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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.

Financial support for the work of the Working Group was provided by the World Meteorological Organization (WMO) and the United Nations Environment Programme (UNEP).

Contents

Page

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.

It should be noted that there are analytical difficulties in the determinations of CH_3SH and CS_2, and that the results obtained depend upon the method of analysis used.

Dimethyl disulphide: Concentrations of this species in all known sea surface environments are much lower than those of DMS and CH_3SH (from which it is probably formed). For this reason, no significant sea-to-air transfer is to be expected for this compound. It reaches high levels in marine sediments and some releases may occur from tidal flats and salt marshes.

Hydrogen sulphide: While this gas is produced in large amounts in marine sediments, it is rapidly reoxidized at the sediment/water interface and in the seawater column. Therefore, no important release occurs from the ocean surface, and the emissions of H_2S are restricted to tidally exposed environments. Some release occurs from terrestrial biota. Source strength estimates range from 10^{12} - 10^{13} g yr^{-1}. Emissions of this gas may be of importance in the coastal zone in particular.

The gases discussed so far in this section all have a net flux out of the seawater. For other sulphur compounds the direction of the net flux can be in the opposite sense, i.e. from the marine atmosphere into the sea. It is known that the oceans are the major sink for the excess sulphate present in marine aerosols. In addition, dimethylsulphoxide and methanesulphonic acid present in atmospheric aerosols (Panter and Penzhorn, 1980) and precipitation are being deposited on the ocean surface. However, no adequate data are available at present to quantitatively estimate the fluxes of these two substances.

Rather better studied is the one-way flux of sulphur dioxide into the ocean from the marine atmosphere. The SO_2 can come either from land, where anthropogenic releases are becoming increasingly important, or from the oxidation of reduced sulphur gases, such as DMS, where part of the atmospheric burden comes from the oceans, as discussed above. The atmospheric residence time of DMS is known to be short (hours-days) and its rapid reaction in the marine boundary layer of the atmosphere offers the possibility that a fraction of the gaseous sulphur compounds emitted from seawater is returned to the ocean surface which is then acting as a sink. Measurements of SO_2 concentrations on a cruise of the R.V. "Meteor" from Hamburg to Rio de Janeiro and of the Swedish icebreaker "Ymer" into Arctic regions show the existence of SO_2 in the marine boundary layer in regions far from the continents. Concentrations were found in the range between 0.07 - 0.7 μg $S(SO_2)$ m^{-3} (Ockelmann and Georgii, 1984). Considering the relatively short atmospheric residence time of SO_2 of one to a few days, and the fact that samples were taken in areas where anthropogenic influence can be excluded, it is suggested that a fraction of the SO_2 measured in the marine boundary layer originates from biogenic gaseous sulphur compounds. If this can be supported by further measurements, then the ocean can be considered as a secondary source for SO_2 and a primary sink for SO_2. Sulphur dioxide measurements made several years ago in the temperate latitudes of the North Atlantic between the North American and the European continents showed SO_2 concentrations of 0.5 - 1.5 μg $S(SO_2)$ m^{-3} within the Westerlies. This rather high SO_2 concentration can most certainly be attributed to the plume from the many anthropogenic sources near the east coast of North America extending many hundred kilometers over the North Atlantic ocean. Present best estimates give the global air-sea flux of SO_2 as approximately 10^{13} g S yr^{-1}.

1.3 Aerosols and Trace Elements

Recent years have seen the publication of a considerable amount of new data on the concentrations and behaviour of aerosols and trace elements in the marine environment (see Buat-Ménard, 1983 for a review). More and more substances are being investigated in the context of large-scale programmes, both national and international.

In the early seventies, most of our knowledge was restricted to major components, such as sea-salt, continental dust, and associated major elements. Since then, many trace elements and compounds, such as heavy metals and organic compounds, have been identified and studied. Most of this is the result of improved sampling and analytical techniques. Collection artifacts are now well documented in many cases. Also, stringent precautions against local contamination during sampling and sample contamination during handling have proven to be an absolute necessity, especially for sampling in remote areas. Although vertical distributions of atmospheric concentrations are still poorly known (primarily because of sampling difficulties), latitudinal and longitudinal distributions, based on the analysis of samples collected from ships, coastal areas and remote islands, are beginning to be reasonably well-documented both for regional seas and remote oceanic regions. Since the marine aerosol is a variable mixture of modified marine and continental source material, source identification for a given element or compound is a crucial aspect of ongoing research. Together with the use of reference elements (Na for sea-salt aerosols, Al, Si or Fe for coastal aerosols), other tools such as the determination of elemental concentrations as a function of particle size (which aids in the discrimination between primary and secondary sources) have proved to be very useful. Also, other criteria have been used that are more specific for the substance and source being investigated. These include: chemical analysis of individual particles, measurements of the isotopic composition of some elements and radioisotopes, analysis of "source markers" such as organic compounds or classes of compounds, chemical speciation studies, and carefully designed laboratory experiments.

Recent data, such as those obtained during the SEAREX (Sea-Air Exchange) Programme indicate that the continental component of marine aerosols is highly variable in space and time. This is true both for aerosols from natural and anthropogenic sources. For example, Table 1 shows that, on the average, the rate of input of metals from the atmosphere to the sea-surface decreases by many orders of magnitude from coastal areas to the remote regions of the Tropical North Pacific. For mineral aerosols originating from arid regions and deserts, the long-range transport of Asian dust has been documented over the entire North Pacific ocean. A seasonal transport pattern was found at most of the sites, together with a latitudinal gradient in the mean-annual atmosphere dust concentration, with the greatest concentrations occurring in mid-latitudes. As has been found previously for Saharan dust transported over the North Atlantic, Asian dust is a significant source of sedimentary material for the North Pacific.

Different source regions for pollutant lead aerosols, the North Pacific (Japan and North America), have been found on the basis of lead isotope measurements. In the same context, study of the mineralogy of aluminosilicate dust particles appears to be a promising tool for allocating sources. Also, significant progress in source identification has been achieved for a number of elements or compounds. For example, chemical speciation studies have allowed estimation of the respective proportions of marine-derived, crustal-derived and anthropogenically-derived phosphorus in marine aerosols. With respect to organic compounds, carbon isotope measurements as well as biological source marker measurements have allowed successful distinction to be made between marine and land-derived sources for organic matter in marine aerosols.

The importance of the ocean surface as a source of aerosols is still receiving attention. New estimates of sea-salt production rates and concentrations as a function of wind speed have been published. For trace elements, more accurate sea-to-air fluxes, based on the analysis of aerosol particles artificially produced from bursting bubbles, have been obtained, since such data take into account the enrichment of these elements in sea-source aerosols. They indicate that, outside the well-documented alkali and alkaline-earth metals, the ocean could be a significant source of V and perhaps Cd to the

TABLE 1

Estimated Mean Fluxes of Trace Metals from the Atmosphere to the Sea Surface (ng cm^{-2} yr^{-1})‡

Element	New York Bight (Duce et al., 1976a)	North Sea (Cambray et al, 1975)	Western Mediterranean (Arnold et al., 1982)	South Atlantic Bight (Windom, 1981)	Bermuda (Duce et al., 1976b)	Tropical North Atlantic (Buat-Ménard & Chesselet,1979)	Tropical North Pacific (Duce et al., 1982)
Al	6,000	30,000	5,000	2,900	3,900	5,000	1,900
Sc	-	5	1	-	0.6	1.1	0.4
V	-	480	-	-	5	1.7	2.8
Cr	-	210	49	-	9	14	6
Mn	-	920	-	60	45	70	18
Fe	5,700	25,500	5,100	5,900	3,000	3,200	1,300
Co	-	39	3.5	-	1.2	2.7	0.6
Ni*	-	260	-	390	3	20	-
Cu*	-	1,300	96	220	30	25	2
Zn*	1,400	8,950	1,080	750	75	130	13
As*	-	280	54	45	3	-	-
Se*	-	22	48	-	3	14	4.5
Ag*	-	-	3	-	-	0.9	0.2
Cd*	30	43	13	9	4.5	5	0.5
Sb*	-	58	48	-	1.0	3.5	0.1
Au*	-	-	0.05	-	-	0.1	-
Hg*	-	-	5	24	-	2.1	-
Pb*	3,900	2,650	1,050	660	100	310	7
Th	-	4	1.2	-	-	0.9	0.9

* Designates elements generally enriched in marine aerosols

‡Flux estimates are based upon a variety of assumptions, not necessarily the same among the listed investigators.

atmosphere. However, for many trace substances, the existence of a significant recycling across the air-sea interface makes it difficult to evaluate the net input of these substances from the continent to the oceans via atmospheric deposition. For enriched metals and organic carbon, it appears that measured total dry deposition fluxes may be mostly due to the sea surface derived fraction, which typically resides on the largest particles which have the highest deposition velocities. The presence of a recycled component in marine rain may also affect the significance of direct measurements of net fluxes to the ocean. This question is still open to debate since the answer depends on our knowledge of the scavenging efficiency of aerosol particles as a function of their size, and washout factors are still not known with accuracy. Very recent data indicate, however, that in clean marine air the aerosol scavenging efficiency is apparently not particle-size-dependent, so that the relative contribution of the recycled component to elemental concentrations in rain is probably not enhanced compared to what is observed in the marine aerosol. In any case, it can now be inferred that atmospheric net fluxes to the ocean surface are primarily due to wet deposition in the remote marine atmosphere. This is particularly true for pollution-derived elements which are generally found on submicron sized aerosols. Dry deposition, on the other hand, is certainly significant for sea source aerosols as well as for continental dust derived from soil erosion.

The high efficiency of aerosol scavenging by rain has led to some interesting findings with respect to elements or components which are present both in the particulate form and the gaseous form in the remote marine atmosphere. For Hg and some organic compounds, it has been found that although the concentration in the gaseous form dominates the concentration in the particulate form, the rain content of that element or compound is controlled mainly by the scavenging of the particulate form.

With all this new information, some conclusions on the role of air-sea particulate exchange in geochemical cycling have become possible. For regional seas, it appears that the atmospheric delivery from the atmosphere to the ocean is higher than or at least comparable to the riverine dissolved delivery for many trace elements (Table 2). Due to anthropogenic perturbations of Pb and Sn atmospheric cycles, the cycles of these elements in the ocean are not longer at steady state and show enhanced concentrations over natural levels in the upper water column. The level of the enhancement reflects the level of the atmospheric input rate. For these and other elements predictive modeling of the influence of natural anthropogenic inputs from the atmosphere on their cycles in the ocean has been proposed and clearly indicates that the deep ocean is no longer free from anthropogenic inputs from the atmosphere.

Future research should concentrate on the following topics: i) Investigation of sources, sinks and transport processes on the regional scale (enclosed seas - pericontinental areas); ii) The need for reliable data in remote parts of the Southern Hemisphere; iii) Improvement in the understanding of the biological availability of atmospheric inputs of particulate matter to the ocean surface through "in situ", or carefully designed laboratory experiments: iv) The need for data on the chemical composition of oceanic precipitation as well as much better data on the distribution and quantity of global rainfall.

1.4 Low Molecular Weight Halocarbons

The air-sea exchange of low molecular weight halocarbons is important for several aspects of atmospheric and oceanographic science. For example, methyl chloride produced naturally in the oceans enters the atmosphere across the sea surface and constitutes a significant source of chlorine to the troposphere, and especially the stratosphere. In a similar way, methyl iodide produced by marine microorganisms is an important component in the global geochemical cycle of iodine. Conversely, anthropogenically produced compounds, such as the Freons and carbon tetrachloride, are injected into the atmosphere and any net flux across the sea surface must be directed downwards. Quantification of such fluxes is important for assessing the importance of the oceans as a sink for these man-made compounds. Furthermore, tracking of their seawater distributions both horizontally and vertically is providing a valuable tool for the tracing of water movements in the oceans.

Estimation of the flux of these compounds across the surface presents most of the usual difficulties with such calculations. In this case, some simplification is possible because we are dealing with simple gases, i.e. small size and low molecular weight, which are generally rather unreactive in the aqueous phase.

Of the chlorine-containing gases, the principal one whose net flux is out of the ocean is methyl chloride (CH_3Cl). This global sea-to-air flux has been estimated to be in the range $3\text{-}8 \times 10^{12}$ g yr^{-1} (Singh et al., 1979, 1983, Watson et al., 1980). The sea appears to be the largest source of CH_3Cl to the atmosphere, with biomass burning as the next most prolific contributor (Watson et al., 1980). The reason for estimating the flux of this compound to the atmosphere is because it is probably comparable to the man-made Freons as a natural source of chlorine atoms to the stratosphere, and may also be of importance for the behaviour of gases in the troposphere (Rasmussen et al., 1980). Recently Khalil et al. (1983) have used measurements of chloroform ($CHCl_3$) in marine air and surface seawaters to calculate the flux of this compound across the sea surface. They obtain a global flux of 0.35×10^{12} g yr^{-1} from the sea to the air. This result may imply that much of the chloroform in the atmosphere is natural and not anthropogenic, as thought previously.

TABLE 2

Ratio of Atmospheric Flux to Riverine Flux (dissolved) of some Trace Elements in Coastal and Semi-remote Oceanic Areas

Element	South Atlantic Bight (Windom, 1981)	New York Bight (Duce et al., 1976a)	North Sea (Cambray et al., 1975)	Western Mediterranean Sea (Arnold et al., 1982)
As	2.1	1.0	1.7	-
Cd	2.7	3.1	1.1	-
Cu	1.9	-	1.9	-
Fe	5.8	6.4	1.7	-
Mn	0.6	-	0.8	-
Hg	22	-	2.1	0.8
Ni	1.7	-	1.3	-
Pb	9.5	20	6.8	6.2
Zn	2.3	3.1	1.9	0.8

Of the low molecular weight brominated compounds, methyl bromide (CH_3Br) has recently been measured in surface seawater, and a global flux from sea to air of 0.3×10^{12} g yr^{-1} calculated (Singh et al., 1983). Bromoform ($CHBr_3$) has been observed in Arctic surface waters (Dyrsson and Fogelqvist, 1981), although no air-sea flux calculations appear to have been attempted for this compound.

Methyl iodide measurements in surface ocean waters show them to be substantially supersaturated with respect to levels in the marine atmosphere, implying a flux of the gas out of the oceans. This flux has been estimated as between 3×10^{11} g yr^{-1} (Liss and Slater, 1974) and 13×10^{11} g yr^{-1} (Rasmussen et al., 1982) on a global basis. Even the lower estimate constitutes an important component of the global iodine cycle.

Anthropogenically produced halocarbons injected into the atmosphere whose air-to-sea transfer has been examined are principally various Freons (e.g. F-11 or CCl_3F, and F-12 or CCl_2F_2) and carbon tetrachloride (CCl_4). Based on measurements made in the North and South Atlantic in the early 1970s (Lovelock et al., 1973), Liss and Slater (1974) calculated the net global air-sea flux of F-11 and CCl_4 to be 5.4×10^9 and 1.4×10^{10} g yr^{-1}, respectively. A decade later, Hunter-Smith et al. (1983) sampled on an almost identical cruise track and found the air and seawater to be essentially at equilibrium for CCl_4, implying no net flux. Similarly, recent measurements of F-11 in the North Pacific (Gammon et al., 1982) indicate almost precise saturation equilibrium between atmosphere and surface ocean for this gas. In view of the levelling off and recent decrease in release of F-11 to the atmosphere, it may well be that the change found in the air-to-sea flux over the last decade is real. At the beginning of the period atmospheric releases (mainly in the Northern Hemisphere) were still increasing and this led to a significant difference in air concentrations between the Northern and Southern Hemispheres. In these circumstances, a flux into the oceans was to be expected - the figure given above corresponds to approximately 2% of the anthropogenic production rate of F-11 at that time. The recent changes in release rates have led to a decrease in this N-S difference in air levels (Hunter-Smith, et al., 1983), and may have allowed the surface oceans and the atmosphere to come close to equilibrium.

The input of F-11 and F-12 into the oceans, which has occurred over the last two to three decades since these compounds came into widespread use, has recently begun to be successfully exploited as a tracer of water movements in the oceans (Gammon et al., 1982, Bullister and Weiss, 1983).

1.5 Heavy Chlorinated Hydrocarbons

The ever-increasing production of synthetic organic chemicals and the relatively high vapour pressure of many of these substances has led to considerable concern about their transport to open ocean regions via the atmosphere. Some of these substances may be lipophilic and subject to concentration up the food chain, as such they may present a hazard to marine organisms either through direct exposure or via their food. Data on the distribution of most synthetic organic substances in the atmosphere and in rain in remote marine regions are very sparse (Duce et al., 1983). Some new data on the distribution of heavy chlorinated hydromcarbons such as DDT, DDE, PCBs, chlordane, hexachlorocyclohexane, etc., have become available during the past 3 to 5 years, however. Recent data are presented in Table 3. Even though these are relatively high molecular weight compounds, there is continuing evidence that they exist in the atmosphere almost entirely in the vapour phase. These compounds have no natural sources and it is clear from the data in Table 3 that they are transported in the atmosphere thousands of kilometres from their source.

There are marked regional differences in the concentrations of some substances (e.g. p,p^1-DDT), while others appear to be more uniformly distributed (e.g. chlordane). While these different distribution patterns are at least partly a result of regional differences in the use of the various chemicals, differences in atmospheric residence times undoubtedly also play a major role. The relatively uniform concentrations for such compounds as PCBs (Arochlor 1242), chlordane, dieldrin, and hexachlorocyclohexane suggest a reasonably long (at least from weeks to several months) atmospheric residence time for many of them. These relatively long residence times have been confirmed over the North Pacific by the general lack of correlation of these organic substances with mineral aerosol concentrations. Mineral aerosol, largely derived from Chinese deserts in that area, has a residence time of a few days to a week or so.

There are few atmospheric data available for these substances in the Southern Hemisphere, but preliminary data from the SEAREX Programme in American Samoa suggest concentrations of heavy chlorinated hydrocarbons 3 to 5 times lower than those measured by the same SEAREX group at Enewetak in the North Pacific. Additional data for these substances from SEAREX studies at a remote New Zealand site in 1983 should be available in the near future.

There is still considerable uncertainty about the primary pathway by which atmospheric heavy chlorinated hydrocarbons enter the ocean. Rain is apparently a relatively inefficient removal mechanism for the vapour phase of most of these substances. While the particulate fraction of most of the heavy chlorinated hydrocarbons represents considerably less than 5% of their total mass in the atmosphere, evidence suggests that most of these substances in rain may be derived from scavenging of the particulate phase.

TABLE 3

Concentration of Heavy Synthetic Organic Compounds in the Vapour Phase

Compound	Arabian Sea*	Persian Gulf*	Red Sea*	Barbados*	Newfoundland*	North Atlantic Trades	Enewetak Atoll +
p, p'-DDT	75	90	132	2.5	2.7	5.0*	
p, p'-DDE						6+	3
Chlordane	7.8	8.0	16	9.6	35	19*	13
Dieldrin	3.9	10	13	5.2	7.3	16+	10
Hexachlorobenzene						150+	100
α -Hexachlorocyclohexane						390+	250
γ -Hexachlorocyclohexane							15
Toxaphene					109	50*	
PCB (Arochlor 1242)						1840+	540

Concentrations are in picograms m^{-3}(STP)

* Bidleman and Leonard (1982)

\+ Atlas and Giam (1981)

Laboratory measurements of Henry's Law constants (partition coefficients) have recently been made for several of these chlorinated hydrocarbons in seawater systems. Using film model calculations, it appears that direct gas exchange with the ocean may be the primary removal mechanism for many of these compounds in the marine atmosphere. For example, preliminary calculations (Atlast and Giam, 1981, Atlas et al., 1982) suggest that the direct gas flux of PCB (Arochlor 1242) from the atmosphere to the ocean in the North Pacific is perhaps 60 times the precipitation flux. Additional laboratory studies measuring partition coefficients for other synthetic organic compounds between air and both fresh water and sea water and at near ambien concentration levels are needed before adequate evaluations can be made of the sea/air exchange of these substances. Even then, it must be emphasized, the resulting gas exchange fluxes will be calculated, not measured, for these substances, and will still be subject to considerable uncertainty.

Many more field measurements of heavy chlorinated hydrocarbons in air and precipitation over open-ocean regions of the Atlantic, Pacific and Indian Ocean are needed. Such measurements, particularly in precipitation, should be relatively straightforward to make and are strongly encouraged. Of particular importance will be measurements in the Southern Hemisphere, where source strengths for synthetic organic chemicals are considerably lower than in the Northern Hemisphere, but may be on a rising trend. Information on vertical distributions of these substances would also be very useful, but is presently very difficult to obtain owing to the long sampling times (a day or two) required to collect sufficient material for analysis. It must be emphasized that local sources of contamination can pose serious problems in the collection of air and precipitation samples for analyses of trace organic materials, but these problems can be avoided with careful planning (Atlas and Giam, 1981, Bidleman and Leonard, 1982).

1.6 The Air-Sea Transfer of Man-Made Radionuclides

Most of the research on air-sea transfer of man-made radionuclides has been conducted in relation to radioactive fallout from nuclear weapons testing in the atmosphere and at the sea or land surface. Since the limited test ban treaty of 1963, there has been a general decline in fallout of radionuclides. A marked latitudinal variation in fallout of all fission-product radionuclides has been noted, with most of the fallout occurring in the Northern Hemisphere, predominantly at mid-latitudes. This global distribution is in part related to the source of radionuclides, which has been largely from testing north of the equator, and partly due to the nature of the stratospheric and tropospheric wind systems transporting nuclear debris globally.

While most of the fallout studies have been conducted on Sr^{90} and Cs^{137}, because of their relatively long half-life (28 and 30 years, respectively) and potential hazard to human health, there have been fallout records maintained also on $Pu^{239,\ 240}$ and Pu^{238}. Parallel with the year-to-year trends of Sr^{90} and Cs^{137}, reflecting the intensity of atmospheric nuclear weapons testing, there was an increase of $Pu^{239,\ 240}$ to a peak in 1963 at 0.62 mCi km^{-2} and then a decline to 0.01-0.03 mCi km^{-2} during 1970-1974, as measured in New York. Tokyo fallout records showed a peak for $Pu^{239,\ 240}$ and Pu^{238} at 0.200 and 0.0073 mCi km^{-2} in 1963, and then a decline during 1970-1978 to levels of 0.001-0.013 and 0.0002-0.0019 mCi km^{-2}, respectively.

Data reported for surface seawater in the North Pacific Ocean sampled in 1977-1978 showed concentrations of $Pu^{239,\ 240}$ at $0.6\text{-}6 \times 10^{-4}$ pCi l^{-1}, with the highest levels at mid latitude. In the Southern Ocean the concentrations ranged from $0.2\text{-}3 \times 10^{-4}$ pCi l^{-1}. Am^{241} exhibited concentrations of $0.1\text{-}1.1 \times 10^{-4}$ pCi l^{-1} in the North Pacific and $0.2\text{-}0.5 \times 10^{-4}$ pCi l^{-1} in the Southern Ocean during the same period.

It can be inferred from measurements of natural radionuclides, e.g. K^{40}, in the atmosphere and comparing the ratios to salt in the sea and atmosphere that there can be a flux of artificial radionuclides from the sea to the atmosphere. As well documented for metals, radionuclides can be concentrated in the surface microlayer and transferred to the atmosphere through bubble bursting and wind spray.

Atmospheric measurements of radionuclides previously discharged to the sea were made at coastal stations in northwest England in the neighbourhood of a nuclear reprocessing facility (Pattenden et al, 1981). It was concluded that a number of the discharged radionuclides were being returned to land from the sea via the atmosphere. It was postulated that for some of the actinides, there was enrichment in the seasurface microlayer and/or sediments, and that seaspray and surf transferred them into the atmosphere in concentrations greater than that found in seawater.

A need exists for measurements of fluxes of radionuclides from the sea to the atmosphere for a better understanding of behaviour of radionuclides released into rivers or directly into the sea from nuclear reactors and other peaceful uses of radioactivity.

1.7 Particulate Carbon in the Marine Atmosphere

Carbon is present in marine aerosols largely as organic matter and as black soot particles. Recent investigations have shown that soot carbon is present in the marine aerosol over most oceanic areas at concentrations of 10-100 ng C m^{-3} (Andreae, 1983 et al., 1984). The ratio between soot carbon and total carbon is relatively constant as long as significant amounts of soot are present. This suggests that the continents are the dominant source of both organic and soot carbon. Only over the most remote oceanic areas does organic carbon of marine origin make up a significant component of the organic aerosol (Andreae et al., 1984, Chesselet et al., 1981). Correlations between soot carbon and other aerosol constituents suggest that comparable amounts of the global burden are contributed by biomass burning and by fossil fuel combustion.

Since soot carbon is the only important visible light absorbing component of atmospheric aerosols (Ackerman and Toon, 1981), the ratio of soot carbon to total aerosol mass determines the net effect of the atmospheric aerosol on the global enbergy budget. Under certain conditions, e.g. the arctic haze layer, significant effects have been prediced from current levels of atmospheric soot carbon (Rosen et al., 1983). In addition, carbon must be expected to contribute a large proportion of the number of cloud condensation nuclei of continental origin.

Recently, a catalytic effect of soot carbon on the oxidation of SO_2 to H_2SO_4 has been suggested (Novakov, 1983), although the details of the interaction are complex and not yet well understood.

2. SOME PROCESSES AND MECHANISMS IMPORTANT FOR THE AIR-SEA INTERCHANGE OF POLLUTANTS

2.1 The Atmospheric Transport of Materials To and From the Oceans

The oceans can act as both a source and a sink of materials which are transported by the atmosphere. Particularly on a global basis, the atmosphere plays an important role as a conduit of such substances as sulphur compounds, trace metals, desert dust, organic materials and other natural and man-made substances. Close to continents, input into the oceans via rivers may be much higher for a given compound than input via the atmosphere. Such direct transport from land sources is being reviewed by the GESAMP working group on Land-Sea Boundary Flux of Pollutants. However, far from the continents, the atmosphere is the major path of transport for many materials in the ocean.

How a given substance is transported via the atmosphere depends on a number of factors. One of the most important is the form in which it is released. A non-reactive gas will be transported much farther than an aerosol, all other things being equal. Other factors that influence transport are the elevation of release, the state of the atmosphere, the location of the source with respect to the oceans, particle size, amongst others. However, physical transport is not the only factor that influences the lifetime of material in the atmosphere.

Two other factors beside transport affect the residence time of a substance in the atmosphere. First, chemical transformation can have an important effect on the lifetime of a gas or aerosol through photochemical processes or through in-cloud chemical reactions. In both cases, the end product will be in a different chemical and/or physical form (for non-reactive species this process is not important). Second, physical capture or scavenging of particles and gases by aerosols and cloud droplets may occur, and in this manner substances can be deposited in the oceans. These three processes - transport, transformation and scavenging - determine the distribution of substances to the oceans (Prospero, 1978).

Atmospheric transport can be defined simply as the movement of materials by the winds. This process is purely a physical one; transformation and scavenging, mentioned above, would have to be included if a complete picture of emission/deposition is drawn. A number of methods can be applied in evaluating transport, such as: climatological studies, single-trajectory analysis, and complex transport models. These types of analysis have been applied on a regional basis, such as eastern North America and Western Europe. Another approach is to use global-scale climatological models with a chemical module to study cycles of chemicals over long time scales. In all approaches, the lack of meteorological and chemical data over the oceans is a major disadvantage. Whatever the approach, the difficulties of describing transport over the oceans is a complex one. The following summarizes three of the most frequently used methods that could be applied to the evaluation of the atmospheric transport of pollutants.

Climatological studies: The climatological method involves such studies as producing average monthly and yearly weather maps, calculating one station climatology over decades, satellites summaries, and analogue techniques. These methods are successful in describing average conditions but are not applicable in interpreting individual chemical measurements made on ships or remote islands (Holzworth, 1972, Korshover, 1976, Eichenlaub, 1979, Rahn and McCaffrey, 1980).

Single-Trajectory Analysis: In recent years, computer techniques have allowed the calculation of forward or back air trajectories on a routine basis and have thus enabled researchers to use daily trajectories on an operational basis. These trajectories, along with the chemical data, yield a qualitative evaluation of the trasnport. An example of this type of trajectory analysis is that by Jickells et al., 1982, which showed the large transport of sulphate and nitrates from North America to the Western Atlantic. Other works in this area include those by Pack et al., 1978, Peterson et al., 1980, Heintzenberg and Larssen, 1983, and many others. Because of the large areal sources that contribute to ocean deposition, forward trajectories are probably not useful in evaluating transport but could be applied to point sources from continents.

Transport models: In recent years, the transport of materials in the atmosphere has been approached by the use of atmosphere models that take emission values, meteorological data and other parameters and attempt to show the final deposition of the material being studied. These models use either a Lagrangian or a Eulerian framework. Most of these models have been applied to land areas, where emission and meteorological data are more extensive. Application to ocean areas has not been attempted (Eliassen, 1980).

The techniques to describe transport to and from the oceans are still in their infancy. Most of the work to date has concentrated on transport over continents. As more atmospheric chemical measurements are made over the oceans, companion meteorological models, which include the chemical changes determining both the chemical forms and residence times of the transformed materials, must be developed to help in the interpretation of these data.

2.2 Formation and Distribution of Cloud Condensation Nuclei

As noted previously, sulphur dioxide in the atmosphere has two main sources, viz. from the oxidation of reduced sulphur gases, some of which are formed biologically in the surface oceans, and from burning of fossil fuels containing sulphur. Whatever its source, atmospheric SO_2 is rather rapidly oxidized by homogeneous or heterogeneous reactions leading to the formation of sulphate aerosols. The oxidation rate can be assumed to be between 0.1 and 10% hr^{-1}, and is dependent upon other substances in the atmosphere. These particles being in the size range 0.01-0.3 μm radius can act as cloud condensation nuclei in the marine atmosphere. Measurements of Aitken nuclei (size range below 0.1 μm radius) made before 1975 showed concentrations around 300 cm^{-3} in maritime air far from continents, and cloud condensation nuclei concentrations around 100 to 150 cm^{-3}. More recent measurements, for instance by Gravenhorst (1978), show Aitken nuclei concentrations of 500 to 800 cm^{-3} in mid-Atlantic air and also higher values for cloud condensation nuclei. All samples analyzed for SO_4^{2-}, Na^+, Cl^-, showed excess sulphate concentrations compared with the sulphate concentrations in sea water. This was not only the case for small nuclei which were produced by gas-to-particle conversion but was also the situation for sea-salt particles. In the latter case, it is assumed that SO_2 was absorbed on the surface of the sea-salt particles, indicating that coagulation between small sulphate particles and sea-salt particles took place. Both mechanisms seem likely.

It is expected that the concentration of cloud condensation nuclei over the North Atlantic ocean has increased during the last two or three decades although the data and the information available are very scarce and insufficient. A long-term increase in the concentration of cloud condensation nuclei in the marine atmosphere over the North Atlantic ocean would certainly have consequences for the microstructure of maritime clouds and for the mechanism leading to precipitation from clouds in the temperature regime warmer than freezing level. The consequence would be an increase in the droplet number in maritime clouds and a decrease in the average size of cloud droplets. This again will lead to a reduction of the efficiency of the coalescence process necessary to form precipitating droplets in maritime clouds. Therefore, it has been suggested that climate may be affected through man-made changes in the number and composition of cloud condensation nuclei which in turm would alter the distribution of precipitating clouds over the Atlantic. This suggestion has yet to be substantiated.

It seems necessary to conduct measurements of the distribution of cloud condensation nuclei over the Atlantic ocean on board ship and by aircraft ascents, with special consideration of the middle latitudes. It also seems necessary to intensify the study of microphysical parameters of maritime clouds by extended aircraft measurements.

It is assumed that anthropogenic impact on the concentration and distribution of cloud nuclei and on the microstructure of maritime clouds is restricted at the present to the North Atlantic ocean (and perhaps to the Indian ocean), although this has not yet been proven. Comparative measurements over the South Atlantic and Pacific oceans are therefore also very desirable.

2.3 An Inversion in the Sea-Salt Mass Concentration in the Marine Atmosphere

It has generally been assumed that the mass concentration of the aerosol produced by the sea decreases steadily with altitude, but a recent study (Blanchard and Woodcock, 1980) suggests that an inversion in the sea-salt concentration exists between altitudes of about 300 and 600 m. For example, at wind speeds of 8 $m\ s^{-1}$ the salt concentration at 10 m above the sea is about 20 $\mu g\ m^{-3}$ and decreases steadily to about 10 $\mu g\ m^{-3}$ at an altitude of about 300 m. However, from 300 to 600 m the salt mass increases to about 14 $\mu g\ m^{-3}$. Above 600 m the salt mass decreases again, reaching values of 1 $\mu g\ m^{-3}$ at the temperature inversion at about 2000 m.

The cause of the sea-salt inversion is not known. However, since both the top of the inversion and cloud base are at about the same altitude, 600 m, it is probable that it is produced by a cycling of salt through the clouds. This interaction between cloud dynamics and the sea-produced aerosol poses a number of interesting problems. Not the least of these is the great difficulty in predicting the vertical distribution and ultimate fate of pollutants in the sea that are carried into the atmosphere by the droplets of water that become the sea-salt aerosol.

2.4 Bubble and Aerosol Spectra Produced by a Laboratory "Breaking Wave"

Bubbles from breaking waves burst at the surface of the sea to produce the major part of the water-to-air transfer of particulate material. It has long been known that both film and jet drops are produced by bursting bubbles, the number of jet drops per bubble decreasing with bubble size and the number of film drops increasing. Thus, the relative flux of these two types of drops is critically dependent on the shape of the whitecap-produced bubble spectrum. In as much as the enrichment mechanism for a variety of materials is different for these two classes of drops, a knowledge of the bubble spectrum is necessary to understand the enrichment of pollutants in the sea-produced aerosol.

The only published work on bubble spectra obtained directly in a breaking wave is that of Blanchard and Woodcock (1957). Since experimental difficulties prevented them from sampling large bubbles, a laboratory experiment was performed recently in which the complete bubble and aerosol spectrum was obtained in a steady-state "breaking wave" generated by letting seawater fall into seawater from a height of 33 cm at a rate of 410 $cm^3 s^{-1}$ (Cipriano and Blanchard, 1981). The bubble concentration produced was about 20 cm^{-3}, and the flux to the surface about 200 $cm^{-2} s^{-1}$ one third of which was composed of bubbles from 1 to 10 mm diameter. The estimated film-drop flux (calculated from the bubble spectrum) was 6,400 $cm^{-2} s^{-1}$, of which 88% was produced by bubbles > 1 mm. It is felt that the film-drop flux, which greatly exceeds that of the jet drops, provides most of the number concentration of the sea-salt aerosol, while jet drops provide the mass.

This new-found importance of large bubbles in the production of film drops is significant, since it is known that surface-active materials profoundly affect film-droplet production. Thus, pollutants, in monolayers, either on the surface of the sea or absorbed to a rising bubble, can become not only enriched in the aerosol but also modify the size distribution itself.

2.5 Petroleum Films at the Sea Surface

Evaluation of MAPMOPP Data

The existing processed MAPMOPP (The IOC/WMO Marine Pollution (Petroleum) Monitoring Pilot Project) data were reviewed to evaluate the possible impact of petroleum hydrocarbons on the properties of the upper ocean and the air-sea interface and the possible consequences on weather and climate.

Dissolved/dispersed petroleum hydrocarbons were found generally at the part-per-billion level in ocean water, a value too low to affect the physicochemical properties of the sea surface. It was noted that dispersed petroleum droplets could act as an accumulation site for other oleophilic pollutants. Subsequently, the dispersed pollutant matrix could be incorporated into particulate matter or returned to the sea surface by upward vertical transfer processes, such as rising air bubbles and upwelling.

Tar on Beaches: the effects of oil spills and tar residues on the natural movement of beach sand and of water in sand were considered. It was concluded that while tar balls reduced the amenities of beaches, they do not greatly influence sand migration. On the other hand, a continuous large quantity of oil from a recent spill, being fluid, could penetrate the sand, reduce its wettability and modify its normal transport patterns. Freshly spilled fluid oil, therefore, causes the greater effects on beach sand distribution. A secondary effect lies in the fact that a spoiled beach requires removal of sand by man which in effect constitutes a transport event.

Petroleum residues (tar balls): the distribution of petroleum residues is governed by physical processes and large current flow patterns. However, it was concluded that the low concentration levels of tar (several $mg.m^{-2}$ in the North Atlantic) should not alter physical processes in seawater, at the air-sea interface or in the atmosphere. This conclusion was based not only on the fact that concentrations of tar are low, but also that the tar is generally composed of small discrete particles, unable to spread into continuous films of the type which have been shown to modify small-scale air-sea interfacial parameters.

As it has been shown in GESAMP Reports and Studies No. 13 (GESAMP, 1980) there are a number of important processes at the sea surface as well as air-sea interfacial exchanges of material and energy which may be modified by films of petroleum (slicks) at the sea surface. Consequently, MAPMOPP data on visual observations of oil slicks on the ocean (Global Oil Pollution, Levy and al., 1982) were considered to be of considerable value since they had been used for calculations of the extent of oil slicks at sea.

Surface Area of the Oceans Covered by Petroleum Films: using analysis of IGOSS MAPMOPP data produced by the German Oceanographic Data Center, Hamburg, calculations have been made of several important features of petroleum films on the sea. Using data on visual observations of oil slicks, calculations indicate that the percentage of the ocean surface covered by oil films at a particular time is between 0.05 and 0.1% for the monitored ocean areas. On a global basis considering both monitored and unstudied regions, the coverage of the sea surface by oil is calculated to be about 0.015%. It is emphasized that these values are averaged over vast oceanic areas, whereas in reality the oil slicks are preferentially distributed in "hot spots", usually along shipping routes. These calculations provided, in part, support for the conclusion that, at the present time, petroleum films do not modify the interfacial exchange of matter or energy significantly on a global scale. It is possible, however, that in certain coastal areas and seas (e.g. the Mediterranean, see later), especially along shipping routes, such films will be more prevalent and could modify interfacial properties and exchange processes on a smaller scale.

Characteristics of Marine Petroleum Films

Measurements made in the North Atlantic by scientists from the U.S.S.R. indicate that, as expected from the surface coverage results discussed above, concentrations of petroleum hydrocarbons are spatially very variable. The data indicate that more than 99% of the petroleum hydrocarbons in the marine water column are concentrated in the surface microlayer (as sampled by a Garrett screen harvesting approximately the upper 300 mm of the water). The hydrocarbon content of the near-water atmopheric layer does not exceed 0.2% of the amount in the water. A linear correlation was found between the dissolved form of petroleum hydrocarbons in the surface microlayer and in the near-surface layer of the atmosphere. Petroleum hydrocarbons in the surface microlayer are present in a dissolved state (approximately 60% of the total), with the remainder in suspended forms. These latter rapidly lose their reactivity and do not participate in exchange between the oceans and the atmosphere, but probably take part in the formation of tar balls.

Biodegradation of Petroleum and Other Organic Pollutants

There are a number of physical and chemical processes which degrade the disperse oil spilled onto the sea. These include spreading, entrainment and emulsification by wind and waves, photocatalyzed oxidation, evaporation, dissolution, and others.

It is clear that bacterioneuston in the sea surface microlayer also play an important role in the biological degradation of petroleum and other organic pollutants in the marine environment. Chemical compounds deposited on the surface of the ocean are accumulated in organic slicks, suspended aggregates, and oil films. They affect the neuston community, which plays an important role in the larval stage of many valuable food fishes. In the surface microlayer exists a specific zone of life with its peculiar characteristics under the special physical-chemical processes that exist there. The near-surface micro-horizons contain a complex of microorganisms of large specific diversity which constitute the bacterioneuston.

The bacterioneuston can be subdivided into two fractions: epibacterioneuston, which are microorganisms developing in the sea foam; and hypobacterioneuston associated with the surface film or accumulated under it. Surface films have been shown to be particularly rich in microflora, the number of microorganisms being 10-10,000 times higher there than in the lower layers. The main factor determining the vertical distribution of microorganisms is the amount of nutrients present. Air bubbles migrate to the surface from the water column and carry with them organo-phosphorus substances absorbed on the surface. The flow of organic matter to the sea surface is increased during wind and wave activity. It has been found that the number of heterotrophic, saprophytic microflora in the sea foam exceeds by two or three orders of magnitude those in the lower layers. For bacterial growth, it is important that foam consists of three phases: gas, liquid and particles. Bacterial cell numbers increase during wave activity.

From the point of view of microbial degradation of oil, marine bacteria may be subdivided into three groups: (1) bacteria destroying mainly n-paraffins; (2) bacteria preferring aromatic hydrocarbons; and (3) bacteria which more actively oxidize iso-pariffin hydrocarbons. A few microorganisms are capable of complete degradation of oil but such forms are rarely found in the sea. Microbial cultures from the surface film of the Black Sea destroyed 16.6-47.6% of the oil used in laboratory experiments. Cultures separated from the surface microlayer of the Caspian Sea oxidized 0.7-30 mg l^{-1} day^{-1} at 22-24°C and the Black Sea cultures 5-7 mg l^{-1} day^{-1} at 22-23°C. The total proportion of oil destroyed in laboratory experiments was 23-80% over 4-6 days. It was estimated that the bacterioneuston of the Caspian Sea is capable of oxidizing during a summer season approximately 9000 tons of oil. The total amount of petroleum hydrocarbons which could be oxidized by the Baltic Sea bacterioneuston was estimated at 7000 to 8000 tons. Microbial cultures, isolated from southern Baltic Sea water and sediments, assimilated from 40 to 60% of benz(a) pyrene during 9 days of incubation at 20°C.

2.6 Residence Times of Pollutants in the Sea Surface Microlayer

In comparison with other marine interfaces, the transit time for most pollutants across the air-sea boundary is relatively short. The estimated residence time for water wettable particulate trace metals is about 2 seconds. When the trace metal particulates are surface stabilized by less wettable organic coatings, the particles have estimated residence times in the surface microlayer of from 1 to 30 minutes.

Lipophilic pollutants (e.g. PCBs, chlorinated pesticides, organic forms of heavy metals, etc.) may be accumulated by natural or pollutant organic surface films. Lifetimes of pollutants in natural slicks are probably measured in hours, but uner extended periods of calm marine weather, a lifetime of a day or two may occur. The persistence of organic sea surface films is governed by the dynamics of the air-sea interface, and when winds exceed 4-5 m s^{-1} natural slicks usually disappear. When calm conditions recur there is a potential for lipophilic pollutants to return to the sea surface. Oil spills may survive as continuous films and emulsions at the air-sea interface for hours or days depending upon environmental conditions and the nature of the petroleum product spilled.

It is essential to predict the frequency, distribution and longevity of natural and petroleum slicks, in order to ascertain the importance of organic films as collectors of oleophilic pollutants at the sea surface. The most influential factors limiting the existence of organic surface films are air-sea dynamics, breaking waves, bursting bubbles, sea spray, and wave processes which disperse the films by entrainment, turbulent transport, etc. In addition, constituents of a surface film are selectively removed by dissolution, evaporation, biological degradation, spreading and photocatalytic oxidation. The lifetime and fate of natural and petroleum slicks in the marine environment has been related to such dispersive processes. Because of the great influence of wind and waves, the probability of encountering slicks or persistent oil films in the open ocean may be related to average wind conditions. Data on visual observation of oil slicks on the Mediterranean Sea derived from the IGOSS Pilot Project on Marine Pollution (Petroleum) Monitoring show that greater than 10% of visual observations indicated the presence of oil over most of the sea surface. This rate of positive observations is considerably higher than the corresponding rate generally found for the open ocean, as discussed earlier. Consequently, there is a corresponding potential for the incorporation and concentration of other oil-soluble pollutants into the petroleum films on the Mediterranean and other similar areas, a condition which can lead to an increases sea surface lifetime for the solubilized pollutants.

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

3.1 Critical Pollutants

The following substances have been selected on the basis of current knowledge concerning their significance as pollutants. It is clear that lists of critical pollutants must be reviewed periodically and the lists revised.

Metals: The metals selected by the WMO Technical Conference on Air Pollution Measurement Techniques (Gothenburg, Sweden, 11-15 October 1976) would be appropriate as a core group in a measurement programme. In addition, those metals whose concentrations in the sea or atmosphere are affected by anthropogenic input should be considered. These can be selected on the basis of atmospheric concentrations of the metals exceeding those derived from the ratio of natural concentrations to concentrations predicted from crustal weathering or bulk seawater sources. The present list includes lead, mercury, arsenic, selenium, antimony, zinc, cadmium, copper, nickel, chromium and vanadium.

High Molecular Weight Halogenated Hydrocarbons: DDT and polychlorinated biphenyls have always been considered good representatives of this group of compounds because of their persistence and the ecological damage that they are known to cause. They are declining in the oceans of the Northern Hemisphere because their use has been restricted in many countries. There has been a shift in the use of these organochlorines, however, to tropical areas and the Southern Hemisphere. Perhaps the replacement chemicals, such as toxaphene, should be examined as candidates for this group.

Low Molecular Weight Halogenated Hydrocarbons: The halocarbons (chlorofluorocarbons, chlorocarbons and bromocarbons) continue to be substances of environmental concern. They should be acceptable candidates for the list of critical pollutants.

Petroleum Hydrocarbons: The report "Implementation Plan for the Determination of the Atmospheric Contribution of Petroleum Hydrocarbons to the Oceans" by R.A. Duce (1977), published by WMO, could provide a suitable basis for developing a programme for measurement of petroleum hydrocarbons in the atmosphere. Techniques for detection and measurement of petroleum hydrocarbons in the sea are well developed. The important point to note is that measurements should be capable of distinguishing the anthropogenic contribution.

Radionuclides: Transuranium radionuclides, particularly plutonium isotopes and Am^{241} should be included in the set of critical pollutants, because of their environmental presence from various nuclear sources and the potential long-term hazard that they pose to human health.

Pollutants Having Effects on Atmospheric Properties and Processes: The gases having a known impact on atmospheric properties and processes are the ones that should be considered in an international programme. These include carbon dioxide, sulphur dioxide and oxides of nitrogen.

The impact of increasing atmospheric CO_2, leading to rises in temperature via the "greenhouse effect", is generally accepted. Sulphur dioxide is an important contributer to acid precipitation and thus has an undesirable impact on terrestrial and freshwater ecosystems. Halocarbons should be included, because of possible global impacts on the ozone layer and the effects on the amount of ultra-violet radiation reaching the earth. Particulate materials alter visibility and could affect global temperature because of inhibition of light penetration. Sulphates, in addition to having undesirable terrestrial and freshwater effects, have an impact on visibility in the atmosphere.

3.2 Selected Areas and Sites for Measurement

There continues to be a need for suitable sites for measurements well removed from direct man-made input. Oceanic islands remote from continents have proved suitable for ocean air-sea exchange studies. However, selection of similar sites in enclosed seas is more difficult.

Weatherships have been identified as suitable platforms for certain types of atmospheric and oceanographic measurements, recognizing that contamination problems are inherent in shipboard sampling. Unfortunately, weatherships are being phased out by a number of countries and are being replaced by deep-sea buoy systems.

Arctic and Antarctic stations are still relatively well removed from anthropogenic sources of pollution and are used quite extensively for atmospheric and snow/ice sampling.

3.3 Measurement Techniques

Standardization of methods: Many methods are available for measurements of pollutants in the atmosphere and in seawater. Different techniques may measure different constituents or characteristics, e.g. measurement of petroleum hydrobarbons by gas chromatography/mass spectrometry vs. fluorescence spectroscopy. It is essential that methodology is standardized so that data are comparable. It is also essential that the accepted methods are not only sensitive and reliable but can be adopted by most laboratories participating in the programme.

Quality Control: It is important that the quality of data acquired by different laboratories meets minimum requirements. This can usually be achieved by intercalibration exercises involving participating laboritories. Those laboratories that cannot meet quality requirements will need upgrading.

3.4 Data Processing and Analysis

Standardization of Data Processing: Agreement should be reached early in the development of a programme on the processing of data in an acceptable format for analysis.

Central Data Bank: A data centre should be designated for archiving the data acquired in the programme in order to aid in its ready retrieval. Possibly existing national meteorological data centres and the World Oceanographic Data Centres could adequately meet this requirement. The experience available there could avoid much data archiving development work. A data centre is particularly vital for data exchange between laboratories.

Analysis of Data to Meet Objectives: The purpose of the data should be clearly spelled out in the objectives developed for the programme. The final analyses should provide information on: (1) processes of transfer of pollutants; (2) sources and sinks; and (3) fluxes.

Symposia and Workshops: Workshops and symposia for presentation of findings and exchange of information are vital for proper evaluation of data and methods of measurement at various stages in the programme, once it is underway.

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ANNEX

LIST OF PARTICIPANTS

Members of the Working Group	Participation in meetings			
	Miami 1980	Tallinn 1981	Hamburg 1981	London 1983
W.D. Garrett (Chairman)	+		+	+
D.C. Blanchard	+	+		
R.P. Chesselet	+			
P.S. Liss	+			+
V. Pravdic	+	+		
M. Waldichuk	+	+		
V. Smaguine (Technical Secretary)	+	+	+	+
I.M. Zrajevskij		+		
U. Siegenthaler		+		
V.M. Koropalov		+	+	
R.A. Duce				+
P.E. Buat-Menard				+
J.M. Miller				+
M.O. Andreae				+
H.W. Georgii				+
D. Kohnke			+	
E. Levy			+	

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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