



UNITED NATIONS ENVIRONMENT PROGRAMME

Interaction of the oceans with greenhouse gases and atmospheric aerosols

UNEP Regional Seas Reports and Studies No. 94

Prepared in co-operation with





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1. EXECUTIVE SUMMARY

The Sixth Session of the GESAMP Working Group on the Interchange of Pollutants between the Atmosphere and the Oceans stressed the impact of contaminants on climate. This included the effects of such "greenhouse" gases as CO_2 increasing temperature and aerosols decreasing temperature, as well as contaminants and processes at the air-sea interface that affect the interchange of energy and material which could affect climate regionally and even globally.

Carbon dioxide is clearly increasing in the atmosphere at the rate of about 1 ppmv (parts per million by volume) per year, starting at 315 ppmv in 1958 when good records commenced. It is estimated that the near-surface global temperature will increase by 1.5° to 4.5° K with a doubling of the atmospheric CO₂.

The global cycle of carbon dioxide indicates that the terrestrial biosphere and the oceans each cycle about 10^2 Gt (1 gigaton = 10^{15} g) carbon per year between themselves and the atmosphere, in a two-way flux if the system is in a steady state. This equilibrium has been perturbed naturally in the last 10^4-10^5 years at least, as shown by the analysis of air trapped in bubbles of glacial ice cores. Since the start of the agricultural/industrial revolution, man has added another perturbation by burning fossil fuels and mobilizing CO₂ from the fixed carbon in the land biosphere. For the period around 1980, the release of CO₂ from fossil fuel combustion is about 5 GtC yr⁻¹ and estimates of the release from biomass destruction, e.g., deforestation, ranges from 0 to 2 GtC yr⁻¹, depending on the technique of estimation. The major sink for man-mobilized CO₂ is the ocean which is estimated to accept above 2-3 GtC annually. The atmosphere retains about 2.5 GtC yr⁻¹; it is this residual CO₂ that contributes to the annual increase in atmospheric CO₂ concentration. The discrepancy between sources and sinks of man-made CO₂ is in the range of 0.5 to 1.5 GtC yr⁻¹, depending on the net biospheric input. Arguments are presented to show that the current input of CO₂ from the biosphere is no more that 1 GtC yr⁻¹, but uncertainty regarding the biomass contribution of CO₂ continues.

Some of the factors affecting the oceanic uptake of CO_2 from the atmosphere are presented. The gas transfer velocity is controlled mainly by the wind speed. The other variable that controls the CO_2 exchange flux is the partial pressure difference between the air and the sea. It is noted that there is a latitudinal variation in CO_2 flux, based on the observed CO_2 partial pressure distribution in the surface ocean. A net CO_2 flux of the order of 2 GtC yr⁻¹ emanates from the sea in the equatorial region between 16°S and 16°N. To balance this contribution, there would have to be a net flux of about 4 GtC yr⁻¹ from the atmosphere to the ocean north and south of this region.

Various models of the oceanic carbon cycle exist to estimate uptake of atmospheric CO_2 by the oceans. Diagnostic models have been developed in which the ocean is subdivided into a few well-mixed reservoirs connected by first-order exchange fluxes. Stationary tracers (e.g., natural 14C) and transient tracers (e.g., bomb-produced ¹⁴C and ³H, ⁸⁵Kr, halocarbons) have been used to calibrate the models by circulating the advective and diffusive fluxes between the various boxes. Effects of the marine biosphere and its associated cycle of nutrients have been included.

Recently, new types of circulation models of the oceanic carbon cycle, based on a realistic three-dimensional flowfield and mixing parameters of a general circulation model of the global ocean, have been introduced. These models make it possible to assess the effects of changes in the oceanic circulation, arising from climatic changes, on tracer distributions and the oceanic uptake capacity for CO_2 . They are preliminary, however, and lack certain features of the real ocean, particularly a realistic representation of the surface layer, including the marine biosphere.

With increasing temperatures due to rising atmospheric CO_2 concentration, inhomogeneities in sea-surface warming are expected owing to faster surface warming in areas with a shallow mixed layer and a strong thermocline than in areas of deep winter mixing or upwelling. Cold sea-surface temperature anomalies (SSTAs), relative to the temperature pattern expected at equilibrium with the CO_2 increase, would likely develop. SSTAs influence global weather patterns, as has been demonstrated by numerical experiments with weather forecast models. Good agreement has been found between the numerical experiments and available observations for both middle-latitude and tropical SSTAs. Rainfall increased near to warm anomalies and decreased in adjacent tropical regions. Major associated changes in atmospheric circulation arose. The response to equatorial SSTAs in middle latitudes is two to three times greater than for mid-latitude SSTAs of similar magnitude.

A second way that the ocean may modify the climatic response to a CO_2 increase is through the effect on ocean circulation and the distribution of temperature and salinity of changes in the atmospheric forcing at the surface due directly to the increase in CO_2 . Increased high-latitude precipitation would cause greater annual mean run-off, thus decreasing coastal salinities. Changes in the tropical rainfall distribution would effect changes in the density structure of the tropical oceans.

It was recognized that other man-made substances besides CO_2 , e.g., chlorofluorocarbons, nitrous oxide, methane and ozone, could influence the earth's radiative energy balance. Many authors claim that these radiatively active trace gases could cause a warming of the surface-tropospheric system of the same magnitude as that projected for increases in CO_2 . Such trace gases pose radiative/chemical/dynamical problems that are distinctly different and more complex than those of CO_2 . They could influence global climate through the greenhouse effect, but unlike CO_2 , they exhibit no important exchange processes with the oceans.

Both natural and man-made aerosols may influence climate by direct reduction of solar insolation transfer to the earth's surface and by change in the earth's albedo through aerosol interaction with cloud processes. Natural aerosols, e.g., volcanic emission, may play a more important role in climate changes than anthropogenic aerosols. During periods of extended air stagnation, accumulation of aerosols could be enough to change the solar energy input to coastal areas and regional seas. But it is not expected that anthropogenic aerosols would have much influence on global ocean climate through direct intervention with solar energy. The interaction of aerosols and clouos, on the other hand, may have a more significant impact on climate. Recently, investigators have postulated that natural sources of sulfur over the oceans may play an important role in regulating the cloud-condensation nuclei and hence the albedo. Others conclude that the effects of aerosols will probably not overshadow the impact of greenhouse gases as the most important cause of climate change over the next century.

2. CARBON DIOXIDE

2.1 Introduction

There is considerable evidence from climate models that the observed increase in the atmospheric concentration of carbon dioxide (CO_2) will lead to a significant warming of the atmosphere-ocean system [e.g., see the Villach, October 1985, Conference Report (WMO, 1986)].

In the models, this warming is due to the direct radiative effect of CO_2 enhanced by positive feedbacks due to water vapour, snow and ice and cloud extent. The equilibrium global near-surface warming for a doubling of CO_2 is estimated to be 1.5° to 4.5°K, with most recent results with model-dependent cloud cover nearer to the larger figure. This warming is larger in middle and high than in low latitudes.

The ocean is expected to modify this climate response directly in two ways. Firstly, the ocean's large thermal inertia will cause the ocean (and atmosphere) warming to lag behind that which would be in equilibrium with the CO_2 increase. Secondly, the atmospheric forcing of the ocean through momentum, heat and water transfer will be changed, thus modifying the ocean circulation and temperature and salinity structure. These aspects are discussed in Section 2.7.

The ocean's role in the global carbon cycle is crucial to predictions of future atmosphere CO₂ levels. Increases in other trace gases including methane, chlorofluorocarbons and nitrous oxide are together expected to lead to a warming of comparable magnitude to that caused by CO₂ (see Section 3). The following discussion of CO₂ can also be applied to these gases except that the ocean plays a lesser part in their geochemical cycles.

2.2 The global carbon cycle

A summary of the principal carbon reservoirs on the earth and the major fluxes between them is given in Figure 1. Examination of the reservoir sizes immediately highlights the smallness of the atmosphere as a reservoir for carbon relative to the land biosphere, sedimentary deposits, the oceans and fossil fuel reserves. This means that even small transfers of carbon as CO₂ from the other reservoirs to the atmosphere can have a disproportionately large effect on the latter.

Both the land biosphere and the oceans each cycle approximately 10^2 Gt^{*}C yr⁻¹ between themselves and the atmosphere; this is a balanced two-way flux if the system is stationary. Perturbation of the steady-state situation can come about when the two-way fluxes are out of balance, which is what must have happened in the past to explain the atmospheric CO₂ variations over at least the last 10^4 - 10^5 years, shown by analysis of air trapped in ice cores (Neftel et.al., 1982).

Since the industrial/agricultural revolution, man has applied another perturbation by burning fossil fuel and by net conversion of land biosphere (fixed carbon) to CO_2 . The sizes of these anthropogenic mobilizations are currently 5 GtC yr-1 from fossil fuel burning and anywhere from 0 to 2 GtC yr-1 from deforestation and changes in land use (see Section 2.6). The CO_2 enters the atmosphere and about 2.5 GtC yr-1 appears to remain there and leads to the well documented increase observed in atmospheric CO_2 partial pressure.

The major sink for man-mobilized CO_2 is the ocean which, according to current estimates, could get 2-3 GtC yr-1 of CO_2 during the last 25 years.

2.3 Ocean carbonate chemistry

In pure water CO₂ gas, although reasonably soluble, can be accommodated to only a very limited extent. Seawater, on the other hand, due to dissolved carbonates, contains about 150 times more carbon in the form of dissolved ionic species, primarily HCO₃, than does an equal volume of air at normal CO₂ partial pressure in equilibrium with it.

This fact makes the ocean the most important reservoir taking up CO_2 released by man to the atmosphere (Liss and Crane, 1983). As we shall see, however, the accommodating capacity of the ocean is much smaller than it might look at first sight. This is so for two reasons: (1) the time needed to spread the CO_2 taken up over the whole ocean depth is considerable (see below); and (2) the uptake capacity of seawater is about a factor of 10 (the so-called buffer or Revelle factor) smaller than anticipated from the static equilibrium partition factor of 150 quoted before. As a consequence of both (1) and (2), it turns out that the oceans take up the equivalent of half of the CO_2 released by fossil fuel combustion.

1 Gt (gigaton) = 10¹⁵ g



Glubal carbon reservoirs and present natural and anthropogenic fluxes between reservoirs in GtC year⁻¹. Anthropogenic fluxes are circled. Figure 1

2.4 Transfer of CO₂ between the air and the sea

The net flux (j) of CO₂ across the air-sea boundary can be expressed as the product of essentially two factors, the gas transfer velocity w and the difference ($\Delta pCO_2 = p_a - p_s$) between the partial pressures of CO₂ in the atmosphere p_a and the surface layer p_s of the ocean:

$j = w \alpha \Delta p C O_2$

Hence both quantities may be assessed separately. The third factor, the gas solubility α (i.e., the amount of CO₂ dissolved in a unit volume of water per unit CO₂ partial pressure) is a quantity comparatively easy to estimate and therefore of minor interest here.

The gas transfer velocity is controlled primarily by wind speed driving the near-surface turbulence in the water and thus enhancing gas transfer. In the absence of surface waves, the gas transfer velocity w is a linear function of wind speed or rather of the friction velocity and nicely follows the hydrodynamical prediction by Deacon (1977). Laboratory experiments (Jähne <u>et.al.</u>, 1986) show, however, that with the onset of wind-induced surface waves the transfer velocity starts to exceed Deacon's prediction by up to a factor of 10. This excess factor can reasonably well be correlated with the mean square slope of the surface waves. This indicates that a highly irregular wind-induced wave field enhances surface renewal by the generation of additional turbulence. Since surface films damp or even suppress waves, they also reduce gas transfer to the predictions of the smooth surface model. Whether, and if so to what extent, over the open ocean surface films do reduce gas exchange, at a given wind speed, is essentially unknown. The definite degree of gas transfer enhancement by air bubbles at very high wind speed is also still an open question.

Nevertheless, it seems (Broecker et.al., 1986) that laboratory experiments, field experiments by the radon deficiency method, and the geochemical 14 C techniques yield consistent global average values for w. However, uncertainty still exists concerning the dependence of w on wind speed, which is knowledge required to estimate the latitudinal dependence of w needed for ocean CO₂ uptake modelling and for local estimates of air-sea CO₂ fluxes.

The other quantity which determines the CO_2 exchange flux is the partial pressure difference ΔpCO_2 between air and sea. Considerable efforts have been undertaken to document this quantity on a global scale (Keeling, 1968; Takahashi et.al., 1983).

The seasonal variation of the atmospheric CO₂ mixing ratio varies from a few ppm in the southern hemisphere to not more than 20 ppm in high northern latitudes (Pearman et.al., 1983; Convay et.al., 1985). Furthermore, annually averaged mean mixing ratios vary less than 4 ppm as a function of geographic location (Pearman et.al., 1983; Pearman and Hyson, 1986). On the other hand, the partial pressure of CO₂ in the surface ocean varies spatially and temporally by up to \pm 100 ppm and occasionally more. Hence its influence on the distribution of Δ pCO₂ is much more pronounced.

The partial pressure of CO₂ at a given location in the surface ocean is determined by the complex interaction of several processes:

- gas exchange with the atmosphere;
- chemical equilibrium with the different components of dissolved inorganic carbon;
- depth of the mixed surface ocean layer;
- upwelling of and mixing with subsurface water;
- horizontal advection of waters with different history; and
- activity of the marine biosphere.

In particular, the effects of the marine biosphere are still poorly understood.

The general pattern of the mean annual distribution of ΔpCO_2 consists of an equatorial belt of supersaturated waters with excess ΔpCO_2 of up to 100 ppm, which is flanked by regions of undersaturated waters to the north and south. The distribution of ΔpCO_2 in higher latitudes, however, is less well known owing to a seasonal bias in the available measurements.

The present distribution does not represent a steady state situation, since the anthropogenic input of CO_2 into the atmosphere has created a perturbation flux into the oceans on the order of 2 GtC yr⁻¹, that is included in the pattern of the net flux as inferred from the measured ΔpCO_2 distribution.

Based on a global average value of α w derived from the pre-bomb ¹⁴C⁴ distribution, a net CO₂ flux on the order of 2 GtC yr⁻¹ emanates from the sea in the equatorial region between 16°S and 16°N. Correspondingly, a net flux of about 4 GtC yr⁻¹ would have to enter the ocean north and south of this region. The relative partitioning of this flux between the hemispheres may be inferred from the observed meridional atmospheric gradients of CO₂ concentration and its isotopic 13C/12C ratio (Keeling <u>et.al</u>., 1985).

The evolution of the ΔpCO_2 distribution with time as a consequence of increasing atmospheric CO₂ levels has not been observed accurately enough to estimate directly any changes in the air-sea fluxes of CO₂.

In order to clarify the role of the pCO₂ in the surface ocean in driving the air-sea flux, measurements of that property at a number of key locations for several years would be very valuable.

2.5 Models of the oceanic carbon cycle

The uptake of atmospheric CO_2 by the oceans can be estimated by means of a model of the oceanic carbon cycle. In the past, several models have been constructed that divide the ocean into a few well-mixed reservoirs (boxes), which are connected by first-order exchange fluxes. The exchange rates are then calibrated by tuning the predicted distributions of various stationary (e.g., natural ^{14}C) and transient tracers (e.g., the bomb-produced ^{14}C and ^{3}H , ^{85}K , halocarbons) to the observations (Keeling, 1973b; Oeschger <u>et.al</u>., 1978; Siegenthaler, 1983; Broecker and Peng, 1982).

This type of diagnostic ocean model has been optimized by increasing the subdivision of the oceans, inclusion of effects of the marine biosphere and its associated cycle of nutrients, and the use of inverse methods to obtain the unknown advective and diffusive fluxes between the various boxes (Bolin <u>et.al.</u>, 1983). Since all of these models are calibrated with essentially the same transient-tracer data, it is not surprising that their predicted uptake capacity of excess CO_2 is rather similar (Peng and Broecker, 1985), amounting to about 2 GtC yr⁻¹ around 1980.

Recently, new types of circulation models of the oceanic carbon cycle have been introduced. These models are based on the realistic three-dimensional flowfield and mixing parameters of a general circulation model (GCM) of the global ocean. This approach is promising in several ways:

- ⁰ There is no need to tune any transport parameters, since they are derived directly from the primitive hydrodynamic equations and the boundary conditions imposed at the surface in the oceanic GCM. Therefore, the wealth of available tracer data may be used to validate the model.
- D The fairly high horizontal resolution of the model (on the order of 500 km) allows model predictions of tracer distributions and fluxes on a regional scale.

⁰ The model is prognostic; therefore, it is possible to assess the effects of changes in the oceanic circulation on tracer distributions and the oceanic uptake capacity for CO_2 . This is important if the influence of climatic changes on the global carbon cycle is to be investigated.

The presently existing models of this type (Sarmiento, 1985; Maier-Reimer <u>et.al.</u>, 1985; Bacastow and Maier-Reimer, 1985) are, however, still preliminary, in that they lack certain features of the real ocean, most notably a realistic representation of the surface layer including the marine biosphere.

2.6 The effect of the biosphere on CO2

Estimates based on 13 C/ 12 C recorded in tree-rings (Broecker and Peng, 1982) and on the atmospheric CO₂ history of the last 200 years determined from air bubbles trapped in Antarctic ice-cores (Siegenthaler and Oeschger, 1987), indicate, besides the known input from fossil fuel, an additional source of CO₂ <u>ettimated</u> to the terrestrial biosphere. This source shows a peak around 1900 and a decline since then. During the time period 1959-1983 the net biospheric source contribution is estimated to lie between 0.0-1.0 GtC year⁻¹. These estimates are based on an assumed oceanic uptake capacity for CO₂ as given by state-of-the-art ocean carbon cycle models; which, however, have been validated by independent data (see section 2.5).

Woodwell <u>et.al.</u>, (1983), based on population and land use statistics, estimated that during 1980 between 1.8 GtC and 4.7 GtC year⁻¹ was released by the biosphere due to deforestation (80%) and changes in land use, primarily in the tropics. A subsequent study by the same group of investigators resulted in somewhat lower figures, giving as best estimate an annual release of 1.8 GtC for the year 1980 (Houghton <u>et.al.</u>, 1987). Bolin (1986) reviewed these estimates and concluded that this source contributed 0.8-2.4 GtC year⁻¹ during the last decade.

Elliot <u>et.al.</u> (1985) analyzed indepth the CO_2 concentrations measured at the Mauna Loa Observatory. They came to the conclusion that the CO_2 record at Mauna Loa is not consistent with net annual additions or subtractions of CO_2 other than from fossil fuels unless such additions have closely followed the trend of the fossil fuel input. Given the uncertainties, a net biotic addition between +0.7 and -0.2 GtC year⁻¹ is allowed by the analysis.

There is some evidence that increased plant production could have lead to a net uptake of CO_2 in the biosphere. Such a carbon flux has not been considered in the analysis by Woodwell <u>et.al.</u>, (1983) and by Houghton <u>et.al.</u>, (1987). Stimulation of land plants could have been effected either directly as a consequence of increasing atmospheric CO_2 levels (Kohlmaier <u>et.al.</u>, 1987) or from increased use of fertilizing agents in agriculture. Peterson and Mellillo, (1987), however, estimated the latter effect to contribute not more than 0.2 GtC year⁻¹, based on the assumption of a constant element ratio of carbon to phosphorus and nitrogen in terrestrial organic material. On the other hand, changes during the last 200 years in physiological parameters of plants growing in remote areas have been observed, such as a reduction of pore density per unit leaf area (Woodward, 1987) and increased in the size of tree-rings (LaMarche <u>et.al.</u>, 1984). Kohlmaier <u>et.al.</u>, (1987), find by means of a biota model that the increased storage of carbon in the biosphere due to the CO_2 fertilization effect could amount of 0.7-2.1 GtC year⁻¹.

If the CO_2 fertilization effect is real the net biospheric release of carbon to the atmosphere presently (deforestation minus fertilization) would lie in the range from 0 to 1 GtC year⁻¹, thus almost balancing the global carbon budget. Otherwise, an imbalance of 1 to 2 GtC year⁻¹ results, which has to be explained either by an oceanic sink being greater than currently acceptable, or by one or several, heretofore not yet identified sinks.

The foregoing discussion deals only with the terrestrial biosphere. It is uncertain how the marine biosphere has responded to changing CO_2 concentrations in the atmosphere or what contribution it has made to atmospheric CO_2 . Generally, it has been assumed that on an annual basis, the uptake of CO_2 by photosynthesis by marine plant life has been balanced by release of CO_2 from respiration and decay of marine plant and animal organisms. This may not be true. Increased input of nutrients from land as a result of agricultural practices, e.g., soil fertilization, could result in greater marine plant production. If the plants are harvested by marine fauna or man, or if they die and sink to enter the sediments, then CO_2 is removed from the surface layer of the sea, and ultimately from the atmosphere. The marine biosphere would become an enhanced sink for CO_2 .

In the foregoing connection, recent studies of the mid-Atlantic Bight of the U.S.A., the south-eastern Bering Sea, and the Peruvian coast (Walsh <u>et.al.</u>, 1985) estimate that the present carbon loading to the continental slopes of the world, as a result of export of organic carbon from continental shelves, ranges from about 0.3 to 0.48 Gt C yr^{-1} . In earlier reports, it was proposed that the increased carbon to slope standard or the mid-Atlantic coast may have occurred in response to eutrophication (Walsh <u>et.al.</u>, 1981), and off Peru in response to overfishing the anchovy, the major herbivore (Walsh, 1981), creating transient gradients in the vertical profiles of sediment carbon. Walsh <u>et.al.</u> (1985) used a combination of sediments, and the amount of nitrogen thought to be released from the coastal zone to make an independent estimate of anthropogenic carbon loading to world slopes of about 0.3 to 0.5 GtC yr^{-1} . Although the authors note that additional measurements are required to test their conclusions, they feel that their data set is consistent with the hypothesis that continental slopes are now depocentres for storage of anthropogenic releases of CO₂.

Another possible biogenic route for CO_2 uptake in the ocean is by dissolution of calcium carbonate mineral phases. The general situation is that near-surface waters are supersaturated with respect to calcitic solid phases, so that dissolution by excess CO_2 taken up from the atmosphere is not expected; only further down the water column (several km depth) does the system become undersaturated with respect to calcite. However, recent work in the N. Pacific (Betzer <u>et.al.</u>, 1984) has indicated that aragonite pteropods are subject to dissolution in quite shallow water (<2200m), and this may be an important mechanism for uptake of additional anthropogenic CO_2 by the near-surface oceans.

Other effects of CO_2 on the marine environment include changes in pH and temperature in the surface seawater layer. Projected increases in atmospheric CO_2 have been shown (Liss and Crane, 1983) to reduce pH by 0.3 for a doubling in atmospheric pCO_2. Increased atmospheric temperature by $1.5^{\circ}-4.5^{\circ}K$, with a doubling of atmospheric CO_2 concentration, would also increase the temperature of the surface seawater. What impact these physical and chemical changes in the seawater would have on the marine biota can only be speculated at present. The effect of pH change within the normal range for seawater, i.e., 7.5 to 8.5, would probably be insignificant, in that marine organisms should be able to adapt to such changes. However, a decrease in pH below the normal lower limit experienced by marine organisms could have adverse effects. Similarly, a temperature increase above the upper normal limit could cause population changes. Moreover, if temperature is an important variable triggering phytoplankton blooms, increased temperature due to higher CO_2 concentrations could temporally advance such blooms and disrupt the marine ecosystem.

2.7 Oceanic modification of climatic effects of increasing CO2

The ocean would be expected to warm as a result of increasing atmospheric CO₂ content. Because of the dependence of the ocean's thermal inertia on the depth of mixing, faster surface warming would be expected in areas with a shallow mixed layer and strong thermocline than in areas where deep mixing occurs in winter or upwelling of water from a few hundred metres is prevalent. These inhomogeneities in surface warming would lead to the development of cold sea-surface temperature anomalies (SSTAs), relative to the temperature pattern which would pertain at equilibrium with the CO₂ increase, and so also relative to the thermal forcing of the land. A first estimate of these cold SSTAs is obtainable from results published by Bryan <u>et.al.</u> (1982) on the response to a sudden quadrupling of CO_2 . However, it should be remembered that the thermal lag obtained in such an experiment will be larger than that with a gradual CO_2 increase. Firstly, one may note in Bryan <u>et.al.</u>'s results a faster warming near the ocean surface than at depth. After 10 years the surface warming is 1.5° to 3°K, compared with less than 0.5°K, at most depth below 600 m. The thermocline would thus be more stable with probable impacts on vertical mixing. The zonal mean surface changes show that the approach of SST to equilibrium was faster at 20°-45° latitude over the first 15 years. However, by 25 years, from the CO_2 increase, the response was much more uniform with the surface warming near 70% of the equilibrium figure at most latitudes. With an equilibrium warming of about 3°K in the tropics and 5° to 6°K at 45°-60° latitude, similar to more recent results for a doubling of CO_2 , the implied zonally-averaged cold anomalies, are about 1° and 2°K in tropics and middle latitudes, respectively. Regional anomalies could be substantially larger.

Such SSTAs would be near the maximum currently observed on large horizontal scales. Thus the results of observational eine fractioning studies on the atmospheric effects of such anomalies may be relevant to CO_2 climate impact studies. The effects of SSTAs in models have been reviewed by Rowntree (1986, and personal communication at the meeting). Generally, both for middle latitude and tropical SSTAs, good agreement has been found between numerical experiments and between experiments and available observational studies. Tropical SSTAs had major effects on tropical climate; rainfall was increased near warm anomalies and decreased in adjacent tropical regions. There were major associated changes in circulation. For example, with warm anomalies over the equatorial Pacific, upper troposphere anticyclonic cells develop near 15°N and S in the longitude of the SSTA, with increased easterly flow on the equatorial side (above decreased surface easterlies) and an enhanced subtropical jet to poleward. Further poleward, a mid-latitude trough is introduced throughout the troposphere. Both in models and the real atmosphere, a downstream wavetrain can usually be identified, with an anticyclonic response near 60°-70° latitude and a cyclonic response further downwind. These features appear to depend on the location of the SSTA relative to climatological flow (see also Simmons, 1982).

The response to mid-latitude SSTAs was found to be generally consistent with earlier theoretical work, with a surface low near the warm SSTA and a middle tropospheric ridge at some 20° longitude downstream. In middle latitudes, the response to equatorial SSTAs is two to three times greater than that for mid-latitude SSTAs of similar magnitude. Thus, for the cold anomalies relative to the equilibrium state for increased CO_2 , the mid-latitude responses to tropical and extra-tropical features could be of similar magnitude. However, non-uniformity of the heating of the tropical oceans could dominate the response both in the tropics and at middle latitudes. Such non-uniformity could be caused by the distribution of mixed-layer depth or upwelling or by anomalous atmospheric circulation in the tropics, in the same way that the onset and maintenance of equatorial Pacific anomalies can be attributed to particular wind patterns.

The second way in which the ocean may modify the climate response to a CO_2 increase is through the effect, on ocean circulation and the distribution of temperature and salinity, of changes in the atmospheric forcing at the surface due directly to the increase in CO_2 . There is little agreement as yet concerning such changes. One feature noted in the Villach 1985 Conference statement (WMO, 1986) is that increased high-latitude precipitation may lead to greater annual mean run-off, so decreasing coastal salipities. Increased precipitation over high-latitude oceans may have a similar effect away from coasts. A reduction in sea ice would also modify the salinity distribution in the mixed layer, and it is possible that the impact of these changes on the density structure would have significant effects on temperature, the ocean circulation and marine life, additional to those resulting directly from the general warming. The density structure of the tropical oceans would also be affected by changes in the tropical rainfall distribution and a probable general 'increase in ocean evaporation. More modelling studies are needed to quantify these and other possible impacts, including those associated with the lag in ocean temperature response discussed above.

3. OTHER RADIATIVELY ACTIVE TRACE GASES

Besides the influence of CO_2 on climate as detailed in the last section, other trace gases may also act as "greenhouse" gases. In the last fifty years, the number of anthropogenic gases released to the atmosphere has risen substantially. A decade ago, researchers first suggested that other man-made substances, e.g. chlorofluorocarbons, nitrous oxide, methane, tropospheric ozone and others, could influence the radiative energy balance just as well as carbon dioxide (Ramanathan, 1975; Wang <u>et.al.</u>, 1976). Recently, this suggestion has been definitively reviewed by Ramanathan et.al. (1985).

Table 1 lists trace gases that are currently considered to be the most important for the future state of the global atmospheric environment and gives average rates of this increase. The best known example is the well-documented increase of CO_2 as measured over nearly three decades. More recently, the concentration increases of several other trace gases were also documented, the foremost being methane mitrous oxide and carbon monoxide. These trace gases have

Table 1

Gas A	Rate of increase Nve. % per yr (range)	Effects	Sources	Lifetime (years)
Carbon dioxide	0.4 (0.2–0.7)	Added greenhouse effect	Natural; combustion	10-15
Methane	1.3 (1-2)	Added greenhouse effect; OH cycle; ozone (tropospheric and stratospheric)	Natural; food production	7-10
Nitrous oxide	0.3	Added greenhouse effect; ozone depletion (strato- sphere)	Natural; combustion; agriculture	100
Carbon monoxide	5	Indirect effects, OH depletion (troposphere)	Natural; combustion; automobiles	0.2
F-11 and F-12	5	Added greenhouse effect; ozone depletion (strato- sphere)	Anthropogenic .	50-100
Others F-113	10	Ozone depletion	Anthropogenic	Long
F-22	11	(stratosphere)		15
Methylchloroform	n 5	Added greenhouse		6
Carbontetra-	3	effect		50

Concentration increases and effects of trace gases





probably existed in the Earth's atmosphere for aeons, but are now being increased by anthropogenic activities. In addition, there are several fluorocarbon compounds in the atmosphere which are entirely man-made. The most important of them are trichlorofluoromethane (CCl₃F or F-11) and dichlorodifluoromethane (CCl₂F₂ or F-12). Other man-made chlorocarbons and fluorocarbons could also contribute to the possible depletion of the ozone layer in the stratosphere and to climate changes. These trace gases include methylchloroform (CH₃CCl₃), F-113, F-22, F-114 and CCl₄ (Rasmussen and Khalil, 1986).

The present sources of these trace gases appear to be as follows. For methane, wetlands and marshes are thought to be the largest natural sources, while the oceans, tundra, lakes, insects and other sources together contribute about as much as the wetlands. Rice paddy fields and domestic cattle appear to be the largest sources affected and controlled by human activities, while biomass burning and direct emissions also contribute significant amounts. The total yearly emissions are estimated to be 550Tg (1 Tg = 1 teragram = 10^{12} g), about half of which comes from anthropogenic activities. For <u>nitrous oxide</u> the major natural sources are the soils and oceans, whereas combustion processes and acriculture constitute the anthropogenic sources. The total emissions are 30 Tg year⁻¹, of which about 25% are anthropogenic. The sources of <u>CO</u> are many and varied. It was estimated that, in total, about 2,400 Tg of CO are emitted into the atmosphere every year, of which perhaps half is due to various human activities. No natural sources of the <u>fluorocarbons</u> have been found; the present anthropogenic emissions of F-11 and F-12 are about 0.4 Tg year⁻¹ for each.

The increasing levels of the trace gases are likely to be caused by increasing emissions. For methane and CO, some of the increase may also stem from the fact that their cycles are related to that of OH radicals. As CO increases the concentrations of OH radicals may diminish. This would in turn remove less methane (and other trace gases) than under natural, undisturbed conditions of the atmosphere. Therefore, a possible depletion of OH may be the main effect of increasing CO and could then disturb many chemical cycles and indirectly contribute to global warming and climatic changes. Based on measurement of old air in polar ice cores, there is some evidence that OH radicals may already have been reduced by perhaps 20% over the past century. Moreover, the same studies have shown that the atmospheric levels of methane several hundred years ago were less than half of the present level.

The problem concerning the greenhouse effects of human activities has broadened its scope from the CO_2 -climate problem to the trace gas-climate problem. Non- CO_2 greenhouse gases in the atmosphere are now adding to the greenhouse effect by an amount comparable to the effect of CO_2 (see Figure 2). This is a fundamental change from the situation during the period of 1850-1960 (WMO, 1985).

If the growth rates of trace gas concentration (or their emission rates) that were observed during the decade of the 1970's continue unabated for the next several decades, non-CO₂ trace gases can have as much impact as CO₂ on future trends of surface and atmospheric temperatures. In addition to the direct radiative effect, many of the trace gases have indirect effects on climate. For example, addition of gases such as CH₄, CO and NO_x can alter tropospheric O₃, which is a radiatively active gas. Within the troposphere, the indirect climate effects can be as large as the direct effects. On the other hand, within the stratosphere, temperature changes are largely determined by indirect effects of CFC's. Stratospheric H₂O will increase owing to the oxidation of the increasing concentrations of CH₄, and can be influenced by the trace gases through their effect on tropical tropopause temperatures. Furthermore, increases in tropospheric H₂O, through the temperature - H₂O feedback, can perturb tropospheric chemistry and alter the concentration of CH₄ and O₃.

Contamination of the atmosphere influences the marine environment in two ways: (1) directly through the input of pollutants into the sea, changing the physical, chemical and biological processes in the upper mixed layer and sea-surface microlayer; and (2) indirectly through modification of atmosphere and ocean-related processes, especially those pertinent to climate, and

the energy balance of the oceans. As a source or sink, the ocean plays an important role in the global cycles of radiatively active gases, i.e. CO_2 , N_2O , O_3 and halocarbons, which can affect biogeochemical processes in the marine ecosystems through long-term climatic changes and <u>vice versa</u>.

For this report, which deals with process modifications over the oceans, the influence of these gases is only indirect in that they will influence global climate.

4. ATMOSPHERIC AEROSOL PARTICLES

Through man's activities, considerable amounts of particulate matter and aerosol-forming gases are released to the atmosphere. Though much of this material is deposited close to its source, some pollutants can be transported thousands of kilometres and affect the chemistry of the atmosphere far from their origin. Scientists have been concerned that besides changing the natural chemical cycles of the atmosphere, these pollutants would also have an influence on the global climate (Wilson and Matthews, 1971). Although these concerns were first expressed over a decade ago, there are still many unknowns in understanding pollutant transport and interactions in the atmosphere. The form in which the materials are released, the chemical reactions that take place both inside and outside of clouds and the final deposition of the given pollutant substances are still poorly known.

Whatever the uncertainties, some evaluation can be made of the role of man-made atmospheric pollutants on the climate. However, before this can be done, a distinction must be made between natural and anthropogenic materials put in the air. The recent eruption of the volcano El Chichon has caused scientists to review more closely the importance of such a natural phenomenon on climate (Deluisi <u>et.al.</u>, 1983). Other more seasonal aerosol transport, such as that of Gobi and Sahara desert dust, may also be important in climate variations (Parrington <u>et.al.</u>, 1983; Heintzenberg, 1985). In both examples above, the natural aerosol would reduce the solar radiation reaching the earth's surface. It is thus important at the outset to realize that natural aerosols may play a more significant role than anthropogenic aerosols on climatic change (Deepak and Gerber, 1983).

Aerosols both natural and man-made may influence the climate of the oceans in two ways:

(1) The direct reduction of insolation transfer to the earth's surface; and

(2) Aerosol interaction with cloud processes that in turn change the earth's albedo.

For man-made aerosols, the first effect is probably only important for very limited regional areas, such as the northern coast of North America, parts of the Mediterranean and other industrial areas that border on the oceans. In general, these anthropogenic aerosols would not be expected to have much influence on the global ocean climate through the direct intervention with solar energy. Only during periods of extended air stagnation would the accumulation of aerosols be enough to change the solar energy input to regional seas and coastal areas.

The second effect, i.e., the interaction of aerosols and clouds, may have more important impact on climate. Pollution increases the number of dark light-absorbing particles in the atmosphere and, on the other hand, may also increase the atmospheric concentration of cloud-nucleating particles. Elemental carbon is believed to dominate the absorption, whereas sulfates are the major nuclei which influence droplet number. Though emission may vary for these two substances, under present industrial conditions, both should increase globally. This means either a decrease in global mean cloud albedo (because of increased absorption by carbon particles) or an increase in it (because of increasing cloud-drop concentrations). Twomey et.al. (1984) suggest that the latter effect (brightening) is the dominant one for the global climate. They state that a 2% increase in the earth albedo caused by the increased cloud-drop concentration would be equal (in the opposite sense) to the doubling of CO_2 . This hypothesis by Twomey <u>et.al.</u> (1984) requires extensive measurements in order to quantify how such a mechanism would affect the world climate. It probably does not overshadow the effects of the greenhouse gases as the most important cause of climate change over the next century (WMO, 1986).

More recently, Charlson <u>et.al.</u>, 1987 have postulated that dimethylsulphide, which is produced over the oceans and oxidizes to form sulphate aerosol, will influence the albedo of the clouds. The formation of cloud-condensation nuclei through this process could be an important method of biological regulation of the climate.

5. PROCESS MODIFICATION BY POLLUTANTS IN THE MARINE ENVIRONMENT

The effect of contaminants in modification of processes in the atmosphere, at the air-sea interface and in the sea, in the context of weather and climate modification is considered in this section. It is clear that certain processes are affected by contaminants (GESAMP, 1980 and 1985), but the significance of these alterations in terms of climate modification cannot be assessed at present. It is likely that some of the effects are confined to local areas, e.g., regions with oil films, and the global impact is inconsequential. The effects on processes are summarized in Table 2.

Certain of these process modifications might influence weather and climate either regionally or on a global scale. Specific examples of pollutant effects on important processes in the marine environment related to climate are as follows:

- Increased nutrient inputs and ocean heating due to CO₂-induced climatic changes may alter type, number and distribution of organisms in the marine biosphere.
- 2. In the marine atmosphere anthropogenic carbonaceous material, i.e., soot and dust, in sufficiently large quantities could alter the direct solar input to the seas, and consequently alter the thermal characteristics of the sea and the troposphere. The introduction of cloud-condensation nuclei, mainly sulfur compounds, into the marine atmosphere modifies the physics of clouds by increasing the number of drops per unit volume. Through this process the clouds become more reflective and hence change the earth's albedo.
- 3. At the air-sea interface, pollutant organic films from petroleum and/or detergents are known to modify a number of interfacial properties and exchange processes. However, the Working Group has determined that, at the present time, petroleum films probably do not modify the interfacial exchange of matter or energy on a global scale, but that in certain coastal areas and seas, especially those affected by oil production and transportation, oil films could influence interfacial exchange processes on a smaller scale. Altered air-sea interfacial processes may influence the ocean-atmosphere exchange of CO₂ and Freons, and of natural substances as sources of atmospheric acidity, but further research is required to establish whether this influence really exists, and if so, to what extent.
- 4. Turbidity increases at sea from man-mobilized solids, e.g. from farming and construction in riverine inputs, will influence light penetration and possibly alter ocean thermal structure and biological uptake of CO₂ in the photic zone. Such effects would be of greatest concern in marine areas in the vicinity of river discharges and near disposal sites for municipal wastes.

TABLE 2. MODIFICATION OF PROCESSES BY CONTAMINANTS

PROCESS	TROPOSPHERE	AIR-SEA INTERFACE	SEA
PHYSICAL	Soot and dust could alter the solar input and change the thermal characteristics of the troposphere. Cloud- condensation nuclei in the marine atmosphere modify the physics of clouds which may result in the modifica- tion of cloud formation patterns and the earth's albedo.	Organic films from petroleum hydro- carbons and/or detergents modify interfacial properties and exchange process- es. Altered air-sea interfacial processes may influence the ocean-atmosphere exchange of gases (CO ₂ and acid rain precursors) that are sources of acidity in coastal areas and seas. especially those affect- ed by oil production and transportation.	Agricultural, forestry and construction silt runoff influences light penetration and possibly alters thermal structure in the euphotic zone. Estuar- ine areas and sites of municipal and industri- al waste disposal would be of greatest concern.
CHEMICAL	Ozone is the source of the highly reactive radicals that control the chemistry of the troposphere. Changes in ozone can alter the concentrations of these radicals. Vari- ous atmospheric pollutants, e.g., nitrogen oxides and hydrocarbons, con- tribute to ozone through photo- ox fation processes.	Enrichment of organic films with petroleum hydrocarbons, organochlorines and metals occurs. This prevents ready transfer to the water column and enhances transfer to the atmos- phere by bubble bursting. Exposure of substances in the surface film to the atmosphere and solar radiation promotes oxidation and photo- chemical processes.	Increased input of sub- stances from man-made sources can change the minor element composi- tion of seawater. Metal concentrations can be increased. Input of CO_2 can change the pH of seawater with certain consequences to chemi- cal equilibria of ionic composition.
BIOLOGICAL	Transfer of bacteria, viruses and fungus spores from the sea to the atmosphere and potential transport to land by winds. This is a possible route for pathogens from sewage- polluted coastal areas to land animals and humans.	Pathological micro- organisms could be concentrated in the surface film. Neuston- ic organisms can be affected by pollutants concentrated in the surface film. Erosion of the ozone layer by freons could lead to more UV light imping- ing on the sea surface and could affect the neuston adversely.	Dissolved constituents from municipal and industrial wastes, as well as from runoff, could be toxic to marine organisms or be bio- accumulated by them, posing a threat to consumers including man. Turbidity from suspended matter can reduce light penetra- tion and primary productivity. Silt and other suspended mater- ials can have adverse effects on sensitive marine organisms and habitats, e.g., coral reefs and mangroves.

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Annex I

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Annex II

NOTE ON GESAMP

GESAMP, the Joint Group of Experts on the Scientific Aspects of Marine Pollution, was established in 1969 and is today co-sponsored by the United Nations, United Nations Environment Programme (UNEP), Food and Agriculture Organization of the United Nations (FAO), United Nations Educational, Scientific and Cultural Organization (UNESCO), World Health Organization (WHO), World Meteorological Organization (WMO), International Maritime Organization (IMO) and International Atomic Energy Agency (IAEA).

According to its peresent terms of reference, the functions of GESAMP are:

- to provide advice relating to the scientific aspects of marine pollution $\frac{1}{2}$; and
- to prepare periodic reviews of the state of the marine environment as regards marine pollution and to identify problem areas requiring special attention.

Since its beginning GESAMP involved a large number of experts as members of GESAMP or GESAMP Working Groups and produced, at the request of the sponsoring organizations, numerous reports on a variety of scientific problems related to marine pollution $\frac{2}{2}$.

^{1/} GESAMP defined marine pollution as "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."

^{2/} V. Pravdic: GESAMP, The First Dozen Years. UNEP, 1981.

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