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Relating major ions and nutrients to watershed conditions across a mixed-use, water-supply watershed

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Abstract. Stream inorganic chemistry was sampled under summer baseflow conditions from 2000 to 2002 at 60 sites as part of a large-scale, enhanced water-quality monitoring project (the Project) across New York City's drinking-water-supply watersheds. The 60 stream sites were evenly divided between regions east and west of the Hudson River (EOH and WOH, respectively). EOH sites had generally higher ionic concentrations than WOH sites, reflecting differences in land use and geology. Within each region, variability in inorganic chemistry data between sites was far greater than annual variability within sites. Geology was an important factor controlling underlying baseflow chemistry differences within and between regions. However, after taking into account geological controls, anthropogenic land uses primarily defined ion and nutrient baseflow chemistry patterns at regional and watershed levels. In general, watershed-scale landscape attributes had either the strongest relationships with analytes or had relationships with analytes that did not differ fundamentally from relationships of riparian- or reach-scale landscape attributes. Individual analyses indicated no dominant watershed-scale landscape attribute that could be used to predict instream inorganic chemistry concentrations, and no single ion or nutrient was identified as the best indicator of a given anthropogenic land use. Our results provide a comprehensive baseline of information for future water-quality assessments in the region and will aid in examining other components of the Project.

Key words: anions, cations, nutrients, land use, scale, New York.

In 2000, a large-scale enhanced water-quality monitoring project (the Project) was initiated in New York City's (NYC) drinking-water-supply watersheds to enhance routine stream monitoring conducted by NYC and other agencies (Blaine et al. 2006). The project incorporated novel tools, such as ecosystem processing (Newbold et al. 2006) and molecular tracers (Aufdenkampe et al. 2006), which were intended to augment more traditional stream-monitoring techniques, such as sampling inorganic chemistry (e.g., major anions and cations) and nutrients. Monitoring inorganic chemistry and nutrients offers valuable information on the influence of watershed landscape attributes on stream water quality; moreover, it provides a bridge between the novel techniques used in the Project and other regional monitoring efforts, both past and present.

A primary goal of many inorganic water-quality research/monitoring projects has been to relate instream measures of inorganic water quality to type, extent, and proximity of land use. (In our paper, land use implies both land use and land cover.) These empirical and quantitative analyses have indicated many relationships between land use and instream inorganic chemistry concentrations, but they left unresolved many apparent contradictions as to which landuse variable is most useful in predicting certain chemical constituent concentrations and which spatial scale is best for assessing defined landuse influences (Allan 2004).

Osborne and Wiley (1988) were among the first to use Geographic Information Systems (GIS) to quantify land use both across an entire watershed and within a defined stream–riparian area. They determined that urbanization was more important than agriculture in predicting instream nutrient (P) concentrations in a Midwestern stream. Jordan et al. (1997a) found that various forms of N, but not P, were positively related to the proportion of cropland in Mid-Atlantic Coastal Plain watersheds. Cl^- concentrations were the strongest indicator of general human disturbance in streams

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across the Mid-Atlantic region (Herlihy et al. 1998), whereas K^+ concentrations were the most strongly associated of all measured ions with urban and agricultural land uses in a Massachusetts watershed (Williams et al. 2005). These few examples demonstrate the apparent contradictions among studies associating stream chemistry responses to watershed landscape conditions.

Embedded in many of these studies were questions related to scale (or proximity) of influences on perceived relationships between water quality and watershed landscape variables, variation of defined relationships among regions, and multicollinearity among various land uses in these defined relationships. Allan (2004) noted that anthropogenic land uses often covary with natural (e.g., geological) landscape features, a factor that can lead to overestimation of the associated landuse influence on stream water quality. King et al. (2005) specifically explored spatial covariance issues within the context of water quality vs watershed landscape relationships and demonstrated, among other things, the danger of using univariate correlation between stream water-quality measures and landuse type and extent without accounting for correlations among differing land uses. Strayer et al. (2003), Allan (2004), and King et al. (2005) all highlighted the variability in assessing landuse effects across differing scales (e.g., watershed, riparian, reach; after Allan 2004). In fact, Strayer et al. (2003) specifically acknowledged the heterogeneity in water-quality responses across scales and stressed that no single scale should be expected to control a broad number of stream water-quality response variables.

Implicit in the definition of scale for our paper is that delivery of inorganic chemical inputs to streams is such that the closer a given source is to a stream, the greater the potential signal (i.e., concentration) in the stream. Here, land uses and related watershed landscape features are considered proxies for inorganic chemistry sources, whereas proximity between these sources and a sampling site is specifically quantified at 3 scales: watershed, riparian, and reach. Proximity also implies mechanisms for source-material delivery to a stream. Mechanisms specific to our study would be those processes that support stream baseflow (i.e., subsurface hydrology) including wastewater treatment plant and septic system effluent. Within the Croton River watershed (NYC watershed), Heisig (2000) demonstrated that concentrations of all selected baseflow chemical constituents were higher in small unsewered residential watersheds than in undeveloped or sewered watersheds, presumably because of greater septic effluent inputs. This result was supported by later work examining baseflow discharge in similar-sized watersheds within the same study area (Burns et al. 2005). Another aspect of scale or proximity is the attenuation, or lack thereof, of upslope sources resulting from undisturbed or minimally disturbed riparian landuse conditions. Many researchers have documented the instream water-quality benefits of an intact, forested riparian area, but others have found no such benefit. For instance, Jordan et al. (1997b) found cases of poor hydrologic connection between near-stream forested areas and adjacent streams, allowing nutrients such as NO_3^- originating from upland land uses to have a much more direct impact on corresponding instream concentrations than near-stream land use.

The intent of our study was to attempt to define these uncertainties in the study region as part of an overall objective of the Project rather than to provide an in-depth analysis of the sources of uncertainty when examining inorganic water-quality relationships with respect to watershed conditions. The goal of the Project was to provide a baseline of information that could be used to assess future changes in conditions across the entire NYC drinking-water-supply watershed. This baseline of information required investigation into how the instream measures of water inorganic chemistry were related to current watershed conditions and quantification of the variability within those relationships. Therefore, the objectives of our paper were to provide an overview of inorganic chemical composition for streams across NYC's drinking-water-supply watersheds and to provide an assessment of the present-day watershed landscape factors that potentially influenced stream water chemistry.

Methods

Study sites and watershed characteristic data

The 60 sites included in our study were split between 2 major regions: west of the Hudson River (WOH; $n = 30$ sites) and east of the Hudson River (EOH; $n = 30$ sites) in the southeastern part of New York (fig. 1 in Blaine et al. 2006; figs 1 and 2 and table 1 in Arscott et al. 2006). Study-site selection criteria, specific location information, and details regarding land use and related watershed characteristic data are reported in Arscott et al. (2006).

Study sites were selected in an attempt to capture the range of land uses and geological conditions across both regions, to coincide with past and current monitoring conducted by other agencies such as the US Geological Survey (USGS), and to ensure feasibility in conducting the various tasks of the overall monitoring project. Study sites were located using a

Trimble GPS Pathfinder^{TM} ProXR receiver, and corresponding watershed boundaries were derived from a NYC Department of Environmental Protection (NYC DEP) watershed boundary layer based on surface topography with some onscreen digitizing (using USGS 1:24,000 topographic maps) necessary to modify existing boundaries relative to exact study-site locations.

Study-site landuse data were compiled from an existing NYC DEP data set based primarily on 2001 Landsat Enhanced Thematic Mapper Plus satellite imagery with other data sources incorporated to obtain a composite landuse data layer at a 10-m resolution. Population density data were derived from 2000 census data using census blocks as the base population unit. Road densities were based on either 1996 NY Department of Transportation planimetric images (EOH sites) or 1993 USGS DLG (WOH sites) data layers. Point-source discharges (as mean annual watershed-area-normalized effluent volumes over the 2000–2002 study period), were compiled from NYC DEP monitoring data of State Pollution Discharge Elimination System (SPDE) monitored sites.

Bedrock and surficial geology across the study region was summarized from the 1:250,000 bedrock geology or surficial geology maps of New York State (NYS Geological Survey Map and Chart Series Number 15 and Number 40). Map interpretation was guided by a publication on NY state geology (Isachsen et al. 2000), the NY State Museum web site, and metadata for these GIS data layers (http://www.nysm.nysed.gov/).

Mean annual (October–September water year) watershed-area-normalized discharge over the 2000 to 2002 period was lowest for USGS gauging stations located EOH at 44 ± 3.9 cm (±1 SD; $n = 8$) and highest for Neversink/Rondout gauging stations at 86 ± 12 cm ($n = 10$). Total annual discharge was higher in 2000 than in 2001 and 2002 and was >75th percentile of annual discharges measured from 1964 to 1999 at 8 WOH USGS gauging stations. In contrast, both 2001 and 2002 total annual discharges measured at these same 8 WOH USGS stations were <25th percentile of measured discharges for the same historical time period.

Stream sampling and laboratory analyses

Stream sampling was conducted during baseflow conditions at each of the 60 study sites from mid June through late September 2000 to 2002 (1 sample was collected on 3 October 2000). Baseflow conditions were defined as relatively constant stream flow, changing <10% over the 24 h preceding sampling, based on either co-located or nearby real-time USGS gauging stations. Major ions and nutrients were sampled once per y ($n = 3$/site) in coordination with collection of molecular tracers (Aufdenkampe et al. 2006), organic particles (seston), and dissolved organic C (DOC)/biodegradable DOC (Kaplan et al. 2006) samples when possible. Inorganic chemical analyses included cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) and anions (Cl^-, SO_4^{2-}), pH, specific conductance, and alkalinity. Nutrient chemistry analyses included NO_3-N, NH_4-N, soluble and total Kjeldahl N (SKN and TKN, respectively), soluble reactive P (SRP), total dissolved P (TDP), and total P (TP). Analyzed nutrient values were used to calculate the following derived nutrient values: total N (TN = TKN + NO_3-N), total dissolved N (TDN = SKN + NO_3-N), dissolved organic N (DON = SKN – NH_4-N), particulate N (PN = TN – TDN), and particulate P (PP = TP – TDP). SKN and TKN were not used in any subsequent analyses.

A grab sample (500-1000 mL) for nutrients and major ions was taken from the thalweg of each stream using acid-washed 1-L Nalgene® bottles. Samples were chilled to ~4°C in coolers until they could be processed. An Orion® field pH meter, and a YSI® conductivity/temperature meter were used to measure pH, specific conductance (T_{ref} = 25°C), and temperature in situ. Immediately upon return from the field, the grab sample from each site was divided into 5 to 6 split samples for subsequent analysis of nutrients and major ions. One split was frozen for analysis of TKN (semi-automated phenate block digester method, modified from EPA methods 351.2 and 350.1, USEPA 1983) and TP (EPA method 365.1) (see USEPA 1983 for all EPA methods). A 2nd split was refrigerated at 4°C for subsequent alkalinity analysis (EPA method 310.1). An additional split sample for alkalinity analysis was collected for WOH sites because low alkalinities, which required a modified titration analysis using an increased sample volume, were expected (APHA Standard Method 2320, APHA 1995). The remaining water was then filtered through a cellulose-nitrate membrane filter (0.45-μm), divided among three 125-mL polyethylene bottles, and stored for later analysis of dissolved nutrients, anions, and cations. One filtered split was frozen for subsequent analysis of SKN (semi-automated phenate block digester method, modified from EPA methods 351.2 and 350.1, USEPA 1983), NO_3-N and NO_2-N (EPA method 353.2), NH_4-N (EPA method 350.1), SRP (EPA method 365.1), and TDP (EPA method 365.1). A 2nd filtered split was refrigerated at 4°C for analysis of Cl^- (EPA method 325.3) and SO_4^{2-} (EPA method 375.4). The last filtered split was acid-fixed with 0.2 μL HNO_3/mL for later analysis of Ca^{2+}, K^+, Na^+, and

Mg^{2+} (EPA method 200.7). All nutrient and major ion analyses were done by the Patrick Center for Environmental Research at the Academy of Natural Sciences of Philadelphia.

Data analyses

Intersite vs interannual variability.—Within- and between-year Principal Components Analysis (wbPCA; Thioulouse et al. 1997) was used to partition site and year variance associated with the suite of nutrient and ion variables. Separate wbPCAs were run for WOH and EOH sites. Sites 43, 49, and 58 in the EOH region were removed from the analysis because of the influence of very high NH_4-N (site 49) and NO_3-N (sites 43 and 58) concentrations. Each wbPCA was done with ADE-4 software (Thioulouse et al. 1997), which is freely available with full documentation via an anonymous FTP web site (http://pbil.univ-lyon1.fr/ADE-4/). wbPCA standardizes data ($X_i - \bar{X}/SD$) prior to analysis to remove magnitude and range differences among variables. Analysis of variance (ANOVA) was used to test for significant site and year effects for each analyte within each region.

Inorganic chemistry vs watershed characteristics: multivariate relationships.—A 3-step multivariate analysis was conducted to assess geological and landuse influences on nutrient/ion chemistry and then to determine the interaction of these 2 classes of independent variables using variance partitioning techniques (Borcard et al. 1992). Redundancy Analysis (RDA), a constrained linear ordination technique, was used to assess the ability of geological variables (selected following visual inspection of an initial Principle Components Analysis [PCA], see below) to describe nutrient/ion concentrations. A separate RDA with automatic forward selection was used to select 5 landuse variables that best described among-site variation in nutrient/ion concentrations. Last, variance partitioning analysis on an RDA including both geological and landuse variables was done to assess the interactions between these 2 classes of independent variables. All analyses were done using CANOCO (version 4.0, Microcomputer Power, Ithaca, New York). Only 5 variables were selected from each class to build a balanced model and to ensure that <10 variables were included in the variance partitioning procedure because the arch effect (Lepš and Šmilauer 2003, Palmer 2006) is more likely to appear as the number of independent variables approaches the number of sites included in the analysis.

Geology variables were summarized as percentages of each watershed from 2 different GIS data layers (described above): surficial geology and bedrock geology (Table 1). Five variables that best described among-site differences in the geology were selected based on 1st and 2nd axis loadings from a PCA for each region. Variables selected among WOH sites included kame (steep-sided mounds of sand and gravel deposited by glacial meltwater), till (poorly sorted sand-rich deposit containing a wide range of particle sizes resulting from deposition beneath glacier ice), outwash sand and gravel deposits from the surficial-bedrock data layer, and 2 bedrock-geology types. Both bedrock types originated from the middle and late Devonian (360–408 million years before present [ybp]) and are sedimentary rocks dominated by shales, sandstone, and conglomerates.

Variables selected to describe the geology template among EOH sites included till, outwash sand and gravel from the surficial-bedrock data layer, and 3 bedrock types that were associated with 2 distinct geological regions (Isachsen et al. 2000), the Hudson Highlands (Middle Proterozoic, ~1100 million ybp) and the Manhattan Prong (~500 million ybp). The Hudson Highlands region crosses the northwestern portion of the EOH and the representative bedrock type (BG in Table 1) is composed of layered and unlayered metamorphic rocks highly resistant to erosion and consisting of biotite granitic gneiss. In general, Hudson Highlands bedrock layers can contain deposits of magnetite, biotite, mica, quartz, and feldspar gneiss (Isachsen et al. 2000). The Manhattan Prong dominates the southern portion of the EOH region but is also present across the most northeastern tip of the region. Rock composition of the Manhattan Prong includes Fordham gneiss folded together with inwood and dolomite marble, calcshist, chert, argillite, and granulite (primarily composed of pyroxene, plagioclase feldspar, and accessory garnet, oxide, and amphibole).

The forward selection procedure included in CANOCO was used to select 5 independent variables from the suite of landuse variables (see below) that best explained among-site variation in the 19 nutrient/ion response variables. Landuse and related variables were summarized as % cover or density at 3 different spatial scales: 1) watershed, 2) riparian (30 m on each side of entire stream network upstream of a site), and 3) reach (same as riparian, but truncated 1 km upstream of the study site) (Table 2; see also Methods in Arscott et al. 2006). Seven landuse variables were not scaled (Table 2) but were important descriptors of other anthropogenic influences or of the physical environment (e.g., point-source discharge, watershed area). Significance of each of the 5 forward-selected variables in each class (geological or landuse) was assessed using a Monte Carlo permutation test ($n =$

TABLE 1. Watershed surficial and bedrock geology variables initially considered for use in the Redundancy Analysis. Variables were derived from Geographical Information System data layers for west of Hudson River (WOH) and east of Hudson River (EOH) regions of New York City's drinking-water-source watersheds.

Geological variables	Abbreviation	Applicable region
Surficial geology		
Till	Till	WOH/EOH
Bedrock	BEDR	WOH/EOH
Outwash sand and gravel	OUTW	WOH/EOH
Kame deposits	KameD	WOH/EOH
Swamp deposits	SwampD	WOH/EOH
Recent alluvium	RAlluv	WOH/EOH
Alluvial fan	AlluvF	WOH/EOH
Kame moraine	KameM	WOH
Till moraine	TillM	WOH
Bedrock geology		
Lower Walton formation	DSW	WOH
Upper Walton formation	DWW	WOH
Oneonta formation	DGO	WOH
Slide Mountain formation	DWS	WOH
Honesdale formation	DWH	WOH
Unadilla formation	DGU	WOH
Manhattan formation	OM	EOH
Biotite granite gneiss	BG	EOH
Biotite-hornblende granite and granite gneiss	BPQC	EOH
Fordham gneiss	F	EOH
Amphibolite, pyroxenic amphibolite	AM	EOH
Inwood marble	OCI	EOH
Walloomsac formation	OWL	EOH
Stockbridge marble	OCST	EOH
Bedford gneiss	OB	EOH
Muscovite-biotite granondiorite	DPGD	EOH
Rusty and gray biotite-quartz-feldspar paragneiss	RG	EOH
Poundridge gneiss	PG	EOH
Pyroxenite	OPX	EOH
Muscovite-biotite granite	DPGR	EOH
Garnet-biotite-quartz-feldspar gneiss	QTCS	EOH
Gabbro or norite to hornblende diorite	OGB	EOH
Muscovite-biotite granite gneiss	DBG	EOH
Poughquag quartzite	CPG	EOH

1000 iterations) to test if variation in water chemistry among sites was independent of the environmental variables (Lepš and Šmilauer 2003).

Percent landuse data were arcsine-square-root(x) transformed to minimize bimodality and all other environmental variables (except for the categorical lake-code variable) were $\log_{10}(x)$ transformed prior to analysis. The 3-y means of summer baseflow nutrient/ion concentrations were used in this analysis because the wbPCA indicated that year-to-year variance within a site was small compared to site-to-site variation. All nutrient and ion variables except pH were $\log_{10}(x)$ transformed prior to analysis. Four sites (39, 43, 49, and 58) in the EOH region had undue influence on initial ordinations because of high 3-y mean concentrations of NO_3-N (site 39: 1.7 mg/L, site 43: 6.9 mg/L, site 49: 2.2 mg/L, site 58: 5.7 mg/L) or NH_4-N (site 43: 0.3 mg/L, site 49: 17.8 mg/L). NO_3-N and NH_4-N concentrations at these sites were down-weighted prior to analysis (sites 39, 43, 49, 58: $[NO_3\text{-N}] = 0.5[NO_3\text{-N}]$; site 43: $[NH_4\text{-N}] = 0.5[NH_4\text{-N}]$; site 49: $[NH_4\text{-N}] = 0.4[NH_4\text{-N}]$). The influence of down-weighting on the structure of the ordination was assessed by comparing RDA output before and after down-weighting. The arrangement of sites in the 2-dimensional ordination space and trajectories of independent and dependent variables did not change between analyses, but the down-weighting did have the anticipated effect of decreasing distances of sites 38, 43, 49, and 58 from the remaining sites.

Geology and landuse RDAs were run separately for WOH and EOH regions, and variances explained in each analysis were noted. A variance partitioning procedure (Borcard et al. 1992, Richards et al. 1996, Lepš and Šmilauer 2003) was used to decompose the total variability into parts that could be explained solely by geology, solely by land use, or by the interaction (covariance) of these 2 classes of independent variables.

Means of the sum of base cations ($Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}$) were plotted as a function of alkalinity (Rhodes et al. 2001) by region to provide added perspective regarding landuse vs geological influences on stream chemistry. A 1:1 line in these plots indicates that stream chemistry is controlled solely by mineral weathering (Rhodes et al. 2001). A watershed baseline also was defined for each region by regressing the mean base cation sum against mean alkalinity for the sites with the least-disturbed watersheds in each region. In the WOH region, these watersheds had >97% forested area with no known point-source discharges: sites 22 and 24 from the Esopus Creek watershed, sites 27, 28, and 29 from the Neversink River watershed, and site 30 from the Rondout Creek watershed. In the EOH region, the least-disturbed watersheds had >75% forested area with no known point-source discharges: sites 31, 34, 36, 37, and 48 from the northern and eastern portion of the EOH region (see table 1 and fig. 2 in Arscott et al. 2006).

Inorganic chemistry vs landuse variables: individual analyte relationships.—The 3-y mean ion and nutrient chemistry values were related separately to landuse variables (% land use, road density, and point-source discharge) using multiple linear regression (MLR).

TABLE 2. Landuse variables derived from Geographical Information System data layers and quantified at the watershed (W), riparian (b), and reach (1k) scales. Variables were used in the Redundancy Analysis (complete set) and multiple linear regressions (subset, see text for specific variables used). NA = not applicable.

Landuse variables	Abbreviation	Scale	General classification
Scale-defined variables			
% residential	RESD	W, b, 1k	Urban
% commercial	COMM	W, b, 1k	Urban
% industry	INDU	W, b	Urban
% transportation	TRAN	W, b, 1k	Urban
% other urban	OURB	W, b, 1k	Urban
% cropland (and pasture)	CROP	W, b, 1k	Agriculture
% orchard	ORCH	W, b, 1k	Agriculture
% farmstead	FMST	W, b, 1k	Agriculture
% grassland	GRAS	W, b, 1k	Agriculture
% shrubland	SHRB	W, b, 1k	Undisturbed
% mixed brush-grassland	MBRH	W, b, 1k	Undisturbed
% deciduous forest	DECD	W, b, 1k	Undisturbed
% coniferous forest	CONF	W, b, 1k	Undisturbed
% mixed forest	MFOR	W, b, 1k	Undisturbed
% water	WTER	W	Undisturbed
% wetland	WETL	W, b, 1k	Undisturbed
2000 population density (ind./km^2)	PDNS	W, b, 1k	Urban
Road density (m/km^2)	RDNS	W, b, 1k	Urban
Unscaled variables			
Point-source discharge (mean annual watershed-area-normalized State Pollution Discharge Elimination System effluent volume) (cm^3/cm^2)	SPDE	NA	Urban
Total number of active SPDE-permitted dischargers	SPDE#	NA	Urban
Stream network density (km/km^2)	SDNS	NA	NA
Upstream lake density (ha/km^2)	LDNS	NA	NA
Area of 1st upstream lake (ha)	LUPS	NA	NA
Lake code[a]	LCOD	NA	NA
Watershed area (km^2)	WTSD	NA	NA

[a] 0 = no lake on mainstem, 1 = lake on mainstem >3 km upstream (<5 ha in size), 2 = lake on mainstem <3 km upstream (>5 ha in size)

RDA provides an overall picture of the chemistry–landuse relationships within the study regions, but MLR analysis examines individual relationships between each ion or nutrient and land use. The 3-y mean values of all water-chemistry variables (except pH and PN) were $\log_{10}(x)$ transformed; PN values were $\log_{10}(x + 0.01)$ transformed, and pH was not transformed. All scaled landuse variables listed in Table 2 (except % transportation, % water, and population density) were used in the MLR analyses; the only other variable included was point-source discharge. All % landuse variables were arcsine square-root(x) transformed, road density was $\log_{10}(x + 1)$ transformed, and point-source discharge was $\log_{10}(x + 0.001)$ transformed. Stepwise variable selection with a variable significance cutoff of 0.05 was used in selecting independent variables in the MLR models (SAS/STAT, version 9, SAS Institute, Cary, North Carolina).

Separate MLR analyses were run for each analyte at each scale at which landuse variables were quantified: watershed, riparian, and reach. Additional effects of scale on the chemistry–landuse variable relationships were analyzed by running the MLR analyses using data from sites grouped into regions/watersheds. These regions/watersheds were: 1) all WOH sites, 2) West and East Branch of the Delaware River sites (WOHdel: site numbers 1–15), 3) Schoharie, Esopus, Neversink, and Rondout sites (WOHcat: site numbers 16–30), and 4) all EOH sites. More refined grouping of sites was not possible because the number of observations would have been too low for the MLR analyses.

The best model for each variable from the scale comparison was the model with the highest overall adjusted R^2 value and no significant multicollinearity. Multicollinearity was assessed using the variance inflation factor (VIF). VIF values >10 for any independent variables suggest problems associated with multicollinearity in the regression model (Myers

1990). The best model was considered unique relative to the models from the remaining scales if: 1) the adjusted R^2 of the best model was $\geq$10% of the adjusted R^2 for models at the other scales, and 2) if no strong relationship (e.g., $R^2 > 0.50$) could be found for a regression between the strongest predictor from the best model using either group of significant predictors from the models for the other scales.

PCAs were run based on the landuse variables used in the MLR analyses described above. Each landuse variable was included in the PCA 3 times, once at each spatial scale, and separate PCAs were run for each region/watershed. This analysis complimented MLR analyses by examining similarities among landscape data across the 3 landscape scales. All data transformations were identical to those described above.

Inorganic chemistry vs landuse variables: univariate relationships.—Linear regression was used to illustrate relationships between Cl^- and K^+ with watershed-scale road density and % cropland to emphasize the variability in univariate relationships that can occur across regions. Cl^- and K^+ were selected because previous work had identified each as the strongest predictors of anthropogenic influences on stream water quality (Cl^-: Herlihy et al. 1998, K^+: Williams et al. 2005). Road density and % cropland were selected as predictor variables because each was the significant predictor in at least one of the MLR analyses for both analytes, and each represented 1 of the 2 primary anthropogenic landuse influences on stream water quality (urbanization and agriculture). The univariate relationships were examined in 3 of the 4 regions/watersheds used in the MLR analyses: EOH, WOHdel, and WOHcat. Data were not transformed so that the effects of outlier values on results could be seen.

Results

General instream inorganic chemistry patterns

Stream baseflow inorganic chemistry differed strongly between and within WOH and EOH regions (Figs 1A–D, 2A–D). Ion and nutrient concentrations were higher in EOH streams than in WOH streams. Ion-equivalent concentrations differed by ~1 order of magnitude between the 2 regions. Regional differences in nutrient concentrations were not as striking, but 3 sites in the EOH region had extremely high concentrations of N species (Fig. 2B). Concentrations of P species at these 3 sites were not as extreme (Fig. 2D). These 3 sites were affected greatly by point-source discharges (see Arscott et al. 2006 for watershed-area-normalized effluent discharges across all sites), and the point-source discharge at one site (49) has a well-documented history of capacity exceedance.

Differences in stream chemistry were observed within each region, especially in WOH. A clear gradient of decreasing ion and nutrient concentrations occurred across the WOH region, from higher concentrations for West Branch Delaware sites to very low concentrations for Neversink River and Rondout Creek sites (Fig. 1A, C, Fig. 2A, C). Ion and nutrient concentrations did not appear to follow any clear gradients across the EOH region, and within-region differences were primarily related to point-source discharges (Fig. 1B, D, Fig. 2 B, D). Three Muscoot River and north of Croton Reservoir sites (43, 49, and 58) were strongly influenced by point-source discharges (Fig. 2B, D). Interbasin transfer, a very different type of point source, had an apparent influence on water chemistry at one West Branch Croton (41) site (Fig. 1B, D). Site 41 was below an EOH reservoir that received interbasin water from the Ashokan and Schoharie reservoirs (in the WOH region) that had the relatively low ionic composition of WOH streams. As a consequence, site 41 had the lowest cation and anion (Fig. 1B, D) concentrations of any EOH stream site. Site 26 (in the Esopus Creek watershed of WOH sites; Fig. 1A, C) also received substantial interbasin transfers of water from the Schoharie Reservoir, but the effects were not apparent from baseflow samples of inorganic chemistry concentrations.

Intersite vs interannual variability

Results from the wbPCA revealed that variance among sites within a year accounted for 97.3% and 95.2% of site variation in EOH and WOH watersheds, respectively. Variance among years within a site was minimal (EOH: 2.7%, WOH: 4.8%). Only 1 of 19 variables (pH) at EOH sites and 6 of 19 variables (pH, specific conductance, K^+, Na^+, Cl^-, and NH_4-N) at WOH sites varied significantly by year (ANOVA, $p < 0.05$). No EOH and only 1 WOH variable (pH) varied significantly by year (ANOVA, $p < 0.0025$) when Bonferroni criteria were applied to the results of the multiple ANOVAs for interannual differences. Low variability among years suggests that, collectively, baseflow inorganic chemistry variables provided a consistent measure of water quality among sites across years even though values for any single analyte may have varied from year to year.

Inorganic chemistry vs watershed characteristics: multivariate relationships

WOH RDA.—All 5 variables (kame, till, outwash sand and gravel deposits, and 2 bedrock geology

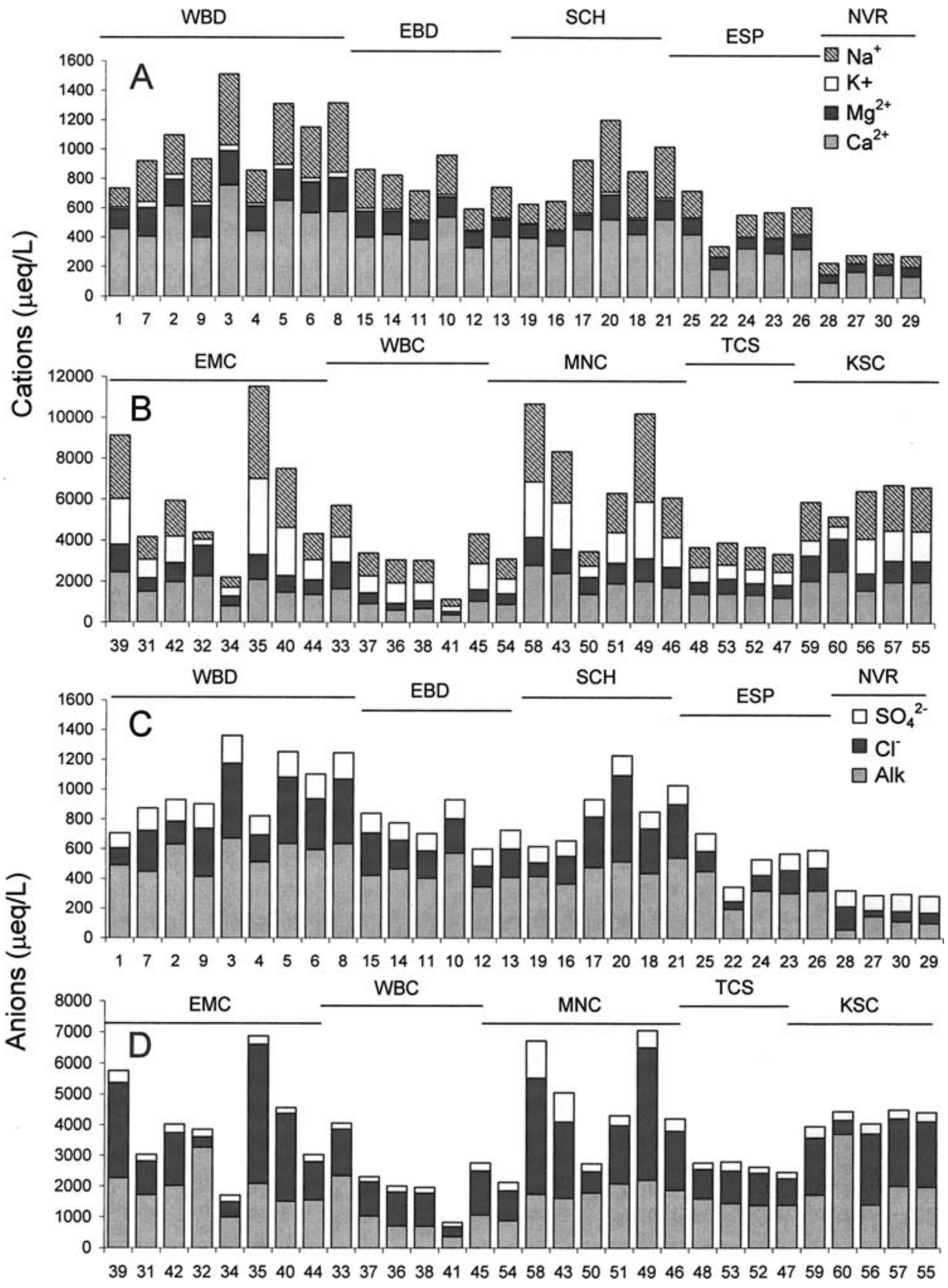


FIG. 1. Three-year mean concentrations for major cations (A, B) and anions and alkalinity (Alk) (C, D) in stream water collected during summer baseflow from 30 west of Hudson River (WOH: A, C) and 30 east of Hudson River (EOH: B, D) study sites on streams contributing to New York City's drinking-water-supply reservoirs (see figs 1 and 2 and table 1 in Arscott et al. 2006 for site numbers and locations). Sites in each panel are arranged by geographical watershed and are sorted from smallest to largest watershed area within each watershed. Watershed abbreviations are: WOH–WBD = West Branch Delaware River, EBD = East Branch Delaware River, SCH = Schoharie Creek, ESP = Esopus Creek, NVR = Neversink River and Rondout Creek; EOH–EMC = East and Middle Branch Croton River, WBC = West Branch Croton River, MNC = Muscoot River and other sites north of Croton reservoir, TCS = Titicus, Cross, and Stone Hill rivers, KSC = Kensico Reservoir and other sites south of Croton Reservoir. $n = 3$ in most cases.

types) selected to describe the geological template at the 30 WOH sites contributed significantly to the RDA model explaining variability of nutrient/ion concentrations in terms of geology ($p < 0.03$). The 1st axis and all RDA axes combined were statistically significant ($p < 0.001$). The resulting RDA model explained 70% of the variance in nutrient/ion concentrations among sites.

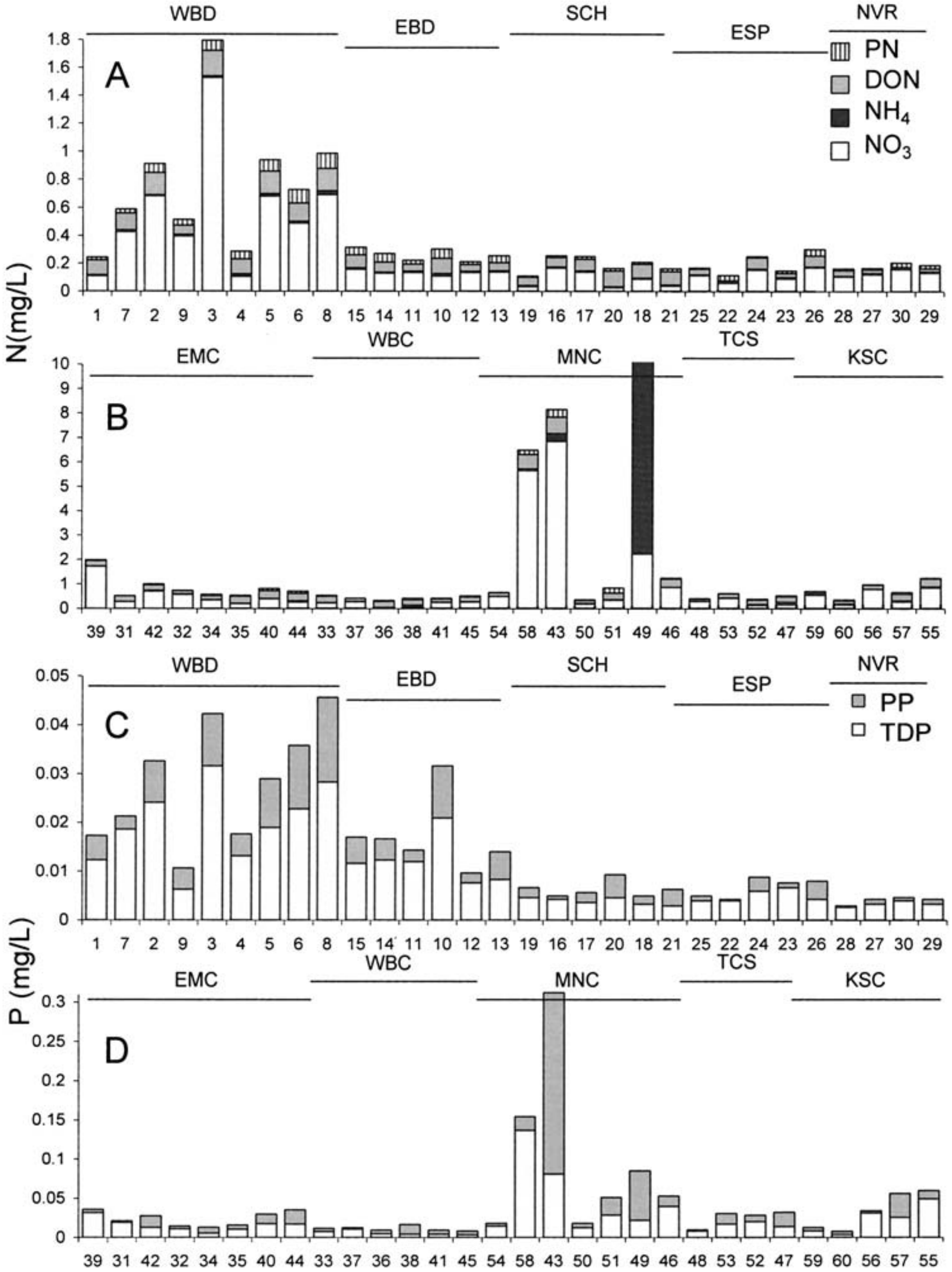


FIG. 2. Three-year mean concentrations of N (A, B) and P (C, D) species in stream water collected during summer baseflow from 30 west of Hudson River (WOH; A, C) and 30 east of Hudson River (EOH; B, D) study sites on streams contributing to New York City's drinking-water-supply reservoirs (see figs 1 and 2 and table 1 in Arscott et al. 2006 for site numbers and locations). Sites in each panel are arranged by geographical watershed and are sorted from smallest-to-largest watershed area within each watershed. See Fig. 1 legend for watershed abbreviations. PN = particulate N, DON = dissolved organic N, PP = particulate P, TDP = total dissolved P. Site 49 (panel B) is attenuated because of extremely high NH_4-N concentration (NH_4-N = 17.8, DON = 1.1, PN = 0.38 mg/L). $n = 3$ in most cases.

Four watershed-scale landuse variables (% residential, % coniferous forest, % cropland, and population density) and 1 riparian-scale landuse variable (% coniferous forest) were selected from the suite of 58 landuse variables (Table 2) to describe the landuse template at the 30 WOH sites. All 5 variables contributed significantly to the RDA model explaining variability in nutrient/ion concentrations in terms of land use ($p < 0.02$). The 1st axis and all RDA axes combined were statistically significant ($p < 0.001$). The

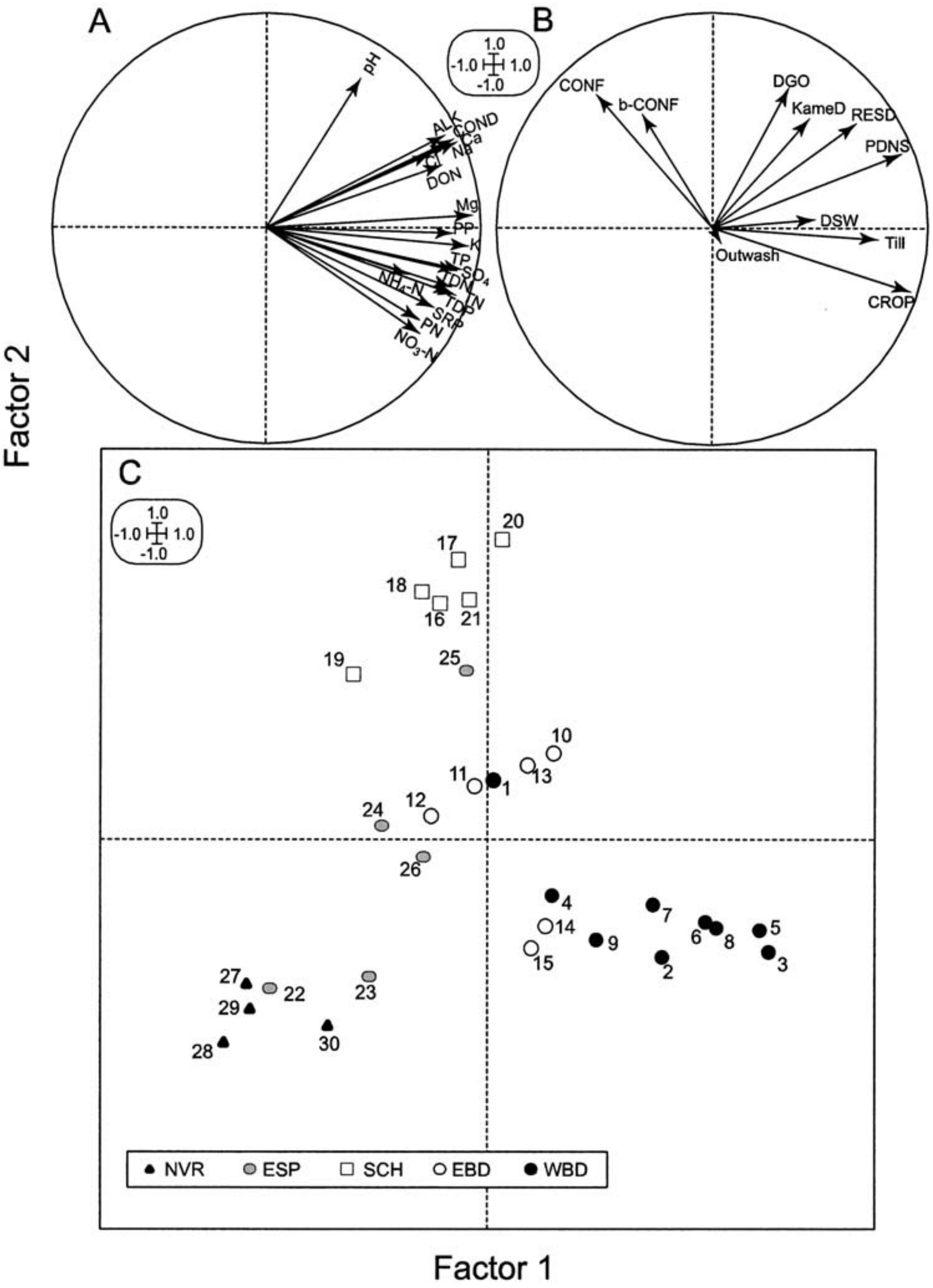


FIG. 3. Redundancy Analysis plots of spatial variability of summer baseflow nutrient/ion concentrations explained by selected landuse and geological variables in the west of Hudson River region (see text for selection procedures/criteria). A.—Factor loadings (factors 1 and 2) for each analyte (see Table 3 for analyte abbreviations). B.—Factor loadings (factors 1 and 2) for landuse and geological variables (see Table 1 for geological abbreviations and Table 2 for landuse abbreviations). C.—Plot of factor 1 and factor 2 scores for each site (see Fig. 1 for watershed abbreviations). Insets indicate axis scales.

resulting landuse RDA model explained 81% of the among-site variability in nutrient/ion concentrations.

An RDA model that included all 10 independent variables (see above) explained 87% of the among-site variability in nutrient/ion concentrations (Fig. 3A–C). The 1st axis and all RDA axes combined were significant ($p < 0.001$). Most (67%) of the among-site variance was explained by the 1st axis, and the 1st and 2nd axes together explained 79% of the total variance in nutrient/ion concentrations. Variance partitioning highlighted the tight multicollinearity between geological variables and landuse variables (Fig. 4A). The

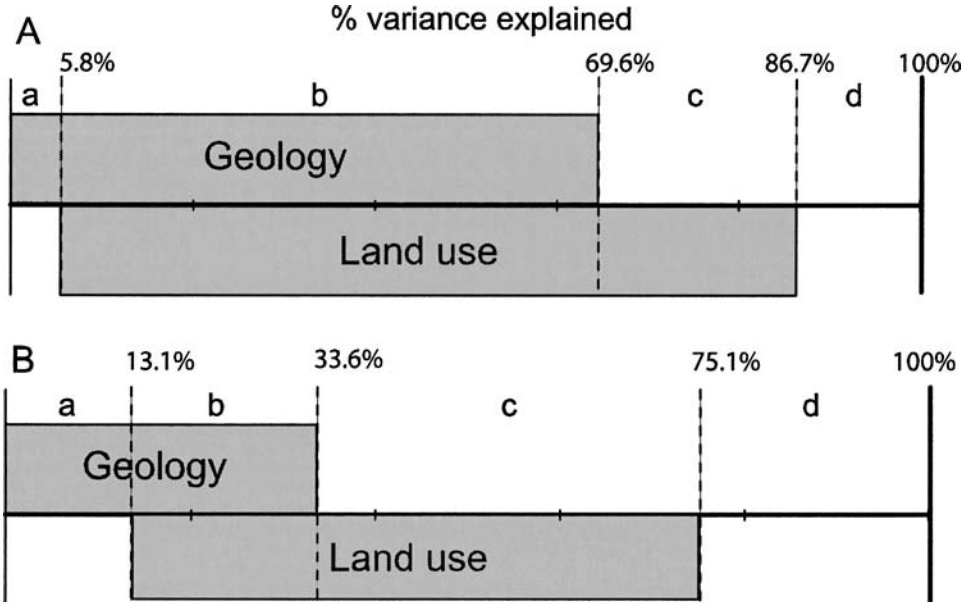


FIG. 4. Redundancy analysis of spatial (among-site) variance in summer baseflow nutrient/ion concentrations among west of Hudson River (WOH; A) and east of Hudson River (EOH; B) sites accounted for by all landscape factors. Total variance was partitioned by geology (a), the interaction of geology and land use (b), land use (c), and unexplained variance (d).

interaction between the geological and landuse classes of independent variables (inseparable variance) accounted for ~64% of the explained variance (Fig. 4A). Landuse variables alone accounted for ~17% of the explained variance in nutrient/ion concentrations, and the 1st axis and all axes combined of the resulting RDA model were significant ($p < 0.001$). Geological variables alone accounted for 5.8% of the explained variance in nutrient/ion concentrations, but the resulting RDA model was only marginally significant (1st axis: $p = 0.11$, all axes: $p = 0.048$).

Despite the high multicollinearity between geological and landuse variables, the way in which the explained variances of specific nutrients and ions were partitioned between geological and landuse variables differed appreciably (Fig. 5A). Landuse variables alone accounted for greater proportions of the explained variances of N and P species than of specific conductance, alkalinity, and many base cations. In fact, the explained variance of specific conductance, alkalinity, and many base cations could not be partitioned (i.e., large interaction between geological and landuse variables).

EOH RDA.—Only 3 of the 5 variables (till, outwash sand and gravel, and 3 bedrock types) selected to describe the geological template at the 30 EOH sites contributed significantly to the RDA model explaining variability of nutrient/ion concentrations in terms of geology ($p < 0.05$). The 1st axis of the RDA was not significant ($p = 0.12$), but all RDA axes combined were statistically significant ($p = 0.016$). The resulting RDA model explained 34% of the variance in nutrient/ion concentrations among sites.

Four watershed-scale variables (road density, % industry, % wetland, and upstream lake density) and point-source discharge were selected from a suite of 58 landuse variables (Table 2) to describe the landuse template at the 30 EOH sites. All 5 variables contributed significantly to the RDA model explaining variability in nutrient/ion concentrations in terms of land use ($p < 0.02$). The 1st and all RDA axes combined were statistically significant ($p < 0.001$). The resulting landuse RDA model explained 62% of the among-site variability in nutrient/ion concentrations.

An RDA model that included all 10 independent variables (see above) accounted for 75.1% of the among-site variability in nutrient/ion concentrations (Fig. 6A–C). The 1st axis and all RDA axes combined were significant ($p < 0.001$). Most (52.5%) of the among-site variance was explained by the 1st axis, and the 1st and 2nd axes together explained 62.9% of the total variance in nutrient/ion concentrations. Variance partitioning indicated that multicollinearity between geological variables and landuse variables was less important in the EOH region than in the WOH region (Fig. 4B). The interaction between the geological and landuse variables (inseparable variance) accounted for 20.5% of the explained variance (Fig. 4B). Landuse variables alone accounted for 41.5% of the explained variance in nutrient/ion concentrations. Geological

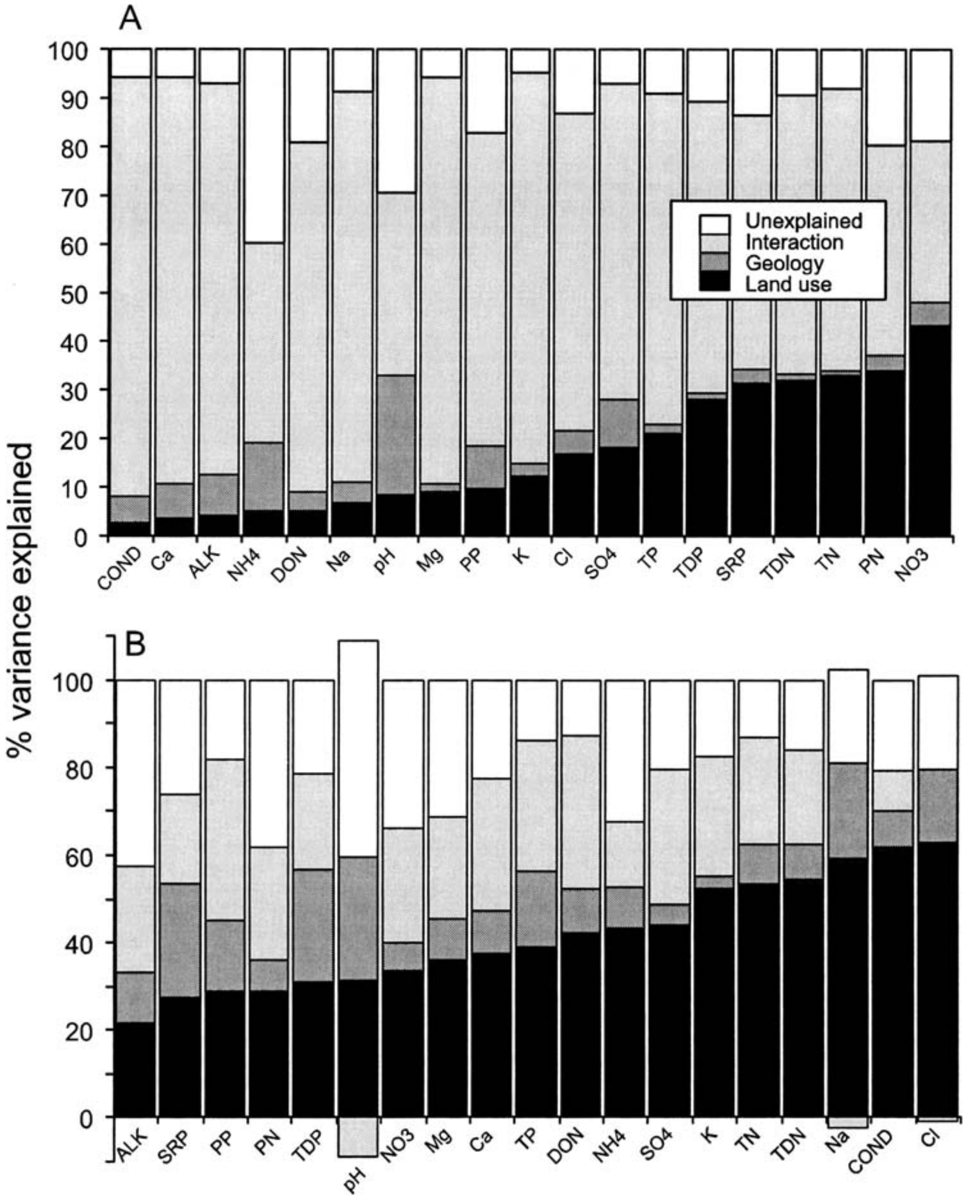


FIG. 5. Results of spatial variance partitioning of Redundancy Analysis for nutrient/ion concentrations among west of Hudson River (WOH; A) and east of Hudson River (EOH; B) sites. Bars indicate the % of the spatial variance explained for each analyte (nutrient /ion) by land use, geology, the shared variance between the 2 classes of variables, and unexplained variance. Note that pH, Na^+, and Cl^- each resulted in a negative interaction term for the EOH model. See Table 3 for analyte abbreviations.

variables alone accounted for 13.1% of the explained variance in nutrient/ion concentrations, but the resulting RDA model was only marginally significant (1st axis: $p = 0.14$, all axes: $p = 0.003$).

Variance in nutrient and ion concentrations could more easily be explained by land use at EOH sites than at WOH sites (Fig. 5B), and the EOH RDA model suffered less from multicollinearity between geological and landuse variables. For the EOH variance partitioned RDA model, concentrations of Na^+, Cl^-, TN, TDN, and specific conductance were best explained by landuse variables (Fig. 5B).

Alkalinity and base cations.—In plots of the sum of base cations vs alkalinity, sites that plot above the defined watershed baseline probably have anthropogenic contributions to base cation concentrations within a watershed (Rhodes et al. 2001). The WOH watershed baseline regression had a slope of 1.2 and an x-intercept of −120 μeq/L (Fig. 7A). This x-intercept value can be interpreted as a loss of alkalinity caused by regional acid inputs and is consistent with the ~100

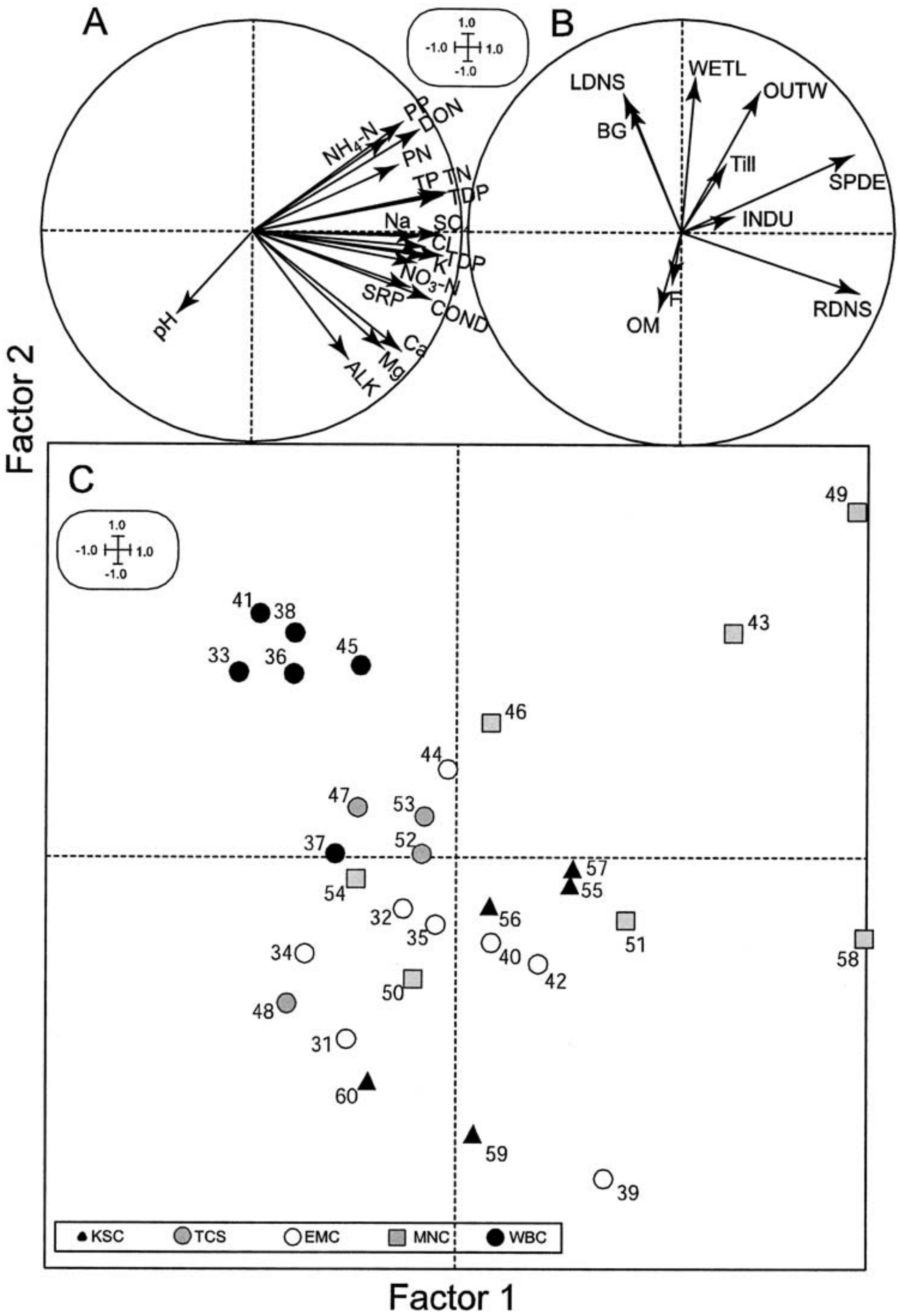


FIG. 6. Redundancy Analysis plots of spatial variability of summer baseflow nutrient/ion concentrations explained by selected landuse and geological variables in the east of Hudson River region (see text for selection procedures/criteria). A.—Factor loadings (factors 1 and 2) for each analyte (see Table 3 for analyte abbreviations). B.— Factor loadings (factors 1 and 2) for landuse and geological variables (see Table 1 for geological abbreviations and Table 2 for landuse abbreviations). C.—Plot of factor 1 and factor 2 scores for each site (see Fig. 1 for watershed abbreviations). Insets indicate axis scales.

μeq/L loss in acid-neutralizing capacity from acid inputs reported by (Rhodes et al. 2001) for minimally disturbed watersheds in western Massachusetts. In addition, the effects of acid deposition in the Neversink watershed have been well documented (Lawrence et al. 2001). The EOH watershed baseline regression had a slope of 1.2 with an x-intercept of −783 μeq/L. The inferred loss of alkalinity caused by regional acid

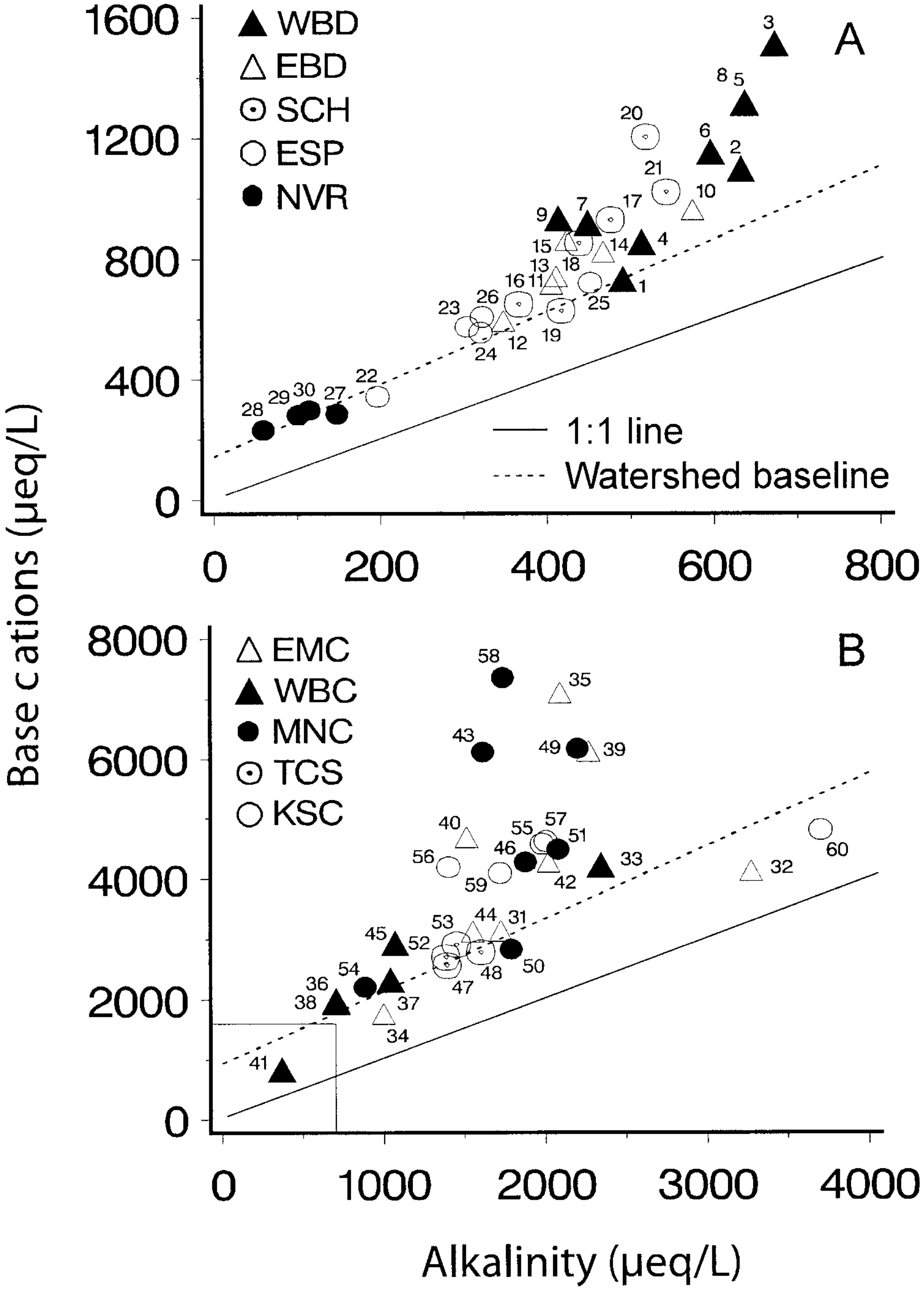


FIG. 7. Plot of the sum of base cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) vs alkalinity for west of Hudson River (WOH; A) and east of Hudson River (EOH; B) sites. Base cations were summed within each year and the sums were averaged over the 3-y study period. The watershed baseline is based on a regression using the least-disturbed sites as defined by the % forested area in the watershed (see text for details). The box in the lower-left portion of the EOH plot panel (B) indicates the range of values for WOH sites. See Fig. 1 for watershed abbreviations; see figs 1 and 2 and table 1 in Arscott et al. (2006) for site names.

inputs is greater for EOH watersheds than for WOH watersheds, but this result may actually indicate that the least-disturbed sites selected from the EOH region were not 'minimally disturbed'. The facts that some EOH sites are below the defined watershed baseline and that the % forested area is much lower for EOH least-disturbed sites relative to WOH least-disturbed sites suggest that the true watershed baseline for the EOH region may be much lower than defined here.

The plots of the sum of base cations vs alkalinity indicate that geology is one of the driving factors behind differences in stream chemistry between the WOH and EOH regions. None of the EOH sites (except site 41) overlapped with WOH sites in these plots (Fig. 7A, B). EOH sites have higher base cation sums and higher alkalinities than WOH sites, and both variables reflect underlying differences between the 2 regions in the geological influences on stream chemistry. Within the WOH region, subtle differences in stream chemistry are also attributable to geology. The clear gradient of decreasing ion/nutrient concentrations across the WOH region (Fig. 1A, C, Fig. 2A, C) appears to be caused, in part, by geology. Gradients of high-to-low base cations and alkalinity exist from west to east (from the West Branch Delaware sites to the Esopus sites) and from north to south (from the Schoharie sites to the Neversink sites) (Fig. 7A).

Inorganic chemistry vs landuse: individual analyte relationships

Significant MLR models were generated for almost every analyte in all 4 regions/watersheds (WOHdel, WOHcat, WOH, EOH) at $\geq$2 of the 3 spatial scales. The single exception was that PN did not generate any significant models at any scale in the WOHcat watershed (Table 3). Each of the landuse variables (Table 2) was included in at least 1 model, and 14 of the 16 landuse variables were the most significant predictors (i.e., highest partial R^2) in at least 1 model. For the WOH models, ~37% (7 of 19) of the most significant predictors could be classified as urban, ~42% (8 of 19) as agricultural, and ~21% (4 of 19) as undisturbed (not urban or agriculture). In the WOHdel watershed, ~32% (6 of 19) of the most significant predictors could be classified as urban, ~47% (9 of 19) as agricultural, and ~21% (4 of 19) as undisturbed (not urban or agriculture). In the WOHcat watershed, ~67% (12 of 18) of the most significant predictors could be classified as urban, ~11% (2 of 18) as agricultural, and ~22% (4 of 18) as undisturbed. In the EOH region, ~89% (17 of 19) of the most significant predictors could be classified as urban, and the remaining ~11% (2 of 19) as undisturbed.

The best predictor variable in 70 of the 75 significant models contributed $\geq$50% to the variance explained by the model (i.e., partial R^2 of the best predictor relative to the overall unadjusted model R^2; R^2 values in Table 3 are the adjusted model R^2). The 5 models in which the partial R^2 of the best predictor was $\leq$50% were for alkalinity, PN, and TDP in the WOHdel watershed and pH and PP in the EOH region. These results imply that the most important predictor variable in any given model had most of the power to explain variability in ion and nutrient concentrations across the region/watershed, regardless of the number of significant predictors in the model.

The watershed-, riparian-, and reach-scale MLR models were compared for each analyte in each region/watershed (75 comparisons), and the best (highest adjusted R^2, no multicollinearity) of the 3 models in each comparison was identified (Table 3). The best MLR models came from all 3 spatial scales within each region/watershed, except that no riparian-scale models were selected in the EOH region (Table 3). In the EOH region, most of the best models were based on landuse variables quantified at the watershed scale whereas, in the WOH region and the WOHdel and WOHcat watersheds, the best models were evenly distributed between the watershed and riparian scales. In the EOH region, 5 of the best models were based on landuse variables quantified at the reach scale, whereas only 2 of the best models in WOHdel and WOHcat watersheds and 1 of the best models for the WOH region were based on landuse variables quantified at the reach scale. Most of the best models in the EOH region were considered unique, whereas <½ of the best models in the WOHdel and WOHcat watersheds and <¼ of the best models in the WOH region were considered unique.

More than 50% of the variability among sites in the WOH region and the WOHdel and WOHcat watersheds was explained by the first 2 axes of the PCAs based on landuse variables quantified at 3 scales (Fig. 8A, C, E), whereas only 32% of the variability among sites in the EOH region was explained by the first 2 axes of the PCA (Fig. 8G). Individual landuse variables quantified at the watershed scale tended to be more closely associated with the same variable quantified at the riparian scale (along both axes) in PCAs for the WOH region (i.e., short solid lines; Fig. 8F) and for the WOHdel and WOHcat watersheds (Fig. 8B, D) than in the PCA for the EOH region (i.e., long solid lines; Fig. 8H). The only landuse variable that did not follow this general pattern was road density. In the WOHdel and WOHcat PCAs, riparian-scale road density was more closely aligned with other riparian-scale urban land uses than with watershed-scale road density (Fig. 8B, D). In the WOHcat PCA, riparian-scale road density was more closely aligned with other reach-scale urban land uses than with watershed-scale road density (Fig. 8B).

In general, sites tended to be separated more on the basis of landuse variables than on the basis of the scale at which those characteristics were quantified in all of the PCAs. Only the WOHcat PCA showed any tendency toward separation of sites based on scale (Fig. 8C, D). The distinctly different landuse variables

Table 3. Adjusted R^2 values and significant predictive variables (partial R^2, direction of slope) for the best (highest adjusted R^2, no multicollinearity) model among scales for each analyte in each region/watershed. Models were derived from stepwise multiple linear regressions (MLR) of mean analyte concentration as a function of watershed landuse characteristics quantified at the watershed (W), riparian (b), or reach (1k) scales. The best MLR is indicated in bold and marked with an asterisk (*). See text for definition of a unique model. See Table 2 for landuse variable codes. WOH = west of Hudson River geographic region, EOH = east of Hudson River geographic region, WOHdel = East and West Branches of the Delaware River watershed, WOHcat = Schoharie, Esopus, Neversink, and Rondout watershed, DON = dissolved organic N, TDN = total dissolved N, PN = particulate N, TN = total N, SRP = soluble reactive P, TDP = total dissolved P, PP = particulate P, TP = total P, Y = yes, N = no, – indicates no significant model found.

	Model adjusted R^2				
Analyte	W	b	1k	Unique	Significant predictors
WOHdel					
Alkalinity	0.43	**0.91***	0.33	Y	CROP (0.46, +) COMM (0.19, +) WETL (0.15, −) ORCH (0.07, +) MBRH (0.06, +)
Specific conductance	**0.93***	0.88	0.89	N	FMST (0.65, +) SPDE (0.16, +) OURB (0.07, +) CONF (0.04, −) ORCH (0.03, +)
pH	**0.52***	0.45	–	N	SHRB (0.41, +) CONF (0.18, −)
Cl^-	**0.85***	0.75	0.77	Y	RDNS (0.66, +) SPDE (0.15, +) MFOR (0.07, −)
SO_4^{2-}	0.96	**0.97***	0.85	N	FMST (0.62, +) SPDE (0.29, +) WETL (0.07, +)
Ca^{2+}	**0.73***	0.70	0.35	Y	DECD (0.52, −) SHRB (0.25, +)
Mg^{2+}	0.89	**0.94***	0.84	N	DECD (0.87, −) SPDE (0.05, +) MFOR (0.03, −)
Na^+	**0.95***	0.87	0.83	N	FMST (0.71, +) SPDE (0.17, +) RDNS (0.04, +) MFOR (0.04, −)
K^+	0.94	**0.95***	0.72	N	CROP (0.89, +) COMM (0.05, +) WETL (0.02, +)
NH_4-N	0.37	–	**0.63***	Y	COMM (0.36, +) CROP (0.18, +) WETL (0.17, +)
NO_3-N	0.87	**0.93***	0.69	N	CROP (0.65, +) COMM (0.21, +) OURB (0.07, −) SHRB (0.03, −)
DON	**0.65***	0.62	–	N	CROP (0.67, +)
TDN	0.92	**0.96***	0.67	N	CROP (0.71, +) COMM (0.20, +) OURB (0.04, −) SHRB (0.02, −)
PN	0.91	**0.92***	0.34	N	SHRB (0.46, +) SPDE (0.33, +) GRAS (0.14, +)
TN	0.93	**0.95***	0.66	N	CROP (0.72, +) COMM (0.22, +) OURB (0.03, −)
SRP	0.21	**0.40***	–	Y	RESD (0.44, −)
TDP	0.33	0.41	**0.67***	Y	COMM (0.35, +) CONF (0.21, +) CROP (0.19, +)
PP	**0.41***	0.41	0.41	N	SPDE (0.45, +)
TP	0.35	**0.56***	0.34	Y	RESD (0.41, −) SPDE (0.21, +)
WOHcat					
Alkalinity	**0.73***	0.73	0.58	N	RESD (0.67, +) MFOR (0.10, −)
Specific conductance	**0.93***	0.89	0.70	N	RESD (0.89, +) INDU (0.03, +) RDNS (0.03, −)
pH	0.82	0.79	**0.85***	N	SPDE (0.51, +) GRAS (0.25, −) SHRB (0.08, +) MFOR (0.05, −)
Cl^-	0.83	**0.89***	0.84	N	COMM (0.82, +) CROP (0.09, +)
SO_4^{2-}	0.48	**0.59***	–	Y	INDU (0.48, +) CROP (0.17, +)
Ca^{2+}	0.72	**0.75***	0.71	N	RESD (0.76, +)
Mg^{2+}	0.87	**0.94***	0.69	N	RESD (0.84, +) MBRH (0.08, +) SHRB (0.04, +)
Na^+	**0.98***	0.97	0.89	N	RESD (0.93, +) INDU (0.05, +)
K^+	**0.90***	0.84	0.68	N	GRAS (0.87, +) FMST (0.04, +)
NH_4-N	–	**0.63***	0.22	Y	CROP (0.41, −) OURB (0.28, +)
NO_3-N	**0.69***	0.28	–	Y	RDNS (0.40, +) GRAS (0.33, −)
DON	**0.70***	0.62	0.47	N	DECD (0.62, −) INDU (0.12, +)
TDN	**0.45***	–	0.30	Y	RDNS (0.34, +) GRAS (0.19, −)
PN	–	–	–	N	
TN	0.28	–	**0.41***	Y	OURB (0.45, +)
SRP	0.43	**0.50***	–	Y	MFOR (0.54, −)
TDP	0.46	**0.54***	–	N	MFOR (0.57, −)
PP	0.54	**0.57***	–	Y	MFOR (0.36, −) OURB (0.27, +)
TP	0.41	**0.58***	–	Y	RESD (0.47, +) CONF (0.17, −)
WOH					
Alkalinity	0.64	**0.71***	0.18	N	COMM (0.47, +) MFOR (0.22, −) RESD (0.05, +)
Specific conductance	0.78	**0.85***	0.53	N	COMM (0.65, +) MFOR (0.18, −) WETL (0.03, +)
pH	**0.47***	0.32	0.15	Y	WETL (0.35, +) SHRB (0.15, +)
Cl^-	0.82	**0.89***	0.57	N	DECD (0.64, −) SPDE (0.21, +) OURB (0.03, −) RESD (0.03, +)
SO_4^{2-}	**0.88***	0.83	0.73	N	FMST (0.78, +) SPDE (0.08, +) SHRB (0.03, −)
Ca^{2+}	0.66	**0.75***	0.40	N	COMM (0.55, +) MFOR (0.21, −)
Mg^{2+}	0.83	**0.93***	0.41	Y	CROP (0.75, +) RESD (0.13, +) WETL (0.04, +) SHRB (0.02, +)

TABLE 3. Continued.

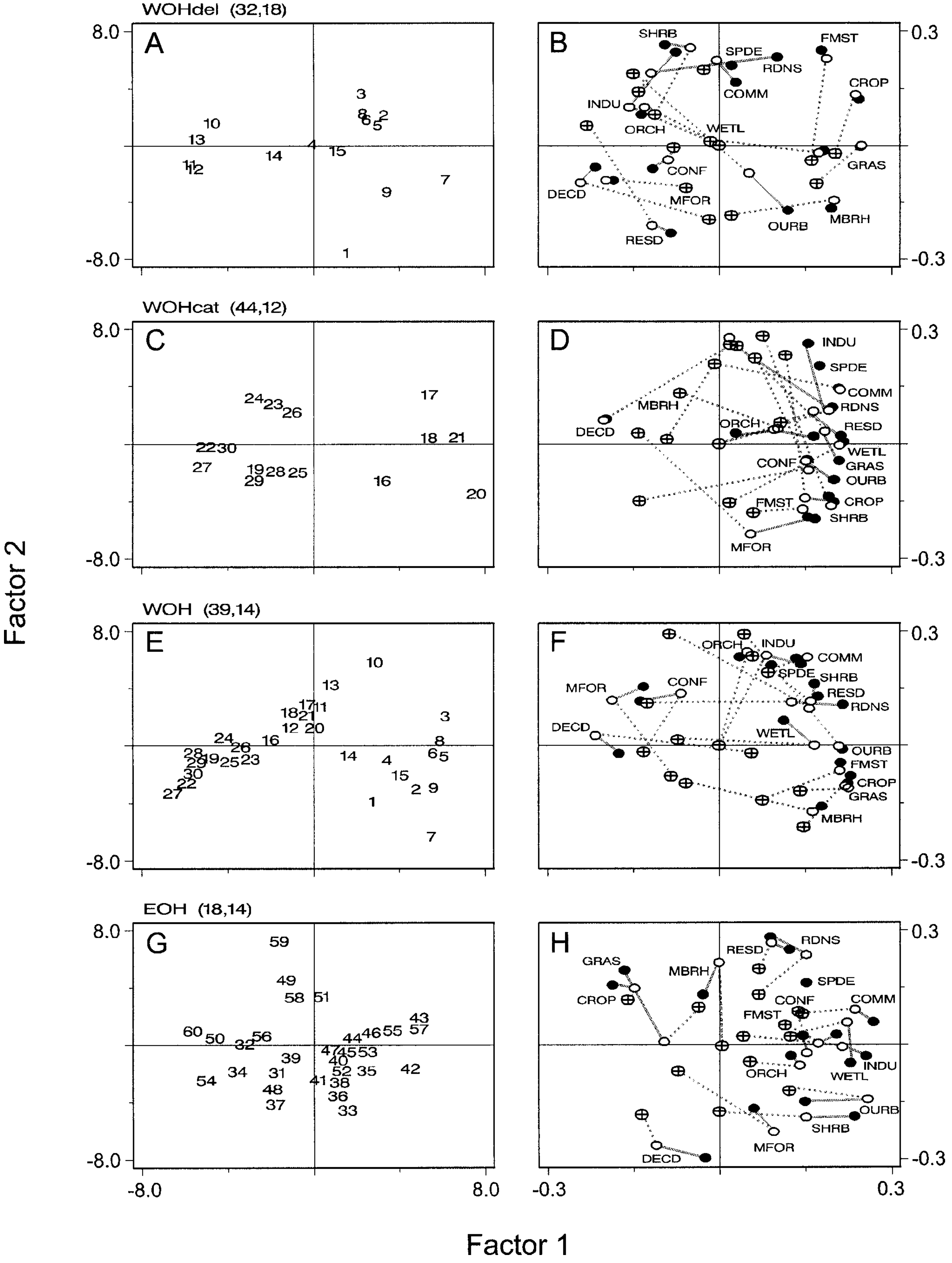
Analyte	Model adjusted R^2			Unique	Significant predictors
	W	b	1k		
Na$^+$	**0.88***	0.86	0.63	N	COMM (0.69, +) FMST (0.13, +) OURB (0.04, −) RESD (0.04, +)
K$^+$	**0.96***	0.95	0.65	N	FMST (0.87, +) GRAS (0.06, +) WETL (0.03, +)
NH$_4$-N	0.42	0.42	**0.52***	Y	COMM (0.32, +) CROP (0.23, +)
NO$_3$-N	**0.69***	0.63	0.58	N	CROP (0.61, +) GRAS (0.10, −)
DON	0.75	**0.76***	0.63	N	COMM (0.51, +) MFOR (0.22, −) CONF (0.05, +)
TDN	**0.86***	0.83	0.63	N	CROP (0.78, +) SPDE (0.05, +) RESD (0.04, −)
PN	**0.81***	0.64	0.53	Y	CONF (0.54, −) COMM (0.21, +) SHRB (0.05, +) RESD (0.04, −)
TN	**0.91***	0.87	0.64	N	CROP (0.82, +) SPDE (0.05, +) RESD (0.04, −) RDNS (0.02,+)
SRP	**0.80***	0.78	0.37	N	CONF (0.66, −) INDU (0.12, +) CROP (0.04, +)
TDP	**0.87***	0.87	0.51	N	CROP (0.73, +) CONF (0.09, −) INDU (0.06, +)
PP	0.77	**0.78***	0.47	N	OURB (0.59, +) COMM (0.13, +) MFOR (0.08, −)
TP	**0.94***	0.88	0.63	N	GRAS (0.75, +) MFOR (0.09, −) INDU (0.08, +) ORCH (0.02, +)
EOH					
Alkalinity	**0.34***	0.32	–	Y	DECD (0.25, −) MBRH (0.13, +)
Specific conductance	**0.57***	0.40	0.28	Y	RDNS (0.54, +) SPDE (0.06, +)
pH	0.36	0.34	**0.37***	Y	RESD (0.18, −) MFOR (0.14, +) OURB (0.13, +)
Cl$^-$	**0.71***	0.54	0.41	Y	RDNS (0.49, +) SPDE (0.10, +) DECD (0.08, +) MFOR (0.08, +)
SO$_4^{2-}$	**0.61***	0.52	0.59	N	RDNS (0.43, +) SPDE (0.15, +) SHRB (0.07, −)
Ca^{2+}	**0.57***	0.37	–	Y	RDNS (0.47, +) CROP (0.13, +)
Mg^{2+}	**0.34***	0.30	–	Y	DECD (0.37, −)
Na$^+$	**0.67***	0.49	0.38	Y	SPDE (0.40, +) RDNS (0.15, +) MFOR (0.09, +) DECD (0.08, +)
K$^+$	**0.64***	0.47	0.40	Y	RDNS (0.42, +) SPDE (0.16, +) CROP (0.09, +)
NH$_4$-N	0.29	0.29	**0.47***	Y	SPDE (0.32, +) COMM (0.13, +) ORCH (0.08, −)
NO$_3$-N	**0.69***	0.59	0.41	Y	RESD (0.41, +) WETL (0.14, −) SPDE (0.11, +) FMST (0.07, +)
DON	0.64	0.64	**0.65***	N	SPDE (0.61, +) COMM (0.07, +)
TDN	**0.60***	0.49	0.49	Y	SPDE (0.51, +) RESD (0.12, +)
PN	0.60	0.54	**0.64***	N	SPDE (0.48, +) DECD (0.13, −) OURB (0.06, −)
TN	**0.67***	0.51	0.51	Y	SPDE (0.53, +) RESD (0.12, +) CROP (0.05, +)
SRP	**0.49***	0.18	0.32	Y	RDNS (0.39, +) OURB (0.14, +)
TDP	**0.51***	0.32	0.39	Y	RDNS (0.42, +) OURB (0.13, +)
PP	0.57	0.51	**0.85***	Y	SPDE (0.42, +) FMST (0.14, +) COMM (0.11, +) ORCH (0.06, −) CONF (0.05, +) MFOR (0.04, −) MBRH (0.04, −)
TP	**0.54***	0.46	0.52	Y	RESD (0.42, +) SPDE (0.15, +)

of sites in WOHdel and WOHcat watersheds can be seen clearly in the WOH PCA (Fig. 8E, F), which includes all WOHdel and WOHcat sites. The 1st axis corresponded to a gradient from high % forested area (on the left) to high urban/agricultural land uses (on the right). All WOHcat sites (sites 16–30) plotted to the left along the 1st axis, whereas all WOHdel sites (sites 1–15) plotted to the right along the 1st axis (Fig. 8E). The association between the watershed and riparian scales for a given land use was weaker for the EOH PCA (Fig. 8H) than for WOH PCA models, but the association between those 2 scales and the corresponding reach-scale land use was stronger for the EOH PCA models relative to the WOH PCA models.

Inorganic chemistry vs landuse variables: univariate relationships

Cl$^-$ and K$^+$ concentrations were significantly related to road density in the WOHdel and WOHcat watersheds and the EOH region ($p < 0.05$; Fig. 9A, C, E), but the relationships between Cl$^-$ and K$^+$ and road density were not strong in the EOH sites (both R^2 values <0.50; Fig. 9E). Cl$^-$ and K$^+$ concentrations were significantly related to % cropland in the WOHdel and WOHcat watersheds ($p < 0.05$; Fig. 9B, D), but not in the EOH region ($p > 0.05$; Fig. 9F). Cl$^-$ concentrations were most strongly related to road density in the WOHcat sites ($R^2 = 0.64$; Fig. 9C). K$^+$ concentrations were most strongly related to % cropland in WOHdel sites ($R^2 = 0.92$; Fig. 9B).

Differences between the WOH and EOH regions in water-chemistry and landuse variables were evident in these relationships. The maximum road density in watersheds upstream of WOH sites (1300 m/km^2) was lower than any EOH road-density value. All % cropland values were lower at WOHcat sites than at WOHdel sites. Only 4 EOH sites had mean Cl$^-$ concentrations that were lower than the maximum


WOHdel (32,18)
A
B
WOHcat (44,12)
C
D
WOH (39,14)
E
F
EOH (18,14)
G
H
8.0
-8.0
0.3
-0.3
-0.3
0.3
Factor 1
Factor 2
SHRB
SPDE
RDNS
FMST
CROP
COMM
INDU
ORCH
WETL
GRAS
CONF
DECD
MFOR
OURB
MBRH
RESD
WETL
RESD

WOH Cl^- concentration (~600 μeq/L), and only 3 EOH sites had mean K^+ concentrations that were lower than the maximum WOH K^+ concentration (~40 μeq/L).

Notable outliers in the Cl^- and K^+ plots are identified in Fig. 9. In the WOHdel watershed, Cl^- concentrations were lower at sites 2 and 7 than at other sites with similar % cropland values (Fig. 9B) and K^+ concentrations were higher at sites 2 and 7 than at other sites with similar road densities (Fig. 9A). Neither site had any identified point-source discharges. In the WOHcat watershed, site 20 was a potential outlier in the Cl^- and K^+ relationships (Fig. 9C, D). Site 20 did not have the highest road density in this watershed but did have the highest % cropland value (<1%). Site 20 also had identified point-source discharges, but the mean annual watershed-area-normalized effluent volume (0.03 cm) was an order of magnitude lower than the maximum value for sites in the WOHcat watershed (0.33 cm for a site upstream of site 20). In EOH, sites 35, 49, and 58 were potential outliers in the Cl^- relationships, and sites 49 and 58 were potential outliers in the K^+ relationships (Fig. 9E, F). Sites 49 and 58 (along with site 43) had very high point-source discharges relative to the other EOH sites. Site 35 also had identified point-source discharges, but the corresponding mean annual watershed-area-normalized effluent volume was only 0.10 cm.

Discussion

Effects of temporal variability on results of synoptic surveys

Synoptic surveys of water quality depend upon the assumption that relationships derived from the spatially intensive sampling effort are representative of the sampled area both spatially and temporally. It follows, then, that such relationships should not change when another synoptic survey is conducted in the same region during a different time period. Wayland et al. (2003) suggested that proper definition of watershed-scale influences on stream water quality requires a number of synoptic surveys throughout a given year to capture seasonal (i.e., temporal) variation in stream chemistry properly. In contrast, Dow and Zampella (2000) found that relationships for pH and specific conductance vs the proportion of altered land in a watershed (i.e., sum of agricultural and urban/suburban development) were similar regardless of the season and that summarizing chemistry data across seasons did not enhance predictive power. Furthermore, including seasonal variability in stream chemistry data sets actually may confound attempts to develop stream water-chemistry vs watershed-condition relationships by capturing within-year variability.

In our study, interannual variability, rather than intra-annual variability (i.e., seasonal), was captured by sampling stream water quality during a single season (summer). The wbPCA results indicated that interannual variability was minor relative to intersite variability, strengthening the robustness of the relationships between chemical water quality and watershed conditions presented in our study. However, the applicability of the relationships between summer baseflow chemistry and watershed condition to other seasons should be explored further. Heisig (2000) observed that seasonal differences in baseflow concentrations of several analytes from EOH streams did not substantially alter relationships with land use or watershed condition. However, Heisig (2000) also observed that certain land uses (e.g., housing density) had greater influence (steeper regression slope but similar R^2) on stream chemistry (i.e., NO_3-N) in January than in August. In another study, Kaushal et al. (2005) reported that Cl^- concentrations were greatest in late winter, but relationships between Cl^- and road density were evident even during summer.

The effect of underlying geology on detection of landuse impacts

Beyond any issues of temporal consistency, another important issue in defining watershed controls on stream chemistry lies within the realm of spatial variability. The RDA constrained ordinations helped describe site similarities within each region and further

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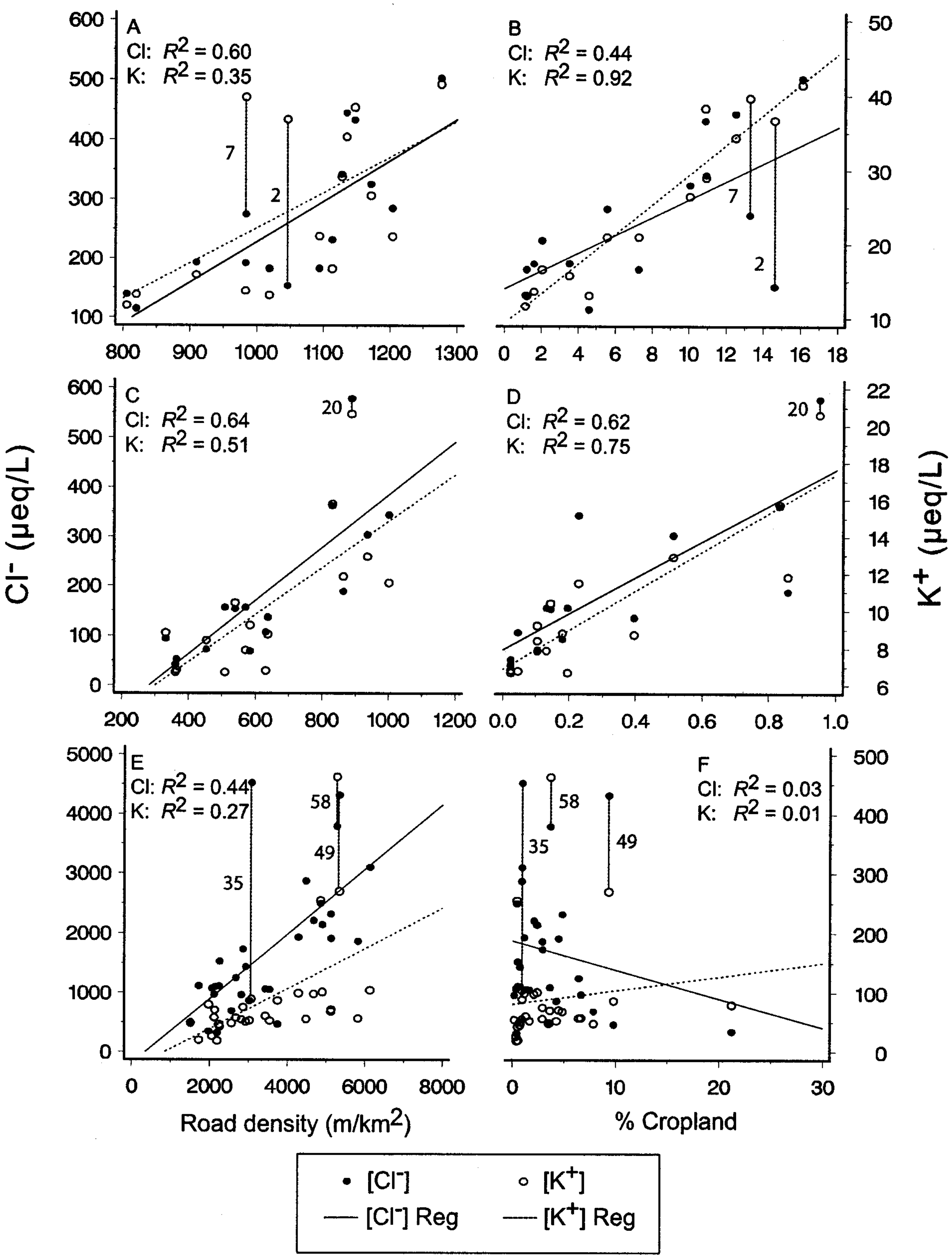
FIG. 8. Principal Components Analysis (PCA) of watershed characteristics (e.g., landuse variables, road density, mean annual watershed-area-normalized State Pollution Discharge Elimination System [SPDE] effluent volume) quantified at watershed, riparian, and reach scales (see text for detailed explanation). PCA scores (left column; see figs 1 and 2 and table 1 in Arscott et al. 2006 for site names) and landuse variable loadings (right column; see Table 2 for landuse abbreviations) are given for sites in the East and West Branches of the Delaware River (WOHdel; A, B) and Schoharie, Esopus, Neversink, and Rondout (WOHcat; C, D) watersheds, and the west of Hudson River (WOH; E, F), and east of Hudson River (EOH; G, H) regions. The % of variation in the data explained by axes 1 and 2 are shown in parentheses above panels A, C, E, and G. The lines in panels B, D, F, and H connect landuse variables quantified at the 3 spatial scales: solid lines connect watershed (solid circles) to riparian scales (open circles); dotted lines connect riparian to reach scales (circles with crosshairs). The positions of some sites in panels A, C, E, and G were moved to ease interpretation.


A
Cl: $R^2 = 0.60$
K: $R^2 = 0.35$
B
Cl: $R^2 = 0.44$
K: $R^2 = 0.92$
C
Cl: $R^2 = 0.64$
K: $R^2 = 0.51$
D
Cl: $R^2 = 0.62$
K: $R^2 = 0.75$
E
Cl: $R^2 = 0.44$
K: $R^2 = 0.27$
F
Cl: $R^2 = 0.03$
K: $R^2 = 0.01$
7
2
20
58
49
35
Cl^- (μeq/L)
K^+ (μeq/L)
Road density (m/km^2)
% Cropland
600
500
400
300
200
100
0
5000
4000
3000
2000
1000
800
900
1000
1100
1200
1300
200
400
600
800
1000
1200
6000
8000
0
2
4
6
8
10
12
14
16
18
0.0
0.2
0.4
0.6
0.8
1.0
20
30
50
40
22
18
16
14
12
10
8
6
● $[Cl^-]$
○ $[K^+]$
— $[Cl^-]$ Reg
---- $[K^+]$ Reg

related the collective suite of summer baseflow analytes to dominant landuse and other watershed-condition variables. Other studies in the WOH and EOH regions have described patterns similar to those described in our study for various ions and nutrients (e.g., Stoddard 1991, Heisig 2000, Mehaffey et al. 2001), but no single published study has provided either the perspective across both regions for all nutrients and major ions or the spatial extent presented here. Perhaps the most revealing feature in the RDA ordinations is the apparent degree of interaction between geology and land use in defining stream chemistry patterns, particularly in the WOH region. Separating geological controls and other natural controls on stream chemistry from anthropogenic landuse impacts remains a challenge, especially across large regions such as the one covered in our study.

Past research involving both geology and land use has demonstrated varying degrees of interaction. For instance, Miller et al. (1997) found a potential synergism between geology and land use in the Potomac River watershed, where watersheds draining predominantly agricultural areas were underlain by carbonate lithology that allowed greater hydrologic transport of the agriculturally available N. Johnson et al. (1997) determined that seasonal differences in central Michigan stream chemistry were attributable to sampling the falling limb of stream hydrographs during summer months. These seasonal differences resulted in a stronger landuse effect on summer-sampled stream chemistry than on autumn-sampled stream chemistry and masked geological controls on stream chemistry. Several definable interactions between geology, land use, and stream chemistry (e.g., streams in deciduous forest areas underlain by carbonate bedrock have high ion concentrations) were found for streams and rivers of the Baden–Württemberg region of Germany (Xie et al. 2005).

Implicit, though not necessarily directly acknowledged, in studies examining geological vs landuse interactions is that geology is important in defining a stream chemistry signal, and it is *equally* important in defining landuse patterns. For example, row-crop agriculture generally will be found in landscapes conducive to growing crops, and the suitability of landscapes for growing crops is a function, at least in part, of geology. The WOH region is a case in point: agricultural land uses are much more prevalent in the West and East Branch Delaware watersheds than in the eastern ½ of the region that includes the Schoharie Creek, Esopus Creek, Neversink River, and Rondout Creek watersheds because the geological setting in the Delaware watersheds resulted in deeper and probably more-nutrient-rich soils, gentler slopes, etc. (Arscott et al. 2006). The question, then, is 2-fold: 1) to what extent is agriculture affecting stream chemistry above and beyond geologic controls, and 2) are landuse vs stream-chemistry relationships developed for the entire WOH region simply a reflection of the geological controls on landuse patterns across the region rather than regional landuse impacts on stream chemistry?

Approaches to separating the effects of geology and land use

Three separate approaches, all having different objectives, were taken in our study in an attempt to separate geological controls from landuse effects on stream chemistry. First, the RDA ordinations represented a statistical approach meant to clarify the level of interaction between geology and land use in defining stream chemistry. RDA is a powerful tool that provides a holistic view of the various landscape features and their interactions in defining baseflow chemistry because it incorporates all inorganic chemistry analytes, geological variables, and landuse variables. Second, plotting base cation sums against alkalinity (adapted from Rhodes et al. 2001; Fig. 7) was a process-based approach to separating the influences of natural landscape features on stream chemistry from anthropogenic impacts. The WOH region plot (Fig. 7A) shows the utility of this approach for defining a regional (e.g., watershed) baseline for stream chemistry that should reflect geological controls on stream chemistry and for indicating the subsequent anthropogenic influences acting to modify stream chemistry beyond the defined baseline within a watershed. Third, an attempt was made to remove altogether the variation in stream chemistry attributable to geology by defining geological regions/watersheds that presumably reflected unique gradients of stream chemistry and the factors affecting or controlling stream chemistry (see discussion of this 3rd approach in *model domain* below).

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FIG. 9. Univariate relationships between ion concentrations and watershed-scale road density or watershed-scale % cropland for sites in the East and West Branches of the Delaware River (WOHdel; A, B) and Schoharie, Esopus, Neversink, and Rondout (WOHcat; C, D) watersheds, and the east of Hudson River (EOH; E, F) regions. Regression lines and corresponding R^2 values are provided (all regressions were significant [$p < 0.05$ level] except for the EOH K^+ relationships). Vertical lines with site numbers (see figs 1 and 2 and table 1 in Arscott et al. 2006) denote outlier values in each relationship. Reg = regression line.

Influence of scale

Among other spatial considerations is the relative importance of local- vs watershed-scale influences on stream water chemistry (e.g., Allan 2004, King et al. 2005). Results from both the RDAs and MLR analyses suggested that landuse patterns at the watershed and riparian scales were more important than patterns at the reach scales in defining most individual ion and nutrient analyte gradients in both WOH and EOH regions. All but one of the landuse variables selected in the RDAs was quantified at the watershed scale, and the single exception was a variable quantified at the riparian scale. In the EOH region, watershed-scale MLR models were most often selected as the best models and were usually considered unique relative to models at riparian and reach scales in explaining or predicting ion and nutrient baseflow chemistry. Furthermore, 2 of the 3 EOH MLR models that were not considered unique included the single variable that was not scale dependent, SPDE-permitted discharge volume (i.e., point-source discharge).

In the WOHdel and WOHcat watersheds, MLR models at the riparian or reach scales were often selected as the best models, indicating that local conditions, either at the riparian or reach scales, appeared to be more relevant to water chemistry than conditions at the watershed scale. However, many of these best MLR models were not unique. This lack of uniqueness for many WOH, WOHdel, and WOHcat results implies that no particular scale (especially watershed vs riparian scales) was better than another at explaining variability in concentrations of any given analyte. For certain analytes, notably nutrients, the lack of unique results among scales may also reflect inadequacies in defining riparian-scale land use. Riparian area influences on streams were defined from the perspective of source proximity to streams in our study, but more effective riparian landscape metrics may result from a perspective focusing on riparian functional attributes, an idea being pursued by Baker et al. (in press).

The RDA and MLR analyses suggest that baseflow inorganic chemistry, especially among major cations and anions, is influenced more by watershed-scale conditions than by local conditions. Several studies have reported that watershed- rather than riparian- or reach-scale factors best explained concentrations of certain baseflow chemistry analytes (Osborne and Wiley 1988, Johnson et al. 1997, Gergel et al. 1999, Sponseller et al. 2001). However, other studies have reported opposite results (reviewed in Gergel et al. 2002), and this apparent contradiction is certainly related to differences in specific analytes, geological and anthropogenic settings, legacy effects, and other methodological considerations.

The importance of the watershed-scale influence observed in our study is probably related to geological controls on the ions measured and to the likelihood that any landscape controlling factors were acting in concert with the geological controlling factors (Allan 2004). Nevertheless, a certain amount of caution should accompany this conclusion. King et al. (2005) pointed out that landuse classes often are not independent, and this lack of independence occurs among as well as within scales as shown in the PCA results involving land use across all 3 scales. A second important point is the resolution of the landuse data (Stewart et al. 2001). The 10-m resolution of the landuse data source used in our study is comparatively good relative to the resolution used in other similar studies (often 30 m), but it probably is not adequate to capture the variability of near-stream conditions fully.

Importance of model 'domain'

The differences in MLR models between regions point to the spatial issue that Strayer et al. (2003) and Allan (2004) termed model 'domain.' The important watershed conditions influencing stream conditions, the scales at which those watershed conditions operate, and the degree to which those conditions are influencing factors can be quite different on a regional basis. The question remains whether these model domains reflect actual differences in how watershed conditions influence stream water chemistry, or whether the watersheds simply reflect different endpoints along the same response gradient. For instance, % cropland was the primary predictor of K^+ in the WOHdel model, % grassland was the primary predictor in the WOHcat model, and % farmstead was the primary predictor in the WOH region model (Table 3). All 3 models identified some type of agricultural land use at either the watershed or riparian scales as the primary predictor (none of the models were unique), and all explained approximately the same overall proportion of the variance in K^+ (all $R^2 \geq 0.90$). On the other hand, the best alkalinity model for the WOHdel watershed was unique at the riparian scale, with % cropland as the strongest predictor and $R^2 = 0.91$. This model was quite different from the best alkalinity model for the WOHcat watershed, which was at the watershed scale and not unique, with % residential as the strongest predictor and $R^2 = 0.73$.

Partitioning of variation within the RDA ordinations among the individual chemical analytes revealed varying influence of geology vs land use (Fig. 5) within and between regions. Especially in the WOH region, land use explained some of the variability of instream nutrient concentrations, but the influences of land use and geology could not be partitioned effectively to explain instream ionic concentrations because of multicollinearity between the 2 sets of explanatory variables. The nutrient relationships for sites in different WOH watersheds might be applicable across the entire WOH region because they reflect landuse gradients, but the ionic relationships for the 2 WOH watersheds should remain as separate watershed-defined relationships because they reflect geological differences between the watersheds. These examples suggest that the question of model domain, at least for the study region, was analyte specific, and they demonstrate the difficulty of selecting a single instream chemical response that will be representative of a certain type of watershed-level influencing factor across a broadly defined geographic region.

Monitoring stream inorganic chemistry has a long history as a tool for assessing the impact of changing watershed conditions. This history has brought a myriad of conclusions documenting: 1) a suite of watershed conditions that affect a given set of analytes, 2) certain geographic scales that influence baseflow stream chemistry, and 3) analytes that are considered the best indicators of anthropogenic watershed effects on stream water quality. This extensive history of monitoring inorganic stream chemistry provides an important frame of reference for current and future studies, but the variability of responses found in past work demonstrates the ongoing need to assess these measures as indicators of stream water quality.

The results of our study indicate that relationships between stream inorganic chemistry and watershed condition show distinct regional differences that are manifested in differences in geological and specific landuse linkages to a given analyte and, to a lesser degree, in the scale (i.e., watershed vs riparian vs reach) at which the specific land uses were operating. The influence of particular anthropogenic landuse classes, whether urban/suburban or agricultural, varied regionally and by analyte. Conversely, no single ion or nutrient was found to be the strongest indicator of either urban or agricultural impacts on stream inorganic chemistry across the study area.

Further work in the study region, including sampling at nearly 50 new sites and continued sampling at a handful of current sampling sites, will provide further evidence of the adequacy of the temporal and spatial relationships between stream inorganic chemistry and watershed conditions presented here. Work also continues on integrating the inorganic chemistry sampling effort with the other components of the Project, including molecular tracers, macroinvertebrates, and measures of ecosystem function.

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