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 µatm) and high CO2 fluxes (280 ± 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 ± 17 µmol.kg−1 for DIC, by 80 ± 14 µeq.kg−1 for Total Alkalinity (TA) and by 684 ± 142 µatm for pCO2. In parallel, oxygen decreased by 65 ± 12 µmol.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.

1. 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 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 (neap-spring) 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.

2. 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−1 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 out 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 ± 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.
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 ±4 μeq.kg⁻¹) on 0.7 mm filtrate samples and oxygen with an automated Winkler method (±2 μmol.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 water-air 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

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.

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 μmol.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 ± SD: 43 ± 27% sat) and CO₂ oversaturated.
(pCO2 = 2960 ± 2060). Anoxia and a pCO2 maximum of 10500 µatm (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 ± 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].

Table 1. Average (±Standard Deviation) Changes in Concentration (in µmol.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)

<table>
<thead>
<tr>
<th></th>
<th>Change in Concentration, µmol.kg−1</th>
<th>Rate Per Surface Unit, mmol.m−2.d−1</th>
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</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>−65 ± 12</td>
<td>−327 ± 62</td>
</tr>
<tr>
<td>DIC</td>
<td>+106 ± 17</td>
<td>+530 ± 85</td>
</tr>
<tr>
<td>EDIC</td>
<td>+43 ± 12</td>
<td>+217 ± 62</td>
</tr>
<tr>
<td>TA</td>
<td>+80 ± 14</td>
<td>+400 ± 72</td>
</tr>
</tbody>
</table>

3.2. Origin of the DIC Release

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.l−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.l−1 in dissolved organic carbon (DOC), by 70 µmol.l−1 in dissolved organic nitrogen and by 25 µmol.l−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.l−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

Before starting fluxes calculations at the whole estuarine scale, it is necessary to carefully examine the time-scales 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...
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 ~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 sphere, either in the estuary itself or in the adjacent coastal.

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

<table>
<thead>
<tr>
<th></th>
<th>Lateral Transfers</th>
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<tbody>
<tr>
<td></td>
<td>DIC, tC.d⁻¹</td>
<td>EDIC, tC.d⁻¹</td>
<td>TA, tC.d⁻¹</td>
</tr>
<tr>
<td>River input</td>
<td>495</td>
<td>615</td>
<td>120</td>
</tr>
<tr>
<td>Output to ocean before resuspension</td>
<td>10</td>
<td>90</td>
<td>80</td>
</tr>
<tr>
<td>Difference output-input before resuspension</td>
<td>490</td>
<td>540</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vertical Transfers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resuspension input at spring tide</td>
<td>635</td>
<td>260</td>
<td>480</td>
</tr>
<tr>
<td>Resuspension input averaged over neap-spring</td>
<td>90</td>
<td>35</td>
<td>70</td>
</tr>
<tr>
<td>Atmospheric input</td>
<td>320</td>
<td>320</td>
<td>0</td>
</tr>
</tbody>
</table>

* River discharge (198 m³.s⁻¹) multiplied by the river concentrations (DIC = 2.407; EDIC = 0.041; and TA = 2.389 mmol.kg⁻¹).
* River 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, R² = 0.99; EDIC = 0.474, R² = 0.99; TA = 2.625, R² = 0.96.

* Estuarine surface (102 km²) multiplied by the average changes in concentration between days 2–3 and days 4–5 from Table 1.
* Estuarine surface multiplied by the average CO₂ fluxes measured during the ruise in the inner estuary (salinity 0.1–25).

References


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