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.

Financial support for the work of the Working Group was provided by the United Nations Environment Programme (UNEP).

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_2, sulphur compounds, and some of the low-molecular-weight chlorinated hydrocarbons 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 acqueous 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 soluable 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 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. H_2O, 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 IOC/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.   <u>INTRODUCTORY REVIEW OF STATE OF KNOWLEDGE</u>

        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_2 concentration from
below 300 ppm to about 330 ppm in 1976.   However, the magnitude of the flux of this
anthropogenic CO_2 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 ^{137}Cs and ^{90}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.[a]

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.[b]

Radionuclides, particularly plutonium and americium.

Pathogenic bacteris and viruses.

[a]No effort is made here to specify the most important fractions.

[b]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_3, Cl_2.

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 surfacant 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 GEOSECS 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_2 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 μm) 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^{-2} μm, 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	Liquid		
Petroleum Hydrocarbons	+	+	+	+	+	U	U
High M.W. Halogenated Hydrocarbons	+	+	+	(+)	(+)	↓	↓
Low M.W. Halogenated Hydrocarbons							
– Chlorocarbons	+	(+)	?	+	(+)	↓	↓
– Fluorochlorocarbons	+	(+)	?	+	(+)	↓	↓
CO_2	+	(+)	-	+	(+)	↓	U
SO_2	+	+	-	-	-	↓	↓
SO_4^{2-}	-	+	+	-	+	↓	↑
Metals							
Pb	?	+	+	?	+	↓	U
Hg	(+)	+	+	(+)	+	↓	U
As	(+)	+	+	(+)	+	↓	U
Se	?	+	+	?	+	↓	U
Sb	?	+	+	?	+	↓	U
Zn	?	+	+	?	+	↓	U
Cd	?	+	+	?	+	↓	U

SUBSTANCE	Air ——→ Sea Gas	Liquid	Solid	Sea ——→ Air Gas	Liquid	Open-Ocean Net Pollutant Transfer	Open-Ocean Net Natural and Pollutant Transfer
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