Comparison of regional stream and lake chemistry: Differences, similarities, and potential drivers

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Abstract

We compared lakes and streams in northern Wisconsin to ask how regional patterns of water chemistry differed, and how ecosystem size relates to water chemistry. By applying traditional statistical approaches in novel ways, we identified factors influencing regional chemistry of lakes and streams. Chemistry differed significantly among the two ecosystem types ($p = 0.01$), and two distinct variable groups were apparent. Almost two thirds of the variation in 16 constituents was associated with concentration gradients related to groundwater inputs (group 1, represented by Ca) and adjacent wetlands (group 2, represented by dissolved organic carbon [DOC]). Largest differences were observed in groundwater-associated variables. Median Ca concentrations in lakes were an order of magnitude lower than in streams (lake = 1.43 mg L^{-1}, stream = 12.45 mg L^{-1}), and indicate that regional lake chemistry is strongly influenced by precipitation or short groundwater flow paths, whereas streams are more affected by groundwater with substantial mineral water contact. In contrast, variables reflecting wetland influence (e.g., DOC) did not differ between streams and lakes. Despite these differences, as lake and stream size increased, their biogeochemical attributes converged, likely reflecting increased diversity of flow paths to larger systems, greater biogeochemical processing, and changes in landscape composition. Our results have identified critical differences (groundwater inputs) and similarities (organic carbon dynamics) between lakes and streams and emphasize the importance of ecosystem size in interpreting these observations at the regional scale. Studies such as this will provide essential pieces of information for regional and global biogeochemical studies of freshwater ecosystems.

Freshwater ecosystems are increasingly recognized as important components of regional and global biogeochemical cycles (Cole et al. 2007; Wollheim et al. 2008). This new appreciation underscores the importance of analyses of biogeochemical inputs and processing in various types of freshwater environments, not only individually as lakes, reservoirs, streams, and wetlands, but also as a collective whole by considering the inherent connectivity of these different types of aquatic systems in a complex network, or "hydroscape."

In the most basic sense, the concentration of a chemical constituent in an aquatic system is a function of inputs to the system and subsequent processing. Inputs reflect availability in the surrounding environment coupled with transport to the ecosystem, whereas the extent of processing is dependent on processing rates and residence time. We expect that, in general, the relative importance of inputs and processing differs in streams vs. lakes, and across streams or lakes of different sizes. Conventional wisdom suggests that stream chemistry is more strongly affected by inputs from the surrounding terrestrial environment than by processing because of limited processing opportunities, whereas greater residence times in lakes increases the contribution of processing in determining water chemistry of lakes (Gergel et al. 1999; Kling et al. 2000; Green and Finlay 2008). However, when comparable aspects of

different aquatic ecosystems have been studied simultaneously, surprising similarities have been observed between lakes and streams. For example, nutrient cycling rates are similar between lakes and streams after accounting for differences in residence time (Essington and Carpenter 2000), and no significant differences were found for N retention among lakes, streams, and wetlands after accounting for differences in discharge (Saunders and Kalff 2001). Finally, a national survey of Swedish lakes and streams revealed shared drivers of water chemistry for both types of ecosystems (Stendera and Johnson 2006).

The relative size of lakes or streams is expected to influence the relative importance of input vs. processing in determining their chemical charactistics as well. Conceptual models for both streams and lakes describe an increased diversity of flow paths with increases in ecosystem size (Wood et al. 1988; Kratz et al. 1997; Winter 2001). Systems with a higher diversity of incoming flow paths would be expected to have more similar water chemistry that is reflective of regional landscape characteristics. In contrast, the chemistry of lakes or streams with a smaller number of incoming flow paths might differ from one another because the water chemistry inputs would be more strongly influenced by the idiosyncracies of individual flow paths (Asano and Uchida 2010). Thus one might expect the chemisty of inputs in large systems, whether they are lakes or streams, to be similar within a region. However, size may not affect processing in the same way in lakes and streams. Even though residence time generally increases with increased lake or stream size (Downing et al. 2006), increased stream channel size decreases the extent of

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sediment–water contact. Because biogeochemical processing in fluvial systems is predominantly a benthic phenomenon, decreasing sediment–water contact reduces processing rates exponentially (Alexander et al. 2000). In contrast, although littoral production can be significant in lakes, its relative contribution declines and gives way to water-column processes as lake size increases (Vadeboncoeur et al. 2008). Hence, unlike in streams, increased hydrologic residence time should translate to greater processing in lakes (Essington and Carpenter 2000).

In heterogeneous hydroscapes, approaches that focus on a single hydroscape component are likely to be less effective than integrative approaches (i.e., Lovett et al. 2005). Further, because lakes and streams have generally been studied in isolation (Kling et al. 2000; Stendera and Johnson 2006; Soranno et al. 2010), much is yet to be learned about how the regional chemistry of lakes and streams compares and what insights this type of information can provide about chemical inputs and processing in aquatic ecosystems at regional scales. Here we address two questions about water chemistry of lakes and streams in the Northern Highland Lake District (NHLD) of Wisconsin. To the best of our knowledge, this is one of the first studies to examine regional lake and stream chemistry with the larger goal of greater conceptual integration of lakes and streams into the aquatic landscape. Do regional distributions of water chemistry in lakes and streams differ and, if so, how? Similar chemical profiles would indicate similar inputs and processing in both types of systems, whereas differing chemical profiles would indicate either different chemical inputs into lakes and streams or greater residence times and thus greater opportunity for biogeochemical processing in lakes. How does ecosystem size affect water chemistry? Regardless of the outcome of our initial lake–stream comparison, we expect water-chemistry patterns to be tempered by ecosystem size because transport of chemicals to the freshwater environment and processing of those chemicals within the system should change along a size gradient. By addressing these questions, we have an opportunity to assess the spatial heterogeneity of water chemistry and infer regional processes that create these patterns—information that is critical for understanding the movement of chemicals and energy across the landscape (Cardille et al. 2007; Buffam et al. 2011).

Methods

Study region—The NHLD (ca. 5000 km^2) of Wisconsin contains more than 7500 lakes and 1500 streams. Forty-one percent of the landscape is covered by lakes and wetlands (13% and 28%, respectively), with only minor (< 5%) amounts of agriculture and urban development present (Homer et al. 2004). Glaciation affected the surficial geology of the region between 10,000 and 12,000 yr ago, leaving approximately 30–50 m of sandy, noncalcareous till across the landscape (Magnuson et al. 1997). As a result, surface waters are embedded in a medium- to coarse-grained sandy matrix with high hydraulic conductivity, and often receive substantial groundwater inputs (Webster et al. 2006; Cardille et al. 2007). Water budgets of most regional

lakes are dominated by groundwater or precipitation inputs (or both) and evapotranspirational outputs (Elder et al. 1992). Lakes range in size from small dystrophic bog lakes less than 0.01 km^2 to clear-water lakes more than 25 km^2, whereas streams range from small intermittent channels to large-order systems such as the Wisconsin, Chippewa, and Wolf rivers. Drainages within the NHLD flow either into the Mississippi River or the Laurentian Great Lakes.

Site selection and sampling—Physical and chemical characteristics of streams were determined from a regional synoptic survey at base flow conditions during June–August 2006. Because lakes are a dominant feature of the region (Hanson et al. 2007), we classified streams into two categories as a function of their hydrologic connections to lakes (streams with upstream lakes and streams without upstream lakes). We selected streams from these two categories using a stratified random design based on the distribution of stream categories in the region. This was done to ensure that the set of randomly selected streams represented the actual distribution of all streams in the region. To determine the distribution of stream types and potential sampling locations, all streams identified on 1 : 24,000 U.S. Geological Survey topographical maps that intersected access points were identified. Access points ranged from recreational trails and abandoned logging roads to major highways. More than 500 sampling points were identified and classified as streams with or without upstream lakes. Of these 500 potential sampling locations, 52 sites were randomly sampled on the basis of the distribution of aforementioned stream types. Selected sites were all located in independent drainage networks. All streams were sampled 7–10 channel widths upstream of an access point to minimize any influences of culverts or other features (Fitzpatrick et al. 1998). Water samples were collected from the center of the channel using a peristaltic pump. Discharge was measured using cross-sectional area and multiple measurements of water velocity (Marsh-McBirney model 2000 portable flowmeter).

Lake characteristics were determined by a regional synoptic survey during July–August 2004 (Hanson et al. 2007). Briefly, 170 of the more than 7500 lakes within the region were sampled for a range of chemical and physical characteristics using a stratified random approach on the basis of lake surface area. All samples were collected from the middle of the epilimnion in the approximate center of the lake using a peristaltic pump.

The Hanson et al. (2007) lakes data set contained ca. three times more sites than the stream survey. We subsampled the lake data set to generate a set of 60 lakes to create comparable stream and lake data sets. Differences in median values of individual variables between the original and subsampled data set averaged $\sim$ 4% with a maximum of 9%. No significant differences in median values were observed (Wilcoxon sign rank test, $n = 13$, $S = 5$, $p = 0.733$), suggesting that the smaller data set used here represents the distribution of variables observed in all 170 lakes.

Differences in annual climate could cause some lake–stream chemistry differences since samples were collected in

different years. Data collected as part of the North Temperate Lakes Long-Term Ecological Research (NTL-LTER) program were used to test for differences between years (http://lter.limnology.wisc.edu unpublished data). Over the prior 20 yr, annual temperatures in the region ranged from $-41°C$ to $36°C$ and precipitation ranged from 0.4 m to 1.0 m. With respect to the years in which data were collected from lakes (2004) and streams (2006), air temperature ranges were similar for 2004 (-32–$35°C$) and 2006 (-33–$30°C$), but 2004 (0.6 m precipitation) was a wetter year than 2006 (0.4 m precipitation). To determine if there were differences in chemistry between summer 2004 (lake sampling) and summer 2006 (stream sampling), we examined water chemistry of the seven NHLD lakes that are monitored as part of the NTL-LTER program. Comparison of the 16 chemical constituent concentrations in 2004 and 2006 (data not shown) using a nonparametric multivariate analysis of variance (npMANOVA; Anderson 2001) demonstrated that concentrations were not significantly different ($F_{1,46} = 0.59$, $p = 0.58$) between years, suggesting that interannual variability between 2004 and 2006 in lakes does not contribute substantially to any potential differences observed between lake and stream constituents.

Water chemistry analyses—All samples for both studies were collected and processed following the NTL-LTER protocols (http://lter.limnology.wisc.edu). Samples were filtered in the field using a 0.45-μm membrane filter, stored on ice, and returned to the laboratory where they were preserved according to NTL-LTER protocols. Acid-neutralizing capacity (ANC) was determined by Gran titration (APHA 2005). Dissolved organic carbon (DOC) was measured on a Shimadzu total organic carbon (TOC)-V analyzer. Total nitrogen and phosphorus (TN and TP) and total dissolved nitrogen and phosphorus (TDN and TDP) were quantified with an Astoria-Pacific segmented flow autoanalyzer after digestion. Chloride and SO_4 were measured using a Dionix DX-500 ion chromatograph and cations (Ca, Mg, Na, K, Fe, K, and Mn) using a Perkin Elmer inductively coupled plasma–optical emissions spectroscopy.

Two parameters were quantified differently in the lake and stream data sets. For the lake data, dissolved inorganic carbon (DIC) was determined on water samples collected in gas-tight containers and analyzed using a Shimadzu TOC-V carbon analyzer. DIC for streams was determined by acidifying the sample in the field in a sealed container to convert all DIC to CO_2. After acidification, a small headspace was created and the sample was allowed to equilibrate ~ 1.5 min before collecting a headspace sample for CO_2 determination on a Shimadzu gas chromatograph (Cole et al. 1994). DIC was then calculated using headspace CO_2 and Henry's constant (Cole et al. 1994). The second parameter that was measured differently in the two data sets was pH. Measurements for the lakes data set were quantified on nonair-equilibrated samples in the lab with an Accumet 950 pH meter. In streams, pH was measured in the field using a hand-held Orion model 266 pH meter that was allowed to equilibrate ~ 20 min in the center for the stream channel.

Data analysis—Individual or groups of chemical constituents are often used to characterize external drivers of freshwater biogeochemistry. Ca, Mg, DIC, and ANC characterize the influence of groundwater in NHLD lakes and streams (Webster et al. 1996, 2000; Walker et al. 2003) as precipitation and surface runoff have significantly lower base cation and weathering ion concentrations than groundwater (Hurley et al. 1985; Kenoyer and Anderson 1989). DOC is a strong indicator of wetland extent in lakes and streams (Gergel et al. 1999; Mulholland 2003). The extent of wetlands often explains more than 50% of the variation in freshwater DOC concentrations (Mulholland 2003) and up to 69% in NHLD streams (Lottig 2009). Thus, although these constituents are not direct measures of relative groundwater inputs or wetland extent, they provide an indication of the importance of these influences on NHLD streams and lakes and are used extensively in our analyses and interpretations of the results.

Ecological data often fail to meet normality assumptions, and data that are transformed to meet normality requirements for parametric analyses can be difficult to interpret (Limpert et al. 2001). Thus, we elected to use nonparametric analyses that are robust to nonnormal distributions for most analyses. Three analytical strategies were used to answer the question: do the chemistries of lakes and streams differ in this region, and if so, how? First, we tested for differences between streams and lakes using npMANOVA. On the basis of npMANOVA results, post hoc comparisons of individual constituents were performed by assessing differences in the distributions of observed values between lakes and streams. Distributions were determined using univariate kernel density estimates calculated with a nonparametric smoothing coefficient (Bowman and Azzalina 1997). Because we sampled lakes and streams randomly, kernel density estimates can be used to estimate the actual probability density function of each chemical constituent. The regional (i.e., combined lake and stream) distribution for each constituent was determined by bootstrapping the density estimates in both lakes and streams 1000 times. Finally, a bootstrapped hypothesis test of equality was conducted to determine if the combined distribution for each constituent was significantly different from the individual distributions observed in lakes and streams (Bowman and Azzalina 1997). On the basis, in part, of visual analysis of these distributions, variates with similar distributional patterns were identified and grouped together. Spearman rank correlation coefficients were used as an additional approach to aid in identifying variates that displayed similar patterns in either lakes or streams.

Second, we compared variances of individual constituents from lakes vs. streams using a nonparametric analog of coefficient of variation (C.V.). Instead of normalizing the variation of a constituent by dividing the standard deviation by the mean as in the C.V., we used the median absolute deviation (MAD) divided by median (i.e., nonparametric [np]C.V.). MAD is a robust measure of variability and influenced less by skewed distributions than the standard deviation (Hoaglin et al. 1983). Normalized variances were compared with an *F*-test similar to the approach used for C.V.s (Lewontin 1966).

The third and final strategy for comparing lake and stream chemistry involved principal components analysis (PCA) to reduce the dimensionality of the data and determine if lakes were chemically distinct from streams, or if both system types showed similar variation across composite chemical gradients. In the first case, lake and stream points would each form their own discrete groupings in the PCA and examination of the axis responsible for this separation should allow us to infer processes responsible for the lake–stream separation. For example, a high DOC loading for an axis along which lakes and streams separate could be interpreted as a differential influence of wetlands on lakes vs. streams. In the second case, lakes and streams would be interspersed along one or more PCA axes, indicating that some larger-scale phenomenon (e.g., climate, parent geology) likely drives variation in surface water chemistry in a similar fashion for both lakes and streams. The number of PCA axes included in the analysis was determined with a scree test (Cattell 1966). To simplify the interpretation of the results, data were orthogonally rotated using the varimax method so that chemical variables were associated with only a single axis. We tested the robustness of the PCA to lack of normality and differences in the magnitude among variables in the two data sets by analyzing the data using nonmetric multidimensional scaling and PCA on log-transformed data. In both cases, results were almost identical to the original PCA, so only the original PCA results are presented.

To address our second question of how ecosystem size affects water chemistry, we examined trends in lake and stream water chemistry across the range of ecosystem sizes occurring in the NHLD. We used surface area as a measure of lake size (Downing et al. 2006) and base flow discharge for stream size (Wetzel 2001). These metrics were selected because they could be determined easily and accurately, and have proven to be reliable measures of system size. In contrast, watershed area is difficult to determine from surface water features in the NHLD because groundwater-contributing areas often differ substantially from the contributing area defined by surface topographic features (Pint et al. 2003). Because sizes of lakes and streams were quantified by distinctly different attributes, we used a measure of relative size so that changes in chemistry could be compared across a common gradient. Nonparametric standard scores of ecosystem size were calculated as the number of MADs the size of a lake or stream was away from the median lake or stream size. Computationally this is identical to a standard Z-score but uses median and MAD values instead of mean and standard deviation. This approach will maintain the original distribution of the data but normalizes for differences in scale and units. It is important to note that we are not suggesting that these comparisons are of equally sized ecosystems, but rather the systems occupy a similar relative position within the size distribution of specific ecosystem types (e.g., smallest streams are compared with the smallest lakes).

Concentrations of biogeochemical variates were plotted as a function of relative ecosystem size and both linear and nonlinear exponential models were fit to the lake and stream data separately. We used Akaike information criterion (AIC) to determine if a significant difference existed between linear and exponential fits and assumed that differences existed when AIC values differed by more than two (Burnham and Anderson 2002). When the same model (e.g., linear in lakes and streams) explained a trend in constituent concentrations, we determined if a difference existed between the lake and stream trend using analysis of covariance (ANCOVA). If no difference in slope and intercept existed, a single trend line was fit to the data. In all other instances, the central trends in lakes and streams were fit individually. Finally, quantile regression was used to estimate the spread of constituent concentrations around the central trend line(s). For all quantile regressions, 0.875 and 0.125 quantiles were used as the upper and lower boundaries, respectively. These regressions identify the upper and lower concentration ranges containing 75% of the data across the entire size gradient.

Results

Nonparametric MANOVA indicated significant chemical difference between lakes and streams in the NHLD ($F_{1,85} = 86.1$, $p = 0.01$). Comparisons of probability distribution functions of individual constituents between lakes and streams suggested three general patterns. First, large differences in lake and stream distributions were observed for ANC, Ca, Mg, and DIC (Fig. 1A–D). The ranges for these four constituents were similar but median concentrations were typically an order of magnitude lower in lakes (Table 1). Consequently, the combined lake–stream distributions were bimodal. Second, SO_4, DOC, TN, TDN, and K represent the other end of the spectrum, with no significant differences between lakes and streams in the NHLD (Fig. 1L–P, Table 1). The variables within each of these two groups were tightly correlated; correlation coefficients between ANC, Ca, Mg, and DIC exceeded 0.69 and 0.63 in lakes and streams, respectively (Tables 2, 3). Similarly, TN and TDN were well correlated with DOC in lakes ($\rho > 0.71$) and streams ($\rho > 0.91$).

Although significant differences were observed for other constituents (e.g., Na, TP, Cl), the third pattern appeared to be an intermediate between the two groups noted above (Fig. 1). In some cases, significant shifts of the central tendency were observed, but were not large enough to result in bimodal distributions for the combined data (Fig. 1E–I). For example, TP and TDP were more concentrated in streams than in lakes, with the medians shifted by approximately a factor of 2 (Table 1). Other variables such as Cl had similar ranges in lakes and streams and only small differences in median concentrations, resulting in slight overall differences in distributions that were ambiguous and difficult to categorize (Fig. 1J,K). Constituents in the first group with substantial distributional differences also displayed the greatest differences in variance, as Ca, Mg, ANC, DIC, and Na were significantly more variable in lakes than in streams. Conversely, variables with similar lake and stream distributions (e.g., DOC, SO_4, Cl) had similar regional variances (Table 1).

Sixty-four percent of the variance in the 16 biogeochemical variables could be explained by two PCA axes
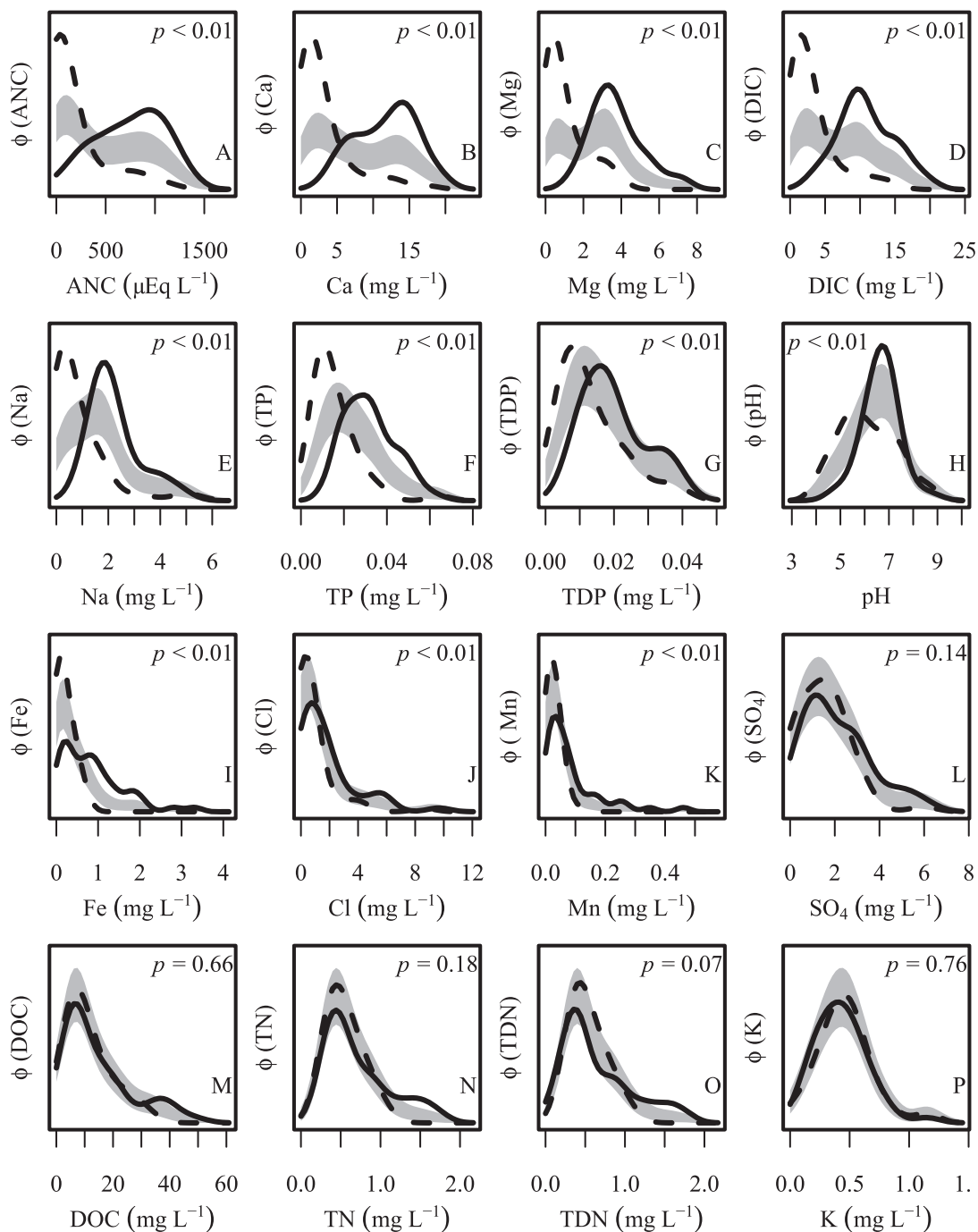
Fig. 1. Frequency distributions (φ) of 16 biogeochemical constituents quantified in randomly sampled streams and lakes. Dashed lines are lakes, solid lines are streams, and shaded region is the combined lake and stream distribution determined from bootstrapping the prior distributions 1000 times. *p*-values are derived from bootstrapped hypothesis test of equality to determine if significant differences exist between the frequency distributions in lakes and streams.

(Fig. 2A). The primary variables loading axis 1 were Ca (0.89), Mg (0.90), DIC (0.89), and ANC (0.87), whereas axis 2 was influenced by DOC (0.86), TDN (0.88), and TN (0.85). Ca could explain 85% of the variance in PCA axis 1 (Fig. 2B), whereas 76% of the variance in PCA axis 2 was explained by DOC (Fig. 2C). Although minor overlap exists, streams and lakes separated into distinct clusters because of differences in concentrations of the Ca group of variables (i.e., PCA axis 1). Although streams and lakes both separated along a DOC gradient (PCA axis 2), the degree of separation was not as large in lakes because of a lack of large positive axis 2 scores (stream max. ~ 6, lake max. ~ 3) even though minimum scores (~ −3) were similar. This is reflected in the actual DOC concentrations

Table 1. Summary of 16 lake and stream biogeochemical constituents. Values presented are mean, median, and (range). *p*-values indicate overall differences in distributions (bootstrapped hypothesis test of equality) and variances (npC.V. *F*-test) between lakes and streams.

Constituent*	Lake data set			Stream data set			*p*-value	
	Mean	Median	Range	Mean	Median	Range	Distribution	Variance
ANC (μEq L^{-1})	172	42	86–1137	749	804	20–1382	<0.01	<0.01
Ca (mg L^{-1})	2.95	1.43	0.39–17.30	11.73	12.45	3.42–19.18	<0.01	<0.01
Mg (mg L^{-1})	1.00	0.52	0.13–4.00	3.72	3.41	0.16–7.31	<0.01	<0.01
DIC (mg L^{-1})	3.10	1.73	0.44–14.47	10.85	10.25	2.68–19.81	<0.01	<0.01
Na (mg L^{-1})	0.83	0.36	0.00–5.31	2.22	1.95	1.16–7.31	<0.01	<0.01
TP (mg L^{-1})	0.015	0.012	0.004–0.065	0.032	0.031	0.012–0.062	<0.01	0.09
TDP (mg L^{-1})	0.013	0.010	0.002–0.039	0.020	0.018	0.010–0.041	<0.01	0.09
pH	6.1	5.9	4.1–8.8	6.7	6.7	4.7–8.9	<0.01	<0.01
Fe (mg L^{-1})	0.19	0.13	0.00–0.69	0.85	0.73	0.08–3.31	<0.01	0.24
Cl (mg L^{-1})	0.73	0.31	0.00–8.65	1.80	1.16	0.17–9.66	0.01	0.30
Mn (mg L^{-1})	0.026	0.022	0.000–0.117	0.089	0.050	0.030–0.462	<0.01	0.39
SO$_4$ (mg L^{-1})	1.48	1.49	0.00–5.96	2.12	1.68	0.18–6.18	0.14	0.28
DOC (mg L^{-1})	11.28	8.38	0.80–32.14	14.52	9.16	2.53–48.84	0.66	0.35
TN (mg L^{-1})	0.55	0.50	0.23–1.07	0.71	0.56	0.12–1.78	0.18	0.22
TDN (mg L^{-1})	0.53	0.46	0.23–1.07	0.65	0.49	0.12–1.76	0.07	0.13
K (mg L^{-1})	0.46	0.45	0.00–1.16	0.42	0.41	0.20–0.85	0.76	0.39

* ANC, acid-neutralizing capacity; DIC, dissolved inorganic carbon; TP, total phosphorus; TDP, total dissolved phosphorus; DOC, dissolved organic carbon; TN, total nitrogen; TDN, total dissolved nitrogen.

as well. Maximum DOC concentrations in streams were markedly higher (48.8 mg L^{-1}) than in lakes (32.1 mg L^{-1}), whereas minimum concentrations were similar (Table 1).

Given that Ca and DOC appear to be strong indicators of potential regional determinants of spatial variability in lake and stream biogeochemistry in the NHLD (Fig. 2) and the fact that they represent contrasting patterns in lake vs. stream frequency distributions (Fig. 1), we focus our analyses of ecosystem size on these two constituents. The standardized size distributions (i.e., ecosystem size) of streams and lakes in the NHLD were not significantly different (*p* = 0.98, Fig. 3A). In relation to ecosystem size, both Ca and DOC converged toward similar concentra-

tions in the largest lakes and streams, although large systems became more Ca rich but more diluted in DOC (Fig. 3B,C). The Ca concentration–size relationships were distinctly different for lakes and streams; an exponential model best described the lake relationship and the quantile regression illustrated that the range of Ca concentrations increased with size. In contrast, stream Ca concentrations increased in a linear fashion for streams, and the concentration range containing 75% of the data decreased as stream size increased. Unlike Ca, very similar trends were observed for DOC as a function of ecosystem size in lakes and streams (ANCOVA, $F_{1,101}$ = 1.86, *p* = 0.18). Quantile regressions revealed that the largest ranges

Table 2. Spearman correlation coefficients for 16 biogeochemical constituents quantified in a random sampling of 52 streams in the Northern Highland Lake District, Wisconsin.

	ANC*	pH	DIC	DOC	TDN	TN	TDP	TP	Cl	SO$_4$	Ca	Mg	Na	K	Fe	Mn
ANC	1.00	0.74	0.84	−0.58	−0.52	−0.50	−0.26	−0.16	−0.12	0.43	0.96	0.75	0.07	0.40	−0.46	−0.27
pH		1.00	0.41	−0.75	−0.64	−0.57	−0.37	−0.24	0.03	0.47	0.68	0.56	0.12	0.33	−0.60	−0.51
DIC			1.00	−0.40	−0.39	−0.40	−0.15	−0.02	−0.09	0.36	0.81	0.63	0.10	0.21	−0.18	−0.02
DOC				1.00	0.92	0.91	0.48	0.32	−0.07	−0.52	−0.46	−0.22	−0.22	−0.33	0.58	0.42
TDN					1.00	0.96	0.52	0.36	0.04	−0.51	−0.38	−0.18	−0.15	−0.33	0.59	0.44
TN						1.00	0.49	0.42	−0.02	−0.41	−0.34	−0.15	−0.18	−0.31	0.54	0.38
TDP							1.00	0.81	0.25	−0.19	−0.21	−0.06	0.22	0.04	0.39	0.41
TP								1.00	0.14	−0.04	−0.11	0.01	0.14	0.08	0.39	0.39
Cl									1.00	−0.08	−0.11	−0.08	0.76	0.11	0.07	0.04
SO$_4$										1.00	0.35	0.46	0.26	0.40	−0.36	−0.43
Ca											1.00	0.75	0.03	0.30	−0.36	−0.19
Mg												1.00	0.12	0.33	−0.19	−0.16
Na													1.00	0.27	−0.10	−0.18
K														1.00	−0.34	−0.14
Fe															1.00	0.73
Mn																1.00

* ANC, acid-neutralizing capacity; DIC, dissolved inorganic carbon; DOC, dissolved organic carbon; TDN, total dissolved nitrogen; TN, total nitrogen; TDP, total dissolved phosphorus; TP, total phosphorus.

Table 3. Spearman correlation coefficients for 16 biogeochemical constituents quantified in a random sampling of 60 lakes in the Northern Highland Lake District, Wisconsin.

	ANC	pH	DIC	DOC	TDN	TN	TDP	TP	Cl	SO$_4$	Ca	Mg	Na	K	Fe	Mn
ANC	1.00	0.91	0.69	−0.40	−0.11	−0.09	0.03	0.09	0.42	0.11	0.78	0.79	0.70	0.56	−0.21	−0.32
pH		1.00	0.51	−0.61	−0.33	−0.31	−0.18	−0.09	0.53	0.31	0.68	0.68	0.64	0.47	−0.44	−0.55
DIC			1.00	0.00	0.14	0.16	0.03	0.07	0.27	−0.10	0.69	0.73	0.59	0.48	0.08	−0.16
DOC				1.00	0.73	0.71	0.48	0.44	−0.32	−0.36	−0.06	−0.05	−0.11	−0.08	0.71	0.61
TDN					1.00	0.99	0.62	0.74	−0.16	−0.26	0.11	0.15	0.03	−0.01	0.56	0.59
TN						1.00	0.59	0.74	−0.16	−0.29	0.12	0.16	0.05	0.01	0.55	0.57
TDP							1.00	0.81	−0.32	−0.26	0.00	0.04	−0.04	−0.05	0.44	0.43
TP								1.00	−0.20	−0.24	0.08	0.10	0.03	0.02	0.39	0.40
Cl									1.00	0.50	0.53	0.49	0.52	0.38	−0.22	−0.47
SO$_4$										1.00	0.25	0.32	0.29	0.10	−0.46	−0.22
Ca											1.00	0.95	0.84	0.55	0.07	−0.11
Mg												1.00	0.84	0.55	0.05	−0.10
Na													1.00	0.52	0.02	−0.26
K														1.00	−0.01	−0.01
Fe															1.00	0.50
Mn																1.00

* ANC, acid-neutralizing capacity; DIC, dissolved inorganic carbon; DOC, dissolved organic carbon; TDN, total dissolved nitrogen; TN, total nitrogen; TDP, total dissolved phosphorus; TP, total phosphorus.

occurred in the smallest systems, although highest concentrations and greatest ranges across the entire size gradient were almost always observed in streams (Fig. 3C).

Discussion

How do chemical characteristics of lakes and streams differ?—We observed strong within-group similarities among the constituents making up either the Ca or DOC groups (Ca, Mg, ANC, DIC in the first group and DOC, TN, TDN in the second) in both lakes and streams. Variables within each of these two groups exhibited similar concentration distributions, similar changes over gradients of ecosystem size, and similar statistical characteristics (e.g., variation in concentrations among lakes and streams, correlations among variables within each group, and PCA loadings). These common patterns observed among variables suggest two potential drivers determining biogeochemical distributions in both lakes and streams: groundwater inputs from the surrounding aquifer and organic carbon inputs and processing from adjacent wetlands.

In previous studies variables in the Ca group have been shown to be associated with the relative importance of groundwater inputs, relative to precipitation and runoff, to area lakes (Webster et al. 1996; Kratz et al. 1997; Riera et al. 2000). The concentrations of some variables within this group such as DIC are likely influenced by other processes, but the effects of those processes appear to be minimal on the basis of strong similarities between these variables and more conservative variates such as Ca. Because Ca behaves conservatively in many aquatic systems (Wetzel 2001), including those in the NHLD, the effects of internal processing are minimal (Webster et al. 1996). Therefore, significant differences in this constituent group between lakes and streams are likely caused by differences in inputs to lakes vs. streams rather than by differences in processing rates, regardless of residence time differences between the two ecosystem types. In the NHLD, Ca in precipitation averages < 0.20 mg L^{-1} (NADP 2010), which is a much lower concentration than observed in most aquatic systems. Surface and groundwater Ca concentrations < 10 mg L^{-1} are characteristic of short mineral–water contact (e.g., precipitation and groundwater flow paths $<$ 100s of meters), whereas concentrations > 20 mg L^{-1} result from long mineral–water contact times (e.g., $>$ kilometer-long flow paths; Walker et al. 2003). Thus, a median lake Ca concentration of 1.43 mg L^{-1} and the rarity of lakes with $>$ 5 mg Ca L^{-1} provide strong evidence for precipitation and short groundwater flow paths as the dominant hydrologic inputs to lakes in this region, as in other regions (Momen and Zehr 1998). Even though median concentrations were low, the relatively high lake Ca variance further suggests that there is substantial variability in the mixture of these and other hydrologic sources among lakes in this geologically homogeneous region (Vano et al. 2006; Webster et al. 2006; Cardille et al. 2007). Compared with lakes, streams had an order-of-magnitude greater median concentration of Ca, and Ca-poor streams (< 5 mg L^{-1}) were rare, indicating long groundwater flow paths to NHLD streams. The low across-site variability observed in stream base cations and carbonate species relative to lakes also suggests a consistent contribution of groundwater to regional streams—likely the result of sampling during the summertime groundwater-dominated base-flow period.

In contrast to the calcium group, the across-site distribution of concentrations of constituents in the DOC group likely reflects both differences in inputs and in processing. Wetlands occupy 28% of the landscape in the NHLD (up to 100% in some watersheds) and are a substantial source of DOC to adjacent freshwater ecosystems, explaining up to 69% of the variance in surface-water concentrations in the region (Gergel et al. 1999; Lottig 2009; Buffam et al. 2011). The similarity of lake and stream concentration patterns suggests that the net effect of wetlands on surface-water DOC is the same for both lakes and streams. This influence extends beyond DOC and can
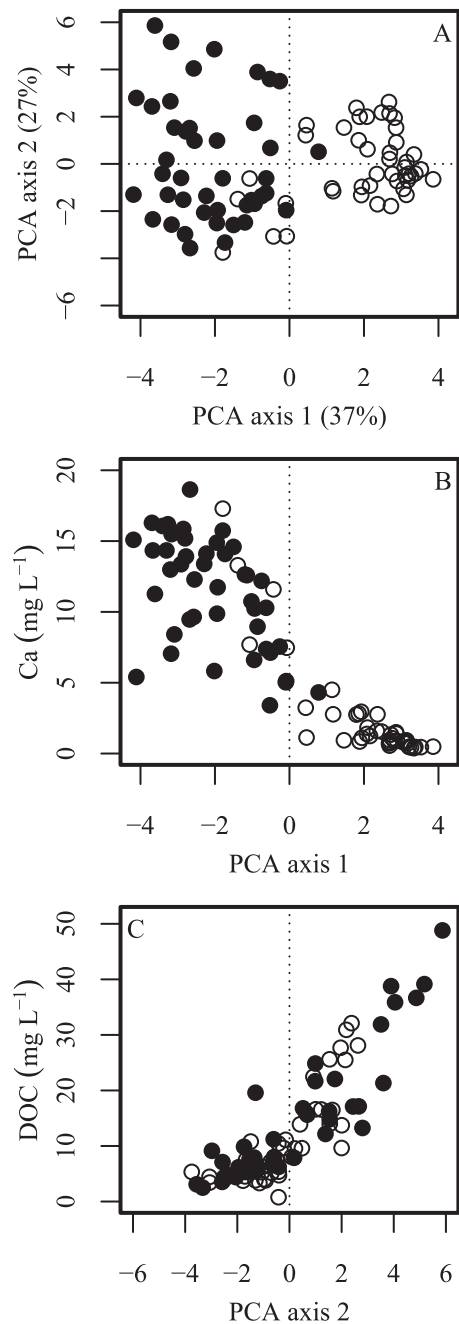
Fig. 2. Principal components analysis (PCA) result on the basis of 16 chemical constituents quantified in randomly selected lakes and streams. Lakes (open circles), streams (closed circles).
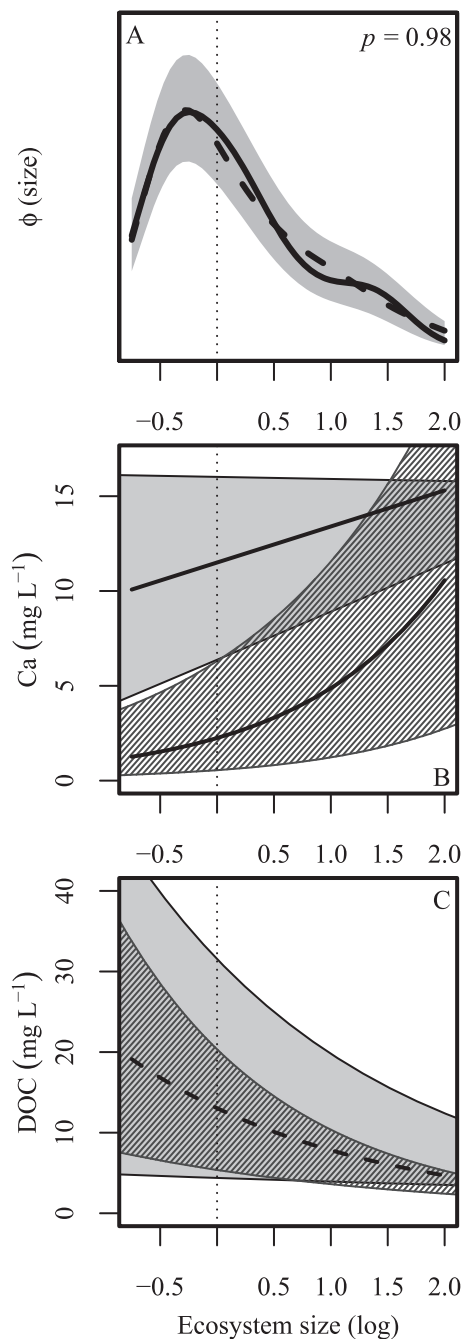

Fig. 3. The influence of lake and stream size on Ca and dissolved organic carbon (DOC) concentrations in streams and lakes. (A) Frequency distribution of standardized lake and stream sizes. Dashed line is the distribution of lakes and solid line is the distribution of streams. Ecosystem size of zero (dotted vertical line) is the median stream (23 L s^{-1}) and lake (0.025 km^2) size. (B, C) Relationship between ecosystem size and Ca and DOC concentrations, respectively. Shaded areas (solid: streams; hashed: lakes) bound 75% of the data determined through quantile regression analysis. Trend lines are the best fit to the data. Solid lines indicate distinctly different trends in lakes and streams, whereas dashed line indicates that lakes and streams are described by the same trend.

affect, among other solutes, iron, phosphorus, and nitrogen in freshwater systems (Dillon and Molot 1997; Pellerin et al. 2004). Thus, strong correlations between DOC and other constituents in the group such as N and SO$_4$ might also be explained by wetlands as critical sources of chemical constituents to both streams and lakes.

In the basic framework of inputs and processing, similar DOC concentrations among lakes and streams can result from either similar inputs and processing in both types of systems, or offsetting changes in inputs and processing in one system type (e.g., increase DOC inputs and processing

in lakes) relative to the other. The first scenario of equal inputs and processing is supported by the fact that streams have the potential to process large quanties of organic carbon (Battin et al. 2008; Stanley et al. in press) much like what has been observed in lakes (Cole et al. 2007; Battin et al. 2008). Consequently, if inputs and processing of carbon in streams and lakes are of similar magnitude, one would expect to see similar distributions as observed here.

On the other hand, the second scenario of elevated processing in one ecosystem type is consistent with observations that lakes are hot spots of organic carbon processing (Cole et al. 2007; Battin et al. 2008). In the NHLD, organic matter processing rates are high in DOC-rich lakes (Hanson et al. 2004) and could explain why DOC in lakes never reached the same maximum concentrations that are found in streams with similar wetland cover (Lottig 2009; P. C. Hanson unpubl. data). However, because the DOC distributions were identical in lakes and streams, the elevated processing in lakes would have to be offset by increased carbon inputs. One potential source of carbon in lakes is from riparian wetlands (Gergel et al. 1999). Ca-poor, short flow-path water that strongly affects lakes should include precipitation falling on adjacent wetlands and seeping into lakes, providing potentially DOC-rich water to these systems. In contrast, older groundwater paths that dominate in streams can bypass or short-circuit organic matter-rich wetland soils (Lowry et al. 2007). Additionally, internal production of DOC may provide another source of organic carbon to lakes (Kling et al. 2000), although this appears not be the case in the NHLD (Larson et al. 2007). Although it is unclear which scenario is driving the similar distributions of DOC in NHLD streams and lakes, the results clearly indicate that additional information is needed to unravel the processes affecting regional organic carbon inputs and processing in freshwater systems.

How does ecosystem size affect water chemistry?—Changes in Ca concentration as a function of ecosystem size generally confirmed our existing understanding of changes in hydrology across large gradients of stream and lake sizes (Riera et al. 2000; Asano and Uchida 2010). In NHLD streams, we observed an increasing trend in concentrations as sites became larger, along with a decrease in the variance around the trend. Increases in base cation concentrations are often observed in streams along longitudinal gradients (Kling et al. 2000; Temnerud et al. 2007; Buffam et al. 2008), which would be anticipated from longer flow paths in larger systems (Walker et al. 2003). Likewise, variation in conservative solute chemistry of groundwater tends to decrease with increasing watershed size because, in part, of mixing of multiple different water sources (Wood et al. 1998; Asano and Uchida 2010).

Lake characteristics also change in predictable ways on the basis of the location of lakes in the landscape. Lakes located high in the landscape are typically small and their primary source of water is precipitation or runoff, whereas lakes low in the landscape are often larger drainage lakes that receive a large part of their water from stream and groundwater inputs (Kratz et al. 1997). It is clear from

results in this study that the aforementioned landscape position patterns correlate with lake size as well. Small lakes have very low Ca concentrations and little across-lake variation in concentration, suggesting that the hydrologic budgets are dominated by precipitation and discharge of groundwater that has had only minor mineral contact. On the other hand, larger lakes typically had higher Ca concentrations, likely reflecting an increase in connectivity with streams and groundwaters (Riera et al. 2000; Quinlan et al. 2003; Martin and Soranno 2006). However, increased variance in Ca concentrations in the largest systems indicates that these basic patterns are not universal in the NHLD and that hydrologic setting is important for understanding the dynamics of individual systems (e.g., not all large lakes have surface water connections).

Unlike Ca, patterns in DOC across the entire size distribution of streams and lakes were remarkably similar, supporting the hypothesis that wetlands exert a similar effect on lakes and streams. The largest variation in DOC concentrations occurred in the smallest systems and average DOC concentrations along with variation in concentrations decreased as lake and stream size increased. These patterns in regional stream and lake DOC likely reflect an interaction between watershed size, variability in wetland land cover (Strayer et al. 2003), and processing along the hydrologic continuum (Cole et al. 2007). In the NHLD, small watersheds can be composed entirely of wetlands or contain no wetlands (Lottig 2009; Hanson unpubl. data), which undoubtedly has important implications for DOC loading to freshwater ecosystems and the wide range in DOC concentrations observed in small lakes and streams. As watersheds become larger, they integrate more of the regional landscape, converging on the regional land-cover characteristics. Consequently, as observed, we would expect to see DOC concentrations trend toward a value consistent with loading from the regional wetland extent and variation in DOC concentration to decrease as watershed attributes become more similar in the largest systems.

The most striking result of this analysis is that, as lakes and streams increase in size, their biogeochemical attributes converge. The convergence of Ca in large surface water bodies is likely attributable to the increasing importance of groundwater and hydrologic connections between lakes and streams (Riera et al. 2000; Quinlan et al. 2003; Martin and Soranno 2006). The consistently similar patterns in stream and lake DOC concentrations support earlier observations that wetlands are influencing lakes and streams in a similar manner, not just at the regional scale, but at a local scale as well. The combined effect of these two patterns is that across a gradient of lake and stream size, we observe converging trajectories in the biogeochemical characteristics of lakes and streams toward similar Ca and DOC concentrations. Results suggest that these two trajectories are likely influenced by changes in hydrology and increased connectivity of surface waters (Walker et al. 2003; Webster et al. 2006), processing of biogeochemically reactive constituents (Cole et al. 2007; Battin et al. 2008), and changes in landscape composition (Gergel et al. 1999; Mulholland 2003). Consequently, these patterns clearly

emphasize the potential importance of considering ecosystem size in biogeochemical studies of surface waters.

Broader implications—Our analyses comparing patterns in lake and stream chemistry showed that regional factors can explain variation in surface-water chemistry. Two of the most surprising results from these analyses were first that, in a groundwater-dominated region, precipitation or short groundwater signals in lakes relative to streams were very important, and second, there was chemical convergence of large lakes and streams. These results were revealed through using multiple complementary analyses designed to answer similar questions from different angles, which we feel may not have been as apparent if we had relied on more traditional statistical approaches or a consideration of only one type of freshwater ecosystem.

Understanding the spatial distribution, movement, and transformations of solutes in surface waters across a landscape is fundamental for identifying the sensitivity of freshwater ecosystems to changes in exogenous drivers such as land use and climate change. Likewise, integrating studies of lakes and streams will be critical to addressing regional and global stressors on the freshwater landscape (Soranno et al. 2009). Our results have identified critical differences (groundwater inputs) and similarities (organic carbon dynamics) between lakes and streams and emphasize the importance of ecosystem size in interpreting these observations at the regional scale. As a result, studies such as this will provide essential pieces of information for regional and global biogeochemical studies of freshwater ecosystems.

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