

Sinks and sources of CO₂ in coastal seas: the North Sea

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ABSTRACT

Alkalinity, Σ CO₂ and pH were measured and the respective PCO₂ was calculated for over 1000 water samples from the North Sea. Distribution of these parameters in the surface waters in May–June, 1986, shows that three principle water masses exist in the North Sea: North Atlantic water, Skagerrak water and German Bight water. The carbonate parameters of the German Bight water are indicative of an intense plankton bloom which reduced the PCO₂ to values as low as 88 ppmv. Assuming an average thickness of the stagnant boundary layer of 40 μ m, the CO₂ flux entering the areas with a PCO₂ below that of ambient air (346 ppmv in 1986) amounted to 3.1×10^9 moles CO₂ d⁻¹. However, at the same time, areas with a PCO₂ up to 518 ppmv and therefore higher than the atmospheric PCO₂ co-existed in the central North Sea and near the British coast. These areas formed a source for CO₂ to the atmosphere in the size of 1.1×10^9 moles CO₂ d⁻¹. Taken together, the North Sea had an area-averaged PCO₂ of 323 ppmv and formed a net sink for CO₂ in the range of 2.0×10^9 moles d⁻¹ or 7.5×10^4 moles km⁻² d⁻¹ or 24×10^3 t C d⁻¹ in summer 1986. It is estimated that a total of 4.3×10^6 t C enters the North Sea in the warm season. This size is comparable to the additional CO₂ uptake by phytoplankton induced by the anthropogenic input of nutrients which amounts to $5\text{--}6 \times 10^6$ t C a⁻¹.

1. Introduction

The rapid anthropogenic release of CO₂ from fossil fuel and from biosphere destruction has upset the natural carbon cycle (e.g., Degens et al., 1984). Roughly half of the surplus CO₂ stays in the atmosphere, while half enters the ocean because of the chemical buffer capacity of the aqueous carbonate system. Additionally, phytoplankton might sequester CO₂ in coastal seas because of ongoing eutrophication. It is estimated that phosphorus and nitrogen inputs to coastal seas have increased by a factor of ten since 1850 (Walsh et al., 1985). One of the most polluted coastal seas is the North Sea (Kempe et al., 1988). It is situated between 51°N and 61°N and 4°W and 9°E and covers an area (A) of 525,000 km². It receives an excess of nutrients from British and Central European rivers (Kempe et al., 1989, 1990). The annual load of phosphorus and nitrogen to the North Sea is estimated to be 120×10^3 t and 970×10^3 t, respectively (ICES, 1978). The elemen-

tal ratio of C:N:P of phytoplankton (Redfield ratio, 105:15:1; Broecker and Peng, 1982) suggests an additional sequestering of carbon of roughly $5\text{--}6 \times 10^6$ t C annually.

However, several questions remain unclear in this approach. First, it is not certain that this carbon is derived from the atmosphere, it may be derived from the high carbonate alkalinity of rivers entering the North Sea. Second, phosphorus may be buried bound to inorganic compounds and nitrate might be denitrified, thus diminishing the nutrients available for plankton blooms. Third, much of the organic matter produced is respired again leading to interannually increasing nutrient concentrations and an increase in the annual amplitude of plankton blooms, but not necessarily to a net subtraction of organic matter with settling sediments. These increases are in fact observed in the long-term record of nutrient concentrations and primary productivity at Helgoland (Radach and Berg, 1986).

Permanent deposition of additionally fixed

carbon is also hampered by the shallow depth of the North Sea (average 80 m; Anon. 1980). Much of its southern reaches are even less than 40 m deep. Storms can thus resuspend fine-grained sediments. In fact, permanent deposition of fine sediments is, except for a few isolated small areas, possible only in the Skagerrak and in the Norwegian Trough where water depths exceed 100 m (Salge and Wong, 1988).

In order to gain more insight into the question of CO₂ fixation in eutrophied coastal seas we attempt in this study to calculate the CO₂ exchange between the North Sea surface and the atmosphere.

2. Material and methods

For this purpose we investigated the carbonate system in the North Sea 1985 and 1986 on four cruises during the project "Biogeochemistry and Distribution of Suspended Matter in the North Sea and Implications to Fisheries Biology" funded by the German Minister for Research and Technology (BMFT). At 205 stations a total of 1000 water samples were taken and their pH values, alkalinities and total inorganic carbon concentrations (ΣCO_2) measured (Pegler, 1989). Salinity, temperature, oxygen, chlorophyll, POC, and nutrient concentrations were simultaneously measured by other colleagues. The most extensive

data set was obtained during the R/V Planet and R/V Gauss cruises 2 May–13 June 1986, which were organized by the BMFT project "Circulation and Pollutant Transfer in the North Sea." Results from that cruise allow one to draw maps of the summer conditions of the total North Sea surface with regard to the parameters of the carbonate system.

Alkalinity and ΣCO_2 were determined with a high precision, computerized, automatic Gran titration using similar equipment and software as described by Bradshaw et al. (1981). Titration was done at 25°C with 20 or 25 mm³ increments of 0.2 eq dm⁻³ HCl + 0.45 eq dm⁻³ NaCl as a titer. The closed cell had a volume of $137.75 \pm 0.1 \text{ cm}^3$ which gives a precision of $\pm 2 \mu\text{eq kg}^{-1}$ at average alkalinities of 2.3 meq kg⁻¹. Further details of the method are given in Pegler and Kempe (1988). The pH was measured immediately after recovery of the sample with a WTW-pH91 meter and an INGOLD combination electrode PT-408 standardized against

pH = 7.385 at 25°C/INGOLD 9806,

pH = 9.180 at 25°C/INGOLD 9807

(DIN 19266 and NBS).

Repeated pH-measurements differed by ± 0.01 and drift between standardizations stayed below ± 0.02 pH. Thus total accuracy of pH determination was probably better than ± 0.03 pH.

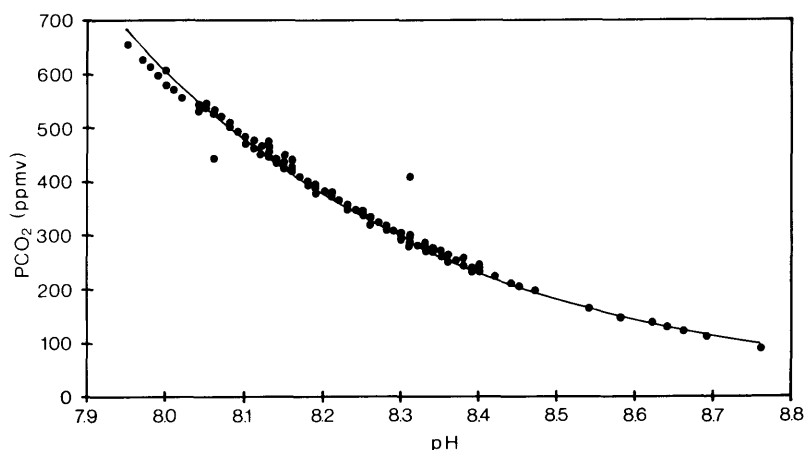


Fig. 1. Empirical transfer function $\text{PCO}_2 = 158.06 \times 10^3 \times e^{(-2.422 \times \text{pH})}$ with a correlation coefficient $r = -0.97$ as derived from $N = 528$ water samples taken throughout the North Sea and from various depths in May–June 1986.

From the pH, salinity, temperature, and alkalinity data the PCO_2 , the carbonate ion concentrations, and the calcite saturation index was calculated with the program WATMIX of Wigley and Plummer (1976). The program uses a full ionic model and is valid for all salinities. This approach was chosen because of the wide range in salinities, alkalinities and pH values encountered in the North Sea instead of the calculation of PCO_2 using the apparent carbonate system equilibrium constants for seawater (e.g., Broecker and Peng, 1982).

As is expected from carbonate thermodynamics, the results of this procedure show that the relation of pH to PCO_2 is exponential and highly signifi-

cant ($\alpha < 0.1\%$). The relation is described by the equation (Fig. 1):

$$\text{PCO}_2 = 158.06 \times 10^9 \times e^{(-2.4220 \times \text{pH})}.$$

This transfer function is based on 528 water samples taken in May and June 1986 from various depths in the North Sea and is valid between 700 and 100 ppmv PCO_2 and 7.95 and 8.75 pH and for a wide range of salinities, alkalinities, ΣCO_2 , and temperatures. It allows to calculate PCO_2 reasonably accurately from simple pH measurements and makes thus fast surveys of PCO_2 in the North Sea feasible without complicated titration of alkalinity and ΣCO_2 and complex computations.

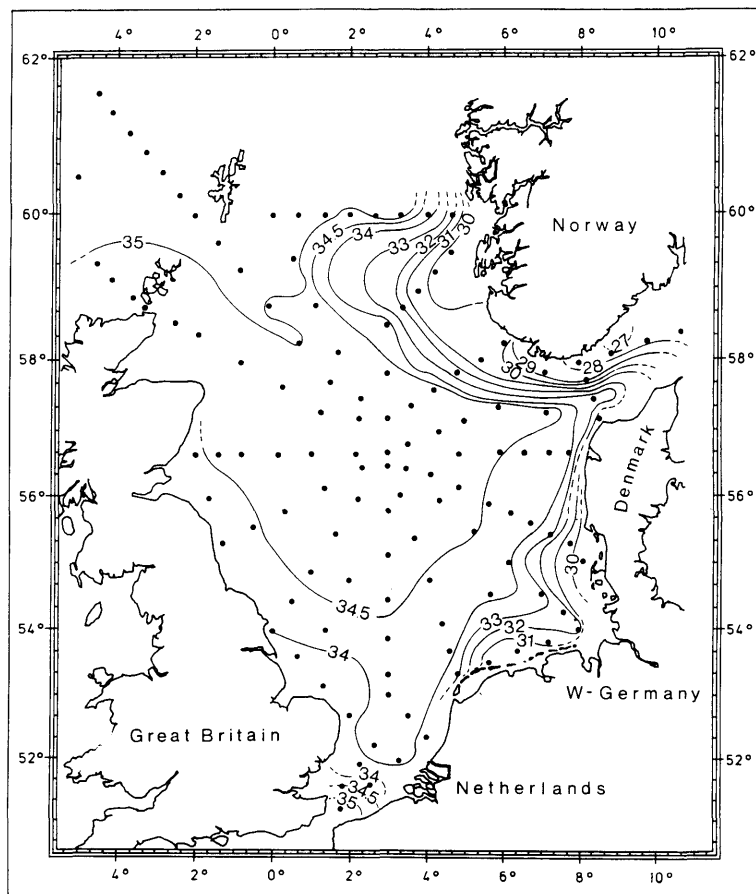


Fig. 2. Distribution of salinity (5 m depth) in the North Sea in May-June 1986.

3. Water masses of the North Sea

The distributions of the salinity, alkalinity and ΣCO_2 (Figs. 2–4) show that essentially three water masses exist in the North Sea.

(1) The North Atlantic water mass which enters the North Sea from the Northwest and through the English Channel and carries high salinity (> 35 permil) and ΣCO_2 (> 2.10 mmol kg⁻¹) and an intermediate alkalinity (2.32–2.34 meq kg⁻¹).

(2) The Skagerrak water mass which is formed by the outflow of Baltic Sea water and which is characterized by low salinities (27–32 permil),

low ΣCO_2 (2.05–1.90 mmol kg⁻¹) and low alkalinities (2.32–2.12 meq kg⁻¹). And

(3) the German Bight water mass which is influenced by the fresh water input of Central European rivers. It has low salinities (34–30 permil), a low ΣCO_2 (2.05–1.90 mmol kg⁻¹) and high alkalinities (> 2.34 meq kg⁻¹).

The mixing of these three water masses is quite evident in the alkalinity-salinity scatter plot (Fig. 5, top). Two linear trends appear, one, with a negative slope, encompassing the data from the German Bight and one, with a positive slope, including the Skagerrak samples. Both regressions

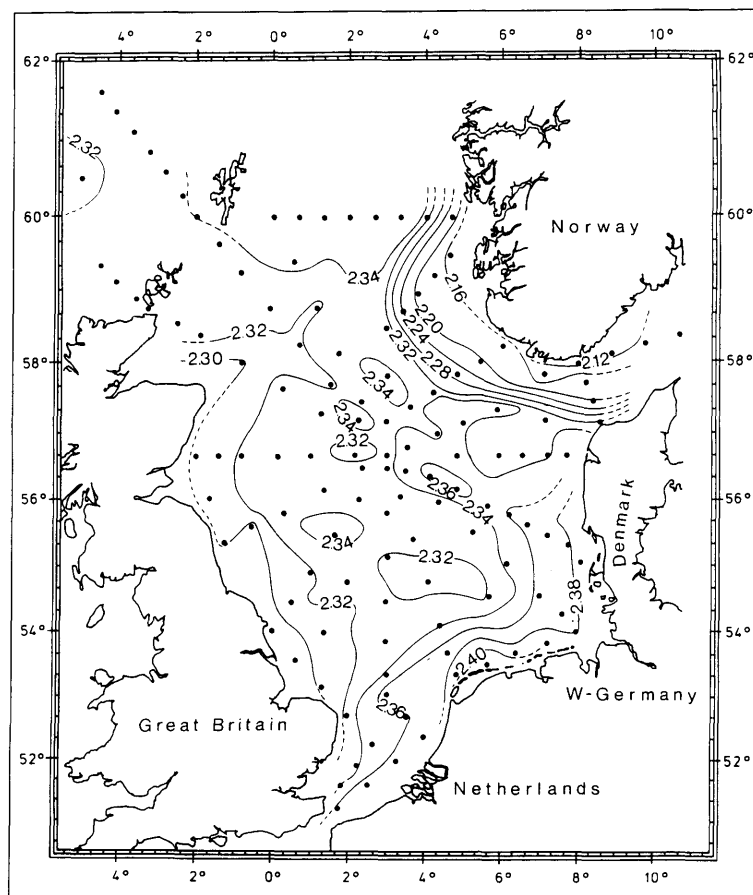


Fig. 3. Distribution of alkalinity (5 m depth) in the North Sea in May–June 1986.

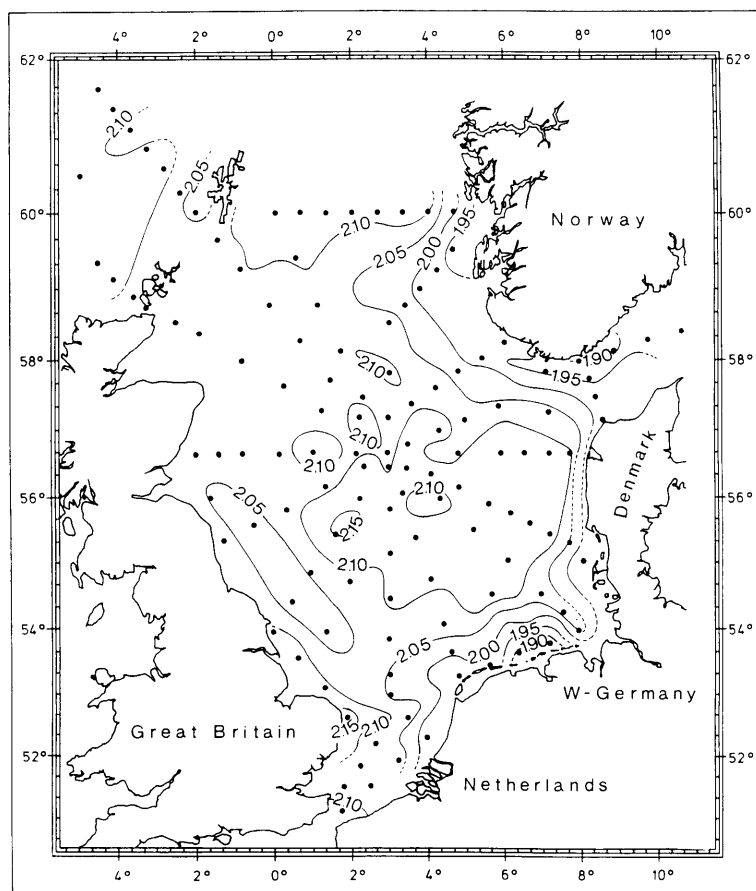


Fig. 4. Distribution of ΣCO_2 (5 m depth) in the North Sea in May–June 1986.

converge towards the North Atlantic water mass of S ca. 35 permil and Alk. ca. 2.35 meq kg^{-1} . The salinity- ΣCO_2 scatter plot (Fig. 5, bottom), however, does not show these two mixing lines and both the Skagerrak and the German Bight water masses appear to fall on the same mixing line.

The explanation of this difference between the mixing lines of alkalinity and ΣCO_2 is the eutrophication of the German Bight. Originally the rivers Rhine, Weser and Elbe discharged water high in alkalinity and high in ΣCO_2 (Kempe, 1982a, b). Because they have a very high PCO_2 (and a low pH) they do not have any appreciable carbonate ion content. Therefore alkalinity (in meq kg^{-1}) and ΣCO_2 (in mmoles kg^{-1}) must

have the same numerical values (i.e., 2.6 according to the Y-axis intersect in the regression equation of Fig. 5, top). Since alkalinity is largely a conservative property, the ΣCO_2 must have been diminished by photosynthesis and by the production of organic carbon.

4. The CO_2 budget

This interpretation is substantiated by the distribution of the pH and the PCO_2 in North Sea surface waters (Figs. 6 and 7). The northern North Sea and the Skagerrak have pH values of between 8.2 and 8.4 corresponding to PCO_2 values of 300

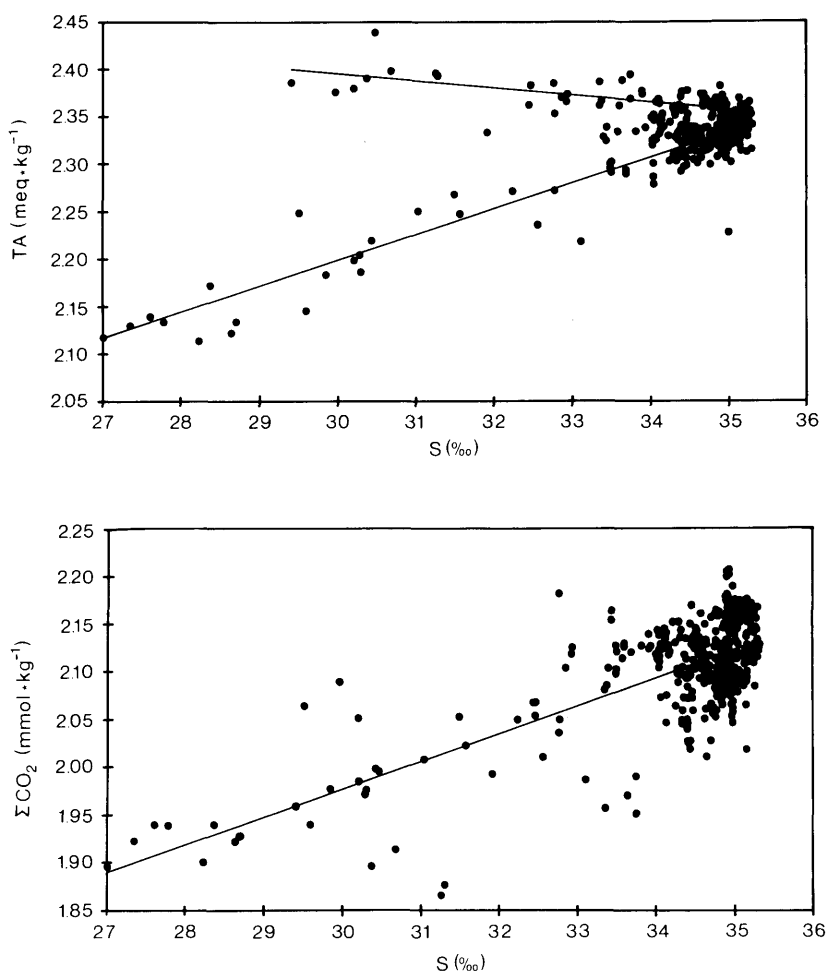


Fig. 5. Relation between salinity and alkalinity (top) and salinity and ΣCO_2 (bottom) for all North Sea samples of May–June 1986. The linear regressions are: $\text{TA} = -0.0074 \times S + 2.6150$ for $\text{TA} \geq 2.35$ ($r = -0.70$; $N = 119$), $\text{TA} = 0.0272 \times S + 1.3830$ for $\text{TA} < 2.35$ ($r = 0.91$; $N = 406$), and $\Sigma \text{CO}_2 = 0.0294 \times S + 1.0966$ ($r = 0.70$; $N = 525$).

to 400 ppmv, i.e., similar to atmospheric pressure (in 1986: 346 ppmv). The central North Sea and the British coast have low pH values corresponding to PCO_2 values of above 400 ppmv, indicative that the North Sea gives off CO_2 to the atmosphere. Values were as high as 518 ppmv near the Humber mouth, indicating that this part of the North Sea suffers from exceptionally high rates of respiration, possibly due to waste inputs. The German Bight, however, has very high pH values, up to 8.7, corresponding to very low PCO_2 values, indicative of CO_2 uptake from the atmosphere.

One coastal station has a PCO_2 of <100 ppmv. In this region an extremely active plankton bloom was encountered clearly seen in simultaneous high chlorophyll values. From Fig. 7, it is clear that during early summer the North Sea functions both as a sink and as a source for atmospheric CO_2 .

If the North Sea were devoid of life, it should function in summer as a source for CO_2 , simply because the solubility of CO_2 in warm water is less than in cold water. At winter temperatures of 3–7°C, 22.3 $\mu\text{mol} \text{CO}_2 \text{ kg}^{-1}$ are needed to maintain a PCO_2 of 346 ppmv, while in summer at

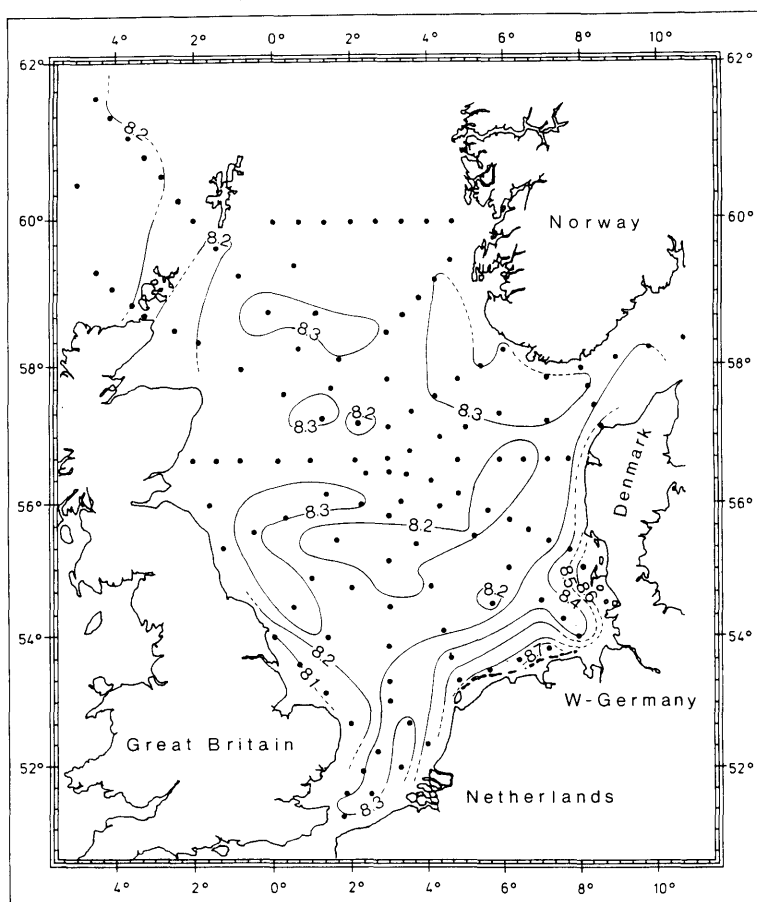


Fig. 6. Distribution of pH (5 m depth) in the North Sea in May-June 1986.

temperatures of 13–17°C, 16.2 $\mu\text{moles CO}_2 \text{ kg}^{-1}$ maintain the same PCO_2 . Compared to the annual average temperature of 10°C (corresponding to 19.0 $\mu\text{moles CO}_2 \text{ kg}^{-1}$) this would call for a daily flux of 4.5×10^9 moles CO_2 or $54 \times 10^3 \text{ t C d}^{-1}$ into the water in winter and out of the water in summer.

However, large parts of the North Sea act as a CO_2 sink also in summer. In order to estimate the total summer CO_2 flux the PCO_2 surface measurements were transferred to an area correct map (Fig. 7). Next, the areas between the isolines were integrated. Results are given in the bar-graph of Fig. 8, top, for 10 PCO_2 classes between 50 and 550 ppmv. The area weighted average PCO_2 of the North Sea derived from these values is 323 ppmv,

i.e., the North Sea acts in fact as a net CO_2 sink during summer.

Finally, the mass flux (FCO_2) across the air sea interface was calculated using the equation (e.g., Broecker and Peng, 1982):

$$\text{FCO}_2 = D \times ([\text{CO}_2]_{\text{air}} - [\text{CO}_2]_{\text{water}}) \times z^{-1}$$

where D is the diffusion coefficient ($1.32 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ or $1.14 \times 10^{-4} \text{ m}^2 \text{ d}^{-1}$ at the average temperature of 8.6°C during May-June 1986), $[\text{CO}_2]_{\text{air}}$ is the CO_2 concentration at 346 ppmv (i.e., 19.9 mmoles m^{-3}), $[\text{CO}_2]_{\text{water}}$ is the CO_2 concentration in the respective class and z is the thickness of the boundary layer (in μm). If we assume an average thickness of $z = 40 \mu\text{m}$

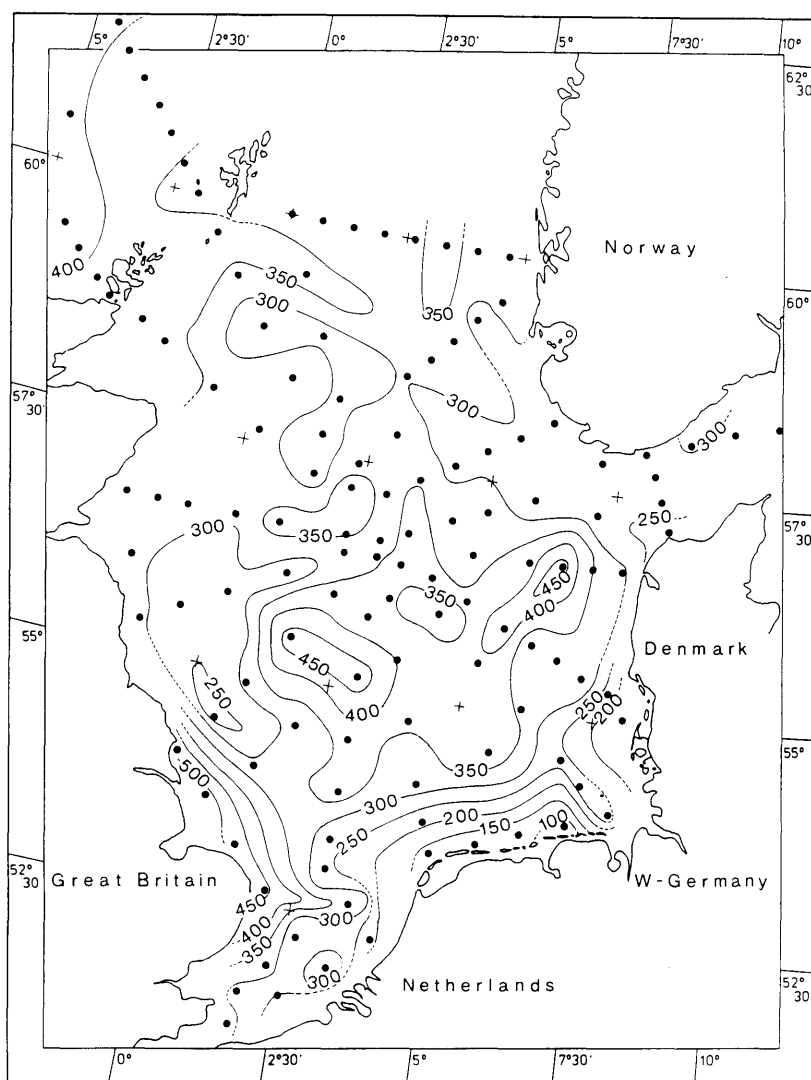


Fig. 7. Distribution of calculated PCO₂ (5 m depth) in the North Sea in May-June 1986 and locations of stations.

(Broecker and Peng, 1982), then the area averaged PCO₂ of 323 ppmv (= 18.6 mmol CO₂ m⁻³) yields a net flux of

$$\begin{aligned} \text{FCO}_2 &= 1.14 \times 10^{-4} \times (19.9 - 18.6) \times 10^{-3} \\ &\quad \times (40 \times 10^{-6})^{-1} \\ &= 3.705 \times 10^{-3} \text{ moles m}^{-2} \text{ d}^{-1} \\ &= 44 \text{ mg C m}^{-2} \text{ d}^{-1}. \end{aligned}$$

If one repeats this calculation for the ten PCO₂ classes and their areas separately (Table 1 and bar-graph Fig. 8, bottom) the net uptake of the North Sea becomes 2×10^9 moles CO₂ or 24×10^3 t C daily. This flux figure is valid for $z = 40 \mu\text{m}$. During storms, z becomes smaller, at $z = 30 \mu\text{m}$ the flux would increase roughly by 25% (Table 1). The inaccuracy in estimating z is the largest inaccuracy in assessing CO₂ fluxes across the air-sea interface.

Table 1. Daily area-weighted CO_2 fluxes (FCO_2) for 10 PCO_2 classes between 50 and 550 ppmv (column 1) between atmosphere and the surface layer of the North Sea in May/June 1986

PCO_2 Classes [ppmv]	Area (A) [km^2]	$\text{FCO}_2 \text{ A}^{-1} \times 10^{-4}$ for $z = 30 \mu\text{m}$ [moles $\text{km}^{-2} \text{ d}^{-1}$]	$\text{FCO}_2 \text{ A}^{-1} \times 10^{-4}$ for $z = 40 \mu\text{m}$ [moles $\text{km}^{-2} \text{ d}^{-1}$]	$\text{FCO}_2 \times 10^{-6}$ for $z = 40 \mu\text{m}$ [moles $\text{A}^{-1} \text{ d}^{-1}$]
50–100	932	+5.928	+4.446	+41.4
100–150	5,852	+4.826	+3.620	+211.8
150–200	16,931	+3.724	+2.793	+472.9
200–250	22,691	+2.660	+1.995	+452.7
250–300	103,867	+1.558	+1.169	+1,214.2
300–350	218,113	+0.456	+0.342	+745.9
$\Sigma < 350$	368,386	-	-	+3,138.9
350–400	115,008	-0.646	-0.485	-557.8
400–450	20,704	-1.710	-1.283	-265.6
450–500	9,162	-2.850	-2.138	-195.9
500–550	4,212	-3.914	-2.936	-123.7
$\Sigma > 350$	149,086	-	-	-1,142.0
Σ total	517,364	-	-	+1,996.9

CO_2 fluxes (moles $\text{km}^{-2} \text{ d}^{-1}$) are calculated for boundary layer thicknesses of $z = 30 \mu\text{m}$ and $z = 40 \mu\text{m}$ (column 3 and 4). For $z = 40 \mu\text{m}$ total fluxes for areas (A; column 2) are given (column 5). Positive values indicate sinks of atmospheric CO_2 and negative values sources for atmospheric CO_2 .

All other inaccuracies like measurements errors, inaccuracies in chemical constants and contouring errors are small compared to the difficulties in establishing z . The calculated fluxes are therefore rough estimates only. The fluxes calculated are representative of an area of 517,000 km^2 since the Wadden Sea areas were excluded from the calculation (total North Sea area is 525,000 km^2). Since the data span a time period of one and a half month in May and June one can, as a first approximation, assume that the daily flux is representative of the conditions of the warm season. The total net uptake becomes then $4.3 \times 10^6 \text{ t C}$ within half a year (Fig. 9). This figure compares favourably well with the organic carbon production calculated from the nutrient input which was $5\text{--}6 \times 10^6 \text{ t C a}^{-1}$.

This flux is still small when compared with the total primary productivity in the North Sea (Fig. 9). According to Aletsee and Rick (1988) the gross primary productivity reaches $170 \times 10^6 \text{ t C}$

in summer. $20 \times 10^6 \text{ t C}$ are consumed for autorepiration resulting in a net primary productivity of $150 \times 10^6 \text{ t C}$. The total ΣCO_2 in the euphotic zone of the North Sea (assumed to have a depth of 20 m) is estimated to $270 \times 10^6 \text{ t C}$ which implies that the average carbon atom has only a residence time of 1.6 years in the inorganic pool. It also implies that the NPP is quickly recycled by heterotrophic respiration because otherwise the ΣCO_2 concentration would decrease to less than 50% its average value during plankton blooms. This, however, is not the case as can be seen from Figs. 4 and 5. The total phytoplankton mass in the North Sea is estimated to $1.4 \times 10^6 \text{ t C}$ (Aletsee and Rick, 1988) which suggests a turnover of its carbon every 1.3 days.

An extremely fast recycling of organic carbon is also indicated by the size of the vertical carbon flux leaving the euphotic zone. This flux was measured by two sediment traps, one moored in the Norwegian Trough, one moored in the Skagerrak

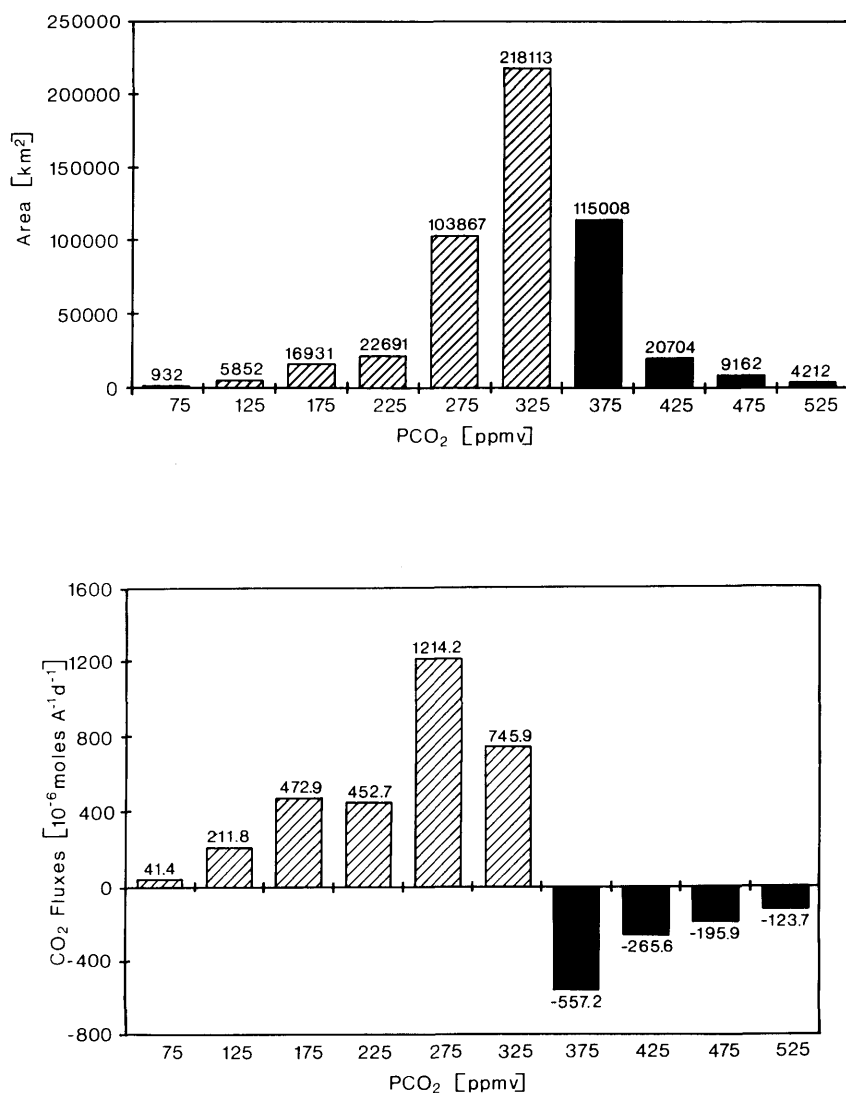


Fig. 8. Sizes of North Sea surface areas ($A = 517,000 \text{ km}^2$) in various PCO₂ classes (top) and resulting daily net CO₂ fluxes (bottom). The North Sea gains $3.139 \times 10^9 \text{ moles CO}_2 \text{ A}^{-1} \text{ d}^{-1}$ from the atmosphere and loses $1.142 \times 10^9 \text{ moles CO}_2 \text{ A}^{-1} \text{ d}^{-1}$ to the atmosphere. The net CO₂ flux amounts to $1.997 \times 10^9 \text{ moles A}^{-1} \text{ d}^{-1}$.

(Kempe and Jennerjahn, 1988). Their average summer C_{org} fluxes amounted to 8.7 and 27 mg C m⁻² d⁻¹, respectively, while their CaCO₃-C_{inorg} flux amounted to 2.4 and 8.0 mg C m⁻² d⁻¹. Taking averages from these figures and assuming that this flux is representative for all of the North

Sea, a total vertical carbon flux of $1.5 \times 10^6 \text{ t C}_{\text{org}}$ per half year and $0.3 \times 10^6 \text{ t C}_{\text{inorg}}$ per half year is indicated. This figure is small compared to the NPP, indicating that only 1% of the organic carbon produced in the North Sea has a chance to reach the sediment.

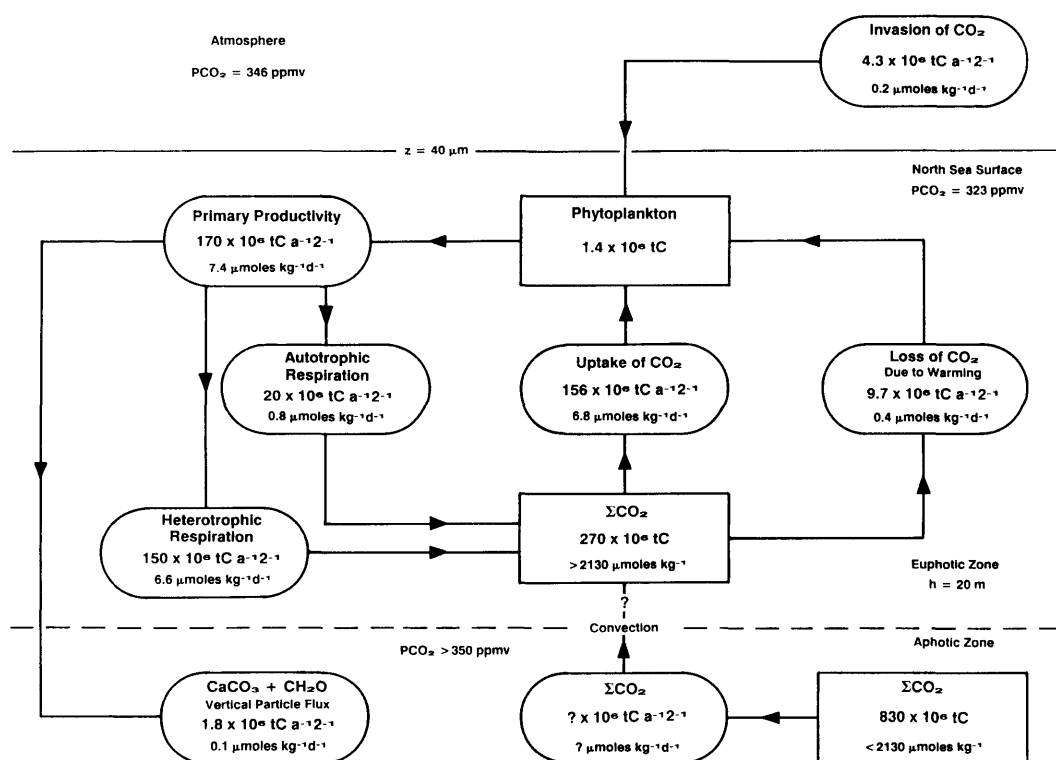


Fig. 9. Pools and fluxes of CO₂ in the North Sea according to various sources. For further explanations see text.

6. Conclusions

In summer, the North Sea is a net sink for atmospheric CO₂. This is in spite of the seasonal warming, which tends to cause degassing. The cause of this reversal in trend is intensive photosynthesis. The question remains, if in winter respiration will cause the release of enough CO₂ to cause the North Sea to become a source of CO₂ in spite of seasonal cooling. Data by Weichert (1985) suggest that in fact CO₂ is degassed from the surface of the German Bight in winter. If this degassing is, however, large enough to make the entire North Sea a source for CO₂ and if this is more than the summer uptake, remains to be shown.

The magnitude of the summer sink of CO₂ in the North Sea, an estimated $4.3 \times 10^{12} \text{ gC}$, is by no

means trivial for the global carbon cycle. This is especially so because the North Sea represents only 1.9% of the $27.4 \times 10^6 \text{ km}^2$ of continental shelf area of the world ocean, all of which is potentially vulnerable to anthropogenic eutrophication.

7. Acknowledgements

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