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**The role of ocean biota in the CO₂ drama
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PREFACE

In 1989 I received a scholarship from the Swedish Council for Planning and Coordination of Research to participate in the young scientist summer program at IIASA (International Institute for Applied Systems Analysis), Laxenburg, Vienna. Before going there I had never studied oceanography or global change. However, my supervisor at IIASA, professor Michael Antonovsky had an idea of looking into ocean biology and its interaction with climate change. Thus I started to study this problem and presented a first draft of an article before I left IIASA.

Since I caught an interest for the question, I have tried to follow the development in climate change research, especially in connection with ocean biota and ocean circulation. This interest has now resulted in this contribution. As I am not myself involved in the research about climate change I apologize for any mistakes or misconceptions. The value of the article, I think, is that it summarizes many thoughts about ocean biology and climate change. Further, one can still hear arguments for ocean biota having no significant importance in rapid climate change scenarios, and I think that this article at least shows that this is a doubtful assumption. My thanks to doctors Erik Danfors and Gunno Renman who has given valuable editorial remarks on different versions of the manuscript before publishing.

Stockholm in January 1992

Thomas Gumbricht

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ABSTRACT

Gumbricht, T. (1992); **The role of ocean biota in the CO₂ drama**. Royal Inst. of Technology, Department of Land and Water Resources. Research report, TRITA-KUT 92:1069, 32 pp.

In this review article it is suggested that ocean biota largely determines the climatic regime on earth by controlling the carbon cycle. This implies that ocean biota also can play a significant role in the present scenario of more rapid climate change.

On geological time scales the carbonate-silicate geochemical cycle largely controls the atmospheric carbon dioxide content. As ocean life determines the amount and distribution of carbonate sedimentation, it also controls the long run atmospheric $p\text{CO}_2$.

Measurements in ice cores have revealed that the ice age oscillation in temperature is strongly correlated to $p\text{CO}_2$ and ocean productivity. The most probable sequence of climatic control in the 100 kyr cycle interpreted from those and other data is that ocean productivity induces $p\text{CO}_2$ change in turn inducing climate change. There are, however, several other suggestions that rely more heavily on changes in ocean general circulation pattern bringing about the ice age cycles.

Estimates of productivity and sinking carbon fluxes in the present ocean are very inconsistent. However, most recent investigation show higher productivity and fluxes than older results indicate. Productivity is probably limited by nitrogen and phosphorus in the warm ocean, and apart from those nutrients also by iron, light and temperature in the cold ocean. All those factors are subject to change in a rapid climate change scenario as well as by other anthropogenic disturbances. This implies that primary production in the ocean will change, and hence also the ocean carbon distribution and net carbon uptake.

Keywords: global climate change, biogeochemical feedback, ocean biota, ocean primary production, ocean circulation, nitrogen, ice age cycle.

1 INTRODUCTION

Although the atmosphere is nearly transparent to shortwave radiation, it readily absorbs terrestrial infrared radiation. The major natural absorbers being water vapour, carbon dioxide, methane and ozone (Sellers, 1965). Of these all except water vapour have increased since the onset of the industrial revolution due to anthropogenic activity (Watson et al., 1990). Also CFCs, a group of completely anthropogenic derived products, are potent absorbers of infrared radiation (*ibid.*). The atmosphere, in turn, reradiates the absorbed terrestrial radiation partly back to space and partly back to the earth's surface. If it was not for this greenhouse effect the temperature at the surface of the earth would be about minus 16 centigrades, or 33 centigrades colder than at present (IPCC, 1990).

The importance of water vapour as a greenhouse gas was discovered already in 1861 by Tyndall (Cess, 1989). Arrhenius (1896) discovered that the same is true for CO₂, and also predicted, with surprisingly good accuracy, that changes in atmospheric CO₂ would bring about climate change. More than a century after Tyndall's discovery Möller (1963)

suggested that water vapour could act as a positive feedback (Cess, 1989), and thus increase climatic changes.

A doubling of atmospheric $p\text{CO}_2$ is expected to bring about a temperature rise of 1.5-4.5 °C, with a best estimate of 2.5 °C (IPCC, 1990; Mitchell et al., 1990). This is roughly expected to happen in the middle of the next century. During this century the best estimate is that temperature has risen about 0.5 °C (Folland et al., 1990; Jones and Wigley, 1990). There are however, still large uncertainties about this figure (Barnett, 1990)

The range of uncertainty of temperature predictions is rather large due to the many feedback mechanisms in the climate system. Particularly the role of cloud formation and ocean uptake/release of greenhouse gases are not fully understood (Cess et al., 1989; Cubasch and Cess, 1990; Dickinson, 1986b; Hansen et al., 1984; Lashof, 1989; Leggett, 1990; IPCC, 1990; Peng et al., 1987; Ramanathan, 1988; Schimel, 1990; Schneider, 1989).

The feedback mechanisms can be divided into physical and biogeochemical loops, of which, surprisingly as it might seem, most are positive (Lashof, 1989; Schimel, 1990; Watson et al., 1990).

The physical loops are the most important with atmospheric water vapour as the outstanding contributor to magnified climatic change (Cess et al., 1989; Cubasch and Cess, 1990; Hansen et al., 1984; Lashof, 1989; Raval and Ramanathan, 1989). Also the cover of snow and ice is a strong positive feedback, and the base for glacial theories, as first suggested by Milankovitch (1941). The role of clouds is more unpredictable and one of the major uncertainties in climatic change scenarios (Cess et al., 1989). For recent overviews of physical feedback mechanisms see Lashof (1989), Hansen et al. (1984) Schimel (1990) or Dickinson (1986a;b).

The biogeochemical feedback loops are not as influential as the physical, but taken together they can play a pronounced role on climatic change (Lashof, 1989). The most important probably being release of methane hydrates from the ocean continental slope sediments (*ibid.*). As the oceans contain vast amounts of methane hydrate, and solubility decreases with temperature, it can magnify climate change significantly.

Oxidation of frozen soils, peatbogs and wetlands will also increase, causing release of both CO_2 and CH_4 (Nisbett, 1989; Schimel, 1990). Changes in soil-water may affect carbon fixation, but those changes are not possible to predict at present (Watson et al., 1990).

Carbon dioxide fertilization effect (Melillo et al., 1990; Schimel, 1990; Strain and Cure, 1985) together with higher efficiency for water, light and nitrogen use (Gates, 1985; Melillo et al., 1990) will cause the earths vegetation to act as a negative feedback system. Normally it is thought that C3 plants will increase their growth more than C4 plants, unless there is water stress.

However, if climate change is fast, some species (and ecosystems) might not be able to adapt fast enough (Huntley, 1990; Melillo et al., 1990; Woodwell, 1990), particularly loss of forest ecosystems will enhance the CO_2 release from the terrestrial vegetation (Watson et al., 1990). Further, vegetation changes are expected to bring about a world wide net decrease in albedo (Lashof, 1989). And probably the most important vegetation effect is that respiration rates increases more than photosynthetic rates as temperature rises, thus enhancing climate change (Houghton and Woodwell, 1989; Lashof, 1989; Melillo et al.,

1990; Schimel, 1990). The additional CO₂ flux might be significant, perhaps a few GtC per year. Taken together the terrestrial vegetation net effect is unpredictable, but it is more likely to act as a positive than as a negative feedback system (Lashof, 1989; Melillo et al., 1990; Schimel, 1990; IPCC, 1990; Woodwell, 1990). However, I shall argue that the same mechanisms that lead to terrestrial biota acting as a positive feedback at climate warming, causes ocean biota to act as a negative feedback.

An increase in ocean temperature will cause an increase in ocean $p\text{CO}_2$ (Stumm and Morgan, 1981), tending to decrease the ocean net uptake, thus acting as a positive feedback. The ocean surface temperature is expected to increase faster than the deeper ocean, creating a more stable thermocline, and, hence, an ocean more resistant to vertical mixing. (The best estimate is that also the ocean surface temperature has risen during this century with approximately 0.5 °C - Folland et al., 1990). However, the ocean general pattern of circulation might be significantly altered, as suggested by historical data (Boyle and Keigwin, 1982; 1987; Boyle, 1988a; Broecker, 1987; Broecker et al., 1985; 1990a; Duplessy and Shackleton, 1985). Coupled to shifts in salinity and/or alkalinity circulation changes can explain much of the glacial-interglacial oscillation of $p\text{CO}_2$ (Broecker and Peng, 1989; Broecker et al., 1985; 1989; 1990b).

Also changes in wind pattern and forces might change the transfer of CO₂ across the air-sea interface. Finally, and not least important, life in the oceans might change, and severely interact with climate change. Changes in photosynthesis, respiration and net primary production (NPP) can be brought about by changes in temperature, circulation pattern, nutrient availability or species composition. Anthropogenic activity like eutrophication might cause enhanced NPP, whereas toxification can cause a decrease in NPP (Watson et al., 1990). This suggests that ocean life plays a crucial role in controlling atmospheric $p\text{CO}_2$, and that it does so through linkage with other biogeochemical cycles (McElroy, 1983; Shaffer, 1989; Sharp, 1991). Probably the most important part of the ocean in this respect are high latitude waters, acting as windows to the deep sea (Sarmiento and Toggweiler, 1984; Knox and McElroy, 1984).

The objective of this study is to show that ocean biota, even though its standing crop is very small, can effect the carbon cycle in timespans of decades to eons. That the biological pump of the ocean can have withdrawn the missing sink of atmospheric carbon. The study put emphasis on qualitative mechanisms and only briefly discusses the quantitative interpretation.

Since a lot can be learnt from examining the carbon cycle and processes that have determined climate change in the past, the report starts with a brief description of the carbon cycle and atmospheric CO₂ control on different time scales.

1.1 The carbon cycle

Even though the periodic table consists of about a 100 elements, life is built up around a few of the lighter elements (Deevey, 1970). One of the central elements around which life revolves is carbon. And thus, life itself has a big role in the way in which carbon cycles between lithosphere, hydrosphere, atmosphere, pedosphere and the biosphere itself (Bolin, 1970; Holser et al., 1987).

The by far largest carbon reservoir is the lithosphere (table 1). The largest fluxes are between atmosphere and terrestrial biota and atmosphere and ocean. Carbon, in its volatile forms, CO₂ and CH₄, is also the major greenhouse gas. Anthropogenic activity has increased CO₂ levels since 1700 from about 280 to 353 ppm in 1990 and CH₄ levels from 0.8 ppm to 1.72 ppm (Watson et al., 1990).

Table 1. Reservoirs, total fluxes and detention times of carbon in the carbon cycle (mainly after Eppley, 1989; Holser et al., 1987; Olson et al., 1985; Solomon et al., 1985; Sundquist, 1985; Watson et al., 1990).

Reservoir	Reservoir Mass (10 ¹⁸ g)	Fluxes (10 ¹⁸ g C yr ⁻¹)		Detention time (yr)
		Range	Best estimate	
I Atmosphere	0.75+0.003yr ⁻¹	0.15-0.23	0.19	4 ^a
II Hydrosphere				
Fresh water	0.048	0.0003-0.0013	0.0008	60
Ocean surface	0.63+0.001yr ⁻¹		0.1	6
Intermediate and deep ocean	38+0.002yr ⁻¹		0.04	1000
III Biosphere				
Terrestrial life	0.56-0.0016yr ⁻¹	0.045-0.078	0.060	9
Oceanic life	0.004	0.02-0.06	0.03	0.1
IV Pedosphere				
Soil and detritus	1.5		0.05	30
Subfossile	1.0		0.001	1000
Soil carbonates	1.1		0.00003	37 000
V Lithosphere				
Carbonates	60 000		0.00018	345 000 000
Org. sediments	10 000		0.000037	278 000 000
Recov. foss.	4-0.0057yr ⁻¹	0.0052-0.0062	0.0057	-
Fuel				

a) This means that on average it takes about 4 years before a molecule of CO₂ is taken up by plants or dissolved in the ocean. However, this must not be confused with the time it takes to adjust to a new equilibrium if sources or sinks change. This time is of the order of centuries (Watson et al., 1990).

As seen from table 1 there is a discrepancy between present reservoir changes (boldface figures) of about 0.0013 *10¹⁸ g C yr⁻¹. This is the "missing sink" that generally is thought to have gone into the ocean, however so far all explanations of the mechanism for this has failed (Watson et al., 1990).

2 CO₂ CONTROL ON GEOLOGICAL TIME SCALES

The illumination of the sun has increased by a about 25 % during the last two billion years (Budyko et al., 1985). This suggests that the earth was a frozen planet in the Precambrian. Evidently this was not the case, and it is thought that both CO₂ and methane were more important heat trappers during earlier eras (Henderson-Sellers, 1986; Lovelock, 1988). CO₂ was the dominating greenhouse gas before life evolved, but as photosynthesis began, CO₂ was withdrawn from the atmosphere and methane emitted instead. When the atmosphere became oxygenated methane was oxidated. Large drops in temperature probably marked both occasions.

The decrease of atmospheric CO₂ has since continued and that is thought to be a result of the decreasing content of radioactive elements in the earths interior, decreasing the driving

force of magmatic and volcanic processes releasing carbon from the lithosphere (Budyko et al., 1985). If the processes stopped the CO₂ content of the atmosphere would be depleted in about 10 000 years (Berner and Lasaga, 1989). An alternative explanation is that plateau uplift have exposed more rock to the atmosphere, increasing *p*CO₂ consumption through weathering processes (Berner et al., 1983; Ruddiman and Kutzbach, 1991).

The major processes controlling the long term atmospheric content of CO₂ is the carbonate-silicate geochemical cycle (Holland 1978 and 1984; Budyko et al. 1985), as suggested by Urey in his classical work (Urey, 1952). Apparently, the large amount of carbon in the lithosphere (table 1) also suggests that the long-term control mechanism lies here.

In short the processes of weathering and sedimentation withdraw carbon from the atmosphere, whereas metamorphic and magmatic processes are followed by degassing of CO₂:

I	Carbonate rock weathering:	$\text{CO}_2 + \text{H}_2\text{O} + \text{CaCO}_3 \leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$
II	Silicate rock weathering:	$2\text{CO}_2 + \text{H}_2\text{O} + \text{CaSiO}_3 \leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- + \text{SiO}_2$
III	Carbonate formation in oceans:	$2\text{HCO}_3^- + \text{Ca}^{2+} \leftrightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$
IV	(II + III) Classical Urey reaction:	$\text{CO}_2 + \text{CaSiO}_3 \leftrightarrow \text{CaCO}_3 + \text{SiO}_2$
V	Metamorphic/magmatic breakdown:	$\text{CaCO}_3 + \text{SiO}_2 \leftrightarrow \text{CaSiO}_3 + \text{CO}_2$

Reaction V means a net release of CO₂ to the atmosphere, the corresponding sink is reaction II that consume two molecules of CO₂ of which one, through reaction III enters the lithosphere.

Budyko et al. (1985) have shown the relationship between those processes and the atmospheric CO₂ content in the geological past, and Berner and co-workers (1983 and 1989) presents a mathematical model predicting atmospheric *p*CO₂.

Volk (1989) has pointed at the importance of the ocean regional distribution of carbonate burial. Regeneration of pelagic carbonate is about one magnitude faster than continental carbonate (i.e. due to plate-tectonics and subduction zones). During the last 100 Myr pelagic burial has increased, which perhaps have prevented glaciations and balanced the decrease in volcanic and magmatic activities.

As oceanic life largely determines deposition rate and distribution of organic matter and calcium carbonate on the sea floor (Lyle et al., 1988; Jahnke, 1990, also see below), ocean biota plays a crucial role feeding the endogenic carbon cycle, thus determining the climatic regime on geological time scales.

3 THE ICE AGES AND THE MILANKOVITCH CYCLES

It is commonly accepted that the onset of glacial periods is due to changes in the earth's orbital pattern (Henderson-Sellers, 1986; Imbrie, 1985), as first suggested by the Serbian mathematician Milankovitch (1941). His basic idea was that it is the summer illumination that plays the critical part. In periods with decreasing summer radiation, the ice line would gradually advance. Higher earth albedo, and further lowering of the temperature would follow this. In periods with increasing radiation the processes would go the other way around. The historical record show periods with colder climate in sequences of about 100 000, 59 000, 41 000, 23 000 and 19 000 years (Barnola et al., 1987; Imbrie, 1985). Except

for the 100 000 year cycle, this clearly coincidence with what could be expected from the earths orbital pattern (Imbrie, 1985; McElroy, 1986). Further the CO₂ record for the last 160 000 years also show a major 100 000 year cycle and a minor cycle of 21 000 years (Barnola et al., 1987).

Later investigations indicate that orbital changes and ice-albedo alone are not strong enough to explain the rapidity and magnitude of the quaternary climatic past (Pisias and Shackleton, 1984; Genthon et al., 1987; Schneider, 1989). The changes must be amplified by one or several of the feedback mechanisms mentioned above. Ruddiman and Kutzbach (1991) have suggested that the ice plateaus formed during ice-ages changes atmospheric circulation pattern leading to further cooling, thus being an additional positive feedback mechanism.

It has been revealed (through measurements in ice cores) that the atmospheric CO₂ level went up from about 200 to 280 ppm rather quickly towards the end of the last ice age (Barnola et al., 1987; Neftel et al., 1982 and 1988). This has been interpreted as a sign of decreased biological activity in the oceans due to withdrawal of phosphorus as suggested by Broecker (1981 and 1982) or nitrogen as suggested by McElroy (1983). The mechanism for withdrawal being that the sea level transgression following melting of the glaciers, causes increased deposition of nutrients. During glaciation the opposite would occur. The regression of the sea level causes leakage of nutrients, leading to eutrophication of the ocean. Shaffer (1990) have brought this concept further, including also denitrification changes he has shown that the productivity of a nitrogen-starved ocean can explain much of the 100 kyr *p*CO₂ oscillation (Shaffer, 1990).

Since later investigations have indicated that the *p*CO₂ change took place during centuries rather than millenas (Stauffer et al., 1984), and that production changes seem to lead sea-level changes (Shackleton and Pisias, 1985), this hypothesis has been questioned (Broecker et al., 1985). Also, based on Cd data, it has been argued that oceanic P inventories have changed less than approximately 20 % (Boyle and Keigwin, 1985). Instead the rapid rise is suggested to have been brought about by change in C:N and/or C:P ratio in the organic residues falling through the thermocline, or by increases in high latitude deep water formation (i.e. increased ocean circulation), possibly in combination with a drop in nutrient use efficiency followed by increases in high latitude water nutrient content (Broecker et al, 1985; Peng and Broecker, 1984; Sarmiento and Toggweiler, 1984; Knox and McElroy, 1984; Sarmiento and Toggweiler, 1984). The latter hypothesis is supported by the findings of for instance Boyle and Keigwin (1982; 1987), Boyle (1988a), Duplessy and Shackleton (1985) and Broecker et al. (1990a) that indicates drops in North Atlantic deep water (NADW) formation during glacial times.

Boyle (1988b) showed that a decrease in NADW were followed by an increase in alkalinity, which led Broecker and Peng (1989) to suggest that this alkalinity increase coupled to a shallowing of ocean nutrient maximum, could explain glacial to interglacial CO₂ changes (the relation between alkalinity and *p*CO₂ is explained in section 5). Thus this hypothesis demands no change in high latitude nutrient content.

Broecker et al. (1985 and 1989) suggested a mechanism for glacial-interglacial circulation with meltwater inflow to the Northern Atlantic causing the thermohaline circulation, or conveyer belt, to halt. As Fairbanks (1989) could prove that meltwater

production ceased during the Younger Dryas, Broecker et al. (1990b) instead suggested thermohaline circulation to oscillate naturally due to cyclical salinity changes in the Atlantic contra the rest of the ocean.

However, it seems obvious that ocean photosynthetic activity was higher during the last glaciation in comparison with the present ocean. Evidence for this lies in the ratios of ¹³C/¹²C in upper and lower ocean. There is a preferential uptake of ¹²C in photosynthesis, whereas the transfer of C over the air-sea interface is without fractionisation. This enriches the surface water with ¹³C and the deeper ocean with ¹²C. The relative abundance of ¹³C to ¹²C is specified by δ¹³C, proportional to the ratio of concentrations ¹³C/¹²C. Differences in levels of δ¹³C between upper and lower ocean should therefore reflect higher productivity in the oceans. Peaks in the ocean productivity measured in this way is negatively coupled to p CO₂ and temperature, showing sequences of approximately 100 000, 40 000 and 20 000 years (McElroy, 1986).

Martin (1990) suggest that iron limits nitrogen assimilation, and thus also carbon withdrawal in part of the present ocean, and since iron input was higher during the last glaciaton (De Angelis et al., 1987) ocean biota more efficiently withdrew CO₂ during that time.

Increased biological activity in the ocean obviously is followed by withdrawal of atmospheric CO₂. But not only the amount of carbon incorporated in biological tissue will be withdrawn (as this amount is very small, table 1). The increase in biological growth will also increase the precipitation of organic matter from the photic zone (see below). In the deep ocean this organic matter will be oxidized. As long as oxygen is present it will be the oxidizing agent, but if the productivity of the oceans increase further first nitrate (NO₃) and then sulphate (SO₄) will act as oxidizing agents (Shaffer, 1989). Present Holocene ocean is not anoxic except in eutrophied estuaries like the Baltic Sea and other stagnant basins, where nitrate is an important oxidizing agent (Holland, 1978; Wulff et al., 1990). However, the δ¹³C data during Pleistocene glacials (Mix, 1989; Sarnthein et al., 1988; Shackleton et al., 1983) suggests 30-40 % higher NPP indicating anoxic conditions (Shaffer, 1989). Thus a low content of O₂ in the deep ocean will be followed by low content of CO₂ in the atmosphere, and a higher content of CO₂ in the deep ocean. This processes is sometimes referred to as the ocean biological pump. Perturbation in the biological pump can strongly affect the atmospheric content of carbon (Baes, 1982; Peng and Broecker, 1984; Knox and McElroy, 1984; Sarmiento et al., 1988; Southam and Peterson, 1985). There is also evidence that this pump has had a major influence on climate in the geological past (Arthur et al., 1988).

The conclusion of the ice age theories is that climate change is induced by physical factors, but the change is not sufficient to bring about climate change magnitudes as revealed by the quaternary history. This is most likely brought about by ocean biota that amplifies the change and thus determines the ice age climate regime on earth. This suggests a sequence of ocean NPP change inducing pCO₂ change inducing climate change (Genthon et al., 1987; Southam and Peterson, 1985).

4 CARBON FLUXES DURING THE LAST 200 YEARS

The burning of fossil fuels since 1850 is calculated to have brought with it an effluent of about 200*10¹⁵ g C (Solomon et al., 1985). Today the emissions have stabilized around 5

$\cdot 10^{15}$ g C yr⁻¹. Of the total amount burnt only about 40 %, the airborne fraction is still in the atmosphere (Watson et al., 1990).

Until the mid 70:s it was thought that the terrestrial biota had acted as a sink for CO₂ (Broecker et al., 1979; Zimen, 1979). However, investigations based on ¹³C/¹⁴C record in tree rings revealed not only that terrestrial biomass changes had contributed as a source of atmospheric CO₂, but also the magnitude of this source (Peng, 1985; Stuiver, 1978). Today there is consensus about the terrestrial biota having acted as a source for atmospheric carbon since the beginning of the industrial era (Bolin, 1986; Detwiler and Hall, 1987). The total release having been $150 \cdot 10^{15}$ g (range: 90 - $180 \cdot 10^{15}$ g C) since 1800 (Solomon et al., 1985; Watson et al., 1990), with approximately half being released before the year 1900 (Siegenthaler and Oeschger, 1987). This means that the contribution of CO₂ from deforestation and land conversion historically has been of the same magnitude as fossil fuel burning. Today the annual net carbon flux from land conversion is approximately 1.5 - $3 \cdot 10^{15}$ g C (Woodwell, 1990; Solomon et al., 1985; Watson et al., 1990).

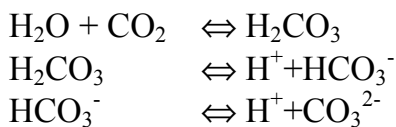
However, later investigations indicate that part of the missing sink has probably been incorporated in forests in the northern hemisphere that has increased their biomass due to changed forest management, including nitrogen fertilization (Tans et al., 1990; Watson et al., 1990).

Suggested additional sinks for the atmospheric carbon are increased weathering of rocks (through increased *p*CO₂ and temperature), incomplete litter decomposition and accumulation of peat and charcoal (Hampicke, 1979; Seiler and Cruzen, 1980; Zimen, 1978 and 1979). However, from table 1 it is evident that these processes only can be of minor importance in shorter time span. Smith (1981) suggested marine macrophyte biomass accumulation of carbon being an additional sink. As the annual NPP of macrophytes is about $1.0 \cdot 10^{12}$ g C this seems highly unlikely. A potential negative feedback is coral reefs that might double their growth in a greenhouse scenario of centuries as temperature and the sea level rises (Feary et al., 1991; Kinsey and Hopley, 1991). So far, however, there is no evidence that coral reefs have acted as negative feedback systems.

5 SOME PHYSICAL AND CHEMICAL PROPERTIES OF THE OCEAN

The net flux of CO₂ through the air-sea interface is controlled by the liquid phase (Liss and Merlivat, 1986). The transfer is given by the product of a gas transfer coefficient and partial pressure difference between atmospheric and upper ocean *p*CO₂. The former is proportional to wind speed, wave activity, and, most probably bubble frequency (Liss, 1982). The convection motion in the near surface, driven by evaporative cooling is of less importance, except during exceptionally calm conditions. During condensing conditions its significance is even further decreased. The transfer of trace gases from air to sea is also performed by rain fall in sequence of several steps (Peters, 1982). For CO₂, the chemical equilibria (see below) means a chemical transfer of CO₂ into other species, and an upkeep of the concentration gradient than would else have been the case. This chemical enhancement is more likely to be apparent under calm rather than rough regimes (Liss, 1982). However, CO₂ uptake by the ocean is probably controlled by vertical mixing in the ocean and not by air-sea transfer (Oeschger et al., 1975; Watson et al., 1990). Most of the carbon in the ocean is in the form of bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻). CO₂ is rather soluble in water, and its solubility decreases with temperature (Stumm and Morgan,

1981). In water CO₂ hydrates under the formation of carbonic acid (H₂CO₃), which dissociates into bicarbonate and carbonate:



The first reaction reaches equilibrium within minutes, the two dissociations more or less instantaneous.

The oceans contain about 60 times more carbon than the atmosphere (table 1). This suggests that the ocean could swallow 60 times more than the atmosphere of the anthropogenic output of CO₂. In reality there are two constraints to this; the long turnover time of the oceans and the buffer effect.

The carbon content in the upper mixed layer is of the same magnitude as that in the atmosphere (table 1). The equilibrium reactions above reaches equilibrium in about 1 - 3 months in the mixed layer (Bolin, 1986, Crane and Liss, 1986). The further transfer of gases takes place through the downward directed flux at the poles, eddy diffusion, and break-ups of the thermocline. The downwelling of CO₂-enriched cold surface water is sometimes referred to as the carbon physical or solubility pump (Volk and Hoffert, 1985). Thus, in the short run, only the mixed layer reflects information about changes in atmospheric *p*CO₂.

The turnover time of the whole ocean is calculated to be approximately a millennia (Björkström, 1983). Hence the shortest time for the atmosphere and ocean to reach equilibrium is in the order of thousands of years.

Changes in *p*CO₂ will bring about changes in total inorganic dissolved carbon (TC) in the oceans, according to the equilibrium reactions above. However, depending on the constituents that make up seawater the change is not linear (see Baes, 1982 and 1983, Bolin, 1986 or Björkström 1983, for a closer discussion). *p*CO₂ in the atmosphere is only in equilibrium with the CO_{2(g)} in the oceans (which make up only about 2 % of TC). This disproportionality is called the buffer effect (or Revelle-factor), defined as:

$$\xi = (\Delta p\text{CO}_2 / p\text{CO}_2) / (\Delta \text{TC} / \text{TC})$$

The value of ξ in today's ocean is about 10. This means that the capacity of the oceans for storing excess carbon in the time span of decades to centuries is reduced by a factor 10, as compared with what might be expected from just looking at reservoir sizes (table 1). The value of ξ increases with decreasing temperature and increasing TC (Bolin, 1986).

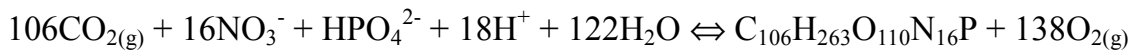
6 THE ROLE OF OCEAN BIOTA

It has become more and more evident that the oceanic carbon cycle is intimately connected to the biogeochemical cycles of phosphorus, nitrogen, oxygen, sulphur, iron, manganese and molybdenum (Howarth et al., 1988b; Shaffer, 1989; Sharp, 1991; Martin et al., 1990a;b). The connecting pathway is through limiting growth factors in the upper mixed layer (nitrogen, phosphorus, iron and manganese) and oxidation agents in the reduction of organic material in the deep ocean (oxygen, nitrogen and sulphur).

Previously ocean biota was neglected as having any importance in the distribution of carbon between the atmosphere and the hydrosphere. The reason for this seems to be the smallness of the standing crop of this biota (Oeschger and Siegenthaler, 1978). However, Baes (1982 and 1983) showed the importance of the ocean biota by comparing a hypothetical lifeless ocean with the present ocean.

The standing biomass in the ocean is in the range $3 - 4 \cdot 10^{15}$ g C, whereas the annual Net Primary Production (NPP) is estimated to lay in the range $20 - 60 \cdot 10^{15}$ g C yr⁻¹ (Eppley, 1989; Sundquist, 1985).

When photosynthesis occurs in the photic zone TC is reduced. This decrease is followed by a small increase in total alkalinity (TA), as seen from the formula for photosynthesis (using the widely accepted Redfield ratios - Redfield, 1963):



Part of the formed tissue falls to the deep ocean as marine snow in the form of particulate organic carbon (POC). It is generally accepted that the sinking fraction is correlated with NPP (Suess, 1980; Sundquist, 1985). Eppley and Peterson (1979) emphasized the correlation between new NPP entering the euphotic zone (NPP supported by new nitrogen - Dugdale and Goering, 1967) and sinking particle fluxes, and estimated the flux of POC to the deep ocean to approximately 4 GtC, which is in agreement with several other earlier estimates (see Sundquist, 1985 - table 7).

More recent studies, measuring oxygen utilization rates (OUR) below the photic zone (Jenkins, 1982; Jenkins and Goldman, 1985), have indicated several times higher NPP and a sinking flux as high as 15 GtC yr⁻¹. This has recently also been confirmed using the traditional ¹⁴C method (Pace et al., 1987; Martin et al., 1987; Karl et al., 1988; Laws et al., 1989), indicating a sinking POC flux of approximately 7 GtC yr⁻¹. If ocean CO₂ uptake is limited by vertical mixing, as inferred above, this is a true net sink for CO₂.

New measurement techniques further indicate dissolved organic carbon (DOC) in the deeper ocean being more than double traditional levels throughout the water column and even more so in the region several hundred meters below the bottom of the photic zone (Sugimura and Suzuki, 1988; Sharp, 1991). The "new" DOC found is probably of recent biological origin and there are indications that to a large extent it consist of particles of zooplankton origin, including fecal pellets (Pilskaln and Honjo, 1987; Wakeham and Canuel, 1988). Bacastow and Maier-Reimer (1991) including DOC advection fluxes found better agreement between observed and predicted oceanic phosphate and oxygen concentration in comparison with modelling only sinking POC fluxes.

Thus the structure of the food-web is important in determining the cycling and sinking of POC, DOC and nutrients. It is generally accepted that a large part of the phytoplankton is consumed by herbivores (Valiela, 1984). Azam et al. (1983) suggested bacteria as an important intermediate step, a concept known as the microbial loop. There are indications that the bacteria recycle nitrogen more efficiently than carbon, even accumulating rather than releasing nutrients (Koop et al., 1982), thus withdrawing nitrogen from the phytoplankton (Bratbak and Thingstad, 1985; Caron et al., 1988; King, 1987). However, the sinking POC is most probably dominated by phytoplankton input (Allredge and Gottschalk, 1990; Jackson, 1990; Simon et al., 1990).

Regeneration of POC is fast just below the photic zone and most of the sinking POC is oxidized within the first 1000 meters (Jenkins and Goldman, 1985; Martin et al., 1987). In the deeper ocean the particulate carbon flux is made up of larger particle fractions less favourable as bacterial habitats (Karl et al., 1988; Caron et al., 1989), and thus fairly constant as breakdown is minimal during their descent (Suess, 1980; Noriki and Tsunogai, 1986).

There is also an increase in detritus flux due to eutrophication of the ocean, which is estimated to be 0,04 - 0,3 GtC per year (Baes et al., 1985). As ocean biota do not directly respond to excess CO₂, the IPCC scientists draw the conclusion that the biological pump can not help to sequester anthropogenic CO₂. Thus the particle flux is kept constant in most climate modelling scenarios (Watson et al., 1990).

Only about 1% of the originally formed organic carbon reaches the bottom, and Berner (1982) calculates the present rate of burial for in situ formed organic carbon for the entire ocean to be about 0.020 Gt C yr⁻¹. Other sources (see Sundquist, 1985 - table 19) indicate higher burial rate, with Walsh (1984) giving the value 1.35 Gt C yr⁻¹. However, the hypothesis of Walsh et al. (1981 and 1988) that shelf primary production is exported in large quantities to deep slope water sediments is highly questionable (Carpenter, 1987; Falkowski et al., 1988; Rowe, et al., 1988; Shaffer, 1987).

Thus burial of carbon in the deep ocean is not a significant carbon sink in shorter time spans, not even in an extreme eutrophication scenario (Shaffer, 1987). It is the transfer of carbon to the deep ocean that is of importance.

Regeneration is also fast and almost complete in highly productive shallow coastal waters (McNichol et al., 1988; Tribble et al., 1990), as well as in estuaries (Hedges et al., 1988; Turner et al., 1987). In those waters, however, nitrogen is lost through denitrification when nitrate is used as electron acceptor instead of oxygen during anaerobic conditions. Thus nitrogen cycling in coastal waters can be said to be carbon controlled (Smith and Hollibaugh, 1989; Smith et al., 1989). In a scenario of a higher NPP in the ocean, anoxia could appear in larger parts of the deep ocean, eliminating nitrogen availability, thus being a negative feedback in such a scenario (Shaffer, 1989; 1990). Also phosphorus removal is enhanced in such a scenario by increased precipitation of phosphates (Froelich et al., 1982).

Nitrogen and phosphorus are generally released preferentially during the decomposition of organic matter in aquatic environment (Bordowskiy, 1965; Golterman, 1973; Granéli and Solander, 1988; Nichols, 1983). Thus several sources indicate that the C:N and C:P ratios of organic matter increases with depth in the ocean (Erhardt, 1969; Holland, 1978; Knauer et al., 1979; Martin et al., 1987; Peng and Broecker, 1987; Shaffer and Rönner, 1984). And in permanently buried material the C:N and C:P ratios may be twice the Redfield ratios (Rosenfeldt, 1981; Froelich et al., 1982).

The formation of shells and skeletons (CaCO₃) in the surface of the ocean show a slightly different cycle. The formation of CaCO₃ in the euphotic zone is followed by a decrease in alkalinity and a rise in *p*CO₂. Thus the initiate effect of for instance increased coral reef growth as a response of rising sea level (Kinsey and Hopley, 1991) or temperature rise (Feary et al., 1991) will be an increase in surface ocean *p* CO₂. In the open ocean, less CaCO₃ is recycled in the mixed layer, and the dissolution as a whole occurs at greater depth. Nevertheless the larger part of the calcium carbonate is dissolved (less than 1 GtC

yr⁻¹ is buried - see Sundquist, 1985 - table 18). The effect of this carbonate pump is thus a decrease in surface ocean alkalinity, followed by an increase in $p\text{CO}_2$, and increases of alkalinity at depth by dissolution of CaCO_3 . The carbonate pump has a potential of changing $p\text{CO}_2$ to a very high extend, at least up to 1100 ppm (Sarmiento et al., 1988). Obviously the relative magnitude of the pumps is important for the role of ocean biota in the CO_2 drama. (In addition to the three pumps mentioned; the soft tissue, the hard tissue and the physical pump, the fact that a saltier ocean increases $p\text{CO}_2$ is sometimes referred to as the oceanic salt pump - Broecker and Peng 1987).

To sum up: ocean productivity is higher than previously thought, and the carbon flux across the thermocline is greater. As regeneration is fast and N and P preferentially released, new nitrogen and new phosphorus supply can trigger off a significant increase in NPP and thus in carbon flux across the thermocline. The exportation of particulate organic matter to the deep ocean will thus be enriched in carbon. The relative magnitudes of the carbonate and the soft-tissue biological pumps have the potential of strongly influencing the $p\text{CO}_2$ (Westrich and Berner, 1984; Noriki and Tsunogai, 1986).

A useful diagram, summarizing the ocean biological pumps is shown in figure 1 (after Baes, 1982; 1983). The isolines within the diagram represents partial pressure of CO_2 . As seen those are distributed in a logarithmic way, reflecting the buffer effect mentioned above.

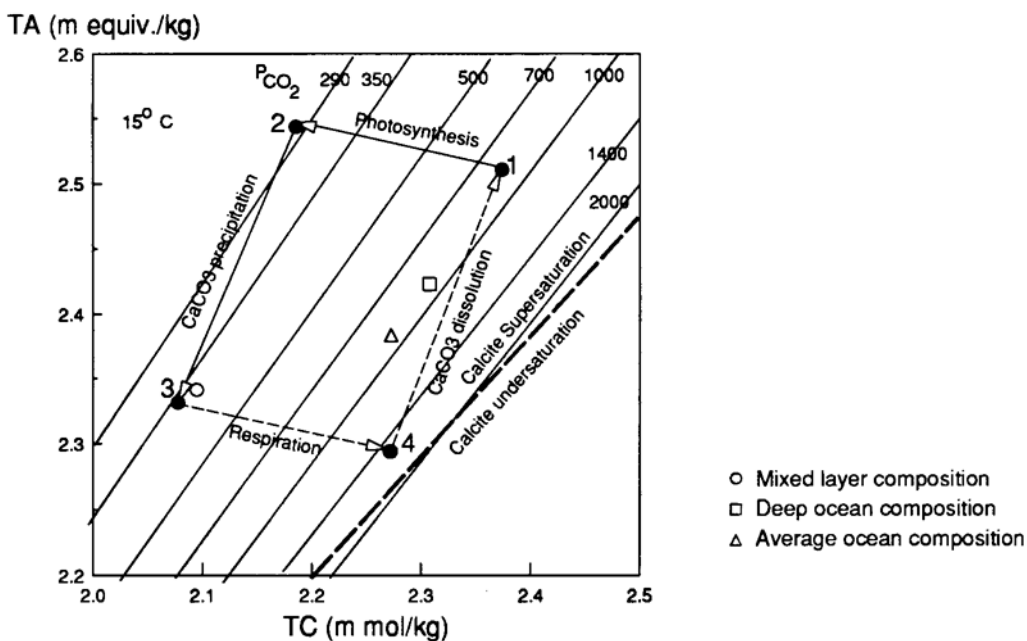


Figure 1. Schematic representation of the effect of biological process on water composition. Composition of upwelling water at point 1 is changed by photosynthesis to point 2 and by CaCO_3 precipitation to point 3. The change to point 4 occurs as organic detritus decays and finally back to point 1 in the deep ocean as the CaCO_3 dissolves (from Baes, 1982; 1983, partly using figures from Sundquist, 1985).

6.1 Polar regions - windows to the deep sea

Several authors have suggested that the cold high latitude ocean plays a crucial role in ocean circulation, acting as windows to the deep sea. And the most important part of today's ocean for deep-water formation is the North Atlantic (Dickson et al., 1990). Hence also the

most important transfer of atmospheric carbon to the deep sea would be the polar regions (Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984; Knox and McElroy, 1984).

Concentrations of NO₃⁻ and PO₄³⁻ are undetectable low in surface waters with temperature above 20°C. The concentrations increase steadily with decreasing temperature, reaching values of about 23 and 1.5 mole*kg⁻¹ respectively in cold waters (Takahashi et al., 1981). This suggests that nitrogen and phosphorus are limiting for growth at low latitudes but not at high. The obvious candidates are light and temperature. However, recent investigations have shown that nitrogen and phosphorus can be limiting for growth, part of the year, even at the edge of the ice (Cota et al., 1987; Sakshaug and Skjodal, 1989).

The biological activity in polar waters show annual cycles (Cota et al., 1987; Enoksson et al., 1990; Nelson et al., 1987; Rydberg et al., 1990; Sakshaug and Skjodal, 1989). When the ice melts in spring and/or the water temperature rises a density layer is formed, which prevents vertical mixing. In this layer a spring bloom, nourished by the winter nutrients and driven by the increasing light regime, evolves. The bloom starts with an exponential phase (doubling of arctic phytoplankton takes about 1 to 2 days, antarctic two days or more, in temperature range -1.8 to 6 °C). The bloom can be prolonged by local upwelling, and is by and large supported by new nitrogen (Cota et al., 1987). As the spring bloom consists of many larger species more susceptible to sedimentation (Enoksson, 1990) up to 50-70 % may sink toward the bottom (Sakshaug and Skjodal, 1989). During summer NPP depend almost exclusively on recycled "old" nitrogen, species are smaller, and thus sedimentation is less. However, even during this period phytoplankton biomass can be relatively high (Nelson et al., 1989). A second bloom occur during autumn, and sinking toward the bottom can again become significant (Enoksson, 1990).

Martin et al. (1990a;b) have also inferred that iron can be the limiting growth factor (regulating phytoplankton nitrate uptake) in high latitude waters. They found that small Fe additions to Antarctic water samples created 2-10 fold increases in nitrate uptake. Martin (1990) calculated that NPP could increase from less than 0.1 GtC*yr⁻¹ to approximately 2-3 GtC*yr⁻¹ if substantial amounts of Fe were added to the Antarctic ocean, thus potentially sequestering a large part of the fossil fuel emitted CO₂. Dugdale and Wilkerson (1990), repeating the experiment, found no increase in net growth or nitrate uptake, and suggested that Fe instead might have affected zooplankton and grazing pressure to lessen. However, Young et al. (1991) observed a 60 % increase in NPP following dust deposition in the North Pacific Ocean, and concluded that it was the Fe content of the dust that caused the increase.

Later model studies indicate that large efforts would be needed if iron fertilisation should effect atmospheric p CO₂. Peng and Broecker (1991) calculated that 34 ppm could be withdrawn from the preindustrial atmosphere fertilising 10 % of the ocean, Joos et al. (1991), fertilising 16 % of the ocean calculated a withdrawal of 60 ppm. With increasing pCO₂ also more carbon can be withdrawn, and thus it is, at least theoretically, possible to sequester some of the anthropogenic CO₂ emissions by fertilizing the ocean.

In comparison with N and P, Fe sinks faster toward the ocean floor, and there is net downward flux through the ocean. Thus iron is almost exclusively supplied from the surface through atmospheric and river input (Duce, 1986).

Annual NPP in Arctic and Antarctic regions may range from 10 to 100 g C m⁻²yr⁻¹, and total NPP is about 0.7*10¹⁵ g yr⁻¹ in Arctic and 0.6-4.5*10¹⁵ g yr⁻¹ in Antarctic. This is about 10 % of the total oceanic NPP. As for other ¹⁴C measurements of ocean productivity, earlier values of NPP were probably underestimated. Further, earlier calculations excluded the ice-edge zone (see Nelson et al., 1987).

6.2 Nitrogen - the key element?

There are a few reports that indicate CO₂-limited growth in aquatic environments under extreme conditions (Talling, 1976; Bowes and Beer, 1987; Kozak and Bishop, 1987; Rast et al., 1989). However, even if *p*CO₂ was about 1000 times higher when life began it is probably not impairing oceanic primary production (Broecker, 1974; James and Lee, 1974; Lovelock and Whitfield, 1982).

Instead, since Ryther and Dunstan (1971) published their paper, marine scientists have generally favoured nitrogen limitation (Glibert, 1988; Howarth, 1988; Paasche, 1988). However, phosphorus limitation has been inferred (Chiaudani and Vighi, 1982) and ecosystem-level production is not necessarily nitrogen limited because algal growth is (Howarth, 1988). Smith (1984) and Capone and Carpenter (1982) argues that nitrogen can not be limiting since nitrogen fixation should be able to match any nitrogen deficiency. However, as shown by Howarth et al. (1988b) nitrogen fixation might be limited by trace metal availability.

The ratio of new production supported by nitrate fluxes in upwelling waters (PN) to total (PT) production is often called the *f*-ratio, and has a value of approximately 0.05 in the oligotrophic ocean (Eppley et al., 1973), thus nitrogen is recycled 20 times in the euphotic zone before sinking to the deep ocean. This implies that a small support of new nitrogen can trigger off large increases in NPP (Eppley and Peterson, 1979; Glibert, 1988).

Pace et al. (1987) found that 13-25 % of primary production in the North-East Pacific was supported by new nitrogen (Dugdale and Goering, 1967), and Eppley (1989) reports NPP supported from new-nitrogen to be 5-10 GtC yr⁻¹ (equivalent to 10-20 %) for the whole ocean. However, as pointed out of Jenkins and Goldman (1985) the supply of new nitrogen can potentially support a much higher NPP. McCarthy and Goldman (1979) hypothesized that rapid nitrogen turnover between phytoplankton and grazers occur in microenvironments virtually unobserved with standard sampling technology, and other reports (see Legendre and Gosselin, 1989) indicate that nitrogen fixation and atmospheric input might be higher (i.e. higher support of new nitrogen) than previously thought. This shows that the steady state assumption made by Eppley and Peterson (1979) and others does not hold. Instead the concept of regenerated production and export is dependent on the food web structure and thus a dynamic process (King, 1987; Legendre and Le Fèvre, 1989; Legendre and Gosselin, 1989).

6.3 Ocean nitrogen budget

For a steady state ocean, sources and sinks of N can be formulated as:

$$L - BR + NF - DN = 0$$

where L = external load, BR = burial, NF = nitrogen fixation and DN = denitrification. All of these terms probably have changed or are likely to change due to anthropogenic activity and thus coincidence with climate change.

The external load of nitrogen from rivers is in the order of 14-43 Tg yr⁻¹ (Meybeck, 1982; Richey, 1983). However, Ittekkot and Zhang (1989) estimated the particulate nitrogen transport to be larger than previously thought, thus indicating a total nitrogen transport as high as 50 Tg yr⁻¹. Present estimates of pre-industrial N input is about 36 Tg (Meybeck, 1982).

Most estimates of ocean plankton nitrogen fixation falls in the range 2-90 *10⁻³ g N m⁻² y⁻¹, equivalent to 7-325 *10¹¹ g yr⁻¹ (Howarth et al., 1988a), which is less than 1 % of total nitrogen input. Major exceptions are nitrogen fixation rates found in the Peel-Harvey estuary and parts of the Baltic Sea. Rates of fixation in estuarine and coastal sediments tend also to be low to moderate with reported values in the range 0.002 - 1.56 g N m⁻²y⁻¹, with higher rates in organic rich near shore sediments, and most sources normally consider N-fixation to be of minor importance also in this environment. Nitrogen fixation in deep ocean sediments is reported in one study only (Hartwig and Stabley, 1978 quoted in Howarth et al., 1988a), and the reported rate is 0-0.4 *10⁻³ g N m⁻²yr⁻¹. However, saltmarshes, seagrass beds, and mangrove swamps (near-shore ecosystems) show moderate to high nitrogen fixation ranging from 0.24 to 50 g N m⁻²y⁻¹ (Howarth et al., 1988a), with the range 0.24 to 7.7 for the more reliable short-term incubation method though. Capone and Carpenter (1982) estimated that, worldwide, saltmarshes contribute 6.3 *10¹² g N yr⁻¹ equivalent to 40 % to the total nitrogen fixed in the oceans. However, Howarth et al. (1988a) using the short term incubation figures, suggests that only 0.7 *10¹² g N yr⁻¹ is fixed in saltmarshes.

The biogeochemical control of nitrogen fixation is complicated, and connects the nitrogen cycle with several other elements (Howarth et al., 1988b). Significant nitrogen fixation by planktonic organisms generally occurs only when the N:P ratio is near or below the Redfield ratio of 16:1. The lower N fixation in marine environment than in lakes may be due to lower availability of one or more trace elements such as iron or molybdenum required for nitrogen fixation. Iron concentration is generally low in marine waters, and molybdenum availability is blocked by the presence sulphate.

Denitrification is probably insignificant in the large oceanic photic zone which in principle is oxygenated. However, in eutrophic estuaries it might be a large sink for nitrate (Shaffer and Rönner, 1984; Rönner and Sörensen, 1985; Wulff et al., 1990), and total water column denitrification is estimated to be in the range 50 - 60 Tg N yr⁻¹ (Christensen et al., 1987).

Earlier estimates of the total denitrification in continental shelf sediments pointed at 5-25 Tg yr⁻¹ (Hattori, 1983; Liu and Kaplan, 1984), whereas later investigations have shown that this figure is too low. Most literature figures lay between approximately 20 and 100 Tg yr⁻¹ with the range 50 - 75 being the most probable (Christensen et al., 1987). Oceanic nitrogen fluxes are summarized in table 2. The oceanic nitrogen cycle is summarized in figure 2.

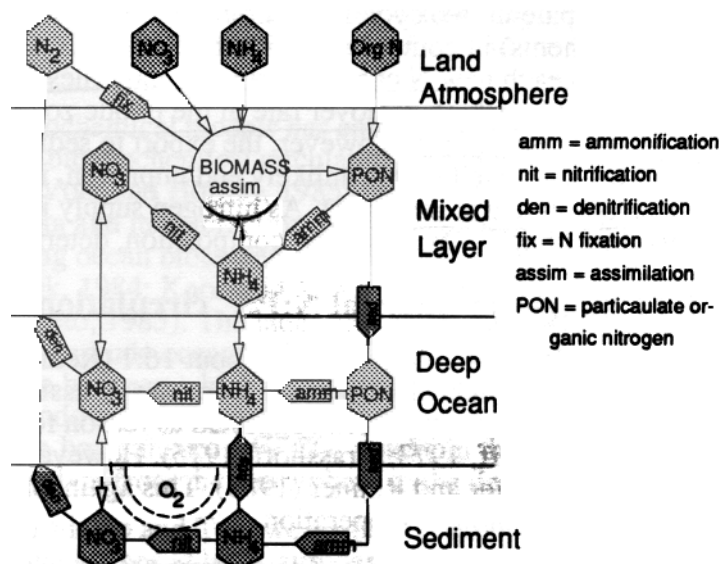


Figure 2. Oceanic nitrogen cycle, fluxes are given in table 2.

Table 2 Nitrogen fluxes to the ocean photic zone (mainly after Capone and Carpenter, 1982; Christensen et al., 1987; Holland, 1978; Howarth et al., 1988a; Meybeck, 1982)

Nitrogen source/sink in the photic zone	Flux Tg yr ⁻¹ Range	Flux Tg yr ⁻¹ Best estimate
New N-input		
River runoff	14-50	43
Planctonic N-fixation	1-32	10
Shelf sediment and estuarine N-fixation		
Near-shore ecosystem N-fixation	6.5-12.1	6.5
Deposition	6-80	8
Thermocline flux	500-2000	1000
Old N-input		
Euphotic zone respiration	3000-10000	8000
N-losses		
Pelagic denitrification	50-60	50-60
Sediment denitrification	20-100	50-75

To sum up, the nitrogen cycling in the ocean is a complex process, probably limiting phytoplankton growth and thus CO_2 withdrawal. The quantitative importance of different processes is not very well understood, not even in small sub-basins (Enoksson et al., 1990; Wulff, 1990). The ocean is probably a heterotrophic system, were total nitrogen losses exceed total nitrogen input (table 2), and nitrogen fluxes probably do not balance in less than 105 yr (McElroy, 1983; Christenson et al., 1987; Smith et al., 1987).

6.4 The human impact

Peng and Broecker (1984) suggested three ways in which anthropogenic activity could change the capability of oceanic biota to withdraw carbon from the atmosphere: (1) Changes in the C:N and C:P ratio in organic residues falling from the surface. (2) Eutrophication of oceanic waters and (3) changes in oceanic internal recycling of nitrogen and phosphorus. A further impact, suggested by Knox and McElroy (1984), is change in

efficiency of nutrient use. Martin (1990) suggested that efficiency in nitrogen uptake is being brought about by iron availability. Legendre and Gosselin (1987) suggested that nitrogen deposition and fixation is greater than previously thought, thus perturbing the nitrogen and carbon cycles in the ocean.

6.4.1 Changes in species composition

Based on the record of the past, there is little doubt that global warming will result in changed distributions of marine planktonic organisms than those of today (CLIMAP Project, 1976). Temperature has also long been considered a primary factor in determining phytoplankton succession (Tilman et al., 1982). Also changes in nutrient availability can impair species changes in both the phytoplankton and zooplankton communities (ibid.).

One group of organisms that are favoured by increasing temperature are Coccolithophorids. Those carbonate shell forming organisms are important rock formers since Jurassic time, and also important DMS producers. Also the growth of coral reefs are supposed to increase with temperature and rising sea-level (Feary et al., 1991; Kinsey and Hopley, 1991). However, as pointed out above, the initial effect of increased CaCO₃ formation in the upper ocean is an increase in p CO₂.

6.4.2 Eutrophication of the ocean

The anthropogenic input of nutrients to the ocean is very small in comparison with the recycled amount (table 2). However, as stated above, the productivity seems to be determined by the input of new nutrients.

Peterson and Melillo (1985) estimated that eutrophication could give rise to an extra ocean storage of 90 Tg annually, which is a negligible amount, unable to explain the missing sink. Their starting point was the Redfield ratio of C:N:P and they calculated that each N or P could participate in two cycles thus doubling their effect in withdrawing C (mainly to the coastal sediments) in comparison with the Redfield ratio. As emphasized by Walsh et al. (1981; 1988) each new N can withdraw several times the Redfield ratio amount of C. This is brought about by a high turnover rate in the photic zone, coupled to preferential release of nitrogen and phosphorus. However, the export to sedimental burial that Walsh and co-workers suggested seems unlikely and unproven, instead it is the DOC and POC fluxes to the deep ocean that is important. As nitrogen supply is dependent on N-fixation, several factors, including shifts in species composition, determining N-fixation also can change NPP.

6.4.3 Changes in internal N:P:C circulation

The atomic N:P ratio in the ocean is about 16:1 (Redfield et al., 1963), whereas it is about 7:1 in the Baltic sea. Radically different processes of assimilation and regeneration of nutrients and phosphate release has been suggested as reason for the deviation (Sen Gupta, 1973; Sen Gupta and Koroleff, 1973; Grasshoff, 1975). However, it is most likely due to denitrification as shown by Shaffer and Rönner (1984). This again tells us that the ocean might have different quasi stable modes of operation.

When oxygen becomes depleted and nitrate acts as oxidizing agent, the efficiency of nitrogen recycling lessens, as is the case in the Baltic Sea today (Wulff et al., 1990). This

implies that nitrogen (i.e. denitrification) acts as a negative feedback for ocean eutrophication, and thus prevents global cooling (Shaffer, 1990). In today's ocean increased N supply however, probably does not enhance denitrification equally much (Seitzinger, 1988).

The most important change in the ocean biogeochemical cycling is probably that regeneration rate increases as temperature rises (see Valiela, 1984). Assuming that the preferential release of nutrients over carbon will persist, potentially more carbon can be withdrawn for every molecule of nitrogen (or phosphorus) per unit of time.

7 MODELS OF THE OCEANS AND THEIR CAPACITY AS SINKS

Quantitative models that adequately describe the distribution of carbon in the sea in the framework of global climatic change, would be of great help. Applicable models for this falls into two general categories; Biogeochemical box-models and General Circulation Models (GCMs). The biogeochemical models divides the ocean into a few boxes, related to biological processes (i.e. photosynthesis, respiration, carbonate formation and dissolution etc). The GCMs put emphasis on ocean circulation and physical and chemical composition, using a finer (but still very coarse) grid resolution, however, paying less or no attention to biological processes.

7.1 Biogeochemical box-models

The first model developed to understand the ocean biogeochemical cycles was Craig's two-box model using the thermocline as boundary (Bolin, 1986). This model was further developed by Bolin and Eriksson (1959) and analysed in detail by Keeling (1973) (see Bolin, 1986). Those models could not explain the ocean uptake of CO₂, and got an airborne fraction that was too high. To overcome this problem Oeschger et al. (1975) developed this concept further, including a transfer of carbon thanks to eddy diffusion between the two boxes (the so called box-diffusion, BD, model). The mixed layer was given a depth of 75 meters. Later other researches increased the eddy-diffusion of the model in the thermocline region for better accordance with available data on vertical mixing of the ocean and the airborne fraction (Bolin, 1986).

As model results were not consistent with the ocean chemical composition a further extension of this model to include the polar zones was done by Siegenthaler (1983) (the so called Outcrop Diffusion, OD, model).

In comparison with observational data that gives an estimate of net ocean CO₂ uptake to be about 1.6 GtC annually (Tans et al., 1990), the BD model yields 2.4 GtC and the OD model 3.6 GtC (Watson et al., 1990).

Further development of the simple biogeochemical models has emerged into two different groups. To understand the ocean interior biogeochemical circulation and interaction, models with high vertical resolution developed (Volk and Hoffert, 1985; Shaffer, 1989). With the increased understanding of the ocean biota and its interaction with atmospheric p CO₂ a second group of new models incorporating ocean biota were developed (Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984; Knox and McElroy, 1984; Broecker and Takahashi, 1984; Toggweiler and Sarmineto, 1985). The latter models all emphasize on the physical and biological dynamics of high-latitude oceans.

The $p\text{CO}_2$ of these models depend upon changes in circulation and exchange between a high latitude surface box and the deep ocean. The high latitude box acts as a window with formation of deep water. A reduced exchange rate of water in the cold surface box enhances the CO_2 uptake in this part, thus increasing its potential in withdrawing carbon from the atmosphere to the deep ocean.

Knox and McElroy (1984 and 1985), Sarmiento and Toggweiler (1984) and Toggweiler and Sarmiento (1985) assumed that insolation changes at high latitudes induced changes in biological production and preformed nutrients, a phenomenon observed in the present ocean by Walsh (1989). An alternative explanation for changes in high latitude biological production is the iron hypothesis inferred by Martin (1990) (see above). The Sarmiento and Toggweiler model could explain the ice-age $p\text{CO}_2$ by reducing ocean circulation by a factor 5 in comparison with the present ocean, and depleting the high latitude ocean in preformed nutrients, which is in agreement with historical data (Boyle and Keigwin, 1982 and 1987; Boyle, 1988a; Broecker et al., 1990; Shackleton et al., 1983). Lately Shaffer (1990) presented a biogeochemical model that, based on changes in ocean NPP governed by nitrogen availability, was able to explain the ice-age cycle climate changes.

Siegenthaler and Wenk (1984) and Wenk and Siegenthaler (1985) attributed the change in $p\text{CO}_2$ to changes in ocean circulation and concluded that reduced ocean circulation could explain the lower $p\text{CO}_2$ during the last glaciation. Both the Siegenthaler and Wenk model and the Knox and McElroy model explain the major part of the glacial-interglacial $p\text{CO}_2$ changes by changes in the carbon solubility pump (Volk and Hoffert, 1985).

7.2 General circulation models

Only few results from ocean GCMs have been reported, and as yet it seems that the coarser biogeochemical models have better ability to predict ocean biogeochemical response to climate change. The IPCC report (Houghton et al., 1990) contains a good summary of modelling and validation of ocean 3-dimensional GCMs.

One of the greatest problems with GCM models is the parameterisation (i.e. the sub-grid averaging of parameters), especially so when it comes to coupled ocean-atmosphere models (Bretherton et al., 1990; Gates et al., 1990). One example is the parameterisation of the carbonate and soft-tissue biological pumps (Cubasch and Cess, 1990). Most ocean GCM-models thus excludes ocean biota or treat it ad hoc (Bretherton et al., 1990). Also the IPCC report (Houghton et al., 1990) by and large ignore effects of ocean biota and dismiss the ocean biological pump as having no significant importance.

8 DISCUSSION

Eventhough much effort is put into understanding the long and short term patterns of atmospheric carbon dioxide cycling, there is still much uncertainty. As carbon is perhaps the most central element for life, life obviously by and large determines the distribution of carbon between atmosphere, hydrosphere, pedosphere and lithosphere. Thus, to neglect the biotic linkage in the carbon cycle, as is often done, seems a dangerous approach.

To reveal the response of the ocean to increases in $p\text{CO}_2$ several investigations have focused on the transition from the last glaciation to the present interglaciation. Some earlier hypothesis emphasised the role of ocean biota and the biological pump (Knox and McElroy,

1984; Sarmiento and Toggweiler, 1984). However, most recent suggestions (Broecker et al., 1989; 1990a; Ruddiman and Cutchbach, 1991; Houghton et al., 1990) rely almost exclusively on changes in the ocean general circulation pattern, neglecting ocean biota.

Most models also use figures of ocean productivity and POC and DOC fluxes derived from Eppley and Peterson (1979), but as shown by several more recent investigations (Jenkins, 1982; Jenkins and Goldman, 1985; Martin et al., 1987; Sugimura and Suzuki, 1988), they most probably underestimate both productivity and fluxes. There is also a potential increase in nutrient availability in climate warming scenarios, from increased rates in respiration, and from external anthropogenic eutrophication. As changes in species composition is highly likely, there is also a potential shift in the relative formation of hard and soft tissue, which in turn changes the relative magnitudes of the soft and hard tissue biological pumps, thus affecting $p\text{CO}_2$. Changes in species composition can also bring about changes in N-fixation and denitrification activity, changing nitrogen availability. As nitrogen is probably limiting production in the ocean, changes in N-fixation and/or denitrification also can impair ocean productivity (Shaffer, 1990). Further, there is still very large uncertainties quantifying the ocean nitrogen cycle, thus also in determining the important relationship between new production, supported by nitrogen input to the photic zone, and regenerated production (Dugdale and Goering, 1967; Eppley and Peterson, 1979).

Changes in runoff pattern, or melting of glaciers can also cause changes in high-latitude waters, leading to changes in productivity in those vital regions for deep water formation. One example being iron-fertilization as inferred by Martin and co-workers (Martin, 1990; Martin et al., 1990a;b), who also suggested that iron-fertilization of antarctic waters could be a mean of managing global warming. Even if connected with great problems, others (Joos et al., 1991; Peng and Broecker, 1991) have confirmed that this scenario can not be dismissed without further research.

9 REFERENCES

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