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ABSTRACT

The North Sea carbon cycle encompasses many carbon reservoirs, both inorganic and organic, and their interactions. By advection dissolved inorganic, dissolved organic and particulate organic carbon are transferred into the North Sea mainly from the North Atlantic Ocean, the English Channel, and the rivers, whereas approximately the same amount of carbon is exported, mainly to the North Atlantic ocean. The annual flowthrough is about $1.5 \cdot 10^{15}$ g C. The major carbon flux caused by in situ processes within the North Sea is brought about by primary production, amounting to about $150 \cdot 10^{12}$ g C per year. Primary production in turn drives other fluxes, such as between the water and the atmosphere and between the water column and the sediments. Almost all carbon fixed as organic matter is returned to the large inorganic reservoir in the same year by remineralization, but a small portion («1%») escapes this cycle in order to be permanently deposited in some special areas, the most important ones of which are the Skagerrak and the German Bight.

The anthropogenic impact on the North Sea carbon cycle derives from two different mechanisms: Toxic wastes, that affect various levels within the ecosystem, and supply of nutrients, which affects primary production and through this the rest of the ecosystem. While some effects of toxic compounds at organism level are well known, at ecosystem level the impact is less clear. On the other hand, an enhanced anthropogenic load of nutrients to the coastal waters (eutrophication) is the likely cause of observed increases of primary production and bottom fauna biomass, but also negative effects such as oxygen depletion with accompanying mass mortality. Other anthropogenic impacts to the North Sea carbon cycle comprise the discharge of organic wastes with eutrophication-like effects, changing carbonate chemistry due to changed CO_2 levels in water and atmosphere, atmospheric deposition of nutrients, sea level rise, fisheries, and oil pollution. As far as the effects of the latter impacts are known and quantifiable, they are of local nature and/or not significant. Enhanced primary production represents a substantial change on the carbon cycle level, yielding an enhanced, but minor sink for carbon through the permanent deposition of part of the primary produced organic matter in the depo-centres of the North Sea. By the same cause significant increases of standing stocks of phytoplankton and macrozoobenthos have come into existence. The other substantial change in the carbon cycle is the increased extraction of calcium carbonate from the seawater by enhanced formation of shells through molluscs. This may, however, have led to more atmospheric CO_2 by rearrangements within the inorganic carbon system.

The oceans are only a minor (<5%) source of methane (CH_4) to the atmosphere. The North Sea indeed is slightly supersaturated with respect to methane, indicating that it is only a small source. In the near-coastal areas the situation appears different with large supersaturations. In situ production of methane is minor, though. Although there may be some more in situ anthropogenic sources of methane, the rivers appear to be the ultimate sources for nearly all methane release by the North Sea. The source strength of the North Sea for methane possibly increased due to anthropogenic activity, but compared to the global source strength this increase is trivial.

The oceans are a significant source of nitrous oxide (N₂O). Within the oceanic environment the coastal seas and estuaries are an important representative of N₂O production. On an average the North Sea is slightly supersaturated with respect to N₂O. In the German Bight about half of the entire N₂O release from the North Sea to the atmosphere occurs. There are indications that the North Sea is a more than proportional source of N₂O compared with its surface area. In situ production may be important, but also wastewater discharges, river runoff and sediments are substantial suppliers of N₂O. Eutrophication is likely to have increased N₂O production in the North Sea.

Dimethyl sulfide (DMS) is the main volatile organic compound in the global sulfur cycle, with the oceans as the prime DMS source. DMS production is strongly associated with phytoplankton, which is evident from the large seasonal variation of the DMS concentration in the seawater. The DMS source strength of the North Sea is more than proportional compared with its surface area. Because of eutrophication and the concomitant increase of phytoplankton production the DMS release from the North Sea to the atmosphere is estimated to have increased with some 10%, especially since the abundance of a well-known DMS producer (*Phaeocystis pouchetii*) increased so dramatically. As a consequence of this link with eutrophication the increased DMS release is likely confined to the inshore area.

As apparent from Table 0.1 the North Sea is a disproportionally large source for atmospheric methane, nitrous oxide and dimethyl sulfide compared with the total oceanic source of these gases.

Table 0.1: Annual release of some radiatively-active gases from the North Sea to the atmosphere and their relative importance compared to the overall oceanic source of these gases. The surface area of the North Sea is 0.16% of the total oceanic surface area.

	flux to the atmosphere	% of total oceanic flux
methane	$2.7 \cdot 10^{10}$ g C	0.3
nitrous oxide	$6 \cdot 10^9$ g N	0.3
dimethyl sulfide	$2 \cdot 10^{11}$ g S	0.5

1. INTRODUCTION

The increase of atmospheric CO₂ has been well established by an excellent set of measurements started by Keeling in 1958 (e.g. Keeling et al., 1989). Compared to the estimated preindustrial level of about $270 \cdot 10^{-6}$ atm (270 ppmv) in the nineteenth century the rise has been considerable and is still going on, the present value being about 351 ppmv. The increase of atmospheric CO₂ is worrisome because of the capacity of CO₂ to absorb radiation in the infrared. In the natural Earth atmosphere CO₂, besides some other gases, is an important contributor to the greenhouse warming of the Earth's surface, meaning that heat radiation from the Earth, which would otherwise escape into space, is absorbed hence raising the temperature of the Earth surface. By this mechanism the temperature of the Earth is maintained at a level convenient for life. The possible warming of the Earth above the natural level by an increase of atmospheric CO₂ (and other greenhouse gases) is commonly referred to as the 'greenhouse effect'. Although the evidence is not yet 100% firm there is a major consensus within the scientific community that increasing atmospheric CO₂ levels will cause an enhanced mean global temperature. The most convincing demonstration of a relation between the atmospheric CO₂ concentration and temperature was obtained from the Vostok ice core which showed a clear co-variation of these two parameters over the last 160,000 years (Barnola et al., 1987).

The atmospheric CO₂ increase does not cope with the statistics of the emission rates derived from fossil fuel burning. About half of the CO₂ released is not present in the atmosphere and this CO₂ is presumably taken up by the oceans. The details of the uptake mechanism are still unclear (see also De Baar & Stoll, 1989). Clearly, the oceans by their vast reservoir size impose a large control on the global carbon cycle and thus on the atmospheric CO₂.

Only relatively recently other potential greenhouse gases have received attention. Methane and nitrous oxide also show an upward trend in their atmospheric abundances due to human activity (Blake & Rowland, 1988; Weiss, 1981). Their overall atmospheric concentration is much smaller than that of CO₂, their warming capacity per molecule, however, is much larger which makes them significant greenhouse gases in the present-day atmosphere. The global budgets and the factors that determine their concentrations are only partially understood, yet the oceans are, in contrast with the case of CO₂, a net source for both of these gases.

Another radiatively important gas which originates mainly from the marine environment is dimethyl sulfide (DMS). DMS is not a greenhouse gas but, on the contrary, may be counteracting the greenhouse effect. DMS might achieve this by entering a complicated feedback loop involving the rapid oxidation to sulfate aerosols in the marine atmosphere, the latter of which may serve as cloud condensation nuclei that in turn control the Earth's albedo and through this temperature (see Charlson et al., 1987). All radiatively important gases (CO₂, CH₄, N₂O and DMS) have in common that the oceans play an important role either as a source or as a sink.

1.1. Rationale

The ocean margins and continental shelves are special oceanic environments. They are very productive, and while only covering a small surface area they represent a large part of all organic carbon fixed in the world oceans. This means that ocean margins have substantial impact on the global budgets of several elements. This holds especially for some radiatively-important gases such as nitrous oxide and DMS. On the continental shelves the impact of human activity on the marine environment is most pronounced. The best studied example is eutrophication of coastal waters. Eutrophication has the potential to influence biological activity because more nutrients become available for growth. The release of biogenic gases to the atmosphere may thus be influenced as well. However, the sources and sinks of the radiatively-important gases are poorly known, and so are the biogeochemical processes that are responsible for their production and consumption. Eutrophication (and other anthropogenic impact on the shelves) is a local impact in the marine environment, but through subsequent processes could have globally important consequences for certain compounds.

1.2. Objective

The present overview provides an assessment of the current knowledge of the anthropogenic impact on the possible emission or uptake of the radiatively-important gases CO₂, CH₄, N₂O and DMS by the North Sea, with special emphasis on the continental shelf waters of the Netherlands. The final objective would be to describe the undisturbed biogeochemical cycles in which these gases are involved, but unfortunately in most cases anthropogenic influence has been exerted for many years and in the absence of historical records of measurements it is impossible to reconstruct the original situation (~1860). Therefore, one is restricted to a description of the present-day cycles along with an assessment of the changes that already took place.

For understanding the changes in the cycling of radiatively-important gases caused by anthropogenic activity it is necessary to know the processes and mechanisms that determine biogeochemical transformations within these cycles. For this purpose the most important production and consumption processes and the transfers of the matter through the overall North Sea reservoir were treated as well.

1.3. Acknowledgements

We acknowledge the use of the BEWON North Sea model for the required model runs and in particular we thank P. Ruardij who performed the runs. Advice and literature was received from very many colleagues, both from our institute and others, in particular the Plymouth Marine Laboratory which we visited. Thanks are due to J.W. Baretta, A.J. van Bennekom, M.J.N. Bergman, J.J. Beukema, G.C. Cadée, D. Eisma, E. Epping, M. Fonds, W. Helder, J.H.F. Jansen, L. Lohse, J. van der Meer, H. Postma, W. van Raaphorst, R. Riegman, P. Ruardij, M.H.C. Stoll, M.J.W. Veldhuis, J.H. Vosjan, P. de Wolf from NIOZ to P.R. Dando, I. Joint, N.J.P. Owens, A. Watson, P. Williamson from PML, as well as S. Kempe, K. Pegler (University Hamburg) and M.I. Scranton (SUNY Stony Brook). The contact with the Ministry of the Environment was very pleasantly maintained through L.H.J.M. Janssen and M.J.M. Hootsmans.

2. THE CARBON CYCLE IN THE NORTH SEA

A general scheme representing the carbon cycle in the North Sea ecosystem is shown in Fig. 2.1. It is composed of biotic and abiotic reservoirs. Between these reservoirs fluxes occur, which can be subdivided into gross and net fluxes. The fluxes between the compartments are not uniformly distributed, neither in place nor in time. The main pathway is from inorganic carbon being incorporated in phytoplankton and from phytoplankton to the higher trophic levels or to non-living organic matter, the latter possibly through heterotrophs and benthic organisms. The input of carbon to the system, both organic and inorganic, comes from the Atlantic ocean, the English Channel, estuaries/rivers, coasts, and waste dumping. On the other hand, carbon is also exported to the Atlantic ocean.

Carbon in the seawater system can be divided into an organic and an inorganic fraction. The former fraction is further subdivided into living biomass and non-living organic material. Carbon is present as dissolved substance, dissolved inorganic carbon and dissolved organic carbon (DOC), and as suspended material, particulate organic carbon (POC) and particulate inorganic carbon (PIC). The distinction between particulate and dissolved matter is rather arbitrary, because actually there is a continuous size spectrum of particles. The difference is merely imposed by the (effective) pore size of the filter commonly used to separate particles from the seawater. In this chapter reservoir sizes and gross fluxes will be dealt with for the whole North Sea, and special emphasis will be laid on the Dutch coastal waters.

2.1. Carbon reservoirs

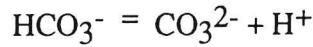
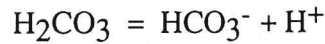
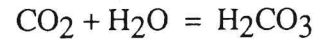
2.1.1. Atmosphere

Carbon in the atmosphere is mainly present as carbon dioxide (CO_2) and methane (CH_4). In addition, a range of natural (Lovelock, 1975; Freyer, 1979) and man-made compounds containing carbon (Atlas & Giam, 1981, 1986) have been detected, but their concentration is relatively insignificant. The content of particulate carbon is still at least one order of magnitude smaller than that of the gaseous trace compounds (Duce, 1978). Methane will be treated in a separate section (chapter 5).

The atmosphere is a relatively well-mixed reservoir with a CO_2 concentration of 351 ppmv (in 1989, Keeling et al., 1989). Very well known are the measurements by C.D. Keeling at Mauna Loa that show a steady increase of CO_2 of 315 ppmv in 1958 until the present value. The atmospheric CO_2 concentration displays a seasonal variation which reflects the consumption and production of CO_2 by the terrestrial biosphere. In urban areas with dense populations the CO_2 concentration may be higher than average (Janssen et al., 1990), a similar situation could also apply to (parts of) the North Sea.

2.1.2. Dissolved Inorganic Carbon (DIC) in seawater

The major part of carbon in seawater is involved in the inorganic carbon system. CO₂ is hydrated to carbonic acid (H₂CO₃) which in turn loses part of its hydrogen ions, according to the following reactions:



The carbonate system constitutes the buffering-capacity of seawater, which is conveniently described by the composite reaction:

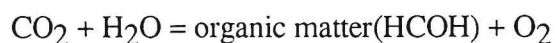


This equilibrium governs the pH of seawater which is on the alkaline side of neutrality (~8.2). Under natural conditions the species CO₃²⁻ and CO₂/H₂CO₃ make up 10% and <1%, respectively of the total inorganic carbon, and the rest is HCO₃⁻ (Skirrow, 1975). The total inorganic carbon is defined as

$$\text{TCO}_2 \text{ (mmol.kg}^{-1}\text{)} = [\text{CO}_2/\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

The position of the equilibrium within the carbonate system is dependent on salinity, temperature, and pressure. This implies that at constant salinity and pressure in cold water (winter) TCO₂ is higher than in warm water (summer).

Through the properties of carbonic acid as a weak acid that forms ions the capacity of seawater to take up CO₂ is strongly augmented compared to the situation if CO₂ would be an inert gas. Another important quantity to describe the state of carbon in seawater is the partial pressure of CO₂ (pCO₂). As HCO₃⁻ and CO₃²⁻ are non-volatile species, pCO₂ is solely determined by dissolved CO₂/H₂CO₃. Without interferences (like biological activity) pCO₂ would be virtually in equilibrium with its atmospheric counterpart. In natural seawater greater or smaller deviations do occur, however. The seawater is then called to be supersaturated or undersaturated with respect to the atmosphere. Photosynthetic fixation of CO₂ is the major cause for undersaturation (and supersaturation of O₂), whereas the reversed process mineralization (respiration) may lead to CO₂ supersaturation.



Surface seawater (and thus also continental shelf water) is supersaturated with respect to calcium (magnesium) carbonate, which enables organisms to extract this from the seawater in order to form skeletal parts. The degree of saturation is determined by the position of the equilibrium

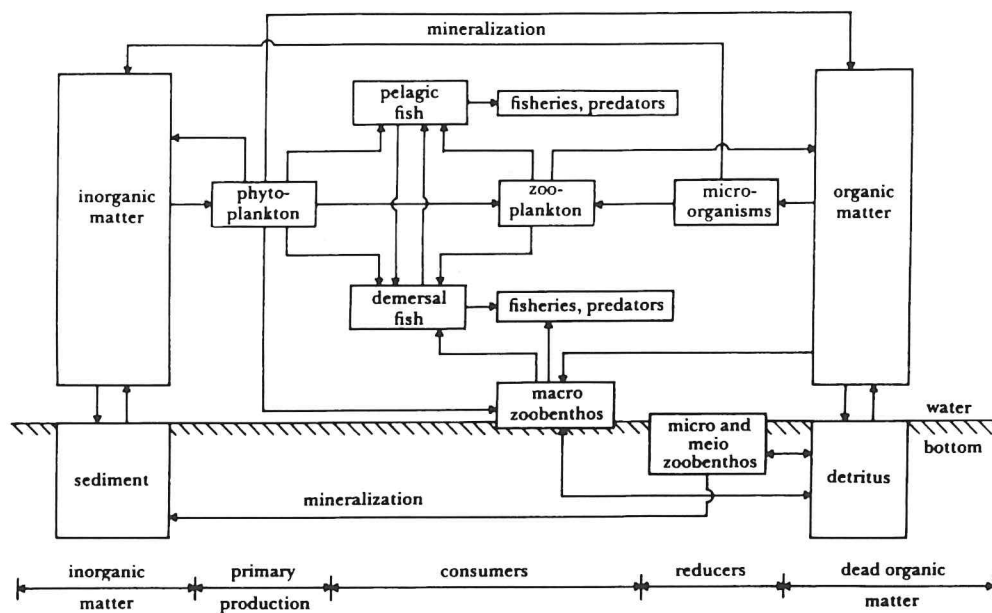


Fig. 2.1: General scheme of the reservoirs and the flow of material (in our case carbon) in the North Sea (from Anonymous, 1985).

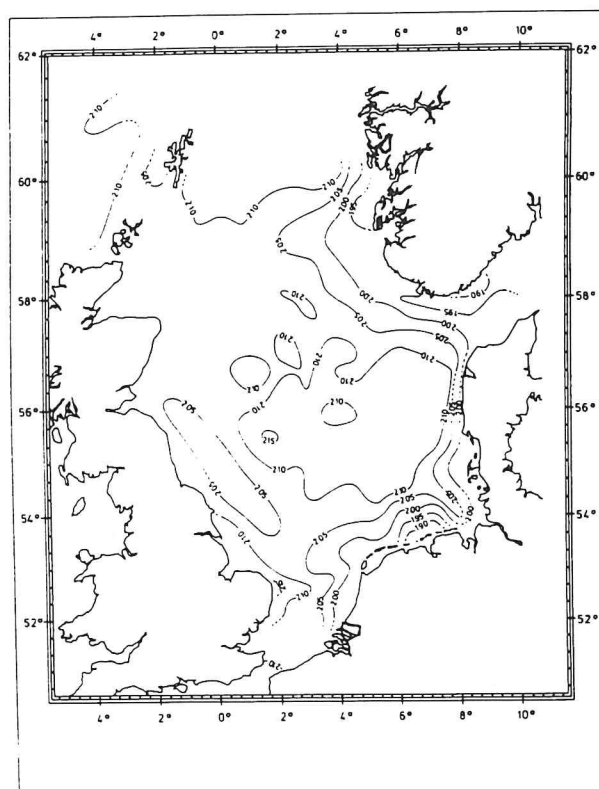


Fig. 2.2: Distribution of total dissolved inorganic carbon, TCO₂ in mmol.kg⁻¹, for the North Sea surface in May/June 1986 (from Pegler & Kempe, 1988).

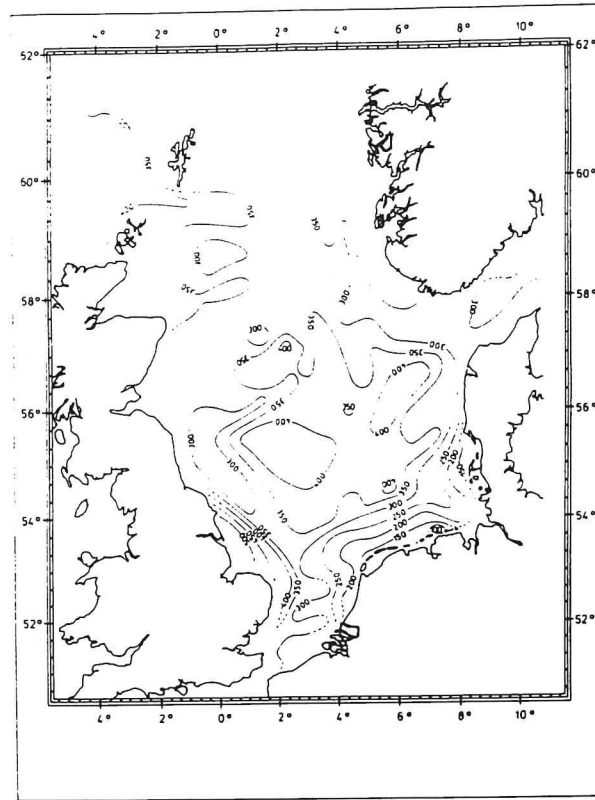


Fig. 2.3: Distribution of pCO₂ (ppmv) in the North Sea surface water in May/June 1986 (from Pegler & Kempe, 1988).

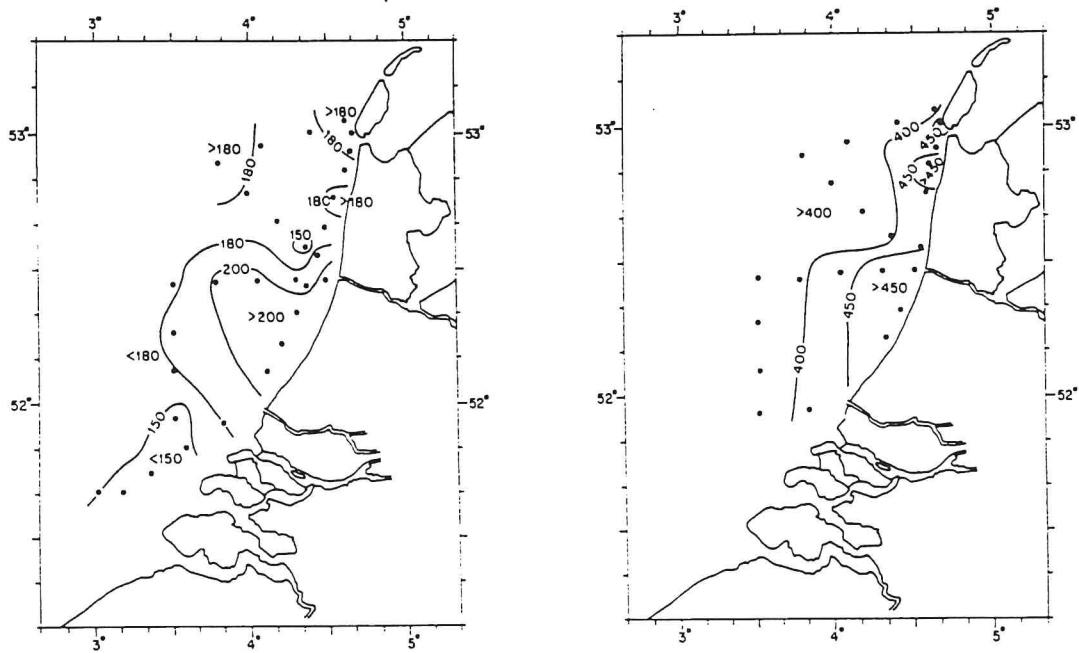


Fig. 2.4: Distribution of pCO₂ (µatm) in the North Sea off the Netherlands in April (left) and November (right) (from Hoppema, 1991).

within the carbonate system. Abiotic precipitation of CaCO_3 hardly ever occurs (Pytkowicz, 1983).

The concentration of TCO_2 in the seawater reservoir is much larger than that of CO_2 in the atmosphere (Fig. 2.2), in May/June the mean for the whole North Sea being $2.10 \text{ mmol.kg}^{-1}$ (Pegler & Kempe, 1988). Assuming this concentration to be uniform over the water column this means an inorganic carbon reservoir size of $9.4 \cdot 10^{14} \text{ g C}$ (water content of the North Sea: $40,300 \text{ km}^3$, ICES, 1983). This is only $2.4 \cdot 10^{-3} \%$ of the global oceanic inorganic C. Parts of the North Sea are supersaturated with CO_2 and others undersaturated (Fig. 2.3). Especially in the coastal regions large deviations from the atmospheric value occur. The data of Pegler & Kempe (1988) are the only complete coverage of inorganic C for the North Sea. However, the data are confined to the May/June period, whereas TCO_2 is expected to show a seasonal variation. An indication for this is found in Fig. 2.4 for the Dutch coastal area (Hoppema, 1991). In May/June the North Sea is on average undersaturated, 323 ppmv (Pegler & Kempe, 1988). It is likely that in the autumn/winter season the mean CO_2 -saturation for the North Sea is higher than shown in Fig. 2.3, due to mineralization of organic matter. Differences in pCO_2 are much more pronounced than for TCO_2 (Hoppema, 1991).

2.1.3. Dissolved Organic Carbon (DOC) in seawater

Dissolved organic matter constitutes the largest pool of organic carbon in seawater (Mopper & Degens, 1979). The exact chemical composition of DOC is not very well known, but we may expect to find in seawater almost any compound known to exist in living matter. A large range of organic molecules has been identified, for example, amino acids, proteins, carbohydrates, fatty acids, phenols, sterols, hydrocarbons, chlorophyll and other photosynthetic pigments, vitamins and halogenated compounds (e.g. Gagosian & Lee, 1981; Hellebust, 1974; Lee & Wakeham, 1989).

There are two sources for DOC in seawater, allochthonous (input from rivers) and autochthonous (production by organisms, mainly plankton). Within the seawater reservoir roughly two DOC fractions can be distinguished based on reactivity; a labile fraction which is easily consumed by heterotrophs, and a more inert or refractory fraction. The proportion of both of these fractions varies both spatially and temporally. The allochthonous DOC consists primarily of refractory material, which can be traced well into the deep ocean using specific biomarkers of landplants (e.g. lignin, Hedges, 1981). The labile DOC is mainly produced in situ by plankton. Its link with the plankton assures that the DOC shows a pronounced seasonal cycle. In winter the DOC concentration in the North Sea is low and it consists mainly of fluorescent substance, which is part of the refractory DOC pool. In situ production of this refractory DOC is small (Laane & Kramer, 1990). During plankton blooms DOC increases spectacularly, sometimes with one order of magnitude difference (Duursma, 1963; Laane, 1982a; Ittekkot, 1982; Postma & Rommets, 1984). In the North Sea highest DOC concentrations are found along the continental coasts (Fig. 2.5), which suggests that they are caused by continental runoff (Beckmann & Liebezeit, 1988). The mean concentration for the North Sea during May/June amounts to 1.1 mg C.dm^{-3} (Pegler & Kempe, 1988). This means a total DOC content of $4.4 \cdot 10^{13} \text{ g C}$ for the whole North Sea, which is a minor amount compared to the dissolved inorganic carbon. DOC values up to 5 mg C.dm^{-3} were measured in summer in specific areas (Postma & Rommets, 1984; Cadée, 1986).

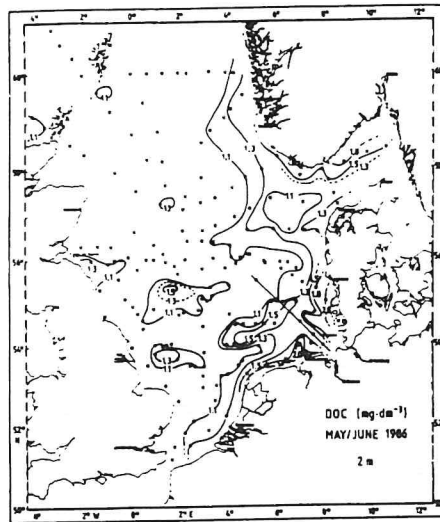


Fig. 2.7: Distribution of DOC in the surface waters of the North Sea in May/June 1986 (from Beckmann & Liebezeit, 1988).

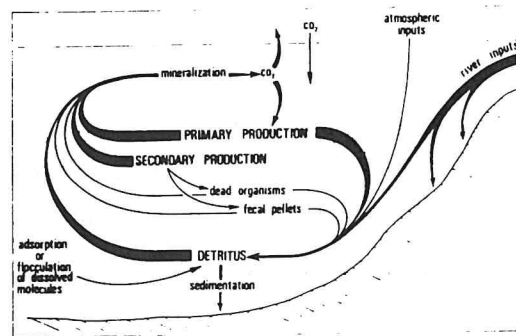


Fig. 2.6: Situation of POC in the carbon cycle (from Cauwet, 1981).

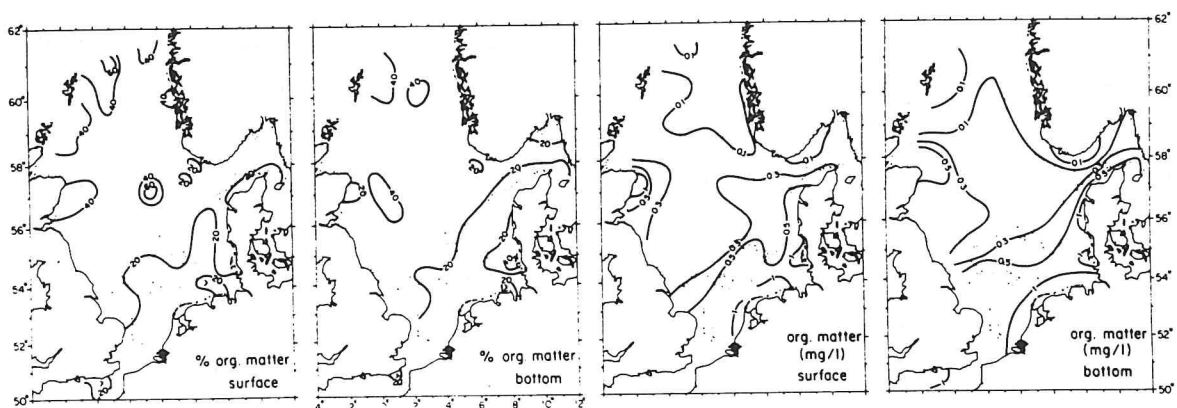


Fig. 2.7: Distributions of organic matter and proportion of organic matter in suspended matter in January 1980 (from Eisma & Kalf, 1987a).

The DOC figures presented above were measured with traditional wet oxidation methods (e.g. Menzel & Vaccaro, 1964). However, Sugimura & Suzuki (1988) using a new method for DOC determination suggested that the older DOC values were underestimates by a factor 2 to 3. If this were true - and this seems to be the case - a major DOC fraction exists that was previously not determined. In vertical profiles in the ocean the new DOC values show a correlation with the apparent oxygen utilization which was not found before, suggesting that there is a labile DOC part that is rapidly recycled. At the same time it means that particle sedimentation out of the euphotic zone becomes less important than thought earlier. For the North Sea a possibly higher DOC pool could have many major implications as well, among which are different advective carbon fluxes, different nutrient circulation and DOC possibly being an extra sink for the carbon cycle by transport to the ocean.

2.1.4. Particulate Organic Carbon (POC) in seawater

POC constitutes the smallest carbon reservoir in the carbon cycle as shown in Fig. 2.1. As for DOC, a labile and a refractory part of POC can be distinguished. The labile POC fraction consists mainly of living and dead plankton and faecal pellets, and it is rapidly converted. Refractory POC (partly) originates from DOC (Parsons, 1975) and in the deep oceans is much older than the labile DOC (hundreds to thousands of years, Mopper & Degens, 1979). Another part of the refractory POC derives from the river water. Generally POC shows a linear correlation with salinity, indicating that no degradation occurs in the estuary and the coastal region (Eisma et al., 1982; Beckmann & Liebezeit, 1988). The sub-cycle in which POC is involved is shown in Fig. 2.6 (Cauwet, 1981). Also for POC there are both autochthonous and allochthonous sources (see sections 2.3 and 2.4). Because of the link between POC concentration and primary production a pronounced seasonal cycle of POC is observed (Brockmann et al., 1983; Beckmann & Liebezeit, 1988) with the highest values in the spring and summer. In the vegetative season 25-65% of POC in the North Sea consists of living phytoplankton (Gieskes & Kraay, 1984), while in dense algal blooms this is almost 100% (Reid et al., 1991). The part of POC consisting of bacteria amounts to 10-20% (Van der Werf & Nieuwland, 1984). In the northern and central North Sea the detritus concentration (i.e. the non-labile part of POC), calculated from the relation between POC and chlorophyll a, amounts to ca. 40 $\mu\text{g C.dm}^{-3}$ (Steele & Baird, 1965; Postma & Rommets, 1984).

A POC distribution covering the whole North Sea is shown in Fig. 2.7, values range from 0.03-2.70 mg C.dm^{-3} in June and 0.08-1.13 mg C.dm^{-3} in January (Eisma & Kalf, 1987a). High values particularly occur along the continental coasts (Eisma et al., 1982; Ittekkot et al., 1982; Beckmann & Liebezeit, 1988) and in the Wadden Sea (Cadée, 1982; Laane, 1982b). Lowest values were measured in the central North Sea (Brockmann et al., 1983; Hölemann & Wirth, 1988). The high values along the coasts are caused by riverine material which stays there concentrated by the general circulation pattern in the North Sea, but these higher values are augmented by resuspension and erosion of sedimentary organic matter (Eisma & Kalf, 1987b; Eisma & Irion, 1988). Related to the latter process is the observation of somewhat higher POC values near the bottom as compared to the surface waters (Beckmann & Liebezeit, 1988).

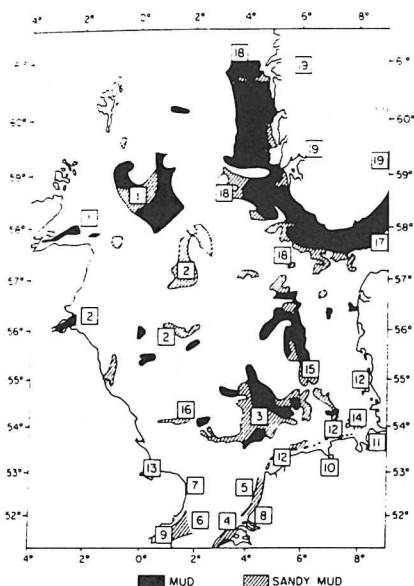


Fig. 2.8:

Distribution of mud and sandy mud in the North Sea (from Eisma 1981). 1, Northern North Sea (chiefly Fladen Grounds); 2, Central North Sea (chiefly Devils Hole and NW of Doggerbank); 3, Oyster Grounds; 4, Flemish Banks; 5, Dutch coastal area; 6, East Anglia Coast; 7, Yarmouth-Lowestoft; 8, Rhine-Meuse-Schelde estuaries; 9, Thames estuary; 10, Ems estuary; 11, Elbe-Weser estuary; 12, the Waddensea; 13, the Wash; 14, the German Bight; 15, Elbe Rinne; 16, Outer Silver Pit area; 17, Skagerrak; 18, Norwegian Channel; 19, Norwegian and some Swedish fjords.

(after Eisma & Kalf, 1987b)

Fig. 2.9: Distribution of the weight content of total sedimentary carbon (from Wirth & Wiesner, 1988).

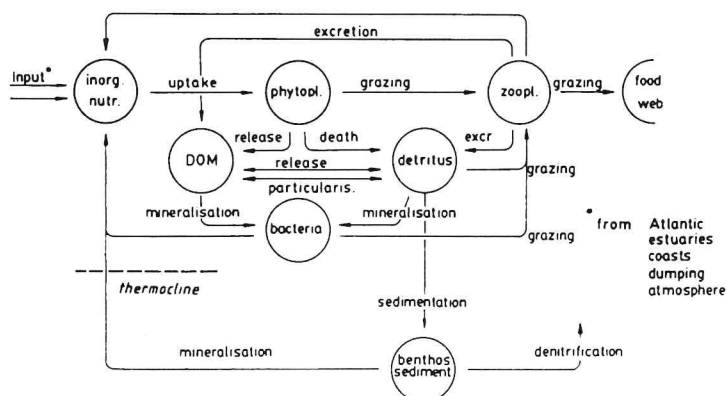
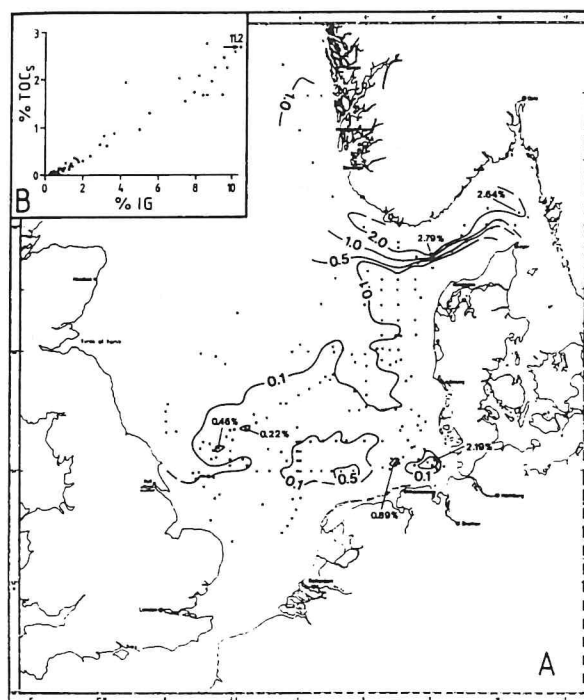


Fig. 2.10: Schematic representation of the main fluxes within the pelagic ecosystem (from Brockmann et al., 1988).

2.1.5. Carbon in the sediments

In the sediment carbon is present as organic matter or as biogenic carbonate (calcite, aragonite). The North Sea sediment mainly consists of sand, with at some places admixed in it gravel, and at some specific locations mud (Veenstra, 1970; Kersten & Klatt, 1988). Due to their recent formation history, variable local environments and rapidly changing external conditions shelf sediments are variable in texture and composition, which in the North Sea resulted in a mosaic of sediment types (Fig. 2.8, Eisma & Kalf, 1987a). Sand and gravel contain recent admixtures of organic matter and carbonate fragments, originating from benthic organisms and plankton (Eisma & Kalf, 1987a). In addition, the seafloor of the North Sea has received a high load of anthropogenic wastes such as harbour dredgings, drilling muds and sewage sludge (Carlson, 1986), which at least locally influenced the sediments. Dumping sites are mainly situated close to the coasts.

In Fig. 2.9 the distribution of organic carbon in the surface sediment (upper 2 cm) is shown. It largely reflects the distribution of the various sediment facies (Wirth & Wiesner, 1988). The organic carbon content is generally <0.1% (Wirth & Wiesner, 1988), except for some localized areas like the inner German Bight and the Norwegian Channel, where large contemporary mud sediments are found (Van Weering et al., 1987). The organic carbon content in the deeper parts of the Skagerrak is about 3% (Van Weering et al., 1987) and along the margins varies between 1.5 and 3% (Olausson, 1975; Van Weering, 1981). In the German Bight organic carbon is up to 2.2% of the sediment (Wirth & Wiesner, 1988). The distribution of organic matter in the North Sea appeared to be controlled by grain-size, and concentrated in the <20 µm (mud) fraction (Wirth & Wiesner, 1988), which is easily transported along the main water transport routes. Creutzberg et al. (1984) already demonstrated that mud content and organic carbon are clearly positively correlated.

Almost all along the Dutch coastline, in the estuaries, and in the Wadden Sea areas with sandy mud are found (Creutzberg & Postma, 1979; Eisma, 1981; Eisma & Irion, 1988). On a tidal flat in the western Dutch Wadden Sea the organic content was found to be 0.4% (Vosjan & Olanczuk-Neyman, 1977), that is, higher than in the open North Sea.

The average CaCO₃ content in the <20µm fraction of the North Sea sediments was about 11%, with a maximum of up to 46% (Kersten & Klatt, 1988), which makes it a substantial component in the recent North Sea sediments. Also in the Skagerrak-Kattegat the carbonate content is related to the fine-grained sediment (Van Weering, 1981). The carbonate content is generally 10-15% there, but sometimes values up to 30% are found.

2.2. The biotic part of the carbon cycle

By the process of photosynthesis inorganic carbon is taken up by phytoplankton to produce organic matter. Phytoplankton uses light as an energy source, and apart from carbon many other macro- and micronutrients. Not all carbon taken up is used for the production of biomass. Products of photosynthesis are consumed in respiration, both during the night and the day. Besides that, a great variety of organic substances are excreted by the phytoplankton (Hellebust, 1974). The amount of substances excreted (exudates) may be considerable, up to 16% of photosynthesis in the North Sea (Reid et al., 1991). Different types of primary producers differ in their amounts of exudates. Also

secretion occurs, the production of organic substance outside the cells, for example by the colonial flagellate *Phaeocystis* (Veldhuis et al., 1986), which is abundant in the North Sea. By the process of excretion the DOC pool is partly filled. These molecules are directly available for consumption by heterotrophic bacteria.

Apart from excretion phytoplankton carbon is transferred to other pools by zooplankton grazing, death and subsequent lysis of the cells and sinking out of the surface layer in order to be deposited on the seafloor (Reid et al., 1991). An overview of main pools, transfer routes and processes involved in biotic carbon cycling is shown in Fig. 2.10. It used to be believed that the main pathway of primary produced carbon was to the zooplankton pool (Harvey, 1945; Steele, 1974). However, recently it has become clear that as much as 10-50% of photosynthesis can be consumed by microbes (Williams & Yentsch, 1976; Azam et al., 1983) through the uptake of DOC released by phytoplankton. This is not only DOC released through excretion, but also due to autolysis or mechanical breakage by grazing zooplankton (Lee & Wakeham, 1989). This constitutes the "microbial loop" (Pomeroy, 1974). The microbial loop appears to be especially effective in coastal regions. Also in the North Sea observations regarding the microbial loop were done (Joiris et al., 1982; Fransz & Gieskes, 1984; Lancelot & Billen, 1984). Fransz & Gieskes (1984) showed that during the phytoplankton bloom more carbon is channelled through the microbial loop than through the zooplankton. During summer, however, zooplankton grazing matches phytoplankton production. The response time of bacteria on the phytoplankton production is usually only a few days (Lancelot & Billen, 1984). Presently it is estimated that zooplankton consumes about 10% of primary produced carbon in the coastal zone and about 20% in the central and northern parts of the North Sea (Joiris et al., 1982; Fransz & Gieskes, 1984). Zooplankton consumes perhaps some non-living particles as well (Lee & Wakeham, 1989).

In shallow areas like the North Sea a considerable part of the primary production may reach the sediments (Billen, 1978; Joiris et al., 1982; Peinert et al., 1982), and this can be as much as 20-35% (Davies & Payne, 1984; Cadée, 1985). However, there is a large variation. Cadée (1986) found that only 1% sank out in the Fladen Ground area. Settling particularly takes place during and at the end of the phytoplankton bloom (Gieskes & Kraay, 1984a; Cadée, 1985). The phytoplankton remains that reach the seafloor are a food source for the benthic community, which consists of both macro-, meio- and microzoobenthos, as well as bacteria (De Wilde et al., 1984; Cadée, 1984). In the continental coastal zone of the North Sea 25-50% of the primary production is consumed by benthic bacteria and meiofauna together, but in the central and northern parts this is probably less (Billen et al., 1991). The response time of the benthos to freshly deposited planktonic material, in terms of mineralization activity, is less than one day (Brockmann et al., 1988).

In another part of the microbial loop microheterotrophic zooplankton consumes bacteria (Williams, 1981; Azam et al., 1983). Through this pathway DOC, consumed by bacteria and thus transformed into POC, is again a food source for grazers (Lee & Wakeham, 1989). It has been suggested by several authors that this is the main function of bacteria in the carbon cycle, rather than being the remineralizers of organic matter (e.g. Andersson et al., 1985), their predators being the remineralizers instead.

By consuming phytoplankton zooplankton takes part in the mineralization process by excreting CO₂, nutrients and DOC (Le Borgne, 1986). Zooplankton is also a link in the fast POC transport

from the surface layers of the water column to the bottom through their capacity of producing faecal pellets. These particulates have high sinking speeds (Bishop et al., 1977; Honjo & Roman, 1978; Honjo, 1980). However, the relative importance of this process compared to the direct sinking of dead phytoplankton is unclear (Fasham, 1984).

From the primary producers (phytoplankton) and primary consumers (zooplankton) the food chain (or carbon chain) broadens out and extends to higher trophic levels via secondary (invertebrate carnivores) and tertiary consumers (fish, birds, mammals and man) at the end of the chain. The total landings of fish and shellfish from the North Sea amounted to about 2.6 million tonnes in 1984 (McIntyre, 1988), a figure that varies considerably between different years. Total fish production makes up about 1% or less from the total primary production in the North Sea (see Jones, 1984, for a review of estimates).

2.3. Hydrography and advective transport

The present description of the hydrography will only be superficial, roughly setting the scene for processes and transport routes that are important for the carbon cycle. The present discussion is essentially based on Eisma (1987) and Anonymous (1985).

The North Sea is a shallow shelf sea which is bordered by land at three sides, except in the north. Water flows in from the North Atlantic, mainly along the western side of the connection with the Atlantic Ocean between the Shetlands and Norway. Other major water inflows come from the English Channel through the Straits of Dover, from the Baltic through the Skagerrak, and from the rivers, especially in the Southern Bight (Rhine/Meuse and Thames) and in the German Bight (Elbe). The major water outflow is along the Norwegian coast to the N Atlantic ocean. The general circulation pattern that results is directed counterclockwise (Fig. 2.11), reinforced by the tides, the prevailing winds, and by density differences, the latter mainly resulting from the freshwater discharges from the continent. Variability in this circulation pattern is large, and is brought about predominantly by variable wind-induced water movements, both inside the North Sea as well as already in the Atlantic Ocean. On longer time scales also climate variations contribute to this variability. The mean residence time of the water in the North Sea is 1-2 years, but again, this figure varies for different areas, for example, in the German Bight the water on average resides longer.

The tidal currents are strong, especially in the shallow Southern Bight. In other parts the wind-induced currents are relatively more important. The Southern Bight is vertically well-mixed with respect to salinity and temperature, while both in the central and northern North Sea seasonal or permanent stratification may develop. Along the Dutch coast the mean residual current is directed to the north. However, wind-forcing may change this current pattern for shorter or longer periods. The concurrent inflow of river water results in a permanently present strip of lower salinity water off the Dutch coast. This feature induces a quasi-estuarine circulation between inshore and offshore waters based on density differences. The lighter inshore water tends to move away from the coast over the heavier offshore water, that thus has a shoreward direction. This mechanism accumulates suspended sediments, which move close to the sea bottom, near the coasts.

The transport of suspended material roughly follows the main transport routes of the water masses, in the meantime going through several cycles of deposition and resuspension before it is

Fig. 2.11: General water circulation in the North Sea (from Eisma & Kalf, 1987b).

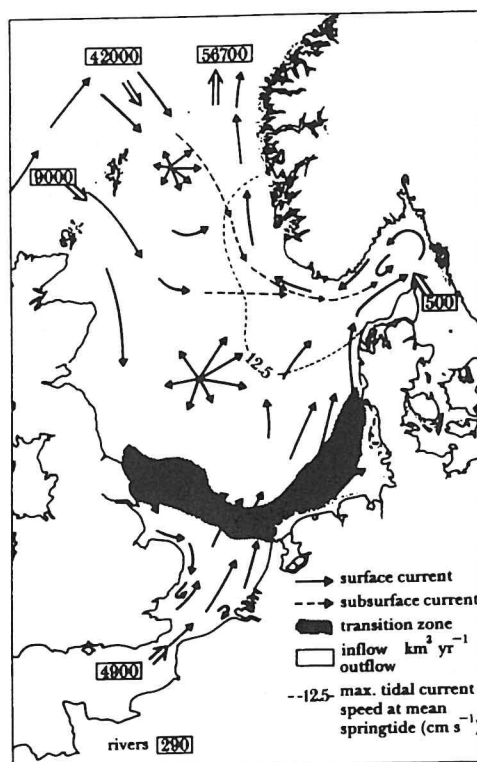


Table 2.1: A water budget for the North Sea in 10^3 km^3 (after Brockmann et al., 1991).

	IN	OUT
North Atlantic	33	37
English Channel	3	
Baltic	1.7	1.2
rivers	0.2	
atmosphere	0.3	

Table 2.2: Estimates of primary production ($\text{mg C} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) in different seasons based on measurements between 1971 and 1981 in the North Sea (after Fransz & Gieskes, 1984).

	Jan-Feb	Mar-May	Jun-Sep	Oct-Dec	Annual estimate ($\text{g C m}^{-2} \text{ yr}^{-1}$)
Southern Bight, coast	100	1 000	1 000	100	200
Southern Bight, offshore	100	1 200	700	500	250
Central North Sea, 1981	100	1 000	800	400	200-250
Northern North Sea (FLEX)	300	1 000	-	-	>>100

permanently deposited. Strong tidal currents, waves and wind events cause rapid resuspension, particularly in the shallow areas, such as the Southern Bight.

All of these water movements are appropriately brought together in a water budget. Recently, a budget was constructed by Brockmann et al. (1991), shown in Table 2.1. The annual amount of water entering and leaving the North Sea is comparable to its volume. It should be realized that these figures are highly variable (Anonymous, 1985). The water budget is the basis for other material budgets.

2.4. Main fluxes between the carbon reservoirs

2.4.1. Primary production

In the light of carbon cycling primary production should refer to the uptake of inorganic carbon to be incorporated in the particulate carbon pool. However, the methods implemented and the definitions used for the concept of primary production are not unequivocal (Jones, 1984; Reid et al., 1991), and neither is the phytoplankton behaviour under different environmental and physiological conditions. A first distinction can be made between gross and net primary production, where the former includes the total photosynthetic carbon uptake and the latter the total uptake minus respiration. Apart from being used for respiration photosynthetically fixed carbon is also used for the synthesis of reserve products that can be catabolized to support further growth in the dark. The extent to which these processes take place is dependent on external conditions. Net primary production may refer to the phytoplankton carbon fixation only (net particulate production) or to the fixation by phytoplankton and bacteria together, called net particulate + soluble production or net community production. In addition, these net production definitions could be valid for the daylight period only, or for the whole 24 hours period (Jones, 1984). The use of any of these definitions of primary production is posed by the aim.

Superimposed on the definitions problem is the question of the validity of experimental primary production measurements and their meaning with respect to the interpretation of the results (Gieskes & Van Bennekom, 1973; Reid et al., 1991). The most widely used method is the ^{14}C method based on Steemann Nielsen (1952), which has undergone several modifications since (Schindler et al., 1971; Gieskes & Kraay, 1984b). The ^{14}C method is certainly a very sensitive and applicable method, but still it suffers from serious experimental uncertainties, summarized by De Vooy (1979). The most serious drawback is that from ^{14}C data no respiration can be determined. It is not clear either whether the ^{14}C method gives net or gross primary production figures, although the opinion tends towards net primary production (De Vooy, 1979). Fransz & Gieskes (1984) actually found that the ^{14}C measured production value was embraced by the gross and net production measured with the oxygen method. For carbon cycle purposes it is suitable to work with net particulate production or net particulate + soluble production; the soluble fraction is incorporated because it provides a transfer pathway between two carbon reservoirs, the inorganic and DOC.

Many measurements have been performed in the North Sea, mainly for restricted areas, while the seasonal coverage has been very poor. Data are summarized by Jones (1984) and Reid et al. (1991). Jones (1984) estimated the mean net annual primary production for the whole North Sea to

be $130 \text{ g C.m}^{-2}.\text{y}^{-1}$, based on values ranging from $60\text{-}200 \text{ g C.m}^{-2}.\text{y}^{-1}$ for various areas. Fransz & Gieskes (1984) came to a much higher annual estimate of $200\text{-}250 \text{ g C.m}^{-2}.\text{y}^{-1}$ for the southern and central North Sea, the seasonal variation of which is shown in Table 2.2. Production in the northern North Sea is probably somewhat lower (Gieskes & Kraay, 1986). Along the Dutch coast the annual production in the inshore area is smaller than offshore (Fransz & Gieskes, 1984), although in the former area nutrients are in excess supply because of river discharges. This apparent paradox is caused by a reduced length of the vegetative season, possibly by light limitation in the more turbid coastal area (Nelissen & Stefels, 1988).

Aletsee & Rick (1988) measured primary production both in summer and in winter covering the entire North Sea (Fig. 2.12). The general picture they obtained was quite comparable with the composite of local studies. Features that emerged were high values in summer off the Dutch and German coasts and off northern England, and much lower values in the central and northern North Sea. This also agrees very well with the one other complete coverage of the North Sea in summer by Owens et al. (1990). Also in winter the highest values were measured in the Southern Bight, but besides also on the Dogger Bank (Aletsee & Rick, 1988). In contrast with Fransz & Gieskes (1984) in winter a decrease off the Dutch coast was found.

In the Southern Bight more than 50% of the primary production was attributed to organisms $>5 \mu\text{m}$ (Owens et al., 1990). According to Aletsee & Rick (1988) 60% of the total North Sea production was accounted for by organisms $>20 \mu\text{m}$. The latter authors estimated the total net production of organic carbon for the entire North Sea at $150\cdot 10^6$ tonnes per year, which is equivalent to ca. $260 \text{ g C.m}^{-2}.\text{y}^{-1}$, higher than all other estimates. Considering the inorganic carbon reservoir size ($9.4\cdot 10^{14} \text{ g C}$, section 2.1.2) and the primary production according to Aletsee & Rick (1988) an inorganic carbon atom will be exchanged every 6 years. Off the Dutch coast the exchange is likely to be faster because there the North Sea is shallower and primary production above average. However, before all inorganic C atoms can be exchanged between the inorganic and POC reservoirs the whole North Sea has already been flushed, the water mass residence time being only 1-2 years (section 2.3).

2.4.2. Seawater-atmosphere fluxes

Due to seasonal heating and cooling the North Sea would be a modest source for CO_2 in summer and a sink in winter, because the solubility of CO_2 in cold water is higher than in warm water. This physical process would result in annual fluxes of $9.8\cdot 10^{12} \text{ g C}$ balancing each other (Kempe & Pegler, 1990). However, instead of a source, the North Sea is a major sink for CO_2 in summer. The driving force for the undersaturation of CO_2 in summer is the extraction of it by the phytoplankton. Kempe & Pegler (1990) derived a flux of $4.3\cdot 10^{12} \text{ g C}$ entering the sea in summer. This combined with the above theoretical efflux due to physical processes yields a total flux of $14.1\cdot 10^{12} \text{ g C}$ taken up every summer by photosynthesis. Assuming steady state, mineralization in winter releases the same amount of carbon to the atmosphere. On a total inorganic reservoir of $9.4\cdot 10^{14} \text{ g C}$ (see section 2.1.2), this implies that an inorganic carbon atom in the North Sea is exchanged every 67 years with one carbon atom of the atmosphere. The above assessment is for the North Sea as a whole. Near the Dutch coast the extremes in super- and undersaturation are larger (Hoppema, 1991), and therefore the

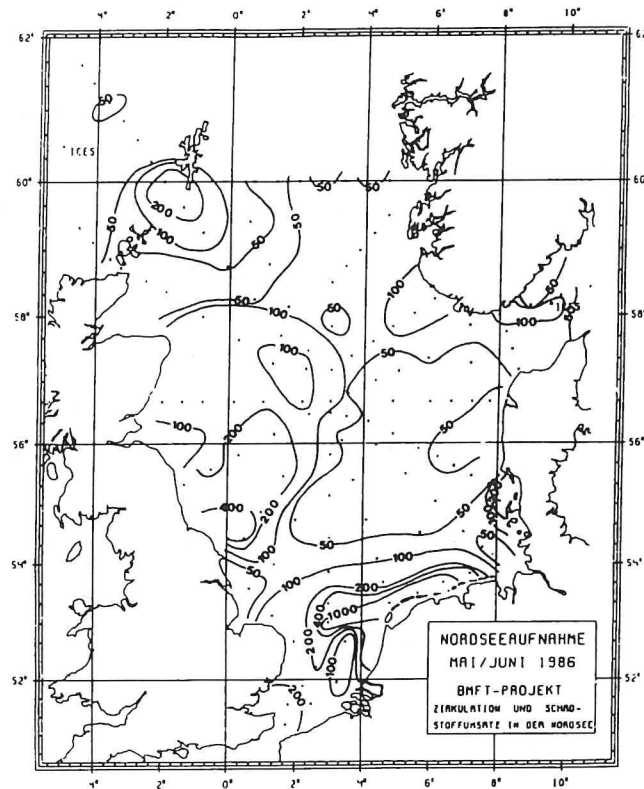


Fig. 2.12: Distribution of primary production ($\text{mg C.m}^{-2}.\text{h}^{-1}$) over the 20 m water column during May/June 1986 (from Aletsee & Rick, 1988).

Table 2.3: Suspended sediment in the North Sea (from Eisma & Irion, 1988).

Supply	10^6 t a^{-1}
North Atlantic Ocean	10.4
Channel	22-30
Baltic	0.5
Rivers	4.8
Seafloor erosion	9-13.5 (+ ?)
Coastal erosion	2.2
Atmosphere	1.6
Primary production	1
	51.5-64.0 (+ ?)
Outflow + Deposition	
Outflow	$11.4 + < 3$
Deposition	
Estuaries	1.8
Waddensea + the Wash	5
Outer Silver Pit	1-4 (?)
Elbe Rinne	?
Oyster Grounds	2(+ ?)
German Bight	3-7.5
Kattegat	8
Skagerrak + Norwegian Channel	17(+ ?)
Dumped on land	2.7
	51.9-62.4(+ ?)

exchange time is probably shorter.

2.4.3. Sediment-suspended particle exchange

Deposition or sedimentation is the process in which particles in suspension are brought down to the seafloor; by the process of resuspension this pathway is reversed. After resuspension the particles may be transported away, along with the water masses. The rate of sedimentation is dependent on the size of the particles through Stokes' law and the bulk density (Leeder, 1982). In fact the situation is more complicated because of phenomena like flocculation, very common for silty sediments. Sedimentation is also dependent on turbulence and wave activity, especially in shallow areas. Resuspension mainly occurs with the small grain-size fractions. These fractions also contain the highest load of POC (Wirth & Wiesner, 1988). Resuspension is also highly determined by currents, waves and wind events (Eisma & Kalf, 1987b).

Suspended matter consists mainly of particles smaller than 60-70 μm (Lee & Folkard, 1969; Eisma & Kalf, 1979), while mud can be considered to be the deposit of suspended matter (Eisma, 1981). Suspended matter subject to deposition-resuspension processes contains carbon as organic matter (POC) or as (calcium)carbonate (PIC). The POC content is quite variable, due to the uneven distribution of primary production over the year. In winter, when there is virtually no primary production, 40% of the suspended matter is organic (Eisma & Irion, 1988). In the Southern Bight this is 20% due to the shallowness through which particles originating from seafloor erosion constitute a larger part than in the northern North Sea. In the vegetative season the POC content may be close to 100% (Eisma & Kalf, 1987a). The suspended organic matter in winter probably finds its origin in bottom deposits, coastal sediments, river supply, primary production and bottom-dwelling organisms together (Eisma, 1981). The organic matter is the glue for aggregates of particles, where bottom organisms are an important intermediate through their production of faeces and pseudo-faeces (Eisma, 1981). Calciumcarbonate in suspended matter originates from the tests of coccolithophorids (Kempe & Jennerjahn, 1988) and other organisms. According to Eisma & Kalf (1979) hard parts of plankton (carbonate shells) are rarely found in suspension during the winter.

There is a supply of particles to the North Sea from several sources (McCave, 1973; Eisma, 1981; Eisma & Irion, 1988; see section 2.3.). A very large supply of carbon to the bottom derives directly from primary production. As much as 20-35% of the production in the North Sea may reach the sediment (Davies & Payne, 1984; Cadée, 1985). This large supply is only temporary since bottom organisms utilize 50-75% of the deposited organic matter, which is evidenced by the fact that in suspended matter the POC is much higher than in the sediments (Olausson, 1975; Eisma, 1981; Van Weering, 1982). On top of that, in the shallow North Sea, and in particular in the non-stratified Southern Bight, the depositions are readily resuspended by strong currents, turbulence, waves and occurrence of storms.

2.4.4. Carbon burial

It is obvious that sedimentation as such is not a useful measure, because most material is modified after sedimentation or resuspended again and dispersed. However, the unbalance between supply and

outflow of suspended matter indicates that within the North Sea material must be deposited permanently (Eisma & Kalf, 1987a; Eisma & Irion, 1988). Mud on the seafloor may be an indication for deposition areas (see Fig. 2.8), but unfortunately such evidence is not conclusive. There are some areas, like the Fladen Grounds and the Oyster Grounds, where the mud deposition is not Recent, but dating back to the early Holocene. These surfaces are a little reworked and usually contain an admixture of small amounts more recently deposited POC and organic carbonate (Eisma & Kalf, 1987b). Permanent deposition of suspended (organic) matter of the North Sea occurs in the southern estuaries, the Wadden Sea and the Wash, the Outer Silver Pit, the German Bight and the Skagerrak-Kattegat-Norwegian Channel (Fig. 2.8). Their relative importance is obvious from Table 2.3.

From these locations the Skagerrak-Kattegat-Norwegian Channel is by far the most important (Rohde, 1973; Eisma, 1981; Van Weering, 1981; Jørgensen et al., 1981; Van Weering et al., 1987; Salge & Wong, 1988; Kempe & Jennerjahn, 1988), amassing 50-70% of all deposited suspended matter of the North Sea (Eisma & Kalf, 1987a). This means that in this area material originating from various parts and various sources of the North Sea settles down (Van Weering et al., 1987). The pattern of supply is roughly with the current along the continental coasts, thereby picking up material from the seafloor and the rivers. Sedimentation occurs right in this area because the typical current structure of the North Sea is favourable and because it is much deeper (700 m) than the rest of the North Sea, hence rapid resuspension is impossible.

Owing to its importance for the North Sea the Skagerrak-Kattegat-Norwegian Channel is well investigated. Kempe & Jennerjahn (1988) measured verticle particle fluxes in this area with sediment traps. They found that fluxes were determined by biological processes, evidenced by the fact that the largest fluxes occurred in summer (in the Skagerrak 79% of total flux). Both in winter and summer fluxes were dominated by CaCO_3 , mainly consisting of coccoliths. The average flux rate of CaCO_3 measured with a sediment trap in the Norwegian Channel amounted to $17.9 \text{ mg.m}^{-2}.\text{d}^{-1}$ (39% of total flux), while in the Skagerrak this was $34.6 \text{ mg.m}^{-2}.\text{d}^{-1}$ (13.6% of total flux). The organic matter fluxes were high as well. The carbonate content of the sediments in the Skagerrak is between 10 and 15% and shows a similar distribution as the mud (Van Weering, 1981). This indicates that this area is a major sink for carbonate carbon. In the Norwegian Channel the sedimentary carbonate content is much higher, 30-50% (Van Weering, 1981). This difference between Skagerrak and Norwegian Channel may be caused by the dissolution of carbonates (Alexanderson, 1978, 1979). Another explanation of this difference is the formation of carbonate rocks associated with methane seepage (section 5.3), which were observed in the Kattegat (Jørgensen, 1989). Therefore, the size of the sink for carbonates is uncertain.

In estuaries and in the Wadden Sea suspended matter is trapped (Eisma & Kalf, 1987b; Eisma & Irion, 1988), the mechanism was described by Van Straaten & Kuenen (1957) and Postma (1961). Sedimentation is related to the turbidity maximum in natural estuaries, and to artificial (harbour) basins and navigation channels in largely constructed river mouths, like the one of the Rhine/Meuse near Rotterdam. In most estuaries the suspended matter trapped largely originates from the sea, like in the Rhine, Ems and Weser (Eisma et al., 1982; Irion et al., 1987). Although the trapping mechanism is very effective only some 3-4% of the deposited material in the North Sea accumulates in the estuaries (Eisma & Irion, 1988). This percentage is so low because of extensive dredging activity in

harbour basins. The dredged material is dumped in the coastal area or on land. In the Wadden Sea (and also in a comparable area along the English coast, the Wash) mud is trapped particularly by the tidal watersheds and tidal flats, because there it is shallower and the suspended matter reaches the bottom sooner. Wave effects counteract this accumulation. Therefore, large deposits are mainly found in sheltered embayments, such as the Dollard and the Jadebusen (Eisma & Irion, 1988). Benthic organisms promote deposition by producing faeces. The ultimate sources for mud deposits in the Wadden Sea are the rivers, of which the Rhine/Meuse is the most significant (Postma, 1982; Eisma & Kalf, 1979).

In the other major depo-centre of the North Sea, the German Bight, deposition of mud occurs in spite of high currents. This can be explained by a tidal concentration mechanism of suspended matter, temporarily low wave activity and a relatively large water depth (40 m) at such a nearcoastal site (Eisma & Kalf, 1987b). The Elbe and dumping of dredged material and sewage are important sources for the mud accumulation, but the high rate of deposition requires that also supply from elsewhere has to take place (Eisma & Kalf, 1987b; Irion et al., 1987).

The order of magnitude of the total deposition in the North Sea, i.e. the net flux between the suspended matter and the sediments, is estimated as follows. The total deposition of suspended matter in the North Sea is $40.5\text{--}51 \cdot 10^{12} \text{ g.y}^{-1}$ (Eisma & Irion, 1988). Suspended matter is generally assumed to be the small particle fraction, operationally defined as $<63 \mu\text{m}$. Knowing the organic matter content of this small fraction, found on the seafloor as mud, an estimate is obtained of the total deposited organic carbon. Wirth & Wiesner (1988) determined the organic content of mud on the North Sea bottom in the $<20 \mu\text{m}$ fraction and arrived at a mean of about 2.5% organic C. Thus $1.0\text{--}1.3 \cdot 10^{12} \text{ g C}$ is estimated to be annually deposited in the whole North Sea, assuming that there is not much difference between the $<20 \mu\text{m}$ and the $<63 \mu\text{m}$ fractions.

Other estimates reported in the literature are $2.0 \cdot 10^{12} \text{ g C.y}^{-1}$ by Brockmann et al. (1991), and $1.5\text{--}2.0 \cdot 10^{12} \text{ g.y}^{-1}$ (Eisma & Kalf, 1987b) for the total deposition of organic matter, equivalent to $0.6\text{--}0.8 \cdot 10^{12} \text{ g C.y}^{-1}$ when assumed that 40% of the organic matter consists of carbon. The latter figure is based on an old, too low value for the total suspended matter deposition (Van Weering et al., 1987). Another approach emanates from the measured organic C fluxes in the Skagerrak and the Norwegian Channel (Kempe & Jennerjahn, 1988), the annual mean being $34.9 \text{ mg.m}^{-2}.\text{d}^{-1}$ and $12.8 \text{ mg.m}^{-2}.\text{d}^{-1}$, respectively. Taking the mean flux of both to be valid for the rest of the North Sea this gives a total organic C flux of $2 \cdot 10^{12} \text{ g C.y}^{-1}$. However, 50-75% of the settled organic material is mineralized in the bottom, this leaves $0.5\text{--}1 \cdot 10^{12} \text{ g C.y}^{-1}$. According to Eisma (1981) and Eisma & Irion (1988) of the $40.5\text{--}51 \cdot 10^{12} \text{ g}$ suspended sediment only $1 \cdot 10^{12} \text{ g}$ derives from in situ primary production in the North Sea. This means that only 2-2.5% (or $0.02\text{--}0.05 \cdot 10^{12} \text{ g C}$) of the deposited carbon was formed in the North Sea. The total primary production of the North Sea being $150 \cdot 10^{12} \text{ g C.y}^{-1}$ (Aletsee & Rick, 1988) the amount of organic C that is withdrawn from the carbon cycle every year by permanent deposition is in the order of 0.02%.

The calculation of the buried CaCO_3 has to be based on the measured flux rates in the Skagerrak and the Norwegian Channel (Kempe & Jennerjahn, 1988). The annual means for both areas are 4.2 and $2.1 \text{ mg C.m}^{-2}.\text{d}^{-1}$, respectively. Because these CaCO_3 fluxes derive mainly from coccoliths and coccolithophorids only occur in the central and northern North Sea (Reid et al., 1991) the assumption is made that the mean flux ($3.2 \text{ mg C.m}^{-2}.\text{d}^{-1}$) of CaCO_3 is confined to half of the

North Sea area. The annual flux of CaCO_3 then becomes $3.4 \cdot 10^{11} \text{ g C.y}^{-1}$. This is much higher than the flux of organic matter derived from primary production in the North Sea, and about 20% of the total deposition of organic carbon.

3. CHANGES IN THE NORTH SEA CARBON CYCLE

The anthropogenic impact on the North Sea carbon system is very diverse. There are many disturbing human activities that can influence several carbon reservoirs, fluxes and processes. Superimposed on the humanly induced changes are changes due to natural causes, such as climate or the variable hydrodynamics. Human influence on the North Sea occurs through the air or with the river water (organic contaminants, metals, organic wastes and nutrients) or directly by dumping of dredged spoils, oil spills, sewage sludge etc.

Anthropogenic wastes will very likely affect the North Sea ecosystem. There are two ways anthropogenic compounds can have impact on the carbon cycle (Anonymous, 1985). An increased nutrient load will have an expected influence on the primary production of organic matter only, and in a later stage this possibly affects the consumers of primary produced material. On the other hand, micropollutants or other contaminants may cause toxicological effects on both primary producers and/or consumers (Fig. 3.1). Due to the complexity of the ecosystem and the range of primary and higher order effects it is generally very difficult to unravel clear cause and effect relationships as a consequence of human disturbances.

Until now there are no indications that contaminants, through lethal effects, significantly changed the structure of the North Sea ecosystem (Anonymous, 1985), although some effects on, in particular, fishes and mammals have been observed that were attributed to contaminants (Roskam, 1966; Koeman & Van Genderen, 1972; Reijnders, 1980, 1982). Moreover, the intricacy of the marine ecosystem and the lack of knowledge about many fundamental processes affecting abundance of species quantitatively inhibits a reliable estimate of the overall changes on ecosystem carbon level, even if all effects of contaminants on individual species would be known. Therefore, we will not go into further detail on the effects of these toxic anthropogenic influences. Rather we will concentrate on the direct and indirect effects of eutrophication, which are better documented.

3.1. Eutrophication

The loads of nutrients (N, P) of the southern rivers, in particular the Rhine, increased dramatically due to anthropogenic activities (Van Bennekom et al., 1975; Postma, 1978; Van Bennekom & Wetsteijn, 1990). Due to the restricted water exchange in the North Sea the river water concentrates along the coasts (e.g. Van Bennekom et al., 1975) and this caused the nutrient concentrations along the Dutch coast to increase by 3 to 5 times compared to 50 years ago (Postma, 1978, 1985). Also in the German Bight great changes in nutrient concentrations were observed (Hagmeier, 1978; Radach et al., 1990). In all other parts than coastal areas that receive fresh water no nutrient increases are found. This means that only 5-10% of the North Sea (surface) suffers from enhanced nutrient concentrations (Duursma et al., 1988).

With eutrophication is meant the disturbances in the ecosystem caused by an increased external load of nutrients. These may include enhancement of primary production and phytoplankton biomass, changes in secondary or higher consumer abundances, reduction of species diversity, and oxygen depletion. When nutrients are in short supply we may indeed expect an increase of primary production of phytoplankton and algal biomass. More phytoplankton means more food for the next

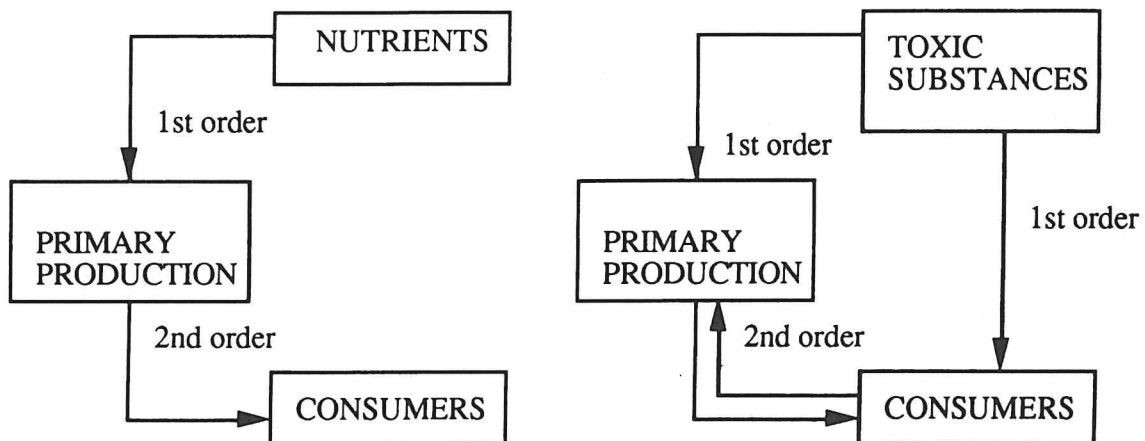


Fig. 3.1: Scheme showing the different effects of nutrients and toxic substances on consumers in an ecosystem (after Anonymous, 1985).

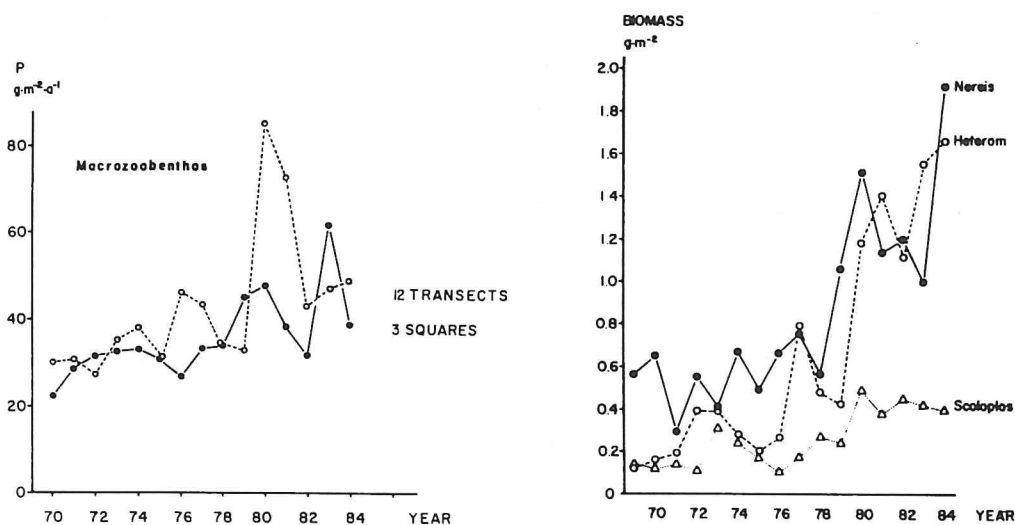


Fig. 3.2: Changes in total macrozoobenthos production (left) and standing stocks of three species of worms (right) on the Balgzand tidal flat area in the western Dutch Wadden Sea (from Beukema & Cadée, 1986 and Beukema, 1987).

trophic level, the herbivoric zooplankton, through which the production of the latter can increase. Eventually we may end up with higher fish biomass and other animals at the top of the foodweb. If, however, one of the trophic levels is not food limited this simple sequence will not continue. For instance, when phytoplankton grazing occurs only to a small extent (as in the coastal zone) a large part of the primary produced matter may settle down to the bottom, where it is a food source for the benthic animals, or it may be deposited. It is evident that in this way the excess produced organic matter is dispersed over many different parts of the foodweb via many different connections. In a highly variable environment this strongly complicates the true assessment of eutrophication effects.

3.2. Changes due to eutrophication

The primary effect of increased nutrients should be an increased primary production and phytoplankton biomass. Fortunately, some long time series of phytoplankton measurements are available. The longest series is the one with the Continuous Plankton Recorder (CPR) (Reid, 1975, 1978; Colebrook, 1986; Dickson et al., 1988; Owens et al., 1989). The silk colour of the CPR, thought to be indicative of the plankton biomass, decreased significantly from 1950 to 1980, where especially diatoms declined. Since the eighties again an increase was observed. However, in Dutch coastal waters an increase by a factor 2.4 was observed from 1950 to 1970 (Gieskes & Kraay, 1977). While the first observation probably is a climatic effect (Radach, 1984; Dickson et al., 1988), and moreover, eutrophication effects are not expected in offshore waters, the second observation seems to be related to the near-coastal eutrophication.

Another valuable record was obtained near Helgoland in the German Bight (Hagmeier, 1978; Gillbricht, 1983; Radach & Berg, 1986; Radach et al., 1990). Also a simultaneous nutrient record is available there. In this area, which also suffers from a high nutrient load (river Elbe) phytoplankton biomass increased two- to threefold in the period 1962 to 1984, mainly as a result of the extreme increase of flagellates. On the other hand, diatoms decreased slightly. These changes were attributed to the increased concentrations of phosphate and nitrate (Radach et al., 1990). The spectacular increase of flagellates compared to diatoms is in line of expectance because the silicate concentration in the German Bight did not increase (diatoms need silicate).

In Dutch coastal waters Cadée started a time series in the Marsdiep tidal inlet in 1969. His measurements roughly show the same trends as the Helgoland data, that is, a doubling of primary production and phytoplankton biomass (Cadée, 1984, 1986a, 1986b; Cadée & Hegeman, 1986). Comparable results were found in the eastern Wadden Sea, the Ems estuary.

It is evident that the concurrent changes of nutrients and algal biomass and production in (Dutch) coastal waters strongly suggest a cause-effect relationship. Comparing the changes it is noticed that nutrients increased by a factor 2 to 5, and phytoplankton only by a factor 2. Apparently, other factors are important as well. These include increased turbidity (Beukema, 1987), diffusion of phytoplankton or nutrients towards offshore waters (Fransz & Verhagen, 1985), or, possibly, contaminants originating from the river water, that would hamper production (Fransz, 1986). The shift of the North Sea phytoplankton population from diatom to flagellate domination (Gieskes & Kraay, 1977; Cadée & Hegeman 1986; Lancelot et al., 1987; Radach et al., 1990) is consistent with the increased P and N concentrations and stationary (or even lower) silicate, and is thus a strong

argument for a eutrophication effect. Still, scientists are cautious to attribute the changes unequivocally to eutrophication, because long-term climatic effects are certainly important as well (Dickson et al., 1988).

Did the structure of the marine ecosystem change due to these higher loads of nutrients? In other words, are the effects noticed on the phytoplankton passed on to higher trophic levels? For the Dutch Wadden Sea this question could be answered with yes. In the period 1970 to 1985 the total biomass of the macrozoobenthos on the tidal flats in the western Wadden Sea roughly doubled (Fig. 3.2, Beukema & Cadée, 1986). Also in other parts of the Wadden Sea increases were observed (Beukema & Essink, 1986). This doubling agrees very well with the concurrent increases of the phytoplankton and microphytobenthos production in the same area (Cadée, 1986a, 1986b; Cadée & Hegeman, 1986). Also in the well investigated German Bight increases of the zoobenthos population have been found, which were positively attributed to eutrophication (Rachor, 1990).

Other observations which might be related to eutrophication are increases of the density of shrimps in the Dutch near-coastal North Sea (Boddeke, 1978; Boddeke et al., 1986). In addition, along the English coast the biomass of the benthos increased between 1971 to 1985 (Buchanan & Moore, 1986) and for the German Bight the same holds, comparing measurements from the 1920's and 1960's with the 1970's (Salzwedel et al., 1985). In the open North Sea the zooplankton abundances, as obtained with the CPR decreased from 1948 to 1980 (Colebrook, 1982) but partially recovered after 1980 (Dickson et al., 1988). These differences between the open North Sea and the coastal areas serve the argument for the existence of eutrophication effects. At a still higher trophic level, the fishes, the effects of eutrophication are uncertain. Fish catches increased (Daan, 1986) and the composition shifted from pelagic to demersal, but changing and more effective fishery techniques would appear the prime explanation of these facts.

Until now it seemed as if eutrophication effects are mainly beneficial to the ecosystem (and to the economical exploitation of marine resources). This is, however, misleading. In the first place, shifts of species composition occur within the ecosystem, which are disadvantageous for the ecosystem as a whole. The opportunistic species with a large reproduction capacity and adaptive feeding behaviour benefit as opposed to the ones with longer reproductive cycles (Beukema & Cadée, 1987; Rachor, 1990). This causes a decline in species diversity and extremities in the total ecosystem abundances. Until now a reduced species diversity was only observed in a small part of the German Bight (Rachor, 1985, 1990). Plankton blooms are an example of an ecosystem extremity. Although they already occurred prior to eutrophication (Van den Ende, 1849 as cited in Van Bennekom et al., 1975), their frequency seems to have increased (e.g. Cadée, 1990) as well as the length of the blooming period (Cadée & Hegeman, 1986). The possible sequence of events during a bloom was discussed by Kempe et al. (1988) as follows: During blooms the phytoplankton takes up a lot of CO_2 within a relatively short time span. This lowers the pCO_2 to values as low as <100 ppm as compared to the equilibrium value of ~ 350 ppm (Pegler & Kempe, 1988) and increases pH and calcite saturation by rearrangement within the inorganic CO_2 -system (see section 2.1). Not all organisms can stand such high pH and/or calcite supersaturation and therefore only a few specialized species will benefit from the changed conditions, thereby reinforcing the diminishing of species diversity. Particularly feared are the plankton blooms that produce toxic substances, killing many marine organisms, also the economically exploited ones.

Secondly, due to the decay of the excess produced organic matter much more oxygen is needed which in turn may lead to oxygen deficiency. This may occur in particular in areas with a stratified water column and during stable conditions, when the exchange with the overlying well oxygenated surface water is limited. Anoxia will lead to the dying or migration of organisms. Areas which are particularly sensitive to the phenomenon because of their typical topographical, hydrographical and biological characteristics are the German Bight and the Skagerrak (or for that matter the Baltic as a whole). In the eighties oxygen depletion was frequently observed in the German Bight (Rachor & Albrecht, 1983; von Westernhagen & Dethlefsen, 1983; Gerlach, 1984; Brockmann & Eberlein, 1986) with accompanying negative effects on the bottom fauna (von Westernhagen & Dethlefsen, 1983; Rachor, 1985).

The Wadden Sea is an accumulation area of organic matter (Postma, 1954, 1981) which makes it potentially vulnerable to the eutrophication effects leading to oxygen deficiency. However, mixing in the Wadden Sea is very effective in preventing stratification and no severe, long-lasting oxygen depletion has been observed until now (Tijssen & Van Bennekom, 1976; Hoppema, 1991).

3.3. Other changes in the carbon cycle

Eutrophication directly affects the North Sea ecosystem but calls for responses in other carbon reservoirs as well. Changes that are treated here may be either related to eutrophication, or are being caused by other anthropogenic activities. The line that divides natural and humanly induced changes is hard to draw, because of high variability in the system.

3.3.1. Deposition and transport

Due to eutrophication there is an excess production of organic matter, which is occurring in a short time span as evidenced by plankton blooms. Part of the excess primary produced organic matter is incorporated in increased algal biomass, part in higher trophic levels. Another part of this organic matter escapes the food chain as detritus (POC) or as DOC. After several cycles of sedimentation and resuspension a part of the excess POC will be permanently deposited in one of the deposition areas of the North Sea, mainly the Skagerrak-Kattegat-Norwegian Channel. By this mechanism extra carbon is removed from the system which would otherwise be part of the seawater-atmosphere system and thus would have led to a higher atmospheric carbon content. This deposition mechanism is particularly effective in the North Sea because eutrophication effects are mainly confined to the coastal area and the general circulation in the North Sea drives the coastal water masses to the main depo-centre.

In addition to deposition the export of suspended particulate carbon to the North Atlantic ocean is also expected to increase. In this way extra refractory carbon will end up in the oceanic pool. It is believed that through enhanced production and deposition the continental shelves of the world are an important additional sink for the anthropogenically increased atmospheric CO₂ (Walsh, 1984; Baes et al., 1985).

The possibly increased phytoplankton excretion due to eutrophication (accompanying enhanced primary production) will likely result in higher DOC concentrations in the coastal waters and

ultimately more DOC will be exported from the North Sea to the North Atlantic via the prevailing water transport route (section 2.3), adding to the refractory oceanic DOC pool. A possibly higher DOC concentration in the North Sea is difficult to quantify for several reasons. DOC data for the North Sea are incomplete, no time series is available and comparing recent results with older ones is difficult because through the last decades the determination of DOC changed. Moreover, superimposed on the possible in situ organic carbon enhancement the organic carbon brought in the coastal regions by river discharges is also thought to have changed. No data set is available to evidence this, but Meybeck (1982) observed organic C concentrations two to four times greater in some European rivers than in rivers in less populated areas. For POC (i.e. primary produced material) a similar mechanism exists (see above), with similar drawbacks. For the fresh water from the IJsselmeer, discharging into the western Wadden Sea no increase of POC was found from the 1950's to the 1980's, but this may be due to the use of different methods of determination (Cadée, 1984; Dankers & Laane, 1983). The river Rhine showed a high organic carbon content due to heavy pollution in the fifties and sixties (IAWR, 1986/ 1987; RIWA, 1984/1985) but since the 1970's a decreased load was measured. However, POC and DOC in the Rhine (Eisma et al., 1982), and also DOC in other estuaries, like the western Wadden Sea (Duursma, 1961; Cadée, 1982) and the Ems, Weser and Elbe (Ittekkot et al., 1982; Laane, 1980) behave conservatively, i.e. the mainly refractory material will eventually leave the North Sea unaltered to the North Atlantic ocean. Interfering with this simple conclusion is that accompanying the organic C enhancement is an increased input of inorganic carbon due to the oxidation of organic carbon already in the river reaches (Meybeck, 1982; Kempe, 1984). For the Rhine Kempe (1982a) found an increasing $p\text{CO}_2$ until 1972 attributed to organic pollution, indeed indicating an enhancement of inorganic carbon discharge.

3.3.2. Organic wastes

Organic wastes are introduced in the marine environment as sewage sludge by dumping from ships or by pipelines. Clearly, also with river water organic wastes will end up in the coastal regions. The composition strongly differs from place to place. The effects of organic wastes bear strong resemblance to those of eutrophication, in fact they are a form of eutrophication, because sewage sludge is a source of nutrients as well. The organic matter in wastes may act as a food source for plankton or bottom fauna. In the Thames estuary, which is a disposal site, no adverse effects on bottom fauna were observed, and possibly faunal enrichment occurred (ap Rheinallt, 1988). At disposal sites zooplankton biomass may also be high.

A recognized potential effect of organic waste dumping in the marine environment is the disturbance of the oxygen balance, caused by degradation. In Fig. 3.3 the effect of an increasing organic matter load is shown. Eventually, anoxia will develop and this will lead to a lifeless seafloor (left in Fig. 3.3). The occurrence of oxygen depletion will depend on the rate of dilution and dispersion (ap Rheinallt, 1988).

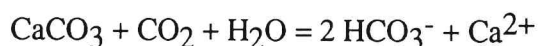
Effects of organic pollution should be considered compared to the naturally produced organic matter in situ. For a relatively small area such as the Wadden Sea organic waste input is relatively small compared with in situ primary production and North Sea input of organic matter (Essink & De Wolf, 1978). For the much larger North Sea this will certainly be the case as well. This means that

adverse effects of organic pollution are of local nature. Eutrophication-like effects were observed in the German Wadden Sea, where algal mats were found near places with domestic sewage loading (Reise, 1984). Under these mats anoxia developed, which led to an impoverishment of the bottom dwelling fauna. In the Dutch Wadden Sea a local decline in macrobenthos was found as a consequence of organic wastes (Essink, 1978).

In analogy to eutrophication it is the topographical and hydrographical setting of the German Bight that makes it also vulnerable to organic waste input. Indeed, negative effects were observed on the bottom fauna (Rachor, 1980), but here these changes were probably a combined action of sewage and eutrophication due to increased nutrient loading of the river Elbe. In 1983 the dumping of sewage in the German Bight ceased.

3.3.3. Changed carbonate chemistry

There are several solid carbonates present in the marine environment, in suspended matter and in the sediments. Calcite, aragonite and vaterite are different crystal forms of pure CaCO_3 . Minor amounts of Ca-ion can be replaced by other ions. Dolomite, with the formula $\text{CaMg}(\text{CO}_3)_2$, also occurs in the sediments. In addition there is magnesian calcite, which is a solid solution of MgCO_3 in calcite with up to 28 mol % MgCO_3 (Pytkowicz, 1983). It occurs in shells and skeletons of marine organisms. The formation of carbonates in the marine environment is largely a biologically mediated process, where mainly calcite and aragonite are formed and vaterite is found only in small quantities, for example in coccoliths (Pytkowicz, 1983). Despite the high supersaturation of CaCO_3 (calcite and aragonite) in surface seawaters inorganic precipitation seldom occurs. Solubilities of carbonates increase with amount of Mg incorporated, thus magnesian calcites with high Mg content are the most soluble. Solubility is dependent on the pCO_2 . High pCO_2 enhances the solubility, which is evident from the dissolution equilibrium of CaCO_3 :



By this reaction one molecule of CO_2 is hydrated and ionized simultaneously with the dissolution of CaCO_3 . Due to the increased atmospheric level of CO_2 (and the pCO_2 in seawater) more CaCO_3 is redissolved. This process causes a CO_2 uptake as well and thus is a sink for part of the excess atmospheric CO_2 . The CaCO_3 involved in this process will mainly be the more easily soluble magnesian calcites with high MgCO_3 content.

Not only the increased atmospheric CO_2 level causes an enhanced dissolution of carbonates. Increased primary production due to eutrophication and increased mineralization of organic matter attendant upon it will cause on average higher pCO_2 levels in mineralization periods and this will in turn cause extra carbonate dissolution (Baes et al., 1985). It is expected that the effect of the latter process will be greater than of the general atmospheric pCO_2 increase, since the pCO_2 enhancement due to mineralization is superimposed on the general pCO_2 increase.

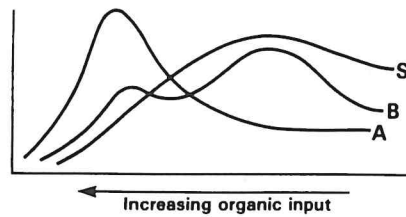


Fig. 3.3: Diagram of changes in species number (S), biomass (B), and total abundance (A) along a gradient of increasing organic input (taken from Rheinallt, 1988).

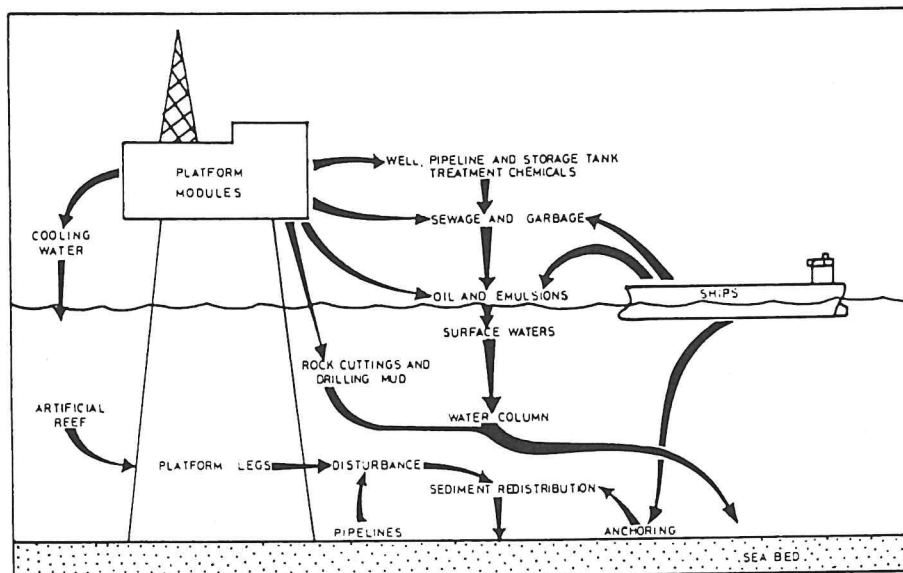


Fig. 3.4: Discharges and sources of disturbance arising from offshore installations and associated activities (from Dicks et al., 1988).

A third case of the above principle is related to the estuaries. River water generally has a very high $p\text{CO}_2$, up to thousands of ppm, and is undersaturated with respect to calcite (Kempe, 1982a). Therefore, rivers have a huge potential to buffer their high $p\text{CO}_2$ with marine carbonates during the mixing with seawater in the estuary. That is, when marine carbonates are available, otherwise degassing of the CO_2 will occur. Additional carbonate dissolution in the estuary may result from a considerably enhanced $p\text{CO}_2$ when river water and seawater with different $p\text{CO}_2$ values meet (Kempe, 1982b). A non-conservative behaviour of free CO_2 and thus higher $p\text{CO}_2$ arises due to non-linear rearrangements within the CO_2 -system as a cause of salinity changes (Mook & Koene, 1975; Whitfield & Turner, 1986). By this process, called mixing corrosion, even river water that is supersaturated with respect to CaCO_3 can cause dissolution of carbonates. Kempe (1982b) showed that the buffering of riverine CO_2 with marine carbonates is effectively occurring in the estuaries of some German rivers, such as the Elbe. The Rhine has a corrosion potential as well (Kempe, 1982b). It is evident that on top of this a further $p\text{CO}_2$ increase in the estuary or river due to an increased mineralization of organic matter would enhance the corrosion potential of the estuary and prevent more CO_2 to escape to the atmosphere. Therefore, the estuaries of rivers with a high load of anthropogenic organic matter form an extra sink in the carbon cycle. In the Rhine changing $p\text{CO}_2$ values were found related to pollution (Kempe, 1982a; see section 3.3.1.) which means that in its estuary the natural CO_2 sink will be enlarged.

3.3.4. Miscellaneous effects

Human activities cause enhanced inputs of atmospheric material to the seawater (Preston, 1989). Since the continental shelves are mostly bordered by large population centres the impact of atmospheric deposition on shelf waters is larger than on the more remote oceanic waters. Among the atmospheric inputs are many metals, but also N and P. The atmospheric load for the southern North Sea was estimated at $1000 \text{ kg.km}^{-2}.\text{y}^{-1}$ for N and $45 \text{ kg.km}^{-2}.\text{y}^{-1}$ for P (Anonymous, 1985). It is unknown what part of this figure is of anthropogenic origin. In the central and northern North Sea this will probably be somewhat less. For P the contribution is very small compared to other, natural and anthropogenic, sources, while the atmospheric N input is of some importance (Nelissen & Stefels, 1988). The contribution of atmospherically derived N to the seawater concentration may amount to 5% in the German Bight and 13% in the central North Sea (Anonymous, 1985). The difference between these two is caused by the dominating riverine N load in the German Bight. Because in the northern North Sea the phytoplankton growth is N-limited (Bauerfeind et al., 1990) the atmospheric N contribution does have a eutrophying effect by increasing phytoplankton production. Direct N_2 -fixation from the atmosphere by algae is on the other hand not a significant contribution to the atmospheric input (Brockmann et al., 1988). Subsequently, the whole line of events up to increased deposition of organic matter (as treated in section 3.3.1) is thought to occur, which renders an extra carbon sink for the North Sea. Along the Dutch coast phytoplankton growth is probably P-limited (Veldhuis et al., 1987) and considering the very small atmospheric P input the

effect is negligible.

Fisheries represent an important direct human impact on the North Sea ecosystem (Heessen, 1988). The North Sea is heavily exploited, in a way that the composition of fish stocks is definitely determined by the fisheries. Intensive fisheries resulted in fish stocks that are dominated by young species. The mean age stays low since by heavy exploitation the fishes will be caught before they can become old. Through this practice, however, fish production is relatively high. The total annual catches in the North Sea in recent years amounted to about 2.5 million tonnes, which is lower than in the seventies but higher than before the seventies. It is estimated that annually about 25% of the total fish biomass is caught. In terms of carbon the total fish catch is only $1.7 \cdot 10^{11} \text{ g C.y}^{-1}$, small compared to other carbon sinks. Moreover, ultimately when fishes are eaten the fish-carbon will be respired and returned to the atmosphere, so fish-carbon removal represents no net effect whatsoever on carbon cycle level.

By the use of beamtrawls with tickler chains fisheries cause massive damage to the benthos of the North Sea (e.g. Bergman et al., 1990). The species composition has probably changed due to this. On carbon cycle level these changes are less clear, but probably negligible.

The influence of temperature on the carbon cycle should be considered, since it is a parameter of prime concern in an anthropogenically disturbed carbon system. This is due because the atmospheric temperature (and with it the temperature of the oceans) is supposed to rise as a consequence of the greenhouse effect. A rise of seawater temperature from 1962 to 1983 amounting to 1.08°C was already observed in the German Bight (Gerlach, 1988), but this was caused by an increase of anthropogenic heat discharges in the river water of the Elbe (thermal pollution). Temperature has an important influence on almost all biological processes, hence also on phytoplankton growth (Eppley, 1972). Translating this to the level of community biomass and production is, however, impossible with the present state of knowledge. Phytoplankton standing stocks are the resultant of both growth and consumption rates (death, grazing etc.). For example, temperature might trigger or intensify the grazing by zooplankton, which entangles the size of the phytoplankton standing stock in the intricate foodweb. A probable effect of a temperature rise is a shift in species occurrence (personal communication, R. Riegman). The overall effect in terms of carbon fluxes seems to be small. The start of the growing season in the Wadden Sea is not correlated with temperature (Cadée & Hegeman, 1986), neither is this the case in the southern North Sea (Gieskes & Kraay, 1975). Bottom fauna is very sensitive to temperature (Beukema, 1990; De Vooys, 1990), a rise in temperature will cause a species enrichment, but the effects on the size of the total biomass are still unclear. The effect of increasing temperature on the inorganic carbon content (TCO_2) of seawater is well known. In warm water TCO_2 is lower than in cold water. With an expected rise of temperature as a consequence of the greenhouse effect the North Sea, as part of the shallow oceans, would lose CO_2 to the atmosphere. In the German Bight (and possibly in some other coastal areas under the influence of thermally polluted river water) the surface area, which shows an increased seawater temperature is too small to be a significant CO_2 source already.

Another phenomenon related to the seawater chemistry is the uptake capacity for excess CO₂. This is essentially CO₂ derived from fossil fuel burning. When CO₂ is released into the atmosphere it is partly redistributed to the seawater and the pCO₂ in seawater roughly approaches that of its atmospheric counterpart. The increase from the preindustrial 270 ppmv to the present day ~350 ppmv caused a concurrent increase in TCO₂ concentration of about 0.05 mol.kg⁻¹. A fractional change in pCO₂ causes a smaller fractional change in TCO₂. This is expressed in the buffer factor:

$$B_f = (d\text{TCO}_2/\text{TCO}_2)_{\text{SW}} / (dp\text{CO}_2/p\text{CO}_2)_{\text{atm}}$$

which roughly equals 0.1 in surface seawater. This means that when the atmospheric pCO₂ would increase 10% TCO₂ would increase only 1%. Unfortunately, B_f decreases when more CO₂ is absorbed and pH decreases (Keeling, 1973) and thus the uptake capacity for excess CO₂ will decrease. The exact extent to which this process will occur is uncertain because some other processes might counteract, like faster weathering on the land, enhanced photosynthetic activity in the sea and dissolution of shallow carbonates (Pytkowicz, 1983). For the North Sea the prerequisites for all of these counteracting processes exist: pCO₂ changes in the Rhine have been observed (Kempe, 1982a) which would enable faster weathering; enhanced primary production occurs in eutrophicated areas (section 3.2) and carbonate sediments are present in parts of the North Sea.

Eutrophication may indirectly also affect the uptake capacity of seawater for excess CO₂. An effect observed in the coastal North Sea probably caused by eutrophication is a shift in phytoplankton species composition, with silicate-forming diatoms making room for other species like flagellates. The proportion silicate-forming to carbonate-forming and hence the alkalinity will change, which in turn will affect the ability of the seawater to take up atmospheric CO₂. However, the typical time scales for this effect are in the order of tens of years.

Assuming sea level rise (SLR) to be largely a natural process till now, human impact on this phenomenon is dawning. An additional rise in sea level, which could already have started, is expected as a consequence of greenhouse warming. A doubling of atmospheric CO₂ in the next century could cause a rise of 80 cm (Robin, 1987). SLR has relatively most influence on estuaries and tidal areas such as the Wadden Sea. As with many future changes concerning anthropogenic impact on natural systems deliberation on the consequences is highly hypothetical (Brouns, 1988; Eisma, 1988). Intertidal areas in the Wadden Sea are deposition centres for silt, and a sink in the North Sea carbon cycle. Due to SLR part of them together with other tidal flat areas might disappear (Misdorp et al., 1990). However, at other locations an enhanced import of suspended silt (caused by the larger water volume entering the Wadden Sea) sedimentation might increase. It is impossible to predict the position of the balance between these two processes, and thus if silt (and carbon) is gained or lost. The ecosystem will respond to changes associated with SLR (Brouns, 1988; Misdorp et al., 1990). For example, the increased influx of suspended matter will be beneficial to the bottom fauna. It should be realized that these thoughts are highly speculative and certainly not quantifiable, as they

are depending on many assumptions. They merely serve to signal changes to be expected.

Apart from the effects on the North Sea carbon cycle treated so far many more anthropogenic activities exert influence on the system. They all have in common that their impact is local and their overall influence on the carbon budget is (probably) negligible.

Dredging of sediments in harbour mouths removes organic carbon from the marine environment. However, for about one third the material is returned to the sea on a dumping site and for about two thirds it is disposed on land (Förstner & Salomons, 1988). On land the organic fraction will eventually be oxidized, returning CO₂ to the atmosphere.

Micropollutions occur in the North Sea and the Wadden Sea at a relatively high level (Wolff, 1988; Ernst et al., 1988; Duinker, 1988; Salomons, 1988), and these include heavy metals and organochlorines like PCB's. They find their origin in river water, dumping, atmospheric deposition and waste incineration. Adverse effects of these compounds on individual species have been demonstrated (e.g. Zitko, 1988; Reijnders, 1988), but on ecosystem level the effects are very difficult to account for, and no report is known about this issue. Ultimately, almost all organic pollutants will be degraded, although this could take many years.

More or less the same could be said about oil pollution. The total input of petroleum hydrocarbons in the North Sea in 1986 was 107-165·10⁶ kg (Bedborough & Blackman, 1986), which is in itself a small carbon source compared to the natural reservoirs. Oil production at sea is a source of disturbance in many ways (Fig. 3.4). The effects of oil pollution on organisms will in general have disappeared after a period of time (Wolff, 1988), which may however last for some years. Particularly notorious and well known to the public eye are oil spills by tankers and platforms causing vast mortality among birds. Biological impact from platforms is well established (Mulder et al., 1988; Daan et al., 1990). It is estimated that the ca. 200 oil rigs influence ca. 0.1% of the total North Sea area (Dicks et al., 1988).

Other human impact on the sea comes from flotsam and jetsam (Nassauer, 1981; Hartwig et al., 1985), acid waste water (Wienecke, 1982), radioactive substances (Kautsky, 1988), enhanced UV-B radiation (Hardy & Gucinski, 1989; Kramer, 1990) and waterworks, such as the dams in Zeeland and the closing of the Zuiderzee. As such their influences are generally detrimental. On carbon cycle level no quantification is possible, but the impact is still likely to be negligible.

3.4. Quantification of effects on the carbon cycle

Quantification is only possible to some extent and when it is the assumptions are large. However, it may be useful to get insight in the order of magnitude of the changes. All figures regarding the North Sea carbon cycle and the inferred changes are given in Table 3.1.

The primary effect of eutrophication is the raise of phytoplankton primary production and biomass. Taking the biomass increase in the German Bight from 9 to 37 µg C.l⁻¹ (Radach & Berg, 1986), i.e. an increase by a factor 4, to be representative for 5% of the North Sea (by volume, which might be an overestimation) the phytoplankton biomass increased by 5.6·10¹⁰ g C between 1962 and 1984.

The part of the primary produced organic matter that is deposited permanently will be assumed

Table 3.1: Summary of the North Sea carbon cycle. Units g C for reservoirs and g C.y⁻¹ for others. Given are figures, single values or ranges, taken from various authors and calculated to the total North Sea area. More specifics about them can be found in the text. The uncertainty ranges of the figures given in the second column are typically 20-100 %, where it is hard to indicate which belongs to which. This is caused by the generally poor coverage, high variation and extrapolation to the large North Sea area. References refer both to chapters 2 and 3.

		changes	period
advection import (NE Atlantic, Channel, rivers)			
TCO ₂	~1.5·10 ¹⁵		
POC	4.4-6.1·10 ¹²		
DOC	4.7·10 ¹³ (old values)		
advection export (NE Atlantic)			
TCO ₂	~1.5·10 ¹⁵		
POC	1.8·10 ¹²		
DOC	4.6·10 ¹³ (old values)		
reservoir size			
DIC	9.4·10 ¹⁴ (Pegler & Kempe, 1988)	+2.4·10 ¹³	1860-1990
DOC	4.4·10 ¹³ (Pegler & Kempe, 1988) or probably ~1·10 ¹⁴ according to recent DOC determination	+?	
POC	1.6·10 ¹³ (Eisma & Kalf, 1987a)		
of which			
phytoplankton	9·10 ¹¹ (Aletsee & Rick, 1988)	+5.6·10 ¹⁰	1962-1984
zooplankton	7.5·10 ¹¹ (De Wolf & Zijlstra, 1988)	?	
bacteria	1.6-3.2·10 ¹² ; 10-20% of POC (Van der Werf & Nieuwland, 1984)		
zoobenthos	2.5-5.3·10 ¹² (De Wolf & Zijlstra, 1988)	+2.3·10 ¹¹ +1.7·10 ¹¹ *)	1969-1984 1969-1984
fish biomass	6.5·10 ¹¹	+	
gross fluxes			
primary production	150·10 ¹² (Aletsee & Rick, 1988)	+~14·10 ¹²	~1930-1990
POC-sediment	15-50·10 ¹² ; 10-35% of primary production (Davies & Payne, 1984)	+	
water-atmosphere	4.3·10 ¹² (Pegler & Kempe, 1988)	+	
net fluxes			
deposition total	1-2·10 ¹²		
of which originates in situ	2-5·10 ¹⁰ (Eisma & Irion, 1988)	+2-3·10 ⁹	~1930-1990
CaCO ₃ -coccoliths	3.4·10 ¹¹ (Kempe & Jennerjahn, 1988)		
dumping	6.5·10 ¹² (Brockmann et al., 1991)	+6.5·10 ¹²	~1930-1990
oil pollution	1.1-1.7·10 ¹¹ (Bedborough & Blackman, 1986)		
atmosphere-water due to fossil fuel burning	~4.8·10 ¹¹	+4.8·10 ¹¹	1860-1990
water-atmosphere due to biogenic carbonate	<1.7·10 ¹¹	+<1.7·10 ¹¹	1969-1984

* biogenic carbonate by Wadden Sea shell-fish

to have increased concurrently with the increase of primary production. When 10% of the North Sea surface area is affected by eutrophication and thus supports an enhanced primary production the increase of the amount of annually buried carbon ($2\text{--}3 \cdot 10^{10}$ g C, section 2.4.4.) has been about $2\text{--}3 \cdot 10^9$ g C. It should be realized that this amount is withdrawn from the carbon cycle every year, in contrast with the enlarged phytoplankton biomass reservoir, which represents a changed state within the carbon cycle. As opposed to primary production there are no indications that the flux of biogenic carbonate to the sediments increased due to eutrophication.

A secondary effect of eutrophication observed in the western Wadden Sea was a doubling of the macrozoobenthic biomass (Beukema & Cadée, 1986). The present value of the biomass is about $40 \text{ g} \cdot \text{m}^{-2}$ (Dekker, 1989), which is a value also found in other parts of the Wadden Sea (see Dekker, 1989). Assuming this doubling to have taken place in the whole Wadden Sea, the German Bight, and some inshore British areas (about 5% of the North Sea surface area) this yields an organic carbon reservoir increase of $2.3 \cdot 10^{11}$ g C, or about 2.5 times the increase in phytoplankton biomass.

In the Wadden Sea the mollusc population extracts large amounts of calcium carbonate from the seawater. Beukema (1982) calculated this to be $156 \cdot 10^9$ g for all cockles on the tidal flats in the Dutch Wadden Sea. This figure should be multiplied with 3 to comprise all molluscs (Beukema, personal communication), with 2 to include subtidal areas, and again with 3 to cover the entire Wadden Sea. This yields $2.8 \cdot 10^{12}$ g CaCO_3 , equivalent to $3.4 \cdot 10^{11}$ g C per year that is extracted by the macrozoobenthos of the Wadden Sea. According to Beukema & Cadée (1986) the shell production roughly doubled between 1969 and 1980/4, meaning that annually about $1.7 \cdot 10^{11}$ g C is extracted more than before. About 3/4 of the amount of shells in the Dutch Wadden Sea is removed by shell fishers. The withdrawal of carbonates is not just simply a sink in the carbon cycle. The removal of carbonate causes a shift in the equilibrium of the inorganic carbon system (section 2.1.2.) through which the concentration of dissolved free CO_2 increases. This will lead to an enhanced atmospheric exchange of CO_2 . Therefore, it is likely that accompanying this CaCO_3 removal from the seawater is an enhanced degassing of CO_2 to the atmosphere. The maximum amount of CO_2 that will be lost to the atmosphere in this manner will be about the same as the amount of CaCO_3 that is formed. On the other hand, CaCO_3 that will be incorporated into the sediments will partly redissolve via the reversed process. This causes undersaturation of CO_2 with a subsequent influx of CO_2 from the atmosphere. The time lag between these two processes is in the order of years to tens of years.

All removal processes quantified so far cause changing carbon fluxes several orders of magnitude smaller than the regular cycling of carbon like primary production ($150 \cdot 10^{12}$ g $\text{C} \cdot \text{y}^{-1}$) and advection of inorganic carbon ($\sim 1500 \cdot 10^{12}$ g $\text{C} \cdot \text{y}^{-1}$). The only substantial increase in reservoir size, that of the amount of DIC, is caused by the uptake of fossil fuel CO_2 that was released into the atmosphere. Compared with the anthropogenic release of carbon by the Netherlands ($50 \cdot 10^{12}$ g $\text{C} \cdot \text{y}^{-1}$) the anthropogenic modification of the carbon fluxes in the North Sea is quite small.

4. MODELLING THE NORTH SEA CARBON CYCLE

From field measurements an instant assessment of the parameter of interest is obtained. With a time series some more information is available but its overall value is still limited when one is interested in the consequences of the observed changes on other, dependent parameters or reservoirs. For the latter purpose a 'best professional judgment' can be made but the complexity of natural systems inhibits a thorough examination (Van der Meer, 1986). Alternatively, major progress has been made with the construction of ecosystem models, which contain all important elements and their interdependencies represented by mathematical expressions (e.g. Fransz & Verhagen, 1985; Anonymous, 1985). With models the ecosystem as a whole can be studied and interconnections or feedbacks between processes which would otherwise stay obscured can become visible. Ecosystem models have the potential to detect or predict relations that would be hard to track without them. Yet one must remain cautious while interpreting model results. Ecosystem models are set up with a particular objective and with that objective only. Also they use certain initial values and boundary conditions that may not represent the real situation and assume certain processes to occur while other (possibly unknown) processes may in some situation be more important. Moreover, extrapolating to another situation (which is inherent to the objective of predicting) introduces uncertainties which in principle cannot be quantified. Consistency of the outcomes then is a minimum requirement. However, at this level using model results in principle is a matter of believe.

As we saw in chapter 3 changes have been taking place in the North Sea ecosystem, whereas scientists are still very cautious to ascribe them to eutrophication. Model calculations could give additional indications as regards to the role of increased nutrients on the North Sea ecosystem. Moreover, the model can be fed with even higher nutrient concentrations and from that the future effect on phytoplankton production and biomass and on sedimentation of organic material may appear. These model runs furthermore serve as a basis for assessing the role of DOC when its input concentration is increased to the level as expected according to the new DOC determination.

4.1. The North Sea model ERSEM

The European Regional Seas Ecosystem Model (ERSEM) is presently being developed by the BEWON-group (Applied Scientific Research NIOZ) in cooperation with scientific groups from other EC countries. A scheme of all flows through the model is shown in Fig. 4.1. It should be noticed that the boxes 'sea mammals' and 'higher trophic levels' are not yet incorporated at this stage of the model development, but considering the relatively small material flows to and from these reservoirs combined with the main objectives of the present study, being the relations between nutrients, phytoplankton and DOC, this will have only a minor influence on the outcomes.

An extensive description of ERSEM is beyond the scope of the present report. Here it is confined to mention general features of the model. For a thorough description one is referred to Baretta & Ruardij (1988) and EON(1988) in which the two precursors of ERSEM are extensively treated. The basics of these models are essentially the same.

For the present study an unstratified box of water is considered, such as can be found off the Dutch coast, although the model also has the possibility for simulating a stratified water column.

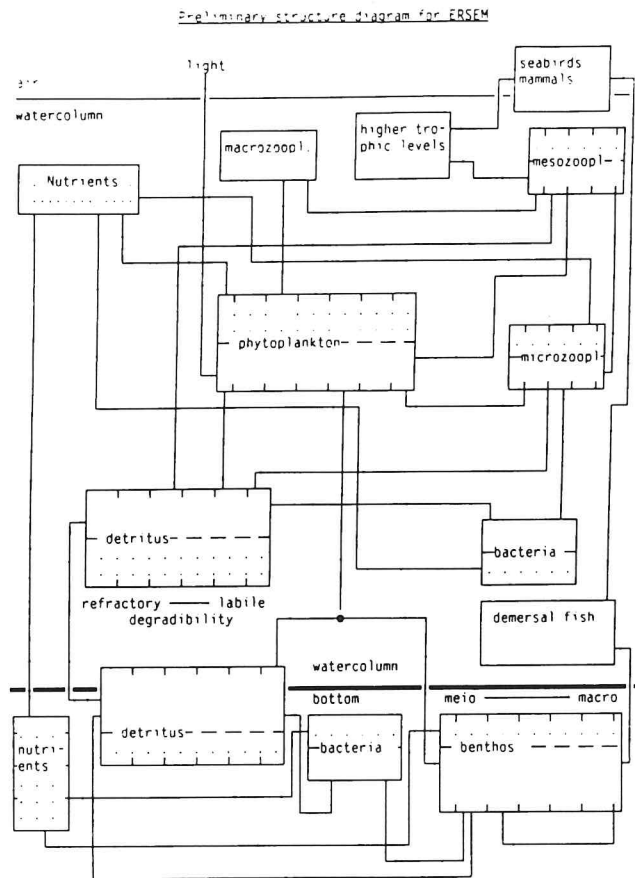


Fig. 4.1: Scheme showing the carbon and nutrient flows in ERSEM.

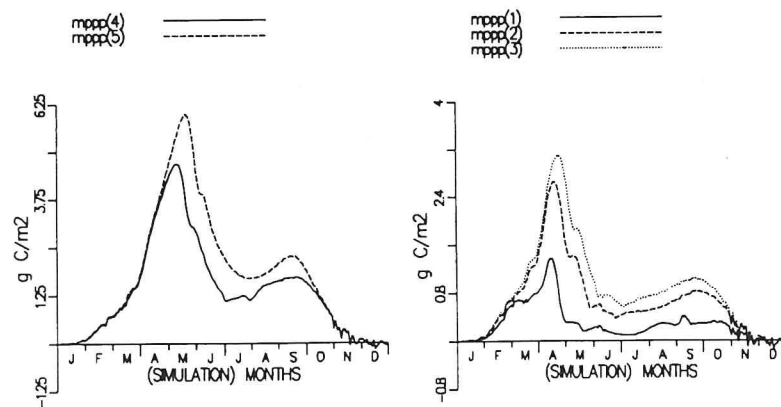


Fig. 4.2: Seasonal cycles of primary production (g C.m^{-2}), diatom and flagellate biomass (mg.m^{-3}) and nitrate (mmol.m^{-3}) simulated with ERSEM.

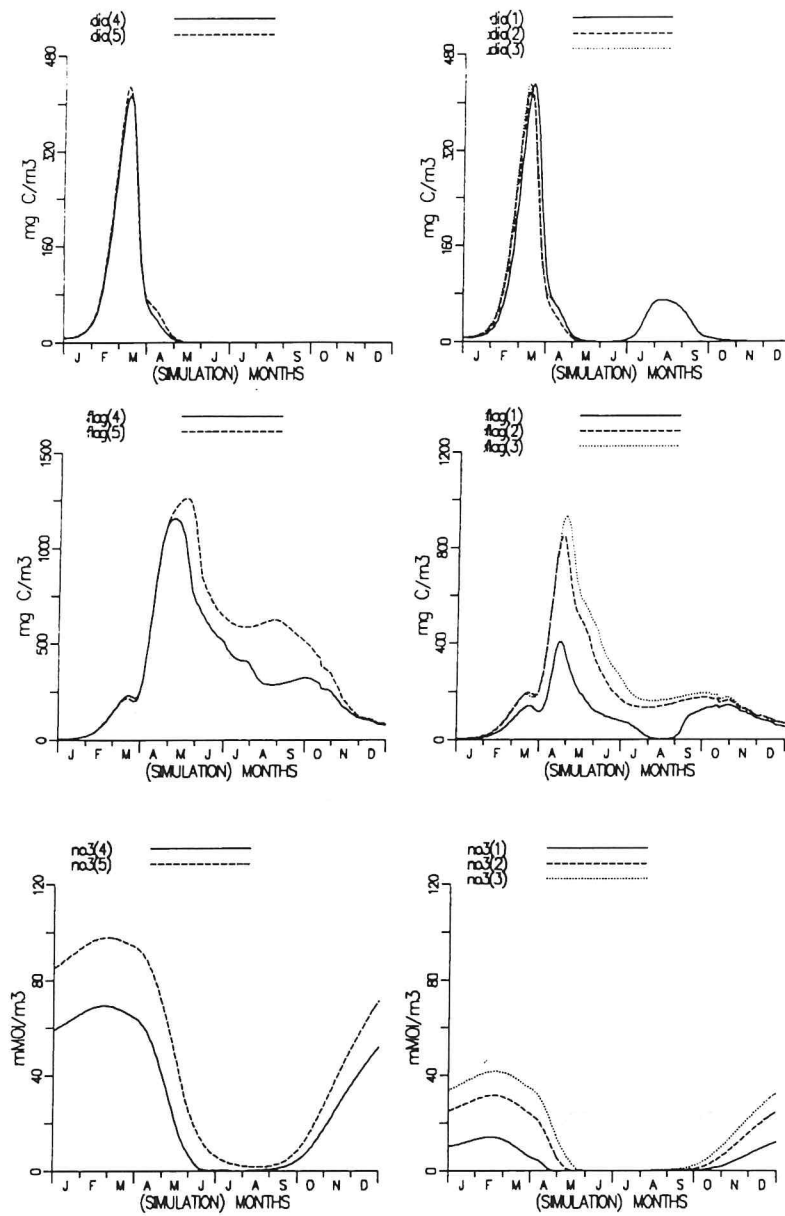


Fig. 4.2: (continued)

Table 4.1: Nutrient inputs to the model runs for different situations, corresponding with three periods and certain salinities (S).

	S=32	S=33	S=32	S=33	S=32
	1930	1986		fictitious	
PO4-P	0.62	1.10	1.37	2.25	3.10
NO3-N	11.4	24.9	33.6	59.2	85.1
NH4-N	1.66	2.61	3.83	2.61	3.83
Si	17.6	14.1	18.1	14.1	18.1
situation	1	2	3	4	5

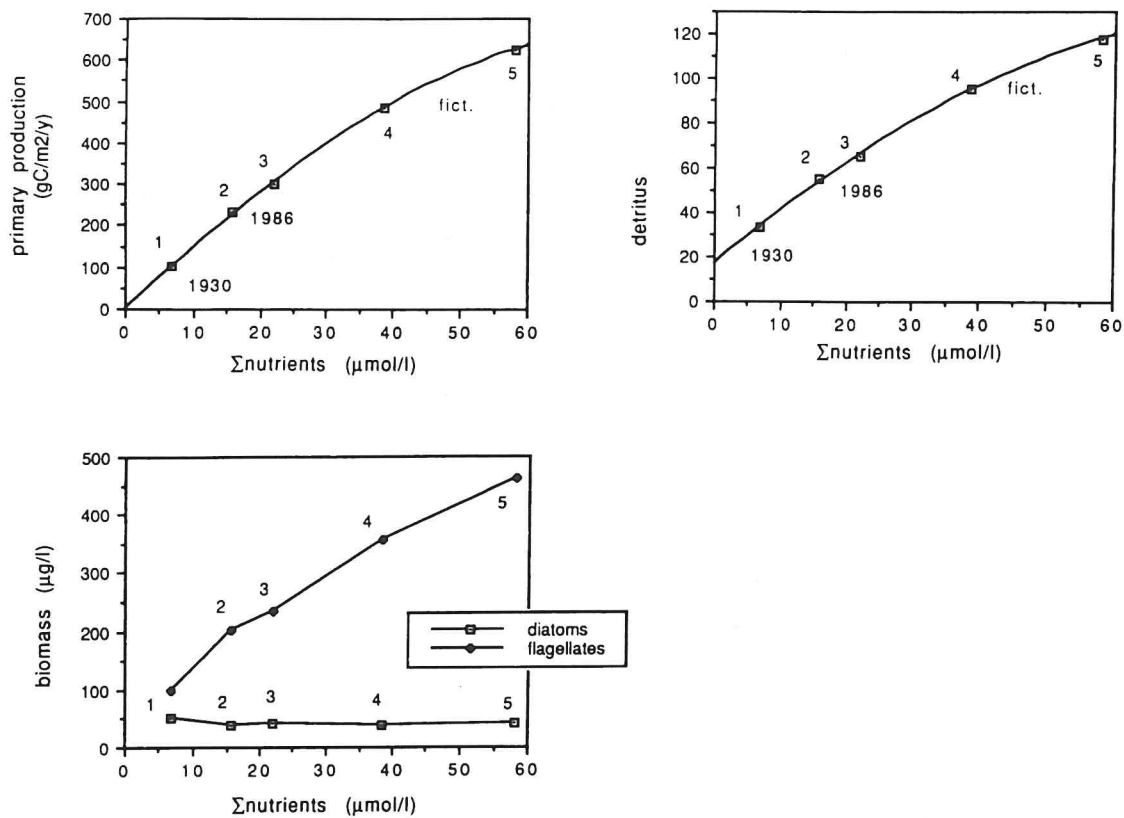


Fig. 4.3: Graphs showing the influence of eutrophication, expressed by the quantity $\Sigma\text{nutrients}$, on primary production, phytoplankton biomass and detritus for five different nutrient situations (see Table 4.1).

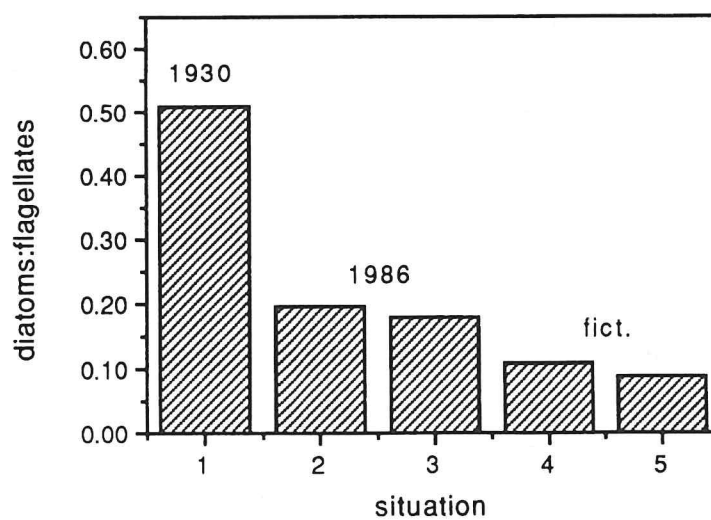


Fig. 4.4: The ratio diatoms to flagellates for five different nutrient regimes (see Table 4.1), corresponding to the situation in 1930 (1), 1986 (2 and 3), and a fictitious one (4 and 5).

Furthermore, no water and material transport to and from this box are as yet incorporated in the model. This necessitated locating the box not too close to the coast, for transport terms contribute at a maximum inshore. Model simulations were performed for three different nutrient (P, N, Si) situations in the southern North Sea, corresponding to ~1930 (before the start of eutrophication), 1986 and a fictitious situation with three times enhanced river concentrations of N and P. The initial nutrient concentrations that were fed to the model, representing the situation at 1 January, were obtained in the following manner. With the values of the nutrients in the Strait of Dover from 1961 and the values for the Rhine in 1932, 1986 (Van Bennekom et al., 1975; Van Bennekom & Wetsteijn, 1990) and fictitious (x3) values salinity-nutrient relationships were calculated, presuming that off the Dutch coast the water is composed of these two end-members of mixing. Hence, nutrient values for S=32 and S=33 were calculated which should reflect the fact that such salinities are generally found sufficiently far offshore as to comply with the condition that transport terms be negligible in comparison to in situ nutrient uptake and release rates.

As regards to DOC ERSEM assumes that only a labile fraction is formed after degradation of phytoplankton, bacteria and microzooplankton. DOC develops through lysis of the plankton, which dies mainly after nutrient stress. The only other degradation pathway is through particulate detritus which is only very slowly remineralized (refractory). The ratio labile DOC to refractory detritus is arbitrarily set to 1:1. In the original concept of ERSEM no standing stock of DOC was formed, for all labile DOC was assumed to be taken up by the pool of bacteria instantaneously. This model approach was prompted by the lack of knowledge about production and consumption processes of DOC. For the first suite of model runs the original model set-up was used.

However, according to recent insights a certain DOC fraction exhibits a finite turnover time (Ducklow et al., 1990). Therefore, before doing the second suite of model runs ERSEM was modified to incorporate a first order rate constant of DOC consumption at the same time introducing a DOC standing stock. The rate constant was varied to investigate the effects on other pools and processes.

The model simulations that are presented here have to be considered against the background that, although the basis of the model is firm due to many years of experience at the NIOZ, ERSEM is not yet in a definite stage. For example, transport terms were neglected. Results should be interpreted to indicate the trends only, actual values are not necessarily significant.

4.2. Results and interpretation

Because in the model there are processes such as nutrient exchange between the bottom and the water column that require equilibration times longer than one year, a number of annual cycles were run before the definitive simulation experiments were conducted. The different situations that were simulated as expressed by the nutrient inputs to the model are shown in Table 4.1. The simulated seasonal cycles of some selected variables at different nutrient regimes (Fig. 4.2) are in general in accordance with the trend obtained from field measurements. We can see that there is an early diatom peak followed by the flagellates, while total primary production has its peak in April/May depending on the initial availability of nutrients, such that with increasing amounts of nutrients the peak shifts to later in this period. The absolute value of the simulated annual primary production in 1986 agrees

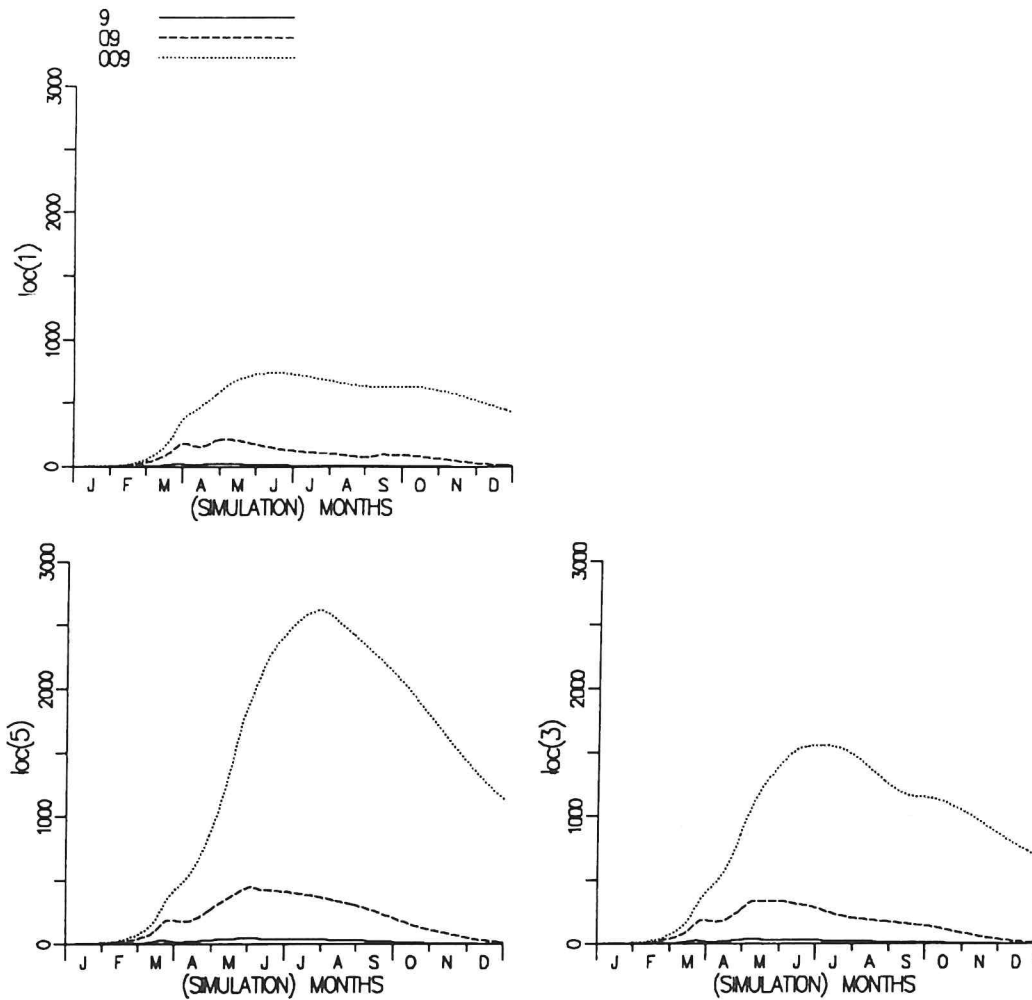


Fig. 4.5: Simulated seasonal cycles of LOC as a function of the turnover rate ($k_L = 9, 0.09$, and 0.009). The three graphs were obtained under different nutrient regimes (situation 1, 3, 5, see Table 4.1).

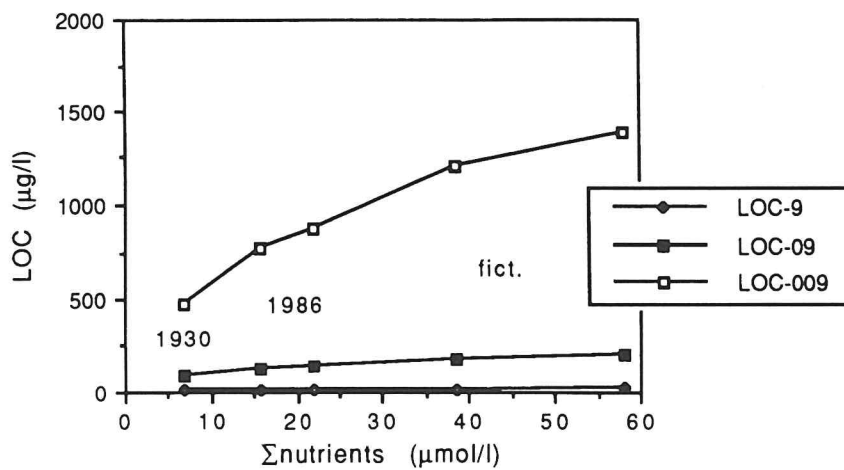


Fig. 4.6: Graph showing the influence of eutrophication on the LOC standing stock for three different turnover rates ($k_L = 9, 0.09, 0.009$).

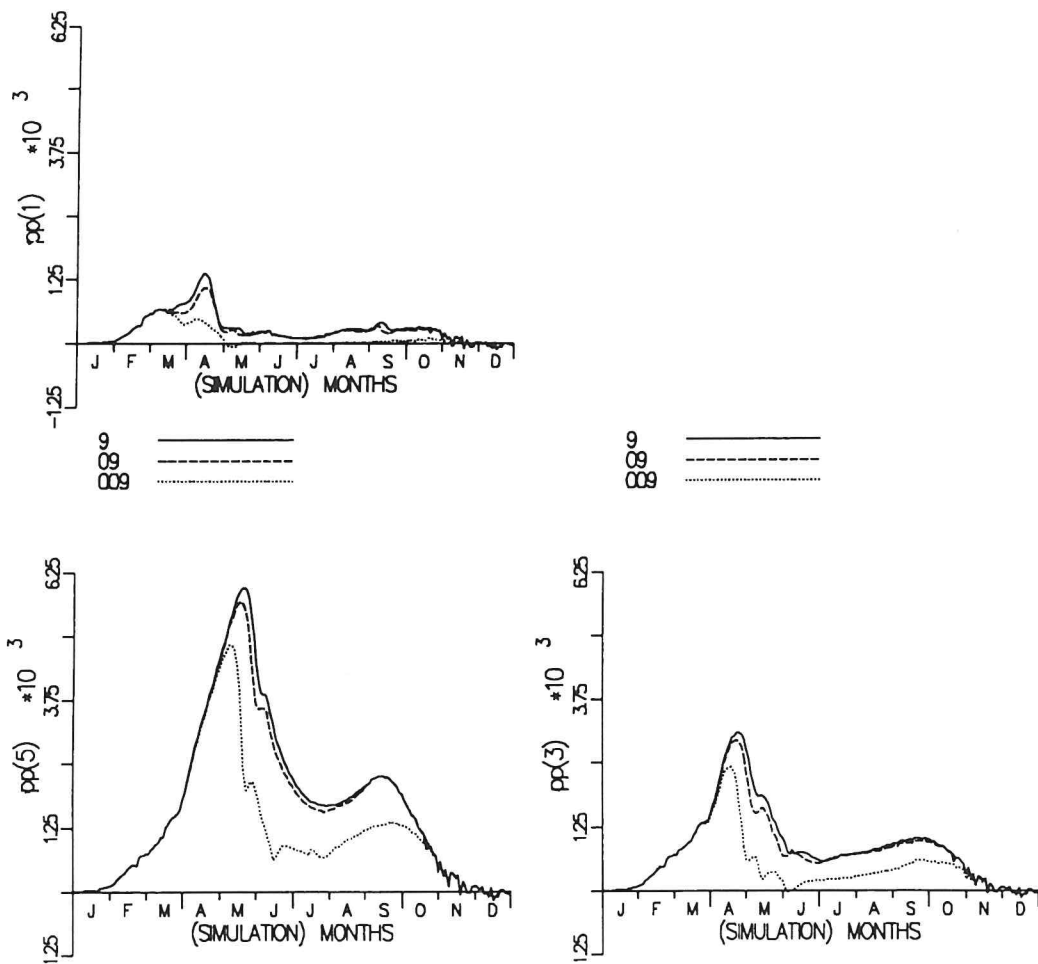


Fig. 4.7: Simulated seasonal cycles of primary production with three different turnover rates for LOC used ($k_L = 9, 0.09, 0.009$). The three graphs were obtained using different nutrient regimes (situation 1, 3, 5, see Table 4.1).

quite well with typical values found in the field. The diatom peak appears to be relatively independent on the nutrient concentrations reflecting that for this kind of phytoplankton silicate is limiting (the silicate concentration did not change much for the different runs). Of the nutrients nitrate is depleted during most of the summer period, even in runs with large initial nutrient availability.

From situation 1 through 5 (Table 4.1) all nutrients inclined simultaneously. As a (rather arbitrary) measure of eutrophication the sum of all nutrients (annual means, silicate excepted) was used. It appeared that the annual primary production as well as the amount of detritus increased strongly with increasing nutrient concentrations, i.e. with eutrophication (Fig. 4.3). The model results say that from ~1930 till the 1986 the annual primary production increased about two to three times (Fig. 4.3). The flagellate biomass also increased as a consequence of eutrophication, however, the diatoms were unaffected. A major effect of eutrophication therefore appears to be a shift in relative abundances of diatoms to flagellates (Fig. 4.4). It can also be deduced from these simulation results that as a consequence of eutrophication more organic matter may be buried after being transferred to the detritus pool. A general conclusion of these ample simulations is that ERSEM is producing realistic and reproducible output, which agree with field observations.

In the real North Sea there is a standing stock of DOC consisting of two pools: 1) a large portion of inert (refractory) matter, and 2) a labile reactive fraction. In the model we only consider the reactive portion, which will henceforth be called LOC (labile dissolved organic carbon). The amount of refractory DOC, which is dependent on the salinity and for our case in the order of $1000 \mu\text{g.l}^{-1}$, should be added to the simulation results to get comparable figures. The model was run again but now modified to have three different turnover rates (k_L) for LOC. The seasonal cycle of LOC is shown in Fig. 4.5 in three different graphs, representing three different nutrient regimes. The three curves in each graph depict three k_L values (units day^{-1}). The largest k_L value approaches the case when LOC is immediately transferred to the bacteria pool, i.e. LOC values stay very low. For all three nutrient regimes LOC gets larger when k_L was made smaller. Such higher LOC values do obviously agree better with the real situation. When k_L is 0.009 d^{-1} , which may however be rather low, LOC values were obtained that, upon addition of the large refractory portion, would amount to DOC values in the North Sea. In Fig. 4.6 it is shown that the standing stock of LOC increases as a consequence of eutrophication; this holds for all three k_L values used. The conclusion as drawn before that primary production and other variables respond positively to eutrophication stays unaffected by the introduction of a slower rate for LOC degradation.

The introduction of a substantial LOC pool through finite turnover rates for LOC causes some serious changes among the other simulated variables in the model, for example primary production (Fig. 4.7). These changes refer to constant nutrient situations. The deviation becomes particularly apparent some time after primary production has started, i.e. when LOC is being formed. The same trend is seen in all three nutrient regimes. Not only primary production but also detritus and diatom and flagellate biomass declined dramatically as a consequence of an enhanced LOC standing stock. On the other hand, the mean nutrient concentrations did not change much.

Comparing the model output for $k_L=9$ and $k_L=0.009$ the annual primary production is 50-100% lower in the latter case, while for the amount of detritus this is 20-30% (Depending on the nutrient regime). Reversing the argument, for obtaining a realistic standing stock for LOC using a

realistic value for k_L (which will be somewhere between these two extremes) a larger primary production would be needed. This suggests that the primary production values that are commonly found would be possibly too low. It remains to be decided on the basis of further research how the apparent discrepancy between LOC and primary production levels can be solved.

It is evident that the introduction of a high LOC standing stock in the model seriously disrupts the present-day insights into the functioning of the North Sea ecosystem. The subcycle of DOC appears to be intimately connected with primary production and detritus formation, which in turn determine the magnitude of the permanent sink in the North Sea carbon cycle. It should furthermore be kept in mind that ERSEM presumes only labile DOC to be formed from the degradation of organic material, whereas in real perhaps also some refractory DOC will emerge. However, because the knowledge about this process is insufficient it was until now not incorporated in the model. This refractory DOC will be transported with the water masses and may be a possible sink in the North Sea carbon cycle. Therefore, there is an urgent need to investigate the position of DOC in the carbon cycle of the North Sea.

5. METHANE CYCLING

Methane (CH_4) is a reduced form of carbon. Albeit the environments of the global reservoirs are generally oxidizing methane occurs in significant amounts. In the atmosphere it is the most abundant C-compound after CO_2 , the concentration currently being 1.7 ppmv in the northern hemisphere (Rasmussen & Khalil, 1986; Steele et al., 1987; Blake & Rowland, 1988), corresponding to an atmospheric reservoir size of 4600 Tg. The atmospheric methane concentration has been increasing at a rate of about 1% per year until the early eighties (Rasmussen & Khalil, 1981; Blake & Rowland, 1988; Steele et al., 1987).

Methane constitutes a separate, significant part of the global C-cycle, justifying its treatment separately in this report. Like CO_2 it is a true greenhouse gas, its infrared absorbing capacity per molecule being 21 times larger than for CO_2 (IGBP, 1990). In addition, the oxidation of CH_4 in the stratosphere yields water vapour and CO_2 (Crutzen, 1983), in this way newly producing two other greenhouse agents. In the troposphere methane oxidation in the presence of NO may give rise to ozone (O_3) (Crutzen, 1983), while in the stratosphere a potential positive effect of CH_4 is its reaction with Cl-radicals, thereby slowing down the O_3 destruction rate by these radicals.

5.1. Global budget

The major sink for methane is the troposphere, where it reacts with the hydroxyl (OH) radical and is converted to CO (Sze, 1977; Crutzen, 1983). Currently, the troposphere represents a sink of 400-600 Tg $\text{CH}_4 \cdot \text{y}^{-1}$, on an atmospheric reservoir size of 4600 Tg. The atmospheric lifetime based on the reaction of CH_4 with the OH radical is 8-12 years (Khalil & Rasmussen, 1990). The rise of atmospheric methane in turn is partly caused by a depletion of OH radicals (Khalil & Rasmussen, 1985), the other part being caused by increased (anthropogenic) methane emissions. Another minor sink for methane may be the soils.

There is a great number of sources of methane, comprised in a great number of constructed budgets (Table 5.1). In a budget analysis study Khalil & Rasmussen (1990) concluded that only two of these budgets (Khalil & Rasmussen, 1983 and Cicerone & Oremland, 1988) meet the requirements posed by the measured scientific data on atmospheric abundance, increase, and lifetime. Hence, taking the most recent budget as a reference it is noticed that the total source strength amounts to 535 Tg $\text{CH}_4 \cdot \text{y}^{-1}$ with a range of 371-880 Tg $\text{CH}_4 \cdot \text{y}^{-1}$. This range leaves more than adequate room for balancing the estimated range of sinks, indicating that large uncertainties are involved. The oceans have been estimated as a source of 5-20 Tg $\text{CH}_4 \cdot \text{y}^{-1}$ (Cicerone & Oremland, 1988), which represents only a very small part (<5%) of the total source strength.

5.2. Methane in the marine environment: Production, consumption and fluxes

The surface oceans are generally slightly supersaturated with respect to atmospheric methane (Lamontagne et al., 1971, 1973; Brooks & Sackett, 1973; Scranton & Brewer, 1977; Burke et al.,

Table 5.1: Estimates of methane emissions from various anthropogenic and natural sources: 1978-1988 (taken from Khalil & Rasmussen, 1980).

	Ehhalt and Schmitt (1978)	Donahue (1979)	Shep- pard et al. (1982)	Crutzen (1983)	Khalil and Ras- mussen (1983)	Blake (1984)	Seiler (1984)	Crutzen (1985)	Seiler (1986)	Bingemer and Crutzen (1987)	Cicerone and Oremland (1988)									
ruminants	100-220	160	100-220	160	90	60	60	120	70-160	115	70-100	85	60	60	70-100	85	70-80	75	65-100	80
rice paddy fields	280	280	140-280	210	39	30-60	45	95	149-189	165	30-75	53	120-200	160	70-170	120	18-91	54	60-170	110
biomass burning				60		30-110	70	25	25-110	68	50-100	75	20-70	45	55-100	78	30-100	65	50-100	55
landfills																	30-70	50	30-70	40
coal mining	8-28	18	16-50	33					30	30	34	34	35	35	35	35	35	35	25-45	35
natural gas flaring				50	20	20	40		20-30	25	33	33	30-40	35	0-35	18	25-50	45		
automobiles	1	1											1-2	2						
other anthropogenic	7-21	14	110-210	160	100		40		62-100	81										
d.S	0-50	25	0-50	25	18	0-25	13	20	0-25	13	0-30	15		0-10	5					
swamps and marshes	190-300	245	200-300	250	39	30-220	25	150	120-190	155	15-60	38	70-90	80	25-70	48	26-137	82	100-200	115
lakes	1-25	13		35			10		13	13	1-7	4			15-35	25		1-25	5	
oceans	1-17	9		30			13		5-21	13								5-20	10	
tropical forests				767					60-400	230										
tundra	0-3	2	3-50	27			12													
other natural					150	150	48		5-15	10					0-30	15	10-100	40		
total anthropogenic	396-550	473	366-760	563	339	140-250	195	320	297-560	429	200-335	268	267-397	332	261-447	354	183-411	297	255-535	365
total natural	192-345	269	203-350	277	871	180-370	275	233	198-624	411	21-82	52	70-90	80	40-105	73	26-167	97	116-345	170
total	588-895	741	569-1110	840	1210	320-620	470	553	495-1184	840	221-417	319	337-487	412	301-552	427	209-578	394	371-880	535
F	67-61	64	64-68	67	28	44-40	41	58	60-47	51	90-80	84	79-82	81	87-81	83	87-71	75	69-61	68

Notes: The first column under each budget is the range of estimated emissions, the second column is the central value. *F* is the ratio of anthropogenic emission to total emissions.

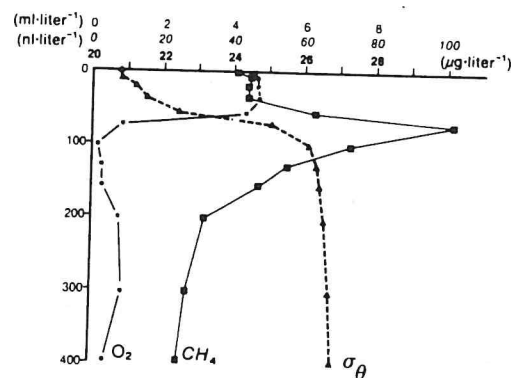


Fig. 5.1: Vertical profile of methane in oceanic water (from Burke et al., 1983).

1983; Ward et al., 1987; Conrad & Seiler, 1988). This appears to be a permanent feature. Frequently, subsurface maxima are observed at 50-150 m (Fig. 5.1; Scranton & Brewer, 1977; Scranton & Farrington, 1977; Brooks et al., 1981; Burke et al., 1983). In surface ocean waters saturation factors of methane are generally in the range 1-1.5 (Lamontagne et al., 1973; Ward et al., 1987; Conrad & Seiler, 1988), the concentration being about 2-2.5 nmol.l⁻¹. The temporal and spatial variation of the surface methane concentrations is relatively small. In upwelling and coastal areas and estuaries these saturation factors are generally much higher (Sackett & Brooks, 1975; Scranton & Farrington, 1977; Lilley et al., 1982; De Angelis & Lilley, 1987). Off Walvis Bay, where intense upwelling is common, up to 300 times methane supersaturation was observed (Scranton & Farrington, 1977). These higher supersaturations appear to be associated with areas of high nutrients and high productivity. High CH₄ concentrations coincide with high chlorophyll values (Conrad & Seiler, 1988), although no strict proportionality is observed (Lamontagne et al., 1975; Burke et al., 1983).

Several workers attributed the methane supersaturation to in situ biological production in the upper water column (Lamontagne et al., 1973; Seiler & Schmidt, 1974; Scranton & Brewer, 1977; Traganza et al., 1979; Brooks et al., 1981). Methane production is known from several species of bacteria, the methanogens (for a recent review, see Oremland, 1988), as the final step of the decomposition of organic matter. The substrates for the methane production by methanogenic bacteria are mainly acetic acid, carbon dioxide and hydrogen (Rudd & Taylor, 1980) (Fig. 5.2), but also dimethyl sulfide can serve in this capacity (Kiene et al., 1986). However, the complication arises that these methanogens are strictly anaerobic (Wolfe, 1971), whereas the upper oceans are well oxygenated. This discrepancy is accounted for by assuming the existence of reducing microenvironments in an oxic surrounding (Scranton & Brewer, 1977; Brooks et al., 1977; Traganza et al., 1979; Burke et al., 1983; Sieburth, 1987). These microenvironments could be faecal pellets or dead cells. In addition, methane production associated with phytoplankton, as by-product of their metabolism has been suggested (Scranton & Brewer, 1977), but also bacterial production in the intestinal tracts of zooplankton and higher animals (Traganza et al., 1979; Oremland, 1979; Lilley et al., 1982). Brooks et al. (1981) pointed out the possible relationship between the suspended particle maximum in subsurface waters and the methane concentration. Rudd & Taylor (1980) questioned the importance of faecal pellets as a source of methane in subsurface waters, because the density of methanogenic bacteria in the pellets would not be large enough. Moreover, the particles would sink out of the surface waters rapidly (Brooks et al., 1981), since to maintain anoxia inside them rather large particles would be required (Jørgensen, 1977). Simultaneously, the CH₄ production accompanying photosynthetic activity could only account for a small fraction of the total methane production (Rudd & Taylor, 1980). A second argument against the latter source is that no diurnal variations in methane concentration are observed (Conrad & Seiler, 1988). Burke et al. (1983) opposed that also in smaller particles reducing conditions are possible and the residence time of the particles in the surface layers of the ocean is significantly enhanced due to repetitive zooplankton grazing on the particles. These anoxic microenvironments are therefore a large potential source of methane, which could also contribute to the methane flux to the atmosphere (Ward et al., 1987).

Not surprisingly, the methane concentration in anoxic sediments and waters is much higher than in oxygenated waters (e.g. Martens & Berner, 1974; Reeburgh, 1976; Ward et al., 1987;

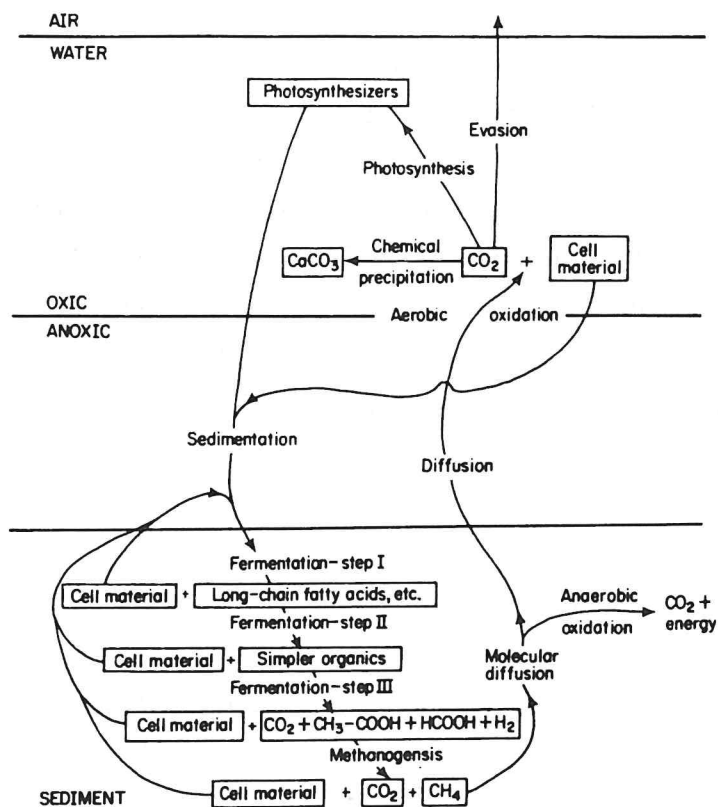


Fig. 5.2: Schematic representation of methane cycling in a stratified water column (taken from Rudd & Taylor, 1980).

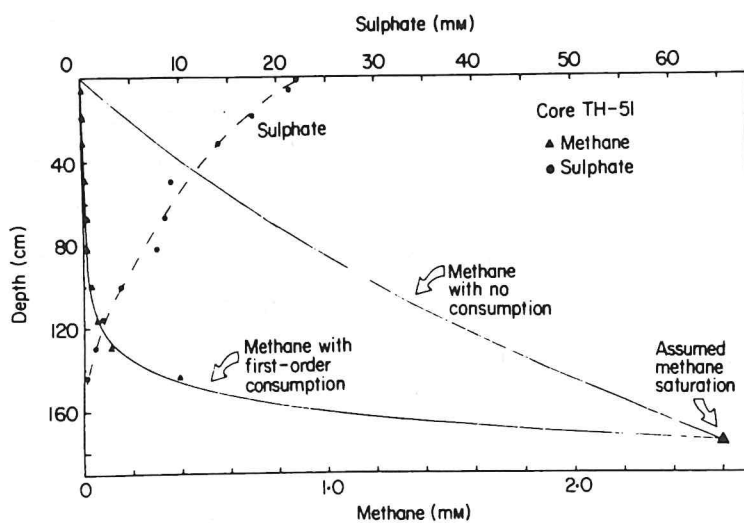


Fig. 5.3: Methane and sulfate concentration versus depth for a sediment core (taken from Rudd & Taylor, 1980).

Scranton, 1988), due to a high production by the anaerobic methanogenic bacteria. Highest methane concentrations are generally observed in the deeper parts of the sediments, where the sulfate concentration is low (Martens & Berner, 1977; Bernard, 1979). The cause for this observation is generally thought to be a competition for substrates between methanogens and sulfate reducing bacteria, where the latter outcompete the former, leaving the methanogens essentially below the zone of sulfate depletion (Cicerone & Oremland, 1988; Rudd & Taylor, 1980). Hence, sulfate reducing bacteria would largely determine the rate of methanogenesis (Rudd & Taylor, 1980).

In oxygenated waters methane is oxidized. This is evidenced by a decrease of methane with depth in the deep oceans, levels decreasing to undersaturation (Lamontagne et al., 1973; Scranton & Brewer, 1978). The aerobic oxidation of methane in seawater is a microaerophilic process, meaning that it solely takes place within a certain range of oxygen concentrations (Sansone & Martens, 1978). The process is inhibited by anoxia. The oxygen range found by Sansone & Martens (1978) suggests that the oxygen conditions in the upper water layers are unfavorable for aerobic methane oxidation. However, at high dissolved inorganic nitrogen concentration the sensitivity towards oxygen was not observed and aerobic methane oxidation could take place (Sansone & Martens, 1978). In oligotrophic regions indeed a low methane oxidation rate in the surface layers was found (Ward et al., 1987).

In anoxic waters and sediments methane generally displays a zone of low concentrations near the oxic-anoxic interface with a slightly concave upward gradient extending downward (Fig. 5.3; Rudd & Taylor, 1980; Reeburgh & Heggie, 1977). From these profiles it was deduced that methane oxidation should also occur anaerobically (Martens & Berner, 1977), possibly by sulfate reducing bacteria (Reeburgh, 1976, 1980; Devol, 1983; Lidstrom, 1983). The evidence for the sulfate reducing bacteria is still mainly circumstantial (see Rudd & Taylor, 1980 and Oremland, 1988), efforts to detect methane oxidation by sulfate reducers microbiologically meeting with complications. In marine environments in particular two factors determine the concentration and distribution of methane (Reeburgh & Heggie, 1977). The first is the relatively large abundance of sulfate, and consequently the high sulfate reduction rates. The second is the availability of organic matter, which is generally low. In the top layer of marine sediments, which receive organic matter in order to be degraded, sulfate reduction is the most important process to accomplish this. Only below the zone of sulfate reduction methanogenesis occurs. Methane diffusing upward will be oxidized anaerobically, mostly before it can pass the sediment-water interface. Henrichs & Reeburgh (1987) estimated that in oceanic sediments anaerobic methane oxidation provides a sink for $5.2 \text{ Tmol CH}_4 \cdot \text{y}^{-1}$. In the water column methane concentrations will be relatively low.

Only in shallow marine environments which receive a heavy load of organic material high decomposition activity in the bottom may deplete sulfate near the sediment-water interface and permit methane production, simultaneously decreasing the relative importance of anaerobic methane oxidation (Rudd & Taylor, 1980). In this case methane might escape the sediment through ebullition (bubbling). On its way through the water column partial dissolution occurs, thus increasing the methane concentration. However, the major part of the bubbles will be released to the atmosphere. Ebullition was observed in several coastal marine environments (Reeburgh, 1969; Martens & Berner, 1974; Hammond et al., 1975). Martens & Klump (1984) estimated that up to 16% of the carbon input to the marine sediment they investigated may be released as methane by ebullition.

The occurrence of anaerobic methane oxidation could be a major controlling factor for the

concentration of dissolved methane and methane fluxes in the marine environment (Rudd & Taylor, 1980), because right here the sulfate concentration is high.

It has been suggested that methane oxidation rates rather than production determines the methane concentration in marine waters and sediments (Reeburgh & Heggie, 1977). The poor relationships of methane with other biologically associated parameters may be explained by different kinds of oxidation activity (Burke et al., 1983). Methane oxidizing bacteria were actually isolated from seawater (Sieburth, 1987).

For the Atlantic Ocean with an average saturation factor of 1.1 Conrad & Seiler (1988) calculated a mean methane flux to the atmosphere of $12.7 \mu\text{g.m}^{-2}.\text{d}^{-1}$. For the western subtropical Atlantic Scranton & Brewer (1977) reported fluxes of $3.43 \mu\text{g.m}^{-2}.\text{d}^{-1}$, while Ward et al. (1987) give $3.68 \mu\text{g.m}^{-2}.\text{d}^{-1}$ for the Cariaco Basin. In estuaries the fluxes are much higher ranging from $0.04\text{--}21 \text{ mg.m}^{-2}.\text{d}^{-1}$, with the highest fluxes at the riverine end of the estuary (De Angelis & Lilley, 1987). The incomplete global coverage and the large variability for similar environments strongly complicates the reliable assessment of the oceanic methane flux to the atmosphere.

5.3. Methane in the North Sea: Concentration, sources and sinks

Only two reports are known to us of measurements in the water column of the North Sea. One very restricted data set is found in Conrad & Seiler (1988). Based on a few samples they reported that the saturation state, amounting to ~ 1.4 , in the North Sea was higher than in oceanic waters, and that it was comparable with other areas that receive enhanced levels of nutrients, like upwelling areas and estuaries. It was suggested that the enhanced supersaturation of methane could have been caused by the influence of river runoff. The enhanced methane concentrations in the North Sea coincided with enhanced chlorophyll a concentrations, which indicates that CH_4 production may also be related to algal production. However, this is not necessarily a direct cause-effect relationship.

Another more extensive study was performed by Scranton & McShane (1990), which was aimed at the Dutch coastal area. As opposed to Conrad & Seiler (1988) they reported that offshore ($>35 \text{ km}$) methane was generally near saturation with the atmosphere, although some exceptions to this trend were observed with concentrations up to 372 nmol.l^{-1} . In the lower salinity nearshore area which extends all along the coastline the water was highly supersaturated with methane (up to 120 times). Unlike Conrad & Seiler (1988), Scranton & McShane (1990) did not see a correlation between methane and chlorophyll. In the well-mixed Southern Bight of the North Sea the methane concentration was independent on depth.

There are several natural and anthropogenic sources of methane to the water column. The discussion on these sources will mainly be qualitatively due to the lack of measurements in the North Sea.

1. In situ production. Although the evidence is conflicting, there is a rough relationship between methane and chlorophyll in the North Sea (Conrad & Seiler, 1988), suggesting that in situ production is probably taking place. When the generally proposed mechanism of production within reducing microenvironments is correct, the methane production in the near-coastal area could possibly be higher than in open sea areas because the concentration of suspended particles in the former area is the highest. However, the offshore near-saturation as observed by Scranton & McShane (1990)

ranging from 95-130% of the equilibrium value, suggests that in situ production is only a minor source. In the deeper, stratified parts of the North Sea a subsurface maximum may exist, like observed in other coastal areas (Lilley et al., 1982). Methane diffusing to the surface layers could in that way also form a source for the atmosphere.

2. River runoff. Rivers have been shown to carry waters highly supersaturated with respect to methane (Swinerton et al., 1969; Lamontagne et al., 1973; Wilkniss et al., 1978; De Angelis & Lilley, 1987; Butler et al., 1987). The saturation factor can be as high as 600 ($1730 \text{ nmol CH}_4 \cdot \text{l}^{-1}$, De Angelis & Lilley, 1987). The variability, however, is large, both within the river as well as between different rivers (De Angelis & Lilley, 1987). Large supersaturations may be caused by pollution (Swinerton et al., 1969; Brooks & Sackett, 1973), but pristine rivers also display high supersaturations (Wilkniss et al., 1978). De Angelis & Lilley (1987) reported no significant difference between relatively undisturbed and polluted rivers. From the observations of Scranton & McShane (1990) it appeared that the rivers Rhine/Meuse and Schelde are probably the most important sources of methane to the North Sea. This was evidenced by the linear correlation between methane concentration and salinity, with low salinity corresponding to a high methane concentration. The mean riverine concentration was estimated from the methane-salinity plots to be $420\text{-}470 \text{ nmol} \cdot \text{l}^{-1}$, whereas the methane concentration in the Schelde was about $600 \text{ nmol} \cdot \text{l}^{-1}$. It was moreover striking that only in the area where river water exerts significant influence enhanced methane concentrations were observed. Several other rivers discharging on the North Sea as well as the Baltic are also likely to be methane sources.

3. Sediments. Methane production in the surface layers of marine sediments is rare due to the abundance of sulfate. Only in some special cases methane release to the overlying water column was observed (section 5.2). This implicates that most North Sea sediments are probably not a major methane source. Only some nearshore sediments that receive enhanced amounts of organic material may be sources, since here sulfate may be depleted due to the high rate of decomposition of organic matter. Scranton & McShane (1990) suggested that the coastal sediments near the mouth of the Schelde may be a significant methane source. In the western Wadden Sea release of methane by ebullition was actually observed (by eye) on a tidal flat area (Vosjan, 1978). It is expected that also in other parts of the Wadden Sea, in particular near the tidal watersheds where silt accumulates, methane release from the sediments will occur. Another area in the North Sea where methane release from the seafloor is possible is the German Bight, which is an accumulation area of organic material as well. In addition, several estuarine sediments could release methane. Unfortunately, no measurements are known of methane in North Sea sediments so the total source strength remains unknown.

4. Wastewater. Butler et al. (1987) attributed the high methane concentration measured in an estuary to municipal wastewater. During the anaerobic digestion of sewage methane is generated. They estimated the methane concentration in wastewater to be as high as $1 \text{ mmol} \cdot \text{l}^{-1}$. Along the North Sea coasts wastewater is discharged in rivers and estuaries, but also directly into the sea. Probably most of the methane originating from wastewater is already included in river runoff.

5. Offshore oil and gas production. The North Sea is rather densely populated with oil and gas rigs. Normal handling procedures and minor accidents probably result in only minor losses of hydrocarbons (Sackett & Brooks, 1975). There are, however, two standard operations that may result in significant losses of light hydrocarbons, including methane (Sackett & Brooks, 1975):

Underwater venting of waste gases and discharge of co-produced water/brines. Measurements near underwater vents showed methane levels enhanced by 5 orders of magnitude with respect to atmospheric values. Calculations by the latter authors revealed that especially the first operation is responsible for much of the enhanced methane concentration in offshore waters in the Gulf of Mexico. Sackett & Barber (1988) estimate that on a global scale about $1 \text{ Tg CH}_4 \cdot \text{y}^{-1}$ is released in this way. In the North Sea no enhanced methane concentration was measured within one mile of offshore installations (Scranton & McShane, 1990), suggesting that oil and gas production are either small sources or possibly significant intermittent sources.

6. Land-based petrochemical industry, refineries. As part of the total input of petroleum hydrocarbons also methane is discharged into the sea, especially near estuaries (Sackett & Brooks, 1975). For the North Sea the most important releases will probably occur from the industrial area of Rotterdam in the Rhine/Meuse estuary, where extensive petrochemical industry is situated.

7. Transportation. Losses by normal shipping practice will probably be minor, but tankers may be a more important source of light hydrocarbons, including methane. Tank washing by the load-on-top procedure could be a major source of methane in the open sea (Sackett & Brooks, 1975). According to this method the tanks are cleaned with water, whereby the light, most soluble hydrocarbons end up in the wastewater and are discharged. Sackett & Brooks (1975) measured a methane concentration increased by several orders of magnitude in the neighbourhood of a tanker that just washed its tanks.

8. Natural seepage. In the sediments below the zone of sulfate reduction methanogenesis occurs. In continental shelf areas the sediment column above methane occurrence may be several meters. Still methane may escape to the overlying water column by diffusion and bubbling. In shallow areas like the North Sea the gas from seeps can reach the sea surface and escape to the atmosphere directly. The seeps are associated with several types of geological settings (Sackett & Brooks, 1975; Hovland & Judd, 1988; Dando & Hovland, 1991). In the North Sea pockmarks are associated with the release of methane, and there may be up to 40 per km^2 (Dando & Hovland, 1991). Seep gas is mainly composed of methane ($>99.9\%$), with only minor amounts of other gases (CO_2 , H_2 , H_2S). Perhaps also petrogenic gas seepage will occur, but this was not demonstrated (Sackett & Brooks, 1975). In the North Sea natural seeps were reported by Bedborough & Blackman, (1986), to amount to $0.3\text{-}0.8 \cdot 10^9 \text{ g} \cdot \text{y}^{-1}$. This figure may be underestimated because research on gas seeps in the North Sea is very recent and data necessarily undergo frequent revisions, the more so as it concerns point sources. Off the Netherlands no seeps were observed by Scranton & McShane (1990). Many seeps have been found in the central and northern North Sea and in the Skagerrak (Schmaljohann & Flügel, 1987; Hovland & Judd, 1988; Dando & Hovland, 1991).

In contrast with the many sources of methane there are only a few sinks.

1. In situ oxidation. In the well-oxygenated waters of the North Sea the most likely oxidation process in the water column is aerobic. In the 110 m surface layer of the Cariaco Basin an oxidation rate of $0.002 \text{ nmol} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ was measured (Ward et al., 1987), i.e. $1.8 \cdot 10^{-4} \text{ nmol} \cdot \text{l}^{-1} \cdot \text{d}^{-1}$. On the Atlantic continental shelf of the U.S.A. the average oxidation rate amounted to $10 \text{ nmol} \cdot \text{l}^{-1} \cdot \text{d}^{-1}$ (Sansone & Martens, 1978). From the data of Ward et al. (1987) it is estimated that $<20\%$ of the methane production in the surface layers is oxidized in situ. Butler et al. (1987) reported very low oxidation rates relative to the high methane concentration in an estuary. For the offshore North Sea typical methane oxidation rates are $2.3 \cdot 10^{-4} \text{ nmol} \cdot \text{l}^{-1} \cdot \text{d}^{-1}$, while inshore the value seems to be higher

for some orders of magnitude (Scranton & McShane, 1990).

2. Atmospheric release. This is generally considered to be the most important loss mechanism. This holds particularly for shallow areas like the North Sea because downward diffusion is impossible. Methane exchange across the air-sea interface is relatively rapid. The calculated flux to the atmosphere using the data of Conrad & Seiler (1988), i.e. a mean saturation of 1.4 for the entire North Sea, amounts to $\sim 2.1 \mu\text{g CH}_4 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$. According to Scranton & McShane (1990) the methane release from the North Sea to the atmosphere ranges from 0.6 to $60 \text{ nmol} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$, which equals $4\text{-}400 \mu\text{g CH}_4 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$. In the nearshore area up to 39% of the methane concentration may be lost to the atmosphere each day.

3. Estuaries. The loss of methane from estuaries was deduced from the non-linearity of CH_4 -salinity plots (Butler et al., 1987). They calculated that 30-40% of the methane in the estuary studied was lost each day, mainly to the atmosphere. Much smaller losses were caused by oxidation. In other estuaries De Angelis & Lilley (1987) found essentially conservative behaviour of methane, meaning that consumption processes were virtually absent. Clearly, differences between estuaries, such as flushing times, are obviously large and determine the behaviour of methane to a great extent.

The observations by Scranton & McShane (1990) clearly demonstrated that by far the most important source of methane to the North Sea are the rivers. Due to the typical current regime the fresh water stays near the coasts and in that way maintains considerable methane supersaturations. The in situ source strength of the North Sea for methane is negligible compared to the riverine source. The main sink for the North Sea is the atmosphere. Not surprisingly, the atmospheric exchange is dominated by the coastal water masses. This can be demonstrated using the data of Scranton & McShane (1990). To obtain the atmospheric loss of methane for the entire North Sea we assume that 10% of the North Sea surface area is coastal, and the gas exchange is $5.1 \text{ nmol} \cdot \text{l}^{-1} \cdot \text{d}^{-1}$. For the rest of the area we assume the latter figure to be $0.008 \text{ nmol} \cdot \text{l}^{-1} \cdot \text{d}^{-1}$. The annual methane release from the coastal regions then is $3.6 \cdot 10^{10} \text{ g CH}_4$, whereas for the rest of the North Sea $4.8 \cdot 10^8 \text{ g CH}_4$. This figure would imply that the North Sea is a somewhat more than proportional source of methane to the atmosphere based on its surface area, but as we saw river water is in fact the ultimate source. A summary of the fluxes of methane within the North Sea is given in Table 5.2.

A potential large influence on the global atmospheric methane level comes from gas hydrates containing methane. Solid gas hydrates are chemical substances in which the gas is tightly and densely packed in cages of water molecules. They only form under special pressure-temperature conditions. Methane hydrates are widespread in outer continental margin sediments (and in permafrost regions), whereas the upper limit of occurrence within the sediment is the seafloor (Kvenvolden, 1988). They also occur in the North Sea shelf area. Nisbett (1990) believes that the release of methane from hydrates due to global warming reinforced this warming at the end of the last glaciation. It is likely that the release of methane from hydrates will be a positive feedback for global warming induced by CO_2 increase, but the extent to which is highly uncertain. At present it seems as if offshore permafrost hydrates are the most vulnerable to global warming, while those hydrates on the continental margins are less vulnerable (Kvenvolden, 1988). However, much more research is needed.

Table 5.2: Summary of the natural and anthropogenic fluxes of methane within the North Sea. Units g C.y⁻¹.

	sources	changes 1930-1990
In situ production	only minor	+
River runoff	major	+
Sediments-water column	minor	+
Wastewater discharges	minor (regional only)	+
Offshore oil and gas	small intermittent	+
Refineries	minor (regional only)	+
Transportation	small	+
Natural seepage	0.3-0.8·10 ⁹ or +?	no
	sinks	
Atmospheric release	2.7·10 ¹⁰ ?	++
In situ oxidation	minor	+
Estuaries	unknown (regional)	+

5.4. Possible changes in methane fluxes in the North Sea due to anthropogenic activity

Because sources and sinks are being known only qualitatively the proper assessment of anthropogenic influence is difficult to achieve. However, from related changes the methane development may possibly be deduced. The following contentions can be made.

The strong increase of offshore oil and gas production activities with concurrent increased oil spills (Dicks et al., 1988) is likely to have been accompanied by an increased source strength of methane from this source. Because we cannot even estimate the importance of offshore activity for the present CH₄ budget we can neither assess the importance of the increase. On the other hand transportation activity appears to have decreased in the last decade and so methane from this source probably lost importance.

The increased organic load of the North Sea by anthropogenic impact, both directly through wastewater and dumping as well as indirectly by eutrophication, is likely to have increased sulfate reduction in the sediments and hence moved the oxic-anoxic boundary closer to the sediment-water interface. This would cause a higher flux of methane from the sediment to the water column. The German Bight, the Wadden Sea and some near-coastal areas are likely to be affected by these changes. Due to the lack of knowledge on the interrelationships between organic matter content and methane concentration in the water column even a rough estimate on these changes would not be possible. Simultaneously, it is impossible to predict the eventual effect of the enhanced primary production on the methane concentration, simply because it is unclear if there is either an additional source or sink.

With some confidence we may assume that the CH₄ load of the rivers has increased during the last decades due to the increased load of organics and wastewater discharges. Summarizing, although speculative, we believe that anthropogenic activity has enhanced the methane emission from the North Sea. However, depending on the magnitude of the natural sources it remains unsolved if the increased source strength due to offshore activity and river discharge contributes significantly to an enhanced methane concentration level in the North Sea. Considering the methane flux from the North Sea to the atmosphere of 3.6·10¹⁰ g.y⁻¹ against the background of the total oceanic flux of 5-20 Tg.y⁻¹, which in turn is very small compared to the global source strength, the possible increase is futile.

6. NITROUS OXIDE CYCLING

In analogy with the global cycle of carbon the nitrogen cycle (Fig. 6.1) contains important gaseous components. Gaseous nitrogen compounds are dinitrogen gas (N_2), ammonia (NH_3), nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2) and nitrous acid ($HONO$). In the atmosphere and oceans N_2 -gas is by far the most abundant nitrogen compound (>99.999%). It comprises 78% of the entire atmosphere. However, N_2 -gas is relatively unreactive and its abundance is barely affected by biological processes. In the atmosphere N_2O is the most abundant after N_2 , accounting for 99.5% of all atmospheric combined nitrogen (Rosswall, 1983). N_2O is quite reactive and has drawn considerable scientific interest. Initially the atmospheric conversion of N_2O to NO



with the subsequent reaction



was the focal point as it is a route for destruction of ozone in the stratosphere (Crutzen, 1971; Johnston, 1971; McElroy et al., 1977). It is well known that the stratospheric ozone layer governs the UV climate on earth, whereas ozone also serves as an insulating or 'greenhouse' gas on its own. Secondly, nitrous oxide is in itself a greenhouse gas (Wang et al., 1976). On a molecular basis N_2O has a much greater capacity to absorb infrared radiation than CO_2 , yet the abundance of N_2O is considerably less. The steady rise of the N_2O concentration in the atmosphere (Weiss, 1981; Khalil & Rasmussen, 1983) has raised considerable concern with regard to these properties.

6.1. Nitrogen compounds in the marine environment

Like in the atmosphere the most abundant nitrogen compound in seawater is N_2 . The other gaseous nitrogen compounds are also found dissolved in seawater. In addition, several ionic species of nitrogen occur, such as nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+), as well as trace amounts of dissolved organic nitrogen compounds. Nitrate is the next most abundant dissolved nitrogen species after N_2 . In the presence of dissolved oxygen (O_2) nitrate is in fact the thermodynamically stable form of nitrogen in the marine environment. The reduced forms nitrite and ammonia are much less abundant as they are produced and consumed rapidly through microbial pathways. Nitrite and ammonium are in fact intermediates in the very complicated nitrogen cycle (von Brand et al., 1937 as cited in Sharp, 1983). Nitrogen is an essential nutrient element, utilized by all organisms to grow soft tissue, notably amino acids as building blocks of proteins. Nitrate, nitrite or ammonium can be utilized by organisms, where latter reduced forms are energetically more favorable for conversion to amino groups but nitrate is usually much more abundant. Because

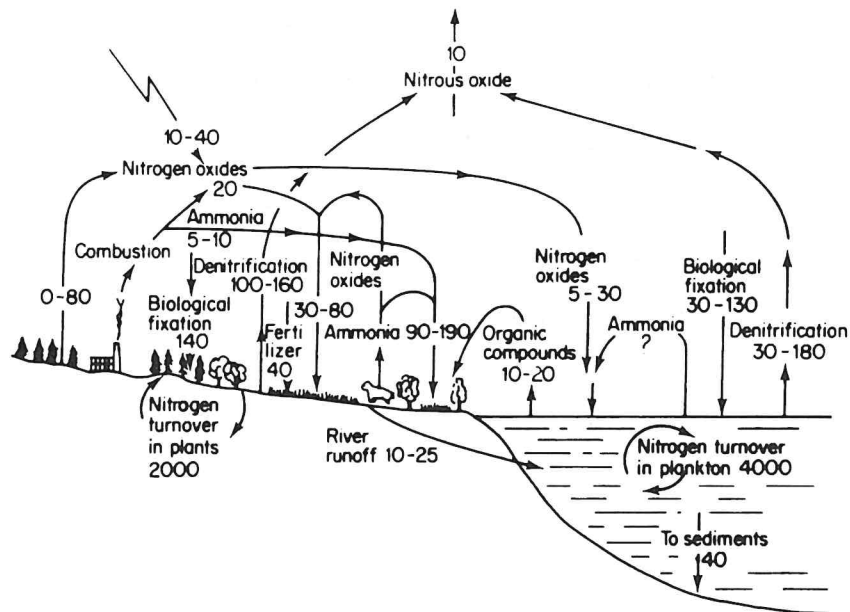


Fig. 6.1: A global nitrogen cycle, units 10^{12} g N.y⁻¹ (from Rosswall, 1983).

Table 6.1: A global budget of nitrous oxide, units 10^{12} g N.y⁻¹ (from Bouwman, 1989 based on Seiler & Conrad, 1987).

Sources

fossil fuel burning	2
biomass burning	1.5
oceans, estuaries	2
fertilized soils	1.5
natural soils	6
plants	<0.1
gain of cultivated land	0.4
Total sources	14 ± 7

Sinks

stratospheric loss	9 ± 2
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nitrogen is incorporated in organisms dissolved and particulate organic forms of nitrogen (living and non-living) also exist. Among the dissolved organic N classes the groups of amino acids and methylamines are relatively well-studied (e.g. Gagosian & Lee, 1981). Their occurrence is, of course, similar to that of organic carbon, so it is referred to in chapter 2 dealing with the latter compounds (but see also Sharp, 1983).

N₂ and N₂O are in more or less equilibrium with their atmospheric counterparts (Scranton, 1983). Particularly for N₂, due to the very high background level, deviations from the solubility value are small, although a process is known (denitrification) that produces N₂. In fact through geological times this process has caused N₂ to be more abundant than the thermodynamically more stable nitrate (Scranton, 1983). For N₂O the deviations from solubility equilibrium are in general more pronounced, where both super- and undersaturation occur (Hahn, 1974; Weiss, 1978), although the latter is rare (Elkins et al., 1978).

6.2. Nitrous oxide budget

The main sink for N₂O is the stratosphere, where it reacts photochemically to NO (Crutzen, 1971; McElroy & McConnell, 1971). In the troposphere N₂O is inert. The loss rate in the stratosphere was estimated at 8.4 Tg N.y⁻¹ by Johnston et al. (1979) and at 10.5 Tg N.y⁻¹ by McElroy & Wofsy (1986) on a total atmospheric reservoir of about 1400 Tg N.y⁻¹ (Rosswall, 1983) (1 Tera g = 10¹² g). Note the approximately three orders of magnitude difference in abundance of N₂O compared to CO₂. From the above we deduct that the natural atmospheric lifetime (turnover rate) is in the order of 100-200 years, which indicates that removal of excess N₂O would be slow. The net accumulation in the atmosphere amounts to 2.8 Tg.y⁻¹ according to McElroy & Wofsy (1986), which means an increase of the atmospheric N₂O content with ca. 0.2% annually (Weiss, 1981).

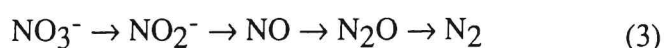
Opposite to the one sink stand several N₂O sources (Table 6.1). It must be realized that the budget for N₂O contains some entries that are poorly understood and/or quantified. Weiss (1981) suggested that the increase of atmospheric N₂O is predominantly caused by the increased rate of fossil fuel combustion. The increased use of fertilizers might also contribute to the increasing atmospheric content of nitrous oxide, but probably this is less important (Seiler & Conrad, 1981). The fossil fuel input may well be dominant, yet it has little or no impact on the aquatic part of the N₂O cycle which is the subject of this report.

From the initial measurements of N₂O concentrations in seawater it was thought that the oceans are a major source of N₂O compared to the stratospheric sink (Junge & Hahn, 1971; Hahn, 1974). More recent measurements provided substantially lower oceanic N₂O concentrations (Yoshinari, 1976; Cohen & Gordon, 1978), the aforementioned initial measurements presumably being incorrect. Weiss (1978, 1981) found generally near-atmospherically equilibrated N₂O concentrations during extensive surveys in the surface oceans and only locally some important sources. In coastal seas and estuaries generally higher N₂O supersaturations can be found than in the oceans (e.g. Butler et al.,

1987; Law & Owens, 1990). This means that coastal seas may be a significant source of atmospheric nitrous oxide.

6.3. Production and consumption of nitrous oxide: Nitrification and denitrification

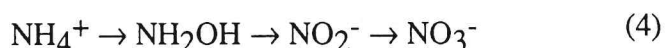
Nitrous oxide distributions are mainly controlled by biological processes. During the breakdown of organic matter the bacteria commonly prefer oxygen (O₂) as the energetically most favourable electron acceptor. In conditions where oxygen replenishment is restricted (for example, within sediments) the oxygen becomes depleted and at low enough oxygen levels (~5-20 μM) the bacterial community changes to nitrate as an electron acceptor. In this process, called denitrification or dissimilatory nitrate reduction, nitrate is converted to dinitrogen gas through the following pathway:



(Payne, 1973). In this process N₂O (and also NO₂⁻) is a stable intermediate (Hattori, 1983). During denitrification N₂O is commonly found as a byproduct of N₂, but only in very small amounts. Several factors determine the rate of each of the above reaction steps, i.e. the extent to which overall denitrification occurs or nitrous oxide is accumulated. Oxygen is an obvious inhibitor of denitrification. The relative abundance N₂O:N₂ is increased with increasing O₂, H₂S and nitrate or decreasing pH and temperature (Tiedje et al., 1981). Denitrification was established to occur within marine sediments, and also in the water column in oxygen poor conditions.

With adequate supply of nitrate the overall denitrification reaction yields mostly N₂ but also minor amounts of N₂O. At low supply of nitrate some bacteria are able to use nitrite and nitrous oxide as electron acceptor, reducing it to N₂ (Cohen, 1978; Scranton, 1983). In this way denitrification becomes a sink for N₂O instead of a source. Thus, it depends on the external conditions if denitrification is a source or a sink of nitrous oxide.

The other process which is now recognized to be the major producer of nitrous oxide is nitrification. During nitrification NH₄⁺ is oxidized to NO₃⁻. Ammonium ion is released during the mineralization of organic matter. The pathway of nitrification involves at least the following steps:



(Kaplan, 1983). Hydroxylamine (NH₂OH) is unstable in aqueous solutions and decomposes to N₂, N₂O or NH₄⁺ (Rajendran & Venugopalan, 1976). Thus, nitrous oxide is a byproduct of nitrification. For every 1000 molecules of ammonium oxidized about 1-2 molecules of nitrous oxide are released (Cohen & Gordon, 1979; Elkins et al., 1978). Like denitrification nitrification occurs in the sediments and in the water column (Goreau et al., 1980), but under aerobic conditions. This means that in the water column and the top (oxygenated) layer of the sediment it is more common than denitrification.

Nitrous oxide is also produced by non-denitrifying bacteria in assimilatory and dissimilatory nitrate reduction to ammonia (Pierotti & Rasmussen, 1980; Bleakley & Tiedje, 1982). It concerns insignificant amounts of N_2O produced by these organisms. Similarly, heterotrophs are able to perform nitrification (Painter, 1970; Bleakley & Tiedje, 1982), and thus produce nitrous oxide. Chemodenitrification is the generating of nitrogen containing gases (catalyzed) by abiotic agents. However, as an N_2O determining process it is relatively unimportant (Tiedje, 1988).

In Fig. 6.2 the processes involved in the marine nitrogen cycle are summarized in a scheme.

6.4. Nitrous oxide in the North Sea

Although in the last 20 years many studies were performed on nitrous oxide in the oceanic water column, only one study is known to us dealing with the North Sea. Some more work has been done on N_2O in the North Sea sediments, but these were largely confined to the fringes, like the Wadden Sea and the estuaries.

The present discussion of the N_2O distribution in the North Sea water column is almost entirely based on an extensive investigation by Law & Owens (1990), covering the entire North Sea (excluding the Wadden Sea). The atmospheric N_2O concentration was determined as well, and was found to be approximately 10% lower than the generally accepted value of 300 ppb. In the surface distribution of the N_2O saturation (Fig. 6.3) remarkable deviations from atmospheric equilibrium are noticed. However, this only applies to the coastal areas and in particular to the German Bight. In the central and northern North Sea the deviation from the value representing equilibrium with the atmospheric N_2O is generally less than 5%, which denotes that these anomalies cannot be attributed to processes other than physical (air injection, temperature anomalies, atmospheric pressure) (Bieri et al., 1968; Carritt, 1954). The German Bight is a large source of nitrous oxide to the atmosphere, the mean saturation being 130% opposed to the central and northern North Sea 102%. Also in front of the Dutch coast supersaturation was observed in surface waters, but undersaturation near the bottom. The coastal supersaturation seems to be related to the nutrient discharges from the land. Because the surface water in the North Sea is well oxygenated nitrification must be the cause for the build-up of N_2O . Law & Owens suggest that also algae and associated microflora produce significant amounts of nitrous oxide.

According to the N_2O profiles consumption should occur in the bottom waters. However, oxygen concentrations were too high for denitrification, the main consumption process, to happen. The authors suggested that faecal pellets, suspended in the bottom waters, possess anoxic microzones (microniches) where denitrification may occur (see also Jenkins & Kemp, 1984). Nitrous oxide fluxes of the sediment to the overlying water column were small, and did not happen at all at many sites. Van Raaphorst et al. (1991) measured the seasonal cycle of nitrous oxide fluxes from the sediment at two positions on the Dutch continental shelf area (Fig. 6.4). The data of Law & Owens (1990) at corresponding positions show agreement in that there is also uptake of nitrous oxide in summer. However, the data of Van Raaphorst et al. (1991) demonstrate that in other seasons the fluxes are quite different, in fact, that there is mostly a release of nitrous oxide to the overlying water

Fig. 6.2: Portions of the marine nitrogen cycle influencing dissolved gaseous nitrogen compounds (taken from Scranton, 1983).

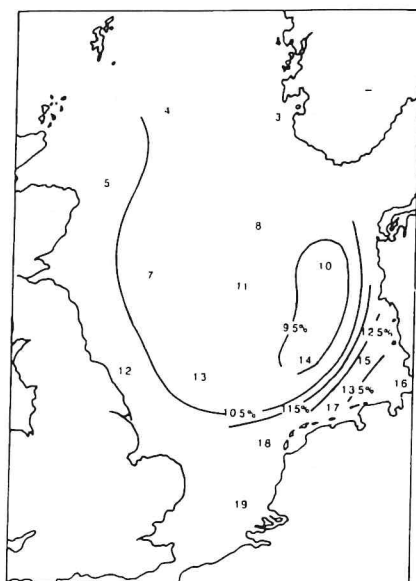
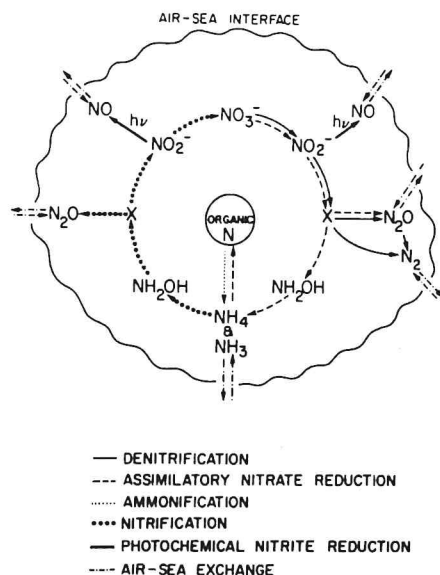
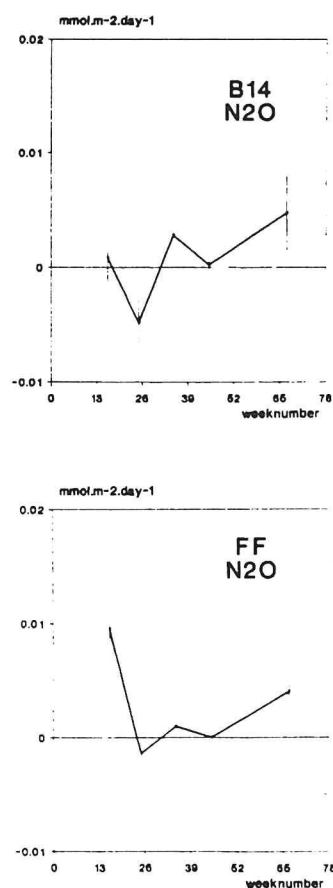


Fig. 6.4: Seasonal variation of nitrous oxide fluxes from two sediment cores in the southern North Sea (from Van Raaphorst et al., 1991).

Fig. 6.3: Surface nitrous oxide saturations. The position of each station is indicated by number (taken from Law & Owens, 1990).



Law & Owens (1990) came to an estimate of the total flux of N_2O from the North Sea to the atmosphere of $9.5 \cdot 10^9 \text{ g N}_2\text{O} \cdot \text{y}^{-1}$ ($=6.0 \cdot 10^9 \text{ g N} \cdot \text{y}^{-1}$), of which more than half originated from the German Bight. When the global source strength (= stratospheric loss + atmospheric accumulation) is about $12 \text{ Tg N} \cdot \text{y}^{-1}$, the North Sea contributes $5 \cdot 10^{-2}\%$ to the worldwide N_2O production. Comparing the N_2O production of the North Sea with the estimated global oceanic source of ca. $2 \text{ Tg N} \cdot \text{y}^{-1}$ (Seiler & Conrad, 1987), this would be a contribution of 0.3%. This is much more than expected on the basis of proportionality of the North Sea surface area. It gets even more interesting when it is realized that most of this production occurs in a small sub-area, the German Bight. This may indicate that some local sources are very important for the global N_2O budget. We should however also be cautious to draw too rigid conclusions, because major assumptions were made with respect to the calculation of both the flux of the North Sea and of the total oceanic flux. Measurements by Law & Owens were performed in the productive summer season in which the N_2O production is expected to be higher than in other seasons. Consequently, the annual N_2O flux is probably overestimated. Indeed, variability of N_2O cycling (be it in the sediments) was shown to be large by Van Raaphorst et al. (1991) and Lohse (1990). Nevertheless, support for the occurrence of locally important N_2O fluxes is found in a paper by Rönner (1985), who estimated that the Baltic Sea was an even greater N_2O source for the atmosphere ($2.8 \cdot 10^{10} \text{ g N} \cdot \text{y}^{-1} = 1.3\%$ of the overall oceanic source) than the North Sea. However, Rönner (1985) also warned for a probable overestimation of his figure for the flux.

On the other hand, the relatively high production figures for small areas like the North Sea and the Baltic may cast some doubt on the global estimates for the oceanic N_2O source. Possibly the shelf seas are not sufficiently accounted for and represent a greater source than assumed till now.

6.5. Sources and sinks of nitrous oxide in the North Sea

In the previous section it was discussed that the North Sea is a net source of nitrous oxide, but this tells little about the actual fluxes through the system. Unfortunately, there is a huge lack of knowledge regarding almost all possible N_2O fluxes in the North Sea. Therefore, the following discussion will be only qualitative, and mainly based on studies in other areas (where the data are also far from complete). There are several possible sources of nitrous oxide to the North Sea.

1. In situ production in the water column. This was treated to some extent in the previous section. Because of the generally high level of oxygen this will mainly occur by nitrification. However, denitrification is also suggested to occur in anoxic microenvironments (Jenkins & Kemp, 1984; Butler et al., 1987). Production by heterotrophs is another possibility (Bleakley & Tiedje, 1982; Law & Owens, 1990). It is generally thought that nitrification is the major source of nitrous oxide (Yoshinari, 1976; Elkins et al., 1978; Cohen & Gordon, 1978; Kaplan, 1983). However, in a small Pacific estuary nitrification was reported to be an insignificant contribution to the N_2O production in the water column (Butler et al., 1987). Law & Owens (1990) demonstrated that in situ production in the North Sea does occur, although the processes that caused it were sometimes

unclear.

2. Wastewater discharge. In several investigations it was reported that wastewater and sewage plant effluents are a major source of nitrous oxide (Cicerone et al., 1978; Kaplan et al., 1978; McElroy et al., 1978; Seitzinger et al., 1983). The N_2O concentration in effluents can amount to more than 100 times the saturation value (Cicerone et al., 1978; Seitzinger et al., 1983). As along the North Sea and Wadden Sea coasts at many locations wastewater is discharged (e.g. Carlson, 1986) it is expected to be an important source of nitrous oxide for the North Sea as well.

3. River runoff and estuaries. Besides direct wastewater discharge on the sea, rivers also receive effluents (wastewater and septic tank leachate), which finally will go to the sea. Nitrification in the river water is another source of elevated nitrous oxide levels, and since ammonia concentrations in fresh water are usually higher than in seawater nitrification will probably occur even to a greater extent. A third possible cause for enhanced N_2O concentrations in river waters is soil runoff from the watershed (Dowdell et al., 1979), due to the extensive use of fertilizers. This is particularly important in the rainy season (De Angelis & Gordon, 1985; Butler et al., 1987). Elevated nitrous oxide levels in rivers were observed by Kaplan et al. (1978), McElroy et al. (1978), Cicerone et al. (1978), De Angelis & Gordon (1985) and Butler et al. (1987). Very few measurements are known for rivers discharging on the North Sea. The Schelde is a very polluted river, where nitrification (Billen, 1975) and denitrification (Billen et al., 1985) rates are very high. Within the estuary nitrous oxide is produced (Somville, 1980 as cited in Wollast, 1983). Another advective source of nitrous oxide for the North Sea is the Baltic, which has an elevated concentration of N_2O (Rönnner, 1985).

4. Diffusion from sediments. The sediments represent an environment likely to display great nitrification and denitrification activity (Sørensen, 1978; Hansen et al., 1981). The two processes can occur concomitantly (Grundimanis & Murray, 1977; Knowles, 1978; Jenkins & Kemp, 1984). In some studies nitrous oxide release from marine sediments to the overlying water column was actually established (Sørensen, 1978; Seitzinger et al., 1980, 1983, 1984; Jensen et al., 1984; Jørgensen & Sørensen, 1985; Lohse, 1990). Sedimentary N_2O fluxes are particularly important in nearshore areas, estuaries and coastal wetlands, i.e. in shallow areas. In such areas the N_2O release from the sediments is comparable to fluxes from autochthonous sources (Seitzinger et al., 1983; Jørgensen & Sørensen, 1985). In areas remote from the coast the sedimentary N_2O flux is minor, as was demonstrated in the more remote North Sea areas by Law & Owens (1990). At some sites the latter authors even found influxes into the sediment. The sedimentary N_2O fluxes show a distinct seasonal pattern with the higher fluxes in winter and lower in summer (Jensen et al., 1984; Van Raaphorst et al., 1991; Lohse, 1990) and during certain periods the sediments even act as a sink for nitrous oxide. Also in other areas nitrous oxide sinks in summer are reported (Kaplan et al., 1978; Elkins et al., 1978). Comparison of nitrous oxide fluxes from open North Sea sediments (Law & Owens, 1990) with those from coastal North Sea sediments (Jensen et al., 1984) learns that the former are much lower. Therefore, also for the North Sea the coastal area, with the Wadden Sea and the estuaries, is the important environment for nitrous oxide release.

A summary of the fluxes of nitrous oxide within the North Sea is given in Table 6.2. Because the information available is limited mainly qualitative estimates are given.

Table 6.2: Summary of the fluxes of nitrous oxide within the North Sea, units g N.y⁻¹.

	sources	changes	1930-1990
In situ production	major		+
Wastewater discharge	possibly major		+
River runoff and estuaries	major		+
Sediments-water column	minor		+
	sinks		
Atmospheric release	6·10 ⁹		+
In situ oxidation	minor		?

6.6. Possible changes in the aquatic nitrous oxide fluxes due to anthropogenic activity

Because of the only recent interest in nitrous oxide no time series or whatsoever is available, even the undisturbed N₂O cycle is hardly satisfactory understood. However, the research that has been done so far does give us some clues on the sensitivity of nitrous oxide fluxes to disturbance.

Firstly, as wastewater is a source of nitrous oxide to the North Sea it is expected that with the changing (=increasing) load of wastewater through the last decades the load of nitrous oxide changed accordingly. This holds both for direct wastewater discharge on the North Sea as for discharge into the rivers. Thus, the nitrous oxide load carried to the North Sea by rivers may also have increased above the natural level.

Secondly, it was shown that the nitrous oxide release from the North Sea water seemed to be related to the high nitrate content near the coast (Law & Owens, 1990) and in the estuaries (Jørgensen & Sørensen, 1985). In the seasonal cycle of nitrous oxide fluxes from the sediments in the western Wadden Sea the nitrate control was established as well (Lohse, 1990). Therefore, it is likely that the nitrous oxide emission increased in response to the eutrophication of the coastal waters, by which the nitrate concentration along the coasts increased.

Thirdly, eutrophication has a pronounced influence on the sediments, for instance, it leads to a higher load of organic matter. This has impact on the chemical regime in the sediment; the oxygen demand increases, which in turn affects the rates of nitrification and denitrification. In end effect, eutrophication will be of importance for the sedimentary source or sink function for nitrous oxide. Seitzinger et al. (1983) demonstrated that nitrous oxide production by sediments in a relatively unpolluted area was smaller than in a eutrophic area. Extrapolating this to the North Sea and Wadden Sea situation means that the sedimentary nitrous oxide production probably increased concurrently with the ongoing eutrophication.

Summarizing, it is probable that nitrous oxide emission from the North Sea and the bordering seas and estuaries increased during the last decades. Nothing can be said quantitatively about this. Eutrophication may have been an important cause. It is illustrative that the eutrophic German Bight is currently responsible for a major part of the nitrous oxide release from the North Sea.

7. DIMETHYL SULFIDE CYCLING AND POSSIBLE CHANGES

Dimethyl sulfide (DMS) is by occurrence only a very insignificant sulfur (S) compound in the global sulfur cycle. Sulfur compounds are distributed over all the main reservoirs, the atmosphere, oceans, lithosphere and biosphere. Large amounts of S occur in the lithosphere (mainly as metal sulfides and -sulfates) and in the oceans (mainly as dissolved sulfate), where the size of the latter is in the order of magnitude of 10^{21} - 10^{22} g S (Freney et al., 1983). The sulfur content of the atmosphere is only very small (4.8 Tg S), and the main components are carbonyl sulfide (COS), sulfur dioxide (SO₂), sulfate in aerosols and reduced gases, like dihydrogensulfide (H₂S). Even within this very small atmospheric S-reservoir DMS, (CH₃)₂S, is insignificant. However, among the natural gaseous emissions of sulfur the DMS emission is by far the most important (Table 7.1, after Andreae, 1990). Simultaneously it appears from Table 7.1 that this emission occurs mainly from the oceans. In seawater sulfate may be by far the major sulfur compound, DMS is the most abundant volatile sulfur compound (Barnard et al., 1982; Andreae et al., 1983; Andreae & Raemdonck, 1983; Cline & Bates, 1983; Nguyen et al., 1983). Thus, DMS is an important transfer route within the global sulfur cycle in the exchange between the oceans and the atmosphere.

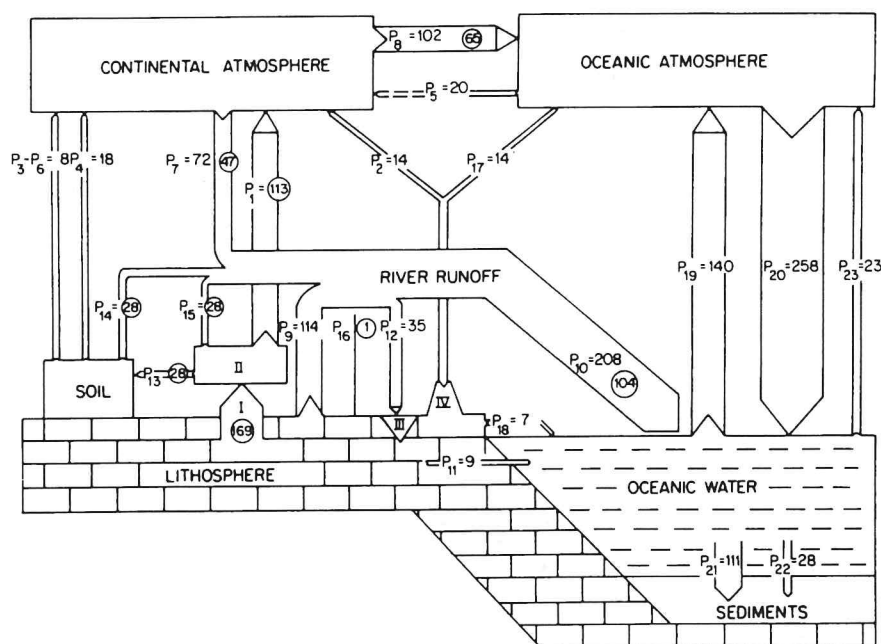
Sulfur is a building block for all living organisms. It is incorporated in organic tissue predominantly via assimilatory sulfate reduction (Anderson, 1980), where it is converted to cysteine and subsequently to the amino acids homocysteine and methionine. The main degradation product of organic sulfur is H₂S gas. The reason that H₂S is not the most abundant sulfur containing gas in the sea is that it is easily oxidized in the presence of oxygen. Also other sulfur containing compounds are released by organisms or are produced chemically from organic sulfur and are thus found in the (marine) environment. These include amino acids, proteins, and gaseous compounds such as carbonyl sulfide, carbon disulfide (CS₂), methylmercaptan, and dimethyl disulfide.

In Fig. 7.1 the fluxes between the reservoirs of the global sulfur cycle are shown. The actual figures are from about 1980 and rather uncertain, still subject to change due to ongoing research. About half of the biogenic flux of sulfur to the atmosphere originates from the oceans (Andreae, 1985a, 1986; Bates et al., 1987b) and this oceanic flux is almost entirely composed of DMS (Andreae, 1986). In the atmosphere DMS is rapidly converted, predominantly via a reaction with hydroxyl and nitrate radicals (Graedel, 1979; Atkinson et al., 1984; Andreae et al., 1985a) to sulfur dioxide and sulfate. Hence, oceanic DMS affects the acidity of the precipitation (Charlson & Rohde, 1982). The residence time of DMS in the atmosphere is only 0.2-0.8 days. A main interest of DMS production is its possible involvement in a climatic feedback loop (Charlson et al., 1987). The oxidation products of DMS in the atmosphere, such as sulfate aerosols, serve as cloud condensation nuclei (CCN)(Fig. 7.2). These CCN largely control the Earth's albedo (Bonsang et al., 1980; Bates et al., 1987a), which in turn is important for the global radiation balance and temperature. Not all interdependencies within this system are well-understood (Andreae, 1990), but the potential of this feedback loop is powerful. For example, an increase in DMS production, which might possibly be the consequence of an enhanced primary production, may counteract a greenhouse warming.

Table 7.1: Estimates of natural sulfur emissions, units Tmol S.y⁻¹ (taken from Andreae, 1990).

	SO ₂	H ₂ S	COS	DMS	CS ₂	Sulfate	Other	Total
Seaspray						1.2-10		1.2-10
Dust						0.1-1		0.1-1
Total particulates						1.3-11		1.3-11
Volcanoes	0.23-0.29	0.03	0.0003	-	0.0003	<0.1	?	0.3-0.4
Soils and plants	-	0.1-0.3	±0.02	0.006-0.12	0.02-0.025	-	0.03	0.15-0.4
Coastal wetlands	-	0.03	0.004	0.02	0.002	-	0.004	0.06
Biomass burning	0.08	?	0.003	-	?	?	?	≥0.08
Oceans (gases)	-	0.05-0.2	0.011	0.6-1.6	0.01	-	?	1.1-1.8
Total gases	0.3-0.4	0.2-0.6	0.00-0.04	0.6-1.7	0.03-0.04	≤0.1	0.03	1.2-2.8*

*Equivalent to 38-89 Tg S year⁻¹.



Roman figures denote:

- I — output of sulfur-containing minerals;
- II — industrial treatment of the sulfur-containing raw materials;
- III — inland water bodies;
- IV — volcanoes.

Fluxes:

P₁ — fuel combustion and metal smelting; P₂ and P₁₇ — volcanic emission; P₃ — aeolian dust; P₄ — biogenic emission from land; P₅ — sea air-land air transport; P₆ — deposition of large dust particles; P₇ — wash-out and dry deposition; P₈ — land air-sea air transport; P₉ — weathering; P₁₀ — river runoff to oceans; P₁₁ — transport to ocean in underground water; P₁₂ — runoff to inland water bodies; P₁₃ — input in fertilizers; P₁₄ — leaching of fertilizers; P₁₅ — efflux from chemical industries; P₁₆ — efflux of acid mine water; P₁₈ — abrasion of shores; P₁₉ — sea spray; P₂₀ — wash-out and dry deposition; P₂₁ — sedimentation of reduced sulfur; P₂₂ — sedimentation of sulfate; P₂₃ — biogenic emission from oceans.

Fig. 7.1: The major natural and anthropogenic (circled) fluxes of the global biogeochemical sulfur cycle, units Tg S.y⁻¹ (from Rosswall, 1983).

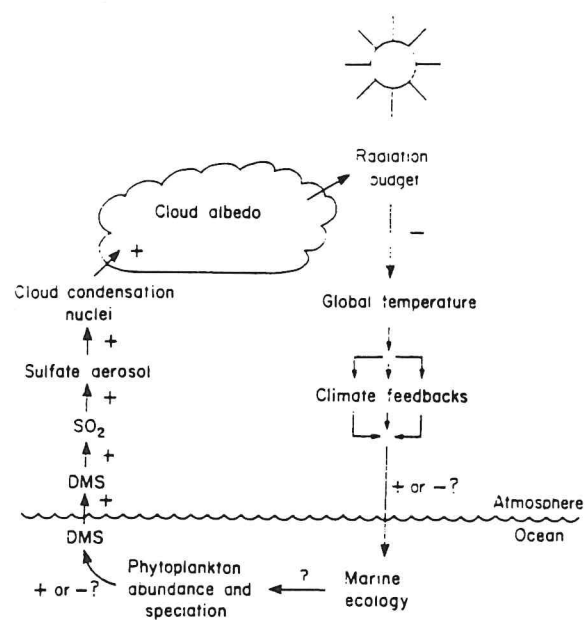


Fig. 7.2: Proposed feedback cycle between climate and marine DMS production (from Andreae, 1990).

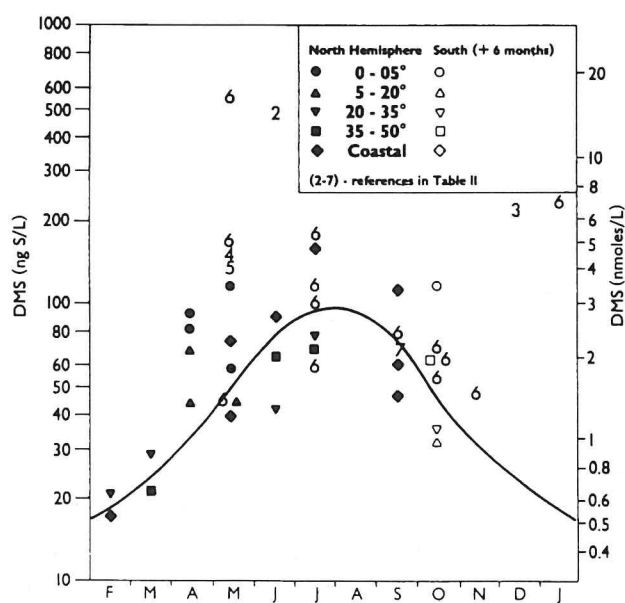


Fig. 7.3: The seasonality of oceanic DMS concentrations (from Bates et al., 1987b).

7.1. Occurrence, sources and sinks of dimethyl sulfide

The concentration of DMS in surface seawater is extremely variable both spatially and temporally. The concentration differences are orders of magnitude ranging from less than 1 to more than 1000 ng S(DMS).l⁻¹ (Barnard et al., 1982; Andreae & Raemdonck, 1983; Andreae & Barnard, 1984; Bates et al., 1987b). In coastal and shelf waters the concentrations of DMS are often higher than in open ocean waters (Andreae & Barnard, 1984; Holligan et al., 1987; Turner et al., 1988), although conflicting observations have been reported (Andreae, 1986). DMS is present in oceanic surface waters in concentrations far above the expected level of equilibrium with the atmosphere (Lovelock et al., 1972; Andreae & Raemdonck, 1983; Andreae, 1986). The concentration of DMS in the marine atmosphere is generally so small (Barnard et al., 1982) that the flux across the air-sea interface is completely determined by the DMS concentration in the seawater (Andreae, 1986). The estimated annual flux of DMS from the oceans to the atmosphere is 27-40 Tg S.y⁻¹ (Nguyen et al., 1978; Andreae & Raemdonck, 1983; Andreae, 1986; Bates et al., 1987b), with the higher estimate being the most probable according to recent insights (Andreae, 1986). This natural flux is comparable to the total anthropogenic sulfur flux to the atmosphere due to fossil fuel burning of ca. 80 Tg S.y⁻¹ (Cullis & Hirschler, 1980; Möller, 1984).

The seasonal variation of DMS in surface ocean waters is shown in Fig. 7.3. Clearly, in the summer months the concentration is the highest. Another feature of DMS is its positive correlation with chlorophyll, primary productivity and phytoplankton abundance (Cline & Bates, 1983; Andreae & Barnard, 1984; Andreae et al., 1985; Turner et al., 1988). These facts indicate that phytoplankton is responsible for the production of DMS. DMS was found to be produced from a precursor present in algal tissue, named dimethyl sulfonium propionate (DMSP) or alternatively dimethylpropiothetin (Challenger & Simpson, 1948; Ackman et al., 1966; Vairavamurthy et al., 1985). The latter compound may well be involved in regulating the osmotic pressure in algal cells (Reed, 1983; Vairavamurthy et al., 1985). Algae also release DMSP, which is subsequently decomposed to DMS in the seawater (Turner et al., 1988). The content of DMSP and the DMS release vary greatly from species to species (Ackman et al., 1966; White, 1982; Turner et al., 1988). The DMS release is associated with both metabolism and senescence of the algae (Nguyen et al., 1988). The DMS release from phytoplankton occurs continuously, the rate in a monoculture being estimated as low as 4.10⁻⁵ ng S(DMS) per cell per day (Vairavamurthy et al., 1985). This rate increases steeply when the plankton is subjected to stress, such as salinity changes or exposure to the atmosphere (Andreae, 1986). The most dramatic release of DMS by phytoplankton is reportedly caused by zooplankton grazing (Dacey & Wakeham, 1986). DMS production due to grazing may be the major production mechanism in the marine environment (Dacey & Wakeham, 1986).

Another source of DMS is the decomposition of organic sulfur by bacteria (Zinder et al., 1977; Wakeham et al., 1984; Andreae, 1985b). On the other hand, bacteria are also able to consume DMS, both under aerobic and anaerobic conditions (Zinder & Brock, 1978; Kiene et al., 1986; Wakeham et al., 1987). The main pathway DMS follows in the marine environment is schematically shown in Fig. 7.4 (note that the consumption of DMS by bacteria is not included in this Figure). Andreae (1985b) estimated that in an upwelling area ca.1% of the sulfur assimilated by the phytoplankton is released as DMS.

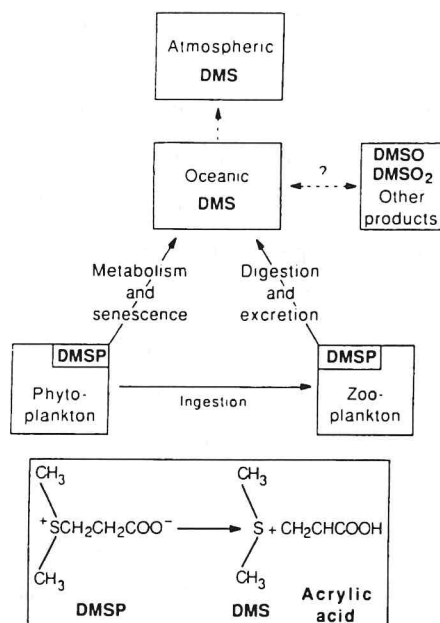


Fig. 7.4: Scheme showing the formation of DMS in oceanic waters (from Dacey & Wakeham, 1986).

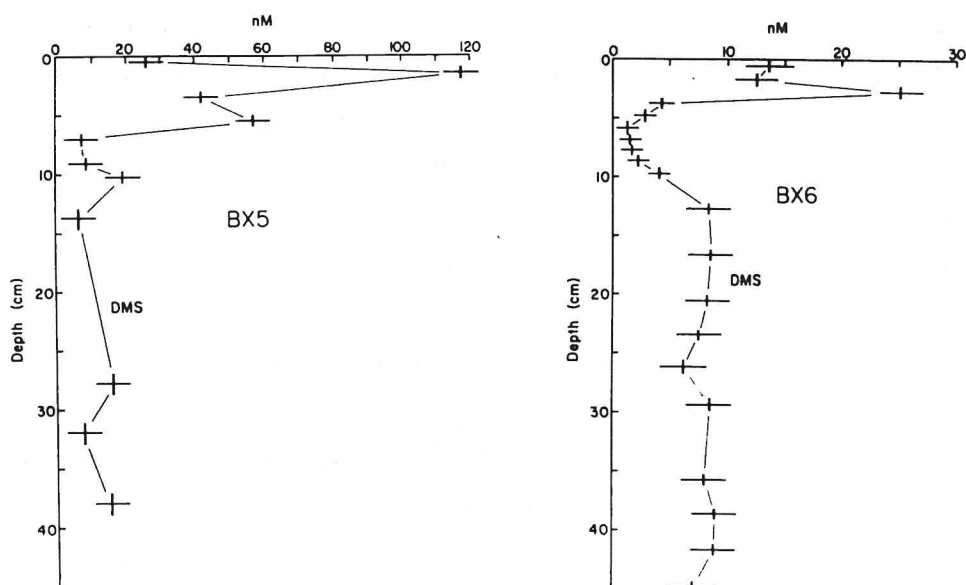


Fig. 7.5: Vertical profiles of DMS in the porewaters from two sediment cores from organic-rich sediments (from Andreae, 1985b).

According to Andreae (1986) the DMS concentration in oceanic surface waters is the result of the combined action of production by phytoplankton, consumption by bacteria, volatilization across the air-sea interface and downward transport into the deep ocean by eddy diffusion (see also Andreae & Barnard, 1984). Other sinks of DMS are possible, such as photochemical oxidation or adsorption on suspended matter (Brimblecombe & Shooter, 1986). The presence of DMS even in the deep oceans at a relatively constant level suggests that abiotic removal mechanisms are relatively unimportant (Andreae & Barnard, 1984; Shooter & Brimblecombe, 1989).

7.2. Sources and sinks of dimethyl sulfide in the North Sea

Some studies have been performed on DMS which included North Sea waters (Turner & Liss, 1985; Turner et al., 1988, 1989; Barnard et al., 1982). Sources and sinks are brought together in Table 7.2. The most important source of DMS to the North Sea is the in situ production by algae (Turner et al., 1988, 1989). Especially coccolithophorids and dinoflagellates were held responsible for a large production of DMS, but also the flagellate *Phaeocystis pouchetii* (see also Barnard et al., 1984; Holligan et al., 1987). In winter slightly elevated levels of DMS were found along the coasts, which were associated with river water input from the Rhine (Turner et al., 1988). Rasmussen (1974) reported DMS release by freshwater algae. Bacteria produce DMS during the degradation of organic matter and when organic sulfur is present (Bremner & Steele, 1978; Kadota & Ishida, 1972). The high organic waste load of rivers may thus cause elevated levels of DMS in river waters. A third reason why DMS in river water may be high is industrial activity, for example paper mills (Sivelä & Sundman, 1975, as cited in Balzer, 1981). Thus, river water is a source of DMS to the North Sea. In summer one would expect the source strength to be greater than in winter because of higher algae activity in the river water.

Indirectly the rivers are an additional source of DMS for two reasons. Firstly, they bring nutrients to the coastal waters, causing blooms of phytoplankton and accordingly elevated DMS production in the coastal regions. Secondly, at the freshwater-seawater transition the phytoplankton experiences salinity stress, which causes them to release extra DMS (Andreae, 1986).

The sediments are another potential source of DMS (Kiene & Visscher, 1987). Andreae (1985b) reported enhanced DMS concentrations in the sediment porewaters of the upwelling area near Peru. He calculated that the possible fluxes of DMS to the overlying water column were small compared to the surface water DMS production. The elevated DMS concentration in and the DMS flux from the sediment porewaters is caused by the decomposition of sedimented algal material (Zinder et al., 1977), which reached the seafloor either by direct settling or through faecal pellets via the zooplankton. Andreae (1985b) found that sedimentary DMS fluxes from a shallow area were higher than from a deeper area. This was explained by differences in time available for settling dead phytoplankton to be degraded, such that in the shallower area more degradation will have to occur in the bottom, with accordingly higher DMS production. The DMS production in the sediments was consistent with the part of the primary production that settled down from the euphotic zone, which in his case was only minor. This implies that the sedimentary DMS flux in the first place should be in some way dependent on the magnitude of the primary production in the overlying water column. In the North Sea and bordering areas on the contrary a much larger part of the primary production sinks

out (up to 35%, chapter 2) and therefore it is expected that in the North Sea the sediments might cause the overall DMS release to be more important than the ~1% of all sulfur assimilated as estimated by Andreae (1985b). Continuing the comparison, the coastal sediments will probably be a larger source than the central and northern North Sea sediments. Unfortunately, no measurements are available to support these hypotheses.

In another way the Wadden Sea sediments are possibly a source of DMS. A large part of the bottom emerges around each tidal period of low water. The bottom algae will then be exposed to the atmosphere, which will cause an increased excretion of DMS (Andreae, 1986). Again, no data are available to quantify this. On the other hand, DMS may also be consumed in the bottom, as evidenced by the profiles measured by Andreae (1985b) (Fig. 7.5). The source or sink function of the bottom is determined by the interplay between production and consumption. In the sediment cores measured by Andreae (1985b) it appears that consumption occurs essentially below the zone of nitrification, while the DMS peak appeared to coincide with the nitrate maximum. This means that sediments will generally be a net source of DMS. Through advection DMS is transported into and out of the North Sea as well. Possibly the Baltic will have an elevated DMS concentration due to high primary production, industrial inputs (e.g. paper mills and waste streams) and salinity stress. The concentration in the English Channel is relatively small compared to the North Sea (Turner et al., 1988), but in the northern North Sea and the North Atlantic concentrations are high due to coccolithophorid blooms. The main sink of DMS for the North Sea is emission to the atmosphere (Turner et al., 1988, 1989; Turner & Liss, 1985), although consumption in the water column might also occur. The magnitude of the latter sink term is not quantified.

7.3. Estimates of the dimethyl sulfide flux from the North Sea to the atmosphere

Assessment of DMS emissions to the atmosphere contain uncertainties due to several causes. Not all different kinds of DMS source areas are known well enough to obtain a sufficiently resolved spatial distribution that covers the entire North Sea. For instance, bordering seas and estuaries may be more significant sources than the open sea. Secondly, there is a very large seasonal amplitude of DMS production which is hard to take into account properly. Thirdly, patchiness of the DMS distribution is large due to different DMS production rates for different phytoplankton species, and rapidly changing external conditions. And fourthly, the methods to calculate fluxes contain intrinsic uncertainties (see also Liss & Merlivat, 1986).

Turner et al. (1988) for the waters around Britain came to winter and summer fluxes of 16 and 935 $\mu\text{g S(DMS).m}^{-2}.\text{d}^{-1}$, respectively, while Turner et al. (1989) calculated a mean spring/summer flux of 1030 $\mu\text{g S.m}^{-2}.\text{d}^{-1}$. The global mean DMS flux amounts to ~290 $\mu\text{g S.m}^{-2}.\text{d}^{-1}$ (Andreae, 1986). The seasonal amplitude on the European shelf is striking (factor 60), where on the western U.S. shelf only a factor 3 difference was calculated (Bates & Cline, 1985). The total North Sea emission of DMS to the atmosphere, based on the figures of Turner et al. (1988) amounts 0.2 Tg S.y^{-1} ($= 0.006 \text{ Tmol S.y}^{-1}$). Other estimations of DMS release by the North Sea were given by Colijn et al. (1988), based on 2 other methods. Their first method emanates from the mean primary production in the North Sea and a fixed S-content of the algae, whereas the second from the mean DMS production per cell. Calculated DMS emissions range from 0.4-1.0 Tg S.y^{-1} (corrected for the

Table 7.2: Summary of the DMS fluxes within the North Sea, units g S.y^{-1} .

	sources	changes 1930-1990
In situ production	major	++
River runoff	minor	+
Sediment-water column	major	+
Emerging tidal flats	unknown	no
Advection	minor	no
	sinks	
Atmospheric release	$2 \cdot 10^{11}$	$+2 \cdot 10^{10}$
Advection	minor	no
Bacterial consumption	minor	+
Photochemical oxidation	negligible	no
Adsorption on suspended matter	negligible	no

different surface area of the North Sea that was used by them). These methods are however less reliable than the direct flux calculations.

Although the idea of localized 'hot-spots' - i.e. relatively small, high productivity areas that dominate the global S-flux to the atmosphere - has been abandoned (Andreae, 1985b, 1986), the measurements by Turner et al. (1988) suggest that the North Sea is a greater source than expected on the basis of its surface area. The North Sea contribution to the world production of DMS by the oceans ($1.2 \text{ Tmol S.y}^{-1}$, Andreae, 1986) would be about 0.5%, not much within global perspective but quite significant when realizing that the North Sea covers only 0.16% of the world oceans. Alternatively, these considerations may indicate that other shelf or ocean areas, with high primary production driven by the proper (i.e. DMS-producing) algal species, are underestimated as DMS sources. Once measured this would yield a larger total world DMS flux from the seas to the atmosphere, yet the relative contribution of the North Sea would diminish accordingly.

7.4. Possible changes in dimethyl sulfide release from the North Sea due to anthropogenic activity

Because the production of DMS is largely mediated by phytoplankton it is expected that any changes in phytoplankton abundance or production would also affect DMS. For the North Sea changes in DMS are not documented, but changes in phytoplankton are (see also chapter 3). Major DMS changes are only expected when algae species increased which concurrently produce large amounts of DMS. For the North Sea particularly interesting is the flagellate *Phaeocystis pouchetii*, which fulfils both conditions. The production of DMS by this species was established at sea to be significant (Barnard et al., 1984; Holligan et al., 1987). In Dutch coastal waters *Phaeocystis* cell numbers increased fourfold and the bloom period from 20 to 100 days during the time span 1973-1985 (Cadée & Hegeman, 1986). Based on these figures and assuming 10% of the North Sea to be affected by *Phaeocystis* increase Colijn et al. (1988) estimated that the DMS flux to the atmosphere increased with $0.019 \text{ Tg S.y}^{-1}$ (which is 10%). This estimate is probably too high, because *Phaeocystis* did not increase that much along the whole coastline. On the other hand, the microphytobenthos in the Wadden Sea also increased significantly (Cadée, 1984), which might have enhanced the DMS flux upon their exposure to air. This contribution was not included in the above estimate. It is however not quantifiable due to lack of data on this phenomenon.

It can safely be concluded that the DMS flux to the atmosphere must have increased significantly due to eutrophication, where the (Dutch) coastal waters undoubtedly play an important role.

8. RECOMMENDATIONS

The present overview again stresses that our understanding of the North Sea carbon cycle is far from complete. Without such complete knowledge it is difficult to assess the influence of human activity on the carbon cycle and to predict future developments. Partly we have tried to meet this problem using model calculations for predicting changes due to increased amounts of nutrients. Exactly this problem of increased nutrients was selected because eutrophication of the coastal waters appears to be the most severe human impact on the North Sea carbon cycle. As part of these model calculations the influence of DOC was investigated as well since recent improvement of the method of determination of DOC provided a major change in our thinking about carbon cycling and the role of DOC therein. Based on the present limited knowledge the modifications of the North Sea carbon cycle appear quantitatively minor compared to the direct fossil fuel CO₂ emissions by The Netherlands. However, future changes in the North Sea system might give a different picture.

We need a better understanding of processes and fluxes and their mutual interdependencies, hence more emphasis should be placed on investigating these processes directly rather than deriving them from distributions and standing stocks of elements or groups of organisms. One process of primary concern is primary production. Standardization of its determination is a challenge and consecutively a more intense coverage, both in space and time, is necessary. Also the influence of enhanced nutrient loads needs to be resolved unequivocally, both with respect to primary production and to higher levels within the ecosystem. In addition, knowledge has to be gained about what eventually happens with the primary produced matter, notably quantifying the flows of carbon leaving the system by sediment burial or along with the water mass transport towards the Atlantic Ocean. Connected with this issue is the question if the carbon cycle of the North Sea is in a steady state on an annual basis or not. The effects of toxic substances at the ecosystem level and carbon cycle level constitute a major lack of knowledge. While given the current limited knowledge long-term time series such as those of phytoplankton, zoobenthos and nutrients will stay of utmost importance for signalizing changes. Moreover, these time series will also provide insight in the complex and variable nature of the shallow North Sea. In the same line of thought lies the need for good indicators (organisms or substances) for detecting or predicting changes.

Through the finding that DOC values were previously probably taken 2 to 3 times too low carbon cycling needs a new context to be placed in. New and extensive measurements of DOC with the improved method are needed, which will certainly lead to much larger DOC values for the reservoir and its turnover than previously thought. Besides, the consequences of these new DOC distributions for the other reservoirs and for fluxes have to be investigated. Because DOC follows the water movements it possibly constitutes a major transport route (and sink) of primary produced material to the ocean. The composition of DOC is hardly known and also needs investigation, for certain compounds included in it may play a role in other processes, like phytoplankton growth. In addition, typical components may be reliable indicators for changes or may have predictive value.

As regards to the other radiatively-active gases CH₄, N₂O and DMS all sources and sinks in the North Sea should be properly documented and in particular the effect of eutrophication on their emission needs more reliable quantification. The North Sea may well be one of the disproportionately major sources for these gases in the global context.

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