



REGIONAL SEAS

GESAMP:

***Atmospheric input of trace species
to the world oceans***

UNEP Regional Seas Reports and Studies No. 119

GESAMP Reports and Studies No. 38

Prepared in co-operation with



United Nations



FAO



UNESCO



WHO



WMO



IMO



IAEA

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.

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

TABLE OF CONTENTS

EXECUTIVE SUMMARY	1
INTRODUCTION	6
Selection of Chemical Species	6
Organization of Report	7
History of the GESAMP Study	8
DEPOSITION PROCESSES	9
Introduction	9
Direct Measurement of Atmosphere-Ocean Mass Fluxes	9
Indirect Estimates of Atmosphere-Ocean Mass Fluxes	10
ATMOSPHERIC TRANSPORT AND PRECIPITATION CLIMATOLOGY	16
Introduction	16
Climatological Data over the Oceans	16
Lagrangian and Eulerian Models	17
Framework for the Calculation	18
Summary	22
THE ATMOSPHERIC INPUT OF TRACE ELEMENTS AND MINERAL AEROSOL TO THE WORLD OCEAN	23
Introduction	23
Methodology	25
Results	31
Regional Seas	36
THE ATMOSPHERIC INPUT OF NITROGEN SPECIES TO THE WORLD OCEAN	42
Introduction	42
Oxidized Nitrogen Species	42
Reduced Nitrogen Species	48
Summary and Discussion	50
Comparison With Other Estimates of Global Ocean Fluxes of Oxidized Nitrogen	58
Comparison of Atmospheric and Riverine Inputs of Dissolved Nitrogen	59
Regional Seas	61
Conclusions	61
THE ATMOSPHERIC INPUT OF SYNTHETIC ORGANIC COMPOUNDS TO THE WORLD OCEAN	62
Introduction	62
Choice of Compounds	62
Data Selection and Extrapolation	65
Data Sources - Atmospheric Concentrations	68
Methods of Calculation	68
Flux Estimates	76
Results	77
Regional Seas	83
RECOMMENDATIONS	89
REFERENCES	90
WORKSHOP PARTICIPANTS	109

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 (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.

预览已结束，完整报告链接和二维码如下：

https://www.yunbaogao.cn/report/index/reportId=5_15469

