CO₂ Input Dynamics and Air–Sea Exchange in a Large New England Estuary

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Abstract Repeated surveys of the Kennebec estuary, a macrotidal river estuary in Maine, USA, between 2004 and 2008 found spatial and temporal variability both in sources of carbon dioxide (CO₂) to the estuary and the air–sea flux of estuary CO₂. On an annual basis, the surveyed area of the Kennebec estuary had an area-weighted average partial pressure of CO₂ (pCO₂) of 559 μ atm. The area-weighted average CO₂ flux to the atmosphere was 3.54 mol C m⁻² year⁻¹. Overall, the Kennebec estuary was an annual source of 7.2×10^7 mol CO₂ to the atmosphere. Distinct seasonality in estuarine pCO₂ was observed, with shifts in the seasonal pattern evident between lower and higher salinities. Fluxes of CO₂ from the estuary were elevated following two summertime storms, and inputs of riverine CO₂ outweighed internal estuarine CO₂ inputs in nearly all months. River and estuarine inputs of CO₂ represented 68 and 32 % of the total CO₂ contributions to the estuary, respectively. This study examines the variability of CO₂ in a large New England estuary, and highlights the comparatively high contribution of CO₂ from riverine sources.

Keywords Estuary · River · Carbon dioxide · Dissolved inorganic carbon

Introduction

The flux of water through estuaries represents a relatively small portion of the global water budget, and the surface area of estuaries is small relative to the surface area of the coastal

ocean over the continental shelves. However, estuaries play a disproportionate role in the transport and transformation of carbon, both organic and inorganic, from land to sea (Borges 2005; Gattuso et al. 1998). Through coupled biological and physical processes, estuaries are generally strong sources of carbon dioxide (CO₂) release to the atmosphere (Borges 2005; Cai et al. 2006; Laruelle et al. 2010; Borges and Abril 2011). The partial pressure of CO₂ (pCO₂) in estuaries, while usually above atmospheric levels, can range over several orders of magnitude. In an extreme example, pCO₂ in the Indian Chilka lagoon ranged from 83 to 6,522 μ atm (Gupta et al. 2008). Some recent work has suggested that the release of CO₂ from estuaries is high enough in magnitude to offset the uptake of CO₂ over the continental shelves (Cai 2011).

The typical high rates of estuarine outgassing of excess CO₂ are sustained by organic and inorganic carbon from two sources: river and groundwater inputs and inputs from the surrounding estuary and coastal wetlands and marshes. Estuaries receive large loads of allochthonous carbon from rivers, and can modify these inputs as they are mixed through the estuaries and into the coastal ocean (Salisbury et al. 2009). At the same time, estuaries can also provide large inputs of autochthonous carbon through in-stream heterotrophy and lateral inputs from tidal marshes (Cai 2011). While river inputs alone could support the observed levels of estuary outgassing for many estuaries, recent work in southeastern American estuaries suggests that the majority of CO₂ comes from estuarine sources such as tidal floodplains and salt marshes instead of riverine sources (Jiang et al. 2008; Cai 2011). The same authors suggest that riverine inputs of organic carbon are remineralized in the estuarine plume or coastal waters, areas outside of the estuary itself. However, work in several smaller Northeastern American river estuaries showed that riverine sources of carbon dioxide were dominant, while the estuaries were smaller sources or even sometimes sinks of CO₂ (Salisbury et al. 2008; Hunt et al. 2010).

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Here, we present a study of the large, river-dominated macrotidal Kennebec estuary in Maine, which was surveyed 44 times from 2004 through 2008. This time-series of data allows us to examine the atmospheric CO₂ exchange of the Kennebec estuary over monthly to annual time scales, and also allows us to examine the temporal variability of internal and riverine sources of CO₂.

Methods

Study Site The Kennebec estuary is located along the central Maine (USA) coast (Fig. 1). It is supplied with freshwater from two large adjacent rivers: the more western Androscoggin and the eastern Kennebec. The combined Kennebec and Androscoggin river system, which drains 24,389 km², represents one of the largest freshwater inputs to the Gulf of Maine system. Both the Androscoggin and Kennebec rivers are overwhelmingly forested (88.3 %), with a relatively small fraction of urban area (2.4 %), agricultural land (5.8 %), wetlands (3.4 %), and range (0.1 %, NOAA-CCMA). The geology of the river basins is characterized by till-covered bedrock with narrow valleys of stratified drift,

with some fine-grained marine deposits in the lower watersheds. The rivers join at Merrymeeting Bay to form the Kennebec estuary, which extends about 35 km to the coast. The Kennebec's tidal prism—the volume of water flowing into and out of the estuary on each tide—is large compared to inflows of Androscoggin and Kennebec river water (1×10^8 m³, or 1600 % of the average river discharge), and ebb currents are stronger than flood currents, especially during the spring freshet period (FitzGerald et al. 2000). During periods of low river flow the salinity =2 isohaline can be located 30 km or more upstream of the estuary mouth—at Bath or even further north (Fig. 1)—while high river flows during the spring freshet can push the same isohaline completely out of the estuary and onto the adjacent shelf (Kistner and Pettigrew 2001). The residence time of water in the Kennebec estuary is estimated as 4 days (NOAA-CCMA). River end-member data were bucket samples collected from the center of bridges in Brunswick and Richmond, Maine for the Androscoggin and Kennebec rivers, respectively.

Sampling and Analytical Methods Surveys of the Kennebec estuary were conducted on a roughly monthly basis between September 24, 2004, and June 10, 2008, aboard the UNH research vessel *R/V Gulf Challenger*. A total of 44 surveys were conducted, with 22 of these on consecutive days while the ship docked overnight at Bath. Tidal state during the surveys covered the range from low tide to high, with most surveys conducted at mid-tide. Some single-day surveys turned around after sampling at Fiddler's Reach (Fig. 1). A shipboard flow-through system was used to continuously measure physical and chemical properties of surface water. Temperature and salinity were determined by a Sea-bird SBE-45 thermosalinograph, while dissolved oxygen was measured with a Sea-bird SBE-43 sensor (Sea-bird electronics, Bellevue, WA). A temperature offset was observed between the sea surface temperature measured by the continuous-flow SBE-45 and that measured at the water surface by a SBE-37 thermosalinograph deployed as part of a profiling package. For each estuary survey, the average temperature offset between the continuous-flow and profiler sea-surface temperature was removed, to bring the continuous-flow temperature into agreement with in situ sea surface temperature. The SBE-45 thermosalinograph and SBE-43 oxygen sensor received annual manufacturer calibrations, but were not calibrated in the field against discrete measurements. The oxygen percent saturation was calculated according to Sea-bird Electronics Application Note 64 (Sea-bird Electronics 2013).

Flow to the shipboard flow-through system was also pumped to an equilibrator, similar to that described by Wanninkhof and Thoning (1993), but consisting of three Plexiglas chambers instead of a single chamber. Equilibrated air was drawn out of the third chamber, while ambient air was drawn into the first chamber and passed through the second

Fig. 1 Map of the study site, located along the central Maine (USA) coast. The *inset map* shows the approximate location of the Kennebec estuary within the continental USA. River end-member sampling sites at Brunswick and Richmond are shown, as are sampling sites at Fort Popham and Fiddler's Reach. The ten *shaded regions* outlined in *black* show the subregions of the estuary used for area-averaging calculations

and third chambers, equilibrating with the pumped water supply at each step. Equilibrated air was drawn at 100 mL/min through tubing containing a Nafion selectively permeable membrane (Perma Pure, Toms River NJ) with a counter-flowing stream of dry nitrogen, which dried the sample gas stream of water vapor. Due to the short run of tubing between the water source for both the continuous-flow system and the gas equilibrator, no water temperature difference was observed between that measured by the continuous-flow SBE-45 and the outflow from the equilibrator (measured with a handheld meter—YSI Yellow Springs, Ohio—manufacturer accuracy ± 0.2 °C). Temperature from the continuous-flow SBE-45 was used in sea-surface temperature corrections during the calculation of $p\text{CO}_2$. After drying, the sample was pumped to a non-dispersive infrared gas analyzer (Li-cor, LI-6262 or LI-840), which measured the molar fraction of carbon dioxide ($x\text{CO}_2$) of the sample stream. The Li-cor was calibrated several times each survey with pure nitrogen (0 ppm CO_2 molar fraction) and one span tank. Over the study period we employed a succession of span tanks containing a gas mixture with CO_2 molar fraction between 819 and 851 ppm (Scott-Marin, Riverside, CA). Corrections of the data for water vapor pressure and sea surface temperature and conversion from $x\text{CO}_2$ to the partial pressure of carbon dioxide ($p\text{CO}_2$) were carried out according to standard methods (Dickson et al. 2007). Atmospheric $p\text{CO}_2$ was periodically measured as well while the ship was underway. Ambient air was drawn from the ship's bow through a length of tubing and pumped into the non-dispersive infrared gas analyzer described above. The estimated uncertainty of $p\text{CO}_2$ measurements is ± 3 μatm . All $p\text{CO}_2$ data have been banked with the Carbon Dioxide Information Analysis Center (http://cdiac.ornl.gov/oceans/Coastal/unh_ts.html).

Discrete samples were collected from Niskin bottles in the Kennebec estuary, and transferred to sample bottles through silicone tubing to prevent bubbling. At the end-member sites, a bucket was lowered from a bridge upstream from each river's most downstream dam, thoroughly soaked in the river water, and raised slowly to avoid promoting gas exchange. Samples for pH and total alkalinity (TALK) were transferred without bubbling into 60-ml glass BOD bottles with greased stoppers. Beginning in 2006, dissolved inorganic carbon (DIC) was sampled from the same bottles. These were filled to leave less than 1 % headspace in the bottle, preserved with 0.1 ml of saturated mercuric chloride solution, and immediately cooled. Samples for TALK and DIC were generally stored for several weeks before analysis, allowing for settling of particulate material, with the supernatant sample drawn for analysis. The in situ temperature of bucket samples was measured with the handheld YSI meter. DIC was measured first from each sample bottle, followed sequentially by pH and TALK. Dissolved organic carbon (DOC) samples were collected according

to JGOFS protocols (JGOFS 1996) into acid-washed high-density polyethylene bottles, and measured using a Shimadzu high temperature catalytic oxidation analyzer with chemiluminescent detection.

DIC of unfiltered water was determined using an automated analyzer built by Apollo SciTech (Bogart, GA). Immediately after opening the sample bottle, a digital syringe withdrew a small amount of sample (0.5 mL), acidified it with 10 % phosphoric acid and subsequently measured the evolved CO_2 with a Li-Cor 6262 non-dispersive infrared gas analyzer (similar to the method described by Cai and Wang 1998). Certified seawater reference materials from Dr. A. Dickson were used to determine DIC concentration by preparing a calibration curve covering the range of DIC from 200 to 2000 $\mu\text{mol kg}^{-1}$ (Dickson et al. 2003), with a resulting precision ranging from 0.05 to 0.5 % (or 0.1–10 $\mu\text{mol kg}^{-1}$), with an average of ~ 0.1 % (2 $\mu\text{mol kg}^{-1}$).

TALK and pH of unfiltered water were simultaneously measured by the same instrument, and thus pH and TALK measurements are both based on the same pH electrode. The pH electrode used in the TALK titration (Orion 3-Star, Thermo Fisher Inc.) was calibrated using three low ionic strength pH buffers certified on the U.S. National Bureau of Standards (NBS) scale to ± 0.01 , and the initial reading before the addition of acid titrant was taken as the sample pH_{NBS} (pH on the NBS scale, hereafter simply referred to as pH).

TALK was measured by Gran titration (Gran 1952) with 0.1 N HCl using an automated titrator. This method adds an initial aliquot of acid to the sample in an open cell, generally lowering the sample pH_{NBS} below 3, and then adds subsequent aliquots of titrant until the pH_{NBS} changes linearly with the volume of acid added. The TALK endpoint is then obtained from linear regression of the change of pH_{NBS} against the volume of acid added, according to a Gran transformation:

$$\text{GF} = (v + V_o)/V_o \times 10^{-\text{pH}} \quad (1)$$

where GF is the resulting Gran Function, v is the volume of acid added to the sample, V_o is the original sample volume, and pH is the pH value (in this case, on the NBS scale) measured after each successive addition of volume v . Multiple analyses of the Dickson reference material resulted in a calculated precision of this method of about 0.1 % (or $\sim \pm 2$ $\mu\text{mol kg}^{-1}$). The accuracy of the TALK automated system, also calibrated with multiple batches of the Dickson CRM as discussed above, was ± 3 –4 $\mu\text{mol kg}^{-1}$.

Non-Carbonate Alkalinity Correction Recent work in New England rivers, including the Androscoggin and Kennebec rivers, indicates that non-carbonate species comprise a

substantial portion of TALK (Hunt et al. 2011). These non-carbonate species can include inorganic nutrients, metal complexes, and weak organic acids. Inclusion of these non-carbonate species in calculations to derive carbonate parameters can result in the overestimation of $p\text{CO}_2$ and CO_2 concentration. To account for this, we followed the methodology of Hunt et al. (2011) to derive $\text{TALK}_{\text{DIC-pH}}$ from DIC and pH_{NBS} measurements, with the resulting difference between measured TALK and $\text{TALK}_{\text{DIC-pH}}$ representing non-carbonate alkalinity (NC-Alk). All TALK data presented in this work have been corrected for NC-Alk at levels that will be discussed later.

Air–Water CO_2 Flux Estimation The air–water flux of CO_2 (F , in millimole per square meter per day) was calculated using the equation:

$$F = k \times K_0 \times (p\text{CO}_{2\text{water}} - p\text{CO}_{2\text{air}}) \quad (2)$$

where k (centimeters per hour) represents the piston velocity of CO_2 , K_0 (in mole per cubic meter per atmosphere) is the solubility coefficient of CO_2 at measured salinity and temperature, and $p\text{CO}_{2\text{water}}$ and $p\text{CO}_{2\text{air}}$ (in microatmosphere) are the measured partial pressures of CO_2 in water and air, respectively. In this work, the term $p\text{CO}_2$ will refer to $p\text{CO}_{2\text{water}}$, unless otherwise indicated. Positive values of F indicate outgassing of CO_2 from the water to the atmosphere. Due to a lack of appropriate equipment, the piston velocity was estimated from wind speed instead of measured directly. There has been much discussion of the best method to estimate the piston velocity of CO_2 in estuaries, which is heavily dependent upon wind, but may also be affected by wave slope, surface films, rain, bottom-generated turbulence, surface turbulence, turbidity, and fetch limitation (Raymond and Cole 2001; Zappa et al. 2007; Borges et al. 2004a; Abril et al. 2009). A paper by Ho et al. (2011) examined the estimation of air–water gas exchange in the Hudson River, another northeastern USA estuary. The authors compared observed gas exchange rates measured using a dual tracer technique with those estimated from four wind-only k_{600} parameterizations: Raymond and Cole (2001), Borges et al. (2004b), Ho et al. (2006), and Jiang et al. (2008), finding that the Ho et al. (2006) parameterization most closely matched observed gas exchanges during two years of the study, while the Raymond and Cole (2001) parameterization most closely matched observations in a third year. The Jiang et al. (2008) and Borges et al. (2004b) parameterizations always overestimated the observed exchanges.

While discussion of gas flux results from the Kennebec estuary using the four parameterizations mentioned above will be presented later, fluxes in this work were estimated using the

“tracers only” relationship from Raymond and Cole (2001) to calculate k_{600} :

$$k_{600} = 1.58e^{0.30 \times U} \quad (3)$$

where k_{600} (in centimeter per hour) is the piston velocity at the Schmidt number of 600 and U is the wind speed (in meter per second). Hourly wind data were obtained from the Brunswick Air Station, just west of Bath.

To calculate area-averaged CO_2 fluxes, the Kennebec estuary was broken into 10 segments (Fig. 1), although the upper segments were not accessible during some surveys, and are thus only included when data were available. The area-averaged flux was calculated from each segment as:

$$F_{\text{area-average}} = \frac{\sum F_i \times S_i}{\sum S_i} \quad (4)$$

where $F_{\text{area-average}}$ is the area-averaged flux of all segments surveyed, F_i is the average of all fluxes within segment i , and S_i is the surface area of segment i .

Temperature-Normalized $p\text{CO}_2$ Influences upon estuarine $p\text{CO}_2$ include factors both physical (water temperature, horizontal and vertical mixing) and biological (primary production and respiration). To examine the impact of seasonal water temperature changes and to contrast the influence of temperature to the aggregate influence of other factors, we calculated a temperature-normalized $p\text{CO}_2$ at a temperature of 12 °C ($p\text{CO}_{2\text{obs}@12^\circ\text{C}}$, Eq. 5), which is the mean area-averaged temperature measured in the Kennebec estuary during the surveys, according to the method of Takahashi et al. (2002):

$$p\text{CO}_{2\text{obs}@12^\circ\text{C}} = p\text{CO}_{2\text{obs}} \times \exp[0.0423(T_{\text{mean}} - T_{\text{obs}})] \quad (5)$$

where $p\text{CO}_{2\text{obs}}$ is the $p\text{CO}_2$ at in situ temperature, T_{mean} is the mean area-averaged temperature (12 °C), and T_{obs} is the in situ temperature in degrees Celsius.

Changes in $p\text{CO}_{2\text{obs}@12^\circ\text{C}}$ represent the combined influences of horizontal mixing, vertical mixing, and biology if the water temperature remained at a constant 12 °C. In contrast, to calculate the effect of only temperature upon the mean annual $p\text{CO}_2$, we again followed the method of Takahashi et al. (2002):

$$p\text{CO}_{2\text{mean}@T_{\text{obs}}} = p\text{CO}_{2\text{mean}} \times \exp[0.0423(T_{\text{obs}} - T_{\text{mean}})] \quad (6)$$

where $p\text{CO}_{2\text{mean}@T_{\text{obs}}}$ is the area-averaged mean $p\text{CO}_2$ at in situ temperature for each point during each survey and $p\text{CO}_{2\text{mean}}$ is the mean area-averaged $p\text{CO}_2$.

Results

Hydrographic Conditions Combined discharge data from the Androscoggin (USGS gage 1059000) and Kennebec (USGS gage 01049265) rivers is shown in Fig. 2, together with daily precipitation from the Portland International Jetport, located 50 km to the southwest of Bath. Generally, flow in the rivers is highest during two periods of the year: springtime, when snowmelt dominates the hydrograph, and fall, when rainfall from seasonal storms generates large amounts of rain and subsequent runoff, as seen in October and November 2005 and October 2006. Both the Androscoggin and Kennebec rivers trace their sources to large reservoirs, and are dammed at multiple points. These multiple impoundments increase the residence time of water in the rivers, and smooth out the hydrograph during larger precipitation events (Hunt et al. 2005). Surveys of Kennebec estuary $p\text{CO}_2$ were conducted over a wide range of river flow conditions (Fig. 2). The highest-flow survey was conducted October 18, 2005, during a fall storm, while the lowest-flow survey was conducted July 19, 2007. The average combined river flow on days when surveys were conducted ($485 \text{ m}^3 \text{ s}^{-1}$) was lower than the average of all daily river flow measurements taken over the time period of this study ($566 \text{ m}^3 \text{ s}^{-1}$). For 2005, 2006 and 2007, the 3 years of the survey period with relatively complete temporal coverage (at least 11 transects per year), the average annual combined discharge of the rivers was 713, 588, and $501 \text{ m}^3 \text{ s}^{-1}$, respectively. Long-term flow data from the USGS indicates that the combined average daily discharge is $459 \text{ m}^3 \text{ s}^{-1}$.

Salinity at the top of the estuary transect (Figs. 1 and 3) was below 1.0 for 32 of the 44 surveys. Months where salinity at the uppermost transect reach was higher than 1.0 were typically the low-flow summer and fall months of August, September, and October (Table 2). In general, however, the

Fig. 2 Combined average daily discharge from the USGS gages 1059000 (Androscoggin river) and 01049265 (Kennebec river, solid line). Filled circles indicate dates of Kennebec estuary surveys, while filled bars show NOAA National Climate Data Center daily precipitation from the Portland International Jetport, 50 km southwest of Bath

surveys were able to satisfactorily cover the full salinity gradient, perhaps with the exception of October 18, 2005, when salinity at Fort Popham was only about 15. Annual, area-averaged salinity for the whole Kennebec estuary was lower in 2005 (11.4) than in 2006 (12.7) or 2007 (17.9, $\sigma=5.9$, 3.3, and 6.2 respectively), which agrees with the annual differences in combined river discharge.

Water temperature at the upper transect reach was more variable than at Fort Popham (Fig. 3). During the winter months, water temperature was lower at the uppermost transect reach than Fort Popham, while during the summer months, the uppermost transect reach was warmer than Fort Popham. For some time in the spring (usually April or May) and in the fall (usually October), the water temperature was essentially the same along the entire transect.

River Chemistry The Kennebec and Androscoggin rivers, like many rivers in the New England region, have lower TAlk and are more acidic (Table 1) than other rivers around the USA (Hunt et al. 2011; Salisbury et al. 2008). On average, half of the alkalinity leaving the rivers is composed of non-carbonate species (Hunt et al. 2011). This may be explained in part by the presence of organic acids as a component of DOC (Eshleman and Hemond 1985; Cai et al. 1998), although borate, inorganic nutrients, and metal complexes may be contributors to NC-Alk as well. Concentrations of DOC in the Androscoggin and Kennebec rivers are of the same order of magnitude as TAlk (Table 1), and the presence of organic acids in the DOC pool would contribute to both the lower pH and higher levels of NC-Alk. DIC was also relatively low for northeastern rivers (Raymond et al. 2004), and $p\text{CO}_2$ derived from DIC and pH river end-member measurements was both always above atmospheric levels and always above the highest $p\text{CO}_2$ measured in the Kennebec estuary (Table 2).

Kennebec Estuary $p\text{CO}_2$ In general, Kennebec estuary $p\text{CO}_2$ decreased from the river to the ocean, and followed a seasonal pattern of lower $p\text{CO}_2$ in the winter and spring and higher $p\text{CO}_2$ in the summer and fall (Fig. 3). For the period of this study, the area-averaged $p\text{CO}_2$ in the Kennebec estuary was $558 \mu\text{atm}$ ($\sigma=167 \mu\text{atm}$), while the average observed $p\text{CO}_{2\text{air}}$ was $383 \mu\text{atm}$ ($\sigma=8 \mu\text{atm}$). The lowest measured $p\text{CO}_2$ was $203 \mu\text{atm}$ (at salinity 9.78) in April 2008, while the highest $p\text{CO}_2$ was $1,771 \mu\text{atm}$ (at salinity 1.17) in June 2005. While an overall seasonal pattern of $p\text{CO}_2$ was observed, storm events had a dramatic effect on $p\text{CO}_2$ on shorter time scales. The two surveys with highest $p\text{CO}_2$ (Fig. 3) were conducted on June 29, 2005, ($1,725 \mu\text{atm}$) and June 28, 2006 ($1,771 \mu\text{atm}$). River discharge on the days of these surveys was not especially high (Fig. 2), but both surveys followed very large storm events which released large amounts of river water into the estuary. A survey of three New Hampshire estuaries located approximately 150 km from the Kennebec

Fig. 3 Variations of Kennebec estuary salinity, water temperature, $p\text{CO}_2$ and CO_2 flux over the sampling period from the estuary mouth (43.74° latitude at Fort Popham) to Fiddler's Reach (43.88° latitude). Circles on the x-axis mark dates when the estuary was surveyed. Bilinear interpolation was used between surveys

estuary, which also experienced the same large June 2006 storm event, showed elevated $p\text{CO}_2$ as well (Hunt et al. 2010). Storm events, especially during the warmer months when the ground is not frozen, can presumably flush out soil and groundwater enriched in CO_2 (Paquay et al. 2007) as well as large amounts of labile particulate and dissolved organic matter, which could support bacterial respiration and CO_2 production in the estuary (Abril et al. 2000; Abril and Borges 2004). The elevated $p\text{CO}_2$ observed in the June 2005 and 2006 surveys was more than twice the $p\text{CO}_2$ levels in

June 2007 (highest $p\text{CO}_2$: 780 μatm) and June 2008 (highest $p\text{CO}_2$: 604 μatm) when river discharge was at typical low-flow summer levels (Fig. 2).

Data from each survey was binned by salinity and averaged every five salinity units (Fig. 4). The lowest salinity bin (salinity 0–5) never had $p\text{CO}_2$ below atmospheric levels, and $p\text{CO}_2$ ranged as high as 1,711 μatm (in June 2005) for this bin, with a mean $p\text{CO}_2$ of 888 μatm ($\sigma=304$ μatm). At the high-salinity end of the estuary (25–30 salinity), the $p\text{CO}_2$ ranged from 199 to 608 μatm , with a mean $p\text{CO}_2$ of 392 μatm ($\sigma=78$ μatm). The bin with $p\text{CO}_2$ most closely resembling the whole-estuary area-averaged $p\text{CO}_2$ was salinity 10–15, as illustrated by the difference between the binned $p\text{CO}_2$ and the estuary-average $p\text{CO}_2$ (Figs. 4 and 5). It is noteworthy that the difference in $p\text{CO}_2$ between salinity bins was always highest between the 0–5 and 5–10 salinity bins, except in the month of September when the 0–5 salinity $p\text{CO}_2$ values decreased from 1,130 to 891 μatm . This suggests that the largest changes in CO_2 along the salinity gradient occur at low salinities, when river water is initially mixed with water from the estuary.

To examine the annual pattern of CO_2 in the Kennebec estuary, we constructed a yearly climatology. We combined the area-averaged $p\text{CO}_2$ values into monthly averages, repeated the annual cycle of monthly values three times (to obtain reasonable boundary values for January and December), ran a 60-day Matlab smooth function over the resulting timeseries

Table 1 Summary of constituent concentrations from the Androscoggin and Kennebec rivers. The (stdev) value after each average value represents one standard deviation around the mean. Values of $p\text{CO}_2$ were computed from pH_{NBS} and DIC measurements, together with in situ temperature, while NC-Alk % was determined by the difference between measured TAlk and $\text{TAlk}_{\text{DIC-pH}_{\text{NBS}}}$ estimated from DIC- pH_{NBS} pairs, as described in Hunt et al. (2011). A regression between NC-Alk% and pH_{NBS} yielded the relationship $\text{NC-Alk}\% = -0.31 \times \text{pH}_{\text{NBS}} + 2.45$ ($R^2=0.70$)

	Range	Average (stdev)
TAlk ($\mu\text{mol kg}^{-1}$)	87–510	284 (85)
NC-Alk %	30–90 %	40 % (11 %)
pH_{NBS}	4.9–7.0	6.6 (0.38)
DIC ($\mu\text{mol kg}^{-1}$)	110–557	311 (93)
$p\text{CO}_2$ (μatm)	1,231–6,703	3,064 (1,410)
DOC ($\mu\text{mol kg}^{-1}$)	120–626	412 (119)

Table 2 Summary of monthly Kennebec estuary physical observations, with *n* indicating the number of cruises performed in each month. Discharge data were summed from the USGS gages 1049265 and 1059000 to estimate total freshwater input to the estuary. Ranges of

observed data are shown for estuary water temperature, salinity, pCO₂ and CO₂ flux, with the area-averaged mean of each range shown in parentheses

	<i>n</i>	Average 10-day antecedent discharge (m ³ s ⁻¹)	Estuary surface water temperature (°C)	Estuary surface salinity	Estuary pCO ₂ (µatm)	Estuary CO ₂ flux (mmol m ⁻² day ⁻¹)
	No.	Average	Range (area average)	Range (area average)	Range (area average)	Range (area average)
Jan	1	630	0.6–2.9 (1.3)	0.4–21.8 (6.7)	341–744 (535)	–4.0–34.8 (13.0)
Feb	4	422	0.3–4.2 (2.3)	0.4–31.8 (14.3)	286–1,018 (417)	–16.0–45.6 (0.7)
Mar	2	516	2.6–4.4 (3.6)	0.6–24.8 (12.6)	284–623 (351.0)	–9.6–13.2 (–1.1)
Apr	4	1,094	3.7–9.8 (6.5)	0.0–26.5 (6.5)	203–813 (503)	–57.4–105.3 (20.5)
May	5	1,101	7.6–17.5 (11.8)	0.1–29.9 (8.8)	289–1,126 (515)	–21.7–88.2 (9.4)
Jun	5	462	11.9–24.0 (18.1)	0.1–29.2 (12.0)	312–1,771 (668)	–4.6–77.6 (10.6)
Jul	3	283	12.8–26.9 (19.5)	0.9–30.0 (14.6)	355–1,295 (687)	–1.4–68.2 (12.0)
Aug	6	206	13.9–24.7 (18.9)	2.1–29.5 (17.2)	443–1,339 (721)	1.0–56.5 (12.0)
Sep	5	225	13.8–21.3 (17.7)	1.1–30.7 (16.0)	428–1,127 (652)	2.4–53.3 (9.0)
Oct	1	1,449	12.3–14.1 (13.1)	1.7–15.2 (6.1)	372–1,082 (739)	–0.3–19.4 (8.9)
Nov	3	595	6.7–10.0 (8.6)	0.6–31.5 (12.6)	320–750 (495)	–2.5–16.6 (5.4)
Dec	5	464	–0.1–9.0 (4.2)	0.2–31.0 (14.6)	342–825 (419)	–3.6–43.2 (2.7)

(‘smooth’, The MathWorks, Inc., Natick MA), then took the middle year as the final climatology (Fig. 5). The resulting line shows a clear drop in pCO₂ during the late winter and early spring (February and March), a steady rise in pCO₂ through the spring and summer, more or less constant pCO₂ over the fall months, then a sharp decline in pCO₂ through November and December. Opposing trends were seen in the saturation of dissolved oxygen (Fig. 5), which rose through the winter to a peak in April (a month later than the lowest pCO₂ in March), then dropped through the late spring and summer to a low in September (a month before the peak pCO₂ in October). This seasonal coupling between pCO₂ and dissolved oxygen

indicates that biological activity contributes noticeably to overall pCO₂ in the Kennebec estuary. The cycle of pCO₂ in Fig. 5 also bears a strong resemblance to the annual cycle observed at inner shelf coastal stations in the Gulf of Maine (Vandemark et al. 2011), as well as the BATS site near Bermuda (Takahashi et al. 2002) and a Spanish coastal site (Ribas-Ribas et al. 2011).

The solubility of CO₂ decreases with increasing water temperature (Carroll et al. 1991), and in the New England region warmer water temperatures in the summer and fall increase pCO₂, while cooler temperatures in the winter and spring months drive pCO₂ lower. If water temperature was the sole control upon pCO₂, the pCO_{2,obs}@12 °C should be fairly constant over the course of the year. We repeated the above process to construct salinity-binned climatologies of temperature-normalized pCO₂ (pCO_{2,obs}@12 °C, Fig. 6). The annual patterns of pCO_{2,obs}@12 °C reflect how the observed pCO₂ would change if the water temperature in the estuary were held at a constant 12 °C, and differ from those of pCO₂ at in situ temperature (Fig. 4). Seasonal patterns of pCO_{2,obs}@12 °C are markedly different from the cycle of pCO₂ at in situ temperature, and differ between salinity bins. The highest pCO_{2,obs}@12 °C was generally in winter (December or January), followed by a steady decrease similar to that seen at in situ temperature. For the lowest-salinity bin, this decrease continued through the spring and summer, to an annual minimum in September. For all other salinity bins the annual pCO_{2,obs}@12 °C minimum was much earlier—in April or May. Mid-salinity bins (salinities 5–10, 10–15, 15–20, and 20–25) all had a secondary pCO_{2,obs}@12 °C maximum in August. While pCO_{2,obs}@12 °C rose sharply between September and October in the 0–5 salinity bin, pCO_{2,obs}@12 °C dropped in the same time period in the

Fig. 4 Monthly, area-averaged pCO₂ values by salinity bin. Error bars represent one standard deviation of the mean binned measurements for each month. Salinity bins 20–25 and 25–30 had no pCO₂ measurements in October

Fig. 5 Monthly mean values of area-averaged $p\text{CO}_2$ (open circles), climatology of $p\text{CO}_2$ after 60-day smooth (solid line), monthly mean of area-averaged oxygen saturation (plus signs), and climatology of the percent saturation of oxygen (dashed line), constructed using the same smoothing method as area-averaged $p\text{CO}_2$

higher-salinity bins. In all salinity bins, $p\text{CO}_{2\text{obs}}@12^\circ\text{C}$ rose through late fall back to the annual winter maximum. The observed difference between the climatologies of $p\text{CO}_2$ and

$p\text{CO}_{2\text{obs}}@12^\circ\text{C}$ indicate that temperature variability is one important process controlling seasonal $p\text{CO}_2$ changes. In addition to temperature, $p\text{CO}_2$ is influenced by the seasonality of

Fig. 6 Salinity-binned climatologies of temperature-normalized observed $p\text{CO}_2$ at 12°C ($p\text{CO}_{2\text{obs}}@12^\circ\text{C}$, solid line) and the mean, area-averaged $p\text{CO}_2$ at in situ temperature through the year ($p\text{CO}_{2\text{mean}}@T_{\text{obs}}$, dashed line). The mean $p\text{CO}_2$ values for each bin were 857, 619, 471, 424, 407, and 396 μatm for salinities 0–5, 5–10, 10–15, 15–20, 20–25, and 25–30, respectively. The dashed vertical arrow in the salinity 0–5 panel shows the magnitude of $\Delta p\text{CO}_{2\text{temp}}$, while the solid vertical arrow in the same panel shows $\Delta p\text{CO}_{2\text{bio}}$

river/ocean mixing in the estuary and net community productivity.

Air-Water CO_2 Fluxes Estimates of k_{600} in the Kennebec estuary using the Raymond and Cole (2001) parameterization resulted in area-averaged CO_2 fluxes (average = $8.6 \text{ mmol m}^{-2} \text{ day}^{-1}$) that were higher than those calculated according to Ho et al. (2004, average = $6.3 \text{ mmol m}^{-2} \text{ day}^{-1}$), but lower than those from Jiang et al. (2008), average = $12.4 \text{ mmol m}^{-2} \text{ day}^{-1}$ or Borges et al. (2004b), average = 16.1 . Paired t tests showed that the average fluxes from all four parameterizations were significantly different ($p < 0.01$). As no site-specific parameterization of gas exchange is available for the Kennebec estuary, we chose to use the Raymond and Cole (2001) parameterization, as it demonstrated reasonable results in the Hudson estuary (Ho et al. 2011), and represents a flux estimate bracketed by other published estimates. Thus, all further CO_2 fluxes presented in this work were calculated using the Raymond and Cole (2001) parameterization.

Area-averaged fluxes in the Kennebec estuary were mostly positive in sign, meaning that CO_2 was released from the estuary to the atmosphere. The Kennebec estuary released CO_2 to the atmosphere in 38 of the 44 surveys performed. There was no significant correlation observed between tidal height and area-averaged CO_2 flux ($r^2 = 0.0024$), indicating that other factors controlled CO_2 fluxes more than the tide. The overall area-averaged CO_2 flux from the estuary was $8.6 \text{ mmol m}^{-2} \text{ day}^{-1}$ ($\sigma = 8.9 \text{ mmol m}^{-2} \text{ day}^{-1}$). The flux of CO_2 decreased in late winter (February) to a minimum in early spring (March), then increased rapidly to an annual peak in April, before leveling out and gradually decreasing through the summer and fall to another minimum in December. The lowest value of area-averaged CO_2 flux was on February 23, 2006 ($-11.5 \text{ mmol m}^{-2} \text{ day}^{-1}$), while the largest area-averaged flux was on April 19, 2005 ($31.7 \text{ mmol m}^{-2} \text{ day}^{-1}$). When the daily fluxes provided by the climatology are summed and multiplied by the total surface area of the estuary ($2 \times 10^7 \text{ m}^2$), the result is an annual flux of $7.2 \times 10^7 \text{ mol C}$, or 3,160 metric tons of CO_2 .

Temperature played a role in suppressing the flux of CO_2 on an annual basis, as the average CO_2 flux estimated at a constant temperature of 12°C ($11.4 \text{ mmol m}^{-2} \text{ day}^{-1}$) was well above the annual average flux calculated at in situ temperature ($8.6 \text{ mmol m}^{-2} \text{ day}^{-1}$). However, the large CO_2 flux decrease between January and March (Fig. 7), and the subsequent CO_2 flux increase from March to April, appear to be caused by factors apart from temperature, as does the CO_2 flux increase later in the year (November and December).

Salinity-binned fluxes (Fig. 8) exhibited similar monthly trends, apart from the 0–5 salinity data. This lowest salinity bin mirrors the monthly pattern of overall CO_2 flux in the estuary depicted in Fig. 7, with a decline in CO_2 flux in March

Fig. 7 Monthly mean values of CO_2 flux at in situ temperature (open circles) and temperature-normalized CO_2 flux (at 12°C , triangles). Error bars represent one standard deviation of the mean fluxes for each month

and a sharp peak in CO_2 flux in April. Despite the same wind data being used in all salinity bins, the higher salinity bins show the spring decline a month later, in April, followed by a steady increase in CO_2 flux until August or September. It is apparent from the binned flux data that the 0–5 salinity bin exerts a strong influence on overall fluxes from the estuary. The area of the estuary represented by the 0–5 salinity bin, calculated assuming a consistent average channel width and averaging the latitudinal distribution of salinity, varies widely due to seasonal and episodic changes in river discharge (Fig. 2), ranging from 0 to 60 % of the estuary area, with a mean of 18 % ($\sigma = 17\%$) of the estuary area. Thus, especially in the spring months of March and April when river discharge is high and estuary salinity is low, CO_2 fluxes from the 0–5 salinity bin may play a disproportionately large role in the overall flux of CO_2 from the estuary.

Fig. 8 Monthly area-averaged CO_2 fluxes, grouped into salinity bins. Error bars represent one standard deviation of the mean binned measurements for each month

Discussion

The $p\text{CO}_2$ in estuaries is controlled by inputs of CO_2 from rivers, the ocean, and within the estuary itself, together with water temperature, horizontal and vertical mixing, and net community productivity. In the following sections, we will discuss the effects of changing water temperature and inputs of CO_2 from river and within-estuary sources, and compare results from the Kennebec estuary to some other estuaries. It is important to note that the data presented here, particularly CO_2 fluxes, represent the surveyed portion of the Kennebec estuary, not the entire estuary. Merrymeeting Bay (Fig. 1) is the upper tidal portion of the estuary, with a surface area more than twice that of the lower portion of the estuary we surveyed. So, although the surveyed portion of the estuary represented almost the entire salinity gradient (Table 1), a rigorous definition such as that of Perillo (1995), “a semi-enclosed coastal body of water that extends to the effective limit of tidal influence” would include Merrymeeting Bay and some lower portion of the Androscoggin and Kennebec rivers; thus total fluxes, as well as average $p\text{CO}_2$ and area-specific CO_2 fluxes (i.e., in millimole per square meter per day), are underestimates. Indeed, since the Merrymeeting Bay portion of the estuary would fall into the 0–5 salinity bin—the bin with highest $p\text{CO}_2$ —estimates of CO_2 flux from the whole Kennebec estuary, including Merrymeeting Bay, are likely to increase by a factor of three or more.

Changes in water temperature in a northern latitude estuary occur on a seasonal basis, resulting in higher $p\text{CO}_2$ in the summer and lower $p\text{CO}_2$ in the winter. The temperature of the Androscoggin and Kennebec rivers varies from a low of nearly 0 °C to a high of over 25 °C, while the ocean end-member water temperature ranges from 1.4 to 16 °C. The timing of maximum and minimum temperatures also differs between the rivers and ocean end-member. River temperature reaches its minimum in January and February, while the surface ocean temperature minimum is later, in April. Additionally, the rivers warm up faster in the spring, so that by May the rivers are warmer than the ocean end-member. Maximum river water temperature is in July or August, while the maximum ocean end-member temperature occurs in September or October. The Androscoggin and Kennebec rivers spend much of the winter covered in ice, usually from December until spring snowmelt in March or April. When the spring snowpack melts, there is a large pulse of very cold freshwater discharged to the estuary, which lowers water temperature and $p\text{CO}_2$ and also delivers inorganic nutrients (Oczkowski et al. 2006) and presumably DOC to the estuary.

Temperature affected both $p\text{CO}_2$ and CO_2 flux in the Kennebec estuary, as seen by the differences between temperature-normalized $p\text{CO}_2$ and CO_2 flux and the observed patterns at in situ temperatures (Figs. 4, 5, and 6). While the observed $p\text{CO}_2$ is lowest in March or April, the lowest

$p\text{CO}_{2\text{obs}}@12\text{ °C}$ occurs in May or later in all salinity bins. This suggests that cold inputs of river water in the spring act to lower the $p\text{CO}_2$ in the estuary. This can also be seen in Fig. 4, since the lowest $p\text{CO}_2$ in the 0–5 salinity bin at in situ temperature occurred in March, while the lowest $p\text{CO}_2$ in the other salinity bins was observed later, in April. Increasing water temperature in the estuary from March through July was also responsible for the rise of $p\text{CO}_2$ through the same time period. The yearly progression of temperature-normalized $p\text{CO}_2$ shows that seasonal water temperature changes do not explain all observed variability of Kennebec estuary $p\text{CO}_2$. Temperature-normalized $p\text{CO}_2$ decreased during the spring as in situ $p\text{CO}_2$ also decreased, but while in situ $p\text{CO}_2$ rose from May to August due to increasing water temperatures, $p\text{CO}_{2\text{obs}}@12\text{ °C}$ in the 0–5 salinity bin continued decreasing. This suggests two possible scenarios: one, that decreasing river flow through the spring into the summer resulted in lower inputs of terrestrial DIC and organic carbon to the estuary, or two, that in situ primary production at low salinities through the spring into mid-summer drew down the $p\text{CO}_2$, while increased respiration through late summer and the fall raised the $p\text{CO}_2$. Patterns of $p\text{CO}_{2\text{obs}}@12\text{ °C}$ in the other salinity bins more closely resembled those at in situ temperature, but with the annual $p\text{CO}_2$ minimum shifted a month or two later. Takahashi et al. (2002) calculated the effect of biology on surface water $p\text{CO}_2$ as:

$$\Delta p\text{CO}_{2\text{bio}} = (p\text{CO}_{2\text{obs}}@12\text{ °C})_{\text{max}} - (p\text{CO}_{2\text{obs}}@12\text{ °C})_{\text{min}} \quad (7)$$

where $(p\text{CO}_{2\text{obs}}@12\text{ °C})_{\text{max}}$ and $(p\text{CO}_{2\text{obs}}@12\text{ °C})_{\text{min}}$ are the maximum and minimum values of $p\text{CO}_{2\text{obs}}@12\text{ °C}$ in the time-series, respectively. Correspondingly, we calculated the effect of changing temperature on the mean surface $p\text{CO}_2$ value in each salinity bin ($p\text{CO}_{2\text{mean}}@T_{\text{obs}}$) according to Takahashi et al. (2002):

$$\Delta p\text{CO}_{2\text{temp}} = (p\text{CO}_{2\text{mean}}@T_{\text{obs}})_{\text{max}} - (p\text{CO}_{2\text{mean}}@T_{\text{obs}})_{\text{min}} \quad (8)$$

The value of $\Delta p\text{CO}_{2\text{bio}}$ also includes the effects of horizontal and vertical mixing for the Kennebec estuary. We believe the effects of vertical mixing to be relatively small in the Kennebec estuary; however, horizontal mixing appears to contribute to $\Delta p\text{CO}_{2\text{bio}}$, especially in the 0–5 salinity bin as the $p\text{CO}_{2\text{obs}}@12\text{ °C}$ continues to decrease as river inputs decrease through the late spring into the summer and fall. The difference between $\Delta p\text{CO}_{2\text{temp}}$ and $\Delta p\text{CO}_{2\text{bio}}$ ($T-B$, Table 3), together with the ratio of $\Delta p\text{CO}_{2\text{temp}}/\Delta p\text{CO}_{2\text{bio}}$ (T/B , Table 3) yield the relative importance of temperature and biology/mixing on the Kennebec estuary as a whole; in this case temperature changes have about twice the effect of biology/mixing on $p\text{CO}_2$ for salinities 0–15 ($T/B \sim 2$, Table 3), while for salinities greater

Table 3 Values of $\Delta p\text{CO}_{2\text{temp}}$ and $\Delta p\text{CO}_{2\text{bio}}$ for each salinity bin, as well as calculated values of $T-B$ and T/B

	Salinity 0–5	Salinity 5–10	Salinity 10–15	Salinity 15–20	Salinity 20–25	Salinity 25–30
$\Delta p\text{CO}_{2\text{temp}}$ (μatm)	875	559	371	283	229	174
$\Delta p\text{CO}_{2\text{bio}}$ (μatm)	460	265	198	173	166	181
$T-B$ (μatm)	415	294	173	110	63	–7
T/B	1.9	2.1	1.9	1.6	1.4	1.0

than 15 the T/B drops steadily to a value of 1.0. Thus, while both $\Delta p\text{CO}_{2\text{temp}}$ and $\Delta p\text{CO}_{2\text{bio}}$ decrease with increasing salinity, $\Delta p\text{CO}_{2\text{temp}}$ decreases more. This decreasing influence of temperature with increasing salinity is reasonable, as the range of river water temperatures is greater than that at the ocean end-member. The $\Delta p\text{CO}_{2\text{bio}}$ decreases with increasing salinity to a minimum in the 20–25 salinity bin, perhaps indicating a decreasing influence of river CO_2 input to salinity 20, followed by an enhanced ocean biologic CO_2 signal at salinities greater than 25 due to upwelling or some other factor. In Takahashi et al. (2002), the temperature effect in the Gulf of Maine exceeded the effect of biology, indicating that the effects of biology/mixing at the mouth of the Kennebec estuary are stronger than those generally observed in the Gulf of Maine.

For 2005, 2006, and 2007, the 3 years with the best survey coverage, the mean area-averaged CO_2 fluxes were 13.9, 5.4, and 5.8 $\text{mmol m}^{-2} \text{day}^{-1}$, respectively ($\sigma=9$, 9 and 7 $\text{mmol m}^{-2} \text{day}^{-1}$, respectively). The year-to-year variation in annual mean CO_2 flux may be partly explained by river discharge. Annual river discharge in 2005 was the highest measured for the Kennebec river in 24 years, and the second-highest in the Androscoggin river for 82 years of record. Elevated river discharge delivers large fluxes of CO_2 and DOC to estuaries, resulting in elevated CO_2 fluxes from the estuary (e.g., Hunt et al. 2011). Additionally, elevated river flow in 2005 reduced the overall surface salinity in the estuary, and since lower salinity is generally associated with high $p\text{CO}_2$ in the Kennebec estuary, the higher proportion of low-salinity waters in the estuary resulted in elevated fluxes of CO_2 from the estuary as a whole.

The average annual flux of CO_2 to the atmosphere from the Kennebec estuary was 3.5 $\text{mol m}^{-2} \text{year}^{-1}$ ($\sigma=1.0 \text{ mol m}^{-2} \text{year}^{-1}$) over the study period. A review of estuary CO_2 fluxes (Borges and Abril 2011) provides a reference for CO_2 fluxes from estuaries similar to the Kennebec, with the range of fluxes from “tidal systems and embayments” reported as 1.1–76 $\text{mol m}^{-2} \text{year}^{-1}$. This places the CO_2 flux from the Kennebec estuary on the low end of the range. The Kennebec flux is consistent with data from five other estuaries in the region, which only range from 1.1 to 4.0 $\text{mol m}^{-2} \text{year}^{-1}$ (Raymond and Hopkinson 2003; Hunt et al. 2010). One

possible explanation as to why the Kennebec and other New England estuaries seem to have lower $p\text{CO}_2$ and CO_2 fluxes than their global counterparts is a lack of CO_2 input from the estuaries themselves. Some estuaries have been shown to enhance CO_2 levels (Cai 2011; Gupta et al. 2009; Jiang et al. 2008; Raymond et al. 2000). In fact, some researchers have observed that the majority of CO_2 in the estuary is produced internally from the lateral transport of DIC produced by microbial organic matter respiration in tidal marshes or mangroves which fringe the estuary (Cai 2011; Cai and Wang 1998, 2004), although CO_2 production via respiration in the water column or sediments is also a potential contributor (Raymond et al. 2000). The Kennebec estuary does have some tidal marshes, particularly around smaller tributaries, but overall they are not a large presence along the steep, rocky shoreline. In other New England estuaries the majority of CO_2 came from the rivers, and during the spring (and fall to a lesser extent) the estuarine areas removed CO_2 (Salisbury et al. 2008; Hunt et al. 2010). Another possible explanation for the seeming lower CO_2 fluxes from the Kennebec estuary as compared to other global estuaries is that fluxes from Merrymeeting Bay, which covers a large amount of area at the freshwater end of the estuary, were not measured and would presumably reflect high $p\text{CO}_2$ from river inputs, raising the overall CO_2 flux from the estuary as a whole.

To examine the inputs of CO_2 from river and estuary sources, we followed the approach of Jiang et al. (2008), who partitioned dissolved CO_2 concentrations into ocean, river and estuary sources according to conservatively mixed salinity. Specifically, the CO_2 contribution from the estuary ($\Delta[\text{CO}_2]_{\text{estuary}}$) to in situ estuarine dissolved CO_2 ($[\text{CO}_2]_i$) is calculated as the difference between $[\text{CO}_2]_i$ and the CO_2 concentration if the ocean and river end-members mix conservatively ($[\text{CO}_2]_{\text{mixing w/R}}$). The CO_2 concentration of river input ($\Delta[\text{CO}_2]_{\text{river}}$) was calculated as:

$$\Delta[\text{CO}_2]_{\text{river}} = [\text{CO}_2]_{\text{mixing w/R}} - [\text{CO}_2]_{\text{mixing w/O}} \quad (9)$$

where $[\text{CO}_2]_{\text{mixing w/R}}$ is the CO_2 concentration if the ocean and river end-members mix conservatively, and $[\text{CO}_2]_{\text{mixing w/O}}$ is the CO_2 concentration if the ocean end-member is diluted by fresh water with a CO_2 of zero. Conservative mixing of TALK and DIC (calculated from either TALK and pH or TALK and $p\text{CO}_2$, since DIC was not measured in 2004 and 2005) was used to calculate the mixing curves. Observed oceanic concentrations of DIC and TALK were conservative with salinity, and there was no evidence of a seasonal change in oceanic DIC or TALK concentration with respect to salinity. Inputs from the river end-members were controlled by river flow, with the highest fluxes of TALK and DIC observed during spring snowmelt and storms in the late fall (Fig. 2).

The results of these analyses showed that both the river and estuary made positive contributions to CO_2 in the Kennebec estuary in all months (Fig. 9). The river was generally the dominant source of CO_2 to the estuary- the only month that the estuary input of CO_2 exceeded that of the river was June (56 % of CO_2 was from estuary). Overall, the monthly estuary contribution of CO_2 ranged from 14 to 56 %, with an average contribution of 33 % ($\sigma=12$ %). On an annual basis, the average contributions of the Kennebec estuary to CO_2 were indistinguishable at 36, 32 and 38 % in 2005, 2006, and 2007, respectively ($\sigma=38, 41, 47$ %, respectively). Both the estuary and river contributed the most CO_2 in 2005 (14.4 and $8.2 \mu\text{mol L}^{-1}$, respectively), and the least CO_2 in 2007 (6.6 and $4.1 \mu\text{mol L}^{-1}$, respectively). This is in contrast to estuaries in the Southeastern USA, such as the river-dominated Satilla (Cai and Wang 1998) and Altamaha (Jiang et al. 2008) river estuaries and the marsh-dominated Sapelo and Doboy sounds (Jiang et al. 2008). In all these Southeastern systems, a seasonal pattern of increased marsh influence has been discussed, from low marsh inputs in spring, increasing inputs through summer into fall and early winter, then decreasing inputs through winter back into spring (Cai 2011). However, the input of CO_2 from the Kennebec estuary does not appear to show a seasonal progression that would be associated with the growth and die-off of marsh plants.

Our observations in the Kennebec estuary suggest a system whose main CO_2 source is the degassing of river-borne DIC, with in-channel heterotrophy being a secondary input, and marsh inputs representing a small contributor of CO_2 . A study of 11 European and American estuaries calculated the median contribution of riverine DIC to estuary CO_2 degassing at 10 % of total CO_2 release, with heterotrophic activity accounting for the remaining 90 % of CO_2 release, and riverine contributions increasing with decreasing estuary residence time (Borges et al. 2006). This seems consistent with our observations in the Kennebec estuary, as the Kennebec residence time is quite short (4 days, NOAA-CCMA) and the riverine CO_2 contribution is relatively high as discussed above.

The balance of river and marsh DIC contributions to global estuaries remains unclear. Coastal marshes are generally found in northern temperate areas from about 30°N to 65°N , with mangroves becoming dominant south of 30°N (Ibanez et al. 2012), although the seagrasses which typically dominate marsh vegetation can also be found throughout the tropics (UNEP-WCMC 2005). Overall, seagrass and salt marsh together cover an order of magnitude more area than mangroves (158×10^6 and 15×10^6 ha, respectively, Duarte et al. 2008). There are large areas of the global coastline, notably the western African and South American coasts and higher-latitude coasts, which do not support documented marsh or mangrove areas (UNEP-WCMC 2005). Additionally, marsh habitat is being lost at a rapid pace- estimated to be up to 2 % per year- with over 30 % of total habitat lost since the 1940s (Duarte et al. 2008). As discussed above, CO_2 release from numerous estuaries has been shown to be marsh-dominated; however, we speculate that higher-latitude temperate areas such as the Kennebec estuary may be more river-influenced, presenting a scaling challenge to integrating studies of individual estuaries into a global whole. Finally, as marsh areas continue to decline, riverine inputs of DIC could begin to dominate in more systems.

Conclusions

The seasonal cycle of Kennebec estuary pCO_2 displayed a pattern of decreased pCO_2 in late winter and early spring, coincident with colder water temperatures and the annual spring phytoplankton bloom, followed by increasing pCO_2 through late spring and summer, then decreasing pCO_2 through the fall and early winter. The Kennebec estuary was a net source of CO_2 to the atmosphere, and monthly fluxes of CO_2 from the Kennebec estuary were positive except for the month of March as the spring bloom drew down CO_2 . Warmer water temperatures in New England promote increased pCO_2 in the summer and fall months, while cooler temperatures lead

Fig. 9 Inputs of dissolved CO_2 , normalized to 12°C and area-averaged, from river (dark bars) and estuary sources (open bars)

to decreased $p\text{CO}_2$ in the winter and spring. The yearly progression of temperature-normalized $p\text{CO}_2$ showed that water temperature was not the only factor controlling Kennebec estuary $p\text{CO}_2$, as $p\text{CO}_{2\text{obs}}@12^\circ\text{C}$ decreased during the spring as did in situ $p\text{CO}_2$, but unlike in situ $p\text{CO}_2$ continued decreasing into the late spring or even summer, well past the time when in situ $p\text{CO}_2$ was rising due to increasing water temperatures. Overall, temperature changes accounted for more of the $p\text{CO}_2$ variability than biological activity and mixing. The balance between the influences of biology and mixing is not clear, but both appear to be important processes in the Kennebec estuary. Storm events, which generated large amounts of rainfall and subsequent river discharge to the estuary, were shown to produce elevated $p\text{CO}_2$ in the estuary in June in two consecutive years, and these events may affect overall annual rates of CO_2 efflux from estuaries. River discharge also appears to influence the CO_2 flux from the estuary on an annual scale. The highest annual average flux of CO_2 from the Kennebec estuary to the atmosphere was in 2005, the year with the highest annual river discharge and lowest annual average salinity. While both the estuary and river contributed to overall estuary CO_2 , contributions from the river were twice the magnitude of those from the estuary. The monthly estuary contribution of CO_2 ranged from 14 to 56 %, with an average contribution of 33 %. There was no discernible seasonality in estuary or river contributions to overall estuary CO_2 . Future work should extend the findings presented here to the coastal ocean, and examine how inorganic and organic carbon releases from the Kennebec estuary spread into the coastal Gulf of Maine, as well as the persistence and fate of these fluxes.

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