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

## **REPORTS AND STUDIES**

No. 48

**GLOBAL CHANGES AND THE AIR-SEA  
EXCHANGE OF CHEMICALS**

391  
61.48



**WORLD METEOROLOGICAL ORGANIZATION**

**1991**

8/11/75-34

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)

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"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."

\* \* \*

For bibliographic purposes, this document may be cited as:

GESAMP - IMO/FAO/UNESCO/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Pollution. Global Changes and the Air-Sea Exchange of Chemicals, 1991. Rep. Stud. GESAMP (48).

## 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.

# GESAMP REPORTS AND STUDIES PUBLICATIONS

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2.	Review of Harmful Substances	1976	E
3.	Scientific Criteria for the Selection of Sites for Dumping of Wastes into the Sea	1975	E,F,R,S
4.	Report of the Eighth Session	1976	E,F,R
5.	Principles for Developing Coastal Water Quality Criteria (Published also as UNEP Regional Seas Reports and Studies No. 42)	1976	E
6.	Impact of Oil on the Marine Environment	1977	E
7.	Scientific Aspects of Pollution Arising from the Exploration and Exploitation of the Sea-bed	1977	E
8.	Report of the Ninth Session	1977	E,F,R,S
9.	Report of the Tenth Session	1978	E,F,R,S
10.	Report of the Eleventh Session	1980	E,F,S
11.	Marine Pollution Implications of Coastal Area Development	1980	E
12.	Monitoring Biological Variables related to Marine Pollution	1980	E,R
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14.	Report of the Twelfth Session	1981	E,F,R
15.	The Review of the Health of the Oceans (Published also as UNEP Regional Seas Reports and Studies No. 16)	1982	E
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18.	Report of the Thirteenth Session	1983	E,F,R,S
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20.	Marine Pollution Implications of Ocean Energy Development	1984	E
21.	Report of the Fourteenth Session	1984	E,F,R,S
22.	Review of Potentially Harmful Substances	1985	E
23.	Interchange of Pollutants Between the Atmosphere and Oceans (Second report)	1985	E
24.	Thermal Discharges in the Marine Environment	1984	E

Rep. & Stud. No.	Title	Date	Language
25.	Report of the Fifteenth Session	1985	E,F,R,S
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
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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

# 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  $\text{CO}_2$  by the oceans using integrated values for  $p\text{CO}_2$  and  $K$ , which are both quite variable, are probably uncertain by a factor of two. For example, small scale variability (10-100 km) in  $p\text{CO}_2$  is  $\sim 30 \mu\text{atm}$ , while a systematic error of  $1 \mu\text{atm}$  over the world ocean would lead to an error in the integrated  $\text{CO}_2$  flux of  $0.2 \times 10^{15} \text{ g C yr}^{-1}$ . 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  $\text{CO}_2$  flux which ignore such skin temperature effects may be in error by  $0.5\text{-}1 \times 10^{15} \text{ g C yr}^{-1}$ . Increasing sea surface temperature will result in increasing  $p\text{CO}_2$ , with an extra atmospheric  $p\text{CO}_2$  of  $\sim 5\%$  of the initial perturbation.

The most important future effects on surface ocean  $p\text{CO}_2$  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  $\sim 0.3$  units for a doubling of  $p\text{CO}_2$ , reducing the capacity of the ocean to take up  $\text{CO}_2$ . 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<sub>4</sub> and CO without increasing NO<sub>x</sub>, whereas OH may increase in the northern hemisphere due to increasing NO<sub>x</sub>. Changes in the OH concentration will affect the lifetimes and transport to the ocean of a number of natural and pollutant gases, including HNO<sub>3</sub> and SO<sub>2</sub>.

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  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , 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  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  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 ( $\text{O}_3$ ) 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  $\text{O}_3$  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

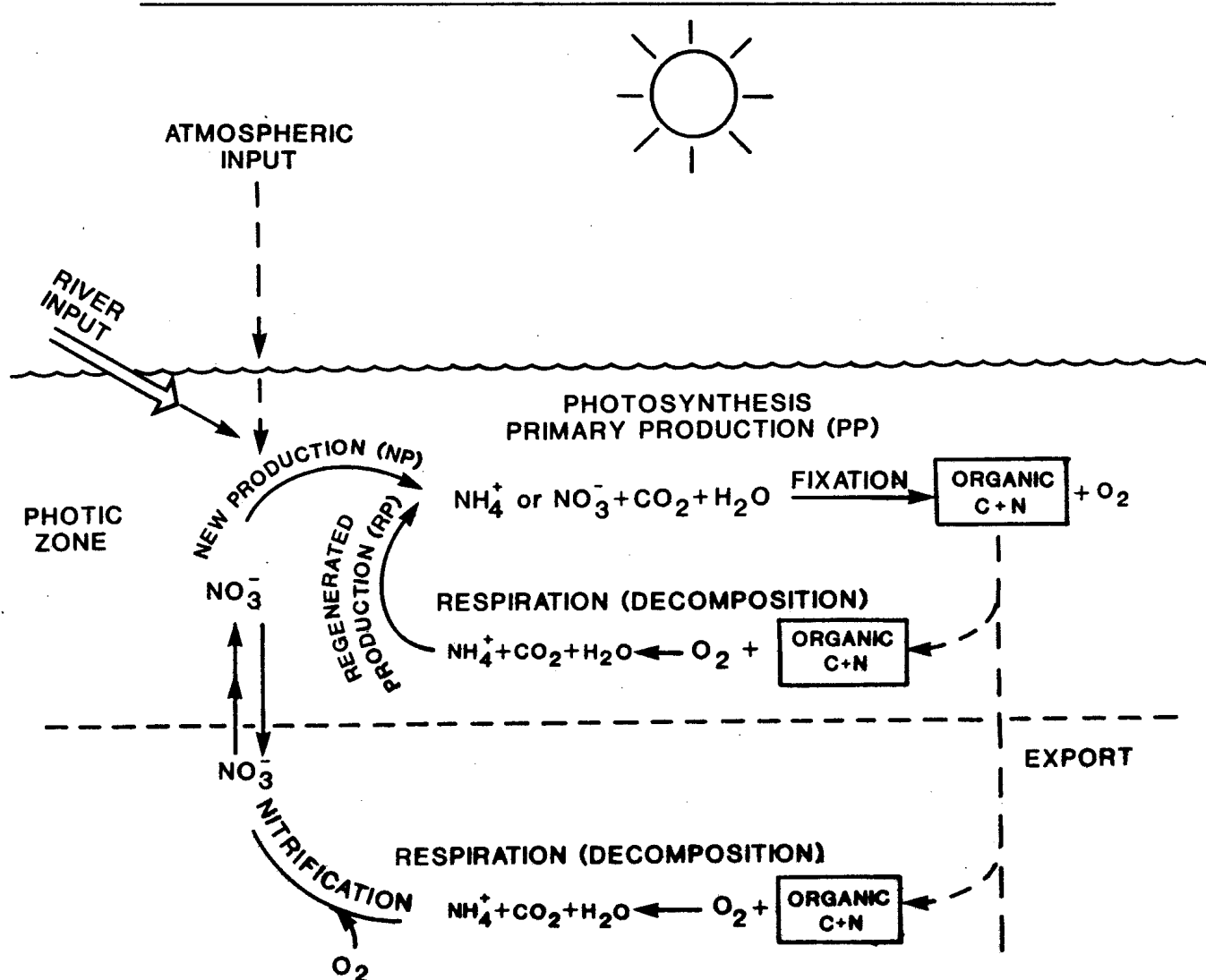


Figure 1. Schematic of the important carbon and nitrogen transfers in surface waters associated with the biological pump.

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<sub>2</sub> 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 ( $>3 \text{ g C m}^{-2} \text{ d}^{-1}$ ) 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



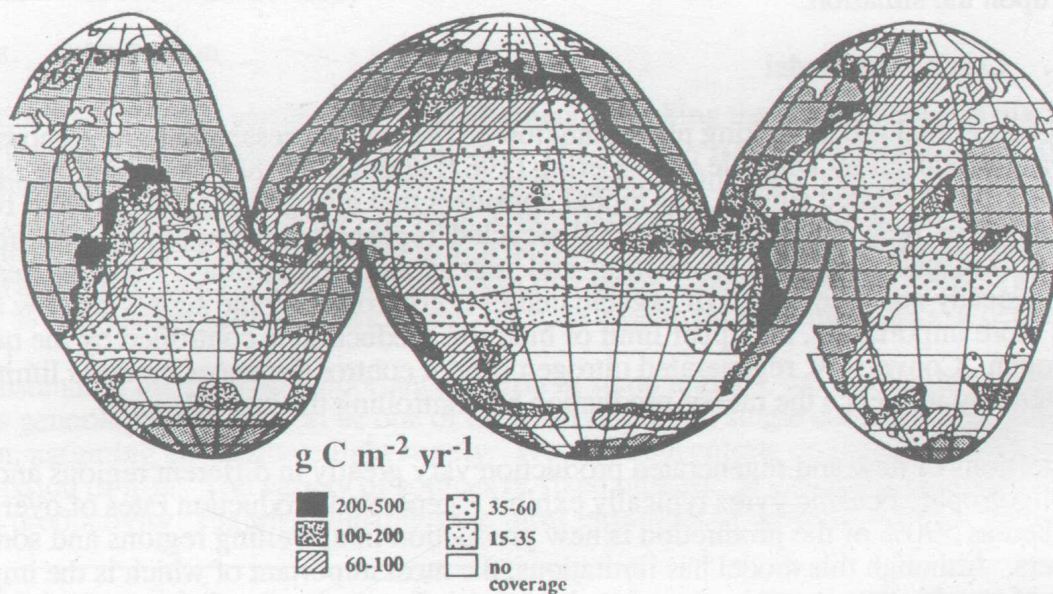


Figure 2. Average annual primary productivity of the ocean (Jahnke, 1990; Berger et al., 1988).

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 variability 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  $\text{NH}_4^+$  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  $200 \mu\text{m}$  (bacteria, protozoans, micro-zooplankton) that have been found to be the most quantitatively important (Glibert, 1982a; Harrison, 1978). Although the usual end-product of regeneration is  $\text{NH}_4^+$ , other regeneration



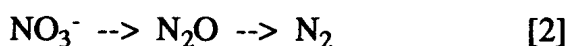
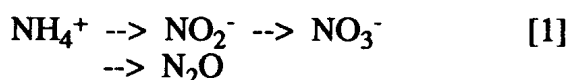
products include organic forms of nitrogen, some of which (e.g., urea) may be utilized directly by phytoplankton. Other organic forms require further bacterially-mediated breakdown before being available to re-enter the assimilation cycle. The role of organic nitrogen, particularly DON, in biological 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,  $\text{NH}_4^+$  may undergo further decomposition or be reassimilated directly by phytoplankton. Generally,  $\text{NH}_4^+$  does not accumulate in seawater because of rapid reassimilation, even if concentrations of  $\text{NO}_3^-$  greatly exceed those of  $\text{NH}_4^+$ . This apparent paradox is well documented and results from the fact that phytoplankton expend less energy in the uptake of  $\text{NH}_4^+$  than  $\text{NO}_3^-$ , which must be reduced before it can be assimilated (Owens et al., 1985). Concentrations of  $\text{NH}_4^+$  in seawater are typically  $<0.2 \mu\text{mol l}^{-1}$ , but may increase to  $1-5 \mu\text{mol l}^{-1}$  in narrow zones associated with the pycnocline, where regeneration exceeds assimilation. In general, however, production rates of  $\text{NH}_4^+$  are quantitatively similar to assimilation rates (Glibert, 1982b; Harrison, 1978; Owens et al., 1985).

A key regeneration pathway is nitrification ( $\text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$ ). 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-photoc 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  $\text{NH}_4^+$  production) to be important in that region. Although  $\text{NO}_2^-$  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  $\text{N}_2\text{O}$  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  $\text{NO}_3^-$ ) 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  $\text{N}_2\text{O}$ . This can be formed by both nitrification and denitrification according to the following simplified scheme:



Reaction [1] is nitrification, and  $\text{N}_2\text{O}$  may be formed under certain conditions as a by-product. This is in contrast to reaction [2] (denitrification) where  $\text{N}_2\text{O}$  is an intermediate. The conditions under which  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  does not always accumulate. There is invariably a strong relationship between  $\text{N}_2\text{O}$  concentration and the apparent oxygen utilization.  $\text{N}_2\text{O}$  is apparently in equilibrium with the atmosphere over the