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REPORTS AND STUDIES

No. 48

GLOBAL CHANGES AND THE AIR-SEA EXCHANGE OF CHEMICALS

WORLD METEOROLOGICAL ORGANIZATION

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Reports and Studies No. 48

IMO/FAO/UNESCO/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on
the Scientific Aspects of Marine Pollution (GESAMP)

GLOBAL CHANGES AND THE AIR-SEA EXCHANGE OF CHEMICALS

World Meteorological Organization, 1991

(RDP 788)

NOTES

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Definition of Marine Pollution by GESAMP

"POLLUTION MEANS THE INTRODUCTION BY MAN, DIRECTLY OR INDIRECTLY, OF SUBSTANCES OR ENERGY INTO THE MARINE ENVIRONMENT (INCLUDING ESTUARIES) RESULTING IN SUCH DELETERIOUS EFFECTS AS HARM TO LIVING RESOURCES, HAZARDS TO HUMAN HEALTH, HINDRANCE TO MARINE ACTIVITIES INCLUDING FISHING, IMPAIRMENT OF QUALITY FOR USE OF SEA WATER AND REDUCTION OF AMENITIES."

* * *

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EXPLANATORY NOTE

The global environmental change, especially the change in composition of the atmosphere and related climate change resulting from the increasing atmospheric concentrations of greenhouse gases is one of the most urgent issues facing the society. Noting the need for better understanding of the impact of global change on the marine environment, the Commission for Atmospheric Sciences of the World Meteorological Organization recommended that a study on atmospheric-ocean interaction of pollutants and of the relationship of marine pollution and climate change, should be conducted to contribute to the WMO Global Atmosphere Watch programme. In line with this recommendation GESAMP was requested to establish a working group to study the problem.

The GESAMP Working Group No. 32 on the Global Changes and the Air-Sea Exchange of Chemicals was established at the twentieth session of GESAMP (Geneva, May 1990) with WMO being the lead agency and UNEP and Unesco being the co-operating agencies. The Group was requested to prepare a review on the following subjects: exchange of nutrient nitrogen between the ocean and the atmosphere, global warming and air-sea exchange of gases and the changing oxidizing capacity of the atmosphere and the ocean.

To fulfil the above tasks a meeting of the Working Group No. 32 was held at the University of Rhode Island, USA, from 17 to 21 December 1990. A draft report prepared during and after the meeting was submitted to the twenty-first session of GESAMP (London, 18 to 22 February 1991) which considered the report and recommended that comments and proposals made by GESAMP Members should be reflected in the final version and the report should be published in the GESAMP Reports and Studies Series. Final amendments to the present report were made at a meeting of the core group of the Working Group No. 32 held at the University of East Anglia, Norwich, UK from 22 to 26 July 1991. Both meetings were financially supported by WMO, UNEP and Unesco.

GLOBAL CHANGE AND THE AIR-SEA EXCHANGE OF CHEMICALS

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EXECUTIVE SUMMARY

Global environmental change is one of the most important issues facing society over the next several decades. Present and potential future changes to the global environment have important implications for marine pollution and for the air-sea exchange of both anthropogenic and natural substances. This report addresses three issues related to the potential impact of global change on the air-sea exchange of chemicals:

- **Global change and the air-sea transfer of the nutrients nitrogen and iron.**

The deposition of atmospheric anthropogenic nitrogen has probably increased biological productivity in coastal regions along many continental margins. Atmospheric deposition of new nitrogen may also have increased productivity somewhat in mid-ocean regions downwind from significant population and industrial centers as (e.g., the central North Atlantic Ocean).

The projected future increases of nitrogen oxide emissions from Asia, Africa and South America will provide significant increases in the rate of deposition of oxidized nitrogen to the central North Pacific, the equatorial Atlantic, and the equatorial and central South Indian Oceans. It is likely that this nitrogen will increase primary productivity in these regions, as well as coastal regions, but the magnitude of the increase is unknown. It is unlikely that atmospheric nitrogen inputs significantly influence phytoplankton production in upwelling regions or the polar oceans. It is possible that ice-edge blooms may be a special case.

Atmospheric iron may be an important nutrient in certain open ocean regions. Future changes in the delivery to the ocean of atmospheric dust containing iron are uncertain, but will likely occur if there are changing patterns of aridity and wind speed as a result of climate change. Current climate models cannot adequately predict changes in the atmospheric transport paths for atmospheric nitrogen and iron species to the world ocean as a result of possible future climate change. This is, however, a potentially important issue that should be evaluated carefully once appropriate climate models have been developed.

- **Global change and the air-sea exchange of gases.**

Present estimates of the net global uptake of CO_2 by the oceans using integrated values for p_{CO_2} and K, which are both quite variable, are probably uncertain by a factor of two. For example, small scale variability (10-100 km) in p_{CO_2} is ~30 μatm, while a systematic error of 1 μatm over the world ocean would lead to an error in the integrated CO_2 flux of 0.2×10^{15} g C yr^{-1}. Small differences between the temperature of the skin of the ocean and water just below the surface can be very important. Calculations of the global CO_2 flux which ignore such skin temperature effects may be in error by $0.5\text{-}1 \times 10^{15}$ g C yr^{-1}. Increasing sea surface temperature will result in increasing p_{CO_2}, with an extra atmospheric p_{CO_2} of ~5% of the initial perturbation.

The most important future effects on surface ocean p_{CO_2} will likely be caused by changes in ocean circulation, although we cannot say with certainty whether the resultant amplification of temperature changes will be positive or negative. The pH of the ocean would decrease by ~0.3 units for a doubling of p_{CO_2}, reducing the capacity of the ocean to take up CO_2. However, it seems unlikely that the pH decrease, or the concomitant change in the speciation of inorganic carbon, or the corresponding increase in water temperature will have any substantial direct effects on ocean productivity, at least for several decades.

There is increasing evidence that dimethyl sulfide from the ocean is a source of cloud condensation nuclei and thus a factor controlling cloud albedo. However, it is still not possible to

predict even the sign of any feedback mechanism in the dimethyl sulfide-climate link.

- **Oceanic responses to radiative and oxidative changes in the atmosphere.**

By 2060 in the southern hemisphere reduction in total column stratospheric ozone from recent levels could reach 2 to 5% in the tropics, 10% at mid latitudes, and over 20% at 60°S. Smaller, but significant, reductions are likely in the northern hemisphere. In this same time frame increases in ground-level effective UV-B radiation could reach 5%, 26% and 66% at low, mid, and high latitudes in the southern hemisphere.

Tropospheric ozone will continue to increase throughout the northern hemisphere outside the tropics but will likely decrease in the southern hemisphere. It is uncertain how the concentration of OH will change, but it will likely decrease in the southern hemisphere as a result of increasing CH_4 and CO without increasing NO_x, whereas OH may increase in the northern hemisphere due to increasing NO_x. Changes in the OH concentration will affect the lifetimes and transport to the ocean of a number of natural and pollutant gases, including HNO_3 and SO_2.

Increased UV-B could result in significantly decreased primary productivity at the sea surface, and perhaps throughout much of the photic zone, particularly at southern hemisphere mid and high latitudes. However, further detailed modeling efforts will be needed to assess the magnitude of such an effect. OH-sensitive processes, such as degradation of natural and xenobiotic substances in the sea, could intensify with increasing UV-B, but the complexity of these photochemical processes does not allow us at present to predict quantitatively the effects of global changes.

The region of the ocean most sensitive to UV-B, both with respect to photochemical and biological processes, is the sea surface microlayer, and changes in photochemical processes in the surface waters of the ocean could have significant effects on the air-sea exchange of a number of compounds in the carbon, nitrogen, sulfur and halogen cycles.

I

INTRODUCTION

Global environmental change is one of the most urgent issues that will face society over the next several decades. Global change is a result of the rapid growth of world population and their increasing demand for energy and economic development.

Among the most significant changes resulting from the increased growth and industrialization of our global society is the possibility of global atmospheric and oceanic warming and related climate change, particularly as a result of the increasing atmospheric concentrations of infra-red active gases such as CO_2, N_2O, CH_4, etc. Climate change would also result in the alteration of precipitation and wind flow regimes in some regions as well as changes in the atmospheric residence times of some chemical species, thus altering the patterns of atmospheric pollution transport and exchange with the ocean. Other important changes include the increased production and emission to the atmosphere and ocean of a variety of harmful pollutants; changes in the oxidation capacity of the troposphere; and reduction of stratospheric ozone, resulting in increased quantities of ultraviolet radiation reaching the earth's surface. The impact of global change on the oceanic coastal zone could be particularly important, resulting in increasing pressure on that part of the marine environment that is most biologically and economically productive.

These present and potential future changes to the global environment have important implications for marine pollution and for the air-sea exchange of both anthropogenic and natural substances. This report will address three issues related to the potential impact of global change on the air-sea exchange of chemical species. These are summarized below.

A. GLOBAL CHANGE AND THE AIR-SEA EXCHANGE OF THE NUTRIENTS NITROGEN AND IRON

Increased industrialization and burning of fossil fuel has resulted in greater emissions of the oxidized and reduced forms of nitrogen to the atmosphere, with subsequent enhanced transport over and into the ocean. Current evidence indicates that the oxidized forms of nitrogen, primarily nitric acid and nitrate aerosol, over the North Atlantic are probably an order of magnitude higher than they are over the South Atlantic, primarily due to major anthropogenic sources in North America and Europe. This has led to increasing quantities of nitrogenous nutrient material being delivered to certain open ocean regions as well as to coastal regions. In coastal areas such increased emissions from non-point sources are difficult to control, and deposition of these nutrients to the water could lead to increased eutrophication. Recent studies suggest that the atmosphere is the primary source of the micronutrient iron in the surface waters of many open ocean regions. In some areas iron may be the nutrient that is limiting biological productivity. Future climate change may alter the source regions and transport paths for the mineral particles that are the source of the atmospheric iron.

B. GLOBAL CHANGE AND THE AIR-SEA EXCHANGE OF GASES

Increasing concentrations of CO_2 and other infra-red active gases in the global atmosphere will likely result in a rise in the temperature of both the atmosphere and surface seawater, thus possibly altering the equilibrium conditions for some gases, both natural and anthropogenic, in the ocean/atmosphere system and possibly affecting productivity in the oceans. Increasing atmospheric CO_2 concentrations may also result in shifts in the oceanic carbonate system and may lower the pH of seawater slightly. This in turn could affect the lysocline and processes of carbonate sedimentation as well as the sea/air transfer of other trace gases whose exchange is pH-dependent. However, our present quantitative understanding of the temporal and spatial

distribution of the global flux of CO_2 across the air-sea interface is still quite primitive. In addition, dimethyl sulfide produced by certain marine plankton escapes from the ocean into the atmosphere, where some fraction of it is oxidized to form sulfate aerosol particles. These particles are effective cloud condensation nuclei and may play an important role in the earth's radiation budget. Climate change could affect the production and oxidation of dimethyl sulfide.

C. RESPONSES OF THE OCEANIC SYSTEM TO RADIATIVE AND OXIDATIVE CHANGES IN THE ATMOSPHERE

In the upper atmosphere (stratosphere) ozone (O_3) filters out much of the incoming solar ultraviolet radiation of wavelengths 290-320 nm (UV-B radiation). Anthropogenic trace gases are depleting the stratospheric ozone layer. Depletions have been greatest over Antarctica and at high southern latitudes, but recent evidence suggests that depletion is also occurring in the northern hemisphere. Because of the long lifetimes of these anthropogenic trace gases, stratospheric ozone is expected to continue to decrease for the next few decades. Decreasing stratospheric O_3 results in increasing quantities of harmful ultraviolet radiation reaching the land and ocean surface. This increasing UV-B radiation could alter a number of important biological and chemical processes involved in regulating the Earth's climate. Radiative changes could affect the chemistry of the lower atmosphere (troposphere). Increased UV-B radiation could result in increased production of tropospheric ozone and reactive free radicals such as the hydroxyl radical (OH). Such free radicals largely control the oxidizing capacity of the ocean and atmosphere and thus play an important role in the chemical destruction of many anthropogenic and natural chemical substances and their residence time in the oceanic and atmospheric environment. Also, increasing quantities of air pollution on a global scale will result in changes in the concentration of OH in the atmosphere due to various types of reactions with these substances. The sign and magnitude of these changes will be quite variable geographically. Increased UV-B in the upper layers of the ocean will decrease the photosynthetic productivity of marine phytoplankton and, thus could alter the oceanic uptake of atmospheric carbon dioxide. Changes in radiative flux could also alter important photochemical processes in the upper water column. Photochemical and biological change will be greatest in the sea-surface microlayer. Effects could extend through much of the photic zone of the water column, but overall impacts will require further evaluation.

II

GLOBAL CHANGE AND THE AIR-SEA EXCHANGE OF THE NUTRIENTS NITROGEN AND IRON

A. INTRODUCTION

1. Background

There has been a growing recognition of the potential importance of the atmosphere as a transport path for certain nutrients entering the ocean. For example, our increasing population and industrialization are resulting in continually increasing emissions to the atmosphere of both the oxidized and reduced forms of nitrogen, with subsequent enhanced transport over the ocean. In some regions of the atmosphere, nitrogen species from anthropogenic sources (e.g., power plants, automobiles, and industrial combustion) dominate those from natural sources (e.g., nitrogen oxides from soils and the ocean as well as ammonia from decaying organic matter). Current evidence indicates that the oxidized forms of nitrogen, primarily nitric acid and nitrate aerosol, over the North Atlantic are probably a number of times higher than they are over the South Atlantic, primarily due to major anthropogenic sources in North America and Europe (Duce et al., 1991). These higher concentrations of atmospheric nitrogen species have led to increasing quantities of nitrogenous nutrient material being delivered to certain open ocean as well as coastal regions. This is of particular concern since the emissions from non-point sources are difficult to control, and the deposition of these nutrients to coastal waters can be a significant source. For example, in the western Mediterranean recent estimates suggest that, integrated over a broad area, nitrogen inputs from the atmosphere and rivers are approximately equal (Martin et al., 1989), while roughly one third of the nitrogen input to the North Sea is from the atmosphere, most of it human-derived (North Sea Conference, 1987).

There has also been considerable interest in the possibility that iron, derived primarily from atmospheric input, may limit primary productivity in some open ocean regions. Calculations by Duce (1986) and Martin and Fitzwater (1988) showed that as much as 95-98% of the dissolved iron in the surface waters of the central oceanic gyres in the North Atlantic and North Pacific may be derived from the input of mineral matter (dust) transported from continental regions. In this case the source of most of the atmospheric iron is natural, not human-derived. In high latitude regions, and in some equatorial regions characterized by strong upwelling, there are often excess concentrations of such nutrients as nitrate and phosphate, suggesting that these nutrients are not limiting production. These areas often have extremely low iron concentrations and are the most likely locations where atmospheric delivery of iron might have the most significant influence on primary productivity.

In this section the potential impact of the input of human-derived atmospheric nitrogen species on marine biological productivity and eutrophication in the coastal zone, central ocean gyres, upwelling and polar regions will be evaluated. Potential future changes in the anthropogenic emissions and fluxes of atmospheric nitrogen species to the ocean as a result of global environmental change will also be considered. Our understanding of the input of atmospheric iron to the open ocean, its potential impact on biological productivity, and possible future changes to its input to the ocean will also be reviewed.

2. Dynamics of Phytoplankton Production

a. Introduction

The major state and rate variables and transformations linking the atmosphere and marine production processes are summarized in Figure 1. The primary route for the production of organic carbon is through photosynthesis in the marine photic zone. This results in the fixation of inorganic carbon and nutrients (N, P, S, etc.). Once fixed as organic carbon and nitrogen this material either undergoes decomposition *in situ* or is lost from the system, either vertically through sedimentation or laterally via horizontal transport processes. Consumption processes (grazing) can contribute to both the recycling or loss fluxes; bacteria are the primary mediators of decomposition.

Notwithstanding the possible importance of iron in some regions, the availability of fixed nitrogen is generally considered to be one of the most important single controls on phytoplankton production, assuming an adequate light supply. We will concentrate on the role of nitrogen, with a brief discussion of iron. The variety of sources of fixed nitrogen in the ocean play a critical role in biological productivity. Figure 1 illustrates the most important of these. The input pathways for

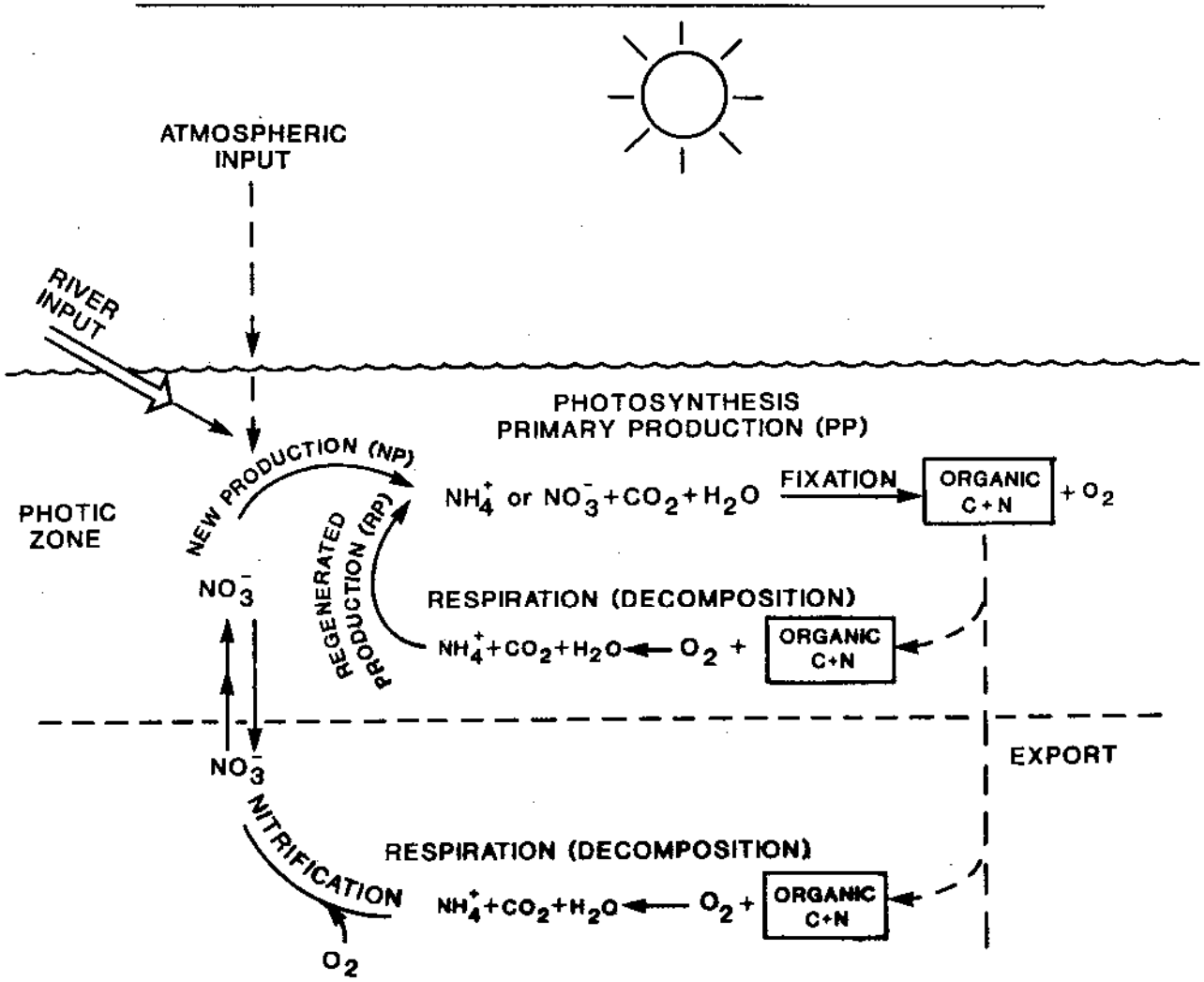

Figure 1. Schematic of the important carbon and nitrogen transfers in surface waters associated with the biological pump.

individual nitrogen species are frequently different, and their relative importance will also differ depending upon the situation.

b. Conceptual Model

A useful conceptual model linking phytoplankton production processes and nitrogenous nutrients was introduced by Dugdale and Goering (1967) and was further developed by Eppley and Peterson (1979). Stated simply, this model considers that nitrogen is supplied from two sources: external or 'new nitrogen' and internal recycled 'regenerated nitrogen'; the production that these support is respectively 'new production' and 'regenerated production'. The significance of this is that in steady state the export of organic matter is controlled by the supply of 'new nitrogen', or, perhaps more importantly, the upper limit of biomass production is controlled by the quantity of new nitrogen. Conversely, regenerated nitrogen cannot control the upper biomass limits, but can fundamentally influence the rate of production by controlling the rate of supply.

The proportions of new and regenerated production vary greatly in different regions and seasons. Oligotrophic oceanic gyres typically exhibit regenerated production rates of over 80% (up to 99%), whereas >90% of the production is new production in upwelling regions and some coastal waters. Although this model has limitations, the most important of which is the implicit assumption of steady state, it can be seen that the supply of new nitrogen from external sources is of fundamental importance, particularly for the amount of carbon that can be immobilised, with obvious consequences for the ability of the ocean to act as a sink for anthropogenic CO_2 emissions.

c. Assimilation of Nitrogen

i.) Spatial variability

All of the processes outlined in Figure 1 are highly variable in both space and time; the scales of variability range from meters to ocean basins and minutes to millenia. An important space scale is the geographic variability of primary production (Figure 2). It is well established that coastal regions are more productive than mid-oceanic gyres, in large part because of the extra availability of nutrients; variations in production within coastal zones are frequently controlled by the availability of light. Wind and geostrophic current-induced upwelling regions also have high productivity; indeed the highest levels of production (>3 g C m^{-2} d^{-1}) in the open ocean have been recorded in these locations. Wind-induced upwelling systems are typically located on the western boundaries of the continents, although a unique and biogeochemically important wind driven upwelling is associated with the monsoon in the Arabian Sea. Upwelling related to geostrophic currents occurs in a circum-global band associated with the equatorial divergence.

The polar oceans exhibit some unique features. First, because of their high latitude they are directly controlled by the ambient insolation to a much greater degree than the tropical oceans. Second, they are influenced significantly by the intensity of storm-induced turbulence, particularly in the Southern Ocean, which further reduces light availability. Third, they are uniquely influenced by the seasonal presence of sea-ice, which is known to induce relatively short lived, intense phytoplankton blooms, but these blooms contribute a quantitatively important proportion of the annual production.

ii.) Temporal variability

The seasonal cycle is probably the most important time scale affecting production in the ocean. It is driven fundamentally by the annual variation in solar irradiance, which clearly influences

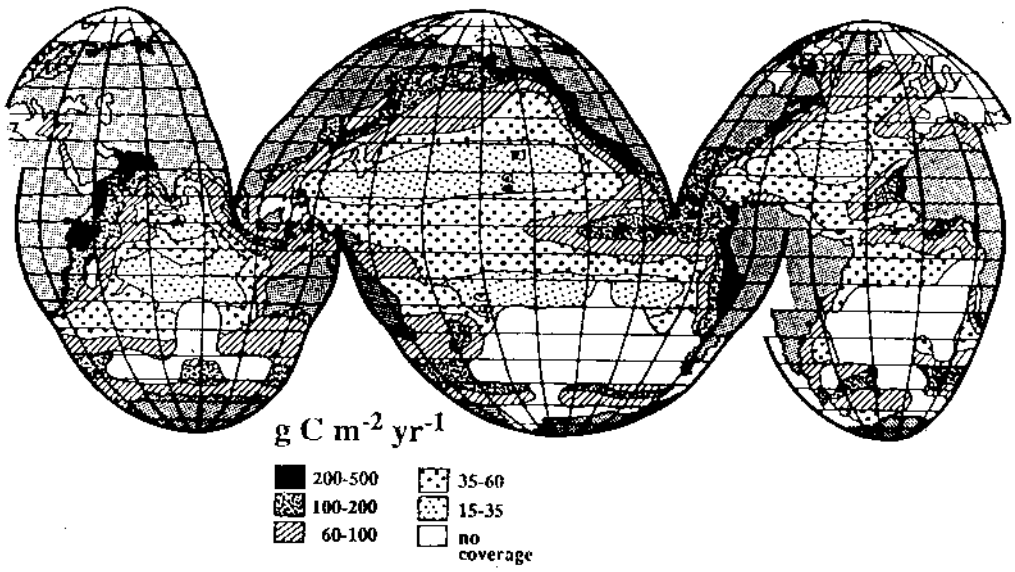

Figure 2. Average annual primary productivity of the ocean (Jahnke, 1990; Berger et al., 1988).

higher latitudes to a greater degree than the tropics. Indeed, tropical oceans generally do not exhibit any significant seasonal variability. Associated with the annual variation in solar irradiance is the equally fundamental development of seasonal density (temperature-induced) stratification, which enhances the availability of light and which is invariably a requirement for significant production to develop in mid-latitude regions. In some nearshore regions, salinity stratification, which may or may not be seasonal, can contribute significantly to the levels of biological production. It is clear that this wide geographic and temporal variablility in marine productivity must be influenced to varying degrees by atmospheric inputs of nitrogen and by climate change.

d. Regeneration of Nitrogen

Regeneration pathways of nitrogen, both in the photic zone and in the deep ocean, are of fundamental importance to phytoplankton production (Figure 1). However, they also have important implications for both the atmospheric inputs of nitrogen and the exchange of some biogenic gases.

Of pre-eminent importance is the first step in the regeneration pathway - the formation of NH_4^+ from organic nitrogen. This is primarily a biologically induced transformation and, as noted above, is mediated through the activity of both herbivorous grazers (zooplankton) and bacteria. The relative importance of these two groups varies in space and time, and it depends to a large degree on whether the organic nitrogen is in the particulate (PON) or dissolved (DON) form. PON can be utilized directly by consumers, whereas bacteria must first convert PON to DON before its utilization. This results in a significant proportion of bacterial regeneration being found on particles sinking out of the photic zone, away from the centers of assimilation. Sediments in shallow water are sites of intense bacterial regeneration as a result of this sinking flux.

Large zooplankton are generally considered not to contribute a significant proportion of the regeneration flux, but rather it is organisms less than approximately 200 μm (bacteria, protozoans, mico-zooplankton) that have been found to be the most quantitatively important (Glibert, 1982a; Harrison, 1978). Although the usual end-product of regeneration is NH_4^+, other regeneration

products include organic forms of nitrogen, some of which (e.g., urea) may be utilized directly by phytoplankton. Other organic forms require further bacterially-mediated breakdown before being available to re-enter the assimilation cycle. The role of organic nitrogen, particularly DON, in biological processes in the ocean is currently undergoing a fundamental reappraisal, and it may prove to be of greater significance than previously believed (Flynn and Butler, 1986).

Once formed, NH_4^+ may undergo further decomposition or be reassimilated directly by phytoplankton. Generally, NH_4^+ does not accumulate in seawater because of rapid reassimilation, even if concentrations of NO_3^- greatly exceed those of NH_4^+. This apparent paradox is well documented and results from the fact that phytoplankton expend less energy in the uptake of NH_4^+ than NO_3^-, which must be reduced before it can be assimilated (Owens et al., 1985). Concentrations of NH_4^+ in seawater are typically <0.2 μmol l^{-1}, but may increase to 1-5 μmol l^{-1} in narrow zones associated with the pycnocline, where regeneration exceeds assimilation. In general, however, production rates of NH_4^+ are quantitatively similar to assimilation rates (Glibert, 1982b; Harrison, 1978; Owens et al., 1985).

A key regeneration pathway is nitrification (NH_4^+ --> NO_2^- --> NO_3^-). This is the only biologically mediated process leading to the oxidation of nitrogen, and it essentially closes the nitrogen cycle. Although Figure 1 shows nitrification occurring in the sub-photic zone, it does proceed in the upper ocean as well. However, its rate is generally considered to be too slow (compared with the assimilation of nitrogen and NH_4^+ production) to be important in that region. Although NO_2 is an intermediate in nitrification, it rarely accumulates in the ocean, and where it is found it is probably the result of denitrification. Nitrification can be important in the upper ocean because of its role in N_2O production (see below).

The regeneration pathways outlined above are aerobic processes and thus only occur in oxygenated waters. Anaerobic regeneration pathways are important in some oxygen-depleted environments (e.g., sediments and anaerobic microsites) and the unique environment of anaerobic water columns (e.g., the deep oxygen minima of the sub-tropical Pacific Ocean, Baltic Sea, Arabian Sea, and some Mediterranean deep basins). The most notable regeneration pathway in these environments is denitrification, which is the dissimilatory reduction of oxidized nitrogen (primarily NO_3^-) to gaseous end-products. This pathway leads to a loss of combined nitrogen from the environment, which in some areas is quantitatively important (e.g., the Arabian Sea (Law and Owens, 1990a; Mantoura et al., 1992) and the sub-tropical Pacific Ocean (Cline and Richards, 1972)).

A special case of regeneration is the production of N_2O. This can be formed by both nitrification and denitrification according to the following simplified scheme:

$$NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^- \quad [1]$$
$$\rightarrow N_2O$$

$$NO_3^- \rightarrow N_2O \rightarrow N_2 \quad [2]$$

Reaction [1] is nitrification, and N_2O may be formed under certain conditions as a by-product. This is in contrast to reaction [2] (denitrification) where N_2O is an intermediate. The conditions under which N_2O is formed and whether it accumulates in the ocean are only poorly known. It is believed that reaction [1] proceeds under conditions of reduced oxygen concentration, and particularly at oxic/anoxic interfaces. Reaction [2] is the 'normal' denitrification pathway, but N_2O does not always accumulate. There is invariably a strong relationship between N_2O concentration and the apparent oxygen utilization. N_2O is apparently in equilibrium with the atmosphere over the

majority of the world's ocean (Weiss, 1978), and thus its exchange has generally been considered to be unimportant. However, supersaturated surface concentrations of N_2O are known to occur in localized regions, (upwelling areas and waters overlying anoxic basins, Ronner (1981)), and recent evidence has suggested that the marine flux of N_2O to the atmosphere may be greater than previously thought (Law and Owens, 1990a). Significant concentrations of N_2O have also been recorded associated with the pycnocline in areas of the North Sea (Law and Owens, 1990b) and North Atlantic (Kiescamp and Helder, 1990), although surface supersaturation was not always apparent. These data strongly suggest that the role of oceanic sources of N_2O requires reevaluation.

3. Geographical Regions to be Considered

Three geographical regions will be considered in our evaluation of nitrogen inputs to the ocean: coastal, mid-ocean gyre, and upwelling/polar regions. Each region has a unique blend of sources for nitrogen. Thus, each region will be impacted by changes in anthropogenic activities in a different way. The coastal region receives most of its nitrogen from rivers, with the atmosphere as a secondary source. Land-use changes in coastal watersheds as well as changes in the rate of atmospheric deposition can impact coastal productivity. Mid-ocean gyres receive their new nutrients from atmospheric deposition and transport from deeper water. Increased emission of nutrients to the atmosphere with subsequent long range transport and deposition, or climate change-induced alterations in atmospheric and/or oceanic circulation will affect the productivity of these oligotrophic regions. Upwelling/polar ocean regions receive most of their nutrients from waters below the photic zone. Ice-edge blooms are a special feature of polar regions. Again, climate change-induced alterations in atmospheric and/or oceanic circulation will affect the productivity of these regions.

B. NITROGEN INPUT TO THE OCEAN

1. Assessment of the Current Situation

a. Coastal Regions

i.) Important fluxes

There are many transport paths for chemical species, both natural and anthropogenic, entering the coastal zone. These include rivers and streams, sewage outfalls, dumping of wastes, and the atmosphere. Probably less is known quantitatively about the atmospheric input of nitrogen species to our estuaries and near-shore waters than any of the other transport paths. Most studies have concentrated on evaluating the other pathways, but recently there has been increasing interest in the potential of the atmosphere to supply significant quantities of both oxidized and reduced forms of nitrogen to the coastal marine environment. Atmospheric input to the watersheds of rivers can often provide a significant fraction of the riverine nitrogen as well.

ii.) Have fluxes increased?

Concentrations of inorganic nitrogen have increased markedly over the last three or more decades in most European rivers. The majority of data are for rivers entering the North Sea, and they all show similar trends. Typically, concentrations have increased two to threefold. In recent years the concentrations of NH_4^+ have begun to decline, in line with improvements in sewage treatment, and the most recent data have also shown a levelling off (and in some cases a decrease) in nitrate concentrations (Brockmann et al., 1988).

Although relatively long term concentration data sets are available for most major European

rivers, these are almost exclusively for sites at the upper limit of tidal influence, i.e., they represent gross inputs into the estuaries. Since estuaries are important sites of nitrogen cycling, and may act as efficient 'nitrogen filters' through denitrification and/or assimilation and immobilisation, the data cannot be used as indications of the net nitrogen inputs to the coastal ocean. Relatively few long term data are available for coastal water concentrations, and where they exist they are equivocal. Radach and Berg (1986) show a linear trend of increasing winter nitrate concentrations in the inner German Bight. However, Dickson et al. (1988a) have examined data from nearshore and offshore regions of the North Sea, and although they showed trends in winter nitrate concentrations, these were cyclical rather than a consistent increase. Cadee (1986) has examined nutrient concentrations in nearshore Dutch waters since the 1970's and has demonstrated a consistent increase in nutrient concentrations. The consensus appears to be that nutrient concentrations in some coastal areas have increased over the latter half of this century due to anthropogenic inputs, but that the area impacted in these regions is confined to localised, nearshore (one to tens of kilometers) regions.

Smith et al. (1987b) reported that of 383 reporting stations on rivers in the United States, nitrate concentrations increased from 1974 to 1981 at 116 stations, decreased at only 27 stations, and showed no statistical trend at the remaining sites. At the 116 sites with higher nitrate concentration the median increase was about 6.5%. Most of the increases occurred in the heavily industrialized eastern United States. Smith et al. also pointed out that atmospheric deposition has become a major source of nitrate in these rivers, particularly in the eastern United States and the northern parts of the Midwest, and that much of the increased riverine concentrations of nitrate in these regions is likely related to increased atmospheric deposition. These authors estimate that riverine delivery of nitrate to the Northeast Atlantic coast has increased by ~26-32%, to the southeast Atlantic coast by ~20-28%, and to coastal regions of the Gulf of Mexico by ~46%. The west coast of the United States has seen little change in the riverine input of nitrogen.

One of the publications that has most effectively galvanized interest and research on atmospheric input to coastal waters was the report by the Environmental Defense Fund (Fisher et al., 1988) on the role of acid rain, and its associated nitrogenous material, in supplying nutrients to polluted coastal waters of the northeastern United States. These authors indicated that approximately 40% of all the nitrogen contributed by human activity to the Chesapeake Bay enters via acid rain falling directly on the Bay or its watershed. The input of nitrate in rain (25% of the total input) exceeded that from animal waste runoff, was approximately the same as the input from point sources such as sewage treatment plants, and was exceeded only by fertilizer runoff (34% of the total). Fourteen per cent of the total input was ammonium in precipitation, resulting in atmospheric input accounting for almost 40% of the total nitrogen input to Chesapeake Bay. Of the total atmospheric input, about 25% fell directly on the Bay, while the remaining 75% fell on the watershed. As an interesting comparison, the application of nitrogen fertilizer to the watershed of the Bay is about 5.4 g m^{-2} yr^{-1}, while the atmospheric input of nitrate nitrogen is about 3.1 g m^{-2} yr^{-1}

Table 1, derived from Duce (1991) and GESAMP (1989a), provides a comparison of the atmospheric input of nitrogen species to that from all other sources for several European semi-enclosed seas and for several areas on the east coast of North America. The data in this table are reasonably consistent and suggest that when atmospheric input to a watershed (with subsequent input to the water body of some fraction of that total) and directly to the coastal water are considered, roughly 20-30% of the total can be traced to an atmospheric pathway. When only riverine and atmospheric input are compared, the atmospheric percentage is somewhat higher. When only direct deposition to the water surface is considered, the atmospheric percentage is probably in the 10-25% range.

It must be noted that calculations of the relative importance of atmospheric input, as determined by comparing the total inputs from the various sources or transport paths, can be misleading unless very carefully used and described. This is because chemical species in rivers and from sewage

outfalls enter the coastal waters directly at or very near the coast, providing very high concentrations, and their impact on productivity very near the coastline is large. The atmospheric input is spread more uniformly over the entire coastal area and beyond. For example, Duce et al. (1976) calculated that only 6% of the atmospheric lead transported offshore near New York City would be deposited within the first 100 km of the coast, assuming no rain. The remainder would be transported further out to sea. Thus, the atmospheric input generally becomes a proportionally more important source for material in the water at increasing distances from the coastline.

With increasing global population and industrialization and the associated increase in the emissions of nitrogen oxides, there is no question that the atmospheric input of oxidized nitrogen species to the coastal zone has increased over the past several decades. To a large extent this increase paralleled the acidity increase of rain in urbanized and industrialized regions, since many of the same types of anthropogenic processes that are associated with the increased acidity of rain are also important sources of oxidized nitrogen. Indeed, a significant fraction of the acidity of rain in these regions is due to nitric acid.

Table 1

Input of Nitrogen to Coastal Areas

Region	Total Atmospheric Input* (10^9 g yr^{-1})	Total Input All Sources (10^9 g yr^{-1})	Percent Atmospheric Input (%)	Ref.
New York Bight	--	--	13+	(1)
Chesapeake Bay	54	140	39	(2)
Long Island Sound	11	49	23	(2,3)
Neuse River Estuary, NC	1.7	7.5	23	(2,4)
North Sea	400+	1500	27+	(5)
Western Mediterranean Sea	350+	753++	46+	(6)
Baltic Sea	--	--	25+	(7)

*Total from direct atmospheric deposition and runoff of atmospheric material from the watershed.
+Direct atmospheric deposition to the water only.
++Total from atmospheric and riverine input only.
(1) Sinderman and Swanson (1979)
(2) Fisher et al. (1988)
(3) Farro et al. (1986)
(4) North Carolina Div. of Environmental Management (1985)
(5) North Sea Conference (1987)
(6) Martin, J.-M., et al. (1989)
(7) Roenner (1985)

iii.) Has productivity increased?

Considerable attention has been directed toward the question of increased biological production (eutrophication) in European waters in recent years. As with the nutrient data, the evidence is

rather equivocal. Radach and Berg (1986) have shown a marked increase in the abundance of flagellates and a decline in diatoms coincident with changes in nutrient concentrations in the German Bight. This is thought to be a response to the change in the relative abundance of nutrients, particularly the Si/N ratio, rather than the absolute quantity of nutrients present. Similar findings have been reported off the Dutch coast (Cadee, 1986). Unfortunately the data sets are rather short in time scale, and the interannual variability is frequently larger than the trend. While some studies suggest that increases in nutrients have led to increases in phytoplankton production, others have shown that local weather patterns are more important (Maddock et al., 1989). The situation in more open waters is also not clear. Excellent long-term (since the late 1940's) data are available for a large number of taxa (phytoplankton and zooplankton) from the Continuous Plankton Recorder (CPR) survey of the North Atlantic and North Sea. This unique data set has demonstrated the close links between the plankton community and weather patterns over the North Atlantic over time scales of decades (Colebrook, 1985; Dickson et al., 1988b; Owens et al., 1989). The mechanisms of interaction are not clear, but are probably associated with changes in turbulence, which will affect light availability and the development of the seasonal thermocline. Changes in atmospheric transport pathways during this time period also cannot be ruled out. These studies provide some of the few data that can be used to evaluate the consequences of climate change on plankton populations.

The specific case of *Phaeocystis spp.* is worth highlighting because of its potential links with DMS production. *Phaeocystis* is known to produce significant quantities of DMS (Gibson et al., 1990), and there are indications that this genus has increased in abundance in some regions in recent years. Some time series data are available for the eastern sector of the southern North Sea which suggest a marked increase in *Phaeocystis* since the mid 1970's (Cadee, 1986). Studies of the offshore regions of the North Sea and North Atlantic, however, have shown that the species has generally declined since the 1940's, with a slight increase over the last 5 years. The most recent increases are not thought to be associated with increases in nutrient inputs, but rather reflect the overall change in the phytoplankton composition of the North Atlantic, with which it shows a marked correspondence (Owens et al., 1989).

The combined evidence of primary production trends in European waters have, therefore, been equivocal. Some data clearly demonstrate increases coincident with increased nutrient concentrations. It is probable that if anthropogenic inputs have led to increases in production in European waters this is confined to localized, enclosed inshore waters, e.g., the Wadden Sea in the Netherlands and the northern Adriatic.

In the United States there is some evidence that increased productivity has taken place in coastal waters as a result of greater quantities of nitrate entering the coastal zone. For example, Kemp et al. (1983) has indicated that the significant decline in certain rooted plants in Chesapeake Bay probably resulted from growing turbidity in the water and from growth of algae on the blades of these plants that resulted from higher nutrient concentrations. D'Elia (1987) and D'Elia et al. (1986) also pointed out that the productivity in estuarine coastal waters has increased as a result of increased nitrogen loadings. Swanson and Parker (1988) pointed out that nutrient nitrogen enrichment in the New York Bight has been a significant factor in the low oxygen levels reported there every year since 1976. High levels of chlorophyll *a* and low levels of dissolved oxygen are now frequently observed in the spring in Delaware Bay, which is one of the most nitrate-enriched estuaries in the United States (NOAA, 1986). Similar problems have been found in the Albemarle-Pamlico Sound area of North Carolina (North Carolina, 1987). Paerl (1987) has shown that the severity of summer blooms of algae in the Neuse River estuary, North Carolina are directly related to the quantity of nitrogen in the river. It appears that the increased input of nitrogen from rivers and the atmosphere in industrialized regions can have some impact on the biological productivity of the adjacent coastal waters.

b. Mid-Ocean Gyres

i.) Important fluxes

Mid-ocean gyres are isolated from coastal nutrient sources; their nutrient supply is dominated by atmospheric deposition and tranport from deeper waters. By virtue of their oligotrophic nature, they are sensitive to added nutrients, either from increased atmospheric deposition or from changes in the rate of supply from below the photic zone.

ii.) Have fluxes increased?

Wet deposition of inorganic nitrogen has increased in mid-ocean regions downwind of continents with significant industrial activities. For example, Duce et al. (1991) show that the deposition of nitrogen to the North Atlantic Ocean is about 11 mmol m^{-2} yr^{-1}, compared to 3 mmol m^{-2} yr^{-1} for the South Atlantic Ocean. The higher values in the North Atlantic are due to the large anthropogenic sources in North America and Europe. The magnitude of such increases can also be determined by comparing nitrogen deposition rates at specific sites in remote regions to those in regions directly downwind from continental sources. For example, from a ten year record of precipitation composition at Amsterdam Island, a remote island in the southern Indian Ocean, Galloway (personal communication) calculated a deposition rate of 4 mmol m^{-2} yr^{-1}, while from a similar record at Bermuda, only about 1000 km downwind of North America, the deposition rate is about 8 mmol m^{-2} yr^{-1}. The relatively good agreement between these two methods of evaluating anthropogenic impact suggests that the deposition of nitrogen to mid-ocean regions that are impacted by anthropogenic emissions has probably increased by roughly a factor of 2 to 4.

However, primary production does not occur on an "annual-average" basis. It is an episodic event, and thus the impact of anthropogenic activities on the episodic deposition of nitrogen should also be considered. As an illustration, the ten year record of nitrogen deposition from Amsterdam Island shows that the median and maximum rates of episodic nitrogen deposition are ~22 and ~510 μmol m^{-2} $event^{-1}$, respectively, while at Bermuda, they are several times larger: ~85 and ~1500 μmol m^{-2} $event^{-1}$ (see Figure 3). These increases in episodic deposition supply a large amount of nitrogen relative to internal marine sources and will probably have a significant impact on productivity.

iii.) Has productivity increased?

The impact of atmospheric deposition of nitrogen on phytoplankton productivity in mid-ocean gyres has primarily been investigated in the North Atlantic Ocean, with a focus on the Sargasso Sea (Duce, 1986; Knap et al., 1986; Glover et al., 1988; and Hitchcock et al., 1990) A common thread in these papers is that, on the average, nitrogen deposition is not a dominant source. For example, at Bermuda an average nitrogen deposition rate of about 10 mmol m^{-2} yr^{-1} is substantially less than the nitrogen requirement for new production of approximately 70-200 mmol m^{-2} yr^{-1} in that region. We have attempted to show the global distribution of the importance of atmospheric inputs to the annual mean new production in Figure 4. Although a number of assumptions have been made in the construction of this figure, it can be seen that up to 15% of the annual new production can be met by atmospheric input over large areas of the ocean, predominantly in the central gyres. However, atmospheric deposition contributes significantly less than this over much of the ocean.

We have investigated the possible contribution of episodic events by comparing the 10 year frequency distribution of deposition at Bermuda with a realistic range of nitrogen assimilation. We have assumed a range of new nitrogen demand of 277 μmol m^{-2} d^{-1} (= 100 mg C m^{-2} d^{-1}, using an f ratio [the ratio of new production to total primary production] of 0.2) to 1400 μmol m^{-2} d^{-1}

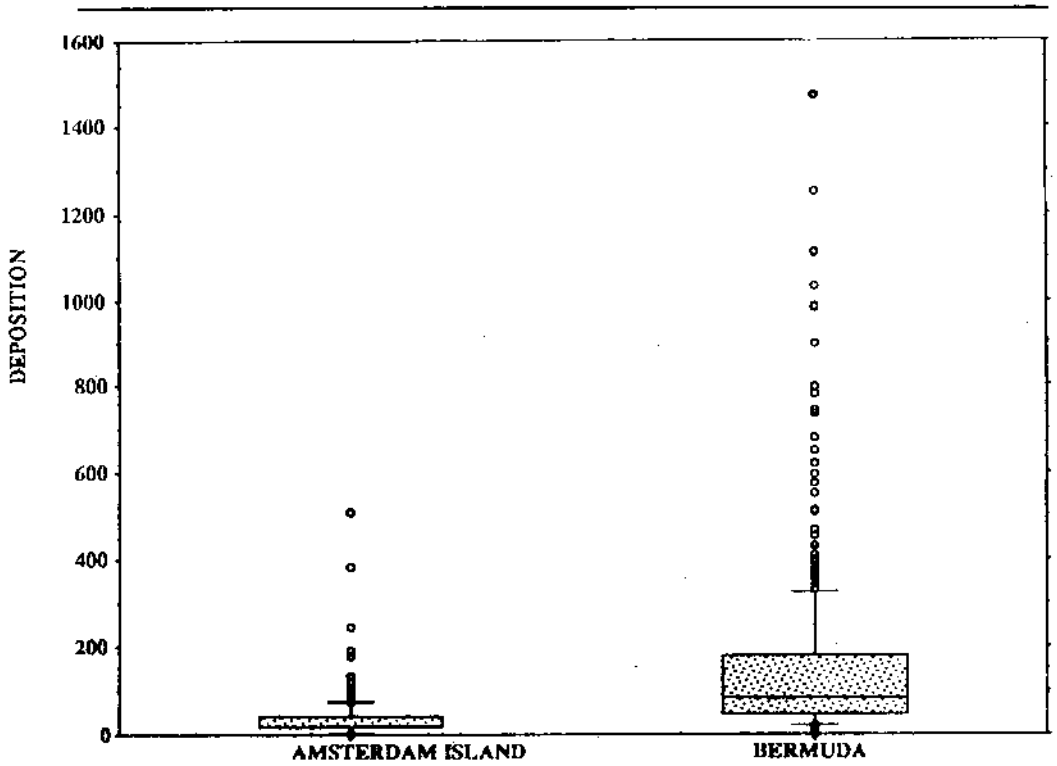

Figure 3. Percentile distributions of nitrate plus ammonium per-event deposition (μmol m^{-2} $event^{-1}$) over a ten year period at Amsterdam Island and Bermuda. The lower and upper bars represent the 10th and 90th percentile, respectively. The lower and upper outlines of the box represent the 25th and 75th percentile, respectively. The line in the box represents the median. The dots represent those events that fall below the 10th or above the 90th percentile.

(= 500 mg C m^{-2} d^{-1}, using an f ratio of 0.6). It can be seen (Figure 5) that under certain circumstances episodic deposition events can be highly significant.

This can be further demonstrated by examining the possible change in inorganic nitrogen assimilation during such an event. Mid-ocean surface nitrogen concentrations are typically on the order of 10-50 nmol l^{-1} NO_3^- (Garside, 1985; Eppley and Renger, 1988; Mantoura et al., 1991). Although NH_4^+ concentrations are not known with a similar accuracy, they are undoubtedly of a similar order (if not lower). The median and maximum atmospheric nitrogen deposition rates at Bermuda are ~85 and ~1500 μmol m^{-2} $event^{-1}$ (Galloway, personal communication). Assuming that these fluxes are dispersed through a surface mixed layer 75 m deep, the concentration of inorganic nitrogen could be increased in this layer by approximately 1-20 nmol l^{-1}, a highly significant increase. Similar conclusions have been drawn by Glover et al. (1988) and Hitchcock et al. (1990). Similarly low inorganic nitrogen concentrations are found in seas considerably closer to land than the mid-ocean gyres - e.g., the North Sea and the northwestern Mediterranean Sea, where NO_3^- concentrations <20 nmol l^{-1} have been measured during the summer, only tens of kilometers from the coast (Woodward and Owens, 1990).

These data strongly support the idea that atmospheric deposition is an important source of new nitrogen during episodic events in certain regions of the world ocean, especially in areas downwind of continents with significant anthropogenic nitrogen emissions.

c. Upwelling and Polar Regions

By definition, the most important flux of inorganic nitrogen to surface waters of upwelling regions is the wind or geostrophic current-driven injection of deep water containing high nutrient concentrations. Such systems are among the most productive ecosystems in the world ocean, and wind-driven upwelling regions typically exhibit surface nitrogen concentrations of several $\mu mol\ l^{-1}$. Such systems are themselves not nitrogen limited, although they are usually surrounded by regions which are typically nitrogen limited. With such high nitrogen concentrations, atmospheric nitrogen inputs are not important. Upwelling regions are not constant features but respond to variations in the physical environment which generate them (e.g., wind fields). Some systems are highly seasonal. For example, the upwelling off the Arabian peninsula is driven by the northern summer southwest monsoon. Equatorial upwellings are generated by current-induced divergence, and result in a circum-global band of elevated production (see Figure 2). Here, inorganic nitrogen concentrations are ~0.5-1.0 $\mu mol\ l^{-1}$, and extreme atmospheric nitrogen deposition events would probably only elevate the inorganic nitrogen concentrations by a few percent.

The polar oceans, particularly the Southern Ocean, are dominated by upwelling, but this is not ubiquitous, and extreme geographic variations exist. Indeed, there are large areas of the polar ocean where downwelling occurs. Inorganic nitrogen concentrations in the Southern Ocean are typically 15-25 $\mu mol\ l^{-1}$ (Jennings et al., 1984), the system is not nitrogen limited, and thus atmospheric nitrogen inputs will generally be insignificant. However, atmospheric iron deposition may be of significance in these regions (see later in this section). Areas of the Arctic Ocean do exhibit periods of nitrogen depletion (Smith et al., 1987a), and atmospheric nitrogen inputs could be significant during these periods (*cf* mid-ocean gyres).

A unique feature of the polar oceans is the development of ice-edge blooms. These are spring-time phenomena, largely induced by salinity stratification from melting ice. Ice-edge blooms can contribute to a significant quantity of the annual productivity of the high latitude oceans (Smith et al., 1987a; Smith and Nelson, 1990). The high concentrations of inorganic nitrogen present prior to the onset of the bloom, coupled with advective/upwelling supplies, are usually sufficient to supply the nitrogen demand for these blooms. Extremely low (possibly limiting) nitrogen concentrations have been reported during ice-edge blooms (Smith et al., 1987a), and it is conceivable that if an episodic event coincided with this period, a significant contribution might result. However, direct atmospheric inputs are in general a trivial source of nitrogen. The contribution of nitrogen of atmospheric origin from melting ice is possibly of greater significance. Ice contains significant concentrations of nitrogen, and it is possible that this contributes to the ice-edge bloom as the ice melts. Ice-edge blooms are also significant sources of DMS. Indeed, the highest absolute concentrations of DMS, and concentrations of DMS per unit of chlorophyll, have been recorded at Antarctic ice-edges (Gibson et al., 1990). These features are clearly important interfaces between biological productivity and the atmosphere.

It is not known whether production in upwelling regions or the polar oceans has increased as a result of human activities, but overall it is unlikely that atmospheric nitrogen inputs are important in influencing phytoplankton production in upwelling regions or the polar oceans. Ice-edge blooms may be a special case. Because of the potential significance of ice-edge blooms as a link between biological productivity and the atmosphere, this possibility is worthy of further consideration.

2. Projections for the Future

a. Introduction

It is likely that marine productivity has increased in some coastal regions over the past decades due to enhanced riverine and atmospheric inputs of nitrogen. The increases due to atmospheric

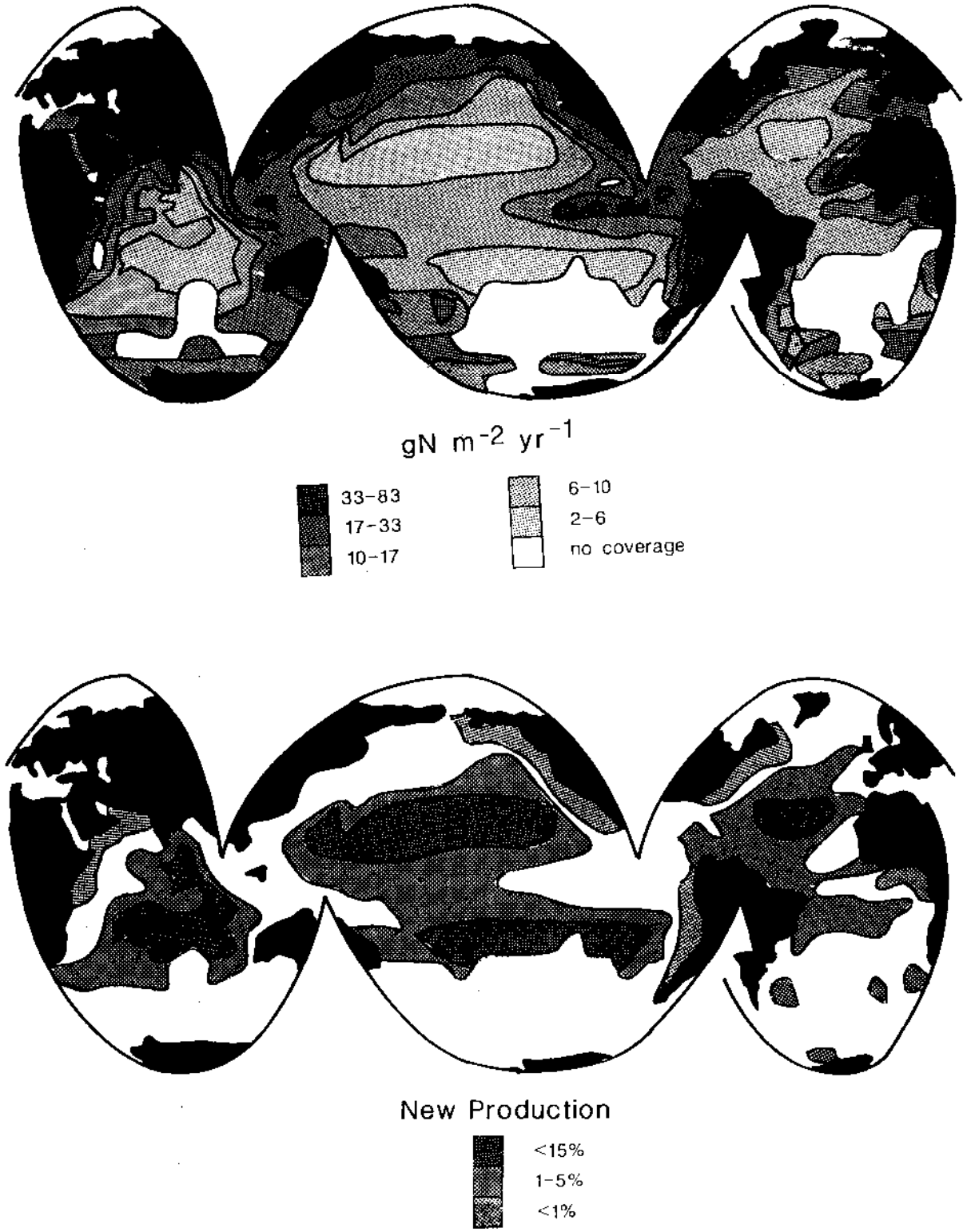

Figure 4. Top: Nitrogen required for primary productivity (derived from Figure 2). Bottom: Fraction of that nitrogen that is provided through atmospheric input.

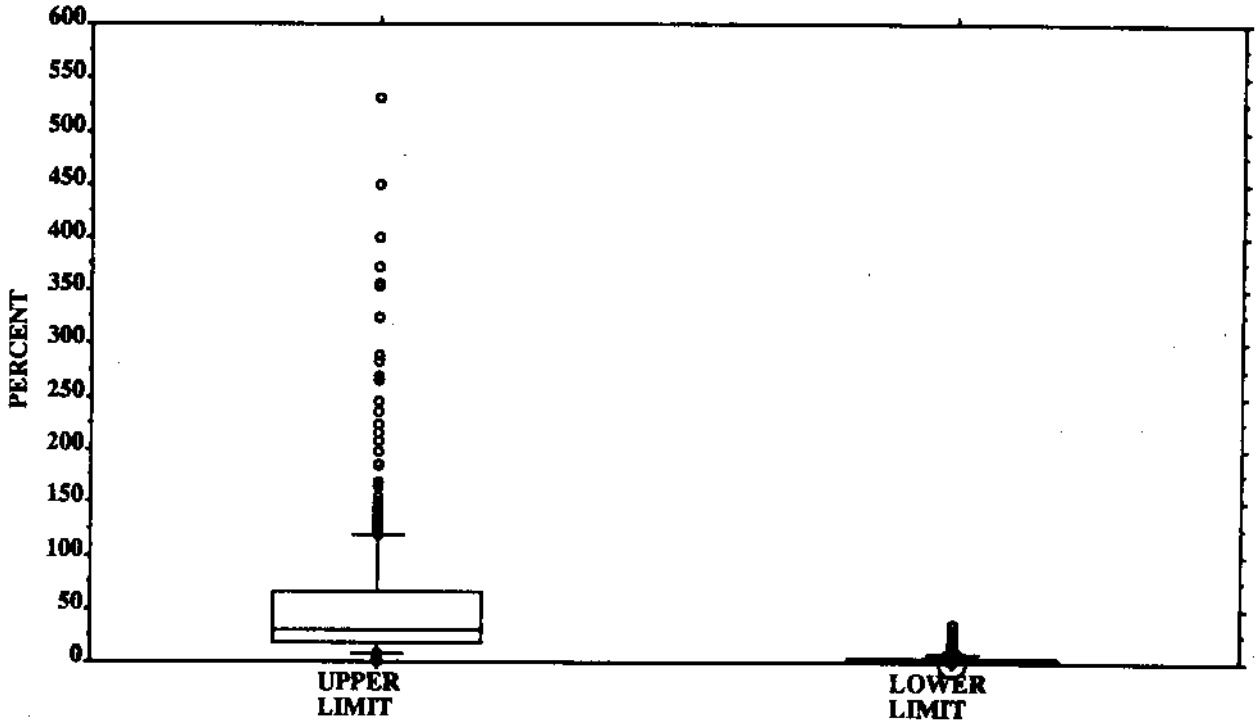

Figure 5. Percentile distribution of upper and lower limits on the contribution of atmospheric nitrogen to new production at Bermuda. The lower and upper bars represent the 10th and 90th percentile, respectively. The lower and upper outlines of the box represent the 25th and 75th percentile, respectively. The line in the box represents the median. The dots represent those events that fall below the 10th or above the 90th percentile.

input are most obvious downwind of regions of intense industrial activity. In the future, changes in marine productivity in response to human actions will continue to occur for three reasons. First, regions adjacent to or downwind of more developed countries (MDCs) will continue to impact marine ecosystems by virtue of their continued anthropogenic nitrogen emissions and land-use practices. Second, increases in the population and per-capita energy usage of less developed countries (LDCs) will result in increased nitrogen inputs in new regions of the world. Third, changes in atmospheric and marine turbulence induced by climate change could result in changes in all three sources of nitrogen - rivers, atmospheric deposition and upwelling. This section briefly discusses these three aspects.

b. Future Impacts on Marine Regions Adjacent to MDCs

Chesapeake Bay provides a good example of what we may expect in the future for regions next to MDCs (Fisher et al., 1988). In this region there are goals to reduce significantly the input of nitrogen from such point sources as municipal and industrial waste facilities and agricultural runoff. Planned agricultural management procedures may help reduce the emission of ammonia to the atmosphere. However, unless there are additional, more stringent nitrogen oxide emission controls, atmospheric emissions will continue unabated, and in fact are forecast to increase by about 44% by 2030. If the deposition of oxidized nitrogen species to the Bay increases proportionally, atmospheric deposition of nitrate to the watershed and directly to the Bay will become the dominant single source of nitrogen in Chesapeake Bay waters by 2030, contributing well over 40% of the total input, with all atmospheric species, including ammonium, contributing

about 55% of the total input.

It is apparent that unless stringent controls on the emissions of nitrogen oxides are developed, there will be increasing quantities of oxidized nitrogen entering the coastal zone. This source of nitrogen could well become the dominant source of nitrogen entering the coastal zone in many highly populated and industrialized regions of the world.

c. Future Impacts on Marine Regions Adjacent to LDCs

In 1980 the global population was 4.4 billion. By the year 2020, it is projected to almost double to 8.3 billion (Population Data Sheet, 1989, Population Reference Bureau, Washington, D.C.). The primary regions that will experience this increase will be Asia, Africa and South America. Increases in population, together with increases in per capita energy usage, will result in increases in riverine and atmopheric inputs of nitrogen in the ocean downstream and downwind of these regions. These increases are projected to be large. For example, Galloway (1989) estimated that increases in population and per-capita energy usage would cause marked increases in the emission of nitrogen oxides in Asia, with smaller absolute increases in Africa and South America (Figure 6). These increases in emissions have the potential to influence the productivity of marine regions downwind of these continental regions (shaded areas, Figure 6). It is recommended that these regions be the focus of future investigations, not only to understand the current role of atmospheric deposition on marine productivity, but also to provide baseline data by which the significance of future changes can be determined.

d. Climate-Induced Changes

Equatorward alongshore wind stress that drives coastal upwelling has trended significantly upward during the past 40 years (Bakun, 1990). This trend may represent an early signal of global warming. Continuing future increases in upwelling of nutrient-rich water could intensify productivity and oceanic carbon assimilation in these areas. Future climate changes will also likely result in changes in population and industrialization in many regions, which in turn could result in different patterns of nitrogen oxide emissions than at present. In addition, changes in precipitation and wind patterns could significantly affect the transport and distribution of anthropogenic nitrogen species over and into the ocean. Since the transport from source regions is related to local and regional meteorological regimes, and since present climate models do not have sufficient resolution on these spatial scales, it is difficult, if not impossible, to predict quantitatively at present any future changes in the delivery of nitrogen to the ocean from the continents. This is, however, a potentially important issue that should be evaluated carefully when appropriate climate models have been developed.

C. IRON INPUT TO THE OCEAN

1. Assessment of the Current Situation

It is apparent that if iron is a limiting nutrient for marine primary productivity anywhere in the ocean, it is probably in open ocean regions. There are plentiful supplies of iron in coastal areas due to riverine input and resuspension from sediments. The most likely locations for iron limitation are polar regions and equatorial upwelling regions, where other nutrients are quite abundant and where sources for iron are minimal. It is in these regions that atmospheric input may also be most important. It must be pointed out, however, that the entire issue of iron limitation in the ocean is still quite controversial.

The atmospheric transport of iron and its deposition to the ocean has recently been reviewed by Duce and Tindale (1991). Atmospheric iron is present on mineral particles, which are primarily generated in arid regions on the continents. For example, over China local episodic meteorological

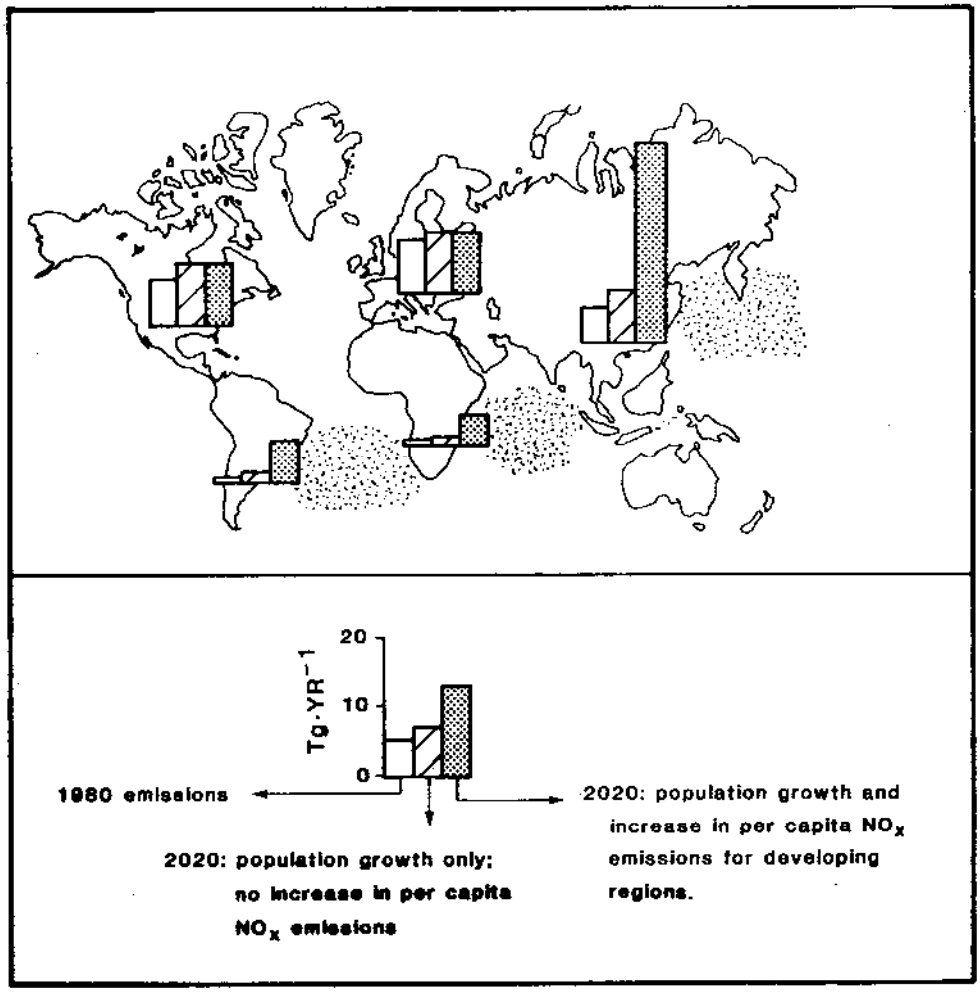

Figure 6. Estimates of NO_x emissions based on continental population growth and increases in per capita NO_x emissions by 2020. The units are Tg (10^{12} g) N yr^{-1}. From Galloway (1989).

events, such as strong frontal passages or thunderstorms, form large dust clouds which are often carried into the upper levels of the troposphere and are transported rapidly by strong upper level winds out over the open North Pacific Ocean. This dust gradually settles into the lower troposphere as it moves over the ocean, where it is primarily removed to the ocean surface by rain (Uematsu et al., 1985). Most dust storms in China occur in the spring following the passage of a cold front. At this time of year the winter snows have melted and there is little or no vegetation. The dust arrives at mid-Pacific islands such as Midway and Oahu from 5 to 10 days after an event in China. Deposition is thus very episodic, with most of the dust entering the ocean in from 3 to 5 events in the spring, each of which is perhaps 1 to 3 days in duration. Since most of the removal is via rain, the input to any particular location depends largely on the extent and duration of local precipitation. This likely results in rather spatially patchy inputs of the mineral material in these oceanic regions. Very large mineral particles have been observed at mid-Pacific locations (as large as 300 μm aerodynamic equivalent diameter (Betzer et al., 1988)), although the mass median diameter for mineral particles over open ocean regions is typically a few micrometers.

Biological systems utilize iron in the form of ionic species of Fe(II) and Fe(III). Chloride,

hydroxide, carbonate and sulfate complexes and ion pairs as well as organic iron complexes likely are included in the collection of iron species present in seawater, rainwater, and marine aerosols. A variety of particulate forms of iron, including inorganic colloids, mineral particles and adsorbed iron on biological and inorganic particles are also common. The thermodynamically stable oxidation state of iron in seawater and rainwater is Fe(III), but photochemical or microbial reduction of Fe(III) to Fe(II) may provide significant concentrations of Fe(II). For example, recent measurements suggest that in aged mineral aerosol samples collected over the Pacific, Fe(II) may account for approximately 50% of the total iron (Zhuang et al., 1991), while other studies support the belief that Fe(II) is an important photo-active species in clouds and rainwater (Behra and Sigg, 1990; Faust and Hoigne, 1990). The Fe(II) is probably rapidly oxidized to Fe(III) when the aerosols or rain enter the ocean, but Fe(II) can be regenerated to some extent by photochemical or microbial reduction in seawater, as mentioned above (see also Section IV). Fe(III) is very insoluble in seawater, forming amorphous colloidal hydrous ferric oxide at seawater pH.

Zhuang et al. (1990) have used mineral aerosol particles from samples collected over the central North Pacific to investigate in the laboratory the dissolution of iron from these particles. Defining dissolved iron as that iron which passes through a 0.4 μm pore size Nuclepore filter, Zhuang et al. found that as much as 40-60% of the iron would dissolve if the total iron in the seawater was only a few nmol kg^{-1}. It was observed that the maximum concentration of dissolved iron in these experiments was ~10-20 nmol kg^{-1}, which is very similar to the saturated concentration of hydrous ferric oxide in seawater (Byrne and Kester, 1976). The aerosol iron was released in just a few minutes, suggesting that most of the dissolved iron will enter the euphotic zone before the aerosol particles can settle into deeper water. It is likely that the aerosol iron dissolves rapidly because the mineral particles are part of a mixed, highly acidic aerosol that also contains sea salt and sulfuric acid (Zhuang et al., 1990; Andreae et al., 1986). This mixed aerosol is likely formed as a result of coalescence processes within clouds. Thus, the iron dissolution probably takes place primarily during the atmospheric transport, so the iron can be rapidly released when the particles enter the sea.

To assess whether or not iron may be a limiting nutrient in the ocean, Martin and Fitzwater (1988) and J.H. Martin et al. (1989, 1990) have undertaken shipboard enrichment studies in which they have added ferrous iron to three-liter vessels containing ambient plankton populations and exposed to ambient light conditions on deck. Studies in the Gulf of Alaska and the Southern Ocean showed significant growth, as indicated by the increased concentrations of chlorophyll *a*, in the growth chambers. However, other investigators (de Baar et al., 1990; Banse, 1990 and 1991; Dugdale and Wilkerson, 1990) have questioned whether the growth observed by Martin and co-workers actually indicates that productivity in those oceanic regions is limited by iron. Recently Martin, Tindale and Duce (unpublished data) added aerosol material collected over the North Pacific to growth chambers containing ambient seawater and phytoplankton populations in the central Pacific equatorial upwelling region. Significant production of chlorophyll *a* took place, indicating that iron, or some other material in the aerosol, was apparently enhancing phytoplankton growth. Clearly considerable additional research is required before the question of the importance of iron as a limiting nutrient in open ocean regions is resolved.

2. Projections for the Future

Since atmospheric iron over the ocean is almost exclusively derived from natural sources, the primary factors effecting future changes in the delivery of atmospheric iron to the ocean would be related to possible changes in climate in the source regions. Of particular importance would be changes in aridity of continental regions, particularly in those areas where atmospheric wind patterns could effectively transport the iron to open ocean regions. This would include areas directly downwind of major desert regions. Decreasing precipitation could result in more frequent and severe dust storms. Changes in the atmospheric circulation patterns would also effect the areas

impacted by atmospheric transport from continental regions, as is the case for nitrogen. Similarly, changes in the frequency and strength of the type of events (e.g., strong fronts, thunderstorms, etc.) that generate large dust storms would also significantly affect transport to the ocean. As for nitrogen, present climate models do not have sufficient resolution to enable realistic quantitative predictions to be made of changes in the transport of iron to the ocean from the continents.

D. LINKAGES WITH OTHER ENVIRONMENTAL CHANGES

Human activities have directly increased the biological productivity of some marine regions due to increased nitrogen inputs. Other human activities have contributed to decreases in stratospheric ozone (Section IV), increases in tropospheric concentrations of radiatively active gases (Section III), and increases in cloud condensation nuclei (CCN)(Section III). It is possible that there may be linkages, or feedbacks, between the impacts of these other environmental changes and the productivity of the surface ocean. This section very briefly examines some of those linkages.

Increases in quantities of sulfate aerosol particles, derived from human activities, in the northern Hemisphere has the potential for increasing the cloudiness and decreasing both the temperature of the surface ocean and the amount of light reaching the surface ocean (Charlson et al., 1987). Both effects could decrease marine productivity. Currently, any impact is expected to be most marked over the North Atlantic Ocean.

The decrease in stratospheric ozone at high latitudes, which apparently is spreading to lower latitude regions, will lead to an increase in incident of UV-B radiation, which could cause a decrease in marine productivity.

Changes in productivity can lead to secondary effects. For example, decreased productivity would lead to a decrease in DMS production, which might effect the formation of CCN. Decreases in productivity would result in lower carbon fluxes to the marine sediments. Alternatively, increases in productivity could result in increased cloudiness and an increased carbon flux to marine sediments.

As complicated as the impacts of increased CCN and decreased ozone are on marine productivity, they are relatively simple compared with the linkages between increases in the concentrations of radiatively active trace gases and the biological productivity of the surface ocean. The increase in temperature due to increased concentrations of carbon dioxide, ozone, CFC's, methane, etc. is hypothesized to result in changes in present patterns of precipitation, wind speed and atmospheric transport, among other factors. Changes of this type have the potential to affect very significantly all aspects of the delivery of nitrogen and iron to the surface of the ocean.

E. CONCLUSIONS

1. The deposition of atmospheric anthropogenic nitrogen has probably increased the productivity in coastal regions along many continental margins. Atmospheric deposition can be an important source of new nitrogen and may have increased productivity somewhat in mid-ocean regions downwind from significant population and industrial centers (e.g., the central North Atlantic Ocean).

2. The projected future increases of nitrogen oxide emissions from Asia, Africa and South America will provide significant increases in the rate of deposition of oxidized nitrogen to the central North Pacific, the equatorial Atlantic, and the equatorial and central South Indian Oceans. It is likely that this nitrogen would increase primary productivity in these regions, but the magnitude of the increase is unknown.

3. It is apparent that unless stringent controls on the emissions of atmospheric nitrogen oxides are

developed, there will be increasing quantities of oxidized nitrogen entering the coastal zone in the future.

4. It is unlikely that atmospheric nitrogen inputs significantly influence phytoplankton production in upwelling regions or the polar oceans. It is possible that ice-edge blooms may be a special case. Because of the potential significance of ice-edge blooms as a link between biological productivity and the atmosphere, this possibility is worthy of further consideration.

5. Atmospheric iron may be an important nutrient in certain open ocean regions. Future changes in the delivery to the ocean of atmospheric dust containing iron are uncertain, but will likely occur if there are changing patterns of aridity as a result of climate change.

6. Current climate models cannot adequately predict changes in the atmospheric transport paths for atmospheric nitrogen and iron species to the world ocean as a result of possible future climate change. This is, however, a potentially important issue that should be evaluated carefully when appropriate climate models have been developed.

III

GLOBAL CHANGE AND THE AIR-SEA EXCHANGE OF GASES

A. INTRODUCTION

Increasing concentrations of CO_2 and other radiatively important trace species in the global atmosphere are predicted to lead to significant increases in both atmospheric and surface ocean temperatures in the next century. A very important factor in determining the amount of CO_2, either that emitted from fossil fuel burning or that from biomass destruction, which remains in the atmosphere is the rate at which it is taken up by the oceans. Thus, a major task is to assess our current quantitative understanding of the net flux of CO_2 and other radiatively important trace species from the atmosphere to the oceans. The many uncertainties in estimating the oceanic sink are discussed in this section, together with a description of the possible directions for future research. A necessarily speculative account of future global changes in the oceanic uptake of CO_2 is also presented.

Another gas that is of potential climatic significance is dimethyl sulfide (DMS). DMS is formed by algae in seawater, and some fraction of it is released to the atmosphere where it is oxidized to sulfate aerosols, *inter alia*. In the remote marine atmosphere these aerosols are an important source of cloud condensation nuclei, which in turn are important in the climatology of clouds. In this case we examine the various uncertainties of this proposed DMS-climate link and how marine emissions of DMS may change in the future. The flux of ammonia out of the oceans is also examined, as is the interaction of the ammonia cycle with that of DMS and its atmospheric oxidation products to form ammonium (bi)sulfate aerosols.

The emphasis in this section is clearly on the air-sea exchange of CO_2 and DMS, with some reference to ammonia. A number of other gases were also considered, but are not dealt with here. The sea is a net source for all of these gases in the atmosphere: carbonyl sulfide (COS), CO, non-methane hydrocarbons (NMHC) and N_2O. There is evidence for photochemical production of COS, CO, and probably NMHC in surface seawater. These gases are discussed in Section IV, which deals with photochemical processes. N_2O was discussed briefly in Section II.

B. THE AIR-SEA EXCHANGE OF CO_2

1. The Global Carbon Budget

A balanced budget for anthropogenic CO_2 continues to elude the scientific community despite the passing of more than five decades since the papers of Callendar (1938), who first investigated in a systematic way the increase in the atmospheric CO_2 concentration. The only relatively firm constraints on this budget are the increase in atmospheric CO_2, measured at monitoring stations since the late 1950s, and the quantitative information on the release of CO_2 by the burning of fossil fuels (and to a small extent the production of cement). By contrast, quantitative estimates of the oceanic sink and the terrestrial biospheric sources due to deforestation and land use changes have large uncertainties associated with them. Table 2 presents the different terms in the CO_2 budget for the period from 1980-1989 as reported by IPCC (1990). We note that the budget is unbalanced, and that the oceanic sink and the deforestation source are known with only poor certainty.

2. The CO_2 Flux Across the Air-Sea Interface

a. Modeling Approach

The flux of carbon absorbed by the ocean has been computed by models, either box models or

Table 2

1980 to 1989 Budget for CO_2 Perturbation+

	Average Perturbation (10^{15} g C yr^{-1})
Sources	
(1) Fossil fuel combustion	5.4 ± 0.5
(2) Deforestation	1.6 ± 1.0
TOTAL	7.0 ± 1.2
Sinks	
(1) Atmosphere	3.4 ±0.2
(2) Oceans (Steady State Models)	2.0 ± 0.8
TOTAL	5.4 ± 0.8
Sinks Unaccounted For	
	1.6 ± 1.4

+IPCC (1990)

3-D general circulation models. Recently, Sarmiento et al. (1990) have used the model developed at the Geophysical Fluid Dynamics Laboratory (GFDL) to develop a perturbation simulation of CO_2 uptake by the ocean for the 1980-1989 period. They computed an average flux of CO_2 into the ocean of 1.9 x 10^{15} g C yr^{-1}. It is worthwhile pointing out the good agreement between the output of the simple models used by IPCC (1990) (given in Table 2) and that of the 3-D general circulation model used by Sarmiento et al. (1990), particularly since the latter gives a more realistic description of the oceanic circulation. In fact the distribution of "bomb" ^{14}C, as measured during the GEOSECS program, was used to calibrate the transport coefficients used in both types of models. It would thus seem logical that they obtain similar values for the quantity of CO_2 taken up by the ocean.

However, this apparent consensus between model results has recently received a severe challenge as a result of work by Tans et al. (1990), confirming the studies of Keeling et al. (1989). These authors have produced new estimates of the terrestrial and oceanic sources and sinks by an analysis of atmospheric and oceanic CO_2 observations in combination with a 3-D model of atmospheric CO_2 transport. Their model of CO_2 transport, when constrained by the observed interhemispheric CO_2 gradient, does not permit a sufficiently large transport from the regions of anthropogenic production in the northern hemisphere to a proposed southern hemisphere oceanic sink. These authors conclude that the total oceanic sink must be less than 1 x 10^{15} g C yr^{-1} over the period 1981-87. This is half of the value presented in Table 2. This in turn implies that the net carbon budget imbalance that would have to be accounted for by terrestrial biota sinks is greater than 2.6 x 10^{15} g C yr^{-1}, with much of this uptake occuring in the temperate latitudes of the northern hemisphere. The conclusions drawn from the atmospheric model used by Tans et al.

(1990) appear fairly robust. However, their calculation of the ocean-atmosphere flux may be in error, as discussed further below.

b. Direct Flux Calculations

The flux of CO_2 between the atmosphere and the ocean is estimated from a bulk formula that takes the product of the CO_2 exchange coefficient (which parameterizes the physical driving force) and the CO_2 partial pressure difference between the ocean and atmosphere (the chemical driving force). To integrate this flux over an ocean basin it is necessary to estimate the values of the gas exchange coefficient and the partial pressure difference over large areas. For CO_2 we may write,

$$F = K \bullet \Delta p_{CO_2} \qquad (1)$$

where F is the flux (mol m^{-2} yr^{-1}), K is the exchange coefficient (mol m^{-2} yr^{-1} μatm^{-1}) and Δp_{CO_2} is the partial pressure difference of CO_2 (μatm) between the ocean and atmosphere.

Direct calculation of the air-sea flux of CO_2 requires that equation (1) be spatially integrated over the entire surface of the global ocean and be temporally integrated over an annual cycle. To do this it is necessary to know the spatial and temporal variation of both surface Δp_{CO_2} and the gas transfer coefficient, K. These quantities are quite variable, both temporally and spatially, making the integration very difficult. We estimate that at present the oceanic flux calculated using this method is uncertain by a factor of two.

i.) Gas exchange coefficient

The gas exchange coefficient, K, has a strong positive correlation with wind speed. Liss and Merlivat (1986) proposed a set of linear relationships based on wind tunnel experiments and the lake measurements of Wanninkhof et al. (1985). This relationship has been supported by recent measurements made in the North Sea under more realistic conditions (Watson et al., 1991). Different authors (Etcheto et al., 1991; Heimann and Monfray, 1991; Erickson 1989; Etcheto and Merlivat, 1988) have used the Liss and Merlivat relationship to compute the space and time variability of the CO_2 exchange coefficient at the air-sea interface for the world ocean using wind fields derived from wind climatology data sets, from outputs of atmospheric circulation models or from satellite data (see Figure 7). It is then possible to compute the mean value of the exchange coefficient for the global ocean. The computed values reported in the literature range between 3.3 and 3.6 x 10^{-2} mol m^{-2} yr^{-1} μatm^{-1}. These numbers are significantly different from the value based on the distribution of bomb ^{14}C in the ocean, which is ~6.1 x 10^{-2} mol m^{-2} yr^{-1} μatm^{-1}. It is worthwhile investigating possible reasons for the discrepancy between these sets of data.

The ^{14}C-based exchange coefficient has been carefully computed by Broecker et al. (1985), who indicated that all the bomb ^{14}C injected into the atmosphere since the beginning of the 1960s has entered the ocean by gas exchange. Knowledge of the time history of both the atmospheric $p^{14}CO_2$ and the total inventory of bomb ^{14}C in the ocean allows computation of the value of the mean global gas exchange coefficient. The atmospheric part of the calculation is quite straightforward. The oceanic inventory is more difficult to evaluate for the following reasons. The bomb ^{14}C signal in the ocean must be distinguished from the natural ^{14}C background, which is not well known in certain areas. Moreover, the inventory is based on measurements made at the GEOSECS stations, which represent a limited number of sampling points relative to the entire area of the oceans. This undersampling is quite critical in the computation of the bomb ^{14}C inventory, as we know that the tracer is primarily confined to the upper layers of the ocean, which show a large variability. This was certainly not taken into account very well by the sampling strategy

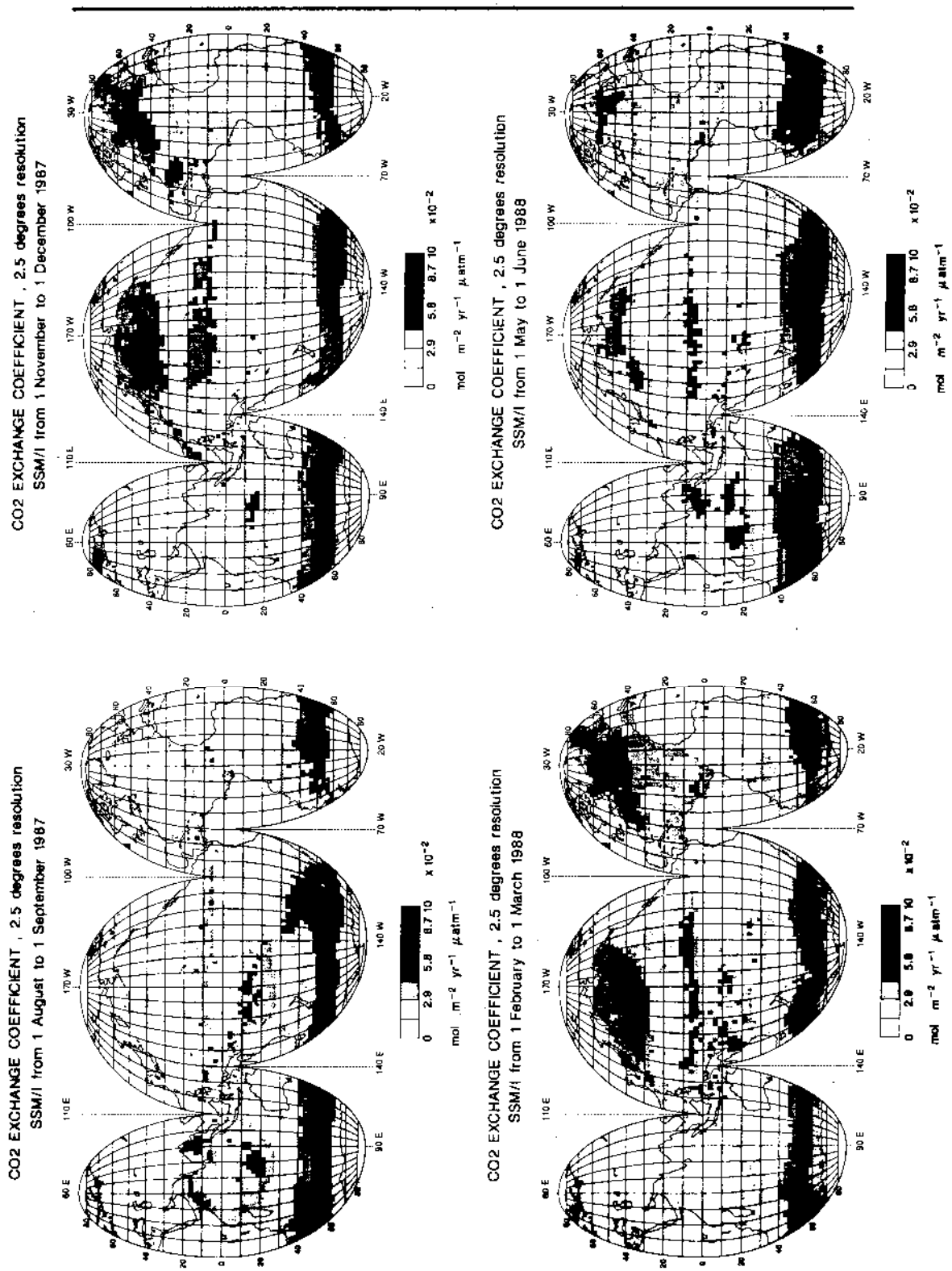

Figure 7. Maps of CO_2 exchange coefficients for different months in 1987 and 1988. From Etcheto et al. (1991).

during GEOSECS. For these reasons the error of 20% often quoted for the ^{14}C exchange coefficients seems to be overly optimistic.

Etcheto et al. (1991) computed monthly values for the world ocean using microwave radiometer data (Wentz et al., 1986). The results show very large temporal and spatial variability for this parameter (see Figure 7). In the near future it should be possible to document this variablity more accurately with the launch of satellites dedicated to oceanic observations (ERS-1 and 2 and NSCAT).

ii.) Specification of the air-sea concentration difference

Determination of Δp_{CO_2} presents a more difficult problem. No method has so far been suggested to obtain directly surface water p_{CO_2} from satellites. Measurements available to date have been made from research vessels or ships of opportunity. Such measurements have been undertaken over approximately the past 20 years, but the data base is still inadequate to make the global flux calculation with sufficient accuracy (i.e., to within 0.5×10^{15} g yr^{-1}) to answer the major questions concerning the carbon budget.

If surface water p_{CO_2} changed smoothly and slowly with location and time, then a relatively small number of measurements would suffice to define the concentration field. While in some regions of the world this may be true (the interiors of the sub-tropical gyres, for example), there are many regions where p_{CO_2} appears to be highly variable on short space and time scales. For example, recent data from the North Atlantic collected during the 1989 JGOFS (Joint Global Ocean Flux Study) Bloom experiment indicates that small-scale (10-100 km) variablity on the order of 30 µatm, associated with patchiness in biological productivity, was the norm (Watson et al., 1991, see Figure 8). To obtain sufficient measurements to enable adequate averaging of such a "noisy" field is a daunting task, made even more difficult by the rapid seasonal shifts observed. We note that a systematic error of 1 µatm over the entire oceans would lead to an error in the integrated flux of about 0.2×10^{15} g C yr^{-1}.

One such systematic error that does not appear to have been taken into account in the recent estimates of the CO_2 flux into the ocean (see above) is that due to the bulk-skin temperature difference, ΔT, at the surface of the ocean. This effect depends on actual weather conditions that specify the heat and momentum fluxes through the sea surface. The surface skin layer, through which molecular transport is dominant, regulates the fluxes of shortwave and longwave radiative energy as well as the sensible and latent turbulent energy fluxes across the sea surface.

Recent values of ΔT have been reported by Schluessel et al. (1990) based on measurements made during a six week cruise in the North Atlantic Ocean. It is shown that the bulk-skin temperature difference varies between day and night with mean values respectively equal to 0.11°K and 0.30°K, the skin layer being colder than the bulk water. A cooling of 0.2 degrees will have the effect of lowering the effective p_{CO_2} of water in contact with the atmosphere by 3 µatm, because p_{CO_2} is a sensitive function of temperature. Calculations which ignore this effect will underestimate the oceanic sink by 0.6×10^{15} g C yr^{-1}. We must point out that a cooling effect will be the most important in the high latitude areas where the momentum and latent heat fluxes are large; these areas represent the main zones for invasion of CO_2 from the atmosphere to the ocean. In consequence, neglecting the skin effect underestimates the magnitude of the invasion flux in these areas.

In the outgassing regions, e.g., tropical areas, the skin effect must be smaller (radiative fluxes are more important). However, if we neglect it, we overestimate the evasion flux and consequently we add again an underestimation of the total net ocean sink. These qualitative

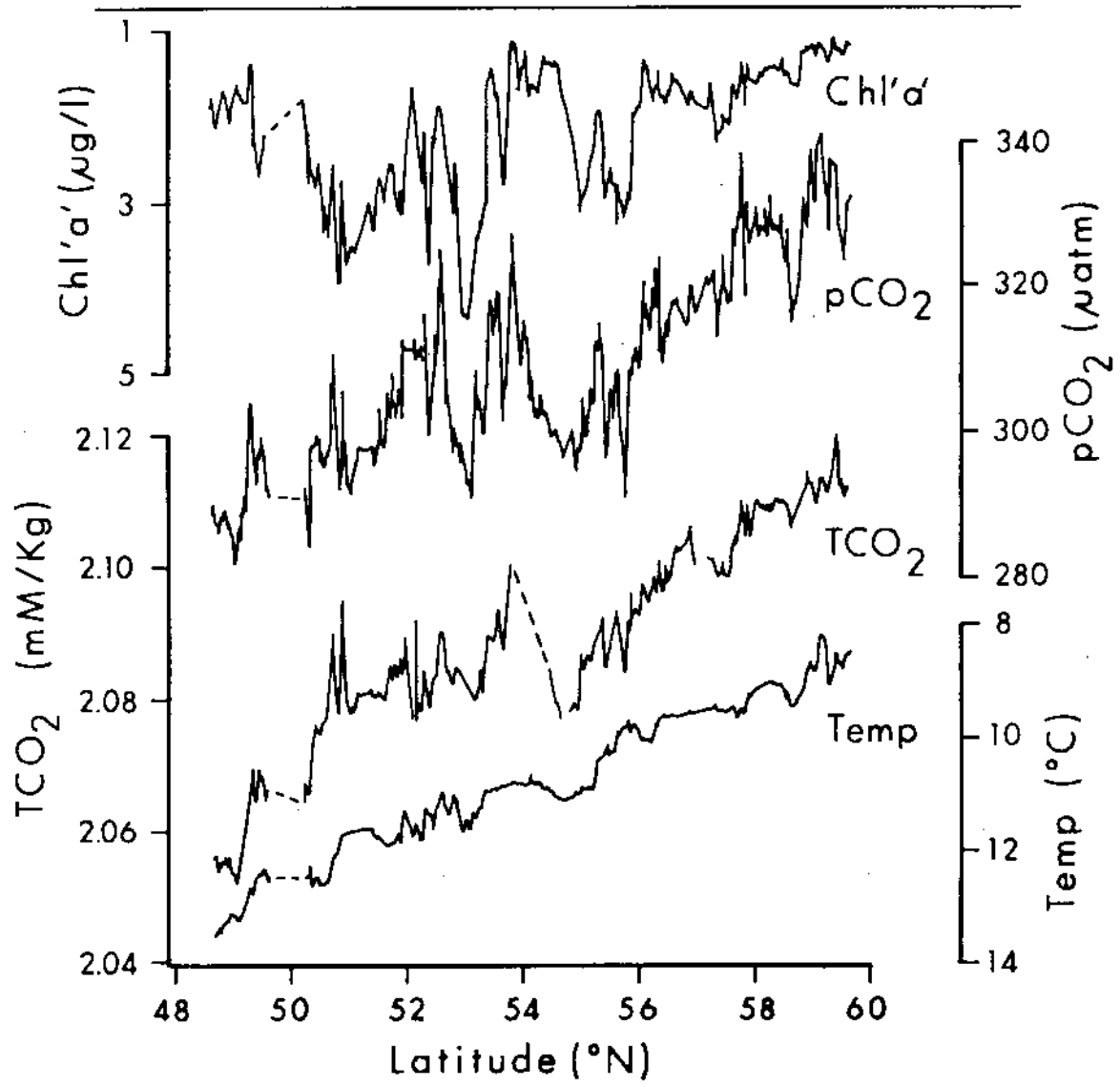

Figure 8. Surface chlorophyll, p_{CO_2}, T_{CO_2}, and temperature between 48°N, 20°W and 60°N, 20°W in the North Atlantic, May 1989. Note the large spatial variation in all parameters, and the locally good correlation between p_{CO_2}, chlorophyll and temperature. From Watson et al. (1991).

arguments show that it is important at the global scale to pay attention to the skin effect as it is a cause of a systematic error in the computation of the net flux of CO_2 absorbed through the atmosphere-ocean interface.

It has become apparent that p_{CO_2} in oceanic surface waters probably varies dramatically with season in parts of the world away from the tropics, due both to biological and temperature effects. Heating of the surface results in an increase in p_{CO_2} such that, other things being equal, summertime values should be higher. However, biological productivity fixes carbon from the water and has the opposite effect. Which effect "wins" depends on the location. For example, in the North Atlantic north of 40°N there is substantial summer drawdown of CO_2 due to phytoplankton productivity, but south of this latitude the seasonal effect tends to be in the other

direction. The transfer coefficient also varies seasonally, because in winter at temperate latitudes winds are higher. The seasonality of the transfer coefficient is out of phase with the dominant biological effect on p_{CO_2} at higher latitudes, so that the flux through the sea surface tends to remain reasonably constant through the year. For example, we calculate that for the North Atlantic north of 40°N, using transfer coefficients of 2×10^{-2} and 6×10^{-2} mol m $^{-2}$ yr^{-1} µatm^{-1} and Δp_{CO_2} values of 50 and 20 µatm (values are for summer and winter respectively, and the references are Etcheto et al., 1991 and Watson et al., 1991), the summertime flux is 1.0 and the wintertime flux is 1.2 mol m^{-2} yr^{-1}, both fluxes being into the water. Most of the seasonal change in atmospheric concentrations observed in the northern hemisphere is therefore due to uptake and release from land vegetation, with only a small oceanic component.

Most of the surface p_{CO_2} data so far collected are in the process of being collated by Takahashi and co-workers, and some maps of global Δp_{CO_2} have recently been published by Tans et al. (1990). These maps are based on a combination of all the data collected between 1972 and 1988 into a single seasonal cycle. There are substantial regions where there are essentially no measurements, particularly in the Southern Ocean, South Pacific, and close to ice edges in polar regions where high Δp_{CO_2} values are known to occur. Even in the relatively better sampled regions the data may be inadequate to define properly the regional fluxes. It is therefore apparent that to improve estimates of the global flux of carbon ways must be found to increase substantially both the coverage and density of oceanic p_{CO_2} measurements in the future. Possible methods for achieving this are discussed below.

c. Future Strategies

If we must rely on measurements of p_{CO_2} from research vessels alone it will be many years before we are satisfied with the coverage of the data base. Alternative techniques are also required. Among those which are being developed are:

i.) Use of ships of opportunity

Commercial vessels can be used to collect data on a much more regular basis than can be obtained from research ships. These have already been used to good effect by, e.g., Takahashi et al. (1986), who used technicians aboard selected cargo ships. To make the best use of commercial vessels, reliable instrumentation to measure p_{CO_2} for long periods of time without attention will be required. This is now under development at several laboratories in the United States, the United Kingdom and France. Development of existing methods (gas chromatography or infra-red absorption) for use on ships of opportunity has the advantage that data of high accuracy and reasonable density of coverage could be obtained for some important ocean regions which are frequently travelled by ships. We note, however, that some of the least sampled regions of the ocean are also virtually untravelled by commercial vessels.

ii.) Buoy-mounted probes

At least two laboratories (Woods Hole Oceanographic Institution in the United States and Laboratoire d'Oceanographie dynamique et de Climatologie in France) are currently developing optical devices for measurement of p_{CO_2}. These are designed to be mounted on free-drifting buoys. Once developed, these instruments could obtain time-series data that have been rarely available to date. These instruments could be deployed in remote areas that have previously been severely under-sampled. The first of these instruments may be available within 2-3 years.

iii.) Process studies

Recent work as part of JGOFS has shown that p_{CO_2} can be related to surface chlorophyll and temperature in a manner which is reasonably in accord with present understanding of surface productivity (Watson et al., 1991; Taylor et al., 1991). Since both temperature and chlorophyll from ocean color measurement are measurable from satellites, it should be possible to predict p_{CO_2} by using satellite observations to constrain models of the surface carbon system. This approach requires an understanding of the processes controlling surface p_{CO_2}, but this is also required if we are to predict how the oceanic sink may change in response to future climate changes. It is likely that such models would be "region specific" and would need to be developed with the help of detailed process studies in many different parts of the world.

iv.) Measurements of total CO_2 (T_{CO_2}) on oceanographic sections

It has recently been pointed out by Brewer et al. (1989) that it is possible to obtain quite accurate estimates of the net carbon flux through selected oceanographic sections by combining high quality total CO_2 data with estimates of the net currents through the section. If the ocean were in steady state with respect to CO_2 transport, the fluxes so obtained could be used to deduce the net air-sea flux for each ocean region. For example, since the North Atlantic is nearly closed off to the north, the net flux to the south through any section between the Americas and Africa would, in steady state, equal the net air-sea flux into the ocean north of that section. Since the industrial revolution the ocean has demonstrably **not** been in steady state with respect to carbon, but the perturbation from the steady state remains relatively small (about 20%) and can be corrected for. This technique could provide a valuable check on direct air-sea flux estimates made by integrating equation (1) over the ocean surface. A data set of global high-quality T_{CO_2} and hydrographic data should be collected during the coming decade by a joint effort between the World Ocean Circulation Experiment (WOCE) and JGOFS.

None of the above approaches will by itself be sufficient to specify the global air-sea flux to the desired accuracy. However, it is possible that through a synthesis of these efforts we will have attained this goal by the end of the decade. Some international co-ordinating body is required to ensure that measurements are of sufficient accuracy, that they are referenced to common standards, and that there is a minimum duplication of effort. The JGOFS Committee on Climate Change and the Ocean should be supported in fulfilling that role.

3. The Effect of Global Change on the Air-Sea Exchange of CO_2

The climatic changes which we anticipate over the next century, caused in large part by increasing atmospheric CO_2, will in turn affect the air-sea exchange of this gas, further perturbing the carbon cycle (IPCC, 1990). A number of different possible feedbacks of this type are identified below, but our knowledge of the behavior of the global system is as yet too uncertain for us to be able to predict quantitatively the total feedback effect. We cannot even be certain of its sign, although most of the possibilities identified are positive feedbacks, i.e., they will tend to increase atmospheric CO_2 further.

a. Increasing sea surface temperatures will tend to increase surface p_{CO_2}, slowing the net uptake by the oceans. This effect is relatively simple to quantify, and at steady state it would result in an extra atmospheric p_{CO_2} rise of 5% of the initial perturbation (IPCC, 1990).

b. Global salinities may be expected to decrease as icecaps and glaciers melt and dilute the salt in the sea, tending to reduce surface p_{CO_2}. This effect will eventually largely cancel the temperature effect, but probably will take substantially longer (up to a thousand years) to be fully

felt (IPCC, 1990).

c. Ocean uptake of CO_2 will lead to a lowering of seawater pH (approximately 0.3 units for a doubling of p_{CO_2}), which will in turn cause the inorganic carbon speciation to move from left to right in the series $CO_3^{=}$ --> HCO_3^{-} --> CO_2. This will both raise surface water p_{CO_2} and also reduce the buffering capacity of the ocean to take up CO_2 as more is added (Liss and Crane, 1983; GESAMP, 1989b).

d. The gas exchange coefficient for CO_2 will probably be affected by changes in global winds. At present there is no consensus as to whether the wind will increase or decrease. However, there is some evidence that in eastern margin areas alongshore wind speeds have increased in the last 20 years, increasing coastal upwelling (Bakun, 1990). Through the increased availability of nutrients, this would tend to increase the rate of CO_2 uptake by the oceans, although (since the interfacial exchange is not in itself thought to be the primary limiting factor for CO_2 absorption) we can expect the total effect on atmospheric CO_2 to be quite small (IPCC, 1990).

e. The most important effects on surface ocean p_{CO_2} are likely to be caused by changes in ocean circulation -- both its direct effect on uptake (e.g., upwelling of nutrient-rich deep water) and indirectly via its impact on the biota of the ocean. We know that such changes have been very important in the past. During previous glacial-interglacial transitions the natural oscillations in atmospheric CO_2, as observed in the ice-core record, are thought to have been driven by these changes, and several hypotheses have been advanced to explain them (Siegenthaler and Wenk, 1984; Sarmiento and Toggweiler, 1984; Knox and McElroy, 1984). During the glacial cycles these processes worked as positive feedbacks, tending to amplify temperature changes, but we are unable to say whether the same will happen in the present case.

C. THE AIR-SEA EXCHANGE OF DIMETHYL SULFIDE AND ITS ROLE IN CLIMATE

1. Introduction

Dimethyl sulfide (DMS) is produced in surface seawater by certain species of marine algae. The DMS is formed by cleavage of the precursor molecule dimethyl sulfoniopropionate (DMSP), which is thought to be used by the phytoplankton as an osmolyte. Measurements of DMS in surface seawater and in marine atmospheric samples indicate that the water is highly supersaturated with respect to the air concentrations, implying a net flux out of the oceans. In the atmosphere DMS is oxidized to form sulfur dioxide, methane sulfonic acid (MSA) and non sea-salt (NSS) sulfate as the primary products. Estimates of the sea-to-air flux of DMS indicate that it is an important component in the global cycling of sulfur, and since its main oxidation products are acidic it also plays a significant role as a source of atmospheric acidity, particularly in the remote marine atmosphere. Sulfate particles formed by the oxidation of DMS are also important as cloud condensation nuclei (CCN). Further details on several of the aspects of the production and reactions of DMS mentioned above are given in the review by Andreae (1986).

Charlson et al. (1987) stressed the importance of marine DMS as a provider of CCN, particularly in regions far from land sources of these particles. These authors went further and speculated that since the number of CCN in the atmosphere is important in the cloud formation process, and hence in affecting the Earth's albedo, it is possible to hypothesize that the DMS-CCN link might act as a climate regulating mechanism. Figure 9 shows the basic elements of their proposal. A simple example of how climate regulation might work, according to this scheme, is as follows: If the temperature of the atmosphere increases, it will lead to some concomitant increase in ocean water temperatures. If this in turn results in an increase in DMS production by marine algae, then the enhanced flux of sulfur across the sea surface will lead to formation of more sulfate aerosol (CCN). (Even if there were not increased production at the warmer temperatures, p_{DMS}

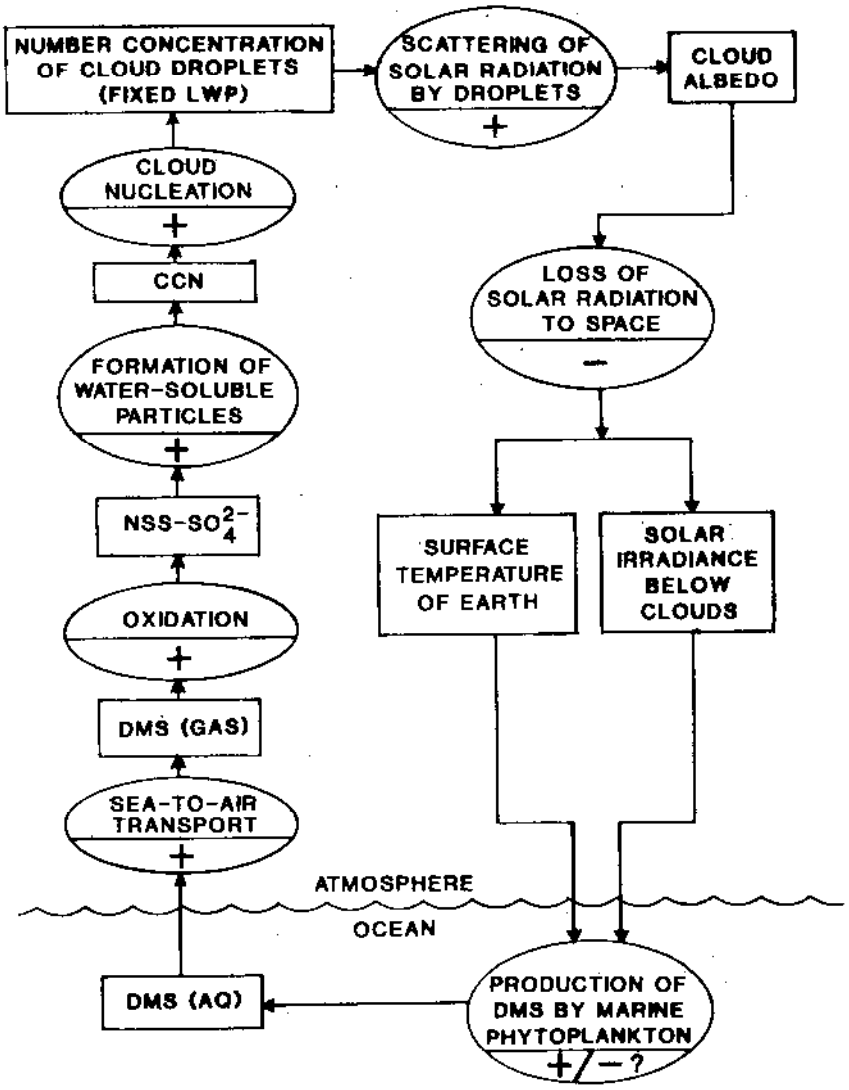

Figure 9. Conceptual diagram of a possible climatic feedback loop. The rectangles are measurable quantities, and the ovals are processes linking the rectangles. The (+ or -) in the oval indicates the effect of a positive change of the quantity in the preceding rectangle on that in the succeeding rectangle. LWP refers to liquid water path. From Charlson et al. (1987).

would be higher, leading to increased fluxes out of the ocean.) Finally, this will produce an increase in cloud albedo and the reflection back into space of a greater fraction of the incoming solar energy, tending to cool the atmosphere. Thus, the system, as described above, provides a negative feedback mechanism which can potentially lead to some degree of climate stabilisation.

2. Assumptions and Uncertainties in the DMS/Climate Connection

It is clear from the above that there are several important assumptions and uncertainties involved in the DMS-climate hypothesis. We examine some of them here, concentrating on those which are concerned with DMS production in the sea, its air-sea exchange and subsequent atmospheric chemistry.

a. DMS Production/Consumption in the Ocean

In view of the importance of DMS oxidation products in several areas of atmospheric chemistry, it is not surprising that the factors controlling the formation and consumption/destruction of this gas in seawater have received considerable attention. Figure 10 (Malin et al., 1991) summarizes our current understanding. Water temperature, light and nutrient supply are all important factors in the production of DMSP by phytoplankton. A minimum light level is required for growth, but as discussed elsewhere in this report it may be that excess UV is detrimental, such that any future increase in UV-B radiation due to stratospheric ozone depletion could lead to a decrease in phytoplankton and less DMS production. Relative to water temperature, there are very few data that would provide information on the sign of the temperature effect on DMS production. Although measurements of the DMS oxidation products MSA and NSS sulfate in ice cores (Saigne and Legrand, 1987; Legrand et al., 1988) indicate higher concentrations of these species during the last glacial period, this does not necessarily imply that the sign is negative, i.e., less DMS production in warmer water. During the last glacial period oceanic production in general appears to have been significantly higher than at present, and this may well be a more important factor than the effect due to temperature alone.

Another important determinant of DMS production is probably the nutrient concentration in the water. There is some evidence that DMS production is favored in waters low in nitrate (Turner et al., 1988; Leck et al., 1990). It is speculated that in nitrate-rich waters the plants utilise an alternative osmolyte (glycine betaine) which is the nitrogen analog of DMSP (Andreae, 1986). There is also considerable evidence that the production of DMS is species specific, with some organisms making large amounts of DMSP/DMS (e. g., coccolithophores, *phaeocystis*) whereas others (e.g., diatoms) make little or none (Turner et al., 1988). This means that a clear-cut

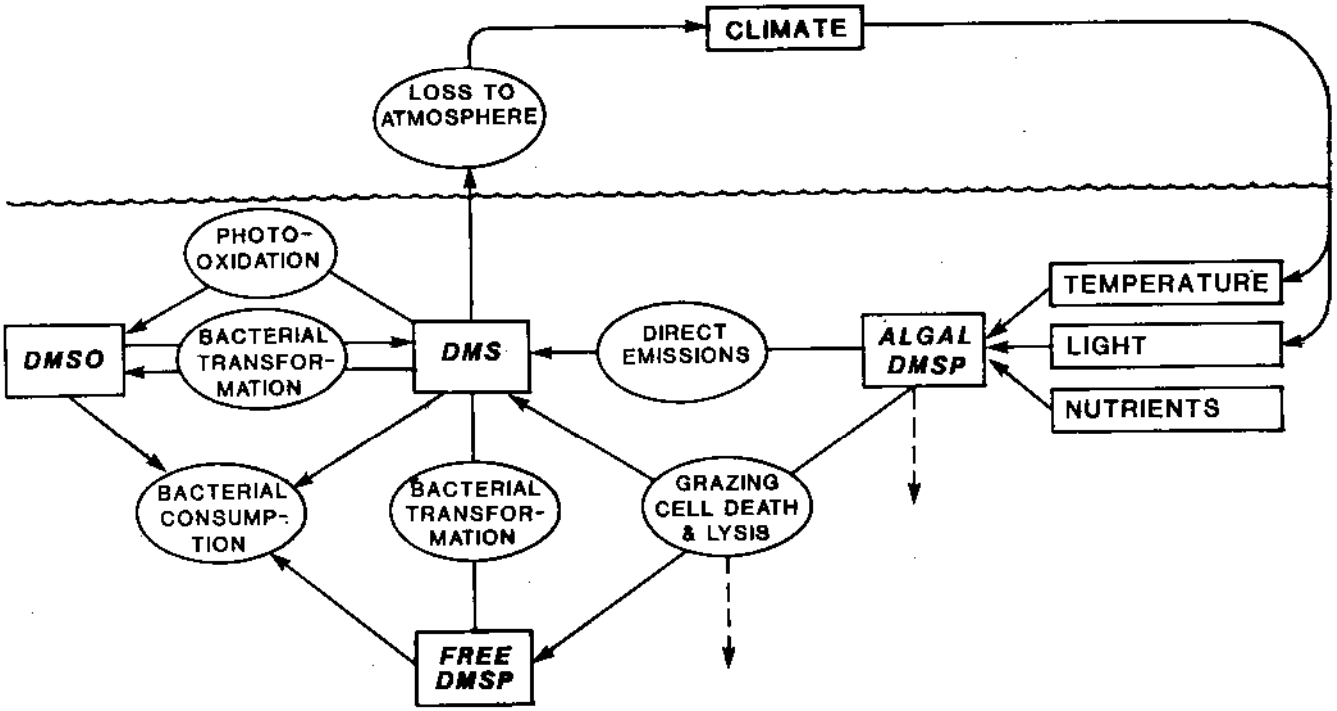

Figure 10. The marine biogeochemical cycle of sulfur; production, transformation and utilisation pathways which may ultimately influence the quantity of DMS lost to the atmosphere. From Malin et al. (1991).

relationship between DMS concentration and simple measures of algal production (such as fluorescence, chlorophyll *a*) is not found, except in limited situations where a single organism is dominant.

An increase in ocean productivity due to iron addition (Section II) would not necessariily lead to an increase in DMS production of equivalent magnitude. For example, if added iron leads to a relative enhancement of diatoms then because of their poor ability as DMS producers there could, in these circumstances, be a rather small increase or even possibly a decrease in formation of the gas. Another possible link between the sulfur and iron cycles is worth noting. On release to the atmosphere DMS is oxidised to soluble acidic products which are easily taken up by rain drops and aerosols. The decrease in pH coupled with photochemical reduction will lead to solubilisation of particulate iron, so that on deposition to the sea surface the iron will be more readily available to marine organisms (Zhuang et al., 1991). Even though the iron will probably be rapidly oxidised in seawater, the iron colloids formed are likely to be more readily assimilated by plankton than iron-containing particles from the continents.

Once formed, DMS is subject to a number of bacterial and photochemical consumption/ transformation processes (Figure 10) so that the ambient concentration of DMS, which is the driving force for exchange to the atmosphere, is the resultant of all of them. For example, Kiene and Bates (1990) have recently presented results which imply that the rate of DMS loss by bacterial consumption can be significantly greater than that by air-sea gas exchange. Because of the complexity of the production/consumption processes discussed above, it is clearly very difficult to calculate *a priori* DMS concentrations in seawater under present conditions. To estimate what might happen in the future under globally changed conditions is even more difficult.

b. Oxidation of DMS in the Atmosphere

The next stage in the proposed DMS-climate link is the formation of aerosol particles (CCN) by oxidation of DMS in the atmosphere. Evidence for this comes from a very recent study by Ayers et al. (1991), which shows a strong relationship between DMS, MSA and NSS sulfate concentrations in the air at Cape Grim, Tasmania. The relationship is seasonally dependent, with highest values in spring and summer (Figure 11). In another study presented in Bell (1986), Ayers and Bigg find a similar seasonal dependence for atmospheric particle numbers in the southern hemisphere, the effect showing a marked enhancement with increased incident sunlight at southerly latitudes between 14 and 68° (Figure 12). These results, coupled with the finding that in temperate latitudes the production by plankton is also strongly seasonal (Turner et al., 1989) point to a linkage between DMS production and the formation of sulfate particles, which are the primary source of CCN in remote marine areas. As Ayers et al. (1991) point out, in view of the strong seasonality in the production of CCN a test of this link would be to determine if there is a corresponding variation in cloud albedo. This should be examined in future studies.

With respect to the DMS-climate link proposed by Charlson et al. (1987), it is probably reasonable to conclude that there is increasing evidence for the oceans as a source of CCN and hence as a factor controlling cloud albedo. However, in view of the complexity and current lack of knowledge of what controls DMS formation in the sea and what factors determine cloud albedo, it is not possible to predict the sign of any feedback mechanism between these two processes that result from future climate change.

3. Ammonia Production and its Relation to the DMS Cycle

The oceans also appear to be a significant source of ammonia in the atmosphere. The flux of ammonia is of interest since much of the aerosol sulfate in the remote marine atmosphere has

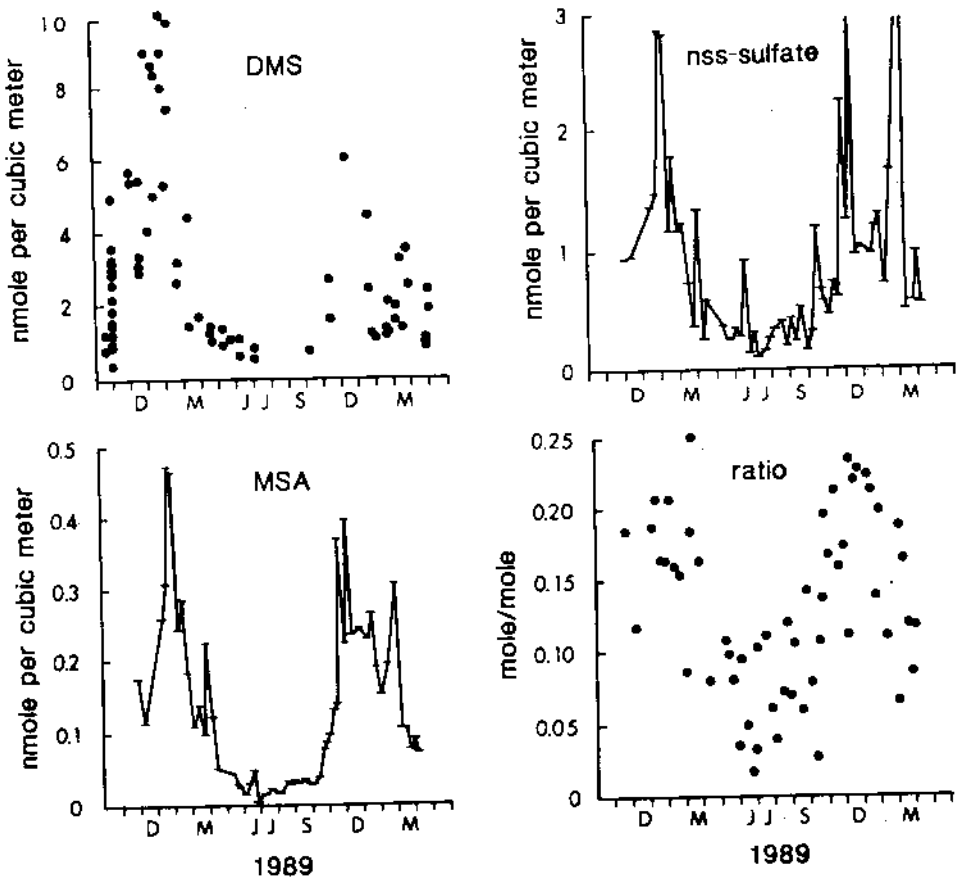

Figure 11. Time series plots of gaseous DMS concentration, sub-micrometer aerosol MSA concentration, sub-micrometer NSS sulfate concentration, and the MSA/NSS sulfate ratio in "baseline" air at Cape Grim, Australia. From Ayers et al. (1991).

ammonium as the companion cation. The ratio of sulfate to ammonium generally varies within the molar range 1 to 2, i.e., as NH_4HSO_4 to $(NH_4)_2SO_4$. In a recent paper describing work in the northeast and equatorial Pacific, Quinn et al. (1990) calculate the sea-to-air fluxes of both DMS and ammonia. Although there appears to be little spatial correlation between the two fluxes, they are of similar magnitude. This implies that, in this study region, essentially all the ammonia and sulfur needed to form the aerosol is supplied from the oceans. It is remarkable how closely the two fluxes balance, producing a largely neutralized aerosol. If they did not balance, the aerosol would be considerably more acidic or alkaline than at present. As with DMS formation in seawater, the analogous cycle for ammonia production is complex and poorly known. It is also very difficult to predict how it might change in the future. Alterations in one or both of these cycles resulting from global change might well lead to substantial alteration in the chemical and cloud-forming properties of marine aerosols.

D. CONCLUSIONS

1. Present estimates of the global flux of CO_2 across the air-sea interface by calculations using

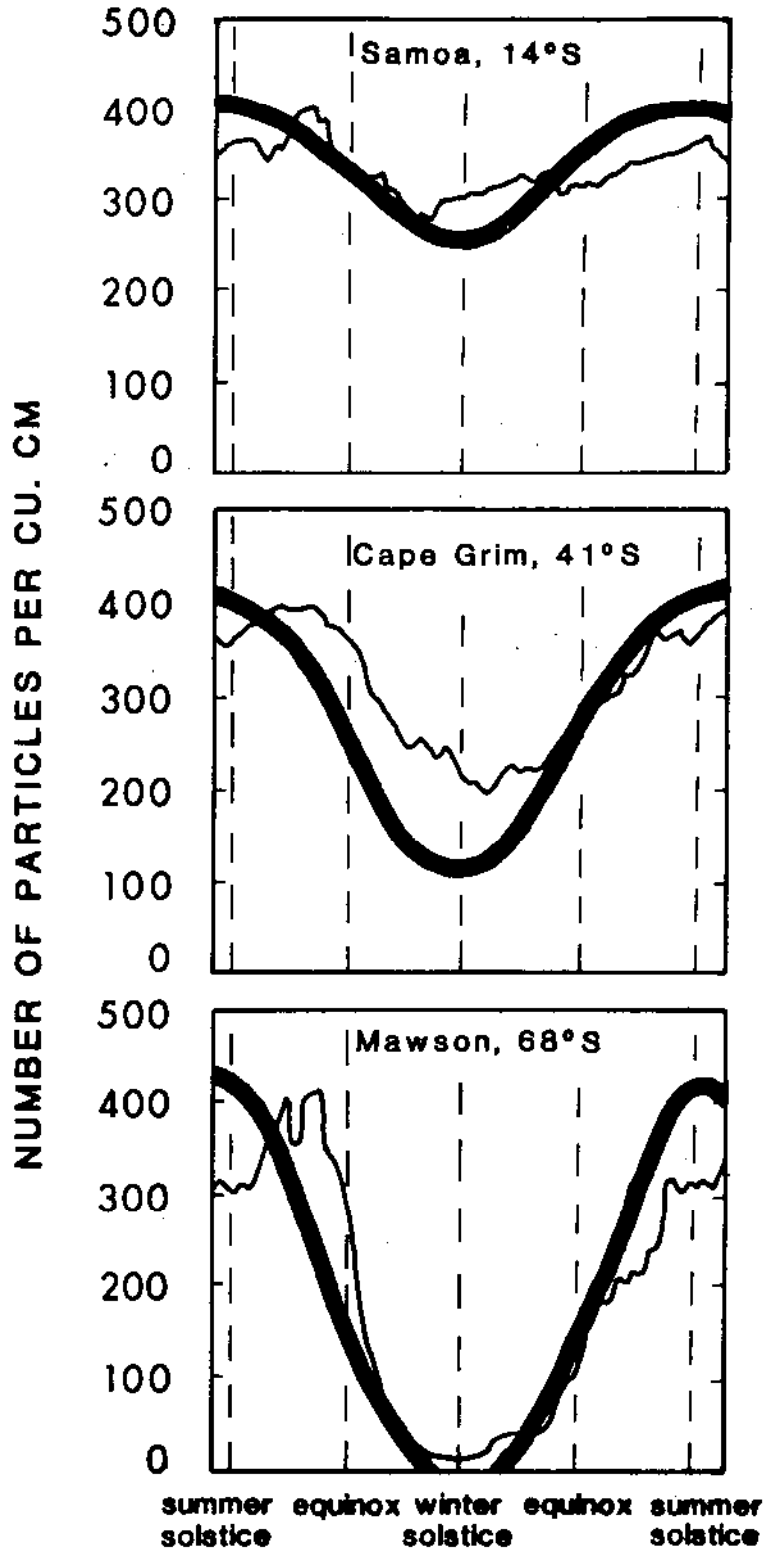

Figure 12. Seasonal variation of incident sunlight (heavy curve) and particle number at Samoa, Cape Grim, and Mawson. From Bell (1986).

integrated values for p_{CO_2} and K, which are both quite variable, are probably uncertain by a factor of two.

2. Small scale variability (10-100 km) in p_{CO_2} is ~30 μatm, while a systematic error of 1 μatm over the world ocean would lead to an error in the integrated CO_2 flux of 0.2×10^{15} g C yr^{-1}.

3. Calculations of the global CO_2 flux which ignore the skin temperature effect may be in error by $0.5\text{-}1 \times 10^{15}$ g C yr^{-1}.

4. Increasing sea surface temperature will result in increasing p_{CO_2}, with an extra atmospheric p_{CO_2} of 5% of the initial perturbation.

5. The pH of the ocean would decrease by ~0.3 units for a doubling of p_{CO_2}, reducing the capacity of the ocean to take up CO_2. It seems unlikely that the pH decrease, or the concomitant change in the speciation of inorganic carbon, or the corresponding increase in water temperature will have any substantial direct effects on ocean productivity, at least for several decades (Fogg, 1991; GESAMP, 1989b).

6. Improved estimates of the global carbon flux across the air-sea interface require a substantial increase in both the coverage and density of oceanic p_{CO_2} measurements. New approaches and techniques, including modelling efforts, are required.

7. The most important future effects on surface ocean p_{CO_2} will likely be caused by changes in ocean circulation, although we cannot say with certainty whether the resultant amplification of temperature changes will be positive or negative.

8. There is probably increasing evidence that the oceans are a source for CCN and thus are a factor controlling cloud albedo. However, it is still not possible to predict the sign of any feedback mechanism in the DMS-climate link.

9. The ammonia and DMS fluxes from the ocean are remarkably balanced, resulting in a largely neutralized marine aerosol.

IV

RESPONSES OF THE OCEANIC SYSTEM TO RADIATIVE AND OXIDATIVE CHANGES IN THE ATMOSPHERE

A. INTRODUCTION

1. Interactions of Solar Radiation with the Atmosphere and Biosphere

Biological and chemical processes on Earth are strongly influenced by the spectral composition and energy of solar radiation penetratiing the atmosphere. Much of the solar radiation shorter than 300 nm is attenuated by gases present in the Earth's atmosphere. Solar radiation in the stratosphere is capable of photolysing molecular oxygen (<242 nm) and the resulting oxygen atom reacts with oxygen to form ozone. Oxygen absorbs most radiation below 200 nm and ozone absorbs strongly between 230 and 290 nm. However, the remaining solar ultraviolet between wavelengths of 290 - 320 nm (UV-B), passes through the lower atmosphere (troposphere) where it produces ozone and highly reactive hydroxyl radicals.

Finally, UV-B reaches the Earth's surface where it is an important environmental factor affecting both biological and chemical components of aquatic ecosystems (Jagger, 1985). It is damaging to a great variety of living organisms and biological processes. UV-B radiation also penetrates into the upper layers of the ocean where it has important effects on photochemical and biological processes.

2. Changes in the Upper Atmosphere

Anthropogenically-induced changes in atmospheric chemistry are altering this radiative environment and could, in turn, affect air-sea exchange and the Earth's climate in general. In particular, recent and future changes in the flux of ultraviolet radiation of differing wavelengths through the atmosphere are likely to alter photochemical and photobiological processes.

The stratospheric ozone layer, at an altitude between 10 and 50 km, reduces much of the incident flux of solar UV-B. However, anthropogenic releases of chlorofluorocarbons (CFCs), nitrous oxide, bromine-containing halons, and solvents such as methyl chloroform and carbon tetrachloride are causing a decrease in stratospheric ozone (NRC, 1989; WMO, 1988) and an increase in incident solar UV-B radiation. Thus, destruction of stratospheric ozone could lead to perturbation of natural chemical systems and could negatively impact marine organisms important in the cycling of radiatively important natural trace gases between the ocean and atmosphere.

3. Changes in the Lower Atmosphere

Increases in UV-B radiation could affect the oxidizing capacity of the troposphere. Atmospheric oxidants primarily responsible for the chemical changes in the troposphere include oxygen atoms, ozone, hydrogen peroxide, and hydroxyl and peroxy radicals, all of which are formed photochemically. With the exception of oxygen atoms, these oxidants do not react with major atmospheric constituents such as molecular oxygen, nitrogen, water vapor or carbon dioxide, but are responsible for the removal of most trace gases from the atmosphere. Their concentrations are sensitive to changes in photon flux and water vapor and to changes in the concentration of a few trace substances such as the oxides of nitrogen, carbon monoxide and hydrocarbons, which are capable of being influenced by human activity. Substantial changes are, therefore, likely to occur in the natural distribution of oxidant species in the future. In some cases these changes may already have occurred. There are several good reviews on the subject of tropospheric oxidants

(Isaksen, 1988, a and b; Rowland and Isaksen, 1988).

4. Changes in the Upper Ocean

Predicted increases in incident solar ultraviolet radiation, as well as changes in the chemistry of the troposphere are likely to have a number of effects on photochemistry and biology of the ocean, particularly the upper water column and near-surface layers. These oceanic changes, through a number of feedback loops could, in turn, affect the chemistry of the atmosphere. The influence of such changes on air-sea exchange processes is discussed in sections D and E below.

B. RADIATIVE CHANGES FROM STRATOSPHERIC OZONE DEPLETION

1. Recent Change

During the past 10 years UV-B irradiance reaching the ground has increased about 1% per year at mid-northern latitudes (Blumthaler and Ambach, 1990). In the spring over Antarctica measurements indicate springtime increases of nearly 100% during occurence of the "ozone hole" (Lubin et al., 1989), increasing the annual UV dose by 20 to 25% (Dahlback et al. 1989).

2. Future Change

The Montreal Protocol, limiting substances that deplete stratospheric ozone, was strengthened and the time frame for emission reductions was accelerated at a London Conference in June, 1990. However, because of the long residence time of different CFC compounds in the atmosphere (8 to 380 years), stratospheric ozone is likely to continue to decrease from present levels well into the middle of the next century. Based on the London agreements, future emissions of stratospheric ozone-depleting chemicals may approximate the D2 scenario presented by Watson et al. (1990), i.e., a maximum stratospheric chlorine content of about 4.2 ppbv by the year 2060.

Increases in incident solar UV-B radiation are likely to continue over the next few decades. What can we expect in terms of future increases in UV-B in the marine environment? Table 3 presents estimates of the changes from the present to 2060 in both stratospheric O_3 and UV-B in the southern hemisphere (Watson et al., 1990; Green, 1983). Obviously significant increases in incident UV-B, particularly at high latitudes, are possible.

C. RADIATIVE CHANGES IN THE LOWER ATMOSPHERE

1. Photochemical Production of Ozone and Other Oxidants in the Troposphere

Oxidants are produced in the troposphere from the photolysis of ozone and of nitrogen dioxide. The chemical scheme linking these different oxidizing species is outlined below:

$$O_3 \xrightarrow[\lambda < 310\ nm]{h\nu} O(^1D) + O_2 \qquad [3]$$

$$O(^1D) + H_2O \longrightarrow OH + OH \qquad [4]$$

$$OH + CO \longrightarrow CO_2 + H \qquad [5]$$

Table 3

Latitudinal Distribution of Stratospheric Ozone and UV-B Changes from the Present to 2060*

D2 Scenario:

95% reduction of CFCs by 2000
50% reduction of CFC surrogates by 2000
7×10^9 g yr^{-1} CFC-22 growth per year
Total atmospheric chlorine loading by 2060 down to 4.2 ppb

Result:

No change in O_3 at the equator
2-4% reduction in O_3 in mid-latitudes
4-12% reduction in O_3 in high latitudes
No improvement in the antarctic O_3 hole until 2075
~5% increase in UV-B in the tropics
~26% increase in UV-B at 40°S
~66% increase in UV-B at 60°S

*Adapted from Watson et al. (1990) and Green (1983)

$$H + O_2 \text{ ----> } HO_2 \qquad [6]$$

The HO_2 formed via reactions [5] and [6] and in the course of oxidation of methane and other hydrocarbons by hydroxyl radicals has three primary reaction possibilities:

$$HO_2 + NO \text{ ----> } NO_2 + OH \qquad [7]$$

$$HO_2 + HO_2 \text{ ----> } H_2O_2 + O_2 \qquad [8]$$

$$HO_2 + O_3 \text{ ----> } OH + 2O_2 \qquad [9]$$

Reaction [7] is a source of ozone due to NO_2 photolysis:

$$NO_2 \xrightarrow[\lambda < 400 \text{ nm}]{h\nu} O(^3P) + O_2 \qquad [10]$$

$$M + O_2 + O(^3P) \text{ ----> } O_3 + M \qquad [11]$$

Reaction [8] produces hydrogen peroxide and reaction [9] is a substantial sink for ozone, at least as large as the loss of ozone which occurs in reactions [3]+[4]. In [11] M refers to any other gas present.

In the global atmosphere about one-third of the HO_x (OH and HO_2) produced by CO and hydrocarbon, (primarily methane) oxidation leads to ozone production, one-third to ozone destruction and one-third to hydrogen peroxide production (Crutzen et al., 1991). The atmospheric hydrogen peroxide concentration is much lower than the ozone concentration primarily

because its atmospheric lifetime is much shorter due to efficient removal in rain.

2. Trends in Concentrations of Tropospheric Ozone and Its Precursors

Trends have been observed in tropospheric ozone over a relatively short period in the twentieth century. In the northern hemisphere it is almost certain that the tropospheric ozone concentration is increasing, particularly at mid to high latitudes, and in the southern hemisphere a decrease in the ozone concentration may be occurring. Both trends are, in all probability, associated with increasing emissions of precursor gases (Bojkov, 1986; Logan, 1985)

The average rate of increase of tropospheric ozone observed at remote sites in the northern hemisphere is nearly 1% per year (Penkett, 1988). Between 1969 and 1988 the average ozone concentration has decreased in the stratosphere and increased in the troposphere (Figure 13). The increase in tropospheric ozone is maintained up to the tropopause in the atmosphere above Payerne, Switzerland (Staehelin and Schmidt (1991), suggesting that the increase could be typical of all stations at mid-latitudes in the northern hemisphere. An even more dramatic change is

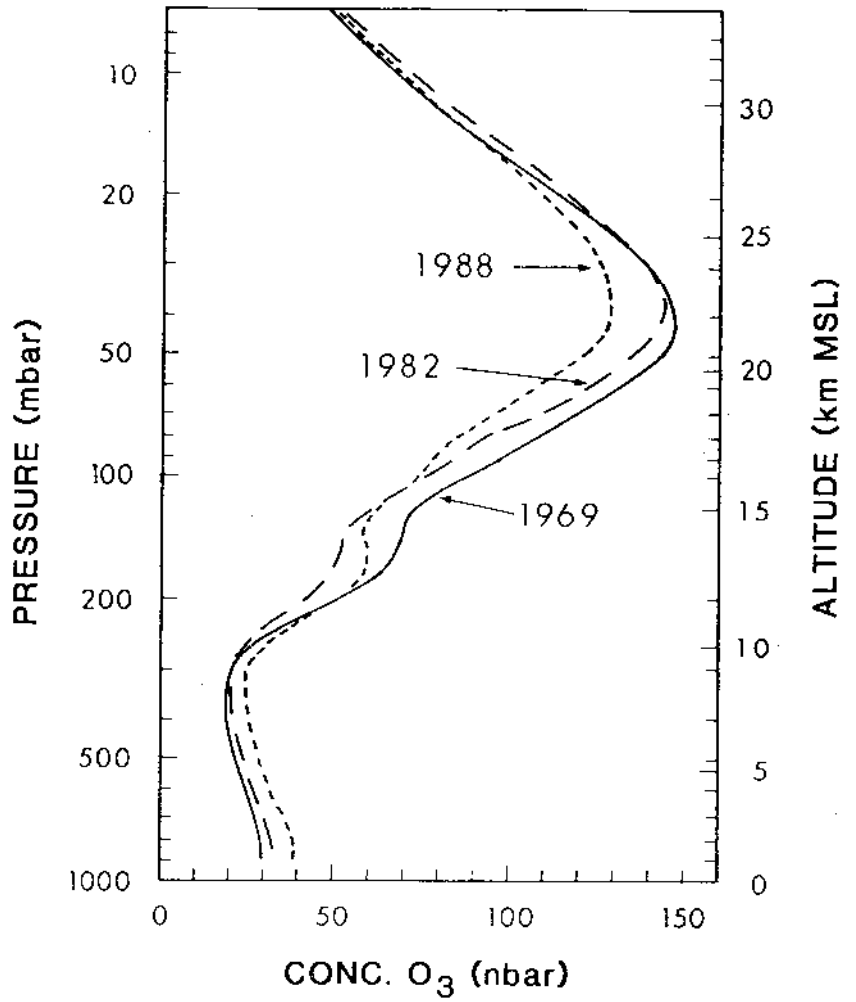

Figure 13. The change recorded in the annual average vertical profile of ozone above Payern, Switzerland over the years 1969-1988. The mean altitude of the tropopause in this region is ~12 km. From Staehelin and Schmidt (1991).

occurring to ozone in the lower stratosphere (Figure 13). This decrease in northern hemisphere ozone may be associated with the same type of chemistry responsible for the Antarctic ozone hole (United Kingdom Stratospheric Ozone Review Group, 1990). Most of the increase in tropospheric ozone concentration has occurred between 1950 and the present which would coincide with known trends in the atmospheric abundance of precursors, particularly NO_x. There is presently much more ozone in the lower atmosphere at all times of the year (Figure 14), and the spring maximum is seen to be a recent phenomenon associated with the increase in ozone concentrations (Volz and Kley, 1988). It is only weakly associated with seasonal changes in the flux of ozone from the stratosphere to the troposphere (Penkett, 1988).

Although the data shown in Figures 13 and 14 are from European sites, the phenomenon of tropospheric ozone increase almost certainly prevails thoughout the northern hemisphere outside the tropics. Various calculated estimates of the size of the global ozone perturbation in the troposphere agree with the observed data on an annual basis (Dignon and Hameed, 1985), and they also show the same changes in seasonal variation (Hough and Derwent, 1990). This would also be expected from the changes in emissions of precursor compounds and their measured or inferred concentration increases.

Increases in atmospheric concentrations have also been recorded for methane (Rasmussen and Khalil, 1989), carbon monoxide (Rinsland and Levine, 1985), and non-methane hydrocarbons such as ethane (Levine, personal communication). Some of these data are extracted from the ice core record, which provides information on changing atmospheric composition over time. This record also indicates that the abundance of oxidized nitrogen compounds in the form of nitrate ions is increasing in the northern hemisphere (Neftel et al., 1985)(See Section II). The methane increase is worldwide since methane has a long atmospheric lifetime. The carbon monoxide

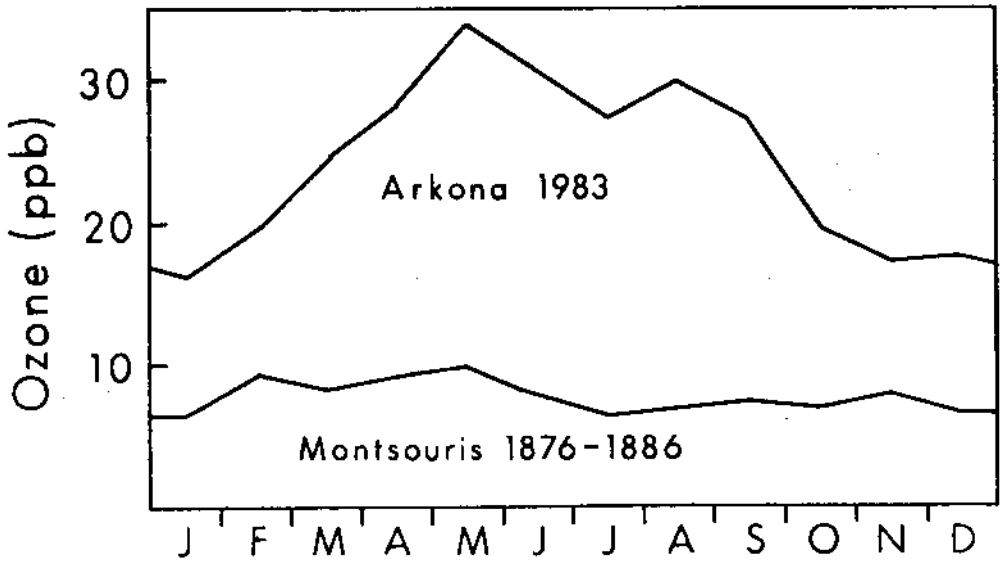

Figure 14. A comparison of the seasonal variation of ozone recorded at Cape Arkona (Baltic Coast) in 1983 with that recorded at Montsouris (Paris) in the last century. From Volz and Kley (1988).

increase may be limited to the northern hemisphere, and the increase in nitrogen oxides may be primarily associated with continental and near shore marine areas because of their relatively short lifetimes (also see Section II). However, the influence of nitrogen oxides may be spreading due to

a greater number of source areas associated with increasing economic activity in the developing world (Galloway, 1989), and due to reservoir species such as peroxyacetyl nitrate (PAN), which have relatively long atmospheric lifetimes and can dissociate to produce NO_2 far from source regions (Crutzen, 1979). More NO_x in the atmosphere will adjust the balance of reactions [7], [8] and [9], leading to more ozone production, rather than loss. In the absence of NO_x, which is a more typical situation in the southern hemisphere, reaction [8] will produce peroxide and reaction [9] will cause ozone loss.

Recently, Sigg and Neftel (1991) report that the hydrogen peroxide concentration in Greenland ice has increased by over 50% compared to the natural background values. Since this is occurring simultaneously with the recorded tropospheric ozone increase, it must mean that more peroxy radicals are being produced and that the overall oxidation capacity of the northern hemisphere troposphere has increased.

3. Trends in Tropospheric OH

The primary chemical reagent determining the atmospheric lifetime of most trace gases is the hydroxyl radical, OH. This radical is produced via reaction [4] and [7] and lost via reaction [5] and similar reactions with methane (reaction [12]) and other hydrocarbons (reaction [13]) and with nitrogen dioxide (reaction [14]).

$$CH_4 + OH \text{ ----> } CH_3 + H_2O \qquad [12]$$

$$RH + OH \text{ ----> } R + H_2O \qquad [13]$$

$$NO_2 + OH \text{ ----> } HNO_3 \qquad [14]$$

Overall the OH concentration can be shown to be:

$$[OH] = \frac{2k_4[O(^1D)][H_2O] + k_7[HO_2][NO] + k_9[HO_2]\,[O_3]}{k_5[CO] + k_{12}[CH_4] + k_{13}[RH] + k_{14}[NO_2]} \qquad (2)$$

where the k's refer to the reaction rate constants, the subscripts refer to the reaction number and the brackets refer to the species concentration. Because of the complex links existing between the various species it is difficult to say exactly what will happen to the concentration of OH as the concentration of the other gases change. However, increasing CH_4 and CO alone without increasing NO_x will decrease OH. This may be happening in the southern hemisphere. Increasing all three reactants will probably keep OH constant, and increasing NO_x faster than the others will probably cause OH to increase.

4. Effect on Trace Gas Lifetimes and Transport

The OH radical concentration has a controlling influence on the lifetime of many trace gases. Increases in [OH] will shorten the lifetime of NO_2 for instance, converting it to HNO_3, which is removed more rapidly from the atmosphere, either by rain or dry deposition. Similarly, more SO_2 would be oxidized either by increased OH or by increases in H_2O_2, which may occur simultaneously.

Decreases in lifetimes for many trace gases will probably decrease the proportion that can be transported from land over the ocean. Similarly, increases in lifetimes, due to reduced OH, will probably increase the influence of continental sources on the remote ocean. There are many other instances which could be quoted here.

5. Effects of a Changing Radiative Flux on Tropospheric Ozone and OH

The effects produced by loss of ozone in the stratosphere, particularly the greater flux of UV into the troposphere, will enhance the perturbations expected in ozone and OH in the two hemispheres due to changing concentrations of other gases.

In the case of tropospheric ozone, the photochemical rate of production of $O(^1D)$ via reaction [3] will be enhanced, leading to more OH and more HO_2, which in the presence of sufficient NO_x, will produce more ozone. This is the likely situation in the northern hemisphere, and more ozone in the troposphere there will offset, to a large extent, the effect of the loss of stratospheric ozone on the penetration of UV-B radiation to the Earth's surface. Ozone in the troposphere is more effective in absorbing UV-B radiation than ozone in the stratosphere because the path length of the UV is longer due to greater molecular scattering and due to the presence of clouds, which also scatter light. The southern hemisphere situation is different, certainly over the remote oceans, because the NO_x concentrations will be lower than in the northern hemisphere. Ozone will therefore be removed more efficiently, both by direct photolysis (reaction [3]) and by removal by HO_2 (reaction [9]), thus leading to even larger quantities of solar UV-B radiation reaching the earth's surface.

In the case of the OH radical, equation (2) (and reaction [4]) shows that increased levels of $O(^1D)$, produced from ozone photolysis, will increase OH. However, in the event of large ozone losses, such as may happen in the southern hemisphere, OH may actually decline since the overall rate of production of $O(^1D)$ may decrease. In the northern hemisphere it is much more likely that increased UV radiation would produce more OH. Another aspect, which is of some relevance to both ozone and OH, is that a warmer world would cause the concentration of water vapor to increase thereby increasing the efficiency of reaction [4], producing more OH.

In summary, all these changes, i.e., increased emission of trace gases, mostly occurring in the northern hemisphere, increased solar UV-B reaching the troposphere, and increased water vapor concentration should lead to lower ozone in the southern hemisphere and therefore more UV-B reaching the surface. It is also possible that higher ozone concentrations and more OH may occur in the northern hemisphere, leading to some reduction in the level of UV-B reaching the surface there.

D. RADIATIVE CHANGES IN THE UPPER OCEAN

1. Introduction

The predicted increases in UV-B and changes in the oxidative capacity of the troposphere described above are likely to affect a number of important processes in the ocean. Possible changes include photochemicaly-induced changes in dissolved organic matter, reduction in photosynthetic productivity, and changes in the production of a number of biogenic and radiatively important gases. These changes are discussed below.

Estimates of UV-B effects must take into consideration the spectral distribution of the incident energy. For biological processes, within the UV-B range, shorter wavelengths are much more biologically damaging than longer wavelengths. For photochemical reactions absorption and reaction optima occur at different wavelengths, depending upon the parent compound. Therefore, in estimating UV-B-induced change, it is necessary to use an action spectrum, where the energy at each wavelength is multiplied by a weighting factor to derive the biologically or chemically "effective" irradiance. Action spectra have been developed for a number of processes, including DNA damage, loss in plant productivity and changes in photochemical reaction rates (Calkins, 1982). Since different investigators have used different exposure methodologies, action spectra,

and end points, one must use caution in comparing the results of individual studies. All references to biological effects of UV-B in this chapter are based on "effective irradiance" weighted by a DNA action spectrum normalized to 300 nm.

2. UV-B In the Ocean

In marine and freshwaters UV-B radiation is attenuated by dissolved and particulate materials in the water column. The total diffuse attenuation coefficient, k, relates the spectral irradiance just beneath the surface, E_o, to the downward spectral irradiance, E_d, at depth d:

$$E_d = E_o\, e^{-kd} \qquad (3)$$

Considerable UV-B radiation penetrates the water column. Attenuation is wavelength-dependent and depends upon the biological and chemical characteristics of the water column (Figure 15). In nearshore water 1% of the total effective surface incident UV-B radiation typically penetrates to a depth of about 30 m (Jerlov, 1976; Baker and Smith, 1982). In very clear waters, with low plankton and dissolved organic carbon content such as the central South Pacific gyre, measurements indicate a 1% penetration depth of up to 66 m (Hardy, personal communication).

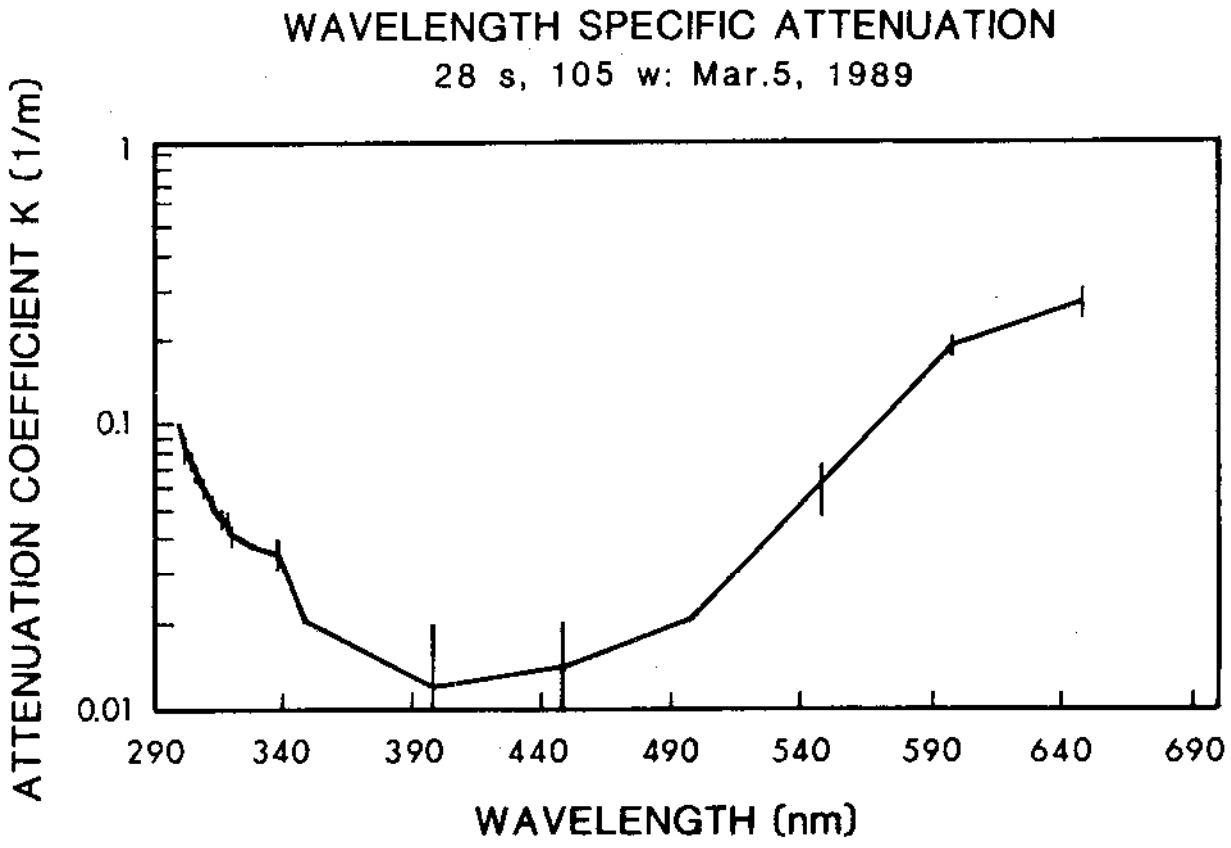

Figure 15. Wavelength-specific attenuation of effective (DNA 300nm) UV-B in the central Pacific Ocean (Hardy, personal communication)

3. Biological Responses

a. UV-B and Marine Organisms

A variety of marine organisms, including phytoplankton, zooplankton, macroalgae, seagrass, corals and fish eggs or larvae, are damaged by very similar, and rather small, doses of UV-B radiation. Seventeen studies spanning a wide variety of organisms, exposure conditions, and locations all suggest that an increase in daily UV-B dose of 900± 450 J m^{-2} (DNA weighted-normalized to 300 nm) can have a variety of negative impacts on marine biota (Hardy and Gucinski, 1989). Predicting biological effects over the wide range of seasons, latitudes, water types and ozone depletion scenarios is beyond the scope of this report. However, for clear water at mid-latitudes in summer, a 16% ozone depletion would lead to an additional daily UV-B irradiance of about 900 J m^{-2} at a depth of 1 meter. Such an increase would exceed the daily dose found to cause a significant reduction in survival of most zooplankton species examined (Damkaer and Dey, 1983) and could reduce the fecundity of marine copepods (Karanas et al. 1981).

Marine organisms can produce UV-B-absorbing compounds that protect them from damage, but the value or time scale of such adaptation remains unclear. One study suggests that phytoplankton are unable to adapt to increases in UV-B over the course of many generations (Behrenfeld and Hardy, personal communication).

b. UV-B and Photosynthetic Carbon Fixation

Phytoplankton exhibit decreased photosynthetic rates, changes in species composition, decreased community chlorophyll-a concentrations, and decreased reproductive rates when irradiated with levels of UV-B radiation that would result from predicted stratospheric ozone depletion (Hardy and Gucinski, 1989). In summer, at temperate northern latitudes, even current levels of UV-B radiation can reduce photosynthesis in marine phytoplankton.

Studies were conducted on the effects of enhanced UV-B radiation and natural levels of UV-A radiation (321-400 nm) and photosynthetically-active radiation (PAR, 401-750 nm) on the primary production of natural marine phytoplankton assemblages sampled over a wide latitudinal gradient in the South Pacific Ocean (Behrenfeld, 1989). Results indicated that primary production decreased with increasing UV-B radiation, independent of geographic location, according to: $Y = 0.22X$, where Y = percent decrease in primary production and X = the total dose of UV-B radiation, in J m^{-2}.

Using the D2 emissions scenario of ozone depletion (section IV A above), the predicted increase in UV-B at the sea surface (Green , 1983), and the UV dose-photosynthetic response relationship (above), future decreases in sea surface primary productivity in the South Pacific would be ~5% at the equator, ~15% at 40°S and ~30% at 60°S. An effect of this magnitude would be limited to approximately the upper meter of the ocean. Both the abundance of plankton and the flux of UV-B differ greatly both spatially in the water column (in 3 dimensions) and temporally (over both diel and seasonal time scales). Therefore, overall effects, integrated through the water column and over large geographic areas, are much more difficult to estimate.

In order to estimate the dose of UV-B received by a plankton population many factors must be considered. Chief amongst these are the incident surface irradiance based primarily on latitude and season, the attenuation of UV-B with depth in the water column, and the depth distribution and "residence time" of the population within the UV-B photic zone. Incident UV-B can be estimated from theoretical models (Green , 1983) or empirical measurements (Hardy, personal communication). Attenuation of UV-B in the water column can be approximated from chlorophyll concentrations (Hardy, personal communication).

The combined effects of water column density gradients, phytoplankton sinking rates, and near-surface photoinhibition alter the depth distribution of phytoplankton productivity. Subsurface population maxima are common, especially in summer at temperate latitudes. The residence time of plankton in the UV-B photic zone can differ greatly, based on a number of factors, including vertical mixing and population age. The buoyancy of phytoplankton cells changes in response to nutrient and light conditions. Young, actively dividing cells tend to sink less rapidly than older and nutrient deficient cells (especially in darkness). Thus, estimates of phytoplankton sinking rates vary from 0.02 to 20 meters per day (Akinna, 1969) to 1.4 to 4.0 meters per day (Steele, 1956).

Futher complicating an estimate of population dose is the fact that different phytoplankton species show a wide range in sensitivity (Karentz, 1991). Thus, one of the most likely effects of increasing UV-B may be a shift in the species composition of phytoplankton populations from sensitive to more tolerant species. Since higher trophic levels are dependent on primary production, a decrease in marine primary production or a shift in species composition resulting from increased UV-B radiation would likely decrease fisheries yield (Nixon, 1988).

In conclusion, future increases in UV-B, particularly in the southern hemisphere, are likely to have significant impacts on near-surface marine plankton and could alter the cycling of biogenic radiatively-important trace gases between the water and atmosphere. However, present unknowns, particularly the residence time of plankton populations at different depths in the water column, make an estimation of exposure to and resultant effects from UV-B radiation difficult.

4. Photochemical Responses

a. Background

Increases in UV-B may also change photochemical reactions in the photic zone of the water column. Many natural and xenobiotic components are oxidized or altered at significant rates in the upper ocean by direct or indirect photolysis (for reviews and background, see Zafiriou et al., 1984; Waite et al., 1988; Cooper et al., 1989; Hoigne et al., 1989; Zafiriou et al., 1990; Calkins, 1982; and Blough and Zepp, 1990). Direct photolysis rates are controlled by the substrate-specific rate of absorption of photons and hence by (1) the light spectrum and intensity, (2) the optical absorption spectrum of the substrate, and (3) its decomposition probability or quantum yield. Indirect photolyses are initiated by the absorption of light by substances other than the substrate. These substances are called chromophores. Indirect photolysis rates may exhibit complex kinetics, but for trace substances in a given medium, rates are often proportional to the product of the chromophore's photoexcitation rate and the freely dissolved or locally "bound" substrate concentrations.

b. Natural Chromophores

Both direct and indirect mechanisms are important in the natural photochemical cycles and in the removal of xenobiotic compounds (Zepp, 1982; Zepp et al., 1985). Such substances as hydrogen peroxide, nitrite, nitrate, methyl iodide, flavins, Fe colloids, etc. participate in direct photolyses. However, the principal chromophores in both mechanisms are an ill-defined pool of natural substances. This has led to a confusion of terms in the literature - gelbstoffe" (yellow substances), colored organic matter (COM), or unknown photoreactive chromophores (UPCs). We will use the term COM in this report. COM is principally dissolved or colloidal, substances, but they may be particulate. They also may contain bound metals. COM exhibits a broad, featureless optical absorption spectrum increasing exponentially with decreasing wavelength in the UV region of the spectrum (Figure 16).

The direct photolysis of COM yields a variety of reactive species and products. Taken together, these reactive transients constitute an important part of the natural photochemistry of seawater and

the sensitized degradation of xenobiotics. Mechanisms involving COM may be responsible during the photodegradation of highly hydrophobic xenobiotics such as PCB's and chlorinated dibenzodioxins (Shiu et al., 1988; Friesen et al., 1990; Nestrick et al., 1980). Photolysis of COM is also a source of important trace gases (CO, COS) (see page 54), possibly a sink for DMS (Brimblecombe and Shooter, 1986), and produces fragments that can be metabolized (Geller, 1986). These include low molecular weight acids and carbonyl compounds (Mopper and Stahovec, 1986).

Unfortunately the concentrations, structures, and biogeochemical cyles of COM are poorly understood. COM is a complex, molecularly heterogeneous pool (Kouassi et al., 1986; Blough et al., 1991). It is largely of natural origin, but it may not be in geochemical steady state. This is because sources (e.g., riverine input, sedimentary diagenesis, and decomposition in the water column) may be perturbed by alterations in the hydrological cycle, deforestation and biomass burning, and riverine inputs. Sinks for COM are also poorly known. For "refractory" humic-fulvic components the principal sinks are believed to be photochemical destruction (or photobleaching) in surface waters and slow coagulation/adsorption/absorption reactions leading ultimately to deposition in sediments.

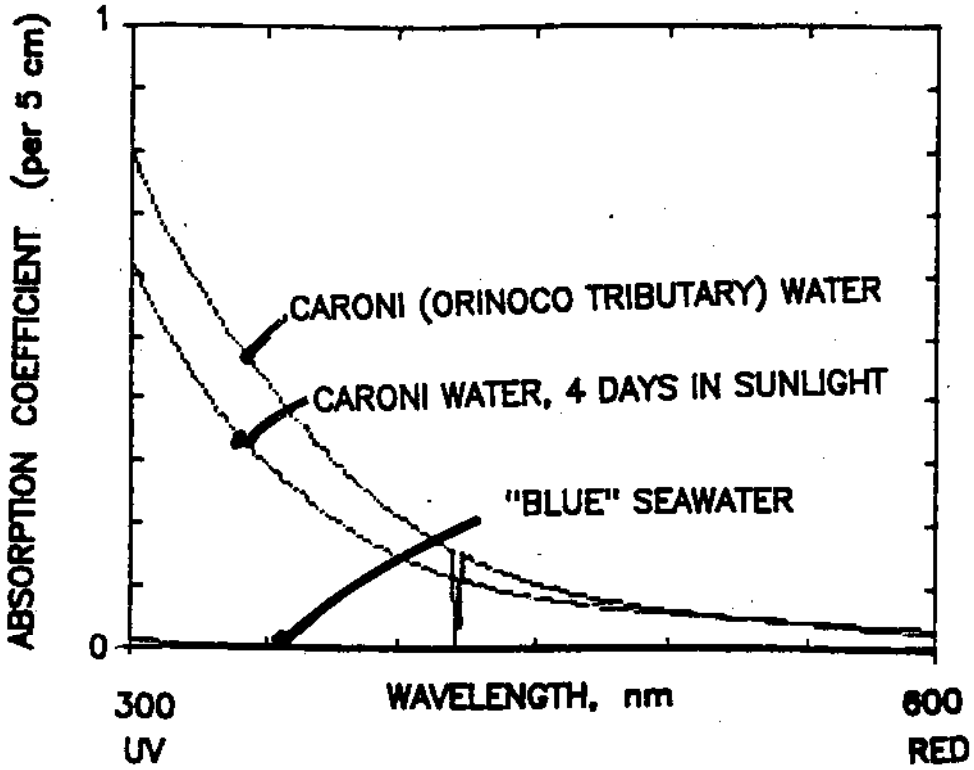

Figure 16. Spectrum of water of the Caroni (a major Orinoco tributary) before and after exposure to 4 days of summer sun at 41°N.

c. Optical Effects

Photobleaching of COM is detectable within hours in a closed container in full surface sunlight in the tropics (Kouassi et al., 1986; unpublished results by Blough, Mopper, Zafiriou, and Zika). This suggests that significant depletion of COM throughout the euphotic zone is possible on a time.scale of weeks to years. The rate of COM excitation per unit area will then decrease, and the

penetration of light (including wavelengths longer than the UV-B) into the water column will increase. The possibility that this change in optical properties might significantly affect the heat budget of the water or its properties as a biological environment appears not to have been addressed.

d. COM and Xenobiotic Organic Compounds

i.) Case I - light-limited rates

In Case I we assume that only the incident light field changes; supply rates of COM, other natural chromophores, and xenobiotic compounds are fixed. This case resembles that expected just after a sudden change in atmospheric transmission (e.g., the ozone hole springtime scenarios). At that time insolation, specifically increasing UV-B, increases the rates of all photoprocesses in proportion to the increased excitation rates of the chromophores involved.

Sensitivities of individual processes (i.e., the percent response per percent UV-B increase) will vary widely, depending on the optical and quantum yield properties of the substrate. For example, Zepp (1982) calculated that DDT and methoxychlor photolysis sensitivities are in the range of 1 - 10, i.e., in the range of the biological sensitivity discussed above. Xenobiotics absorbing throughout the UV-visible range may have sensitivities as low as 0.01.

Direct photolysis of COM and the processes associated with it (e.g., H_2O_2 formation, total radical formation, O_2^- formation, bleaching) also generally have a low sensitivity to UV-B changes because their wavelength-dependence tends to follow the absorption spectrum of COM (Figure 16). Thus, the sensitivity of most COM-driven processes to changes in UV-B appears to be low (~0.1) because most of the effective light at >320 nm does not change significantly. However, additional UV could lead to less COM, which would result in further UV penetration into the water column. This could lead to an enhanced depth range of UV effects.

It was recently reported that the quantum yield for photochemical reactions with COM resulting in the production of the OH radical, an important oxidant in seawater (Zafiriou, 1974), rises steeply from zero at 320 nm to high values at 280 nm (Mopper and Zhou, 1990). Hence the sensitivity of OH formation rates to UV-B is high. Thus OH-sensitive processes, which may well include degradation of relatively refractory natural and xenobiotic materials, could intensify greatly in response to increases in solar UV-B entering the sea.

The above analysis of photochemical changes related to COM is preliminary and possibly fragile because it is based on samples that are geographically restricted to 9.5-42.5°N in the coastal western Atlantic. Regions most strongly affected by UV-B changes, such as high latitudes, central gyres, and equatorial upwellings, should be studied directly.

ii.) Case II - Supply-limited rate

It is also not clear that the simple conclusion above is robust on the time scales of interest in global change. In many regions the supply rates of xenobiotics may change faster than the insolation field due to changing source strengths and patterns, changes in transport, etc. For species undergoing direct photolysis, their local degradation rates in the sea will still increase on a per molecule basis with increasing insolation.

The response situation may be quite different for all the natural photoprocesses and for those degradations driven by the interactions with COM and products derived from COM (Table 4) discussed above. Assuming an insolation increase in the absence of any other change in the supply of COM or its cycling, the system must adjust by decreasing the steady state concentrations of

COM. The additional UV could lead to less COM surviving transport out of the source regions, which would result in more remote regions being deprived of COM. The supply/formation and destruction of COM thus limits the rates. If there are other significant light-absorbers in the water that compete with COM for light, total excitation rates of COM per unit volume of water will decrease at steady state relative to those present just after the increased UV input, e.g., Case I above.

However, the most dramatic changes in processes driven by COM could arise from nonphotochemical changes in the supply rates of COM. "Conventional wisdom" (Hojerslev, 1982) is that riverine material is the dominant source of COM, although marine chemists now have some evidence for a second marine-derived source. The relative importance and chemical reactivity spectra for these two potential sources of COM is controversial and poorly understood. The equatorial Pacific, central gyres, and water around Antarctica are the most likely to be supply-limited due to their distance from major riverine inputs. It is unlikely that coastal and estuarine waters will become starved of COM.

The photoreactivity of water below the mixed layer in temperate and tropical regions is several times greater than that of surface waters (Zafiriou et al., 1990; Mopper and Zhou, 1990). Thus, this material may also be upwelled from deep waters. It is not clear whether this COM is from high-latitude rivers whose waters mix and sink during deepwater formation or whether it is "marine" COM associated with decomposition processes. It has also been suggested that antarctic waters contain high concentrations of marine detrital particulate COM, especially near the surface, and that these materials may exert a photoprotective influence on the biota. Since primary productivity is expected to decrease in response to rising UV-B, this supply of COM might decrease also.

In summary, there is insufficient information to specify even the sign of the response of these photochemical processes to global change on relevant time scales. Critical issues include (1) the unknown sources and supply rates of COM, (2) the unknown balance between the direct and sensitized pathways, which respond differently at steady state, (3) the possibility that the estimates above, based on short-term incubations and limited sample suites, do not represent the relevant behavior of COM, (4) plausible large changes in supply rates of COM (especially riverine/estuarine supply) due to changes in inputs and circulation, and (5) uncertainties as to whether the pool of COM is best treated as a mixture of substances, each associated with a specific process or product, or a homogenous array of molecules, each of which can give a variety of photoproducts.

e. Metal Speciation

The cycling of such biologially important metals as Cu, Fe, and Mn is influenced in various ways by photoprocesses. Examples include colloidal Fe and Mn dissolution, Cu(II) reduction to Cu(I) (Waite et al., 1988); Fe(III) reduction to Fe(II) (see Section II); and destruction of Cu(II) organic ligands (Moffett and Zika, 1987). These processes are too poorly characterized at present for us to perform a sensitivity analysis. As these materials differ substantially from COM in the distribution of their sources and transport mechanisms on regional scales, in any given region the perturbation of their chemistries may be quite different from that of COM.

E. IMPACTS ON AIR-SEA EXCHANGE.

1. The Air-Sea Interface and Near-Surface Layers

The atmosphere-ocean interface represents a boundary with unique physical, biological and chemical features (Hardy, 1982) (Figure 17). Within the upper 50 meters a static boundary layer reduces turbulent mixing compared to the air above or the water below. Atmosphere-ocean exchange of gases and particles may be greatly influenced by the properties of this thin boundary

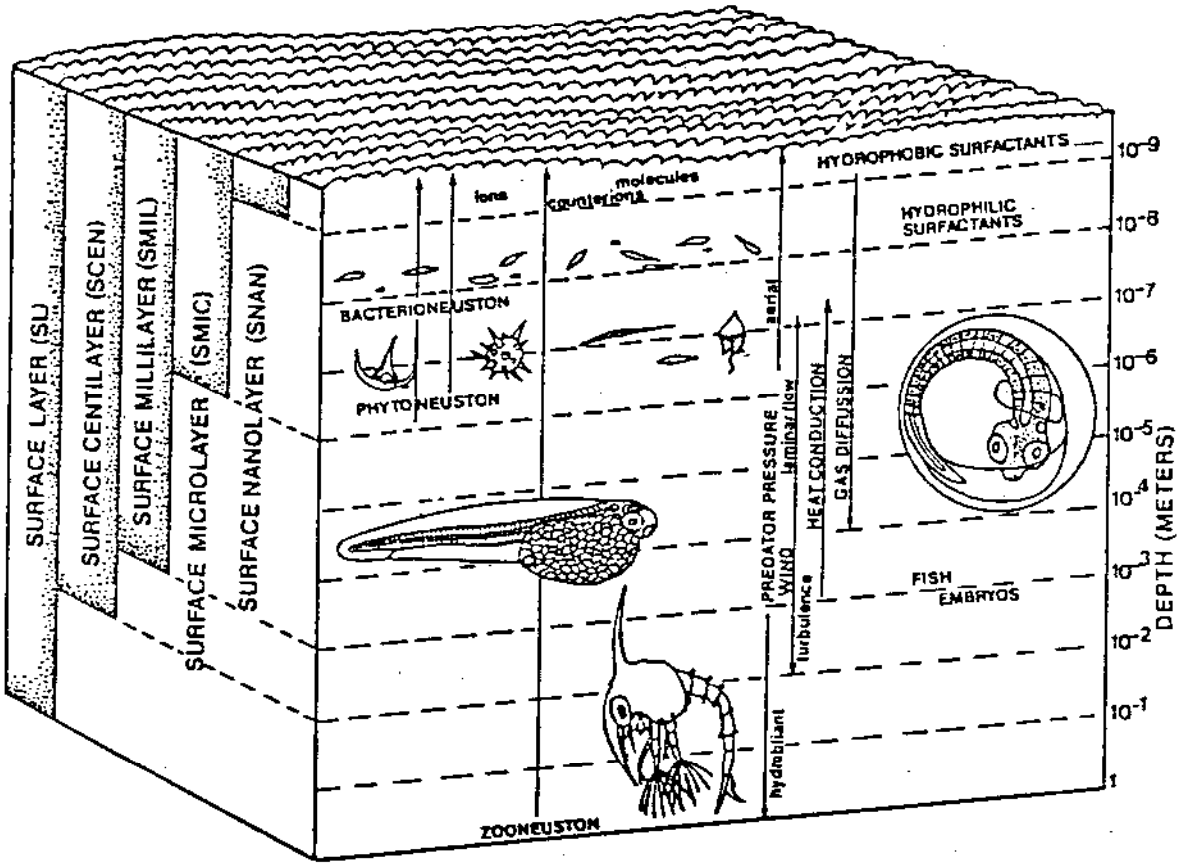

Figure 17. Logarithmic representations of sub-layers within the upper meter of the ocean surface. From Hardy and Word (1986).

layer (Liss and Slater, 1974). Both natural biogenic and anthropogenic chemicals concentrate at this interface due to their hydrophobic properties or by association with floatable particles.

The surface microlayer is a biologically-active interface and is generally highly enriched in microorganisms (GESAMP, 1980). Photosynthetic rates within the microlayer can be one or two orders of magnitude greater than those in an equal volume of subsurface water (Hardy and Apts, 1989). The microlayer also represents an important concentration point for anthropogenic pollutants (Hardy, 1987), and evidence suggests that for some contaminants it represents an important site of photodegradation. The flux of UV-B radiation is greatest at the sea surface. Increased UV-B could reduce photosynthesis and affect other important photochemical and biological processes in the sea surface microlayer (the upper 50 μm of the ocean surface) and affect air-sea exchange processes.

2. Response to Increases in UV-B and Tropospheric Ozone

Unique processes occur in the microlayer associated with atmospheric inputs (dry deposition, rain, and atmospheric gases) and with the unique biogeochemistry associated with the specialized biota, visible and invisible sea-surface films, bubbles and wave-breaking processes. For example, the input of gaseous ozone to the sea surface has been addressed. Ozone appears to react within a fraction of a second (Garland et al., 1980; Thompson and Zafiriou, 1983) and it may affect (1)

oxidation of nitrite to nitrate, (2) oxidation of iodide to HOI and (3) oxidation of organic materials, including COM-type molecules. Increasing tropospheric ozone will initially increase the sum of these rates, but the partitioning between (1), (2), and (3) and their sensitivity to change is unclear.

In temperate gyres nitrite concentrations are too low to be an important factor (Zafiriou et al., 1990). Iodide production is thought to be driven by assimilatory nitrate uptake and thus should correlate positively with local new production. The ozonation of humic acid, perhaps similar in this respect to COM/UPC, takes place readily and decreases the hydrophobicity and color of humic material (Arai et al., 1986). As ozone reactions occur directly at the sea surface, any gases produced would likely escape to the atmosphere. A strong positive feedback cycle, based on oxidant (especially ozone) fluxes driving HOI-organic reactions and the subsequent photolysis of reactive C-I bonds, has recently been proposed (Figure 18).

F. IMPLICATIONS FOR BIOGEOCHEMICAL CYCLES

The importance of biological processes as sources and sinks for atmospheric chemicals is becoming increasingly clear. In fact, the present composition of the atmosphere is closely coupled to biological systems. Important biogenic compounds released to the atmosphere from the oceans include several species of reduced sulfur compounds, CH_3Cl and CH_3I. Productive ocean areas are also important contributors to biogenic N_2O, sulfur, and possibly CO (Cicerone et al., 1984). Increases in UV-B radiation could affect marine organisms and alter the biogeochemical cycles of

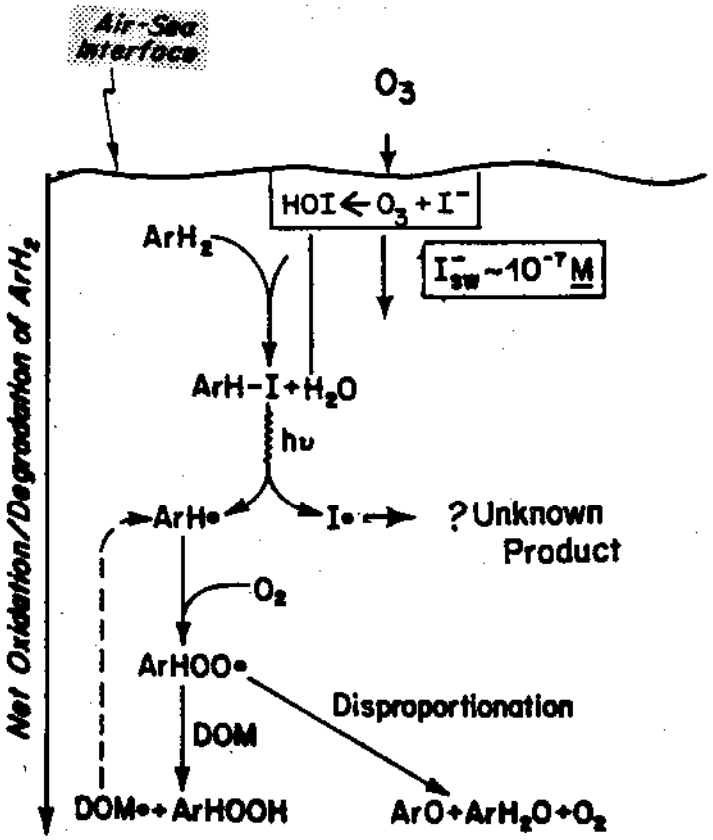

Figure 18. Possible role of an O_3 - I^- - COM feedback loop in photodegradation of dissolved organic matter at the air-sea interface (Modified from Waite et al., 1988). Ar refers to aryl groups.

the following substances:

Carbon dioxide - A decrease in marine primary productivity in response to increasing UV-B would decrease the ocean's capacity as a sink for anthropogenic CO_2, thus exacerbating the problem of global greenhouse warming. Reduction in populations of phytoplankton could decrease the sinking of carbon to the deep ocean.

Sulfur - Marine phytoplankton produce dimethylsulfide (DMS), which after entering the atmosphere, is oxidized to form particles that serve as CCN (see Section III). Production of DMS may be reduced in response to higher levels of solar radiation (Gucinski et al., 1990). Although direct empirical evidence is lacking, it is conceivable that, through a positive feedback loop, an inhibition of sulfur production by increased UV-B could reduce cloud formation, leading to an additonal increase in UV-B flux.

Nitrogen - Uptake of nitrogen by marine phytoplankton can be reduced by increased UV-B radiation and may be even more sensitive to UV-B than carbon assimilation. Phytoplankton utilization of NH_4^+ was found to be more sensitive to UV-B than NO_3^- utilization (Dohler, 1990).

Carbonyl sulfide - COS is produced by photochemical processes in the surface layers of the ocean (Ferek and Andreae, 1984). Increased solar UV reaching the ocean surface could cause more COS to be produced. The lifetime of COS in the troposphere is quite long, since it is not removed by reaction with hydroxyl radicals. Greater emissions of COS would therefore lead to greater amounts of COS reaching the stratosphere, where it is photolysed to form the stratospheric sulfate layer. If this happened on a large scale it could cause many effects. For instance, it could lead to an increase in planetary albedo and a reduction in the temperature of the lower atmosphere. It might also reduce the UV flux reaching the troposphere, since more solar UV would be backscattered. In addition, it might allow more rapid ozone removal throughout the stratosphere because it would provide a particulate surface on which the heterogeneous chemistry responsible for ozone removal in polar regions could proceed. The feedbacks could therefore either be positive or negative.

Methyl chloride and brominated methanes - Oceanic methyl chloride is the primary natural source of chlorine in the stratosphere. About 2.5×10^{12} g yr^{-1} is emitted, largely from the ocean, compared with about 0.7×10^{12} g yr^{-1} of CF_2Cl_2 and $CFCl_3$ the major anthropogenic chlorine-containing gases. The influence of the natural chlorine emissions is considerably reduced since most of the methyl chloride is removed by reaction with hydroxyl radicals in the troposphere. Reductions in the atmospheric concentration of hydroxyl radical will, therefore, allow more of the naturally emitted chlorine to reach the stratosphere and visa versa. The effects produced by increasing UV on the global hydroxyl radical concentration are therefore of considerable importance. If there is an overall reduction of OH, due primarily to loss of ozone in areas where NO_x is low, the feedback will be positive and more stratospheric ozone could be lost. If there is an overall increase in OH, perhaps due to a combination of increased $O(^1D)$ production and more water vapor, then the feedback will be negative. The same comments apply to the brominated methanes, which, while largely destroyed in the troposphere, supply a substantial fraction of the bromine observed in the stratosphere.

Nitrous oxide - Increased nitrous oxide emissions would probably lead to more ozone loss, while reduced emissions would result in less ozone loss. While the primary source of nitrous oxide is believed to be located on the land surfaces at present, recent studies indicate that oceanic sources may be more important than previously thought (see Section II).

Carbon monoxide and non-methane hydrocarbons - Oceanic photochemistry represents a

source of about 20 to 200 x 10^{12} g of CO per year to the global atmosphere (Gammon and Kelly, 1990. High CO concentrations in surface waters correlate well with local light levels and productivity indices (e.g., nutrients and chlorophyll) and correlate inversely with wind speed. In addition, the lifetime of CO in the atmosphere is related to photochemical processes. Thus, changes in radiation (especially UV-B) could influence the formation of CO in the water column and its lifetime in the atmosphere. Changes in the supply rate of starting material might significantly perturb this flux.

In the event that non-methane hydrocarbons such as ethene and propene are sensitive to UV fluxes, then it is possible that ozone concentrations over the remote ocean could be further reduced if greater quantities of UV reach the ocean surface. This is because the HO_2 radicals produced in the course of oxidation of hydrocarbons by OH could constitute a significant sink for ozone (reaction [9] above). This would give rise to a positive feedback.

G. CONCLUSIONS

1. In the southern hemisphere, by 2060 reduction in total column stratospheric ozone from recent levels could reach 2 to 5% in the tropics, 10% at mid latitudes, and over 20% at 60°S. Smaller, but significant, reductions are likely in the northern hemisphere.

2. By 2060, increases in ground-level effective UV-B radiation could reach 5%, 26% and 66% at low, mid, and high latitudes in the southern hemisphere.

3. Tropospheric ozone will continue to increase throughout the northern hemisphere outside the tropics but will likely decrease in the southern hemisphere.

4. It is uncertain how the concentration of OH will change, but it will likely decrease in the southern hemisphere as a result of increasing CH_4 and CO without increasing NO_x, whereas OH may increase in the northern hemisphere due to increasing NO_x.

5. Changes in the OH concentration will affect the lifetimes and transport to the ocean of a number of natural and pollutant gases, including HNO_3 and SO_2.

6. Increased UV-B could result in significantly decreased primary productivity at the sea surface, and perhaps throughout much of the photic zone, particularly at southern hemisphere mid and high latitudes. However, further detailed modeling efforts will be needed to asses the magnitude of such an effect.

7. OH-sensitive processes, such as degradation of natural and xenobiotic substances in the sea, could intensify with increasing UV-B, but the complexity of these photochemical processes does not allow us at present to predict quantitatively the effects of global changes.

8. The region of the ocean most sensitive to UV-B, both relative to photochemical and biological processes, is the sea surface microlayer.

9. Changes in photochemical processes in the surface waters of the ocean could have significant effects on the air-sea exchange of a number of compounds in the carbon, nitrogen, sulfur and halogen cycles.

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GESAMP WORKING GROUP 32

Workshop at the University of Rhode Island
Alton Jones Campus
16-21 December 1990

ATTENDEES

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26.	Atmospheric Transport of Contaminants into the Mediterranean Region	1985	E
27.	Report of the Sixteenth Session	1986	E,F,R,S
28.	Review of Potentially Harmful Substances. Arsenic, Mercury and Selenium (Published also as UNEP Regional Seas Reports and Studies No. 92)	1986	E
29.	Review of Potentially Harmful Substances. Organosilicon Compounds (Silanes and Siloxanes) (Printed in limited number by IMO and published also as UNEP Regional Seas Reports and Studies No. 78)	1986	E
30.	Environmental Capacity. An approach to Marine Pollution Prevention (Published also as UNEP Regional Seas Reports and Studies No. 80)	1986	E
31.	Report of the Seventeenth Session	1987	E,F,R,S
32.	Land-sea Boundary Flux of Contaminants: Contributions from Rivers	1987	E
33.	Report of the Eighteenth Session	1988	E,F,R,S
34.	Review of Potentially Harmful Substances. Nutrients	1990	E
35.	The Evaluation of the Hazards of Harmful Substances Carried by Ships: Revision of GESAMP Reports and Studies No. 17	1989	E
36.	Pollutant Modification of Atmospheric and Oceanic Processes and Climate: Some Aspects of the Problem (Printed in limited number by WMO and also published as UNEP Regional Seas Reports and Studies No. 117)	1989	E
37.	Report of the Nineteenth Session	1989	E,F,R,S
38.	Atmospheric Input of Trace Species to the World Ocean	1989	E
39.	The State of the Marine Environment	1990	E
40.	Long-Term Ecological Consequences of Low-Level Contamination of the Marine Environment	1989	E
41.	Report of the Twentieth Session	1990	E,F,R,S
42.	Review of Potentially Harmful Substances. Choosing Priority Organochlorines for Marine Hazard Assessment	1990	E
43.	Coastal Modelling	1990	E
44.	Report of the Twenty-first Session	1991	E
45.	Global Strategies for Marine Environmental Protection	1991	E
46.	Carcinogens: Their Significance as Marine Pollutants (in press)		
47.	Reducing Environmental Impacts of Coastal Aquaculture (in press)		
48.	Global Change and the Air/Sea Exchange of Chemicals	1991	E