1 Title: Surface fCO₂ variability in the Loire plume and adjacent shelf waters: high
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3 2 spatiotemporal resolution study using ships of opportunity.
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Abstract:

To investigate the seasonal and spatial variability of the CO₂ uptake across the Loire estuary plume and the adjacent continental shelf, a two-year (November 2002 to December 2004) high-frequency time series of the surface CO₂ fugacity (fCO₂^{sw}) and the air-water CO₂ exchange is reported and discussed. Continuous measurements of salinity, temperature, fCO₂^{sw}, dissolved oxygen (O₂) and Chl *a* were performed, on a commercial route between Vigo (Spain) and St. Nazaire (France).

A significant biogeochemical gradient is observed along this hydro-geographical continuum, in both space and time. The biogeochemical response to these inputs in the inner shelf is suggested to be closely related to the river discharge enriched in CO₂ and the spreading of the plume. This region is oversaturated for most of the year, excepting when favourable conditions for phytoplankton blooms are created by the availability of light, the inputs of riverine nutrients and the haline stratification of the water column. On a yearly scale, the non-thermodynamic processes (biological, riverine inputs, etc) exert more control than the thermodynamic (changes in temperature and salinity) over the pattern of CO₂ flux in the inner shelf. The biogeochemical imprint of the Loire River is noticeable in the mid-shelf during high river flow events and favourable winds, but almost negligible in the outer shelf, where temperature is the main mechanism controlling the seasonal variability of the fCO₂^{sw}. During the two-year study period, the estimated air-water CO₂ flux is -5.2 mmol·m⁻²·d⁻¹ and -7.5 mmol·m⁻²·d⁻¹, in the middle and outer shelf respectively.

Keywords: fCO₂, Loire plume, air-sea exchange, continental shelf, ship of opportunity, outer estuaries, seasonal variability.

1. Introduction:

Despite accounting for a relatively small surface area (7% of the global ocean surface), coastal environments constitute important pathways between land and the open ocean. These areas play a significant role in modifying the flows of matter and energy between these two systems and are characterised by high temporal and spatial heterogeneity in carbon flows; this variability is the main difficulty in establishing the carbon cycle in these zones. Unlike the ocean, where different approximations can be used because behaviour is more homogeneous, the main carbon fluxes involved in coastal zones have only been estimated very roughly using models of interaction on a global scale. At present, work is in progress to set up the largest possible database on carbon fluxes in coastal systems that should serve to validate the available (global) models, for example the SOCAT project (Surface Ocean CO₂ Atlas) what make an special effort for including the coastal ocean. The key questions still unresolved centre firstly, on the metabolic status of the coastal areas, and secondly, on their role as a sink or source of CO₂ with the atmosphere. Concerning the second question, one of the major scientific issues to be addressed by an enhanced global data-set is to reconcile opposing views on carbon cycling in the coastal ocean: namely, whether the continental shelf or distal ocean act as sinks, and near-shore ecosystems or the proximal ocean act as sources of CO₂ to the atmosphere. Some models (Rabouille et al., 2001; Chen, 2004) state that the subdivision of the coastal ocean is necessary to account properly for the distinct differences in the observed biogeochemical processes, between proximal and distal regions. In the proximal zone, large inputs of particulate and dissolved matter are received from the rivers into a relatively small reservoir volume. In addition, there is a strong degree of coupling between respiratory and primary production processes. In the distal zone, matter inputs are received from the open ocean and the proximal coastal zone, and less importantly from the atmosphere. This zone can be divided into

two sub-reservoirs: the upper water column, where light availability is responsible for the dominant process being primary production; and the lower water column, which is dominated by mineralization and the transfer of particles to the sediment. From the results of the model proposed by Rabouille et al. (2001), it has been concluded that the proximal coastal zones are CO₂ sources (0.1 Pg C yr⁻¹), whereas the distal coastal zones act as CO₂ sinks (0.34 Pg C yr⁻¹). Consequently, the continental margins are considered to be a net sink of 0.24 Pg C yr⁻¹ in the pre-anthropogenic state, and that adjustments for present day conditions lead to the continental margins acting as a net sink of the order of 0.34 Pg C yr⁻¹, for the year 2000 (Chen and Borges, *in press*). In addition to the modelling approaches for assessing the role of the continental margin as sink or source of atmospheric CO₂, recent efforts have been based on the worldwide measurement of the pCO₂ in diverse coastal systems, taking into account their geographical and ecological diversity (Borges et al., 2005; Cai et al, 2006). The results of these exercises indicate that most open continental shelves in temperate and high latitude regions are CO₂ sinks, whereas low latitude shelves seem to be CO₂ sources. One of the most recent scaling of air-sea CO₂ fluxes based on pCO₂ measurements and carbon mass balance calculations, indicates that the continental shelves absorb between 0.33 and 0.36 Pg C yr⁻¹, and that they account for an additional sink of 27 to 30 % of the CO₂ uptake by the open ocean (Chen and Borges, *in press*); these values match the 0.34 Pg C yr⁻¹ estimated with previous models by Rabouille et al. (2001). Nevertheless, there remains a high degree of uncertainty associated with some of these near-shore systems, such as inner and outer estuaries and river-dominated margins, especially given the scarcity of studies with a proper seasonal and spatial coverage (Borges, 2005). Outer estuaries are characterised by less intense carbon and nutrient cycling and air-water CO₂ aerial fluxes than inner estuaries (Brasse et al., 2002; Borges and Frankignoulle, 2002); they show considerable spatial and seasonal variability, and in

some cases shift between over-saturation and under-saturation of CO₂ (Frankignoulle and Borges, 2002; Brasse et al., 2002). Nevertheless, air-water CO₂ fluxes in outer estuaries have been satisfactorily integrated at an annual scale only for a few rivers such as for the Amazon (Koertzing et al., 2003) and the Scheldt (Schiettecatte et al., 2006). In inner and outer estuaries and adjacent continental shelves, the presence or absence of seasonal or permanent stratification seems to be a critical factor controlling air-water CO₂ fluxes. In stratified systems the organic matter produced by primary production can escape from the surface layer down through the pycnocline, and the CO₂ produced by degradation processes in the lower layers is not available for exchange with the atmosphere. Permanently well-mixed systems behave differently: the decoupling between production and degradation of organic matter can occur in time but does not occur throughout the water column; this usually causes such systems to be neutral, or else to act as sources of CO₂ to the atmosphere (Borges, 2005).

The main objective of the present paper is to investigate the surface fCO₂ dynamics in the plume of the Loire River and adjacent continental shelf, from recent data sets obtained using ships of opportunity. Underway measurements were performed along 150 tracks from November 2002 to December 2004. The seasonal variability, the across-shelf gradient of surface fCO₂, the air-water CO₂ fluxes and their underlying controlling mechanisms have been assessed based on the river discharge, and the role of temperature and biological activity. Ships of opportunity provide a valuable platform for studying these highly variable systems both in space and on shorter time-scales. Furthermore, an additional contribution of this study is the reporting of information on the carbonate system and air-water CO₂ exchange in this oceanic region, which has not previously been available.

2. Material and Methods:

2.1. Study area:

The river Loire is the longest river in France; it flows for more than 1000 km, collects water from catchment areas equal to 1/5 of the total surface of France (118,000 km²), and 5 million inhabitants live along its banks (Staebler, 2006). The average annual fluvial flow volume is 850 m³ s⁻¹, for the last century. An historic high of 6400 m³ s⁻¹ was attained during the floods of 1910, and the lowest water volume on record (50 m³ s⁻¹) occurred in August 1949 (Dauvin, 2008). At St. Nazaire, located at the mouth of the estuary, the proportion of seawater at low tide at Saint Nazaire ranges between 10 and 40% and the maximum tidal amplitude is 6 m (Meybeck et al, 1988). In the inner estuary, fluid mud only forms during neap tides, when the weak current and increasingly long slack tides encourage the sediment in the maximum turbidity to settle. The Loire is one of Europe's most turbid rivers, with turbidity values ranging from 100 to 150 g L⁻¹. Furthermore, the Loire River estuary is highly eutrophic, with chlorophyll (Chl a) concentrations exceeding 100 µg L⁻¹ in summer (Meybeck et al., 1988). The eutrophication of the river waters leads to a precipitation of authigenic carbonates, which account for up to 37% of material in suspension in summer (Meybeck et al., 1988). Previous studies have shown that the estuary is highly heterotrophic (Rellexans et al., 1988) and all the riverine material is mineralised in the estuarine turbidity maximum (ETM), where waters are dramatically oxygen-depleted. Rellexans et al. (1988) studied the algal and microbial processes. They describe two typical contrasting situations: (i) during winter and early spring, when discharge increases beyond 1000 m s⁻¹, heterotrophic activity inside the estuary always dominates over primary production but remains moderate because of low temperature and the non-biodegradable nature of organic carbon; (ii) during low discharge periods, phytoplankton production in the river increases the O₂, but the accumulation of phytoplanktonic material in the highly turbid estuary results in highly heterotrophic activities. The intense bacterial activity in the zone of maximum turbidity results in the regeneration of large quantities of nutrients (nitrates, phosphates and silicates) that are

1 163 subsequently exported to the sea. As a result of the relatively long residence time of
2
3 164 freshwater within the Loire estuary (ranging from 3 days in floods to 30 days in times of
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5 165 low river flow, Gallene, 1974) conservative behaviour is observed for most of the river's
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7 166 nutrients that enter the estuary and that eventually reach the coastal zone (Guillaud et
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9 167 al., 2008).

11 168 The hydrodynamic settings of the Loire River plume were modelled by Lazure and
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13 169 Jegou, (1998), who developed a 3D model of the Atlantic shelf that combined the
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15 170 effects of the wind, river discharges and surface heat fluxes. This model shows that the
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17 171 plume evolution depends on the high variability of river runoff and winds, and highlights
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19 172 several features of the plume: 1) in early winter and periods of high river runoff, the
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21 173 plume usually spreads northward and along the shore; 2) during winter, vertical
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23 174 stratification is weak on the shelf; 4) When river discharges are reduced and prevailing
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25 175 winds are from the north-west, the northward spread of the plume may be stopped. In
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27 176 that case, the plume may be driven offshore or southwards. This change of path
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29 177 usually occurs in spring. Late March and April clearly marks the change between winter
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31 178 conditions (freshwater extending northwards of the inner shelf) and summer conditions
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33 179 (freshwater spreading offshore and mixing with seawater). Seasonal and inter-annual
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35 180 fluctuations of the freshwater supply and wind stress lead to high variability of the low
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37 181 salinity expanse over the shelf.

41 182 The outflow of continental waters from the Loire river also modifies the hydrographic
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43 183 pattern in the northern Bay of Biscay. From January to June, the haline stratification is
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45 184 strong on a large part of the shelf, in response to high Loire river runoff. Between May
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47 185 and September, thermal stratification occurs in a layer that can reach 50 m in thickness
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49 186 (Puillat et al., 2004). These driving physical variables, associated with inputs of riverine
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51 187 nutrients and meteorological conditions, can influence the seasonal behaviour of
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53 188 phytoplankton in the northern part of Biscay.

2.2. Sampling and methods:

The data set presented in this paper was collected on board of ships of opportunity operated by the company Flota Suardiaz (the RO-RO ferries “L’Audace” and “Surprise”) between November 2002 and December 2004, in the framework of the Spanish founding ECO project. This regular shipping route links Vigo (Spain) and St. Nazaire (France). The focus of this paper is on the measurements made between the port of St Nazaire and the outer shelf, covering a distance of 250 km seaward (Figure 1).

Seawater was continuously pumped from 3 m below waterline at a high flow rate, although only a reduced flow was conducted to the analytical system in order to minimize warming on the way. This supply of uncontaminated seawater was bifurcated to pass through an analytical system consisting of a thermosalinometer (SBE-45-MicroTSG), oxymeter (SBE-43) and fluorometer (WETLabs) and a home-made $f\text{CO}_2$ analyser. The underway measurements of sea-surface salinity (SSS), sea surface temperature (SST), oxygen (O_2) and chlorophyll *a* (Chl *a*) concentration were recorded, together with the CO_2 fugacity in seawater ($f\text{CO}_2^{\text{sw}}$).

The measurements of CO_2 mole fraction ($x\text{CO}_2$) were performed with a non-dispersive infrared gas analyzer (Li-6262, LI-COR). This analyzer was calibrated at the beginning and at the end of each transit using two gases: one of CO_2 -free air and one of high CO_2 standard gases with a certified concentration of 375 ppm (Instituto Meteorológico Nacional, Canary Islands, Spain). The drift was calculated by means of a linear interpolation between the zero and span standards between the two calibrations. The CO_2 values measured at the riverine end of the Loira plume occasionally reach 1500 ppm whereas the CO_2 system is calibrated up to 375 uatm ppm. A test was carried out to check the validity of the measurements. The test consisted of calibrating the LiCOR-6262 using a CO_2 -free standard (zero) and a second one of 400 ppm (span). Then, two certified standards out of the calibrated range, one of 600 ppm and other of 800 ppm, were

measured as shown, and then the differences between expected (certified) values and measured concentrations were compared. The results obtained show that, if the zero and span values are adjusted on a daily basis, the average standard error is 0.8 % and the maximum error that has been calculated is 1.6% for the concentrations beyond the calibration range. These errors may be acceptable for the data-base available in the Loire plume and French shelf obtained in this study, because the error only represents 0.5 % of the measured values.

$x\text{CO}_2$ was converted into $f\text{CO}_2$ in saturated water vapour pressure using the atmospheric pressure as described in the DOE Handbook (1994). Subsequently $f\text{CO}_2$ values were corrected for the temperature shift using an empirical equation proposed by Takahashi et al. (1993). The temperature difference between the seawater inlet and the equilibrator system was typically less than 1 °C. During the ECO voyages, atmospheric $x\text{CO}_2$ ($x\text{CO}_2^{\text{atm}}$) was measured every hour, recording 20 observations within 5 min. Subsequently, a selection criterion was applied to eliminate spurious values to identify representative data for $x\text{CO}_2^{\text{atm}}$. These data were fitted to a seasonal curve, consisting of two harmonics of an annual trend plus a seasonal cycle (Padin et al., 2007). In this study, $x\text{CO}_2^{\text{atm}}$ values have been calculated using the sinusoidal expression proposed by Padin et al. (2007) for the French offshore.

Discrete samples were collected at four locations along the commercial track to calibrate the different sensors (Fig. 1). The calibration frequency changed during the ECO project from three per month during 2003 to one per month during 2004.

Alkalinity (A_T) and pH measurements were taken to study the internal consistence of *in situ* $f\text{CO}_2^{\text{sw}}$ measurements. Poisoned A_T samples, as the DOE handbook (DOE, 1994) recommends, were determined by automatic potentiometric titration with HCl at a final pH of 4.40 (Pérez and Fraga, 1987, Mintrop et al., 2000). The electrodes were standardised using a buffer of pH 4.42 made in CO_2 -free seawater (Pérez et al., 2002).

The method has an accuracy of $\pm 1 \mu\text{mol kg}^{-1}$, which was estimated using certified reference material (CRM). The pH samples were kept refrigerated after collection until the spectrophotometric determination, following Clayton and Byrne (1993). This method has a precision of 0.0004 (Clayton and Byrne, 1993) and accuracy of 0.002 (DeValls and Dickson, 1998). The comparison between the *in situ* and the computed fCO_2 from pH and A_T using the carbonic system constants of Lueker et al. (2000), showed a consistence error of $\pm 6 \mu\text{atm}$ ($n = 365$, $r^2 = 0.91$).

O_2 samples were stored in the dark and analysed by the Winkler method 24 h after collection. The potentiometric end-point determination of oxygen has an estimated accuracy of $\pm 2 \mu\text{mol kg}^{-1}$. Oxygen saturation was calculated following the Benson and Krause equation (UNESCO, 1986). The underway fluorescence measurements, determined with a WETLabs fluorometer, were calibrated with chlorophyll extracted by 25 mm Whatman GF/F filters and analysed after 90% acetone extraction in a 10,000 R Turner fluorometer (Yentsch and Menzel, 1963). The precision was $\pm 0.05 \text{ mg m}^{-3}$.

The values of daily river flows are given by the “Banque Nationale des Données pour l'Hydrométrie et l'Hydrologie” (<http://www.hydro.eaufrance.fr/accueil.html>).

The exchange of carbon between the atmosphere and the ocean (F) was calculated with the following equation:

$$F = k S (\text{fCO}_2^{\text{sw}} - \text{fCO}_2^{\text{atm}})$$

where seawater CO_2 solubility (S , $\text{mol L}^{-1} \text{atm}^{-1}$) was calculated from Weiss (1974) and the piston velocity (k , cm h^{-1}) was computed using the expression proposed by Wanninkhof et al. (1992) for short-term winds. The wind speed used in our computations was provided by the NCEP/NCAR re-analysis project (Kalnay et al., 1996) from the web site of the NOAA-CIRES Climate Diagnostics Center, Boulder, CO, USA (<http://www.cdc.noaa.gov/>).

3. Results and discussion

3.1. Surface water biogeochemical distribution and its seasonal variability

The Loire river discharge has a wide range of seasonal variability, the maximum values of $4430 \text{ m}^3 \text{ s}^{-1}$ and $4710 \text{ m}^3 \text{ s}^{-1}$ being recorded in January 2003 and 2004 respectively, and the minimum values of 140 and $148 \text{ m}^3 \text{ s}^{-1}$ being recorded in August 2003 and 2004 respectively. Figure 2 shows how the seasonal pattern and values for the river discharge were fairly reproducible from 2003 to 2004. In general, salinity traces the presence of the plume and the percentage of riverine influence over the studied track, then, if the outer limit of the plume is defined at SSS 34 (a SSS value of 1 less than the adjacent oceanic basin has been used arbitrarily as the offshore boundary, in Abril and Borges, 2004) the resulting hypothetical line can be used as an approximation to the extent of the plume over the studied track (Figure 2). The extent of the plume closely follow the river discharge most time of the year, excepting from May to July, when a maximum extent of the plume is detected despite of the decrease in the river discharge. This late-spring maximum not related to river discharge can be explained as being due to the seasonal variability of the wind pattern. This wind-plume interaction is in agreement with previous studies in the area (Lazure et al., 1998; Puillat et al., 2004) which describe that during the winter, the north-eastward winds are intense and dominant causing the northward propagation of the Loire plume, whereas under low river discharge periods coinciding with prevailing southward winds, the plume may be driven offshore or southward, and thus the low salinity stripe could be detected in our studied track.

FIGURE 2

The spatial-temporal variability of the sea surface chemistry properties in the plume of the Loire and offshore waters from November 2002 to December 2004 shows a marked seasonality. The figure 3 show the complete database obtained in this study (Figure 3). Minimum salinity at Saint Nazaire is observed during January and February (around 2) and maximum salinity values are recorded in September (around 30), corresponding to maximum and minimum river discharge periods respectively.

FIGURE 3

For the purpose of a clearer discussion, the track studied has been operatively divided in three parts characterised by different hydrodynamic regimens and riverine inputs, which account for the maximum biogeochemical gradient across the continental shelf: the inner shelf, from river mouth to the 10 m isobath (i.e. to a distance of 25 km from the river mouth), the middle shelf, between the 10 m and 100 m isobaths (between 25 km and 100 km from the river mouth), and finally the outer shelf, from the 100 m isobath to the continental slope (between 100 km and 250 km distance from the coastline). Each of these regions will exhibit different seasonal features and controlling mechanisms that will be analysed separately here. Maximum and minimum track-averaged values for the variables measured are shown in Table 1.

TABLE 1

3.1.1. Variability in the inner shelf

The $f\text{CO}_2^{\text{sw}}$ for all seasons exhibited a large cross-shelf gradient, especially in the inner shelf, where the direct freshwater influx is a determining factor of the biogeochemical variability, and the river plume covers the entire inner shelf all year long, except during

October (figures 2 and 3). The seasonal amplitude for the track-averaged $f\text{CO}_2^{\text{sw}}$ is ~ 700 μatm , with maximum $f\text{CO}_2^{\text{sw}}$ values observed from late-summer to late-winter; the upper $f\text{CO}_2^{\text{sw}}$ limit value is ~ 940 μatm and then, during the spring and early summer, the $f\text{CO}_2^{\text{sw}}$ decreases the lower limit being ~240 μatm . The track-averaged salinity also oscillates in a wide range from 11.1 to 34.6. In turn, $f\text{CO}_2^{\text{sw}}$ values at the surroundings of the river mouth tend to be higher and decrease toward the shelf; and for most of the time, this region shows an inverse correlation between $f\text{CO}_2^{\text{sw}}$ and SSS ($r^2 = 0.4$), typical for estuarine environments (figure 4a). This dependence of $f\text{CO}_2^{\text{sw}}$ on salinity suggests that the biogeochemical signal generated in the plume, and hence in the inner shelf, is highly affected by riverine and inner estuarine inputs. This fact is in agreement with previous studies in the Loire inner estuary, where waters are characterised by higher nutrients, $f\text{CO}_2^{\text{sw}}$ and oxygen deficit values than the surface waters of the shelf (Rellexans et al., 1988; Abril et al., 2000, 2003, Loyer et al., 2006). Exceptionally, $f\text{CO}_2^{\text{sw}}$ values equal to ~1590 and ~1455 μatm have been recorded at the mouth of the river in July and November 2003 respectively. The high dependency of these high $f\text{CO}_2^{\text{sw}}$ values with salinity and with very low O_2 saturation (see figure 4) suggests they are linked to intense respiratory processes and that the high organic matter remineralization event was produced in the inner estuary instead of in the plume. These high $f\text{CO}_2^{\text{sw}}$ concentrations may be associated with a phenomenon previously described by Abril et al (2003; 2004), related to episodes of resuspension of anoxic fluid-mud in the inner estuary of the Loire during low river discharge periods, which cause oxygen depletion and $f\text{CO}_2^{\text{sw}}$ values up to a maximum of 10500 μatm in the ETM. These previous studies also support the high seasonal variability of C_T observed in this study at the river mouth; which concentration varies between 1755 $\mu\text{mol kg}^{-1}$ in February 2003 and 2533 $\mu\text{mol kg}^{-1}$ measured in October 2003. This C_T variability is related to river discharge (Figure 5), with higher values during low discharge periods and lower values during high river discharges; as a result, the C_T

concentrations in the estuary and in the river mouth are usually lower than offshore during the winter, but higher during the summer. However, during periods of high river discharge, dilution with freshwater is responsible for reducing the C_T in the estuary and in river mouth. Despite the observation of some authors that C_T was highly non-conservative within the inner estuary (Abril et al., 2003), the results obtained in this study on each cruise show a nearly conservative behaviour in the plume.

FIGURE 4

FIGURE 5

River-to-shelf gradient concentrations for O_2 saturation and Chl *a* generally show higher values near the riverine endmember throughout the year. For this inner region of the shelf, the track-averaged O_2 saturation varies between 63 and 152% and Chl *a* ranges from 0.16 to 11.45 $mg\ m^{-3}$ (Table 1). In general, the minimum O_2 saturation in this region occurs during autumn and early winter (~60%), due to intense heterotrophy in the inner estuary, and maximum values are found in late spring and early summer, particularly in June 2003, when the saturation reached 166% coinciding with the development of a phytoplankton bloom (15.9 $mg\ m^{-3}$) at the river mouth; this signal extends beyond the area dominated by the plume, that during this period of the year spread up to the middle shelf. The seasonal succession of the phytoplankton blooms in the shelf nearby the Loire during June 2003 has been extensively documented from data of the VILOIR cruise using both in-situ and remote sensing measurements (Lunven et al., 2005; Guillaud et al., 2008; Gohin et al., 2005). Gohin et al. (2005) described how the horizontal and vertical distribution of in situ Chl *a* revealed the presence of two distinct maxima: first one located in the mouth of the Loire river, where the Chl *a* was homogeneously distributed in the mixed water column, and a second maximum that was measured in the middle shelf, in the stratified area. The biogeochemical consequences of these previously described blooms are apparent in

the O₂ saturation, fCO₂ and Chl *a* distribution obtained in this study. In the figure 3 and 4 it can be observed how the maximum O₂ saturation is related to very low fCO₂ values and that in turn, maximum Chl *a* concentrations are observed in a narrow salinity gradient characteristic of June; furthermore, the figure shows how it affect similarly to the inner and middle shelf.

The relationship of the Chl *a* versus salinity (figure 4c) suggests two different origins for the pigments in the inner shelf: first, the flushing of degraded old pigments from the inner estuary, which occurs mainly at high river discharge in late winter and is associated to lower salinity values; second, the production of marine phytoplankton generally observed in coastal waters in early spring and summer, this observations are in agreement with previous studies in the inner estuary (Relexans et al., 1988).

3.1.2. Variability in the middle shelf

In this river-ocean transition region of the shelf the direct inputs of continental or estuarine materials are less continuous and the biogeochemical gradient is less intense than in the inner shelf described above (Table 1, Figure 3). The presence of the plume along the studied track in the mid-shelf is highly dependent not only on the river discharge but also on the wind regime. Despite the relatively low discharge during early summer, the predominance of north-easterly winds at this time of the year favours the southwest-ward spreading of the plume (Figure 2). The plume is present in this region for about 75% of the year, but it only covers more than half of the extension for 20% of the year.

The seasonal amplitude for the track-averaged temperature and salinity is 9 °C and 7.7 respectively, which is considerably lower than in the inner shelf as a result of the reduced river water influence.

Maximum track-averaged $f\text{CO}_2^{\text{sw}}$ values are observed in early winter (431 μatm) and decrease progressively as spring approaches, due to the photosynthetic activity. Minimum values for this variable of ~ 244 μatm are observed in late spring and early summer (May-June). Minimum values recorded in June 2003 for $f\text{CO}_2^{\text{sw}}$ (166.3 μatm) coincide with maximum O_2 oversaturation (168 %) and Chl *a* (9.3 mg m^{-3}) corresponding to the summer bloom previously described and simultaneous to the one in the river mouth. Guillaud et al., (2008) observed that, over the mid-shelf, where thermal stratification starts to be established in mid-spring, pico-phytoplankton, which are better competitors during periods of low nutrients, are largely present; however, in the plume itself, growth of diatoms is favoured by the continued enrichment from nutrient inputs, and the decreasing river flow that leads to lower turbidity. The resulting biochemical imprint that extends from the river mouth to the outer shelf would be the appearance of a minimum for $f\text{CO}_2^{\text{sw}}$ values and a maximum for Chl *a* and oxygen over-saturation (figure 3); that appear earlier in the mid-shelf than in the inner shelf due to the expected higher light availability (Guillaud et al., 2008).

3.1.3. Variability in the outer shelf

This coastal region is characterised by the almost complete absence of the Loire plume, except for occasional instances occurring during February 2003, due to a peak in river discharge, and in June 2004, due to the north-easterly winds that cause the plume spreading toward the southwest (Figure 2). Track-averaged salinity in the outer shelf stays between 34.7 and 35.5, indicating that influence of the water discharge of the Loire river in this area is not significant; consequently oceanic rather than coastal processes are responsible for the biogeochemical features in this region. In the outer shelf, $f\text{CO}_2^{\text{sw}}$ shows much less variability, both spatially and temporally: the seasonal

amplitude for $f\text{CO}_2^{\text{sw}}$ is ten times lower than in the inner shelf. The winter season is characterised by slightly undersaturated $f\text{CO}_2^{\text{sw}}$ (370 μatm) values due to winter cooling; there is a progressive decrease during spring, when minimum $f\text{CO}_2^{\text{sw}}$ values (~292 μatm) are reached coinciding with maximum Chl *a* and O_2 oversaturation (at ~2.7 mg m^{-3} and ~130 % respectively). These biogeochemical signals are the response to the start of thermal stratification in the region, from May to September, as described by Puillat et al. (2004). During the summer, maximum $f\text{CO}_2^{\text{sw}}$ values (~380 μatm) are observed due to the thermodynamic increase caused by the higher SST and also coinciding with the lower Chl *a* concentrations, then suggesting the decrease in the photosynthetic activity possibly caused by the nutrient depletion. In autumn, a decrease in $f\text{CO}_2^{\text{sw}}$ values is observed, linked to an increase in Chl *a*, probably related to the breakdown of the summer stratification (Puillat et al., 2004). This breakdown provokes the upward inputs of nutrients to the sea surface reactivating phytoplankton activity.

The biogeochemical pattern found in the outer shelf is similar to that observed by Padin et al. (2008), who studied the $f\text{CO}_2^{\text{sw}}$ variability in the adjacent waters of the Bay of Biscay following a similar sampling strategy. These authors recorded minimum $f\text{CO}_2^{\text{sw}}$ values in spring and maximum in summer, with a range of 72 μatm for the two seasonal cycles.

3.2. Evaluation of temperature, water masses mixing and biology in the $f\text{CO}_2$ variations

In order to evaluate the relative importance of temperature compared to other effects on the $f\text{CO}_2^{\text{sw}}$ dynamics over an annual cycle, an approach to the method proposed by Takahashi et al. (2002) has been applied. Similarly to Takahashi et al (2002) and in

order to remove the temperature effect from the observed fCO_2 (represented by $fCO_2@T_{mean}$), the observed fCO_2 values are normalised to a constant temperature, this is the mean annual temperature. The effect of temperature changes on fCO_2 has been computed by perturbing the mean annual fCO_2 for each region with the difference between the mean and observed temperature (represented by $fCO_2_{mean}@T_{obs}$); the values obtained for $fCO_2_{mean}@T_{obs}$ indicate the fCO_2 values that would be expected only from temperature changes, if a parcel of water having a fCO_2 value equal to the its annual average is subjected to seasonal temperature changes under isochemical conditions.

Temperature ($fCO_2_{mean}@T_{obs}$) and non-temperature ($fCO_2@T_{mean}$) effects respectively were calculated applying the following equations:

$$fCO_2_{mean}@T_{obs} = fCO_2(T_{obs}) = \text{mean annual } fCO_2 \cdot \exp [0.0423 \cdot (T_{obs} - T_{mean})] \text{ (I)}$$

$$fCO_2@T_{mean} = fCO_2(T_{mean}) = fCO_2(obs) \cdot \exp [0.0423 \cdot (T_{mean} - T_{obs})] \text{ (II)}$$

where T is the SST and the subscripts “mean” and “obs” indicate the annual average and the observed values, respectively. It has been used an annual average of 15 °C for SST in the inner, middle and outer shelves.

Contrary to oceanic regions, where the non-temperature effect can be attribute almost entirely to the “net biology effect”, the non-temperature term for coastal waters contains all the biochemical processes acting on the net CO_2 utilization (primary production and respiration), including other processes also governing the CO_2 such as riverine input, changes in C_T by advection or air-sea CO_2 fluxes, which can be significantly important in the coastal ocean and that in the original method of Takahashi et al. (2002) would be inherently attributed to the biological signal.

The seasonal evolution of $f\text{CO}_2^{\text{obs}}$ and the monthly increase/decrease of $f\text{CO}_2 @T_{\text{mean}}$ and $f\text{CO}_2 @T_{\text{obs}}$ (Figure 6) give three contrasting pictures as a function of the distance from the coastline; the main difference between these pictures is the amplitude of the seasonal variability.

FIGURE 6

The effect that the annual temperature cycle cause on the $f\text{CO}_2$ is reflected on the $f\text{CO}_{2\text{mean}}@T_{\text{obs}}$, which general pattern is similar for our three notional regions of the continental shelf, in a marked sinusoidal trend with a winter minimum and a summer maximum; the seasonal amplitude $f\text{CO}_2 @T_{\text{obs}}$ in the inner shelf (248 μatm / 181 μatm for year 2003/2004) is twice that in the middle (163 μatm / 129 μatm for year 2003/2004) and outer regions (154 μatm / 114 μatm for year 2003/2004) of the shelf. As solar radiation decreases in autumn, temperature drops more quickly in the inner shelf than in the middle and outer regions, owing to the shallower water depth and the input of colder river discharges. In contrast, in summer inner shelf waters get warmer than in the outer and middle regions.

The effects of the other processes not related to temperature cause that the general pattern for $f\text{CO}_2 @T_{\text{mean}}$ shows a similar tendency during the year and is a mirror image of the $f\text{CO}_2 @T_{\text{obs}}$, with much higher seasonal amplitude on the inner (329 μatm / 351 μatm for year 2003/2004) than in the middle (176 μatm / 179 μatm for year 2003/2004) and outer shelf (104 μatm / 145 μatm for year 2003/2004). Unlike $f\text{CO}_2 @T_{\text{obs}}$, the evolution of $f\text{CO}_2 @T_{\text{mean}}$ in the inner shelf is particularly irregular, accounting for the short temporal scale as well as by the intensity of the underlying mechanism involved in the $f\text{CO}_2$ variability in the coastal waters.

The evaluation of the biogeochemical factors others than the temperature component affecting the $f\text{CO}_2^{\text{sw}}$ seasonal variability has been extended performing multiple lineal

regressions. In order to make a better picture of the seasonal variability of the $fCO_2 @T_{mean}$ for each region of the French shelf, the values used in the multiple linear regressions are the track-averaged values of $fCO_2 @T_{mean}$, SST, SSS, O_2 Sat, and Chl a. So, the role of river-ocean mixing, remineralization and organic matter synthesis respiration/production has been assessed for the inner, middle and outer shelves. From here, the relationship considering only the significant variables were established (Table 2). The total regression coefficients for each region were 0.70, 0.81 and 0.90 for the inner, middle and outer shelf respectively suggesting that most of the non-thermodynamic variability on fCO_2 can be fairly well predicted using these four variables. The relative explanatory weight for each contributory factor has been computed as the ratio of the sum of squares of the partial residuals associated with each variable over the total sum of squares of residuals of the total regression. No statistical correlation has been found between the independent variables of the lineal multiple regression

Table 2

In the inner shelf, most of the variability of the $fCO_2 @T_{mean}$ is explained together by temperature (33%) and salinity (29%), and in a lesser proportion by the O_2 Sat (8%), whereas Chl a does not appear significantly correlated. $fCO_2 @T_{mean}$ increases as salinity decreases, suggesting that the fresher riverine Loire waters are a significant source of fCO_2 to the inner shelf. The coefficient for salinity (-13.87) is double the one for temperature (-5.67). Given the fact these two parameters and their variations ranges were in a similar order of magnitude with a track-averaged salinity range of 11.2-34.6 and a temperature range of 5.6-27.0 °C, the much higher coefficient for salinity clearly indicated that water mixing is more important than the temperature annual cycle. The higher $fCO_2 @T_{mean}$ at lower temperature could be explained by several processes masked by the annual temperature cycle: for instance, higher riverine inputs are expected during higher river discharge periods, which occur mainly

in winter, whereas maximum primary production activity has been observed in summer when temperature is higher.

Figure 3 shows that the $f\text{CO}_2^{\text{sw}}$ increases as the O_2 Sat decreases. Based on the fact that local consumption or production of oxygen is proportional to CO_2 , it would be possible to separate the two processes responsible for CO_2 variations by analysing the variation of O_2 Sat. Nevertheless, there are two deficiencies in this method that may result in considerable errors (Dai et al., 2009). First, the ratio between the biological production or utilization of O_2 and CO_2 is different from place to place (Chen et al. 1996). Second, the O_2 air-sea exchange rate is much faster than that of CO_2 . The result of these two considerations could be that, although intense biological activity is expected in the inner shelf, this fact is not as obvious as expected in the weight of the O_2 Sat in the multiple linear regression, since the relationship between $f\text{CO}_2^{\text{sw}}$ and O_2 Sat (figure 4) in the inner shelf shows a wide range of possibilities for a theoretical linear slope.

Regarding the middle shelf, the SST explains most of the $f\text{CO}_2 @T_{\text{mean}}$ variability (66 %) whereas O_2 consumption/production and Chl a only explain much smaller proportions of this variability (13% and 3%, respectively). In contrast, SSS is not significantly correlated on an annual scale with the $f\text{CO}_2$ variability in this region. The higher weight in the $f\text{CO}_2 @T_{\text{mean}}$ of SST in the middle shelf compared to the inner shelf suggests that the seasonal sequence of the diverse biogeochemical processes is more synchronized with the annual temperature cycle in the more offshore region. $f\text{CO}_2 @T_{\text{mean}}$ increases as SST decreases, as a consequence of prevailing respiration during the winter time and the phytoplankton bloom appearing during the summer (and consequently $f\text{CO}_2 @T_{\text{mean}}$ consumption). In turn, O_2 Sat is correlated slightly more closely in the middle shelf than in the inner shelf, suggesting that in-situ biological processes are responsible for the O_2/CO_2 variations, rather than inner-estuarine processes.

Finally, SST explains almost the entire $fCO_2 @T_{mean}$ variability in the outer shelf (85%), but is only slightly correlated with SSS (1%), O2 Sat (2%) and Chl a (2%). As with the middle shelf, the high inverse correlation between the SST and $fCO_2 @T_{mean}$ suggests that the factors affecting the $fCO_2 @T_{mean}$ variability are overshadowed by the annual cycle temperature. Apart from the decoupling between winter respiration and spring/early summer production, there are processes other than biological that could possibly influence the $fCO_2 @T_{mean}$ variability. The positive relationship between SSS and $fCO_2 @T_{mean}$, an inverse relationship for the inner shelf affected more by riverine freshwater, could be explained by the disappearance of the water column stratification during the winter, which can inject deeper water enriched in CO_2 into the surface layer. The reason why the correlation of the $fCO_2 @T_{mean}$ with temperature is much weaker than that with salinity is probably because salinity is much more conservative than temperature: salinity oscillates within a narrow range of 34.7-35.5.

These results obtained can be compared with those from the original method proposed by Takahashi et al. (2002), which has been applied here to compare the relative weight of the effects of changes in water temperature on fCO_2 versus other non-temperature factors (attributed entirely to biology in the Takahashi method) affecting the fCO_2^{obs} variability. Seasonal effects of non-temperature processes (B) and temperature (T) were determined, respectively, from the annual amplitudes of $fCO_2 @T_{mean}$ and $fCO_2^{mean}@T_{obs}$; the net annual effect is expressed by the ratio T/B. In the method of Takahashi et al (2002), T/B ratios greater than 1 mean that the effects of temperature changes on surface-water fCO_2 exceed the biological effects, whereas in areas where biology effects exceed the temperature effect, the T/B ratio is less than 1.

Therefore, the net effect of temperature changes on surface-water fCO_2 versus other processes can be assessed by the annual (T/B) ratio, which is 0.75 ($T/B = 248/329$) for

2003 and 0.52 ($T/B = 181/351$) for 2004. The middle shelf shows that processes other than changes in water temperature control the fCO_2 variability from February to May, and that changes in temperature control this variability for the rest of the year. The T/B ratio in the middle shelf is 0.93 and 0.72, for 2003 and 2004 respectively, showing that changes in water temperature and the rest of the processes are almost in equilibrium on an annual scale, with changes in water temperature being only slightly less influential. The seasonal signal for fCO_2^{obs} in the outer shelf is controlled by changes in water temperature from June to November, with the rest of the processes (biology, water mixing and advection, etc) being more significant from December to May; on an annual scale the changes in water temperature are the controlling mechanism (T/B ratio is 1.48 in 2003 and 0.79 in 2004).

Like the interannual variability found in the T/B ratio, significant inter-annual differences were observed by Padin et al. (2008) in the adjacent waters of the Bay of Biscay, where the fCO_2^{sw} variability associated with biology control for 2004 was 10% stronger than the changes in water temperature component, due to intense fertilization in winter 2004 by the late shoaling of the mixed layer. Nevertheless, the T/B ratio is systematically higher in 2003 than in 2004 from the coastline to the continental slope. It is possible that the inter-annual variations found in the T/B ratio may be derived from the sampling strategy. During 2004, the surface water fCO_2 , was measured less frequently, and the maximum fCO_2^{temp} that is expected in August may not have been detected, producing an underestimation of the fCO_2^{temp} amplitude, a lower T/B ratio and consequently underestimation of the net annual temperature control.

Although similar results are obtained from the application of the method of Takahashi et al. (2002) and multiple linear regressions, certain considerations arise from their comparison. First, the interannual variability obtained in the T/B ratio shows that the application of the Takahashi approach is very susceptible to the sampling strategy,

especially in inshore waters, where short-time scale processes are very significant. Second, as the biological term in Takahashi et al (2002) accounts for all the processes except the changes in water temperature, other methods need to be used to discern the different processes (mixing, biology, water-sediment fluxes, etc) included in the biological term, especially in inshore waters.

3.3 Air-water CO₂ exchange

The annual trend of the air-water CO₂ gradient, and hence the air-water exchange, show different patterns from the river mouth to the continental slope (Figure 7). The direction of the CO₂ flux is imposed by the sign of the air-water CO₂ gradient. Hence, the inner shelf is affected strongly by the direct inputs of excess CO₂ from the Loire estuary, resulting in CO₂ oversaturation during most of the year. Minimum (maximum) values for the $\Delta f\text{CO}_2$ in this region, averaged for each cruise, are -113(581) μatm in 2003 and -132(314) μatm in 2004, with maximum oversaturation occurring during the summer and CO₂ undersaturation linked to the bloom periods at the river mouth during late spring and early summer.

As a consequence, the seasonal and inter-annual variability for air-water CO₂ fluxes in the inner shelf is rather irregular both in direction and in magnitude. The higher values for air-water CO₂ fluxes are modulated by the higher wind speed values during winter (figure 2), resulting in 364 mmol m⁻²d⁻¹ for 2003 and 102 mmol m⁻²d⁻¹ in 2004; these values correspond to high wind events of 18.7 and 11 m s⁻¹ respectively. Maximum CO₂ water uptake values in this region are relatively low compared to the CO₂ outgassing rates, with values around -28 and -13 mmol m⁻² d⁻¹ for 2003 and 2004 respectively. Annual fluxes were calculated by direct lineal interpolation of the cruise-averaged fluxes in each region. Consequently, the inner shelf region behaves yearly as

a CO₂ source to the atmosphere; the averaged CO₂ fluxes in the inner shelf are 30.2 ± 27.55 and 15.1 ± 27.55 mmol m⁻²d⁻¹ for 2003 and 2004 respectively.

FIGURE 7

The general trend in the mid-shelf during 2003 and 2004 is CO₂ undersaturation, with higher uptake capacity in spring and CO₂ fluxes equal to -11.6 and -16.8 mmol·m⁻²d⁻¹ in 2003 and 2004 respectively, and minima during autumn of 0.16 and -1.2 mmol·m⁻²d⁻¹ in 2003 and 2004 respectively. Exceptionally in autumn 2003, mid-shelf surface waters are almost in equilibrium, acting finally as a slight source of CO₂ to the atmosphere due to the slight dominance of heterotrophic over thermodynamic processes. On a yearly scale, the mid-shelf behaves as a net CO₂ sink with CO₂ flux values equal to -4.6 ± 8.2 and -7.5 ± 7.7 mmol·m⁻²d⁻¹ for 2003 and 2004 respectively. The middle and outer shelf share a similar seasonal pattern for CO₂ fluxes, showing undersaturated CO₂ waters all through the year, with higher uptake capacity in spring (-10.8/-19.2 mmol m⁻²d⁻¹ for 2003/2004) and less in autumn. Unlike the inner shelf, no clear seasonal correlation is observed between wind speed and sea surface fCO₂ in the middle and outer shelf: thus CO₂ fluxes are primarily controlled both in direction and in magnitude by the air-water CO₂ gradient, the maximum of which occurs in spring. Some differences are seen in the seasonal distribution of CO₂ fluxes between 2003 and 2004 especially in summer; in 2003 the minimum CO₂ fluxes occur in summer (-1.8 mmol·m⁻²d⁻¹), whereas in 2004 they occur in autumn. This may also be explained by the less frequent CO₂ data obtained during summer 2004.

Comparing the resulting CO₂ fluxes in the Loire plume and in the adjacent shelf for 2003 (when better temporal coverage was achieved), the CO₂ fluxes reported in this study highlight the diversity of patterns identified in the coastal ocean. The inner shelf is

a relatively important CO₂ source to the atmosphere ($30.3 \pm 52.6 \text{ mmol m}^{-2} \text{ d}^{-1}$), and the mid-shelf ($-4.6 \pm 8.2 \text{ mmol m}^{-2} \text{ d}^{-1}$) and outer shelf ($-6.3 \pm 6.3 \text{ mmol m}^{-2} \text{ d}^{-1}$) are net CO₂ sinks. The fCO₂^{sw} in the estuarine plume depends on its primary production/respiration balance but also on the quantity of excess dissolved CO₂ advected from the inner estuary.

In turn, CO₂ atmospheric exchanges in plumes are affected by many parameters, among which the river discharge, the degree of heterotrophy in the inner estuary, the availability of nutrients and light, and the stratification of the water column are worthy of mention. If the plume extent is delimited by salinity 34, the resulting annual flux in the Loire plume for our study period is $16.90 \text{ mmol m}^{-2} \text{ d}^{-1}$, which can be contrasted with previous studies in the adjacent areas and in similar systems. For instance, previous studies carried out by Abril *et al.* (2003, 2004) show that much more intense fluxes occur in the inner estuary than in the plume, possibly due to the dilution effect, and the dominance of the in-situ production versus respiration processes. The flux in the Loire inner estuary varies between 30 and $280 \text{ mmol m}^{-2} \text{ d}^{-1}$ in summer (September 1998), and accounts for a total emission of 110 TC d^{-1} for the entire estuary (Abril *et al.*, 2003), which puts the Loire in second rank among the European estuaries with very high CO₂ emissions, after the extremely polluted Scheldt (Frankignoulle *et al.*, 1998). From 13 voyages studying 7 European Atlantic and North Sea estuarine plumes, Frankignoulle *et al.* (1998) observed variations in pCO₂ from $240 \text{ } \mu\text{atm}$ in the Scheldt plume at salinity 34, in March, to $1330 \text{ } \mu\text{atm}$ at the mouth of Douro in September. The studies of air-water CO₂ exchange available for outer estuaries are very few and are particularly difficult to integrate on a yearly scale, since they show a very arbitrary seasonal coverage. Most of the available studies were carried in spring and summer, hence winter periods are understudied. One of the most intensively studied plumes is the Scheldt plume, where the yearly integration of air-sea CO₂ fluxes shows that this

system acts a net source to the atmosphere of $1.9 \text{ mmol m}^{-2}\text{d}^{-1}$ (Schiettecatte et al., 2006), due to a combination of the high excess CO_2 exported by the heterotrophic Scheldt inner estuary, and to a completely mixed water column on the shelf during the whole year.

4. Summary and concluding remarks

Conclusions from the underway measurements performed during the ECO voyages using ships of opportunity, from November 2002 to December 2004, emphasise the biochemical differences on seasonal scales between the near-shore and distal hydrographical continuum in the Loire plume and the adjacent French continental shelf. The CO_2 exchange estimated for 2003 and 2004 on a yearly data base is $22.7 \pm 42.6 \text{ mmol m}^{-2}\text{d}^{-1}$ in the inner shelf, dominated by the riverine inputs from the eutrophic Loire River. The biochemical response to these inputs in the inner shelf is closely related to the river discharge and expanse of the plume, as well as to the heterotrophic status within and beyond the river. This region is oversaturated for most of the year, except when the light availability, together with the inputs of riverine nutrients and the haline stratification of water column, create favourable conditions for phytoplankton blooms. The biochemical imprint of the Loire River is noticeable in the mid-shelf during high river flow events and favourable winds and almost negligible in the outer shelf, where temperature is the main controlling mechanism in the seasonal variability of the fCO_2^{sw} . During the study period (Nov 2002-Dec 2004), the estimated air-water CO_2 flux is $-6.04 \pm 8.08 \text{ mmol}\cdot\text{m}^{-2}\text{d}^{-1}$ and $-8.46 \pm 9.5 \text{ mmol}\cdot\text{m}^{-2}\text{d}^{-1}$ in the middle and outer shelf respectively. These atmospheric CO_2 absorption rates highlight the uptake capacity of the continental shelves and match the general pattern for shelves in middle and high latitudes to act as sinks of atmospheric CO_2 (Borges et al., 2005).

Very few studies have been made of the carbonate system in the Loire inner estuary and river (Abril et al., 2003, 2004), and those available are limited to the summer season. This paper provides a broader coverage in space and time in the study of CO₂ flux along the hydrological continuum of the Loire plume and the adjacent continental shelf. The authors are in agreement with others who have concluded that inner estuaries and near-shore systems are effective filters for terrestrial and/or riverine organic inputs and impose a by-pass of carbon towards the atmosphere for the global carbon (Chen and Borges, 2009).

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Figure captions:

Figure 1. Map of the study area showing the regular ECO route and the biogeochemical regions differentiated in the discussion: inner (red), middle (dark grey) and outer (light grey) shelf. The approximate location for the four discrete sampling stations has been also indicated in the map (●)

Figure 2. River discharge, plume expanse, wind module and direction from December 2002 to December 2004. The black continuous line in the wind module plot depicts the monthly averaged wind module.

Figure 3. Spatio-temporal variability of temperature (SST, °C), salinity (SSS), O₂ saturation (%), fCO₂^{sw}, chlorophyll a in the Loire plume and offshore waters and Loire river discharge at St. Nazaire. Notes: 1). the continuous line at salinity plot marks the isohaline 34; 2) the 100% saturation isopleths; 3) the continuous line at the surface fCO₂^{sw} is equal to fCO₂^{atm} (i.e. equilibrium with the atmosphere).

Figure 4.a) fCO₂ versus salinity, b) fCO₂ versus OD Sat and c) Chl a vs salinity

Figure 5. C_T in the inner shelf plotted against river discharge at the mouth.

Figure 6. Temporal evolution of $f\text{CO}_2^{\text{obs}}$, $f\text{CO}_2 @ T_{\text{mean}}$, $f\text{CO}_2 \text{ mean}@T_{\text{obs}}$ and $(\delta f\text{CO}_2 \text{ mean}@T_{\text{obs}} - \delta f\text{CO}_2 @ T_{\text{mean}})$ for the ECO voyages in the three regions: inner shelf (to 25 km out), middle shelf (25-100 km) and outer shelf (100-250 km).

Figure 7. Spatio-temporal variability of: a) the air-sea CO_2 gradient, and b) air-water CO_2 fluxes. The continuous line traces the zero values for the air-water $f\text{CO}_2$ gradient and air-sea CO_2 fluxes in the respective graphs.

Table 1

		SST psu		SSS		Chl a		O ₂ Sat		fCO ₂ ^{sw}	
		°C	Date	psu	Date	mg m ⁻³	Date	%	Date	µatm	Date
Inner shelf	min	5.63	14 Jan 03	11.15	19 Jan 04	0.16	28 Jul 04	63	28 Jul 04	240.6	09 May 04
	max	26.97	01 Sep 03	34.68	08 Jul 04	11.45	03 Jun 03	152	03 Jun 03	937.7	01 Sep 03
Middle shelf	min	9.09	29 Jan 03	27.71	19 Jan 04	0.17	28 Jul 04	91	09 Dec 02	244.1	14 May 04
	max	21.03	31 Aug 03	35.38	20 Jan 03	5.60	13 Jun 03	143	03 Jun 03	430.8	04 Dec 02
Outer shelf	min	10.70	27 Feb 03	34.73	10 Jul 03	0.11	29 Jul 04	94	10 Dec 02	292.3	27 Apr 03
	max	21.73	02 Sep 03	35.54	06 Nov 03	2.70	04 May 04	130	12 Mar 03	370.8	18 Jan 04

Table 1. Minimum and maximum values for track-averaged temperature (SST), salinity (SSS), Chlorophyll *a* (Chl *a*), oxygen saturation (O₂Sat) and fugacity of CO₂ (fCO₂) in the inner, middle and outer shelves, and the specific dates when the variables were measured.

Table 2

	SST	SSS	O ₂ Sat	Chl <i>a</i>	<i>r</i> ² Total
Inner shelf	-5.67 ± 2.48	-13.87 ± 1.80	-4.15 ± 0.77	--	
<i>r</i> ²	0.33	0.29	0.08	n. s	0.70
Middle shelf	-14.00 ± 0.69	--	-2.53 ± 0.34	-12.60 ± 3.14	
<i>r</i> ²	0.66	n. s.	0.13	0.03	0.81
Outer shelf	-13.7±0.5	20.3±6.9	-0.7±0.2	-17.5±3.5	
<i>r</i> ²	0.85	0.01	0.02	0.02	0.9

Table 2. Coefficients of empirical relationship between fCO₂ @T_{mean} and every significant variable showing the coefficient of each variable, the partial regression coefficient (*r*²), and the total regression coefficient (*r*²) (n. s.: non significant)

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