

# Identifying Relationships between Baseflow Geochemistry and Land Use with Synoptic Sampling and R-Mode Factor Analysis

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## ABSTRACT

The relationship between land use and stream chemistry is often explored through synoptic sampling of rivers at baseflow conditions. However, baseflow chemistry is likely to vary temporally and spatially with land use. The purpose of our study is to examine the usefulness of the synoptic sampling approach for identifying the relationship between complex land use configurations and stream water quality. This study compares biogeochemical data from three synoptic sampling events representing the temporal variability of baseflow chemistry and land use using R-mode factor analysis. Separate R-mode factor analyses of the data from individual sampling events yielded only two consistent factors. Agricultural activity was associated with elevated levels of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , alkalinity, and frequently  $\text{K}^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ . Urban areas were associated with higher concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cl}^-$ . Other retained factors were not consistent among sampling events, and some factors were difficult to interpret in the context of biogeochemical sources and processes. When all data were combined, further associations were revealed such as an inverse relationship between the proportion of wetlands and stream nitrate concentrations. We also found that barren lands were associated with elevated sulfate levels. This research suggests that an individual sampling event is unlikely to characterize adequately the complex processes controlling interactions between land use and stream chemistry. Combining data collected over two years during three synoptic sampling events appears to enhance our ability to understand processes linking stream chemistry and land use.

LAND USE CHANGE has been shown to be a significant threat to aquatic ecosystems (Allan and Flecker, 1993; Sala et al., 2000; International Joint Commission, 1997; Tufford et al., 1998), yet the understanding of linkages between land use and water quality is limited. Relationships between land use and stream chemistry are often explored through synoptic, or "snapshot," sampling in which surface water is collected from a large number of sites across a watershed in a short period of time (Clow et al., 1996; Eyre and Pepperell, 1999; Fetter, 1994; Grayson et al., 1997). If flow remains relatively constant during the sampling period, synoptic sampling can often be used to study the spatial variability of stream chemistry (Grayson et al., 1997). Most synoptic studies are conducted during baseflow conditions when ground water dominates streamflow. The chemistry of baseflow represents an integrated signal of the climate, geology, and historical land use patterns throughout the water-

shed, and thus baseflow sampling should help link surface water quality to land use distributions.

Research has shown that the source of water in streams during nonstorm periods exhibits spatial and temporal variability. Hinton et al. (1993) observed that topography, hydraulic conductivity, and sediment thickness affected the magnitude and spatial distribution of ground water discharge to streams. Rose (1996) suggested that some baseflow contributions may come from vadose zone drainage during cooler or wetter months. Such hydrologic studies may explain why baseflow chemistry can be temporally variable in some watersheds (Clow et al., 1996), while remaining relatively constant in others (Pionke et al., 1999).

Given the likelihood that baseflow chemistry varies temporally as well as spatially, it is necessary to examine further the usefulness of the synoptic sampling approach for identifying consistent and reliable biogeochemical fingerprints across a watershed. The first objective of this paper is to compare biogeochemical data collected during three synoptic sampling events in a rapidly urbanizing watershed to characterize the temporal variability of baseflow chemistry. The second objective is to identify the effects of land use on surface water chemistry using factor analysis, and to examine how temporal variations in baseflow chemistry affect the identification of consistent land use fingerprints. Factor analysis has been applied to stream chemistry data collected at permanent sampling stations (Cameron, 1996; Evans et al., 1996; Puckett and Bricker, 1992) and during synoptic sampling surveys (Miller et al., 1997; Clow et al., 1996; Eyre and Pepperell, 1999). Although researchers frequently interpret associations of chemical species by considering land use near sampling sites, few studies include variables other than chemical species, such as land use distributions or environmental attributes, in the databases used in factor analyses. Our research combines geographical information systems (GIS)-derived land use distributions and biogeochemical data into a single database for use in R-mode factor analysis, thus examining the strength of relationships between land use categories and surface water chemistry.

## MATERIALS AND METHODS

### Study Site

Our study is located in the 2600-km<sup>2</sup> Grand Traverse Bay watershed (GTBW; Fig. 1) in the northwestern portion of Michigan's Lower Peninsula. The thick surficial sediments (up to 290 m) of the watershed are predominantly glacial outwash,

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**Abbreviations:** DO, dissolved oxygen; GTBW, Grand Traverse Bay watershed.

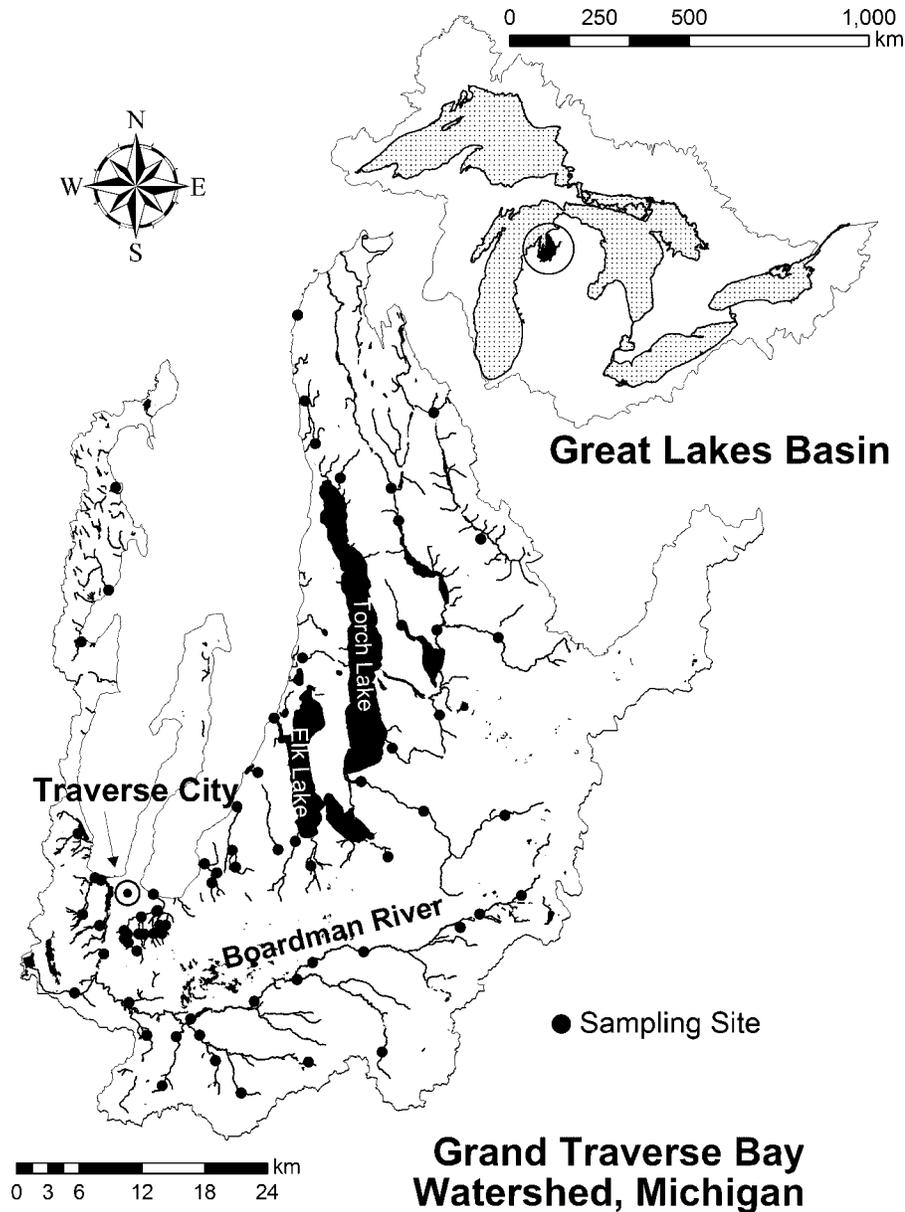


Fig. 1. Location of Grand Traverse Bay watershed, Michigan, and sampling sites.

till, lacustrine sand and gravel, and dunes, all overlying shale and limestone bedrock (Boutt et al., 2001). Oil and gas wells are located in the southern half of the watershed; brines associated with oil production are often applied to dirt roads in the region to control dust.

Land use and cover in the GTBW is predominantly forest (49%) and agriculture (20%) (Fig. 2). The diverse agricultural land uses include orchards, vineyards, row crops, and livestock production. Urban land use composes about 6% of the watershed, with Traverse City as the main urban area on the shores of Grand Traverse Bay. The other main land cover categories are shrub-brush (15%), water (9%), and wetlands (1%). Limited research has been conducted in the GTBW to examine relationships between land use and water quality. Cherry (*Prunus* spp.) orchards have been linked to high nitrate concentrations in wells in some areas of the watershed (Rajagopal, 1978). A weak correlation has been found between nitrate concentrations in ground water and nitrogen loading from precipitation, animal waste, septic tanks, and fertilizers (Cummings et al.,

1990). Results from a regional ground water flow and solute transport model for the GTBW indicate that the dissolution of road salt (halite) may be the most significant source for  $\text{Cl}^-$  in surface waters (Boutt et al., 2001), typical for many areas (e.g., Ostendorf et al., 2001). However, road salt alone cannot account for observed  $\text{Cl}^-$  concentrations and other sources, such as from wastewater, probably contribute  $\text{Cl}^-$  to surface waters.

Superimposed on this relatively healthy ecosystem is some of the greatest population growth and land use change in the Great Lakes region (Vesterby and Heimlich, 1991). The population of the watershed is approximately 100 000, but the summer recreational population can exceed 200 000. The population of Grand Traverse County is expected to double by the year 2020 (Grand Traverse County, 1996), so the effects of these changes on the water quality are of great concern to land use planners and resource managers. Beginning in 1998, surface water sites from an earlier U.S. Geological Survey study (Cummings et al., 1990) were resampled at least annually; preliminary analysis of the two datasets suggests that only

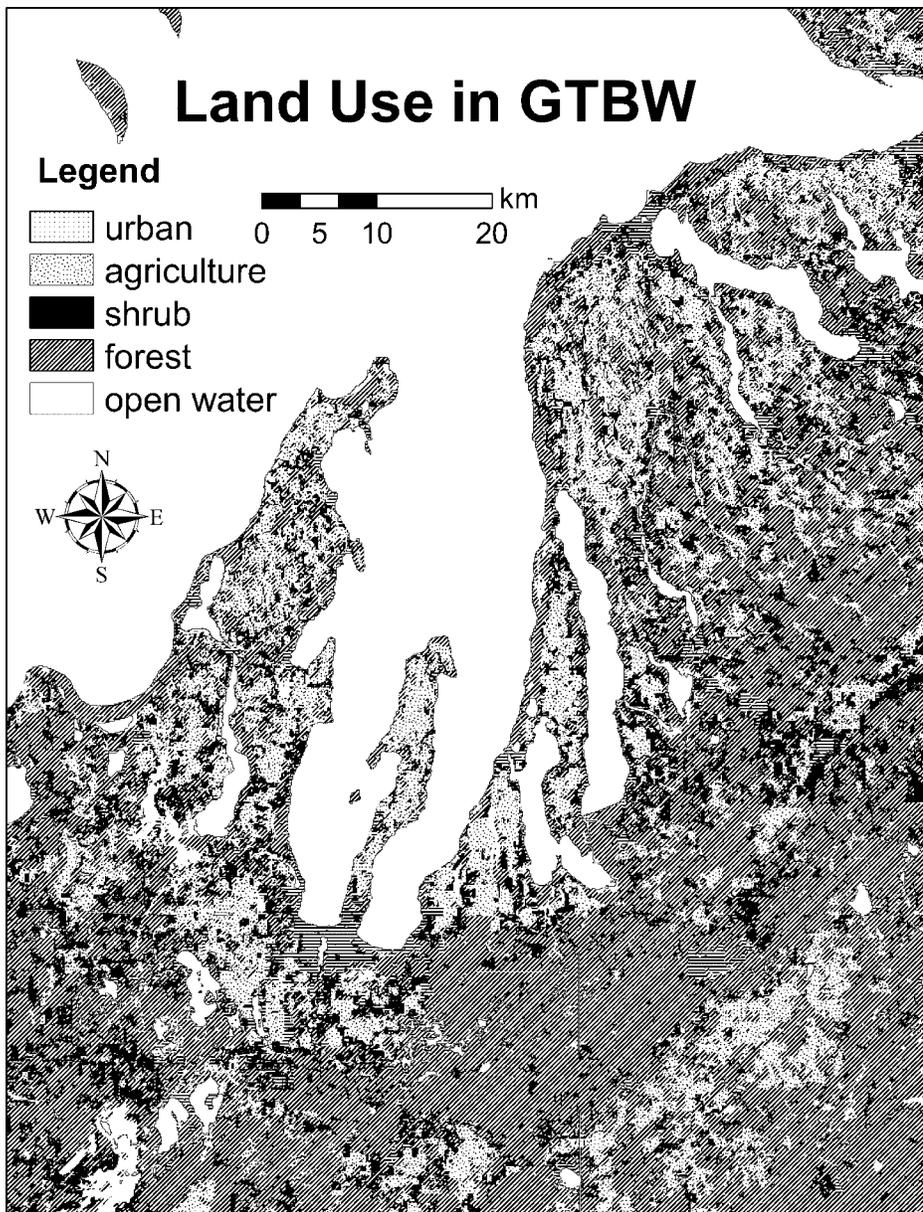


Fig. 2. Selected land use distributions in the Grand Traverse Bay watershed.

minor changes in the biogeochemistry of the watershed have occurred (Woodhams et al., 1998).

**Synoptic Sampling and Laboratory Analyses**

Biogeochemical data were collected during three baseflow synoptic sampling events in September 1997 and May and October 1998. Sampling events occurred during low flow conditions on the recession limb of the hydrograph as recorded for the Boardman River, the major river draining the GTBW. We consider baseflow to be the period between storms when the hydrograph is in the later stages of the recession limb (Pionke et al., 1999). Discharge was nearly constant during each synoptic sampling event, but varied among sampling events. Discharge at the U.S. Geological Survey Boardman River gauging station was 2.77, 3.45, and 2.52 m<sup>3</sup> s<sup>-1</sup> for the September 1997, May 1998, and October 1998 sampling events, respectively (Fig. 3).

The sampling sites (Fig. 1) were located at bridges or other easily accessible locations to facilitate rapid sample collection. Three crews of two to four people each were used to visit up to 75 sites across the watershed in 2.5 d. Although we identified approximately 80 potential sampling sites, some streams were dry during at least one of the sampling events.

At each site, samples were taken from the thalweg of the river with a plastic bucket or bottle on the upstream side of bridges. Buckets and bottles were rinsed three times with river water before samples were collected. Dissolved oxygen, specific conductance, temperature, redox potential, and pH were measured at each site with a HydroLab (Austin, TX) or YSI (Yellow Springs, OH) multiparameter probe. Alkalinity was determined in the field by the Gran titration method (Stumm and Morgan, 1981). As necessary, samples were filtered (0.45-µm Millipore [Bedford, MA] filters) in the field, acidified with concentrated nitric acid (Optima; Fisher Scientific, Chicago, IL) to a pH near 2 (cations), preserved with formaldehyde

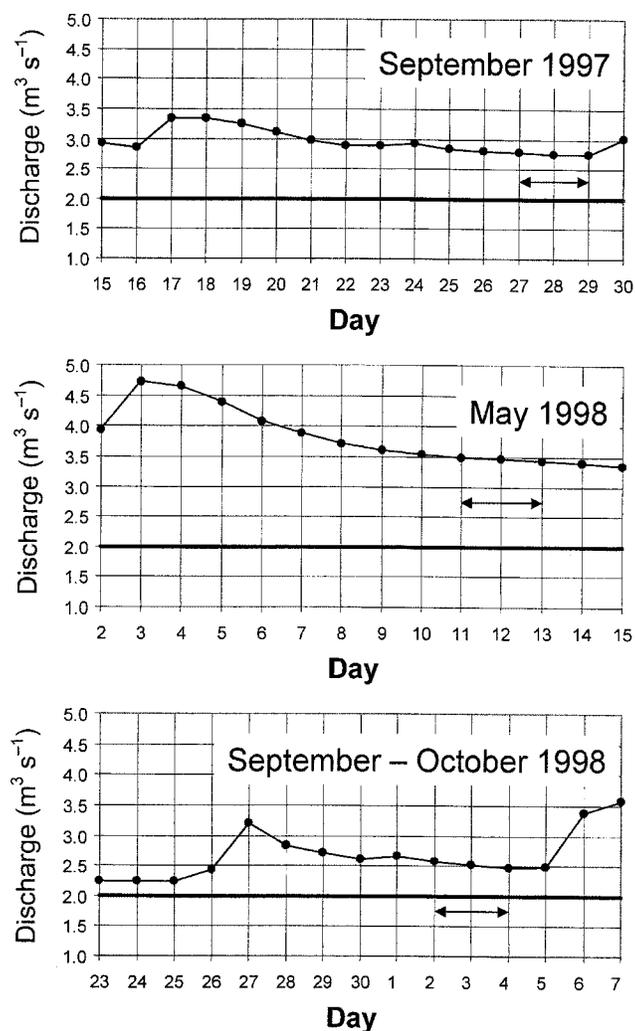


Fig. 3. Flow at the U.S. Geological Survey Boardman River gauging station for three synoptic sampling events and two-week period prior to sampling. The sampling dates are shown by the double arrow lines. Discharge of  $2 \text{ m}^3 \text{ s}^{-1}$  is highlighted as a common reference.

(sulfate), and/or flash frozen with dry ice (other anions). Samples that were not flash frozen with dry ice were stored on ice until return to the laboratory. All sample bottles were pre-cleaned by acid washing with distilled-deionized water rinses.

In addition to the field measurements described above, samples were analyzed for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{SiO}_2$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ . Cations were analyzed by flame atomic absorption (PerkinElmer [Wellesley, MA] 5100 PC). Chloride, nitrate, nitrite, sulfate, and fluoride were analyzed by selective ion electrode or capillary electrophoresis (Hewlett-Packard [Palo Alto, CA] 3DCE) and silica by colorimetry (Milton Roy Spectronic 1001 UV-Vis; Fisher Scientific, Chicago, IL).

#### Sourcesheds and Land Use Distributions

Land use and sampling points were related through the development of surface water sourcesheds with  $30\text{-} \times 30\text{-} \times 1\text{-m}$  vertical digital elevation model (DEM) data from the U.S. Geological Survey. A sourceshed is defined as the total area that contributes to a selected drainage point, or sampling site (Fig. 4). A raster drainage network was generated in Arc/INFO GRID with the FLOWDIRECTION and FLOWAC-

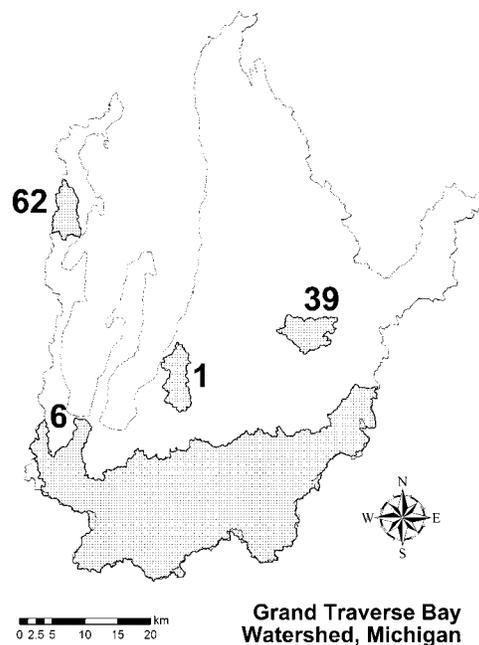


Fig. 4. Sourcesheds for Sample Sites 1, 6, 39, and 62. A sourceshed is defined as the total area that contributes to a selected drainage point, or sampling site. Sourcesheds were generated using the GIS software package Arc/INFO (Environmental Systems Research Institute, 2001).

CUMULATION commands (Environmental Systems Research Institute, 2001). Small sinks in the DEM were first removed from this analysis with the FILL command. Each sampling point was then assigned to a grid cell within the drainage network and sourcesheds were then created within GRID with the WATERSHED command. Each sourceshed was then converted to polygons for further analysis.

The polygon layer was then intersected with gridded ( $100\text{-} \times 100\text{-m}$  cell size) Level 1 Anderson land use–land cover data from the 1980 Michigan Resource Information System (MIRIS). The total number of cells of each land use type (urban, agriculture, shrub–brush, forest, water, wetland, and barren) was calculated for each sourceshed with ArcView 3.2's Spatial Analyst Extension 1.1 Tabulate Area function. The proportion of each land use class was computed for sourcesheds and exported to Excel (Microsoft, 1999) for use in statistical analyses. Brief descriptions of each land use category from Anderson et al. (1976) are listed in Table 1.

#### Statistical Procedures

All statistical procedures were conducted with SAS software (SAS Institute, 1998). Factor analysis is a common statistical approach for examining and quantifying the factors that control biogeochemical distributions in both surface and ground water (Drever, 1997; Gupta and Subramanian, 1998; Ramanathan et al., 1996; Abu-Jaber et al., 1997; Long et al., 1988, 1992). A previous analysis of the GTBW data with Q-mode factor analysis revealed that all sampling sites appeared to cluster together as a single population (Woodhams et al., 1998), and therefore data from all sampling sites could be used for R-mode factor analysis. For the R-mode factor analysis, biogeochemical data for each sampling point were merged with land use distributions for the corresponding sourceshed; the resulting database contained the proportion of each land use in the sourceshed contributing to the sampling point and biogeochemical data for the three sampling events. The database was struc-

**Table 1. Description of Level I Anderson land use–land cover classification scheme used in the Michigan Resource Information System database (MIRIS).**

Land use category	Description
Urban	Single and multiple unit residential areas; educational institutions; commercial and industrial areas; recreational facilities, such as marinas, fairgrounds, and sports complexes; transportation and utility infrastructure, mixed urban land, parks, zoos, landfills, golf courses, and cemeteries.
Agriculture	Cropland, pasture, orchards, vineyards, nurseries, confined feeding operations, and farmsteads.
Shrub–brush	Young shrub and brush, mature shrub and brush, and fallow cropland.
Forest land	Deciduous, evergreen, and mixed forest.
Water	Streams, lakes, reservoirs, bays, and estuaries.
Wetlands	Forested and nonforested wetlands.
Barren	Beaches, sand dunes, exposed rock, surface excavations, transitional areas, and mixed barren land.

tured so that columns contained biogeochemical and land use variables, and rows contained sample locations.

Factor analysis returns a quantitative assessment of the strength of a series of factors in explaining the variance of variables in the dataset (Gorsuch, 1974). These factors are based on eigenvalues derived from a correlation matrix (Davis, 1986; Evans et al., 1996). R-mode analysis requires that the number of factors be specified before the analysis; if the number of factors is not known prior to analysis, factors are retained based on subjective constraints imposed on the analysis by the modeler (Davis, 1986). We used the most common method for retaining factors when the actual number is unknown, which is to consider only those factors whose eigenvalues are greater than 1, the default procedure in SAS (e.g., Cody and Smith, 1997; Lee et al., 2001).

Interpretation of factors in the context of biogeochemical sources and processes can be difficult (Drever, 1997; Gorsuch, 1974; Child, 1990) and can be facilitated by rotating the factors in multidimensional space. Rotation can be either orthogonal or oblique. Varimax is a common orthogonal method that results in stronger factor loadings at the extremes (0 and  $\pm 1$ ), while oblique rotations (e.g., Promax) result in correlated factors and may improve the ability to interpret factors (Davis, 1986). A comparison of rotation methods indicated that the Promax rotation returned similar but slightly more easily interpreted factors than the Varimax procedure, so the Promax rotation was used for all analyses. Variable loadings are correlation coefficients between the variable and the factor. A loading close to  $\pm 1$  indicates strong correlation between a variable and the factor, while a loading close to 0 indicates weak correlation (Davis, 1986; Evans et al., 1996). Variables that exhibited a rotated loading greater than 0.5 were considered moderately loaded on a factor, while variables with loadings greater than 0.75 were considered strongly loaded on a factor. Values of 0.4 to 0.5 have been used as the lower end of moderate loading (Evans et al., 1996; Miller et al., 1997; Puckett and Bricker, 1992).

Factor analysis does not require normalized data sets as long as data are not excessively skewed (Child, 1990), but data transformation may result in an improved ability to interpret factors (Gorsuch, 1974). Data can be log-transformed (Schot and van der Waal, 1992; Cameron, 1996), rank-ordered (see Miller et al., 1997), or converted to z-scores with a mean of 0 and variance of 1 (see Ravichandran et al., 1996). However, the last method is not recommended for water quality studies in which the relative magnitudes of variables are important (Davis, 1986). Although raw GTBW data were not normally distributed, log-transformation did not noticeably improve the interpretability of factors from GTBW data and thus this transformation was not used. Rank order has the greatest influence on the correlation matrix upon which factors are based (Gorsuch, 1974). Log-transformation does not change rank order, so this normalization procedure has little effect on correlation coefficients. Because factor analysis should be most sensitive

to rank order, all factor analyses reported in this paper were performed on ranked data.

Most factor analyses reported in the literature use only water quality data to identify factors that explain the dominant controls on stream chemistry. In our research, factor analysis was performed on a database of land use and chemical variables to identify associations of land use and chemical species. Factors were calculated for each individual sampling event and for all events combined. We recognize that using land use distributions together with chemistry is a relatively novel approach that mixes two types of data (chemical concentrations and land use proportions). To investigate whether the chemical groupings, or fingerprints, remained the same if land use variables were excluded from the database, factor analysis was also performed on the combined biogeochemical dataset for all sampling events without land use variables. If our overall approach is able to link land use with process, the chemical associations we identify should remain the same whether we include or exclude land use.

## RESULTS AND DISCUSSION

### Variability of Baseflow Chemistry

The surface waters of GTBW are well buffered, with alkalinity values from 98 to 355 mg L<sup>-1</sup> HCO<sub>3</sub><sup>-</sup> and pH values from 7.39 to 8.58 (Table 2) over the three sampling events. The dominant cations are Ca<sup>2+</sup> and Mg<sup>2+</sup>, and the dominant anion is HCO<sub>3</sub><sup>-</sup>. The concentrations of other chemical species indicate that water is of good quality in this area. For example, dissolved oxygen levels are high, in some cases exceeding saturation, and the mean nitrate concentration for each sampling event ranges from 0.25 to 0.59 mg L<sup>-1</sup> NO<sub>3</sub>-N. The mean and median values exhibit small fluctuations, but the maximum values show more dramatic differences among sampling events (Table 2). The nonparametric Kruskal–Wallis test was used to test the hypothesis that populations from which the three datasets were drawn have equivalent means (Gilbert, 1987) (Table 2). A probability <0.05 indicates that the chemical parameter is significantly different over the three sampling events. Only Na<sup>+</sup> and Cl<sup>-</sup> concentrations were not significantly different at the 95% confidence limit. Baseflow chemistry varied significantly for most parameters over the three sampling events. This variability may be related to differences in flow and local inputs during each sampling event, and to seasonal effects (Clow et al., 1996; Puckett and Bricker, 1992).

**Table 2.** Minimum, maximum, and mean concentrations and chi-squared values from the Kruskal–Wallis test.

Variable	September 1997				May 1998				October 1998				$\chi^2$	Prob > $\chi^2$
	Minimum	Mean	Median	Maximum	Minimum	Mean	Median	Maximum	Minimum	Mean	Median	Maximum		
pH	7.39	8.05	8.06	8.41	7.44	8.16	8.17	8.58	7.64	8.09	8.09	8.54	8.0327	0.0171
Temperature, °C	8.50	12.1	12.7	17.9	9.53	15.0	14.6	23.9	6.78	9.92	9.52	15.2	77.4813	<0.0001
Alkalinity, mg HCO <sub>3</sub> L <sup>-1</sup>	98	199	192	323	163	236	232	310	172	235	215	355	17.402	0.0002
	mg L <sup>-1</sup>													
Dissolved oxygen	6.89	9.42	9.57	10.82	5.18	9.04	9.18	11.6	7.40	11.2	10.6	16.2	53.3642	<0.0001
Ca <sup>2+</sup>	49.3	71.5	68.4	101	41.0	62.6	60.0	94.0	36.3	58.7	53.5	84.1	21.3048	<0.0001
Mg <sup>2+</sup>	8.50	12.9	12.4	20.5	10.2	14.0	13.7	20.3	8.60	13.0	12	19.2	8.4402	0.0147
Na <sup>+</sup>	1.50	5.37	4.87	13.7	1.2	5.94	4.3	40.7	1.03	5.5	4.23	21.5	0.3439	0.842
K <sup>+</sup>	0.50	0.96	0.90	1.67	0.5	0.82	0.8	2.00	0.50	0.91	0.8	2.6	11.1779	0.0037
SiO <sub>2</sub>	4.20	9.14	8.6	20.6	2.5	7.42	7.6	10.2	2.45	9.79	9.75	21.6	60.8893	<0.0001
Cl <sup>-</sup>	0	13.1	9.96	45.4	0.68	10.5	6.87	76.0	0.54	10.7	7.32	43.1	1.8611	0.3943
SO <sub>4</sub> <sup>2-</sup>	0	18.2	17.1	73.4	2.93	9.36	8.65	24.7	4.86	12.8	10.4	48.1	8.0646	0.0177
NO <sub>3</sub> -N	0	0.25	0.12	0.94	0	0.58	0.33	2.45	0.01	0.59	0.31	2.7	14.4538	0.0007
F <sup>-</sup>	NA†	NA	NA	NA	0	0.23	0.19	0.78	0	0.17	0.10	1.89	16.5708	<0.0001

† Not available.

### Comparison of Factors from Three Sampling Events

For the comparisons (Table 3), there are no data for F<sup>-</sup> and dissolved oxygen (DO) concentrations in the September 1997 samples. Six factors had eigenvalues >1 for the September 1997 dataset and seven factors for May 1998 explained approximately 91 and 85%, respectively, of the variability in the land use—biogeochemistry databases. The six October 1998 factors explained nearly 100% of variability in the data (Table 3). The high percentage is likely a result of rounding during different stages of calculations and is not indicative of a perfect model.

The factors from the three analyses are not identical, although variable loadings on Factors I and II are similar among dates. Common variables in Factor I are proportion agriculture, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and alkalinity, all of which have positive loadings on the factor. Other variables that load positively in one or two of the analyses include proportion shrub–brush, K<sup>+</sup>, SiO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup>; proportion water and proportion forest have a negative loading when present in Factor I. For all sampling events, common variables with positive loadings on Factor II are Na<sup>+</sup>, K<sup>+</sup>, and Cl<sup>-</sup>. Sodium, potassium, and chloride also appear along with proportion urban in Factor III of the October 1998 sampling event. Positive loadings for proportion urban and temperature and a negative loading for proportion forest also appear but are not common to Factor II for all sampling events.

For all sampling events, Factors I and II are the only factors that are easily interpreted in the context of biogeochemical processes. We interpret Factor I as the biogeochemical fingerprint of agricultural activity and Factor II as the signature of halite dissolution. These factors appear in other analyses, and therefore our rationale for these interpretations will be discussed in greater depth below. The remaining factors are not consistent from date to date and are also more difficult to interpret.

Evans et al. (1996) also observed that factors from a multivariate dataset of water quality parameters (without land use variables) exhibited temporal variability, with different variables loading on a factor or with the

magnitude of a variable loading changing with season. They combined their data from different seasons into a larger database for factor analysis. This approach has the advantage of increasing the ratio of observations to variables that can improve interpretability of factors (Child, 1990). In fact, Evans et al. (1996) were able to include two new biogeochemical variables in their combined data analysis because the number of observations increased. The ratio of cases, or samples, to variables needed to produce factors with significant meaning is debated, with rules varying from 1:1 to 10:1 (Child, 1990). For the GTBW data, although the ratio of observations to variables for the individual sampling events does not violate any rules of factor analysis, a larger number of cases may produce clearer factors with better explanatory power. To test this hypothesis, factor analysis was conducted on a new dataset comprised of all data collected over the three sampling events.

### Factor Analysis of Combined Data from Three Sampling Events

By combining datasets from the three sampling events, the number of observations increased to 176, but 26 observations were omitted because of missing values. Factor analysis on the remaining 150 observations provided seven factors that explain approximately 88% of the variability of the data (Table 4). Proportion of agriculture exhibited strong loadings on Factor I, along with Ca<sup>2+</sup>, Mg<sup>2+</sup>, and alkalinity. Proportion of forest had a strong negative loading on Factor I, and K<sup>+</sup> and NO<sub>3</sub><sup>-</sup> had moderate positive loadings. Alkalinity, Ca, Mg, and K loadings on Factor 1 can be explained by the increased dissolution of soil minerals, such as calcite (CaCO<sub>3</sub>), dolomite [CaMg(CO<sub>3</sub>)<sub>2</sub>], and potassium feldspar (KAl<sub>3</sub>Si<sub>3</sub>O<sub>8</sub>), during soil cultivation. Other researchers have observed similar loadings of alkalinity, Ca, and Mg on a factor, which they interpreted as a mineral weathering signal (Schot and van der Waal, 1992; Puckett and Bricker, 1992); however, land use variables were not included in their analyses. Collins and Jenkins (1996) reported elevated base cation and bicarbonate concentrations associated with terraced agriculture and attrib-

Table 3. Factors for September 1997, May 1998, and October 1998 datasets. Factor loadings > 0.5 or < -0.5 are shown. Numbers in italic type indicate loadings > 0.75 or < -0.75. Cumulative percentage of variability in the data is explained by factors is shown in the last line.

Variable	September 1997						May 1998						October 1998							
	I	II	III	IV	V	VI	I	II	III	IV	V	VI	VII	I	II	III	IV	V	VI	
Urban	0.575	0.599	0.546	-0.543	0.634	0.833	0.670	0.7197			0.586			0.644	0.709	0.764				
Agriculture							0.672							0.631						
Shrub-brush							-0.760							-0.576	-0.766					
Forest							-0.553							-0.6536						
Water	-0.665				-0.552															
Wetlands			0.840					0.774												0.795
Barren				0.779																0.653
pH						0.667											0.753			
Dissolved oxygen													0.722							
Temperature													0.863							
Ca <sup>2+</sup>	0.886				-0.555															
Mg <sup>2+</sup>	0.843				0.505				0.698											
Na <sup>+</sup>		0.899					0.924							0.880	0.757					
K <sup>+</sup>		0.672	0.724				0.903							0.833	0.649	0.870	-0.645			
SiO <sub>2</sub>	0.766						0.906							0.833	0.914	0.504	-0.572	0.562		
Alkalinity	0.809						0.657							0.800						
Cl <sup>-</sup>							0.898													
SO <sub>4</sub> <sup>2-</sup>																				
NO <sub>3</sub> <sup>-</sup>																				
F <sup>-</sup>																				
Cumulative variance, %	21.8	39.7	54.5	67.2	80.3	91.1	26.5	42.4	56.5	70.4	78.0	85.4	85.4	27.7	50.1	67.3	83.8	94.5	~100	0.783

uted this effect to higher weathering rates of soil overturned during tillage. Other variables that load on Factor I in this analysis (K<sup>+</sup> and NO<sub>3</sub><sup>-</sup>) are frequently associated with agricultural activities, such as land applications of fertilizer and animal wastes.

Factor II had strong loadings of Na<sup>+</sup> and Cl<sup>-</sup> and moderate loadings of proportion urban and K<sup>+</sup>. As was suggested in the previous section, Factor II reflects the use of halite and potassium salts on roads, particularly in urbanized regions where road density is higher (e.g., Long and Saleem, 1974). There are other sources of Na<sup>+</sup>, K<sup>+</sup>, and Cl<sup>-</sup> in the watershed, such as wastewater and oilfield brines (Boutt et al., 2001), but these sources probably play a minor role in controlling the distribution of these ions across the GTBW. The molar ratio of Na<sup>+</sup> to Cl<sup>-</sup> in halite is 1:1; Fig. 5 shows that the majority of samples at the lower concentrations collected during the three sampling events fall near a line with a slope of 1:1, as would be expected if halite were the dominant source of these ions. Wastewater is enriched in Na<sup>+</sup> relative to Cl<sup>-</sup> (Vengosh and Keren, 1996), and therefore septic systems and animal waste may influence samples that lie above the halite line. A cluster of samples has excess Cl<sup>-</sup>, which could be the result of a number of processes. Sodium may exchange with soil pools of potassium, which may also explain the shift in the Na to Cl molar ratio toward Cl, as well as the association of potassium concentrations on this factor. A reduction in the Na to Cl ratio with time and/or distance as a result of the exchange of Na with other cations has been observed in studies of deicing salts (Rhodes et al., 2001; Shanley, 1994; Driscoll et al., 1991) and wastewater (Vengosh and Keren, 1996). Shanley (1994) summarized a series of studies reporting Na to Cl ratios of less than 1, with the lowest ratio equal to about 0.6. Therefore, even if halite is the dominant source of Na and Cl in the watershed, the molar ratio will vary spatially and temporally as a result of cation exchange. The sample sites with excess Cl<sup>-</sup> all occur outside Traverse City, and therefore may also be influenced by the application of brines to dirt roads. The typical Na to Cl ratio in brines from the GTBW region is approximately 0.61 (Wilson and Long, 1992) (Fig. 5). This ratio should also decrease due to cation exchange of Na<sup>+</sup> as brines move through the aquifer, which would explain Cl<sup>-</sup> enriched samples that fall below the brine line.

Temperature was inversely related to DO and SiO<sub>2</sub> concentrations in Factor III, with these three variables having strong loadings on the factor. Biological activity, particularly photosynthesis by diatoms, is probably responsible for this association of variables. As temperature rises, diatom productivity should increase, consuming SiO<sub>2</sub> (Wetzel, 1983). At the same time, the solubility of DO will decrease, so DO concentrations will also be lower as temperature rises. Warmer temperatures also increase respiration rates, and the combined effects of lower solubility and increased respiration may counteract the production of O<sub>2</sub> by photosynthesis at high temperatures. No particular land use showed significant association with this factor. Since we sampled the watershed from early morning to late afternoon, Factor III

**Table 4.** Factors for September 1997, May 1998, and October 1998 combined datasets with land use and without land use. Factor loadings  $>0.5$  or  $<-0.5$  are shown. Numbers in italic type indicate loadings  $>0.75$  or  $<-0.75$ . Cumulative percentage of variability in the data explained by factors is shown in the last line.

Variable	Combined data with landuse							Combined data without landuse				
	I	II	III	IV	V	VI	VII	I	II	III	IV	
Urban		<b>0.594</b>		<b>0.539</b>								
Agriculture	<b>0.879</b>											
Shrub-brush				<b>0.751</b>								
Forest	<b>-0.791</b>											
Water												
Wetlands					<b>0.746</b>							
Barren							<b>0.743</b>					
pH						<b>0.888</b>						<b>0.781</b>
Dissolved oxygen			<b>0.783</b>								<b>0.751</b>	
Temperature			<b>-0.870</b>								<b>-0.866</b>	
Ca <sup>2+</sup>	<b>0.775</b>							<b>0.807</b>				
Mg <sup>2+</sup>	<b>0.780</b>			<b>0.6158</b>				<b>0.899</b>				
Na <sup>+</sup>		<b>0.8892</b>							<b>0.864</b>			
K <sup>+</sup>	<b>0.600</b>	<b>0.7224</b>							<b>0.854</b>			
SiO <sub>2</sub>			<b>0.824</b>							<b>0.819</b>		
Alkalinity	<b>0.711</b>			<b>0.6148</b>				<b>0.869</b>				
Cl <sup>-</sup>		<b>0.8498</b>							<b>0.868</b>			
SO <sub>4</sub> <sup>2-</sup>							<b>0.640</b>					
NO <sub>3</sub> <sup>-</sup>	<b>0.503</b>					<b>-0.630</b>						
F <sup>-</sup>				<b>0.525</b>					<b>0.565</b>			
Cumulative variance, %	<b>23.1</b>	<b>30.0</b>	<b>51.7</b>	<b>64.5</b>	<b>72.0</b>	<b>80.7</b>	<b>87.8</b>	<b>26.6</b>	<b>49.9</b>	<b>68.8</b>	<b>81.1</b>	

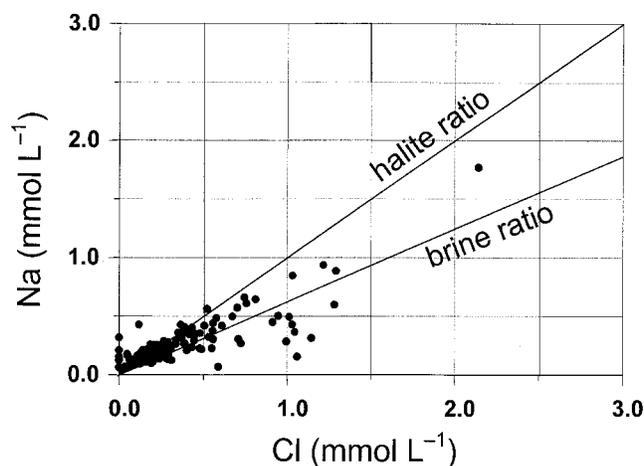
may reflect daily cycles in SiO<sub>2</sub> and DO concentrations in the streams.

Factor IV included proportion urban, proportion shrub-brush, Mg<sup>2+</sup>, alkalinity, and F<sup>-</sup>, with only shrub-brush exhibiting strong loadings. Weathering of disturbed soils in urban regions and shrub-brush may account for the associations of Mg<sup>2+</sup> and alkalinity with these land uses. The presence of fluoride is more difficult to explain. There is no major source of F<sup>-</sup> in the GTBW, but a significant anthropogenic source could be fluoridated toothpaste. In areas of the watershed without sewers, septic systems may be the principal source of fluoride to surface waters (Vengosh and Pankratov, 1998). Nonsewered residential areas in the GTBW include urban areas outside the Traverse City sewer system, pasture-shrubland that has been developed since the Michigan Resource Information System database, and forested land that has recreational housing. Proportion of wetlands and NO<sub>3</sub><sup>-</sup> had moderate but opposite loadings on Factor V that may be related to the reduction of nitrate in wetland environments.

The only variable that loads on Factor VI is pH, which suggests that pH is an independent factor controlling stream chemistry. Factors that load with a single variable can be difficult to interpret. Clow et al. (1996) explained the fact that nitrate was the only variable strongly associated with a factor as indicating that nitrate concentrations varied independently of other solutes. This is not the case with pH, which cannot vary independently of most of the other solutes we measured. More likely, so many processes influence the relationship between pH and other solutes that no other solutes have strong loadings on Factor VI.

Finally, proportion of barren and SO<sub>4</sub><sup>2-</sup> have moderate loadings on Factor VII. Atmospheric deposition is a major source of SO<sub>4</sub><sup>2-</sup> to watersheds of the Midwestern USA (Drever, 1997). Other sources in the GTBW may

include sulfate-bearing fertilizers, sediments, and bacterial oxidation of sulfur compounds (Sidle et al., 2000). Some farmers in the watershed also apply elemental sulfur to agricultural areas to reduce high soil pH, and copper sulfate is a commonly used pesticide in fruit production. Two major controls on sulfate mobility are the amount of anion exchange sites present in soil and biological uptake (Drever, 1997). In the GTBW the land use category "barren" is primarily beach, dunes, and unvegetated riverbank (Table 1), because there is very little exposed bedrock or quarries in the watershed. These areas probably have sandy soils with few exchange sites and little vegetation, and hence SO<sub>4</sub><sup>2-</sup> should be more mobile in this environment, leading to higher concentrations of SO<sub>4</sub><sup>2-</sup> associated with the barren land use category.



**Fig. 5.** Ratio of Na<sup>+</sup> to Cl<sup>-</sup> (mol L<sup>-1</sup>) in all samples for three sampling events. The Halite line represents the 1:1 molar ratio that would result from halite dissolution. The brine line represents the typical Na to Cl ratio in Michigan brines (Wilson and Long, 1992).

Previously published factor analyses of the dominant controls on stream chemistry rarely included variables representing land use or environmental attributes (Cameron, 1996; Evans et al., 1996; Miller et al., 1997; Clow et al., 1996; Puckett and Bricker, 1992). Our results link certain land uses with groupings of chemicals, and we are able to explain these relationships based on hydrological and geochemical processes. However, the combination of different types of data may influence factor loadings and thus the chemical associations within each factor. Therefore, we also conducted factor analysis on the biogeochemical data alone to examine whether groupings of chemicals were consistently loading together as factors both with and without the inclusion of land use variables.

### Factor Analysis of Combined Data without Land Use

Factor analysis was conducted on the combined, ranked biogeochemical data without land use proportions to investigate the effects of the use of different types of variables (land use and chemical concentrations) on factors (Table 4). The inclusion of chemical parameters only for factor analysis is the standard approach for most studies of stream chemistry that use factor analysis (Cameron, 1996; Evans et al., 1996; Miller et al., 1997; Puckett and Bricker, 1992; Clow et al., 1996). In our analysis of chemical variables, four factors were retained, each of which has a corresponding factor when land use proportions are included in the factor analysis. The first factor (Table 4) has strong loadings of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and alkalinity, and a moderate loading of  $\text{F}^-$ . This factor reflects mineral weathering, similar to the first factor in all the previous analyses. The association of  $\text{F}^-$  with this factor may indicate that areas with enhanced mineral dissolution resulting from soil disturbance are also experiencing the influence of septic systems. The second factor has strong loadings of  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cl}^-$ . This factor is similar to Factor II when land use is included, primarily reflecting the dissolution of halite, but also the potential influence of wastewater and brines. The third factor has strong positive loadings of DO and  $\text{SiO}_2$  and a strong negative loading of temperature, which is identical to Factor III in the previous analysis. As described above, this factor probably reflects biological productivity, primarily by diatoms. The final factor has a strong loading of pH, as in Factor VI of the analysis with land use. These results show that stream chemistry in the GTBW can be characterized by associations of chemical species that consistently load together on factors, whether or not land use variables are included.

### CONCLUSIONS

The primary objective of this research was to identify consistent biogeochemical fingerprints of land use in surface waters with baseflow synoptic sampling and factor analysis. Other researchers have used synoptic sampling to capture a watershed-scale representation of en-

vironmental conditions at a point in time. However, conclusions based on a single round of synoptic sampling may be compromised by temporal variations in stream flow and chemistry (Puckett and Bricker, 1992). To examine the effects of baseflow variability on the results of factor analysis, we conducted three synoptic sampling events and compared factors produced from each individual sampling event and from a combined dataset of all events. We included land use variables in the datasets used for factor analyses, which is a relatively new application of the statistical method to the study of land use-stream chemistry relationships.

The concentrations of all solutes measured in baseflow varied significantly among three synoptic sampling events that occurred over a period of two years, with the exception of sodium and chloride. Factor analysis of the datasets from individual sampling events yielded only two consistent factors that we attributed to agricultural activity and the dissolution of halite, respectively. The other factors retained in the analyses were not consistent among sampling events, and most were also difficult to interpret in the context of biogeochemical sources and processes. Our research suggests that the temporal variability of baseflow chemistry limits the usefulness of one-time synoptic sampling for identifying easily interpretable factors that describe the variability of stream chemistry.

Despite variability in baseflow quantity and chemistry over our study period, our results show that the effects of land use are expressed through changes in the relative abundances of major ions even in aquatic ecosystems that are relatively unimpaired by human activities. When all data were combined, the factor analysis produced a set of factors that could be clearly interpreted in light of biogeochemical processes. In the GTBW, agricultural activity is associated with elevated levels of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , alkalinity, and frequently  $\text{K}^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ . Urban areas are associated with higher concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cl}^-$ , probably as a result of road salting. These two relationships were apparent even within individual sampling events. When all data were combined, associations of  $\text{Mg}^{2+}$ , alkalinity, and  $\text{F}^-$  with urban areas and shrub-brush were revealed. This factor suggests that septic systems may be starting to affect the chemistry of streams in the GTBW, since there is no major natural source of  $\text{F}^-$  in the watershed. Wetlands were inversely related to nitrate concentrations, and further research may confirm the importance of wetlands in maintaining water quality in the GTBW. Barren lands were associated with elevated levels of sulfate, indicating that sulfate mobility may be higher in these areas than in other land uses. Factor analysis also helped identify the influence of temperature-dependent diatom productivity on the watershed's stream chemistry.

The results of this research suggest that an individual sampling event is unlikely to characterize adequately the complexity of processes controlling the interactions between land use and stream chemistry. The pathways of water to the stream may differ seasonally or with short-term variations in antecedent moisture conditions, and thus the water-rock, microbial, and dilution pro-

cesses that influence baseflow biogeochemistry are also likely to vary. Variability in baseflow chemistry may limit the usefulness of one-time synoptic sampling for characterizing land use–surface water quality relationships. The use of data collected over two years during three synoptic sampling events appears to enhance our ability to understand the processes controlling relationships between land use and stream chemistry. However, all analyses produced two similar factors that we believe are the biogeochemical fingerprints of agricultural activity and urban areas. More work is necessary to characterize the biogeochemical fingerprints of other land uses, which may be facilitated by comparing stream chemistry to more specific indicators of land use, such as housing, road and population densities, agricultural crop types and practices, the presence or absence of wastewater treatment facilities, and more refined land use classifications. Our analyses may also be improved by the use of ground water sourcesheds that better reflect flowpaths of ground water moving through a watershed. Riparian sourcesheds composed of all land within a given buffer width from surface waters may show that land use in close proximity to streams has a greater influence on stream chemistry than upland uses. Finally, historical land use patterns and the residence time of ground water within a watershed must be considered to account for the effects of land use legacy on baseflow chemistry.

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