Estuaries and Coasts
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Contrasting Carbon Dioxide Inputs and Exchange in Three Adjacent New England Estuaries

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Abstract Four surveys of the adjacent Cocheco, Bellamy, and Oyster estuaries reveal spatial heterogeneity with respect both to river-born carbon dioxide (CO_2) fluxes and CO_2 exchange with the atmosphere (−17 to 51 mmol m^{-2}day^{-1}), a finding partially explained by CO_2 inputs from contributing watersheds. Nonuniform nutrient and organic carbon loading from upstream rivers and within the estuaries is considered as a mechanism resulting in the variability between estuaries. Conditions during the surveys included spring river runoff and phytoplankton blooms, drought with baseline river flow, and a historic flood which led to a large CO_2 release to the atmosphere. This study highlights the variability of CO_2 transport and release found between proximate estuaries over a wide range of flow conditions.

Keywords Inorganic carbon · Macro-tidal estuary · Carbon dioxide · Flood

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Introduction

Estuaries are commonly described as being heterotrophic, where community respiration exceeds gross primary production, and thus estuaries are generally cited as net sources of CO_2 to the atmosphere (Borges 2005). Some estuaries have aquatic partial pressure of carbon dioxide (pCO_2) higher than atmospheric levels by an order of magnitude, including the Pearl River estuary in China (2,000–10,000 µatm, Zhai et al. 2005) and the Scheldt estuary in the Netherlands/Belgium (125–9,425 µatm, Borges et al. 2006). However, other estuaries, including the Scheldt, the York River estuary (Raymond et al. 2000), and the marine-dominated region of the Elbe estuary (Brasse et al. 2002) have been shown to occasionally have sub-atmospheric pCO_2 levels and may act as moderate sinks of atmospheric CO_2 over time scales of weeks to months.

Net ecosystem metabolism is controlled by physical factors (temperature, light limitation, stratification, residence time), and inputs of organic matter and nutrients. Very high pCO_2 levels, such as those documented in the Pearl and Scheldt estuaries, have been attributed to the bacterial respiration of inorganic and organic carbon, much of which comes from human pollution, since both these estuaries drain heavily developed watersheds. By contrast, low or subatmospheric pCO_2 is attributed to primary production by phytoplankton, both in relatively pristine watersheds like that of the York River and even in highly developed watersheds such as the Elbe River, where remineralization of organic matter is outweighed by nutrient-enhanced productivity. However, varying inputs of organic carbon and inorganic nutrients affect community metabolism in different ways (Hitchcock et al. 2010), and the net effect of these inputs upon CO_2 remains unclear.

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The influence of storms and river discharge dynamics upon carbon dioxide in estuaries could represent an increasingly important influence upon carbon exports, as global warming has been predicted to lead to an accelerated hydrologic cycle (Douville et al. 2002, Labat et al. 2004). In New England (USA), increased precipitation, earlier snowmelt, and extreme weather and discharge events are predicted (e.g., Hurtt et al. 2001; Hodgkins et al. 2003). In the York River (Raymond et al. 2000), higher discharge in the winter and spring coincide with minimum pCO_2 levels. High flushing rates of the soil and groundwater pools following heavy rains in the Wailuku River of Hawaii promoted increased pCO_2, but a flood event in the neighboring Wailoa River produced lowered pCO_2, probably due to the input of low-alkalinity freshwater (Paquay et al. 2007). The five European rivers which empty into the Scheldt estuary also offer similar contrasts: the Scheldt, Dender and Nete rivers all showed at least an occasional rise in pCO_2 during flood events, while the Zenne river showed a decrease in pCO_2 (Abril et al. 2000). The response of river pCO_2 to flooding varies according to, among other factors, the balance of entrainment of organic carbon from floodplains and upstream areas (Richey et al. 2002) against the effects of dilution (Koné et al. 2009).

Here, we present a study of three adjacent New England estuaries which drain similar (in terms of land use, geology, climate, and population) watersheds but receive varying nutrient and carbon inputs. The examination of these estuaries provides an opportunity to examine the influence of these inputs upon estuary CO_2 in several systems as well as the impact of a flooding event.

Methods

Study Site The Cocheco, Bellamy, and Oyster estuaries empty into the Great Bay, which lies primarily in Strafford, Rockingham, and Carroll counties in New Hampshire, with the northern end of the Salmon Falls River drainage basin extending into York County in southwestern Maine (Fig. 1). Elevation in the Great Bay watershed ranges from sea level to approximately 300 m with most of the area located within the flat-lying coastal plain. The Great Bay covers a surface area of 44 km^2 enclosed by 230 km of shoreline, with generally steep banks and narrow salt marshes, and the contributing watershed geology is mostly metamorphosed sedimentary rocks overlain with glacial deposits of till, sand and gravel, and glacio-marine clay. This region is characterized by strong seasonal variations, with warm summers and cold winters, where precipitation in the form of snow is held above ground until temperatures warm, usually resulting in a hydrographically dominant spring runoff period. Land-use statistics (Oczkowski 2002) for the three estuary watersheds are relatively similar (Table 1), with the exception of the Oyster watershed population density, which is higher due to the presence of the University of New Hampshire campus.

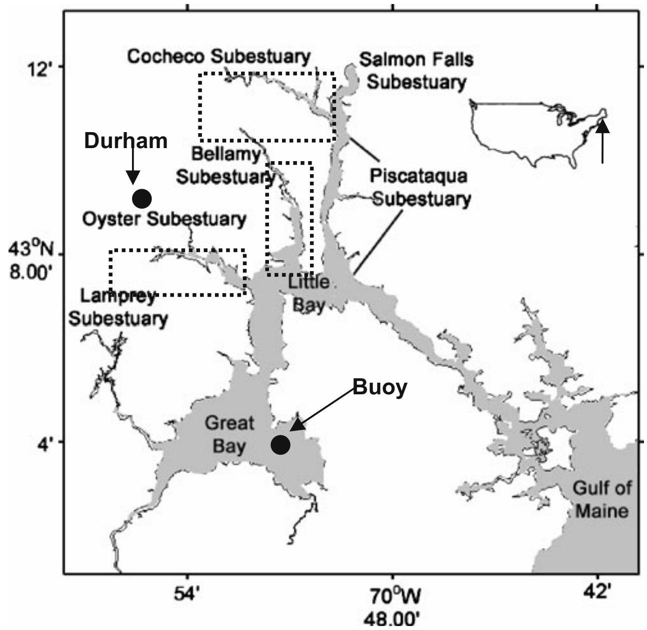

Fig. 1 Map of the study site, located in the southeastern corner of New Hampshire, USA, with the Salmon Falls River in Maine. The inset map and *arrow* (*upper right*) show the approximate location of the Great Bay within the continental USA. *Dashed rectangles* show the area boundaries used to subset data from individual estuaries. *Solid circles* note the locations of wind measurement stations

For this study, we defined each estuary as the area from a river's dammed outflow downstream to the meeting of the estuary with the wider Great Bay. The upstream extent of the estuaries shown in Fig. 1 represents the tidal portion of each estuary—each is dammed above the extent shown. Henceforth, we will refer to the area above the dam as a river, and the area from below the dam to the confluence with Great Bay as an estuary. Seven estuaries drain into Great Bay, three of which were surveyed for this work. These are the Cocheco, Bellamy, and Oyster estuaries. Below their confluence, the combined Cocheco and Salmon Falls estuaries are conventionally renamed as the Piscataqua, but for the purposes of this study we will refer to the Piscataqua and Cocheco estuaries simply as the Cocheco estuary.

The Cocheco River supplies 21% of the freshwater to Great Bay, while the Bellamy (2.2%) and Oyster (1.7%) rivers are relatively minor contributors. Nutrient inputs from the three rivers have been shown to be heterogeneous (Table 1), as the Cocheco River expresses higher concentrations of inorganic nitrogen and phosphorous (Jones 2000; Oczkowski 2002). Several municipal wastewater

Table 1 Summary of basin statistics for rivers described in this work

Basin	Lat, Lon of mouth	Basin size (km^2)	Urban (%)	Agricultural (%)	Forested (%)	Wetlands (%)	Cleared (%)	Population Density (people km^{-2})	Average DIN ($\mu molL^{-1}$)	Average PO_4^{3-} ($\mu molL^{-1}$)
Bellamy	43.13°N 70.85°W	6,183	8	3	74	6	9	85	9.2	0.26
Cocheco	43.12°N 70.82°W	42,562	12	3	71	5	9	93	42.0	0.85
Oyster	43.12°N 70.87°W	7,811	8	3	75	4	9	158	18.1	0.40

Excerpted with permission from Oczkowski (2002). DIN and $PO4^{3-}$ values are averages of spring, summer, fall, and winter values reported in Oczkowski (2002)

treatment facilities (WWTFs) discharge directly to Cocheco River, while the Cocheco estuary receives direct discharge from one WWTF. A similar facility located in the Oyster estuary discharges treated waste only to the tidal estuary waters, bypassing the river. The Bellamy River and estuary do not receive any WWTF input (Table 2). Thus, the Cocheco River is a high-nutrient, WWTF-influenced river, while the Oyster and Bellamy are presumably lower-nutrient rivers (Oczkowski 2002). Total nutrient inputs to the Cocheco estuary (river and direct-to-estuary) are highest, those to the Oyster estuary are lower, and the Bellamy estuary received no WWTF inputs (Table 2).

The estuarine water column is well mixed due to strong tidal action and shallow depths. Residence times have not been estimated for the estuaries discussed here, but data for average freshwater input and freshwater volume (Table 2) yield short freshwater replacement times (Trowbridge 2007). Bilgili et al. (2005) estimated a residence time of 13.1 days for a water parcel entering the Cocheco estuary, and residence times of 20.4 and 15.7 days for water parcels from Great and Little Bays, respectively (Fig. 1).

Sampling and Analytical Methods

Four surveys of the estuaries were conducted in October 2005 and April, June and October 2006 (referred to as Oct05, Apr06, Jun06, and Oct06) aboard a small research vessel. A shipboard flow-through system was used to continuously measure physical and chemical properties of surface water. Water was pumped from a seacock located at the stern at a depth of 0.5 m. Temperature and salinity were determined by a Sea-bird (Bellevue, WA) SBE-45 thermosalinograph. In addition, a debubbled line supplied water to a WetStar fluorometer for chlorophyll fluorescence (f-chl, WetLabs, Philomath OR).

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 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. After drying, the sample was pumped to a nondispersive infrared gas analyzer (Li-cor, LI-6262 or LI-840), which measured the molar fraction of carbon dioxide (xCO_2) of the sample stream. The Li-cor was calibrated several times per day with pure nitrogen (0 ppm CO_2 molar fraction) and a gas mixture with CO_2 molar fraction of 832 ppm (Scott-Marin, Riverside, CA). Corrections of the data for water vapor pressure and sea surface temperature and conversion from xCO_2 to the partial pressure of carbon dioxide (pCO_2) were carried out according to standard methods (Dickson et al. 2007). Atmospheric pCO_2 was periodically measured as well while the ship

Table 2 Hydrologic characteristics of the Cocheco, Bellamy, and Oyster estuaries

Estuary	Estimated estuary surface area (km^3)	Mean depth (m)	Range of tidal amplitude (m)	Freshwater replacement time (days)	Mean river Q (m^3s^{-1})	WWTF permitted discharge (m^3s^{-1})	Estuary freshwater volume (m^3)
Cocheco	4.1	1–2.6	2.2–3.3	4.9	8.6	0.22	3,652,900
Bellamy	1.4	1.0–1.6	1.7–2.4	6.6	1.3	0	756,200
Oyster	1.1	1.5	1.8–2.2	8.0	0.9	.06	658,100

was underway. Ambient air was drawn from the ship's bow through a length of tubing and pumped into the nondispersive infrared gas analyzer described above. All pCO_2 data have been banked with the Carbon Dioxide Information Analysis Center (http://cdiac.ornl.gov/oceans/Coastal/unh_ts.html).

Total alkalinity (TA) of unfiltered water was measured by end-point titration with 0.1 N HCl to pH4.5 using an automated titrator (reproducibility ±2–4 μmol/kg TA). The pH electrode was calibrated using a range of 3 pH buffers on the US National Bureau of Standards scale (now known as the US National Institute of Standards and Technology). Certified reference materials from Dr. A. Dickson were used to ensure the accuracy of TA determination (Dickson et al. 2003). TA, pH and inorganic carbon dissociation constants (Millero et al. 2006) were used as inputs to the CO2SYS program (Lewis and Wallace 1998) to calculate dissolved inorganic carbon (DIC) at the river endmembers. Ocean DIC endmembers were calculated from CO2SYS using the measured TA, pCO_2, salinity and temperature at the highest salinity of each survey. Discrete nutrient samples (nitrate, nitrite, ammonium, phosphate) were taken periodically, preserved with chloroform and frozen, and analyzed using a Smartchem automated analyzer (Westco Scientific) by standard colorimetric methods (Strickland and Parsons 1972). Dissolved organic carbon (DOC) samples were collected according to JGOFS protocols (JGOFS 1996) and measured using a Shimadzu high-temperature catalytic oxidation analyzer with chemiluminescent detection.

Additional discrete endmember water samples from contributing rivers were collected for TA/pH, DOC, and nutrient analysis using buckets lowered from bridges, located a short distance upstream of each river's most downstream dam. Temperature was measured at the time of collection using a handheld digital thermometer.

Air–water CO_2 flux estimation The air–water flux of CO_2 (F, mmol $m^{-2}day^{-1}$) was calculated using the equation:

$$F = k^*K_0^*(pCO_{2water} - pCO_{2air}) \quad (1)$$

Where k (cm h^{-1}) represents the piston velocity of CO_2, K_0 (mol $m^{-3}atm^{-1}$) is the solubility coefficient of CO_2 at measured salinity and temperature, and pCO_{2water} and pCO_{2air} (μatm) are the measured partial pressures of CO_2 in water and air, respectively. Positive values of F indicate outgassing of CO_2 from the water to the atmosphere.

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. 2004; Abril et al. 2009). For the purpose of this paper, the “tracers only” relationship from Raymond and Cole (2001) was used as a minimal estimate of k_{660}:

$$k_{660} = 1.58e^{0.30^*U} \quad (2)$$

where k_{660} (cm h^{-1}) is the piston velocity at the Schmidt number of 660 and U is the wind speed (m s^{-1}). Hourly wind data for the October 2005, June 2006, and October 2006 surveys were obtained from a mooring in Great Bay, while wind speed for the April 2006 survey was obtained from a weather station in Durham, NH (Fig. 1).

To calculate area-averaged CO_2 fluxes, the estuaries were broken into segments (ten for the Cocheco estuary, seven each for the Bellamy and Oyster estuaries, although the upper segments were not accessible during some surveys, and are thus only included when data were available), and the area-averaged flux was calculated from each segment as:

$$F_{area-average} = \frac{\sum F_i^*S_i}{\sum S_i} \quad (3)$$

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

Temperature-normalized pCO_2

To more closely examine aqueous pCO_2 dynamics due to biogeochemical processes, we also calculated the temperature-normalized pCO_2 at a temperature of 16°C (pCO_2@16°C), which is the mean temperature measured in Great Bay from 2004 to 2006. We used a linear relationship between salinity and river and ocean end-member TA to estimate TA for each pCO_2 measurement, then calculated DIC from TA and pCO_2 at in situ temperature and salinity using the inorganic carbon dissociation constants (Millero et al. 2006). These DIC estimates were then combined with the linear TA at in situ salinity and a constant temperature of 16°C to calculate pCO_2@16°C using the same dissociation constants.

Results

Hydrographic data Conditions varied widely over the course of the four surveys, especially in terms of rainfall and subsequent river discharge (Fig. 2). The Oct05 survey followed a long drought period, the Apr06 survey came after winter snowmelt, and the Jun06 survey was conducted immediately after a flood that produced the highest

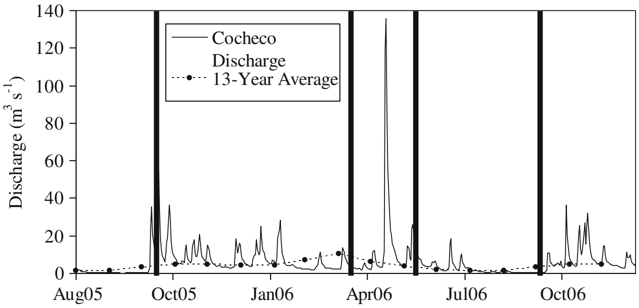

Fig. 2 Hydrograph of the Cocheco River discharge at USGS gage 01072800, located above the tidal section of the river. *Dash-dotted line* represents the average monthly discharge for the 13 years of record at the gage. *Black vertical lines* mark the dates of the four surveys in Oct05 and April, June and Oct06. The large peak immediately prior to the Jun06 survey represents the highest discharge measured at this gage and was concurrent with the highest discharge measured at the Lamprey River USGS gage (01073500) in 70 years of data. Hydrographs for all other rivers discharging into the Great Bay were comparable

recorded river discharges on record. The Oct06 survey followed another period of approximately 6 weeks of little to no rainfall and low river discharge, which are typical late summer/fall conditions in this region.

The influence and variability of river discharge is reflected in Table 3, where the mean salinity was highest during the two October surveys and lowest in the Jun06 survey. Data from a buoy located in the eastern portion of Great Bay showed that salinity variability between high and low tides was low during the two October surveys (only varying by 1–2), moderate in Apr06 (varying by 4) and high in Jun06 (ranging from about 5 at low tide to about 17 at high tide). Surface water temperature was coldest during the Apr06 survey and warmest during the Jun06 survey. The upstream portions of the estuaries generally showed higher temperatures than those closer to Great Bay, the lone exception being the upstream reaches of the Cocheco estuary in Apr06, which were colder than the water in Great Bay.

Surface water pCO_2– During the four surveys surface pCO_2 varied seasonally and across the estuaries (Table 3). The lowest recorded pCO_2 (84 µatm in the Cocheco estuary) was measured in Oct05, while the highest pCO_2 (2,007 µatm in the Oyster estuary) was measured in Jun06. There was a strong CO_2 drawdown during the Apr06 survey. This occurred during the time period when annual phytoplankton blooms and colder water temperatures combine to lower pCO_2. The opposite was observed during the Jun06 survey two months later, when all pCO_2 measurements were significantly above atmospheric levels as high river flows had presumably flushed out both high-CO_2 soil and groundwater (e.g., Paquay et al. 2007) and large amounts of labile particulate and dissolved organic carbon, which could sustain bacterial respiration and CO_2 production (Abril et al. 2000; Abril and Borges 2004). To test the assumption that groundwater can sustain high pCO_2 levels, sampling in July 2008 of a USGS well in Deerfield NH found TA of 254 µmol/kg and DIC of 443 µmol/kg, which combine to yield a calculated pCO_2 of 3,481 µatm, demonstrating that groundwater in this region can contain very high concentration of inorganic carbon species. Overall, pCO_2 levels during the four surveys were within the reported lower ranges of inner estuaries (Borges 2005).

The pCO_2 in many river estuaries increases with decreasing salinity to a maximum, often coincident with the estuary turbidity maximum, before decreasing again as salinity declines to zero. The Bellamy and Oyster estuaries appear to follow this general pattern, with higher pCO_2

Table 3 Ranges of estuary physical and chemical measurements, with area-averaged means in parentheses

		Water temperature (°C)	Salinity	f-CHL (mgm^{-3})	pCO_2 (µatm)	pCO_2@16°C (µatm)
Cocheco	Oct05	13.1–18.8 (16.8)	9.4–30.8 (22.9)	4.0–68.7 (35.2)	84–496 (286)	75–550 (285)
	Apr06	5.9–7.0 (6.3)	2.0–9.4 (4.5)	3.3–4.4 (4.0)	250–633 (460)	357–892 (649)
	Jun06	15.8–16.3 (16.1)	0.1–4.1 (0.7)	5.7–7.8 (7.0)	846–1,187 (1,040)	848–1,181 (1,038)
	Oct06	14.7–17.9 (16.5)	0.2–30.3 (13.5)	3.2–25.1 (6.2)	527–1,052 (756)	540–1,045 (744)
Bellamy	Oct05	15.5–18.3 (17.2)	28.5–30.4 (29.6)	3.7–7.4 (4.7)	478–757 (593)	485–700 (570)
	Apr06	9.2–11.8 (10.6)	9.6–20 (15.3)	2.5–6.5 (3.9)	148–192 (164)	188–243 (206)
	Jun06	18.6–19.7 (19.3)	3.8–11.1 (7.9)	4.1–5.4 (4.8)	1,192–1,515 (1,314)	1,062–1,362 (1,185)
	Oct06	16–16.8 (16.5)	27.2–29.2 (27.8)	3.4–4.7 (4.0)	531–596 (570)	529–580 (558)
Oyster	Oct05	14.6–18.6 (17)	27.3–30.6 (29.5)	3.1–7.2 (4.4)	427–549 (455)	404–495 (438)
	Apr06	9.6–10.7 (10.1)	3.7–17.9 (13.6)	3.8–5.2 (4.5)	141–418 (178)	182–509 (228)
	Jun06	17.1–19.3 (18.5)	0.9–8.4 (5.3)	4.7–5.9 (5.2)	1,581–2,003 (1,771)	1,438–1,867 (1,638)
	Oct06	15.8–17.1 (16.5)	27.8–29.5 (28.4)	–	537–770 (586)	520–543 (531)

Area-averaged means were calculated by substituting the respective measurement for the F term in Eq. 3. No chlorophyll fluorescence data were taken in the Oyster estuary in Oct06 due to sensor malfunction associated with lower salinity, and above-atmospheric pCO_2 throughout the estuary except during the April spring phytoplankton bloom. However, we observed strikingly different conditions in the Cocheco estuary on several surveys. In Oct05, the pCO_2 in the Cocheco decreased upstream to below-atmospheric levels. The Oct05 pCO_2 minimum in the Cocheco (84 µatm) was located in an area of high in-situ chlorophyll fluorescence (f-chl) roughly equivalent to chlorophyll-a concentrations of over 70 mg m^{-3}. During Apr06, the Cocheco was colder than the other two estuaries, but had the only above-atmospheric pCO_2 measured during that survey, despite the fact that colder temperatures lower pCO_2. In Jun06, the f-chl levels in the Cocheco were again higher (approximately 7.5 mg m^{-3}) than those of the rest of the Great Bay system (4–5 mg m^{-3}), and the short distance surveyed upstream in the Cocheco showed decreasing pCO_2, in contrast to the Bellamy and Oyster estuaries. Atmospheric pCO_2 measured during the surveys ranged from 368 µatm (Jun06) to 400 µatm (Oct05).

Air−water CO_2 fluxes Area-averaged air−water CO_2 fluxes from the three estuaries were sometimes positive (releasing CO_2 to the atmosphere), and sometimes negative (absorbing CO_2 from the atmosphere). The highest flux of 51.5 mmol $m^{-2}day^{-1}$ was in the Oyster estuary in Jun06, while the most negative flux of −17.2 mmol $m^{-2}day^{-1}$ was also in the Oyster in Apr06 (Fig. 3). The highest air−water CO_2 fluxes were during the post-flood survey in Jun06, when salinity was very low throughout the estuaries. There was significant spatial variation in the calculated CO_2 flux. Air–water CO_2 fluxes in the Bellamy and Oyster estuaries were positive except during the spring drawdown. The CO_2 flux from Cocheco estuary, however, appeared to be distinct, with a negative flux in Oct05, positive flux in Apr06, and lower flux in Jun06 than the other two estuaries. Overall, degassing of CO_2 from the Cocheco estuary was lower than that from the Oyster or Bellamy estuaries except during the spring bloom period.

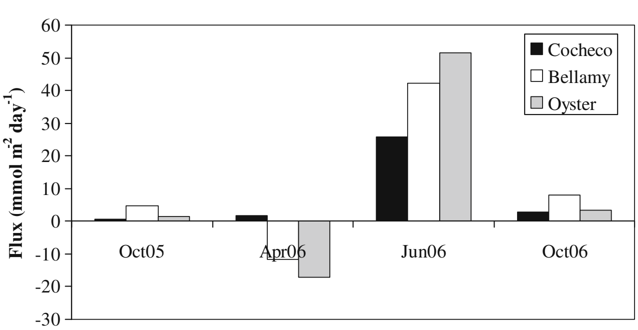

Fig. 3 Area-averaged CO_2 fluxes. Positive fluxes indicate CO_2 release from water to the atmosphere, negative fluxes indicate CO_2 uptake from the atmosphere to the water

Total Alkalinity and pH Endmember TA was low and variable in the rivers entering the estuaries (Table 4). To allow the calculation of CO_2 mixing curves, high-salinity endmember TA and pCO_2 from station WB7, a nearby ocean station sampled as part of a monthly monitoring program were used (Salisbury et al. 2009). River endmember TA covaried with river discharge—higher river flow yielded lower TA—but pH did not show a similar trend. The TA variability agrees with data from the nearby Kennebec River (Salisbury, personal communication) and other reports showing diluted TA concentration with increased river discharge, even though increased discharge also increases weathering dissolution (e.g., Gislason et al. 2009).

Nutrients and Dissolved Organic Carbon Nutrient data from the rivers showed the dominant form of inorganic nitrogen was nitrate (NO_3^-), with negligible nitrite concentrations. Generally, ammonium (NH_4^+) represented less than 15% of dissolved inorganic nitrogen (DIN=NO_3^-+ NH_4^+), although the proportion was higher (~28%) in the Oyster River in Oct05 and Jun06. DIN concentrations during the Oct05 survey were high, especially in the Cocheco estuary (Fig. 4). River inputs are usually the largest source of nutrients to an estuary, and the Oct05 survey followed a prolonged drought, with extremely low river flows. Possible nutrient sources are the municipal WWTFs which discharge directly into both the Cocheco River and Cocheco estuary as well as the Oyster estuary. These WWTFs represent point sources of nutrients, and these nutrient inputs may have had less river water to dilute them during periods of low river flow. DIN in the Cocheco River in Oct05 was very high (165 µmol L^{-1}), and DIN concentration was also high in the upper reaches of the Oyster River estuary (33 µmol L^{-1}). In Apr06, the highest DIN concentrations were also found in the Cocheco and Oyster Rivers. Bellamy River DIN was highest in Apr06, which agrees with earlier findings detailing snowmelt enriched in nitrate (Oczkowski et al. 2006). Data from Jun06 show a reversal of the nutrient dynamics, as the highest nutrient concentrations were found in the main area of Great Bay (DIN=17 µmol L^{-1}) and at the mouth of the Oyster estuary (DIN=18 µmol L^{-1}). This could presumably be due to early flushing of much of the watershed's nutrients into the bay during the flood. In Oct06, the highest DIN and phosphate concentrations were in the mid-salinity reaches of the Cocheco (DIN=28 µmol L^{-1}) and Oyster estuaries (DIN=19 µmol L^{-1}), possibly indicating inputs of nutrients from WWTFs discharging directly into these estuaries.

River DOC inputs also varied across the surveys (Fig. 4). Bellamy River DOC was much higher than DOC in the Cocheco or Oyster Rivers in the low-flow surveys

Table 4 TA, pH and pCO_2 values at low- and high-salinity endmembers for each estuary, with calculated $[CO_2]$ and DIC

		Salinity	Water temperature (°C)	TA (μmol kg^{-1})	pH (NBS scale)	pCO_2 (μatm)	$[CO_2]$ (calculated, μmol kg^{-1})	DIC (calculated, μmol kg^{-1})
Oct05	Cocheco River	0	17.70	542	7.227	–	114	656
	Bellamy River	0	17.70	764	7.137	–	198	962
	Oyster River	0	19.00	1,085	7.327	–	179	1,263
	High salinity	32.08	10.33	2,094	–	355	16	1,927
Apr06	Cocheco River	0	9.80	290	7.384	–	49	339
	Bellamy River	0	11.40	177	6.499	–	222	399
	Oyster River	0	11.40	411	6.882	–	213	624
	High salinity	32.47	8.40	2,269	–	224	11	2,011
Jun06	Cocheco River	0	15.40	142	7.062	–	46	188
	Bellamy River	0	17.90	386	7.233	–	80	466
	Oyster River	0	17.90	385	7.249	–	77	463
	High salinity	32.459	6.45	2,180	-	503	25	2,075
Oct06	Cocheco River	0	15.90	548	7.751	–	35	582
	Bellamy River	0	10.00	620	7.086	–	206	826
	Oyster River	0	10.00	736	7.136	–	218	954
	High salinity	30.93	8.81	2,193	–	450	21	2,063

Oct05 and Oct06. DOC was very similar for all three rivers in Apr06, while Cocheco River DOC was lower than Bellamy or Oyster River DOC during the Jun06 flood survey. For three of the four surveys, the ratio of DOC to DIN for the Bellamy River was much higher than that of the Cocheco or Oyster Rivers. In our case, a simplistic way to consider the potential balance of production to respiration that is modulated by river inputs is a comparison of DOC to DIN, assuming DOC to be a crude proxy for labile carbon, when in fact only a percentage of allochthonous organic matter is usually metabolized (e.g., Hopkinson and Vallino 1995; del Giorgio and Davis 2003).

Discussion

The factors which combine to control the pCO_2 in estuaries are water temperature and CO_2 inputs from the ocean, rivers, and within each estuary. Temperature affects estuary pCO_2 on a seasonal basis, increasing pCO_2 in the warm months and decreasing pCO_2 in the colder months. Processes within an estuary that can affect pCO_2 include net ecosystem metabolism, DIC inputs from tidal marshes, groundwater inputs, air–water exchange, the formation or dissolution of calcium carbonate, and other processes excluding inputs from the river or ocean endmembers. Nutrient and organic matter inputs to each estuary vary

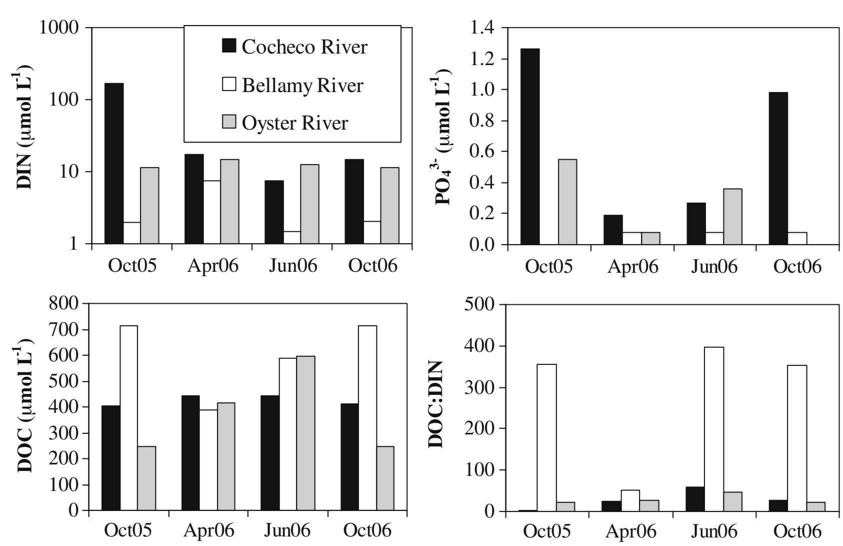

Fig. 4 River endmember concentrations of dissolved inorganic nitrogen (*DIN*), inorganic phosphate (*PO_4^{3-}*), dissolved organic carbon (*DOC*), and the ratio of DOC/DIN. Note the logarithmic scale of DIN

according to river flow, watershed characteristics, and anthropogenic inputs, and these inputs influence the net ecosystem metabolism of the estuary, with more inorganic nutrients generally promoting production and organic matter supporting respiration. In the following sections the effects of temperature, nutrient and labile carbon inputs, and inputs of CO_2 from river, ocean and within-estuary sources are discussed.

Warmer temperatures in New England increase pCO_2 in the summer and fall months, while cooler temperatures decrease pCO_2 in the winter and spring. Trends in temperature-normalized pCO_2 (pCO_2@16°C) indicate that temperature was not the only factor controlling estuarine pCO_2 (Table 3), as pCO_2@16°C in Jun06 is much higher than pCO_2@16°C in other surveys, and pCO_2@16°C in April is lower than other surveys. Water temperature lowered pCO_2 in the colder month of Apr06 (by 25–41%), but raised the pCO_2 in Oct05 (by 3%), Jun06 (by 2–9%) and Oct06 (by 2%). The percentage changes in Jun06, Oct05 and Oct06 appear small, but the in situ temperatures during those surveys were close to 16°C (Table 3).

The Cocheco River has been shown to deliver water with unusually high concentrations of DIN and phosphate to the Great Bay, particularly during the summer and fall months, when streamflows are the lowest (Jones 2000). Additionally, the Cocheco (combined with the Salmon Falls River) accounts for between 50–80% of river-borne DIN entering Great Bay, and 60–90% of river-borne phosphate (Oczkowski 2002), which would presumably lead to greater primary productivity and DIC uptake in the Cocheco River and estuary. This helps to explain the very low pCO_2 levels in the Cocheco estuary during the low-flow two Oct05 and Oct06 surveys, and the depressed pCO_2 levels in comparison to the Bellamy and Oyster estuaries in Jun06 when pCO_2 was very high across the system. Samples taken at the river endmembers of the Cocheco and Bellamy Rivers emphasize the different magnitudes of nutrient input from high nutrient (Cocheco) and low-nutrient (Bellamy) rivers (Fig. 4). The Cocheco River and estuary receive large inputs of nutrients from multiple WWTFs, the Oyster estuary receives discharge from one WWTF, and the Bellamy River receives no WWTF inputs. Since the nutrient concentrations in Fig. 4 were measured above the dams on each river, the nutrient inputs to the Cocheco and Oyster estuaries are even larger when the discharge from the WWTFs directly to these two estuaries is taken into account.

The large disparity of the DOC/DIN ratio between the Bellamy River and the Cocheco and Oyster Rivers (Fig. 4) suggests that the CO_2 flux from the Bellamy estuary would be enhanced relative to the Cocheco and Oyster estuaries, due to proportionally higher inputs of organic matter to sustain respiration. Bellamy estuary CO_2 flux was higher during the low-flow Oct05 and Oct06 surveys, when the Bellamy River DOC concentration was also very high. Low DOC:DIN in the Cocheco and Oyster Rivers also corresponded to lower CO_2 fluxes from their respective estuaries in Oct05 and Oct06, and in Apr06 the Cocheco River had the highest DOC:DIN while the Cocheco estuary had the largest CO_2 flux. After the flood of Jun06 the DOC:DIN in the Bellamy River was much higher than that of the Cocheco or Oyster Rivers, but the Bellamy estuary CO_2 flux was not enhanced (Fig. 3), although residence time in the estuaries was much reduced by the extremely high river flows.

To examine the inputs of CO_2 from river, estuary, and ocean sources, we followed the approach of Jiang et al. (2008), which partitions dissolved CO_2 concentrations ($[CO_2]$, μmol/kg) into oceanic, riverine and estuarine sources. Specifically, the estuarine contribution ($\Delta[CO_2]_{estuarine}$) to in situ estuarine dissolved CO_2 ($[CO_2]_i$) is calculated as

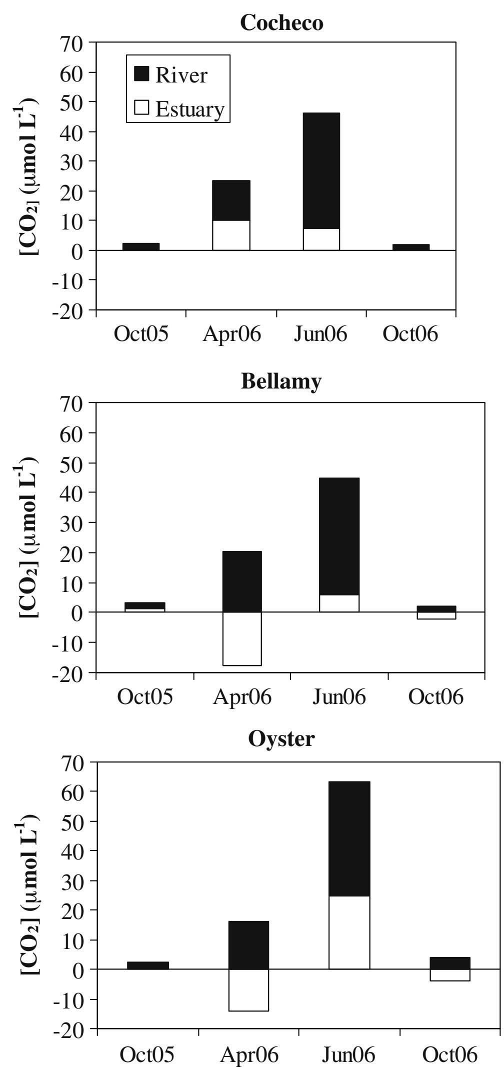

Fig. 5 Inputs of dissolved CO_2 (area-averaged and normalized to 16°C) from riverine (*dark bars*) and estuarine sources (*open bars*)

the difference between $[CO_2]_i$ and the CO_2 concentration if the ocean and river endmembers mix conservatively ($[CO_2]_{mixing\ w/R}$). The CO_2 concentration due to input from the river ($\Delta[CO_2]_{river}$) was calculated as the difference between $[CO_2]_{mixing\ w/R}$ and the CO_2 concentration if the ocean endmember is diluted by fresh water with a CO_2 of zero ($[CO_2]_{mixing\ w/O}$) . Conservative mixing of TA and DIC (calculated from either TA and pH or TA and pCO_2) was used to calculate the mixing curves (Table 4).

Results of this analysis show that the Cocheco River and estuary made positive contributions to CO_2 in the estuary during the four suveys, with the river always contributing more than the estuary (Fig. 5). Generally, $\Delta[CO_2]_{river}$ in the Cocheco estuary was not different than $\Delta[CO_2]_{river}$ in the Bellamy or Oyster estuaries. The Bellamy and Oyster Rivers were also contributors to CO_2 in their estuaries during the four surveys, but in Apr06 and Oct06 $\Delta[CO_2]_{estuarine}$ in the Bellamy and Oyster estuaries was negative. The most apparent difference between the estuaries is in Apr06, when both the Bellamy and Oyster estuaries showed negative $\Delta[CO_2]_{estuarine}$, while the Cocheco estuary $\Delta[CO_2]_{estuarine}$ was positive. The CO_2 contribution from the Bellamy and Oyster estuaries was also negative in Oct06, while that of the Cocheco estuary was small but positive. The flood in Jun06 provided a large pulse of river-borne CO_2 to all three estuaries, and the Oyster estuary contributed proportionally more CO_2 than the Cocheco or Bellamy estuaries during the event. The three estuaries also contributed significant CO_2 inputs during the flood as well, despite the presumably very short water residence time during the flood event.

Conclusions

The distribution of pCO_2, as well as the magnitude and direction of air-water CO_2 flux, varied across the three estuaries in this study. A lower DOC/DIN ratio in the contributing river coincided with smaller air–water CO_2 fluxes in the Cocheco estuary. River inputs of CO_2 were fairly consistent between the three rivers, while CO_2 contributions or withdrawals in the estuaries showed more variability between systems. The large influx of freshwater during a summer storm resulted in a large release of CO_2 to the atmosphere, primarily from riverine CO_2, but with a sizeable fraction of CO_2 released from estuarine processes as well. Flood events appear to contribute to large releases of CO_2 to the atmosphere, and should be taken into account for carbon budgeting and CO_2 flux calculations, especially as precipitation and the frequency of floods in some areas are projected to increase under climate change scenarios. Time-series monitoring data of CO_2 in the estuarine environment is needed to capture the impact of storm and flood events, and how these episodic events affect the carbon transport and degassing properties of coastal and estuarine systems on time scales of months to years.

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