

**Title:** Seasonal response of air-water CO<sub>2</sub> exchange along the land-ocean aquatic continuum  
of the **Northeast** American coast

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**Abstract:**

This regional study quantifies the CO<sub>2</sub> exchange at the air-water interface along the land-ocean aquatic continuum (LOAC) of the [Northeast](#) American coast, from streams to the shelf break. Our analysis explicitly accounts for spatial and seasonal variability in the CO<sub>2</sub> fluxes. The yearly integrated budget reveals the gradual change in the intensity of the CO<sub>2</sub> exchange at the air-water interface, from a strong source towards the atmosphere in streams and rivers ( $3.0 \pm 0.5$  TgC yr<sup>-1</sup>) and estuaries ( $0.8 \pm 0.5$  TgC yr<sup>-1</sup>) to a net sink in continental shelf waters ( $-1.7 \pm 0.3$  TgC yr<sup>-1</sup>). Significant differences in flux intensity and their seasonal response to climate variations is observed between the North and South sections of the study area, both in rivers and coastal waters. Ice cover, snow melt and [intensity of the carbon removal efficiency through the estuarine filter](#) are identified as important control factors of the observed spatio-temporal variability in CO<sub>2</sub> exchange along the LOAC.

## 1. Introduction

Over the past decade, several syntheses have highlighted the significant contribution of the Land-Ocean Aquatic Continuum (LOAC) to the global atmospheric CO<sub>2</sub> budget (Cole et al., 2007; Battin et al., 2009; Mackenzie et al., 2012; Bauer et al., 2013; Ciais et al., 2013; Raymond et al., 2013; Regnier et al., 2013). In a recent review, Regnier et al. (2013) proposed that inland waters (streams, rivers and lakes) and estuaries outgas 1.1 and 0.25 PgC yr<sup>-1</sup>, respectively, while continental shelf seas take up 0.2 PgC yr<sup>-1</sup>. However, CO<sub>2</sub> data are too sparse and unevenly distributed to provide global coverage and large uncertainties remain associated to these estimates. The inland water outgassing could for instance reach 2.1 PgC yr<sup>-1</sup> with 86% coming from streams and rivers (Raymond et al., 2013), a value which is about twice that reported in Regnier et al. (2013) and in the 5<sup>th</sup> assessment report of the IPCC (Ciais et al., 2013). The most recent global budgets for the estuarine CO<sub>2</sub> source and the continental shelf CO<sub>2</sub> sink also reveal significant discrepancies, both falling within the 0.15-0.4 PgC yr<sup>-1</sup> range (Laruelle et al., 2010; Cai, 2011; Bauer et al., 2013; Dai et al., 2013; Laruelle et al., 2013). None of these estimates, however, fully resolves the seasonality in CO<sub>2</sub> fluxes because temporal coverage of the global data is insufficient. Complex seasonal dynamics of CO<sub>2</sub> exchanges between the atmosphere and individual components of the LOAC have been reported in previous studies which have highlighted the potential importance of the intra-annual variability for local and regional CO<sub>2</sub> budgets (e.g. Kempe 1982; Frankignoulle, et al., 1998; Jones and Mulholland, 1998; Degrandpré et al., 2002; Thomas and Schneider, 1999; Wallin et al., 2011; [Regnier et al., 2013](#); Rawlins et al., 2014). Here, we extend the analysis to the sub-continental scale, and present the spatial and seasonal variability of CO<sub>2</sub> fluxes at the air-water interface (FCO<sub>2</sub>) for the entire [Northeast](#) American LOAC, from streams to the shelf break. This region of unprecedented data coverage allows us producing, for the first time, empirically-derived monthly maps of CO<sub>2</sub> exchange at 0.25° resolution. Our results allow

investigating the seasonal CO<sub>2</sub> dynamics across the inter-connected systems of the LOAC and elucidating their response to contrasting intra-annual changes in climate conditions.

## 2. Methods

Our study area is located along the Atlantic coast of the Northern US and Southern Canada and extends from the Albemarle Sound in the South to the Eastern tip of Nova Scotia in the North. It corresponds to COSCAT 827 (for Coastal Segmentation and related CATchments) in the global coastal segmentation defined for continental land masses by Meybeck et al. (2006) and extrapolated to continental shelf waters by Laruelle et al. (2013). COSCATs are homogenous geographical units that divide the global coastline into homogeneous segments according to lithological, morphological, climatic and hydrological properties. The area corresponding to COSCAT 827 comprises 447 10<sup>3</sup> km<sup>2</sup> of watersheds and 357 10<sup>3</sup> km<sup>2</sup> of coastal waters, amongst which 15 10<sup>3</sup> km<sup>2</sup> of estuaries. It is one of the best monitored regions in the world with several regularly surveyed rivers (Hudson, Susquehanna, York, Connecticut) and some of the most extensively studied coastal waters (Degrandpré et al., 2002; Chavez et al., 2007; Fennel et al., 2008; Fennel and Wilkin, 2009; Previdi et al., 2009; Fennel, 2010; Shadwick et al., 2010; 2011; Signorini et al., 2013). For the purpose of this study, the area was divided in a North and a South section (Fig. 1). The boundary is set on land, to delineate the regions subject to seasonal ice freeze and snowfalls from those that are not (Armstrong and Brodzik, 2001). This delineation attributes 96% of the estuarine surface area to the South section due, for the most part, to the contribution of Chesapeake Bay which accounts for about two thirds of the estuarine area. The delineation extends further into the coastal waters in such a way that the Scotian Shelf and the Gulf of Maine correspond to the North section and the Mid-Atlantic Bight and Georges Banks to the

South section. The riverine data are calculated from pH and alkalinity measurements extracted from the GLObal River CHemistry Database (GLORICH, previously used in Lauerwald et al., 2013) while continental shelf values are calculated from the Surface Ocean CO<sub>2</sub> Atlas (SOCAT v2.0) database which contains quality controlled direct pCO<sub>2</sub> measurements (<http://www.socat.info/>, Bakker et al., 2014).

## 2.1. Rivers

CO<sub>2</sub> evasion from rivers (FCO<sub>2</sub>) was calculated monthly per 15s grid cell (resolution of the hydrological routing scheme Hydrosheds 15s, Lehner et al., 2008) from estimates of the effective stream/river surface area  $A_{eff}$  [m<sup>2</sup>], gas exchange velocity  $k$  [m d<sup>-1</sup>], and water-atmosphere CO<sub>2</sub> concentration gradient  $\Delta[CO_2]$  [μmol l<sup>-1</sup>]:

$$FCO_2 = A_{eff} \times k \times \Delta[CO_2] \quad (\text{Eq. 1})$$

The calculation of  $A_{eff}$  first requires estimation of the total stream/river surface area,  $A$ . The latter was calculated from the linear stream network derived from the Hydrosheds 15s routing scheme using a minimum threshold on the catchment area of 10 km<sup>2</sup> and estimates of stream width derived from the annual mean discharge  $Q_{ann}$  using the equations of Raymond et al. (2012, 2013) (Eqs. 2,3).  $A$  values were not calculated for each individual month, as the discharge-stream width relations only hold true for  $Q_{ann}$  (Raymond et al., 2013).  $Q_{ann}$  was obtained using Hydrosheds 15s to route the gridded data of average annual runoff from the UNH/GRDC composites (Fekete et al., 2002).

$$\ln(B \text{ [m]}) = 2.56 + 0.423 \cdot \ln(Q_{ann} \text{ [m}^3\text{s}^{-1}\text{]}) \quad (\text{Eq 2, after Raymond et al., 2012})$$

$$\ln(B \text{ [m]}) = 1.86 + 0.51 \cdot \ln(Q_{ann} \text{ [m}^3\text{s}^{-1}\text{]}) \quad (\text{Eq. 3, after Raymond et al., 2013})$$

with

$B$  stream width [m]

107  $Q_{ann}$  annual average discharge [ $m^3 s^{-1}$ ]

108 For each 15s raster cell covered by lake and reservoir areas as represented in the  
109 global lake and wetland data base of Lehner and Döll (2004), A was set to 0 km<sup>2</sup>.  $A_{eff}$  was  
110 then derived from A to account for seasonal stream drying and ice cover inhibiting FCO<sub>2</sub>.  
111 Seasonal stream drying was assumed for each 15s cell and month when the monthly average  
112 discharge  $Q_{month}$  is 0 m<sup>3</sup>s<sup>-1</sup>. Values of  $Q_{month}$  were calculated similarly to that of  $Q_{ann}$  using the  
113 gridded data of average monthly runoff from the UNH/GRDC composites (Fekete et al.,  
114 2002). Ice cover was assumed for each 15s cell and month when the mean air temperature  
115 ( $T_{air}$ ), derived from the worldclim data set of Hijmans et al. (2005), is below -4.8°C  
116 (Lauerwald et al., under revision). In case of ice cover and/or stream drying,  $A_{eff}$  is set to 0  
117 m<sup>2</sup>. Otherwise  $A_{eff}$  equals A.

118 Values of k were first calculated as standardized values for CO<sub>2</sub> at a water temperature  
119 ( $T_{water}$ ) of 20°C ( $k_{600}$ ), from stream channel slope CS and estimates of flowing velocity V (Eq  
120 4). Using the Strahler order (Strahler, 1952) to perform the segmentation of the stream  
121 network, CS was calculated for each segment by dividing the change in its altitude by its  
122 length. Information on altitude was derived from the Hydrosheds elevation model. V was  
123 calculated from  $Q_{ann}$  based on the equations of Raymond et al. (2012, 2013) (Eqs. 5, 6).  
124 Similarly to the stream width, the V-Q relations only hold true for  $Q_{ann}$  (Raymond et al.,  
125 2013), and this is why only annually average values for V and  $k_{600}$  could be calculated. The k  
126 value for each month was calculated from  $k_{600}$  an estimate of the average monthly water  
127 temperature  $T_{water}$  (Lauerwald et al., under revision; Raymond et al., 2012).

128  $k_{600} [m d^{-1}] = V [m s^{-1}] \cdot CS [1] \cdot 2841 + 2.02$  (Eq. 4, after Raymond et al., 2012)

129  $\ln(V [m s^{-1}]) = -1.64 + 0.285 \cdot \ln(Q_{ann}[m^3 s^{-1}])$  (Eq. 5, after Raymond et al., 2012)

130  $\ln(V [m s^{-1}]) = -1.06 + 0.12 \cdot \ln(Q_{ann}[m^3 s^{-1}])$  (Eq. 6, after Raymond et al., 2013)

131 with

132  $k_{600}$  Standardized gas exchange velocity for CO<sub>2</sub> at 20°C water temperature [m d<sup>-1</sup>]

133  $Q_{\text{ann}}$  annual average discharge [m<sup>3</sup> s<sup>-1</sup>]

134  $V$  stream flow velocity [m s<sup>-1</sup>]

135  $CS$  channel slope [dimensionless]

136

137 Values of  $\Delta(\text{CO}_2)$  were derived from monitoring data with calculated  $\text{pCO}_{2\text{river}}$  (12,300

138 water samples, from 161 locations, Lauerwald et al., 2013), an assumed  $\text{pCO}_{2\text{atmosphere}}$  of 390

139  $\mu\text{atm}$ . Lauerwald et al. (2013) calculated  $\text{pCO}_{2\text{river}}$  values from pH, alkalinity, water

140 temperature, and, where available, major ion concentrations, using the hydrochemical

141 modelling software PhreeqC v2 (Parkhurst & Appelo, 1999). The  $\text{pCO}_2$  values were

142 converted into concentrations,  $[\text{CO}_2]$ , using Henry's constant (Henry, 1803) for each sample

143 at its observed temperature  $T_{\text{water}}$  using the equation of Telmer and Veizer (1999). In order to

144 minimize the influence of extreme values, the results were aggregated to median values per

145 sampling location and month for which at least three values were available. These median

146 values per sampling location and month were then used to calculate maps of  $\Delta[\text{CO}_2]$  at a 15s

147 resolution. To this end, an inverse distance weighted interpolation was applied. This method

148 allows predicting a value for each grid cell from observed values at the four closest sampling

149 locations, using the inverse of the squared distance between the position on the grid and each

150 sampling locations as weighting factors. To account for downstream decreases in  $\text{pCO}_{2\text{river}}$ ,

151 which are often reported in the literature (Finlay, 2003; Teodoru et al., 2009; Butman and

152 Raymond, 2011), the interpolation was applied separately to three different classes of streams

153 and rivers defined by  $Q_{\text{ann}}$ , for which sufficiently large subsets of sampling locations could be

154 retained: 1)  $Q_{\text{ann}} < 10 \text{ m}^3 \text{ s}^{-1}$  ( $n = 76$ ), 2)  $10 \text{ m}^3 \text{ s}^{-1} \leq Q_{\text{ann}} < 100 \text{ m}^3 \text{ s}^{-1}$  ( $n = 47$ ), and 3)  $Q_{\text{ann}} \geq 100 \text{ m}^3 \text{ s}^{-1}$  ( $n = 38$ ). The three maps of  $\Delta[\text{CO}_2]$  per month were then recombined according to the

spatial distribution of  $Q_{\text{ann}}$  values. The  $\text{FCO}_2$  values were first calculated using equation (1) at the high spatial resolution of 15s for each month. The results were then aggregated to a  $0.25^\circ$  resolution and three-month period and reported as area specific values referring to the total surface area of the grid cell. At the outer boundaries, only the proportions of the cell covered by our study area are taken into account. The difference between the  $\text{FCO}_2$ s calculated using the equations of Raymond et al. (2012) and Raymond et al. (2013) was used as an estimate of the uncertainty of the mean yearly  $\text{FCO}_2$ . This method is consistent with the approach of Raymond et al. (2013), which used two distinct sets of equations for  $k$  and  $A$  to estimate the uncertainty in these parameters and their combined effect on the estimated  $\text{FCO}_2$ .

## 2.2. Estuaries

The yearly averaged  $\text{CO}_2$  exchange at the air-water interface was obtained from local estimations of emission rates in seven estuaries located within the study area (see Table 1). The limited number of observation does not allow resolving the seasonality in  $\text{CO}_2$  emissions. The yearly-average local  $\text{CO}_2$  emission rates range from  $1.1 \text{ molC m}^{-2} \text{ yr}^{-1}$  in the Parker River to  $9.6 \text{ molC m}^{-2} \text{ yr}^{-1}$  in the Hudson River estuary, for a mean value of  $4.2 \text{ molC m}^{-2} \text{ yr}^{-1}$  for the seven systems. This value was then multiplied by the estuarine surface areas extracted from the SRTM water body data set (NASA/NGA, 2003), to estimate the bulk outgassing for the North and South sections of COSCAT 827. It should be noted that the methods used to estimates the  $\text{CO}_2$  emission rates differ from one study to the other (i.e. different relationships relating wind speed to the gas transfer coefficient). However, in the absence of consistent and substantial estuarine  $\text{pCO}_2$  database for the region, we believe that our method is the only one which allows deriving a regional data driven estimate for the  $\text{CO}_2$  outgassing from estuaries. Similar approaches have been used in the past to produce global estuarine  $\text{CO}_2$  budgets



(Borges et al., 2005; Laruelle et al., 2010; Cai, 2011; Chen et al., 2013; Laruelle et al., 2013). Similar approaches have been used in the past to produce global estuarine CO<sub>2</sub> budgets (Borges et al., 2005; Laruelle et al., 2010; Cai, 2011; Chen et al., 2013; Laruelle et al., 2013). The standard deviation calculated for the emission rates of all local studies was used as an estimate of the uncertainty of the regional estuarine FCO<sub>2</sub>.

### 2.3. Continental shelf waters

Monthly CO<sub>2</sub> exchange rates at the air-water interface were calculated in continental shelf waters using 274,291 pCO<sub>2</sub> measurements extracted from the SOCAT 2.0 database (Baker et al., 2014). For each measurement, an instantaneous local CO<sub>2</sub> exchange rate with the atmosphere was calculated using Wanninkhof's equation (Wanninkhof, 1992) which is a function of a transfer coefficient ( $k$ ), dependent on the square of the wind speed above sea surface, the apparent solubility of CO<sub>2</sub> in water ( $K'_0$ ) [moles m<sup>-3</sup> atm<sup>-1</sup>], which depends on surface water temperature and salinity, and the gradient of pCO<sub>2</sub> at the air-water interface ( $\Delta pCO_2$ ) [ $\mu$ atm].

$$FCO_2 = A_s \times k \times K'_0 \times \Delta pCO_2 \quad (\text{Eq. 2})$$

The parameterization used for  $k$  is that of Wanninkhof et al. (2013) and all the data necessary for the calculations are available in SOCAT 2.0 except for wind speed, which was extracted from the CCMP database (Altas et al., 2011). The resulting CO<sub>2</sub> exchange rates were then averaged per month for each 0.25° cell in which data were available. Average monthly CO<sub>2</sub> exchange rates were calculated for the North and South sections using the water surface area and weighted rate for each cell and those averages were then extrapolated to the entire surface area  $A_s$  of the corresponding section to produce FCO<sub>2</sub>. In effect, this corresponds to applying the average exchange rate of the section to the cells devoid of data.

To refine further the budget, a similar procedure was also applied to 5 depth segments (S1 to S5) corresponding to 0-20m, 20-50m, 50-80m, 80-120m and 120-150m, respectively, and their respective surfaces areas were extracted from a high resolution bathymetric files (Laruelle et al., 2013). The choice of slightly different methodologies for FCO<sub>2</sub> calculations in rivers and continental shelf waters stems from the better data coverage in the continental shelf, which allows capturing the spatial heterogeneity within the region without using interpolation techniques. The standard deviation calculated for all the grid cells of the integration domain was used as uncertainty of the yearly estimates of FCO<sub>2</sub>. A more detailed description of the methodology applied to continental shelf waters at the global scale is available in Laruelle et al. (2014).

### 3. Results and Discussion

Figure 2 shows the spatial distribution of FCO<sub>2</sub> along the LOAC integrated per season. Throughout the year, river waters are a strong source of CO<sub>2</sub> for the atmosphere. Significant differences in the intensity of the CO<sub>2</sub> exchange at the air-water interface can nevertheless be observed between the North and South sections, both in time and space. During winter, there is nearly no CO<sub>2</sub> evasion from rivers in the North due to ice coverage and stream drying. Over the same period, the CO<sub>2</sub> emissions from the South section range from 0 to 5 gC m<sup>-2</sup> season<sup>-1</sup>. During spring, the pattern is reversed and northern rivers exhibit higher outgassing rates than in the South with maximum emissions rates of >10 gC m<sup>-2</sup> season<sup>-1</sup>. This trend is maintained throughout summer while during fall, the entire COSCAT displays similar emission rates without clear latitudinal signal.

Continental shelf waters display a very different spatial and seasonal pattern than that of rivers. During winter, the North section is predominantly a mild CO<sub>2</sub> sink, with rates

comprised between  $+2$  and  $-5 \text{ gC m}^{-2} \text{ season}^{-1}$ , which intensifies significantly in the South section ( $-2$  to  $>-10 \text{ gC m}^{-2} \text{ season}^{-1}$ ). During spring, an opposite trend is observed with a quasi-neutral  $\text{CO}_2$  uptake in the South and a strong uptake in the North, especially on the Scotian Shelf. The entire COSCAT becomes a net  $\text{CO}_2$  source in summer with emission rates as high as  $5 \text{ gC m}^{-2} \text{ season}^{-1}$  in the Mid-Atlantic Bight. During fall, the Gulf of Maine and Georges Banks remain  $\text{CO}_2$  sources while the Scotian Shelf and the Mid-Atlantic Bight become again regions of net  $\text{CO}_2$  uptake.

The monthly integrated  $\text{FCO}_2$  for the North and South sections provides further evidence of the contrasting seasonal dynamics for the two areas (Fig. 3a and 3b). In the North section,  $\text{CO}_2$  evasion from rivers is almost zero in January and February, rises to a maximum value of  $0.26 \pm 0.05 \text{ TgC month}^{-1}$  in May, and then progressively decreases until the end of the year. These low winter values are explained by the ice cover inhibiting the gas exchange with the atmosphere. The steep increase and  $\text{FCO}_2$  maximum in spring can be related to the flushing of water from the thawing top-soils, which is rich in DOC and  $\text{CO}_2$ . Additionally, the temperature rise also induces an increase in respiration rates within the water streams (Jones and Mulholland, 1998; Striegl et al., 2007). Rivers and the continental shelf in the North section present synchronized opposite behaviors from winter through spring. In the shelf, a mild carbon uptake takes place in January and February ( $-0.04 \pm 0.25 \text{ TgC month}^{-1}$ ) followed by a maximum uptake rate in April ( $-0.50 \pm 0.20 \text{ TgC month}^{-1}$ ). This  $\text{CO}_2$  uptake in spring has been attributed to photosynthesis associated to the seasonal phytoplankton bloom (Shadwick et al., 2010). Continental shelf waters behave quasi neutral during summer ( $<0.05 \pm 0.09 \text{ TgC month}^{-1}$ ) and emit  $\text{CO}_2$  at a high rate in November and December ( $>0.15 \pm 0.21 \text{ TgC month}^{-1}$ ). Overall, the rivers of the North section emit  $1.31 \pm 0.24 \text{ TgC yr}^{-1}$  while the continental shelf waters take up  $0.47 \pm 0.17 \text{ TgC yr}^{-1}$ . The very limited estuarine surface area ( $0.5 \cdot 10^3 \text{ km}^2$ ) only yields an annual outgasing of  $0.03 \pm 0.02 \text{ TgC yr}^{-1}$ . The shelf sink calculated for the

region differs from that of Shadwick et al. (2011) which reports a source for the Scotian Shelves, in contrast to the current estimate. Our seasonally resolved budget is however in line with the  $-0.6 \text{ TgC yr}^{-1}$  sink calculated by Signorini et al. (2013) using a 8 years dataset as well as with the simulations of Fennel and Wilkin (2009) which also predict sinks of  $-0.7 \text{ TgC yr}^{-1}$  and  $-0.6 \text{ TgC yr}^{-1}$  for 2004 and 2005, respectively. No similar analysis was so far performed for inland waters.

In the South section of the COSCAT, the warmer winter temperature leads to the absence of ice cover (Armstrong and Brodzik, 2001). Our calculations predict that the riverine surface area remains stable over time, favoring a relatively constant outgassing comprised between  $0.1$  and  $0.2 \text{ TgC month}^{-1}$  throughout the year, adding up to a yearly source of  $1.69 \pm 0.31 \text{ TgC yr}^{-1}$ . Estuaries emit  $0.73 \pm 0.45 \text{ TgC yr}^{-1}$ , because of their comparatively large surface area ( $14.5 \cdot 10^3 \text{ km}^2$ ), about one order of magnitude larger than that of rivers ( $1.2 \cdot 10^3 \text{ km}^2$ , Table 2). It should be noted that our estimate of the estuarine outgassing is derived from a limited number of local studies, none of which were performed in the two largest systems of COSCAT827, that are, the Chesapeake and Delaware Bays (>80 % of the total estuarine surface area in COSCAT827). These estuaries are highly eutrophic (Cai, 2011), which suggests that they might be characterized by lower  $\text{pCO}_2$  values and subsequent  $\text{CO}_2$  exchange than the other systems in the region. On the other hand our regional outgassing of  $50 \text{ gC m}^{-2} \text{ yr}^{-1}$  is already well below the global average of  $218 \text{ gC m}^{-2} \text{ yr}^{-1}$  calculated using the same approach by Laruelle et al. (2013) for tidal estuaries. The continental shelf  $\text{CO}_2$  sink is strongest in January ( $-0.47 \pm 0.30 \text{ TgC month}^{-1}$ ) and decreases until June, when a period of moderate  $\text{CO}_2$  emission begins (max of  $0.13 \pm 0.08 \text{ TgC month}^{-1}$  in August) and lasts until October. Finally, November and December are characterized by mild  $\text{CO}_2$  sinks. Such seasonal signal, following that of water temperature, is consistent with the hypothesis of a

CO<sub>2</sub> exchange in the South section regulated by variations in gas solubility, as suggested by Degrandpré et al. (2002) for the Mid-Atlantic Bight.

The analysis of the intensity of the river CO<sub>2</sub> outgassing reveals that the smallest streams ( $Q < 1 \text{ m}^3 \text{ s}^{-1}$ , Q1 in [table 2](#)) display the highest emission rates per unit surface area, with values ranging from  $1961 \text{ gC m}^{-2} \text{ yr}^{-1}$  in the South section to  $2893 \text{ gC m}^{-2} \text{ yr}^{-1}$  in the North section. These values gradually decrease with increasing river discharge to  $729 \text{ gC m}^{-2} \text{ yr}^{-1}$  in the South section and  $891 \text{ gC m}^{-2} \text{ yr}^{-1}$  in the North section for  $Q > 100 \text{ m}^3 \text{ s}^{-1}$  (Q4, [table 2](#)). The emission rates for this latter class of rivers are consistent with the median emission rate of  $720 \text{ gC m}^{-2} \text{ yr}^{-1}$  proposed by Aufdenkampe et al. (2011) for temperate rivers with widths larger than 60-100m. Aufdenkampe et al. (2011) also report a median emission rates of  $2600 \text{ gC m}^{-2} \text{ yr}^{-1}$  for the smaller streams and rivers, which falls on the high end of the range calculated for Q1 in the present study. The surface area of the river network is relatively evenly distributed amongst the four discharges classes of rivers ([Table 2](#)). Yet, river sections for which  $Q < 10 \text{ m}^3 \text{ s}^{-1}$  (Q1+Q2) contribute to 65% of the total CO<sub>2</sub> outgassing although they only represent 51% of the surface area. This result therefore highlights that streams and small rivers are characterized by the highest surface-area specific emission rates. The higher outgassing rates in the North are a consequence of higher  $\Delta\text{CO}_2$  values since average  $k$  values are similar in both sections. In rivers with  $Q_{\text{ann}} < 10 \text{ m}^3 \text{ s}^{-1}$ , the  $\Delta\text{CO}_2$  is about twice as high in the North than in the South from April to August ([Table 2](#)). The calculation of  $\text{pCO}_2$  from alkalinity and pH presumes however that all alkalinity originates from carbonate ions and thus tends to overestimate  $\text{pCO}_2$  because non-carbonate contributions to alkalinity, in particular organic acids, are ignored in this approach. The rivers in Maine and New Brunswick, which drain most of the Northern part of COSCAT 827, are characterized by relatively low mineralized, low pH waters rich in organic matter. In these rivers, the overestimation in  $\text{pCO}_2$  calculated from the carbonate alkalinity only was reported to be in the range 13%-66% (Hunt

et al., 2011). Considering that rivers in the Southern Part of COSCAT827 have lower DOC concentrations and higher DIC concentration, the higher FCO<sub>2</sub> rates per surface water area reported in the Northern part could partly be due to an overestimation of their pCO<sub>2</sub> values. However, a direct comparison of average pCO<sub>2</sub>'s does not confirm this hypothesis. For the two Maine rivers (Kennebec and Androscoggin Rivers), Hunt et al. (2014) report an average pCO<sub>2</sub> calculated from pH and DIC of 3064 µatm. In our data set, three sampling stations are also located in these rivers and present lower median pCO<sub>2</sub> values of 2409, 901 and 1703 µatm for Kennebec River at Bingham and North Sidney and for Androscoggin River at Brunswick, respectively. A probable reason for the discrepancy could be that we report median values per month while Hunt et al. (2014) report arithmetic means, which are typically higher.

On the continental shelf, the shallowest depth interval is a CO<sub>2</sub> source in the North Section while all other depth intervals are CO<sub>2</sub> sinks (Table 2). The magnitude of the air-sea exchange for each segment is comprised between the values calculated for estuaries (50 gC m<sup>-2</sup> yr<sup>-1</sup>) and the nearby open ocean (~20 gC m<sup>-2</sup> yr<sup>-1</sup>, according to Takahashi et al., 2009). This trend along a depth transect, suggesting a more pronounced continental influence on near-shore waters and a strengthening of the CO<sub>2</sub> shelf sink away from the coast was already discussed in the regional analysis of Chavez et al. (2007) and by Jiang et al., (2013) specifically for the South Atlantic Bight. Modeling studies over a larger domain including the upper slope of the continental shelf also suggest that the coastal waters of the Northeast US are not a more intense CO<sub>2</sub> sink than the neighboring open ocean (Fennel and Wilkin, 2009; Fennel, 2010). Our analysis further suggests that the continental influence is more pronounced in the North section. Here, the shallowest waters (S1) are strong net sources of CO<sub>2</sub> while the intensity of the CO<sub>2</sub> sink for the other depth intervals gradually decreases, but only to a

maximum value of  $-4 \text{ gC m}^{-2} \text{ yr}^{-1}$  for S5. This value is about 3 times smaller than in the South section ( $-12 \text{ gC m}^{-2} \text{ yr}^{-1}$ ).

Annually, river and estuarine waters of the entire COSCAT 827 outgas  $3.0 \pm 0.5 \text{ TgC yr}^{-1}$  and  $0.8 \pm 0.5 \text{ TgC yr}^{-1}$ , respectively, while continental shelf waters take up  $1.7 \pm 0.3 \text{ TgC yr}^{-1}$  (Fig. 3c). The total riverine carbon load exported from rivers to estuaries for the same area has been estimated to  $4.65 \text{ TgC yr}^{-1}$ , 45% as dissolved and particulate organic carbon ( $2.10 \text{ TgC yr}^{-1}$ , Mayorga et al., 2010) and 55% as dissolved inorganic carbon ( $2.55 \text{ TgC yr}^{-1}$ , Hartmann et al., 2009). The ratio of organic to inorganic carbon in the river loads is about 1 in the North and 1.4 in the South. This difference stems mainly from a combination of different lithogenic characteristics in both sections and the comparatively higher occurrence of organic soils in the North (Hunt et al., 2013; Hossler and Bauer, 2013). Estimates of the total amount of terrestrial carbon transferred to the riverine network are not available but the sum of the river export and the outgassing, which ignores the contribution of carbon burial and lateral exchange with wetlands, provides a lower bound estimate of  $7.65 \text{ TgC yr}^{-1}$ . Under this hypothesis, ~40% of the terrestrial carbon exported to rivers is emitted to the atmosphere before reaching estuaries. In spite of higher emission rates per unit surface area in the North (Table 2), the overall efficiency of the riverine carbon filter is essentially the same in the two sections (40% and 38% outgassing for the North and the South, respectively). On the shelf, however, the South section exhibit a significantly more intense  $\text{CO}_2$  sink ( $-1.25 \pm 0.2 \text{ TgC yr}^{-1}$ ) than in the North ( $-0.47 \pm 0.2 \text{ TgC yr}^{-1}$ ). A possible reason for this difference can be found in the contribution of the estuarine carbon filter. In the South, where 96% of the estuarine surface area is located, these systems contribute to an outgassing of  $0.73 \text{ TgC yr}^{-1}$  while in the North, their influence is negligible. Cole and Caraco (2001) estimated that 28% of the DOC entering the relatively short Hudson River estuary is respired in-situ before reaching the continental shelf and it is thus likely that the estuarine outgassing in the South section is

fueled by the respiration of the organic carbon loads from rivers. In contrast, the absence of estuaries in the North favors the direct export of terrestrial organic carbon onto continental shelf waters where it can be buried and decomposed. The respiration of terrestrial organic carbon could therefore explain why the strength of the shelf CO<sub>2</sub> sink is weaker in this portion of the domain. This view is further substantiated by the similar cumulated estuarine and continental shelf FCO<sub>2</sub> fluxes in both sections (Fig. 3a and b). Naturally, other environmental and physical factors also influence the carbon dynamics in shelf waters and contribute to the difference in CO<sub>2</sub> uptake intensity between both sections. For instance, in the North, the Gulf of Maine is a semi-enclosed basin characterized by specific hydrological features and circulation patterns (Salisbury et al., 2008; Wang et al., 2013) which could result in longer water residence times promoting the degradation of shelf-derived organic carbon. Other potential factors include the plume of the Saint Lawrence estuary, which has also been shown to transiently expend over the Scotian Shelf (Kang et al., 2013), the strong temperature gradient and the heterogeneous nutrient availability along the region which may result in different phytoplankton responses (Vandemark et al., 2011; Shadwick et al., 2011). Additionally, modeling studies evidenced the potential influence of sediment denitrification on water pCO<sub>2</sub> through the removal of fixed nitrogen in the water column and consequent inhibition of primary production (Fennel et al., 2008; Fennel, 2010). This removal was estimated to be of similar magnitude as the lateral nitrogen loads, except for estuaries of the MAB region (Fennel, 2010). It can nonetheless be suggested that the estuarine carbon filter in the South section of COSCAT 827 is an important control factor of the CO<sub>2</sub> sink in the Mid-Atlantic Bight, which is stronger than in any other area along the entire Atlantic coast of the US (Signorini et al., 2013).



376

## 377 4. Conclusions

378 Our data driven spatially and seasonally resolved budget analysis captures the main  
379 characteristics of the air-water CO<sub>2</sub> exchange along the LOAC of COSCAT 827. It evidences  
380 the contrasting dynamics of the North and South section of the study area and an overall  
381 gradual shift from a strong source in small streams oversaturated in CO<sub>2</sub> towards a net sink in  
382 continental shelf waters. Our study reveals that ice and snow cover are important controlling  
383 factors of the seasonal dynamics of CO<sub>2</sub> outgassing in streams and rivers and account for a  
384 large part of the difference between the North and South section. The close simultaneity of the  
385 snow melts on land and of the phytoplankton bloom on the continental shelf leads to opposite  
386 temporal dynamics in FCO<sub>2</sub> in these two compartments of the LOAC. In addition, our results  
387 reveal that estuaries filter significant amounts of terrestrial carbon inputs, thereby influencing  
388 the continental shelf carbon uptake. Although this process likely operates in conjunction with  
389 other regional physical processes, it is proposed that the much stronger estuarine carbon filter  
390 in the South section contributes to a strengthening of the CO<sub>2</sub> sink in the adjacent continental  
391 shelf waters.

392

## 393 Acknowledgements

394 The research leading to these results has received funding from the European Union's  
395 Seventh Framework Program (FP7/2007-2013) under grant agreement no. 283080, project  
396 GEOCARBON. Goulven G. Laruelle is 'Chargé de recherches du F.R.S.-FNRS' at the  
397 Université Libre de Bruxelles. Ronny Lauerwald was funded by the French Agence Nationale  
398 de la Recherche (n° ANR-10-LABX-0018). Jens Hartmann was funded by DFG-project EXC  
399 177. The Surface Ocean CO<sub>2</sub> Atlas (SOCAT) is an international effort, supported by the

International Ocean Carbon Coordination Project (IOCCP), the Surface Ocean Lower  
Atmosphere Study (SOLAS), and the Integrated Marine Biogeochemistry and Ecosystem  
Research program (IMBER), to deliver a uniformly quality-controlled surface ocean CO<sub>2</sub>  
database. The many researchers and funding agencies responsible for the collection of data  
and quality control are thanked for their contributions to SOCAT. This work also used data  
extracted from the SOCAT/MARCATS segmentation (Laruelle et al., 2013), the CCMP wind  
database (Atlas et al., 2010), GLOBALNEWS2 (Mayorga et al., 2010; Hartmann et al., 2009),  
the SRTM water body data set (NASA/NGA, 2003), Hydrosheds 15s routing scheme, the  
average annual runoff data extracted from the UNH/GRDC composites (Fekete et al., 2002),  
the global lake and wetland data base of Lehner and Döll (2004) and mean air temperature  
derived from the worldclim data set of Hijmans et al. (2005).

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**Figure captions:**

Figure 1: Geographic limits of the study area with the location of the riverine (Glorich database, in green; Lauerwald et al., 2013) and continental shelf waters data used for our calculations (SOCAT 2.0 database, in red; Bakker et al., 2014). The location of the estuarine studies used is indicated by purple squares.

Figure 2: Spatial distribution of the CO<sub>2</sub> exchange with the atmosphere in rivers and continental shelf waters aggregated by seasons. The fluxes are net FCO<sub>2</sub> rates averaged over the surface area of each 0.25° cells and a period of 3 months. Positive values correspond to fluxes towards the atmosphere. Winter is defined as January, February and March, Spring as April, May and June and so forth.

Figure 3: Areal-integrated monthly air-water CO<sub>2</sub> flux for rivers and the continental shelf waters in the North section (a), South section (b), and entire study area (c). Positive values correspond to fluxes towards the atmosphere. The boxes inside each panel correspond to the annual carbon budgets for the region including the lateral carbon fluxes at the river-estuary interface, as inorganic (IC) and organic carbon (OC). The values in grey represent the uncertainties of the annual fluxes.

656 **Table 1:** Summary of the data used for the FCO<sub>2</sub> calculations in compartment of the LOAC.

| Compartment | Parameter      | Description  | Source                           | Reference  |
|-------------|----------------|--|----------------------------------|--|
| Rivers      | $pCO_2$        | CO <sub>2</sub> partial pressure                         | GLORICH                          | Hartmann et al., 2014;<br>Lauerwald et al., 2013   |
|             | -              | River network, digital elevation model (DEM)             | Hydrosheds 15s                   | Lehner et al., 2008  |
|             | -              | Runoff   | UNH/GRDC                         | Fekete et al., 2002  |
|             | $T$            | Air-temperature  | -                                | Hijmans et al., 2005   |
| Estuaries   |                | Lake surface area  | Global Lake and Wetland Database | Lehner and Döll, 2004  |
|             | $As$           | Surface Area   | SRTM water body data set         | NASA/NGA, 2003   |
|             | -              | CO <sub>2</sub> exchange rate                            | Average of local estimates       | Raymond et al., 1997;<br>Raymond et al., 2000;<br>Raymond and Hopkinson, 2003; Hunt et al., 2010 |
| Shelves     | $As$           | Surface area   | COSCAT/MARCATS Segmentation      | Laruelle et al., 2013  |
|             | $\Delta pCO_2$ | pCO <sub>2</sub> gradient at the air-water interface     | SOCAT database                   | Bakker et al., 2014  |
|             | $k$            | calculated using wind Speed                              | CCMP database                    | Altas et al., 2011   |
|             | $K'_0$         | Solubility, calculated using salinity, water temperature | SOCAT database                   | Bakker et al., 2014  |

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660 **Table 2:** Surface areas, CO<sub>2</sub> exchange rate with the atmosphere and surface integrated FCO<sub>2</sub> for the North and South sections of COSCAT 827,  
 661 subdivided by river discharge classes and continental shelf water depth intervals.

|  | <b>North</b>                    |                                    |                                     | <b>South</b>                    |                                    |                                     | <b>Total</b>                    |                                    |                                     |
|--|---------------------------------|------------------------------------|-------------------------------------|---------------------------------|------------------------------------|-------------------------------------|---------------------------------|------------------------------------|-------------------------------------|
|  | Surface Area                    | Rate                               | FCO <sub>2</sub>                    | Surface Area                    | Rate                               | FCO <sub>2</sub>                    | Surface Area                    | Rate                               | FCO <sub>2</sub>                    |
|  | 10 <sup>3</sup> km <sup>2</sup> | gCm <sup>-2</sup> yr <sup>-1</sup> | 10 <sup>9</sup> gC yr <sup>-1</sup> | 10 <sup>3</sup> km <sup>2</sup> | gCm <sup>-2</sup> yr <sup>-1</sup> | 10 <sup>9</sup> gC yr <sup>-1</sup> | 10 <sup>3</sup> km <sup>2</sup> | gCm <sup>-2</sup> yr <sup>-1</sup> | 10 <sup>9</sup> gC yr <sup>-1</sup> |
| <b>Rivers</b>  |                                 |                                    |                                     |                                 |                                    |                                     |                                 |                                    |                                     |
| <b>Q1 (Q &lt; 1m s<sup>-1</sup>)</b>                           | 0.14                            | 2893±521                           | 391±70                              | 0.27                            | 1961±353                           | 532±96                              | 0.41                            | 2271±409                           | 924±166                             |
| <b>Q2 (1m s<sup>-1</sup> &lt; Q &lt; 10m s<sup>-1</sup>)</b>   | 0.21                            | 2538±457                           | 525±95                              | 0.32                            | 1570±283                           | 506±91                              | 0.53                            | 1948±351                           | 1032±186                            |
| <b>Q3 (10m s<sup>-1</sup> &lt; Q &lt; 100m s<sup>-1</sup>)</b> | 0.16                            | 1476±267                           | 237±43                              | 0.30                            | 1307±235                           | 392±71                              | 0.46                            | 1366±246                           | 629±113                             |
| <b>Q4 (100m s<sup>-1</sup> &lt; Q)</b>                         | 0.17                            | 891±160                            | 152±27                              | 0.36                            | 729±131                            | 261±47                              | 0.52                            | 781±141                            | 412±74                              |
| <b>Sub-total</b>   | <b>0.67</b>                     | <b>1939±349</b>                    | <b>1305±235</b>                     | <b>1.25</b>                     | <b>1351±243</b>                    | <b>1692±305</b>                     | <b>1.92</b>                     | <b>1557±280</b>                    | <b>2997±539</b>                     |
| <b>Estuaries</b>   | <b>0.53</b>                     | <b>50 ± 31</b>                     | <b>27 ± 19</b>                      | <b>14.51</b>                    | <b>50 ± 31</b>                     | <b>731 ± 453</b>                    | <b>15.04</b>                    | <b>50 ± 31</b>                     | <b>758 ± 469</b>                    |
| <b>Shelf</b>   |                                 |                                    |                                     |                                 |                                    |                                     |                                 |                                    |                                     |
| <b>S1 (depth &lt; 20m)</b>                                     | 11.21                           | 5 ± 1                              | 53 ± 19                             | 24.28                           | -3 ± 1                             | -79 ± 11                            | 35.49                           | -1 ± 1                             | -27 ± 5                             |
| <b>S2 (20m &lt; depth &lt; 50m)</b>                            | 26.25                           | -1 ± 1                             | -35 ± 12                            | 63.88                           | -8 ± 1                             | -521 ± 70                           | 90.13                           | -6 ± 1                             | -556 ± 108                          |
| <b>S3 (50m &lt; depth &lt; 80m)</b>                            | 39.28                           | -3 ± 1                             | -128 ± 45                           | 48.63                           | -7 ± 1                             | -359 ± 126                          | 87.91                           | -6 ± 1                             | -488 ± 95                           |
| <b>S4 (80m &lt; depth &lt; 120m)</b>                           | 60.69                           | -3 ± 1                             | -209 ± 73                           | 25.18                           | -8 ± 1                             | -199 ± 27                           | 85.87                           | -5 ± 1                             | -409 ± 80                           |
| <b>S5 (120m &lt; depth &lt; 150m)</b>                          | 34.73                           | -4 ± 1                             | -151 ± 18                           | 7.63                            | -12 ± 1                            | -91 ± 12                            | 42.36                           | -6 ± 1                             | -242 ± 47                           |
| <b>Sub-total</b>   | <b>172.17</b>                   | <b>-3 ± 1</b>                      | <b>-472±166</b>                     | <b>169.59</b>                   | <b>-7 ± 1</b>                      | <b>-1250±169</b>                    | <b>341.77</b>                   | <b>-5 ± 1</b>                      | <b>-1722±335</b>                    |

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