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- GESAMP -

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No. 23

Interchange of Pollutants between the Atmosphere and the Oceans (part II)

World Meteorological Organization

Reports and Studies No. 23

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

INTERCHANGE OF POLLUTANTS BETWEEN THE ATMOSPHERE AND THE OCEANS

World Meteorological Organization, 1985

NOTES

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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

The report summarizes the results of the following four meetings of the WMO-led GESAMP Working Group on the Interchange of Pollutants between the Atmosphere and the Oceans (INTERPOLL) established by GESAMP in 1975: i) Third Session held 27-31 October 1980 in Miami, USA, ii) Ad Hoc Meeting held 19-23 May 1981 in Tallinn, USSR, iii) Expert Consultation held 27-29 August 1981 in Hamburg, Federal Republic of Germany and iv) Expert Consultation held 2-4 September 1983 in London, U.K. This report supplements the first report entitled "Interchange of Pollutants between the Atmosphere and the Oceans", which was published in 1980 as the GESAMP Reports and Studies No. 13 and presented the results of the first two sessions of INTERPOLL held in 1977 and in 1978. These two reports should be taken together, since material included in the first part is generally not repeated in the second.

The present report, which is available in English only, has been discussed and approved by the Fourteenth Session of GESAMP.

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Rep. & Stud. No.	Title	Date	Language
1.	Report of the Seventh Session	1975	E,F,R,S
2.	Review of Harmful Substances	1976	E
3.	Scientific Criteria for the Selection of Sites for Dumping of Wastes into the Sea	1975	E,F,R,S
4.	Report of the Eighth Session	1976	E,F,R
5.	Principles for Developing Coastal Water Quality Criteria	1976	E
6.	Impact of Oil on the Marine Environment	1977	E
7.	Scientific Aspects of Pollution Arising from the Exploration and Exploitation of the Sea-bed	1977	E
8.	Report of the Ninth Session	1977	E,F,R
9.	Report of the Tenth Session	1978	E,F,R,S
10.	Report of the Eleventh Session	1980	E,F,S
11.	Marine Pollution Implications of Coastal Area Development	1980	E
12.	Monitoring Biological Variables related to Marine Pollution	1980	E,R
13.	Interchange of Pollutants between the Atmosphere and the Oceans	1980	E
14.	Report of the Twelfth Session	1981	E,F,R
15.	The Review of the Health of the Oceans	1982	E
16.	Scientific Criteria for the Selection of Waste Disposal Sites at Sea	1982	E
17.	The Evaluation of Hazards of Harmful Substances Carried by Ships	1982	E
18.	Report of the Thirteenth Session	1983	E,F,S,R
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,R,S
22.	Review of Potentially Harmful Substances - Cadmium, Lead and Tin	1985	E
23.	Interchange of Pollutants Between the Atmosphere and Oceans (part II)	1985	E
24.	Thermal Discharges in the Marine Environment	1984	E
25.	Report of the Fifteenth Session	1985	E
26.	Atmospheric Transport of Contaminants into the Mediterranean Region	1985	E

Contents

EXECUTIVE SUMMARY

The present document summarizes the results of the work of the WMO-led GESAMP Working Group on the Interchange of Pollutants between the Atmosphere and the Oceans (INTERPOLL) subsequent to its first report which was published in the GESAMP Reports and Studies series No. 13 (GESAMP, 1980). These two reports should be taken together, since material included in the first report is generally not repeated in the second. If a distinction can be made between the two reports, then the first constitutes a rather broad overview of the whole topic, whereas the present report is more concerned with the behaviour of specific pollutants, or group of pollutants, including those related to fossil fuel burning and those which have a potential for altering climate.

The present report has three main sections. The first deals with the air-sea exchange of specific substances, and the second reviews some processes important in effecting this exchange. In the final section an outline is given of the criteria which need to be considered in designing a global programme to study pollutant interchange at the air-sea interface.

1. Air-sea exchange of particular pollutants or groups of pollutants

Carbon Dioxide: In order to enter the oceanic reservoir CO_2 has to pass the air-sea interface, although this barrier is generally not the main obstacle controlling the magnitude and timing of the uptake. Rates of lateral and, especially, vertical mixing of surface waters constitute the main factors controlling the rate of uptake of CO_2 by the oceans.

Sulphur Gases: The oceans can act as both a source and a sink for atmospheric sulphur gases. The principal gas identified for which the oceans are a net source is dimethyl sulphide (DMS). For this gas the magnitude of its sea-to-air flux is currently estimated to be about 40×10^{12} g S(DMS) yr^{-1}, i.e. of about the same size as the global production rate of sulphur dioxide from fossil fuel burning (Turner and Liss, 1983). Once emitted from the oceans the dimethyl sulphide is subject to rather rapid oxidation in the atmosphere, to form a variety of compounds including sulphur dioxide. The SO_2 will contribute to the acidity of rain, with the DMS-SO_2 route being proportionately more important over remote marine areas far removed from anthropogenic sources of sulphur dioxide. Other gases emitted from the ocean surface include carbonyl sulphide and carbon disulphide. Along with DMS, these gases are ultimately oxidised in the atmosphere to form sulphate aerosol particles. This process is especially important in the stratosphere where sulphate aerosols play an important role in controlling the radiation balance, and hence the climate of the Earth (Sze and Ko, 1979; Turco et al., 1980). Recently, Shaw(1983) has even speculated that changes in amounts of sulphate aerosols may be much more effective in altering climate than changes in atmospheric partial pressures of carbon dioxide.

Aerosols and Trace Elements: Early studies of particles collected from the marine atmosphere concentrated on sea-salt and insoluble continental dust, together with their associated major components. More recently it has become possible to examine substances present in only trace amounts, such as heavy metals and organic compounds. This advance has taken place in part because of improvements in the sensitivity of the necessary analytical techniques, but perhaps even more important has been the recognition of the importance of collecting samples free of contamination. Results obtained by the use of such techniques have considerably advanced our knowledge of the sources of particulate material found in the marine atmosphere. More specifically, they have made it possible to begin to establish how much of a particular trace element or substance is derived from pollution, as opposed to natural terrestrial or oceanic sources. Recent data indicate that both natural and pollutant components of the continentally-derived part of the marine aerosol are highly variable in concentration spatially as well as temporally. For many of the pollutant substances examined wet deposition appears to be the major mechanism by which they are transferred from the marine atmosphere to the oceans, at least in remote regions. It is clear that for the open oceans it is transported via the atmospheric, as opposed to the riverine, route which is the principal supplier of several trace metals (e.g. Pb, Sn) to the ocean.

Low Molecular Weight Halocarbons: The air-sea exchange of low molecular weight halocarbon gases has received some attention over the last decade or so. The sea is an important source of methyl chloride for the atmosphere, especially the stratosphere where the gas constitutes a source of chlorine atoms (with their potential for ozone destruction) comparable in size to the man-made Freons. Although the oceans are not thought to be the major sink for man-made halocarbon gases, such as carbon tetrachloride and the Freons, the distributions of the latter class of compounds as tracers of oceanic water movements has recently begun to be exploited.

Heavy Chlorinated Hydrocarbons: Synthetic heavy chlorinated hydrocarbons, such as DDT, PCBs, chlordane, hexachlorocyclohexane, etc., are being produced in ever increasing amounts. Since they have relatively high vapour pressures, concern has been expressed about their transport to remote marine areas via the atmosphere. Recent data confirms that these compounds do indeed exist in the vapour phase in remote marine air and that they are transported in the atmosphere thousands of kilometres from their sources on the industrialised land masses. Concentrations of heavy chlorinated hydrocarbons measured in marine air in the Southern Hemisphere appear to be between 3 and 5 times lower than amounts measured at equivalent sites in the Northern Hemisphere. The main route by which these compounds are removed from the marine atmosphere into seawater appears to be by direct gas exchange. For example, present best estimates indicate that for PCBs air-sea transfer of gas is approximately 60 times more important than the flux in rain.

Man-Made Radionuclides: Environmental measurements of radionuclides from nuclear weapons testing have yielded valuable information on rates and modes of deposition onto land and water surfaces. What is much less well understood is the way in which man-made radionuclides transfer by natural processes from the sea to the atmosphere. There is some evidence that transuranic radionuclides, like various trace metals, occur at elevated levels in the sea surface microlayer. They may then be transferred to the atmosphere via bubble bursting and wind spray which in coastal areas may allow radionuclide transport back to land by onshore winds. Further work is required, and such studies will tell us not only about the behaviour of the nuclides themselves, but by analogy may also provide more generally applicable information on microlayer enrichments and air-sea transfer mechanisms.

Particulate carbon: In marine aerosols the particulate carbon is composed largely of organic matter and black soot particles. The latter, whose concentration over oceanic areas ranges 10-100 ng C m^{-3}, is derived approximately equally from biomass burning and consumption of fossil fuels. It is suggested that soot carbon, because it absorbs visible light, can affect the global energy budget. It may also play a role in the atmospheric oxidation of sulphur dioxide to sulphuric acid.

2. Some processes and mechanisms important for the air-sea interchange of pollutants

Atmospheric Transport: Factors controlling the atmospheric transport of pollutants to and from the oceans are reviewed. After outlining the important properties affecting transport, methods for evaluating it are discussed under the headings of climatological studies, single-trajectory analysis, and transport models.

Cloud Condensation Nuclei: Submicron sulphate aerosol particles, formed by oxidation of sulphur dioxide in the atmosphere, play important roles in the microstructure of maritime clouds and in the processes leading to the formation of precipitation. There is some evidence that the concentrations of such cloud condensation nuclei over the North Atlantic have significantly increased over the last two to three decades. Although by no means proven, such an increase might lead to a reduction in the efficiency of the coalescence process necessary for the formation of precipitation.

Sea-Salt Inversion: It is generally assumed that the profile of sea-salt particles above the oceans shows a steady decrease in concentration with height. Recent measurements indicate that this is not necessarily always the case, and that inversions in the concentration profile just below cloud base can occur. The reasons for this effect are not known, but it is probably related to the cycling of salt through the clouds. Such uncertainties create problems in trying to predict the vertical distribution, and hence the fate, of pollutants in the sea which are resuspended along with the seawater electrolyte which forms the sea-salt aerosol.

Bubbles from Breaking Waves: Recent laboratory studies of the bubbles produced by waves breaking at the sea surface have confirmed the role of jet drops in producing most of the aerosol mass. More importantly, the experiments have highlighted the significance of large bubbles in the formation of film drops. Since it is known that surface-active materials can profoundly affect film-drop production, surface-active pollutants in seawater can become not only enriched in the aerosol produced when the bubbles burst, but can also modify the bubble size distribution itself.

Petroleum Films: Using visual observations, it has been estimated that at any particular time the amount of the sea surface which is covered by oil films is approximately 0.015%. This finding implies that petroleum films are unlikely to modify the exchange of matter or energy significantly on a global scale. However, in certain coastal regions, and especially along shipping routes, films will be more prevalent and could alter interfacial exchange processes. There are a number of natural processes which degrade and dispense oil films on the ocean. These include spreading of the oil film, the evaporation and dissolution of certain constituents, photocatalyzed oxidation, the entrainment and emulsification of the oil slick by wind and waves, etc. In addition, where oil films exist, rich populations of bacterioneuston play an important role in biologically degrading the oil. Laboratory experiments indicate that as much as 80% of the oil can be broken down within a matter of days. At sea degradation rates may be slower than this because the numbers of microorganisms in the surface microlayer are dependent on an adequate supply of nutrients from below.

Microlayer Residence Times: Compared with other marine interfaces the transit time of pollutants in the sea surface microlayer is generally short. For example, the residence time for water wettable particulate trace metals is estimated to be about 2 seconds. If the trace metal particulates are surface stabilized by less wettable organic coatings then their residence time in the microlayer can be in the range of 1-30 minutes. For lipophilic pollutants, such as PCBs, chlorinated pesticides, and organic forms of trace metals, which may accumulate in natural or pollutant organic films, microlayer lifetimes will be considerably extended and can be up to several days under extended periods of calm marine weather.

3. Development of scientific bases for future international programmes related to air-sea interchange of pollutants and the effects of such pollutants on atmospheric properties and processes

Presented here is the outline of a plan for a future international research programme on air-sea exchange of pollutants on a global basis. Critical pollutants for study in such a programme are identified, as are areas and sites where the measurements should be made. It is stressed that analytical methods as well as data collection and processing facilities will have to be standardized, as far as possible. Methods selected must not only be sufficiently sensitive and reliable, but also able to be adopted by all laboratories participating in the programme. Data quality will have to be rigorously checked. This can often be achieved by intercalibration exercises involving the participating laboratories under the coordination of a lead laboratory. The purpose of the programme needs to be clearly defined and its major objectives must have at their core a better understanding of processes of air-sea pollutant transfer, increase in knowledge concerning sources and sinks, and improved estimates of air-sea fluxes of pollutants.

1. AIR-SEA EXCHANGE OF PARTICULAR POLLUTANTS OR GROUPS OF POLLUTANTS

1.1 Carbon Dioxide

It is clearly necessary to improve our quantitative understanding of the oceanic exchange rate for anthropogenic CO_2, especially in order to predict future atmospheric levels of the gas, since these are required in order to model the time-scale of any resulting climatic changes. The size of the net flux to the ocean depends on three processes: i) the equilibrium capacity of seawater for CO_2 uptake, determined by chemistry; ii) gas exchange between air and sea; and iii) transport of CO_2-laden surface water to the deep ocean. Of these, the first two are relatively well known (Liss and Crane, 1983), while the oceanic circulation has been simulated in global carbon models in a rather simple way only. A test of the carbon cycle models is possible by the penetration of bomb-produced C^{14} and H^3 into the ocean; the simulations agree reasonably well with the observed depth distribution (Oeschger et al., 1975; Broecker et al., 1979). The mean depth of penetration of artificially produced C^{14} and H^3 is only a few hundreds of metres, indicating also that anthropogenic CO_2 cannot have been transported in significant amounts to the huge reservoirs of the deep ocean. In certain restricted areas of the cold ocean surface, where vertical exchange with deeper water occurs much faster than elsewhere, CO_2 uptake is more effective than on the average. This feature is in general not explicitly included in existing models; estimates show that the additional CO_2 uptake may amount to several percent of the fossil CO_2 uptake (Crane, 1982; Siegenthaler, 1983). When describing the exchange between atmosphere and ocean it is evidently necessary to take into account its geographical variability.

It has also been proposed that sedimentation of fixed carbon in coastal waters contributes an important CO_2 sink. A related possibility is increased biological CO_2 uptake in seawater (and ultimately an increase in fixed carbon sedimented out of the system) as a result of increased nutrient inputs (Walsh et al., 1981).

Although it is true that industrial production of phosphorus and nitrogen-containing fertilisers has increased enormously over the last century along with CO_2 emission from hydrocarbon burning, it is not at all clear how much of the increased nutrients are lost from the agricultural land to which they are applied and eventually reach the oceans.

Obviously, these various possibilities should be thoroughly investigated. However, probably the most obvious way in which present models may underestimate the ocean sink for CO_2 is in the rate at which the gas is mixed into the huge reservoir of the deeper layers of the oceans.

1.2 Sulphur Gases

The ocean surface acts as a source for a number of gaseous (organo) sulphur compounds which are produced in seawater by biological and/or chemical processes. Since direct flux measurements across the air/sea interface are not yet able to reproduce realistically actual environmental conditions, the fluxes for all these gases are currently being estimated using the film transfer model on the basis of oceanic and atmospheric concentration measurements. This introduces a significant uncertainty into all the estimates discussed below. At this time, the following volatile sulphur compounds have been identified in sewater, dimethylsulphide(DMS), carbonyl sulphide(COS), carbon disulphide(CS_2), methylmercaptan(CH_3SH) and dimethyldisulphide(DMDS). Hydrogen sulphide(H_2S), sometimes present in coastal waters, is rarely detectable in the open ocean. These compounds will be discussed in more detail in the following paragraphs.

Dimethylsulphide: This is the most abundant volatile sulphur compound detectable in seawater. Extensive data on its distribution in the major oceans (with the exception of the Indian and Southern oceans) have been reported by several groups (Andreae, Florida State University; Bingemer, Frankfurt; Cline, NOAA/PML). On the basis of

700 data points in the Atlantic and Pacific oceans, Andreae and Raemdonck (1983) estimated a sea-to-air flux of about 40×10^{12} g S(DMS) yr^{-1}. The results of the other groups concur with this estimate. There is also evidence for a correlation between DMS concentrations in the water and marine primary production. Recent observations in coastal water by Turner and Liss (1984) show a pronounced seasonal variability of DMS and suggest the possibility of a microlayer enrichment of the gas under some circumstances.

Despite a relatively large number of measurements of the atmospheric concentration of DMS by the Frankfurt and Florida State groups, substantial uncertainty persists regarding the fate of DMS in the atmosphere. Two rather distinct types of behaviour have been observed both over the Atlantic and the Pacific oceans, one is characterized by relatively high DMS levels (about 100 ng S(DMS) m^{-3}) and a pronounced diurnal variation, the other by low concentrations (5 ngS(DMS) m^{-3}) and the absence of diurnal changes. The DMS levels in the underlying seawater are comparable in both cases. The high DMS case agrees extremely well with the behaviour predicted by current photochemical models, while the low DMS case suggests the presence of an additional, rapid, non-photochemical sink. The low DMS case is usually related to detectable continental influence on airmass composition.

Current estimates of the deposition rate of non-seaspray derived (excess) sulphate aerosol over remote regions, where anthropogenic sulphur dioxide(SO_2) is not expected to be a significant source, are of the order of 50% of the input estimate of DMS from sea-to-air transfer in these areas. The presence of relatively constant concentrations of SO_2 over remote marine regions also supports the existence of a significant seawater source of volatile sulphur.

The results of kinetic experiments on the photochemical oxidation of DMS suggest that SO_2 and methanesulphonic acid are the major reaction products. The latter compound has been recently observed in marine rain (Saltzman et al., 1983).

Carbonyl sulphide: This compound is persistently supersaturated in surface seawater (Ferek and Andreae, 1983, 1984; Rasmussen et al., 1982a). In the open ocean, the supersaturation ratio is near 2, which corresponds to a sea-to-air flux of about 0.5×10^{12} g S(COS) yr^{-1}. This flux is of the same order of magnitude as the other natural sources of COS (soils 0.4×10^{12} g yr^{-1}, volcanos 0.02×10^{12} g yr^{-1}, marshes 0.03×10^{12} g yr^{-1}) and the anthropogenic emissions (biomass burning 0.3×10^{12} g yr^{-1}, fossil fuel burning 0.06×10^{12} g yr^{-1}). A potentially large source exists in the photo-oxidation of CS_2 in the atmosphere. The sum of these fluxes is substantially larger than the only known sink of COS, its photo-oxidation in the stratosphere ($\sim 0.3 \times 10^{12}$ g yr^{-1}).

COS is produced in surface seawater by the reaction of photochemically produced oxidants with dissolved organosulphur compounds probably of biological origin (Ferek and Andreae, 1984). No evidence exists for the direct production of this gas by microbes in seawater.

Carbon disulphide: The oceanic source of this substance has not yet been adequately evaluated. Studies on its concentration in seawater suggest that it is normally near equilibrium, with a possible upward flux of about $0.15\ 10^{12}$ g S(CS_2) yr^{-1}. Higher supersaturations have been observed in coastal waters (Turner and Liss, 1984) but may not contribute strongly to the global budget. Substantial emission from land, including anthropogenic releases, have been suggested (Adams et al., 1981).

Methyl mercaptan: CH_3SH is often present in surface seawater, especially from coastal regions. No good quantitative data are yet available; estimates of seawater concentrations are in the range of up to 10 ng S(CH_3SH) l^{-1}. It may thus represent a significant source to the marine boundary layer.