Biogeosciences

Contribution of non-carbonate anions to total alkalinity and overestimation of pCO$_2$ in New England and New Brunswick rivers

C. W. Hunt, J. E. Salisbury, and D. Vandemark

Ocean Process Analysis Laboratory, University of New Hampshire, Durham, NH, USA

Abstract. Total alkalinity (TAlk) has long been used to evaluate the buffering capacity of aquatic systems. TAlk has also been used, together with measurements of either pH or dissolved inorganic carbon (DIC), to indirectly estimate the partial pressure of carbon dioxide (pCO$_2$) in inland waters, estuaries, and marine systems. These estimates typically assume that carbonate and bicarbonate ions comprise nearly all the species contributing to TAlk; however, other inorganic and organic acids have the potential to contribute significant non-carbonate alkalinity. To evaluate the potential for error in using TAlk to estimate pCO$_2$, we measured pH, TAlk, and DIC in samples of river water. Estimates of pCO$_2$ derived from TAlk and pH measurements were higher than pCO$_2$ estimates derived from DIC and pH by 13–66 %. We infer that this overestimate is due to the presence of significant non-carbonate alkalinity (NC-Alk). This study also describes the relative proportions of carbonate- and non-carbonate alkalinity measured in 15 river systems located in northern New England (USA) and New Brunswick (Canada). NC-Alk represents a significant buffering component in these river systems (21–∼100 % of TAlk), and failure to account for NC-Alk (which cannot directly contribute to pCO$_2$) leads to the overestimation of carbon dioxide release to the atmosphere.

1 Introduction

Inland waters (lakes, rivers and reservoirs) comprise a small component of the global hydrologic and carbon cycles, but are an important connection between terrestrial and oceanic reservoirs (Degens et al., 1991; Cole and Caraco, 2001). In addition to transporting water and carbon, inland waters process a large fraction of the carbon they receive, typically re-

sulting in carbon dioxide efflux to the atmosphere (e.g., Cole et al., 1994, 2007; Sobek et al., 2005; Richey, 2004).

Four commonly measured parameters of the aqueous carbonate system are total alkalinity (TAlk), dissolved inorganic carbon (DIC), the partial pressure of carbon dioxide (pCO$_2$), and pH. The measurement of any two of these parameters allows for the calculation of the remaining carbonate system parameters using equilibrium constants and in-situ temperature data (Stumm and Morgan, 1996). When not measured directly, the partial pressure of carbon dioxide for inland waters is routinely derived from measurements of TAlk and either pH or DIC (e.g., Paquay et al., 2007). The TAlk of natural waters is comprised of a mixture of inorganic and organic bases and acids, and is thought to be dominated by the carbonate species (CO$_3^{2-}$ and HCO$_3^-$) at circum-neutral to alkaline pH (Williams et al., 2009):

$$\text{TAlk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-]$$
$$+ [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{H}_3\text{SiO}_4^-] + 2[\text{H}_2\text{SiO}_4^{2-}] + [\text{HS}^-]$$
$$+ 2[\text{S}^-] + [\text{NH}_3^+] + [\text{Org}^-] - [\text{H}^+] - [\text{H}_3\text{PO}_4] \quad (1)$$

where Org$^-$ represents a collective term for organic acids. Organic acids in river water may be autochthonous (derived from photosynthesis in the river) or allochthonous (leached from plants and soils into the river). Autochthonous organic material usually has a lower molecular weight and is more easily recycled, that of allochthonous origin is higher molecular weight and richer in aromatics, including humic compounds (Degens et al., 1991), and has been associated with NC-Alk (Cai et al., 1998). In the absence of information on organic matter quality, or other chemical species which may contribute to alkalinity, we can group all non-carbonate alkaline species together as NC-Alk and simplify this equation as:

$$\text{TAlk} = [\text{C-Alk}] + [\text{NC-Alk}] + [\text{OH}^-] - [\text{H}^+] \quad (2)$$

where C-Alk is the sum of carbonate and bicarbonate, and NC-Alk is the net contribution of non-carbonate species to

Correspondence to: C. W. Hunt
(chunt@unh.edu)

alkalinity. The magnitude of NC-Alk is often assumed to be small compared to carbonate alkalinity, and the NC-Alk contributions from species of boron, phosphorus, nitrogen and silicon are sometimes estimated or simply ignored when using TAlk to calculate pCO_2 or other carbonate system parameters (e.g., Cole and Caraco, 2001; Cole et al., 1994; Sobek et al., 2005; Paquay et al., 2007). In rivers, the NC-Alk term is often dominated by contributions from organic species such as humic acids (Cai and Wang, 1998, Lozovik, 2005), which can vary in pK and represent a large fraction of TAlk. Some studies (e.g., Cai et al., 1998; Tishchenko et al., 2006; Kim and Lee, 2009) have shown that NC-Alk is sometimes a significant fraction of TAlk in estuarine and coastal ocean waters, and must be taken into account when analyzing the carbonate system in various environments. Here we present data from several Northeastern USA and Canadian rivers showing that NC-Alk represents a significant – and sometimes dominant – fraction of TAlk. Our data demonstrate that failure to account for NC-Alk in these rivers leads to an overestimation of pCO_2. Studies which use alkalinity to estimate carbon dioxide release from inland waters may seriously overestimate this transfer of carbon dioxide to the atmosphere.

2 Methods

2.1 Sample collection

We measured TAlk, pH and DIC periodically from July 2008 to July 2009 at two sites on the Oyster River, which drains a temperate 72 km^2 watershed in southeastern New Hampshire, USA. The bedrock of the Oyster River watershed is primarily metamorphic slate, with other metamorphosed sedimentary rock and some igneous intrusions of diorite and monozonite (Oczkowski, 2002). Land use for the Oyster River watershed is mostly forested (75 %, Oczkowski, 2002). Other categories of land use within the watershed are urban (8 %), agricultural (3 %), wetlands (4 %) and cleared (9 %). The two predominant soil types for the Oyster River watershed are sands, loamy sands or sandy loams, together with loams or silt loams (Oczkowski, 2002). Samples were collected in buckets and transferred without bubbling into 60-ml glass BOD bottles with greased stoppers. 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. Sampling from buckets allowed for potential CO_2 loss during sample transfer; however, as DIC, pH, and TAlk were measured from the same bottle, any CO_2 loss was propagated through all measurements. In-situ temperature was measured with a handheld meter (YSI, Yellow Springs, Ohio). Samples collected from the additional sites listed in Table 2 were obtained using the same procedures. DIC was measured first from each sample bottle, followed sequentially by pH and TAlk.

2.2 Measurement of dissolved inorganic carbon

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 A. Dickson were used to ensure the quality of DIC determination by preparing a calibration curve covering the range of DIC from 200–2000 $\mu eq \, l^{-1}$ (Dickson et al., 2003), with a resulting precision ranging from 0.05–0.5 %, with an average of ~0.1 %.

2.3 Measurement of pH and total alkalinity

TAlk and pH of unfiltered water were both measured using the same titration system. TAlk was measured by Gran titration (Gran, 1952) with 0.1N 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 below 3, and then adds subsequent aliquots of titrant until the pH changes linearly with the volume of acid added. The TAlk endpoint is then obtained from linear regression of the change of pH against the volume of acid added, according to a Gran transformation (Fig. 1):

$$GF = (v + V_o) / V_o \cdot 10^{-pH} \qquad (3)$$

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 measured after each successive addition of volume v.

Multiple analyses of a certified seawater reference material resulted in a calculated precision of this method of about 0.1 % (or $\sim \pm 2 \, \mu eq \, l^{-1}$). The accuracy of the TAlk automated system, also calibrated with the Dickson CRM as discussed above, was ± 3–4 $\mu eq \, l^{-1}$. The pH electrode used in the Gran titration (Orion 3-Star, Thermo Fisher Inc.) was calibrated using three low ionic strength pH buffers certified on the US National Bureau of Standards scale to ± 0.01, and the initial reading (before the addition of acid titrant) was taken as the sample pH. Performance of the TAlk analyzer at zero salinity was checked by preparing solutions of known potassium bicarbonate concentration between 50–400 $\mu eq \, l^{-1}$, analyzing them for DIC and TAlk/pH, and calculating TAlk from DIC and pH. We found good agreement between measured and calculated TAlk for these analyses. We also performed several back-titrations of Oyster River samples, according to a published method (Cai et al., 1998), which involved titrating a sample once according to the Gran method described above, then raising the pH of the titrated sample back to the starting value via incremental additions of NaOH while bubbling nitrogen through the sample to remove acidified CO_2, and finally titrating the sample again according to

Table 1. Comparison of programs used in carbonate system calculations. $TAlk_{DIC-pH}$ is the total alkalinity derived from DIC and pH measurements. $pCO_{2-TAlk-pH}$ is the partial pressure of carbon dioxide derived from TAlk and pH measurements, while $pCO_{2-DIC-pH}$ is the partial pressure of carbon dioxide derived from DIC and pH measurements.

|		PHREEQC	CO2SYS (Salinity = 0 freshwater option)	Cai et al. (1998)
$TAlk_{DIC-pH}$ ($\mu eq\,l^{-1}$)	Mean	356	374	374
	Range	126–729	130–726	130–726
	Std. Dev.	158	153	153
NC-Alk ($\mu eq\,l^{-1}$)	Mean	151	133	133
	Range	81–422	23–393	23–393
	Std. Dev.	69	68	68
$TAlk_{DIC-pH}$ percent difference from PHREEQC results	Mean	–	−3.14 %	−3.14 %
	Range	–	−8.8–0.23 %	−8.8–0.23 %
	Std. Dev.	–	2.85 %	2.85 %
$pCO_{2-TAlk-pH}$ (μatm)	Mean	4626	3944	3941
	Range	1047–12023	1016–11427	1016–11418
	Std. Dev.	2347	2211	2210
$pCO_{2-DIC-pH}$ (μatm)	Mean	2931	2977	2639
	Range	912–5370	929–5455	887–5023
	Std. Dev.	974	988	1004
$pCO_{2-DIC-pH}$ percent difference from PHREEQC results	Mean	–	−0.78 %	6.11 %
	Range	–	−1.63–0.04 %	−3.58–17.4 %
	Std. Dev.	–	0.39 %	5.30 %
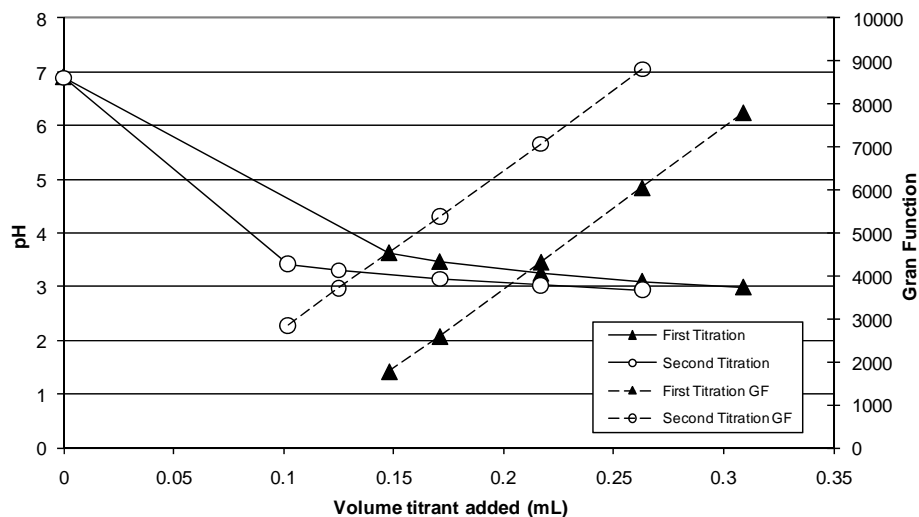
Fig. 1. Example titration curve and Gran function (GF) plot for Oyster River water.

the Gran method (example titration shown in Fig. 1). The difference in alkalinity between the first titration, after which any CO_2 had been removed, and the second titration represented the NC-Alk (Fig. 1). Precision of this back-titration method was poor ($\sim 75\,\mu eq\,l^{-1}$), but the NC-Alk measured by this method, ranging from 160–$220\,\mu eq\,l^{-1}$, was well within the range of calculated values described in this study.

2.4 Carbonate system calculations

Measured TAlk, pH, and DIC data were used as inputs to the PHREEQC program (Parkhurst and Appelo, 1999) to calculate the unknown parameters of the carbonate system. There are several software packages available which perform carbonate equilibria calculations, with a variety of choices of
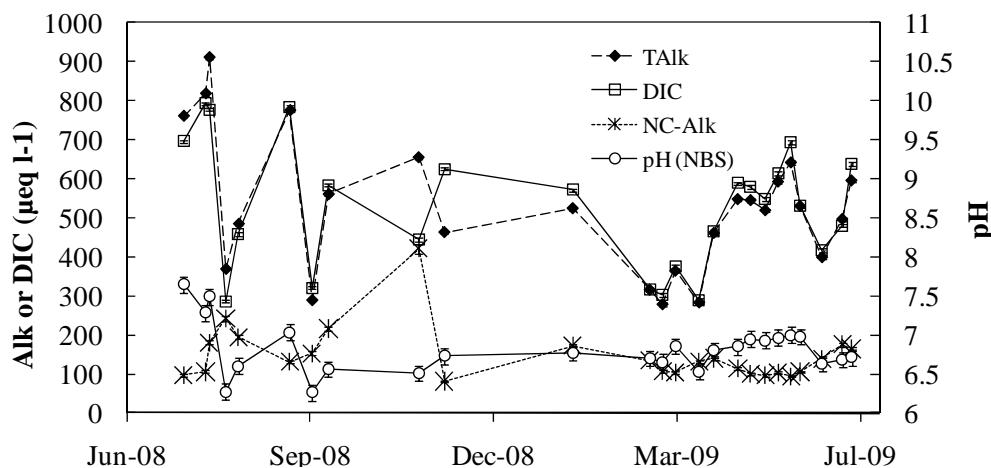
Fig. 2. TAlk, DIC and pH at one sampling location on the Oyster River. NC-Alk was calculated by subtracting $TAlk_{DIC\text{-}pH}$ from $TAlk_{measured}$. Error bars of ± 0.1 in pH are shown, but error bars of $\pm 4\,\mu eq\,l^{-1}$ in TAlk and DIC are too small to appear in the plot.

carbonate dissociation constants. To compare the effect of the selection of the PHREEQC program, pCO_2 and TAlk were also derived using the program CO2SYS ("$S = 0$ freshwater" option, Lewis and Wallace, 1998) and a modified version of CO2SYS which included the constants of Cai et al. (1998), provided by Wei-Jun Cai, hereafter referred to as the CAI program. CO2SYS is a program commonly used for calculations of seawater equilibria, while the CAI program's constants were determined for an estuarine salinity range. All programs were given identical input data of DIC, pH and temperature. The pCO_2 derived by CO2SYS was very close to that returned by PHREEQC (less than 1 % difference), while the pCO_2 derived from the CAI program was somewhat lower than the results from PHREEQC (Table 1). For TAlk, the results from CO2SYS and CAI are nearly identical, and both were somewhat higher than TAlk results from PHREEQC. PHREEQC returns a larger average NC-Alk than CO2SYS or CAI, but the magnitudes of NC-Alk from all three programs is high. As PHREEQC is the more commonly employed tool for freshwater environments such as rivers, we have chosen to present the results from that program in this work.

3 Results and discussion

3.1 Oyster River NC-Alk

TAlk, DIC and pH all followed similar patterns of concentration over the sampling time period (subset of data shown in Fig. 2), where higher river flows generally produced lower TAlk, DIC, and pH. Average TAlk, DIC and pH were $507\,\mu eq\,l^{-1}$, $500\,\mu eq\,l^{-1}$, and 6.8, respectively. The least-squares linear regression of TAlk and DIC showed a fairly strong trend ($r^2 = 0.83$). We calculated NC-Alk by subtracting the calculated TAlk values – derived from DIC

and pH measurements ($TAlk_{DIC\text{-}pH}$) – from measured TAlk ($TAlk_{measured}$). This produced a NC-Alk ranging between 83–$423\,\mu eq\,l^{-1}$, with a mean NC-Alk of $145\,\mu eq\,l^{-1}$. NC-Alk did not show a correlation with river discharge, but did generally increase with lower pH.

It is worth addressing the possibility that calculated NC-Alk is a result of measurement error, and not an actual contribution to alkalinity from non-carbonate materials. The choice to not filter samples may introduce some uncertainty, as particulate matter may provide some NC-Alk; however, this error is probably small. Analyses of TAlk and DIC were calibrated using a certified reference material, with a precision of about $\pm 0.5\,\mu eq\,l^{-1}$ in DIC and $\pm 1.0\,\mu eq\,l^{-1}$ in TAlk. Measurements of pH in natural waters are inherently uncertain due to liquid-junction interferences (Covington et al., 1983). The pH electrode was calibrated with buffers of 4.01, 7.00 and 10.01, each certified to ± 0.01 on the NBS scale, and we estimate the reproducibility of our pH sampling and analysis methods as ± 0.05 based on repeated measurements of the Dickson seawater CRM. When this uncertainty is applied to our measurements the resulting change in $TAlk_{DIC\text{-}pH}$ (on the order of 3–$5\,\mu eq\,l^{-1}$) is far smaller than the calculated values of NC-Alk. So, while measurement error may play some role in the TAlk discrepancies, that role appears to be small. Additionally, the differences in the back-titration curves, an example of which is shown in Fig. 1, lends further support to the presence of NC-Alk. Since all CO_2 had been removed from the sample during the first titration, the steeper slope of the second set of pH titration data, together with the linear GF series during the second titration, indicates acid neutralization must have been produced by non-carbonate species.

As evident in Eq. (1), NC-Alk can be composed of several different constituents. Work by Oczkowski (2002) shows that the concentration ranges of Oyster River dissolved
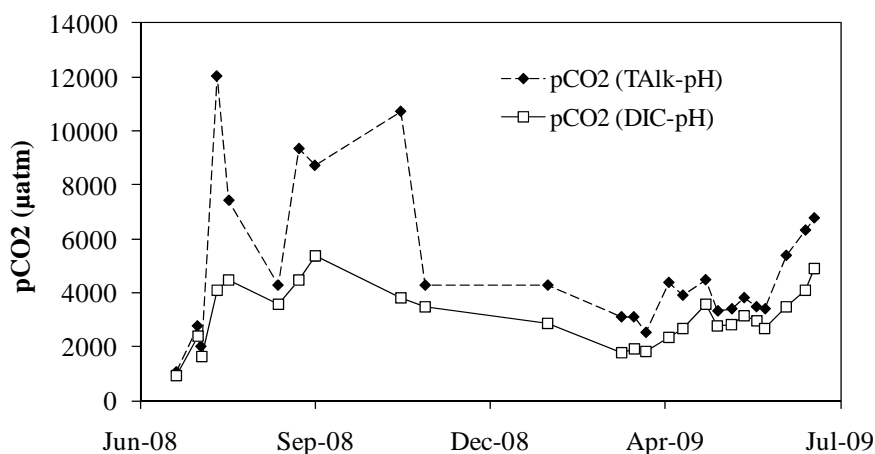
Fig. 3. Partial pressure of carbon dioxide calculated from TAlk and pH ($p\mathrm{CO}_{2\text{-TAlk-pH}}$), as well as from DIC and pH ($p\mathrm{CO}_{2\text{-DIC-pH}}$), at one sampling site on the Oyster River.

inorganic nitrogen (DIN) and phosphorus (P) are small (0–25 µM DIN, 0–0.5 µM P) compared to the calculated range of NC-Alk. Silicates (ranging in concentration from 50–150 µM, Oczkowski, 2002) would represent a very small proportion of NC-Alk over the measured Oyster River pH range of 6.3–7.6. We thus presume that NC-Alk is primarily comprised of a complex mixture of organic acids (Cantrell et al., 1990). Organic acids found in inland waters are a highly complex mixture of proton-accepting compounds, covering a wide spectrum of proton binding sites. Monomeric species of aluminum ($\mathrm{Al(OH)}_2^+$, $\mathrm{Al(OH)}_3^+$) can also contribute NC-Alk, but this phenomenon typically occurs at pH values well below those we observed in the Oyster River (e.g., Hemond, 1990). The range of NC-Alk measured in the Oyster River represented 13–66 % of TAlk$_{\mathrm{measured}}$, with a mean of 32 %, demonstrating that NC-Alk is an important component of alkalinity in this river.

3.2 Organic acid contributions

It is worth noting that the total humic acid concentration could actually be much higher than the estimates we present here. Gran titrations measure the alkalinity of samples for which an acidimetric titration endpoint is not easily found, and are typically performed in the 2–4 pH range where we determined our TAlk$_{\mathrm{measured}}$. However, only about 55 % of humics are typically protonated at this pH range (Morel and Hering, 1993), and only protonated species are counted in the Gran method. Following the calculations of Morel and Hering (1993), we determined that ~55 % of total organic acids are protonated in the Gran titration:

$$\text{Gran-Alk} = \text{C-Alk} + (1.00 - 0.45)\text{HA}_\text{T} \tag{4}$$

where Gran-Alk is the total alkalinity determined by Gran titration, HA$_\text{T}$ is the total organic acid concentration, and C-Alk is the sum of carbonate species which contribute to total alkalinity (estimated from DIC and pH):

$$\text{C-Alk} = [\mathrm{HCO}_3^-] + 2[\mathrm{CO}_3^{2-}] \tag{5}$$

We find that our estimates of NC-Alk represent 48–53 % of the total organic acids (HA$_\text{T}$) predicted to be present in the samples, with a median of 51 %. It is possible that these estimates are high, as the Gran titration data presented here were measured at a somewhat lower pH range (<3.0) than that of Morel and Hering (3.7–2.8), but the overestimate is on the order of 5–10 %.

This is supported by dissolved organic carbon (DOC) data measured during the same time period in the Oyster River. For 23 samples taken between September 2007 and December 2009 DOC ranged from 210–570 µM, with an average concentration of 404 µM (unpublished data from New Hampshire Water Resources Research Center). Thus, the average NC-Alk (145 µeq l^{-1}) measured during this study represents 36 % of the average DOC concentration, and if NC-Alk represents 51 % of total humic concentration, or 290 µM, then humics represent 72 % of the average DOC concentration. This figure is similar to the ~77 % humic fraction of DOC in the Satilla river, another river with a high percentage of NC-Alk (Cai et al., 1998).

3.3 Overestimation of $p\mathrm{CO}_2$ due to NC-Alk

When we examined the difference between $p\mathrm{CO}_{2\text{-TAlk-pH}}$ and $p\mathrm{CO}_{2\text{-DIC-pH}}$ (assuming that $p\mathrm{CO}_{2\text{-DIC-pH}}$ represents the accurate estimate of $p\mathrm{CO}_2$) we found that accounting for the presence of NC-Alk substantially lowers $p\mathrm{CO}_2$ estimates in the Oyster River. In other words, using TAlk instead of DIC to calculate $p\mathrm{CO}_2$ resulted in $p\mathrm{CO}_2$ overestimates (Fig. 3). Direct measurements of river $p\mathrm{CO}_2$ are rare in the literature, but while Cole and Caraco (2001) found

Table 2. Location information and NC-Alk data for northern New England and Canadian rivers. The NC-Alk fraction column lists the proportion of TAlk represented by NC-Alk for each river. NS in the DOC column indicates no DOC sample for that river.

River	Location	Sampling Date	Latitude	Longitude	TAlk (μeq l^{-1})	DIC (μeq l^{-1})	pH	NC-Alk (μeq l^{-1})	NC-Alk fraction	DOC (μmol l^{-1})
Merrimac	Lowell, MA	29 May 2008	42.66	−71.32	411.4	335.8	6.9	160	39 %	NS
Kennebec	Richmond, ME	1 Jun 2008	44.09	−69.79	365.8	325.7	6.6	169	46 %	478.3
Aroostook	Washburn, ME	14 Jul 2008	46.78	−68.16	569.7	524.6	6.7	205	36 %	725.8
Canaan	Coles Island, NB	15 Jul 2008	46.92	−65.79	370.9	231.0	5.9	314	85 %	1480
St. John	Fredericton, NB	15 Jul 2008	46.96	−66.64	730.4	715.8	6.9	155	21 %	772.5
Tobique	Tobique, NB	15 Jul 2008	46.79	−67.49	828.5	775.7	6.9	219	26 %	265
St. John	Perth, NB	15 Jul 2008	46.74	−67.71	884.7	801.4	6.8	293	33 %	530.8
Saco	Fryeburg, ME	15 Jul 2008	44.08	−70.91	232.5	97.4	6.4	183	79 %	381.7
Saco	Crawford Notch, NH	15 Jul 2008	44.18	−71.40	184.3	55.0	6.1	166	90 %	156.7
Kennebecasis	Norton, NB	16 Jul 2008	45.64	−65.70	956.7	873.4	7.1	215	22 %	252.5
Connecticut	Lancaster, NH	16 Jul 2008	44.46	−71.65	364.9	284.6	6.8	162	45 %	438.3
Androscoggin	Brunswick, ME	25 Aug 2008	43.92	−69.97	303.7	241.6	5.7	259	85 %	NS
Pleasant	Columbia Falls, ME	21 Sep 2008	45.65	−67.73	128.9	45.6	5.3	130	101 %	937.5
Narraguagus	Cherryfield, ME	21 Sep 2008	44.61	−67.93	116.4	68.5	5.8	106	91 %	1030.0
Penobscot	Milford, ME	5 Dec 2008	44.94	−68.64	305.6	216.4	5.8	277	91 %	698.3

that direct $p\text{CO}_2$ measurements in the Hudson River corresponded well with $p\text{CO}_{2\text{-DIC-pH}}$, Cole et al. (1994) note that the average $p\text{CO}_{2\text{-TAlk-pH}}$ in lakes was $\sim$8 % higher than the respective $p\text{CO}_{2\text{-DIC-pH}}$. Calculating $p\text{CO}_2$ from TAlk and pH led to an overestimation of $p\text{CO}_2$ in the Oyster river by 138–8000 μatm, with a median overestimate of 1675 μatm. This translates to a range of overestimation of 13–98 %, with an average overestimate of 40 %. The disagreement in the Oyster River data between $p\text{CO}_{2\text{-TAlk-pH}}$ and $p\text{CO}_{2\text{-DIC-pH}}$ is much larger than has been previously reported (e.g., Cole et al., 1994). It is worthwhile to note that $p\text{CO}_2$ in the Oyster River is always above atmospheric levels, and thus the Oyster River represents a source of carbon dioxide to the atmosphere no matter which measurements were used to calculate $p\text{CO}_2$.

While we found $p\text{CO}_{2\text{-TAlk-pH}}$ to be overestimated with respect to $p\text{CO}_{2\text{-DIC-pH}}$, an accurate measure of $p\text{CO}_2$ is still needed. Hope et al. (1995) developed a headspace equilibration method to measure free CO_2, and found that this method yielded much higher $p\text{CO}_2$ than calculated $p\text{CO}_{2\text{-TAlk-pH}}$. Inaccuracy in the measurement of pH in an open cell was cited as one of the reasons why $p\text{CO}_{2\text{-TAlk-pH}}$ was underestimated, with the loss of CO_2 leading to a lower pH (Hope et al., 1995). While the pH measurements in this study are susceptible to the same error, the estimates of NC-Alk are still useful, since the same pH data were used for both $p\text{CO}_{2\text{-TAlk-pH}}$ and $p\text{CO}_{2\text{-DIC-pH}}$.

3.4 Results from other New England and Canadian rivers

We sampled other northern New England USA and Canadian rivers to examine regional levels of NC-Alk (Table 2). The NC-Alk concentrations calculated for each river fall within the range of NC-Alk values we measure in the Oyster River. NC-Alk appears to be widely distributed throughout the Northeast United States and maritime Canada, with the three highest proportions of NC-Alk found in Maine rivers (the Pleasant, Narraguagus and Penobscot rivers). The fraction of TAlk represented by NC-Alk in these three Maine rivers is much higher than the fraction observed in the Oyster River, and in cases such as the Pleasant River, NC-Alk represented all alkalinity in the sample. In the rivers listed in Table 2 the percent difference between $p\text{CO}_{2\text{-TAlk-pH}}$ and $p\text{CO}_{2\text{-DIC-pH}}$ ranges from 24–190 %, with an average of 96 %.

While the NC-Alk concentration is poorly correlated with pH in all the rivers discussed in this study ($r^2 = 0.0001$), there is a good least-squares correlation between pH and the percentage of alkalinity comprised of NC-Alk ($r^2 = 0.9108$), with the apparent exception being the Saco River (Fig. 4). The increased percentage of NC-Alk at lower pH agrees with the carbonate equilibria equations, as increased acidity shifts carbonate to free CO_2 (or H_2CO_3^*). In some of the sampled rivers, such as the Pleasant, Narraguagus and Penobscot, all or nearly all the alkalinity is in the form of NC-Alk. This does not mean these rivers do not release CO_2 to the atmosphere, as dissolved CO_2 is present as H_2CO_3^*, which does not accept protons and thus does not contribute to alkalinity. In fact, $p\text{CO}_{2\text{-DIC-pH}}$ from the rivers in Table 2 averages 3330 μatm, nearly an order of magnitude higher than atmospheric levels, indicating that these rivers represent strong sources of carbon dioxide to the atmosphere. Data from the Oyster River appear to follow the same pattern (Fig. 4) up to pH 7.0; however, the few Oyster River samples above neutral pH show a leveling off of the NC-Alk fraction.

The data from Table 2 and Fig. 4 are indicative of poorly buffered rivers and streams, with relatively low pH and
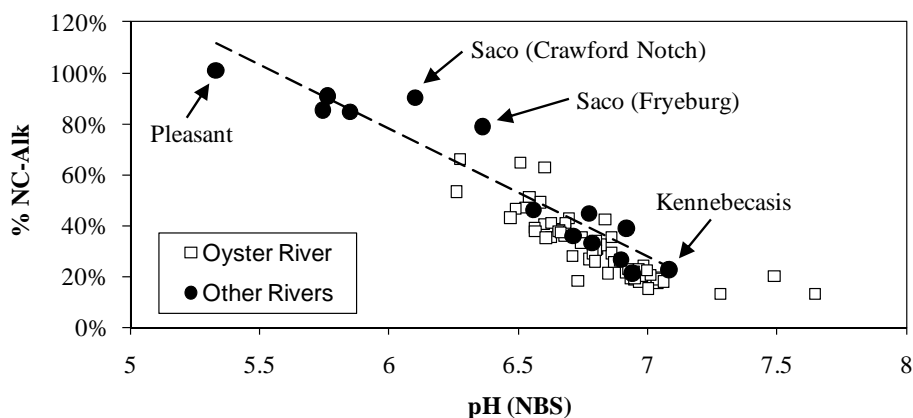
Fig. 4. Relationship between pH (measured in the lab) and the calculated percentage of NC-Alk in the Oyster River and in the sampled rivers in northern New England and Canada (Other Rivers, Table 1). The dotted line shows the linear regression of the Other Rivers, having the equation $\% \text{ NC-Alk} = -0.5 \cdot \text{pH} + 379$.

Table 3. Comparison of pH, TAlk and DOC measurements from this study to data obtained from the USGS.

	# sites	Mean	Median	Minimum	Maximum	Standard deviation
			pH			
This study	16	6.4	6.6	5.3	7.1	0.55
USGS	21 938	7.47	7.7	2.2	11.1	0.91
			TAlk (μeq l^{-1})			
This study	16	454	368	116	956	268
USGS	1173	1064	1086	10	2970	720
			DOC (μmol C l^{-1})			
This study (Oyster River only)	1	472	469	245	665	143
USGS	5417	475	286	8.3	>2000	326

carbonate alkalinity. To examine whether the presented rivers may be representative of national trends, we obtained all pH, TAlk and DOC data (parameter codes 00400, 00419, and 00681, respectively) from the United States Geological Survey (USGS) website (http://nwis.waterdata.usgs.gov/usa/nwis/qwdata,SiteType=''Stream'') for the time period 1 January 1990–1 January 2010. This comparison (Table 3) shows that the pH and TAlk are indeed lower than the national statistics, with significantly different means (Student's t-test, 95 % confidence interval). However, DOC levels in the Oyster are not significantly different than national levels, indicating that NC-Alk contributions from DOC similar to those in New England may be possible elsewhere. The USGS data include more than 4700 sites having a mean pH less than 7.0. This represents about 20 % of all USGS sampling locations in the dataset, and suggests that the occurrence of rivers having high fractions of NC-Alk may extend beyond our region of study.

4 Conclusions

While organic acids and NC-Alk have previously been examined for in-land waters, it has mostly been in regard to their chemical composition, and not their effect upon TAlk measurements and CO_2 efflux estimates. Our data indicate that NC-Alk represents a significant, and sometimes dominant, portion of alkalinity in northern New England and Canadian Maritime rivers. The presented levels of presumed organic acid contribution to TAlk are much higher than in other reports (Lozovik, 2005), although some have found levels of similar magnitude (Cai et al., 1998). The lower average pH of these rivers (Table 3) may be related to acidic precipitation in the region (Dupont et al., 2005), resulting in increased leaching of organic acids from the soils, but this is speculative. The use of total alkalinity to estimate CO_2 efflux in this region is thus problematic, and leads to a presumed overestimate of pCO$_2$. Direct measurements of pCO$_2$ like those of Hope et al. (1995) or Wallin et al. (2010), together

with concurrent sampling of TAlk, DIC and pH, are needed to confirm that $p\text{CO}_{2\text{-DIC-pH}}$ is accurate. Based on the presented data we recommend that estimates of $p\text{CO}_2$ in a studied body of water be made using DIC and pH measurements if the NC-Alk fraction is unknown; however, the simple relationship between % NC-Alk and pH (Fig. 4) shows promise. If this relationship can be extended to other areas and types of water bodies, it may allow for more accurate estimates of $p\text{CO}_2$ as well as a more realistic accounting of carbonate alkalinity in stream water. An investigation into the presence and properties of NC-Alk in alkaline waters is needed as well. Because of the widespread use of TAlk as a carbonate system parameter, research on the quantification, sources, and chemical composition of NC-Alk in inland waters remains a priority.

Edited by: T. J. Battin

References

Cai, W.-J. and Wang, Y.: The chemistry, fluxes and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha Rivers, Georgia, Limnol. Oceanogr., 43, 657–668, 1998.

Cai, W.-J., Wang, Y., and Hodson, R. E.: Acid-base properties of dissolved organic matter in the estuarine waters of Georgia, USA, Geochim. Cosmochim. Ac., 62, 473–483, 1998.

Cantrell, K. J., Serkiz, S. M., and Perdue, E. M.: Evaluation of acid neutralizing capacity data for solutions containing natural organic acids, Geochim. Cosmochim. Ac., 54, 1247–1254, 1990.

Cole, J. J. and Caraco, N.: Carbon in catchments: connecting terrestrial carbon losses with aquatic metabolism, Mar. Freshwater Res., 52, 101–110, 2001.

Cole, J. J., Caraco, N., Kling, G. W., and Kratz, T. K.: Carbon dioxide supersaturation in the surface waters of lakes, Science, 265, 1568–1570, 1994.

Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Downing, J. A., Middelburg, J. J., and Melack, J.: Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget, Ecosystems, 10, 171–184, 2007.

Covington, A. K., Whalley, P. D., and Davison, W.: Procedures for the measurement of pH in low ionic-strength solutions including fresh-water, Analyst, 108, 1528–1532, 1983.

Degens, E. T., Kempe, S., and Richey, J. E. (Eds.): Biogeochemistry of major world rivers, SCOPE, 42, 323–347, John Wiley & Sons, 1991.

Dickson, A. G., Afghan, J. D., and Anderson, G. C.: Reference materials for oceanic CO$_2$ analysis: a method for the certification of total alkalinity, Mar. Chem., 80, 185–197, 2003.

Dupont, J., Clair, T. A., Gagnon, C., Jeffries, D. S., Kahl, J. S., Nelson, S. J., and Peckenham, J. M.: Estimation of critical loads of acidity for lakes in northeastern United States and Eastern Canada, Environ. Monit. Assess., 109, 275–291, 2005.

Gran, G.: Determination of the equivalence point in potentiometric Titrations, Part II, Analyst, 77, 661–671, 1952.

Hemond, H. F.: Acid neutralizing capacity, alkalinity, and acid-base status of natural waters containing organic acids, Environ. Sci. Technol, 24, 1486–1489, 1990.

Hope, D., Dawson, J. J. C., Cresser, M. S., and Billett, M. F.: A method for measuring free CO$_2$ in upland streamwater using headspace analysis, J. Hydrol., 166, 1–14, 1995.

Kim, H.-C. and Lee, K.: Significant contribution of dissolved organic matter to seawater alkalinity, Geophys. Res. Lett., 36, L20603,4 doi:10.1029/2009GL040271, 2009.

Lewis, E. and Wallace, D. W. R.: Program Developed for CO$_2$ SystemORNL/CDIAC-105, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, 1998.

Lozovik, P. A.: Contribution of organic acid anions to the alkalinity of natural humic water, J. Anal. Chem., 60, 1000–1004, 2005.

Morel, F. M. M. and Hering, J. G.: Principles and Applications of Aquatic Chemistry, Wiley-Interscience, New York, 1993.

Oczkowski, A. J.: Riverine inputs of nutrients to Great Bay, NH (USA), MS thesis, University of New Hampshire, 2002.

Paquay, F. S., Macenzie, F. T., and Borges, A. V.: Carbon dioxide dynamics in rivers and coastal waters of the "big island" of Hawaii, USA, during baseline and heavy rain conditions, Aquat. Geochem., 13, 1–18, 2007.

Parkhurst, D. L. and Appelo, C. A. J.: User's guide to PHREEQC (version 2) – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: US. Geological Survey Water-Resources Investigations Report 99-4259, 312 pp., 1999.

Richey, J. E.: Pathways of Atmospheric CO$_2$ through Fluvial Systems, 329–340, in: Toward CO$_2$ Stabilization: Issues, Strategies, and Consequences, A SCOPE/GCP Rapid Assessment Project, edited by: Fields, C., Island Press, 526 pp., 2004.

Sobek, S., Tranvik, L. J., and Cole, J. J.: Temperature independence of carbon dioxide supersaturation in global lakes, Global Biogeochem. Cy., 19, GB2003, doi:10.1029/2004GB002264, 2005.

Stumm, W. and Morgan, J. J.: Aquatic Chemistry, Wiley-Interscience, New York, 1996.

Tishchenko, P. Y., Wallmann, K., Vasilevskaya, N. A., Volkova, T. I., Zvalinski, V. I., Khodorenko, N. D., and Shkirnikova, E. M.: The contribution of organic matter to the alkaline reserve of natural waters, Oceanology, 46, 211–219, 2006.

Wallin, M., Buffam, I., Oquist, M., Laudon, H., and Bishop, K.: Temporal and spatial variability of dissolved inorganic carbon in a boreal stream network: Concentrations and downstream fluxes, J. Geophys. Res., 115, G02014, doi:10.1029/2009JG001100, 2010.

Williams, A. J., Andersen, C. B., and Lewis, G. P.: Evaluating the effects of sample processing treatments on alkalinity measurements, J. Hydrol., 377, 455–464, 2009.