————, AND R. H. PETERS. 1994. Patterns in planktonic *P:R* ratios: Influence of lake trophy and dissolved organic carbon. Limnol. Oceanogr. **39:** 772–787.

DeNIRO, M. J., AND S. EPSTEIN. 1978. Influence of diet on the distribution of carbon isotopes in animals. Geochim. Cosmochim. Acta **42:** 495–506.

ELSER, J. J., AND R. P. HASSETT. 1994. A stoichiometric analysis of the zooplankton-phytoplankton interaction in marine and freshwater ecosystems. Nature **370:** 211–213.

FRANCE, R. L. 1995. Differentiation between littoral and pelagic food webs in lakes using stable carbon isotopes. Limnol. Oceanogr. **40:** 1310–1313.

FRY, B., R. K. ANDERSON, L. ENTZEROTH, J. L. BIRD, AND P. L. PARKER. 1984. ¹³C enrichment and oceanic food web structure in the northwestern Gulf of Mexico. Contrib. Mar. Sci. **27:** 49–63.

————, AND E. SHERR. 1984. $\delta^{13}C$ measurements as indicators of carbon flow in marine and freshwater ecosystems. Contrib. Mar. Sci. **27:** 15–47.

GOERING, J., V. ALEXANDER, AND N. HAUBENSTOCK. 1990. Seasonal variability of stable carbon and nitrogen isotope ratios of organisms in a North Pacific bay. Estuarine Coastal Shelf Sci. **30:** 239–260.

GRIESBACH, S. J., AND R. H. PETERS. 1991. The effects of analytical variations on estimates of phosphorus concentration in surface waters. Lake Reservoir Manage. **7:** 97–106.

GU, B., D. M. SCHELL, AND V. ALEXANDER. 1994. Stable carbon and nitrogen isotopic analysis of the plankton food web in a subarctic lake. Can. J. Fish. Aquat. Sci. **51:** 1338–1344.

HAMILTON, S. K., AND W. M. LEWIS, JR. 1992. Stable carbon and nitrogen isotopes in algae and detritus from the Orinoco River floodplain, Venezuela. Geochim. Cosmochim. Acta **56:** 4237–4246.

JEFFREY, A. W. A., R. C. PFLAUM, J. M. BROOKS, AND W. M. SACKETT. 1983. Vertical trends in particulate carbon ¹³C: ¹²C ratios in the upper water column. Deep-Sea Res. **30:** 971–983.

KLING, G. W., B. FRY, AND W. J. O'BRIEN. 1992. Stable isotopes and planktonic trophic structure in arctic lakes. Ecology **73:** 561–566.

McCONNAUGHEY, T., AND C. P. McROY. 1979. Food-web structure and the fractionation of carbon isotopes in the Bering Sea. Mar. Biol. **53:** 257–262.

MEILI, M. 1992. Sources, concentrations and characteristics of organic matter in softwater lakes and streams of the Swedish forest region. Hydrobiologia **229:** 23–41.

————, B. FRY, AND G. W. KLING. 1993. Fractionation of stable isotopes (¹³C, ¹⁵N) in the food web of a humic lake. Int. Ver. Theor. Angew. Limnol. Verh. **25:** 501–505.

PETERSON, B. J., AND B. FRY. 1987. Stable isotopes in ecosystem studies. Annu. Rev. Ecol. Syst. **18:** 293–320.

————, B. FRY, M. HULLAR, S. SAUPE, AND R. WRIGHT. 1994. The distribution and stable carbon isotopic composition of dissolved organic carbon in estuaries. Estuaries **17:** 111–121.

QUAY, P. D., S. R. EMERSON, B. M. QUAY, AND A. H. DEVOL. 1986. The carbon cycle for Lake Washington—A stable isotope study. Limnol. Oceanogr. **31:** 596–611.

RAU, G. H. 1978. Carbon-13 depletion in a subalpine lake: Carbon flow implications. Science **201:** 901–902.

————, M. HEYRAND, AND T. R. D. CHERRY. 1989. ¹⁵N/¹⁴N and ¹³C/¹²C in mesopelagic shrimp from the northeast Atlantic Ocean: Evidence for differences in diet. Deep-Sea Res. **36:** 1103–1110.

TAKAHASHI, K., E. WADA, AND M. SAKAMOTO. 1990. Carbon isotope discrimination by phytoplankton and photosynthetic bacteria in monomictic Lake Fukami-ike. Arch. Hydrobiol. **120:** 197–210.

ZOHARY, T., J. EREZ, M. GOPHEN, I. BERMAN-FRANK, AND M. STILLER. 1994. Seasonality of stable carbon isotopes within the pelagic food web of Lake Kinneret. Limnol. Oceanogr. **39:** 1030–1043.

# Atmospheric CO₂ 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 mol m$^{-2}$ d$^{-1}$. The estimated flux for the entire estuary amounts to 600 t of C d$^{-1}$ for a river discharge of $<1 \times 10^6$ m$^3$ 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 km³ yr$^{-1}$), this organic matter accumulates preferentially in the upper estuary, between salinities of 2 and 10 (Wollast 1983). In this area,
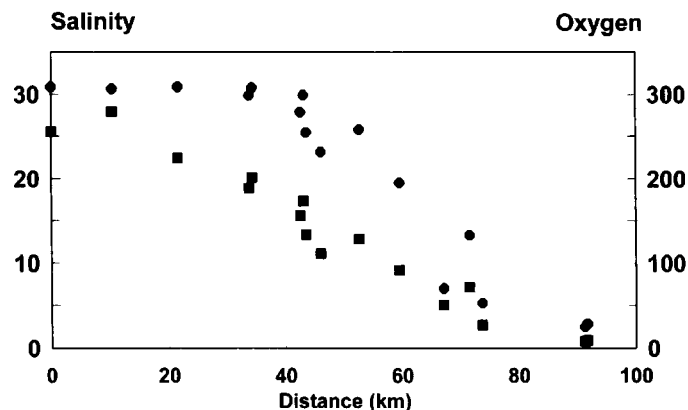
North                    *The Netherlands*

Sea    Vlissingen
       0 km                        Hansweert
        ▪              Baarland    40 km    Bath
       Breskens        20 km         ✦
                         ▪                        Zandvliet
                        Terneuzen        Doel  ✦60 km

            **Western Scheldt**                  ✦80 km
                                            Antwerpen

*Belgium*

                                         ✦100 km
                                      Wintham

Fig. 1.  Map of the Scheldt estuary.



Fig. 2.  Distribution of salinity (■) and oxygen (●, in $\mu$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 $CO_2$ ($pCO_2$) in the water column. As shown in Fig. 3, $pCO_2$ reaches 5,700 $\mu$atm at a salinity of $\sim5$, which also corresponds to the turbidity maximum and where the highest bacterial degradation activity can be expected. The oversaturation of $pCO_2$ with respect to atmospheric equilibrium (presently $\sim355$ $\mu$atm) is close to 1,600%. According to Kempe (1982), marked oversaturation of $CO_2$ occurs in many estuaries, but $pCO_2$ rarely exceeds 2,500 $\mu$atm in his observations.

In our work, $pCO_2$ 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 $\mu$eq kg$^{-1}$. The resulting error on $pCO_2$ depends also on the water buffering capacity and thus on pH, alkalinity, and salinity. In our experimental conditions, this error ranges from 6 $\mu$atm 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 $pCO_2$ (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 $\sim25\%$. The results of these measurements are given in Fig. 3.

In the area of the $pCO_2$ maximum, we observed fluxes as high as 1.2 mol m$^{-2}$ 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 $pCO_2$ 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 mmol m$^{-2}$ 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±4.9 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 ($<3.6$ 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 ($t\sim9°C$), the $CO_2$ Schmidt number is $\sim1210$ (Wanninkhof 1992) and our calculated value of K, corrected to Sc $= 600$ ($K \propto Sc^{-2/3}$), is 8.4±3.1 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
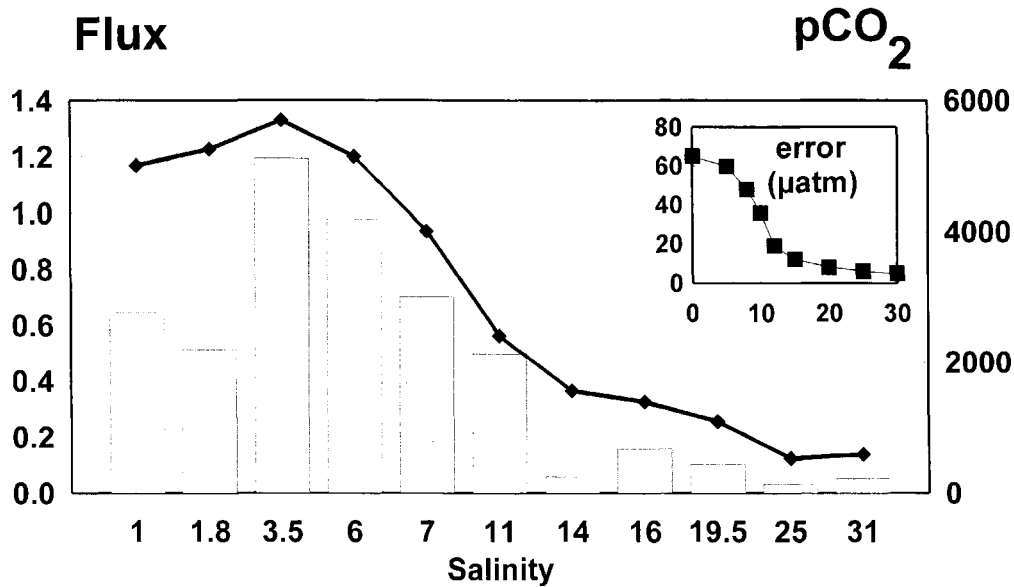
## Flux

## pCO$_2$



Fig. 3. Distribution of the partial pressure (◆, in μatm) and atmospheric fluxes of CO$_2$ (bars, in mol m$^{-2}$ d$^{-1}$) vs. salinity in the Scheldt estuary, March 1993. The error on $p$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 $8 \times 10^6$ m$^3$ d$^{-1}$ of freshwater with DIC ≈ 6 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 $8 \times 10^6$ m$^3$ d$^{-1}$ of freshwater with DIC ≈ 2 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$30 d) (Wollast 1988) and the mean river depth ($\sim$5 m), we obtain a loss to the atmosphere of 4.2 mmol kg$^{-1}$. This loss corresponds to a mean atmospheric flux of 0.7 mol m$^{-2}$ d$^{-1}$. Because

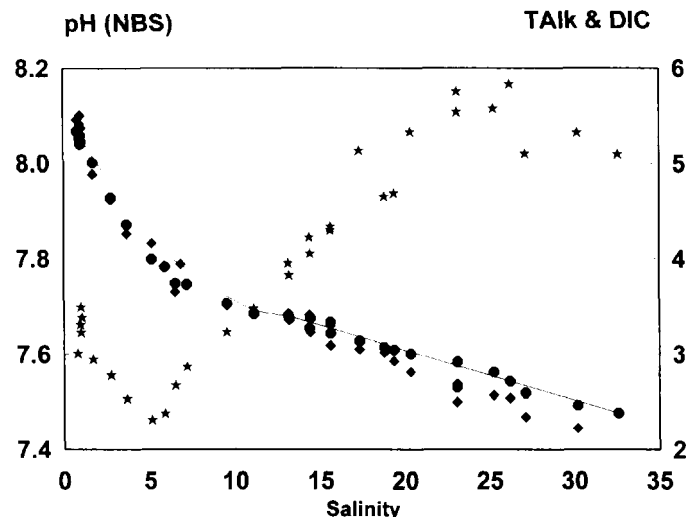### pH (NBS)                               TAlk & DIC



Fig. 4. Distribution of pH (★, NBS scale), TAlk (●, meq kg$^{-1}$), and DIC (◆, 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*).
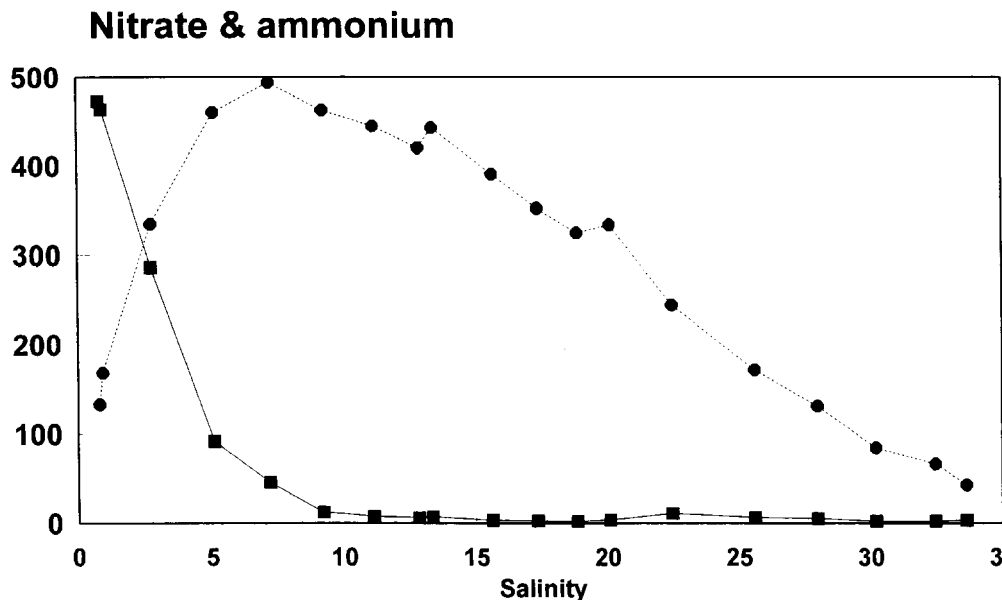
## Nitrate & ammonium



Fig. 5.    Distribution of ammonium (■, in $\mu$mol kg$^{-1}$) and nitrate (●, in $\mu$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 $\mu$mol kg$^{-1}$ and the excess of $CO_2$ is 246 $\mu$mol kg$^{-1}$ (5,000 $\mu$atm, i.e. 1,400% over-saturation). At a salinity of 11, these values are 96 $\mu$mol kg$^{-1}$ for $O_2$ and 103 for $CO_2$ (2,405 $\mu$atm, i.e. 677% oversaturation). Because the exchange coefficients of $O_2$ and $CO_2$ at the air–water interface are also similar (Wan-ninkhof 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 ($\sim 1$ 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 $NH_4^+ + 2O_2 + H_2O \rightleftharpoons NO_3^- + 2H_3O^+$, 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.

*Michel Frankignoulle*
*Isabelle Bourge*

Université de Liège
Laboratoire d'Océanologie
Institut de Chimie (Bât B6)
B4000 Sart Tilman, Belgium

*Roland Wollast*

Université Libre de Bruxelles
Service d'Océanographie Chimique
Campus de la Plaine C.P. 208, Bd. du Triomphe
B1050 Bruxelles, Belgium

## References

BATES, R. G. 1973. Determination of pH. Theory and practice. Wiley-Interscience.

BENNET, J. P., AND R. E. RATHBUN. 1972. Reaeration in open-channel flow. U.S. Geol. Surv. Prof. Pap. 737.

BENSON, B. B., AND D. KRAUSE. 1984. The concentration and

isotopic fractionation of oxygen dissolved in freshwater and seawater in equilibrium with the atmosphere. Limnol. Oceanogr. **29**: 620–632.

BILLEN, G. 1975. Nitrification in the Scheldt estuary. Estuarine Coastal Shelf. Sci. **3**: 79–89.

CLARK, J. F., R. WANNINKHOF, P. SCHLOSSER, AND H. J. SIMPSON. 1994. Gas exchange rates in the tidal Hudson River using a dual tracer technique. Tellus **46B**: 274–285.

FRANKIGNOULLE, M. 1988. Field measurements of air–sea $CO_2$ exchange. Limnol. Oceanogr. **33**: 313–322.

KEMPE, S. 1982. Valdivia Cruise, October 1981: Carbonate equilibria in the estuaries of Elbe, Weser, Ems and in the southern German bight. Mitt. Geol. Paleaontol. Inst. Univ. Hamburg **52**: 719–742.

LISS, P., AND L. MERLIVAT. 1986. Air–sea exchange rates: Introduction and synthesis, p. 113–128. *In* P. Buat-Ménard [ed.], The role of air–sea exchanges in geochemical cycling. Reidel.

LYMAN, J. 1975. Buffer mechanism of seawater. Ph.D. thesis, Univ. California, Los Angeles. 196 p.

MEHRBACH, C., C. H. CULBERSON, J. E. HAWLEY, AND R. M. PYTKOWICZ. 1973. Measurements of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. Limnol. Oceanogr. **18**: 897–907.

WANNINKHOF, R. 1992. Relationship between wind speed and gas exchange over the ocean. J. Geophys. Res. **97**: 7373–7382.

WEISS, R. F. 1974. Carbon dioxide in water and seawater: The solubility of a non-ideal gas. Mar. Chem. **2**: 203–215.

WILCOCK, R. J. 1984. Methylchloride as a gas tracer for measuring stream respiration coefficients. 2. Stream studies. Water Res. **18**: 53–57.

WOLLAST, R. 1983. Interactions in estuaries and coastal waters, p. 385–407. *In* B. Bolin and R. B. Cook [eds.], The major biogeochemical cycles and their interactions. SCOPE 21. Wiley-Interscience.

———. 1988. The Scheldt estuary, p. 185–193. *In* W. Salomons et al. [eds.], Pollution of the North Sea: An assessment. Springer.