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Carbonate dissolution in the turbid and eutrophic Loire estuary

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ABSTRACT: We measured particulate and dissolved organic carbon (POC and DOC), chlorophyll, oxygen, partial pressure of CO_2, pH, total alkalinity (TAlk) and particulate inorganic carbon (PIC) during a late summer cruise in the eutrophic Loire estuary. These parameters reveal an intense mineralisation of organic matter in the estuarine maximum turbidity zone (MTZ) that results in oxygen deficits (down to 20% of the saturation level) and high CO_2 oversaturations (pCO_2 up to 2900 µatm). Several facts revealed the occurrence of carbonate dissolution in the Loire MTZ: large amounts of alkalinity were produced in the upper estuary, increasing its transfer to the ocean by 30%; the calculated saturation index showed a net undersaturation for aragonite and a slight undersaturation for calcite in the MTZ; and PIC decreased from 2.1% (% dry weight) in riverine suspension to 0.4% in the MTZ. A stoichiometric approach is used to assess the coupling between aerobic respiration and carbonate dissolution, where apparent oxygen utilisation, excess CO_2, TAlk and dissolved inorganic carbon are compared quantitatively. About 20% of the CO_2 generated by respiration was involved in carbonate dissolution. The loss of PIC at the river–estuary transition quantitatively corresponds to the amount of authigenic calcite precipitated upstream in the highly eutrophic river. This suggests that CO_2 exchange with the atmosphere along the eutrophic river–estuary continuum is buffered by carbonate precipitation in the autotrophic river and its dissolution in the heterotrophic estuary.

KEY WORDS: Eutrophication · Estuarine turbidity maxima · Heterotrophy · Aerobic respiration · Carbonate dissolution

INTRODUCTION

Estuaries play an important role in the transfer of material from the land to the coastal ocean. This is particularly true for macrotidal estuaries, where the long residence times of both water and suspended matter allow a significant modification in the speciation of chemical compounds by biological activity and physico-chemical processes (e.g. Wollast 1983). The transport of carbon by world rivers is a significant component of the global carbon cycle estimated to ca. 0.9 Gt C yr^{-1}, of which ~60% is inorganic and ~40% is organic (Meybeck 1993a). It is now well established that estuaries are net heterotrophic ecosystems, where total respiration exceeds gross primary production (Smith & Hollibaugh 1993, Gattuso et al. 1998). This respiration is particularly intense in the upper part of estuaries, which generally coincides with the maximum turbidity zone (MTZ), and where oxygen deficits, CO_2 super-saturations and CO_2 fluxes to the atmosphere are highest (Thouvenin et al. 1994, Frankignoulle et al. 1996, 1998, Cai et al. 1999, Raymond et al. 2000). Most of the riverine organic carbon respired in estuaries enters in the particulate form (POC) and originates from soils, freshwater phytoplankton and sewage (Ittekkot & Laane 1991, Abril et al. 2002). On the contrary, riverine dissolved organic carbon (DOC) appears more refractory

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to bacterial degradation, DOC having a conservative behaviour (Mantoura & Woodward 1983) or sometimes being produced in the estuarine zone (Raymond & Bauer 2001).

By contrast to organic carbon, little is known about how estuarine processes could change the net fluxes of inorganic carbon between the land and the ocean. Respiration produces dissolved inorganic carbon (DIC) as CO_2 that rapidly escapes to the atmosphere from the estuary itself or from the adjacent coastal area (Frankignoulle et al. 1996, 1998, Cai et al. 1999, Borges & Frankignoulle 2002). Total alkalinity (TAlk), which is not affected by atmospheric exchange and is weakly affected by aerobic respiration (only through associated ammonification; Brewer & Goldman 1976), has often been considered as a conservative parameter during estuarine mixing (Hoppema 1990). Recently, net changes in TAlk have been reported in relation to different estuarine biogeochemical processes: (1) in the highly polluted Scheldt estuary, ammonification and denitrification on the one hand and nitrification on the other hand, respectively, consume and produce enough protons to significantly affect the alkalinity (Frankignoulle et al. 1996, Abril & Frankignoulle 2001); (2) in estuaries with large tidal marshes, significant amounts of alkalinity were found to be produced by denitrification (Cai et al. 2000) and/or sulfate reduction, when coupled to a net accumulation of sulfides in sediments (Brasse et al. 1999, Cai et al. 1999, Raymond et al. 2000); (3) in the highly turbid Ems and Gironde estuaries, dissolution of calcium carbonate occurs in MTZs, generating alkalinity (de Jonge & Villerius 1989, Abril et al. 1999). Here, we report significant carbonate dissolution also in the Loire estuary, where, in addition, due to a pronounced eutrophication in freshwaters, authigenic carbonate constitutes a significant fraction of the riverine suspensions entering the estuary (Grosbois et al. 2001).

MATERIALS AND METHODS

Study area. The Loire estuary (Fig. 1) on the French Atlantic coast is 100 km long with a surface area of 100 km^2, an average depth of 9 m and a restricted area of tidal flats. The estuary is macrotidal (average tidal amplitude at the mouth ~4 m), well mixed and highly turbid. The MTZ (defined as depth-integrated suspended particulate matter (SPM) >1 g l^{-1}) is 20 to 50 km long, depending on river discharge (Gallene 1974). In the MTZ, surface SPM concentrations can reach 2 g l^{-1} during spring tide, but decrease to a few hundred mg l^{-1} during neap tides, when suspensions are temporarily trapped in fluid mud layers (Le Normant 2000). Long-term budget calculations show that river input is by far the major source of suspensions to the estuary, residence times of waters and suspensions being, respectively, 10 to 30 d and 1 to 2 yr (Migniot 1993).

The Loire River, which drains a 117 000 km^2 area, has an average discharge of 850 m^3 s^{-1}. It is probably one of the most eutrophic large rivers in the world, with chl *a* concentrations exceeding 100 µg l^{-1}, and algal POC representing 60 % of the POC in summer (Meybeck et al. 1988). In addition to a high load of algal POC, a second effect of eutrophication in the Loire River is the chemical precipitation of authigenic carbonates in the river waters, when primary production raises the pH above 8.5 (Manickam et al. 1985). As a consequence, authigenic carbonates represent up to 37 % of the river suspensions in summer (Meybeck et al. 1988, Grosbois et al. 2001). Previous studies have shown that the estuarine zone is highly heterotrophic (Relexans et al. 1988), with all the riverine algal POC being mineralised in the MTZ, where in addition light penetration is too low to sustain important primary production (Billen et al. 1986, Meybeck et al. 1988). As a result, the estuarine waters in the MTZ are dramatically oxygen depleted (Thouvenin et al. 1994).

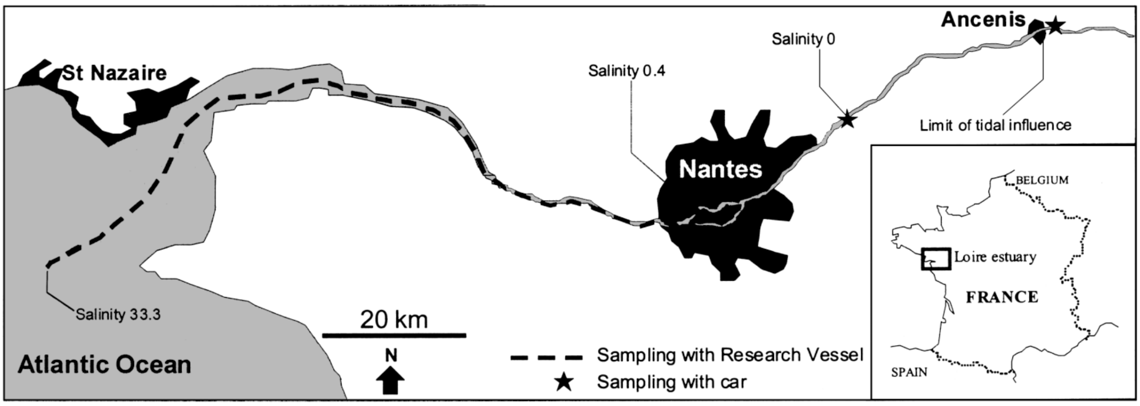

Fig. 1. Map of the Loire estuary with different sampling strategies

Sampling and analytical techniques. During a 5 d cruise in spring-tide conditions, from 10 to 14 September 1998, we sampled surface waters along the whole salinity gradient of the estuary, including a non-tidal river station upstream of Ancenis, a freshwater tidal station upstream from the city of Nantes and a marine station downstream at salinity 33.3 (Fig. 1). We measured salinity and temperature with a Sea Bird Electronics (SBE) 19 probe. Chl *a* was determined on glass fibre filters (porosity 0.7 µm) by fluorescence after extraction in 90% acetone (precision ±10%). Two precombusted and pre-weighed glass fibre filters (porosity 0.7 µm) were used for SPM determination (reproducibility ±15%); one filter was then used for total carbon determination with a LECO analyser; the second filter was acidified with HCl 2N to remove carbonate and then analysed for POC (precision ± 5%). Particulate inorganic carbon (PIC) was determined as the difference between the total carbon and the organic carbon contents of the suspensions, and expressed as percent of total suspended matter (precision ±10%). We measured pH with a Ross combination electrode calibrated against NBS buffers (precision ±0.005 U), TAlk by Gran electrotitration (precision ± 4 µEq kg^{-1}) and oxygen with an automated Winkler method (± 2 µmol kg^{-1}). We calculated the surface partial pressure of CO_2 (pCO_2) and DIC from temperature, salinity, pH and TAlk with the constants from Mehrbach et al. (1973) and Lyman (1975), and the CO_2 solubility coefficient from Weiss (1974). We also calculated the excess carbon dioxide (ECO_2 in µmol kg^{-1}), defined as the quantity of DIC that must be released as CO_2 to the atmosphere to achieve complete air–water equilibration. ECO_2 was calculated as the difference between the *in situ* DIC and the DIC computed at the atmospheric equilibrium of 370 µatm and using the *in situ* TAlk. Oxygen concentrations were compared with the oxygen concentration of air-saturated water computed with the algorithm of Benson & Krause (1984), apparent oxygen utilisation (AOU) being the difference between the 2 oxygen concentrations. Finally, we estimated the saturation index (Ω) of calcite and aragonite, using the solubility coefficients given by Mucci (1983) and, as a first approximation, by considering conservative mixing for Ca^{2+} between the Loire River (September average: 0.9 mmol kg^{-1}; Grosbois et al. 2000) and the sea (10 mmol kg^{-1}; Morse & Mackenzie 1990).

RESULTS

The distributions of POC, DOC and chl *a* (Fig. 2) were very consistent with the ones measured in the 1980s (Meybeck et al. 1988, Relexans et al. 1988). During our cruise, the MTZ was divided in 2 parts (Fig. 2A), one between salinities 0 and 10 and a second between salinities 14 and 18, where SPM at the surface were >100 mg l^{-1} and where fluid-mud layers (height ~50 cm) could be observed using an echo sounder. In between, around salinity 12, surface waters were less turbid and no fluid mud was detected. POC (Fig. 2A) and chl *a* (Fig. 2B) were exceptionally high at the non-tidal river station and rapidly decreased at the entrance of the estuarine MTZ. The % POC stabilised in the MTZ, at a constant value of 3.5%, and chl *a* decreased to less than 2 µg l^{-1} at the estuarine mouth. DOC decreased almost linearly with salinity (Fig. 2B), although some significant peaks at salinities 0, 13 and 20 suggest some input, possibly related to episodic resuspensions of anoxic fluid-mud (Abril et al. 1999). Although the river was rich in chlorophyll, the water remained supersaturated in CO_2 and below the saturation level for oxygen (Fig. 3), either due to a decay of the freshwater phytoplankton bloom during this late summer period and/or inputs from groundwaters (Jones & Mulholland 1998). In the estuary, the distributions of oxygen and pCO_2 showed a remarkable antiparallelism along the salinity gradient (Fig. 3). In the 2 most turbid regions (salinity 0 to 10 and 14 to 23),

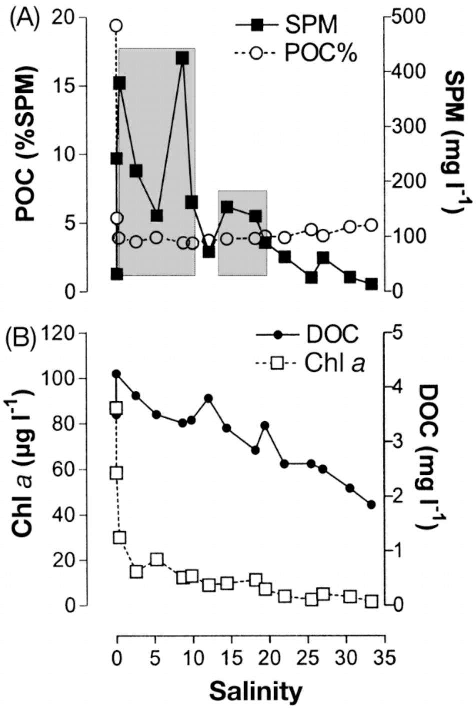

Fig. 2. Distributions of (A) suspended particulate matter (SPM; mg l^{-1}) and particulate organic carbon (POC; % SPM); (B) chl *a* (µg l^{-1}) and dissolved organic carbon (DOC; mg l^{-1}) as a function of salinity in the Loire estuary in September 1998. Shaded areas indicate the 2 regions of the estuarine maximum turbidity zone (MTZ)

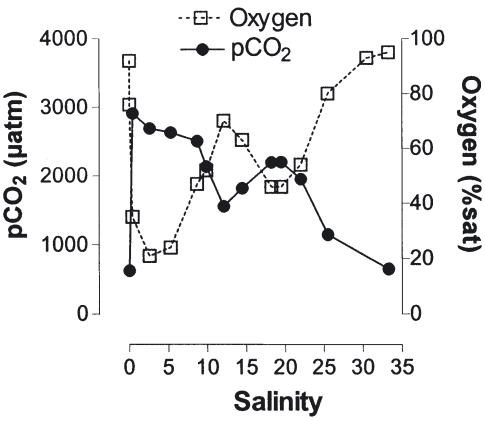

Fig. 3. Distributions of oxygen (% saturation) and partial pressure of CO_2 (pCO_2; µatm) as a function of salinity in the Loire estuary in September 1998

pCO_2 showed a maximum and oxygen a minimum. The decrease of POC and chl *a* at the river–estuary transition, and the oxygen depletion and CO_2 supersaturation in the estuarine MTZ, attest for the marked heterotrophy in the eutrophic Loire estuary (Relexans et al. 1988).

DIC showed a strong non-conservative behaviour, with a steep increase between the river and salinity 0.5 (Fig. 4A). Most of this DIC increase was related to the production of alkalinity at the entrance of the MTZ (Fig. 4B). In parallel, PIC rapidly dropped from 2.1 % in river suspensions to a constant value of 0.4 % in the MTZ suspensions (Fig. 4C), except at salinity 12, where a small PIC peak occurs, probably due to a local precipitation because pH (not shown) re-increased at that location or to grain-size effects associated with the physical mixing of different suspensions. River waters were largely oversaturated with respect to calcite ($\Omega = 5.7$) and aragonite ($\Omega = 3.2$) (Fig. 4C). By contrast, estuarine waters were largely undersaturated for aragonite ($\Omega = 0.56 \pm 0.11$ in the 0 to 22 salinity range) and close to equilibrium for calcite ($\Omega = 1.11 \pm 0.19$ in the 0 to 22 salinity range), with a slight undersaturation (3 Ω values <1 for calcite between the 2.5 and 9 salinity range) (Fig. 4C). This suggests that the thermodynamic conditions required for some carbonate dissolution are locally reached in the estuary.

DISCUSSION

Evidence for carbonate dissolution

When comparing the observed riverine TAlk concentration with the intercept at zero salinity of the line tangent to the curve at high salinities (Fig. 4A), ca. 720 µEq kg^{-1} of TAlk were generated in the Loire estuary during our cruise, apparently in the region with salinity <12. This corresponds to an increase of ~35 % in the net alkalinity flux to the Atlantic Ocean, where it will enter into the oceanic carbonate precipitation/dissolution cycle (Morse & Mackenzie 1990). The distribution of dissolved inorganic nitrogen species during our cruise can be seen in Middelburg & Nieuwenhuize (2001). Nitrate decreased linearly from 70 µM in the river to 10 µM at sea, showing that denitrification was not significant at the estuarine scale, nor were presumably other anaerobic, alkalinity-generating processes such as sulphate reduction. In addition, ammonium was below 10 µM all along the salinity gradient, rejecting the possibility of significant alkalinity changes due

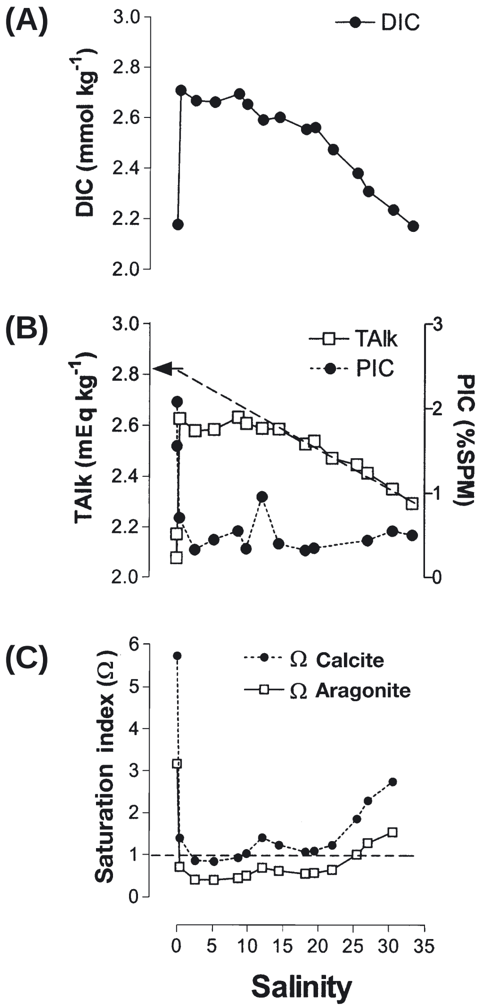

Fig. 4. Distributions of (A) dissolved inorganic carbon (DIC; mmol kg^{-1}); (B) total alkalinity (TAlk, mEq kg^{-1}) and particulate inorganic carbon (PIC, in % suspended particulate matter [SPM]); and (C) the saturation index (Ω) for calcite and aragonite, as a function of salinity in the Loire estuary in September 1998

to ammonification and nitrification (Abril & Frankignoulle 2001). Consequently, such a huge production of alkalinity can only be attributed to carbonate dissolution, which is confirmed here by the significant decrease of PIC from the river to the estuary. This is also consistent with the sediments study of Négrel (1997), who observed a calcium depletion of 50% in estuarine sediments relative to fluviatile sediments. In the estuarine waters, our calculated carbonate saturation states show a large undersaturation for aragonite, but only a slight undersaturation (minimum $\Omega = 0.84$) for calcite in the 0 to 10 salinity region (Fig. 4C). In Canadian shelf sediments, Mucci et al. (2000) made similar observations with calculated Ω values for calcite in porewaters always higher than 0.8 and often above 1, but still the occurrence of carbonate dissolution unequivocally demonstrated by a net Ca^{2+} release to porewaters. In the case of the Loire estuary, the occurrence of intense carbonate dissolution at a relatively high theoretical saturation state might also be due to the presence of fluviatile authigenic calcite (Grosbois et al. 2001), whose solubility has not yet been documented (Morse & Arvidson 2002).

Carbonate dissolution is a chemical process driven by thermodynamic potential, which depends on physico-chemical conditions of both the water and the solid phases. Among the major parameters in the water phase conditioning the occurrence and intensity of carbonate dissolution are pH, pCO_2, ionic strength, and the presence of 'foreign ions' and Ca^{2+} concentration (Morse & Arvidson 2002). At the Loire river–estuary transition (low salinity region), changes in the physicochemical conditions driven by biogeochemical processes, that is by the sharp autotrophy > heterotrophy switch and subsequent changes in pH and pCO_2, are by far the dominant factors for the occurrence of carbonate dissolution (Figs. 3 & 4). This was also the case in the Ems estuary, where, by contrast to the Loire, carbonate suspensions are mainly seaborne, but also are dissolved in the MTZ, where pH is much lower than in the marine area (de Jonge & Villerius 1989). In coastal and marine sediments the biogeochemical factors that control carbonate dissolution are now well understood. Aerobic respiration that produces carbonic acid ($CO_2 + H_2O = H_2CO_3$) promotes carbonate dissolution, whereas most anaerobic processes (Fe[III] and SO_4 reductions), consume protons and lead to a build-up of alkalinity in the porewaters, inhibiting dissolution and sometimes resulting in precipitation (Morse & Mackenzie 1990, Mucci et al. 2000). In addition, the oxidation by oxygen of reduced compounds (ammonia, dissolved iron and sulphides) generates acid (protons), and also stimulates dissolution (Aller 1982, Green & Aller 1998). Estuarine MTZs are sites of intense exchanges of chemical compounds between the particulate and dissolved phases through chemical reactions and adsorption/desorption processes (Van Beusekom & de Jonge 1994). Due to strong tidal currents, particles remain in suspension in the water column under oxic conditions. Anoxic conditions occur in the most concentrated layers of fluid mud but are restricted to short periods, typically ~5 d (Abril et al. 1999, Le Normant 2000). In addition, the periodic resuspensions of the fluid mud prevent carbonate particles from staying in contact with highly alkaline porewater and allow complete oxidation of reduced compounds. This makes the estuarine MTZ fluid-mud system an efficient biogeochemical reactor for carbonate dissolution.

Using a mixing model based on rare earth-element analysis in Loire estuarine suspensions, Négrel (1997) showed that the proportion of fluviatile suspensions in the estuary represented 80 to 90% all along the first

Table 1. Typical particulate organic and inorganic carbon concentrations (POC and PIC, respectively, expressed as % of suspended particulate matter [SPM]) in the Loire riverine and estuarine suspensions. Yearly average (discharge weighed) concentrations are calculated using the reported summer and winter values and the corresponding solid discharges from Meybeck et al. (1988)

	Riverine suspensions			Estuarine suspensions	
	Summer	Winter	Yearly average	Summer	Winter
Total POC	10.5[a]	5.1[a]	6.4	3.5[b]	3.4[c]
Detrital POC	3.0[a]	3.0[a]	3.0	3.5[b]	3.4[c]
Algal POC	7.5[a]	2.1[a]	3.4	0.0[b]	0.0[c]
Total PIC	2.1[d]	0.5[d]	0.9	0.4[e]	–
Detrital PIC	0.4[d]	0.5[d]	0.5	–	–
Authigenic PIC	1.7[d]	0.0[d]	0.4	–	–

[a] Value from Meybeck et al. (1988)
[b] Values from Billen et al. (1986), Meybeck et al. (1988) and this study consistent at ±10%
[c] Values from Billen et al. (1986), Meybeck et al. (1988)
[d] Values from Manickam et al. (1985), Meybeck et al. (1988) and Grosbois et al. (2001) consistent at ±10%
[e] Average value observed in the estuary, this study

50 km in the upper estuary and then decreased to reach 40 to 50 % at the estuarine mouth. This large predominance of fluviatile suspensions in the upper estuary allows us to interpret quantitatively the changes in particulate concentrations between the river non-tidal station and the upstream estuarine stations in the MTZ as the result of biogeochemical processes (particulate carbon removal), rather than particle mixing. Table 1 summarizes the typical POC and PIC concentrations reported so far in the Loire river and estuary during high and low discharge regimes. These carbon concentrations show a remarkable constancy with time, suggesting that little has changed in the eutrophication status of the Loire since the mid-1980s. Previous studies, either process-based, including respiration and primary production measurements (Billen et al. 1986, Relexans et al. 1988), or based on geochemical considerations of changes in carbon concentrations at the river–estuary transition (Meybeck et al. 1988) lead to the same conclusion of a complete mineralization of the riverine algal-POC in the estuarine MTZ. Indeed, the constant POC concentration found at any season in the Loire MTZ (3.5%; Table 1) corresponds to the 'detrital-POC', originating from soils, that is supplied during high river discharges, and is refractory to bacterial decomposition at the scale of its residence time in the estuary (Meybeck et al. 1988). A similar statement can be made with the PIC data in Table 1. Indeed, the total PIC we measured during our cruise in river suspensions (2.1 %) exactly matches values reported previously during the same late summer period, among which ca. 1.7 % is authigenic PIC and 0.4 % is detrital PIC (Manickam et al. 1985, Meybeck et al. 1988, Grosbois et al. 2001). Thus, the residual value we measured in the MTZ (0.4 %) corresponds to the detrital PIC in river suspensions, which strongly suggests that (similarly to algal-POC) only authigenic PIC was lost at the river–estuary transition, detrital PIC (similarly to detrital POC) having a conservative behaviour. This would imply that the authigenic PIC precipitated in the river is more soluble than detrital PIC mechanically eroded from the basin. Dissolution kinetics studies are now required to confirm this hypothesis.

Coupling between aerobic respiration and carbonate dissolution

The data we collected during this study can be used to develop a stoichiometric approach in order to assess the coupling between aerobic respiration and carbonate dissolution in estuarine MTZ. Relexans et al. (1988) showed that, because light penetration (<1 % incident light) in the Loire estuary is only 30 to 50 cm, i.e. <5 % of the water column, primary production represented less than 5 % of heterotrophic activity all year round. It thus appears reasonable to assume that dark processes dominate and that the respiratory quotient is equal to 1. In addition, during our cruise measured respiration rates were ~0.5 µmol l^{-1} h^{-1} (R. Wollast pers. comm.), dark ammonia uptake was ~0.1 µmol l^{-1} h^{-1} (Middelburg & Nieuwenhuize 2000) and the C:N ratio of particulate organic matter was 6 to 7 (J. J. Middelburg pers. comm.). When assuming the same C:N ratio for the organic matter being decomposed, this means that 70 % of the ammonium produced by ammonification is immediately re-incorporated into bacterial biomass in an organic form, thus having no effect on alkalinity. In addition, it implies that nitrification becomes a minor oxygen consuming process. For those reasons, we assume that aerobic respiration is the only process consuming oxygen, and we use a simplified formulation of organic matter that takes into account only carbon. Accordingly, the stoichiometry of aerobic respiration and carbonate dissolution are represented by, respectively:

$$\text{'}CH_2O\text{'} + O_2 \rightarrow CO_2 + H_2O$$

and

$$CO_2 + H_2O + CaCO_3 \rightarrow 2HCO_3^- + Ca^{2+}$$

where 'CH_2O' represents organic carbon.

Only a fraction, α, of the carbonic acid generated by respiration is involved into the carbonate dissolution reaction, which can be written as:

$$\text{'}CH_2O\text{'} + O_2 + \alpha CaCO_3 \rightarrow (1-\alpha)CO_2 + (1-\alpha)H_2O + 2\alpha HCO_3^- + \alpha Ca^{2+}$$

with $0 \leq \alpha \leq 1$. When considering a closed system, where no gaseous exchange occurs with the atmosphere, we can write from the dissolution reaction:

$$(1-\alpha)\Delta AOU_{(cl)} = \Delta ECO_{2(cl)} \quad (1)$$

and

$$2\alpha\Delta DIC_{(cl)} = (1+\alpha)\Delta TAlk \quad (2)$$

where Δ is the variation of a given chemical species and the 'cl' notation refers to a closed system. TAlk is not affected by gaseous exchange, consequently ΔTAlk is identical in closed and open systems.

To investigate the magnitude of a given process in estuaries, one classical approach is to compare the observed profiles as a function of salinity with the theoretical mixing line between 2 given end-members. When making the hypothesis that end-members are constant at the timescale of estuarine mixing, the variation, Δ, of the parameter is the difference between the observed value and the value predicted by the conservative line at the same salinity. Owing to the low discharge condition during our cruise, which makes the steady-state hypothesis

Table 2. Linear regression parameters. Slopes and intercepts are given ±SE. ΔECO_2: Δ excess carbon dioxide; ΔAOU: Δ apparent oxygen utilisation; ΔTAlk: Δ total alkalinity; ΔDIC: Δ dissolved inorganic carbon. Δ refers to the difference relative to conservative mixing in the respective sections (see 'Discussion'). p-values: probability for the slope to be different from 0; ns: not significant

	Salinity 0–12	Salinity 12–33
ΔECO_2 vs ΔAOU	Significant	Significant
Slope	1.71 ± 0.16	0.92 ± 0.11
y-intercept	–8.31 ± 10.85	0.16 ± 7.76
R^2	0.965	0.926
p	0.0005	0.0005
ΔTAlk vs ΔDIC	Significant	ns
Slope	1.18 ± 0.03	
y-intercept	–6.43 ± 6.88	
R^2	0.997	0.523
p	<0.0001	0.0661

acceptable, we performed such calculations for AOU, ECO_2, DIC and TAlk, using first a dilution line between the riverine and the marine end-members. When using these 2 end-members, we obtained a highly significant linear correlation ($R^2 = 0.97$) between ΔDIC and ΔTAlk, but a weak correlation ($R^2 = 0.49$) between ΔECO_2 and ΔAOU (not shown). We then considered separately the 2 regions showing an oxygen minimum and a pCO_2 maximum (Fig. 3) by introducing an intermediate end-member at a salinity of 12, and we obtained significantly different relationships, listed in Table 2 and shown in Fig. 5. In the upper estuary (salinities of 0 to 12), the slope between ΔAOU and ΔECO_2 is 1.71 and is significantly higher than 1 ($p < 0.0001$) This is in agreement with the occurrence of calcite dissolution coupled to aerobic respiration and implies that $\alpha \neq 0$. In addition, the slope between ΔDIC and ΔTAlk is 1.18 and is significantly higher than 1 ($p = 0.001$). This is consistent with a calcite dissolution that involves only a fraction of the CO_2 generated by aerobic respiration, and implies that $\alpha < 1$. In the lower estuary (salinities of 12 to 33), ΔAOU and ΔECO_2 are similar (the slope of the regression line was not significantly different from 1, with $p = 0.058$), in agreement with the occurrence of aerobic respiration alone ($\alpha = 0$). In addition, ΔDIC and ΔTAlk show no correlation, TAlk being almost conservative (ΔTAlk ~ 0), also consistent with aerobic respiration alone occurring in this area. None of the regressions had significant intercepts ($p > 0.05$).

Calcite dissolution appears to occur only in the low salinity (0 to 12) region of the estuary, with the following relationships from Table 2:

$$\Delta AOU_{(op)} = a_1 \Delta ECO_{2(op)} \quad \text{with } a_1 = 1.71 \pm 0.16 \quad (3)$$

$$\Delta DIC_{(op)} = a_2 \Delta TALK \quad \text{with } a_2 = 1.18 \pm 0.03 \quad (4)$$

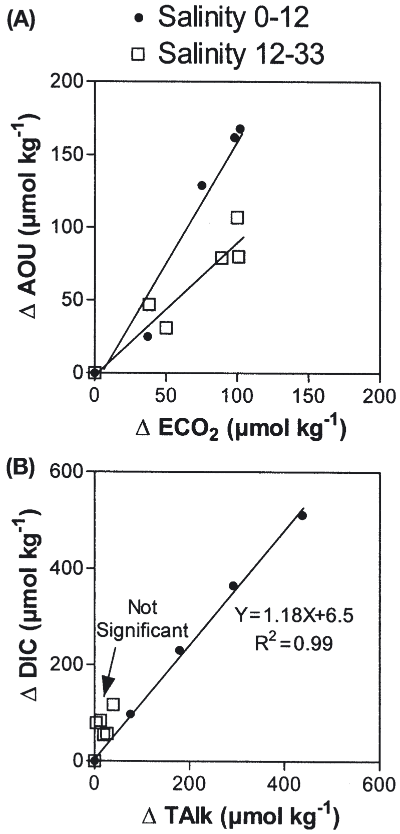

Fig. 5. Relationships between (A) Δ apparent oxygen utilisation (ΔAOU) and Δ excess carbon dioxide (ΔECO_2); and (B) Δ dissolved inorganic carbon (ΔDIC) and Δ total alkalinity (ΔTAlk). Two sections of the estuary were considered separately (Salinities 0 to 12 and 12 to 33). Δ refers to the difference relative to conservative mixing in the respective sections (see 'Discussion')

where the notation 'op' refers to an open system that exchanges gas with the atmosphere.

Because ECO_2 and AOU are of the same order of magnitude, and because the exchange coefficients of CO_2 and O_2 are also similar (Wanninkhof 1992), these 2 gases exchange with the atmosphere at a similar rate. The differences in concentrations between open and closed systems correspond to the loss to the atmosphere, and are thus very close for ECO_2 and for AOU:

$$\Delta ECO_{2(cl)} - \Delta ECO_{2(op)}) = \Delta AOU_{(cl)} - \Delta AOU_{(op)}$$

Using Eqs. (1) & (3) this leads to:

$$\Delta ECO_{2(cl)}\left[1 - \frac{1}{1-\alpha}\right] = \Delta ECO_{2(op)}[1 - a_1]$$

That is rewritten as:

$$\Delta ECO_{2(cl)} = (a_1 - 1)\left[\frac{1-\alpha}{\alpha}\right]\Delta ECO_{2(op)} \quad (5)$$

Similarly, the term ΔTAlk can be removed from Eqs. (2) & (4) to obtain the following relationship:

$$\Delta DIC_{(cl)} = \frac{1}{a_2}\left[\frac{1+\alpha}{2\alpha}\right]\Delta DIC_{(op)} \quad (6)$$

The exchange of DIC with the atmosphere concerns the CO_2 form only, so the differences between open and closed systems, that is the quantity exchanged with the atmosphere, are equal for DIC and ECO_2. Consequently, the 2 coefficients in Eqs. (5) & (6) are equal, and thus:

$$(a_1 - 1)\left[\frac{1-\alpha}{\alpha}\right] = \frac{1}{a_2}\left[\frac{1+\alpha}{2\alpha}\right]$$

and

$$\alpha = \frac{2a_2 - 2a_1a_2 + 1}{2a_2 - 2a_1a_2 - 1}$$

which leads to a numerical value of $\alpha = 0.25 \pm 0.09$. Approximately 25% of the CO_2 generated by respiration is involved in calcite dissolution. In addition, it is possible to estimate the fraction of the produced CO_2 that has escaped to the atmophere using Eq. (6):

$$\Delta DIC_{(cl)} = 2.1\Delta DIC_{(op)}$$

Approximately 52% of the CO_2 produced by respiration had already escaped to the atmosphere. This confirms the fast and dynamic coupling between CO_2 generation and evasion reported by previous DIC studies in estuaries (Frankignoulle et al. 1996, 1998, Cai et al. 1999, 2000, Raymond et al. 2000).

A tentative summer budget of CO_2 for the Loire estuary

To estimate the total CO_2 emissions from the estuary, we considered a gas exchange coefficient of 13 cm h^{-1} as representative for macrotidal estuaries (Frankignoulle et al. 1996), and we integrated the calculated fluxes over the surface of 5 km sections of the Loire estuary. This lead to fluxes between 30 and 280 mmol m^{-2} d^{-1}, and a total emission of 110 tC d^{-1} from the entire estuary, which ranks the Loire among the European estuaries with highest CO_2 emissions after the highly polluted Scheldt (Frankignoulle et al. 1998). The heterotrophic activity in the Loire estuary during summer is well documented by the different approaches, giving very similar results: 150 tC d^{-1} when simply considering that all the riverine algal POC is consumed (Meybeck et al. 1988), 150 tC d^{-1} when using bacterial production (thymidine incorporation) and growth yield (Relexans et al. 1988), and 160 tC d^{-1} during spring tide when using biological oxygen demand and a model of suspended matter dynamics (Thouvenin et al. 1994). Due to light limitation, primary production in the Loire estuary is known to be a very minor component of the carbon cycle, representing about 10 tC d^{-1} (Relexans et al. 1988). Carbonate dissolution can be estimated either by considering that all the riverine autigenic PIC summer input is dissolved (23 tC d^{-1}; Meybeck et al. 1988) or by multiplying ½ of the TAlk increase (360 mmol kg^{-1}) with the river discharge during the cruise (220 m^3 s^{-1}), which results in 80 tC d^{-1}. Using an intermediate value of 30 tC d^{-1} allows an equilibration of the CO_2 budget (Table 3) in which 20% of the respiratory CO_2 is involved in carbonate dissolution. Notwithstanding the large uncertainties probably still remaining with these numbers, we believe they satisfactorily reflect the significance of carbonate dissolution in the Loire estuary during summer.

Table 3. Tentative carbon dioxide budget for the Loire estuary during summer. See 'Discussion' for numbers selection

	Sources (tC d^{-1})	Sinks (tC d^{-1})
Respiration	150	
Atmospheric emission		110
Primary production		10
Carbonate dissolution		30
Total	150	150

As a conclusion, we can define here a 'reverse buffering mechanism' with respect to atmospheric CO_2 exchange along the eutrophic Loire river–estuary continuum: in the river, intense primary production consumes atmospheric CO_2 but also creates conditions for calcite precipitation that releases CO_2, thus buffering the CO_2 influx; in the estuarine MTZ, intense respiration produces atmospheric CO_2 but also results in an almost complete dissolution of the calcite produced upstream, thus consuming water CO_2 and buffering the CO_2 outflux. For future biogeochemical studies in estuaries, calcite precipitation and dissolution might be considered as important processes for the carbon cycle. Furthermore, detailed distributions of Ca^{2+} and Mg^{2+} may provide significant information for the carbonate system of estuaries.

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