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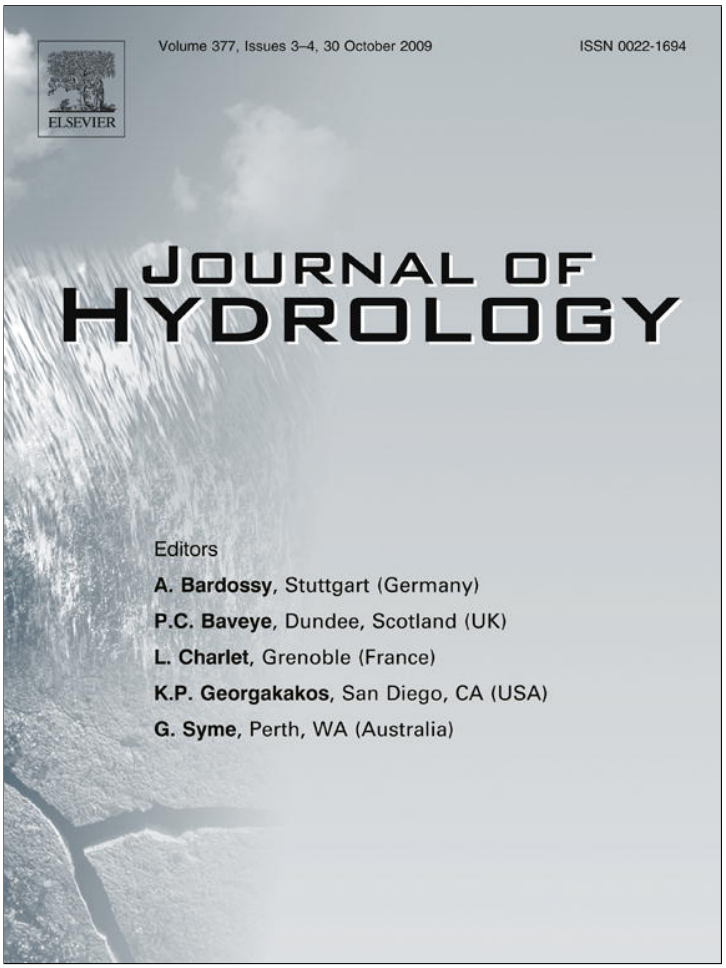

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Evaluating the effects of sample processing treatments on alkalinity measurements

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SUMMARY

The concentration of bicarbonate, the dominant anion in river water, is typically calculated using measured alkalinity concentrations. Alkalinity concentrations also are necessary for analytical charge balance, carbonate speciation, and PCO_2 calculations. Although the Gran titration is the standard method for measuring alkalinity, previous studies have varied in how water samples have been processed prior to analysis. The purpose of this study was to determine whether variation in filtering, refrigeration, and sample storage time leads to statistically significant differences in alkalinity concentrations in oxic, low-turbidity surface waters and groundwaters ranging from undersaturated to supersaturated with respect to calcite. Samples were collected from the Blue Ridge and Piedmont Provinces of northwestern South Carolina and the Valley and Ridge Province of eastern Tennessee. Each sample was analyzed using four processing treatments: filtered and refrigerated, filtered and unrefrigerated, unfiltered and refrigerated, and unfiltered and unrefrigerated ($n = 3$ analyses per treatment combination). All replicates were analyzed within 24 h using the Gran titration method. Samples then were reanalyzed after 17–194 days of storage to determine if storage time affects alkalinity measurements. Overall, alkalinity concentrations ranged from 0.8 to 107 mg/L $CaCO_3$. Statistically significant differences among the treatments and significant interactions between filtration and refrigeration were limited. For samples in which treatment means differed significantly or in which interactions were significant, differences generally were less than 10% and probably of little biogeochemical importance. For all but one sample locality, storage time did not affect alkalinity. Our results show that for oxic waters that have low concentrations of DOC and reduced metals, filtration, refrigeration and storage time are unlikely to affect measured alkalinity concentrations. However, additional research is needed to determine the degree to which sample processing treatment is important to interpreting the alkalinity concentrations of DOC- and metal-rich samples.

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Introduction

Rivers transport carbon (C) between terrestrial sources and the ocean (e.g., Ramesh et al., 1995; Edmond et al., 1995) and release C to the atmosphere during the transport process (e.g., Raymond et al., 1997; Oechel et al., 2000; Richey et al., 2002; Worrall and Lancaster, 2005). Forms of riverine C include dissolved and particulate organic C and dissolved and particulate inorganic C (Meybeck, 1993). Of these forms, dissolved inorganic C (DIC) typically has the highest concentration in both small streams and large rivers (e.g., Meybeck, 1993; Dawson et al., 2002) except for some blackwater streams and rivers (e.g., Neal and Hill, 1994; Richey et al., 1990). Globally, bicarbonate (HCO_3^-) is the dominant inorganic carbonate species in most rivers and many groundwaters (Meybeck, 2003; Eby, 2004). The dominance of HCO_3^- is consistent with the typical pH range of 6.0–8.2 for surface and groundwaters. Thus, HCO_3^- typically will be the dominant species of carbonate and will make the largest contribution to C fluxes to the ocean.

Bicarbonate concentration, however, is difficult to measure directly. Most often, alkalinity is measured directly, and HCO_3^- concentration is calculated assuming that the concentrations of other alkalinity-producing anions are not significant. Water temperature and pH are the two most important controls over inorganic carbon speciation and therefore over the proportion of DIC that is HCO_3^-. Total DIC can be measured directly and HCO_3^- concentrations calculated (e.g., McDowell and Asbury, 1994; Raymond et al., 1997), although this method is less common. More commonly, inorganic C species concentrations are calculated using a thermodynamic model utilizing stream water or groundwater temperature, pH, and alkalinity as model variables, along with other variables for calcite-saturated waters (e.g., Neal et al., 1998). Of these three variables, pH and alkalinity have the greatest uncertainty, with temperature measurements generally being the most precise. The uncertainty in pH measurements in natural

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waters is associated with low conductivity (Neal and Thomas, 1985) and can be attributed to high sample PCO_2 (partial pressure of carbon dioxide) values (Cai and Wang, 1998), variable temperatures, errors due to using a large buffer range (Howland et al., 2000), and analytical error associated with electrode aging and variation in liquid junction (Pytkowicz et al., 1966). Unlike uncertainty in pH measurements, the variation in alkalinity concentrations as caused by sample treatment have not been systematically assessed.

Gran titration is the standard method for measuring alkalinity, although some studies have used end point titration to pH 4.5 (e.g., Neal, 1988). In contrast to the standard titration methods, the processing of water samples has varied considerably in past studies. The standard method (Eaton et al., 1995) recommends that alkalinities be measured within 24 h of collection on unfiltered samples, with a maximum of 14 d of refrigerated storage. However, the basis for this recommendation is unclear. Through the years, a variety of treatment methods have been used to process samples for alkalinity measurements, yet no consensus exists on which method is the most reliable. Although in some studies samples were titrated in the field (e.g., Richey et al., 1990; Piñol and Avila, 1992; Barth et al., 2003), in other studies samples were shipped and stored prior to analysis (e.g., Moon et al., 2007). Samples sometimes have been filtered prior to alkalinity measurement (e.g., Neal and Hill, 1994; Edmond et al., 1995; Wu et al., 2005) and sometimes not (e.g., Lewis and Grant, 1979; Hoffer-French and Herman, 1989; Jones and Mulholland, 1998; Neal et al., 2000). Samples sometimes have been refrigerated prior to analysis (e.g., Hoffer-French and Herman, 1989; Raymond et al., 1997, Neal et al., 2000) and sometimes not (e.g., Lewis and Grant, 1979; Edmond et al., 1995; Howland et al., 2000; Barth et al., 2003).

Very few studies have examined the impact of variation in filtration, refrigeration, or sample storage time in any systematic fashion. Stallard (1980), in his study of the Amazon River, provided limited data showing that filtration and storage time did not affect calcite saturation levels even for supersaturated samples. Still, samples for alkalinity analysis were not collected in some studies because of concerns about the effects of sample transport and storage (Zhang et al., 1995; Nakagawa and Iwatsubo, 2000). The purpose of our study was to determine whether variations in sample processing treatments (filtration, refrigeration, and storage time) significantly affect alkalinity concentrations in freshwater (stream and groundwater) samples from both silicate and carbonate terrains. Given the range of chemistries of our samples, our results apply primarily to oxic waters (>2 mg/L) with low turbidity, dissolved organic carbon, and dissolved iron.

Study areas

Three surface water samples and four groundwater samples were collected from localities in the Blue Ridge of northwestern South Carolina, and four surface water samples were collected from localities in the Valley and Ridge Province of eastern Tennessee (Fig. 1). Sample localities were chosen to represent waters that, as a result of draining either silicate or carbonate rocks, had a wide range of alkalinities.

Piedmont localities

The Piedmont Province of South Carolina is characterized by Paleozoic metamorphic and igneous silicate rocks of the Inner Piedmont terrane (Overstreet and Bell, 1965). These rocks are dominantly gneisses, schists, and granites with minerals of low solubility. Ultisols overlying sandy clay loam saprolites constitute the regolith in this region (Byrd, 1972). Thus, natural surface water

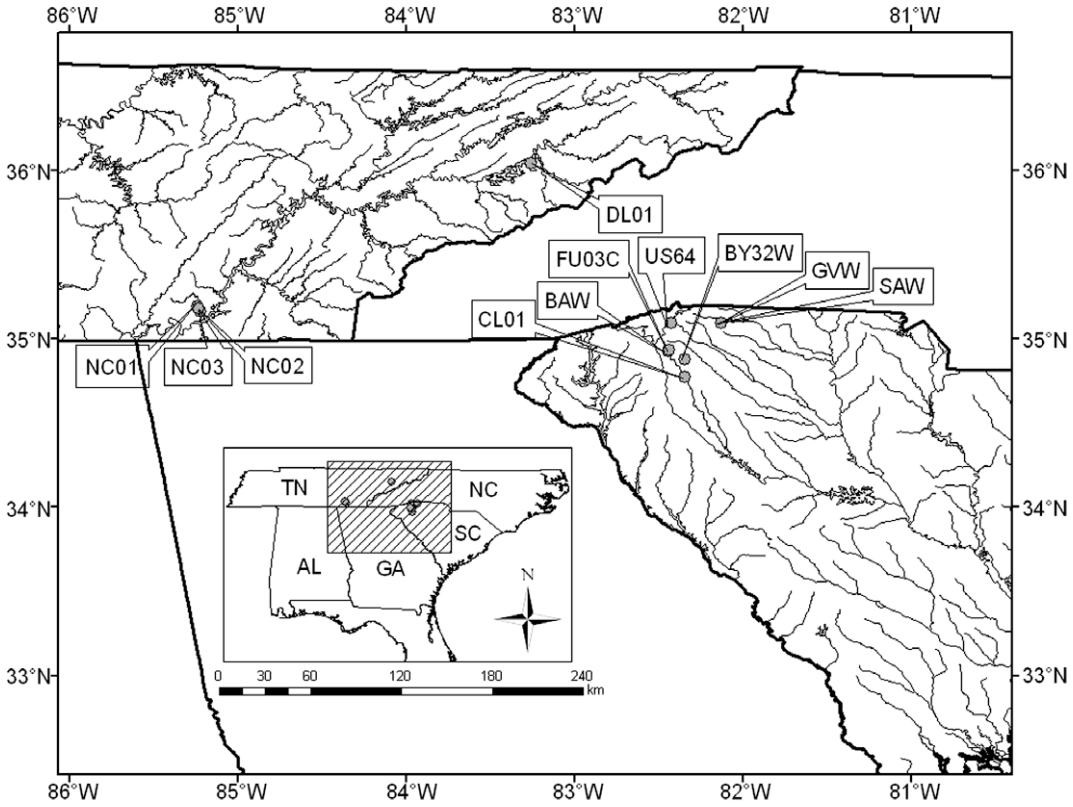

Fig. 1. Location maps for surface and groundwater samples from the Blue Ridge and Piedmont provinces in northwestern South Carolina and the Valley and Ridge Province in eastern Tennessee.

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and groundwater from the Piedmont region typically has low ionic strength and low alkalinity (Andersen et al., 2001; Lewis et al., 2007). The three surface water sample localities were chosen from within the Saluda River basin (Fig. 1) to represent a characteristic range of alkalinities for the Piedmont region. Locality US64 was a headwater stream draining gneisses and schists of the Tallulah Falls Formation in the mountainous terrain of the South Saluda River sub-basin (Garihan, 2007). The other two localities, FU03C and CL01, were surface impoundments within the Reedy River sub-basin whose streams drain biotite gneisses and silmanite schists of the Tallulah Falls Formation or similar rocks (Maybin, 2003; Garihan, 2009).

Groundwater samples were collected from four wells ranging from 5.2 to 101.8 m deep located in the Saluda, Enoree, and Pacolet River basins (Fig. 1). The localities included shallow and deep wells chosen to represent a characteristic range of alkalinities. The well at locality GVW was chosen because it was screened in gneiss bedrock at a depth of 101.8 m. The well at locality SAW was chosen as a comparison for GVW because it was within 1 m of GVW and was screened in saprolite at 24.4 m. The well BY32W was screened in saprolite at a depth of 5.2 m along a branch of Brushy Creek, an urbanized tributary of the Enoree River. The well at BAW, located along a headwater of a tributary to the Reedy River in the Saluda River basin, was screened in saprolite at a depth of 7.25 m.

Valley and Ridge localities

Four localities were located the Valley and Ridge Province of eastern Tennessee, which is characterized by abundant carbonate and carbonate-cemented sedimentary rocks (Fig. 1). Surface water samples were collected from three localities along North Chickamauga Creek in the Lower Tennessee River Basin, which drains Paleozoic sedimentary rocks (Rogers, 1953; Hardeman, 1966). The headwaters originate in Pennsylvanian siliciclastic sedimentary rocks and coals of the Crab Orchard Mountains Group and then flow through Mississippian to Cambrian carbonate rocks and carbonate-cemented siliciclastic sedimentary rocks. Locality NC01 drained Mississippian carbonates of the Newman Limestone, but it also was ~1.5 km downstream of three mines discharging acidic effluent. Localities NC02 and NC03 drained the carbonates of the Ordovician Knox Dolomite and Cambrian Copper Ridge Dolomite, respectively, and were unaffected by acid mine drainage at either location. Locality DL01 was located in the French Broad River basin along the shore of Douglas Lake, an impoundment of the Nolichucky and French Broad Rivers. The headwaters of these rivers drain siliciclastic metasedimentary and sedimentary rocks of the Precambrian Ocoee Supergroup and the Cambrian Chilhowie Group and then flow through carbonates of the Ordovician Knox Group and the calcareous Ordovician Sevier Formation (Rogers, 1953; Hardeman, 1966).

Methods

Samples were collected between October 2005 and March 2007. Each locality was sampled once, with the exception of BY32W, which was sampled twice (November 2006 and February 2007). At each surface water locality, a grab sample was collected in a pre-cleaned 4 L HDPE bottle. At each groundwater locality, water was collected in four pre-cleaned 500 mL HDPE bottles (to be filtered) and twelve pre-cleaned 125 mL HDPE bottles (left unfiltered). At all localities, the sample bottles were rinsed three times with the water from that locality before filling. Also, a sample for turbidity was collected in a separate HDPE bottle at each locality. To minimize degassing, all samples were collected with zero headspace, either by submerging the bottle and capping under water or by filling the bottle to overflowing and then capping. Samples then were transported to the laboratory on ice. Water temperature, pH, conductivity, and dissolved oxygen (DO) were measured in the field at all localities with Fisher Scientific AP62 Accumet pH meters, YSI 30 salinity/conductivity meters, and YSI 55 dissolved oxygen meters.

In the laboratory, samples for alkalinity analysis were processed using four different treatment combinations of filtering and refrigeration with three replicates per treatment. The four treatments were filtered-refrigerated (FR), filtered-unrefrigerated (FU), unfiltered-refrigerated (UR), and unfiltered-unrefrigerated (UU). Filtered samples were passed through a 0.45 μm cellulose membrane filter using a N_2 gas positive pressure filtration system. Refrigerated samples were stored at 4 °C until analysis, and unrefrigerated samples were stored at room temperature. For all samples from each locality, alkalinities were measured within 24 h of sample collection. We made the assumption that titration in the controlled laboratory conditions likely is more accurate than titration in field conditions. In addition, subsamples from each locality were stored for a period ranging from 17 to 51 days before reanalysis of alkalinity. For South Carolina surface water localities, only unrefrigerated filtered and unrefrigerated unfiltered samples were reanalyzed after storage. Additionally, refrigerated filtered samples for locality FU03C were reanalyzed again after 194 days. For South Carolina groundwater and Tennessee surface water localities, samples in all treatment combinations were reanalyzed after storage.

Alkalinity was measured using the Gran titration method. Titrations were performed using Fisher Accumet AR25 dual channel pH/ion meters with Fisher Accumet glass combination electrodes, Kimax "A" 5 mL burets, and either 0.020 N (low alkalinity) or 0.20 N (high alkalinity) sulfuric acid. Cation, anion, dissolved silicon, and dissolved organic C (DOC) analyses were performed within 1 wk of sample collection on single aliquots of filtered and refrigerated (FR) samples. Cation aliquots were preserved with trace metal grade nitric acid, and aliquots for anion, ammonium (NH_4^+), and DOC analyses were left unpreserved. Cation and dissolved silicon concentrations (Na^+, Ca^{2+}, K^+, Mg^{2+}, Fe^{3+}, Si^{4+}) were measured using a Varian 2000 ICP-AES. Anion concentrations (F^-, Cl^-, Br^-, NO_3^-, NO_2^-, $H_2PO_4^-$, SO_4^{2-}) were measured using a Dionex DX-120 ion chromatograph. Ammonium concentrations were measured with a Turner Designs 10-AU fluorometer using Protocol B of Holmes et al. (1999). Dissolved organic C (DOC) concentrations were measured with a Tekmar Dohrmann Phoenix 8000 total C analyzer using a potassium persulfate – UV light oxidation method. Samples FUC03, US64, and CL01 were not analyzed for DOC, so DOC concentrations were estimated based on results from previous studies for purposes of interpretation Andersen and Lewis, unpublished data. Turbidity was measured the same day of sample collection using a LaMotte 2020 turbidity meter.

Charge balance error was calculated using the method of Freeze and Cherry (1979) assuming that all alkalinity was in the form of HCO_3^-. This assumption is reasonable for surface and groundwaters low in phosphate and other alkalinity-generating anions (Andersen, 2002). Because measurements of cation and anion concentrations were not repeated, variation in charge balance error for sample treatments was accounted for by variation in measured alkalinity concentrations.

For the alkalinities measured within 24 h, as well as for the alkalinities of stored samples, we used two-way analysis of variance (ANOVA) tests to determine if mean alkalinities differed significantly among the processing treatment methods. These ANOVAs also allowed us to test for interactions between processing methods (i.e., between filtration and refrigeration methods). We used the Kolmogorov–Smirnov test to test for normality of alkalinity data and the Levene median test to determine if alkalinities in the treatment groups had equal variances. For each locality,

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a paired *t*-test or a Wilcoxon rank sum test was used to compare the alkalinities measured within 24 h to alkalinities measured after storage of the same samples or subsamples. For the South Carolina surface water samples, a *t*-test was used to compare the alkalinities of the FU and UU samples reanalyzed after storage. We considered the results of statistical tests to be statistically significant if $p \leqslant 0.05$. We used SigmaStat software (v. 3.5) to conduct all statistical tests.

Carbonate speciation and the partial pressure of carbon dioxide (PCO_2) were calculated using a simple thermodynamic model modified from Andersen (2002). Equilibrium constants were calculated using the equations of Plummer and Busenburg (1982), and activity coefficients were calculated using the extended Debye–Hückel equation. The ratio of PCO_2 in sample water to PCO_2 in the atmosphere indicates the degree of carbon dioxide (CO_2) supersaturation in the water relative to the atmosphere (Piñol and Avila, 1992; Huh et al., 1998). We refer hereafter to this ratio as PCO_2 saturation. The equation for the PCO_2, which uses measurements of water temperature, pH, and HCO_3^-, was not modified to account for the dissolution of calcite (e.g., Neal et al., 1998) because distinguishing between silicate and carbonate weathering was not relevant to this study.

Results

Field data and chemical analyses

Surface water and groundwater samples collected from the South Carolina Piedmont were dilute (<120 μS/cm) and had circumneutral to slightly acidic pH (Table 1). Locality CL01 was a silted impoundment that had become a wetland. Thus, the surface water at that locality had lower DO than did the other surface waters, which were well oxygenated. Groundwater samples were poorly to moderately well oxygenated. Locality BAW had a nitrate concentration >17 mg/L, which was much higher than in any other sample. Surface water samples collected from the Tennessee Valley and Ridge generally had higher conductivity (>150 μS/cm) than the South Carolina samples, neutral to slightly basic pH, and moderately high oxygenation. However, the sample from NC01 had slightly acidic pH and was relatively dilute. All surface waters had turbidity values <11 NTU. We did not analyze FU03C for turbidity, but the water was clear on collection suggesting an equally low turbidity.

In general, surface water and groundwater samples from the Piedmont had a mixed cation to sodium bicarbonate composition (Fig. 2). The headwater stream at US64 had a higher dissolved silicon concentration than downstream localities (Table 1). CL01 had very low dissolved silicon for the Piedmont and had the highest sodium and chloride concentrations of any locality we sampled. In contrast, the samples from the Valley and Ridge had a calcium bicarbonate composition, with the exception of NC01 which had a calcium sulfate composition (Fig. 2). All of the sample localities from the Valley and Ridge had sulfate concentrations between 10 and 20 mg/L.

Concentrations of DOC were consistently low (<4 mg/L) at all localities. Although we did not conduct DOC analyses on surface waters from the Piedmont in this study (Table 1), samples from these localities collected in other studies had concentra-

Table 1
Chemical composition of surface and ground waters from the Blue Ridge and Piedmont provinces of South Carolina and the Valley and Ridge province of Tennessee. All concentrations in mg/L except for conductivity (uS/cm). All data represent a single sampling event and analysis.

Locality	Temp.(°C)	pH	DO	Cond.	DOC	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	Si^{4+}	Fe^{2+}	Cl^-	NO_3^-	SO_4^{2-}	PO_4^{3-}
US64	17.0	5.3	9.4	16	NA[a]	1.62	0.60	0.53	0.31	NA	6.14	0.11	0.94	<0.05	0.65	<0.10
FUC03	10.7	6.9	9.0	47	NA	3.05	2.52	5.42	1.67	NA	2.45	0.12	3.06	0.13	3.80	<0.10
CL01	9.1	7.1	2.7	99	NA	10.51	3.59	9.98	1.50	NA	0.41	NA	15.21	2.61	8.91	<0.10
NC01	25.6	5.9	7.4	56	0.92	0.59	0.83	3.96	1.85	<0.02	2.04	NA	1.54	0.75	17.15	<0.10
NC02	21.1	7.3	6.1	217	1.57	1.34	0.88	32.49	7.60	0.03	2.60	NA	2.82	2.03	17.26	<0.10
NC03	21.0	7.2	5.9	193	1.32	1.01	0.87	31.25	7.24	0.03	2.53	NA	2.58	1.20	17.37	0.62
DL01	30.3	9.2	7.8	155	2.99	0.95	2.49	16.07	7.24	<0.02	3.32	NA	8.42	<0.05	11.00	0.81
BY32Wa[b]	15.0	6.1	3.8	90	2.69	4.79	2.52	4.85	1.42	0.65	5.98	0.72	4.61	0.14	0.11	<0.10
BY32Wb	12.1	6.1	2.6	81	1.66	4.55	2.64	4.69	1.42	0.47	5.57	0.63	4.78	0.12	0.13	<0.10
BAW	16.6	4.9	6.5	76	3.93	2.42	4.69	6.47	1.08	0.07	4.85	NA	7.69	17.24	0.52	0.31
GVW	19.5	7.7	2.3	118	0.45	7.48	4.65	9.86	3.80	<0.02	1.54	NA	1.23	0.96	0.96	<0.10
SAW	19.3	6.0	6.7	33	0.42	3.22	1.60	0.94	0.37	<0.02	8.30	0.01	1.02	0.76	0.76	<0.10

[a] NA = not analyzed.
[b] BY32Wa sampled in October 2006, BY32W sampled in February 2007.

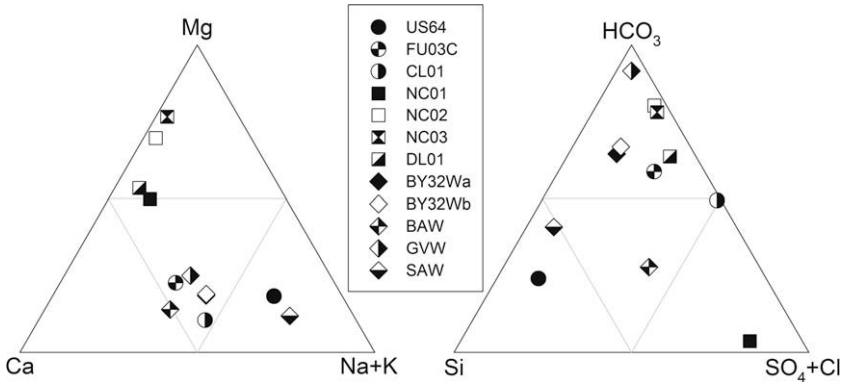

Fig. 2. Ternary plots of the chemical composition of surface and groundwaters from South Carolina and Tennessee. Circles represent surface water sample localities in the Blue Ridge and Piedmont provinces of South Carolina, squares represent surface water sample localities in the Valley and Ridge Province of Tennessee, and diamonds represent groundwater sample localities in the Piedmont Province of South Carolina. Units are in μeq/L, except for dissolved silicon, which is in μmol/L. Average alkalinity concentrations were used to calculate average bicarbonate concentrations.

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tions <5 mg/L Andersen and Lewis, unpublished data. Phosphate concentrations for all samples were very low, with most being below our detection limit of 0.1 mg/L. The three samples with measurable phosphate had concentrations <1 mg/L. Ammonium concentrations were very low in most samples, with only groundwater samples from BY32W having concentrations >0.10 mg/L. Iron concentrations were measured for a subset of samples. Iron concentrations were less than 0.15 mg/L for three sample localities, but exceeded 0.5 mg/L for groundwater samples from BY32W.

Comparison of processing treatments

Alkalinity concentrations ranged widely among localities both in the South Carolina Piedmont and in the Tennessee Valley and Ridge (Table 2). Mean alkalinity concentrations for Piedmont surface water and groundwater samples ranged from 4 to 59 mg/L $CaCO_3$. Mean alkalinity concentrations for Tennessee Valley and Ridge surface waters ranged more widely from 0.8 to 106 mg/L $CaCO_3$.

For most sample localities in both regions, there were no statistically significant effects of filtration or refrigeration on alkalinity concentrations (Tables 3 and 4). Even in comparisons in which treatment effects were statistically significant, the differences between means were relatively small. For example, after 50–57 d of storage of the samples from SAW and NC03, alkalinity concentrations were significantly lower in filtered than in unfiltered samples (Tables 2 and 4). However, mean concentrations in filtered and unfiltered samples differed by <9%. Also, there were significant differences between levels of filtration and levels of refrigeration for samples analyzed within 24 h from localities NC02 and DL01. For NC02, the differences in mean concentrations for the treatments were <3%. The largest difference between treatment means was seen in analyses of the sample from DL01. For DL01, the FR treatment mean was ~13% lower than the means from the other three treatments because two FR replicates had markedly lower alkalinity concentrations than any of the other replicates.

Significant interactions between sampling and filtration were found in three samples (BY32W, NC01, and NC02) analyzed after storage for 33–44 days (Table 4). For two of the samples (BY32W and NC02), the differences among treatment means were small. For the November sample from BY32W, the FR and UU treatments had higher mean concentrations than did the FU and UR treatments (Table 4). The means from the four treatments, however, differed by <5%. Similarly, for the sample from NC02, mean concentrations among treatments differed by <5%. In contrast, for the sample from NC01, the FR and UU mean concentrations were 1.5–2.2 times higher than the means from the FU and UR treatments. All mean concentrations, however, were very low (<1.1 mg/L $CaCO_3$) and likely near the method detection limit for the measurement of alkalinity using 0.020 N acid.

Significant effects of sample storage time on alkalinity concentrations were found only in samples from 3 of the 11 localities (Tables 2 and 4). Two of those three localities were Piedmont groundwater localities (BY32W and GVW). For the November samples from BY32W, the mean concentration after storage was 3% to 24% lower than the original concentration measured within 24 h

Table 2
Mean alkalinity concentrations (mg/L $CaCO_3$) by treatment (n = 3 per treatment).

Sample	Time	Treatment[a]			
		FR	FU	UR	UU
US64	24 h	4.07	4.10	4.20	3.97
	21 days	NA[b]	3.98	NA	4.07
FU03C	24 h	17.97	17.68	17.92	18.13
	51 days	NA	17.90	NA	18.27
CL01	24 h	31.26	30.10	31.11	30.70
	17 days	NA	30.98	NA	29.82
NC01	24 h	0.91	0.87	0.86	0.97
	33 days	1.05	0.55	0.48	0.83
NC02	24 h	104.83	107.53	106.69	109.03
	34 days	103.33	108.17	107.67	108.31
NC03	24 h	105.33	92.94	94.32	92.48
	57 days	91.63	91.3	96.00	93.19
DL01	24 h	44.40	51.00	50.88	51.50
	31 days	48.50	50.33	50.50	49.83
BY32Wa[c]	24 h	30.97	31.46	36.70	29.23
	44 days	28.07	27.47	27.47	28.63
BY32Wb	24 h	36.33	31.73	37.47	32.13
	18 days	26.10	25.33	23.50	24.80
BAW	24 h	7.77	7.87	7.77	7.50
	50 days	8.32	8.40	8.40	7.10
GVW	24 h	58.63	59.10	59.10	58.73
	40 days	58.97	59.47	59.60	59.83
SAW	24 h	11.48	11.53	12.00	11.57
	50 days	11.23	11.54	12.36	12.63

[a] FR = filtered, refrigerated, FU = filtered, unrefrigerated, UR = unfiltered, refrigerated, UU = unfiltered, unrefrigerated.
[b] NA = not analyzed.
[c] BY32W sampled twice, a = November and b = February.

Table 3
P values for comparison of treatments for surface water samples from the Blue Ridge and Piedmont provinces, South Carolina. All $P > 0.05$ indicating no significant differences.

Sample	ANOVA (<24 h)			t-test[a]	Paired t-test[b]
	Filtering	Refrigeration	Interaction		
US64	1.000	0.701	0.610	0.279	0.962
FUC03	0.464	0.890	0.351	0.306	0.270
CL01	0.673	0.166	0.487	0.223	0.970

[a] Comparison of stored unrefrigerated filtered (n = 3) to stored unrefrigerated unfiltered (n = 3) samples.
[b] Comparison of unrefrigerated filtered and unfiltered samples (n = 6) analyzed in <24 h and after respective storage times of 12, 51, and 17 days.

Table 4
P values of Tennessee Valley and Ridge surface water samples and South Carolina piedmont groundwater samples. Bold numbers indicate significant results ($P < 0.050$).

Sample	Storage	ANOVA			Paired t-test[a]
		Filtering	Refrigeration	Interaction	
NC01	<24 h	0.731	0.626	0.299	
	33 days[c]	–	–	**0.020**	**0.046**
NC02	<24 h	**0.024**	**0.003**	0.775	
	34 days	–	–	**0.017**	0.785
NC03	<24 h[c]	0.344	0.248	0.382	
	57 days	**0.039**	0.252	0.358	0.677[d]
DL01	<24 h	**0.044**	**0.037**	0.076	
	31 days	0.459	0.562	0.231	0.898[d]
BAW1	<24 h	0.650	0.832	0.661	
	50 days	0.311	0.311	0.253	0.286
BY32W1a	<24 h	0.422	0.130	0.090	
	44 days	–	–	**0.037**	**0.003**[d]
BY32W1b	<24 h	0.757	0.072	0.882	
	18 days[b]	0.155	0.796	0.331	**<0.001**
GVW1	<24 h	0.914	0.920	0.395	
	40 days	0.174	0.306	0.701	**0.016**
SAW1	<24 h	0.176	0.331	0.229	
	50 days	**0.020**	0.483	0.967	0.272

[a] Paired t-test compares <24 h samples and stored samples (n = 12).
[b] Failed normality test.
[c] Failed equal variance test.
[d] Wilcoxon rank sum test.

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depending on the treatment, with the UU treatment showing the smallest difference and the UR treatment showing the greatest difference. The difference between concentrations before and after storage was greater for the February samples from BY32W, with the mean concentrations after storage between 18% and 37% lower depending on treatment, with the FU treatment showing the smallest difference and the UF treatment showing the greatest difference (Table 2). A Mann–Whitney rank sum comparison of combined measurements from November and February at BY32W ($n = 24$) indicated no statistically significant difference. In contrast to BY32W, the mean alkalinity concentration after storage for GVW was only slightly higher (<2%) than the mean concentration before storage. For locality NC01, the mean concentration after storage was as much as 44% lower for three of the treatments, but this amounted to a difference of only 0.4 mg/L $CaCO_3$ because of the overall low alkalinity concentrations. Although this difference was statistically significant, it was within analytical error for the method.

Charge balance errors

More than 60% of analyses had charge balance errors <±5%, and more than 90% of the analyses had errors of <±10% (Fig. 3). A single replicate of the NC03 FR treatment had an error of −19% with all other errors ranging from −4.5% to −8.5%. Samples from BY32W analyzed within 24 h for both the November and February samplings had a wide range of errors. For the November sampling, all three replicates of the UR treatment and a single replicate of the FR treatment had errors between −10% and −13%. The other eight replicates had charge balance errors between 0% and −4%. For the February sampling, the UR treatment, two replicates for both the FR and FU treatments, and one replicate of the UU treatment had errors that exceeded −10%. For the stored samples from both dates, however, all charge balance errors were within ±3%. A single replicate of the UU treatment for the stored SAW sample had a charge balance error of −13.5%. All other charge balance errors for SAW were between −2% and −10%. Finally, there did not appear to be any relationship between ionic strength of a sample and charge balance error (Fig. 3).

Carbon speciation and PCO_2

Among all samples, total dissolved C (TDC) ranged between 2 and 100 mg C/L, and the proportions of dissolved C species varied considerably (Fig. 4). The headwater Piedmont stream (US64), the acidified stream (NC01), and the shallow groundwater wells had

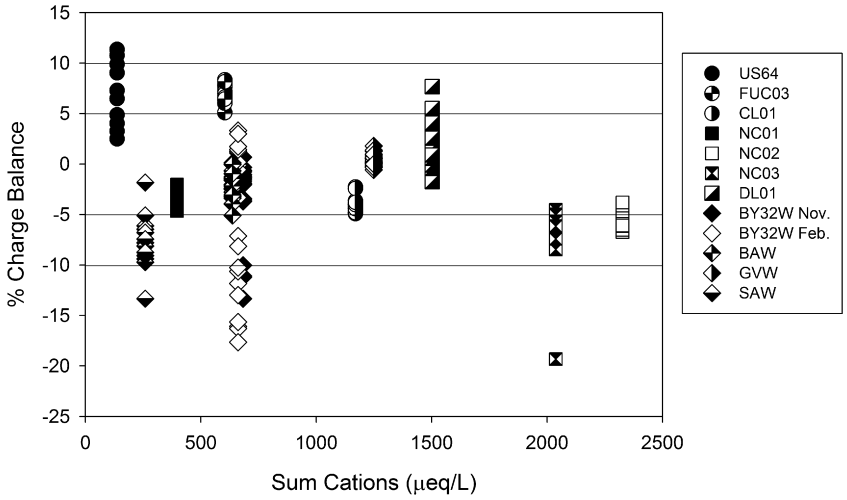

Fig. 3. Charge balance results for all sample treatments for each surface and groundwater locality ($n = 18$ for surface water samples from South Carolina, and $n = 24$ for all other localities) from South Carolina and Tennessee.

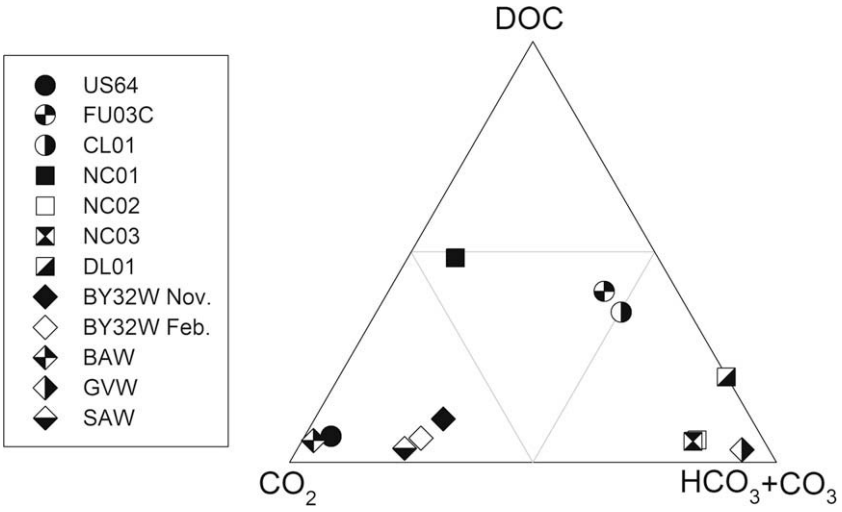

Fig. 4. Ternary plot of dissolved carbon species (μmol/L C) for surface and groundwaters from South Carolina and Tennessee. Concentrations of DOC for samples US64, FU03C, and CL01 are estimated from prior analyses.

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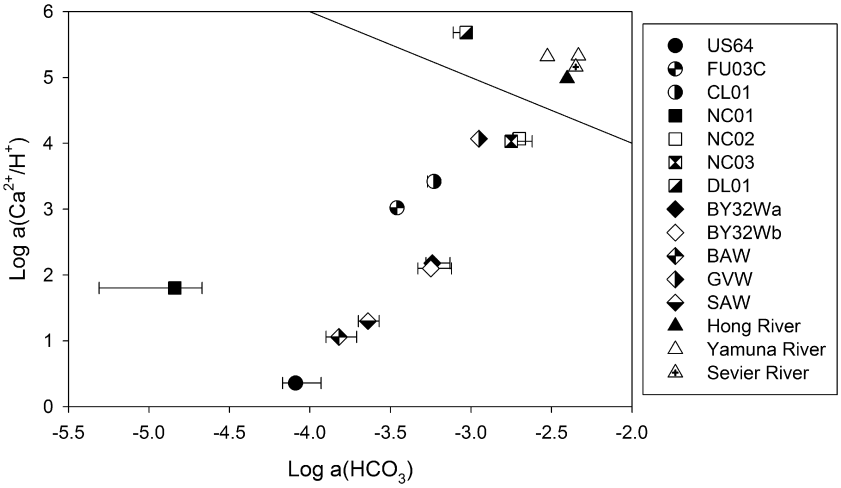

Fig. 5. Calcite saturation diagram for samples from South Carolina and Tennessee. Samples below the line are undersaturated with respect to calcite. A single sample from this study above the line, DL01, is saturated with respect to calcite. Calcite saturated samples from the Hong (Moon et al., 2007), Yamuna (Dalai et al., 2002), and Sevier (Benke and Cushing, 2005) Rivers, show as triangles, are include for comparison.

high proportions of dissolved CO_2. In contrast, the deep well (GVW) and the other streams had high proportions of HCO_3^-. Dissolved organic carbon for these samples was <20% of TDC with the exception of NC01, which had a high proportion of DOC but a concentration of <1 mg C/L. Although DOC concentrations were not measured for the Piedmont surface water samples in this study, addition of DOC data from previously collected samples suggests that the proportion of CO_2 was nearly 90% and HCO_3^- only 5% for the headwater sample US64. In contrast, the proportion of CO_2 was <20%, and HCO_3^- constituted nearly half the carbon in samples from the impoundments.

All samples except DL01 were undersaturated with respect to calcite (Fig. 5) and had PCO_2 oversaturation. DL01 was oversaturated with respect to calcite and had PCO_2 undersaturation. PCO_2 saturation ranged from 0.1 for DL01 to >300 for BAW1. Statistically, all comparisons of PCO_2 among the treatments were the same as for alkalinity concentrations except that there was no statistically significant effect of storage time on alkalinity in the NC01 sample.

Discussion

Dissolved inorganic carbon, particularly bicarbonate, is the most abundant anion in most world rivers (Meybeck, 2003) and in many groundwaters (Eby, 2004). The analytical method for the measurement of alkalinity is central to understanding carbonate speciation, yet sample processing treatments reported in the literature vary considerably with respect to filtration, refrigeration, and storage time. Our results indicate that variation in processing treatments do not appreciably affect the measurements of alkalinity within the range of conditions at our study locations. Even for samples in which we found statistically significant differences among processing treatments, differences among treatment means were small (typically <5%) and thus probably are of minor biogeochemical importance. These results reinforce previous suggestions that processing treatments and storage time do not affect measured alkalinities for surface waters of low ionic strength ($<10^{-3}$ M) in the Amazon and Orinoco basins (Stallard, 1980). Given the general lack of sample processing effects on alkalinities of surface waters from eastern Tennessee, our results also apply to surface waters from carbonate terranes with ionic strengths $<10^{-2.5}$ M. Further, our results suggest that sample treatment and storage time do not affect surface water samples that are supersaturated with respect to calcite.

Alkalinity concentrations in the samples we analyzed ranged over three orders of magnitude and thus spanned the range of bicarbonate concentrations found in the majority of surface waters and many groundwaters globally. The total DIC ranged from 1 to 75 mg C/L, which is about the same as the range reported for major world rivers (Meybeck, 2003). Likewise, the alkalinity concentrations covered most of the range of rivers globally. For example, the range of alkalinity concentrations in our study includes the concentrations reported from 70% of surface waters in a survey of 178 North American rivers (Benke and Cushing, 2005). Our groundwater alkalinity concentrations are representative of groundwaters typically associated with silicate rocks (Eby, 2004). Surface waters draining carbonate rocks in semi-arid and arid regions often have high ionic strengths and are supersaturated with respect to calcite. Our results suggest that variations in treatment or storage do not affect alkalinities of samples supersaturated with respect to calcite.

Our results are supported by the results of Moon et al. (2007) in which samples were collected from the Hong River, Vietnam, filtered in the field, and then shipped to the United States for alkalinity analysis by Gran titration. Similar to DL01, the Hong River sample (Fig. 5) was supersaturated with respect to calcite with a charge balance of −11%, suggesting reasonably accurate analyses. Dalai et al. (2002), in a study of the Yamuna River in India, determined alkalinities on unfiltered samples by endpoint titration both in the field and in the laboratory after shipment and storage. Charge balances for supersaturated samples in that study were generally better than ±10% (Fig. 5). Additionally, Dalai et al. (2002) found that concentrations of Ca^{2+} and Mg^{2+} did not differ between acidified and unacidified samples stored for several weeks. Those authors interpreted their results to mean that kinetic barriers, such as presence of precipitation inhibitors or lack of nucleation processes, prevent the precipitation of calcite (Dalai et al., 2002). Our results confirm that field titrations are unnecessary in most situations and that shipment to distant laboratories is not an obstacle to obtaining accurate results regardless of filtering treatment, even if the sample is supersaturated with respect to calcite. On a cautionary note, warming of samples during transport and storage could cause calcite precipitation, in which case filtration would change the alkalinity (but not the charge balance) of the sample, leading to potential misinterpretation of the results.

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Additional research is required to test the impact of sample treatment on groundwater from carbonate rocks as carbonate mineral precipitation driven by degassing or temperature change could be important. Groundwater, particularly if associated with carbonate rocks, often can have HCO_3^- concentrations over 400 mg/L (in some cases even higher than 600 mg/L) and can be significantly supersaturated with respect to calcite and dolomite (Langmuir, 1997). However, the supersaturation is maintained in aquifers because of kinetic inhibition of precipitation (Langmuir, 1997), which may mean that, as for surface waters, no special treatment would be required prior to alkalinity analysis.

Thus, our results are significant because they imply that (1) alkalinity concentrations are independent of sample treatment method, and (2) extended sample storage and/or shipment should not be an impediment to collection of samples for alkalinity analysis, at least for samples similar to our own. We suggest that for many types of natural waters the standard method for alkalinity titration is overly cautious in the recommendation for sample treatment (Eaton et al., 1995). For example, alkalinity often is measured in the field because of concerns about CO_2 degassing, whereas our results suggest that in most cases analyses can be postponed. In nearly all inland surface waters, partial pressures of CO_2 typically range up to 20 times the atmospheric partial pressure (e.g., Aston, 1984; Stallard and Edmond, 1987; Kling et al., 1991; Cole et al., 1994; Jarvie et al., 1997; Huh et al., 1998; Cole and Caraco, 2001). The main sources of CO_2 are respiration of allochthonous organic matter within surface waters and inputs of groundwater enriched in CO_2 from soil respiration (Cole et al., 2007). The rate at which respired CO_2 is dissolved into surface waters and groundwater exceeds the rate at which CO_2 degasses from the water to the atmosphere, resulting in the observed disequilibrium (Langmuir, 1997). Because of the ubiquitous supersaturation of CO_2 in surface waters, there is some concern that calcite could precipitate if CO_2 degasses during storage from a sample that is at or near saturation with respect to calcite. If the sample then were filtered, alkalinity would be underestimated, leading to a poor charge balance if the cations were analyzed using an acidified aliquot. To prevent degassing, some researchers have collected samples in sealed bottles with zero head space (e.g., Neal and Hill, 1994; Raymond et al., 1997; Cai and Wang, 1998; Dawson et al., 2001) and some have even titrated the samples in the laboratory under controlled nitrogen atmospheres (e.g., Neal and Hill, 1994). We collected groundwater samples for alkalinity and other analyses in separate bottles, but alkalinity concentrations from unrefrigerated filtered samples stored for 50 days and having PCO_2 saturation over 250 times atmospheric partial pressure were not significantly different from alkalinity concentrations in other treatments. Likewise, our results suggest that surface waters up to 75 times supersaturated with CO_2 do not require special treatment. These results suggest that, as with calcite precipitation, PCO_2 disequilibrium is maintained in the sample for significant periods of time during storage, regardless of temperature or filtration. The only exception to this was BY32W, which had significant iron concentrations and had a lower PCO_2 after storage. The lower PCO_2, however, was directly related to the decrease in alkalinity during storage, which was likely a function of the precipitation of iron hydroxide.

Special consideration may need to be given to samples collected under great pressure, such as those collected from deep ocean waters (Edmond, 1970), deep lake waters, or from very deep groundwater wells, if those waters are supersaturated with CO_2. However, our results indicate that groundwaters from wells up to 100 m deep and that are only slightly supersaturated with CO_2 do not require special treatment. Deep lakes receiving large CO_2 influxes due to volcanic activity (e.g., Lake Nyos in Cameroon) also may require special consideration in the processing of samples for alkalinity analysis (Nojiri et al., 1993).

We recognize that our results apply only to oxic samples that have low mineral turbidity and low DOC concentrations. The effect of high turbidity on alkalinity measurement requires further testing. Sample BAW had high turbidity (nearly 300 NTU), but the particulates mainly were organic. Alkalinity concentrations could be overestimated if the acid used for titration dissolves mineral particles in the water, providing that 0.02 N and 0.20 N sulfuric acids are strong enough to dissolve silicate particulates. Neal et al. (1998) only filtered samples with obvious mineral turbidity to avoid degassing, but they did not test whether turbidity increased alkalinity concentrations.

Several studies have indicated that organic anions in DOC can contribute alkalinity in addition to carbonate alkalinity. For example, DOC has been found to comprise all the measured alkalinity in groundwaters associated with oil field brines (Willey et al., 1975). Likewise, DOC also may increase alkalinity significantly in acidic surface waters that are rich in humic compounds, such as bogs, some boreal lakes and brownwater streams (e.g., Oliver et al., 1983; Köhler et al., 2000). Typically DOC contributes between 2 and 12 μeq ANC/mg DOC (Kahl et al., 1989; Cantrell et al., 1990; Wilkinson et al., 1992). Some large rivers, such as the Congo (Coynel et al., 2005), Amazon (Richey et al., 1990), and Rio Negro (Richey et al., 1990) contain up to 10 mg/L DOC and have relatively low bicarbonate alkalinity. Assuming an average of 7 μeq ANC/mg DOC, DOC could provide as much as 50% of the alkalinity in a tropical river such as the Amazon based on DOC data in Richey et al. (1990). However, for samples from the Amazon, no substantial difference was found between the concentration of CO_2 calculated from measured alkalinity concentrations and the concentration of CO_2 measured directly by infrared analysis (Stallard and Edmond, 1987) or gas chromatography (Richey et al., 1990). These results suggest that DOC did not significantly contribute to total alkalinity as the calculated CO_2 concentration would have been significantly higher than the measured CO_2 concentration because of overestimated carbonate alkalinity. Thus, alkalinity results based on titrations of high DOC surface and groundwaters must be interpreted cautiously (e.g., Sullivan et al., 1989; Hemond, 1990). If DOC contributes to ANC as measured by Gran alkalinity, flocculation or degradation of DOC over time could change the alkalinity significantly in high-DOC/low-pH waters. In fact, the results of Hemond (1990) suggest that storage of samples with subsequent flocculation of DOC reduces total alkalinity concentrations, so results more accurately reflect carbonate alkalinity.

Hydrolysable metal ions and hydroxides, such as those of iron and manganese, can undergo hydrolysis reactions during titration, thereby increasing the measured alkalinity (e.g., Sullivan et al., 1989; Hemond, 1990). In contrast, precipitation of metal hydroxides during storage will release H^+, thereby decreasing measured alkalinity. The influence of metal ions on alkalinity has been demonstrated for acid mine drainage (Kirby and Cravotta, 2005) but it may also be important in natural anoxic groundwaters and some surface waters. For example, Roberson et al. (1963) found only minor differences (~2%) between field and laboratory alkalinity for surface waters (streams and springs) with low metal and turbidity concentrations from the Sierra Nevada of California. However, for all groundwater samples they collected from the Englishtown Formation in the coastal plain of New Jersey, laboratory-determined alkalinities were lower than field alkalinities by >5% in almost all cases. Samples in which alkalinity decreased most were those in which it is was visually evident that iron had precipitated, which also tended to be samples with pH < 7.0 which were drawn from aquifers with little or no calcium carbonate material.

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Similar to Roberson et al. (1963), we found a substantial effect of storage time on measured alkalinity and calculated PCO_2 in groundwater from one locality in the South Carolina Piedmont on two separate sampling dates. For the two samples from BY32W, the higher alkalinities associated with samples analyzed within 24 h could skew interpretations of carbonate speciation and PCO_2 made using those data. Assuming that all other anion and cation concentrations were correct, the poor charge balances associated with those samples when measured within 24 h of collection indicated an additional source of alkalinity other than bicarbonate. Both samples had between 0.6 and 0.7 mg/L of iron. Other than the high iron concentrations, we noted nothing unusual about the chemical composition or turbidity of those samples. In contrast, the stored samples, particularly the unfiltered-refrigerated samples, had excellent charge balances and significantly lower PCO_2, indicating that sample storage caused a significant decrease in alkalinity for this particular locality. Thus, hydrolysis of dissolved iron species during titration (e.g., $FeOH^+$ and $Fe(OH)_3^0$) may have consumed hydrogen ions, resulting in the higher measured alkalinity. Dissolution of colloidal ferrhydrite by hydrolysis during titration would have the same effect and may be a common phenomenon as ferrihydrite is a common amorphous nanopartical in rivers around the world (e.g., Hasselöv and von der Kammer, 2008). If so, immediate titration of samples that contain relatively high concentrations of dissolved and colloidal iron likely will result in an accurate measure of ANC but an overestimation of the bicarbonate alkalinity and therefore PCO_2. Therefore, storage of samples with high iron concentrations is preferable if the objective of the study is accurate determination of carbonate alkalinity for calculation of PCO_2.

In conclusion, the alkalinity concentrations in this study represent the range of concentrations documented in most surface waters and many groundwaters throughout the world. Our results show that for oxic waters that have low concentrations of DOC and reduced metals, filtration, refrigeration and storage time are unlikely to affect measured alkalinity concentrations. Sample processing treatment may be important to interpreting the alkalinity concentrations of DOC- and metal-rich samples, although further research is necessary. For samples with relatively high concentrations of hydrolysable metals, precipitation of metals during extended storage will result in more accurate determination of carbonate alkalinity and PCO_2. Ultimately, because alkalinity concentrations are necessary for analytical charge balance, carbonate speciation, PCO_2 calculations, and ANC estimation, concern over effects of sample storage conditions and storage duration should not be an impediment to conducting alkalinity analyses on samples of surface waters and groundwaters.

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