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Discussions

Contribution of non-carbonate anions to river alkalinity and overestimation of $p\mathrm{CO}_2$

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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 ($p\text{CO}_2$) 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 $p\text{CO}_2$, we measured pH, TAlk, and DIC in samples of river water. Estimates of $p\text{CO}_2$ derived from TAlk and pH measurements were markedly higher than $p\text{CO}_2$ estimates derived from DIC and pH. 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 and the Canadian Maritimes. NC-Alk represents a significant buffering component in these river systems, and failure to account for NC-Alk (which cannot directly contribute to $p\text{CO}_2$) 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 (Cole and Caraco, 2001). In addition to transporting water and carbon, inland waters process a large fraction of the carbon they receive, typically resulting 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):

$$\begin{aligned}\mathrm{TAlk} = {} & [HCO_3^-]+2[CO_3^{2-}]+[B(OH)^{4-}]+[OH^-]+[HPO_4^{2-}]+2[PO_4^{3-}]+[H_3SiO_4^-]\\ & +2[H_2SiO_4^{2-}]+[HS^-]+2[S^-]+[NH_3^+]+[Org^-]-[H^+]-[H_3PO_4] \qquad (1)\end{aligned}$$

where Org$^-$ represents a collective term for organic acids. We simplify this equation as:

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

where C-Alk is the sum of carbonate and bicarbonate, and NC-Alk is the net contribution of non-carbonate species to 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). However, 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 can lead to an overestimation of the 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, mostly forested, 72 km^2 watershed in southeastern New Hampshire, USA. Samples were collected in 60-ml glass BOD bottles with greased stoppers, preserved with 0.1 ml of saturated mercuric chloride solution, and immediately cooled. In-situ temperature was measured with a handheld meter (YSI, Yellow Springs, Ohio). Samples collected from the additional sites listed in Table 1 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), which acidified of a small amount of sample (0.5 ml) with 10 % phosphoric acid and subsequently measured the evolved CO_2 with a Li-Cor 6262 non-dispersive infrared gas analyzer. Certified seawater reference materials from A. Dickson were used to ensure the quality of DIC determination (Dickson et al., 2003), with a resulting precision of 0.1 %.

2.3 Measurement of pH and total alkalinity

TAlk and pH of unfiltered water were measured by the same instrument. 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 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):

$$\mathrm{GF}=(v+V_\mathrm{o})/V_\mathrm{o}\cdot 10^{-\mathrm{pH}} \tag{3}$$

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 ∼ ±2 µeq l^{-1}). The accuracy of the TAlk automated system, also calibrated with the Dickson CRM as discussed above, was ±3–4 µeq 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 U.S. 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 µeq 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 $\mathrm{CO_2}$, and finally titrating the sample again according to the Gran method (example titration shown in Fig. 1). The difference in alkalinity between the first titration, after which any $\mathrm{CO_2}$ had been removed, and the second titration represented the NC-Alk (Fig. 1). Precision of this back-titration method was poor (∼75 µeq l^{-1}), but the NC-Alk measured by this method, ranging from 160–220 µeq l^{-1}, was well within the range of calculated values described in this study.

2.4 Carbonate system calculations

TAlk, pH, and DIC were used with carbonate dissociation constants from Millero (1979) as inputs to the CO2SYS program ("Salinity = 0 freshwater; K1, K2 from Millero, 1979" option, Lewis and Wallace, 1998) to calculate the unknown parameters of the carbonate system. The selection of the carbonate dissociation constants is a difficult one, since the CO2SYS program provides twelve sets of constants. To compare the effect of the selection of the "Salinity = 0 freshwater; K1, K2 from Millero (1979)" option, $p\mathrm{CO}_2$ and TAlk were also calculated using the "Millero (2006)", "K1, K2 from Roy (1993)", and "K1, K2 from Goyet and Poisson (1989)" options, with identical input data. The resulting $p\mathrm{CO}_2$ differed from the "$S = 0$ freshwater" results by averages of −5 %, 8 % and 5 %, respectively. For TAlk, the results differed from the "$S = 0$ freshwater" option by 4 %, −6 % and −4 %, respectively. Thus, the choice to use the "$S = 0$ freshwater" option seems to produce calculated TAlk and $p\mathrm{CO}_2$ that fall near the median of the range of values produced by the various sets of carbonate dissociation constants available in CO2SYS.

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 $\mu\mathrm{eq\,l}^{-1}$, 500 $\mu\mathrm{eq\,l}^{-1}$, and 6.8, respectively. The least-squares linear regression of TAlk and DIC showed a fairly strong trend ($r^2 = 0.83$), while a similar linear regression of TAlk and pH was weaker ($r^2 = 0.59$). We calculated NC-Alk by subtracting the calculated TAlk values – derived from DIC and pH measurements ($\mathrm{TAlk}_{\mathrm{DIC\text{-}pH}}$) – from measured TAlk ($\mathrm{TAlk}_{\mathrm{measured}}$). This produced a NC-Alk ranging between 83–423 $\mu\mathrm{eq\,l}^{-1}$, with a mean

NC-Alk of 145 µeq 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. Analyses of TAlk and DIC were calibrated using a certified reference material, with a precision of about ±0.5 µeq l^{-1} in DIC and ±1.0 µeq 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. When this uncertainty is applied to our measurements the resulting change in $\text{TAlk}_{\text{DIC-pH}}$ (on the order of 3–5 µeq 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 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, also called humics (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 ($Al(OH)_2^+$, $Al(OH)_3$) can also contribute NC-Alk, but this phenomena 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 $\text{TAlk}_{\text{measured}}$, with a mean of 32 %, demonstrating that NC-Alk is an important component of alkalinity in this river.

It is also 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 $\text{TAlk}_{\text{measured}}$. 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 find that our estimates of NC-Alk represent 48–53 % of the total organic acids (humics) predicted to be present in the samples, with a median of 51 %. 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 $\mu\text{eq}\,\text{l}^{-1}$) 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.

3.2 Overestimation of $p\text{CO}_2$ due to NC-Alk

When we examined the difference between $p\text{CO}_{2\text{-TAlk-pH}}$ and $p\text{CO}_{2\text{-DIC-pH}}$ (assuming that $p\text{CO}_{2\text{-DIC-pH}}$ represents the accurate estimate of $p\text{CO}_2$) we found that accounting for the presence of NC-Alk substantially lowers $p\text{CO}_2$ estimates in the Oyster River. In other words, using TAlk instead of DIC to calculate $p\text{CO}_2$ resulted in overestimated $p\text{CO}_2$ (Fig. 3). Calculating $p\text{CO}_2$ from TAlk and pH led to an overestimation of $p\text{CO}_2$ 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 pCO_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 pCO_2.

While we found $pCO_{2\text{-TAlk-pH}}$ to be overestimated with respect to $pCO_{2\text{-DIC-pH}}$, an accurate measure of pCO_2 is still be needed. Hope et al. (1995) developed a headspace equilibration method to measure free CO_2, and found that this method yielded much higher pCO_2 than calculated $pCO_{2\text{-TAlk-pH}}$. Inaccuracy in the measurement of pH in an open cell was cited as one of the reasons why $pCO_{2\text{-TAlk-pH}}$ was underestimated, with the loss of CO_2 resulting in 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 $pCO_{2\text{-TAlk-pH}}$ and $pCO_{2\text{-DIC-pH}}$.

3.3 Results from other New England and Canadian Maritime rivers

We sampled other northern New England USA and Canadian Maritime rivers to examine regional levels of NC-Alk (Table 1). The NC-Alk concentrations calculated for each river fall within the range of NC-Alk concentrations we measured in the Oyster River. NC-Alk appears 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 1 the percent difference between $pCO_{2\text{-TAlk-pH}}$ and $pCO_{2\text{-DIC-pH}}$ 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, $p\mathrm{CO}_{2\text{-DIC-pH}}$ from the rivers in Table 1 averages 3330 µatm, nearly an order of magnitude higher than atmospheric levels, indicating that these rivers represent sources of carbon dioxide to the atmosphere. Data from the Oyster River appears 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 1 and Fig. 4 are indicative of poorly buffered rivers and streams, with relatively low pH and 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 to 1 January 2010. This comparison (Table 2) shows that the pH and TAlk are indeed lower than national values, 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 the NC-Alk contributions from DOC similar to those in New England may be possible elsewhere. The USGS data shows more than 4700 unique sites, representing about 20 % of all sites, had a mean pH less than 7.0. This suggests that the occurrence of rivers having high fractions of NC-Alk extends well beyond our region of study.

4 Conclusions

While organic acids and NC-Alk have been examined in inland waters, it has mostly been in regard to their chemical composition, and not their effect upon TAlk measurements and CO_2 degassing 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 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, together with concurrent sampling of TAlk, DIC and pH, are needed to confirm that $pCO_{2\text{-DIC-pH}}$ is accurate. Based on the presented data we recommend that estimates of pCO_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 pCO_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.

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Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◂◂ | ▸▸
◂ | ▸
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

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Table 1. 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.

River	Location	Sampling Date	Latitude	Longitude	NC-Alk (μeq l^{-1})	NC-Alk fraction
Merrimac	Lowell, MA	29 May 2008	42.66	−71.32	161	39 %
Kennebec	Richmond, ME	1 Jun 2008	44.09	−69.79	170	46 %
Aroostook	Washburn, ME	14 Jul 2008	46.78	−68.16	206	36 %
Canaan	Coles Island, NB	15 Jul 2008	46.92	−65.79	315	85 %
St. John	Fredericton, NB	15 Jul 2008	46.96	−66.64	157	21 %
Tobique	Tobique, NB	15 Jul 2008	46.79	−67.49	222	27 %
St. John	Perth, NB	15 Jul 2008	46.74	−67.71	296	33 %
Saco	Fryeburg, ME	15 Jul 2008	44.08	−70.91	184	79 %
Saco	Crawford Notch, NH	15 Jul 2008	44.18	−71.40	166	90 %
Kennebecasis	Norton, NB	16 Jul 2008	45.64	−65.70	217	23 %
Connecticut	Lancaster, NH	16 Jul 2008	44.46	−71.65	163	45 %
Androscoggin	Brunswick, ME	25 Aug 2008	43.92	−69.97	259	85 %
Pleasant	Columbia Falls, ME	21 Sep 2008	45.65	−67.73	130	101 %
Narraguagus	Cherryfield, ME	21 Sep 2008	44.61	−67.93	106	91 %
Penobscot	Milford, ME	5 Dec 2008	44.94	−68.64	278	91 %

Table 2. Comparison of pH, TAlk and DOC data 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						
This study	16	454	368	116	956	268
USGS	1173	1064	1086	10	2970	720
DOC						
This study (Oyster River only)	1	472	469	245	665	143
USGS	5417	475	286	8.3	>2000	326

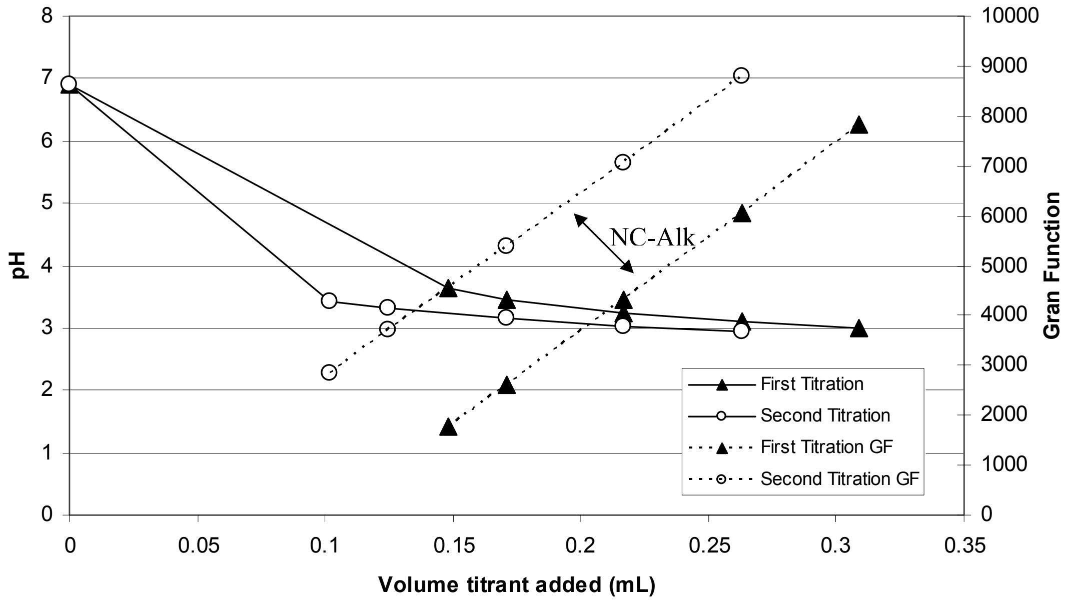

Fig. 1. Example titration curve and Gran function (GF) plot for Oyster River water.

BGD
8, 5159–5177, 2011
Non-carbonate river alkalinity
C. W. Hunt et al.

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀| |▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

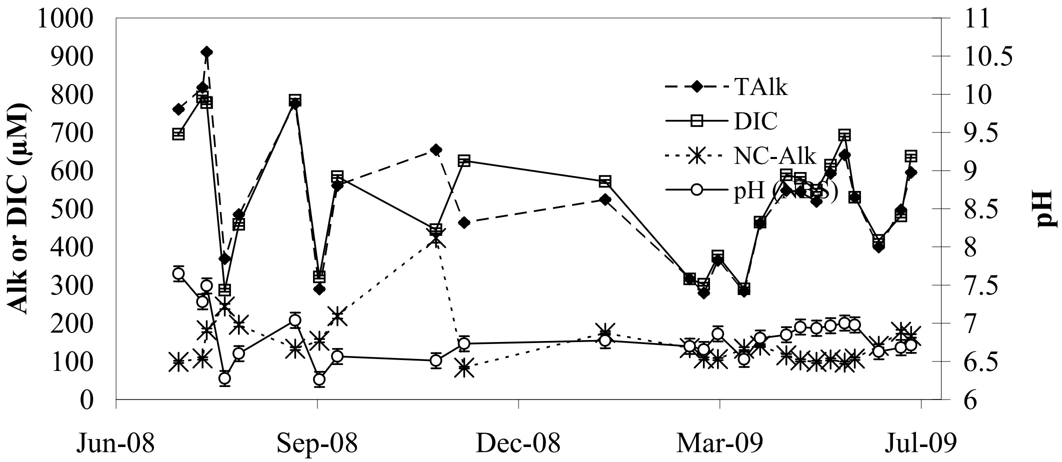

Fig. 2. TAlk, DIC and pH at one sampling location on the Oyster River. NC-Alk was calculated by subtracting $\text{TAlk}_{\text{DIC-pH}}$ from $\text{TAlk}_{\text{measured}}$. Error bars of ±0.1 in pH are shown, but error bars of ±4 $\mu\text{eq}\,\text{l}^{-1}$ in TAlk and DIC are too small to appear in the plot.

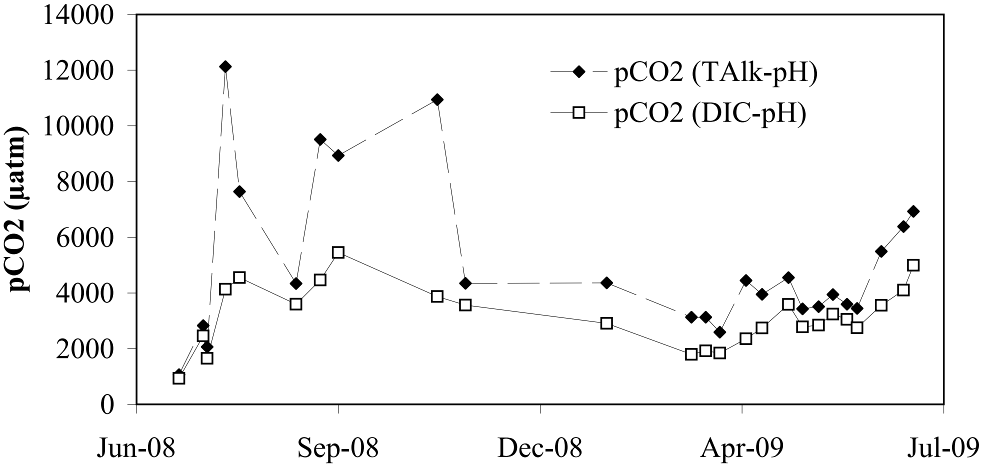

Fig. 3. Partial pressure of carbon dioxide calculated from TAlk and pH ($p\mathrm{CO}_{2\text{-TAlk-pH}}$), as well as from DIC and pH ($p\mathrm{CO}_{2\text{-DIC-pH}}$), at one sampling site on the Oyster River.

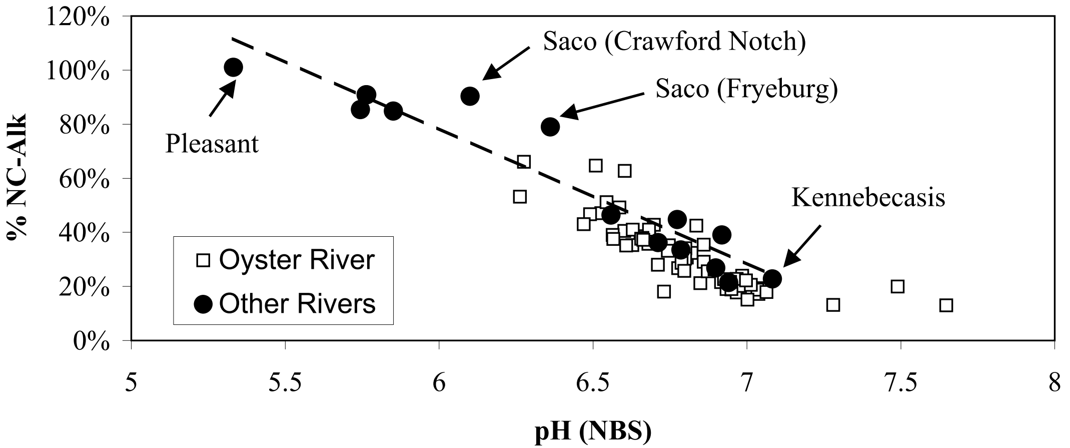

Fig. 4. Relationship between pH (measured in the lab) and the calculated percentage of NC-Alk in the Oyster River and the sampled rivers in northern New England and Canada (Other Rivers, Table 1). The dotted line shows the linear regression of the Other Rivers, having the equation $\%\,\text{NC-Alk} = -0.5 \cdot \text{pH} + 378$.