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The carbon dioxide system in the Elbe estuary

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Abstract. The $p\mathrm{CO}_2$ distribution in the surface waters of the Elbe estuary and German Bight was investigated during high river discharge in April 1997. $p\mathrm{CO}_2$ values of about 1100 μatm found in the upper part of the estuary are, compared to other European rivers, only moderate. In the outer estuary, the enhanced river discharge creates a pronounced river plume reflected in decreased surface salinity. However, $p\mathrm{CO}_2$ in this area (250 μatm) is below atmospheric values due to primary production. Comparison with results we obtained during other measuring campaigns show that in the outer estuary supersaturation of CO_2 with respect to the atmosphere occurs only in early spring during the time of highest river discharge. In late spring and summer, intensive primary production within the surface layer leads to a pronounced undersaturation (141 μatm), despite a temperature increase of more than 20 °C from winter to summer. Undersaturation is enforced by stable stratification of the water column during the productive seasons that diminishes the entrainment of CO_2 from below the thermocline into the surface water. In winter, CO_2 is close to equilibrium with the atmosphere and controlled by physical processes. Our data suggest that the Elbe estuary represents a sink for atmospheric CO_2 over the investigated seasons and that carbon cycling in this area is dominated by biological processes.

Introduction

Generally, the global ocean is considered to be a net sink for atmospheric CO_2. In contrast, coastal seas are thought to be mainly net heterotrophic systems with remineralisation outweighing primary production (Smith & Hollibaugh 1993) and thus possibly constitute a source rather than a sink for atmospheric CO_2. In this context, the role of estuaries is of particular concern even though it is not well understood at present.

European estuaries are subject to considerable human perturbation due to their vicinity to highly industrialised and/or agriculturally used areas, leading to large imbalances in coastal carbon cycling. Especially the southeastern part of the North Sea, receiving the rivers Rhine, Elbe and Weser, is subject to inorganic nutrient input in the same order of magnitude as the load delivered by the 50 times larger discharge of the Amazon river (Degens et al. 1991). As a result, primary production in the coastal North Sea may be enhanced resulting in net autotrophic conditions. On the other hand, rivers also carry large amounts of organic material, either particulate or dissolved, which are additionally transported into the near coastal waters. This favours elevated remineralisation possibly resulting in anaerobic conditions in the water column as well as in a pronounced supersaturation of CO_2 (e.g. Brockmann et al. 1990; Kempe 1982a).

One approach to determine whether coastal seas are sinks or sources for atmospheric CO_2 would be to measure directly the partial pressure of CO_2 (pCO_2) in the surface waters with appropriate spatial and temporal resolution, but such studies are scarce. The most comprehensive study of the pCO_2 distribution covered nine European estuaries and is reported by Frankignoulle et al. (1998). This study revealed a broad range of pCO_2 values between 125–9425 μatm for inner estuaries and 545–1330 μatm for outer estuaries.

Hoppema (1991) obtained pCO_2 values from < 150 μatm in April to $>$ 500 atm in November at a site close to the Dutch coast. These variations were mainly attributed to variations in fresh water input and, to a minor extent, primary production.

Borges and Frankignoulle (1999) reported seasonal pCO_2 variations along the Belgian and Dutch coastal zone ranging between 90–778 μatm. Supersaturation was induced by river input and remineralisation, while undersaturation was attributed to primary production.

Bakker et al. (1996) observed pCO_2 values from 300 to 800 μatm in September 1993 along a 70 km transect perpendicular to the Dutch coast between the North Sea Channel and the Rhine estuary. In this high resolution study, tidal mixing, freshwater input, stratification and coastal upwelling were the main factors controlling the CO_2 distribution in the surface waters.

Although the spatial and seasonal resolution of these studies varies considerably, coastal seas obviously reveal higher variation in pCO_2 than the open ocean where, the seasonal amplitude of pCO_2 in the surface waters rarely exceeds 100 μatm (Takahashi et al. 1997; Bates et al. 1998). For the Elbe estuary and the adjacent southeastern part of the North Sea (German Bight) very few pCO_2 data are available. The only published data are from Kempe (1982b) who determined pCO_2 values between 500–4000 μatm for a transect along the Elbe river into the German Bight during October 1981. In the framework of the BIOGEST program (Biogas transfer in estuaries), we obtained an extensive data set covering not only the river itself but also the outer estuary (German Bight). This enabled us to study riverine processes as well as their influence on the adjoining near coastal area. Beyond that, we made an attempt to assess the different processes which underlie seasonal changes of the $p\mathrm{CO}_2$ distribution in the Elbe estuary by comparing spring 1997 data with $p\mathrm{CO}_2$ distributions in the German Bight obtained during other seasons (winter 1996; spring 1995; summer 1994).

Sampling and methods

The Elbe estuary was investigated as part of the BIOGEST program in April 1997 onboard RV VALDIVIA. During times of enhanced river discharge, surface water (1m below sea-surface) along the Elbe river into the outer estuary was sampled in detail (Figure 1). The samples cover a salinity gradient from 0 to 31. The outer estuary was sampled on the identical sample grid we occupied during earlier investigations during other seasons in 1994–1996 (Reimer et al. 1999). Sampling took place at the end of a period of high river discharge (Figure 2), leading to decreased salinities in the German Bight (Figure 3).

pH was measured immediately after collecting the samples using a Schott CG 841 pH-meter and a combination electrode (Metrohm) standardised against NBS buffers pH 7.413 and pH 9.180 at 25 °C (Ingold). Precision of pH-measurements was ± 0.01. The pH-values at in situ temperature (°C) were calculated by the empirical function $\mathrm{pH}_{\mathrm{insitu}} = \mathrm{pH}_{\mathrm{meas.}} + 0{,}0141\,(\mathrm{T}_{\mathrm{meas}} - \mathrm{T}_{\mathrm{insitu}})$.

Samples were filtered (Whatman GF/F) immediately after collection and then total alkalinity (TA) was measured by computerised potentiometric titration with a closed and constantly temperated (25 °C) titration cell (Dickson 1981; DOE 1994). The calculation of TA from the titration curves was performed with GRANPLOT-algorithms after Stoll et al. (1993). Thermodynamic constants were taken from Goyet and Poisson (1989). The precision of the method was $\pm 5\ \mu\mathrm{mol\ kg}^{-1}$.

Samples for dissolved inorganic carbon (DIC) determination were poisoned with HgCl_2 and stored at 4 °C. DIC was determined by coulometric analysis (model 5011, U.I.C. Inc., USA, method after Johnson et al. 1985; Johnson & Sieburth 1987; Johnson et al. 1993; DOE 1994) immediately after the cruise in the laboratory. Reference standards from A. Dickson (Scripps Institution of Oceanography, San Diego, USA) were used to calibrate the system at a precision of $\pm 2\ \mu\mathrm{mol\ kg}^{-1}$ DIC.

Temperature, salinity, DIC and TA were employed to calculate the partial pressure of CO_2 ($p\mathrm{CO}_2$). Calculations were performed with the program CO_2SYS provided by E. Lewis and D. Wallace (1998, U.S. Department of Energy, Oak Ridge, Tennessee). Constants were taken from Roy et al.

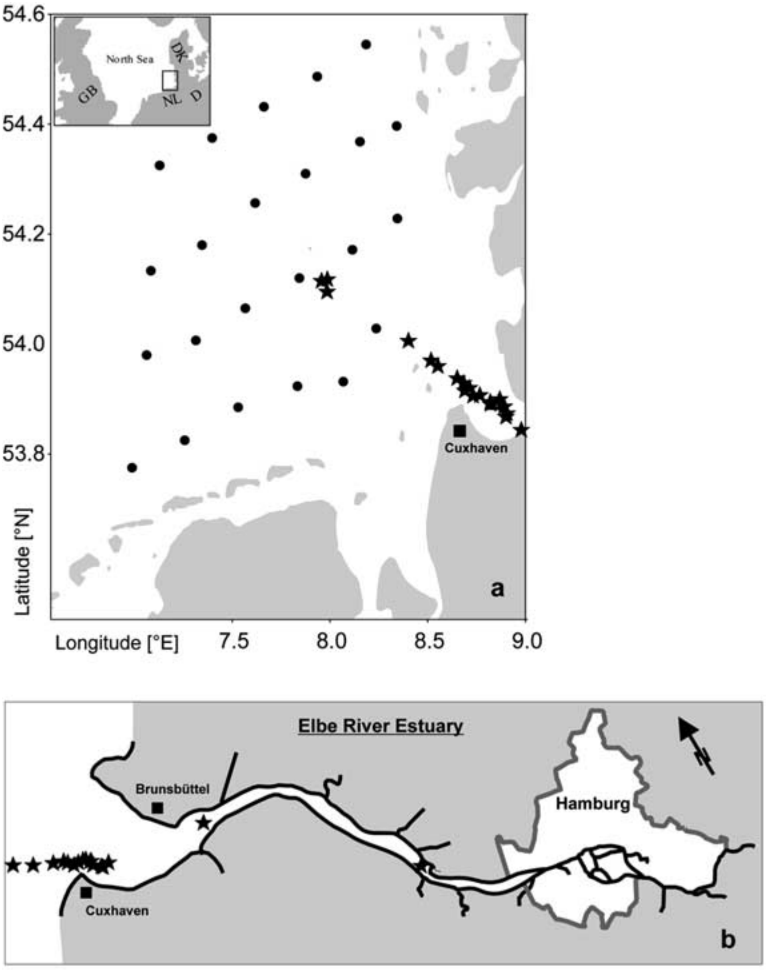

Figure 1. (a) sampling grid (filled circles) and position of the river transect (filled stars) in the outer Elbe estuary. (b) Map of the inner Elbe estuary. Sampling started 20 km downstream the city of Hamburg, still outside the turbidity maximum. One sample was taken in the turbidity maximum. The steepest salinity gradient occurred at the river mouth where, accordingly, the majority of samples was taken.

(1993) and Weiss (1974). The precision of K1 and K2 was 2% and 1.5%, respectively.

For the determination of total suspended matter (SPM) 200–5000 ml of sample were filtered through pre-combusted Whatman GF/F filters. The filters were rinsed with 100 ml deionised water (Millipore) to remove salt and dried at 40 °C. The filters were then re-weighed and subdivided for high

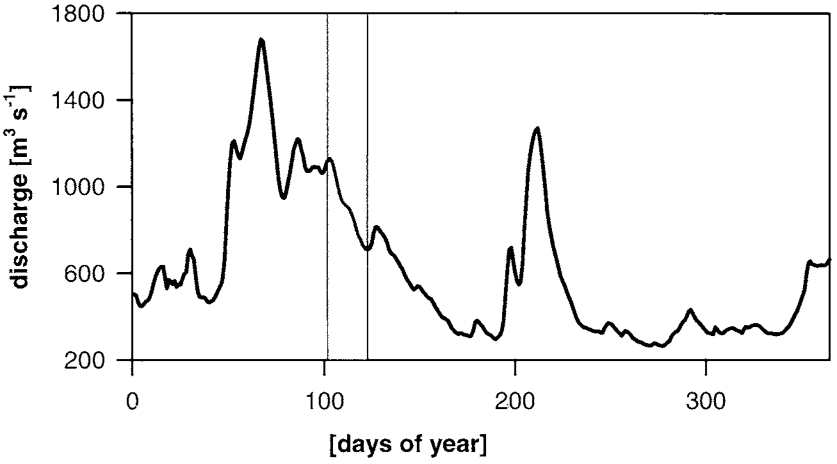

Figure 2. River discharge of the Elbe river in 1997. Shaded bar displays the period of investigation. Discharge data from ARGE Elbe (pers.com).

temperature combustion analysis (Leco 1000 HCN-analyser) of total particulate carbon (PC) and particulate organic carbon (POC). Samples for POC analysis were treated with 2N H_3PO_4 (Merck) at 40 °C to remove inorganic carbon. The precision of the measurements was ± 5%.

Oxygen analyses were carried out according to the Winkler method used by Borges and Frankignoulle (2002). The apparent oxygen utilisation (AOU) was calculated as the difference between oxygen saturation values (Weiss 1970) and in situ concentrations. Discharge and additional oxygen data for the Elbe river were kindly provided by the federal authorities of the city of Hamburg (ARGE Elbe, pers. com.) and measurements of depth integrated primary production rates (^{14}C method) were obtained as part of the KUSTOS project by H.-J. Rick (pers.com.).

Results

Riverine processes

The $p\mathrm{CO}_2$ distribution of the Elbe river reveals only moderate supersaturation in the upper part of the estuary in April 1997 (Figure 4(a)). Highest $p\mathrm{CO}_2$ values were only 1100 μatm in areas of the turbidity maximum (salinity: 1.5), accompanied by a pH of 7.88. Further upstream the $p\mathrm{CO}_2$ dropped to 650 μatm. These $p\mathrm{CO}_2$ values are amongst the lowest measured for the nine European estuaries within the BIOGEST program (Frankignoulle et al. 1998).

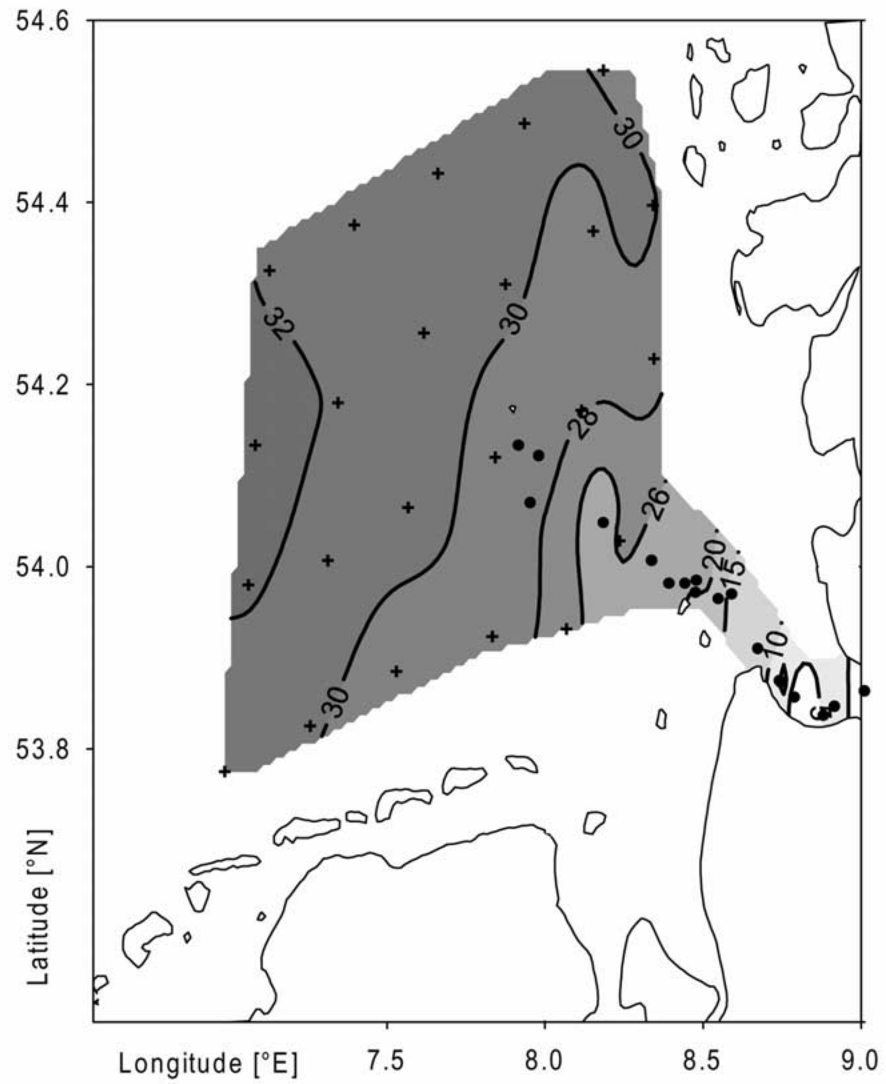

Figure 3. Salinity distribution at 1m depth in the Elbe estuary and German Bight in April 1997.

Lower maximum values were observed only in the Gironde River in February 1998 (980 μatm), while highest values were obtained for the Scheldt River with up to 9425 μatm.

From a salinity of 2 the $p\text{CO}_2$ rapidly declines, reaches atmospheric values at a salinity of $\sim$ 15 and is lower than the atmospheric value in the higher salinity range. These observations are contrary to 1981 data on the $p\text{CO}_2$

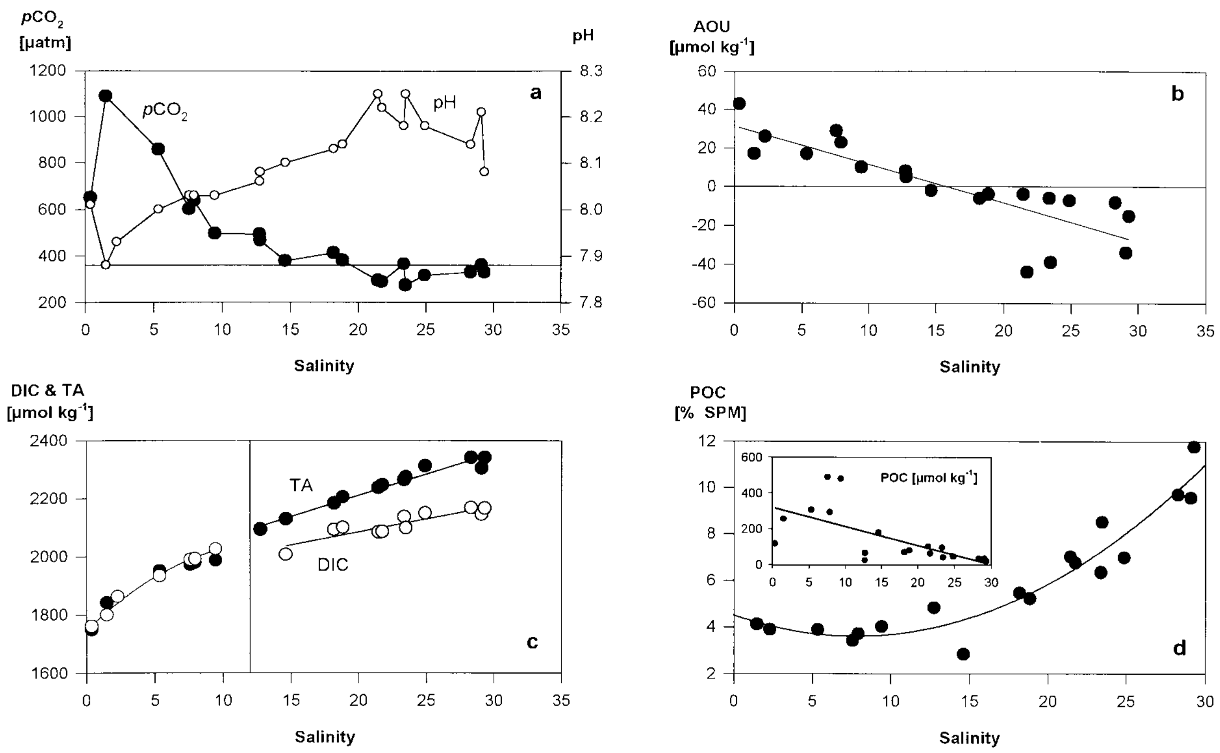

Figure 4. Distribution of (a) pCO$_2$, pH; (b) AOU; (c) DIC, TA and; (d) POC at 1m depth along the salinity gradient of the inner Elbe estuary in April 1997.

distribution in the Elbe estuary found by Kempe (1982a, b). He reported calculated $p\mathrm{CO}_2$ values several times the atmospheric value (up to 4000–6000 μatm) in the river, with values reaching 500 μatm in the high salinity reaches of the estuary. Remineralisation of labile organic matter was identified to be a main source for the increased $p\mathrm{CO}_2$. This is generally supported by very low oxygen concentrations found in the lower reaches of the Elbe river during the seventies and eighties, especially during late spring and summer. These interdependencies are also verified by other rivers, e.g. the Scheldt (Frankignoulle et al. 1996).

The oxygen distribution along the salinity gradient of the Elbe river in April 1997 reveals only moderate oxygen utilisation in the low salinity range and supersaturation at higher salinities (Figure 4(b)). This distribution is not only typical of a high discharge in spring, but is also confirmed at other seasons of the year. Oxygen concentrations in the Elbe river have not been below 3 mg l^{-1} since the early nineties, even in summer (ARGE Elbe 1997). Therefore, aerobic remineralisation of organic matter seems no longer to dominate the $p\mathrm{CO}_2$ distribution of the Elbe estuary and anaerobic remineralisation in the water column is not likely to occur at all. Figure 4(c) displays the DIC and TA distribution along the salinity gradient in April 1997. Both are low compared to many other European rivers in the uppermost estuary (1748 μmol kg^{-1} and 1760 μmol kg^{-1}, respectively) and show a non-linear increase up to a salinity of 10. Downstream, they increase linearly with increasing salinity, but are offset from each other with DIC concentrations being lower than TA. This suggests that two distinct processes determine the distribution of inorganic carbon species along the Elbe estuary. In the low salinity range the non-linear increase can be explained by build-up of the carbonate buffer by "titration" of freshwater with CO_3^{2-} enriched seawater, leading to an increase in HCO_3^- concentration. This is accompanied by a steep decrease in $p\mathrm{CO}_2$. At higher salinities, the reduced increase in DIC concentrations compared to TA can be ascribed to primary production, leading to oxygen supersaturation and a further decrease of $p\mathrm{CO}_2$ below atmospheric equilibrium. This hypothesis is consistent with the POC distribution (Figure 4(d)). Although total amounts of POC decrease with increasing salinity, the percentage of POC increases from 4 to 12% of SPM in the higher salinity range, indicating an in situ production of organic material.

Outer estuary (German Bight)

$p\mathrm{CO}_2$ was below atmospheric equilibrium for the entire German Bight in April 1997 and generally reaches only 200–270 μatm (Figure 5). Areas of higher $p\mathrm{CO}_2$ (up to 350 μatm) were restricted to the vicinity of the river mouth and decreased seaward along the river plume to $\sim$250 μatm (compare

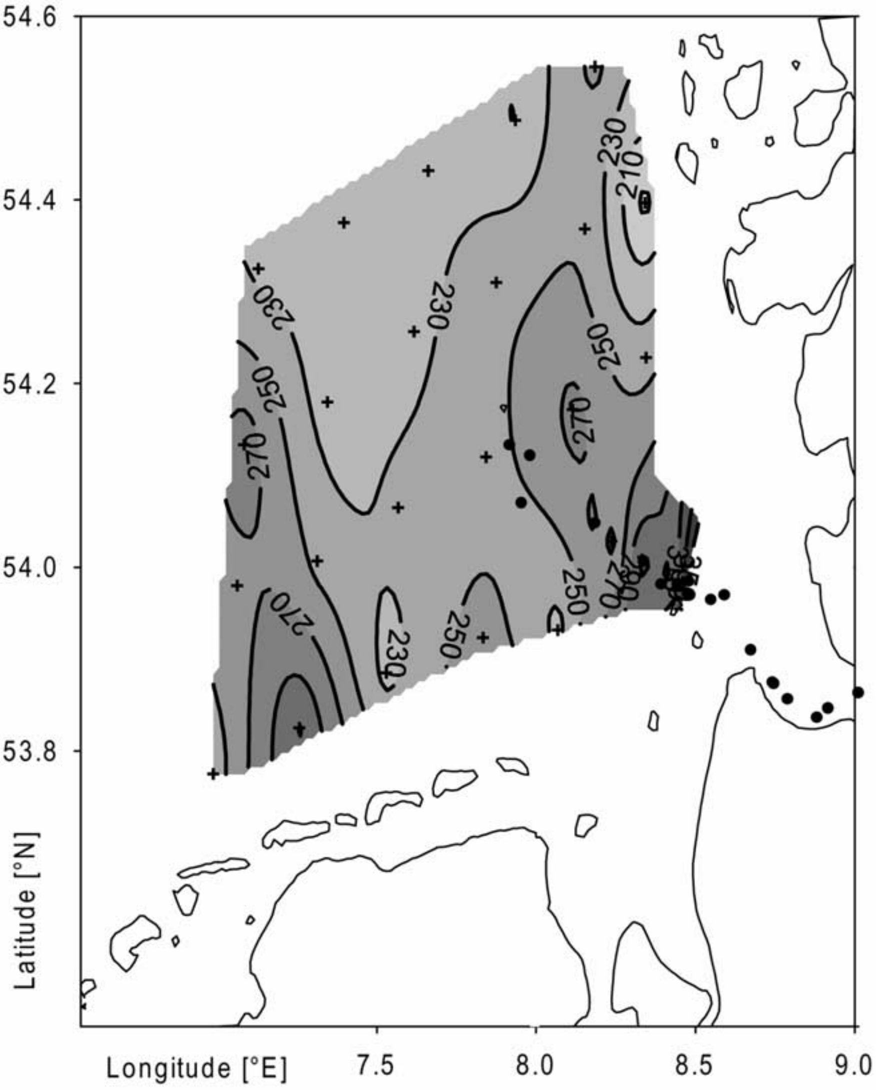

Figure 5. pCO$_2$ [μatm] distribution at 1m depth in waters of the outer Elbe estuary in April 1997.

to Figure 3). Slightly higher values (∼270 μatm) were found at the south-western corner of the sampling grid, while lowest values (200–230 μatm) appear in the northern and north-eastern part of the German Bight.

These low pCO$_2$ values coincide with decreased DIC concentrations. The DIC versus TA plot allows us to separate mixing processes from biological

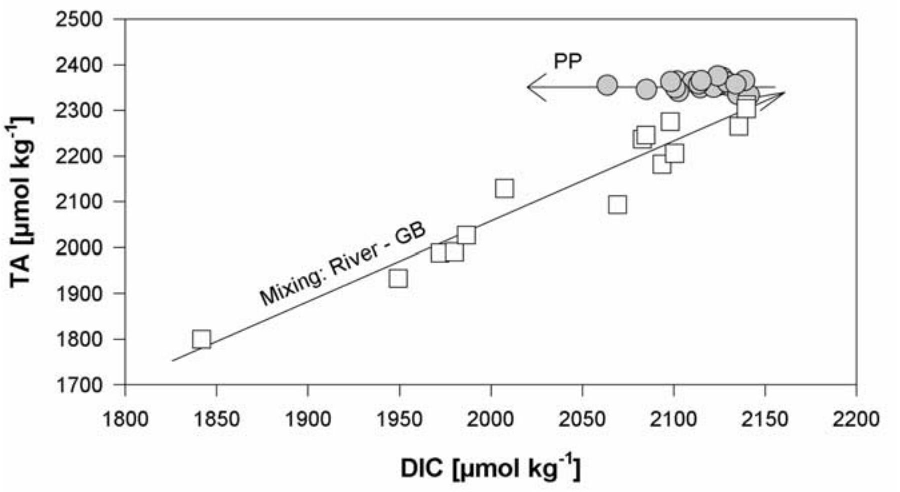

Figure 6. DIC vs. TA for samples along the river transect (squares) and outer estuary (circles) to distinguish mixing processes from primary production (PP). GB = German Bight. For further explanation see text.

CO_2 uptake (Figure 6). Samples of the German Bight (filled circles in Figure 6) show a constant high alkalinity ($\sim$2360 mol kg^{-1}) but decreased DIC concentrations were found in several samples. This departure suggests that these values are not simply the result of mixing with river water low in alkalinity. Mixing is only significant for samples along the river transect (squares in Figure 6). In combination with generally elevated POC concentrations in the German Bight ($>$ 25–100 μmol kg^{-1}), the decreased DIC concentrations suggest primary production (spring bloom) to be the main process controlling the carbon distribution, and therefore also pCO$_2$, in the outer Elbe estuary in April 1997.

Discussion

To discuss the pCO$_2$ distribution found in April 1997 in a broader context, it is compared to results recently obtained by us for the same area as part of the German KUSTOS project. Our aim at this project was to study the carbon cycling in the water column (0–40m depth) of the German Bight during August 1994, April/May 1995 and February/March 1996 (Brasse et al. 1999; Reimer et al. 1999). Apart from inorganic and organic carbon species, we also investigated the distribution of pCO$_2$. In combination with the results from the BIOGEST project in the Elbe estuary, these data allow us to examine processes responsible for inter-annual CO_2 variations.

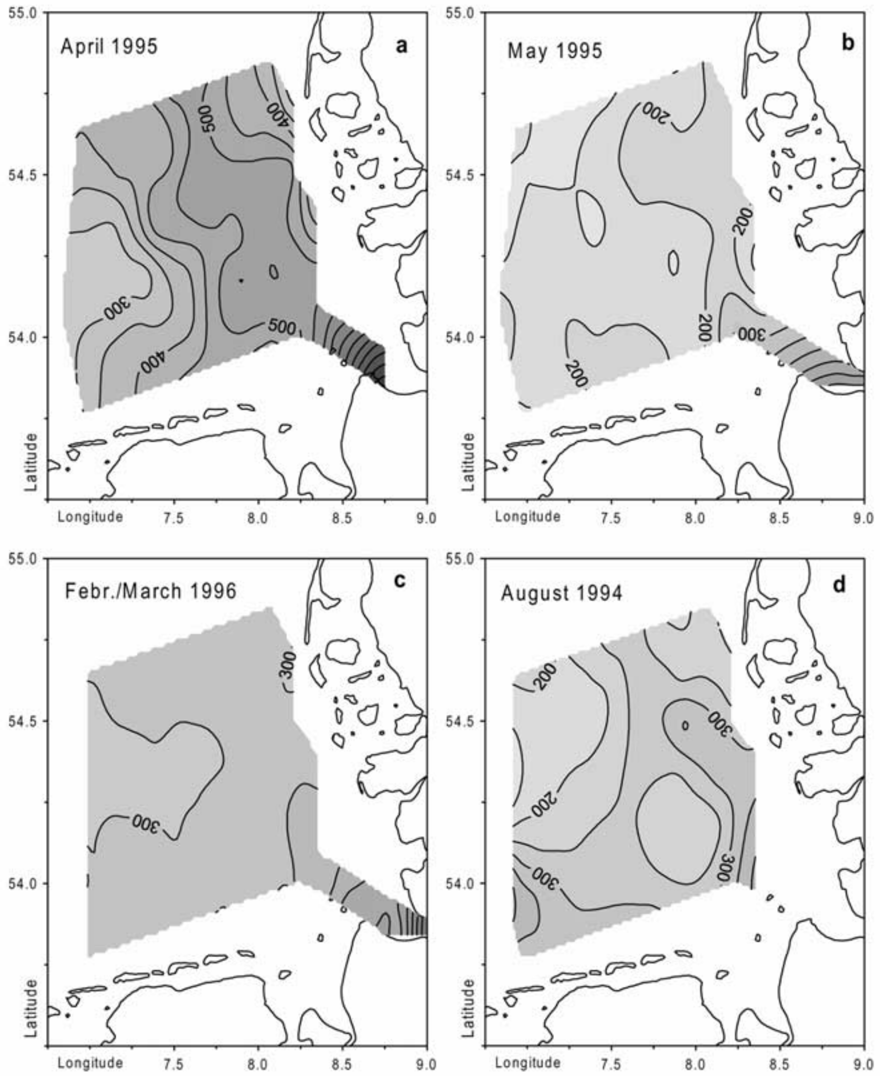

Figure 7. $p\mathrm{CO}_2$ [μatm] distribution at 1m water depth in the outer Elbe estuary for different seasons between 1994–1996.

The peak of high spring discharge (up to 2200 $\mathrm{m}^3\ \mathrm{s}^{-1}$) during early April 1995 led to salinities of < 26 in large parts of the German Bight. Due to relatively low primary production ($\sim$0.5 g C $\mathrm{m}^{-2}\ \mathrm{d}^{-1}$), CO_2 supersaturation of up to 550 μatm was found in the river plume (Figure 7(a)). At either side of the plume, the beginning of the spring bloom led to $p\mathrm{CO}_2$ values of < 300 μatm, accompanied by primary production rates of $\sim$10 g C m^{-2}

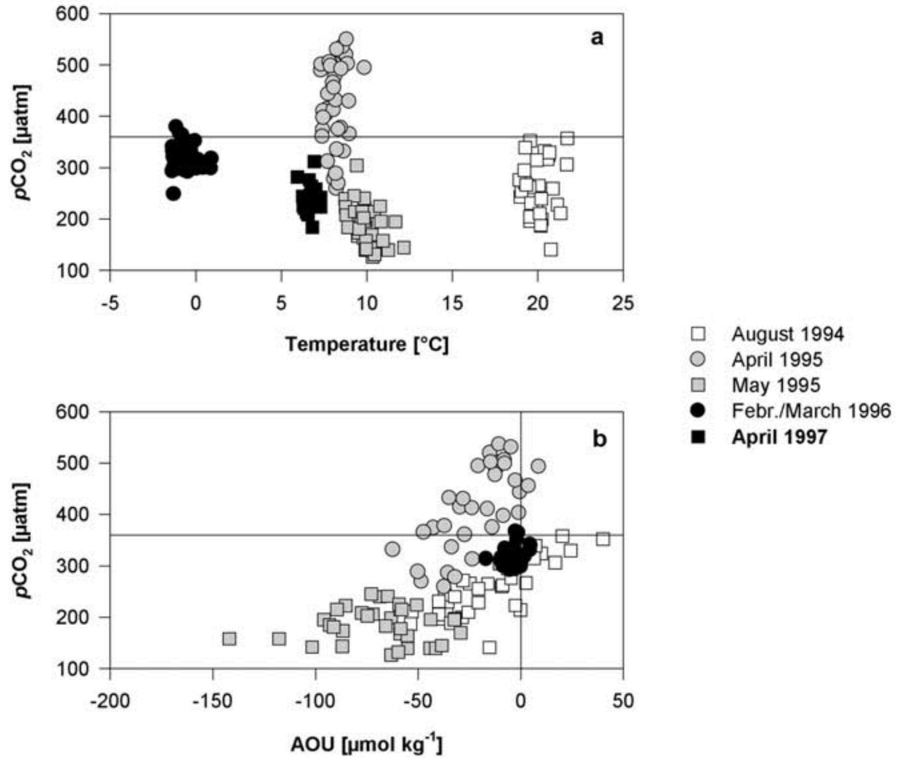

Figure 8. Physical (a) and biological (b) dependencies of pCO$_2$ in surface waters of the outer Elbe estuary for different seasonal situations (oxygen was not measured for the samples of the outer estuary in 1997, therefore missing in (b).

d^{-1}. With the onset of the bloom (PP 15 g C m^{-2} d^{-1}) and a concurrent decrease in discharge in early May, highest pCO$_2$ (up to 300 μatm) were found only at the river mouth and CO$_2$ was undersaturated in all other parts of the German Bight (Figure 7(b)). This is similar to what we observed in 1997. Therefore, supersaturation of CO$_2$ in the German Bight seems to be confined to times of enhanced river discharge accompanied by low primary production; a condition present only during a restricted period in early spring. The pCO$_2$ distributions in April 1997 and May 1995 already display the dominance of biological processes over riverine influences. Furthermore, CO$_2$ is also undersaturated during the other seasons investigated (winter and summer, Figure 7(c), (d)). The pCO$_2$ distribution in winter was mainly governed by enhanced CO$_2$ solubility at low temperatures. River discharge (500–700 m^3 s^{-1}) and biological processes were relatively unimportant at this time of the year (Figure 8(a), (b)). In summer 1994, river discharge was only 300–400 m^3 s^{-1} and had no detectable influence on the $p\mathrm{CO}_2$ distribution. At the same time a stable pycnocline was established throughout the German Bight. Nitrate in the surface water was completely exhausted (Brockmann et al. 1999), but primary production rates still reached 5–15 gC m^{-2} d^{-1}, suggesting a preferential recycling of nutrients which sustained the high productivity (e.g. Thomas et al. 1999). Accordingly, $p\mathrm{CO}_2$ was undersaturated in the surface water of the entire study area, even though the temperature increase from winter to summer amounted to more than 20 °C (Figure 8(a)). A slight oxygen utilisation was observed only in areas of $<$ 10m water depth where no stratification occurred (open squares in Figure 8(b), suggesting net remineralisation. Generally, remineralisation of organic matter was the dominant process in the bottom water in summer 1994, but due to the stable stratification in large areas of the German Bight, nutrients remineralised below the pycnocline could not be mixed back into the surface water. During the period investigated, DIC concentrations in the surface layer were as low as 1930 μmol kg^{-1}, while they reached up to 2250 μmol kg^{-1} below the pycnocline (Reimer et al. 1999). Therefore, the $p\mathrm{CO}_2$ distribution of the surface water in summer is mainly governed by primary production (biological dependency) outweighing the $p\mathrm{CO}_2$ increase due to elevated temperatures and remineralisation.

Conclusions

The Elbe river has generally been classified as one of the most heavily polluted rivers in Europe due to discharge of industrial, municipal and agricultural waste water into the river. Nevertheless, during the last decade the water quality of the Elbe river was considerably improved. Due to remediation of the east-european industrial production sites and the extension of municipal waste water treatments, e.g. the mercury load decreased by 95% and the phosphorous load by 50% since 1985. Also, the frequent occurrence of hypoxia and the concomitant dying of fish was not observed any more due to a decrease in dumping of oxygen utilising substances from the former GDR (ARGE ELBE 1997). This study also confirms an improved water quality of the Elbe river concerning CO_2 supersaturation. $p\mathrm{CO}_2$ values for the upper part of the estuary were only 1100 μatm and an oxygen utilisation reached only 50 μmol kg^{-1} in the turbidity maximum. This has considerable influence on the general controlling mechanisms of riverine carbon cycling. Obviously, remineralisation of labile organic matter no longer plays the major role, like it is the case for many other European rivers (e.g. the Scheldt river, see Borges & Frankignoulle 2002). Also, the outer estuary seems to be CO_2 supersaturated only at times of the most pronounced river discharge in early spring and undersaturated during all other investigated seasons. The $p\mathrm{CO}_2$ distribution in the outer estuary reveals a physical (temperature) dependency in winter and is controlled by in situ biological processes in late spring and summer, namely primary production. Riverine influences are only of minor importance. Although intensive remineralisation of organic material in the bottom water could be observed, undersaturation is enforced by stable stratification of the water column during the productive seasons that diminishes the entrainment of remineralised material from below the thermocline into the surface water. Overall, about 95% of the primary produced biomass was remineralised in the water column, leaving only 5% to reach the sedimentary pool (Reimer et al. 1999). Assuming an averaged residence time of water masses in the German Bight of one month (Otto et al. 1990), net accumulation of organic material is not likely. One probable fate of the organic material would be its transport to deposition areas of the North sea like the Norwegian trench. The above results therefore strongly suggest that the German Bight acts as a sink for atmospheric CO_2 on an annual scale.

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