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The ocean as a source and sink for atmospheric trace constituents

Final Report of
SCOR Working Group 72



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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	—	50 Progress on oceanographic tables and standards 1983-1986. Work and recommendations of the Unesco/SCOR/ICES/IAPSO Joint Panel	1987	—
36 The practical salinity scale 1978 and the international equation of state of seawater 1980. Tenth report of the Joint Panel on Oceanographic Tables and Standards, (JPOTS). Sidney, B.C., Canada, 1-5 September 1980. Sponsored by Unesco, ICES, SCOR, IAPSO. Available in Ar, Ch, F, R, S (Примечание: Этот доклад (текст идентичен) был первоначально издан только на английском языке под заголовком Tenth report of the Joint Panel on Oceanographic Tables and Standards (Десятый доклад Объединенной группы по океанографическим таблицам и стандартам)). Имеется на арабском, испанском, китайском, русском и французском языках.	1981	WG 10	51 Thermodynamics of the carbon dioxide system in seawater Report by the carbon dioxide subpanel of the joint panel on oceanographic tables and standards	1987	—
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42 Carbon dioxide sub-group of the joint panel on oceanographic tables and standards. Report of a meeting Miami, Florida, 21-23 September 1981 sponsored by Unesco, ICES, SCOR, IAPSO	1983	—			

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Final Report of
SCOR Working Group 72

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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 advances in oceanographic research and on recommended research programmes and methods.

The texts in this series are prepared in co-operation with non-governmental scientific organizations. Many of the texts result from research activities of the Scientific Committee on Oceanic Research (SCOR) and are submitted to Unesco for printing following final approval by SCOR of the relevant working group report.

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ABSTRACT

A state-of-the-art review of chemical exchange between ocean and atmosphere is presented, including discussion of flux measurement techniques. The exchange of particulate matter, CO₂, sulphur species, hydrocarbons and halogenated compounds, as well as the role of microbes and phytoplankton in the production of volatile species are discussed. The influence of atmospheric input of nutrients on ocean productivity and the role of photochemical processes in air/sea exchange is explored. Recommendations are made for future research in the field of air/sea exchange, with emphasis on the development of flux measurement techniques, the study of nutrient inputs to the sea, and the role of photochemical processes and biological activity.

RESUME

Présentation de l'état des connaissances relatives aux échanges chimiques entre l'océan et l'atmosphère, comprenant, entre autres, une analyse des techniques de mesure des flux. Les échanges de particules solides, de CO₂, d'éléments sulfureux, d'hydrocarbures et de composés halogénés sont notamment examinés, ainsi que le rôle des microbes et du phytoplancton dans la production d'éléments volatils, l'influence des apports atmosphériques de substances nutritives sur la productivité de l'océan et le rôle des processus photochimiques dans les échanges air/mer. Des recommandations sont formulées au sujet des orientations futures de la recherche relative aux échanges air/mer : elles portent notamment sur la mise au point de techniques de mesure des flux, sur l'étude des apports nutritifs à la mer et sur le rôle des processus photochimiques et de l'activité biologique.

RESUMEN

Se presenta en este documento una recapitulación de los conocimientos actuales sobre intercambios químicos entre el océano y la atmósfera y, particularmente, el examen de las técnicas de medición de los flujos. Se examinan los intercambios de materia particulada, CO_2 , compuestos de azufre, hidrocarburos y compuestos de halógenos y también el papel de los microbios y el fitoplancton en la producción de compuestos químicos volátiles. Se examinan asimismo la cuestión de la influencia de los aportes atmosféricos de nutrientes en la productividad oceánica y el papel de los procesos fotoquímicos en la interacción aire-mar. Se han elaborado recomendaciones para las investigaciones futuras en el campo de la interacción aire-mar, insistiendo en la importancia de perfeccionar las técnicas de medición de los flujos, el estudio de los aportes de nutrientes en el mar y el papel de los procesos fotoquímicos y de la actividad biológica.

РЕЗЮМЕ

Дается обзор уровня современных знаний о химическом обмене между океаном и атмосферой, включая обсуждение методов измерения потоков. Рассматривается обмен вещества в виде частиц, CO_2 , материалов, содержащих серу, углеводородов и галогензамещенных соединений, а также роль микробов и фитопланктона в производстве летучих видов. Рассматривается влияние поступления питательных веществ из атмосферы на продуктивность океана и роль фотохимических процессов в обмене воздух/море. Даются рекомендации в отношении будущих исследований в области обмена между атмосферой и морем с упором на развитие методов измерения потоков, изучение поступления питательных веществ в море и роль фотохимических процессов и биологической деятельности.

مستخلص

يتضمن هذا المؤلف استعراضا للوضع الراهن للمعارف الخاصة بالتبادل الكيميائي بين المحيط والغلاف الجوي بما في ذلك مناقشة تقنيات قياس التدفق . كما يتضمن بحث التبادل المنصب على المادة الجسيمية وثاني أكسيد الكربون ، وأنواع الكبريت والهيدروكربونات والمركبات الهالوجينية وكذلك دور الكائنات الحية الدقيقة والبلانكتون النباتي في إنتاج الأنواع المتطايرة . كما جرى استطلاع تأثير المدخلات الجوية المغذية على إنتاجية المحيط ودور العمليات الكيميائية الضوئية في إطار التبادل بين الجو والبحر . ويتضمن المؤلف توصيات خاصة بالبحوث المستقبلية في مجال التبادل بين الجو والبحر مع إيلاء الاهتمام لتطوير تقنيات قياس التدفق ودراسة المدخلات المغذية إلى البحر ودور العمليات الكيميائية الضوئية والنشاط البيولوجي .

摘 要

现将对海洋与大气层之间化学交流科学发展动态，包括磁通量测量技术的考查提供如下。讨论内容有散式物质、二氧化碳、硫磺种类、碳氢化合物（类）和卤代化合物的交换以及微生物和海洋浮游植物在制造易挥发类中的作用。并探索了大气中营养素输入量对于海洋生产率的影响和光化学作用在空气／海水交换中的作用。对今后空气／海水交换领域的研究提出了建议，建议研究重点放在发展磁通量测量技术、海洋营养素输入量之研究，和光化学过程和生物活动的作用。

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SCOR Working Group 72

THE OCEAN AS SOURCE AND SINK FOR ATMOSPHERIC TRACE CONSTITUENTS (OSSAC)

Final Report by Meinrat O. Andreae (Chairman)

SCOR Working Group 72 was set up during the 16th General Meeting of SCOR held in Halifax, 1982. The terms of reference were:

To review the present knowledge of processes and measurements related to:

1. the flux of gases and particles across the air/sea interface.
2. photochemical processes at the air/sea interface.
3. microbiological processes at the air/sea interface.

The original members of the working group were: R. Duce (USA), R. Chesselet (France), M.O. Andreae (then USA), P. Liss (U.K.), A. Tsyban (USSR) and O. Zafiriou (USA). The group first met in July 1983 at Jouy-en-Josas (France) in conjunction with a workshop on "Dynamic Processes in the Chemistry of the Upper Ocean". The working group discussed its possible future activities and agreed to organize an international workshop on air/sea exchange, with the main emphasis on processes interacting with the flux of trace species through the air/sea interface. Workshop objectives were to review the present knowledge in different fields contributing to the air/sea exchange, and to encourage interdisciplinary discussions among biologists, chemists, physicists and meteorologists.

The group convened for a second time in September 1985 in Bombannes, France, in conjunction with a workshop on "The Role of Air/Sea Exchange in Geochemical Cycling". The major item discussed was preparation for the proposed workshop in Mainz, FRG. It was agreed that the members of WG 72 would act as the programme committee with W. Seiler as the local organizer. A list of invited speakers was composed and a preliminary programme of the workshop was set up. Furthermore, the working group decided to prepare a document which would be presented as a final report to SCOR.

The meeting was held in Mainz on March 16-21, 1986 and was entitled "Biosphere/Atmosphere Exchange". Major sessions were:

- Biosphere and particles.
- Global distribution of biospheric trace constituents.
- Deposition of trace constituents in terrestrial ecosystems.
- Production of trace constituents in terrestrial ecosystems.
- Oxidation of biogenic trace gases in the atmosphere.
- Flux of trace gases from freshwater ecosystems.
- Ocean as source of trace substances.
- Global aspects, budgets.

The meeting was attended by about 150 participants from 25 countries, including Brazil, India, and the Peoples Republic of China. Because of the financial support by SCOR, it was possible to invite scientists from several developing countries. Additional support was made available by the Federal Ministry for Research and Technology (BMFT), the German Meteorological Society, the Fraunhofer Society, and the Max Planck Society.

The symposium provided an excellent opportunity for interdisciplinary discussions among scientists from different disciplines which resulted in the planning of several cooperative, international projects which may contribute to the IGBP (International Geosphere/Biosphere Programme). The chairmen of the individual sessions as well as the participants emphasized the great need for such an interdisciplinary symposium and expressed their hope that future symposia on this topic will be organized in the near future.

Following the symposium on "Biosphere/Atmosphere Exchange", Working Group 72 met in Mainz on 22 March 1986. The meeting was attended by group members Duce, Liss, Andreae and Seiler. In addition, Dr. Norkrans (Sweden), Dr. Roether (FRG), Dr. Buat-Ménard (France) and Dr. Conrad (FRG) were invited as experts to participate in the meeting and to contribute to the proposed summary report on the present knowledge in air/sea exchange. The results of the discussions are summarized as follows:

1. The working group reviewed the symposium. There was general agreement that the symposium was very successful and covered many aspects of air/sea exchange and the biospheric role within the flux of trace constituents between the ocean and the atmosphere. The symposium benefited from the presence of scientists working in terrestrial ecosystems, e.g. on dry deposition, presenting new techniques on deposition studies which may be applied after some modification for flux measurements of trace constituents between ocean and atmosphere. The group recommended to continue the present series of symposia on biosphere/atmosphere exchange in time intervals of two years.
2. The chairman informed the group that Drs. Chesselet and Zafiriou had resigned from Working Group 72. To complement the existing expertise in the Group, the following experts were invited to become members:

Dr. B. Dahlbäck (Sweden)	- Microbiology
Dr. P. Holligan (U.K.)	- Phytoplankton
Dr. R. Zika (USA)	- Photochemistry
Dr. P. Buat-Ménard (France)	- Particle Transfer
Dr. B. Hicks (USA)	- Exchange Mechanisms

In addition, W. Roether (FRG), B. Norkrans (Sweden) and R. Conrad (FRG) were invited to be correspondent members of WG 72. With the exception of Dr. Dahlbäck, all the proposed new members were able to accept the invitation. The members of the Working Group thanked Drs. Chesselet and Zafiriou for their important contributions to the group activities. Dr. Seiler announced his intention to resign as chairman; the working group proposed Dr. Andreae as new chairman.

This proposal was subsequently accepted by the SCOR Executive Committee.

3. Contributions by the group members and invited experts to the proposed document on the "Present state of knowledge in air/sea exchange" were presented and discussed. Contributors were asked to modify their contributions according to the recommendations of the group and to submit the final version to the chairman.
4. The group members discussed the present knowledge and future needs in air/sea exchange. After consideration of papers presented at the symposium on "Biosphere/Atmosphere Exchange" the discussion focused on 4 important areas for future research on which this group proposes to concentrate its future efforts. These areas are:
 - Improvement and development of techniques for measuring transfer velocities at the air/sea interface.
 - Studies on the role of atmospheric input of nutrients on the marine productivity and ocean fluxes.
 - Studies on the role of photochemical processes in the air/sea exchange of chemical species.
 - Studies on the role of biological activities in the exchange of trace constituents between ocean and atmosphere.

The next meeting of SCOR Working Group 72 took place during 15-18 November 1987 at Schloss Ringberg, Bavaria. It was attended by Drs. Andreae (Chairman), Buat-Ménard, Conrad, Duce, Hicks, and Liss. The following members of WG 72 were absent: Drs. Holligan, Norkrans, Roether, Seiler, Tsyban and Zika. Prof. Kirst from the University of Bremen was present as an invited expert on phytoplankton physiology. The Group members and invited experts presented short talks on recent developments in their fields of expertise, which were subsequently discussed by the Working Group. Ongoing international scientific activities were reviewed by Prof. Duce (GTCP, AEROCE, IGAC, IGBP) and Dr. Buat-Ménard (WOCE, JGOFS, EUROTRAC/ASE, and other European activities).

The Working Group examined the options for publishing a report containing a state-of-the-art review and a set of recommendations. Publication as a UNESCO Technical Report was found to be an appropriate medium.

Dr. Graeme Pearman, CSIRO Aspendale, the chairman of the IGAC steering committee had requested that the group make recommendations on the research related to air/sea exchange to be conducted under IGAC. The chairman was instructed to draft a letter to Dr. Pearman, expressing the enthusiastic support of the Working Group for the goals of IGAC and the recommendations of the group for future research.

The Working Group discussed the potential future directions that it should take. It was concluded that the Group should present its final report at the Acapulco Meeting of Joint Oceanographic Assembly, 23-31 August 1988. The Working Group will then conclude its activities at this meeting, as required by the SCOR byelaws. However, it was felt that in the current period of intensive scientific planning activity for international programmes in the marine and atmospheric community, there is a significant need for a group which acts as an information resource and

as a kind of clearinghouse to help coordinate the research in those fields where atmospheric and oceanographic research overlap. Both the International Global Atmospheric Chemistry programme and the Joint Global Ocean Flux Study are aware of this need and have contacted WG 72, or some of its members, to participate in their planning activities. JGOFS has invited the chairman of WG 72 as a Corresponding Member of the JGOFS Steering Committee.

Working Group 72 therefore would like to propose the formation of a new SCOR Working Group: "Biogeochemical Air/Sea Exchange Studies" (BASES) with the following terms of reference:

- 1) Identify research needs and define scientific planning approaches related to:
 - a) Emissions of biologically and photochemically produced trace species from the surface ocean.
 - b) Deposition of atmospheric materials to the ocean surface and its influence on marine chemistry and biology, including their use as tracers.
 - c) Measurement technologies for air/sea exchange fluxes.
- 2) To provide a means of interaction and guidance for the planning activities of the International Global Atmospheric Chemistry and the Joint Global Ocean Flux Studies programmes related to air/sea exchange.

SUMMARY AND RECOMMENDATIONS

In the following paragraphs, a short overview of key issues discussed by Working Group 72 is given together with recommendations for future research related to these issues.

1) Development and Validation of Flux Measurement Techniques

It is only for very few chemicals that exchange rates can now be directly measured, mostly by micrometeorological methods but sometimes using other techniques. In the absence of a well-developed measurement method that is widely applicable, more indirect methods are frequently employed, normally based on measurements of concentration in air, in seawater, and in rain. Correct interpretation of such concentration information requires a good understanding of the processes involved in the exchange, both atmospheric and oceanic. At present, many of the most important processes are poorly understood.

Recommendations

Scientific effort should be directed towards answering several outstanding questions concerning the exchange processes, and towards developing parameterizations suitable for deriving exchange rates from field observations of atmospheric and oceanic concentrations. The necessary studies involve laboratory experiments conducted in controlled conditions (e.g. wind tunnels) as well as field experiments to extrapolate the results to open-ocean conditions.

Techniques for measuring exchange rates must be improved. Possible techniques include micrometeorological methods (requiring the use of towers, buoys, and/or aircraft) and a variety of methods using gases of special interest (e.g. radon, isotopically-labelled carbon dioxide, and other tracers). Since no measurement method can yet be identified as a standard, all opportunities should be taken to use as many as possible of the available methods in field studies. If possible, a variety of observational platforms should be used, combining the benefits of ships, towers, and aircraft.

Methods for assessing particle deposition are presently inadequate, with continuing great differences between the predictions of different models, and with field measurements showing great scatter. Recent studies using micrometeorological methods on towers "of opportunity" appear to offer considerable promise.

The deposition of material in precipitation needs special attention, because of the wide range of efficiencies with which precipitation scavenges materials from the air and the present inability to predict even average scavenging efficiencies as a function of season and location. In practice, the difficulty associated with precipitation itself

requires attention; even the amount of precipitation to the oceans is not well known.

2) Influence of the Atmospheric Input of Nutrients on Marine Productivity

There is evidence that the atmospheric input of certain nutrient species to the ocean may play an important role in biological productivity in surface waters. Nutrients of interest include nitrogen species, phosphorus, iron, silicon, and possibly other trace metals. The temporal and geographical variability of this input and its potential impact may be quite large, although there are few data available at present to assess this problem. The biological and chemical effects of the short-term pulsed input (1-3 days) of large quantities of atmospheric mineral particles to the surface ocean are presently unknown. In some areas of the North Atlantic and North Pacific, temporal variations of a factor of 100 in mineral particle (and thus iron) input from distant desert regions are not uncommon. Similar temporal variability may occur for other nutrients. Although atmospheric input may be particularly important to productivity in some coastal regions and in oligotrophic waters, very few data are available to evaluate this adequately. In addition, accurate estimates of the transport of these nutrients into the oceanic mixed layer from deeper layers are lacking.

Recommendations

Studies to evaluate the net input rate of nutrients from the atmosphere to the ocean surface should be undertaken. These studies should be combined with enhanced efforts to measure the transport of these substances into the euphotic zone from deeper waters to ascertain the role played by atmospherically derived material. Specific geographic regions should be investigated and the temporal variability of the fluxes must be ascertained. At least one coastal region and one open ocean region should be investigated. Close cooperation among atmospheric and marine chemists, biological and physical oceanographers will be needed.

It is emphasized that such a research effort would also increase our understanding of the influence of atmospheric inputs, both natural and anthropogenic, on the concentrations and fluxes of substances from the surface to the deep ocean and marine sediments.

3) The Role of the Photochemical Processes in the Air/Sea Exchange of Chemical Species

Photochemical reactions and reactive products of these reactions can influence the exchange of various chemical species across the air/sea interface. Both photochemical formation and destruction of these exchanging chemical species have been observed. The interfacial region can

be divided into three different zones for these reactions:

- the atmosphere above the interface
- the sea surface microlayer
- the water directly below the interface.

Each of these zones has a different array of photochemical reactions and different reaction characteristics that can affect the transfer of chemical species through the interfacial region. There are a variety of examples in the literature which illustrate the potential importance of these processes, but comprehensive quantitative and mechanistic information is lacking. The complexity of the interfacial environment with respect to its physical and chemical heterogeneity may be the major reason why we have only rudimentary understanding of this very important region.

Recommendations

The photo-processes involved in the production of OCS and the destruction of dimethyl sulphide as well as other sulphur volatiles such as H_2S need further elucidation.

Aside from sulphur compounds there are also a number of other volatiles that can be formed by photochemical reactions in seawater and studies should also be made on these. Some of the other candidates include organic and inorganic halides, organo-mercury compounds, and some of the elements in groups III-VI of the periodic table.

Calculations suggest that iodine in its various forms is one of the most important constituents involved in oxidation reactions above, below, and at the interface. Investigations on its speciation, micro-layer concentration gradients, and photochemical reaction mechanisms need to be conducted.

Many aspects of the physical, chemical, and biological characteristics of the sea surface micro-layer are still not well understood. Efforts should be made to more fully characterize the micro-layer region, with particular emphasis upon those processes and properties that potentially impact upon reactions and fluxes of volatiles.

The transfer of film constituents of the sea surface micro-layer via aerosols into the atmosphere and then back to the ocean is a photochemical recycling process about which little is known. Questions that need to be addressed include:

- What are the extent and nature of the reactions during the atmospheric residence time of the aerosol?
- What impact do chemical species in the return flux to the ocean have upon the interface?

4) Role of Biological Activity in the Exchange of Trace Constituents Between Ocean and Atmosphere

Marine biota act as both sources and sinks of compounds which are exchanged across the air/sea interface. Recent studies have resulted in some understanding of the biological and chemical processes responsible for the production of a few important species, particularly dimethylsulphide (DMS). Due to its importance in the global sulphur cycle, and consequently, its influence on global climate, this compound has recently been the subject of a relatively intensive study. However, large uncertainties remain about the biogenic sources of a number of other substances which are of considerable significance for the chemistry of the atmosphere, e.g. the organohalogens and some volatile carbon and nitrogen species. For most of these substances, both the magnitude of the sea-to-air fluxes, and the processes responsible for their production in the sea remain to be determined.

Recommendations

Future studies should focus on the biological processes which are responsible for the production and removal of DMS and other volatile compounds from the surface waters of the oceans. These studies should include the effects of microbial and algal activity both in the euphotic zone and in the sea-surface microlayer. They should influence the ecophysiology of individual planktonic species and the structure of the marine planktonic community on the production and consumption of volatile chemical species. While the oligotrophic ocean areas appear to be the globally dominant sources of DMS, the highly productive coastal and upwelling regions are significant sources for this and several other trace gases, e.g. carbonyl sulphide, some low-molecular-weight hydrocarbons, and some organohalogens, and should therefore also receive intensive study. It is essential that this research be conducted in close collaboration between atmospheric and marine chemists, as well as marine biologists and microbiologists.

ASSESSMENT OF ATMOSPHERE/OCEAN FLUX MEASUREMENT TECHNIQUES AND CAPABILITIES

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In general, there is no accepted method by which average rates of exchange of trace chemical species between the atmosphere and the ocean can be measured. Instead, we must make use of a limited amount of information on localized exchange and extrapolate this to provide the average values that are truly required. This extension from a small existing data base to global scales can be guided by the considerable experience gained in studies of the exchange of more conventional meteorological properties: momentum, sensible heat, and water vapour.

The case of water exchange is of special relevance. Precipitation is an episodic input of liquid water to the surface, that carries with it the trace chemicals that are of interest here. The average input of precipitation to the oceans is poorly known, and is worthy of increased study in its own right. The rate of transfer of atmospheric trace chemicals to the ocean by wet deposition is correspondingly difficult to assess, and is even more complicated by the undisputed fact that the efficiency of scavenging of atmospheric chemicals from the air by precipitation systems varies greatly with the season and with the location. Scavenging efficiencies associated with intense convective cells are markedly greater than those of large-scale frontal systems. Thus we might expect (but as yet have little data to substantiate) that wet deposition will be most efficient in low latitudes.

In comparison, the evaporation of water from the surfaces of the oceans is a far slower and more continual process. Evaporation has been the target of scientific investigation for more than a century. In early work, evaporation pans were placed aboard the decks of ships, and the loss of water from these pans was measured as the ships passed over their prescribed commercial routes. In later years, more detailed methods have been developed for measuring the flux of water vapour from the surface of the ocean. The rate of water loss has been related to the temperature of the water and to the concentration of water vapour in the air above. The resulting bulk transfer coefficients can then be used (in concept, at least) to derive the evaporation rate data from observations of simpler quantities obtained routinely.

The transfer of trace gases between the surface of the ocean and the air, unassociated with the precipitation phenomenon, can be likened to the case of evaporation. In general, the fluxes that are desired can be computed from observations of concentrations in the air and concentrations in the water, using an exchange coefficient that is a function of controlling variables that can be measured. If some measurement technique were available by which the exchange could be quantified directly, then this exchange coefficient could be calibrated. In practice, the ability to measure exchange rates directly exists only in very few

situations, and consequently we must often rely upon logic to extrapolate existing limited understanding to circumstances where even less knowledge is available.

In general, then, it is useful to distinguish between the complicated research methods used in short intensive studies of the processes of atmosphere/ocean exchange and the far simpler methods that are developed to assess average exchange over large areas and long times. It is an acknowledged purpose of the intensive research studies to develop the techniques to address large areas and long times. It is necessary first to determine the processes of importance, then to formulate them in a manner such that multi-process descriptions of the overall exchange can be constructed. It is such descriptions of the mechanisms of atmosphere/surface exchange that enable trace gas fluxes to be computed from such fundamental information as air and water partial pressures, wind speed, etc. It is clear that the intensive research methods that underlie all parameterizations of atmosphere/surface exchange are themselves not sufficiently robust to permit their routine application. This is sometimes used as an argument against them, but the argument is specious. It is not the intent to refine any of these methods so that they will work in all conditions, but instead, to develop them to a point where adequate answers can be obtained to specific scientific questions related to transfer mechanisms.

Here, the discussion will focus on the research methods that are available, rather than on the methods that have been derived to assess average fluxes from routine data. The latter methods are somewhat developmental at this time; many of the research methods appear capable of yielding high-quality flux information, but only in a limited range of situations.

Many laboratory methods are available to study and formulate exchange across the interface between a water surface and the atmosphere. These techniques, such as wind/wave tunnels (e.g. Coantic and Bonmarin, 1975), provide the capability to scrutinize the behaviour of the surface film in the upper layers of the water body. Although most often used for studies of physical properties of a disturbed water surface, such facilities clearly offer the potential to compare the behaviour of different trace gases as they are influenced by diffusion and chemical reactions occurring near the surface. However, it is clear that the complete range of conditions encountered in natural circumstances cannot be reproduced in any such study. Relationships appropriate to open ocean conditions must be either based upon field experiments conducted at sea, or upon extensions of laboratory work that is subsequently tested and verified in open ocean situations.

Chamber techniques provide an opportunity to extend laboratory techniques to open ocean conditions in an especially rewarding fashion. In essence, the chambers are made of materials that are inert, so that emissions from the sea can be accumulated inside the enclosed volume and measured. A modification of this approach is to make use of a flow-through chamber, in which the air within the controlled volume is replaced at a constant rate and emissions from the surface are quantified from the differences in concentration between input air and output. Techniques of this kind have been applied in open ocean situations but

are limited to relatively calm water conditions. It is under these conditions that the surface film is most continuous, and therefore that exchange rates are likely to be lowest.

Studies of radon exchange have been especially revealing. Radon is a radioactive gas, occurring naturally, which diffuses through the ocean, across the interface, and into the air above. Its radioactive half-life (3.8 days) makes it especially useful for studies of the exchange across the interface over time scales of similar (or greater) magnitude. These techniques have been the basis for much of what is known concerning atmosphere/ocean interaction. Recent applications have included studies of CO₂ exchange, in the context of globally increasing CO₂ levels and possible consequences on climate. However, once again, the techniques appear somewhat limited. In this particular case, doubts arise as a consequence of the averaging time to which the results necessarily apply, and concerning the inability of the experimental technique to be used in very rough conditions.

Several other tracers (radioactive and otherwise) have been used, with great profit, to quantify exchange between the atmosphere and open water surfaces. Studies using ¹⁴C have provided much of the existing understanding of CO₂ exchange rates at sea (see Broecker and Peng, 1983). Both cosmogenic and bomb-produced sources of ¹⁴C have been employed. ³H and ³He have been used together in studies of exchange over lakes, but have not yet been widely applied to the oceanic case. A discussion of many alternative tracer techniques has been presented by Roether (1986).

The methods discussed so far tend to be extensions of laboratory techniques to open ocean conditions. In each case, the techniques are simplest to apply in light winds and quiet seas. Transfer of trace gases across the air/sea interface is likely to be slowest in these conditions, since in light winds it becomes difficult for trace gases to diffuse across the layers of air and water adjacent to the surface. In strong winds, breaking waves are suspected to modify the surface film that otherwise limits the transfer. Droplets evaporating in the spray zone above breaking waves are suspected to have chemical characteristics that could be quite different from the bulk water underneath. All such considerations reinforce the conclusion that exchange between the atmosphere and the surface in rough seas will be quite different from that in calm situations. In rough seas, the techniques discussed above are difficult to use. In these circumstances, another set of measurement methods appears more appropriate. These are the so-called micrometeorological methods.

If conditions are horizontally uniform, not changing rapidly with time, and if there are no sources or sinks of the materials being studied in the lowest few metres of the atmosphere, then the exchange at the surface itself will be the same as the flux through a horizontal layer of the air some metres above the surfaces. In such cases, micrometeorological techniques can be used to measure exchange rates, and hence to formulate behaviour at the surface itself. Suppose that all the requirements are met, and a measurement is made of the concentration of some species of interest at some height a few metres above the surface. If exchange is taking place, then this concentration will not be

constant with time, but will vary slightly from second to second in correlation with wind fluctuations. Suppose, then, that a measurement is made of the wind speed at the same location, and that from this measurement we deduce the vertical velocity component. At every instant, it is possible to compute the product of the concentration and the vertical windspeed, yielding the instantaneous rate of exchange across a horizontal plane at that height. A time average of this quantity is the average rate of exchange -- a direct measure of the flux across a horizontal surface at some height above the sea.

The eddy flux derived as described above is the most direct measure of surface exchange that is possible using micrometeorological techniques. It is appropriate, in passing, to draw attention to a potential limitation of the method. Consider the case of Argon, a gas that is present in measurable quantities, but which is not transferred across the air/sea interface. Suppose that we measure the concentration of Argon as a mass per unit volume, or partial density, in units of mg m^{-3} . Density fluctuations of the air will cause the Argon concentration expressed in this way to change. (Partial density is not a conservative quantity.) If there were a flux of heat or water vapour, then there would be fluctuations occurring that would influence the apparent concentration of Argon. Upon correlation of this concentration signal with vertical velocity, an apparent flux will result*. This flux is clearly an aberration, a consequence of the effects of density fluctuations occurring when there is indeed an exchange of heat and water vapour occurring. In theory, it is necessary to consider the concentration of Argon in terms of mass per unit mass of dry air. (This is a conservative quantity, as required by the basic equations.) Once this is done, effects of density fluctuations caused by heat exchange and water vapour exchange become inconsequential.

The errors that can arise as a result of using an incorrect concentration signal in an eddy correlation application can sometimes be substantial, particularly when the flux of the species of interest is small, and the fluxes of heat and water vapour are large. For the species that are easily transferred, the errors are generally small.

Just as great care must be given to the specification and measurement of concentration, so must care be directed towards the correct derivation of the vertical velocity component. In theory, the velocity of relevance is that normal to the plane across which there is no average transfer of dry air. Over open ocean, this plane is horizontal, and the appropriate vertical is that defined by gravity. The presence of the structure on which the sensors are mounted will necessarily cause the wind flow to be modified, even at the end of the mounting booms normally used to position sensors upwind of supporting towers. The local plane relevant for the determination of the velocity can then no longer be assumed to be horizontal, but instead some variation on it. In practice, the effects of such streamline modification can be taken into

* This illustration of the problems associated with the use of volumetric concentrations instead of mixing ratios in micrometeorological applications is due to Businger (1986).

account in a fairly straightforward manner. If a three dimensional anemometer is used, then appropriate corrections can be applied by coordinate rotation to satisfy the requirement that the average vertical velocity is zero. When such corrections are applied, then the resulting fluxes are essentially corrected for the effects of streamline departure. However, there remain some residual errors associated with the effects of the sensor itself on the turbulence field; these errors can sometimes be considerable.

If three-dimensional anemometers are not available, straightforward mean removal techniques can be used as a first-order approximation to coordinate rotation correction. These simple methods are clearly less attractive than the full treatment, but sometimes permit comparatively easy extraction of meaningful data from otherwise deficient records.

The importance of coordinate rotation and/or mean removal is greater at sea than on land because of the relatively smaller vertical velocity fluctuations that are encountered. The presence of the sensor itself can impart a considerable error in the derived vertical velocity signal; the average "vertical" velocity should be expected to be non-zero even when the supporting structure is arranged to be perfectly vertical. Experience has demonstrated that structures such as drilling platforms can be used as platforms of opportunity. It has been shown that coordinate rotation techniques applied to signals derived from sensors on such platforms can be used to derive meaningful data provided streamline departures are less than about 10 degrees.

The greatest difficulty associated with the application of eddy correlation methods to studies of air/sea exchange of trace chemical species lies in the requirements for the chemical sensor. For operation on a fixed platform at sea, the sensor must resolve concentration fluctuations as fast as 1 Hz; as yet, there are few sensors with this capability. The frequency requirement becomes more difficult when a moving platform is used (typically, 10 Hz is quoted as a target). This special case will be discussed later.

The eddy flux techniques described above are the only direct method by which fluxes can be derived from in-air methods alone. Several less direct methods are available. The most common of these is the so-called gradient technique, in which concentration differences between two different elevations above the surface are interpreted using a turbulent diffusivity as computed on the basis of other data. The method has two shortcomings. First, the concentration differences (computed as mass per unit mass of dry air, as already emphasized) may be sufficiently small that their measurement is exceedingly difficult. Second, the diffusivity may be very hard to specify. Gradient techniques have rarely been successful in oceanic conditions, primarily because of the difficulty in resolving the small vertical differences that exist near the surface. Instead, many workers are attracted by the benefits of turbulent fluctuation interpretation as an indirect method.

Several innovative revisions of standard gradient techniques may have special application over open ocean. The use of a second quantity that can be better measured, as an intermediate in the computation of the air/surface exchange rate, is attractive in some situations. In

general, such approaches are modifications of methods referred to as "Bowen ratio" techniques. Although strongly advocated in some circles, these methods have not been widely applied in oceanic studies of atmosphere/surface exchange. In a similar category are techniques that combine chemical considerations with studies of in-air concentration gradients of reacting chemical species (e.g. Parrish, et al., 1987); these methods have been applied over land, and appear promising for some oceanic situations (Roether, 1983).

The spectrum of turbulent fluctuations that causes the eddy flux extends to very high frequencies, far higher than those which contribute to the flux itself. The behaviour of turbulence at high frequencies is fairly well understood, such that measurements of the intensity of turbulence alone can be used to derive flux data. Once again, there are several difficulties that arise. First, a sensor with sufficiently fast response must be used, typically faster than one second. Second, several fundamental meteorological properties must be known in order to derive the flux from the data that are then obtained. In practice, these difficulties combine to prohibit ready application of this so-called inertial dissipation method. However, it retains the unique attraction that it could be used to derive flux information using floating platforms; platform instability makes eddy correlation exceedingly difficult, and complicates the interpretation of gradient data. A third difficulty that arises with inertial dissipation techniques of this kind is that information on the direction of the flux is lost. The methods yield only the magnitude of the rate of exchange, not whether it is upwards or downwards.

It has been suggested that methods of this kind could be extended to lower frequencies, more within the range of existing concentration sensors, by modifying the usual relationships (Hicks and Dyer, 1972). It seems possible to derive fluxes by relating low frequency concentration fluctuations to temperature and humidity fluctuations at the same frequency. We might expect to see a spate of imaginative exploitation of such methods as improved chemical sensors become available.

Common to all these techniques is the need for basic meteorological information on the exchange of heat, water vapour and momentum. This background information is far from easy to obtain.

The various micrometeorological techniques lend themselves to a wide variety of applications. In particular, it is possible to make use of many different kinds of observational platforms. Eddy correlation techniques require accurate values of vertical velocity, consequently, a fixed platform is required. In practice, it is necessary that the platform not move at the frequencies at which the turbulent transfer occurs; consequently fixed towers and aircraft provide adequate platforms for eddy correlation studies. Floating platforms, such as buoys and ships, are influenced by wave motions in a manner that prohibits easy application of eddy correlation principles. It is for these specific applications that turbulence intensity techniques offer special promise. The possibility of using inertial platforms on buoys and ships to provide the necessary stationary measurement framework has yet to be fully explored. Gradient methods are more tolerant of platform motions; they can be used on a large range of platforms (including ships), although in

some situations there is a need to consider the way in which the obstacle interferes with wind flow and hence modifies the effective height of observation.

Micrometeorological techniques are especially suited to studies of the processes that influence exchange across the air/sea interface. In order to derive the parameterizations for application in other situations, it is necessary to have a wide range of supporting measurements. The most critical of these data are those quantities that determine the credibility of the micrometeorological flux measurements, especially of time stationarity of conditions (that is, rate at which changes are occurring with time), and horizontal homogeneity. At sea, the matter of horizontal homogeneity is of special importance, because of the logistical preference for experimental sites near shores, and because even distant from coasts substantial differences in the nature of the surface can occur, and can influence fluxes measured through the air above the surface. Such changes may be associated with the presence of surface films, with changing depth, with wind streams, etc. Documentation of the average condition of the surface upwind of the measurement location is a matter that could easily require extensive sampling using ships. Likewise, accurate documentation of the chemical characteristics of the air upwind of the measurement location could require extensive use of aircraft. This simple example is adequate to underline the need to consider the roles for different observational platforms to derive the fundamental information that is often required.

Experiments in coastal waters appear especially vulnerable to errors arising from variations in conditions, either with time or space. Recent debate concerning apparent large differences between the results of radon- deficiency and chamber methods of CO_2 exchange at sea and coastal eddy correlation measurements (Broeker et al., 1986) has focussed attention on this issue. Possible explanations for the difference appear to be (a) the role of advection in a spatially non-uniform area, (b) breaking waves, and (c) sub-surface characteristics of coastal waters that are not representative of the open ocean (Wesely, 1986; Smith and Jones, 1986).

Aircraft eddy flux systems provide an additional capacity that complements the surface tower, buoy, and ship approaches considered above. In general, the instrumentation requirements for aircraft eddy correlation are far more demanding than for surface use (typically 10 Hz versus 1 Hz). Typical aircraft eddy flux samples constitute an average over a 20 - 50 km path. The constraints discussed above for the case of tower measurement extend to the aircraft case, sometimes with severe repercussions. For example, the surface constant flux layer extends only to less than 10% of the depth of the convective mixed layer, i.e. to about 50 - 150 m at sea. While there is no difficulty in arranging for tower-mounted sensors to be erected in the surface boundary layer of near-constant flux, aircraft sometimes experience difficulties operating at a sufficiently low altitude. Fortunately, this difficulty is minimized at sea.

Much recent attention has been directed to the "eddy accumulation" method. In this method, the sample is collected in two sample containers, one receiving the air sampled during upward flow, the other

during downward flow. The sampling rate for each container is proportional to the vertical velocity. This technique (in concept, at least) could avoid the need for fast-responding chemical instrumentation while retaining the direct flux-measurement benefits of eddy correlation. Efforts to develop the method have been underway for more than a decade, yet no successful application has yet been reported other than for sensible heat (Desjardins, 1977). It has been demonstrated that the method has several technological difficulties, primarily associated with sampling and with the need for very precise chemical measurement (see Hicks and McMillen, 1984). The method remains an attractive target for developmental effort.

Recommendations

Improved relationships for computing surface fluxes from routine observations of air and water concentrations and supporting atmospheric and oceanic data are badly needed. To this end, improved methods for measuring surface fluxes are required. In particular, fast-response chemical sensors for use with micrometeorological methods, and high-precision sensors for both micrometeorological and chamber methods need to be developed.

In general, chamber and tracer techniques appear to work best in light winds, whereas micrometeorological methods seem to optimize in brisk winds. There is need to compare the results obtained by the various approaches; it is only by successful completion of such comparisons that confidence will be generated in the results. Once the desired confidence is attained, then there is an urgent need to extend studies to conditions of strong winds and breaking waves.

Also, surface observations are best suited for constructing time records at a single location, in air and in water so as to derive parameterizations that describe the range of conditions encountered at that single location. Aircraft are best suited for evaluating spatial averages of fluxes, at specific times. Thus towers are best for investigating changes with time at a single place and aircraft for best for investigating changes in space at specific times. There appears to be a profit in combining these systems wherever possible so as to draw upon the strength of each in order to help interpret the results obtained.

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PROPOSAL FOR A FIELD STUDY ON ATMOSPHERE/OCEAN GAS TRANSFER PARAMETERIZATION

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A capability to convert a measured atmosphere/ocean gas solubility disequilibrium ($c_w - \alpha \cdot c_a$, where c_a , c_w = gas concentrations in air and water, α = Ostwald's solubility) into a net interfacial gas flux density (F) is required in the fields of marine trace gas chemistry, upper-ocean gaseous constituent budgeting, and tracer oceanography.

Such conversion is commonly made via introducing a gas transfer coefficient, k , i.e.,

$$F = k \cdot (c_w - \alpha \cdot c_a) \quad (1)$$

Currently, estimates of k are usually based on field results obtained from ocean basin ^{14}C budgets and the radon deficit method (Broecker and Peng, 1982). These results, however, in the main, represent geochemical averages alone. If more detailed gas transfer estimates are desired, results of laboratory investigations on air/water gas transfer could be taken into account, but the laboratory measurements are restricted to moderate wind velocity and their direct applicability to the ocean is in doubt. While the laboratory measurements are important for understanding the physics of air/water gas exchange, it has become clear that, in order for one to predict atmosphere/ocean gas transfer in any given situation, more detailed field results are needed.

New methods of obtaining such field data have recently been proposed. One method employs certain environmental gases in a micrometeorological gas flux density measurement (air gradient method, because commonly the flux would be determined from the vertical concentration gradient) (Roether, 1983). This method exploits the fact that gases like those listed in Table 1 are produced in the ocean and have an atmospheric life time of no more than a few days. This gives measurable vertical gas concentration gradients in the atmospheric surface layer, which in turn can be converted into a flux density, by, for example,

$$F = u_* \cdot r_{1,2} \cdot (c(z_1) - c(z_2)) \quad (2)$$

where, u_* = non-dimensional transfer resistance between heights z_1 and z_2 above the interface; for neutral stability one has $r_{1,2} = 1/K \cdot \ln(z_1/z_2)$ ($K = v \cdot \text{Karman constant}$). $r_{1,2}$ could be obtained from a parallel measurement of the water vapour gradient and an independent determination of the net water vapour flux density, e.g. by eddy correlation. Measuring a number of gases simultaneously would allow one to check for consistency. Moreover the gases listed in Table 1 cover a considerable range in solubility (if higher alkenes were included, still lower

solubilities could be covered), so that the effect of air bubbles could be studied. Development of the air gradient method is presently being pursued, and the method, if successful, could become operative in 1988. A second new method is a gas balance method for the ocean mixed layer using a deliberately added gas tracer. This method has successfully been used on a lake (Wanninkhof et al., 1985), but its feasibility on the open ocean is uncertain at present. It is believed that these methods have the potential to produce the desired field information on gas exchange.

In order to enable one to use field information obtained with the methods mentioned to predict in detail atmosphere/ocean gas exchange, it will be necessary to construct a parameterization of the gas exchange from it, in terms of relevant external variables, such as wind velocity and sea state. It is believed that appropriate parameterization schemes can be devised on the basis of the ongoing laboratory investigations on gas exchange (Brutsaert and Jirka, 1984). This approach implies that gas exchange measurements would have to be accompanied by measurement or other assessment of relevant meteorological and sea state parameters, including friction velocity, atmospheric boundary layer stability, spectral information on waves and air bubbles, and possibly surface films. Because, as mentioned, gas fluxes in the air gradient method might profitably be deduced from measured concentration gradients by comparison to water vapour flux, the latter would have to be determined as well. It would furthermore be advantageous to parameterize gas exchange in terms of a scatterometer signal, for later use in satellite scatterometry to estimate atmosphere/ocean gas transfer globally.

It is hoped that trace gas chemists, micrometeorologists, wave specialists, and satellite scientists will join forces to devise and carry out a field programme in which, possibly in connection with other studies, detailed gas exchange measurements are to be made with the aim of obtaining a parameterization of atmosphere/ocean gas exchange.

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Table 1: Suitable gases for use in the air gradient method.

	CH_3I	$(\text{CH}_3)_2\text{S}$	^{222}Rn	C_2H_4	C_3H_6
atmospheric lifetime (days)	5	0.5	5.5	1	0.5
solubility (Ostwald)	5	3	0.25	0.1	0.06
expected $(c_2 - c_1)/c_1$ for $z_1 = 3$ m, $z_2 = 20$ m, at $u_* = 0.5$ m/s	2%	20%	2%	10%	20%

AIR-SEA EXCHANGE OF PARTICULATE TRACE SUBSTANCES

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The understanding of the geochemical transport of materials from land to sea and from sea to land via the atmosphere depends to a great degree on a quantitative assessment of the processes by which aerosol particles are removed from the marine atmosphere. The ability to simultaneously differentiate among the various sources which can contribute to the atmospheric burden of materials attached to such particles is necessary for such an understanding. Indeed, marine aerosol particles are not only derived from the ocean. They can be produced by a variety of sources on land: natural and/or anthropogenic (i.e., soil erosion, volcanic activity, emissions from terrestrial biomass and human activity through industrial and agricultural practises). Such a production can be either direct, by mechanical processes, or indirect, due gas to particle conversion. In the size-range of 0.1 to 20 μm where most of the mass of the atmospheric aerosol is found, long-range transport (>1000 km) of materials over ocean waters can be expected before their deposition onto the ocean surface by dry and wet removal processes. Dry deposition, which refers to all deposition processes which occur in the absence of precipitation, may be more or less continuous whereas the removal of aerosol particles by precipitation is discontinuous.

In principle, knowledge of aerosol particle deposition processes combined with atmospheric transport models should allow an evaluation of the net air to sea transfer rate of particulate materials, provided accurate source-emission inventory data are available. At present such an approach is not possible and we must rely on experimental field measurements for such an assessment. One major conclusion which has emerged in recent years is that the deposition rate of particulate material from the atmosphere to the ocean exhibits a strong spatial and temporal variability. This is primarily because of a) meteorological factors (air-mass circulation patterns), b) the geographical variability of continental source strengths and c) the fact that aerosol particles have very short residence times in the troposphere (1 day to 1 month) and cannot therefore be homogeneously distributed.

It should also be pointed out that geographical variability is also a characteristic of the oceanic system especially for trace elements. Thus, any reliable assessment of the role of air to sea transfer of particles on ocean chemistry cannot be obtained simply by a consideration of global mass balance. This applies also to the problem of the assessment of the oceanic source strength for some atmospheric compounds (e.g. biogenic sulfur) when it is inferred from the estimates of the deposition to the ocean surface.

Recent years have seen the publication of a considerable amount of new data on the concentration and behaviour of aerosols and trace

elements in the marine environment. More and more substances are being investigated in the context of large-scale programmes, both national and international.

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

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

Different source regions for pollutant lead aerosols found over the North Pacific (Japan and North America) have been identified on the basis of lead isotope measurements. In the same context, the study of the mineralogy of aluminosilicate dust particles appears to be a promising tool for allocating sources. Also, significant progress in source identification has been achieved for a number of elements or compounds. For example, chemical speciation studies have allowed estimation of the respective proportions of marine-derived, crustal-derived and

anthropogenically-derived phosphorus in marine aerosols. With respect to organic compounds, carbon isotope measurements as well as biological source marker measurements have allowed successful distinction to be made between marine and land-derived sources for organic matter in marine aerosols.

The importance of the ocean surface as a source of aerosols is still receiving attention. New estimates of sea-salt production rates and concentrations as a function of wind speed have been published. For trace elements, more accurate sea-to-air fluxes based on the analysis of aerosol particles artificially produced from bursting bubbles have been obtained, since such data take into account the enrichment of these elements in sea-source aerosols. They indicate that, outside the well-documented alkali and alkaline-earth metals, the ocean could be a significant source of V and perhaps Cd to the atmosphere. However, for many trace substances, the existence of a significant recycling across the air-sea interface makes it difficult to evaluate the net input of these substances from the continent to the oceans via atmospheric deposition. For enriched metals and organic carbon, it appears that measured total dry deposition fluxes may be mostly due to the sea surface derived fraction, which typically resides on the largest particles which have the highest deposition velocities. The presence of a recycled component in marine rain may also affect the significance of direct measurements of fluxes to the ocean. This question is still open to debate since the answer depends on our knowledge of the scavenging efficiency of aerosol particles as a function of their size, and washout factors are still not known with accuracy. Very recent data indicate, however, that in clean marine air the aerosol scavenging efficiency is apparently not particle-size dependent, so that the relative contribution of the recycled component to elemental concentrations in rain is probably not enhanced compared to what is observed in the marine aerosol. In any case, it can now be inferred that atmospheric net fluxes to the ocean surface are primarily due to wet deposition in the remote marine atmosphere. This is particularly true for pollution-derived elements which are generally found on submicrometer sized aerosols. Dry deposition, on the other hand, is certainly significant for sea source aerosols as well as for continental dust derived from soil erosion.

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

With all this new information, some conclusions on the role of air/sea particulate exchange in geochemical cycling are possible. For regional seas, it appears that the atmospheric delivery from the atmosphere to the ocean is higher than or at least comparable to the riverine dissolved delivery for many trace elements. Due to anthropogenic perturbations of the Pb and Sn atmospheric cycles, the cycles of these elements in the ocean are no longer at steady state and show enhanced concentrations over natural levels in the upper water column. The level of the enhancement reflects the level of the

atmospheric input rate. For these and other elements, predictive modeling of the influence of natural and anthropogenic inputs from the atmosphere on their cycles in the ocean has been proposed and clearly indicates that the deep ocean is no longer free from anthropogenic inputs from the atmosphere.

Recommendations

Future research should concentrate on the following topics:

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

In this context, it can be expected that significant advances in flux prediction will come from the use of remote sensing techniques conducted from aircraft or satellites. Indeed such techniques already give us and will give us some of the important parameters needed for such predictions, i.e. precipitation patterns, whitecap-coverage, sea-surface roughness, extent of aerosol-plumes following desert-dust outbreak events, volcanic eruptions, and intense biomass burning activities. Obtaining the latter information may be one of the highest priorities for future studies because of their possible major impact on atmospheric and ocean chemistry.

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EXCHANGE OF PARTICULATE CARBON AND NUTRIENTS ACROSS THE AIR/SEA INTER-FACE

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PARTICULATE CARBON

Carbon is present on marine aerosols in essentially three forms - carbonate-bicarbonate, organic carbon, and elemental carbon or soot. Except in areas downwind from continental or island limestone or coral deposits, carbonate is a small fraction of marine aerosol carbon and will not be considered further here. Hundreds of different organic compounds are present on atmospheric particles and each has its own characteristic physical and chemical properties and associated atmospheric sources, residence times, and sinks. Data are very sparse on individual compounds in the marine aerosol, however (see reviews by Duce et al., 1983 and Gagosian, 1986), so we will restrict our discussion of particulate carbon to total organic carbon.

Organic carbon in the marine aerosol has been measured by several investigators during the past few years. In many cases the concentrations reported for organic carbon probably include some elemental carbon as well. Reported values in the near-surface marine atmosphere (5-90 meters) are presented in Table 1. Note that the mean concentrations observed are rather similar at the various marine sites in the northern and southern hemispheres. Near-coastal sites have higher concentrations than open ocean locations.

Hoffman and Duce (1977) found that about 80 percent of the carbon was on particles with radii $<0.5 \mu\text{m}$ at Bermuda, Hawaii, and Samoa. They suggested that this was the result of gas-particle conversion reactions in the atmosphere. This size distribution of marine aerosol carbon has been corroborated by Chesselet et al. (1981), Andreae et al. (1984), and others. Hoffman and Duce (1977) measured the distribution of organic carbon and Na as a function of particle size for laboratory generated sea salt particles and for a typical atmospheric sample from Bermuda. While the Na size distribution was quite similar in the ambient and laboratory aerosols, the organic carbon distribution was quite different. The organic carbon in the laboratory generated sea salt particles was enriched several hundred-fold over the sea-water concentrations (relative to Na) and was present on generally the same size particles as the Na. This suggests that the large-particle organic carbon is probably present on the sea salt aerosols when they are produced by the ocean, while the small particle, or dominant, organic carbon comes from some other source.

SEAREX studies by Chesselet et al. (1981) utilizing stable carbon isotopes lend support to the suggestion that the small particle organic

carbon is not of marine origin. The authors measured the organic carbon concentration and the $\delta^{13}\text{C}$ value for a size-separated aerosol sample collected at Enewetak Atoll. $\delta^{13}\text{C}$ values for the smallest particles were -26‰ to -28‰ . Chesselet et al. (1981) point out that this range is similar to $\delta^{13}\text{C}$ values for continental vegetation, coal, and the products of petroleum combustion, $-26 \pm 2\text{‰}$, suggesting that the small-particle carbon is of continental origin. The $\delta^{13}\text{C}$ values for the large-particle carbon are -18 to -22‰ . This is similar to $\delta^{13}\text{C}$ for marine organic carbon, which is generally $-21 \pm 2\text{‰}$ in low latitude regions (40°S - 50°N), suggesting that the large-particle organic carbon in the atmosphere is of marine origin.

The global production of aerosol organic carbon is rather poorly known. Duce (1978) estimated a global source strength of organic carbon on primary aerosols of $\approx 5\text{ Tmol/yr}$, of which about half was from natural sources (the ocean, crustal weathering, biomass burning) and about half from pollution sources. Duce (1978) estimates that about 7 to 13 Tmol/yr of particulate organic carbon result from gas to particle conversion processes. This leads to estimates of the total global production rate of organic carbon on aerosols ranging from ≈ 12 to 18 Tmol/yr . This agrees well with the estimate of Jaenicke (1978) of $\approx 17\text{ Tmol/yr}$ with $\approx 13\text{ Tmol/yr}$ from gas-particle conversion and $\approx 4\text{ Tmol/yr}$ from direct production.

Cachier et al. (1985) have investigated the concentration, size distribution, and sources of organic carbon in aerosols in tropical regions on the Ivory Coast. Atmospheric concentrations were considerably higher than in marine areas, and generally ranged from 250 to 1300 nmol/m³. Submicrometer particles accounted for 50 to 80 percent of the total mass. On the basis of stable carbon isotope measurements, Cachier et al. (1985) found that natural emissions from the equatorial forests were the dominant source during the wet season, but that biomass burning was the primary source during the dry season. On an annual basis, biomass burning was the primary source, even though it is only active for about 4 months each year. Cachier et al. (1985) further estimated that the total quantity of fine particle organic carbon emitted from tropical forest regions into the global troposphere is about 2 Tmol/yr, suggesting that this source may be quite significant for fine particle organic carbon found in marine aerosols.

Information on the net input of organic carbon to the ocean from the atmosphere is essentially nil. We have virtually no data on organic carbon in marine rains. Neumann et al. (1959) reported 0.14 to 0.28 mmol/kg organic carbon over Sweden, while Williams (1967) reported 0.06 mmol/kg just north of Samoa and 0.03 mmol/kg on the southern California coast. Gagosian (1981) found a mean organic carbon concentration of $0.05 \pm 0.04\text{ mmol/kg}$ in ten samples collected during the SEAREX Program at Enewetak Atoll. We can estimate the net input of organic carbon to the ocean as follows.

From the data in Table 1 and the finding that ≈ 10 to 20 percent of the organic carbon is found on the largest particles, which are derived from the ocean (Hoffman and Duce, 1977; Chesselet et al., 1981), we may estimate that the mean concentration of ocean-derived organic carbons is $\approx 8\text{ nmol/m}^3$. Cachier et al. (1987) estimate this component as 6 nmol/m^3 .

Data from Table 1 suggest that total organic carbon ranges from 25 to 65 nmol/m³ in the northern hemisphere and 15 to 25 nmol/m³ in the southern hemisphere. Thus the continentally derived organic carbon in the marine atmosphere would range from 17 to 57 nmol/m³ in the northern hemisphere (Cachier et al., 1987 estimate 38 nmol/m³) and 7 to 17 nmol/m³ in the southern hemisphere (Cachier et al., 1987 estimate 5 nmol/m³). Most of the particulate organic carbon input to the ocean is via rainfall (Zafiriou et al., 1985; Arimoto et al., 1985), with only 10-15 percent via dry deposition. If we use the relationship

$$W = C_R \rho / C_A$$

where W = scavenging ratio
 C_R = concentration of organic carbon in rain in mol/kg
 C_A = concentration of organic carbon in aerosols in mol/m³, and
 ρ = density of air = 1.2 kg/m³

and if we assume a value for W of 500 (Zafiriou et al., 1985, although it should be recognized that this value has been determined from convective rains in tropical regions and may not be representative for more stratiform rains in higher latitudes), then the estimated mean rain concentrations of organic carbon derived from organic carbon present on aerosol particles are 0.007 to 0.024 mmol/kg and 0.003 to 0.007 mmol/kg in the northern and southern hemispheres respectively. With a mean annual marine rainfall of 1.8×10^{17} kg in the northern hemisphere and 2.1×10^{17} kg in the southern hemisphere (Baumgartner and Reichel, 1975), the net organic carbon flux to the ocean is ≈ 1.3 to 4.3 Tmol/yr (or ≈ 7.5 to 26 mmol/m² yr) in the northern hemisphere and ≈ 0.6 to 1.5 Tmol/yr (or ≈ 3 to 7 mmol/m² yr) in the southern hemisphere. Note that this calculation does not consider organic carbon in rain that is derived from the scavenging of gas phase organic species. This may be important for such species as formic acid, acetic acid, etc.. With a typical open ocean organic carbon biological productivity value of ≈ 4 mol/m² yr, atmospheric input of organic carbon accounts for no more than ≈ 1 percent of this value. Whether or not this atmospheric organic carbon can be metabolized in the ocean is unknown. The net input of continentally derived organic carbon to the global ocean is ≈ 2 to 6 Tmol/yr. It is interesting to note that the atmospheric input rates are similar to estimates of organic carbon entering the ocean via rivers, 0.8 to 8 Tmol/yr (see, e.g., Duce and Duursma, 1977).

Using a mean atmospheric concentration of marine derived organic carbon of ≈ 8 nmol/m³, we can calculate the recycled organic carbon flux in a manner similar to the calculation of the net flux above. Using this approach results in an estimated recycled flux from the ocean into the atmosphere and back to the ocean of ≈ 1.3 Tmol/yr.

The use of carbon isotopes offers an excellent opportunity for further untangling the relative roles of small (net input) particles and large (recycled material) particles. It eventually may allow us to evaluate the net input of organic carbon to the ocean much more accurately. Measurement of organic carbon concentrations and $\delta^{13}\text{C}$ values in rain, in dry deposition, and in the ambient aerosol as a function of particle size should aid significantly in determining a.) which size

particles are primarily involved in the wet and dry deposition processes and b.) what the net true input of organic carbon is to the ocean.

A complication in the consideration of organic carbon in marine aerosols is elemental carbon. Elemental carbon has been found in marine sediments in the mid-Atlantic and Pacific Oceans (≈ 0.02 to 0.1 percent dry weight; Smith et al., 1973; Griffin and Goldberg, 1975). This material originates from the combustion of coal, wood, and petroleum products (Griffin and Goldberg, 1979). It has been measured extensively in urban areas, but relatively few data are available in remote regions. Rosen et al. (1981) find elemental carbon concentrations ranging from ≈ 8 to 75 nmol/m^3 at Barrow, Alaska, with the higher concentrations being observed in the winter months. The high concentrations coincide with apparent long range transport of pollution across the Arctic during the winter (Rahn and McCaffrey, 1980) and indeed are near typical concentrations in many urban areas (Rosen et al., 1981). Few data for elemental carbon are available from remote marine regions. Recent concentrations reported by Andreae et al. (1984) for marine regions are presented in Table 2. Atmospheric concentrations of elemental carbon in coastal ocean regions appear to be in the range of 8 to 80 nmol/m^3 , while the few remote ocean atmospheric data available suggest a range of 0.8 to 3.3 nmol/m^3 . As pointed out by Andreae (1983) and Andreae et al. (1984), the source of the elemental carbon in marine aerosols is almost entirely continental, with a significant fraction due to biomass burning.

The global production of elemental carbon by fires may be very high. Ryan and McMahon (1976) indicate that as much as 40 percent of the particles produced during burning of temperate forests and agricultural wastes may be elemental carbon. Seiler and Crutzen (1980) estimated that as much as 7.5 to 15 Tmol/yr of aerosol carbon may be produced in this way. Note this is in the range of the total production of aerosol organic carbon estimated by Duce (1978) and Jaenicke (1978). Elemental carbon may thus play a very important role in the global aerosol carbon budget. The historical record of burning is maintained in coastal marine and in lake sediments. As emphasized by UNESCO (1980), the fate of this elemental carbon may be important for the global carbon budget, and its production and distribution should be investigated in more detail.

Recommendations

1. The primary sources for particulate organic carbon in the marine atmosphere are still very poorly understood. In particular the role of terrestrial sources, such as tropical forests, must be investigated in more detail. Further evaluation of the use of stable carbon isotopes to distinguish marine from continental sources should be encouraged.
2. The role of gas/particle conversion as a "source" for particulate organic carbon in the marine atmosphere must be evaluated. Determination of specific organic classes and compounds will aid in this evaluation, as it will in determining the primary sources discussed in 1. above.
3. The role of the ocean as a source for fine particles (e.g. $<0.5 \mu\text{m}$ diameter) which may contain high concentrations of organic carbon has

never been determined. There is increasing evidence that the ocean can produce significant numbers of particles in this size range.

4. The net input of organic carbon (and specific organic compounds) to the ocean by rain and dry deposition should be investigated. It is very possible that this input is at least equivalent to that via rivers, and while probably unimportant compared with in-situ sources of total organic carbon production in the ocean, it may be very significant for certain types of compounds found in the sea.
5. Much better data are required on the spatial and temporal variability of particulate elemental carbon in the marine atmosphere as well as its input rate into the ocean.

NUTRIENTS

There has been growing interest in the possibility that the atmosphere may be an important transport path for certain nutrients found in coastal and open ocean waters. Recent papers by Graham and Duce (1982), McCarthy and Carpenter (1983), Moore et al. (1984), Paerl (1985), Knap et al., (1986), Duce (1986), Talbot et al. (1986), and Martin and Gordon (1988) have looked at various aspects of this question.

Duce (1986) attempted to evaluate the relative importance of the atmospheric input to the photic zone for the nutrients phosphorus, nitrogen and dissolved iron compared with the input of these nutrients from advective and diffusive mixing (and in the case of nitrogen, fixation) from sub-surface waters. He considered open ocean areas in the central North Pacific and North Atlantic Oceans. Relatively simple models were combined with oceanic and atmospheric concentration measurements of these species to calculate their transport into the photic zone from deep water as well as from the atmosphere. Results of the calculations suggested that the atmosphere was a relatively unimportant source for phosphorus in the surface waters of the North Pacific Gyre (less than 1 percent) and the Sargasso Sea (0.2 to 5 percent). Atmospheric input was potentially an important source at times for nitrogen in the North Pacific Gyre (1 to 27 percent) and the Sargasso Sea (8 to 70 percent). However, the atmosphere was calculated to be a very important source for dissolved Fe in the photic zone of the North Pacific (16 to 76 percent) and the Sargasso Sea (30 to 96 percent). The ranges of the calculated fluxes of these nutrients into the photic zone of these regions are presented in Table 3.

Duce (1986) pointed out, however, that the estimates of the mean annual inputs of these nutrients from the atmosphere to the ocean may be misleading, since often the atmospheric input comes in large pulses over short periods of time, in some cases only a few days. The impact on the biological productivity of the surface waters from such a large input of nutrients over such a short time period is unknown. In addition, recent studies suggest that simple diffusion/advection models to estimate the vertical flux of materials into the photic zone may grossly underestimate the overall flux across the thermocline (Jenkins and Goldman, 1985). These authors suggested that most of the transport from deeper waters may be physical entrainment through turbulence that is induced

primarily by wind stress (Klein and Koste (1984)). The entire question of the primary means by which nutrients are transported from deep water across the thermocline is currently a very active area of research.

A recent paper by Martin and Gordon (1988) supports the suggestion of Duce (1986) that the atmosphere may be the most important source for nutrient iron in the photic zone of the North Pacific Gyre. Dissolved iron from the atmosphere is derived from the solubilization of a fraction of mineral aerosol material entering the ocean. The oceanic advective and diffusive flux estimates of Duce (1986) were based on an assumed vertical profile of dissolved iron in that region of the ocean, since no actual data were available. Martin and Gordon (1988) actually measured dissolved iron below the photic zone in the North Pacific and found concentrations approximately an order of magnitude lower than those estimated by Duce (1986) in his model. This resulted in calculated advective and diffusive fluxes from deeper waters into the photic zone that were also about an order of magnitude below those estimated by Duce (1986), thus reducing the importance of marine versus atmospheric sources for the iron. Martin and Gordon (1988) calculated that 98% of the Fe supplied to the photic zone in the North Pacific Gyre is derived from the atmosphere. These authors also showed that the amount of iron transported from deep waters into the photic zone could not support the level of productivity observed in these waters. The difference was obviously supplied by the atmosphere in the North Pacific. In addition, Martin and Gordon (1988) suggested that there may be some regions of the ocean which are characterized by; a) high concentrations of such nutrients as N, P, Si, etc., but very low concentrations of Fe supplied by deeper waters, and also b) very low atmospheric input of mineral material, and thus Fe. In these regions the limiting nutrient could well be iron from the atmosphere. They suggest that this may be the case in the relatively nutrient rich waters in the region of the Antarctic convergence, between $\approx 40^{\circ}\text{S}$ and Antarctica, where atmospheric dust is believed to be very low due to the absence of land masses.

In a different type of approach, Talbot et al. (1986) compared the estimated atmospheric input rate of soluble nitrate and phosphate into both the Caribbean Sea/Gulf of Mexico region and the tropical North Atlantic ($10^{\circ} - 25^{\circ}\text{N}$, $34^{\circ} - 60^{\circ}\text{W}$) with the estimated transport of these species into the ocean via the Amazon River (see Table 4). The atmospheric input of nitrogen ranged from 15 to 24 percent of that from the Amazon River, while the atmospheric input of phosphate ranged from 5 to 9 percent of that from the Amazon. This again shows the potential importance of atmospheric input and also indicates that atmospheric nitrate input is probably more significant than phosphate.

Recommendations

1. Measurements of the atmospheric input of nutrients to the ocean are still very few and cover very restricted geographical regions over rather limited time periods. A much more broadly based set of measurements over the global ocean as well as coastal regions is required.
2. Our understanding of the vertical transport of nutrients from deep waters into the photic zone is very poor at the present time. Addi-

tional model development is required, as are field programmes designed to validate these models.

3. Information on the chemical and physical forms of many nutrients entering the ocean from the atmosphere is lacking. In particular, both laboratory and field programmes are needed to determine what happens physically and chemically to material present on aerosol particles when these particles enter the ocean.

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Table 1. Organic Carbon Concentration in the Marine Aerosol

Location	Mean (nmol C/m ³ STP)	Range (nmol C/m ³ STP)	Reference
<u>Northern Hemisphere:</u>			
Bermuda	24 ± 8	13 - 39	Hoffman and Duce (1974)
North Atlantic	63 ± 35	28 - 130	Ketseridis et al. (1976)
N. Atlantic and N. Sea	77	---	Andreae et al. (1984)
West Ireland	48 ± 24	17 - 72	Eichmann et al. (1979)
Bermuda	31 ± 19	13 - 65	Hoffman and Duce (1977)
Sargasso Sea	37 ± 3	32 - 40	Chesselet et al. (1981)
Hawaii	33 ± 3	30 - 36	Hoffman and Duce (1977)
Enewetak Atoll	74 ± 23	61 - 100	Chesselet et al. (1981)
Eastern Tropical Pacific	41 ± 22	18 - 62	Hidy et al. (1974)
Barrow, Ak (winter)	71 ± 27	31 - 100	Daisey et al. (1981)
Barrow, Ak (summer)	28 ± 10	13 - 30	Daisey et al. (1981)
<u>Equatorial Regions:</u>			
Equatorial Atlantic	10	---	Andreae et al. (1984)
Equatorial Pacific	11	---	Andreae et al. (1984)
Gulf of Guinea	-	75 - 110	Marty and Saliot (1982)
<u>Southern Hemisphere:</u>			
Samoa	18 ± 8	11 - 34	Hoffman and Duce (1977)
Samoa	-	3 - 8	Cachier et al. (1985)
Eastern Tropical Pacific	18 ± 15	6 - 44	Barger and Garrett (1976)
Tasmania	44	---	Eichmann et al. (1979)
Tasmania	19 ± 6	12 - 26	Andreae et al. (1984)
Brazil/Uruguay coast	33	---	Andreae et al. (1984)
Peru coast	13 ± 6	---	Cachier et al. (1985)
Amsterdam Island	13	---	Cachier et al. (1985)
New Zealand	10 ± 2	---	Cachier et al. (1985)

Note:

C_{organic} concentrations from Andreae et al. (1984) calculated

from C_{total} - C_{soot}.

Table 2. Elemental Carbon (Soot) Concentration in the Marine Aerosol*

Location	Mean (nmol C/m ³)
<u>Coastal Ocean:</u>	
N.E. Atlantic and N. Sea	57
Fernando de Noronha	28
Brazil/Uruguay coast	16
Eastern Gulf of Mexico	9
Peru/Ecuador shelf	8
<u>Open Ocean:</u>	
Sargasso Sea	12
Atlantic, biomass burning plume	13
Equatorial Atlantic	3
Equatorial Pacific	1

*All data from Andreae et al. (1984).

Table 3. Comparison of the Fluxes of Nutrients from Deep Water and from the Atmosphere to the Photic Zone in Open Ocean Regions*

Source	<u>Flux ($\mu\text{mol}/\text{m}^2\text{d}$)</u>	
	Sargasso Sea	North Pacific Gyre
<u>Fixed Nitrogen</u>		
Vertical Advection	0 - 40	10 - 22
Eddy Diffusion	22 - 210	60 - 730
Nitrogen Fixation	0.5 - 5	0.2 - 2
Atmospheric Deposition	26 - 54	8 - 26
Total	50 - 310	80 - 800
<u>Phosphorus</u>		
Vertical Advection	0 - 4	2.4 - 4.8
Eddy Diffusion	1.7 - 10	5 - 50
Atmospheric Deposition	.033 - 0.080	0.005 - 0.012
Total	1.7 - 14	7 - 55
<u>Iron</u>		
Vertical Advection	0 - 0.06	0.012 - 0.018
Eddy Diffusion	.034 - 0.4	0.034 - 0.4
Atmospheric Deposition	0.2 - 0.8	0.08 - 0.16
Total	0.2 - 1.3	0.13 - 0.58

*From Duce (1986)

Table 4. Comparison of the Input of Nutrients from the Amazon and the Atmosphere to Selected Regions of the Atlantic Ocean*

Atmospheric Input (Gmol/yr)		Amazon River Input (Gmol/yr)
Caribbean Sea/ Gulf of Mexico	Tropical North Atlantic	
<u>Nitrate</u> (NO_3^-)		
4.2	2.6	19
<u>Phosphate</u> (PO_4^{3-})		
0.2	0.13	2.3

*From Talbot et al. (1986)

EXCHANGE OF CO₂ BETWEEN ATMOSPHERE AND OCEAN

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CO₂ has received considerable attention primarily for two reasons: its anthropogenic increase, and past natural variations. The ocean is the largest CO₂ reservoir in active exchange with the atmosphere, and it essentially controls the atmospheric CO₂ concentration over time scales of 1 to 10⁴ years. In addition, the ocean plays a major passive and active role for natural and man-made climatic changes. There is considerable activity internationally in CO₂ research; at the same time there are still uncertainties and open questions.

Atmospheric observations are performed in a relatively dense global network, which includes oceanic and coastal stations. Valuable information on seasonal and interannual variability has been obtained, and a connection between El Niño/Southern Oscillation events and atmospheric CO₂ has been observed (Thompson et al., 1986). There are only a few high-precision CO₂ monitoring stations in the continental interior, but such stations, such as those situated on high mountains, could provide information on biospheric source strength. The isotopic composition (¹³C, ¹⁴C, ¹⁸O) of atmospheric CO₂ yields information on exchange and sources; more high-precision isotope measurements should be done on a routine basis.

Air/sea gas exchange: The gas transfer velocity depends on the turbulence conditions near the interface. The quantitative dependence on wind, bubbles, etc. under field conditions is not yet understood well enough. New methods for investigating interfacial turbulence, such as by studying heat transfer (as an analogue) using remote sensing methods locally and with high time resolution, promise to give more insight (Libner et al., 1987). Synoptic large-scale wind fields obtained from satellite scatterometer data will become available in the future, so that, given a wind - transfer velocity relationship, it will be possible to compute gas exchange fluxes with high spatial and temporal resolution.

Ocean circulation: The rate of water exchange between the surface and deeper layers is a most important factor for the uptake of anthropogenic CO₂ as well as for natural CO₂ variations. Information on the vertical exchange has mainly come from oceanic data on ¹⁴C and from other isotopic and geochemical data, as provided by GEOSECS, TTO (J.G.R., 1985) and other programmes. The progressive penetration of transient tracers (CFMs, ³He, ⁸⁵Kr and bomb produced ¹⁴C and ³H) into the ocean provides a unique observational opportunity and should therefore also be monitored regularly in the future. More geochemical data of the CO₂-carbonate system are needed, especially for the Southern Ocean and the Equatorial Pacific during El Niño conditions. The Southern Ocean (waters around Antarctica) is the largest area of deep water outcropping

and formation, and it is of major importance for the natural atmospheric CO₂ concentration; at the same time it is a possibly significant sink area for anthropogenic CO₂. The El Niño-related CO₂ concentration variations are probably related to physical and chemical changes in equatorial surface waters, but the mechanism is not well understood because of the lack of observations.

These tracer data do not just serve goals of geochemistry. Modelling of the general ocean circulation is making rapid progress, but existing 3D models still have fundamental problems with the large-scale and long-term processes that are important in the ocean-climate context. Here, tracer measurements, especially ¹⁴C and transient tracer data, can yield direct information, for instance on the rate of ventilation of the deep sea and on distribution and mixing of water masses (Broecker et al., 1985a,b). In addition, the tracer data are a powerful means to verify ocean models (Maier-Reimer and Hasselmann, 1987). In the planning of WOCE, therefore, tracer and geochemical programmes must receive proper attention, since these observations considerably enhance the scope obtained by physical oceanographic methods.

Marine biology exerts a strong control over the carbonate chemistry of surface waters and, therefore, on the atmospheric CO₂ concentration. To understand the causes of natural CO₂ variations, we ought to know more about Redfield ratios: Are they really constant? How do they depend on ecological conditions? Nutrient availability, composition of ecosystems, fractional release of different elements during particle decomposition should be studied. For modelling the natural CO₂ cycle, more information is needed on the factors controlling marine productivity (and thus indirectly chemical conditions near the surface).

Enhanced burial of organic matter in ocean sediments, due to increased nutrient influx, has been postulated as a possible new sink for carbon. Although this is probably not a large sink, further studies on this subject are necessary. A clear distinction between the steady state and the perturbed situation is necessary (and may not be easy); in the past, a confusion of the two has led some authors to high estimates of this sink.

Increased dissolution of carbonates due to the acidification of seawater by increase of CO₂ would lead to higher alkalinity and therefore higher CO₂ uptake capacity of the ocean. Recent results have suggested that the dissolution rate of aragonitic pteropods may be significantly higher than hitherto assumed (Betzler et al., 1984). It is not clear whether this might be relevant for anthropogenic CO₂.

Terrestrial biosphere: The magnitude of present and past CO₂ emissions due to deforestation and land-use have been estimated from statistics of forest area changes, etc. This has yielded a value of 1.6 ± 0.8 Gt C/yr for the current rate of release from the biosphere, compared to 5 Gt C/yr from fossil fuels (Bolin, 1986). A different approach was to deduce the total CO₂ input into the atmosphere by a deconvolution of the anthropogenic CO₂ concentration increase, as known from ice core measurements plus atmospheric data, by means of a carbon cycle model (Siegenthaler and Oeschger, 1987). This method yielded 0 - 1 Gt C/yr for the current non-fossil (i.e. biospheric) CO₂ input, and it indicated

that significant CO₂ emissions already started around 1800. The results of the two methods of assessment agree marginally, and further investigations are necessary. A much discussed question is to what degree additional growth of the land vegetation can be stimulated by the enhanced CO₂ levels. The seasonal CO₂ amplitude at Mauna Loa has increased significantly from 1958 to 1982, which points to an increased large-scale plant activity, possibly due to CO₂ fertilization (Bacastow et al., 1985).

Carbon cycle history: The best way to obtain information on past concentrations of CO₂ (and also CH₄, N₂O etc.), and on its isotopic composition is analysis of polar ice cores. In several cores from Greenland and from Antarctica, CO₂ levels of 180 - 200 ppm during glacial time have been found, compared to 280 ppm during the Holocene; the longest record goes 160,000 years back, i.e. well into the penultimate glaciation (Barnola et al., 1987). The reasons for the natural CO₂ variations are most probably to be found in the ocean and several hypotheses have been formulated; but a consistent explanation has yet to be found. In Greenland ice, rapid CO₂ oscillations have been observed (Stauffer et al., 1984); but the corresponding variations have not been found in analyses of Antarctic ice cores. If the rapid oscillations can be confirmed, they indicate that dramatic changes affecting the atmospheric composition can occur in the ocean on the time scale of a century.

Sediment records have revealed ¹³C fluctuations in the past, related to atmospheric CO₂ changes. A problem with the interpretation of the data is that all planktonic foraminifera do not live in near surface waters, so that recorded changes may be different from those in surface waters. Accelerator-based ¹⁴C measurements on planktonic and benthic foraminifera from the same depth can provide information on past changes of the vertical ¹⁴C gradient in the ocean and therefore on circulation changes (Andrée et al., 1986).

Modelling: Until now, the oceanic uptake of excess CO₂ has been studied mainly by means of relatively simple, low-resolution models (e.g. Oeschger et al., 1975). Higher resolution is required for two reasons: (1) for more realistic simulation of the CO₂ uptake, (2) for being able to analyse and interpret the (existing and expected) large sets of geochemical and tracer data in an optimal way. In addition, studies using dynamic ocean models are required to explore possible changes in ocean circulation due to man-made climatic change and also their feedback on atmospheric CO₂.

In contrast to the perturbation models used for estimating the excess CO₂ uptake, models suited for studying natural CO₂ variations must include the whole spectrum of biological, chemical and physical processes. Such models, consisting of a few boxes, have been used to investigate possible causes of the glacial-postglacial CO₂ variations (e.g. Siegenthaler and Wenk, 1984). Experiments with three-dimensional models of the oceanic carbon cycle have begun (Maier-Reimer and Hasselmann, 1987; Sarmiento et al., 1988); they allow the inclusion of ocean dynamics phenomena. In addition, it appears worthwhile to study two-dimensional models with relatively high resolution, since they are less complex and require less computing time than 3D models.

Recommendations

Detailed recommendations have been included above in the discussion for individual subjects. In summary, observational and modelling efforts are necessary for the following issues:

- atmospheric observations of concentration and isotopic composition of CO_2 ;
- air/sea exchange of CO_2 , especially dependence on wind or other parameters;
- marine chemistry: possible role of CaCO_3 dissolution for sequestering man-made CO_2 ;
- ocean circulation: pathways of man-made CO_2 to depth, with emphasis on the high-latitude regions; possible modifications of the oceanic circulation;
- role of land biomass; CO_2 fertilization;
- natural oceanic carbon cycle: interplay of biological, chemical, and physical processes; data on carbon cycle history from sediments and polar ice cores;
- continuing development of a hierarchy of ocean models.

The carbon cycle is a complex system which has to be studied in an integrated way, and it would not be appropriate to consider only the oceanic part of it in isolation. On the other hand, it is closely linked to other issues, especially the ocean's role in the global climate. For these combined problems, oceanic tracer studies play a very essential role. Geochemical and isotopic tracers, particularly ^{14}C , carry information in an integrated way, e.g. on deep ocean ventilation, and thus are an important complement to the physical oceanographic methods; correspondingly, they have to be incorporated appropriately into future oceanographic programmes, e.g. WOCE. A special effort will be necessary to interpret, in the most efficient way, the results on transient tracer fields. These data contain a wealth of information on oceanic circulation; however, due to their four-dimensional nature, it is not an easy task to extract all the information they contain. Here, a combined effort by physical and tracer oceanographers will be necessary and will be most fruitful for the oceanographic community.

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DISTRIBUTION AND SPECIATION OF THE MICROBIAL POPULATION IN THE OCEAN SURFACE MICROLAYER

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As early as 1917, Naumann drew attention to the surface microlayer at the air/water interface. He coined the term neuston for its microbial components, discriminated between bacterio-, phyto-, and zooneuston and suggested that the neuston communities differed in structure from the plankton communities. Studies performed during the last two decades have confirmed his suggestion and reported the surface microlayer in aquatic environments to have a different microflora and a concentration of microorganisms that per unit volume exceeds that of the subsurface water by orders of magnitude. This ratio is named the enrichment factor, E or EF, and values of 10^2 - 10^3 have frequently been reported, e.g. from the Arctic, the Atlantic and Pacific Oceans.

All natural waters contain dissolved organic matter originating from dead or living organisms (mainly phytoplankton) from the atmosphere, land, or human activity. Among these organic substances, those with high surface activity, low water solubility, and exhibiting surface hydrophobicity tend to accumulate at the air/water interface, offering the bacterioneuston a marked nutrient enrichment in oligotrophic environments. The chemical composition, formation, and stratification of the surface microlayer have been more frequently analyzed than the biological characteristics (for references see Norkrans, 1980; Kjelleberg, 1985). As the data often derive from samples collected in a few locations over brief periods of time, it is difficult to assess the temporal and spatial variability, and patchiness of the microlayer which surely occur (Carlson, 1983).

Interaction between the chemical strata, lipid- and protein-polysaccharide films, and microorganisms has been demonstrated. With the use of membrane samplers operating horizontally with minimum disturbance of strata and at depths in the range of 1-40 μm , i.e. collecting different amounts of subsurface water, the absolute numbers of bacteria in samples of the surface layers at the same sampling station were fairly constant. This indicates that the bacterioneuston layer may extend to a depth of approximately 1 μm . Only a strong interaction between the films and the bacteria seems to render the bacterial collection possible. Protozoa have been found associated with the bacterioneuston layer (Sieburth et al., 1976). Screen and drum microlayer samples (60-250 μm thick) may show the presence of phytoneuston, evidenced by microscopical work and/or deduced from analysis of chlorophyll a and phaeophytin. Flagellates, dinoflagellates, ciliates and diatoms are represented (Sieburth et al., 1976; Wandschneider, 1979), and even zooneuston may be present.

1. The Bacterioneuston Layer

A possible microbial adhesion process at the air/water interface does not take place until the microbes are in close enough proximity to the surface films to allow the physicochemical interactions to come into play. The bacteria can arrive there randomly by long distance transport (e.g. diffusion, convection or upwelling) through the water column or by short distance transport, as by chemotaxis. The most important transport vector, however, is bubbles rising through the bulk water, i.e. a gas/liquid interface system scavenging organic substances, bacteria and other particles. At any moment about 1% of the ocean is covered with bubbles, and approximately 10^{18} bubbles break every second. At the surface, the bubbles eventually burst into jet and film drops. The bacterial concentration in jet drops has been estimated to be 1000 times greater than in the water column. The Blanchard group has summarized the information from their studies of this system with respect to the mechanisms for bacterial interaction at its interface (Blanchard, 1983).

From a taxonomical point of view, the bacterioneuston is poorly characterized. When characterized, the genus *Pseudomonas* has repeatedly been reported as predominant in the Caribbean Sea, and in the Atlantic and Pacific Oceans. Besides *Pseudomonas*, the genera *Chromobacterium* and *Micrococcus* were generally distributed in the Black Sea, the Caspian Sea, and Alaska Bay. In the Pacific Ocean, *Vibrio*, *Aeromonas* and *Spirillum* species occur frequently. The same species were also reported present in the air above the surface of the Pacific Ocean, transferred to the air by bursting bubbles and foam.

Field studies have given phenomenological information about the bacterial enrichment at the air/water interface. To unravel the mechanisms behind this phenomenon, we have to rely on laboratory experiments and model systems initially, even if they inevitably represent great simplifications of the dynamic systems in nature. As always in ecology research, the validity of the concept deduced from a model system approach has to be proved or disproved by renewed field studies.

2. Selection characteristics for adhesion of water column bacteria to the sea surface microlayer.

Molecules adsorbed at a clean air/water interface introduce their surface characteristics onto the water. The new interface, different from that of bulk water, will exert a selection among the bulk water bacteria. Due to their small size, the bacteria may be regarded as non-living colloid particles whose initial interactions are directed by physicochemical reactions such as double layer phenomena, electrostatic attraction, or hydrophobic interaction, which are discussed in bacterial interface studies, e.g. Marshall (1976), or Gristina (1987). The bulk bacteria with the physicochemically best-fitted interaction potential will be selected. In later stages of interaction, when bacteria express their biological activity, nutrient quantity and quality of the surface microlayer can affect the selection. The bacteria may also be selected for their ability to overcome various potentially detrimental conditions at the air/water interface.

2.1 Selection by physicochemical processes

The following refers to model system studies of the bacterial interaction at a surface film. An appropriate film-forming substance, such as, triglycerides, saturated or unsaturated acids, octadecylamine, a zwitterionic phospholipid, or proteins, was applied to the air/water interface of an aqueous subphase containing suspended bacteria, all originally isolated from the marine environment. The amount of film-substances was calculated to correspond to "mono- or decalayer" under the static film conditions used. An enrichment occurred in all experiments and varied with (i) the bacterium used; (ii) the thickness of the film; (iii) the cell density in the bulk solution. E decreased about a hundred fold for *S. marinarubra* with increases in the number of subsurface cells from 2×10^6 to 50×10^6 cells/ml, possibly due to a decrease in available "film-sites" up to a point of saturation (Norkrans and Sörensson, 1977).

The previous proposal of bacterial interaction at sites in, or just beneath, the surface film is supported by surface balance studies in which the behaviour of various monolayered films, with and without bacteria, was compared. The lipids were spread to a gaseous monolayer and compressed to a condensed state by a barrier moving in the surface balance. The bacterial interaction was indicated by an increase in the surface pressure at a given area per molecule. As could be expected from the E values obtained in the accumulation studies, *S. marinarubra* showed the strongest interaction and the greatest strengthening of films among the bacteria examined, except for a cellwall-less *Acholeplasma* sp., which has its lipid bilayered membrane exposed (Kjelleberg et al., 1976). As part, or all, of the outer surface of bacteria is hydrophobic, it can be deduced that bacteria tend, to a varying degree, to adhere to any non-aqueous phase. This is a result of avoidance of water, ultimately due to the strong self-attraction of the water molecules. The hydrophobicity is governed by particular molecules or a group of molecules. These may be proteins, lipoproteins or lipopolysaccharides localized on the cell surface or on appendages, such as fimbriae. The hydrophobicity of *Serratia marcescens* is coupled to surface-localized red pigments, prodigiosins, produced at late growth phases of wild cells but not by white, pigment-less mutant cells, the former being adhered, the latter not.

If a general positive correlation exists between the different degrees of hydrophobicity and the varying tendencies for interaction observed in enrichment experiments, one would expect a higher average hydrophobicity of surface bacteria than of bulk bacteria in natural environments. This idea was supported when bacteria isolated from different stations on the Swedish west coast were metabolically tritiated and run in hydrophobic interaction chromatography. The results indicated a higher degree of hydrophobicity of the bacteria at the interface compared to those in bulk water (Dahlbäck et al., 1981).

Hydrophobic interaction is the most important physicochemical factor for bacterial adhesion at the surface films; it is strong and the adhesion can be irreversible. Surface balance studies (Kjelleberg and Stenström, 1980) also revealed charge-charge interactions which are effected by the surface charge both of the films and the bacterial

surface. Furthermore, the interaction also depends on the architecture of the film which is very much conditioned by the magnitude of lateral cohesive forces between the hydrocarbon chains. If the surface molecules are separated sufficiently to prevent inter-chain reactions, as in the gaseous monolayer, or if the lateral cohesion is strong enough to bring about and maintain island formations, as can be the case for straight-chain fatty acids, the possibility for microbial interaction is enhanced, as reflected in increased surface pressure. In in-situ experiments of sea surface films, a correlation between the total number of bacteria and high surface pressure values has been obtained (Williams et al., 1980).

2.2 Selection by nutritional conditions.

Although ocean water is considered to be the most constant oligotrophic habitat in the biosphere, interfaces on or in the water column offer considerable enrichment of nutrients. In regard to low nutrient conditions, the heterotrophic bacteria have been divided into two large groups, which have been given different names over the year: oligotrophs (K-strategists, autochthonous bacteria) and the copiotrophs (r-strategists, zymogeneous bacteria) even if our classification - as always - is too rigid to fully reflect nature where transition forms appear.

Oligotrophic bacteria have been defined as those whose survival in nature depends on their ability to multiply in habitats with a low average nutrient flux ($C\ l^{-1}\ h^{-1}$ ranging in amounts from undetectable to not exceeding 0.1 mg) and to survive for long, uninterrupted periods without energy-yielding substrates, but also at transient enrichments. In contrast, the copiotrophic bacteria grow where the nutrient flux is at least 50-fold higher than in the former case and does not drop to zero for any prolonged periods. Nutrient abundance favors their competitiveness and survival, but they are able to adapt to low nutrient starvation conditions (Poindexter, 1981).

The adaptation of marine copiotrophic bacteria to starvation conditions involves a miniaturization (Morita, 1985) or a "dwarfing" (Humphrey et al., 1983) by fragmentation and a continuous reduction in size of the cells of up to two thirds. The increased surface/volume ratio favors the uptake potential. The cell numbers increase by up to 80 % at the same time. Almost all cells are viable. The dwarfing phase was shown to be one of intense metabolic activity. In some strains, the small starved cells seem to increase their surface hydrophobicity concomitantly with an increase in binding. Whether an irreversible adhesion at the air/water interface can be strengthened by production of adhesive polymers, as is the case at a solid/liquid interface, is undecided.

Most bacteria in the ocean are small; less than 0.5 μm . The question has been asked: Are these bacteria inherently small oligotrophs that are actively growing in low nutrient waters, or are they copiotrophs in a state of starvation? In spite of their inability to grow in low nutrient water, they can be readily isolated from such sources. Small bacteria found in the deep sea water of the Pacific Ocean have been reported to represent the same species as those in the upper ocean water. They may derive from large bacteria in rich nearshore waters which have been

transported to the open ocean and further down to the deep waters, reduced in size as a response to the ambient low nutrient conditions. Such a course of events has been assumed to be a general one and designates these small bacteria as copiotrophs.

A selective enrichment of copiotrophic bacteria at the nutrient rich surface microlayer can be expected. The expectation is not only founded on the availability of nutrients, but also on the enhanced adhesion potential (the aforementioned increase in surface hydrophobicity) that the copiotrophs may develop during starvation. A larger fraction of copiotrophs, as compared with oligotrophs, at the surface microlayer was concluded from results obtained in the Arctic Ocean (Dahlbäck et al., 1982). The abundance of nutrients does not offer the oligotrophs any advantage. They are most likely outmatched by the copiotrophs. This is all the more probable as their weakly discriminating uptake system involves a lowered ability to restrict the entry of toxic substances reported to be present at high concentrations in the surface microlayer.

Adhesion is not an "all or nothing" phenomenon. An exchange of copiotrophic bacteria between interface and bulk has been shown in experiments (Hermansson and Dahlbäck, 1983) designed in the same way as the early ones for determinations of bacterial enrichment (E) at lipid films, with the exception that in this case a tritiated film substance, shown not to diffuse into the bulk, was spread. Test bacteria with different E-values were used. The enrichment of cells at the interface was negatively correlated to the ratio of labelled cells in the bulk/labelled cells at the interface. It was concluded that high accumulation involves a firm adhesion at the interface, a low exchange between the interface and the bulk, and a long period of adhesion at the interface, factors that may act to stabilize a bacterioneuston layer. The dynamic behaviour of a copiotroph at the interface has been described as a cycle: starved, small, dwarf-like bacteria, suggested to be primary colonizers, adhere to the interface, utilize the accumulated nutrients for growth, increase in size, divide, leave the interface, but return and adhere to an interface after a period of starvation and "dwarfing".

Considering the broad spectrum of organic substances that may be present at the surface microlayer, we would assume a selection process in which heterotrophs will be selected because of their versatility with respect both to kind and number of organic compounds that they can use as energy and carbon sources, e.g. the pseudomonads. We have, however, hardly any experimental support for this assumption, as the degradation potential of bacterioneuston generally has been tested only for lipolytic, proteolytic and amylolytic activity against a very limited number of compounds within the substance classes concerned. Studies of isolates from surface microlayer and bulk water bacteria of the Arctic Ocean (Dahlbäck et al., 1983), suggest that the surface layer bacteria display the highest diversity as concerns degradable substrates, i.e. the highest "capacity index". There are experimental indications that the interface as such, has some influence on the degradability. Surface active substances are more easily degraded at an interface than in the bulk (Hermansson and Dahlbäck, 1983).

2.3 Selection for resistance to detrimental factors.

Intense solar radiation, rapid temperature and salinity fluctuations, and the presence of toxic organic substances and heavy metals at high concentrations are potentially detrimental factors that can exert a selective pressure on the microbes in the surface microlayer and effect the microbial composition of the community.

Microbes surviving and proliferating at the air/water interface must possess high UV-resistance. Isolates from the subsurface water have been reported as markedly more UV sensitive than those obtained from the bacterioneuston layer. Bacteria with DNA with a high GC mole percent value, and consequently a low thymine content and low probability for thymine dimerization, may be able to better withstand insolation (Marshall, 1976). This could be the case for pseudomonads characterized by GC values between 57 and 70%, i.e. in the upper range for bacteria.

Very few genetic aspects of surface microlayer bacteria have been considered. The finding of an increase in hydrophobicity and irreversible binding at the interface as a starvation response (Humphrey et al., 1983) was mentioned above. It has been referred to as a "responsive system" under genetic control (Silverman et al., 1984). The cells sense the environmental nutrient concentration. They respond by a rearrangement of molecules at the cell surface, with or without production of new substances, with an increase in hydrophobicity as a result. The genetic control of an analogous *E. coli* system, which is regulated by the osmolarity of the culture medium has been fully proved. The interest for genetic studies will probably increase now as plasmid control has been evidenced for adhesiveness of some bacteria (Marshall, 1985).

A field study revealed a higher frequency of pigmented, Hg- and antibiotic-resistant bacteria in the surface microlayer than in the bulk water (Hermansson et al., 1987). This may reflect a response to some of the aforementioned detrimental factors at the surface. As the resistances observed are often encoded on plasmids and high numbers of plasmid-carrying strains were found among surface isolates, a genetic exchange at the surface microlayer seems probable. The dense population at the bacterioneuston layer with close cell contacts seems to offer a suitable environment also for other kinds of genetic transfer, such as conjugation. Even extracellular DNA has been discussed for genetic exchange via transformation in the marine environment (Paul et al., 1987).

Recommendations

1. There is a need for in situ studies where the biological composition as well as the chemical composition of the same surface microlayers are analysed.
2. Mechanism studies, in model systems, and a few in situ studies have given some ideas about factors that may govern the selection of interface bacteria and the speciation of the interface population but further investigation is needed to validate them.
3. More studies of systems are needed where the various competitive effects between different interface bacteria can be analysed and the succession of organisms can be followed.
4. Microbial activity, microbial degradation and consumption of the chemical substances in the surface microlayer in situ are almost unknown and need to be investigated.

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MICROBIAL PRODUCTION AND DESTRUCTION PROCESSES IN SEAWATER; ACTIVITIES IN THE OCEAN SURFACE FILM

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Ocean surface layers are conceptual entities used in transport models but, on the other hand, they are also real. A conceptual definition is given by the laminar film model (Liss and Slater, 1974; Broecker and Peng, 1974) which proposes a surface film of approximately 30 μm in thickness (Peng et al., 1979) controlling the flux of substances whose transfer across the air-water interface is limited by liquid transfer resistance (Liss, 1975; Liss and Merlivat, 1986). Ocean surface layers are also defined by real properties, especially by the presence of a physicochemically defined organic film and a biologically defined neuston layer. These properties have been reviewed by several authors (Wangersky, 1976; Norkrans, 1980; Lion, 1984; Lion and Leckie, 1981; Liss, 1975). Chemical fractionation of substances in the surface film has been reviewed by McIntyre (1974) and Duce and Hoffman (1976), and the physical and chemical effects on gas exchange by Liss (1977) and Zafiriou (1986). However, it is unclear whether, and to what extent, microbial activities may be involved. Micro-organisms are well known as powerful mediators of production or destruction of various substances. Microorganisms are living beings and their existence in ocean surface layers occurs under particularly stressful conditions, e.g. intense solar radiation, salinity fluctuations, temperature fluctuations, and adverse effects of chemical films (e.g. Norkrans, 1980). On the other hand, the surface environment may also provide some positive effects for microorganisms, such as better availability of substrates concentrated in the surface film (e.g. Norkrans, 1980). Therefore, it is a priori impossible to decide whether bacteria in the surface film are active at all under in-situ conditions and whether their activity is different from that in bulk water or not. To get this kind of information it is imperative to do experiments.

The main goal of experiments concerning exchange processes between ocean and atmosphere is to establish whether the bacterial activity higher in the surface film than in the bulk water and, if so, by which enrichment factor? Bacterial activity may be understood (1) as the reaction rate per one microbial cell or, (2) as the reaction rate per unit of surface film. In both cases, the surface film has to be sampled. There are many different techniques (see Norkrans, 1980) which collect surface film samples of different thickness, ranging between 1 and 1000 μm .

The lipid film of the surface has a thickness of approx. 1-10 nm. Bacteria which interact with this lipid film form a bacterioneuston layer approx. 1 μm thick. In order to obtain a representative sample of bacterioneuston which is not too diluted with bacteria from the bulk water (the bacterioplankton), it is imperative to use a sampling

technique which removes only a very shallow surface layer. The use of hydrophobic Nucleopore filters gives thinner samples ($\approx 1 \mu\text{m}$), than the use of screens ($\approx 100 \mu\text{m}$) or the use of freezing ($\approx 1000 \mu\text{m}$). In fact, Kjelleberg et al. (1979) found that collecting with Nucleopore filters gives the highest enrichment factor (up to 10^4 with respect to number of bacteria).

There is no doubt that the total number of microorganisms is significantly higher per volume of surface layer than per volume of bulk water, provided the sample thickness is sufficiently thin (Norkrans, 1980; Hardy & Apts, 1984; De Souza Lima, 1985). Very little is known, however, about the enrichment of specific groups of microorganisms. Model studies indicate that the hydrophobicity of the cell coat is an important factor for adhesion to the air-water interface (Dahlbäck et al., 1981), but the actual interaction also depends on the chemical nature of the surface film (see Norkrans, 1980).

More important than the enrichment factor of the number of microbes is the enrichment of their activities, i.e. the enrichment of the total rate of a specific reaction. Although total bacteria are enriched in the surface layer, specific activities may not be enriched, since either the bacteria having this activity do not adhere at the water-air interface, or their activities are inhibited as soon as they attach to the surface layer and experience new environmental stress situations. The assessment of activity enrichment has to be done under in-situ conditions. The sampling of surface film and subsequent assay of activity in test tubes gives unreal results, since surface microorganisms have then been transferred into a bulk suspension. A good example of the conceptual and methodological problems involved is given by Hermansson & Dahlbäck (1983). The results of these authors indicate, however, that the activity per microbial cell may in principle not be much different in the surface film than in bulk water, and that for some substrates (like long chain fatty acids) and for low substrate concentrations, degradation may occur much faster in the surface film. A similar conclusion was drawn by Carlucci et al. (1985) who observed that in oligotrophic water the microbial degradation of amino acids was faster in the surface film than in subsurface water. However, production or consumption by bacterioneuston has to be assessed for each individual trace substance under in-situ conditions. The activity of bacterioneuston (in most cases even of bacterioplankton) towards trace gases such as H_2 , CO , CH_4 , N_2O , $(\text{CH}_3)_2\text{S}$, NMHC, etc. is unknown. It is also unknown how the activity may change with time of day, climate, etc. The assessment of particular microbial activities in the surface film is especially difficult, since on the one side, bacteria permanently exchange between surface film and bulk water (Hermansson & Dahlbäck, 1983) and on the other side, bacteria adapt to the specific conditions of the new environment as soon as they reach the interface (Kjelleberg et al., 1982).

Although there are many uncertainties concerning the actual influence of microbial activities on the exchange of atmospheric compounds over the ocean/air boundary layer, it seems obvious that such processes, in addition to physical factors, have a potential impact on exchange processes. The bacterioneuston may constitute a source and/or a sink for various atmospheric compounds in addition to the source or sink activities in the bulk water. Whereas the latter activities can be deter-

mined by measuring the degree of supersaturation or undersaturation of the surface water with respect to the atmospheric mixing ratios, the former activities can presently not be determined, since techniques for measuring flux rates directly are not available. Recent observations indicate however, that the surface film is active in degrading atmospheric trace gases such as H_2 and CH_4 , and thus, may reduce the net flux of these gases from the surface water into the atmosphere (Schütz et al., 1988; Conrad & Seiler, 1988). In addition to the surface film, microbial activities are of great importance for the formation of vertical gradients in the water column. Production and consumption processes operate independently and their reaction rates may change significantly with water depths. Steep gradients have been observed for some trace gases which, in addition, may exhibit strong diurnal variations (e.g. Conrad & Seiler, 1986; Andreae, 1986). For determination of ocean atmosphere exchange it is absolutely necessary to take into account that microbiologically formed gradients in the upper one meter of the water column as well as microbial production and consumption reactions within the surface film may be existent. Otherwise, flux determinations which are based on concentration measurements in surface water samples may be unreliable.

It is becoming clear, that the concentrations of many trace substances (CO , H_2 , CH_4 , DMS) in marine surface water are partially the result of simultaneous bioproduction and bioconsumption. It is presently unknown which species of bacteria are able to accomplish degradation of atmospheric trace compounds that are so low in concentration that the biosynthesis of the enzyme apparatus to scavenge them may cost more energy than their degradation can provide (Conrad, 1984). The threshold concentration of biodegradability is a central question for the cycling of trace substances in marine environments. To elucidate the mechanisms of microbial production and destruction processes and their role in the transfer of trace compounds between ocean and atmosphere, it will be necessary to concentrate on the following questions:

1. Which microbial species contribute to production and destruction?
2. By which biochemical pathways are the activities accomplished?
3. What are the kinetics (V_{max} , K_m , threshold) of the conversion processes leading to production or destruction?
4. Do the processes contribute to the efficiency of microbial proliferation and what is the productivity of the microorganisms?
5. Are there differences in quality and quantity of microbial processes between bacterioneuston and bacterioplankton?
6. How do these processes interfere with physical transfer between gas and aqueous phase?

To answer these questions it will be necessary to intensify laboratory studies under defined experimental conditions in addition to conducting investigations in-situ.

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MARINE ALGAE AS A SOURCE OF DIMETHYLSULPHIDE EMISSIONS TO THE ATMOSPHERE.

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Many algae produce dimethylsulphonium compounds that react with halides to form methyl halides (White, 1982). The most abundant is dimethylsulphonium propionate (DMSP) which, on cleavage, yields dimethylsulphide (DMS) and acrylic acid. Methyl halides and DMS are emitted to the atmosphere from the oceans as first reported by Lovelock et al. (1972, 1973). Recent work has shown that biogenic DMS is an important component of the global sulphur cycle, yielding a flux of about 1.1×10^{12} mol S y^{-1} across the air/sea boundary (Andreae, 1986). In the atmosphere the oxidation products of DMS include methane sulfonate, sulphur dioxide and sulfate, all of which influence the pH of rainwater (Charlson and Rodhe, 1982). Furthermore, DMS is now considered to be the main source of cloud condensation nuclei over the oceans (Charlson et al., 1987; Bates et al., 1987) with consequent influences on global albedo and climate.

For these reasons there is now considerable interest in the distribution of DMSP as the source of atmospheric DMS. Here we review present knowledge of the occurrence of DMSP in marine algae and of the biological processes that lead to the formation of DMS.

DISTRIBUTIONS AND PHYSIOLOGICAL SIGNIFICANCE OF DMSP

The presence of DMSP has been reported for a range of green, red and brown macroalgae (White, 1982; Reed, 1983), as well as in the seagrass *Zostera* (White, 1982) and the salt marsh grasses *Spartina anglica* (van Diggelen et al., 1986) and *S. alternifolia* (Dacey et al., 1987). Maximum reported concentrations are 15,500 and 9,000 $\mu\text{g S (g d wt)}^{-1}$ for *Polysiphonia* and *S. alternifolia* respectively.

Following the early work of Ackman et al. (1966) many species of marine phytoplankton in culture and from natural populations, including representatives of all the major classes, have been reported to produce DMSP and/or DMS. In a recent survey of cultured organisms, Keller et al. (1988) found that species of dinoflagellates, prymnesiophytes (in particular, coccolithophores) and chrysophytes contained the highest levels of DMSP. Maximum reported concentrations are generally in the range 200-400 mol DMSP m^{-3} cell volume (Dacey and Wakeham, 1986; Dickson and Kirst, 1987a,b; Keller et al., 1988) which are approximately equivalent, on a dry weight basis, to those reported for the red alga, *Polysiphonia* (Reed, 1983). Groups of marine phytoplankton that have been found to synthesise only small amounts of DMSP include the chlorophytes, cryptomonads and cyanobacteria.

The most generally accepted function of DMSP in marine algal cells is as an osmolyte. Changes in external salinity induce rapid changes in turgor pressure or cell volume, depending on whether or not there is a rigid cell wall, as water passes in or out (Vairavamurthy et al., 1985; Dickson and Kirst, 1986, 1987a,b; Young et al., 1987). A slow phase of osmotic adaption follows with the re-establishment of turgor pressure or cell volume. Control of the internal osmotic potential is achieved by changing the concentrations of ions and low molecular weight organic compounds (osmolytes), a process which depends on a supply of metabolic energy. Osmolytes include major photosynthetic products such as sucrose, mannitol and floridoside (Hellebust, 1976), as well as quaternary ammonium compounds (e.g. glycine betaine and homarine) and DMSP (Dickson and Kirst, 1986).

It would require less energy for algal cells to balance osmotic stress by using inorganic ions only. However, organic osmolytes are "compatible osmotica" (Brown, 1976) which also protect enzyme activity under conditions of low water potential. The restricted solubility of these compounds explains why algae often accumulate more than one osmolyte under severe hyperosmotic conditions.

DISTRIBUTIONS OF DMS AND DMSP IN THE OCEANS

There are uncertainties in the interpretation of DMS and DMSP measurements due to changes during sample preparation. It is usually assumed that DMS is in free solution although some may be released by enzymatic cleavage of DMSP when cells are damaged during sparging or filtration procedures. In the case of DMSP, which is generally measured as DMS released by treatment with alkali, such damage also leads to difficulties in distinguishing intra- and extra-cellular levels.

The highest concentrations of DMS and DMSP have been reported for blooms of organisms which show high internal levels of DMSP, in particular of dinoflagellates and of the prymnesiophyte, *Phaeocystis pouchetii*, in coastal waters. Values can reach 2,000 $\mu\text{g S(DMS) m}^{-3}$ and 50,000 $\mu\text{g S(DMSP) m}^{-3}$ (Andreae, 1986; Turner et al., 1988; S. Turner, unpublished observations on *Phaeocystis* blooms in the North Sea). In open ocean waters where phytoplankton blooms are less intense, corresponding values of 1,000 and 10,000 have been measured for coccolithophore populations (S. Turner and G. Malin, unpublished observations). As has been established with cultures (Dacey and Wakeham, 1986), it appears that the highest concentrations of DMS and extracellular DMSP are associated with active grazing by zooplankton.

Being dependent on the species composition as well as the total biomass of phytoplankton, levels of DMS and DMSP are extremely variable in the oceans both temporally and spatially. Andreae (1986) concluded from data on the distributions of DMS that the average annual fluxes of S(DMS) from the ocean to the atmosphere were comparable for tropical and temperate waters (2.2-2.4 $\text{mmol m}^{-2} \text{y}^{-1}$) and highest for coastal seas (5.7 $\text{mmol m}^{-2} \text{y}^{-1}$). However, the database is still small with very little information about DMSP, so that seasonal variability in high latitude oceans and spatial variability in coastal seas for S(DMS) fluxes remain poorly defined.

BREAKDOWN OF DMSP TO DMS

Within marine phytoplankton populations the measured S(DMS) appears to represent only a small proportion (ca. 10%) of the total S(DMS+DMSP). Apart from uncertainties in the actual measurements, there is the more general problem of defining the proportion of algal DMSP that is eventually lost to the atmosphere as DMS.

Several factors affect the conversion of DMSP to DMS, including plant (Cantoni and Anderson, 1956; Kadota and Ishida, 1968) and bacterial (Wakeham et al., 1987) enzymes, and chemical degradation (Dacey and Blough, 1987). Enzyme action appears the most important mechanism, either as a result of damage (e.g. grazing) and senescence of the algal cells leading to the direct release of DMS, or through the action of bacteria on dissolved DMSP. However, oxidation of DMS in the water column yields the non-volatile dimethylsulphoxide (DMSO) as a result of both biologically-mediated (Wakeham et al., 1987) and photochemical (Brimblecombe and Shooter, 1986) reactions. Also all these organic sulphur compounds can be utilised as growth substrates by heterotrophic organisms (de Bont et al., 1981).

The apparent discrepancy between the quantities of DMSP produced by phytoplankton in the oceans and of DMS released to the atmosphere has not been critically evaluated. During the development of algal blooms there is an accumulation of dissolved DMSP, with the possibility of significant utilisation by bacteria and conversion of the sulphur to compounds other than DMS.

FUTURE STUDIES

Physiological studies confirm that, with the relatively constant salinity of ocean water, the main causes of variability in DMSP production are related to taxonomic trends in the succession (both spatial and temporal) of phytoplankton. For this reason remote sensing techniques based on specific absorption and scattering properties of the different cell types are likely to provide important background information on the large scale distributions of source organisms, as shown already for the coccolithophores (Holligan et al., 1983), and the hydrographic conditions under which they occur. Such information will allow the development of improved sampling strategies for further measurements DMSP and DMS in the oceans that are needed for reliable determinations of the global flux of DMS to the atmosphere. Data on DMSP distributions (e.g. Turner et al., 1988) suggest that the potential for DMS emissions is considerably greater than recent estimates (Andreae, 1986), although this apparent discrepancy may well be due to undefined alternative sinks for DMSP.

Coastal seas, the littoral zone and salt marshes are all recognised as strong sources of atmospheric DMS which are of regional, if not global, importance. The main concern here will be responses to human disturbance of these environments. Already the increased frequency and intensity of blooms of *Phaeocystis* in the southern North Sea as a result of eutrophication (Lancelot et al., 1987) are likely to have had a significant impact on DMS emissions.

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FLUX OF VOLATILE SULPHUR SPECIES ACROSS THE AIR/SEA INTERFACE

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Dissolved sulphate ion, a highly soluble, non-volatile species, is the major sulphur reservoir species in the oceans. In order to be transferred across the air/sea interface, sulphur has to be reduced from the oxidation state +6 in sulphate to the oxidation state -2, which is characteristic of biogenic volatile sulphur species. This reduction is mediated by biological organisms, which have developed two major pathways for the reduction of sulphate to organic and inorganic sulphides: assimilatory and dissimilatory sulphate reduction (reviewed in Andreae, 1986). The dissimilatory process serves to support microbial respiration in environments devoid of dissolved oxygen but rich in organic matter, e.g. in the porewaters of anoxic sediments. The product of this process is hydrogen sulphide (H_2S). The fact that dissimilatory sulphate reduction only occurs in the absence of oxygen implies that it will only take place in environments which are essentially uncoupled from the atmosphere. The relatively small amounts of H_2S which can diffuse out of these systems into the overlying water column are usually oxidized biologically or abiotically before they can be exchanged across the air/sea interface. Only under very special circumstances, e.g. in tidal channels, can significant amounts of H_2S from dissimilatory sulphate reduction enter the atmosphere.

Assimilatory sulphate reduction has as its objective the biosynthesis of organic sulphur compounds which are used for various purposes by the organism, e.g. in aminoacids, proteins, etc. In the course of dissimilatory sulphate reduction, sulphate is attached to a protein carrier substance and reduced to the -2 oxidation state; the resulting sulphide is then incorporated into cysteine, which serves as the starting compound for all other biological sulphur compounds. These compounds may then be transformed by several pathways into volatile sulphur species which are eventually transferred from the oceans into the atmosphere.

The major volatile sulphur species in seawater is dimethylsulphide (DMS). This compound is formed by the enzymatic cleavage of its precursor substance, dimethylsulfonium propionate (DMSP), a major metabolite in many benthic and planktonic marine algae. DMSP appears to have an osmotic function in these algae (Vairavamurthy et al., 1985, and references therein). Current data suggest that the use of a sulphur osmolyte may be an adaptation to low nitrogen environments, since DMSP can replace some nitrogen-containing osmolytes of similar structure. This could explain the unexpectedly high DMS concentrations found in marine environments of relatively low productivity, and the consequently high DMS fluxes from these ocean regions to the atmosphere (Andreae, 1986; Cline and Bates, 1983). For as yet unknown reasons, DMSP is

enzymatically cleaved to release DMS and acrylic acid, which are subsequently excreted into the aquatic environment.

On the basis of large data sets from essentially all of the world's ocean regions, we can now estimate the flux of DMS across the air/sea interface: the current best estimate is ca. 1.1×10^{12} mol S yr⁻¹ (Andreae, 1986). This estimate is still subject to a large uncertainty, maybe as much as $\pm 50\%$, mostly due to the problems associated with the use of the "stagnant-film" model of air/sea gas exchange. Other major uncertainties in the air/sea exchange of DMS result from our still inadequate knowledge of the seasonal variability of this flux. Preliminary work suggests that this variability is high, especially in high-latitude regions. In view of the difficulty of representative sampling in these areas when using oceanographic research vessels, it would seem very desirable to have means of estimating DMS flux by remote sensing techniques. However, DMS concentrations in surface seawater seem to be rather poorly related to simple variables describing plankton density, e.g. chlorophyll concentration. This is due to large differences in DMS production rates between algal species. It may be possible to develop more sophisticated techniques involving scanning spectrometers or regionally specific algorithms which would make possible the estimation of DMS fluxes based on remote sensing.

Recent measurements of DMS in the marine boundary layer and in vertical profiles through the marine troposphere show concentrations on the order of 30-150 pptv in the boundary layer, depending on geographical location and sampling season (Andreae et al., 1985; Ferek et al., 1986; Andreae et al., 1987; Andreae, unpublished data). These concentrations are consistent with a flux of DMS on the order of 1.1×10^{12} mol yr⁻¹, as estimated above, and with current views of the reaction rates of DMS with the OH and NO₃ radicals, the main removal mechanisms for DMS. The products of these reactions are SO₂, sulphate, methanesulphonate (MSA), dimethylsulfoxide (DMSO) and possibly other compounds. SO₂, which is subsequently oxidized to sulphate, appears to be the main reaction product in the marine atmosphere, except at high latitudes, where the production of MSA may rival or exceed that of SO₂ (Ayers et al., 1986; Berresheim, 1987). The concentrations and fluxes of these reaction products are also reasonably consistent with a DMS flux of the magnitude indicated above (Andreae, 1986).

Carbonylsulphide (COS) is the most abundant atmospheric sulphur species in the remote troposphere, with an average concentration near 500 pptv. Due to its low reactivity in the troposphere and its correspondingly long residence time (on the order of one year), it is the only sulphur compound which can enter the stratosphere (with the exception of SO₂ injections during violent volcanic eruptions).

COS is present in surface seawater at concentrations of a few tens to hundreds of picomole L⁻¹ (Rasmussen et al., 1982; Ferek and Andreae, 1983, 1984; Turner and Liss, 1985; Andreae, 1986). The observed concentrations are almost always higher than the equilibrium concentration relative to the overlying atmosphere, so that a net sea-to-air flux exists essentially from the entire ocean surface. Johnson (1981) has speculated that the ocean could be a sink for COS due to its hydrolysis at the slightly alkaline pH of seawater. This suggestion is clearly not

supported by the measured COS supersaturation ratios across the air/sea interface.

COS is produced by photochemical reactions from dissolved organic sulphur compounds (Ferek and Andreae, 1984), resulting in strong diel variations of the COS concentration in surface seawater, with a pronounced midday maximum. Laboratory experiments with seawater and with solutions of organosulphur compounds in distilled water showed that seawater sulphate does not participate in the reaction, and that only the presence of dissolved organic sulphur compounds, dissolved O_2 and light are necessary to produce COS. It appears that the role of organisms in the production of COS in seawater is limited to the synthesis of dissolved organic sulphur compounds which are then abiotically photolyzed to COS. The mechanism of this reaction is not known at this time, but it is likely that short-lived, photochemically produced radicals (e.g. OH) are involved.

In order to obtain a realistic estimate of the flux of COS from the oceans to the atmosphere one has to integrate the supersaturation over the diel cycle and over the different light fluxes, dissolved organic sulphur concentrations, and wind conditions found in different ocean regions. Previous estimates clearly do not satisfy this requirement, and can therefore be only considered rough guesses. On the basis of samples collected without consideration of the diurnal cycle and only separated into coastal and open ocean values, Rasmussen et al. (1982) have estimated a global COS flux from the oceans of ca. $10 \times 10^9 \text{ mol yr}^{-1}$. Based largely on coastal data and interpolation from an observed relationship of DMS and COS, Ferek and Andreae (1983) have estimated a global flux of ca. $15 \times 10^9 \text{ mol yr}^{-1}$. The inclusion of more data from the open oceans in temperate and tropical regions resulted in a refined estimate of the global ocean source flux of COS of $11 \times 10^9 \text{ mol yr}^{-1}$ (Andreae, 1986).

There are few data on the concentration of dissolved H_2S in surface seawater, and few reliable measurements of H_2S in the marine atmosphere, therefore the air/sea exchange flux of this compound is difficult to estimate. H_2S is oxidized rapidly in oxygenated seawater: Half-lives on the order of a few hours are reported (Almgren and Hagström, 1974); other workers have found values as high as 50 hours, however (Chen and Morris, 1972). The most reliable measurements appear to be those of Millero et al. (1987), who found a half-life of 26 hours at 25°C . G.A. Cutter (pers.comm., 1987) has recently developed a technique for the determination of H_2S in seawater and has observed concentrations of 0.1 to 1.0 nmol/L in surface seawater from the Atlantic Ocean. The production mechanism of this H_2S remains unclear, but its vertical distribution in the ocean suggests that bacterial reduction in microbial micro-environments may play an important role. It must, however, be remembered that biological processes, e.g. in plants, can result in the production and release of substantial amounts of H_2S even in the presence of oxygen. This is especially true in the presence of high ambient sulphate concentrations, as is the case in seawater.

H_2S has been observed in the marine atmosphere at levels of a few pptv to a few tens of pptv (Slatt et al., 1978; Delmas and Servant, 1982; Herrmann and Jaeschke, 1984; Cooper and Saltzman, 1987). Cooper

and Saltzman (1987) found a positive interference in the determination of H_2S by the method used by the previous authors (trapping on AgNO_3 -impregnated filters and determination by the quenching of the fluorescence of fluorescein mercuriacetate) and suggested that the true concentrations of H_2S in the marine boundary layer do not exceed 10 pptv. At these levels, H_2S in the atmosphere is near thermodynamical equilibrium for the concentrations in surface seawater observed by Cutter.

To obtain an estimate of the rate of H_2S oxidation in the marine atmosphere, we can simply use an average concentration of 10 pptv or $0.4 \text{ nmol H}_2\text{S m}^{-3}$ (STP) with a scale height of 2 km, a diurnally averaged OH concentration of $2 \times 10^6 \text{ molec cm}^{-3}$, and the measured reaction rate for the oxidation of H_2S by OH ($5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$ (Cox and Sheppard, 1980)). The resulting estimate, $90 \times 10^9 \text{ mol yr}^{-1}$, is an upper limit for the sea-to-air flux of H_2S , and is much smaller than the DMS flux of $\text{ca } 1.1 \times 10^{12} \text{ mol yr}^{-1}$. It is not clear, however, if the source of the H_2S found in the marine troposphere is necessarily the ocean surface or if other processes could be responsible for its presence. For example, advection from coastal regions, where H_2S is emitted from salt marshes, may supply some of this H_2S . On the other hand, McElroy et al. (1980) have speculated that atmospheric reactions of COS and CS_2 with OH radical could produce the necessary amounts of H_2S . However, this suggestion has not yet been verified experimentally.

The presence of CS_2 in seawater was first observed by Lovelock (1974) who measured an average concentration of $14 \text{ pmol S}(\text{CS}_2) \text{ L}^{-1}$ in 35 samples taken in the open Atlantic Ocean. Inshore values were about an order of magnitude higher. Turner and Liss (1985) also report the presence of high levels of CS_2 in coastal waters off England, but give quantitative information for only a few samples with values near $300 \text{ pmol S}(\text{CS}_2) \text{ L}^{-1}$. They found substantially higher concentrations in the low salinity region of an estuary (up to $\text{ca. } 2 \text{ nmol S L}^{-1}$). It is possible that much of the CS_2 found in coastal waters is the result of the diffusion of this substance from the porewaters of the underlying sediments. This would be consistent with the relatively high concentrations and fluxes of CS_2 observed in coastal marsh environments (Adams et al., 1981; Steudler and Peterson, 1984). CS_2 could be formed there either by fermentation reactions of organosulphur compounds or by "pulp-mill" type reactions of terrigenous plant matter with dissolved polysulphides originating from bacterial dissimilatory sulphate reduction.

We have recently determined CS_2 in open ocean and coastal seawater from the North Atlantic, and have observed mean concentrations of 16 ± 8 and $33 \pm 19 \text{ pmol S}(\text{CS}_2) \text{ L}^{-1}$, respectively (Kim and Andreae, 1987), somewhat higher than Lovelock's results. From these data, we estimate a flux of $\text{ca. } 7 \times 10^9 \text{ mol S yr}^{-1}$ in the form of CS_2 from the world ocean surface, about 0.6% of the DMS flux.

In coastal waters, we have observed methylmercaptan and its oxidation product, dimethyldisulphide. Due to calibration problems, we have not been able to report quantitative data, but the concentrations of these compounds are always much smaller than those of DMS. The presence of dimethyldisulphide and a compound tentatively identified (on the basis of its retention time) as ethyl propyl sulphide in coastal waters

off England was reported by Turner and Liss (1985). Like CS_2 , these compounds may originate in the sediment porewaters and coastal marshes, rather than in the marine water column. Due to their consistently low concentrations even in coastal waters, and their absence in open ocean waters, they probably do not make a significant contribution to the global sulphur cycle.

We have recently proposed a feedback mechanism, by which the emission of sulphur gases from the sea surface could influence global climate through modification of cloud albedo over the oceans (Charlson et al., 1987): Biogenic DMS appears to be the dominant source of cloud condensation nuclei (CCN) over the remote oceans. Since the albedo of clouds increases with the CCN number density, an increase in CCN would lead to a decrease in the amount of solar radiation absorbed by the earth and consequently a global cooling. This process could be rather sensitive to variations in the global rate of DMS production, with temperature changes on the order of 2°C possibly resulting from a factor-of-two change in DMS flux.

Recommendations

- 1) There is a great need for the development and validation of methods to determine the flux of gases across the air/sea interface. The possibility of applying micrometeorological techniques, e.g. the gradient method, should be investigated for sulphur compounds emitted from the ocean, especially DMS.
- 2) The processes which control the concentration of DMS in surface seawater need to be further elucidated. The role of phytoplankton speciation and abundance in the production of DMS, of the bacterial cleavage of DMSP in seawater, and of the microbial oxidation of DMS deserve special attention here.
- 3) In view of the unsatisfactory state of knowledge on the role of H_2S in the global sulphur cycle, it appears essential that attempts should be made to determine the concentration of H_2S in surface seawater in a representative number of samples. Simultaneous H_2S measurements should be made in the overlying atmosphere, so that the magnitude (and direction, since the sea surface may well be even a sink for H_2S !) of the exchange flux can be estimated.
- 4) The photochemical processes by which COS is produced from dissolved organic sulphur compounds in seawater need to be investigated.

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METHANE AND LIGHT NON-METHANE HYDROCARBONS

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Measurements of the spatial and temporal distribution of methane and light non-methane hydrocarbons (LNMH) in ocean surface water and air can be summarized as follows. Surface waters in the open oceans have measured methane concentrations of about $0.5\text{--}2\text{ nmol L}^{-1}$ (Lamontagne et al., 1974; Scranton and Brewer, 1977). More recent measurements tend to be at the lower end of this range (Weiss, 1981; Seiler, personal communication). These concentrations imply that the surface water is always supersaturated with respect to atmospheric levels, but away from coasts and highly productive areas the degree of oversaturation is generally rather small (50% for the older measurements, but more typically 10-20% for the more recent data). In coastal and other especially productive regions, as well as in areas of anthropogenic hydrocarbon spillage, concentrations are often much higher and supersaturations of several hundred-fold are not uncommon (Scranton and Farrington, 1977; Weiss, 1981).

Measurements of light ($C_2\text{--}C_4$) non-methane hydrocarbons in surface sea waters have been made by Swinnerton and Lamontagne (1974) and recently by Bonsang et al. (1988), and values are typically $0.05\text{--}1.0\text{ nmol L}^{-1}$. Comparison with atmospheric measurements (Rudolph and Ehhalt, 1981; Bonsang et al., 1988) implies substantial supersaturation.

The data base of atmospheric measurements for CH_4 and other light hydrocarbons is considerably more extensive than that available for ocean waters. Methane is the dominant compound with an atmospheric concentration currently about 1.6 ppm (by volume). There is evidence that atmospheric levels of CH_4 are increasing with time at a rate somewhat in excess of $1\% \text{ yr}^{-1}$. This is of concern since methane is a "greenhouse" gas, with a predicted warming due to the present upward trend in concentration of about 20% of the equivalent effect for the current CO_2 increase.

Non- CH_4 light hydrocarbons occur at much lower levels, 0.02-1.5 ppb (see, for example, Bonsang and Lambert, 1985; Bonsang et al., 1988; Ehhalt et al., 1985; and Hov et al., 1984). These gases show distinct seasonal and interhemispheric variations in their atmospheric concentrations (Hov et al., 1984).

The main destruction and production mechanisms in water and air for these compounds can be summarized as follows. In shallow coastal waters methane may enter the water column from reducing bottom sediments. Anthropogenic hydrocarbon extraction activities are also possible entry routes. In the open oceans in situ production in the water column is a much more likely source. Scranton and Brewer (1977) postulate that such production is either by methane forming bacteria living in reducing

micro-environments in the water, or as a by-product of algal metabolism. The mode of formation of LNMH in ocean surface water is unknown, but is assumed to be biological. There is some evidence for higher concentrations in ice covered areas (Lamontagne et al., 1974).

Although thermodynamically unstable in oxygenated environments, there is little evidence for significant microbiological consumption or chemical breakdown of methane in ocean surface waters. The situation with regard to destruction mechanisms for LNMH in the oceans is essentially unknown, although unsaturated compounds are more likely to be subject to microbiological and/or photochemical breakdown than fully saturated ones.

In the atmosphere there are no significant in situ production mechanisms for CH_4 or LNMH, and all of these gases measured in air samples have come from external sources. The principal route for destruction of CH_4 in the atmosphere is reaction with OH radicals. This leads to the formation of CO and lesser amounts of HCHO and $\text{CH}_3\text{O}_2\text{H}$. The fate of LNMH in air is less well studied, but is likely to lead to similar products.

Ehhalt and Schmidt (1978) have calculated the sea-to-air flux of CH_4 to be in the range $0.08\text{--}1.0 \times 10^{12} \text{ mol yr}^{-1}$. Most estimates for open ocean situations are near the lower end of this range: Weiss (1981); Scranton and Brewer (1977) whose calculated flux for the western tropical N. Atlantic extrapolates to a global value of about $0.3 \times 10^{12} \text{ mol yr}^{-1}$; and Liss and Slater (1974) with $0.2 \times 10^{12} \text{ mol yr}^{-1}$. As already mentioned, supersaturations are often considerably greater in shallow coastal areas, leading to substantially higher fluxes from such waters. In spite of this, production by the oceans is still small in comparison with natural terrestrial sources (see later).

Rudolph and Ehhalt (1981) have used their measurements of C_2 and C_3 hydrocarbons in the air over the Atlantic, coupled with data for surface seawater concentrations from Swinnerton and Lamontagne (1974), to calculate sea-to-air fluxes for ethane, propane, ethene and propene. On the assumption that these measurements are representative of all ocean areas, the total global fluxes have been calculated. The flux of all four gases is similar and close to $0.06 \times 10^{12} \text{ mol yr}^{-1}$ for each of them, which is only marginally less than some of the estimates of the CH_4 flux out of the oceans. Using data recently obtained in the Indian Ocean, Bonsang et al. (1988) calculate somewhat higher fluxes which extrapolated globally yield sea-to-air fluxes for the individual gases in the range $0.06\text{--}1.0 \times 10^{12} \text{ mol yr}^{-1}$.

Niki et al. (1984) gives the following values for the fluxes of CH_4 into the atmosphere from various essentially terrestrial sources (all in units of $\text{mol CH}_4 \text{ yr}^{-1}$):

2- 4 x 10 ¹²	from Rice Paddy Fields
2-14 x 10 ¹²	from Natural Wetlands
4 x 10 ¹²	from Ruminants
<10 x 10 ¹²	from Termites
2- 7 x 10 ¹²	from Biomass Burning
1 x 10 ¹²	from Gas Leakage

This sums to a total terrestrial emission of about $20-40 \times 10^{12}$ mol CH_4 yr^{-1} . Comparing this to the ocean-air CH_4 flux given above, shows that at most the oceans contribute 5% of the amount from the land. This is an extreme value since it compares the lowest total land emission with the largest estimate of the ocean output. More realistically, the sea-to-air flux is in all probability less than 1% of the terrestrial input.

Recommendations

On the basis of the above discussion there would seem little reason for giving high priority to future studies of ocean-atmosphere fluxes of CH_4 . The situation may be different for light non-methane hydrocarbons since they have been much less studied. Furthermore, their emissions from the sea are on a par with those for CH_4 , whereas their inputs to the atmosphere from land sources may be substantially smaller than the corresponding fluxes of methane.

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NATURAL LOW MOLECULAR WEIGHT HALOCARBONS

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Measurements of the spatial and temporal distribution of natural low molecular weight halocarbons in ocean surface water and air can be summarized as follows. Methyl chloride, methyl bromide, and methyl iodide concentration data have been obtained in Eastern Pacific surface waters and show mean values of 228, 12.6, and 11.3 pmol L⁻¹, respectively (Singh et al., 1983). These measurements indicate that the oceans are supersaturated with respect to the atmosphere by several hundred per cent. Hoyt and Rasmussen (1985), however, found lower levels of both methyl chloride and methyl bromide, 50-100 pmol L⁻¹ and 2-5 pmol L⁻¹ respectively. Lower levels of methyl iodide in the open ocean have been reported by Lovelock (1975) and Rasmussen et al. (1982), although they did find elevated concentrations in areas of increased primary productivity. The latter data set also suggests some evidence for a seasonal variation.

Khalil et al. (1983) have shown the oceans to be supersaturated with chloroform in northern latitudes, with concentrations ranging from 13 to 33 pmol L⁻¹. Similar levels (9-19 pmol L⁻¹) have been reported by Hoyt and Rasmussen (1985), but Class and Ballschmiter (1986b) have found higher chloroform concentrations in the Atlantic (13-63 pmol L⁻¹). Bromoform concentrations of 3 pmol L⁻¹ have been measured in Atlantic surface water (Class et al., 1986). Elevated bromoform levels, with a mean of 39 pmol L⁻¹, have been reported in the Svalbard area of the Arctic (Fogelqvist, 1985).

Class et al. (1986) have also reported concentrations of dibromomethane (CH₂Br₂), bromodichloromethane (CHBrCl₂) and dibromochloromethane (CHBr₂Cl) at concentrations of 1.5, 0.6, and 0.6 pmol L⁻¹, respectively, in Atlantic waters. Other halocarbons that have been detected in seawater by G.C.-M.S. analysis include bromochloromethane (CH₂BrCl) (Hoyt and Rasmussen, 1985), bromoethane (C₂H₅Br) and bromopropane (C₃H₇Br) (Penkett, et al., 1985).

More data is available on atmospheric concentrations of halocarbons. Methyl chloride has been measured over the oceans in the range of 600-815 pptv (Rasmussen et al., 1980; Singh et al., 1983; Hoyt and Rasmussen, 1985). Rasmussen et al. (1980) found evidence of increased concentrations over equatorial regions compared to higher latitudes. Singh et al. (1983), however, observed no such elevation and concluded that methyl chloride was both temporally and spatially uniformly distributed.

Methyl bromide concentrations have been found to range from 9-26 pptv (Hoyt and Rasmussen, 1985; Singh et al., 1983; Penkett et al., 1985). Mean concentrations were found to be greater in the Northern Hemisphere than the Southern Hemisphere suggesting a significant anthropogenic

input. Methyl iodide concentrations have been reported in the range of 1.5 to 3.0 pptv over the open oceans (Penkett, 1982; Rasmussen et al., 1982; Singh et al., 1983). Elevated levels of both methyl bromide and methyl iodide have been observed by Singh et al. (1983) between latitudes of 30° N and 20° N. A second methyl iodide maximum was found at latitude 10° S. Rasmussen et al. (1982) also noted higher concentrations of methyl iodide in the tropics compared to higher latitudes. Evidence for a seasonal variation of methyl iodide has been found by both Rasmussen et al. (1982) and Singh et al. (1983), while Rasmussen and Khalil (1984) have noted a similar variation in methyl bromide levels in the Arctic. Maxima occur during the summer.

Chloroform has been detected over the oceans in concentrations ranging from 10-50 pptv, with most measurements nearer the lower value (Penkett, 1982; Khalil et al., 1983; Hoyt and Rasmussen, 1985; Class and Ballschmiter, 1986a). Higher levels have been observed in northern than in southern latitudes, consistent with an anthropogenic input. Khalil et al. (1983) have shown that the tropical oceans constitute the major oceanic source. Penkett et al. (1985) have reported measurements of bromoform over the North and South Atlantic of 0.85 and 0.58 pptv, respectively. Atlas and Tong (1987) have recently obtained similar results from the Pacific, although the mean concentration in the Northern Hemisphere (0.9 pptv) was lower than that in the Southern Hemisphere (1.2 pptv). In spite of this, the highest bromoform levels were observed at high northern latitudes. Class, however, has found higher levels of bromoform over the Atlantic (Class et al., 1986; Class and Ballschmiter, 1986a). A maximum of 26 pptv at latitude 10° N and high concentrations (460 pptv) at a ground level coastal site in the Azores were also observed. Berg et al. (1984) measured elevated levels of bromoform in the Arctic ranging from 2-46 pptv, with a seasonal maximum occurring during the spring.

Dibromomethane has been measured over the Atlantic at concentrations of between 1 and 4 pptv (Penkett et al., 1985; Class et al., 1986). Penkett found a mean concentration of 2.7 pptv in the Northern Hemisphere compared to 1.6 pptv in the Southern Hemisphere. Both groups noted maxima at low northern latitudes, while Class et al. also found elevated levels (50 pptv) at a coastal site. Dibromoethane has been detected over the oceans by Class et al. (1986) and by Atlas and Tong (1987) who reported measurements of 0.18 and 0.32 pptv for the North and South Pacific, respectively. Berg et al. (1984) have measured both dibromomethane and dibromoethane in the Arctic in the range of 3-60 pptv and 1-37 pptv, respectively. Rasmussen and Khalil (1984), also in the Arctic, have found lower and less variable levels of 4.7 - 5.6 pptv and 1.0 - 1.9 pptv. In addition, they observed seasonal variations with maxima occurring in late spring.

Dibromochloromethane, bromochloromethane and bromodichloromethane have been measured over the oceans at ranges of 0.1 - 1.0, <1.0, and 0.1 - 1.0 pptv, respectively (Class et al., 1986; Class and Ballschmiter, 1986a; Atlas and Tong, 1987). Bromochloromethane has been detected in the Arctic between 2.3 and 3.1 pptv by Rasmussen and Khalil (1984), who also found evidence of a seasonal variation.

Rather little is known about destruction and production mechanisms for

these compounds in water and air. For example, it is not established whether the halocarbons are produced directly or indirectly by marine organisms. Lovelock (1975) first proposed that the large kelp Laminaria was responsible for the high levels of methyl iodide he measured in a coastal region of South-West Ireland. Methyl iodide production has since been linked with some species of red, brown and green algae (Fenical, 1981; Geschwend et al., 1985; Newman and Geschwend, 1987). Manley and Dastoor (1987) associate the giant kelp Macrocystis with methyl chloride, methyl bromide and methyl iodide production, although the authors estimate that this production is likely to be less than 1% of the total oceanic source strength. In addition to methyl iodide, production of other halocarbons, including bromoform, dibromomethane, various polyhalomethanes, alkyl bromides and alkyl iodides has also been associated with species of macroalgae by the above authors, and also by Class et al. (1986).

Zafiriou (1975) has proposed that methyl chloride and methyl bromide are produced by reaction of methyl iodide with dissolved halide ions. Whether this production mechanism is backed up by oceanic concentration data is a matter of debate (see Singh et al., 1983; and Zika et al., 1984). White (1982) has suggested that production of methyl halides might occur indirectly by reaction of dimethyl sulphonium ions with halide ions.

The possibility of methyl halide hydrolysis has been investigated by Zafiriou (1975) and found to be slow at the temperature of ocean waters. Zika et al. (1984) have concluded that photolysis of methyl iodide in surface waters is also unlikely to be an important destruction mechanism. The use of methyl iodide as a potential mobilising agent in releasing metals from anoxic sediments has been proposed (Thayer et al., 1984), but this reaction is not likely to be an important sink. The behaviour of the other halocarbons in ocean surface waters does not appear to have been studied.

There appear to be no known mechanisms for the production of natural halocarbons in the atmosphere. The main sink of atmospheric halocarbons is by initial reaction with the hydroxyl radical, although methyl iodide has a photolytic sink. It appears likely that the reaction of the hydroxyl radical with methyl chloride is sufficiently slow for some of it to penetrate into the stratosphere where it can become involved in the catalytic destruction of ozone. There is current interest in whether any of the bromine-containing halocarbons have the ability to reach the stratosphere as it has been suggested that bromine is more efficient than chlorine in decomposing ozone (Wofsy et al., 1975).

Some estimates have been made of flux rates of these compounds through the air-sea interface. Singh et al. (1983) have estimated the oceanic source strength of methyl chloride, methyl bromide and methyl iodide to be $100 \times 10^9 \text{ mol yr}^{-1}$, $3 \times 10^9 \text{ mol yr}^{-1}$, and $2-4 \times 10^9 \text{ mol yr}^{-1}$ respectively. Liss and Slater (1974) have calculated a similar flux of $2 \times 10^9 \text{ mol yr}^{-1}$ for methyl iodide, although Rasmussen et al. (1982) proposed a larger source of $9 \times 10^9 \text{ mol yr}^{-1}$.

Khalil et al. (1983) have calculated the oceanic flux of chloroform to be $3 \times 10^9 \text{ mol yr}^{-1}$. The only other source strength that appears to have

been quantified is that of bromoform at $8 \times 10^9 \text{ mol yr}^{-1}$ (Liss, 1986) on the basis of bromoform levels in the Svalbard area that may not be representative of the oceans as a whole, as discussed earlier.

The importance of oceanic production of halocarbons can be seen from an outline of the atmospheric budgets of the methyl halides. Anthropogenic inputs of methyl chloride to the atmosphere have been estimated at $80 \times 10^6 \text{ mol yr}^{-1}$ (Pearson, 1982). The rate of methyl chloride release during biomass burning has been calculated to be $6\text{--}12 \times 10^9 \text{ mol yr}^{-1}$ (Crutzen et al., 1979). Harper (1985) has shown the ability of fungi to produce methyl halides, but as yet no attempt at quantification has been made. These terrestrial sources are, at the most, 10% of the estimated oceanic flux.

The anthropogenic release of methyl bromide to the atmosphere has been estimated to be $0.8 \times 10^9 \text{ mol yr}^{-1}$ (Wofsy et al., 1975). This is about 25% of the oceanic source strength. No significant terrestrial sources of methyl iodide have been suggested.

Recommendations

There are many directions in which future work can be taken. Few measurements of halocarbons, other than the methyl halides, are available in oceanic waters. Data is also needed on halocarbon levels in coastal waters in view of the elevated concentrations found there. Finally, more work needs to be carried out on the production mechanisms of halocarbons, especially as emissions have not yet been directly linked with marine phytoplankton found in the open oceans where macroalgae are absent.

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THE ROLE OF PHOTOCHEMICAL PROCESSES IN THE AIR/SEA EXCHANGE OF CHEMICAL SPECIES

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The physical interactive coupling between the oceans and atmosphere is well recognized and has been studied for many years. Far less attention has been given to the investigation of chemical interactions between the atmosphere and seawater. Most of the information related to such interactions is concerned with gas/liquid exchange processes where the magnitude and direction of a volatile's flux are the prime issues being addressed. The oceans have been found to be an important source or sink for many chemical species found in the atmosphere. Photochemical gas phase and heterogeneous processes in the troposphere are recognized to play an important role in influencing the concentration of many of these chemical species (e.g. CH_4 , CO , NO_x , H_2 , CH_3I , O_3 ,). Much less, however, is known about the nature and extent of photochemical effects on concentration and flux at the air/water interface or in the bulk water.

The interaction of solar radiation with seawater constituents has long been perceived as an important process in the marine environment. During the last 10 years the interest in the study of marine photochemical processes has increased dramatically as demonstrated by the rapid expansion of the associated literature. The literature related to natural waters photochemistry has been extensively covered in several recent general reviews (Zika 1981; Zafiriou, 1983; Zafiriou et al., 1984; Mill and Mabey, 1985; Zika 1987). In addition to the impact of in situ seawater photochemical reactions on air/sea exchange the effect of the deposition of atmospherically derived photo-products must also be considered (Thompson and Zafiriou, 1983). It is apparent from this literature that photochemistry may play a role in air/sea exchange through a number of different mechanisms, involving both formation and destruction of chemical species.

The sea-to-air fluxes of several trace gases are known to be strongly influenced by photochemical reactions that produce them. In each case the elevated mixed layer concentration resulted from the daylight production of the trace gas, causing the oceans's surface layer to become a source. The best documented case for a photochemical driven trace gas flux in the atmosphere is for carbon monoxide. As shown in a number of studies (Conrad et al. 1982; Conrad and Seiler, 1986), the sea surface layer over a wide area of the Atlantic Ocean is supersaturated with CO by factors ranging from 1.5 - 35. The supersaturation is diurnally variable, with a strong light-dependent maximum that is especially well-defined in the tropical Atlantic. The CO supersaturation is apparently controlled by four processes as shown:

dissolved organic carbon (DOC) + $h\nu$ ---> CO_{aq} + other products

biota + $h\nu$ ---> CO_{aq} (minor)

CO_{aq} ---> CO_{g}

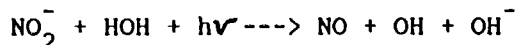
CO_{aq} + biota ---> other products

Photolysis of unknown organic materials in the DOC fraction accounts for the major CO source, far outweighing biological production. Exchange to the atmosphere and microbiological consumption compete as the major sinks for the CO produced. The oceanic CO net production estimates suggest that about 100 ± 90 Tg per year of CO enter the atmosphere, which is about 3% of the estimated global production.

Carbonyl sulphide (COS) is another gas that is generated in the ocean by photolysis (Ferek and Andreae, 1984), resulting in strong diurnal variations of OCS concentration in the surface water. Carbonyl sulphide is the most abundant sulphur containing gas in the atmosphere and is important because its long residence time permits significant penetration into the stratosphere where it is involved in gas phase reactions. Laboratory studies indicate that OCS can be produced at radiation wavelengths found in sunlight in distilled water or seawater solutions containing various dissolved organic sulphur compounds and oxygen. The mechanisms of this reaction is not known, and is puzzling, in that there are no significant light absorbing species present among the reactants in the system. It would appear that the primary excitation step occurs in a low probability transition in the sulphur containing compounds, or involves some unidentified photocatalyst present at trace concentrations.

The implication of these results is that local OCS fluxes from the ocean should vary diurnally and be correlated to solar flux, dissolved sulphur compounds, which are in turn associated with the biota, and possibly some, as yet, unidentified photo-initiator of the reaction. The observed concentrations of OCS in the water, which vary over several orders of magnitude, are almost always higher than the equilibrium concentration relative to the atmosphere. The sea-to-air flux of OCS may be largely controlled by a complex function of the prevailing photo-chemical conditions and the wind stress.

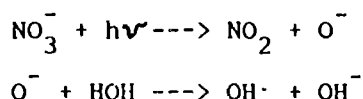
In contrast to CO and OCS, which are relatively inert gases in the water column, NO air/sea flux is complicated by its reactivity, particularly with free radicals. In regions where significant concentrations of NO exist, such as in upwelling areas the surface ocean can be supersaturated with NO as a result of the following reaction:



Because NO is a reactive ground state radical the diffusion of NO through the surface ocean will be dependent on the concentration of and reactivity of other free radicals in the water column. Destruction of NO will be most rapid at the air/sea interface as a combined result of the deposition of atmospheric radicals and high photochemical production rate of radicals in the water. Approximate estimates suggest that

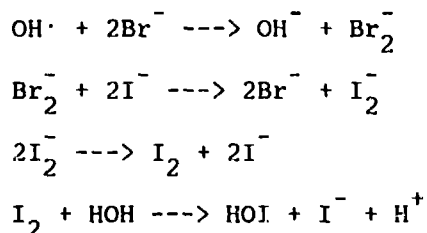
reaction of NO with these radicals may substantially diminish the sea-to-air flux of NO. This flux of NO is not globally significant in any case, but this example shows that the chemistry of these interactions may be important in controlling the flux of reactive gases.

The limited significance of the NO flux from NO_2^- photolysis is largely a function of the low to unmeasurable concentrations of NO_2^- typically found in the ocean photic zone. Nitrate exhibits a photoprocess similar to NO_2^- , but unlike NO_2^- is found in the photic zone at significantly higher concentrations. One of the primary photo-reactions of NO_3^- gives NO_2 as a product,



As a source of NO_2 to the atmosphere this process is minimized by the small absorption cross-section of NO_3^- above 300 nm and by the rapid hydrolysis and decomposition reactions of NO in aqueous solution (Lee and Schwartz, 1981). The secondary reactions of the $\text{OH}\cdot$ on volatiles and other seawater constituents, as well as the solution reactions of NO and NO_2 , maybe the most important consequence of NO_2^- and NO_3^- photolysis.

Although less well defined than the other cases above there is evidence that iodine also produces volatile photo-products. Indirect evidence for iodine volatilization comes from the fact that the comparison of the I/Cl ratios between seawater and the marine atmosphere show that there is large iodine to chlorine enrichment in the atmosphere (Moyers and Duce, 1972). Miyake and Tsunogai (1963) proposed that this enrichment was due to a light initiated reaction that produced a volatile iodine species. They demonstrated this by exposing seawater solutions containing radioactive ^{131}I to near ultraviolet and visible radiation and then measuring the resultant elevated levels of radioactivity in the headspace gas over the irradiated solution. The nature of the reaction and the volatile iodine products remain to be determined, but reaction sequences like the following may be involved.



In the reactions above the $\text{OH}\cdot$ was used as the initiator, however, because I^- is one of the most readily oxidized chemical species present in seawater many photochemically produced transient oxidants will react with it to form $\text{I}\cdot$. The iodine cycle, therefore, should be strongly mediated by photochemical pathways which through volatile product formation provide an important coupling mechanisms with the atmosphere. In view of the recent recognition of the importance of iodine photochemistry in the atmosphere (Chameides and Davis, 1980) the

topic of sea/air transport mechanisms for iodine deserves more attention than it has received to this point.

In addition to the production of volatiles, photochemical reactions near the air/sea interface can inhibit the transport of chemical species across the interface through destructive reactions which modify the hydrophilicity and vapor pressure of species. These processes can be divided into those in which a primary photo-process occurs in the volatile itself and those where a photosensitized or secondary reaction results through the interaction of the volatile with a reactive transient formed from some other photochemical process.

In the troposphere there are a number of species (e.g. O_3 , NO_2 , NO_3 ,...) whose flux is dependent upon their primary photolysis rates. In seawater the only documented example is for methyl iodide which is decomposed by photolysis and competing SN substitution reactions (Zika et al., 1984). In this study the importance of latitude and season on the photochemical and thermal regulation of flux can be seen.

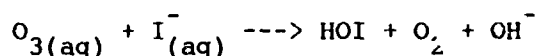
Decomposition by photosensitized or secondary reactions is a more complex situation because of the abundance of possibilities. Firstly, the air/sea interface can be divided into three different regions, each comprising a uniquely different reaction environment. The regions are the atmosphere directly above the interface, the interface itself, and the water directly below the interface.

Reactions above the interface are probably dominated by gas phase reactions which have been extensively reviewed in atmospheric chemistry and will not be considered here. There is far less known about the heterogeneous photo-processes and particularly those occurring in aerosols that originated from the ocean surface. Since most of these aerosols have only a short duration in the atmosphere before returning to the ocean this process represents a potentially important recycling mechanisms for various chemical constituents. Although such aerosols are derived from the ocean surface their properties can be very dissimilar when compared to the bulk seawater from which they originated. Substantial enrichments in transition metals, iodide, and organic materials have been noted. When these changes are coupled with dramatic changes in pH, ionic strength, exposure to gas phase oxidants, and incident near ultraviolet radiation a substantially different reaction environment has been formed when compared to the bulk seawater.

A recent example of this sea-to-air recycling process has been found for amino acids (Mopper and Zika, 1987). In this study marine rain samples collected in the open ocean were found to contain an average of $6.5 \mu M$ dissolved free amino acids. A high ratio of free to combined amino acids and the presence of various amino acid oxidation products indicate that extensive degradation of what were probably originally surface active proteins from the air/sea interface taken place. There is ample evidence to suggest that the interface is the source of these amino acids since a number of studies have shown that experimentally generated aerosols from the seawater are enriched by 100-1000 fold in organic carbon and nitrogen relative to bulk seawater (Gershey, 1983; Hoffman and Duce, 1976). Photochemical initiated degradation in these

transient aerosols may have important consequences for nitrogen, sulphur, and iodine cycling over the ocean.

At the interface photochemical reactions can affect the flux of reactive volatiles from the sea or from the air. Thompson and Zafiriou (1983) have discussed the rates of deposition and the factors controlling the flux of transient atmospheric species to the ocean interface. Of the photochemically derived atmospheric transients O_3 and peroxides, particularly H_2O_2 , have the largest gas phase deposition rates. Hydrogen peroxide is also added to the ocean in precipitation (Cooper et al., 1987) and can potentially reach concentrations in the interface of from 10 to 100 μM . Because of relatively slow reaction rates, most of this peroxide will be rapidly diluted into the underlying water column by mixing. For the more reactive oxidants such as O_3 the transfer to the aqueous layer is faster than can be explained by the oxidant's solubility alone. In the reactive-gas transfer theory, to explain the fluxes inferred from flux-gradient or eddy-correlation measurements, it is necessary to assume an enhanced flux due to chemical reactions in the aqueous stagnant boundary layer. The existence of a chemical reaction sink may be supplied in seawater by the reaction:

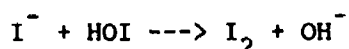


This reaction is thought to have a rate constant near 10^9 l/mole-s; since in surface water the concentration of I^- is 10^{-8} to 2×10^{-7} M, the reaction may proceed rapidly in most surface waters. However, the I^- concentration may be too low to make the O_3 transfer into the sea limited by the transfer resistance of the gas phase boundary layer, so that O_3 flux probably varies in proportion to the I^- concentration or possibly to the concentration of reactive organic constituents of the surface film.

Reactive transient production at the interface can also result from photochemical reactions of accumulated organic substances. For example, enrichments of phenolic substances have been reported in sea surface microfilms (Carlson 1982), and many of these are good chromophores in the near ultraviolet region. It is believed that phenolic moieties in marine humic substances are the principal photochemical reaction centers and lead to a variety of reactive excited and ground state transients in seawater (Mopper et al. 1988).

The combined effect of reactive transient deposition from the atmosphere and enhanced photochemical production in the vicinity of the microlayer may have the net effect of either decreasing or increasing the flux of volatiles across the interface. Labile volatiles such as sulphides and NO_x may find an increased barrier in sea-to-air transfer. The opposite will be true for the air to sea transfer of species such as O_3 , NO_x and SO_2 where an increased rate of transfer should occur as a result of fast reactions in the aqueous boundary layer.

One consequence of these oxidation reactions near the interface is that iodine may be released to the atmosphere. This could result from the following reaction:



The resulting equilibrium concentration of volatile I could then escape to the atmosphere. Laboratory experiments suggest that ozone may be the agent responsible for the flux of iodine to the atmosphere (Garland and Curtis, 1981), but there are a host of other possibilities which need to be considered.

Secondary photo-reactions in the bulk water beneath the interface can also impact the sea-to-air fluxes of volatiles through what are most likely to be oxidation reactions. Brimblecombe and Shooter (1986) have measured the photo-oxidation rate of dimethyl sulphide in seawater solutions and found a first order rate constant of $2.4 \times 10^{-5} \text{ s}^{-1}$. This rate is rapid enough to make the photochemical loss approximately the same as the loss to the atmosphere. The reaction appears to be initiated by photosensitizers and may involve reactions with singlet oxygen or free radicals. The fluxes of other volatiles such as NO should also be sensitive to the concentrations of reactive secondary photochemical transients in water. Because of the diurnal variations in the standing concentrations of these reactive transients a similar signature should be imposed on the flux of the volatiles.

Recommendations

- 1) The photo-processes involved in the production of OCS and the destruction of dimethyl sulphide as well as other sulphur volatiles such as H_2S need further elucidation.
- 2) There is evidence for the photochemical¹ production of a number of volatiles in seawater, and there are a number of others which have not yet been subjected to serious investigations. Some of the other candidates include organic and inorganic halides, organo-mercury compounds, and some of the elements in groups III-VI of the periodic table.
- 3) Calculations suggest that iodine in its various forms is one of the most important constituents involved in oxidation reactions above, below, and at the interface. Investigations on its speciation, microlayer concentration gradients, and photochemical reaction mechanisms need to be conducted.
- 4) Many aspects of the physical, chemical, and biological characteristics of the sea surface microlayer are still not well understood. Efforts should be made to more fully characterize the microlayer region, with particular emphasis upon those processes and properties that potentially impact upon reactions and fluxes of volatiles.
- 5) The transfer of film constituents from the sea surface microlayer via aerosols into the atmosphere and then back to the ocean is a photochemical recycling process about which little is known. Questions that need to be addressed include:
 - what are the extent and nature of the reactions during the atmospheric residence time of the aerosol, and
 - what impact do chemical species in the return flux to the ocean have upon the interface?

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ONGOING INTERNATIONAL ACTIVITIES RELATED TO AIR-SEA EXCHANGE

AEROCE

AEROCE (the Atmosphere/Ocean Chemistry Experiment) is a coordinated multi-institutional atmospheric and marine chemistry research programme centered in the North Atlantic Ocean region. The ultimate goal of the AEROCE Program is the development of a predictive capability for the continentally derived species observed in the marine boundary layer over the North Atlantic. During its early years the AEROCE Program will concentrate on the AEROCE Network Studies, which will include continuous measurements of certain atmospheric species at island sites.

The overall objectives of the AEROCE Network Studies are:

1. To understand the chemical climatology over the North Atlantic Ocean. This can be attained through the use of chemical tracers and modeling techniques:

a.) to understand the atmospheric transport of chemical species from the continents over the North Atlantic Ocean;

b.) to evaluate the continental and marine sources for these atmospheric species observed over the North Atlantic Ocean;

c.) to determine the importance of chemical transformation processes during the transport of trace species across the North Atlantic Ocean; and

d.) to determine the rates and primary processes of removal of trace species from the atmosphere to the North Atlantic Ocean.

2. To understand the impact of atmospheric deposition of trace species on chemical cycles in the North Atlantic Ocean.

Atmospheric measurements will be made initially from sampling stations on the coasts of Barbados, Bermuda, and Ireland as well as from a station at 2300 meters above sea level on Tenerife in the Canary Islands. Twenty meter high walkup sampling towers will be used at the sea level stations. Laboratory facilities, computer based data acquisition systems, etc. will be available at each site, as will full time technical support. Network instrumentation will be reliable and proven in the field. All four sites should be operational by 1989. For the first several years species being measured will be limited to ozone, radon-222, and certain long lived gas species as well as a wide range of inorganic species and mineral matter in the aerosol phase and in precipitation.

The AEROCE Network Studies has a steering committee responsible for the overall direction of the programme. Members are:

J. Prospero, University of Miami, Chairman
R. Duce, University of Rhode Island
J. Galloway, University of Virginia
H. Levy, NOAA, GFDL

IGAC

At a meeting in Stockholm, Sweden in September, 1986 the Commission on Atmospheric Chemistry and Global Pollution (CACGP) of the International Association of Meteorology and Atmospheric Physics (IAMAP) initiated the planning for specific international collaborative research efforts on global atmospheric chemistry, the International Global Atmospheric Chemistry (IGAC) Programme. A subsequent brief workshop was held in Peterborough, Canada in August, 1987. The primary objective of the Peterborough workshop was to provide an open forum for the international atmospheric chemistry community to begin discussions of the objectives and future research strategies for the IGAC Program. In particular, the identification of a set of international activities and research initiatives particularly amenable to international cooperation was given high priority. General recommendations from this workshop included enhancing communications between IGAC and other ICSU organizations, especially IGBP, SCOPE, SCOR, SCAR, and IUPAC, developing an active inventory of international atmospheric chemists, publishing an IGAC Program newsletter, promoting international exchange programmes for faculty and students, developing educational programmes, and developing international intercalibration and standardization programmes for atmospheric chemical measurements.

More specific recommendations for possible scientific cooperation were made in the following five areas:

- 1.) Global distributions and trends in atmospheric trace constituents.
- 2.) Biological and surface exchange processes.
- 3.) Laboratory and field experiments in gas phase atmospheric photochemistry.
- 4.) Laboratory and field experiments in cloud, precipitation, and aerosol chemistry.
- 5.) Theoretical studies and modeling.

CACGP has appointed an international committee to be responsible for the future development of the IGAC Program. Of particular importance will be to provide guidelines for the planning of an extensive IGAC workshop scheduled to be held for one week in Melbourne, Australia in November, 1988. The Melbourne workshop will develop in detail the rationale, objectives, and programme plan for the IGAC Program. The IGAC committee is as follows:

- G. Pearman, Australia (Chairman)
- D. Albritton, USA (Secretary)
- P. Buat-Menard, France
- R. Harriss, USA
- E. Sanhueza, Venezuela
- H. Rodhe, Sweden
- R. Duce, USA (Ex-officio)
- P. Crutzen, Federal Republic of Germany (IGBP representative)
- H. Schiff, Canada (IUPAC representative)

GTCP

In 1984 the United States National Academy of Sciences issued a report entitled "Global Tropospheric Chemistry: A Plan for Action". Because of the growing recognition that human activities can alter the chemistry of the atmosphere on a global scale, with significant consequences to climate, health, agriculture, etc., this report recommended that the United States initiate a comprehensive investigation of the chemistry of the global troposphere. The long term goals of this Global Tropospheric Chemistry Program (GTCP) were as follows:

- 1.) To understand the basic chemical cycles in the troposphere through field investigations, theory aided by numerical modeling, and laboratory studies;
- 2.) To predict tropospheric responses to perturbations, both natural and human induced, of these cycles;
- 3.) To provide the information required for the maintenance and effective future management of the atmospheric component of the global life support system.

In 1985 a workshop was held to define the priorities and assess the funding requirements for the GTCP. These priorities and requirements were defined within 5 research areas: global distributions and trends, biological and surface exchange processes, gas phase photochemistry, multiphase processes, and theoretical studies and modeling. A report from this workshop, entitled "Global Tropospheric Chemistry: Plans for the U.S. Research Effort", was released in December, 1986. This report has been used by U.S. government agencies as a basis for future planning for the resources necessary to undertake the GTCP. Several initiatives have already been started, particularly with NSF, NASA, and NOAA support. Examples include NSF's AEROCE Program, NASA's Global Tropospheric Experiment (GTE), and NOAA's RITS (Radiatively Important Trace Species) study.

In 1987 the U.S. National Academy of Sciences formed a permanent Committee on Atmospheric Chemistry. One of the primary objectives of this committee is to aid in the formulations of future plans for the GTCP, particularly with regard to international cooperative efforts, e.g., with the IGAC (International Global Atmospheric Chemistry) Program. Chairman of the National Academy Committee is R. Sievers of the University of Colorado.

JGOFS

Following a meeting which took place in Paris in 1987, it was agreed that after examination of various national programmes relating to studies of ocean fluxes and major biogeochemical cycles in the ocean there were great benefits to be gained by establishing an international programme which should be known as the Joint Global Ocean Flux Study (JGOFS). The goal of this programme should be : "to determine and understand on a global scale the processes controlling the time varying fluxes of carbon and associated biogenic elements in the ocean, and to evaluate the related exchanges with the atmosphere, sea - floor and continental boundaries". To develop such a programme, it was agreed that

a scientific planning committee should be established under the auspices of SCOR with Dr. B. Zeitzschel (F.R.G) as chairman of this Committee and Dr. P. Brewer (USA) as vice chairman. This committee has the following terms of reference:

- To identify the fundamental scientific issues and detailed goals and objectives for an international Joint Global Ocean Flux Study
- To develop a scientific plan and to establish requirements for carrying it out
- To recommend the necessary actions to be taken to implement the plan and to coordinate and manage the resulting activities
- To collaborate as appropriate with other related programmes and planning activities, such as the World Ocean Circulation Experiment (WOCE), the International Global Atmospheric Chemistry Programme (IGAC) and the International Geosphere/Biosphere Programme (IGBP).
- To report regularly to SCOR and related bodies on the state of planning and accomplishments of JGOFS

A JGOFS North Atlantic Planning Workshop took place in Paris in September 1987 and planned a JGOFS Pilot Study for 1989-90 which will take advantage of existing plans of several countries for research activities in the northeastern region of the Atlantic Ocean. At that meeting several working groups were formed both on process studies and integrative topics. Some of the processes to be studied are particularly relevant to SCOR WG 72. These include: CO₂ air/sea exchange, sulphur cycling in surface waters, temporal and spatial scales of atmospheric inputs of nutrients of other substances. It is suggested that SCOR WG 72 and its possible successor could provide guidance and recommendation for the implementation of these process oriented studies.

WOCE

The World Ocean Circulation Experiment (WOCE) is a part of the World Climate Research Program and is scheduled to begin in the late 1980's. It will provide, over the next decade, the first comprehensive global survey of the physical properties of the oceans, information vitally needed to understand global climate dynamics and to predict climate change on a scale of decades. Of particular interest to SCOR WG 72 is the tracer programme in WOCE. The analysis of the distribution of certain tracers can make important contributions to various aspects of the study of large scale ocean circulation. Some of these tracers are of anthropogenic origin and are mostly deposited to the ocean surface via atmospheric deposition (tritium, fluorocarbons, ¹⁴C, ⁸⁵Kr, ³⁹Ar). The efficient use of these tracers requires an accurate knowledge of their atmosphere-ocean transfer in any given situation. In this respect the WOCE programme would certainly benefit from any improvement and development of techniques for measuring transfer velocities at the air-sea interface.

EUROTRAC

Following the initiative for a European programme on the Transport of Atmospheric Constituents, plans for a subproject related to air-sea exchange studies (ASE) in a European context were initiated in 1986 by P. S. Liss (UK) and P. Buat-Ménard (France). In April 1987 a meeting in Antwerpen (Belgium) gathered 20 scientists from 8 countries from which emerged a proposal with the following major objectives:

- To assess the processes and rates of production of trace gases and aerosol particles from European regional and coastal waters and to examine their role in atmospheric chemistry.
- To investigate the magnitude and processes controlling the deposition of substances of anthropogenic and natural origin from the atmosphere to the regional seas and coastal waters of Europe.

The ASE subproject was reviewed positively by the EUROTRAC Scientific Steering Committee in October 1987. It is divided into 5 topic areas:

- Contribution of biology and photochemistry of surface waters to sea-to-air trace gas fluxes
- Trace emission measurements from surface seawater
- Atmospheric transformation of trace gases and aerosols in marine deposition processes
- Magnitude of the atmospheric flux of anthropogenic and natural substances from land to regional seas
- Factors determining the dynamics near the air/sea interface

The preliminary stage of this project is planned to last for three years during which major efforts would be

- Optimization and intercomparison of sampling and analytical techniques
- Joint laboratory and field experiments
- Development of air/sea exchange models

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