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Atmospheric CO_2 fluxes in a highly polluted estuary (the Scheldt)

Abstract—Dissolved CO_2 concentration and exchange with the atmosphere were investigated simultaneously in the Scheldt estuary. CO_2 partial pressures as high as 5,700 μatm , corresponding to oversaturation with respect to the atmosphere of 1,600%, were observed in the upper estuary. The corresponding atmospheric CO_2 fluxes reached values of up to 1.2 $\text{mol m}^{-2} \text{d}^{-1}$. The estimated flux for the entire estuary amounts to 600 t of C d^{-1} for a river discharge of $<1 \times 10^6 \text{ m}^3 \text{d}^{-1}$.

Estuaries under strong tidal influence are characterized by long residence times of freshwater masses, and this favors chemical and biological transformations of the components carried by rivers. These transformations

deeply modify the fluxes and transport of these components to the sea. Furthermore, estuaries are often centers of intense anthropogenic activities and thereby constitute highly disturbed ecosystems; this is the case for the river Scheldt, which traverses one of the most populated and industrialized areas of Europe (the north of France and Belgium and the south of the Netherlands, Fig. 1). The estuary receives $\sim 100 \times 10^3$ t of organic C per year, mainly of anthropogenic origin, of which a large fraction is respired in the estuarine zone (Wollast 1988). Due to the hydrodynamic conditions imposed by the high tidal regime (mean tidal amplitude at the mouth, 4.5 m) and the relatively low water discharge ($3 \text{ km}^3 \text{ yr}^{-1}$), this organic matter accumulates preferentially in the upper estuary, between salinities of 2 and 10 (Wollast 1983). In this area,



Fig. 1. Map of the Scheldt estuary.

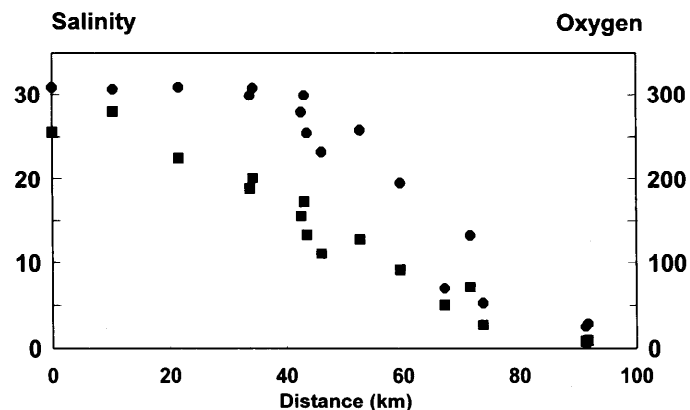


Fig. 2. Distribution of salinity (■) and oxygen (●, in $\mu\text{mol kg}^{-1}$) in the Scheldt estuary, March 1993.

intense bacterial degradation induces permanent anaerobic conditions (Fig. 2).

The tidal prism, which represents the volume of seawater entering the estuary during one tide divided by the volume of freshwater discharged during the same period, amounts to 260 (Wollast and Peters unpubl.). The mixing zone between freshwater and seawater extends, therefore, over 100 km (Fig. 2), and 2 months are required for Scheldt water to reach the sea.

Because of intense bacterial respiration, the long residence time of freshwater in the estuarine region favors buildup of high partial pressure of CO_2 ($p\text{CO}_2$) in the water column. As shown in Fig. 3, $p\text{CO}_2$ reaches 5,700 μatm at a salinity of ~ 5 , which also corresponds to the turbidity maximum and where the highest bacterial degradation activity can be expected. The oversaturation of $p\text{CO}_2$ with respect to atmospheric equilibrium (presently $\sim 355 \mu\text{atm}$) is close to 1,600%. According to Kempe (1982), marked oversaturation of CO_2 occurs in many estuaries, but $p\text{CO}_2$ rarely exceeds 2,500 μatm in his observations.

In our work, $p\text{CO}_2$ is calculated from pH and total alkalinity (TAlk) measurements. The latter is determined by electrotitration (Gran plots) on 100-ml GF/C-filtered samples. pH is measured with a Ross (Orion) combination electrode calibrated against phosphate and phthalate NBS buffers (Bates 1973). The partial pressure of CO_2 is calculated with the constants from Mehrbach et al. (1973) and Lyman (1975) and the CO_2 solubility coefficient from Weiss (1974). Reproducibilities of pH and TAlk measured aboard ship are 0.005 pH unit and 4 $\mu\text{eq kg}^{-1}$. The resulting error on $p\text{CO}_2$ depends also on the water buffering capacity and thus on pH, alkalinity, and salinity. In our experimental conditions, this error ranges from 6 μatm in seawater to 65 in freshwater.

Salinity and temperature are measured with a SBE 19 probe, and dissolved oxygen is determined by the Winkler method. The oxygen saturation level is computed with the algorithm of Benson and Krause (1984).

The flux of CO_2 to the atmosphere induced by this strong oversaturation has been estimated with the bell

method, which consists of continuously recording the change of $p\text{CO}_2$ (infrared analyzer LiCor 6252) in the volume of air entrapped in a floating bell resting at the surface of the water (Frankignoulle 1988). To study the same water mass and to avoid turbulence generated by an anchored bell in a strong current, we adopted a Lagrangien floating system. The surface for exchange in the bell is 0.212 m^2 , and the total entrapped air volume is 0.051 m^3 . The error on flux measurements is estimated to be $\sim 25\%$. The results of these measurements are given in Fig. 3.

In the area of the $p\text{CO}_2$ maximum, we observed fluxes as high as 1.2 $\text{mol m}^{-2} \text{d}^{-1}$. Integration of our observations over the entire surface of the estuary yields a flux of 600 t of C d^{-1} to the atmosphere. This huge flux is due partly to the very high $p\text{CO}_2$ values observed in the upper estuary and also to exchange across the large surface of the lower estuary, where the fluxes remain close to 50 $\text{mmol m}^{-2} \text{d}^{-1}$.

The gas flux at the air-water interface can be expressed as the product of a piston velocity and the difference in CO_2 concentration between the two phases. The calculated piston velocity remains rather constant over the entire estuary, with a mean value and standard deviation of $13.5 \pm 4.9 \text{ cm h}^{-1}$. This value is of the same order of magnitude as the range reported for marine systems (Liss and Merlivat 1986; Wanninkhof 1992) and is typical for moderately turbulent rivers (Bennet and Rathbun 1972; Wilcock 1984) at low wind speeds ($< 3.6 \text{ m s}^{-1}$). Clark et al. (1994) determined the gas exchange rate in the Hudson River with a dual tracer technique and proposed values of K ranging from 1 to 9 cm h^{-1} for a Schmidt number (Sc) normalized to 600. In our experimental conditions ($t \sim 9^\circ\text{C}$), the CO_2 Schmidt number is ~ 1210 (Wanninkhof 1992) and our calculated value of K , corrected to $Sc = 600$ ($K \propto Sc^{-2/3}$), is $8.4 \pm 3.1 \text{ cm h}^{-1}$, which is in good agreement with the results of Clark et al. (1994).

We attempted to evaluate the daily fluxes of organic and inorganic C in the estuary (Table 1) from our data and from the annual averaged fluxes of organic C at the boundaries of the estuary taken from Wollast (1988). This

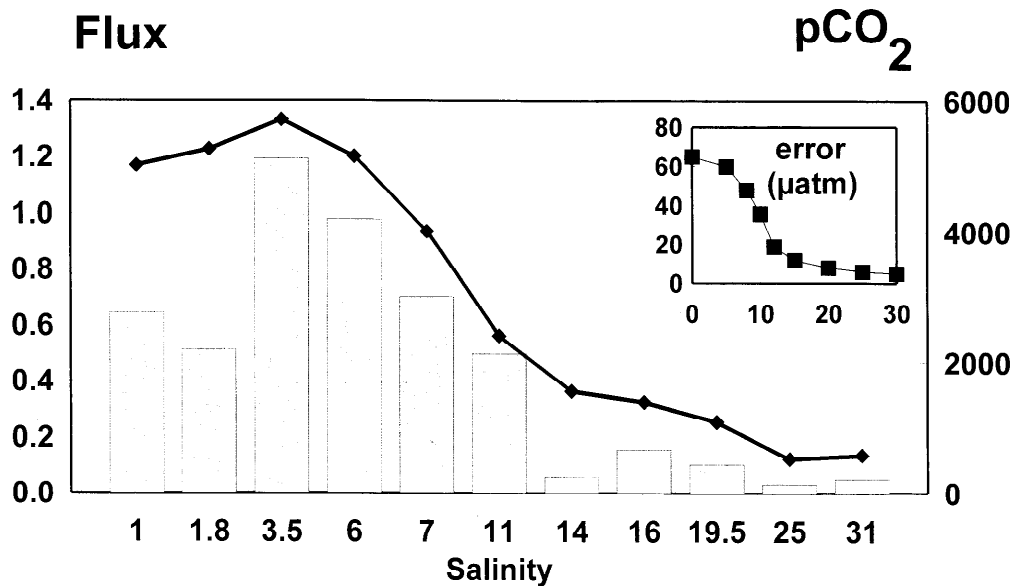


Fig. 3. Distribution of the partial pressure (\blacklozenge , in μatm) and atmospheric fluxes of CO_2 (bars, in $\text{mol m}^{-2} \text{d}^{-1}$) vs. salinity in the Scheldt estuary, March 1993. The error on $p\text{CO}_2$, computed from pH and TALK precision, is given vs. salinity.

Table 1. Estimation of daily carbon fluxes in the Scheldt estuary.

	C (t d^{-1})	Comments
Total organic C loading	300	DOC + TOC averaged discharge (Wollast 1988)
Total inorganic C input	575	Input of $8 \times 10^6 \text{ m}^3 \text{ d}^{-1}$ of freshwater with $\text{DIC} \approx 6 \text{ mol m}^{-3}$
Total C input	875	
Organic C transfer to the sea	75	DOC + TOC averaged discharge (Wollast 1988)
Inorganic C transfer to the sea	190	Output of $8 \times 10^6 \text{ m}^3 \text{ d}^{-1}$ of freshwater with $\text{DIC} \approx 2 \text{ mol m}^{-3}$
Atmospheric output	600	This work
Total C output	865	

budget is surprisingly good—the large uncertainties on individual fluxes notwithstanding. The total dissolved inorganic C (DIC) budget in the estuary is, however, complicated by the fact that the upper part of the estuary is also an area of intense biological activity. The first obvious effect of this activity is to provide a source of inorganic C that compensates for losses of CO_2 to the atmosphere. Nevertheless, a plot of DIC vs. salinity, shown in Fig. 4, indicates that there is a net loss of inorganic C that occurs mainly in the upper part of the estuary. A simple calculation, performed at a salinity of 10 and based on the departure of the composition of the water mass from conservative behavior, indicates a net loss of DIC equal to 1.4 mmol kg^{-1} . On the other hand, the amount of CO_2 transferred to the atmosphere between salinity 0 and 10 can be estimated from the fluxes reported in Fig. 3. Taking into account the residence time of the water masses in the upper estuary ($\sim 30 \text{ d}$) (Wollast 1988) and the mean river depth ($\sim 5 \text{ m}$), we obtain a loss to the atmosphere of 4.2 mmol kg^{-1} . This loss corresponds to a mean atmospheric flux of $0.7 \text{ mol m}^{-2} \text{ d}^{-1}$. Because

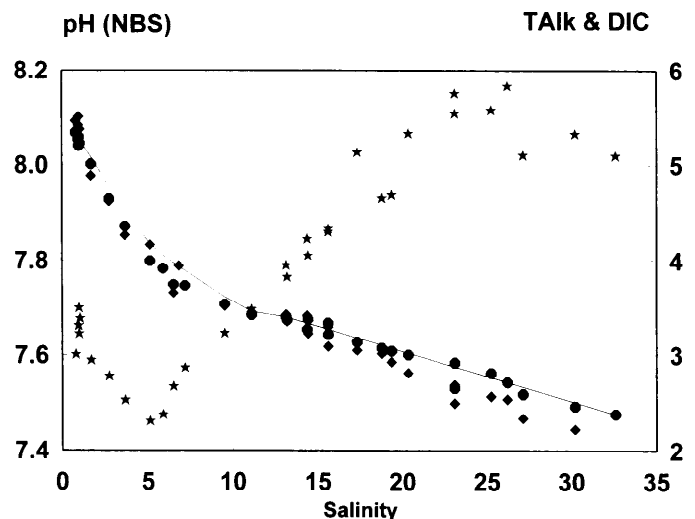


Fig. 4. Distribution of pH (\star , NBS scale), TALK (\bullet , meq kg^{-1}), and DIC (\blacklozenge , mmol kg^{-1}) vs. salinity in the Scheldt estuary, March 1993. Line shows the alkalinity profile calculated from the mixing process of freshwater with seawater and the effect of nitrification on alkalinity (see text).

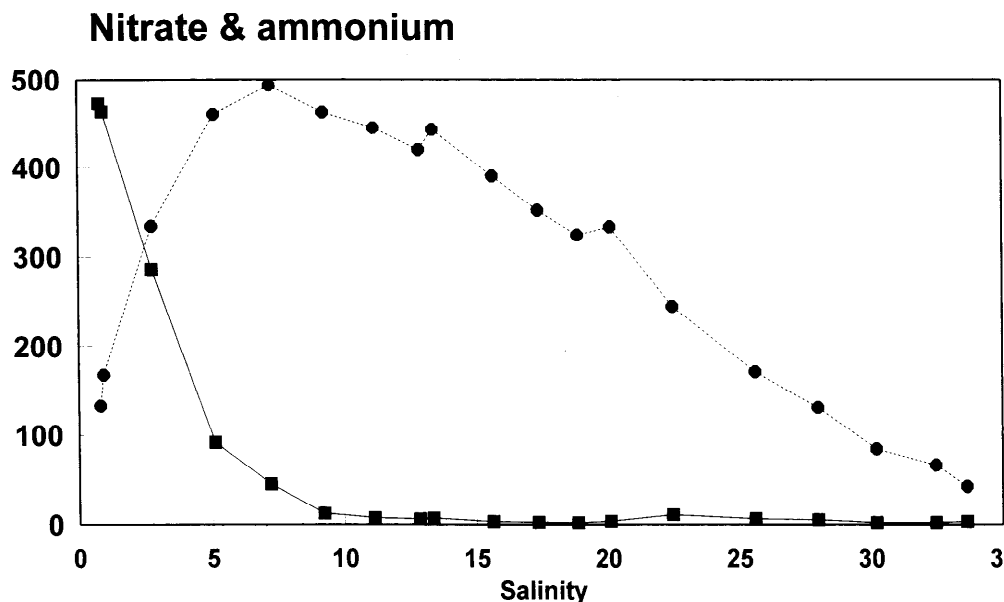


Fig. 5. Distribution of ammonium (■, in $\mu\text{mol kg}^{-1}$) and nitrate (●, in $\mu\text{mol kg}^{-1}$) vs. salinity in the Scheldt estuary, March 1993.

the decrease of DIC in the water column is only 1.4 mmol kg^{-1} , 2.8 mmol kg^{-1} of H_2CO_3 must have been added by degradation of organic matter.

It is also interesting that the deficit of dissolved oxygen with respect to the atmospheric equilibrium in the upper part of the estuary (Fig. 2) is very similar to the excess of CO_2 in the water column. For example, at a salinity of 1, the oxygen deficit is $283 \mu\text{mol kg}^{-1}$ and the excess of CO_2 is $246 \mu\text{mol kg}^{-1}$ ($5,000 \mu\text{atm}$, i.e. 1,400% oversaturation). At a salinity of 11, these values are $96 \mu\text{mol kg}^{-1}$ for O_2 and 103 for CO_2 ($2,405 \mu\text{atm}$, i.e. 677% oversaturation). Because the exchange coefficients of O_2 and CO_2 at the air–water interface are also similar (Waninkhof 1992), the output flux of CO_2 is of the same order of magnitude as the input flux of O_2 . This observation confirms that a large part of the atmospheric flux of CO_2 in that area is directly related to respiration of organic matter, although some of the oxygen input ($\sim 1 \text{ mmol kg}^{-1}$) is used to oxidize ammonium, as shown below.

The release of such large amounts of CO_2 from the water column should have drastic effects on the pH of the system. For example, if we take the water at the fresh end of the estuary (salinity of 0.8) and let it equilibrate with the atmosphere, it is easy to calculate from chemical equilibrium constraints that this water would lose 0.5 mmol kg^{-1} of CO_2 and the pH would rise from 7.60 to 8.82. There is, however, a decrease of pH when the water moves to the sea and loses CO_2 to the atmosphere (Fig. 4). This decrease can be explained by the decrease in alkalinity observed in the same area. As demonstrated in Fig. 4, alkalinity also exhibits a nonconservative behavior that can be explained by bacterially mediated nitrification in the upper estuary when oxygen is restored to the system

(Fig. 5). According to the stoichiometry of the nitrification reaction, given by $\text{NH}_4^+ + 2\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{NO}_3^- + 2\text{H}_3\text{O}^+$, each nitrate produced consumes 2 equivalents of alkalinity. Thus, from the change in nitrate concentration with increasing salinity, it is easy to calculate the decrease in alkalinity. The result of this calculation is given by the curve in Fig. 4, which fits remarkably with the observed values of alkalinity.

The pH of the system is controlled by the values of alkalinity and DIC, and both parameters are strongly affected by bacterial activity—in particular respiration of organic matter and nitrification. Both processes acidify the system, but the release of CO_2 to the atmosphere strongly reduces the decrease of pH.

It should be pointed out that there are strong seasonal fluctuations of the material fluxes and of the biological activity due to changes in river discharge and temperature. Annual budgets require extended coverage over the year.

An unexpected conclusion is that although anaerobic conditions prevail in the upper estuary, oxygen remains the dominant oxidant in this biologically active area. The Scheldt results confirm that estuaries are extremely active systems in which there are intense modifications of the nature and fluxes of many components transported by rivers before these components reach the sea. Furthermore, many estuarine processes produce greenhouse gases. Besides CO_2 discussed here, the Scheldt is also a significant potential source of N_2O due to intense denitrification in the anaerobic zone of the estuary (Billen 1975; Wollast 1983). In addition, high bacterial production of methane can be observed in sediments of the turbidity maximum zone, with massive transfer of this gas to the

water column and the atmosphere. On a global scale, estuaries may act as nonnegligible sources of these gases, and their importance should be more thoroughly investigated.

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