reinhardt, K.H. and D. Wodarg. 1988a). Transport of Organochlorine Compounds. In: Proceedings of the NATO Advanced Workshop. Humidity Exchange over the Sea. Main Experiment (HEXMAX) Analysis and Interpretation. Technical Report, Department of Atmospheric Sciences, University of Washington, Seattle, U.S.A.

Reinhardt, K.H. and D. Wodarg. (1988b). Transport of selected organochlorine compounds over the sea. J. Aerosol Sci., 19: 1251 - 1255.

Rice, C.P., P.J. Samson, and G.R. Noguchi. (1986). Atmospheric transport of toxaphene to Lake Michigan. Environ. Sci. Technol., 20: 1109 - 1116.

Ridley, B.A., M.A. Carroll and G.L. Gregory. (1981). Measurements of nitric oxide in the boundary layer and free troposphere over the Pacific Ocean. J. Geophys. Res., 92: 2025 - 2047.

Risbo, T., H.B. Clausen and K.L. Rasmussen. (1981). Supernovae and nitrate in the Greenland ice sheet. Nature, 294: 637 - 639.

Risebrough, R.W. and G.M. Carmignani. (1972). Chlorinated hydrocarbons in Antarctic birds, In: Proceedings of the Colloquium, Conservation Problems in Antarctica. B.C. Parker, Ed. Allen Press, Lawrence, Kansas, pp. 63 - 78.

Rodhe, H. (1985). The transport of sulfur and nitrogen through the remote atmosphere. In: The Biogeochemical Cycling of Sulfur and Nitrogen in the Remote Atmosphere. J.N. Galloway, R.J. Charlson, M.O. Andreae, and H. Rodhe, Eds. Reidel, Dordrecht, 105 - 124.

Rodhe, H., R. Soederlund, and J. Ekstedt. (1980). Deposition of airborne pollutants on the Baltic. Ambio, 9: 168 - 173.

Roether, W. (1986). Field measurements of gas exchange. In: Dynamic Processes in the Chemistry of the Upper Ocean. J.D. Burton, P.G. Brewer, and R. Chesselet, Eds. Plenum Press, New York, pp. 117 - 128.

Rudolph, J., B. Vierkorn-Rudolph, and F.X. Meixner. (1987). Large-scale distribution of peroxyacetyl nitrate-results from the STRATOZ III flights. J. Geophys. Res. 92: 6653 - 6661.

Ryaboshapko, A.G., V.I. Lepeskin, E.D. Podgurskaya, and V.I. Medinets. (1986). Air pollution monitoring over the North Atlantic. Proc. Int'l. Symp. on Integrated Global Monitoring of the State of the Biosphere, 2, Tashkent, USSR, WMO/TD151, 261 - 282.

Savoie, D. (1984). Nitrate and non-Sea-Salt Sulfate Aerosols over Major Regions of the World Ocean: Concentration, Sources, and Fluxes. Ph.D. Thesis, University of Miami, U.S.A.

Savoie, D.L. and J.M. Prospero. (1982). Particle size distribution of nitrate and sulfate in the marine atmosphere. Geophys. Res. Lett. 9: 1207 - 1210.

Savoie, D.L., and J.M. Prospero. (1983). Nitrate and non-seasalt sulfate concentrations at Bermuda. Paper presented at the WATOX workshop, Bermuda Biological Station for Research, Ferry Reach, Bermuda.

Savoie, D.L., J.M. Prospero, J.T. Merrill, and M. Uematsu. (1989a). Nitrate in the atmospheric boundary layer of the tropical South Pacific: Implications regarding sources and transport. J. Atmos. Chem. In press.

Savoie, D. L., J.M. Prospero, and E.S. Saltzman. (1989b). Nitrate, non-seasalt sulfate, and methanesulfonate over the Pacific Ocean. In: Chemical Oceanography, Vol. 10, J.P.Riley, R. Chester, and R.A. Duce, eds. Academic Press, London. In press.

Savoie, D. L., J.M. Prospero, and R.T. Nees. (1987). Nitrate, non-seasalt sulfate, and mineral aerosol over the northwestern Indian Ocean. J. Geophys. Res. 92: 933 - 942

Schaug, J., J.E. Hansen, K. Nodop, B. Ottar, and J.M. Pacyna. (1987). Co-operative programme on monitoring and evaluation of the long range transmission of air pollutants in Europe (EMEP). Summary Report from the Chemical Co-ordinating Centre for the Third Phase of EMEP.

Schneider, B. (1987). Source characterization for atmospheric trace metals over Kiel Bight. Atmos. Environ., 21: 1275 - 1283.

Schneider, B. (1988). Input of atmospheric trace metals to the Baltic Sea area - an estimate based on the EGAP (HELCOM) monitoring data, submitted for publication to Baltic Environment Protection Commission, HELCOM.

Schneider, J.K., R.B. Gagosian, J.K. Cochran, and T.W. Trull. (1983). Particle size distributions of n-alkanes and 210-Pb in aerosols off the coast of Peru. Nature, 304: 429 - 432.

Scudlark, J.R. and T.M. Church. (1988). The atmospheric deposition of arsenic and association with acid depositon. Atmos. Environ., 22: 937 - 963.

Seiler, W. and P.J. Crutzen. (1980). Estimates of gross and net fluxes of carbon between the biosphere and the atmosphere from biomass burning. Clim. Change, 2: 207 - 247.

Sericano, J., E.L. Atlas, T.L. Wade, and J.M. Brooks. (1989). Chlorinated pesticides and PCBs in oysters (Crassostrea Virginica) and sediments from the Gulf of Mexico, 1986-1987. Mar. Environ. Res. In review.

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

Shen, G.T. and E.A. Boyle. (1987). Lead in corals: reconstruction of historic industrial fluxes to the surface of the ocean. Earth Planet. Sci. Lett., 326: 278 - 280.

Sicre, M.A., J.C. Marty, A. Saliot, X. Aparicio, J. Grimalt, and J. Albaiges. (1987). Aliphatic and aromatic hydrocarbons in the different sized aerosols over the Mediterranean Sea: Occurrence and origin. Atmos. Environ., 12: 2247 - 2259.

Singh, H.B., L.J. Salas, and W. Viezee. (1986). Global distribution of peroxyacetyl nitrate. Nature, 321: 588 - 591.

Slater, R.M. and D.J. Spedding. (1981). Transport of dieldrin between air and water. Arch. Environ. Contam. Toxicol., 10: 25 - 30.

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

Slinn, W.G.N., L. Hasse, B.B. Hicks, A.W. Hogan, D. Lal, P.S. Liss, K.O. Munnich, G.A. Sehmel, and O. Vittori. (1978). Some aspects of the transfer of atmospheric trace constituents past the air-sea interface. Atmos. Environ., 12: 2055 - 2087.

Slutz, R., S.J. Lubker, J.D. Hiscox, S.D. Woodruff, R.L. Jenne, D.H. Joseph, P.M. Steurer, and J.D. Elms. (1985). Comprehensive Ocean-Atmosphere Data Set, Release 1. U.S. Department of Commerce, National Oceanic and Atmospheric Administration, Environmental Research Laboratories, Climate Research Program, Boulder, CO.

Smith, J.H., D.C. Bomberger, Jr., and D.L. Haynes. (1981). Volatilization rates of intermediate and low volatility chemicals from water. Chemosphere, 10: 281 - 289.

Sodergren, A. (1972). Chlorinated hydrocarbon residue in airborne fallout. Nature, 236: 395 - 396.

Soderlund R. and B.H. Svensson. (1976). The global nitrogen cycle. In: SCOPE 7: Nitrogen, Phosphorus and Sulfur--Global Cycles. B.H. Svensson and R. Soderlund, Eds. Ecol. Bull. [Stockholm] 22: 23 - 74.

Sovocool, G.W., R.G. Lewis, R.L. Harless, N.K. Wilson, and R.D. Zehr. (1977). Analysis of technical chlordane by gas chromatography/mass spectrometry. Anal. Chem., 49: 734 - 740.

Statham, P.J. and R. Chester. (1988). Dissolution in sea and rainwater of manganese in atmospheric particulates. Geochim. Cosmochim. Acta, 51: 2433 - 2437.

Stedman, D.H. and R.E. Shetter. (1983). The global budget of atmospheric nitrogen species. In: Trace Atmospheric Constituents, Properties, Transformations, and Fates. S.E. Schwartz, Ed. Wiley, New York, pp. 411 - 454.

Stoessel, R. (1987). Untersuchungen zu Nass und Trockendeposition von Schwermetallen auf der Insel Pellworm. Ph.D. Thesis, University of Hamburg, F.R.G.

Subramanian, A., S. Tanabe, H. Tanaka, H. Hidaka, and R. Tatsukawa. (1987). Gain and loss rates and biological half-life of PCBs and DDE in the bodies of Adelie Penguins. Environ. Poll., 43: 39 - 46.

Subramanian, A., S. Tanabe, Y. Fujise, and R. Tatsukawa. (1986). Organochlorine residues in Dall's and True's porpoises collected from Northwestern Pacific and adjacent waters. Mem. Natl. Inst. Polar Res., Spec. Issue, 44: 167 - 173.

Suntio, L.R., W.Y. Shiu, D. Mackay, J.N. Seiber, and D. Glotfelty. (1987). A critical review of Henry's Law Constants for pesticides. Rev. Environ. Contam. Toxicol., 103: 1 - 59.

Swackhamer, D.L. and D.E. Armstrong. (1986). Estimation of the atmsopheric and non-atmospheric contributions and losses of polychlorinated biphenyls for Lake Michigan on the basis of sediment records of remote lakes. Environ. Sci. Technol. 20: 879 - 883.

Swackhamer, D.L., B.D. McVeety, and R.A. Hites. (1988). Deposition and evaporation of polychlorobiphenyl congeners to and from Siskiwit Lake, Isle Royale, Lake Superior. Environ. Sci. Technol., 22: 664 - 672.

Talbot, R.W., R.C. Harriss, E.V. Browell, G.L. Gregory, D.I. Sebacher and S.M. Beck. (1986). Distribution and geochemistry of aerosols in the tropical North Atlantic troposphere: Relationship to Saharan dust. J. Geophys. Res., 91: 5173 - 5182.

Tanabe, S. (1988). PCB problems in future: Foresight from current knowledge. Environ. Poll., 50: 5 - 28.

Tanabe, S. and R. Tatsukawa. (1980). Chlorinated hydrocarbons in the North Pacific and Indian Oceans. J. Oceanogr. Soc. of Japan, 36: 217 - 226.

Tanabe, S. and R. Tatsukawa. (1983). Chlorinated Hydrocarbons in the Southern Ocean, Memoirs of National Institute of Polar Research Special Issue No. 27, Proceedings of BIOMASS Colloquium in 1982, 64 - 76.

Tanabe, S. and R. Tatsukawa. (1986). Distribution, behavior, and load of PCB's in the oceans. In: PCB's and the Environment, Volume I. J.S. Waid, Ed. CRC Press, Inc., Boca Raton, Florida.

Tanabe, S.H. Hidaka, and R. Tatsukawa. (1983a). PCBs and chlorinated hydrocarbon pesticides in antarctic atmosphere and hydrosphere. Chemosphere 12: 277 - 288.

Tanabe, S., M. Kawano, and R. Tatsukawa. (1982a). Chlorinated hydrocarbons in the Antarctic, Western Pacific and Eastern Indian Oceans. Trans. Tokyo Univ. Fish., 5: 97 - 109.

Tanabe, S., R. Tatsukawa, M. Kawano, and H. Hidaka. (1982b). Global distribution and atmospheric transport of chlorinated hydrocarbons: HCH (BHC) isomers and DDT compounds in the Western Pacific, Eastern Indian and Antarctic Oceans. J. Oceanogr. Soc. Japan, 38: 137 - 148.

Tanabe, S., T. Mori, R. Tatsukawa, and N. Miyazaki. (1983b). Global pollution of marine mammals by PCB's, DDT's, and HCH's (BHCs). Chemosphere, 12: 1269 - 1275.

Tateya, S., S. Tanabe, and R. Tatsukawa. (1989). PCBs in the globe: possible trend of future levels in open ocean environment. Submitted to J. Great Lakes Res.

Tatsukawa, R. and S. Tanabe. (1989). Fate and bioaccumulation of persistent organochlorine compounds in the marine environment. In: Oceanic Processes in Marine Pollution. In Press.

Taylor, G.S., M.B. Baker, and R.J. Charlson. (1983). Heteorgeneous interactions of the C, N, and S cycles in the atmosphere: The role of aerosols and clouds. In: SCOPE 21: The Major Biogeochemical Cycles and Their Interactions. B. Bolin and R. B. Cook, Eds. New York: Wiley, 115 - 142.

Taylor, S.R. and S.M. McLennan. (1985). The Continental Crust: Its Composition and Evolution. Blackwells, Oxford, England, 312 pp.

Tsunogai, S. and T. Kondo. (1982). Sporadic transport and deposition of continental aerosols to the Pacific Ocean. J. Geophys. Res., 87: 8870 - 8874.

Tsunogai, S., T. Suzuki, T. Kurata, and M. Uematsu. (1985). Seasonal and areal variation of continental aerosol in the surface air over the western North Pacific region. J. Oceanogr. Soc. of Japan, 41: 427 - 434.

Turekian, K.K., L.K. Benninger, and E.P. Dion. (1983). 7-Be and 210-Pb total deposition fluxes at New Haven, Connecticut and at Bermuda. J. Geophys. Res., 88: 5411 - 5415.

Unified Deposition Data Base Committee (UDDBC). A unified wet deposition data base for eastern North America: Addendum with results for sulfates and nitrates (1980-1983). Ontario Ministry of the Environment, Toronto, Ont., Canada, 406 pp.

Uematsu, M., R.A. Duce, and J.M. Prospero. (1985). Deposition of atmospheric mineral particles in the North Pacific Ocean. J. Atmos. Chem., 3: 123 - 138.

Uematsu, M., R.A. Duce, J.M. Prospero, L. Chen, J.T. Merrill, and R.L. McDonald. (1983). Transport of mineral aerosol from Asia over the North Pacific Ocean. J. Geophys. Res., 88: 5343 - 5332.

Van Aalst, R.M., R.A.M. Van Ardenne, J.F. de Kreuk, Jr., and Th. Lems. (1982). Pollution of the North Sea from the Atmosphere. TNO, Report CL 82/152, Netherlands Organization for Applied Scientific Research, 124 pp.

Van Bennekom, A.J. and W. Salomons. (1981). Pathways of organic nutrients and organic matter from land to ocean through rivers, In: River Input to the Ocean System, J.D. Burton, D. Eisma, and J.M. Martin, Eds. UNESCO-UNEP, SCOR Workshop, Rome 1979, 33 - 51.

Van Neste, A., R.A. Duce, and C. Lee. (1987). Methylamines in the marine atmosphere. Geophys. Res. Lett., 14: 711 - 714.

Van Vaeck, L., G. Broddin, and K. van Cauwenberghe. (1979). Differences in particle size distributions of major organic pollutants in ambient aerosols in urban, rural, and seashore areas. Environ. Sci. Technol., 13: 1494 - 1502.

Veron, A. (1988). Dynamique du transfert du plomb dans l'ocean Atlantique nord-est depuis l'atmosphere jusqu'au sediment. These Docteur en Sciences, Universite Paris-Sud, France.

Vet, R.J., W.B. Sukloff, M.E. Still, and R. Gilbert. (1986). Canadian Air and Precipitation Network (CAPMoN) precipitation chemistry data summary 1983-1984. Report AQRB-86-001-M, Atmospheric Environment Service, Downsview, Ont., Canada, 544 pp.

Villeneuve, J.-P. and C. Cattini. (1986). Input of chlorinated hydrocarbons through wet and dry deposition to the Western Mediterranean. Chemosphere, 15: 115 - 120.

Volkening, H., H. Baumann, and K.G. Heumann. (1988). Atmospheric distribution of particulate lead over the Atlantic ocean from Europe to Antarctica. Atmos. Environ., 22: 1169 - 1174.

Wade, T.L., E.L. Atlas, J.M. Brooks, M.C. Kennicutt II, R.G. Fox, J. Sericano, B. Garcia-Romero, D. Defreitas. (1988). NOAA Gulf of Mexico Status and Trends Program: Trace Organic Contaminant Distribution in Sediments and Oysters. Estuaries, 11: 171 - 178.

Wagenbach, D., U. Gärlach, K. Maser, and K.O. Münnich. (1988). Coastal Antarctic aerosol: the seasonal pattern and its chemical composition and radionuclide content. Tellus, 40B: 426 - 436.

Walsh, P.R. and R.A. Duce. (1976). The solubilization of anthropogenic vanadium in seawater. Geophys. Res. Lett., 3: 375 - 378.

Walton, J.J., M.C. MacCracken, and S.J. Ghan. (1988). A global scale Lagrangian trace species model of transport, transformation, and removal processes. J. Geophys. Res., 93: 8339 - 8354.

Wanninkhof, R., J.R. Ledwell, and W.S. Broecker. (1985). Gas exchange - wind speed relation measured with sulfur hexafluoride on a lake. Science, 227: 1224 - 1226.

Warneck, P. (1988). Chemistry of the Natural Atmosphere, 757pp., Academic Press, San Diego.

Webb, S.C. and J.V. Walter. (1989). A surface complex reaction model for the pH-dependence of slightly soluble oxides and aluminosilicate dissolution rates. Geochim. Cosmochim. Acta. In press.

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

Wells, D.E. and S.J. Johnstone. (1978). The occurrence of organochlorine residues in rainwaters. Water, Air and Soil Pollution, 9: 271 - 280.

Whelpdale, D.M., W.C. Keene, A.D.A. Hansen, and J. Boatman. (1987). Aircraft measurements of sulfur, nitrogen, and carbon species during WATOX-86. Global Biogeochemical Cycles 1: 357 - 368.

Whelpdale, D.M. and J.L. Moody. (1989). Large-Scale meteorological regimes and transport processes. In: The Large Scale Atmospheric Transport of Natural and Contaminant Substances. A. Knap , Ed. Reidel, Dordrecht. In press.

Whitehouse, B. (1985). The effects of dissolved organic matter on the aqueous partitioning of polynuclear aromatic hydrocarbons. Est. Coastal. and Shelf Sci., 20: 393 - 402.

Wittlinger, R. and K. Ballschmiter. (1987). Global baseline pollution studies XI: Congener specific determination of polychlorinated biphenyls (PCB) and occurrence of alpha and gamma-hexachlorocyclohexane (HCH), 4,4'-DDE and 4,4'-DDT in continental air. Chemosphere, 16: 2497 - 2513.

Wolff, G.T., M.S. Ruthkosky, D.P. Stroup, P.E. Korsog, M.A. Ferman, G.J. Wendel, and D.H. Stedman. (1986a). Measurements of SO_x, NO_x, and aerosol species on Bermuda. Atmos. Environ., 20: 1229 - 1239.

Wolff, G.T., N.A. Kelly, M.A. Ferman, M.S. Ruthkosky, D.P. Stroup, and P.E. Korsog. (1986b). Measurements of sulfur oxides, nitrogen oxides, haze, and fine particles at a rural site on the Atlantic coast. J. Air Pollut. Control Assoc., 36: 585 - 591.

Wollast, R. (1981). Interaction between major biogeochemical cycles in marine ecosystems. In: Some Perspectives of the Major Biogeochemical Cycles, G.E. Likens, Ed. Wiley, New York, pp. 125 - 142.

Wollast, R. (1983). Interactions in estuaries and coastal waters. In: SCOPE 21: The Major Biogeochemical Cycles and Their Interactions. B. Bolin and R.B. Cook, Eds. Wiley, New York, 385 - 407.

Wollast, R. and L. Chou. (1985). Kinetic study of the dissolution of albite with a continuous flow-trough fluidized bed reactor. In: The Chemistry of Weathering. J.I. Drever, Ed. D. Reidel Pub. Co., p. 75 - 96.

Yaaqub, R. (1989). Ph.D. Thesis, University of East Anglia, Norwich, U.K.

Yamasaki, H., K. Kuwata, and H. Miyamoto. (1982). Effects of temperature on aspects of airborne polycyclic aromatic hydrocarbons. Environ. Sci. Technol., 16: 189 - 194.

Zafiriou, D.C., R.B. Gagosian, E.T. Peltzer, J.B. Alford, and T. Loder. (1985). Air-to-sea fluxes of lipids at Enewetak Atoll. J. Geophys. Res., 90: 2409 - 2423.

Zafiriou, O.C., and M. McFarland. (1981). Nitric oxide from nitrite photolysis from the Central Equatorial Pacific. J. Geophys. Res., 86: 3173 - 3182.

Zhuang, G. and R.A. Duce. (1988). The solubility of atmospheric iron in seawater and its impact on marine biological productivity. AGU National Meeting, San Francisco, CA.

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