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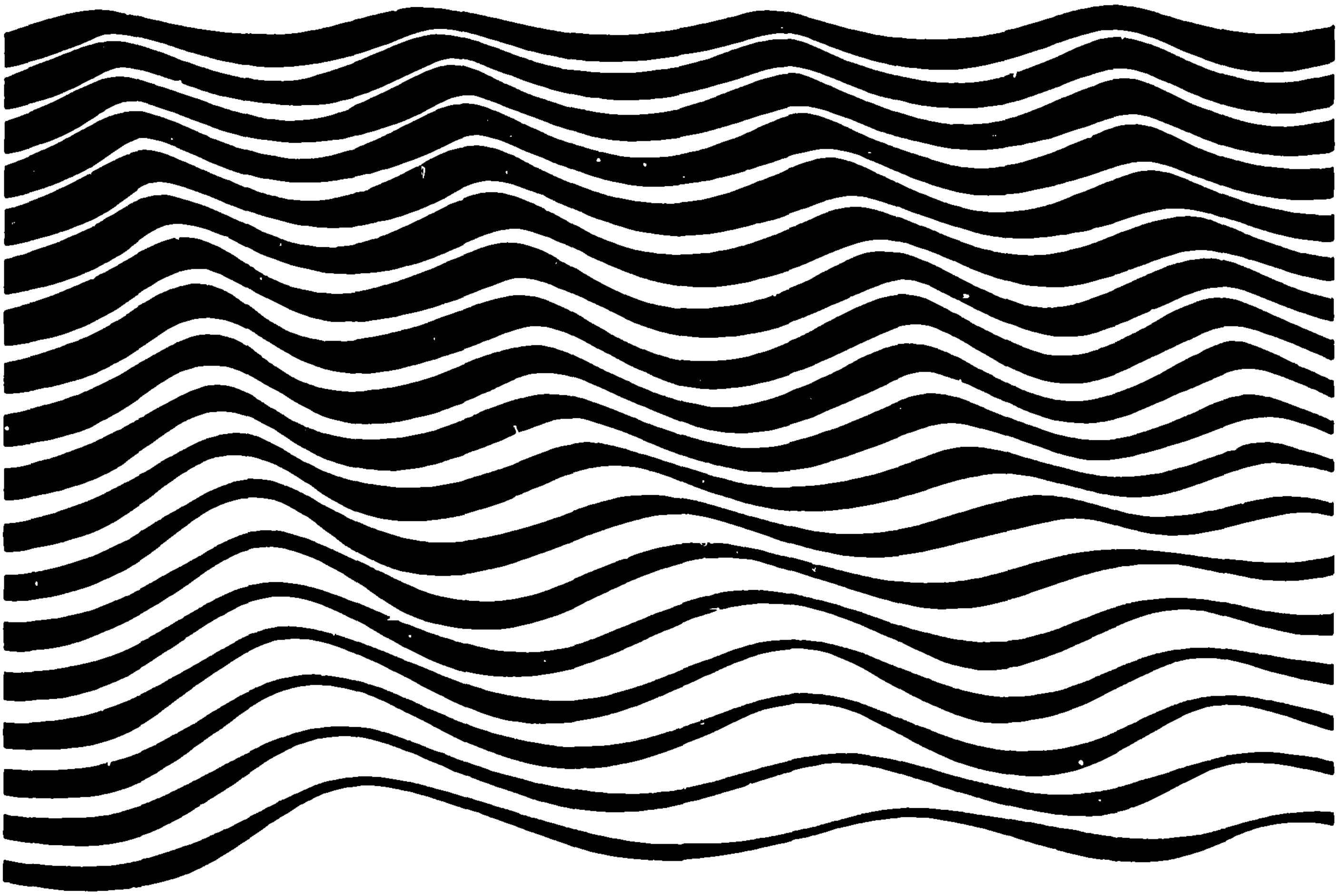
Ocean-Atmosphere Materials Exchange (OAMEX)

Report of SCOR Working Group 44
Unesco, Paris
14-16 November 1979



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29	Committee for the preparation of CLOFETA - Report of the first meeting, Paris, 16-18 janvier 1978	1979	
30	Ninth report of the joint panel on oceanographic tables and standards, Unesco, Paris. 11-13 September 1978	1979	
31	Coastal lagoon survey (1976-1978)	1980	
32	Coastal lagoon research, present and future. Report and guidelines of a seminar, Duke University Marine Laboratory, Beaufort, NC, U.S.A., August 1978. (Unesco, IABO).	1981	
33	Coastal lagoon research, present and future. Proceedings of a seminar, Duke University, August 1978. (Unesco, IABO). *To be published in English and French*	1981	
34	The carbon budget of the oceans. Report of a meeting, Paris, 12-13 November 1979	1980	WG 62
35	Determination of chlorophyll in seawater. Report of intercalibration tests sponsored by SCOR and carried out by C.J. Lorenzen and S.W. Jeffrey, CSIRO Cronulla, N.S.W., Australia, September-October 1978	1980	
36	Tenth report of the joint panel on oceanographic tables and standards, Sidney, B.C., Canada, 1-5 September 1980. Sponsored by Unesco, ICES, SCOR, IAPSO.	1981	WG 10
37	Background papers and supporting data on the Practical Salinity Scale 1978.	1981	WG 10
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40	International Oceanographic Tables, Vol. 4. (To be published)	1982	WG 10

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PREFACE

This series, the Unesco Technical Papers in Marine Science, is produced by the Unesco Division of Marine Sciences as a means of informing the scientific community of recent developments in oceanographic research and marine science affairs.

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ABSTRACT

Present knowledge of processes and methods of measurement related to the exchange between ocean and atmosphere of minor constituents of gaseous and particulate material, both natural and anthropogenic, was reviewed at a meeting of SCOR Working Group No. 44 : Ocean-Atmosphere Material Exchange (OAMEX), Unesco, Paris, November 1979. In this report, problems regarding sea-salt aerosols, mineral aerosols, particulate organic carbon, metals, gases, remote sensing techniques, use of radionuclides, photochemical processes are considered in the context of air-sea exchange studies. Recommendations, particular and general, for further studies are formulated.

I. INTRODUCTION

There has been increasing interest in the possibility that significant quantities of both natural and anthropogenic substances may be transported to the ocean via the atmosphere in mid-ocean regions. An understanding of the importance of the atmosphere as a transport path is critical in determining the basic geochemical cycles and budgets of a variety of naturally occurring substances and in predicting the near-global impact of anthropogenic material in open ocean regions.

In 1977, the Scientific Committee on Oceanic Research (SCOR) with the collaboration of IAMAP* and IAPSO** set up a working group entitled : Working Group 44 (WG-44) : Ocean-Atmosphere Materials Exchange (OAMEX). The following terms of reference were established for the group :

- to review present knowledge of processes and methods of measurement related to the exchange between ocean and atmosphere of minor constituents of gaseous and particulate material, both natural and anthropogenic;
- to propose improved methods for studying the exchange processes and to consider development of relevant co-operative research projects.

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* IAMAP : International Association of Meteorology and Atmospheric Physics.

** IAPSO : International Association for the Physical Sciences of the Ocean.

II. SEA SALT AEROSOLS :

BUBBLES AND THE SURFACE MICRO BOUNDARY LAYERS

The oceans are the source and also the principal sink for sea-salt aerosols. Except under very high wind conditions, this aerosol is produced by the bursting of bubbles. It is now clearly established that the composition of the sea-salt aerosol differs in many respects from that of the seawater from which it is derived. The most marked differences are that the spray is enriched in organic material and in some metals. Evidence suggests that the metals are associated with surface active organic material which is adsorbed to the bubble as it rises through the water column: some of this organic- and metal-enriched spray is injected into the atmosphere when the bubble ruptures. Rising bubbles can also scavenge fine particulate material that likewise can be injected into the atmosphere.

The presence of organic-rich droplets has been conclusively detected while scanning electron microscope photographs of aerosols collected on filters and with impactors. Particles often have an organic "skin" which covers a crystalline nucleus of mixed salts. Organic flakes and clumps are often seen. Microprobe analysis of some of these organic particles has shown high concentrations of zinc in addition to aluminium, iron and titanium; it is believed that the zinc is chemically associated witn the organic material while the other elements are present as mineral particles. Other elements, most notably iodine and phosphorous, have also been shown to be enriched in bubble spray.

It is conceivable that sea-salt aerosol particles could also serve to scavenge material from the atmosphere. It has been argued that the sea-salt aerosol could scavenge small particles by diffusion and that it could serve as a reaction surface for gases. However, at this time, there is no solid evidence to suggest that the aerosol is serving as a major scavenger. Indeed, the exposed surface area on sea-salt aerosols under typical conditions is relatively small compared to the surface of the ocean itself. However, it should be noted that some impactor samples collected in oceanic regions often show a relatively high concentration of Na_2SO_4 on the lowest stages where the sub-micron particles are collected; one interpretation of these findings is that SO_2 has been adsorbed by the smallest droplets (where the surface area is greatest) thereby causing the release of HCl. This reaction could be important for the production of gaseous chloride and other halogens in the marine environment. However, the question is raised as to why these reactions are not taking place to a greater extent in the larger particle size fractions.

Bubbles may also play an important role in the exchange of gases across the sea surface. Especially important may be the role of small bubbles that are driven into solution during downward transport in the water column; such bubbles may be an important mechanism for the production of small particles in seawater.

In the absence of bubble processes, the transport of gaseous materials across the air-sea interface would be a function of the rate of diffusion through the laminar boundary layers that are believed to exist at the sea surface and in the air immediately above. These layers have been estimated by various groups to have a thickness on the order of tens to hundreds of microns and a lifetime of seconds to hours. However, there is considerable controversy about the characteristics and behaviour of these boundary layers. For example, how do their thicknesses vary with environmental conditions and what are the consequent mean residence times of water and air in the layers?

The consideration of boundary layer properties is further complicated by the fact that the sea surface is often covered by a film of organic materials which can serve as the site of greatly enhanced microbial activity. These materials can modify the physical properties of this surface (for example, by the damping of capillary waves) but they also constitute a new chemical phase in the air-sea interface system. In this regard, bubbles serve to scavenge material from the water column and transport it to the surface; on the other hand, the bubbles also serve as a means for breaking the surface film and injecting some of this material into the atmosphere.

At present, information is lacking on the rates of production of bubbles in the oceans as a function of environmental parameters such as wind velocity, sea state, wind duration, etc. Of interest is the concentration and bubble size distribution as a function of depth. Also of interest are the corresponding rates of production and the size distribution of sea-salt aerosol. Nowadays, it is commonly accepted that bubble processes are not effective for the production of sub-micron particles, especially those produced by the rupture of the bubble film; however, to our knowledge, this mode of production has never been adequately investigated using the more sensitive types of aerosol instrumentation that are now available.

If bubbles and spray do indeed play an important role in the air-sea exchange of materials, then the temporal and geographical variability of bubbles and spray production becomes a subject of considerable importance. At present, the global aspects of bubble and spray characteristics are only poorly understood. Some recent work has shown that large gradients in sea-salt aerosol concentration do exist. In the tropical North Atlantic, the mean sea-salt aerosol concentration in the trade wind regime off Africa is about three times that in the intertropical convergence zone which is located only some 5^{o}-10^{o} of latitude to the south. This gradient is related in part to the gradient in sea surface stress and whitecap production. However, the relationship between aerosol concentration and wind speed is not a simple one; the relationship involves other factors such as fetch, boundary layer stability, removal by precipitation and advective contributions. Nonetheless, it is clear that bubble-and-spray related exchanges, if any, will take place most intensively in those relatively localized areas where mean wind velocities are high. In this regard, it is notable that by far the most extensive and intensive region of strong air-sea interaction occurs in the high latitudes in the southern hemisphere; smaller areas in the high latitudes of the northern hemisphere may also be of interest.

Recommendations

1. The basic processes involved in bubble-seawater interaction require further research. Of prime importance is the role of bubbles in the scavenging of various materials from seawater, i.e. dissolved as well as particulate organic and inorganic materials.

2. Aerosol particle production by the bursting of bubbles at the sea surface should be further investigated. Of interest are the aerosol number and size spectrums as a function of bubble size and water properties. The submicron particle spectrum is especially important and has never been adequately studied using the newer techniques.

3. The concentration, size spectrum and vertical distribution of bubbles in the ocean as a function of environmental conditions has never adequately been measured. The small-bubble portion of the spectrum may be especially important as they may play a role in the transfer of gases from the atmosphere to the ocean.

4. The importance of sea-spray aerosols in the scavenging of atmospheric gases and other aerosol materials has never been adequately investigated.

5. The environmental parameters governing the rate of production and character of sea-salt aerosols have not been properly studied to date. Clearly such investigations should be coupled with those measuring environmental bubble interactions.

6. Research on bubble-seawater interactions requires the use of devices capable of producing large numbers of bubbles having a size distribution similar to that in seawater. Such a capability does not currently exist and must be developed.

III. MINERAL AEROSOLS

Mineral matter is a major constituent of aerosols in many ocean regions; clearly, the ocean is a sink for this material. Although the data base is limited, evidence suggests that arid regions and deserts are the major sources of this mineral matter. The concentration of mineral aerosols is greatest in those ocean regions that are traversed by air masses emanating from arid lands.

The best documented case is the transport of Sahara desert particles over the tropical North Atlantic into the Caribbean and North Atlantic. Long range transport has also been documented in the western tropical North Pacific during the recent SEAREX Programme on Enewetak where concentrations of mineral aerosol on the order of $\mu g's/m^3$ were observed; this material apparently originated from arid regions in the People's Republic of China.

Other fragmentary evidence suggests that desert regions such as those in the Middle East, northern India, Australia, the western United States and Mexico may constitute sources of material that could be transported to the ocean in appreciable quantities.

The transport of mineral matter to the oceans is significant from a number of standpoints. First of all, Aeolian dust is a major constituent of the non-biogenic components of ocean sediments in many regions; thus a knowledge of the flux and composition of dust transported to the ocean is necessary in order to determine a proper mass balance for the entire ocean system. Also required is a knowledge of the chemical speciation and behaviour of this particulate matter. For example, the solubility of the particulate species will determine which species are released to the aqueous phase and which are transported directly to the ocean floor sediments. Also, because over half the mineral aerosol mass consists of clay minerals, the dust may play an important role in the adsorption and removal of dissolved species from seawater and in their subsequent transport to the ocean floor.

Secondly, the presence of high concentrations of mineral matter over the oceans may have an impact on oceanic weather and climate. The weather can be affected in several ways :

(1) the particles can directly alter the radiation balance in the atmosphere by absorption and scattering;

(2) they affect cloud microphysics and hence could change the character and distribution of clouds and, consequently, rainfall;

(3) if particles effect a change in the cloud cover, there will be a consequent change in albedo which, in turn, would alter the radiation balance.

The effect of aerosols by mechanism (1) has been well established by measurements made over the tropical North Atlantic. However, in the cases of mechanisms (2) and (3), no significant large-scale impacts have been demonstrated.

Thirdly, the temporal variation in the deposition rate and composition of Aeolian components in sediments can provide important information on the paleoclimatology of the continents. For example, attempts have been made to reach conclusions about past cycles of aridity and the character of the wind field on the basis of the variation in the concentration of quartz in sediments and also the changes in the size distribution of the quartz. However, these efforts suffer from the fact that we have a very poor understanding of the present-day sources of Aeolian material and of how the location of sources and the generation of Aeolian material is affected by changes in meteorological conditions and, over the longer term, by changes in climate. We do know, for example, that at some ocean locations the mineral aerosol concentrations can vary by a factor of a hundred during the course of an annual seasonal cycle; this has been shown for the tropical North Atlantic and the western tropical North Pacific. Also, there is evidence that the dust concentration in the tropical North Atlantic increased by at least a factor of two during the early 1970's as a consequence of the drought in North Africa. Thus, any interpretation of the sedimentary record will be highly speculative until we have a better understanding of the source-transport-sink relationships for mineral dust.

Lastly, we point out that the phenomenon of long range transport of mineral aerosols lends validity to the concern about the possibility that pollutants may also be transported to remote areas. The other major example of long range transport was that obtained from the study of the distribution of nuclear weapon debris; however, this material was injected into the upper troposphere and the stratosphere. Mineral dust, on the other hand, is generated in the boundary layer and hence is subject to the same transporting conditions as pollutants. Thus, the study of mineral dust transport may give us a better understanding of the processes affecting the transport of pollutants over long distances.

Recommendations

1. Studies of mineral aerosols should be carried out in those ocean regions that might be expected to be most susceptible to such inputs. In designing these experiments, an effort should be made to schedule periodic (or, if possible, continuous) measurements over a complete seasonal cycle.

2. In those areas where intensive mineral aerosol transport is occurring on a large scale, measurements should be extended over a period of several years to ascertain if there is any significant year-to-year variability that might be related to changes in weather (or, over a longer term, in climate).

3. Studies of the chemical and mineralogical composition of dust should also include measurements aimed at characterizing the solubility and sorptive properties of the material.

4. Measurements should be made of the removal of dust to the ocean by precipitation. Unfortunately, at present, there does not appear to be any readily usable method for measuring the dry deposition rate of aerosol particles to the ocean surface. The development of a suitable technique should have a high priority.

5. The source areas for mineral aerosol should be accurately located and identified on a global scale. The possibility of using remote sensing techniques should be investigated. In this regard, infra-red satellite photographs have proved to be especially useful in regions that are relatively free of clouds.

6. In regions identified as being major sources, a large-scale multidisciplinary study should be carried out with the following objectives :

   a) to measure the chemical, mineralogical and physical characteristics of the soils (especially as a function of size) as compared to these same characteristics of the dust;

   b) to determine the nature of the physical and chemical processes responsible for the formation of the wind-erodable fraction of the soils;

   c) to perform micrometeorological studies of dust generation;

   d) to ascertain if land use has had a significant impact on the wind erodability of the soils and

   e) to develop a dust storm climatology for the region.

   These studies bear on both the natural and the anthropogenic aspects of dust transport because it is clear that in some regions the mobility of soils has been greatly affected by man's activities. Thus, it is conceivable that these studies could be carried out in conjunction with other land-use studies and soil-mapping and conservation programmes.

7. Programmes to study the wind transport of soil aerosols to the oceans should be designed with the assistance of meteorologists who have a good knowledge of the region being considered. The complexity of atmospheric motions is such that a simplistic approach could lead to erroneous expectations and conclusions.

IV. PARTICULATE ORGANIC CARBON

The concentration of organic carbon on particulate matter in the marine atmosphere appears to fluctuate within a rather narrow range in near surface air over the Atlantic and Pacific oceans, generally between 0.1 to 1.0 μg/m^3 STP. The particle size distribution of the organic carbon is apparently bimodal; the major portion of the mass resides in particles within radii less than 0.5 μm and a secondary maximum occurs in particles with radii of a few μm. Laboratory studies have shown that organic carbon is considerably enriched on atmospheric sea-salt particles produced by bursting bubbles. This enrichment may be attributable to the accumulation of organic substances on the bubble surface as it rises through the water column and to the presence of organic material in the ocean surface microlayer where the bubble ruptures. Laboratory studies also have shown that the particulate organic carbon produced directly by bursting bubbles is concentrated on the larger particles and is probably responsible for the secondary concentration maximum found in the ambient marine atmosphere. While direct particle production from the ocean cannot be ruled out for the small particle organic carbon maximum, it is generally believed that this fraction results primarily from gas-to-particle conversion processes occurring in the marine atmosphere. Little is known about the composition of sources of organic species, in the vapor phase, involved in these conversion processes. Measurements have been made of some of the heavier organic compounds in the vapor phase over the ocean, e.g. the alkanes from C_{12} to C_{30} and the fatty acids. It is not known whether these compounds have a continental or a marine origin. With regard to the fluxes of particulate organic carbon from the atmosphere to the ocean, we are at present unable to distinguish between organic carbon whose source is the ocean and that derived from continental areas. Thus a determination of a net flux of particulate organic carbon into the ocean is difficult. Techniques which might allow us in the future to distinguish between these sources include the use of carbon isotope ratios and the measurement of specific marker compounds known to be derived from certain types of sources.

Recommendations

1. Efforts should be directed toward :

   a) determining the chemical form and quantitative flux of organic substances from the ocean to the atmosphere and

   b) characterizing gas/particle exchange processes in the marine atmosphere.

2. Methods to distinguish between marine and continental sources for atmosphere organic carbon should be developed.

V. METALS

The exchange of trace metals with the ocean is of interest for several reasons. There has been concern that the atmosphere may be a significant transport path for some trace metals, both of pollution and natural origin, to the open ocean and to coastal areas and semi-enclosed seas. However, for most metals there is little information available either to support or allay this concern. Recently, however, some attention has been given to the transport of transuranic elements (e.g. plutonium) to the ocean via the atmosphere. There is also considerable interest in evaluating the importance of the ocean as a source for many metals in the atmosphere. These efforts are related to attempts to understand the atmospheric geochemical cycles of trace metals and the impact of man on these cycles.

The primary source for a number of trace metals over the ocean is well known, e.g. the ocean for Na, K, Ca and Mg, and crustal weathering products (soil) for Al, Fe, Mn, Sc, etc. There is, however, a group of atmospheric metals whose sources cannot be easily identified. These include such metals as Hg, Pb, Cd, Se, As, Zn, Cu, Sn, Sb and Ag among others. Most of these elements, or their simple organic or inorganic compounds, are relatively volatile, and it has been suggested that a vapor phase may be important in the atmospheric cycle of some of these metals. This is supported by measurements which find that a significant fraction of these metals are present on submicrometer particles. Furthermore, it must be noted that systems utilized for marine aerosol collection discriminate against the larger particles, i.e. those greater than 5 to 10 µm. For metals which have most of their mass concentrated in the large particle size range, erroneous conclusions might be drawn as to their atmospheric concentrations and their estimated fluxes to or from the ocean.

With regard to the sources of atmospheric metals, there is much more quantitative data on pollution source strengths than there is for natural sources. Natural sources for atmospheric trace metals which were identified included the ocean, crustal weathering - particularly in desert regions, volcanoes, biomass burning, terrestrial vegetation, and low temperature crustal degassing. With respect to the ocean as a source of atmospheric metals, there is now considerable evidence that a number of metals can be enriched on atmospheric sea-salt particles produced by bursting bubbles : however, we do not have quantitative estimates of the upward flux of metals to the atmosphere via this process. Little is known about the mechanism of this enrichment, although it may be related to metal-organic associations, or about the atmospheric particle size dependence of such enrichment. Also, little is known about the possible importance of gas phase transfer of certain trace metals, e.g. Hg, As, Se, Sn, etc. from the ocean to the atmosphere, although both methylated and protonated forms have been suggested.

Relative to volcanic sources for trace metals, we have few data on the physical or chemical form of volcanic releases and on the variability of releases comparing volcano to volcano and comparing relatively quiescent to violently explosive periods. For desert aerosols, information is lacking on the temporal and geographical variability of their generation and transport.

Virtually no data are available on the release of metals from biomass burning and from terrestrial vegetation. In both cases, information on gaseous versus particulate trace metal releases and the geographical distribution and intensity of the source functions are unknown. The existence of low temperature crustal degassing as a source for atmospheric trace metals has not yet been definitely established. It would be most useful to carry out atmospheric sampling programmes in both the northern and southern hemispheres in order to distinguish between natural and pollution sources for some trace metals. The use of the scanning electron microscope and electron microprobe techniques should prove useful in this regard as particles from various sources often have unique morphologies or elemental composition. For example, small particles containing high concentrations of titanium have been observed in remote areas; these particles are apparently paint pigments.

However, size distribution measurements of particulate trace metals have only been made in a few locations in the marine atmosphere.

There is strong evidence that almost all atmospheric Hg is in the gas phase, primarily as elemental Hg, while less than 5 to 10% of the As is in the gas phase. Information on the vapor phase for other volatile metals is lacking but is important in attempting to assess their sea/air exchange.

There are virtually no direct measurements of the flux of atmospheric metals to the ocean via rainfall or dry deposition in open ocean regions. For rainfall, the collection of contamination-free samples has proved difficult. Controversy continues about measurement techniques and model philosophies, relative to dry deposition. Dry plate and profiling techniques are both being utilized at present, and the results should be compared closely.

Of particular concern to chemical oceanography is the fate of the atmospheric particulate trace metals when they enter the ocean. While a few studies have been undertaken of the seawater solubilization of atmospheric particulate matter collected in urban or near-urban areas, no such studies have been undertaken using aerosols collected in the remote marine atmosphere. Evidence to date suggests that many of the pollution-derived metals present on urban aerosols dissolve to a significant extent in seawater.

At the present time, sampling intervals of several days are required for many trace metals present on atmospheric particles in remote marine areas. These long sampling periods are undesirable as they make it impossible to distinguish concentration fluctuations resulting from changing weather patterns and transport trajectories; also, it is very difficult to measure vertical profiles from aircraft, information which could be of considerable value in evaluating source area and atmosphere residence times for the trace metals. The long collection periods are a result of high concentrations of the trace metals in the blank collection substrate and, in some cases, insufficiently low detection capability of its analytical techniques.

Recommendations

1. Natural sources for atmospheric trace elements should be evaluated carefully. Geographical and temporal variations should be determined for such sources as crustal weathering, biomass burning, volcanoes and vegetation. The mechanisms by which certain trace metals are enriched on particles produced by bursting bubbles in the ocean should be evaluated. Of particular importance is the determination of the nature of the apparent association of these metals with surface active organic material and its seasonal variability.

2. The physical form of trace metals (particle versus vapor) in the marine atmosphere should be determined, as should the trace metal particle size distribution. For the latter, particular care should be taken to assure that discrimination against the larger particles is avoided. If vapor phases are found, their chemical form should be determined.

3. Every effort should be made to collect contamination-free precipitation samples over the ocean at different times of the year. New and imaginative research is required to assess properly the role of dry deposition of particulate trace metals to the ocean surface.

4. The extent of the seawater ability to dissolve trace metals present in marine aerosols over remote marine areas should be determined.

VI. GASES

Studies of the influence of the ocean on the composition of the atmosphere started only recently (within the last 10 years or so) after it became evident that the ocean may play an important role in the cycles of several atmospheric trace gases for which it may serve as both a source and a sink. In the past, the studies had been concentrated predominantly on the determination of the CO_2 and C_2 - fluxes through the air-water interface. These studies have now been extended to a great variety of trace gases such as CO, H_2, CH_4, N_2O, CH_3Cl, CH_3I, CH_3Br, $(CH_3)_2S$, hydrocarbons, and others. Data published so far clearly demonstrate that the ocean - due to its large area - contributes significantly to the budget of these gases in the atmosphere, although the exchange rates per basal area are generally small. In some cases, e.g. N_2O, CH_3Cl, CH_3I, and most probably CH_3Br and also some hydrocarbons, the ocean is the dominant source in the atmospheric budget of these gases.

The reported fluxes from the ocean into the atmosphere have generally been computed from the measured concentration of the gas dissolved in the mixed layer of the ocean (mostly 0.5 to 1m depth) using the "stagnant film model" as proposed by Broecker and Peng. In this model, the flux through the air-sea interface is assumed to be controlled by the molecular diffusion through a hypothetical boundary layer at the sea surface. The thickness of this layer has been calculated from the distribution of the nuclear-weapon-produced ^{14}C, natural ^{14}C, and radon 222 in the upper part of the ocean. The computed global mean values obtained for the layer were 30 ± 10 microns and 46 microns, respectively. Exchange studies suggest that the film is dependent on the wind velocity and increases from about 7 microns at high wind speeds to more than 100 microns at wind speeds $\leqslant$ 5m/sec. Presently, it is not known whether the dependency of the film thickness on the wind velocity is a linear function as expected from radon measurements in the Atlantic and Pacific oceans or an exponential function as expected from laboratory experiments.

Flux calculations of several atmospheric constituents indicate oceanic source strengths of $0.5 - 1.0 \times 10^{14}$g/yr for CO, $0.03 - 0.2 \times 10^{14}$g/yr for CH_4, 0.04×10^{14}g/yr for H_2, $0.7 - 2.1 \times 10^{14}$g/yr for N_2O, 2.7×10^{11}g/yr for CH_3I, and 7.2×10^{12}g/yr for $(CH_3)_2S$. High source strengths are also expected for other biospheric trace gases such as H_2S, NH_3, COS, hydrocarbons and others, indicating that the ocean has an important influence on the composition of the earth's atmosphere. Many of the gases released by the ocean into the atmosphere are involved in chemical and photochemical reaction in the atmosphere, forming and destroying other atmospheric constituents which are of great importance to the earth's environment and climate. Of particular interest are species such as NO, CO, and hydrocarbons; these species and others can affect the concentration and distribution of the highly reactive OH radicals which play a role in a large number of important chemical reactions in the atmosphere.

The ocean acts also as a sink for many atmospheric constituents, both of natural and anthropogenic origin. The transport of gases and particulates from the atmosphere into the ocean is mainly due to rain and wash-out processes. Because of the low concentration of most of these atmospheric trace constituents (with the exception of CO_2) and of their consequently small concentration gradients at the sea-air interface, dry deposition into the ocean surface water is only of minor importance. Despite the relatively small flux rates of several atmospheric constituents into the ocean, e.g. for DDT and PCB, they nonetheless might have a significant impact on biological processes in the ocean surface waters due to their highly toxic character. Thus, it is conceivable that the transport of these substances into the ocean surface water could affect the flux rates of several biospheric trace constituents from the ocean into the atmosphere and, consequently, change the gaseous composition of the atmosphere; such a change could have a significant impact on the climate. Therefore, the exchange rates of several trace substances should be studied carefully so as to detect any changes at an early stage.

The published data on the oceanic source and sink strengths of the individual gaseous atmospheric constituents are highly uncertain. Data reported by different groups sometimes differ by more than one order of magnitude even for measurements which had been carried out in the same ocean area. This discrepancy is very likely caused by the strong temporal variation of the dissolved gas concentration in the water, but in many cases is due to the use of different sampling techniques, different techniques of analysis and different calibration procedures. The sampling depths in "ocean surface waters" vary between 0.5 and 6m depending on the sampling techniques. Changes in the concentration, especially of biospheric gases, very likely occur during the preparation of the water samples, but also during the analytical procedures. The absolute values of calibration standards (as shown recently by an international intercalibration test for the chlorofluoromethanes) used by different groups may differ by more than a factor of 2.

Another reason for the uncertainty of the reported exchange rates at the air-sea interface is the lack of sufficient data on the global distribution and concentration of the individual dissolved gases in the ocean surface water. So far, measurements have been carried out infrequently and only in small areas of the oceans, mainly the open ocean. Most of the data were obtained in the northern hemisphere; there are relatively few measurements in the southern hemispheric oceans. Little information is available about the seasonal variation of the individual gases dissolved in the surface waters. Measurements are almost completely lacking for coastal areas, frontal areas and, most important, areas of extremely high biological activity (such as upwellings) which could be major sources for biologically produced gases.

The uncertainty of the reported fluxes may be due in part to the use of the stagnant film model for the flux calculation. There is little doubt that this model can be used for those gases having physical and chemical properties similar to radon. It is, however, debatable whether the stagnant film model provides realistic flux values for those gases which are produced and consumed by biological activities in the surface water (e.g. CO, CH_3I, CH_3Cl, $(CH_3)_2S$, NH_3, etc.), if values of the thickness derived from the radon distribution are applied. In contrast to radon, these biospheric gases have turnover times in the surface waters in the order of hours or less, and, therefore, show large temporal and spatial variations. As some of the producing and consuming processes are light-dependent, the concentration of biospheric gases in water show generally strong diurnal variations. In addition, measurements indicate strong vertical gradients of some of these gases in the mixed layer of the ocean, particularly in the 10 to 50m depths region where radon is more or less uniformly distributed. Thus it is conceivable that in the stagnant film model, the hypothetical film thickness which one obtains for biospheric gases (or generally for gases with short turnover times in water) may differ significantly from that obtained from the radon distribution.

Little is known about the possible influence of the organic surface microlayer on the air-sea interchange. It is very likely that some of the gases produced in the water are consumed by microbial processes in the microlayer, thereby reducing the flux of these gases from the ocean into the atmosphere. On the other hand, catalytic reactions may take place in the surface microlayers thereby enhancing the gaseous exchange rates between the atmosphere and the oceans. Catalytic reactions have been proposed in the past, e.g. for the CO_2-exchange, but thus far they could not be confirmed by experiments. As the surface microlayers have been observed over large areas of the oceans, these processes may have a considerable influence on the gas exchange rates at the air-sea interface.

The stagnant film model definitely cannot be applied to those gases produced by photochemical, chemical, physical or microbial processes at the ocean surface (e.g. in the organic surface microlayer) and released directly into the atmosphere, e.g. NO. As the turnover time of the individual gaseous components in the microlayer can be expected to be very short ($\leqslant$ hours), the production and destruction processes in this layer may contribute significantly to the flux rates through the air-sea interface. This is of particular interest for a great variety of hydrocarbons which may be produced almost exclusively at the sea surface. On the other hand, the surface microlayer may act as a sink also for those atmospheric constituents having low solubility coefficients and consequently low fluxes into ocean waters which are not covered with an organic surface layer.

Presently, it is not known whether photochemical reactions within the atmospheric laminar boundary layer have any influence on the air-sea interchange of gases. We can assume that this layer contains a variety of reactive gases, produced in the water or at the sea surface, so that photochemical reactions in the gas phase are very likely. It is, however, doubtful whether the residence time of air in the laminar boundary layer is sufficiently long for significant changes of the individual gas concentrations.

Recommendations

A. Techniques

In order to improve the accuracy of the measurements of exchange rates of gases between the ocean and the atmosphere, we recommend that :

a) the sampling and analytical techniques used by the different groups be intercompared preferably on joint expeditions;

b) standards should be intercalibrated on a regular basis, especially before and after longer ship expeditions.

B. Processes

In order to obtain a better understanding of the exchange of gaseous constituents at the air-sea interface, the chemical, physical, biological, photochemical and oceanographic processes involved in the air-sea exchange of the individual constituents have to be better understood. More information is urgently needed on :

a) the influence of microbial processes occurring in the surface microlayer on the air-sea interchange. This programme should include field measurements and laboratory experiments, studying the dependency of the source and sink strengths of these processes on environmental parameters such as wind speed, solar radiation intensity, surface water temperature, nutrient concentration, oxygen concentration, etc.

b) the chemical, photochemical, physical and catalytical processes occurring in the surface microlayer and the sea surface which could alter the flux rates through the air-sea interface;

c) the photochemical reactions taking place in the atmospheric laminar boundary layer;

d) the exchange mechanisms in the ocean surface waters. More studies, both in the field and in the laboratory, should be carried out to determine the dependency of the exchange rates on the wind speed, types of waves, etc. Particular emphasis should be given to studies of the influence of the entrainment of bubbles into the water on the air-sea interchange, e.g. hydrocarbons, trace metals. Exchange rates should also be determined using tracers other than radon or noble gases, e.g. biospheric gases;

e) the spatial and geographical distribution as well as the temporal variations of the organic surface microlayer;

f) the geographical distribution of the film thickness, especially in areas with high biological activities.

C. Distribution

In order to understand the global distribution of gases, we recommended that the measurements of dissolved gases be intensified. Measurements should cover large parts of the ocean, especially in the southern hemisphere, and they should be carried out during different seasons. Intensive measurements in upwellings, coastal areas and frontal areas are urgently needed to improve flux calculations of biospheric gases.

VII. REMOTE SENSING TECHNIQUES - RECOMMENDATIONS

The use of remote sensing techniques to determine the atmospheric functions of gases and particulates and their fluxes into and out of the oceans is just beginning but holds great promise. Already UV laser-induced fluorescence is able to give a measure of organic substances in the surface water of the ocean. It may be possible by Raman scattering techniques to measure carbonate and bicarbonate ions in surface waters in the very near future.

VIII. UTILIZATION OF RADIONUCLIDES FOR THE STUDY OF OAMEX PROBLEMS

Radionuclides are good tools for the study of natural phenomena because they can be used as time markers and because the radioactivity allows them to be used as tracers with high sensitivity. The following studies are recommended as a part of the OAMEX research by coupling with other observations for each research subject.

1. Use of radionuclides as a clock of aerosol transport

The residence time of an atmospheric constituent is important as a measure of its transport from the source to the sink. Radionuclides have been used to determine the residence times of aerosols. The aerosol residence time measured is that of the aerosol to which the radionuclide is attached. Thus the residence time estimated from the radon daughter nuclides (Pb-210, Bi-210 and Po-210) is that of aerosols with a size of about 0.1 μm. The residence time which we have was obtained in about 20 days based on the activity ratio of Po-210/Pb-210. Recently shorter residence times of less than one week have been obtained for rain over the U.S. continent versus the Bi-210/Pb-210 ratio; however, a highly variable residence time of 2 to 50 days has been observed for precipitation over the Japan Islands' using the same Bi-210/Pb-210 ratio. Even though the true residence time of aerosol is 2 weeks, the apparent residence time calculated from the Bi-210/Pb-210 ratio and a steady state model is shown to be less than one week in an air mass increasing its Rn-222 concentration. Therefore, the mean residence time of aerosol of around 0.1 μm in diameter is believed to be 10 to 14 days. An application of the steady state model for each precipitation must be made with care. However, the analysis of the activity ratio for each sample will give useful information on the source and history of aerosol.

The discrepancy between the Po-210/Pb-210 and Bi-210/Pb-210 residence times is due to either the contamination of the surface soil or the addition of long-lived aerosols from the upper atmosphere including the contribution from the volcanic activity. The longer residence time calculated from the Po-210/Pb-210 ratio was always observed for snowfall over the earth's surface already covered with snow. The discrepancy, therefore, will give information about the extra source of aerosol to the tropospheric aerosol.

2. Use of radionuclides as a tracer of material of continental origin

Pb-210 is a daughter of Rn-222 which emanates from the earth's surface. Thus, it is possible to use Pb-210 as a tracer of material of similar origin such as sulphur and nitrogen compounds, and continental dust. The greatest advantage in using Pb-210 is that it is minimizing the problem of contamination. The yearly averaged flux of Pb-210 clearly indicates the global transport or continental aerosols, showing a steep decrease from the continent to the ocean on the continental margins and a rather constant value over the open ocean area. Although the radioactivities are low, it is possible that Be-7 and plutonium can be applied to the study of the transport of material via the upper troposphere and the stratosphere.

3. Application of radionuclides to the removal mechanism of aerosols within an air mass

The radioactive disequilibria between Rn-222 and its short-lived daughters in the atmosphere are caused by the removal of aerosol from the air; thus the degree of disequilibrium can be used for the study of short-lived phenomena occurring within an air mass or cloud.

4. Application of radionuclides to the gas exchange at the air-sea interface

The degree of disequilibrium between the activities of Ra-226 and Rn-222 in the surface seawater can be converted to the exhalation rate of Rn-222 to the air without the measurement of its vertical profile as the surface layer is in a steady state for Rn-222. The steady state condition requires that the surface layer be in the same condition for at least one week; however, even in a non-steady state, we can get useful information on the gas exchange from the measured Rn-222 content, especially in the case where many data are available.

Finally, the profile of H-3 in the surface air as well as that of the H-2/H-1 ratio can be applied to the evaporation problem of water from the ocean surface.

IX. PHOTOCHEMICAL PROCESSES
IN THE OCEAN-ATMOSPHERE INTERFACE*

The photochemical and related photophysical processes of atoms, ions and molecules are now fairly well understood on an experimental basis and also to a considerable extent theoretically. Over the last decade or so, much effort has been expended in applying this knowledge to the study of various environmental problems especially with regard to atmospheric chemical processes. However, surprisingly little work has been directed towards the study of photochemistry in the marine environment including those aspects that might be significant to ocean-atmosphere exchanges.

The air-sea interface represents a dynamic transition zone between the photochemically active troposphere and photic zone of the ocean. Three photochemically distinct regions can be categorized : the water column, the lower troposphere, and the sea surface micro-layer. Each region has unique properties of its own which will determine the nature of the photochemical reactions and the resulting products observed. Historically, researchers have considered the three regions independently with little or no regard for the impact of one upon the other. Yet, it is certain that the three are coupled through the interface in a variety of ways that affect the chemistry of each region.

Perhaps the most obvious interdependence is that of the sources and sinks for reactive volatiles. Photochemical processes may be involved in the formation and destruction of these in all three regions. From the standpoint of possible atmospheric impacts, the most immediate research topics for consideration should probably include volatile inorganic and organic sulphur and halogen compounds, nitrogen oxides, and organo-metallic compounds.

If we are to understand the sources and sinks for these volatiles, it is essential that a major commitment be made to determine the identity, concentration and reactive pathways of important reactive transient species such as hydroxyl radicals, interhalogen radical anions, singlet oxygen, ozone, superoxide radical anion and peroxides. Qualitative and some quantitative evidence already exists which shows that all of these species are present in the environment. However, much more effort in this area is required. A high priority should be placed on the study of the transport of these transient species to the interface from both the water column and atmospheric sources and on their ensuing reactions in the interfacial region.

There are obvious implications in the involvement of the reactive transients with organic material in all three regions. Reactions between these transient species and organic molecules as well as primary photolysis of light-absorbing organic compounds should contribute to chemical and physical modifications of the organic fraction in each of these regions. Such processes probably have a significant role in the transformations between volatile and particulate fractions in the atmosphere.

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* Dr. Ros Zika (R.S.M.R.S., University of Miami) contributed to this section.

X. NOTE ON THE PRESENT STATE OF RESEARCH IN U.S.S.R. ON OAMEX-RELATED PROBLEMS

In the U.S.S.R., the factors governing the exchange of substances between the ocean and the atmosphere have been investigated at the Institute of Oceanology of the Academy of Sciences since 1965, primarily by Bruzvich and Korzh. The chemical composition of precipitation and aerosols over the continent, on the coast and at sea, has been studied by Petrenchuk of the Central Geophysical Observatory. Also, occasional research is carried out in these areas by Savenko (Moscow University) and Supatashvili (Tbilissi University).

Recently, scientists at the Institute of Oceanology have studied the mechanism of iodine ejection into the atmosphere using a "micro-ocean" apparatus in the laboratory. The behaviour of various iodine compounds was investigated by means of $I^{131}$and Na^{22} radioisotopes. The bubbling of artificial seawater containing only inorganic species resulted in the production of aerosol that was only slightly enriched in iodine, the enrichment factor ranging from one to four. When organic compounds were incorporated into the system, the enrichment factor increased markedly, ranging from 60 to 110. These types of studies will be given a high priority in the future and it is hoped that the "micro-ocean" apparatus will be used for the study of heavy metals fractionation as well.

At the Institute of Oceanology, the chemistry of aerosols collected over the oceans and continents, principally the central Atlantic Ocean and the Kara-Kum desert in the U.S.S.R., are also studied. Samples are collected by means of an impactor. Neutron activation and atom absorption spectrometry are the principal analytical techniques employed. In the future, it is planned to conduct studies continuously on board the Institute's research vessels. To this end, a larger impactor (about 100 l/min) of our own design will be used.

XI. GENERAL RECOMMENDATION

An air-sea interaction workshop is proposed for 1982 to emphasize those aspects of ocean-atmosphere exchanges which so far have received inadequate attention at other assemblages but which are nonetheless areas of considerable research activity :

1) direct measurements of the flux of gases and particulates through the air-sea interface;

2) remote sensing techniques for one measurement of the concentration and movement of materials at the air-sea interface;

3) photochemical processes at the air-sea interface, and

4) microbiological processes at the air-sea interface.

XII. WORKING GROUP 44 : OCEAN-ATMOSPHERE MATERIALS EXCHANGE (OAMEX)

April 1981

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