Natural Variation and Current Reference for Specific Conductivity and Major Ions in Wadeable Streams of the Conterminous USA

Author: Griffith, Michael B.

Natural variation and current reference for specific conductivity and major ions in wadeable streams of the conterminous USA

Michael B. Griffith[1,2]

[1]Office of Research and Development, National Center for Environmental Assessment, US Environmental Protection Agency, MS A-130, 26 W. Martin Luther King Drive, Cincinnati, Ohio 45268 USA

Abstract: Variation in specific conductivity and major ions in streams must be understood to assess the effects of changes in ionic strength and salinity on stream biota. I compiled data for randomly selected sites from surveys conducted from 1985 to 2009 by the US Environmental Protection Agency (EPA). I followed EPA methods to estimate reference values for specific conductivity (60 ecoregions) and each major ion (34 ecoregions) as the 25th percentile of values in 1st- to 4th-order streams in Level III ecoregions with data from ≥25 sites (85 ecoregions). The 25th percentiles of specific conductivity were <200 μS/cm for most eastern and western montane ecoregions, except those dominated by limestone or calcareous till. Arid western ecoregions had higher specific conductivities. Ca^{2+} was generally the most abundant cation followed by Mg^{2+}, Na^+, and K^+. HCO_3^- was generally the most abundant anion followed by SO_4^{2-} and Cl^-. Ecoregions where SO_4^{2-} or Cl^- concentrations were greater than HCO_3^- concentration have been affected by acidic precipitation or are influenced by marine air masses, respectively, and have very low specific conductivities. Patterns of variation appear to be associated with 3 processes controlling total and relative concentrations of major ions in freshwaters. In many ecoregions, relative ionic concentrations reflect underlying geology, but in arid ecoregions, relative ionic concentrations show concentration by evaporation. Relative ionic concentrations in coastal ecoregions and those affected by acidic precipitation reflect the ionic content of precipitation. Verification of these factors awaits better quantification of the geological and climatic characteristics of each ecoregion.

Key words: specific conductivity, calcium, magnesium, sodium, potassium, bicarbonate, sulfate, chloride, ecoregions, geographic variation, current reference, wadeable streams

The ionic strength, salinity, or the total concentration of ions in freshwater ecosystems, such as streams, has increased in many regions of the USA because of increasing anthropogenic sources. Anthropogenic sources include rock salt used to melt ice and snow on roads, walks, and parking areas (Jackson and Jobbágy 2005, Kaushal et al. 2005, Kelly et al. 2008); weathering of concrete infrastructure associated with suburban and urban areas (Rose 2007, Wright et al. 2011); produced water and effluents from exploration and production of crude oil or natural gas (Meyer et al. 1985, Boelter et al. 1992, Veil et al. 2004) including coal-bed methane (Jackson and Reddy 2007, Dahm et al. 2011) and shale gas (Entrekin et al. 2011, Gregory et al. 2011); runoff and effluents from coal mining and processing (Zielinski et al. 2001, Kennedy et al. 2003, Kimmel and Argent 2010), particularly mountaintop mines and valley fills (Pond et al. 2008, Griffith et al. 2012); agricultural irrigation return waters (El-Ashry et al. 1985, Dun-

can et al. 2008); and effluent from wastewater treatment plants (Andersen et al. 2004) or industrial processes (Echols et al. 2009). In a few cases, natural sources may include inputs of saline water from deep groundwater (i.e., upper Rio Grande basin; Phillips et al. 2003) or saline springs (i.e., Delores River, tributary to the Colorado River; Blackman et al. 1973, Chafin 2003).

The natural range and variation of these ion concentrations in the absence of anthropogenic sources, particularly in wadeable streams, must be understood before we can fully understand the effects of these elevated ion concentrations on steam biota and ecosystems. Gibbs (1970) and others have described 3 general processes, or axes, that control the total and relative concentrations of major ions in surface waters: 1) the evaporation–crystallization or precipitation process (i.e., increasing ratio of evaporation to precipitation [e.g., rainfall] with differential loss [e.g., mineral precipitation, degassing] of ions), 2) rock dominance

(the mineral composition of the geological strata), and 3) atmospheric precipitation dominance (the ionic content of the original precipitation) (Feth 1971, Gibbs 1971, Stallard and Edmond 1981, 1983, 1987, Kilham 1990). These 3 processes are not independent and interact to produce the natural levels of specific conductivity and concentrations of the individual ions in fresh waters. Concentrations of ions in precipitation are generally low and depend on the sources of aerosols, dusts, and other materials in the atmosphere (Gorham 1958, 1961). Contact to soils and rock increases ion concentrations as a result of weathering unless the geology is resistant to chemical weathering. Evaporation can concentrate these ions, but some ions may be lost by mineral precipitation or degassing.

No investigator has sought to characterize systematically the natural range and variation of ions, measured as total dissolved solids, salinity, or specific conductivity in surface waters of streams in different regions of the conterminous USA. Moreover, no investigator has examined the relative natural concentrations of the major constituent ions in these waters, including the cations: Ca^{2+}, Mg^{2+}, Na^+, and K^+, and the anions: HCO_3^-, SO_4^{2-}, and Cl^-. Specific conductivity is a simple way to measure total ion concentrations in fresh waters (Pawlowicz 2008), but the concentration of individual ions and the relative concentrations of constituent ions may be more important for understanding the adverse effects of elevated ion concentrations on aquatic assemblages (Mount et al. 1997, Tietge et al. 1997). The mechanisms described by Gibbs (1971) can lead to differing relative natural concentrations of constituent ions, whereas anthropogenic sources contribute differing ion mixtures to fresh waters (Andersen et al. 2004, Jackson and Reddy 2007, Duncan et al. 2008, Kelly et al. 2008, Echols et al. 2009, Entrekin et al. 2011, Wright et al. 2011, Griffith et al. 2012).

Many environmental factors, such as flow, nutrients, ion concentrations, bedded or suspended sediments, dissolved O_2, light, and heat, are natural parts of the physicochemical regimes that are fundamental to aquatic ecosystems (Petts 2000, Poole et al. 2004). Each factor has a natural range that is characteristic of particular streams but varies among regions because of differences in geology, climate, and other large-scale factors (Omernik 1995, Naiman and Anderson 1997). Estimates of reference values provide a baseline for assessing human alteration of ion concentrations relative to the regime to which native flora and fauna are adapted. The fauna are likely to be sensitive to this alteration and not to the natural conditions they typically encounter. Fresh waters are generally hypoosmotic, and organisms inhabiting them are exposed to similar osmo- and iono-regulatory challenges (Perry et al. 2003, Evans 2008). Fish, unionid mussels, crayfish, and aquatic insects are hyperregulators that maintain greater internal ion concentrations than are found in fresh waters (Dietz et al. 2000, Bradley 2008, Evans 2008, Charmantier et al. 2009). They maintain ion balance by excreting dilute waste fluids via their renal systems, and maintain salt concentrations with various ion-transporting proteins in epithelial membranes, such as the gills, that allow active transport of ions against concentration gradients (Evans 1980, Burton 1983, Perry et al. 2003). Increased concentrations of different major ions may cause osmotic, ionic, or acid–base imbalances that can eliminate sensitive species from biotic assemblages (USEPA 2011a). Therefore, water-quality benchmarks or criteria are derived for the altered, nonbackground state (USEPA 2011a), and assessment of natural variation of environmental factors among regions and adjustment of benchmarks or criteria for any regional variation is appropriate (USEPA 2000, Smith et al. 2003, Paul and MacDonald 2006).

My goal was to answer the questions: 1) How do current reference specific conductivities and concentrations of major ions in streams vary among Level III ecoregions (Omernik 1987, 1995, USEPA 2011b) in the USA? 2) How do the relative concentrations of the major cations and anions vary among ecoregions? I hypothesized that if the 25th percentiles (used to describe reference conditions for criteria development) for specific conductivity and concentrations of major ions describe current reference conditions in streams within ecoregions, their patterns of variation should be consistent with the 3 processes described by Gibbs (1970).

METHODS

I approached these questions and estimated reference specific conductivity and concentrations of individual ions by compiling water-chemistry data from stream surveys in which selected sites were sampled randomly (Herlihy et al. 2000) by the EPA and cooperating agencies since 1985 (Table 1, Fig. 1). In the National Acid Precipitation Assessment Program (NAPAP) surveys, streams were sampled in selected nascent ecoregions (Omernik 1987), mostly in the eastern USA; in the Environmental Monitoring and Assessment Program (EMAP) and regional EMAP surveys, streams were sampled in selected states, ecoregions, groups of conterminous ecoregions, or river basins in different parts of the USA; and in the National Wadeable Streams Assessment (NWSA) and the National Rivers and Streams Assessment (NRSA) surveys, streams were sampled across the USA.

With the exception of the NRSA and some later EMAP surveys, these surveys were focused primarily on wadeable streams, and my analysis was limited to these streams, defined here as 1st- to 4th-order streams (Strahler 1957) as identified in the National Hydrography Dataset (USEPA 2005). Most sites were only visited once, but some sites

Table 1. Survey data sets included in this study. Years indicates the period during which the survey was conducted, and n is the number of unique sites included in the survey. Western Environmental Monitoring and Assessment Program (EMAP) survey sites are included in the count of sites from the National Wadeable Streams Assessment (NWSA).

Survey	Years	Sample frame	n
National Acid Precipitation Assessment Program (NAPAP)	1985–1986	Blue-line headwater segments or segments between confluences on 1 : 250,000-scale US Geological Survey topographic maps	950
EMAP and Regional EMAP	1993–2003	River Reach File Version 3 (RF3)	2382
NWSA	2000–2004	River Reach File Version 3 (RF3) Alpha	1359
National Rivers and Streams Assessment (NRSA)	2008–2009	National Hydrography Dataset Plus	949

were revisited either within 1 y or in consecutive years to assess between-visit variability. I used data from the 1st visit to a site.

I used Level III ecoregions (Omernik 1987, 1995, USEPA 2011b) to classify sites into groups with similar geology and climate, which are 2 of the mechanisms discussed by Gibbs (1970). Level III ecoregions, as defined by Omernik (1987, 1995), are generally similar to the classic physiographic provinces used by geologists to classify regions with similar geology and geomorphology (Fenneman 1928) but also are related to variations in climate (Carr et al. 2000). I used the hierarchical 6-digit code for the Level III ecoregions (e.g., 08.01.03) published by Wilken et al. (2011) because this approach enabled me to group Level III ecoregions at hierarchical Level II. I referenced the commonly used 2-digit codes in Table S1. I included an ecoregion in the analyses if data were available from ≥25 sites in the ecoregion. Individual ions were not analyzed in some surveys, particularly regional EMAP studies. Dissolved inorganic C (DIC) was not measured in the NRSA, in which only acid-neutralizing capacity was measured. Therefore, data for individual ions, particularly HCO_3^-, were not available for all sites. I ana-
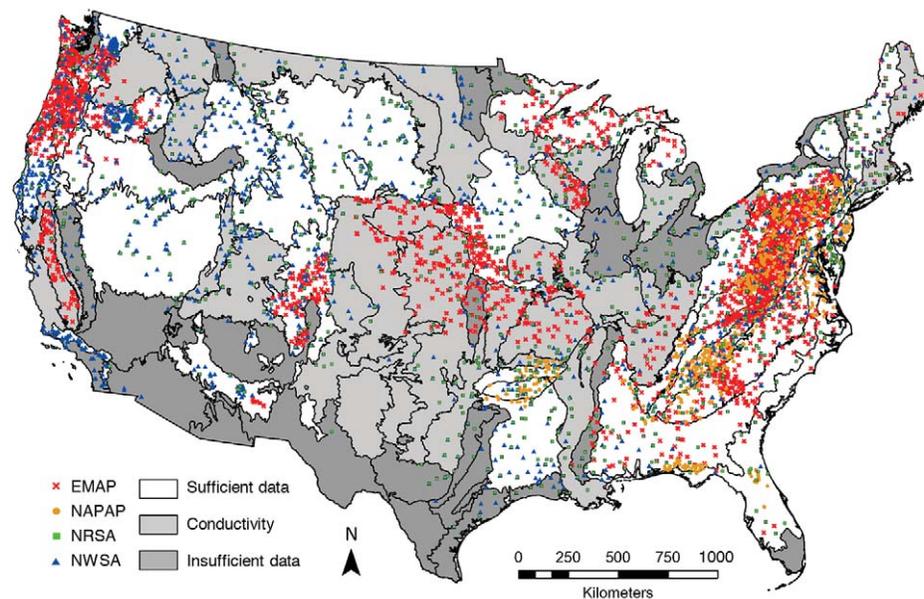

Figure 1. Map showing the sites in each survey and within each Level III ecoregion (outlines). The symbols and their colors differentiate the 4 different surveys: Environmental Monitoring and Assessment Program (EMAP) and regional EMAP, National Acid Precipitation Assessment Program (NAPAP), National Rivers and Streams Assessment (NRSA), and National Wadeable Streams Assessment (NWSA). *Sufficient data* indicates those ecoregions with data from ≥25 sites that were used to characterize specific conductivity and all the ions, *Conductivity* indicates those ecoregions with data from ≥25 sites at least for specific conductivity and often a subset of ions that was used to characterize those variables, and *Insufficient data* indicates those ecoregions with data from <25 sites that could not be used for analysis of either specific conductivity or ions.

lyzed data for each ion only if observations were available from ≥25 sites in an ecoregion. I selected the minimum of 25 sites as a compromise between characterizing as many Level III ecoregions as possible and the uncertainty of characterizing an ecoregion with few sites.

The Ridge and Valley ecoregion (08.03.01) is geologically heterogeneous (Pan et al. 1996, McCormick et al. 2000, Zheng et al. 2008), so I further subdivided the ecoregion into 2 subregions—the Limestone and Shale Valleys and the Ridges—to investigate the effect of this heterogeneity on specific conductivity and ion concentrations. I assigned level IV subdivisions of the Ridge and Valley to these 2 subregions based on descriptions by Woods et al. (1999, 2007).

In most of the surveys, samples were collected at baseflow during a spring (April) to summer (September) index period. Over the entire data set, 10, 10, 12, 22, 23, and 12% of sites were sampled during April, May, June, July, August, and September, respectively. Fewer sites were sampled in March (7%), October (4%), November (0.4%), and December (<0.1%). Preliminary analyses of data from the Central Appalachians (08.04.02) and Western Allegheny Plateau (08.04.03) in West Virginia showed seasonal variation in specific conductivity with higher levels during the April-to-September index period (USEPA 2011a). Therefore, sampling captured these higher levels of specific conductivity and individual ions.

Measured water-chemistry variables included specific conductivity (μS/cm) and the individual concentrations (μeq/L) of 4 major cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) and 3 major anions (HCO_3^-, SO_4^{2-}, and Cl^-). Collection and chemical analysis of water samples in these studies followed EPA procedural and quality-control protocols (Drousé et al. 1986, USEPA 1987, Lazorchak et al. 1998, USEPA 2004a, b, c, 2009a, b, 2010). Water samples generally were collected at midchannel at the lowermost transect of the sampling reach, placed in 4-L cubitainers, and stored on ice for transport to the laboratory. Water samples for analysis of pH and DIC were collected without contact with the atmosphere in 60-mL syringes with Luer-Lok® valves to minimize CO_2 exchange. The water samples for ions were filtered, and samples for cations were acidified with nitric acid (H_2NO_3) until analysis. The water samples for pH and DIC were not filtered. In the laboratory, Cl^- and SO_4^{2-} were analyzed with ion chromatography, and the cations were analyzed with atomic absorption spectroscopy. pH was measured with a calibrated pH meter with a glass electrode, and DIC was measured with a C analyzer equipped with a high sensitivity loop. Specific conductivity was measured with a calibrated conductivity meter, which standardized the measurement to 25°C or, in the case of 1 regional EMAP study of the Southern Rockies ecoregion (06.02.14), was calculated from the measurements of ion concentrations (USEPA 1987). HCO_3^- was calculated from the measurements of pH and DIC. In most studies, specific conductivity also was calculated from measurements of ion concentrations

and compared to the meter specific conductivity measurements as part of quality assurance (USEPA 1987). No data presented an analytical problem that could not be corrected.

EPA (USEPA 2000) guidance has suggested 2 approaches to estimating reference concentrations from survey data. These studies produced probability-based data sets but reference sites frequently were not identified. Therefore, I estimated the upper limit of current reference-site specific conductivity and the concentrations of individual ions as the 25th percentile following EPA (USEPA 2000) guidance. However, I also plotted the maximum, 75th percentile, median, and minimum values for specific conductivity and have presented these data and the mean for specific conductivity, pH, and the individual ions in Table S1.

I calculated Pearson correlations between the 25th percentiles for specific conductivity and the individual ions for each ecoregion with sufficient data to assess the relationships among the different ions. I also plotted the 25th percentile for specific conductivity against the percentile ratio of Na^+ to (Na^+ + Ca^{2+}) for each ecoregion with sufficient data to compare them to the original model by Gibbs (1970). This model describes variation in total dissolved ions and dominance by Ca^{2+} and HCO_3^- vs Na^+ and Cl^- in relation to 3 processes affecting the ionic composition of fresh waters: evaporation–crystallization, rock composition, and atmospheric precipitation composition. I used principal components analysis (PCA) of the $log_{10}(x)$-transformed 25th-percentile concentrations of the individual ions for each ecoregion followed by cluster analysis of the ecoregion scores on the first 3 principal component axes to assess the similarities among sites. I used SAS® (SAS Institute, Cary, North Carolina) to manage the data and the UNIVARIATE, CORR, PRINCOMP, and FASTCLUS procedures for the analyses. The figures were made following the linked micromaps concept of Carr et al. (2000) in which geographically referenced data are presented by combining graphs that display measures of variation with maps (Symanzik and Carr 2008, Carr and Pickle 2010).

RESULTS
Specific conductivity

Specific conductivities ranged from 1.6 to 12,290 μS/cm (median = 132.7 μS/cm, mean = 312.4 μS/cm). Specific-conductivity data were available from ≥25 sites in 60 of 85 Level III ecoregions (Fig. 1). Sufficient data were lacking for all of the warm desert ecoregions in the southwestern USA (Omernik 1995). Among those ecoregions, the 25th percentile for specific conductivity ranged from 16.2 to 563 μS/cm.

For most ecoregions in the eastern USA, the 25th percentiles of specific conductivity were <200 μS/cm, and often the median and 75th percentiles were less than this level (Fig. 2). This level was used by the EPA to characterize

ecoregions with low specific conductivity and its constituent ions (USEPA 2011a). Ecoregions where the 25th percentile was >200 µS/cm included the Interior Plateau (08.03.03), Interior River Valleys and Hills (08.03.02), Ozark Highlands (08.04.05), Erie Drift Plain (08.01.10), Southern

Michigan/Northern Indiana Drift Plains (08.01.06), and Driftless Area (08.01.05).

In the western USA, 25th percentiles of specific conductivity were <200 µS/cm for most montane ecoregions, such as those in the Rockies, the Pacific Northwest, and
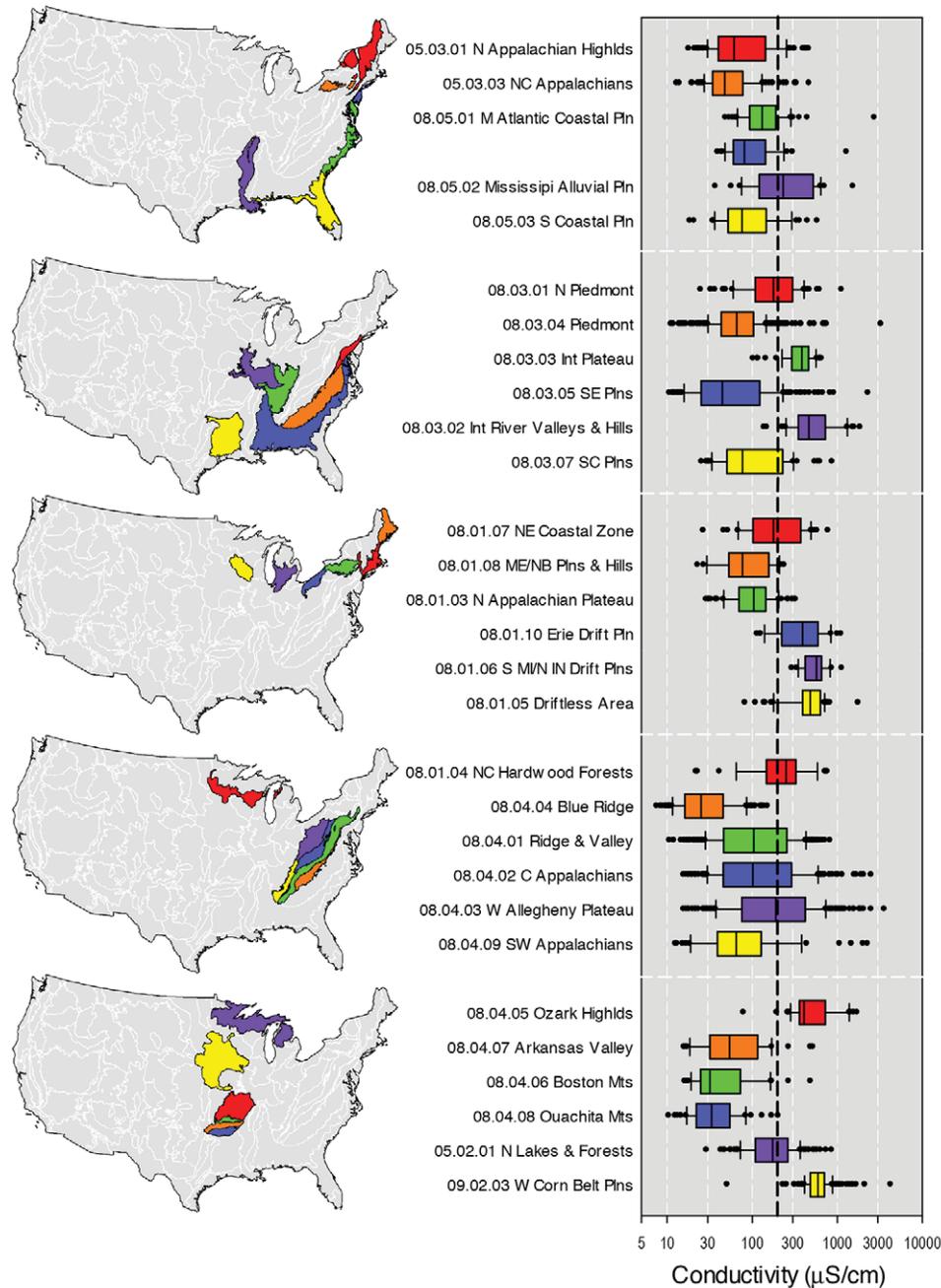

Figure 2. Box-and-whisker plots showing the 90th, 75th, 50th, 25th, and 10th percentiles of specific conductivity (µS/cm) for Level III ecoregions in the eastern conterminous USA and the Western Corn Belt Plains (09.02.03) with sufficient data. Dots represent sites with specific conductivity values >90th percentile or <10th percentile. The vertical dashed line on the graph represents 200 µS/cm. The maps show each plotted ecoregion. The color of the box in the graph (right) matches the color of the ecoregion in the map (left). The abbreviations of the ecoregions include the direction (C = Central, M = Middle, N = Northern, NC = North Central, NE = Northeastern, S = Southern, SC = South Central, SE = Southeastern, SW = Southwestern, W = Western), geographic name (Highlds = Highlands, Int = Interior, Mts = Mountains, Pln/Plns = Plain/Plains), and state or province (IN = Indiana, ME = Maine, MI = Michigan, NB = New Brunswick).

the Upper Gila Mountains (i.e., Arizona/New Mexico Mountains [13.01.01]; Fig. 3). However, for most of the prairie ecoregions and some of the Great Basin or Cold Desert (10.01) ecoregions, the 25th percentiles of specific conductivity were >200 µS/cm. For the ecoregions composing the more eastern Temperate Prairies (09.02, n = 3), the 25th percentiles ranged from 309 to 563 µS/cm, whereas those for the ecoregions composing the West-Central Semi-

arid Prairies (09.03, n = 3) ranged from 160 to 490 µS/cm, and the South-Central Semiarid Prairies (09.04, n = 4) ranged from 291 to 594 µS/cm. The 25th percentiles in the Cold Desert (10.01, n = 5) ecoregions ranged from 98.4 to 405 µS/cm. The Mediterranean California (11.01, n = 3) ecoregions also had 25th percentiles that ranged from 90.3 to 249 µS/cm. I lacked sufficient data to characterize the 25th percentiles of conductivities and ion concentra-

Figure 3. Box-and-whisker plots showing the 90th, 75th, 50th, 25th, and 10th percentiles of specific conductivity (µS/cm) for Level III ecoregions in the western conterminous USA with sufficient data. Figure symbols and abbreviations are as in Fig. 2 except for geographic names (Cstl = Coastal, Fthls = Foothills, Mts = Mountains, Plns = Plains), and states (AZ = Arizona, CA = California, CO = Colorado, NE = Nebraska, NM = New Mexico, ID = Idaho).

tions in streams in the Warm Desert (10.02) ecoregions, but the 8 observations in the data set from these 3 ecoregions ranged from 279 to 12,290 (median = 2622) µS/cm. Within the Ridge and Valley (08.04.01) ecoregion, the 25th percentile for specific conductivity at sites in the Limestone and Shale Valleys was generally greater than that in the Ridges (Fig. 4A).

Concentrations of individual ions

Concentrations of individual cations ranged from 1.9 to 25,694 µeq/L for Ca^{2+}, 2.6 to 44,444 µeq/L for Mg^{2+}, 3.7 to 108,851 µeq/L for Na^+, and 0 to 3406 µeq/L for K^+. Concentrations of individual anions ranged from 0.01 to 16,654 µeq/L for HCO_3^-, 0 to 75,568 µeq/L for SO_4^{2-}, and 0 to 74,750 µeq/L for Cl^-. I had sufficient data for all ions from 34 of 85 ecoregions, and sufficient data for a subset of ions from 24 more ecoregions (Fig. 1).

Among the cations, the 25th percentile concentration of Ca^{2+} either alone or in combination with Mg^{2+} generally exceeded the concentration of Na^+ (Figs 5B, S1–S4), whereas in a few cases, the 25th percentile of Mg^{2+} exceeded that of Ca^{2+}. Exceptions to this pattern included several Eastern Coastal Plain ecoregions: Northeastern Coastal Zone (08.01.07), Atlantic Coastal Pine Barrens (08.05.04), and Southeastern Plains (08.03.05) (Figs 5B, S1, Table S2). The 25th percentiles of Ca^{2+} and Na^+ were similar in several other ecoregions, such as the Middle Atlantic Coastal Plain (08.05.01; Fig. S1), Blue Ridge (08.04.04; Fig. S2), and Coast Range (07.01.08; Fig. S4). In the Arkansas Valley (08.04.07) and Ouachita Mountains (08.04.08) (Figs 5B, S2), the 25th percentiles of Na^+ were greater than those of Ca^{2+} but were less than those of Mg^{2+}. The 25th percentile concentration of K^+ was generally much less than each of the other 3 cations. The 25th percentile

concentration of Mg^{2+} relative to that of Na^+ was more variable. Within the Ridge and Valley (08.04.01) ecoregion, the 25th percentile for concentrations of both cations and anions at sites in the Limestone and Shale Valleys were generally greater than those in the Ridges (Fig. 4B).

The 25th percentiles of the concentrations for the cations Ca^{2+}, Mg^{2+}, Na^+, and K^+ ranged from 37.8 to 3089 µeq/L, 29.8 to 1974 µeq/L, 28.3 to 1316 µeq/L, and 0.0 to 195 µeq/L, respectively. The correlations among these cation concentrations were moderate (Table 2), and r ranged from 0.67 to 0.87. The correlations of the 25th percentiles for each cation and specific conductivity were moderate to strong (Table 2), and r ranged from 0.78 to 0.96.

Among the anions, the 25th percentile concentration of HCO_3^- exceeded the concentrations of either SO_4^{2-} or Cl^-, often by at least an order of magnitude (Figs 5C, S1–S4). Exceptions to this pattern occurred in the Southeastern Plains (08.03.05), Southern Coastal Plain (08.05.03), and Middle Atlantic Coastal Plain (08.05.01) (Fig. 5C, Table S2), where Cl^- concentration exceeded HCO_3^- concentration; the Central Appalachians (08.04.02, Fig. 5C), the ridges of the Ridge and Valley (08.04.01, Fig. 4), and North Central Appalachians (05.03.03, Fig. 5C) where SO_4^{2-} concentration exceeded HCO_3^- concentration; and Atlantic Coastal Pine Barrens (08.05.04, Figs 5C, S1), where both SO_4^{2-} and Cl^- concentrations exceeded HCO_3^- concentration. These ecoregions had low conductivities (25th percentile = 25.0–103 µS/cm; Fig. 5A) and the lowest 25th percentiles for pH (3.96–6.57; Table S1). For many of these ecoregions, the 25th percentile concentrations of Na^+ and Cl^- were similar. Usually, the 25th percentile concentration of SO_4^- exceeded that of Cl^-. However, the reverse occurred in the Marine West Coast Forest (07.01, Fig. S4), Southeastern USA Plains (08.03, Fig. S1), and Mississippi Alluvial and Southeastern USA Coastal Plains (08.05, Fig. S1) ecoregions.

The 25th percentiles of the concentrations for HCO_3^-, SO_4^{2-}, and Cl^- ranged from 0.9 to 4010 µeq/L, 4.1 to 1487 µeq/L, and 5.1 to 441 µeq/L, respectively. The correlation between HCO_3^- and SO_4^{2-} was moderate (Table 2), whereas the correlations between these 2 anions and Cl^- were weaker (Table 2). The correlations of the 25th percentiles for SO_4^{2-} and HCO_3^- with specific conductivity were relatively strong, but the correlation between Cl^- and specific conductivity was weaker (Table 2). The correlations between HCO^{3-} or SO_4^{2-} and the 4 cations were moderate to strong, whereas the correlations between Cl^- and the 4 cations were weaker (Table 2).

When I plotted the ratio of the 25th percentile Na^+ concentration to the summed 25th percentile concentrations of Na^+ and Ca^{2+} (i.e., $Na^+ : [Na^+ + Ca^{2+}]$) against the 25th percentile of specific conductivity for each ecoregion (similar to the method used by Gibbs 1970), several ecoregions with high specific conductivities plotted on the upper part of the graph (Fig. 6), and some ecore-
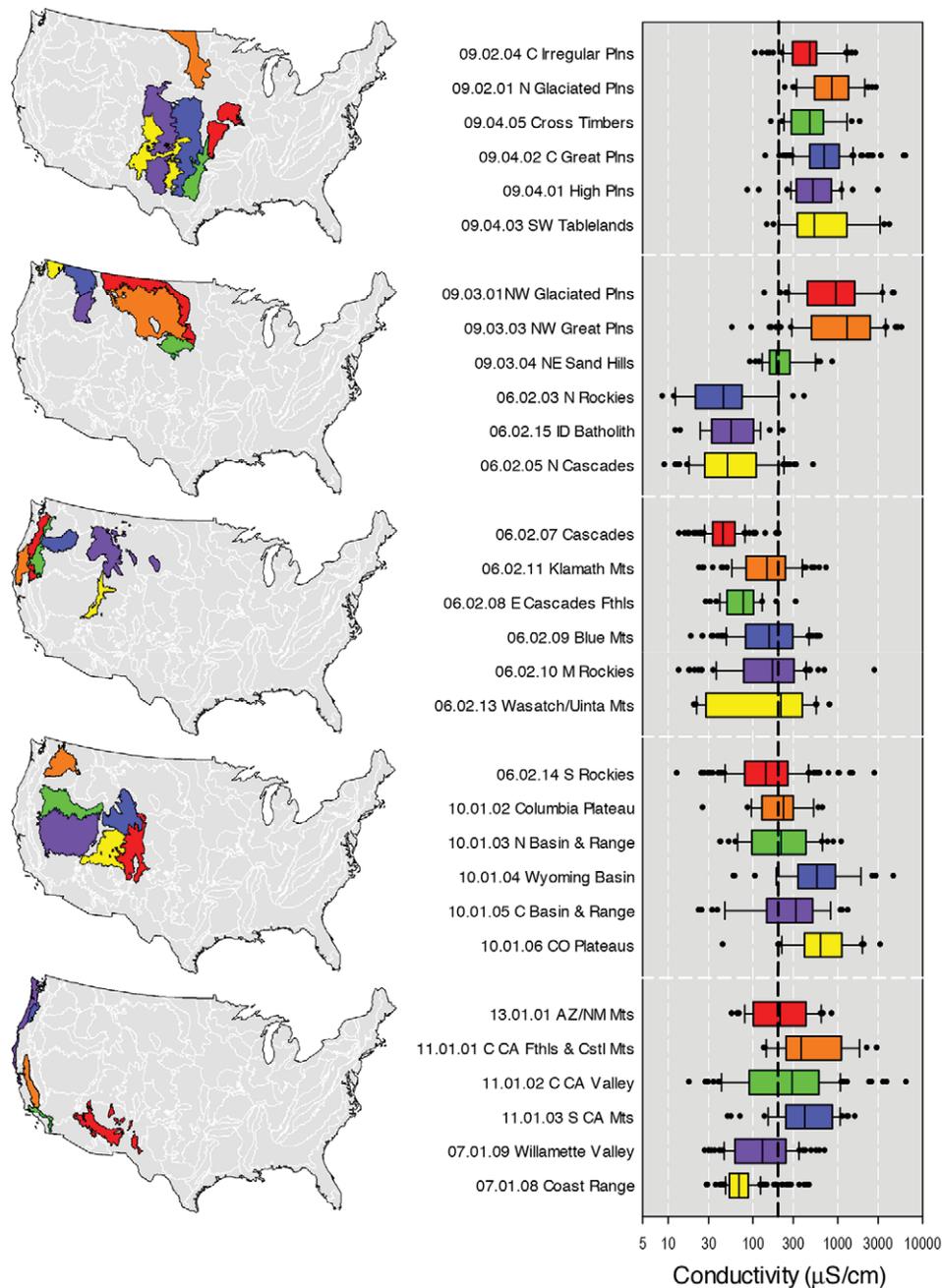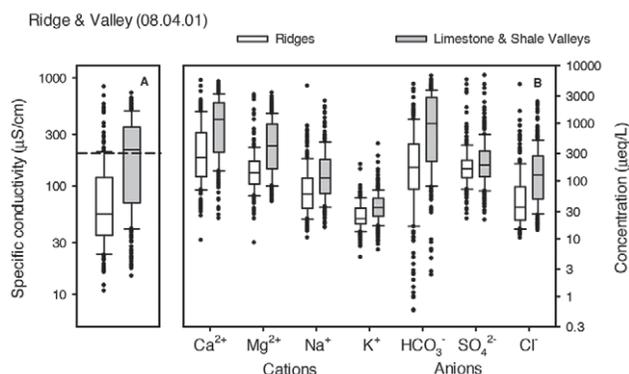

Figure 4. Box-and-whisker plots showing the 90th, 75th, 50th, 25th, and 10th percentiles of specific conductivity (A) and cation and anion concentrations (B). Dots indicate sites that exceeded the 90th and 10th percentiles in the Ridge (n = 222–225 depending on variable) and the Limestone and Shale Valleys (n = 286–295 depending on variable) subregions of the Ridge and Valley (08.04.01) ecoregion. The horizontal dashed line in panel A represents 200 µS/cm.
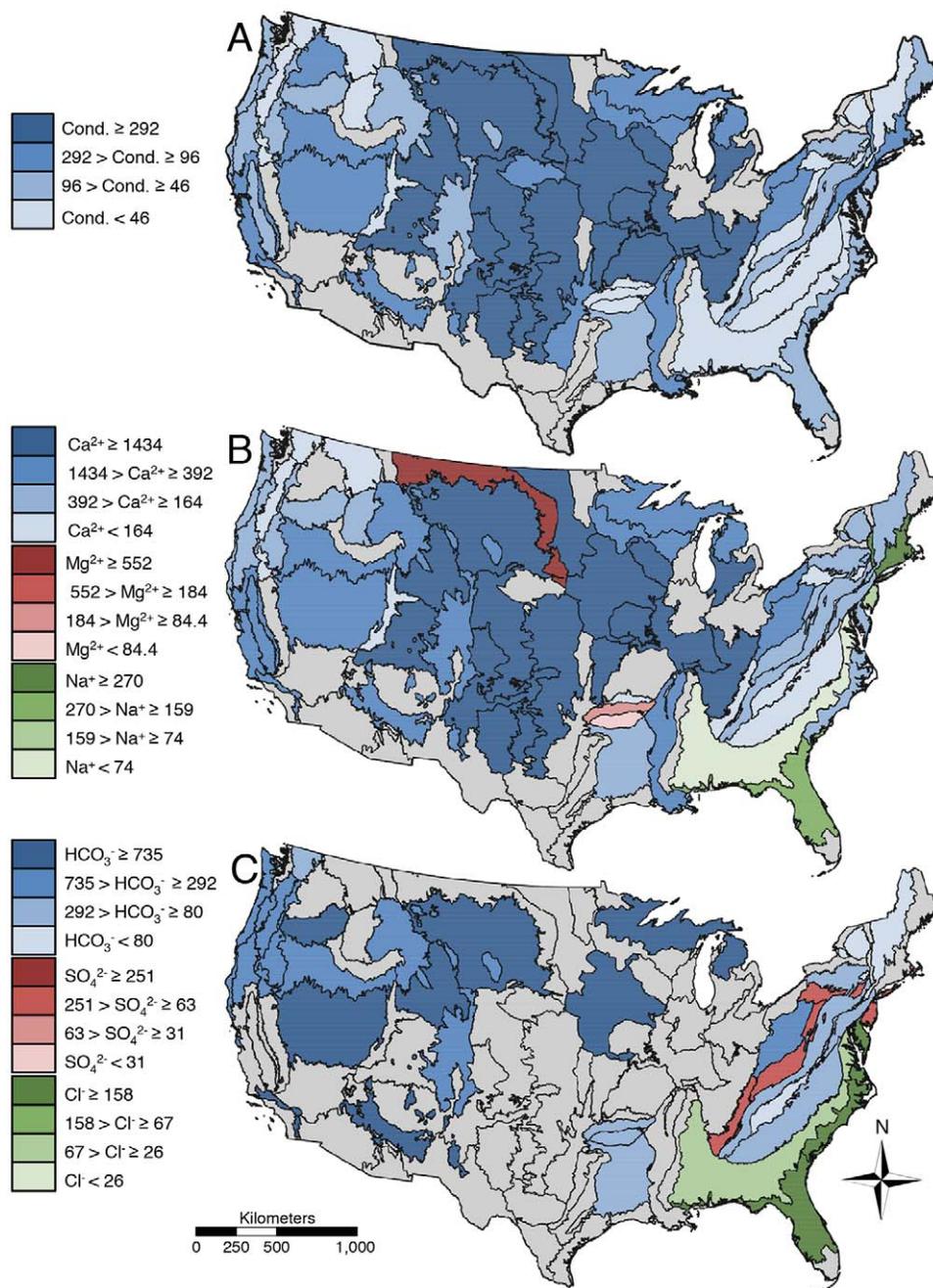
Figure 5. Maps showing the quartiles of the specific conductivity (Cond.) (A) reference values, cations with the greatest reference values (B), and anions with the greatest reference values (C) for each Level III ecoregion. Ecoregions shown in color have data from ≥25 sites for specific conductivity in panel A, all major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) in panel B, or all major anions (HCO_3^-, SO_4^{2-}, Cl^-) in panel C. Ecoregions shown in gray lack sufficient data. The quartile range for each variable is the quartile of the range of all reference values for that variable for ecoregions with sufficient data. See Table S2 for the Level III ecoregions in each group.

gions where Cl^- was greater than HCO_3^- plotted on the lower right part of the graph. However, most sites plotted toward the left center of the graph.

I did not include HCO_3^- in the PCA because the 25th percentiles for HCO_3^- were strongly correlated with those of Ca^{2+} and Mg^{2+} (Table 2). This decision allowed me to in-

clude more ecoregions in the analysis. Axes 1, 2, and 3 explained 75, 10, and 7% of the variance in the ionic concentrations, respectively (Table 3). All 6 ions were positively correlated with Axis 1 (Table 3, Fig. 7), whereas Cl^- was positively and Ca^{2+} and Mg^{2+} were inversely correlated with Axis 2.

Table 2. Pearson correlation (r and associated p-values) matrix of 25th-percentile concentrations of ions (µeq/L) and the 25th percentiles for specific conductivity (µS/cm). n = 55 to 57, except for HCO_3^-, where n = 34.

| Ions | Specific conductivity (µS/cm) | Ions | | | | | |
		Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}
Ca^{2+}	0.96						
	($p<0.001$)						
Mg^{2+}	0.90	0.86					
	($p<0.001$)	($p<0.001$)					
Na^+	0.81	0.67	0.67				
	($p<0.001$)	($p<0.001$)	($p<0.001$)				
K^+	0.78	0.68	0.71	0.87			
	($p<0.001$)	($p<0.001$)	($p<0.001$)	($p<0.001$)			
HCO_3^-	0.97	0.96	0.93	0.80	0.69		
	($p<0.001$)	($p<0.001$)	($p<0.001$)	($p<0.001$)	($p<0.001$)		
SO_4^{2-}	0.86	0.76	0.80	0.83	0.87	0.75	
	($p<0.001$)	($p<0.001$)	($p<0.001$)	($p<0.001$)	($p<0.001$)	($p<0.001$)	
Cl^-	0.59	0.59	0.49	0.46	0.43	0.23	0.43
	($p<0.001$)	($p<0.001$)	($p<0.001$)	($p<0.001$)	($p=0.001$)	($p=0.18$)	($p<0.001$)

I identified 7 groups of ecoregions in the cluster analysis (Fig. 7, Table S3). Cluster A included many of the eastern montane ecoregions, including the Appalachians and the Ozark–Ouachita Highlands, whereas cluster D, which overlapped cluster A along the first 2 axes, included several southeastern lowland ecoregions. Cluster B included a number of Great Plains ecoregions and some more eastern ecoregions influenced by either calcareous bedrock or tills. Cluster G included 7 western montane ecoregions, whereas cluster E included some western montane and Great Basin ecoregions, along with the Willamette (07.01.09) and Central California (11.01.02) valleys and the more eastern Northern Lakes and Forests (05.02.01). Cluster C included 3 eastern coastal or alluvial plain ecoregions, the adjacent Northern Piedmont (08.03.01) and South Central Plains (08.03.07) and the Northern Appalachian Plateau (08.01.03) and North Central Hardwood Forests (08.01.03). Cluster F included a mixture of ecoregions, including 3 eastern ecoregions influenced by calcareous bedrock or tills, 2 Great Plains ecoregions, and 2 basin and range ecoregions along with the Western Allegheny Plateau (08.04.03) and Central California Foothills and Coastal Mountains (11.01.01).

DISCUSSION

Specific conductivity and the concentrations of major ions characteristic of the natural factors originally described by Gibbs (1970) varied in wadeable streams among ecoregions. Such variation must be considered when setting water-quality expectations during stream assessments or when considering management options. Estimates of current reference conditions also are a baseline for future assessment of stream impairments associated with salinity

from anthropogenic sources. The observations by Gibbs (1970) were made in larger rivers. However, within the more-limited range of conditions in wadeable streams and ecoregions sampled during the surveys, I also observed examples that exhibited ionic concentrations and compositions characteristic of rock dominance, evaporation–crystallization, and atmospheric precipitation dominance.

Most ecoregions (75%) appeared to be primarily rock dominant, and the ion signature of the streams was dominated by Ca^{2+}, Mg^{2+}, and HCO_3^- (Gibbs 1970, Stallard and Edmond 1987). In the eastern USA, specific conductivity is generally <200 µS/cm because precipitation is moderate (average annual precipitation = 100–250 cm), but some ecoregions with greater conductivities are generally characterized either by limestone karst (e.g., Interior Plateau [08.03.03], Ozark Highlands [08.04.05], Driftless Area [08.01.05]; Veni et al. 2001), or by calcareous tills (e.g., Southern Michigan/Northern Indiana Drift Plains [08.01.06], Erie Drift Plain [08.01.10]; Smeck and Wilding 1980, Szabo 2006).

The greater conductivities in ecoregions characterized by limestone karst prompted me to investigate whether specific conductivities in streams in the valleys of the Ridge and Valley (08.04.01) ecoregion, which are also characterized by areas of limestone karst, were greater than those of streams on the ridges. They were (Fig. 4), but the 25th percentile of specific conductivity for the limestone and shale valleys was not >200 µS/cm. Moreover, the greater conductivities were associated with greater concentrations of Ca^{2+}, Mg^{2+}, Cl^-, and HCO_3^-. Other investigators have recognized the effects of this heterogeneity in geology (Pan et al. 1996, McCormick et al. 2000, Zheng et al. 2008), and these differences are clearly related to the differences in the li-
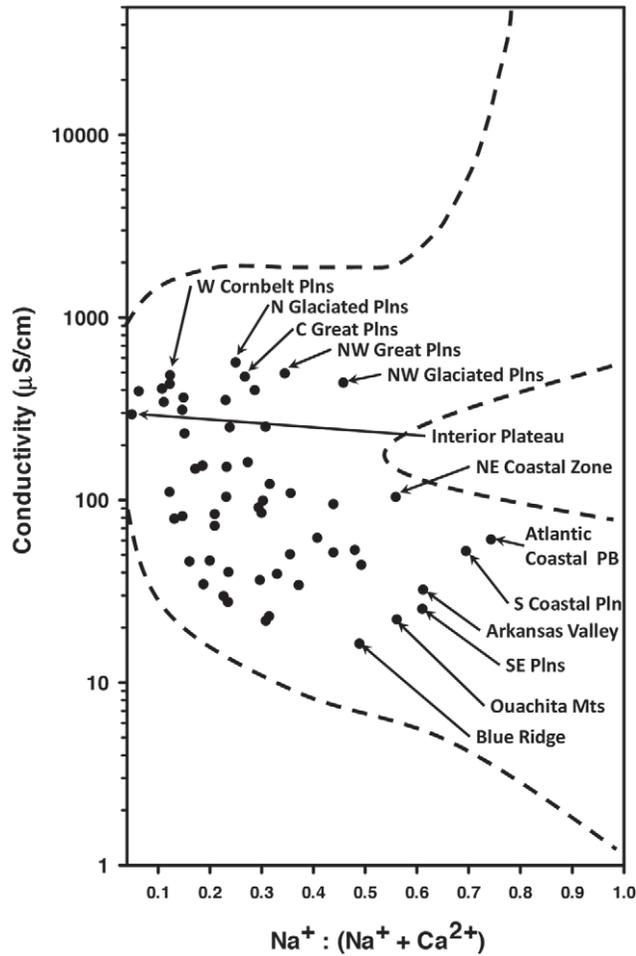
Figure 6. Plot of specific conductivity vs the ratio of $Na^+ : (Na^+ + Ca^{2+})$ (25th percentiles) for each Level III ecoregion with sufficient data. Ecoregions that plot to the upper right (sites with characteristics of the evaporation–crystallization process) or lower right (sites with characteristics of atmospheric precipitation dominance) of the plot are labeled. The dashed lines approximate the outline surrounding the plotted surface waters in fig. 1 by Gibbs (1970). See Figs 2, 3 for abbreviations.

cific conductivity were often >200 µS/cm and ranged up to 563 µS/cm. Yet, the anions were still dominated by HCO_3^-, and Ca^{2+} was the most abundant cation. Some of these same ecoregions (Western Corn Belt Plains [09.02.03], Northern Glaciated Plains [09.02.01], Central Great Plains [09.04.02], Northwestern Great Plains [09.03.03], and Northwestern Glaciated Plains [09.03.01]) occur in the upper part of the graph of specific conductivity vs the Na^+ : $(Na^+ + Ca^{2+})$ ratio (Fig. 6), results suggesting that these increased ion concentrations reflected concentration of the ions by the evaporation–crystallization process (Gibbs 1970).

The eastern ecoregions, where specific conductivities were very low and either SO_4^{2-} or Cl^- were greater than HCO_3^-, are characteristic of dominance by atmospheric precipitation. The North Central Appalachians (05.03.03) and Central Appalachians (08.04.02) both have been affected by acidic precipitation (Herlihy et al. 1991, Kaufmann et al. 1991), which is a source of SO_4^{2-}. However, both ecoregions also have histories of coal mining (Herlihy et al. 1990), and coal-mine drainage is a source of SO_4^{2-}. The Atlantic Coastal Pine Barrens (08.05.04) receives precipitation both from continental air masses, which are a source of SO_4^{2-} as in the 2 Appalachian ecoregions, and marine air masses, which are the source of Na^+ and Cl^- (Raynor and Hayes 1982, Morgan and Good 1988). However, regulation of emissions from coal-fired power plants, the ultimate source of the SO_4^{2-}, has decreased atmospheric deposition of SO_4^{2-} in the northeastern USA (Stoddard et al. 2003).

Similar to the Atlantic Coastal Pine Barrens (08.05.04), the Southern Coastal Plain (08.05.03), Southeastern Plains (08.05.03), and Northeastern Coastal Zone (08.01.07) are influenced by marine air masses (Beck et al. 1974, Richter et al. 1983, Mattson et al. 1992), as is the Coast Range (07.01.08) in the Pacific Northwest (Wigington et al. 1998). Moreover, many of these marine-influenced ecoregions plot in the lower right part of the graph of specific conduc-

thology. Therefore, geological heterogeneity within other ecoregions may affect variation of ambient specific conductivity and concentrations of individual ions. However, the small size and geomorphologic relationship between these Level IV ecoregions are such that many stream sites in the valleys have their headwaters on the ridges, and this relationship may limit variation in specific conductivity and ion concentrations. Level III ecoregions are generally much larger than level IV ecoregions, and I limited the analyses to wadeable streams (1st- to 4th-order). Thus, effects associated with stream sites with at least part of their headwaters in a different ecoregion appear to be uncommon.

In the western USA, particularly outside the montane ecoregions of the Rockies and the Pacific Northwest, where the climate is semiarid, the 25th percentiles of spe-

Table 3. Eigenvectors, eigenvalues, and cumulative proportion of variance for the first 3 axes of the principal components analysis for the 25th percentiles of Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, and Cl^- concentrations for ecoregions with sufficient data ($n = 55$).

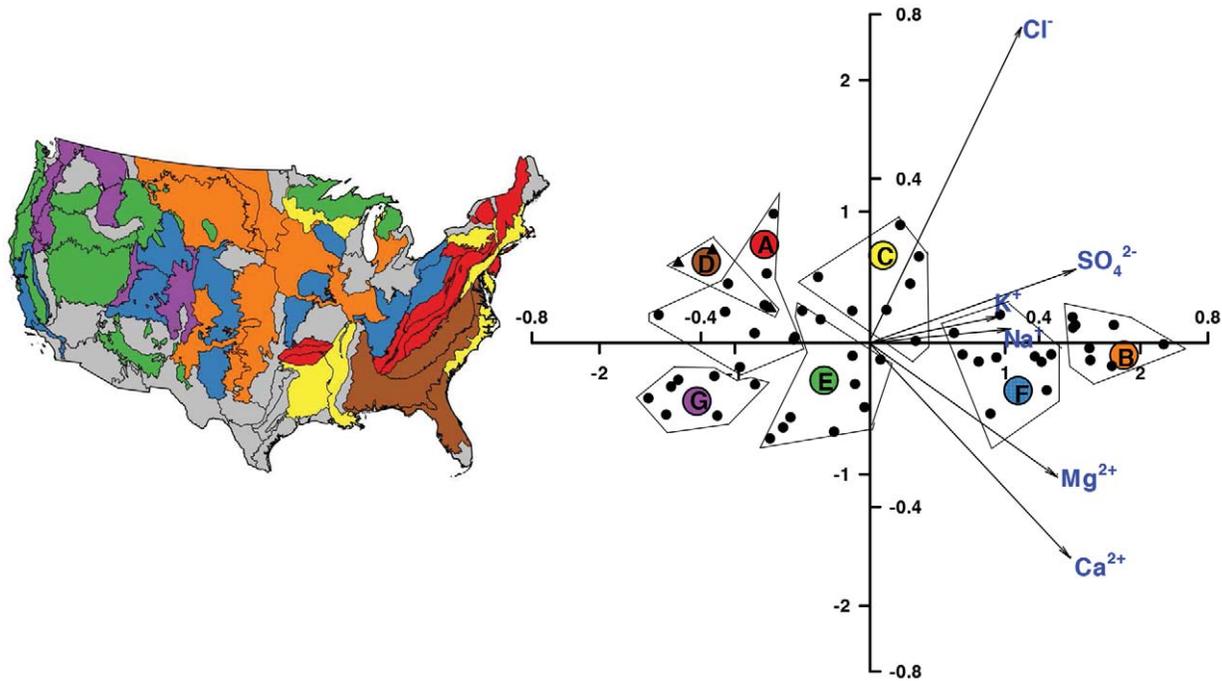| Ion	Axis 1	Axis 2	Axis 3
Ca^{2+}	0.477	−0.523	0.163
Mg^{2+}	0.445	−0.321	0.155
Na^+	0.334	0.032	0.408
K^+	0.308	0.059	−0.053
SO_4^{2-}	0.487	0.179	−0.809
Cl^-	0.361	0.766	0.353
Eigenvalue	1.137	0.157	0.108
Cumulative proportion of variance	0.75	0.85	0.92

Figure 7. Biplot of principal components analysis (PCA) axes 1 and 2 for the ecoregions of the conterminous USA with data from ≥25 sites for the 25th percentiles of Ca^{2+}, Mg^{2+}, Na$^+$, K$^+$, SO$_4^{2-}$, and Cl$^-$. The scale in standard deviation units is –2 to 2 for the ecoregion scores and –0.8 to 0.8 for the ion eigenvectors. The clusters, A–G, are the groups of ecoregions identified by cluster analysis. The triangles are used to differentiate the ecoregions in cluster D where it overlaps with cluster A. The map shows the ecoregions in each cluster. The colors on the map match the colored dot behind each cluster letter. See Table S3 for lists of ecoregions in each cluster.

tivity vs the Na$^+$: (Na$^+$ + Ca^{2+}) ratio (Fig. 6), supporting the model by Gibbs (1970) because specific conductivities are low, whereas relative concentrations of Na$^+$ are greater.

Over all the ecoregions, the 25th percentiles for specific conductivity were most strongly correlated with those of HCO$_3^-$ and Ca^{2+}, which were generally the most common anion and cation, respectively. The correlations of 25th percentiles of the other ions with that of specific conductivity decreased in relation to their general abundance (Table 2). All of these ions contribute to specific conductivity (Pawlowicz 2008), so this decrease is not necessarily surprising. The 25th percentiles of the Ca^{2+} and Mg^{2+} were more closely correlated with each other as were those of Na$^+$ and K$^+$, but the correlations between these 2 pairs of cations were less strong. Similarly, the correlation between HCO$_3^-$ and SO$_4^{2-}$ was greater than the correlation of either anion with Cl$^-$. This result suggests the 3 processes differ in their importance for control of different ion concentrations because Ca^{2+}, Mg^{2+}, and HCO$_3^-$ are associated with rock dominance, whereas Na$^+$, K$^+$, and Cl$^-$ are associated with atmospheric precipitation (Gibbs 1970).

The PCA, followed by cluster analysis, identified many of these patterns. The ions were all positively correlated with the PCA axis 1, whereas the additional axes separated differences among the ions. Ecoregions that are of-

ten grouped together in higher-level classifications, such as those in the Appalachian and Ozark/Ouachita Mountains, the Rocky Mountains, the Great Plains, and Great Basin, were generally grouped by the cluster analysis, but differences exist that are not necessarily explained by geography.

Tests of hypotheses about the variation in specific conductivity and ions among ecoregions require further quantification of climate, geology, and precipitation chemistry for each ecoregion. Such data are not currently available for the entire conterminous USA, but geographic information system (GIS) modeling approaches do exist that could be used to estimate the ratio of evaporation to precipitation at the ecoregion scale (Vörösmarty et al. 1989) and variation in rock chemical and physical properties across map units (Smart et al. 2001). Olson and Hawkins (2012) used GIS modeling of rock chemical and physical properties to predict natural baseflow stream water chemistry in the western USA. This pathway warrants further investigation.

The EPA (USEPA 2000) suggested using either the 25th percentile of randomly selected samples or the 75th percentile of identified reference sites as an estimate of reference values. I chose the 1st approach to make maximum use of the data compiled from the various EPA surveys, which in some cases, did not identify reference sites. Much

discussion exists in the literature as to whether estimates like mine are true estimates of background or at least current reference conditions (Stoddard et al. 2006, Hawkins et al. 2010), but much of this discussion has focused on setting expectations for assessments when biotic assemblages are used to assess biotic integrity. Reference sites should "be stream sites at which biota are exposed to the lowest level of anthropogenic stressors" (Whittier et al. 2007, p. 370). However, professional judgment or the use of objective criteria can be biased. In an analysis of a survey data set from the Western EMAP pilot study, Whittier et al. (2007) found that ~35% of their handpicked reference sites, selected using primarily GIS and other mapped data, could be classified as in least-disturbed condition (75% of reference sites are generally expected to be representative of least-disturbed conditions) compared with 20% for their probability sites (25% of probability sites are generally expected to be in least-disturbed condition). In an analysis of the WSA data, Paulsen et al. (2008) established a condition class as being good based on the 25th percentile of the reference-site distribution of a Multimetric Index of Macroinvertebrate Integrity. This criterion means that 75% of the reference sites were assumed to be representative of least-disturbed conditions. When this threshold was applied to all randomly selected sites sampled nationally, 28% of the stream kilometers were classified as being in good condition, and 18 to 45% of the stream kilometers were classified as being in good condition in the 3 subregions used in their assessment. In many regions, minimally disturbed sites may not exist because of extensive anthropogenic disturbances (Whittier et al. 2007), and the 25th percentile would overestimate undisturbed conditions.

Several investigators have used national survey data for nutrients to compare these approaches (Herlihy and Sifneos 2008, Dodds et al. 2009). In an analysis of WSA data (Herlihy and Sifneos 2008), the 25th percentile of population data was lower for both total P (TP) and total N (TN) than the 75th percentile of reference sites for all national nutrient ecoregions with sufficient probability and reference sites for analysis. In an analysis of national nutrient ecoregions, Dodds et al. (2009) found that 53 to 96% of a probability sample of rivers had higher TP and 69 to 100% had higher TN than the median ecoregion-specific nutrient reference values. However, it seems unlikely that elemental cycles of the major ions have been altered to the extent to which P and N cycles have been altered. Identifying sites that truly represent natural background conditions is prohibitively difficult, so the 25th percentile probably does provide a reasonable estimate of current reference conditions.

The eastern ecoregions that have low specific conductivity, low total ion concentrations, and dominance by SO_4^{2-} have been affected by acidic deposition (Kaufmann et al. 1991, Herlihy et al. 1991). Since 1995, amendments to the Clean Air Act have reduced atmospheric deposition of acidity and SO_4^{2-}, with resultant increases in stream pH and decreases in SO_4^{2-} in most of these ecoregions, except the Blue Ridge (08.04.04), where accumulated SO_4^{2-} appears to be leaching more slowly from soils (Skjelkvåle et al. 2005, Chen and Lin 2009). In these same ecoregions, longer-term effects of acidic deposition may include decreased stream concentrations of some ions, like Ca^{2+}, because of depletion of exchangeable ions in soils (Jeziorski et al. 2008). Moreover, Likens et al. (1970) and others have shown that land disturbances, such as forest cutting, agriculture, and urbanization, may increase mineralization and export of many ions from catchments (Smart et al. 1985, Morgan and Good 1988, Webster et al. 1992, Zampella 1994, Johnson et al. 1997, Herlihy et al. 1998), and Carpenter et al. (2011) describe such landuse change as a pervasive driver of ongoing ecosystem change. Increases in evapotranspiration rates, one of the factors described by Gibbs (1970) that can increase ion concentrations, are occurring as part of climate change (Carpenter et al. 2011). All of these changes have occurred during the 25-y period during which these surveys were conducted (i.e., 1985–2009) and beyond (Drummond and Loveland 2010, Sleeter et al. 2012). However, many ecoregions were not sampled in all surveys, particularly in the earliest survey, NAPAP, in 1985–1986 (Fig. 1).

Based on the definitions proposed by Stoddard et al. (2006), my estimates should be described as "best attainable." They provide a reasonable estimate of current reference levels in these ecoregions in light of increasing anthropogenic sources of salinity to streams and other freshwater ecosystems. However, these estimates are not benchmarks or criteria, which are generally based on adverse effects to biota and would be greater than my estimates of best attainable conditions (USEPA 2011a).

Conclusions

The 25th percentiles of specific conductivity were <200 µS/cm for most ecoregions in the eastern USA and in montane ecoregions in the western USA. Exceptions were some ecoregions dominated by limestone karst or calcareous till. Greater 25th percentiles of conductivity (e.g., 98.4–563 µS/cm) were observed in arid ecoregions of the Great Plains, Great Basins and Ranges, and Mediterranean California. For most ecoregions, $Ca^{2+} > Mg^{2+} > Na^+$, and $HCO_3^- > SO_4^{2-} > Cl^-$. Ecoregions with greater SO_4^{2-} are affected by acidic precipitation and coal mining, whereas those with greater Cl^- are influenced by marine air masses, and streams in these ecoregions have very low specific conductivities.

The patterns of variation appear to be associated with the 3 general processes controlling total and relative concentrations of major ions in freshwaters described by Gibbs (1970). However, better quantification of these re-

lationships will require better quantification of the characteristics of ecoregions relative to these processes. For the 60 Level III ecoregions with sufficient data, the supplementary material (Table S1) provides current reference levels for specific conductivity, and for many of these ecoregions, current reference levels for individual ions. Moreover, I continue to seek additional data from randomly selected sites to characterize the ecoregions for which insufficient data currently exist. In a monitoring and assessment context, the levels are valuable because they estimate the baseline conditions in streams to which the native flora and fauna are adapted. These levels are generally lower than benchmarks or criteria, which are based on adverse effects to biota.

ACKNOWLEDGEMENTS

LITERATURE CITED

Andersen, C. B., G. P. Lewis, and K. A. Sargent. 2004. Influence of wastewater-treatment effluent on concentrations and fluxes of solutes in the Bush River, South Carolina, during extreme drought conditions. Environmental Geosciences 11:28–41.

Beck, K. C., J. H. Reuter, and E. M. Perdue. 1974. Organic and inorganic geochemistry of some coastal plain rivers of the southeastern United States. Geochimica et Cosmochimica Acta 38:341–364.

Blackman, W. C., J. V. Rouse, G. R. Schillinger, and W. H. Shafer. 1973. Mineral pollution in the Colorado River basin. Journal of the Water Pollution Control Federation 45:1517–1557.

Boelter, A. M., F. N. Lamming, A. M. Farag, and H. L. Bergman. 1992. Environmental effects of saline oil-field discharges on surface waters. Environmental Toxicology and Chemistry 11: 1187–1195.

Bradley, T. J. 2008. Hyper-regulators: life in fresh water. Pages 87–110 in Animal osmoregulation. Oxford University Press, Oxford, UK.

Burton, R. F. 1983. Ionic regulation and water balance. Pages 292–352 in A. S. M. Saleuddin and K. M. Wilbur (editors). The Mollusca. Volume 5: Physiology, Part 2. Academic Press, New York.

Carpenter, S. R., E. H. Stanley, and M. J. Vander Zanden. 2011. State of the world's freshwater ecosystems: physical, chemical, and biological changes. Annual Review of Environmental Resources 36:75–99.

Carr, D. B., A. R. Olsen, S. M. Pierson, and J.-Y. P. Courbois. 2000. Using linked micromap plots to characterize Omernik ecoregions. Data Mining and Knowledge Discovery 4:43–67.

Carr, D. B., and L. W. Pickle. 2010. Visualizing data patterns with micromaps. CRC Press, Boca Raton, Florida.

Chafin, D. T. 2003. Effect of the Paradox Valley unit on the dissolved-solids load of the Dolores River near Bedrock, Colorado, 1988–2001. Water Resources Investigation Report 02-4275. US Geological Survey, Grand Junction, Colorado.

Charmantier, G., M. Charmantier-Daures, and D. W. Towle. 2009. Osmotic and ionic regulation in aquatic arthropods. Pages 165–230 in D. H. Evans (editor). Osmotic and ionic regulation: cells and animals. CRC Press, Boca Raton, Florida.

Chen, Y., and L.-S. Lin. 2009. Responses of streams in central Appalachian Mountain region to reduced acidic deposition—comparisons with other regions in North America and Europe. Science of the Total Environment 407:2285–2295.

Dahm, K. G., K. L. Guerra, P. Xu, and J. E. Drewes. 2011. Composite geochemical database for coalbed methane produced water quality in the Rocky Mountain region. Environmental Science and Technology 45:7655–7663.

Dietz, T. H., A. S. Udoetok, J. S. Cherry, H. Silverman, and R. A. Byrne. 2000. Kidney function and sulfate uptake and loss in the freshwater bivalve Toxolasma texasensis. Biological Bulletin 199:14–20.

Dodds, W. K., W. W. Bouska, J. L. Eitzmann, T. J. Pilger, K. L. Pitts, A. J. Riley, J. T. Schloesser, and D. J. Thornbrugh. 2009. Eutrophication of U.S. freshwaters: analysis of potential economic damages. Environmental Science and Technology 43:12–19.

Drousé, S. K., D. C. Hillman, J. L. Engels, L. W. Creelman, and S. J. Simon. 1986. National Surface Water Survey, National Stream Survey (Phase I—Pilot, Mid-Atlantic Phase 1, Southeast Screening and Episodes Pilot) Quality Assurance Plan. EPA 600/4-86/044. US Environmental Protection Agency, Las Vegas, Nevada.

Drummond, M. A., and T. R. Loveland. 2010. Land-use pressure and a transition to forest-cover loss in the eastern United States. BioScience 60:286–298.

Duncan, R. A., M. G. Bethune, T. Thayalakumaran, E. W. Christen, and T. A. McMahon. 2008. Management of salt mobilization in the irrigated landscape – a review of selected irrigation regions. Journal of Hydrology 351:238–252.

Echols, B. S., R. J. Currie, and D. S. Cherry. 2009. Influence of conductivity dissipation on benthic macroinvertebrates in the North Fork Holston River, Virginia, downstream of a point-source brine discharge during severe low-flow conditions. Human and Ecological Risk Assessment 15:170–184.

El-Ashry, M. T., J. van Schilfgaarde, and S. Schiffman. 1985. Salinity pollution from irrigated agriculture. Journal of Soil and Water Conservation 40:48–52.

Entrekin, S., M. Evans-White, B. Johnson, and E. Hagenbuch. 2011. Rapid expansion of natural gas development poses a threat to surface waters. Frontiers of Ecology and the Environment 9:503–511.

Evans, D. H. 1980. Osmotic and ionic regulation by freshwater and marine fishes. Pages 93–122 in M. A. Ali (editor). Environmental physiology of fishes. Plenum Press, New York.

Evans, D. H. 2008. Teleost fish osmoregulation: what have we learned since August Krogh, Homer Smith, and Ancel Keys. American Journal of Physiology 295:R704–R713.

Fenneman, N. M. 1928. Physiographic divisions of the United States. Annals of the Association of American Geographers 18:261–353.

Feth, J. H. 1971. Mechanisms controlling world water chemistry: evaporation–crystallization process. [Comments on Gibbs (1970), "Mechanisms controlling world water chemistry." Science 170:1088–1090]. Science 172:870–871.

Gibbs, R. J. 1970. Mechanisms controlling world water chemistry. Science 170:1088–1090.

Gibbs, R. J. 1971. Reply to Feth (1971), "Mechanisms controlling world water chemistry: evaporation–crystallization process." Science 172:871–872.

Gorham, E. 1958. The influence and importance of daily weather conditions in the supply of chloride, sulphate and other ions to fresh waters from atmospheric precipitation. Philosophical Transactions of the Royal Society of London Series B: Biological Sciences 241:147–178.

Gorham, E. 1961. Factors influencing supply of major ions to inland waters, with special reference to the atmosphere. Geological Society of America Bulletin 72:795–840.

Gregory, K. B., R. D. Vidic, and D. A. Dzombak. 2011. Water management challenges associated with the production of shale gas by hydraulic fracturing. Elements 7:181–186.

Griffith, M. B., S. B. Norton, L. C. Alexander, A. I. Pollard, and S. D. LeDuc. 2012. The effects of mountaintop mines and valley fills on the physicochemical quality of stream ecosystems in the central Appalachians: a review. Science of the Total Environment 417–418:1–12.

Hawkins, C. P., J. R. Olson, and R. A. Hill. 2010. The reference condition: predicting benchmarks for ecological and water-quality assessments. Journal of the North American Benthological Society 29:312–343.

Herlihy, A. T., P. R. Kaufmann, and M. E. Mitch. 1991. Stream chemistry in the eastern United States. 2. Current sources of acidity in acidic and low acid-neutralizing capacity streams. Water Resources Research 27:629–642.

Herlihy, A. T., P. R. Kaufmann, M. E. Mitch, and D. D. Brown. 1990. Regional estimates of acid mine drainage impact on streams in the mid-Atlantic and southeastern United States. Water, Air, and Soil Pollution 50:91–107.

Herlihy, A. T., D. P. Larsen, S. G. Paulsen, N. S. Urquhart, and B. J. Rosenbaum. 2000. Designing a spatially balanced, randomized site selection process for regional stream surveys: the EMAP Mid-Atlantic pilot study. Environmental Monitoring and Assessment 63:95–113.

Herlihy, A. T., and J. C. Sifneos. 2008. Developing nutrient criteria and classification schemes for wadeable streams in the conterminous U.S. Journal of the North American Benthological Society 27:932–948.

Herlihy, A. T., J. L. Stoddard, and C. B. Johnson. 1998. The relationship between stream chemistry and watershed land cover data in the mid-Atlantic region, U.S. Water, Air, and Soil Pollution 106:377–386.

Jackson, R. B., and E. G. Jobbágy. 2005. From icy roads to salty streams. Proceedings of the National Academy of Sciences of the United States of America 102:14487–14488.

Jackson, R. E., and K. J. Reddy. 2007. Geochemistry of coalbed natural gas (CBNG) produced water in Powder River Basin, Wyoming: salinity and sodicity. Water, Air, and Soil Pollution 184:49–61.

Jeziorski, A., N. D. Yan, A. M. Paterson, A. M. DeSellas, M. A. Turner, D. S. Jeffries, B. Keller, R. C. Weeber, D. K. McNicol, M. E. Palmer, K. McIver, K. Arseneau, B. K. Ginn, B. F. Cumming, and J. P. Smol. 2008. The widespread threat of calcium decline in fresh waters. Science 322:1374–1377.

Johnson, L. B., C. Richards, G. E. Host, and J. W. Arthur. 1997. Landscape influences on water chemistry in Midwestern stream ecosystems. Freshwater Biology 37:193–208.

Kaufmann, P. R., A. T. Herlihy, M. E. Mitch, J. J. Messer, and W. S. Overton. 1991. Stream chemistry in the eastern United States. 1. Synoptic survey design, acid-base status, and regional patterns. Water Resources Research 27:611–627.

Kaushal, S. S., P. M. Groffman, G. E. Likens, K. T. Belt, W. P. Stack, V. R. Kelly, L. E. Band, and G. T. Fisher. 2005. Increased salinization of fresh water in the northeastern United States. Proceedings of the National Academy of Sciences of the United States of America 102:13517–13520.

Kelly, V. R., G. M. Lovett, K. C. Weathers, S. E. Findlay, D. L. Strayer, D. I. Burns, and G. E. Likens. 2008. Long-term sodium chloride retention in a rural watershed: legacy effects of road salt on streamwater concentration. Environmental Science and Technology 42:410–415.

Kennedy, A. J., D. S. Cherry, and R. J. Currie. 2003. Field and laboratory assessment of a coal processing effluent in the Leading Creek watershed, Meigs County, Ohio. Archives of Environmental Contamination and Toxicology 44:324–331.

Kilham, P. 1990. Mechanisms controlling the chemical composition of lakes and rivers: data from Africa. Limnology and Oceanography 35:80–83.

Kimmel, W. G., and D. G. Argent. 2010. Stream fish community responses to a gradient of specific conductance. Water, Air, and Soil Pollution 206:49–56.

Lazorchak, J. M., D. J. Klemm, and D. V. Peck (editors). 1998. Environmental Monitoring and Assessment Program—Surface Waters: field operations and methods for measuring the ecological conditions of wadeable streams. EPA 620/R-94/004F. National Exposure Research Laboratory and National Health and Environmental Effects Research Laboratory, Office of Research and Development, US Environmental Protection Agency, Research Triangle Park, North Carolina.

Likens, G. E., F. H. Bormann, N. M. Johnson, D. W. Fisher, and R. S. Pierce. 1970. Effects of forest cutting and herbicide treatment on nutrient budgets in the Hubbard Brook Watershed ecosystem. Ecological Monographs 40:23–47.

Mattson, M. D., P. J. Godfrey, M. F. Walk, P. A. Kerr, and O. T. Zajicek. 1992. Regional chemistry of lakes in Massachusetts. Water Resources Bulletin 28:1045–1056.

McCormick, F. H., D. V. Peck, and D. P. Larsen. 2000. Comparison of geographic classification schemes for Mid-Atlantic stream fish assemblages. Journal of the North American Benthological Society 19:385–404.

Meyer, J. S., D. A. Sanchez, J. A. Brookman, D. B. McWhorter, and H. L. Bergman. 1985. Chemistry and aquatic toxicity of raw oil shale leachates from Piceance Basin, Colorado. Environmental Toxicology and Chemistry 4:559–572.

Morgan, M. D., and R. E. Good. 1988. Stream chemistry in the New Jersey Pinelands: the influence of precipitation and watershed disturbance. Water Resources Research 24:1091–1100.

Mount, D. R., D. D. Gulley, J. R. Hockett, T. D. Garrison, and J. M. Evans. 1997. Statistical models to predict the toxicity of major ions to *Ceriodaphnia dubia*, *Daphnia magna* and *Pimephales promelas* (fathead minnows). Environmental Toxicology and Chemistry 16:2009–2019.

Naiman, R. J., and E. C. Anderson. 1997. Streams and rivers: their physical and biological variability. Pages 131–148 *in* P. K. Schoonmaker, B. von Hagen, and E. C. Wolf (editors). The rainforests of home: profile of a North American bioregion. Island Press, Washington, DC.

Olson, J. R., and C. P. Hawkins. 2012. Predicting natural baseflow stream water chemistry in the western United States. Water Resource Research 48:W02504.

Omernik, J. M. 1987. Ecoregions of the conterminous United States. Annals of the Association of American Geographers 77:118–125.

Omernik, J. M. 1995. Ecoregions: a spatial framework for environmental management. Pages 49–62 *in* W. S. Davis and T. P. Simon (editors). Biological assessment and criteria: tools for water resource planning and decision making. Lewis Publishers, Boca Raton, Florida.

Pan, Y., R. J. Stevenson, B. H. Hill, A. T. Herlihy, and G. B. Collins. 1996. Using diatoms as indicators of ecological conditions in lotic systems: a regional assessment. Journal of the North American Benthological Society 15:481–495.

Paul, J. F., and M. E. McDonald. 2006. Development of empirical, geographically specific water quality criteria: a conditional probability analysis approach. Journal of the American Water Resources Association 41:1211–1223.

Paulsen, S. G., A. Mayio, D. V. Peck, J. L. Stoddard, E. Tarquinio, S. M. Holdsworth, J. van Sickle, L. L. Yuan, C. P. Hawkins, A. T. Herlihy, P. R. Kaufmann, M. T. Barbour, D. P. Larsen, and A. R. Olsen. 2008. Condition of stream ecosystems in the US: an overview of the first national assessment. Journal of the North American Benthological Society 27:812–821.

Pawlowicz, R. 2008. Calculating the conductivity of natural waters. Limnology and Oceanography: Methods 6:489–501.

Perry, S. F., A. Shahsavarani, T. Georgalis, M. Bayaa, M. Furimsky, and S. L. Y. Thomas. 2003. Channels, pumps, and exchangers in the gill and kidney of freshwater fishes: their role in ionic and acid-base regulation. Journal of Experimental Zoology Part A: Comparative Experimental Biology 300A:53–62.

Petts, G. E. 2000. A perspective of the abiotic processes sustaining the ecological integrity of running waters. Hydrobiologia 422/423:15–27.

Phillips, F. M., S. Mills, M. H. Hendrickx, and J. Hogan. 2003. Environmental tracers applied to quantifying causes of salinity in arid-region rivers: results from the Rio Grande basin, southwestern USA. Developments in Water Science 50:327–334.

Pond, G. J., M. E. Passmore, F. A. Borsuk, L. Reynolds, and C. J. Rose. 2008. Downstream effects of mountaintop coal mining: comparing biological conditions using family- and genus-level macroinvertebrate bioassessment tools. Journal of the North American Benthological Society 27:717–737.

Poole, G. C., J. B. Dunham, D. M. Keenan, S. T. Sauter, D. A. McCullough, C. Mebane, J. C. Lockwood, D. A. Essig, M. P. Hicks, D. J. Sturdevant, E. J. Materna, S. A. Spalding, J. Risley, and M. Deppman. 2004. The case for regime-based water quality standards. BioScience 54:155–161.

Raynor, G. S., and J. V. Hayes. 1982. Concentrations of some ionic species in central Long Island, New York, precipitation in relation to meteorological variables. Water, Air, and Soil Pollution 17:309–335.

Richter, D. D., C. W. Ralston, and W. R. Harms. 1983. Chemical composition and spatial variation of bulk precipitation at a Coastal Plain watershed in South Carolina. Water Resources Research 19:134–140.

Rose, S. 2007. The effects of urbanization on the hydrochemistry of base flow within the Chattahoochee River Basin (Georgia, USA). Journal of Hydrology 341:42–54.

Skjelkvåle, B. L., J. L. Stoddard, D. S. Jeffries, K. Tørseth, T. Høgåsen, J. Bowman, J. Mannio, D. T. Monteith, R. Mosello, M. Rogora, D. Rzychon, J. Vesely, J. Wieting, A. Wilander, and A. Worsztynowicz. 2005. Regional scale evidence for improvements in surface water chemistry 1990–2001. Environmental Pollution 137:165–176.

Sleeter, B. M., C. E. Soulard, T. S. Wilson, and D. G. Sorenson. 2012. Land-cover trends in the western United States—1973 to 2000. Pages 3–32 *in* B. M. Sleeter, T. S. Wilson, and W. Acevedo (editors). Status and trends of land change in the western United States: 1973–2000. Professional Paper 1794-A. US Geological Survey, Reston, Virginia.

Smart, M. M., J. R. Jones, and J. L. Sebaugh. 1985. Stream-watershed relations in the Missouri Ozark Plateau province. Journal of Environmental Quality 14:77–82.

Smart, R. P., C. Soulsby, M. S. Cresser, A. J. Wade, J. Townend, M. F. Billett, and S. Langan. 2001. Riparian zone influence on stream water chemistry at different spatial scales: a GIS-based modeling approach, an example for the Dee, NE Scotland. Science of the Total Environment 280:173–193.

Smeck, N. E., and L. P. Wilding. 1980. Quantitative evaluation of pedon formation in calcareous glacial deposits in Ohio. Geoderma 24:1–16.

Smith, R. A., R. B. Alexander, and G. E. Schwarz. 2003. Natural background concentrations of nutrients in streams and rivers of the conterminous United States. Environmental Science and Technology 37:3039–3047.

Stallard, R. F., and J. M. Edmond. 1981. Geochemistry of the Amazon. 1. Precipitation chemistry and the marine contribution to the dissolved load at the time of peak discharge. Journal of Geophysical Research 86:9844–9858.

Stallard, R. F., and J. M. Edmond. 1983. Geochemistry of the Amazon. 2. The influence of geology and weathering environment of the dissolved load. Journal of Geophysical Research 88:9671–9688.

Stallard, R. F., and J. M. Edmond. 1987. Geochemistry of the Amazon. 3. Weathering chemistry and limits to dissolved inputs. Journal of Geophysical Research 92:8293–8302.

Stoddard, J. L., J. S. Kahl, F. A. Deviney, D. R. DeWalle, C. T. Driscoll, A. T. Herlihy, J. H. Kellogg, P. S. Murdoch, J. R. Webb, and K. E. Webster. 2003. Response of surface water chemistry to the Clean Air Act Amendments of 1990. EPA 620/R-03/001. National Health and Environmental Effects Research Laboratory, Office of Research and Development, US Environmental Protection Agency, Research Triangle Park, North Carolina.

Stoddard, J. L., D. P. Larsen, C. P. Hawkins, R. K. Johnson, and R. H. Norris. 2006. Setting expectations for the ecological condition of streams: the concept of reference condition. Ecological Applications 16:1267–1276.

Strahler, A. H. 1957. Quantitative analysis of watershed geomorphology. Transactions of the American Geophysical Union 38:913–920.

Symanzik, J., and D. B. Carr. 2008. Interactive linked micromap plots for the display of geographically referenced statistical data. Pages 267–294 in C. Chen, W. Härdle, and A. Unwin (editors). Handbook of data visualization. Springer, Berlin, Germany.

Szabo, J. P. 2006. Textural and mineralogical characteristics of tills of northeastern and north-central Ohio. Ohio Journal of Science 106:9–16.

Tietge, J. E., J. R. Hockett, and J. M. Evans. 1997. Major ion toxicity of six produced waters to three freshwater species: application of ion toxicity models and TIE procedures. Environmental Toxicology and Chemistry 14:2002–2008.

USEPA (US Environmental Protection Agency). 1987. Handbook of methods for acid deposition studies: laboratory analysis for surface water chemistry. EPA 600/4-87/026. Office of Research and Development, Office of Acid Deposition, Environmental Monitoring, and Quality Assurance, US Environmental Protection Agency, Washington, DC.

USEPA (US Environmental Protection Agency). 2000. Nutrient criteria technical guidance manual: rivers and streams. EPA 822/B-00/002. Office of Water, Office of Science and Technology, US Environmental Protection Agency, Washington, DC.

USEPA (US Environmental Protection Agency). 2004a. Wadeable stream assessment: field operations manual. EPA 841/B-04/004. Office of Water, US Environmental Protection Agency, Washington, DC.

USEPA (US Environmental Protection Agency). 2004b. Wadeable stream assessment: quality assurance project plan. EPA 841/B-04/005. Office of Water, US Environmental Protection Agency, Washington, DC.

USEPA (US Environmental Protection Agency). 2004c. Wadeable stream assessment: water chemistry laboratory manual. EPA 841/B-04/008. Office of Water, US Environmental Protection Agency, Washington, DC.

USEPA (US Environmental Protection Agency). 2005. National hydrography dataset plus. Edition 1.0. Office of Water, US Environmental Protection Agency, Washington, DC.

USEPA (US Environmental Protection Agency). 2009a. National rivers and streams assessment: field operations manual. EPA 841/B-07/009. Office of Water, US Environmental Protection Agency, Washington, DC.

USEPA (US Environmental Protection Agency). 2009b. National rivers and streams assessment: laboratory methods manual. EPA 841/B-07/010. Office of Water, US Environmental Protection Agency, Washington, DC.

USEPA (US Environmental Protection Agency). 2010. National rivers and streams assessment: quality assurance project plan. EPA 841/B-07/007. Office of Water, US Environmental Protection Agency, Washington, DC.

USEPA (US Environmental Protection Agency). 2011a. A field-based aquatic life benchmark for conductivity in central Appalachian streams. EPA 600/R-10/023F. Office of Research and Development, National Center for Environmental Assessment, US Environmental Protection Agency, Washington, DC.

USEPA (US Environmental Protection Agency). 2011b. Level III ecoregions of the continental United States (revision of Omernik, 1987). Map M-1, various scales, and shapefiles. Office of Research and Development, National Health and Environmental Effects Research Laboratory, Corvallis, Oregon.

Veil, J. A., M. G. Puder, D. Elcock, and R. J. Redweik. 2004. A white paper describing produced water from production of crude oil, natural gas, and coal bed methane. Argonne National Laboratory, US Department of Energy, Argonne, Illinois. (Available from: http://s3.amazonaws.com/propublica/assets/natural_gas/doe_produced_water_2004.pdf)

Veni, G., H. DuChene, N. C. Crawford, C. G. Groves, G. H. Huppert, E. H. Kastning, R. Olson, and B. J. Wheeler. 2001. Living with karst: a fragile foundation. Environmental Awareness Series 4. American Geological Institute, Alexandria, Virginia. (Available from: http://www.agiweb.org/environment/publications/karst.pdf)

Vörösmarty, C. J., B. Moore, A. L. Grace, M. P. Gildea, J. M. Melillo, B. J. Peterson, E. B. Rastetter, and P. A. Steudler. 1989. Continental scale models of water balance and fluvial transport: an application to South America. Global Biogeochemical Cycles 3:241–265.

Webster, J. R., S. W. Golladay, E. F. Benfield, J. L. Meyer, W. T. Swank, and J. B. Wallace. 1992. Catchment disturbance and stream response: overview of stream research at Coweeta Hydrologic Laboratory. Pages 231–253 in P. J. Boon, P. Calow, and G. E. Petts (editors). River conservation and management. John Wiley and Sons, Chichester, UK.

Whittier, T. R., J. L. Stoddard, D. P. Larsen, and A. T. Herlihy. 2007. Selecting reference sites for stream biological assessments: best professional judgment or objective criteria. Journal of the North American Benthological Society 26:349–360.

Wigington, P. J., M. R. Church, T. C. Strickland, K. N. Eshleman, and J. van Sickle. 1998. Autumn chemistry of Oregon Coast Range streams. Journal of the American Water Resources Association 34:1035–1049.

Wilken, E., F. J. Nava, and G. Griffith. 2011. North American terrestrial ecoregions—Level III. Commission for Environmental Cooperation, Montreal, Quebec, Canada. (Available from: ftp://ftp.epa.gov/wed/ecoregions/pubs/NA_Terrestrial EcoregionsLevel3_Final-2june11_CEC.pdf)

Woods, A. J., J. M. Omernik, and D. D. Brown. 1999. Level III and IV ecoregions of EPA Region 3: Delaware, Maryland,

Pennsylvania, Virginia, and West Virginia. National Health and Environmental Effects Research Laboratory, US Environmental Protection Agency, Corvallis, Oregon.

Woods A. J., J. M. Omernik, and B. C. Moran. 2007. Level III and IV ecoregions of New Jersey. Map WO-1-07. National Health and Environmental Effects Research Laboratory, US Environmental Protection Agency, Corvallis, Oregon.

Wright, I. A., P. J. Davies, S. J. Findlay, and O. J. Jonasson. 2011. A new type of water pollution: concrete drainage infrastructure and geochemical contamination of urban waters. Marine and Freshwater Research 62:1355–1361.

Zampella, R. A. 1994. Characterization of surface water quality along a watershed disturbance gradient. Water Resources Bulletin 30:605–611.

Zheng, L., J. Gerritsen, J. Beckman, J. Ludwig, and S. Wilkes. 2008. Land use, geology, enrichment, and stream biota in the eastern Ridge and Valley ecoregion: implications for nutrient criteria development. Journal of the American Water Resources Association 44:1521–1536.

Zielinski, R. A., J. K. Otton, and C. A. Johnson. 2001. Sources of salinity near a coal mine spoil pile, north-central Colorado. Journal of Environmental Quality 30:1237–1248.