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**IMO/FAO/UNESCO/WMO/WHO/IAEA/UN/UNEP  
JOINT GROUP OF EXPERTS ON THE SCIENTIFIC ASPECTS  
OF MARINE POLLUTION  
— GESAMP —**

# **REPORTS AND STUDIES**

No. 38

## **THE ATMOSPHERIC INPUT OF TRACE SPECIES TO THE WORLD OCEAN**



**WORLD METEOROLOGICAL ORGANIZATION**

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IMO/FAO/UNESCO/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on  
the Scientific Aspects of Marine Pollution (GESAMP)

THE ATMOSPHERIC INPUT OF TRACE SPECIES  
TO THE WORLD OCEAN

World Meteorological Organization, 1989

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### Definition of Marine Pollution by GESAMP

"POLLUTION MEANS THE INTRODUCTION BY MAN, DIRECTLY OR INDIRECTLY, OF SUBSTANCES OR ENERGY INTO THE MARINE ENVIRONMENT (INCLUDING ESTUARIES) RESULTING IN SUCH DELETERIOUS EFFECTS AS HARM TO LIVING RESOURCES, HAZARDS TO HUMAN HEALTH, HINDRANCE TO MARINE ACTIVITIES INCLUDING FISHING, IMPAIRMENT OF QUALITY FOR USE OF SEA WATER AND REDUCTION OF AMENITIES."

\* \* \*

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## EXPLANATORY NOTE

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.

Financial support for two Working Group meetings was provided by WMO, UNEP and Unesco.

# GESAMP REPORTS AND STUDIES PUBLICATIONS

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19.	An Oceanographic Model for the Dispersion of Wastes Disposed of in the Deep Sea	1983	E
20.	Marine Pollution Implications of Ocean Energy Development	1984	E
21.	Report of the Fourteenth Session	1984	E,F,R,S
22.	Review of Potentially Harmful Substances	1985	E
23.	Interchange of Pollutants Between the Atmosphere and Oceans (Second report)	1985	E
24.	Thermal Discharges in the Marine Environment	1984	E

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Title

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25.	Report of the Fifteenth Session	1985	E,F,R,S
26.	Atmospheric Transport of Contaminants into the Mediterranean Region	1985	E
27.	Report of the Sixteenth Session	1986	E,F,R,S
28.	Review of Potentially Harmful Substances. Arsenic, Mercury and Selenium (Published also as UNEP Regional Seas Reports and Studies No. 92)	1986	E
29.	Review of Potentially Harmful Substances. Organosilicon Compounds (Silanes and Siloxanes) (Printed in limited number by IMO and published also as UNEP Regional Seas Reports and Studies No. 78)	1986	E
30.	Environmental Capacity. An approach to Marine Pollution Prevention (Published also as UNEP Regional Seas Reports and Studies No. 80)	1986	E
31.	Report of the Seventeenth Session	1987	E,F,R,S
32.	Land-sea Boundary Flux of Contaminants: Contributions from Rivers	1987	E
33.	Report of the Eighteenth Session	1988	E,F,R,S
34.	Review of Potentially Harmful Substances. Nutrients (in press)		
35.	The Evaluation of the Hazards of Harmful Substances Carried by Ships: Revision of GESAMP Reports and Studies No. 17	1989	E
36.	Pollutant Modification of Atmospheric and Oceanic Processes and Climate: Some Aspects of the Problem (in press)		
37.	Report of the Nineteenth Session	1989	E
38.	Atmospheric Input of Trace Species to the World Ocean	1989	E

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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  $10^{\circ} \times 10^{\circ}$  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  $10^{\circ} \times 10^{\circ}$  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 ( $\text{NO}_3^-$ ,  $\text{HNO}_3$ ,  $\text{NO}_x$ ), we find about 60% of the amount entering the oceans from the atmosphere is by wet deposition of nitrate and nitric acid. Deposition of  $\text{NO}_x$  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  $\text{NO}_x$  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  $\text{NH}_4^+$  and  $\text{NH}_3$ ) 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,  $\text{N}_2\text{O}$  and  $\text{NH}_3$ ) 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.,  $^{210}\text{Pb}$ ) 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.,  $\text{HNO}_3$  and  $\text{SO}_2$ ) 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 ( $\Delta C$ , 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,

$$F_g = K \cdot \Delta C = K_w [C_{ga}(H/RT)^{-1} - C_{gw}] = K_a [C_{ga} - C_{gw}(H/RT)] \quad (1)$$

$K_w$  and  $K_a$  refer to whether the calculation is made with concentrations expressed on a liquid phase or a gas phase basis.  $C_{ga}$  and  $C_{gw}$  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 ( $r_w$ ),

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

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

In (2),  $k_a$  and  $k_w$  are the transfer velocities for chemically unreactive gases in the air and water, respectively. The factor  $\alpha$  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  $\alpha$  since the compounds of interest do not react rapidly with water ( $\alpha = 1.0$ ).