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A massive dissolved inorganic carbon release at spring tide in a highly turbid estuary

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[1] In September 2003, the highly turbid Loire estuary (France) showed drastic oxygen depletions (down to 11% of saturation), high pCO₂ (up to 3740 μ atm) and high CO₂ fluxes (280 \pm 100 mmol.m⁻².d⁻¹). A rapid rise in Dissolved Inorganic Carbon (DIC) was observed when the tidal amplitude increased from 3.8 m to 5.8 m. In two days, average concentrations in the 0.1-25 salinity range increased by $106 \pm 17 \; \mu \text{mol.kg}^{-1}$ for DIC, by $80 \pm 14 \; \mu \text{eg.kg}^{-1}$ for Total Alkalinity (TA) and by $684 \pm 142 \mu atm$ for pCO₂. In parallel, oxygen decreased by $65 \pm 12 \, \mu \text{mol.kg}^{-1}$. These changes in concentrations were attributed in majority to a massive fluid mud resuspension in the estuarine turbidity maximum. At spring tide, this DIC input was 30% higher than the river input. When averaged over the neap-spring period, resuspension contributed to only 10% of the atmospheric CO₂ flux from the estuary, but to 60% to the net TA production in the estuary. INDEX TERMS: 4235 Oceanography: General: Estuarine processes; 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4806 Oceanography: Biological and Chemical: Carbon cycling; 4820 Oceanography: Biological and Chemical: Gases; 4834 Oceanography: Biological and Chemical: Hypoxic environments. Citation: Abril, G., M.-V. Commarieu, D. Maro, M. Fontugne, F. Guérin, and H. Etcheber (2004), A massive dissolved inorganic carbon release at spring tide in a highly turbid estuary, Geophys. Res. Lett., 31, L09316, doi:10.1029/2004GL019714.

Introduction

[2] Depending on tidal intrusion length, tidal range and residence time, macrotidal estuaries can be extremely turbid [Uncles et al., 2002]. Examples of highly turbid estuaries are the Gironde and Loire in France and the Humber-Ouse in the UK. In these systems, the estuarine turbidity maximum (ETM) extends over a large part of the salinity gradient and suspended particulate matter (SPM) reach several g.l⁻¹ at the surface [Thouvenin et al., 1994; Uncles et al., 2002]. Estuaries are generally net heterotrophic ecosystems and CO₂ sources to the atmosphere [Smith and Hollibaugh, 1993; Frankignoulle et al., 1998]. In turbid estuaries the net heterotrophy is particularly pronounced because primary production is very limited due

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to steep light extinction, whereas respiration and bacterial production are enhanced by the presence of large amounts of particulate organic matter (POM) [Goosen et al., 1999]. In addition, ETMs are highly dynamic systems with intense sedimentation/resuspension cycles at the fortnightly (neapspring) scale [Thouvenin et al., 1994; Uncles et al., 1998; Abril et al., 1999]. Episodic highly concentrated benthic layers called "fluid muds", with SPM concentrations reaching 100 g.l⁻¹ are found at neap and mean tides. They can reach 2 meters in height and are anoxic [Thouvenin et al., 1994; Abril et al., 1999]. In several estuaries, rapid oxygen drops were reported in surface water at spring tide, when fluid mud was resuspended [Parker et al., 1994; Thouvenin et al., 1994; Uncles et al., 1998]. Here we report in the Loire estuary a massive release of dissolved inorganic carbon (DIC) at spring tide, which temporarily constitutes a major component of the carbon budget of the estuary.

Site and Methods

[3] The Loire estuary on the French Atlantic coast is 100 km long with a surface area of 102 km², and an average depth of 9 meters. The estuary is macrotidal, well mixed and highly turbid. Residence times of waters and suspensions are respectively 2-10 days and 1-2 years [Relexans et al., 1988]. The Loire River, which drains a 117 000 km² area, with an average discharge of 850 m.s⁻¹, is highly eutrophic, with chlorophyll-a concentration exceeding 100 μg.l in summer [Meybeck et al., 1988]. In addition, the eutrophication of river waters leads to a precipitation of authigenic carbonates, which represents up to 37% of the river suspensions in summer [Meybeck et al., 1988]. Previous studies have shown that the estuary is highly heterotrophic [Relexans et al., 1988] all the riverine algal material being mineralised in the ETM, where waters are dramatically oxygen depleted [Thouvenin et al., 1994]. In addition, a large part of riverine authigenic carbonates get dissolved in the ETM [Abril et al., 2003].

[4] Sampling was carried during a 5 days cruise (24-28 September 2003, further on referred as days 1 to 5). The river discharge was low and constant (198 \pm 9 m³.s⁻¹) during the sampling period. Tidal amplitude increased from 3.8 m at day 1 to 5.8 m at days 4 and 5 (Figure 1), the latter corresponding to the spring tides. On day 1, a non-tidal river station and a freshwater tidal station were sampled by car. On days 2 to 5, the salinity gradient was sampled with a research vessel. In particular the 0.1-25 salinity range including the ETM was covered twice, once on days 2 and 3 and once on days 4 and 5. Continuous recording of salinity, temperature, oxygen and turbidity was performed

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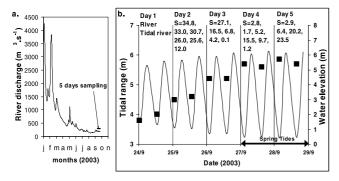


Figure 1. (a) Discharge of the Loire River before and during the field cruise. (b) Tidal amplitude (full squares) and water elevation (line) at 50 km inside the estuary (salinity 2–7) during the cruise; the salinities sampled each day are also reported.

with a YSI- 6920 probe connected to the ship seawater circuit pumping at 0.7 meter below the surface. Discrete samples were taken at ~ 0.5 m below the water surface with a niskin bottle. Contact with air was minimized during sample handling. We measured salinity and temperature with a VTW 325 probe and pH immediately after sampling with a Metrohm 713 pH-meter and a Ross combination electrode calibrated against NBS buffers (precision ±0.005 units). SPM were determined on 0.7 µm glass fibre filters. Total Alkalinity (TA) was measured by Gran electrotitration (precision $\pm 4 \mu eq.kg^{-1}$) on 0.7 μm filtrate samples and oxygen with an automated Winkler method ($\pm 2 \mu \text{mol.kg}^{-1}$). Oxygen concentrations were compared with the oxygen concentration of air-saturated water computed as in Abril et al. [2003], the saturation percentage being the ratio between the two concentrations. We calculated pCO₂ and DIC from temperature, salinity, pH and TA as described in Abril et al. [2003]. We calculated the excess DIC (EDIC in μmol.kg⁻¹), i.e., the quantity of DIC that must be released as CO2 to the atmosphere to achieve complete air-water equilibration, as the difference between the in situ DIC and the DIC computed at the atmospheric equilibrium of 370 μatm and using the in situ TA. CO₂ fluxes across the waterair interface were measured directly using a floating chamber set on a Lagrangian system (rubber boat). Accumulation of CO₂ in the chamber was measured on triplicates during 5 minutes with a LICOR CO₂ analyser as in Frankignoulle et al. [1998]. Salinity was measured at the beginning and end of each flux measurement and fluxes were referred to the average value. Flux data did not always correspond to simultaneous pCO₂ measurements from the research vessel at the same salinity.

3. Results and Discussion

3.1. Heterotrophy and CO₂ Evasion in the Loire Estuary

[5] Continuous turbidity recording on the ship water circuit (not shown) allowed a precise definition of the location of the ETM between salinities 0.1 and 20. However, it could not be used to quantify the total amount of suspended sediment in the water column, not even in the surface waters because of extreme spatial heterogeneity of SPM distribution in subsurface waters. In addition, because

of this heterogeneity, there was no evident correspondence between SPM on discrete samples and the turbidity record. By contrast, the oxygen record was in fair agreement with Winkler titrations on discrete samples. SPM in niskin bottles were low in the river water (28 mg.l⁻¹) and seawater (3 mg.l⁻¹) and highly variable between 100 mg.l⁻¹ and 3 g.l⁻¹ in the ETM.

[6] The spatial distribution of DIC parameters along the salinity gradient confirms the high degree of heterotrophy of turbid estuaries [Frankignoulle et al., 1998; Abril et al., 2003]. Oxygen, DIC, EDIC, and pCO₂ distributions (Figure 2) reflect the high heterotrophy of the estuarine zone, especially the ETM, as well as the abrupt switch from autotrophy to heterotrophy at the river - ETM transition (between the tidal river and salinity 1). River waters were significantly oversaturated in oxygen (291 μmol.kg⁻¹, that is 117% sat at 18.9°C) showing net autotrophy, although pCO₂ was higher (850 µatm) than atmospheric, presumably because of soil and/or groundwater inputs. Seawater was close to equilibrium with the atmosphere in oxygen (229 μ mol.kg⁻¹, that is 97% sat at 17.1°C and salinity 34.8) and oversaturated in CO₂ (570 µatm). In between, estuarine surface waters were drastically oxygen depleted (average \pm SD: 43 \pm 27% sat) and CO₂ oversaturated

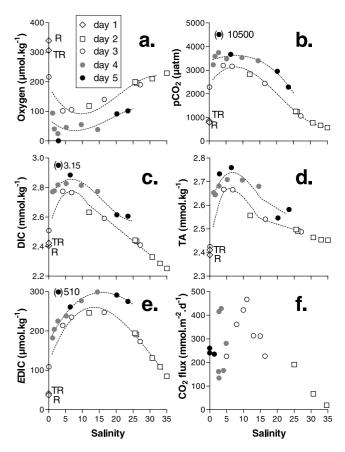


Figure 2. Distribution versus salinity of (a) Oxygen $(\mu mol.kg^{-1})$; (b) pCO₂ (μatm) ; (c) DIC $(mmol.kg^{-1})$; (d) TA $(mmol.kg^{-1})$; (e) EDIC $(\mu mol.kg^{-1})$; and (f) CO₂ flux to the atmosphere $(mmol.m^{-2}.d^{-1})$. Data were grouped $(days\ 2-3$ and $days\ 4-5)$ and simple polynomial and linear segments were fitted for calculation purpose. "R" is the non tidal river station and "TR" is the tidal river station.

Table 1. Average (\pm Standard Deviation) Changes in Concentration (in μ mol.kg⁻¹) Over the 0.1–25 Salinity Range Between Days 2–3 and Days 4–5 and Corresponding Rate Per Surface Unit (mmol.m⁻².d⁻¹)

	Change in Concentration, μ mol.kg ⁻¹	Rate Per Surface Unit, mmol.m ⁻² .d ⁻¹
Oxygen	-65 ± 12	-327 ± 62
DIC	$+106 \pm 17$	$+530 \pm 85$
EDIC	$+43 \pm 12$	$+217 \pm 62$
TA	$+80 \pm 14$	$+400 \pm 72$

(pCO₂ = 2960 \pm 2060). Anoxia and a pCO₂ maximum of 10500 μ atm (pH = 7.10) were detected on day 5 and salinity 2.9 (Figure 2b). This net heterotrophy was accompanied by large CO₂ fluxes to the atmosphere all along the estuary (280 \pm 100 mmol.m⁻².d⁻¹; Figure 2f). In parallel, TA showed a net positive non-conservative distribution, probably due in majority to carbonate dissolution in the ETM [*Abril et al.*, 2003].

3.2. Origin of the DIC Release

[7] The most striking new feature obtained during this cruise was the rapid change in surface water concentrations in the 0.1-25 salinity range with increasing tidal amplitude (Figure 2). Oxygen decreased, whereas DIC and associated parameters increased. In Figure 2, two groups of data with significantly different values could be distinguished: days 2-3 (tidal amplitude = 4.7 ± 0.5 m) and days 4-5 (tidal amplitude = 5.7 ± 0.1 m). Rates of DIC, EDIC and TA releases and oxygen depletions at spring tide can be simply calculated by considering the average changes in concentrations in 2 days over the 0.1-25 salinity range (Table 1). Probably because of the sampling depth (0.7 m), there was no observable increase in turbidity on the ship circuit from day 2 to day 5, the largest variability occurring at the tidal timescale. At an anchor station in the Loire ETM, Thouvenin et al. [1994] reported changes in SPM concentrations from less than 500 mg.1⁻¹ at neap tides to 5-8 g.l⁻¹ at spring tide for a September period. Nevertheless, several facts converge to the idea that the DIC increase and the associated oxygen decrease in surface waters between days 2-3 and days 4-5 were due in majority to fluid mud resuspension. The relationship between hypoxia and resuspension at the neap-spring time scale has been demonstrated in several turbid estuaries including the Loire [Parker et al., 1994; Thouvenin et al., 1994; Uncles et al., 1998]. The DIC released by resuspension can be produced in the water column just after resuspension and/or it can result from the simple mixing of DIC-rich pore waters from fluid mud. In the Loire in summer, the ETM represents approximately 50% of the inner estuarine surface. At neap tides, 90% of the particulate matter is settled as fluid mud with a SPM concentration of 100 g.l⁻¹ [Maurice, 1994]. The fluid mud reaches 2 meters in height with a porewater content of 90%. Maurice [1994] has shown that the anoxic fluid mud in the Loire estuary was enriched by 800 µmol.1⁻¹ in dissolved organic carbon (DOC), by 70 μ mol.1⁻¹ in dissolved organic nitrogen and by 25 μmol.1⁻¹ in ammonium (NH₄) relative to the above water column. No DIC measurements in the fluid mud are available but assuming the same C/N ratio for DIC/NH₄ as for DOC/DON (11.5) gives a DIC enrichment of 280 µmol.1⁻¹. When considering all the DOC accumulated in the anoxic fluid mud is rapidly respired in oxic conditions after resuspension and a 2m/9m dilution ratio of the fluid mud porewater in the water column gives a total potential DIC increase of 240 μmol.kg⁻¹ i.e., 2.4 times higher than the one observed during our cruise. (Table 1). On the one hand this estimates does not take into account carbonate dissolution [Abril et al., 2003] and the enhancement of respiration due to the input of attached bacteria and particulate organic matter [Uncles et al., 1998]. On the other hand it is an overestimate since fluid mud does not occupy all the ETM and the ETM itself occupies only 50% of the estuary area. Anyhow this first order estimate demonstrates the potential for fluid mud resuspension to account for most of the DIC release at spring tide. An alternative processes also linked to the tidal amplitude must however be evoked: enhanced outwelling from tidal marshes. In the marsh dominated Satilla River estuary, Cai et al. [1999] have shown that advection of DIC from marshes with tidal flushing was the major contributor to the CO₂ emissions in the main channel. The marsh/estuary area ratio in the Loire estuary is only 0.2, compared to 3.9 in the Satilla. Applying this ratio and the same marsh respiration rate as Cai et al. [1999] (55 and 40 mmol.m $^{-2}$.d $^{-1}$ for sediment and water respectively) leads to a DIC increase rate in the estuarine water of 20 mmol.m⁻².d⁻¹ i.e., 27 times lower than the one in Table 1. Owing to the fact that only a fraction of the marsh area is additionally flooded at spring tide compared to mean tide, the potential for advection from tidal marshes to raise the DIC at spring tide appears very minor in the Loire estuary.

3.3. Impact on the Carbon Budget of the Loire Estuary

[8] Before starting fluxes calculations at the whole estuarine scale, it is necessary to carefully examine the timescales of each process. Using high frequency turbidity profiles at an anchor station in the Gironde estuary, Abril et al. [1999] showed that the almost complete resuspension of a fluid mud pool may occur during a single tidal cycle. It thus appears reasonable to assume that 2 days are necessary in order to first resuspend all the different fluid mud pool settled in the Loire estuary and second homogenize the water column and affect the surface waters. Consequently, the rates of DIC release calculated in Table 1 occur approximately during 15% of the entire neap-spring period (14 days). In addition, it can be seen in Figure 2 that DIC parameters also increased in the 20-25 salinity range, immediately downstream the ETM, suggesting rapid advection of the released DIC. Indeed, the average residence time of waters in the Loire estuary at low river discharge is about 10 days, meaning that approximately 1.5 days are needed for a water mass to change from salinity 20 to 25 by dilution with seawater. In addition, the salinity at the river mouth was 25 at low tide during our cruise, meaning that rates calculated in Table 1 can reasonably be integrated over the whole surface of the Loire inner estuary and compared to the CO₂ atmospheric emissions calculated the same way. Because residence time of water in the estuary is shorter than the neap-spring period, the water masses sampled on

Table 2. Major Lateral and Vertical Transfers of DIC, EDIC, and TA in the Loire Estuary in September 2003

	DIC, $tC.d^{-1}$	E DIC, tC.d $^{-1}$	TA, tC.d ⁻¹
	Lateral Transfers		
River input ^a	495	10	490
Output to ocean before resuspension ^b	615	90	540
Difference output-input before resuspension	120	80	50
	Vertical Transfers		
Resuspension input at spring tide ^c	635	260	480
Resuspension input averaged over neap-spring	90	35	70
Atmospheric output ^d	320	320	0

^aRiver discharge (198 m 3 .s $^{-1}$) multiplied by the river concentrations (DIC = 2.407; EDIC = 0.041; and TA = 2.389 mmol.kg $^{-1}$).

^bRiver discharge multiplied by the apparent zero end_member concentrations corresponding to the intercepts at zero salinity of the line tangent to the curve at salinities >25 for day 2 (in mmol.kg⁻¹: DIC = 2.983, $R^2 = 0.99$; EDIC = 0.474, $R^2 = 0.99$; TA = 2.625, $R^2 = 0.96$).

^cEstuarine surface (102 km²) multiplied by the average changes in concentration between days 2-3 and days 4-5 from Table 1.

^dEstuarine surface multiplied by the average CO₂ fluxes measured during the ruise in the inner estuary (salinity 0.1-25).

day 2 in the estuarine plume at salinities 25–35 (Figure 2) have passed through the ETM without experiencing any spring tide. The linear distribution of DIC parameters versus salinity in this 25–35 salinity range (Figure 2), together with the constant river discharge before and during the cruise (Figure 1) allow an estimation of the outputs to the ocean before the resuspension event, using the "apparent zero end-member" technique: the 25–35 salinity segment is extrapolated to salinity zero and the obtained apparent concentration is multiplied by the river discharge. Finally, river inputs to the Loire estuary were constant before and during the cruise. Table 2 synthesizes all these budget calculations.

[9] At spring tide, inputs due to resuspension were temporary similar to the river input for TA and $\sim 30\%$ higher for DIC (Table 2). The fraction of DIC released in the form of EDIC will, by definition, further reach the atmosphere, either in the estuary itself or in the adjacent coastal zone, whereas the remaining part, as well as TA will be transferred to the coastal ocean. DIC was released at 40% in the form of EDIC at a rate of 217 \pm 62 mmol.m⁻².d⁻¹ (Table 1). In the 0.1-25 salinity range, CO₂ fluxes were highly variable with no significant change from days $2-3 (315 \pm 98 \text{ mmol.m}^{-2}.\text{d}^{-1})$ to days $4-5 (260 \pm$ 105 mmol.m⁻².d⁻¹). Gas exchange rates calculated for individual fluxes using pCO2 values interpolated at the corresponding salinity slightly decreased from 14.1 ± 6.1 cm.h^{-1} on day 2-3 to $10.3 \pm 4.1 \text{ cm.h}^{-1}$ on day 4-5and showed little correlation with the wind speed recorded from the ship (not shown). Because gas exchange rate is the limiting factor for CO₂ emission, resuspension resulted in an increase in pCO2 and EDIC rather than in an immediate raise in the CO₂ flux. However, when integrated over the entire neap-spring cycle, resuspension of EDIC contributed to only $\sim 10\%$ of the CO₂ atmospheric flux from the inner estuary. Concerning TA, the input due to resuspension was higher than the TA generation in the estuary (difference output-input) before spring tide (Table 2). A major fraction $(\sim 60\%)$ of the TA production in the estuary can therefore be attributed to fluid mud resuspension. Although our observations were restricted to a summer period, resuspension probably plays a significant role on the carbon budget of the estuary also on an annual basis: sedimentation and resuspension cycles are most intense in summer when the ETM

is most concentrated, but also when heterotrophy, CO₂ emission and TA production are highest.

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