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

**REPORTS AND STUDIES**

No. 13

**Interchange of Pollutants  
between the Atmosphere and  
the Oceans**



World Meteorological Organization



## EXPLANATORY NOTE

This report actually presents the results of the two sessions of the WMO-led Working Group on the Interchange of Pollutants between the Atmosphere and the Oceans. The Working Group was established by the interagency Group of Experts on the Scientific Aspects of Marine Pollution in 1975. The first session of the Working Group was held in Dubrovnik, Yugoslavia, in October 1977 and the second one at the Pacific Environment Institute, West Vancouver, B.C., Canada, in September 1978. This report, which is available in English only, has been discussed and approved by the Eleventh Session of GESAMP.

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## EXECUTIVE SUMMARY

The Working Group on Interchange of Pollutants between the Atmosphere and the Oceans was established by GESAMP VIII. Using guidance provided by a previously convened ad hoc group, which met in conjunction with IUGG in Grenoble during September 1975, GESAMP IX developed terms of reference for this working group. These included the selection of pollutants, significant quantities of which are involved in air-sea interchange, and the identification of those pollutants for which an atmospheric pathway might be important in causing adverse effects on marine resources and amenities, and which might directly, or indirectly, affect atmospheric processes and/or modify air-sea interfacial properties. The working group made assessments of fluxes of selected pollutants between the atmosphere and the oceans based on the best available data, reviewed the mechanisms governing pollutant interchange, identified the modes of transport between air and sea for each pollutant, examined the effects of pollutants on chemical and physical air-sea interfacial processes and reviewed the surface-chemical aspects of pollutant interchange. Pollutants which are modified by photochemical reactions and undergo gas-particle interchange in the lower troposphere were tabulated. Consideration was given to biological involvements in pollutant interchange and to the transmission of microorganisms from the sea to the atmosphere. Guidelines were developed for a measurement programme for the determination of air-sea fluxes.

These studies will be useful for a better understanding and/or identification of: (1) the magnitude of the input of pollutants from the atmosphere to the oceans and that of the reverse flux; (2) the distinction between natural and man-induced fluxes of substances which have both natural and anthropogenic sources; (3) the importance of pollutant effects on properties of the air-sea interface and (4) regions of the oceans and marine atmosphere of greatest concern with respect to exchange of material. The review of knowledge and conclusions reported will be of value to both scientists and environmental managers for the development of international programmes in pollutant interchange and may be useful in decision-making processes regarding the eventual management of pollutant sources and marine resources.

### 1. STATE OF KNOWLEDGE AND SELECTION OF POLLUTANTS

A review of the state of knowledge enabled the selection of those pollutants involved in air-sea interchange which might adversely affect marine resources, reduce amenities or alter ocean-related physical processes including climate. The pollutants selected include those substances synthesized by man, such as fluorocarbons, fluorochlorocarbons, high-molecular-weight halogenated hydrocarbons, and the radionuclides of plutonium and americium, a significant fraction of which reaches the ocean via the atmosphere. Having no natural sources, the calculations of air-sea exchange fluxes for these substances is simplified. On the other hand, calculation of fluxes for the heavy metals is complicated by their natural introduction into the atmosphere from crustal weathering, the terrestrial biosphere, volcanoes and the sea. The list of heavy metals selected for study was based on atmospheric concentrations of the metals exceeding those derived from the ratio of baseline marine atmospheric concentrations to concentrations predicted from crustal weathering or bulk seawater composition. Knowledge of the fluxes of CO<sub>2</sub>, sulphur compounds, and some of the low-molecular-weight chlorinated hydrocarbons<sup>2</sup> is also complicated by relatively large natural sources of these materials.

## 2. EXCHANGE MECHANISMS

The most important mechanism for the sea-to-air transport of nongaseous pollutants is the air bubble, which scavenges interfacially active material during its rise through the water and ejects some of the adsorbed material into the atmosphere when it bursts at the sea surface. The enrichment of several pollutants occurs on the bubble surface as well as in the surface microlayer, so that the process of bubble bursting may lead to the enrichment of the adsorbed pollutants in the atmosphere relative to their concentrations in seawater. Gaseous pollutants, on the other hand, exchange mainly by molecular processes at the air-sea interface. The magnitude of oceanic bubble transport for gases is unknown but thought to be less than that due to molecular exchange. In both air and water gases are mixed and transported by turbulent and convective processes, while molecular diffusion dominates near the interface in a thin layer on either side of the sea surface, a zone where turbulent motions perpendicular to the boundary are restricted. The air-sea exchange of a gas can be controlled by the transfer velocity in either the gas phase (e.g.  $H_2O$ ,  $SO_2$ ,  $NO_2$ ) or in the aqueous phase (e.g.  $N_2$ ,  $O_2$ ,  $CO_2$ ,  $CH_4$ ,  $N_2O$ ). In order to calculate fluxes, the value of the transfer velocity of the gas in the rate-controlling phase and the concentration difference driving interfacial exchange are required. This calculation is readily applicable to gases which are gas-phase controlled, but difficulties related to their water solubility and the application of micrometeorological concepts to transfer in the aqueous phase complicate the calculation of transfer velocities for gases subject to liquid-phase control.

The most significant transport modes from air-to-sea were identified for the selected pollutants as follows: The heavy metals, sulfate, radionuclides and micro-organisms move seaward as either dry fallout or as a result of precipitation processes; gases which react with or are soluble in water are transported by precipitation as well as by gas-phase-transport processes (e.g.  $SO_2$ ); while liquid-phase transfer is the principal mode of transport for gases which do not react with or dissolve extensively in water (gaseous hydrocarbons and halogenated hydrocarbons). High-molecular-weight hydrocarbons and halogenated hydrocarbons exist as both gases and particles in the atmosphere and are transported to the sea by all three modes. The net open-ocean transfer for all of the selected pollutants, on which enough information was available to make a judgement, was from the atmosphere to the ocean. In the case of petroleum in seawater, the lighter, more volatile constituents move from sea to air, while the heavier, possibly photochemically reactive components follow the opposite path.

Processes which modify pollutants in the lower troposphere include gas-particle interconversion, photochemical reaction and heterogeneous reactions with water drops. Petroleum hydrocarbons, Hg, As and  $SO_2$  are modified by both processes, while  $CO_2$ , Pu, Am, Cu, Ni, Cr and V are not significantly altered in the lower troposphere. Heavy halogenated hydrocarbons undergo gas-particle exchange, but the group did not have expertise to determine whether photochemical reactions occur with these pollutants. Fluorochlorocarbons do not undergo significant photochemical reaction in the lower troposphere, and there is uncertainty about the importance of their gas-particle interactions.

## 3. EXCHANGE FLUXES

A number of global air-sea fluxes were compiled and/or calculated for gaseous forms of selected pollutants and other substances. The reliability of the air-sea flux calculations is greatly dependent upon the availability of gas concentration values in surface seawater and marine air. Thus it is recommended, THAT THE DATA BASE OF GAS CONCENTRATION MEASUREMENTS IN SURFACE SEAWATER AND IN THE MARINE ATMOSPHERE BE CONSIDERABLY EXPANDED BOTH GEOGRAPHICALLY AND TEMPORALLY FOR ALL SUBSTANCES LISTED IN TABLE 1 OF THIS REPORT, ESPECIALLY FOR GASEOUS FORMS OF THE TRACE METALS. To accomplish these goals encouragement should be given to national



and international research programmes for the measurement of the relevant concentration parameters. Such programmes should also include field and laboratory studies of the mechanisms of interfacial transport.

It is not possible to estimate accurately the global flux of metals from the atmosphere to the ocean because of a complete lack of data from many areas. Even where atmospheric concentration data are available, no direct flux measurements for metals have been made. Values have been calculated in the U.S. National Academy of Science report (1978) for the air-to-sea flux of metals in the North Atlantic Ocean region which are of concern to this group. These calculations are considered to be crude and are based on several critical assumptions. The limitations of the data did not warrant a more sophisticated treatment.

Although the availability of reliable concentration data for substances in solid, liquid and gaseous forms is at present often the limiting factor in flux calculations, more accurate estimates will also require a considerable improvement in our knowledge of the mechanisms by which interfacial exchange takes place and further research in this area is to be encouraged.

#### 4. BIOLOGICAL INVOLVEMENT IN AIR-SEA POLLUTANT INTERCHANGE

Marine organisms, both plants and animals, may be involved in air-sea pollutant interchange in a number of significant ways. 1) They produce and give off surface-active organic material which can alter pollutant exchange through the formation of films both at the air-sea interface and on air bubbles and particles moving toward the interface (see section 5). The organic phases and films may accumulate oleophilic pollutants, such as hydrocarbons, chlorinated hydrocarbons, or organic forms of heavy metals. 2) The substances released or utilized by the organisms may reach the atmosphere by gas or bubble exchange processes. Marine plants floating at or near the sea surface, e.g. kelp and sargassum, may introduce gaseous and volatile organic substances directly into the atmosphere. The most fundamental involvement of marine organisms in air-sea exchange is in utilization of  $\text{CO}_2$  and release of oxygen by marine plants in photosynthetic processes and the reverse utilization-release scheme by bacteria and marine animals. Marine populations play a principal role in maintaining a balance of these gases. They also produce a wide variety of short-chain halogenated hydrocarbons and a variety of both short and long-chain hydrocarbons in addition to lipids, proteins and carbohydrates. 3) Microorganisms and their metabolic products can be transported from the sea to the marine atmosphere by bursting bubbles. However, it is not known whether pathogenic organisms can be transported via this mechanism from coastal municipal dump sites and sewage outfalls through the atmosphere to populated land areas in sufficient numbers to be of epidemiological significance.

#### 5. POLLUTANT MODIFICATION OF PHYSICAL AND CHEMICAL PROCESSES AT THE AIR-SEA INTERFACE

The air-sea interface and interfacial exchange processes may be altered by detergents, petroleum and its derivatives, and the complex mix of surface-active components from municipal wastes and sewage sludge. Petroleum is the most widespread open-ocean pollutant which may affect the properties of the sea surface. Continuous surface films of petroleum oils are required to produce significant effects at the air-sea interface. Such films arise primarily from oil spills and overboard discharges from ships, although natural seeps and offshore petroleum production produce surface films of oils in specific locations.

Field studies have demonstrated that organic surface films and oil spills will attenuate capillary waves, alter surface temperature and modify the reflection and transmission of electromagnetic waves. In addition, laboratory research has shown that continuous petroleum films may reduce the exchange of gases (e.g.  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ),

modify sea foam stability and bubble bursting characteristics, and inhibit micro-scale turbulence and convective processes near the interface. Oil slick effects, such as gravity wave damping, inhibition of breaking waves, and oleophilic pollutant accumulation are possible but have not been proved by either laboratory or field experiments.

Since a number of dynamic air-sea processes act to disperse organic sea surface films, the possible regional and global impacts of petroleum on interfacial processes will require knowledge of the extent of sea surface coverage by continuous films of oil. Recently data collected by the IDC/WMO/IGOSS Marine Pollution (Petroleum) Monitoring Project (MAPMOPP) have been processed and partially analyzed. Oil slicks were reported predominately along shipping routes in the Mediterranean, the English Channel, the southern North Sea, the Caribbean and portions of the Gulf of Mexico, the Red Sea, the Gulf of Aden, and the South China Sea. Further analysis of the MAPMOPP data is being carried out to determine the percentage surface coverage of the oceans and regional seas by oil films and to produce an estimate of the quantities of oil present in various oceanic regions. On the basis of these preliminary analyses, experts in the group concluded that PETROLEUM FILMS AS OBSERVED AT THE PRESENT TIME MAY NOT MODIFY THE INTERFACIAL EXCHANGE OF MATTER OR ENERGY SIGNIFICANTLY ON A GLOBAL SCALE, BUT THAT IN CERTAIN COASTAL ZONES AND SEAS, ESPECIALLY ALONG SHIPPING ROUTES, SUCH FILMS WILL BE MORE PREVALENT AND COULD MODIFY INTERFACIAL PROPERTIES AND EXCHANGE PROCESSES.

Knowledge of the chemical nature and physical properties of the sea surface microlayer is essential to provide "sea truth" for the proper interpretation of data from remote sensing systems. Since pollutant organic surface films modify the properties of the air-sea interface and its associated boundary layers, such films may also influence both passive and active remotely sensed signals. The magnitude of the physical effects of the surface film is a function of its chemical nature, its thickness and the concentration of interfacially - active molecules at the air-sea interface.

Petroleum spills and slicks may be sensed across a broad spectral range by numerous sensor systems. Because oil spills vary greatly in thickness and in their physical and chemical characteristics, the portion of the spill sensed varies according to the type of remote system used for observation. Furthermore, there are numerous false signals due to sea-surface effects when various remote sensors are used to detect petroleum slicks on the sea. Both natural surface films and other pollutant slicks may be incorrectly identified as petroleum by many remote sensing systems. Conversely, pollutant slicks may confuse the interpretation of remotely sensed data when other properties of the sea surface are being studied.

It is recognized that with growing sophistication remote sensing systems are becoming increasingly more useful for many oceanographic applications. However, it should be noted that both natural and pollutant surface films significantly modify the physics and hydrodynamics of the air-sea interface and consequently affect the signals received by a number of remote sensing systems. Thus, WHEN REMOTE SENSING IS USED IN OCEANOGRAPHIC APPLICATIONS, THE PROPERTIES OF THE AIR-SEA INTERFACE (SEA TRUTH) MUST BE KNOWN IN ORDER TO PROVIDE PROPER INTERPRETATION OF THE SIGNALS BEING RECEIVED.

#### 6. GUIDELINES FOR A MEASUREMENT PROGRAMME FOR THE DETERMINATION OF AIR-SEA FLUXES

The primary objectives of the suggested programme are: 1) The quantitative measurement of the fluxes of certain pollutants across the air-sea interface at the present time; and 2) the determination of any significant change in these fluxes with time.

The group considered that two criteria must be met before a long-term monitoring programme for any substance is worthwhile. First, there must be a scientifically substantiated indication that significant changes in the distribution or flux of that substance will result in serious disturbance of physical, chemical or biological processes in the environment. Examples include the injection of quantities of material into the atmosphere which could affect global climate or material into the ocean which could endanger the life cycle of marine organisms. Second, expected changes in concentrations of a particular substance with time must be statistically distinguishable, after considering the natural temporal concentration variations expected for that substance and the analytical precision of the concentration measurements themselves.

On the basis of these criteria, the working group concluded that a continuous, large-scale, long-term monitoring programme for measurement of air-sea fluxes of such substances as heavy metals, petroleum hydrocarbons or heavier chlorinated hydrocarbons, e.g. PCBs and DDT, may not be warranted at present. Collection and analytical methodologies for all these substances in remote regions require considerable development and standardization before measurement accuracies of even a few percent are obtainable. Since all these substances have relatively short atmospheric residence times (a few days to perhaps a few weeks) their concentration variation at a given site may often be quite high. On the other hand, there is reason to believe that the anthropogenic mobilization of some of these substances, e.g. lead, PCBs, DDT, petroleum hydrocarbons, may change significantly over the next few decades, either as a result of specific control measures for these materials or changes in the technologies in which they are utilized.

For these reasons, the Working Group recommends that A MEASUREMENT PROGRAMME FOR THE SELECTED POLLUTANTS SHOULD BE INITIATED IN OPEN OCEAN REGIONS, BUT THAT IT BE DEVELOPED CAREFULLY AND WITHIN A RESEARCH FRAMEWORK, bearing in mind that the concentrations of material to be analyzed will be at the edge of analytical capability, and that sophisticated analytical methodologies will be required. It is further recommended that THE MEASUREMENTS SHOULD NOT BE UNDERTAKEN ON A CONTINUOUS BASIS, BUT THAT THE MEASUREMENT PROGRAMME BE INITIATED AS SOON AS POSSIBLE FOR A RELATIVELY SHORT PERIOD OF ONE TO TWO YEARS, AND THAT ADDITIONAL MEASUREMENT PERIODS BE UNDERTAKEN AT SUBSEQUENT INTERVALS OF PERHAPS 5 TO 10 YEARS TO EVALUATE LONG-TERM CHANGES IN THE DISTRIBUTION AND FLUX OF THESE MATERIALS. To achieve these goals, a site selection rationale is presented along with proposed sampling sites and flux measurement criteria for the determination of pollutant fluxes due to gas exchange, dry deposition and precipitation processes.

It should be stressed that the above recommendations concerning the extremely difficult measurement of air-sea fluxes of pollutants are not necessarily meant to apply to present or planned programmes for the monitoring of pollutant levels in the marine environment, such as the IGOSS Marine Pollution Monitoring (Petroleum) Pilot Project or the IOC/WMO/UNEP Pilot Project on Monitoring Background Levels of Selected Pollutants in Open-ocean Waters.

1. INTRODUCTORY REVIEW OF STATE OF KNOWLEDGE

Several previous reports, covering parts of the brief given to the working group, proved to be of considerable use in the preparation of the present document. The working group, in its discussions, referred to the GESAMP Report "Review of Harmful Substances" (GESAMP, 1976) for some guidance on selection of significant pollutants involved in air-sea interchange. It was aware of the National Academy of Sciences report "Assessing Potential Ocean Pollutants" (NAS, 1975a), where criteria for selection of pollutants are stated. The group liberally utilized the U.S. National Academy of Sciences document "The Tropospheric Transport of Pollutants and Other Substances to the Oceans", arising from the workshop held in Miami, Florida, in December 1975 (NAS, 1978). The background papers (NAS, 1975b) of the Miami Workshop were also available to the group at both sessions. The group was also informed of the SEAREX (Sea-Air Exchange) Programme of the Office of the International Decade of Ocean Exploration of the U.S. National Science Foundation.

Since the beginning of the industrial revolution, man has been introducing increasing amounts of carbon dioxide into the atmosphere from the burning of fossil fuels. So far such activities have increased the atmospheric CO<sub>2</sub> concentration from below 300 ppm to about 330 ppm in 1976. However, the magnitude of the flux of this anthropogenic CO<sub>2</sub> between the atmosphere and the sea is uncertain, and the extent to which the sea acts as a sink is still unknown.

Another problem of atmospheric transport of pollutants and entry into aquatic systems is associated with sulphur dioxide emissions, their washout as acid precipitation and their impact on poorly buffered freshwater ecosystems, for example in Scandinavia and in the eastern USA and Canada. Sulphur dioxide may similarly affect, to some extent, low salinity inland seas such as the Baltic and stratified fjord systems having large inputs of fresh water at the surface. Although this gas is unlikely to have any direct effect on seawater, its uptake by the oceans may be an important route by which it is removed from the atmosphere.

In addition to sulphur and carbon-containing gaseous emissions having significant regional and global impact, there are many other substances involved in air-sea interchange which can be conveniently subdivided into about five categories: petroleum hydrocarbons, halogenated hydrocarbons, metals, radionuclides and microorganisms.

Petroleum hydrocarbon pollutants are widely distributed in the oceans of the northern hemisphere and along tanker routes in the southern hemisphere. Approximately 10% of the estimated input of petroleum hydrocarbons from all sources, is transported to the sea via the atmosphere (NAS, 1975a). Analyses and mass budget computations are complicated by biogenic contributions both in the atmosphere (e.g. terpenoid compounds from the terrestrial vegetation) and in the sea where organisms produce a large variety of n- and iso alkanes.

In the second category are the heavy halogenated hydrocarbons, such as DDT and the PCBs, which are well known for their worldwide distribution particularly in lipid-rich tissues. These compounds are also toxic and may lead to reproductive failure in birds and certain aquatic organisms. In this group are also the lighter halogenated compounds, such as carbon tetrachloride and chlorofluoromethanes, the latter of which may lead to some destruction of ozone in the stratosphere (NAS, 1976). The interchange of these compounds between air and sea has not received much attention.

Among the metals, mercury, cadmium, and lead have received the most attention because of their effects on human health. The metals of greatest concern are those which can be methylated, and in this form become bioaccumulated in marine organisms that serve as food for man.

Fission-products such as <sup>137</sup>Cs and <sup>90</sup>Sr arising from nuclear fallout, have been widely studied in the past. Plutonium and americium have received considerable attention recently, because of the extremely high toxicity and carcinogenic potency of, at least, plutonium.

Pathogenic microorganisms can be spread by the atmosphere as well as by aquatic systems. The possibility has been posed for entry of bacteria and viruses into the atmosphere from contaminated sea water by bubble scavenging through the water column and bursting at the sea surface (Baylor, et al., 1977a, Blanchard, et al., 1974). While transfer of pathogens via the atmosphere has only been demonstrated on land, until the sea-to-air transfer of such microorganisms is better understood it cannot be dismissed.

As well as identification of substances which it is important to study, in order to calculate their air-sea fluxes, it is also necessary to understand the processes by which they are transferred through both the atmosphere and the sea. Realistic models are needed to provide a predictive capability on such transfers. Perhaps the greatest need for a better understanding of interchange of pollutants between the sea and the atmosphere lies at the air-sea interface. Particularly needed is a better measure of the net flux of pollutants across this interface.

The group decided to confine its attention to the substances listed in Table 1, in view of their importance and because transfer across the air-sea interface is a major step in their global cycling. Many of these are known or suspected to have harmful effects on biological organisms.

Table 1

Petroleum hydrocarbons.<sup>a</sup>

High molecular weight halogenated hydrocarbons, including polychlorinated biphenyls, hexachlorobenzene, DDT and other chlorinated pesticides, etc.

Low molecular weight halogenated hydrocarbons, including such chlorocarbons as carbon tetrachloride, chloroform, dichloromethane, perchlorethylene, and the chlorofluoromethanes.

Carbon dioxide.

Sulphur dioxide and its oxidation products, including sulphate.

Heavy metals, including lead, mercury, arsenic, selenium, antimony, zinc, cadmium, copper, nickel, chromium, and vanadium.<sup>b</sup>

Radionuclides, particularly plutonium and americium.

Pathogenic bacteris and viruses.

<sup>a</sup>No effort is made here to specify the most important fractions.

<sup>b</sup>This list was based on atmospheric concentrations of the metals exceeding those derived from the ratio of natural concentrations to concentrations predicted from crustal weathering or bulk seawater sources. It coincides also with the list selected at the WMO Air Pollution Measurement Technical Conference (APOMET) held in Gothenburg, 11-15 October 1976 (WMO, 1976).

Note: The group decided not to study anthropogenically produced or mobilized substances for which any air-sea transfer appears to be on a very local scale, e.g. asbestos, O<sub>3</sub>, Cl<sub>2</sub>.

2. AIR-SEA EXCHANGE MECHANISMS AND PROCESSES MODIFYING POLLUTANTS IN THE LOWER TROPOSPHERE

Exchange of matter across the air-sea interface can occur in a variety of ways, illustrated by the simple outline below:

I. DOWNWARD TRANSPORT

Gaseous

- (1) Wet - incorporation in precipitation
- (2) Dry - direct transfer across interface

Particulate

Wet:

- (3) Rainout
- (4) Washout

Dry:

- (5) Gravitational/Brownian deposition
- (6) Trapping by whitecap bubbles

II. UPWARD TRANSPORT

Gaseous

- (7) Molecular evaporation from surface
- (8) Purging by bubbles

Particulate

- (9) Bursting bubbles and spray

The group was not able to discuss all the above exchange mechanisms, in part because of the almost complete absence of knowledge concerning some of them. Those mechanisms for which information is available are discussed in the next three sub-sections or in later parts of the report.

2.1 Effects of Bursting Bubbles

Present knowledge indicates that accumulation of heavy metals in particular, and possibly other substances, is mediated by surfactant films surrounding air bubbles. Bubbles are produced by breaking waves and other mechanisms. It is still open to further field investigations as to how many bubbles reach the surface per unit time at a given sea state (or wind speed), and their size distribution. At higher wind speed, breaking waves produce white caps, i.e. rafts of bubbles formed from the entrapped air. It is estimated that these white caps on an average cover 4% of the world ocean surface (Blanchard, 1963). The life time of bubbles is of the order of seconds while most of the surface chemical phenomena occurring at the surface of a rising bubble are much faster (Zieminski *et al.*, 1976; Kretschmar, 1972). Thus each rising bubble is scavenging a water column containing natural and man-made surfactants to produce a modified bubble surface film.

Adsorption and ion exchange phenomena will be operative at any film present on the surface of a bubble. Heavy metal ions will be specifically sorbed at this surface and carried upward. Bursting bubbles then eject the heavy metals (and any other species preferentially sorbed in the film) into the air phase.

The electrification of the rising bubble can also be modified by the presence of bubble surface films. Reversal of charge (positive to negative interfacial electrification and vice versa) can be the result of ion-exchange involving heavy metal complexes and thus affect the transfer of trace metals to the atmosphere. Laboratory experimental methodology to measure the electrification of gas bubbles has recently been developed (Vsui and Sasaki, 1978; Collins *et al.*, 1978), and more information of these phenomena can be expected soon.

The bursting bubble process (MacIntyre, 1974) is known to be effective for transport of heavy metals, organic material and micro-organisms from the ocean to the atmosphere. A somewhat similar effect is the ejection of spray from breaking waves, but since in this case the scavenging by the rising bubble is not operative, spray formation is probably less effective for transport.

In addition to their effect in ejecting material into the atmosphere, bubbles also provide added surface for gas exchange. This may work in two ways. Gases entrapped with the air may find time to diffuse into the water before the bubble reaches the surface again. In reverse, gases may diffuse into the bubble and be transported to the surface. At present it is not known how important these processes are. Since the magnitude of gas transfer can be explained reasonably by simple models, gas exchange via bursting bubbles is assumed not to be dominant.

#### Research needs

- (i) Efforts should be made to determine bubble spectra in the open sea under a variety of sea states (together, if possible, with droplet spectra in the air and chemical measurements). This should not only lead to a better description of the processes controlling the transfer of heavy metals, organic material, etc., but also help to assess any possible effect of bubbles in gas exchange.
- (ii) It is necessary to investigate the effectiveness of rafted bubbles, in contrast to isolated bubbles, both in scavenging and ejection of material and in gas transfer.
- (iii) Experiments should be designed to determine the relationship between bubble size and its average lifetime, the rate of film formation and its relaxation times, and the characteristic rates of material transport to the surface of a bubble rising in the water column.

#### 2.2 Gas Exchange

In both air and water gases are mixed by turbulent processes except near the interface where, in both media, molecular transport is assumed to dominate, since turbulent motions perpendicular to the boundary are restricted. It is understood that this is a model only and that turbulent motions intermittently burst into the layers of dominantly molecular transport.

The thickness of the viscous sublayer is proportional to the ratio of the kinematic viscosity to the friction velocity. The influence of occasional turbulent motions very near to the interface increases for smaller diffusivities, i.e. the ratio of the thickness of the layer for molecular transport for other substances to that for momentum varies with the Schmidt number. Also, increase in wind speed produces an approximately proportional decrease in the thickness of the layers and a concomitant increase in the transfer velocities. The mixing in the surface layer of the liquid is mainly mechanical. Only at very low wind speeds does buoyant mixing dominate.

As discussed by Liss and Slater (1974), the air-sea exchange of any particular gas is generally controlled by the transfer velocity in either the gas (e.g.  $H_2O$ ,  $SO_2$ ,  $NO_2$ ,  $NH_3$ ) or aqueous (e.g.  $N_2$ ,  $O_2$ ,  $CO_2$ ,  $CH_4$ ,  $N_2O$ , noble gases) phases. In order to calculate fluxes the value of the transfer velocity of the gas in the rate-controlling phase and the concentration difference driving it across the interface are required.

For gases whose transfer is under gas phase control, the idea outlined above can be applied to the calculation of their transfer velocities. The situation is somewhat more complicated for gases subject to liquid phase control. In this case, their possible reaction with the water must be taken into account. A more important problem is that application of micrometeorological concepts to the calculation of liquid phase transfer velocities can be questioned on theoretical grounds, and such experimental and observational data as exist seem to raise a number of important problems.

The only turbulent boundary layer which has received intensive theoretical and laboratory study in the region very close to the surface, where molecular effects are important, is that over a smooth solid surface. Because of the no-slip condition at such a boundary, within the region strongly influenced by molecular effects fluctuations parallel to the surface decrease linearly with the distance  $z$  from the surface. Continuity considerations require that fluctuations normal to the surface decrease as  $z^2$ . It might be expected that within this region the effective eddy viscosity would vary as  $z^3$ , and Reichard (1951) has shown that the observational data can be well described with such an assumption.

One might expect the eddy diffusion coefficient for a gas to have a similar dependence on distance from the fixed surface. Such a coefficient has dimensions of length times velocity, and in the spirit of Prandtl mixing length theory, the characteristic length will be the distance  $z$  from the wall. However, there is no general consensus as to whether, on theoretical grounds, the sea surface may be treated as if it were a smooth solid wall, as in the Reichard approach. It does seem to be agreed that for the air-sea interface the starting point for theory is that the shearing stress will be continuous across the surface, but beyond this the theoretical treatments diverge.

There does not appear to be any body of experimental or observational data on the detailed behaviour in the viscous sublayer against a free surface. Without such data, one is forced to rely upon indirect evidence for the nature of the near surface phenomena (Deacon, 1977). While we have some such data, the limitations in our understanding require us to be very cautious about any extrapolations. Fortunately, most gases have diffusivities which cover a relatively small range.

Laboratory studies show that gas transfer increases with wind speed, but that this rate of increase is dramatically enhanced after the speed reaches a level such that capillary waves are produced (Jähne et al., 1979). Some arguments can be found for why the existence of capillary waves should increase gas exchange, associated with the increase in surface area and the thinning of the viscous layer in the troughs. However, the magnitude of the effect seems greater than can be accounted for by such reasoning. It may be that there is some non-linear interaction between the strong shear flow, which the surface stress induces in the viscous layer, and the motion or the surface distortion characteristics of the waves. It is possible that turbulent bursts are induced or enhanced. The situation revealed by these laboratory experiments certainly needs further clarification.

Field data similarly have features which are not easily understood. Radon concentrations have been measured as part of the GEOSSECS Programme (Peng et al., 1978). Observations in the upper mixed layer can be interpreted in terms of a transfer velocity through the surface. These indicate a transfer velocity



appreciably greater than would be calculated by applying theory derived from measurements over solids without correcting for wavy surfaces (Hasse and Liss, 1978). As has been indicated above, this is not particularly surprising. What is surprising about the data is the lack of dependence on wind speed. The data are too scattered for one to use them to refute the idea that transfer should be enhanced at higher wind speeds - but they certainly provide no support for such an idea.

While such phenomena remain unexplained, the situation cannot be considered to be well enough understood for one to have great confidence in quantitative calculations of gas exchange fluxes, except on the global scale where averaging will bypass many of the unknown factors.

#### Research needs

- (i) Efforts should be made to increase our understanding of the influence of capillary waves on the physics of air-water gas transfer. Owing to the interest in the field of remote sensing in capillary waves, it is expected that our knowledge in this area will increase rapidly during the coming years. It should be emphasized that with respect to gas exchange the desired information is not really the capillary wave spectra but rather the wave form and the role of capillary waves in bubble production and the energy balance of turbulence.
- (ii) Future studies utilizing radon measurements should concentrate on time series measurements at a fixed point in order to try to better understand the relationship between transfer velocities and meteorological parameters such as wind speed.
- (iii) One obvious difficulty with calculating the gas exchange from radon measurements is that the molecular diffusivity has been determined only once and that in 1917 only at 18°C. It is recommended that the diffusivity of radon be determined again and additionally its variation with temperature.

#### 2.3 Transport Modes Towards the Air-Sea Interface

In Table 2 the ideas developed in this report and elsewhere are used to predict how the substances listed in Table 1 are transported to the interface and to estimate the direction of the net pollutant flux and the net total flux.

In the table modes of transport from air to sea as "liquid" include processes (1), (3), and (4) (Numbers refer to the listing on (p. 8): "Solid" includes (5) and (6); while "gaseous" transport is indicated by (2). In the sea-to-air mode of transport (9) is referred to as "liquid" transport in the table, while (7) and (8) take into consideration "gas" transport.

The net open-ocean flux of the majority of pollutants is from the air to the sea. This occurs because land areas are the only source regions for the anthropogenic substances included in Table 2, and because riverine inputs, although they may be large, are greatly diluted and removed in coastal regions and contribute little to the net flux from sea to air. In the final column of Table 2, net natural and pollutant transport of the critical substances are considered. In several remote regions the calculated enrichment factors, using reference elements from expected sources such as the ocean or the earth's crust, have shown the elements Pb, Hg, As, Se, Sb, Zn, Cd, Cu and V to have concentrations much higher than would normally be expected from simple crustal weathering or injection of bulk seawater into the atmosphere. These relatively high concentrations may be related to anthropogenic activities, but they may also arise from natural geochemical processes which are not fully understood. For example, several recent studies have shown that many of these metals naturally occurring in the sea can be highly enriched, relative to bulk

seawater, on atmospheric sea salt particles owing to fractionation processes occurring during bubble bursting at the air-sea interface. Thus, very significant quantities of these substances are being recycled in both directions across the sea surface, making it very difficult to evaluate the net total downward flux of these metals to the ocean. This is why the final column of Table 2 shows U for many of the metals. Further discussion of the air-sea transfer of metals is to be found in Section 3.2.

Although global models are probably the best currently available method for assessing the amount of CO<sub>2</sub> taken up by seawater, there is still considerable uncertainty concerning the magnitude of the oceans as a sink for this gas.

#### 2.4 Surface Chemical Considerations

Knowledge of the physico-chemical properties of the sea surface is fundamental to an understanding of processes by which chemicals move between air and sea and vice versa. Thus, it is inevitable that surface chemical considerations are discussed in a number of places in this report and in particular in Section 2.2 on the effects of bursting bubbles and Section 5.1 on the influence of pollutant surface films. A number of review articles have been published which deal with the physico-chemical properties of the sea surface and their effects on material exchange across the air-sea interface (MacIntyre, 1974; Blanchard, 1975; Liss, 1975; Duce and Hoffman, 1976). Here attention will be focussed on problems related to present methods of sampling the sea surface for subsequent chemical analysis and also results from laboratory experiments (often using aqueous media other than seawater) which may help in trying to understand the properties of sea surface material and its ability to bind trace substances, especially heavy metals.

To date, most of the chemical analysis of the sea surface have been on samples collected using the mesh screen device invented by Garrett (1965) or by glass plate and rotating drum samplers (Harvey, 1966; Harvey and Burzell, 1972). These harvest a relatively thick slice of the surface (100-300  $\mu\text{m}$ ) and the region sampled is conventionally called the sea surface microlayer. More recently other collectors, which sampler rather thinner layers, have been used. Fasching et al., (1974) have described a Bubble Interfacial Microlayer Sampler (BIMS) which uses artificially produced subsurface bubbles to skim off approximately the top micron of the sea surface. Baier et al., (1974) have sampled very thin films (approximately 10<sup>-2</sup>  $\mu\text{m}$ , i.e. within an order of magnitude of the length of typical surface active molecules) by adsorption onto prisms of germanium.

Not unexpectedly, since the various devices collect layers of different thickness from the sea surface, there is often disagreement between the chemical results obtained. Even for microlayer thick samples there can be divergence between the results from the different collectors (Daumas et al., 1974). Samples obtained using the BIMS device appear to give surface enhancements for several trace metals between one and two orders of magnitude greater than those obtained from microlayer samples. There is major disagreement between the results for the organic chemical composition of the sea surface from screen and germanium prism samples, the former indicating the presence of long chain carboxylic acids and alcohols whereas the latter sees only glycoproteins and proteoglycans in unpolluted waters. It is not possible to be certain whether this last discrepancy is due to the very different thicknesses sampled or is an artefact of the subsequent sample processing and chemical analysis which are completely different for the two techniques. It is apparent that considerable further study is required in this whole area and, for the present, results should be treated with caution.

Table 2. Transport modes towards the air-sea interface

SUBSTANCE	Air → Sea		Sea → Air		Open-Ocean Net Pollutant Transfer	Open-Ocean Net Natural and Pollutant Transfer
	Gas	Liquid	Solid	Gas		
Petroleum Hydrocarbons	+	+	+	+	U	U
High M.w. Halogenated Hydrocarbons	+	+	+	(+)	(+)	↓
Low M.w. Halogenated Hydrocarbons						
- Chlorocarbons	+	(+)	?	+	(+)	↓
- Fluorochlorocarbons	+	(+)	?	+	(+)	↓
CO <sub>2</sub>	+	(+)	-	+	(+)	↓
SO <sub>2</sub>	+	+	-	-	-	↓
SO <sub>4</sub> <sup>2-</sup>	-	+	+	-	+	↓
Metals						
Pb	?	+	+	?	+	↓
Hg	(+)	+	+	(+)	+	↓
As	(+)	+	+	(+)	+	↓
Se	?	+	+	?	+	↓
Sb	?	+	+	?	+	↓
Zn	?	+	+	?	+	↓
Cd	?	+	+	?	+	↓

SUBSTANCE	Air → Sea		Sea → Air		Open-Ocean Net Pollutant Transfer	Open-Ocean Net Natural and Pollutant Transfer
	Gas	Liquid	Solid	Gas		
Cu	-	+	+	-	↓	U
Ni	-	+	+	-	↓	↓
Cr	-	+	+	-	↓	↓
V	-	+	+	-	↓	↓
Radionuclides						
Pu, Am	-	+	+	-	↓	↓
Pathogenic Bacteria	-	+	+	-	↓	↓
Viruses	-	+	+	-	BEG	BEG

+ = Significant transport mode  
 (+) = Less significant transport mode  
 ? = Importance uncertain  
 - = Insignificant transport mode  
 ↓ = Air to sea  
 ↑ = Sea to air  
 U = Unknown  
 BEG = Beyond expertise of the group

There are extensive laboratory studies, for less complex aqueous media than seawater, on the penetration of surface films by various organic components, not necessarily film-forming agents themselves (Cadenhead *et al.*, 1976; Hendrix and Ter-Minassian-Saraga, 1975; Patil *et al.*, 1975). The penetration results both in changes in the elasticity of the surface film and in its chemical reactivity and ion-binding properties. These phenomena have been mostly observed in the laboratory through surface tension and surface potential measurements. There is evidence that interfacial pressure influences chemical rate processes (MacRitchie, 1976); the rate constant for first order reactions decreasing with increase in interfacial pressure. This results from steric hindrance or lateral interaction and is especially important for oxidation processes. There is evidence that petroleum hydrocarbons inhibit decomposition of organic matter in seawater (Chet and Mitchell, 1976).

Studies of the organic chemistry of the sea surface are important with respect to selective complexation of metal ions, speciation of alkali metal and alkaline earth cations, and their accumulation at the ocean surface. Although the exchange chemistry between amino acid metal complexes and fatty acids, or their Ca and Mg soaps, is not well understood, especially so in the case of seawater, it seems likely that the key to speciation phenomena in the interfacial transport of metal ions lies in this type of ion exchange process. In this context, Hunter and Liss (1976) have determined the solubility products of a whole range of metal carboxylates and these have been used to construct a simple model of trace metal binding by organic material in the water near the sea surface (Hunter, 1977). In the model the only functional groups provided by the organic matter are taken to be carboxyl and by assuming a linear free energy relationship between carboxyl-metal binding ability and the experimentally determined solubility products of metal carboxylates a relative binding strength for the various metals is established. This is then used to predict the enhancement to be expected for the metals in microlayer, BIMS and aerosol samples. The agreement between the predicted enhancements and those measured in the field is generally satisfactory, except for Fe and Pb in the microlayer and Hg and Cd in aerosol samples and for these metals other processes must be operative.

## 2.5 Atmospheric Life Cycle of Pollutants in the Lower Troposphere

Before one can accurately evaluate pollutant fluxes and exchange mechanisms across the air-sea interface, it is necessary to know the physical and chemical form of the exchanging pollutant in the atmosphere. The residence time, and thus the horizontal and vertical transport, of atmospheric pollutants is related not only to the chemical properties of the pollutant, but also to its physical form, i.e. whether it is present as a gas or sorbed by solid or liquid particles. Similarly the mechanisms of exchange across the air-sea interface are dependent upon the chemical form and physical phase of the exchanging substance, as discussed in Section 2.3. Thus it is critical to understand the life cycle of these substances in the atmosphere.

Pollutant substances injected into the atmosphere in the vapour, liquid, and/or solid phases may be chemically and physically altered in several ways while in the atmosphere. Some pollutants can undergo photochemical oxidation and degradation reactions resulting in new chemical compounds which can be of lesser or greater environmental concern than the parent compound. In addition, gas-particle interconversion of many substances can take place. This interconversion may involve chemical reactions of the pollutant substance of interest in the gas phase or at the surface of atmospheric particles. It may also simply involve gaseous adsorption or desorption of the substance at a particle surface.

The substances listed as significant atmospheric pollutants in Table 1 have been evaluated relative to their potential for alteration in the lower troposphere in Table 3. For those substances which are believed to undergo

significant alterations, the occurrence of gas-particle interconversion and photo-chemical oxidation and degradation are also indicated. As shown in Table 3, with the exception of CO<sub>2</sub> and certain heavy metals, it is believed that all of the listed pollutants are subject to alterations while in the atmosphere. The evaluation of pathogenic bacteria and viruses was beyond the expertise of the group in this regard.

Table 3. Processes modifying the identified pollutants in the lower troposphere

SUBSTANCE	Altered in lower Troposphere	Gas - Particle Inter-conversion	Photo-chemical Reaction
Petroleum hydrocarbons	+	+	+
High M.W. Halogenated Hydrocarbons	+	+	BEG
Low M.W. Halogenated Hydrocarbons			
- Chlorocarbons	+	?	+
- Fluorochlorocarbons	?	?	-
CO <sub>2</sub>	-		
SO <sub>2</sub>	+	+	+
Metals			
Pb	?	?	?
Hg, As	+	+	+
Se, Sb, Zn, Cd	?	?	?
Cu, Ni, Cr, V	-		
Radionuclides			
Pu, Am	-		
Pathogenic Bacteria and Viruses	BEG		

+ = Yes

- = No

? = Importance uncertain

BEG = Beyond expertise of the group

### 3. EXCHANGE FLUXES

The ideas outlined in Section 2 are used here to make provisional estimates of the air-sea flux for gases, metals and other substances in particulate form and petroleum hydrocarbons.

#### 3.1 Gases

In order to calculate the global air-sea flux for a number of gases the basic approach adopted is that of Liss and Slater (1974), as outlined in Section 2.2, but updated where possible by the use of information which has become available only in the last few years.

From Table 2, the following substances can be identified as having an important transport mode to the oceans from the atmosphere in the gaseous phase: petroleum hydrocarbons, high molecular weight halogenated hydrocarbons, low molecular weight halogenated hydrocarbons (chlorocarbons, fluorochlorocarbons), CO<sub>2</sub>, SO<sub>2</sub>, (Hg), (A<sub>g</sub>). At present, it is not possible to calculate the fluxes for petroleum hydrocarbons, Hg and As through lack of concentration data, although it appears that vapour phase arsenic concentrations over the oceans are less than 5% of particulate arsenic concentrations (Walsh *et al.*, 1978).

In the calculations the values of the gas and liquid phase transfer velocities are taken as 3000 cm hr<sup>-1</sup> (for H<sub>2</sub>O) and 20 cm hr<sup>-1</sup> (for CO<sub>2</sub>), respectively, and are corrected for molecular weight as necessary. As is apparent from the main part of this report, there is some uncertainty concerning the values for these transfer velocities but, as stressed in Liss and Slater (1974), the main factor limiting the accuracy of such flux calculations is the dearth of reliable concentration measurements for the gases of interest in marine air and surface seawater. In view of these caveats the results of the following calculations must be used with circumspection.

##### 3.1.1 High molecular weight halogenated hydrocarbons

###### a). DDT

Using the Henry's law constant (H) for DDT ( $1.6 \times 10^{-3}$ ) given by Junge (1977a), the transfer of this compound as a gas turns out to be controlled by processes in the air. Taking background levels of gaseous DDT in marine air at about  $0.01 \times 10^{-9} \text{ g m}^{-3}$  (Bidleman *et al.*, 1976) and assuming that the sea surface microlayer acts as a perfect sink for DDT, the total oceanic flux is calculated to be  $2 \times 10^8 \text{ g yr}^{-1}$  or approximately 0.2% of the total world production of  $105 \times 10^9 \text{ g yr}^{-1}$  estimated by Bidleman *et al.*, (1976). These should probably be treated as maximum estimates since the marine air concentrations are from the North Atlantic. Measurements in the southern hemisphere, when they are made, may indicate lower values for the background concentration.

###### b). PCBs

The values of H for 4 PCBs given by Junge (1977a) range from  $2.3 \times 10^{-2}$  for Aroclor 1242 to  $2.9 \times 10^{-1}$  for Aroclor 1260. This gives the ratio of gas to liquid phase resistances ( $r_g/r_l$ ) as approximately 0.5 for 1242 and 0.04 for 1260. Thus, even for organic-free water, although liquid phase resistance dominates, that of the gas phase cannot be ignored, especially in the case of 1242. It may be that organic material at the sea surface acts as a perfect sink for PCBs so that the liquid phase resistance tends to zero. Assuming that this is the case (so maximising the flux) and using a background level of  $0.1 \times 10^{-9} \text{ g m}^{-3}$  for total gaseous PCBs in marine air (Bidleman *et al.*, 1976), the total oceanic flux is  $2 \times 10^9 \text{ g yr}^{-1}$  (approximately 4% of world production). As for DDT, in the absence of concentration measurements in the southern hemisphere, these calculations may overestimate the oceanic sink for PCBs.

### 3.1.2 Low molecular weight halogenated hydrocarbons

a). Chlorocarbons, e.g.  $\text{CCl}_4$  and b). Fluorochlorocarbons, e.g. F-11

For both of these examples the best concentration data sets still appear to be those of Lovelock *et al.*, (1973) obtained in the North and South Atlantic and used by Liss and Slater in their 1974 compilation of air-sea fluxes. The latter authors calculated the total global air-sea fluxes of  $\text{CCl}_4$  and F-11 as  $1.4 \times 10^{10}$  and  $5.4 \times 10^9$  g yr<sup>-1</sup> respectively.

### 3.1.3 Sulphur dioxide

The total flux of this gas from the atmosphere to the oceans was also calculated by Liss and Slater (1974). However, the value they obtained ( $1.5 \times 10^{14}$  g yr<sup>-1</sup>) needs to be revised downwards in the light of more recent data on background concentrations of  $\text{SO}_2$  in marine air. Liss and Slater used a value of  $3 \text{ ug m}^{-3}$ . In a recent summary of the available measurements, Meszaros (1978) concluded that the 'true' background level is approximately  $0.1 - 0.2 \text{ ug m}^{-3}$ , but that in the latitude band  $10^\circ - 60^\circ \text{ N}$  higher values are found (almost certainly due to anthropogenic activities) reaching about  $3 \text{ ug m}^{-3}$  at  $35^\circ \text{ N}$ . This means that Liss and Slater's estimate should be decreased by about a factor of ten, so that the global flux of  $\text{SO}_2$  to the oceans is approximately  $10^{13}$  g yr<sup>-1</sup>.

### 3.1.4 Carbon dioxide

Although moderately soluble and somewhat chemically reactive in water, the air-sea transfer of  $\text{CO}_2$  still turns out to be controlled by processes in the liquid phase (Liss, 1973). With this knowledge, it is in principle possible to calculate the net flux of  $\text{CO}_2$  across the sea surface from the state of saturation of the surface water with respect to atmospheric  $\text{CO}_2$  levels. However, as Keeling (1968) has shown, the state of saturation is spatially very variable, with some areas supersaturated and others undersaturated - a situation which, no doubt, also exhibits substantial temporal variability. Thus, a vast number of data points would be needed to obtain the net flux from the difference between the sums of the individual air-sea and sea-air fluxes (although time series measurements at a fixed station of the partial pressure difference between air and sea together with simultaneous meteorological data might be useful in trying to identify the role of, for instance, wind speed in gas transfer). A more effective way of obtaining the amount of  $\text{CO}_2$  taken up by the oceans is to use the distribution of natural and bomb-produced  $^{14}\text{C}$  in the atmosphere-ocean system.

### 3.1.5 Gases whose net flux is from sea to air

For the gases considered so far, the oceans are a net sink. Liss and Slater (1974) have calculated the following global fluxes (in g yr<sup>-1</sup>) for several gases (not necessarily pollutants) whose net transfer is from the oceans into the atmosphere:  $\text{N}_2\text{O}$ ,  $1.2 \times 10^{14}$ ;  $\text{CO}$ ,  $4.3 \times 10^{13}$ ;  $\text{CH}_4$ ,  $3.2 \times 10^{12}$ ;  $\text{MeI}$ ,  $2.7 \times 10^{11}$ ;  $(\text{Me})_2\text{S}$ ,  $7.2 \times 10^{12}$ .

### Recommendations

(i) Since the reliability of air-sea flux calculations is in large measure dependent on the availability of gas concentration measurements in surface seawater and marine air, it is recommended that the data base of such measurements be considerably expanded both geographically and temporally for all the substances listed in Table 1, but especially for gaseous forms of the trace metals.



### 3.2 Metals and Other Substances in Particulate Form

#### 3.2.1 Metals

Metals have always entered the sea from terrestrial sources as part of the natural geochemical cycle. A significant fraction of all metals in the marine environment enters by way of the atmospheric route. Man has added a contribution from his many activities to the flux of metals from land to sea. Presently available data are so sparse that it is impossible to make an estimate of the global flux of metals from land to the sea. In addition, there are few ways in which we can at the present time distinguish the natural from the anthropogenic input of metals. There has been some success in urban and near urban areas in the use of isotope ratio of Pb to distinguish between the natural component of atmospheric Pb and that due to the combustion of leaded fuel. However, this has not been successfully utilized in remote areas to date. As pointed out by NAS (1978), "The magnitude of anthropogenic inputs and the impact of these inputs on the global cycle of metals could be more readily assessed if we had available a chronological record of atmospheric deposition that predates the era of heavy industrialization. Such a record may be obtainable from marine sediments and glaciers." However, in the case of sediments only near-shore ones can be used and the interpretation of the results is then rather difficult owing to the simultaneous input from river, sewage outfalls, etc.

It has been pointed out (NAS, 1978) that there is a great need for data on metals in the atmosphere over the southern oceans, which could provide at least part of the answer on the magnitude of the anthropogenic input of metals into the global atmosphere. Because only 10% of the particulate pollutant sources are located in the southern hemisphere, data from the southern oceans would provide a better basis for assessing anthropogenic impacts.

##### 3.2.1.1 Natural sources of atmospheric metals in the marine atmosphere

There are many possible natural sources of metals entering the marine atmosphere although they have not all been carefully examined. However, there are a number of sources that are reasonably well understood and for which data is available. Crustal weathering contributes a considerable amount of mineral matter to the atmosphere arising from the effects of runoff, freezing and abrasion by wind. It has also been postulated that low-temperature vaporization of some metals or their compounds occurs from crustal rocks (Goldberg, 1976a), although the global importance of this has been questioned (Brimblecombe and Hunter, 1977). A major source of atmospheric mercury has been suggested as arising from degassing of the earth's crust (Weiss et al., 1971). This process may be enhanced by man's activities, such as tilling of the soil and surface mining.

Volcanic activity can contribute metals to the atmosphere and some of the larger and more intense volcanic eruptions have injected particulate and gases into both the stratosphere and troposphere. Such materials at higher altitudes can be transported rapidly around the globe by upper level wind systems and contribute to dry fallout as well as to rainout and washout over the oceans. It has been suggested recently (Hobbs et al., 1977) that yields of particulate material from volcanoes can be quite large. It is noteworthy that metals with high enrichment factors in the crust also have a high enrichment factor in particles collected in the fumaroles and vents of active volcanoes (Mroz and Zoller, 1975; Duce et al., 1976; Buat-Menard and Arnold, 1978).

Heavy metals can be mobilized into the atmosphere by biological activity. Many metals are now known to be methylated by microorganisms and this renders them more volatile, with possible evaporation into the atmosphere. Methylated forms of mercury and sulphur are known to be produced by microorganisms in the marine environment and this has been suggested for arsenic and selenium as well (Wood, 1974). Studies in freshwater environments have shown that lead can also be biologically methylated (Wong *et al.*, 1975). Recent evidence indicates that particles containing high concentrations of zinc can be released into the atmosphere by growing plants (Beauford *et al.*, 1977).

The various physical enrichment processes that occur at the surface of the sea, coupled with mechanisms of injecting the surface sea water into the atmosphere, could contribute to a net flux of metals from the sea to the atmosphere in certain areas. It has been demonstrated by a number of investigators that many metals are concentrated in the top few millimetres of the sea surface (Barker and Zeitlin, 1972; Piotrowicz *et al.*, 1972; Van Grieken *et al.*, 1974; Peirson *et al.*, 1974). However, there has been some disagreement on the scale of enrichment of certain metals in the sea surface microlayer and on the geochemical significance of such enrichment. Iron, zinc, cadmium and copper have been shown to be enriched by a factor of several hundred on atmospheric sea salt particles produced by bubble-bursting in coastal waters (Duce *et al.*, 1976; Piotrowicz *et al.*, 1978; Weisel, 1978). Similar studies conducted recently in the North Sea, remote from any apparent sources of pollution, have shown concentrations of trace elements, including lead, in droplets produced from artificially produced bubbles to be about 100 times higher than those in the bulk seawater (Pattenden and Goodman, pers. comm.). Clearly, this could be a significant source of metals in the marine atmosphere.

### 3.2.1.2 Anthropogenic sources of atmospheric metals

The major anthropogenic sources of atmospheric metals include the combustion of fossil fuels, the incineration of wastes, the emissions from cement plants, contributions from smelters and surface mining operations and other industrial sources. There are other activities which undoubtedly contribute a certain amount of metals into the atmosphere, such as excavations for building construction, gravel washing operations, road building and manufacturing processes of many kinds. There are certain individual man-made sources which contribute particular metals. These include high lead contributions from combustion of lead alkyls in gasoline, arsenic among other metals and metalloids from smelters, cadmium from incinerators and vanadium from residual oils combustion. High-temperature combustion processes release many of these metals to the atmosphere, and in this case, the metals are associated with submicron particulate matter.

### 3.2.1.3 Source identification

Since there are many possible natural sources for the metals present in the atmosphere, it is not easy to assess the anthropogenic contribution to the total atmospheric burden. As pointed out by NAS (1978); "One approach to resolving the inputs from the various sources is to attempt to identify reference elements that are characteristic, or indicative, of specific natural sources. Ideally, a reference element must be amenable to relatively simple and accurate analysis, and it must be present in high concentration in aerosols produced by the source for which it serves as a reference and in low concentration in aerosols from other sources."

"There is general agreement that the major portion of the aerosol mass over the oceans is derived from two sources: the sea itself, as spray from the bursting of bubbles, and the earth's crust, as mobilized soil material. Although a number of major constituents of seawater have been used as reference elements for that source, Na is generally preferred. Commonly used as reference elements for crustal weathering products are Al, Fe, Si and Sc."

"For any element in an aerosol sample, we can define an enrichment factor relative to a reference element in a specific source. For seawater, using Na as the reference element, the enrichment factor,  $EF_{sea}$  for an element X, is

$$EF_{sea} = (X/Na)_{air} / (X/Na)_{sea}$$

where  $(X/Na)_{air}$  and  $(X/Na)_{sea}$  refer, respectively, to the ratio of the concentration of metal X to that of Na in the atmosphere and in bulk seawater. Likewise, for crustal weathering products,

$$EF_{crust} = (X/Al)_{air} / (X/Al)_{crust}$$

If the concentration of any element in an air sample yields an  $EF_{sea}$  or an  $EF_{crust}$  value that is close to unity, then one can assume that the most probable source for that element in the aerosol was, respectively seawater or crustal material."

However, care must be exercised in utilizing enrichment factors. Of particular importance is the fact that atmospheric sea-salt particles produced by bursting bubbles may not have the same chemical composition as bulk seawater owing to the enrichment process discussed previously. Enrichment factors for metals collected over Bermuda are shown in Table 4. Of particular importance are those metals with  $EF_{crust}$  values greater than about 10, which clearly do not have a crustal source.

#### 3.2.1.4 Distribution of metals in the atmosphere

There are now quite a few stations covering the globe in the urban terrestrial environment at which samples are collected for metal analysis. Unfortunately, the sampling of the atmosphere above the oceans is not a simple matter, and data from this source are still rather scanty. However, a few island stations have been occupied over the past decade, and measurements of metal concentrations are becoming available for samples taken at these stations. These include Bermuda and the Shetland Islands in the Atlantic, and Oahu in the Hawaiian Chain. Additional samples have been or are being collected on Enewetak Atoll and American Samoa, the latter being in the southern hemisphere. However, most of the recently available data on the concentrations of metals in the marine atmosphere are for the north Atlantic. There is virtually none for the atmosphere of the oceans in the southern hemisphere. There are also some data for the south pole (90°S) (Maenhaut *et al.*, 1978; Zoller *et al.*, 1974). Some of the available data on concentrations of metals in the marine atmosphere at these stations are given in NAS (1978).

#### 3.2.1.5 Fluxes of metals to the atmosphere

As noted earlier, there is no way at the present time of separating the man-made contribution of metals to the atmosphere from the natural contribution. It has been estimated that there is a total mass flux of crustal material to the atmosphere of  $2.5 \times 10^{14}$  g yr<sup>-1</sup> (Goldberg, 1971), although recent estimates suggest this value may be at least a factor of 3 too low (Junge, 1977b). The flux of sea-salt particles to the atmosphere has been estimated by Eriksson (1959) at  $1 \times 10^{15}$  g yr<sup>-1</sup>, with Blanchard's (1963) estimate higher by a factor of 10. Using the two values given above, the average crustal concentration given by Taylor (1964), and the average seawater concentrations of metals reported by Riley (1975) and by Chester and Stoner (1974), an estimate of the metal fluxes to the atmosphere can be calculated (NAS, 1978). It has been assumed that no elemental fractionation occurs during the sea-salt particle formation. The contribution of heavy metals from the combustion of coal, lignite, oil and natural gas to the atmosphere has been evaluated by Bertine and Goldberg, (1971). Patterson *et al.*, (1976) estimated the flux of submicron lead to the atmosphere from anthropogenic sources, largely the combustion

of leaded gasoline. The global fluxes of metals to the atmosphere from all these sources is given in Table 5.

Obviously, with the level of uncertainty of the source strength estimates themselves, the crustal material and bulk sea-salt values are only order of magnitude estimates. If significant chemical fractionation of these metals occur during bubble bursting, the fluxes calculated from bulk sea-salt concentrations will be too low. In fact, the estimates of metal ejection into the atmosphere from anthropogenic sources are probably considerably more accurate than those from crustal weathering, the ocean, or any other natural sources.

Table 4. Mean crustal enrichment factor for metals in atmospheric particles over Bermuda (from NAS, 1978)

Element	EF <sub>crust</sub>	Element	EF <sub>crust</sub>
Sc	1.1	V	17
Al	1.0	Zn	26
Fe	1.0	Cu	12
Th	2.1	Pb	180
Mn	0.7	As	50
Ce	3.6	Ag	52
Eu	2.5	Hg	≥ 65
Co	1.8		
Cr	1.7	Sb	180
		Cd	570
		Se	2600

#### 3.2.1.6 Fluxes of metals from the atmosphere to the ocean

It is impossible to estimate accurately the flux of metals from the atmosphere to the global ocean because of a lack of concentration data from many areas, particularly in the southern hemisphere. Even in marine areas where there are atmospheric concentration data available, no direct flux measurements for metals have been made. NAS (1978) has made an estimate of the air-to-sea flux of many metals in the region of the North Atlantic using an extremely crude model. Basically, the model assumes that the particles containing the metals are distributed uniformly from the sea surface to a height of 5,000 m. The model also assumes that the particle population in this part of the atmosphere is removed 40 times per year. This very crude calculation yields only a rough approximation of the metal flux in that area, but the limitations of the data do not warrant a more sophisticated treatment. A mean atmospheric concentration for each metal over the North Atlantic was estimated from concentration measurements at Bermuda and over the eastern tropical North Atlantic. As an example of how the flux calculation was made, consider Fe, which had an estimated atmospheric concentration of 130 ng m<sup>-3</sup>STP. The flux is then:

$$130 \text{ ng m}^{-3}\text{STP} \times 40 \text{ washout yr}^{-1} \times 5,000 \text{ m}^3\text{STP m}^{-2} = 2.6 \times 10^{-2} \text{ g m}^{-2}\text{yr}^{-1}$$

Table 5. Global flux of metals to the atmosphere based on total crustal material flux of  $2.5 \times 10^{14}$  g yr<sup>-1</sup>(a) and total sea-salt flux of  $1 \times 10^{15}$  g yr<sup>-1</sup>(b) (from NAS, 1978)

Element	Crustal Material <sup>e</sup> 10 <sup>9</sup> g yr <sup>-1</sup>	Bulk Sea-Salt <sup>d</sup> 10 <sup>9</sup> g yr <sup>-1</sup>	Fossil-Fuel Combustion Products <sup>e</sup> 10 <sup>9</sup> g yr <sup>-1</sup>
Al	20,000	0.15	1400
Fe	14,000	0.5	1400
Na	6,000	$3 \times 10^5$	300
Mn	200	0.005	7
Sc	6	0.000015	0.7
Cu	14	0.04	2
V	30	0.05	12
Se	0.013	0.003	0.5
Pb	3	0.0008	150 <sup>f</sup>
Cd	0.05	0.0008	-
As	0.5	0.05	0.7
Zn	18	0.08	0.5
Sb	0.05	0.007	-
Hg	0.02	0.0005	1.6

<sup>a</sup>Goldberg (1971).

<sup>b</sup>Eriksson (1959).

<sup>c</sup>Using crustal abundances of Taylor (1964).

<sup>d</sup>Using seawater concentrations of Riley (1975) and Chester and Stoner (1974).

<sup>e</sup>From estimates of Bertine and Goldberg (1971).

<sup>f</sup>Estimate of Patterson et al., (1976).

The atmospheric fluxes so calculated were compared with the total input of these metals to this area of the ocean from all sources, as indicated by the metal flux to the marine sediments. The sediment flux was estimated on the basis of the known metal concentration in deep-sea sediments and the accumulation rate of sediments in that area,  $12 \text{ g m}^{-2} \text{ yr}^{-1}$ . (It must be kept in mind that all these calculated fluxes have considerable uncertainty.) The calculated percentage of the total metal flux to the ocean in this area, represented by the atmospheric input, ranged from 0.3 to 13% for Fe, Al, Mn, Sc, Cu, V and As. This range of values appears reasonable. However, the percentage is 51% for Zn and ranges up to 2900% for Cd, Sb, Pb, Hg and Se, i.e., the atmospheric deposition rates to the ocean surface for the latter 5 elements are greater than their deposition rates to the marine sediment. These metals with highly anomalous atmospheric depositions are also among those that have high  $EF_{\text{crust}}$  values.

As pointed out by NAS (1978), there are several possible explanations for the apparently high atmospheric input rates for Zn, Cd, Sb, Pb, Hg and Se.

- \*1. The primary sources of these elements may be anthropogenic, and, thus, the calculated input rates reflect a recent phenomenon in the geological time scale. The sedimentation data are long-term averages spanning many hundreds to thousands of years. Thus, an unusually high-rate, but short-term, injection would not be resolvable in the sediment record.
2. A significant quantity of the metals present in the atmosphere may actually be recycled material that has been resuspended from the ocean surface. Most suspect would be those metals that are enriched in sea-salt aerosols relative to their seawater concentrations. Thus, the calculated atmospheric deposition rate would be artificially high and would not represent a true net input to the ocean.
3. The assumption that the mechanism for the removal of the metals from the atmosphere is equally efficient for all particle sizes may not be valid. Experiments indicate that aerosol removal by precipitation and by dry processes is relatively more efficient for larger particles. Thus, the actual removal rate for small particles over the oceans may be considerably less than that for large particles. Measurements made on Bermuda (Duce *et al.*, 1976) of particle composition as a function of size show that the major fraction of the mass of Cu, Zn, As, Sb, Se, Hg, Pb and Cd is present in submicrometer particles. In contrast, Na, Al, Mn, Fe, Sc, Th and Co are found primarily on the 1- to  $5 \mu\text{m}$  - radius particles."

It is not presently possible to determine which, if any, of these explanations is correct. The first step is obviously to make some direct measurements of the fluxes of these metals to the ocean surface.

### 3.2.2 Other substances in particulate form

There is a vast literature on sulphur compounds entering the atmosphere from various sources (Husar, 1978) and their effects on freshwater environments (Odén, 1976; Schofield, 1976). Anthropogenic sulphur is emitted primarily in the gaseous form as sulphur dioxide and is transformed within several days in the atmosphere to sulphate in the particulate form. Although the flux of gaseous (Liss and Slater, 1974), particulate and precipitation sulphur to the marine environment is significant, its effects there have not yet been established.

Interaction of gaseous substances in the atmosphere may lead to aerosol formation. The significance of this process as a contributor to the atmospheric load of particulate material on a global scale is unknown. It is recognized, although

not quantitatively established, that some gaseous substances are absorbed on existing particles in the atmosphere. This may be a particularly important phenomenon with particles in carbonaceous emissions from forest fires and other combustion processes.

### 3.3 Petroleum Hydrocarbons

The tropospheric transport of petroleum and related natural hydrocarbons to the oceans was reviewed by a working group at the Miami Workshop in December 1975 (NAS, 1978). The budget of particulate and vapour phase non-methane organic carbon in the global troposphere has recently been reviewed by Duce (1978).

It has been estimated that the global atmospheric input of petroleum hydrocarbons to the seas is approximately  $0.6 \times 10^{12}$  g yr<sup>-1</sup> (NAS, 1975c). Garrett and Smagin (1976) estimated that  $1.35 \times 10^{12}$  g yr<sup>-1</sup> is emitted to the atmosphere by natural seeps, transportation sources, and offshore production facilities. However, these hydrocarbons consist mainly of volatile, gas-phase compounds that are highly paraffinic and stable and, thus, not likely to be rapidly converted into particles that would be eventually redeposited in the sea.

The Working Group on Petroleum at the Miami Workshop (NAS, 1978) concluded that: "in addition to continental inputs, it seems likely that there is a cycle of petroleum hydrocarbons between the oceans and the marine atmosphere in which (a) there is a net flux of volatile, low-molecular-weight compounds from sea to air; (b) the less stable compounds undergo gas-to-particle conversion in the atmosphere; and (c) the particulate forms are returned to the sea by precipitation processes and as dry fallout".

Duce (1978a) reviewed available data and concluded that the quantity of organic carbon on large particles ( $d \geq 1 \mu\text{m}$ ) in the global troposphere can be explained by primary emissions from anthropogenic sources and such natural sources as the ocean, crustal weathering and naturally - ignited forest fires. However, primary emissions from pollution and natural sources apparently cannot account for the global tropospheric burden of small ( $d < 1 \mu\text{m}$ ) organic carbon particles, since as much as  $80-160 \times 10^{12}$  g yr<sup>-1</sup> of small particle carbon from some additional source is required to balance the cycle. Possibilities for such a source have been suggested as leaves of vegetation and gas-to-particle conversion of natural and anthropogenic organic carbon compounds.

## 4. BIOLOGICAL CONSIDERATIONS

Marine plants and animals may be involved in the exchange of pollutants between the atmosphere and the sea in a number of significant ways: (a) excrete oily substances, which form a film on the sea surface and alter air-sea exchange (see Section 6); (b) release substances that enter the atmosphere; (c) bioconcentrate certain substances entering the sea from the atmosphere and biomagnify these through the food chain; (d) actute toxicity or sub-lethal effect to organisms in the surface microlayer from substances introduced to the sea through the atmosphere; (e) microorganisms may be concentrated in the surface microlayer and projected into the atmosphere by bursting bubbles, or transferred from the sea surface to the overlying air by wind spray.

### 4.1 The Surface Microlayer

The upper layer of the sea, and particularly the surface microlayer is a unique marine environment (Wangersky, 1976), and plant and animal organisms must become specially adapted to survive the hostile conditions (extreme temperature and salinity fluctuations, intense solar radiation with destructive ultraviolet, and constant agitation) in this habitat. Some microscopic species, particularly bacteria and the heterotrophic microneuston (Bezdek and Carlucci, 1972; Marumo *et al.*, 1971; Sieburth *et al.*, 1976) appear to survive in the surface microlayers of the sea.

Other less resistant species of phytoplankton and microzooplankton inhabit the upper 10 cm of the sea but can still have an impact on the surface microlayer through their metabolic products. Most of the larger marine phytoplankton and zooplankton exist below the upper metre of the sea. The peak production of phytoplankton normally occurs at 5-10 m, removed from the most intense solar radiation at the surface, and zooplankton often undertake diurnal migrations, ascending toward the sea surface at dusk and descending into deeper waters at dawn.

Marine organisms have been recognized for a long time as possible contributors to natural slicks occurring on the sea (Dietz and LaFond, 1950; Ewing, 1950). However, it is only more recently that the chemical properties of sea-surface slicks have been established (Jarvis, *et al.*, 1987; Williams, 1967; Baier, *et al.*, 1974; Berger *et al.*, 1974; Larsson, *et al.*, 1974; Morris, 1974; MacIntyre, 1974; Liss, 1975; Wade and Quinn, 1975; Marty and Saliot, 1976).

Moreover, many of these film-producing substances have been shown to be associated with marine organisms in or near the surface microlayer of the sea (Morris, 1974; Morris and Culkin, 1974; Sieburth *et al.*, 1976; Curtis and Barker, 1977). It is now believed that most of the natural slicks on the sea surface are produced by lipid secretions of marine organisms, and that the intensity and chemical characteristics vary with the state of their development. Unfortunately, it is still difficult to chemically distinguish biogenic hydrocarbons from the petroleum hydrocarbons. In addition to the oils, the glycoprotein fragments (carbohydrate) of dead phytoplankton make an important contribution to the particulate materials in the surface microlayer.

#### 4.2 Biological Contributions to Substances Involved in Air-Sea Exchange

The most fundamental involvement of marine organisms in air-sea exchange is in utilization of carbon dioxide and release of oxygen by plants in photosynthesis, and the use of oxygen and release of carbon dioxide by bacteria and animals in respiration. Clearly, marine organisms have a significant effect in maintaining a balance of these vital gases between the atmosphere and the oceans. In addition to oxygen, marine plants release halogenated hydrocarbons, e.g. methyl iodide, methyl bromide and chloroform, during their growing period and contribute to a net flux of these gases from the sea to the atmosphere (Liss and Slater, 1974). Methyl chloride may also be formed in the sea as a result of the reaction of methyl iodide with chloride ions resulting in a net flux of methyl chloride from the sea to the atmosphere (Zafiriou, 1975). Undoubtedly, there is a release of marine biogenic hydrocarbons from the sea to the atmosphere, as well as a transfer of terrestrial plant hydrocarbons to the sea, although the proportion such hydrocarbons contribute to the total exchanged between the sea and the atmosphere has not been evaluated.

The contribution of marine plants and animals to the global carbon dioxide budget has not been resolved. Atmospheric carbon dioxide concentration shows a distinctive seasonal cycle, with a decrease during the growing season when photosynthesis is high. However, there appear to be erratic CO<sub>2</sub> fluctuations in the surface layer of the sea over a one or two-week period of measurements, unlike the situation in the overlying atmosphere, where CO<sub>2</sub> concentrations appear to be quite stable within such a time frame. The source of the large daily fluctuations of the CO<sub>2</sub> in the upper 15 m of the sea is still not fully understood, but is likely to be related to biological activity and/or temperature changes in the surface water.



#### 4.3 Effects of Pollutant Substances Exchanged Between the Atmosphere and the Sea

Pollutants entering the sea from the atmosphere may be acutely or sublethally toxic to marine organisms. Some may be concentrated by certain species and biomagnified through the food chain. Others may cause tainting of sea food and render it unsuitable for human consumption. Substances that are persistent are usually most likely to be bioconcentrated. Some substances may undergo biotransformation by the action of marine bacteria.

There is a vast literature on bioconcentration of metals by various marine species. Recent studies (Beauford *et al.*, 1977) have shown that zinc compounds can be transmitted into the atmosphere by growing terrestrial plants. It is conceivable that metals could also be released into the atmosphere by marine plants which are partly at the sea surface, e.g. sargassum, giant kelp and laminaria. There is evidence that a number of metals and metalloids, e.g. Hg, Pb, Sn, Se, As, are biomethylated by microorganisms in aquatic environments (Jensen and Jernelöv, 1969; Wong *et al.*, 1975; Wood, 1974), although not all such biotransformations have been demonstrated for the marine environment. Generally, these metallo-organics are more volatile than the inorganic forms, are bioaccumulated by aquatic organisms and may be quite toxic. However, there is no published information on their air-sea exchange.

Synthetic chemicals, e.g. DDT and PCBs, are concentrated by high-lipid marine organisms. Such substances are sometimes found in the surface microlayer in association with films and microorganisms (Bidleman and Olney, 1974; Ahearn *et al.*, 1977). They are readily available for transfer to the atmosphere by bubble bursting and wind spray.

Radionuclides are bioaccumulated by many trophic levels in the marine ecosystem. Plutonium and polonium adsorb on the surfaces of large algae, such as kelp (Folsom *et al.*, 1975).  $^{106}\text{Ru}$ , another alpha emitter, is adsorbed on the sea weed *Porphyra umbilicalis* in the Irish Sea and controls the discharge of radioactive wastes from the Windscale nuclear reactor in the U.K., inasmuch as *Porphyra* is used in laverbread by the Welsh (Preston, 1975). It is uncertain whether any radionuclides are transferred from the sea to the atmosphere through the biota, although it is conceivable that contaminated algae washed up on a beach may dry out, become pulverized and transmit nuclides into the air as dust.

In Table 6 are listed substances produced by and/or which may affect terrestrial and marine organisms and which are involved in air-sea exchange.

#### 4.4 Transmission of Microorganisms from the Sea to the Atmosphere

It has been known for a long time that microorganisms are present in marine air (Zobell, 1942). The marine atmosphere associated with a massive dinoflagellate bloom has been reported to be irritating to the human respiratory system as a result of these organisms or their metabolic products (Woodcock, 1948).

More recently, it has been demonstrated that bacteria and viruses can be enriched in the surface microlayer by bubbles and projected into the atmosphere by bubble bursting and from surf to wind (Baylor *et al.*, 1977 a, b; Blanchard *et al.*, 1974). There is evidence now that some disease-producing microorganisms are transmitted through the atmosphere (Gruft *et al.*, 1975), including the bacterium responsible for the infamous "Philadelphia Legionnaires disease". It has been suggested that certain microorganisms might be encapsulated in oleophilic materials produced by marine organisms at the sea surface and thus preserved for transmission by the atmosphere for long distances. It has been suggested (Blanchard *et al.*, 1974) that surface-active material from slicks could form a coating on airborne cells and depress the normal surface tension at the site of deposition in alveoli.

At the present state of knowledge, it is uncertain how epidemiologically significant the transfer of pathogenic microorganisms from the sea to the land through the atmosphere might be, although Gruft *et al.*, (1975) presented convincing evidence for the transmission of *Mycobacterium intracellulare* (BATTEY) infection from coastal Atlantic waters into the southeastern continental USA. In addition to transport of bacteria and viruses from sea to land via the atmosphere, there is potential for transmission by this mode of spores of fungi and parasites that could infect not only humans and other land animals, but also agricultural products.

Table 6. Biological contributions of substances involved in air-sea exchange

(a) Substances produced or concentrated by terrestrial organisms	Source	Remarks
<u>GASES</u>		
Oxygen	Photosynthesis of terrestrial plants	Forests and grasslands make a major contribution to the global oxygen budget.
Carbon dioxide	Respiration of terrestrial animals and decomposition of plant and animal tissues	Noted to be important in the global carbon cycle (Bolin, 1977).
Terpenoid compounds	Coniferous trees	Terpenes and other organic substances are contributed by the terrestrial biosphere.
Methane	Decomposition of plant life	Swamp areas and peat bogs contribute methane as a major component of decomposition gases.
Ammonia	Metabolic products from animals and decomposition of proteinaceous plant and animal matter	Ammonia is a major excretory product from land animals. Decomposition of animal tissue yields some ammonia.
Hydrogen sulphide	Decomposition of sulphur-containing organic materials	Anoxic conditions lead to hydrogen sulphide formation by reduction of sulphates and other S-compounds
CO, N <sub>2</sub> O, H <sub>2</sub>	Bacteria	Trace gases arising from bacterial activity (Hahn, 1972).

Table 6. (continued)

(a) Substances produced or concentrated by terrestrial organisms	Source	Remarks
<u>METALS</u>		
Metallo-organic compounds of As, Hg, Pb, S and Se	Methylation of metals by microorganisms	Occurs in freshwater sediments. It is noted that other metals and metalloids beside As, Hg, Pb, S and Se may be methylated by aquatic microorganisms (Wood, 1974; Wong <i>et al.</i> , 1975).
Zinc compounds	Growing plants	Noted by Beauford <i>et al.</i> , (1977). May be source for other metals also.
(b) Substances produced or concentrated by marine organisms	<u>HYDROCARBONS</u>	
Paraffins	Algae	Ethylene and propylene related to marine productivity (NAS, 1978).
Branched-chain aliphatic hydrocarbons	Photo- and zooplankton	Common oils produced by marine plankton.
Polycyclic aromatic hydrocarbons	Plants and animals	Noted to be produced naturally in the marine environment (NAS, 1975c).
<u>HALOGENATED SHORT-CHAIN HYDROCARBONS</u>		
Methyl iodide	Growing sea weeds	Contributes to a net flux of this material from the sea to the atmosphere (Liss and Slater, 1974).
Methyl bromide	Growing sea weeds	
Methyl chloride	Possibly by reaction of methyl iodide with chloride ions in seawater (Zafirious, 1975)	
Chloroform	Growing sea weeds	

Table 6. (continued)

(b) Substances produced  
or concentrated by  
marine organisms

Source

Remarks

GASEOUS DECOMPOSITION PRODUCTS

Methane	Decomposition of organic material	Normally occurs in areas of large deposition of decomposable organic materials where waters are not frequently exchanged.
Hydrogen sulphide	Decomposition of organic material (anoxic conditions)	
Dimethyl sulphide	Production by marine bacteria	

METALS

Metals	Concentrated by marine plant and animal organisms	Most marine organisms are capable of bioaccumulating certain metals. Concentrations by micro-organisms in the surface microlayer make the metals available for transfer to the atmosphere.
Metallo-organic compounds of As, Hg, S and Se	Produced by micro-organisms in marine sediments and organisms	Noted by Wood (1974) that methylated compounds of As, Hg, S and Se found in the marine environment. Wong <i>et al.</i> , (1975) reported methylation of Pb in fresh-water sediments.

HALOGENATED HYDROCARBONS

Chlorinated hydrocarbon pesticides, e.g. DDT and industrial chemicals, e.g. PCBs	Concentrated by marine plant and animal organisms	Bioaccumulation of these chemicals by micro-organisms in the surface microlayer make them available for transfer to the atmosphere.
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RADIONUCLIDES

Fission products ( $^{90}\text{Sr}$ , $^{137}\text{Cs}$ , $^{106}\text{Ru}$ , $^{144}\text{Ce}$ , $^{144}\text{Pr}$ ) and neutron-induced radionuclides ( $^{60}\text{Co}$ , $^{32}\text{P}$ , $^{65}\text{Zn}$ , $^{51}\text{Cr}$ ). Plutonium in nuclear power sources	Fallout from nuclear weapons testing. Emissions from nuclear reactors. Reactor accidents.	$^{90}\text{Sr}$ and $^{137}\text{Cs}$ from fallout declining. Plutonium from reprocessing of spent nuclear fuel a major concern. Tritium, radon and krypton-85 potential hazards. Uptake by marine organisms (NAS, 1971; Goldberg, 1976b).
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5. POLLUTANT MODIFICATION OF PHYSICAL AND CHEMICAL PROCESSES AT THE AIR-SEA INTERFACE

5.1 Influence of Pollutant Surface Films

There are three types of organic pollutants which have the potential for modifying the chemical and physical properties of the air-sea interface: detergents, the complex mixture of organics comprising municipal wastes and sewage sludge and petroleum hydrocarbons and their derivatives.

Detergents are short lived in the sea because of their biodegradability. There is no documentation of actual cases in the open oceans where detergents have significantly influenced sea surface properties.

Surface tension reductions due to organic pollutants have been associated with urban waste dump sites (Hardy and Baylor, 1975). A recent workshop report identifies the potential for accumulation of oleophilic pollutants in the surface films associated with such dump sites and the possible transport of the accumulated pollutants into the marine atmosphere (Blanchard et al., 1974).

The third group of organic surface pollutants, petroleum hydrocarbons and their derivatives, influence the physics and chemistry of the air-sea interface in numerous ways. Petroleum films not only affect material transport and physical parameters, but also influence the absorption and reflection of electromagnetic radiation. The various chemical and physical effects of natural and man-made organic films on interfacial properties are summarized in Table 7. Some of the physico-chemical effects of petroleum which might have significant influence on marine organisms were considered recently by a GESAMP Working Group on the Impact of Oil in the Marine Environment (GESAMP, 1977). Of particular interest is the fact that petroleum in and on the sea may influence the pathways of other pollutants by (i) dissolving other oleophilic species such as halogenated hydrocarbons and (ii) by reducing the interfacial pollutant transfer rate when the petroleum exists as a continuous film on the surface of the sea. For example, pollutant exchange rates are decreased by oil films through attenuation of and by alteration of breaking waves, spray and the number and size distribution of bursting bubbles.

The possible regional and global impact of petroleum on interfacial processes will require knowledge of the extent of sea surface coverage by continuous pollutant films. The most influential factors governing the existence of pollutant organic surface films are 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 and photocatalytic oxidation. Because of the great influence of wind and waves, the probability of encountering natural slicks or persistent petroleum films in the open ocean is likely to be a function of average wind conditions. For example, winter meteorological conditions in the North Atlantic and Pacific Oceans would normally preclude the persistence of coherent organic films, while a broad band from the equator to approximately 40 degrees south latitude is relatively calm and has the potential for slick formation and endurance. In summer relatively low-wind conditions exist in some regions of the northern seas, the Black Sea, the Mediterranean, and in a few zones along the Tropic of Capricorn. It must be stressed that coherent films can only be formed when sufficient surface active material is available.

Table 7. Impact of natural and man-made surface films on the properties of the air-sea interface

Surface effect or process modification	Type of organic surface film <sup>†</sup>		
	Natural	Petroleum	Experimental*
Capillary Wave Attenuation	++(33,43,48,122)	++(51)	++(3)
Gravity Waves	-(33)	?	++(3)
Breaking Waves Inhibition	?	?	++(3)
Gas Transport Reduction	-(51)	+(36,51,68,69,90,117)	+(19,51,66,79)
Oleophilic Pollutant Accumulation	++(62,123)	?(54)	?(52)
Foam Stability	+(51)	+(51)	+(49)
Air Bubble Bursting	+(17,50)	+(51)	+(50,112)
Surface Temperature	++(29)	++(42,97)	++(58,78,79)
Electromagnetic Wave Reflection	++(9,23,97)	++(8,26,97)	++(3)
Light Transmission	?	++(54)	?
Light Absorption, Heating	-	?(54)	-

- Significant influence of surface film unlikely

+ Demonstrated in laboratory; field studies if any were inconclusive

++ Effect demonstrated by laboratory and field research

? Potential influence, but not proved by experiment

\* A continuous, monomolecular film added to water surface for research purposes

† Numbers in brackets correspond to entries in the bibliography given in Section 7.

Existing monitoring projects and ongoing basic research will provide valuable information for the further evaluation of surface film impacts. Monitoring data on petroleum slicks will be available from the IGOSS Marine Pollution (Petroleum) Monitoring Pilot Project (MAPMOPP), preliminary results of which have been reported. It is anticipated that this IGOSS Pilot Project and the Joint IOC/WMO/UNEP Pilot Project on Baseline Studies and Monitoring of Oil and Petroleum Hydrocarbons in Marine Waters (Mediterranean) will eventually provide information which can be used to assess the impact of petroleum films at the air-sea boundary. Special attention should be given to coastal areas, estuaries, and certain semi-enclosed areas where oil slicks have been observed to cover a larger percentage of the surface area.

Recently data collected by the IGOSS MAPMOPP Project have been analyzed by the West German Oceanographic Data Centre and presented to the second session of the IOC/WMO Sub-Group of Experts on MAPMOPP, Washington, D.C., 13-17 February 1978. These data had been previously processed in computer-compatible form by the U.S. National Oceanographic Data Centre (acting as an IGOSS RNOOC) and included 25,589 visual observations of oil slicks and 1638 collections of floating particulate petroleum residues (tar balls). Of the visual observations 1778 were positive notifications of oil occurrence. These petroleum data were collected between October, 1974 and May, 1977.

The analyzed data are displayed on world ocean maps and in figures which show spatial and temporal distributions of oil slicks and tar balls. The percentage of positive observations of oil slicks are treated in a similar fashion. Additional analyses of these data by the German NOOC and the Naval Research Laboratory, Washington, D.C., are being attempted to determine the percentage surface coverage of the oceans and regional seas by oil films, and to produce an estimate of the quantities of oil present in these oceanic regions.

On the basis of these preliminary analyses, experts in the group concluded that natural and/or petroleum films may not modify the interfacial exchange of matter or energy significantly on a global scale, but that in certain coastal zones and seas such films will be more prevalent, and a potential for the modification of interfacial properties and exchange processes will exist regionally.

## 5.2 Sea Surface Truth and Remote Sensing: Influence of Natural and Pollutant Organic Surface Films on the Interpretation of Remotely Sensed Signals

Knowledge of the chemical nature and physical properties of the sea surface is essential to provide "sea truth" (the oceanic equivalent of "ground truth") for the proper interpretation of data from remote sensing systems. Since it has been shown in Section 5.1 that organic surface films modify the properties of the air-sea interface and its associated boundary layers, such films may also influence both passive and active remotely sensed signals. The magnitude of the physical effects of the surface film is a function of its chemical nature, its thickness, and the surface concentration of interfacially active molecules at the air-sea interface. Many of the surface effects produced by films can be produced by a layer of adsorbed organic material only one molecule in thickness (approximately 3 nanometers). Films of this kind, e.g. natural sea slicks, require as little as one milligram of organic material per square meter of ocean surface for their formation. Organic films attenuate and resist the formation of capillary waves, modify breaking waves and the resulting distribution of entrained bubbles, influence bubble bursting phenomena, and produce temperature anomalies by various mechanisms.

Table 8. Effects of natural organic seasurface films on remotely sensed signals

<u>Seasurface effect</u>	<u>Sensor approach - spectral region</u>	<u>Influence of signal</u>
Capillary wave damping	Active reflectance - microwave radar	Reduced Backscatter power
	Passive reflectance - UV, visible, near IR	Modified light reflectance
Inhibition of convective overturn at surface	Passive emission - thermal IR	Slicks appear cooler
Inhibition of wave breaking-modified sea foam stability	Passive microwave	Altered sea foam coverage

The influences of natural organic seasurface films on remotely sensed signals are reviewed in Table 8. Since natural slicks attenuate and resist the formation of capillary waves, affected sea surface areas have different reflectance characteristics from those of surrounding nonslicked waters. When passive reflectance is sensed, the relative intensity of the signal is dependent upon the look angle, the relative position of the sensor with respect to the sun, meteorological conditions and other factors. With active sensors such a microwave radar, the power of the backscattered radiation is sharply reduced by the ripple-damped sea surface under the influence of the organic film.

In general, natural slicks appear slightly cooler than adjacent water surfaces when sensed by thermal infrared. Although the emissivity of a water surface is not altered by the presence of a monomolecular layer of organic material, the cool-surface effect is produced by an immobilizing of the near surface water by the "rigid" surface film, which inhibits convective overturn of the surface water cooled by evaporation (Jarvis, 1962). Natural slicks are not expected to retard evaporation to a significant extent. Consequently, warm signatures of sea slicks have not been observed, but appear cooler than the surrounding nonslicked water surface when measured by thermal radiometry (Clark, 1967).

Passive microwave sensors can detect sea foam and white water through a resulting increase of seasurface emissivity. Air bubbles and foam at the air-water interface are responsible for the passive microwave signals, while entrained air bubbles beneath the surface do not participate in the effect. Surface-active material modifies sea foam through several mechanisms. Organic films may resist wave breaking and also act to destabilize foams and bubbles once they reach the water surface. Water-soluble, surface-active materials, on the other hand, are foam stabilizers. The net effect of these opposing processes has not been determined experimentally at sea.

When petroleum spills or municipal effluents are present, thicker films are implicated in the production and modification of remotely sensed signals. The influences of petroleum films on remote sensing are similar to those of natural slicks, except for thermal IR sensors, to which a petroleum surface film may appear either cooler or warmer than adjacent clean water. The sensed IR signal may be due to a number of possible physical effects, the relative importance of which has not been demonstrated by sea-truth experiments.



Table 9. Oil spill detection by remote sensing<sup>†</sup>

<u>Sensor approach</u>	<u>Spectral region</u>	<u>False alarms*</u>
Active reflectance	Microwave radar, 1.05-5cm	Natural organic slicks Wind slicks, ship wakes Pollutant organic slicks (detergents, sewage sludge) Kelp/debris Dense cloud cells Unrippled water under calm conditions
Passive reflectance	UV, < 0.4um	Natural organic slicks Suspended solids
	Visible, 0.4-0.65um	Natural organic slicks Pollutant organic slicks Suspended solids Shallow water Broken cloud deck
	Near IR, > 0.65um	Natural organic slicks Other pollutant slicks
Passive emission	Thermal IR, 3-14um	Natural organic slicks Pollutant organic slicks Ship wakes Thermal discharges and effluents Upwelling
	Microwave, 0.2-1cm	Foam patches Kelp/debris Dense cloud cells

\* Since all of the listed sensors detect oil on water, natural petroleum seeps would be a false target for each sensor.

† Adapted from Maurer and Edgerton, 1975

Petroleum spills may be sensed across a broad spectral range by numerous sensor systems. Because oil spills vary greatly in thickness and in their physical and chemical characteristics, the portion of the spill sensed varies according to the sensing system used for observation. For example, microwave radar senses the entire area affected by the oil in which the capillary wave structure is diminished, whereas dual-frequency, passive microwave radiometry senses only the thicker layers of the spill and can be used to determine spill volume and locate significant quantities of oil to guide spill-removal operations. Table 9 reviews the types of false signals encountered when various sensors are used to detect petroleum slicks on the sea. Both natural surface films and other pollutants may be incorrectly identified as petroleum by many remote sensing systems. The use of multiple sensing systems is required to avoid ambiguities.

In most instances sea truth must be determined if remotely sensed data are to be correctly interpreted. For example, negative seasurface return of side-looking microwave radar signals may be due to the following sea truth situations in which capillary waves are either diminished or absent: (1) zones of calm where no organic film is necessarily involved; (2) hydrodynamic damping in a ship's wake; (3) wind slicks; (4) natural sea slicks caused by organic films which attenuate and resist the formation of capillary waves; and (5) thicker layers or wave-damping petroleum oils or other organic film-forming pollutants. The other sensors used for the detection of oil on water also have a number of possible false alarms which require measurements and observation at the air-sea boundary to ascertain corresponding sea truth.

It is recognized that remote sensing systems are becoming increasingly more sophisticated and useful for many applications. However, it should be noted that both natural and pollutant surface films significantly modify the physics and hydrodynamics of the air-sea interface and consequently affect the signals received by a number of remote sensing systems. Thus, when remote sensing is used in oceanographic applications, the properties of the air-sea interface (sea truth) must be known in order to provide proper interpretation of the signals being received.

#### 6. GUIDELINES FOR A MEASUREMENT PROGRAMME FOR THE DETERMINATION OF AIR-SEA FLUXES

The primary objectives of the suggested programme are the quantitative measurement of the present fluxes of certain pollutants across the air-sea interface, and determination of any significant change in these fluxes with time. The working group considers that two criteria must be met before a long-term monitoring programme for any substance is worthwhile.

First, there must be a scientifically substantiated indication that significant changes in the distribution or flux of that substance will result in serious disturbance of physical, chemical or biological processes in the environment. Examples include the injection of quantities of material into the atmosphere which could affect global climate, or of material into the ocean which might endanger the life cycle of marine organisms.

Second, expected changes in concentrations of a particular substance with time must be statistically distinguishable, after considering the natural temporal concentration variations expected for that substance and the analytical precision of the concentration measurements themselves.

On the basis of these criteria, the working group concluded that a continuous, large-scale, long-term monitoring programme for measurement of air-sea fluxes of such substances as heavy metals, petroleum hydrocarbons and heavier chlorinated hydrocarbons, e.g. PCBs and DDT, may not be warranted at present. Collection and analytical methodologies for all these substances in remote regions

require considerable development and standardization before measurement accuracies of even a few percent are obtainable. Since all these substances have relatively short atmospheric residence times (a few days to perhaps a few weeks) their concentration variation at a given site may often be quite high. Even over the mid North Pacific Ocean daily concentration changes of over a factor of 10 for some of these substances are not uncommon (Hoffman, et al., 1978). On the other hand, there is reason to believe the anthropogenic mobilization of some of these substances, e.g. lead, PCBs, DDT, petroleum hydrocarbons, may change significantly over the next few decades, either as a result of specific control measures for these materials or changes in the technology in which they are utilized. It would be of great value to be able to relate changes in mobilization of these materials to any changes in their distribution and flux across the air-sea interface in open ocean areas.

For these reasons, the working group recommends that a measurement programme for heavy metals, halogenated and petroleum hydrocarbons be initiated in open ocean regions, but that it be developed carefully and within a research framework, as was previously recommended for petroleum hydrocarbons by Duce (1978b). Such measurements have rarely been made for these pollutants, and appropriate analytical and sampling procedures have not been satisfactorily developed in most cases. Problems with sample contamination, in remote areas particularly, will be severe. In many cases, the masses of material to be analyzed will be at the edge of analytical capability, and sophisticated analytical methodologies will be required.

The working group further recommended that the measurement programme be undertaken as soon as possible for a relatively short period of one to two years, but that the measurements not be undertaken on a continuous basis. Sufficient samples must be obtained to adequately ascertain the short-term temporal variations in the distribution of these materials at a particular site. The working group also recommends that additional measurement periods be undertaken at subsequent intervals of perhaps 5 to 10 years to evaluate long-term changes in the distribution and flux of these materials.

## 6.1 Sampling Sites

### 6.1.1 Site selection rationale

#### 6.1.1.1 General

In selecting atmospheric sampling sites for the determination of fluxes between the atmosphere and the ocean, the general criteria for siting WMO Baseline Air-Pollution Stations should be followed. Indeed, these studies should ideally be carried out at WMO Baseline Stations, if possible. The siting criteria are given in WMO Publication No. 491 "International Operations Handbook for Measurement of Background Atmospheric Pollution" (WMO, 1978). Basically the site selected should have no anticipated change in land use for at least 50 years and within 100 km in all directions, be located ~~away~~ from population centres and highways, etc., and should experience only infrequent effects from local natural phenomena such as volcanic activity, forest fires, dust and sandstorms. Baseline air pollution monitoring stations are presently located in the following countries: Argentina, Australia, Canada (Sable Island, Alert, Ocean Ship "P"), Italy\*, Japan, Kenya, Peru, Spain, USSR, USA (Point Barrow\*, Mauna Loa\*, Samoa\*, S. Pole\*). The stations indicated \* are the only ones which are currently fully operational.

For the purposes of this report air-sea exchange will not be considered in the near coastal zone and thus mid-ocean sampling sites are required. This limits the sampling to islands and ships. Both have advantages and disadvantages.

#### 6.1.1.2 Ships and off-shore platforms

Ships have the advantage of mobility and thus can be located geographically in the most interesting areas for sampling. However, a programme which will involve atmospheric sampling over a number of years would require a ship to remain in one location semipermanently. Ships of opportunity have the disadvantage of constant movement, making it impossible to obtain any chemical climatology data from a particular area. For a monitoring programme this limits ships, or platforms, to weather ships and oil rigs.

The primary disadvantage of ships and oil rigs is that they are quite dirty, making it very difficult to collect uncontaminated atmospheric samples (Moyers *et al.*, 1972; Hoffman *et al.*, 1976). Moyers *et al.*, (1972) point out that dirt, paint, rust, etc., from the decks, superstructure, and stacks as well as gases from the stacks and ventilation systems are present all over the ship, including high on the masts and flying bridge. Problems with sea spray were also described. These authors suggest that the only clean area for atmospheric sampling is above and in front of the bow of the ship. Problems with contamination of samples while they are being handled or processed after collection can be minimized by the use of portable clean laboratories or laminar flow clean benches on board ship.

If shipboard sampling must be undertaken it should be carried out from a tower at least 5 to 10m above and slightly in front of the ship's bow and only when the ship is headed into the wind. Laminar flow clean benches or portable clean laboratories should be used when processing the collected samples on board ship.

#### 6.1.1.3 Islands

The most practical way to obtain atmospheric concentrations and fluxes of trace substances in remote marine areas is to have stationary sampling sites on islands operating over a relatively extended period of time. The sampling sites should be located directly on the windward coastline, as far as possible from any human habitation. The samples should be collected from walk-up towers at least 20m high to avoid locally produced surf spray. If the tower is located on a bluff or cliff above the ocean, it may need to be higher than 20m so the top of the tower is above any spray or local soil or vegetation contamination carried up the cliff by on-shore winds.

One of the primary disadvantages of island sites for making flux calculations, using rain and dry deposition measurements, is the strong effect mid-ocean islands often have on precipitation and local wind patterns, both through diurnal surface heating and orographic effects. This can be minimized by selecting very small islands with little topography, or by selecting a site on a peninsula or point which juts relatively far out into the prevailing winds. For many islands, however, this is not possible.

Ideally, a measurement programme should include sites in the major wind regimes in the northern and southern hemispheres. Several sites are suggested below (Section 6.1.2) as possibilities and these have been chosen to be representative of the major global wind regimes. In several cases the particular location was chosen because atmospheric sampling facilities already exist there.

## 6.1.2 Proposed sampling sites

### 6.1.2.1 North hemisphere

- (a) Atlantic Northeast Tradewinds - Barbados ( $13^{\circ}\text{N}$ ,  $59^{\circ}\text{W}$ ) - An atmospheric sampling station operated by the University of Miami has been in use on Barbados for a number of years. This is the easternmost island in the West Indies and is thus subject to little contamination from other islands in the area.
- (b) Pacific Northeast Tradewinds - Hawaii ( $22^{\circ}\text{N}$ ,  $158^{\circ}\text{W}$ ) or Enewetak ( $12^{\circ}\text{N}$ ,  $163^{\circ}\text{E}$ ) - These islands are both in the mid-Pacific, with Enewetak considerably further west than Hawaii. A sampling tower station operated by the University of Hawaii and University of Rhode Island is already located on the east coast of Oahu, Hawaii and Enewetak will be the northern hemisphere station of the SEAREX (Sea-Air Exchange) Programme supported by the U.S. National Science Foundation.
- (c) Atlantic Westerlies
  - (i) Sable Island ( $44^{\circ}\text{N}$ ,  $60^{\circ}\text{W}$ ) or west coast of Ireland ( $53^{\circ}\text{N}$ ,  $10^{\circ}\text{W}$ ) - These sites were selected to evaluate the transport of pollutant substances from the North American continent across the North Atlantic Ocean. Sable Island, near North America, has been used by the Canadians for some atmospheric sampling. Several locations on the west coast of Ireland have also been used for atmospheric sampling by different groups, although no tower facility is presently available there.
  - (ii) Bermuda ( $32^{\circ}\text{N}$ ,  $65^{\circ}\text{W}$ ) is located in a transition zone, with predominantly westerly flow during the winter months and easterly flow during the summer. An atmospheric sampling tower has been in use on Bermuda by the University of Rhode Island for several years.
- (d) Pacific Westerlies - Midway ( $28^{\circ}\text{N}$ ,  $177^{\circ}\text{W}$ ), Adak ( $52^{\circ}\text{N}$ ,  $176^{\circ}\text{W}$ ), or a ship - There are no really satisfactory island sites at mid-latitudes in the Pacific. Midway Island is at  $28^{\circ}\text{N}$  and thus is often in the northeast tradewind regime. Adak Island in the Aleutian chain is perhaps the best island location. Neither of these locations has any atmospheric sampling facilities at present.
- (e) Polar Easterlies - Pt. Barrow, Alaska ( $72^{\circ}\text{N}$ ,  $157^{\circ}\text{W}$ ), Spitzbergen ( $78^{\circ}\text{N}$ ,  $18^{\circ}\text{E}$ ), Novaya Zemlya USSR ( $74^{\circ}\text{N}$ ,  $55^{\circ}\text{E}$ ) or Alert, Ellesmere Island, Canada ( $82^{\circ}\text{N}$ ,  $62^{\circ}\text{W}$ ) - Any of these locations on the Arctic Ocean would be satisfactory. There is presently a WMO Background Air-Pollution Monitoring Station in operation at Pt. Barrow, Alaska and another on Ellesmere Island, Canada.

### 6.1.2.2 Southern hemisphere

- (a) Atlantic Southeast Tradewinds - Ascension ( $8^{\circ}\text{S}$ ,  $15^{\circ}\text{W}$ ) or St. Helena ( $16^{\circ}\text{S}$ ,  $5^{\circ}\text{W}$ ). Both islands are located in mid-ocean regions and would be satisfactory. There are no atmospheric sampling facilities on these islands at present, and access to the islands is limited.
- (b) Pacific Southeast Tradewinds - American Samoa ( $14^{\circ}\text{S}$ ,  $171^{\circ}\text{W}$ ). This is already the site of a WMO Background Air-Pollution Monitoring Station, and an atmospheric sampling tower will be located there as part of the U.S. National Science Foundation's SEAREX Programme in 1980.

- (c) Atlantic Westerlies - Tristan de Cunha ( $37^{\circ}\text{S}$ ,  $12^{\circ}\text{W}$ ). This island is located in the mid-south Atlantic. It also has limited access and no atmospheric sampling facilities.
- (d) Pacific Westerlies - Tasmania ( $41^{\circ}\text{S}$ ,  $141^{\circ}\text{E}$ ), Auckland Islands ( $51^{\circ}\text{S}$ ,  $166^{\circ}\text{E}$ ) or MacQuarie Island ( $54^{\circ}\text{S}$ ,  $158^{\circ}\text{E}$ ). All three of these islands are located between the Australian continent and Antarctica. The Australians have undertaken atmospheric sampling at MacQuarie Island and have a new WMO Background Air-Pollution Monitoring Station on Tasmania. Access to MacQuarie Island and the Auckland Islands is limited.
- (e) Indian Westerlies - Kerguelen ( $49^{\circ}\text{S}$ ,  $70^{\circ}\text{W}$ ) or Amsterdam Island ( $38^{\circ}\text{S}$ ,  $77^{\circ}\text{W}$ ). Both islands are located in the mid-Indian Ocean. Some atmospheric samples have been collected at Kerguelen and the French are planning an atmospheric sampling tower facility on Amsterdam Island.
- (f) Polar Easterlies - South Pole ( $90^{\circ}\text{S}$ ) or Molodezhnaya ( $68^{\circ}\text{S}$ ,  $46^{\circ}\text{E}$ ), Antarctica. Atmospheric samples from the interior polar plateau region of Antarctica can be collected at the WMO Background Air-Pollution Monitoring Station at the South Pole (elevation 2800m). A coastal Antarctic site which is also presently being used for atmospheric sampling is the USSR Molodezhnaya Station.

## 6.2 Flux Measurements

As shown in Figure 1, material enters the ocean from the atmosphere in three ways: by direct gas exchange, on particles by dry deposition, and in precipitation. Precipitation removes both particles and gases from the atmosphere.

### 6.2.1 Gas exchange

The processes controlling gas exchange across the air-sea interface are now reasonably well understood and models have been developed to predict air-sea gas exchange (Liss, 1973; Liss and Slater, 1974; Broecker and Peng, 1974; Hicks and Liss, 1976; Deacon, 1977). For example, using the two layer model described by Liss and Slater (1974), it is possible to estimate the flux of an exchanging gas across the air-sea interface if it obeys Henry's Law and if measurements of the gas in the atmosphere and surface ocean waters are available. Unfortunately, however, very few investigations have attempted to validate the models by directly measuring the flux of any gas across the ambient air-sea interface. To date no procedures exist for direct field measurement of gas fluxes from the atmosphere to the ocean except for  $\text{CO}_2$  in a research mode, although there is promising work underway in this area. Thus, at present, the best estimates would be made using the models above and measurements of the trace gases of interest in seawater and in the atmosphere at a particular monitoring station.

### 6.2.2 Particle dry deposition

The dry deposition flux to the ocean of any substance present on particles is related to its atmospheric concentration through the dry deposition velocity as follows:

$$D_d = v_d C$$

where  $D_d$  is the dry deposition flux of the substance in  $\text{gm}^{-2} \text{sec}^{-1}$ .  
 $v_d$  is the dry deposition velocity of the substance in  $\text{msec}^{-1}$ , and  
 $C$  is the atmospheric particulate concentration of the substance in  $\text{gm}^{-3}$ .

Effective deposition velocities for particles in the stable aerosol size range close to the ground are often near  $0.01 \text{ msec}^{-1}$ , but this varies considerably with particle

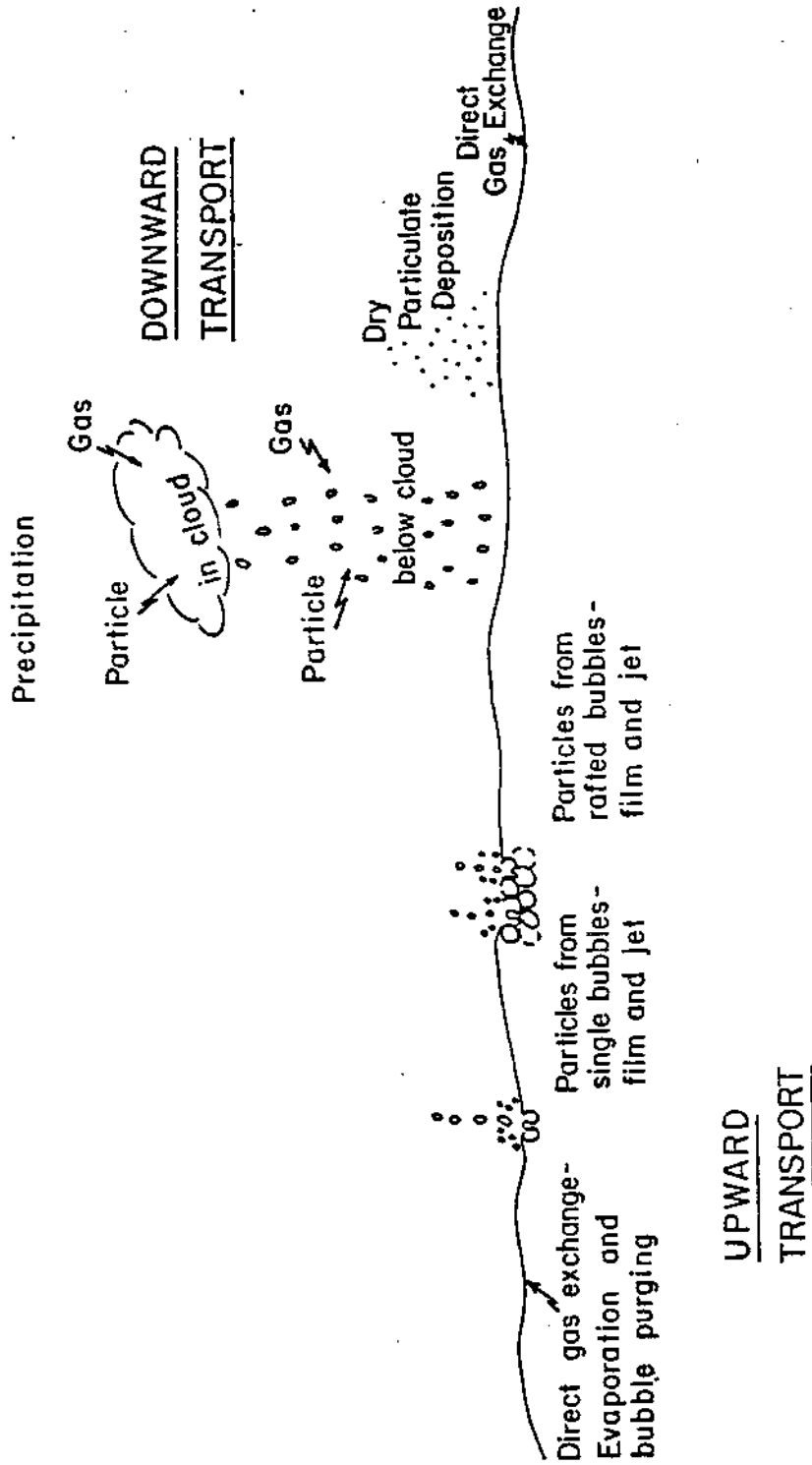


Figure 1. Mechanisms for the exchange of material across the air-sea interface

size, wind speed, and surface roughness. In a laboratory wind tunnel experiment Sehmel and Sutter (1974) investigated particle deposition velocity over a water surface as a function of particle size and wind speed. A summary of their results is presented in Figure 2. There is a general decrease in deposition velocity with decreasing particle size at a given wind speed, with a dramatic drop between 10 and 1  $\mu\text{m}$  diameter. For a given particle size greater than 1  $\mu\text{m}$  diameter, the deposition velocity increases with increasing wind speed. Below approximately 1  $\mu\text{m}$  diameter there appears to be no clear relation between deposition velocity and wind speed. Owing to the strong variation in dry deposition as a function of wind speed and particle size, it is extremely difficult to estimate accurately dry deposition at a particular site. The accurate direct determination of dry deposition over both land and water is presently the subject of considerable controversy, as evidenced by the WADEM Meeting in 1975 (WMO, 1975) and the subsequent WMO Expert Meeting on Dry Deposition Monitoring held in Gothenburg, Sweden in April, 1977. Indeed (NAS, 1978) states that "particle dry deposition is probably the area in which our knowledge of pollutant transfer to the ocean is most limited." Problems include effects of the type of collection surface used, its orientation, ease of contamination, gravitation vs diffusion deposition, etc. For these reasons, dry deposition measurements are not recommended at this time. To obtain some indication of the potential importance of dry deposition, it is recommended that both rain samples and total deposition (rain and dry deposition) samples be collected, as suggested by WADEM (WMO, 1975).

### 6.2.3 Precipitation

The accurate collection of rain or snow, particularly in remote areas, without contamination of the sample is extremely difficult. Galloway and Likens (1976) have evaluated a number of manual and automatic rain-dry deposition systems in the field. In their investigation they evaluated the reliability of collection systems, their construction material, and their efficiency for collecting precipitation. They also evaluated replicability of rainwater chemical data as a function of collector type, and the effects of sampling interval, dry deposition and storage on precipitation chemistry. Galloway and Likens (1976) concluded that of the systems they evaluated the most reliable and accurate automatic rain-dry deposition collector was that developed by Dr. Herbert Volchok at the United States DOE Health and Safety Laboratory (HASL), New York City. This system was also recommended by Garrett and Smagin (1976).

The HASL system consists of two collectors (constructed of glass, aluminum, or stainless steel when used to sample organic material, plastic for sampling inorganic material) which are controlled by a printed circuit rain sensor. The system is designed such that in dry weather, one of the collectors is exposed while a moving cover protects the other container - the precipitation collector. At the first onset of precipitation the cover swings to close the dry deposition container and expose the rain collector. A low wattage heater is attached to the sensor to evaporate moisture so that the system is not triggered by condensation such as dew, and so that the cover will swing from one container to the other soon after the end of a precipitation event. At mid-ocean island sites contaminated samples can be collected if sampling occurs when surface level winds are from the island toward the sampling site rather than from the open water. In any sampling programme where samples will be collected over a period of several days, it is necessary to have a system which controls sampling as a function of surface wind speed and direction, and Aitken nuclei counts, in order to avoid this local contamination. The HASL system should be modified so that it has two covers and can be operated by an environmental control system of the type indicated above. The controller can be integrated into the sampling system so that both collectors would be covered when the wind is from an inappropriate direction of very light, or when the CN counts are above  $200-500\text{cm}^{-3}$ , an average value in clean marine air.



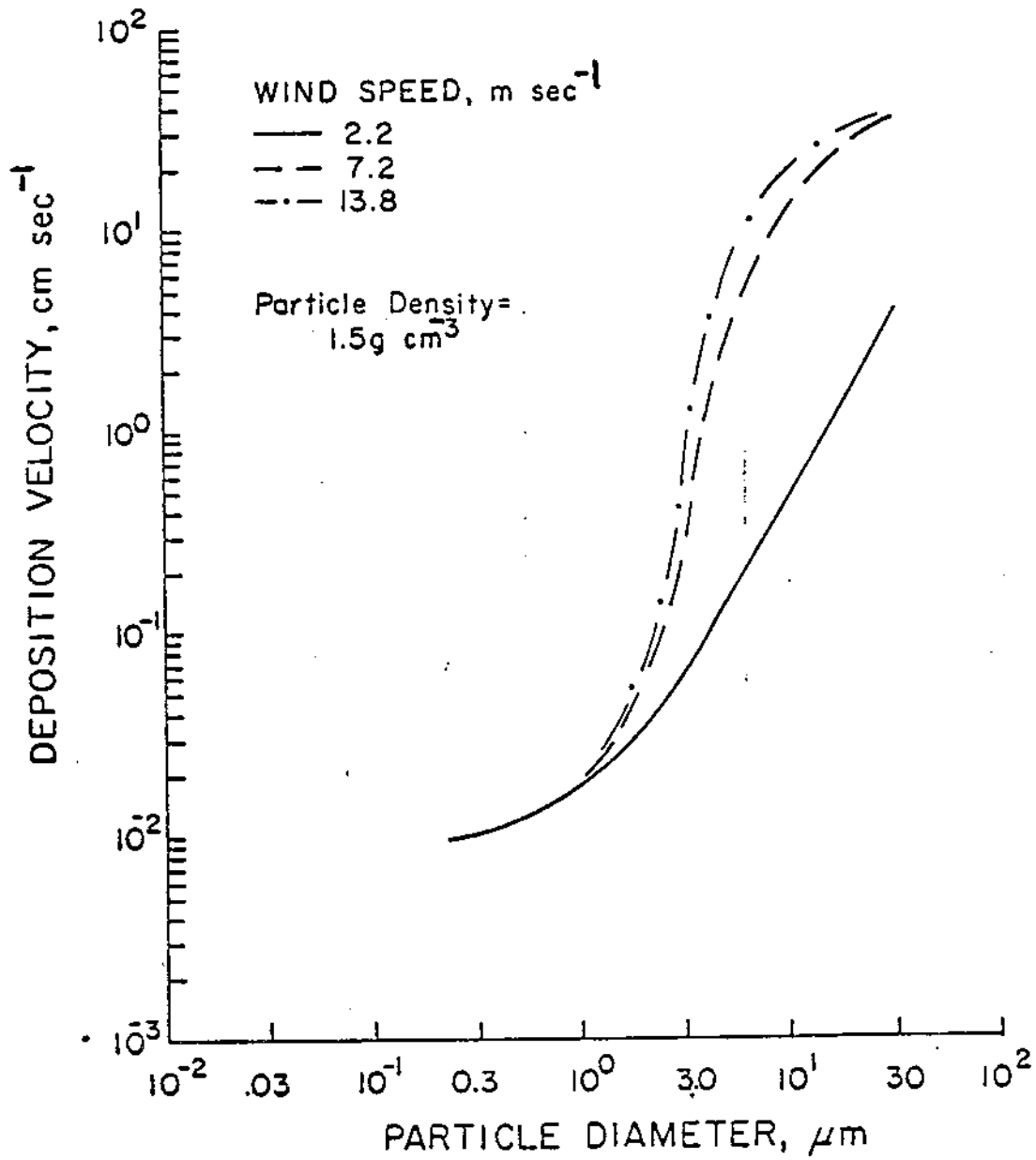


Figure 2. Atmospheric particle deposition velocity to a water surface as a function of particle size and wind speed (After Sehmel and Sutter, 1974)

It is recommended that total deposition samples be collected using the dry deposition bucket of the HASL design rain-dry deposition collector. This second bucket would remain open at all times except when the environmental control system indicated likelihood of local contamination, at which time it would be covered. Recorders or timers would be required to indicate the total time for which both the rain and the total deposition collector were exposed.

Measurement of both rain and total deposition will give at least an approximate indication of the relative importance of rain and dry deposition to the total flux of substances from the atmosphere to the ocean. Samples with visible particulate contamination should be discarded. Appropriate acids or biocides may be added to the collectors, depending on the substance to be analyzed.

Precipitation should be collected on an event basis whenever possible, or during intervals of not longer than one week. Total deposition samples should be collected over no longer than a week as well, with the sampling intervals for both types of samples planned such that direct comparison of the fluxes is possible. To relate the flux measurements to ambient atmospheric concentration, the sampling intervals for the rain and total deposition samples should also be coincident with sampling intervals (or combinations of intervals) for atmospheric particulate and gas phase samples. The environmental control system described above should also be used to monitor the collection of these latter samples.

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