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Distinguishing between physical and biological controls on the spatial variability of pCO_2: A novel approach using OMP water mass analysis (St. Lawrence, Canada)

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ABSTRACT

Present-day air-sea CO_2 flux estimates in the coastal ocean are subject to large uncertainties due to its heterogeneous nature and concomitant lack of data. Factors controlling the dissolved inorganic carbon (DIC) and CO_2 fluxes vary within and between coastal subsystems, hampering the development of robust upscaling and modeling techniques. By applying a multi-tracer, quantitative water mass analysis, physical and biogeochemical factors can be differentiated. This study adopts an expanded version of optimum multiparameter (OMP) water mass analysis, an inverse modeling technique, to estimate the mixing fractions of predefined source water masses as well as the contribution of biological activity (photosynthesis, respiration) at a given observation point in the surface mixed layer that exchanges CO_2 gas with the atmosphere. We apply the method to hydrographic, nutrient, and inorganic carbon data collected in the Estuary and Gulf of St. Lawrence, the world's largest estuarine system and an excellent analogue of the more general coastal environment. Biological activity is identified as the dominant control on mixed-layer CO_2 partial pressure (pCO_2) dynamics along the St. Lawrence land—ocean continuum, explaining the upstream to downstream shift from pCO_2 supersaturation (net heterotrophy) to pCO_2 undersaturation (net autotrophy). Although mixing of freshwater and seawater along the Estuary is the major contributor to the DIC pool, it contributes little (or negligibly) to the spatial variability of surface-water pCO_2.

1. Introduction

The ocean has absorbed ca. 30% of the total anthropogenic carbon dioxide (CO_2) emitted to the atmosphere from fossil fuel burning and land-use changes since the beginning of the industrial era (Doney et al., 2009), yet accurate quantification of organic and inorganic carbon cycling and fluxes in the coastal ocean — where land, ocean and atmosphere interact — remains challenging. The very large uncertainty associated with present-day air-sea CO_2 flux estimates in coastal waters, including rivers, estuaries, tidal wetlands, and the continental shelf, impedes meaningful predictions of the effects of climate change on future fluxes (Bauer et al., 2013). The coastal ocean occupies only ~7% of the global ocean surface area, but it plays a major role in biogeochemical cycles because it (1) receives massive inputs of terrestrial organic matter and nutrients through continental runoff and groundwater discharge; (2) exchanges matter and energy with the open ocean; and (3) is one of the most geochemically and biologically active areas of the biosphere, accounting for significant fractions of marine primary production (~14 to 30%), organic matter burial (~80%), sedimentary mineralization (~90%), and calcium carbonate deposition (~50%) (Gattuso et al., 1998).

Although the carbon cycle of the coastal ocean is acknowledged to be a major component of the global carbon cycle and budget, it is poorly quantified (Bauer et al., 2013). Constraining the exchanges and fates of different forms of carbon along the land—ocean continuum is so far incomplete, owing to limited data coverage and large physical and biogeochemical variability within and between coastal subsystems (e.g., hydrological and geomorphological differences, differences in the magnitude and stoichiometry of organic matter inputs). Changes in freshwater discharge, coupled with higher-frequency (e.g., diurnal and seasonal) and higher-magnitude (e.g., large excursions of salinity and temperature) natural variability compared to the open ocean, further hamper our current understanding of the factors controlling the fluxes and cycling of organic and inorganic carbon in the coastal ocean (Fassbender et al., 2016). The concentration and speciation of dissolved inorganic carbon (DIC) determine the direction and magnitude of air-sea exchanges of CO_2, with the former being influenced by complex interactions between a number of physical and biogeochemical processes. In the surface mixed layer, the effects of transport processes (circulation, mixing), biological activity (photosynthesis, respiration),

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and gas exchange are particularly important.

To differentiate between the physical and biogeochemical drivers affecting DIC fluxes in the coastal ocean, one must estimate the relative contributions of freshwater and seawater to the observed mixture as well as quantitatively assess the influence of important biogeochemical processes. Optimum multiparameter (OMP) water mass analysis, an inverse modeling technique, is a standard tool in oceanography for the quantitative description of water mass structures. It utilizes the observed fields of hydrographic properties (e.g., temperature, salinity, dissolved oxygen, and nutrients) to resolve the distributions of different water masses in a given region of mixing. An expansion of the method to include Redfield stoichiometry corrects for the non-conservative behavior of dissolved oxygen and nutrients resulting from organic matter remineralization (Karstensen and Tomczak, 1998). Although OMP analysis has been successfully applied at both regional and oceanic scales, it does not usually apply to the sunlit surface mixed layer, where water mass properties are non-conservative and display high seasonal variations due to air-sea interaction and CO_2 uptake by photosynthetic organisms (Poole and Tomczak, 1999).

This paper presents a further extension of the OMP analysis method and its application to the surface mixed layer. By incorporating the apparent oxygen utilization (AOU) to determine the sign convention (+/−) for the Redfield ratios, i.e., whether the stoichiometric ratios reflect net respiration or net photosynthesis, our method accounts for the effects of organic matter remineralization and phytoplankton photosynthesis on the observed tracer fields. In this study, we apply the improved method to hydrographic, nutrient, and inorganic carbon data collected in the Estuary and Gulf of St. Lawrence, the world's largest estuarine system and an excellent analogue of the more general coastal environment. The aim of the analysis is to determine the physically- and biologically-induced changes of DIC and the extent to which they control surface-water CO_2 partial pressure (pCO_2) dynamics along the St. Lawrence land—ocean continuum. Multi-tracer, quantitative water mass analysis, as it is shown here, provides a valuable technique for improved mechanistic descriptions of inorganic carbon cycling processes in the coastal ocean — a task of increasing importance for the development of proper upscaling strategies and for achieving closure on the oceanic and global carbon budgets.

2. Data and methods

2.1. Site description—St. Lawrence Estuary and Gulf

The Estuary and Gulf of St. Lawrence, at the southern limit of the subarctic region in eastern Canada, connects the waters of the Great Lakes, the second largest terrestrial freshwater reservoir in the world, with those of the northwest Atlantic Ocean. Because of its large physical dimensions and unimpeded connection to continental shelf and slope waters, the St. Lawrence Estuary (SLE) is fairly unique in that its character is more oceanic than most estuaries. Beginning at the upstream limit of salt water intrusion near Île d'Orléans (~5 km downstream of Québec City), the SLE stretches 400 km seaward to Pointe-des-Monts where it widens into the Gulf of St. Lawrence (GSL) (El-Sabh and Silverberg, 1990), a marginal sea with an area of 250,000 km^2 whose principal connection to the open shelf is through Cabot Strait (Coote and Yeats, 1979). The largest source of freshwater to the SLE is the St. Lawrence River, the second largest river system in North America. Mean annual discharge of the St. Lawrence River near Québec City is ~10,000 $m^3 s^{-1}$, amounting to about 80% of the total freshwater input to the Estuary (Ingram and El-Sabh, 1990), whereas the freshwater runoff from the Saguenay Fjord and Manicouagan River on the north shore contributes about 10–13% and 9–10%, respectively (Tee, 1990).

Traditionally, the SLE is divided into two segments based on bathymetry and hydrographic features. The Upper St. Lawrence Estuary (USLE) is relatively narrow (2 to 24 km) and mostly shallow (< 30 m) with an uneven, fairly complex bottom topography. Although it displays a strong lateral salinity gradient, its water column ranges from well-mixed to partially stratified. In contrast, the Lower St. Lawrence Estuary (LSLE) is wider (30 to 50 km) and deeper (~300 m) and displays a smoother, less variable bottom topography. The dominant bathymetric feature of the LSLE is the Laurentian Channel (or Trough), a deep, central, U-shaped glaciated valley that extends 1240 km from the eastern Canadian continental shelf break through the GSL and into the LSLE (D'anglejan, 1990). In summertime, the SLE can be described as a three-layer system on the basis of its thermal stratification (Gratton et al., 1988), with (1) a warm and relatively fresh surface layer (0–30 m) flowing out from the St. Lawrence River and Saguenay Fjord (Dufour and Ouellet, 2007), (2) a cold (~0 °C) and salty (S_P = 32 to 33) intermediate layer (30–150 m) formed by advection of the wintertime surface mixed layer from the GSL (Galbraith, 2006), and (3) a warmer (2 to 6 °C) and saltier (S_P = 33 to 35) deep layer (> 150 m), of mixed Atlantic and Labrador shelf waters, flowing sluggishly from Cabot Strait into the Lower Estuary (Saucier et al., 2003; Gilbert et al., 2005). A detailed description of the physical oceanography of the St. Lawrence Estuary is given by Saucier and Chassé (2000) and Simons et al. (2010).

2.2. Sampling and sample analysis

The hydrographic data used in this study were collected during ten cruises aboard the R/V *Coriolis II* in the late spring or early summer between 2003 and 2016. Water sampling was conducted mainly along the central axis of the St. Lawrence Estuary and the Laurentian Channel. The sampling locations are shown in Fig. 1. Water samples were taken from discrete depths throughout the water column with 12 12L Niskin bottles mounted on a rosette sampler fitted with a SeaBird SBE 911 conductivity-temperature-depth (CTD) probe as well as a SBE-43 oxygen probe. Although the probes were calibrated by the manufacturer during the winter months preceding the cruises, discrete samples were taken from the Niskin bottles for laboratory measurements of practical salinity (S_P; Guildline Autosal 8400 salinometer calibrated with IAPSO standard seawater) and dissolved oxygen (DO; Winkler titration as described by Grasshoff et al., 1999) and the CTD records re-calibrated post-cruise. In addition, field and laboratory measurements were made of the following physical—chemical properties: pH_{NBS} and/or pH_T, total alkalinity (TAlk), soluble reactive phosphate (SRP), nitrate (NO_3), dissolved silicate (DSi), and the stable oxygen isotopic composition of water ($\delta^{18}O_{water}$).

Water samples for isotopic analysis were taken up into 13 mL screw-top plastic test tubes. Samples were analyzed for the stable oxygen isotope ratio $^{18}O/^{16}O$ using the CO_2 equilibration method (Epstein and Mayeda, 1953) on a Micromass AquaPrep system and the CO_2 analyzed on a Micromass IsoPrime universal triple collector isotope ratio mass spectrometer in dual inlet mode at the Université du Québec à Montréal (Light Stable Isotope Geochemistry Laboratory). Data were normalized against two internal reference waters, both calibrated against V-SMOW and V-SLAP. The oxygen isotope measurements are reported on the δ-scale in ‰ relative to Vienna Standard Mean Ocean Water (V-SMOW): $\delta^{18}O = ((^{18}O/^{16}O)_{sample} / (^{18}O/^{16}O)_{VSMOW} - 1) \times 1000$. Based on replicate analyses of the samples, the average relative standard deviation of the measurements was better than 0.05‰.

Water samples were also analyzed for pH, TAlk, SRP, NO_3, and DSi. A detailed description of the analytical methods is found in Dinauer and Mucci (2017). For the purpose of applying a quantitative water mass analysis to the dataset, in situ temperature was converted to potential temperature and all concentrations were reported in the same units (i.e., μmol kg^{-1}). The potential temperature (θ) along with in situ density (ρ) and pressure (p) were calculated using the Gibbs Seawater (GSW) Oceanographic Toolbox (MATLAB-version 3.05; McDougall and Barker, 2011) of the Thermodynamic Equation of Seawater – 2010 (TEOS-10). The ρ values (kg m^{-3}) were used in the conversion of units.