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AN APPROACH FOR CHARACTERIZING THE BIOGEOCHEMICAL FINGERPRINTS OF LAND USE IN SURFACE WATERS: GRAND TRAVERSE BAY WATERSHED, MICHIGAN

By

Karen G. Wayland

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ABSTRACT

AN APPROACH FOR CHARACTERIZING THE BIOGEOCHEMICAL FINGERPRINTS OF LAND USE IN SURFACE WATERS: GRAND TRAVERSE BAY WATERSHED, MICHIGAN

By

Karen G. Wayland

The potential impact of land use on surface water is an important environmental issue, and a basic understanding of the geochemistry of a watershed undergoing rapid population growth can shed light on the processes through which surface water is affected over space and time. Data from four recent synoptic sampling events and a prior study were analyzed using graphics, statistics, geochemical modeling and groundwater flow and solute transport modeling to examine the relationship between land use and the geochemical evolution of surface and ground water. The concentrations of mineral-derived solutes (i.e., Ca^{2+}, Mg^{2+}, and HCO_3^-) remained relatively constant between groundwater and surface water, and also as water flowed downstream in the Boardman River. In constrast, human-derived solutes showed strong spatial variability. Cluster analysis showed four distinct geochemical fingerprints for surface waters. Waters with high relative concentrations of solutes were associated with agriculture and developed areas, while waters with low solute concentrations were found in forested regions. In the GTBW, Na^+, K^+, SO_4^-, NO_3^-N, and Cl^- appear to be important response variables to human disturbance. Factor analysis identified consistent associations between agricultural activity and Ca^{2+}, Mg^{2+}, alkalinity and frequently K^+, SO_4^{2-}, and NO_3^-. Urban areas were

associated with Na^+, K^+, and Cl^-. The use of data collected over two years appears to enhance our ability to understand the relationship between land use and stream chemistry.

Trace element data were collected using clean techniques to reduce sample contamination. Geochemical fingerprints for trace element cluster suggest that land use distributions alone are unable to explain spatial variability in trace element concentrations. Only Ba and Rb were strongly correlated to land use. Factor analysis of trace element data showed that redox processes may be important controls on the distribution of dissolved trace elements. Concentration profiles along the largest river in the watershed showed that Mn, V, Rb, and Ba behave like solutes of anthropogenic origin, while Sc, Sr, Fe, U, As, and Mo behave like mineral-derived solutes. The Rb/Sr ratio was used to identify areas of the watershed influenced by wastewater from septic systems or wastewater treatment facilities.

The influence of groundwater age on contemporary water chemistry needs to be accurately described to quantify the temporally varying impacts of land use on water quality. Approximately 70 percent of the watershed has a groundwater lag of 30 years or less. Variability in flush times is related both to the size of the sourceshed and its geology. The influence of a particular land use on stream chemistry changes depending on the time scale considered and on the sourceshed in question as a result of landscape diversity. The results suggest that land use management to reduce solute loading to a watershed may not result in water quality improvements for many years, especially if implemented on land far from streams. The influence of long groundwater flow paths that integrate past with current land uses must be considered in the interpretation of land use effects on surface water quality.

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DEDICATION

This dissertation is dedicated to Jack Clausen, my Master's adviser at The University of Connecticut, who saw something in me back then that I did not see in myself. Under Jack's continued mentorship, I have experienced professional and personal growth that is in large part responsible for where I am today.

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KEY TO ABBREVIATIONS

GTBW	Grand Traverse Bay Watershed
ICP-MS	Inductively coupled plasma-mass spectroscopy
MSU	Michigan State University
SI	Saturation index
USGS	United States Geological Survey

CHAPTER 1
INTRODUCTION

Changes in land use from historically undeveloped to agricultural and suburban/urban may be associated with increased imperviousness, loss of wetlands, higher road/traffic density, greater volumes of domestic wastewater, increased chemical use, physical changes to shorelines, and other factors that affect watershed hydrology and biogeochemistry. Aquatic ecosystems can be irreversibly altered by these development-induced changes in chemistry and hydrology; thus, an understanding of the relationship between land use, water movement through a watershed, and water quality is essential for mitigating the effects of land use intensification.

The influence of land use on surface and ground water quality is well documented in the literature. Schot and van der Wal (1992) observed increased solutes in groundwater resulting from urbanization and agricultural activity. Eckhardt and Stackelberg (1995) correlated the presence of groundwater contaminants with population density and agricultural, commercial, and medium to high residential land use. A review of nonpoint source pollution of surface waters concluded that agriculture and urban areas are the primary sources of N and P and that eutrophication of rivers, lakes, estuaries, and coastal waters is a widespread problem (Carpenter et al., 1998). Applications of salt and other chemicals for road de-icing have affected stream chemistry in many areas (Mason et al., 1999; Buttle and Labadia, 1999; Amrhein et al., 1993).

The advent of Geographical Information Systems technology (GIS) has facilitated watershed scale investigations of the relationship between land use and water quality. These investigations are either explanatory or predictive. The term predictive refers to the

use of GIS to model water quality based on measurements of land use/type/cover or geology only. Explanatory applications of GIS use data on land use *and* water quality to develop an enhanced understanding of the processes or factors that relate the two variables. Predictive applications of GIS include assessing aquifer vulnerability for contamination (Laurent et al., 1998); identifying patterns of land use change that may have the greatest impact on water quality (Wear et al., 1998); estimations of nitrogen loading at a watershed outlet over time based on export coefficients from different land uses (Mattikalli and Richards, 1996); and predictions of groundwater recharge and discharge from spatial distributions of aquifer properties, land cover type, and leaf area indices.

Many researchers have used GIS land use coverages and water quality data to correlate observed concentrations with particular land uses. Such applications can be considered explanatory in nature, even though in most cases the researchers were content to make a link between variables rather than exploring processes controlling land use-water quality relationships. Bauder et al. (1993) correlated nitrate concentrations with land use practices, specifically the distribution of dryland crop production and summer fallow. The effects of land use on aquatic biointegrity, defined by macroinvertebrate communities, were studied in seven tributaries of the Blackfoot River in Montana (Rothrock et al., 1998). The researchers found that stream conditions near agricultural sites were worse than conditions in multiple-use or silviculture sites. Wernick et al. (1998) used septic system and animal densities as indicators of residential and agricultural land use; in tributaries, only septic system density could be correlated to nitrate-N.

GIS modeling is rarely (if ever) coupled with geochemical, groundwater flow, and solute transport modeling in watershed studies of land use-water quality relations. Such a coupling would be a powerful explanatory use of modeling technologies as it allows an investigation of the evolution of ground water chemistry from recharge points to discharge points within a watershed in light of the land uses along the flow path. This proposal describes a research approach that utilizes GIS land use/cover databases, multivariate statistics, geochemical modeling, and MODFLOW and MT3D flow and solute transport simulations to explore factors controlling the chemistry of surface and groundwater in a rapidly developing watershed. The research is predicated on the hypothesis that different land uses produce unique multi-element biogeochemical fingerprints that can be identified, quantified, and used to elucidate the processes responsible for these signatures. If land use affects the biogeochemistry of streams and rivers in a predictable manner, the results of this research will facilitate watershed management programs designed to mitigate the environmental impacts of land use change. Furthermore, the approach used in this research can be adapted for use in other watersheds to collect information on the relationship between land use and water quality.

Literature Review

Biogeochemical cycles can be loosely defined as the movement and interaction of chemicals among the hydrosphere, lithosphere, atmosphere, and biosphere. The hydrology and chemistry of watersheds undergoing rapid land use transformation may be profoundly altered, often irreversibly, by human activities. Land use changes cause perturbations in biogeochemical cycling, either from direct inputs of anthropogenic

chemicals or disturbances and interactions of natural processes (Sidle and Hornbeck 1991). Patterns in surface and ground water chemistry are thus related to patterns of land use; both the form and abundance of chemicals may be affected by human activity (Helsel 1995). Human activities such as transportation, energy production, clear cutting, have disrupted natural biogeochemical cycles locally, regionally,and globally (Nriagu, 1996; Larocque and Rasmussen, 1998) and in most cases have resulted in increased loadings of both natural (e.g., nutrients, trace metals) and synthetic (e.g., chlorinated hydrocarbons) constituents to the environment (Hillery et al., 1998). To better understand factors necessary for sustainable development, indicators are necessary to assess the causes for the disruption of the biogeochemical cycles, current status and trends of the disruption, and ecosystem effects from the disruptions.

It appears that major ions can be indicators for natural inputs as well as pollution (Flintrop et al., 1996). Land use and land use change influence species diversity (Sala et al., 2000), nutrient cycling (Motavalli and McConnell, 1998), contaminant cycling (Moore et al., 1998), and surface water-groundwater interactions (Boutt et al., 2000). The resulting effect is that the natural chemical concentrations and distributions in various environmental media (air, water, soils, sediments, biota) have been disrupted (Donigan et al., 1993; Pekarova and Pekar, 1996; Field et al., 1996; Vengosh and Pankratov, 1997; Stone et al., 1998; Boyer and Groffman, 1996; Meissner et al., 1998). For example, it is well known that nutrient cycles such as for nitrogen and phosphorus are highly influenced by agricultural practices (Richards et al., 1993; Stone et al., 1998; Goss and Goorahoo, 1995; Tufford et al., 1998; Withers and Jarvis, 1998).

Nevertheless, such relationships are not always clear, thus making it difficult to construct quantitative models. For example, the disruption of biogeochemical cycles by agricultural and urban land uses can have apparent similar characteristics (Spahr and Wynn, 1997; Collins and Jenkins, 1996). Statistical modeling (regression) of stream chemistry and land cover does not fully explain relations (Herlihy et al., 1998; Battaglin and Goolsby, 1997). It is becoming apparent that various factors may mask relationships among land uses and environmental biogeochemistry. These include influences from local effects such as from microbial processes (Richards et al., 1993); regional effects such as the geologic framework (Allan and Johnson, 1997); hydrologic state and transport pathways (Pekarova and Pekar, 1996; Lapp et al., 1998); and trans-land use effects such as roads and septic systems (Mason et al., 1999; Vengosh and Pankratov, 1998). In addition, the lack of a more detailed biogeochemical characterization (i.e., few parameters) and legacy of land use further contribute to our current inability to fully quantify relationships among land use and environmental biogeochemistry.

As scale increases, the confounding effects of variations in geology, land uses, and ecotomes/ecoregions hamper the identification of land use-water quality patterns at the watershed level. Furthermore, chemicals behave differently in the environment, complicating the interpretation of patterns. For example, nitrate and chloride may both be released to the environment as a result of human activities, but chloride is generally considered conservative as it moves through groundwater, while nitrate can undergo a number of microbially-mediated transformations. Despite extreme variability of land use practices, chemical behaviors, and environmental settings, research has begun to establish water quality patterns associated with individual land uses. There is significant overlap

among patterns of different land uses, and to date, no land use has been characterized by a unique water quality signature. This may be due to the failure of previous research to consider signatures comprised of a large number of elements; the majority of land use/water quality studies reported in the literature have focused on the relationship between a few major ions--especially nutrients--and land use practices or covers. Only recently have analytical methods allowed for more comprehensive inventories of biogeochemical parameters (e.g., trace metals, synthetic organic compounds) associated with land uses.

One of the most widely measured water quality parameters is nitrate, not only because elevated concentrations pose serious health risks and are indicative of anthropogenic sources but also because of relative ease and low cost of measurements. Both urban and agricultural areas are associated with elevated nitrate concentrations in ground and surface waters (Helsel, 1995), but concentrations associated with agricultural areas are generally higher than in other areas (Herlihy et al., 1998; Spahr and Wynn, 1997). The agricultural land use category is broad, encompassing intensive swine farming, row cropping, orchards and pasture. Several studies have compared nitrate levels associated with particular farming practices. Miller et al. (1997) observed higher surface water nitrate concentrations in watersheds with row cropping than in pasture. Jaynes et al. (1999) found lower nitrate concentrations in streams draining agricultural land under corn-soybean rotation than under continuous corn cultivation, probably because fertilizer is only applied every other year in crop rotation schemes. In Australia's Rous River watershed, cane production was associated with the poorest water quality, although other crops, such as bananas, were associated with elevated

concentrations of some nitrogen species (Eyre and Pepperell, 1999). Surprisingly, Bauder et al. (1993) found no correlation between nitrate in ground water in Montana and areas under irrigation, but regions with a predominance of summer fallow exhibited strong correlation with elevated nitrate levels.

Nitrate is also an urban nonpoint source pollutant as a result of lawn fertilizers, pet waste, combined sewer overflows, and septic systems (Clawges and Vowinkel, 1996; Wernick et al., 1998). Clawges and Vowinkel (1996) sampled ground water in urban and agricultural wells and found the highest mean concentration of nitrate in urban residential areas. Other nitrogen species (TKN, ammonia) are also associated with agriculture (Helsel,1995), and to a lesser extent, urban land use (Horner et al., 1994). In general, nitrogen export from a watershed is inversely related to the percent of land in forest cover (Herlihy et al., 1998; Field et al., 1996), so nitrate concentrations should increase in watersheds where land is converted from forest to agriculture or urban uses.

Agriculture has been linked to elevated concentrations of other nutrients in surface and groundwater, particularly phosphorus and potassium, which are included in standard fertilizer mixes (Miller et al., 1997). Associations of land use and phosphorus are not as strong as the relationships observed for nitrate (Tufford et al., 1998; Eyre and Pepperell, 1999), probably because phosphorus is less mobile in the soil. Certain cations (calcium, magnesium) have also been linked to agricultural activity in such disparate regions of the world as the Potomac River Basin (Miller et al., 1997) and the Middle Hills of Nepal (Collins and Jenkins, 1996). Lime applications, the dissolution on carbonate soils, and ion exchange account for the association of calcium and magnesium with agriculture. Collins and Jenkins (1996) measured higher concentrations of the anions

bicarbonate, sulfate, and chloride in agricultural areas of the Himalayas as a result of soil weathering and fertilization. These results illustrate the importance of understanding how chemicals behave in the environment when interpreting biogeochemical signals of land use, as well as recognizing the influence of geological setting on surface water chemistry.

Herlihy et al. (1998) found that nutrients, acid neutralizing capacity, base cations, and especially chloride were the parameters most strongly correlated to land use. Chloride is a general indicator of human disturbance because its presence can be associated with both urban and agricultural land uses: road salt, animal waste, septic systems and sewage sludge, fertilizers and industry all contribute Cl loading to surface and ground water. In addition to elevated chloride levels, wastewater discharges to surface and ground water are associated with overall increases in major ions (Martinelli et al., 1999), trace elements such as boron (Eckhardt and Stackelberg, 1995), and changes in chloride:bromide and chloirde:fluoride ratios (Vengosh and Pankratov, 1998). The application of halite (NaCl) for road de-icing is a major source of chloride (Buttle and Labadia, 1999; Mason et al., 1999). Ion exchange of sodium releases other cations to the environment, so road salting can lead to high concentrations of calcium, potassium and magnesium as well as sodium and chloride (Mason et al., 1999). Road runoff also contains a myriad of other pollutants, such as metals (Perdikaki and Mason, 1999), nutrients, oxygen-demanding substances, petroleum hydrocarbons and synthetic organics (Horner et al., 1994; Thomson et al. 1997). These pollutants are generally associated with urban areas as well as highways (Long and Saleem, 1974; Horner et al., 1994).

The above discussion has focused primarily on patterns of major ions. However, thousands of organic chemicals have been released into the environment over the past

100 years and can be expected to exhibit spatial patterns linked to land use. The pesticides atrazine and alachlor have been measured in shallow groundwater wells in agricultural areas and in streams in an agricultural watershed (Jaynes et al. 1999). Because of the large number of possible chemicals present and the high cost of analysis, water quality monitoring programs infrequently include comprehensive screens for organics. We therefore have an incomplete understanding of the relationship between the production and use of organic chemicals, land use/land cover, and biogeochemistry.

The recent development of sensitive analytical techniques for trace elements, such as inductively coupled plasma mass spectrometry (ICP-MS), has allowed researchers to investigate associations between land use and trace metals that were once below the detection limits of most methods. This work is in its infancy and is expected to reveal new insights into the distribution of trace metals in the environment. Holsen et al. (1993) measured the dry deposition of trace elements to Lake Michigan; these elements were classified by suspected origin as crustal (Al, Ca, Fe, Mg, Si, Ti) or anthropogenic (Cd, Cr, Cu, Mn, Pb, V, Zn). The flux of both crustal and anthropogenic elements was highest over Chicago, intermediate in South Haven, Michigan (a small city), and lowest over Lake Michigan. Elevated concentrations of trace elements in soils and surface waters have been associated with wastewater discharges and industry (Flegal and Sanudo-Wilhelmy, 1993; Sanudo-Wilhelmy and Flegal, 1992); forestry (Mayer, 1998); and agricultural activity (Goulding and Blake, 1998).

Watershed researchers are beginning to use more specific descriptors of the type and intensity of human disturbance in analyses of spatial and temporal trends in water quality across a mixed-use landscape. Land use categories, such as "urban," "forest," and

"agriculture," may be further broken down into variables that describe the land use in greater detail. Miles of road, building density, population density (Bolstad and Swank, 1997), septic system and animal unit density (Wernick et al., 1998) have been related to changes in environmental indicators and further our understanding of the underlying processes that control water chemistry within a particular land use category. As discussed above, agricultural researchers have already noted correlations between particular types of agricultural practices and elevated nutrient levels. The development of GIS technologies has greatly facilitated these analyses, which allows not only for correlations of land use intensity factors with water chemistry but also the study of how distance to water bodies affects these correlations. Tufford et al. (1998) found that nutrient concentrations were more strongly correlated to land cover near stream channels than land uses farther from the channel.

The more recent literature described above follows a new direction in watershed research described by Sidle and Hornbeck (1991) as the "cumulative effects" approach. Such an approach considers the mosaic of land uses in a watershed in combination with geology and naturally occurring solutes to explore how the biogeochemistry of waters changes through a watershed. While it is common to report the effects of individual land uses, only recently have researchers tackled our limited understanding of biogeochemical processes at work as water moves through complex landscapes (Sidle and Hornbeck, 1991). The study of cumulative effects falls in the province of landscape geochemistry, in which the traditional geological approach of mapping and classification is coupled with modeling, statistics, and the methodology of other disciplines (Fortescue, 1990). A major objective of landscape geochemistry is to "provide global databases on the behavior of all

elements (and associated geochemical entities) in landscapes" by studying the interactions of the lithosphere, hydrosphere, atmosphere, and biosphere (Fortescue, 1990).

Research Hypothesis

The goal of this research is to provide an enhanced understanding of the cumulative effects of disturbed land and natural systems on surface water chemistry in a watershed undergoing rapid population growth. ***The working hypothesis is that the effects of land use on the biogeochemistry of streams can be quantified and that an individual land use category has a unique biogeochemical signature or fingerprint.*** If true, then as changes in land use occur, biogeochemical changes that may occur in a watershed can be predicted.

A crucial assumption of this research is that land use fingerprints can be observed by measuring biogeochemical parameters in surface water during baseflow conditions. In humid regions, groundwater discharges to streams and rivers year-round. The chemistry of baseflow thus provides an integrated signal, or fingerprint, of the historical climate, geology, and land use along the groundwater flow path from recharge to discharge areas.

Specific predictions about land use signatures in the Grand Traverse Bay Watershed can be made based on previous work in this watershed and similar work reported in the literature. An urban signature should be characterized by high nitrate levels resulting from lawn fertilizers, wastewater discharges, industry, and construction sites; high chloride from wastewater and road salting; high lead concentrations from paints, structures, and leaded gasoline; and high metals associated with industry, infrastructure, and vehicles (e.g., Cu, Cr, Cd). The trace metals signature of urban areas is

difficult to predict because few studies have reported concentrations for a wide range of elements or land uses. However, the source of enriched concentrations of most metals in surface waters is anthropogenic (Moore, 1990), therefore urban areas should exhibit a biogeochemical signature that has generally higher overall metals concentrations than agricultural or forested land uses, while individual metals (e.g. Cu and Zn in forests) may be higher in other land uses. This research can make a significant contribution to the literature by reporting the distribution of trace elements at low concentrations across a watershed with different land uses.

Wastewater appears to be a significant source of both contaminants and naturally occurring elements in surface water. Domestic wastewater that is treated in municipal plants may lower the concentrations of some of these elements when compared to wastewater discharged to septic systems. Therefore, there may be two distinct signatures from urban areas: one associated with sewered areas, and the other associated with residential zones on septic sytems. Elemental ratios (Na: Cl and Rb:Sr) may provide more information on sources of contamination for the interpretation of biogeochemical fingerprints, especially when concentrations of individual elements cannot be uniquely paired with a land use.

Agricultural areas should be associated with high Ca, Mg, and alkalinity levels because land cultivation increases the dissolution of soil minerals, particularly carbonates that predominate in the glacial tills of the watershed. Nitrogen levels should be high but may not exceed those of urban areas, and therefore may not distinguish an agricultural signature from those of other land uses. Potassium and other minor nutrients added in fertilizers should be higher in agricultural areas, as should sulfate when nutrients are

added to soils as sulfate salts. Copper and other trace metals may show correlations with agriculture because of the metals in pesticides and animal feed. In addition, soil acidification in agricultural areas increases the mobility of metals. However, GTBW soils have relatively high buffering capacity and farmers may apply lime, so soil acidification and the resultant enhanced mobility of metals may be more important in forested areas with high biomass growth and export.

Forested areas should have a biogeochemical fingerprint characterized by lower levels of most chemicals than urban or agricultural land. The exception may be some metals (e.g., Cu and Zn) that move with DOC or are mobilized as soils become acidified by acid deposition and the decomposition of organic matter. Wetlands may also be associated with elevated levels of some metals because these areas are characterized by strong redox- and pH-gradients that affect the mobility of metals. The presence of these gradients should also result in strong associations of DO and pH with the area of wetlands in sourcesheds.

Research Approach

The working hypothesis of this research is that the influence of land use on the biogeochemistry of streams can be quantified and that certain types of land use have a characteristic biogeochemical signature or fingerprint. This hypothesis will be explored through intensive sampling, groundwater and geochemical modeling, and the use of GIS databases of land use distributions. While other research has linked land use to elevated concentrations of a limited number of ions, this research is one of the first multi-element, quantitative characterizations of land use chemical fingerprints. The use of many

biogeochemical indicators should result in a better characterization of the relationship between land use and chemical concentrations in rivers. The analysis presented in this proposal is a step-wise approach for obtaining robust biogeochemical signatures for individual land uses and understanding the geochemistry of a mixed-use watershed.

Chapter 2 provides a basic description of the geochemistry of the study watershed, with an emphasis on linking the spatial and temporal distribution of major ions in surface and ground water with land use patterns. Cluster analysis, statistical comparisons, saturation indices, solute-solute plots and concentration profiles along the watershed's major river shed light on the geochemical evolution of water as it moves through the landscape. Chapter 3 focuses on the processes that control solute distributions in surface waters. The primary analytical tool in Chapter 3 is factor analysis.

Thorndike (1978) wrote of the difference between cluster analysis and factor analysis:

> One of the important differences between cluster analysis and factor analysis is that a variable is assigned to only one cluster, whereas factor analysis...breaks up the variance of a variable into several additive parts. This means that cluster analysis is the proper technique to use when the analysis goal is to build up something, for example, a scale, from several smaller somethings, for example, items. On the other hand, factor analysis is properly used when the objective is to break down the variance of a scale or item into independent parts. We may say that cluster analysis is a method of synthesis, whereas factor analysis is a method of *analysis*.

Cluster analysis is used in Chapter 2 to reduce the complexity of a large, multivariate database by finding similarities among sample sites, while factor analysis is used in the Chapter 3 to reduce the database into a smaller number of factors that explain the variability in the chemical data. Chapter 4 presents the results of ultra-clean sampling for trace elements. No previously published work, to my knowledge, has described a watershed-scale synoptic sampling of stream waters for such a wide range of trace

elements. This dataset is unique, and therefore a chapter is devoted specifically to exploring these data with both cluster and factor analysis and the methods used in previous chapters.

Chapters 2-4 developed statistical relations between land use and stream chemistry variables using a static database of land use distributions. This approach does not take into account the dynamic nature of solute loading to watersheds as land uses change with time. Baseflow in streams is comprised of ground water of varying age, and thus the chemistry of baseflow reflects a time-weighted average of anthropogenic inputs. The use of a "snapshot" land use distribution from one point in time cannot account for the lag time for solutes to travel from the land surface to discharge points at streams and lakes. Chapter 5 describes the first step in understanding how historical land use patterns affect current stream chemistry, which is the development of a groundwater flow and solute transport model that predicts the travel time of water moving through the study watershed.

CHAPTER 2
CHARACTERIZING THE CUMULATIVE EFFECTS OF HUMAN INFLUENCES AND NATURAL PROCESSES ON THE GEOCHEMISTRY OF A WATERSHED UNDERGOING RAPID POPULATION GROWTH

Abstract

The potential impact of land use on surface water is an important environmental issue, and a basic understanding of the geochemistry of a watershed undergoing rapid population growth can shed light on the processes through which surface water is affected over space and time. Data from three recent synoptic sampling events and a prior study were analyzed using graphical and statistical methods to examine the geochemical evolution of surface and ground water. The results show that concentrations of most solutes differ significantly over the short-term, and may show long-term variability. Solute-solute plots indicated that the synoptic sampling events captured baseflow when groundwater inputs dominate stream flow. The concentrations of mineral-derived solutes (i.e., Ca^{2+}, Mg^{2+}, and HCO_3^-) remained relatively constant between groundwater and surface water, and also as water flowed downstream in the Boardman River. In constrast, human-derived solutes showed strong spatial variability. Cluster analysis showed four distinct geochemical fingerprints for surface waters. Waters with high relative concentrations of solutes were associated with agriculture and developed areas, while waters with low solute concentrations were found in forested regions. In the GTBW, Na^+, K^+, SO_4^-, NO_3^-N, and Cl^- appear to be important response variables to human disturbance.

Introduction

The influence of watershed geology and landscape characteristics on stream chemistry is well documented (Herlihy et al. 1998; Puckett and Bricker 1992; Spahr and Wynn 1997; Collins and Jenkins 1996; Evans et al. 1996; Miller and Hirst 1998; Clow et al. 1996; Dow and Zampella 2000), and thus the potential impact of land use on surface water has become an important environmental issue. Land use change has been identified as the most critical driver of biodiversity losses (Sala et al. 2000) and the most serious threat to lotic ecosystems (Allen and Flecker 1993). Agriculture, forestry operations, urbanization, and rural development affect watershed hydrology, vegetative cover, and terrestrial-aquatic linkages (Allen and Flecker 1993). To quantify changes in natural watershed conditions resulting from land transformation, one must have an understanding of the natural and human-influenced processes through which surface water is affected over space and time. A basic research need for furthering this understanding is the study of the geochemistry in disturbed watersheds and empirical studies of key watershed response variables (Sidle and Hornbeck 1991).

Land use change can have subtle effects on watershed geochemistry that may not become apparent over the timeframe in which changes in the landscape occur. It is therefore desirable to have long-term records of water chemistry to understand the temporal effects of land use change on geochemical processes at the watershed scale (Miller and Hirst 1998). However, the expense of collecting detailed chemistry data often prevents long-term continuous monitoring of watershed conditions. This paper describes an approach to watershed sampling and data analysis that allows us to characterize the geochemical evolution of water as it moves through the landscape

without intensive long-term monitoring. We used data from three synoptic sampling events and various graphical and statistical methods to explore the spatial and temporal variability of solutes in a watershed undergoing rapid population growth. The existence of surface and ground water chemistry data from a previous study in one region of the watershed (Cummings et al. 1990) allows us to make some additional comparisons of watershed conditions over a longer time scale. Our approach provides insight on the processes that control surface water chemistry, including the effects of human activities in the watershed, and also produces a robust set of data against which future data collection efforts can be compared to identify long-term trends in watershed geochemistry.

Study Site

Grand Traverse Bay and its watershed (Figure 2.1), located in the northwestern portion of Michigan's Lower Peninsula, are important natural and economic resources for the Great Lakes Region for their great scenic beauty, quality of waters, and recreational opportunities. Grand Traverse is one of the last remaining oligotrophic bays in Lake Michigan, and more than 55 of the over 250 miles of stream are highly prized for trout fishing. Superimposed on this relatively healthy ecosystem is a population growth rate that has been consistently higher than the national average (Michigan Information Center, 1997). The Grand Traverse Bay Watershed (GTBW) was chosen as the research site because of the region's strong population growth and because the GTBW has a diverse landscape, allowing us to examine the influence of different land uses on water chemistry. Furthermore, some data on past biogeochemical conditions and land use are

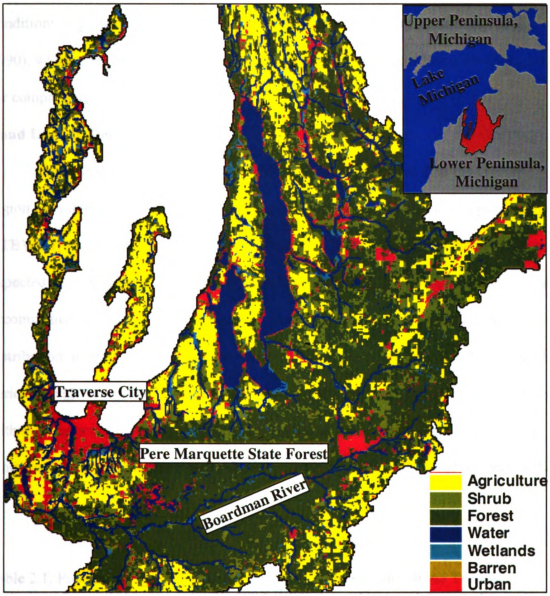

Figure 2.1. Location of Grand Traverse Bay Watershed, Michigan, and land use in the watershed. Land use distribution is from the 1980 MIRIS database (Michigan Resource Inventory System, State of Michigan Department of Natural Resources).

available. In 1985-86, the USGS conducted a study of the chemical and physical conditions of ground and surface water in Grand Traverse County (Cummings et al. 1990), which comprises a large region of the watershed, thus providing a small dataset for comparison with current conditions.

Land Use and Demographics

In the years since the USGS study of 1985-86, the population in the GTBW region has increased by more than 24%. The six contiguous counties encompassing the GTBW have experienced a growth rate of 42% from 1980 to 2000, and the population is expected to increase by 22% from 2000 to 2020 (Table 2.1). This population growth is accompanied by shifts in land use and land cover. Figure 2.1 shows the land use distribution in 1980. Land use/land cover in GTBW is predominantly forest (49%) and agriculture (20%). Urban land use comprises about 6% of the total area of the watershed, with the Traverse City urban region located on the shores of Grand Traverse Bay. The other main land cover categories are shrub/brush (15%), water (9%), and wetlands (1%).

Table 2.1. Population figures for the six counties comprising the Grand Traverse Bay Watershed. Percent change is (2000 – 1980)/1980, as per Census Bureau method. Data compiled from the Michigan Information Center, State Budget office (www.state.mi.us/dmb/mic) and the U.S. Census Bureau.

	Population				% Change	Projected
County	1970	1980	1990	2000	1980-2000	2020
Antrim	12,612	16,194	18,185	23,110	42.7	27,700
Charlevoix	16,541	19,907	21,468	26,090	31.1	31,300
Grand Traverse	39,175	54,899	64,273	77,654	41.4	99,600
Kalkaska	5,372	10,952	13,497	16,571	51.3	21,200
Leelanau	10,872	14,007	16,527	21,119	50.8	22,200
Total	**84,572**	**115,959**	**133,950**	**164,544**	**41.9**	**202,000**

Despite the rapid population growth of the last 20 years, only about 5% of the land in this 2600-km^2 watershed has undergone land use change (*unpublished data???*), primarily because approximately 50% of the landscape is protected state forestland. Therefore, the growing population will probably result in intensification of land use in the other 50% of the watershed in future years.

Geology and Hydrology

The 2600-km^2 watershed contains over 100 lakes, including the Torch and Elk Lakes systems. The Boardman River is the main tributary draining the GTBW and exerts a strong influence on groundwater flow and gradient in the southern half of the watershed (Boutt et al. 2001; Cummings et al. 1990). The surficial sediments of the watershed, which can be as thick as 900 feet, are predominantly glacial outwash, till, lacustrine sand and gravel, and dunes, all of which overlay shale and limestone bedrock (Cummings et al. 1990; Boutt et al. 2001). The water table is close to the surface, and drinking water wells screened in the outwash and lacustrine deposits are from 50 to 150 feet deep and produce at least 20 gallons per minute (Cummings et al. 1990). The water table fluctuates seasonally, with highest levels in the winter and spring and lowest levels in the summer (Cummings et al. 1990). 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.

Water Quality

Limited research has been conducted in GTBW to examine the relationship between land use and water quality on a watershed scale. A 1978 report linked cherry orchards to high nitrate concentrations in wells in some areas of the watershed (Rajagopal

1978). The USGS study of Grand Traverse County in 1985-86 documented potential correlations between nitrate concentrations in groundwater and nitrogen loading from precipitation, animal waste, septic tanks, and fertilizers (Cummings et al. 1990). The USGS results also suggested a possible effect of oil field brines on groundwater quality; in areas with more oil wells, Cl^- concentrations were significantly higher than in other areas of Grand Traverse County. A regional groundwater flow and solute transport model was developed for the GTBW to simulate the flux of Cl^- from roads into Lake Michigan (Boutt et al. 2001). An important conclusion of this model is that the dissolution of halite, probably from road salt, appears to be the most significant source of Cl^- to surface waters. However, halite dissolution alone cannot account for observed Cl^- concentrations at many stream sites, thus wastewater and oilfield brines likely also contribute Cl^- to surface waters. Our recent work (Wayland et al., in press) has identified tentative associations between: Ca^{2+}, Mg^{2+}, K^+ and agriculture; Na^+, Cl^-, and urban areas; and F^- with shrub/pasture areas, possibly as a result of fluoridated toothpaste from septic systems.

While scant data exist on conditions within the watershed, Grand Traverse Bay has been studied more intensively, and a 1998 summary of conditions in the bay indicated that the water quality in nearshore areas has deteriorated as a result of nutrient loading from the watershed (GTBWI 1998). The GTBW Initiative has identified three major threats to the health of the bay: inputs of nutrients, sediment, and toxic substances; the effects of land use and land use management decisions on those inputs; and exotic species (GTBWI 1998). With the exception of exotic species invasions, the roots of these problems lie in the watershed and are common to entire the Great Lakes drainage basin

and beyond, and thus our approach to the study of land use and water chemistry has broad applicability.

Methods

Sampling

Streams and ground water in the GTBW were sampled during synoptic sampling events over the period of 1998-2000 by Michigan State University (MSU) in conjunction with USGS researchers. Because the MSU study was intended in part to compare current conditions with geochemical data collected in 1985-86 by the USGS (Cummings et al. 1990), the earlier USGS sampling design was the starting point for locating sampling points for this research (Figure 2.2). Twenty-seven of the original 34 wells installed for the 1985-86 USGS study (Cummings et al. 1990) could be located and/or opened for resampling of groundwater in August 1998. The USGS study focused on Grand Traverse County, rather than the entire Grand Traverse Bay Watershed, so additional stream sampling sites were added to the MSU study design. Initially, a total of 80 locations representing a range of land uses within the watershed were identified as surface water sampling sites (Figure 2.2). These locations included 13 of the sites originally sampled by the USGS in the 1985-86 study (Cummings et al. 1990); USGS stream sites outside the watershed boundary were not sampled for the MSU research. Sampling sites were located at bridges or other easily accessible locations to facilitate the rapid collection of samples. Three crews of two-four people each were necessary to visit the sites across the watershed in 2.5 days. Sampling occurred in May 1998, October 1998 and October 2000, during low-flow conditions when groundwater was assumed to be the dominant source of

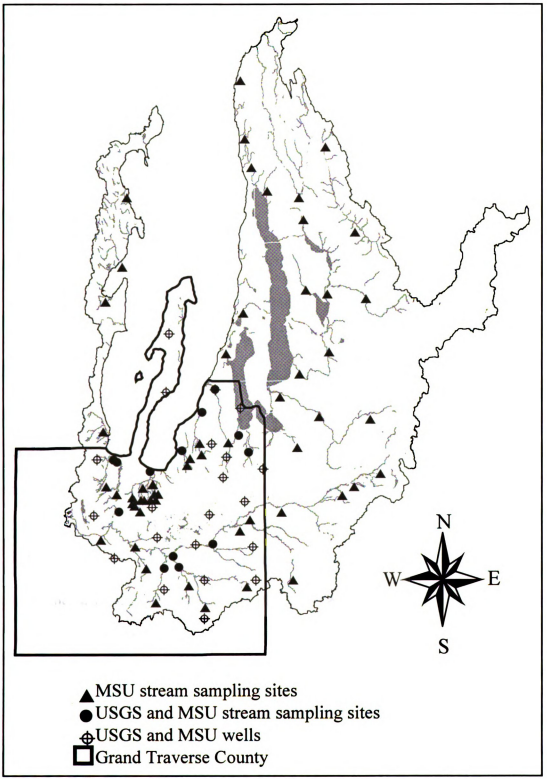

Figure 2.2. Location of surface and ground water sampling sites in the Grand Traverse Bay Watershed

water in streams. Since some sampling sites were either dry or inaccessible during each of the synoptic sampling events, stream samples were collected from between 50 to 70 sites for each date.

At each stream site, samples were taken from the thalwag portion of the river. Sample bottles were rinsed three times with river water before samples were taken. Wells were purged with a bladder pump until specific conductance and pH were constant before sample bottles were rinsed and filled. Dissolved oxygen, temperature, conductance, redox potential, and pH were measured at each site with a YSI or HydroLab multi-parameter probe. Specific conductance and redox potential are not included in this analysis because of the number of missing values. Alkalinity was determined at each sample site by potentiometric titration. As necessary, samples were filtered (0.45 μm acid-washed Millipore filters), acidified with nitric acid to a pH of 2 (cations), preserved with formaldehyde (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.

In addition to the field measurements described above, all samples were analyzed for Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SiO_2, Cl^{-}, F^{-}, Br^{-}, NO_3^{-}, and SO_4^{2-}. Cations were analyzed by flame atomic adsorption (Perkin-Elmer 5100 PC). Chloride and fluoride were analyzed by specific ion electrode or capillary electrophoresis (Hewlett Packard 3DCE). Bromide, nitrate, and sulfate were determined by capillary electrophoresis. Bromide concentrations were below the detection limit for most sites, therefore no bromide data are included in this analysis. Silica was determined by colorimetry (Milton Roy Spectronic 1001 uv-vis) or as silicon by inductively coupled plasma-mass spectrometry (Micromass Platform with concentric nebulizer).

Data Analysis

Temporal changes in surface and ground water chemistry were examined using non-parametric statistical methods. Differences between the USGS and MSU groundwater datasets were analyzed with the Wilcoxon rank sum test. The Kruskal-Wallis test for more than two datasets was used to test for significant differences in the stream chemistry data. Data from 13 stream sites within the GTBW sampled in June 1986 (Cummings et al. 1990) were compared to data collected by MSU at the same sites on May 1998, October 1998, and October 2000. Data from all sites sampled by MSU during these dates were also compared with the Kruskal-Wallis test. In both cases, if the test indicated that a parameter was significantly different from date to date, Tukey's studentized range test was used to identify which dates were significantly different from the others. The Tukey test is a parametric method but is more robust to non-normal data than other methods of distinguishing differences among more than two datasets (Zar 1999). All significance tests were performed with SAS software (SAS Institute, Cary, NC).

To examine the spatial distribution of geochemistry in the GTBW, cluster analysis on the MSU surface water data was conducted using JMP (SAS Institute Inc.). Cluster analysis is a multivariate technique that can identify similarities among sample sites based on correlations of groups of parameters (Thorndike 1978). Clusters were created using Ward's method for building dendograms, or cluster tree, through hierarchal clustering. The cluster analysis was done on the datasets from each individual sampling date. The number of clusters was determined subjectively by choosing obvious groups within the cluster tree; for all dates, four clusters were identified. JMP then assigned

each cluster in the analysis a unique number, and all sample sites in that cluster were labeled with this number. For each date, sample sites were sorted according to the cluster number, and a median value for all parameters in each cluster was calculated. The clusters could then be compared visually to determine which chemical parameters were responsible for cluster membership by graphing the log of the ratio of the median cluster value to the median value for all MSU stream data. Cluster numbers were also mapped for each date using the GIS software package ArcView (ESRI, Inc., Redlands, CA).

The software program AquaChem (Waterloo Hydrogeologic, Waterloo, Ontario) was used for calculating saturation indices and creating Piper diagrams.

As the next step in understanding how water chemistry evolves as it moves through the GTBW, solute concentrations in groundwater and stream samples were graphed in diagrams similar to those used in end member mixing analyses (Hooper et al. 1990; Christophersen et al. 1990; Kleissen et al. 1990; Pionke and DeWalle 1994). In this type of analysis, streamwater chemistry is considered to be a result of the mixing of different endmembers, such as groundwater and the soil solution. These solute-solute diagrams can provide insight on potential sources and processes that control solutes concentrations in streamwater (Pionke and DeWalle 1994) and can give rise to hypotheses concerning other sources affecting stream chemistry that may not have been sampled (Hooper et al., 1990; Christophersen et al., 1990; Kleissen, 1990). Diagrams are constructed as 2-D plots of one solute against another (Hooper et al., 1990) for all sampled end-members. Mixing analysis is typically based on the assumption that the chosen solutes behave approximately conservatively; interpretation of the plots can account for some deviations from conservative behavior (Kleissen, 1990). Hooper and

others (1990) chose six solutes for the analysis (alkalinity, SO_4^{2-}, Na^+, Mg^{2+}, Ca^{2+}, and SiO_2) to represent acid-base reactions and weathering plus ion exchange that affect the evolution of stream chemistry. Chloride was not included in Hooper et al.'s analysis because its main source was atmospheric input and concentrations were therefore constant with depth. In the case of the GTBW, chloride was included in mixing diagrams because its distribution is not constant spatially or temporally (Chapter 3). Magnesium and calcium are so closely correlated in the GTBW that calcium was assumed to act as a surrogate for magnesium, which was then excluded from the analysis. In our analysis, we have chosen solutes that do not necessarily behave conservatively in the GTBW (e.g., SiO_2 and SO_4^{2-}) but should not be affected by terrestrial vegetative uptake, as a means of understanding natural and anthropogenic processes that affect watershed geochemistry. Saturation indices of ground and surface water, as well as plots of concentration changes with distance downstream for the Boardman River, illustrate the continued chemical evolution as water moves through the watershed.

Results

Temporal Changes in Geochemistry

The temporal variability of stream and groundwater chemistry was evaluated with both graphical and statistical methods. The Piper diagrams in Figure 2.3 show that the general chemistry of groundwater in the GTBW has not noticeably changed since the USGS study. Groundwater in the watershed is of a Ca^{2+}-HCO_3^- type, with a few wells showing higher proportions of Na^+ and Cl^- relative to other major ions. The mean and

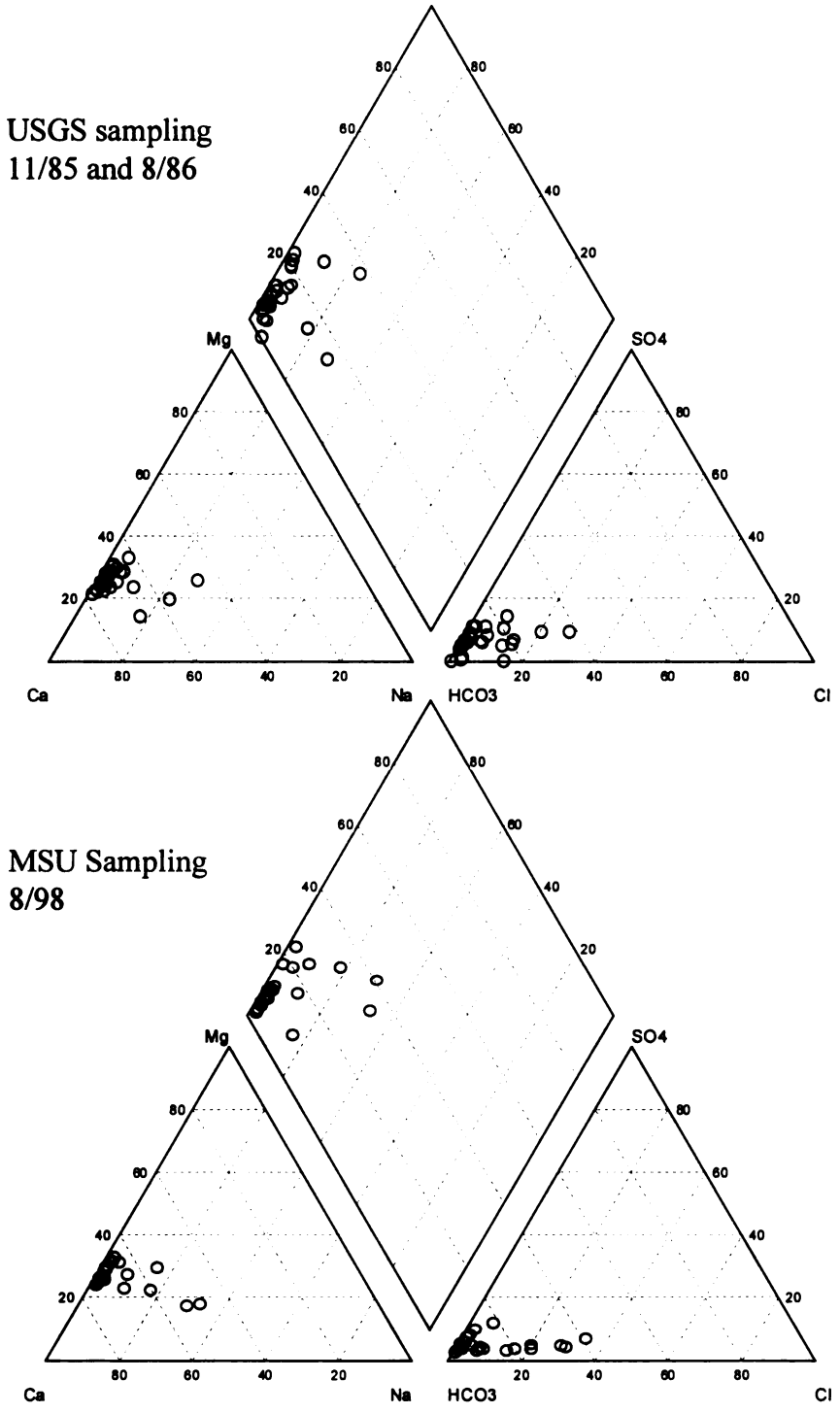

Figure 2.3. Piper diagrams for wells in the Grand Traverse Bay Watershed.

median values of measured parameters for both studies are listed in Table 2.2. The nonparametric Kruskal-Wallis test revealed that only pH and Cl^- concentrations are significantly different ($p < 0.05$) between the 1985-86 and the 1998 samplings (Table 2.2). Mean and median chloride concentrations measured in groundwater during the MSU sampling were higher than during the USGS sampling, while pH values were lower. Temperature was not included in the Kruskal-Wallis test because the USGS sampled in November and August, and the potential difference in air temperature between the two sampling periods could have influenced the measured temperature of groundwater as it was pumped to the surface.

Surface water in the GTBW is dominated by Ca^{2+}, Mg^{2+}, and HCO_3^-, with some sites showing relatively greater influence of Na^+ and Cl^- (Figure 2.4), as suggested by our earlier work (Boutt et al., 2001; Wayland et al., in press). Most sampling sites fall within a tight cluster on the Piper diagrams in Figure 2.4. Long-term temporal changes in stream chemistry were evaluated by looking at data from the 13 sites common to both the USGS and MSU studies (Table 2.3). The Kruskal-Wallis test indicates that only pH and SiO_2 show significant differences ($p < 0.05$) across sampling dates (Table 2.4a and 2.4b). Dissolved oxygen was not included in the Kruskal-Wallis test because of its dependence on temperature and its diurnal cycling with photosynthetic activity. Tukey's test reveals that pH was significantly different between June 1986 and October 1998 (Table 2.5). Silica concentrations differed for all sampling date combinations except June 1986 and May 1998.

Table 2.2. Comparison of well concentration data from USGS and MSU studies. Shaded areas indicate variables that are significantly different between the two sampling dates.

	USGS study		MSU study		Wilcoxon Rank Sum Test		
Variable	Median	Mean	Median	Mean	Z-score	Pr>Z	n (USGS, MSU)
pH	7.7	7.73	7.58	7.54	-2.5927	0.0095	33, 27
Temperature (°C)	9	8.45	9.85	10.15	not included in analysis		
Ca, dissolved (mg/l)	58.5	62.68	53	56.32	-0.9657	0.3342	34, 27
Mg, dissolved (mg/l)	13	14.79	13.55	13.5	-0.4140	0.6789	34, 27
Na, dissolved (mg/l)	2	4.06	1.99	6.2	-0.4502	0.6526	34, 27
K, dissolved (mg/l)	0.7	0.9	0.8	1.3	0.2024	0.8382	34, 27
Cl, dissolved (mg/l)	2.05	8.4	7.26	17	2.3504	0.0221	34, 26
SO_4, dissolved (mg/l)	13	15	10.74	12.3	-1.3187	0.1873	34, 24
NO_3-N, dissolved (mg/l)	2.08	2.12	0.28	1.889	0.2523	0.8008	33, 25
F, dissolved (mg/l)	0.2	0.11	0.0655	0.092	-0.4564	0.6481	34, 25
Alkalinity (mg/l as HCO_3)	219	237	261.5	260.4	1.9603	0.0546	34, 27
SiO_2, dissolved (mg/l)	7.6	8.26	7.85	8.573	0.2489	0.8050	34, 27

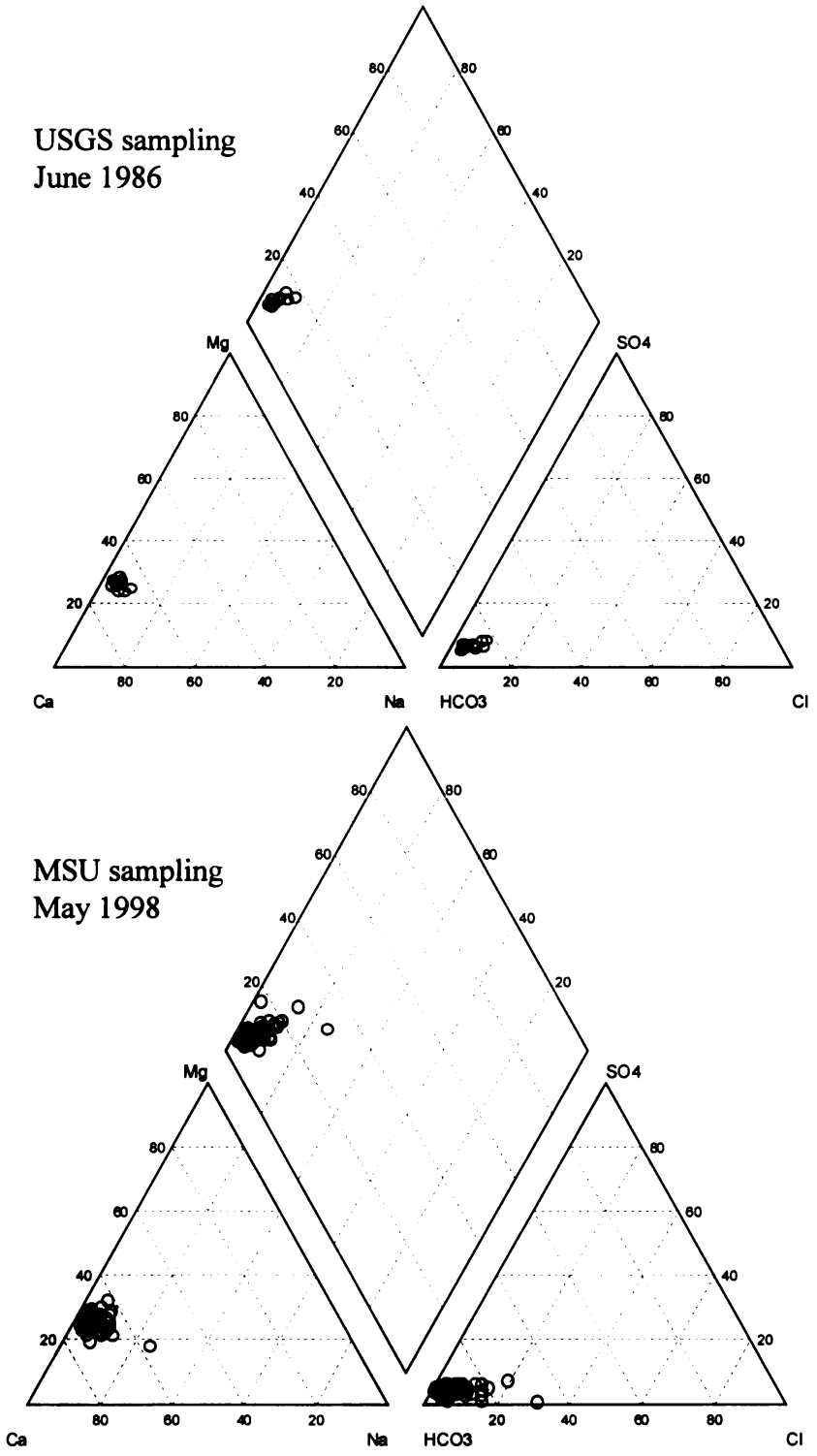

Figure 2.4a. Piper diagrams for streams in Grand Traverse Bay Watershed, June 1986 and May 1998.

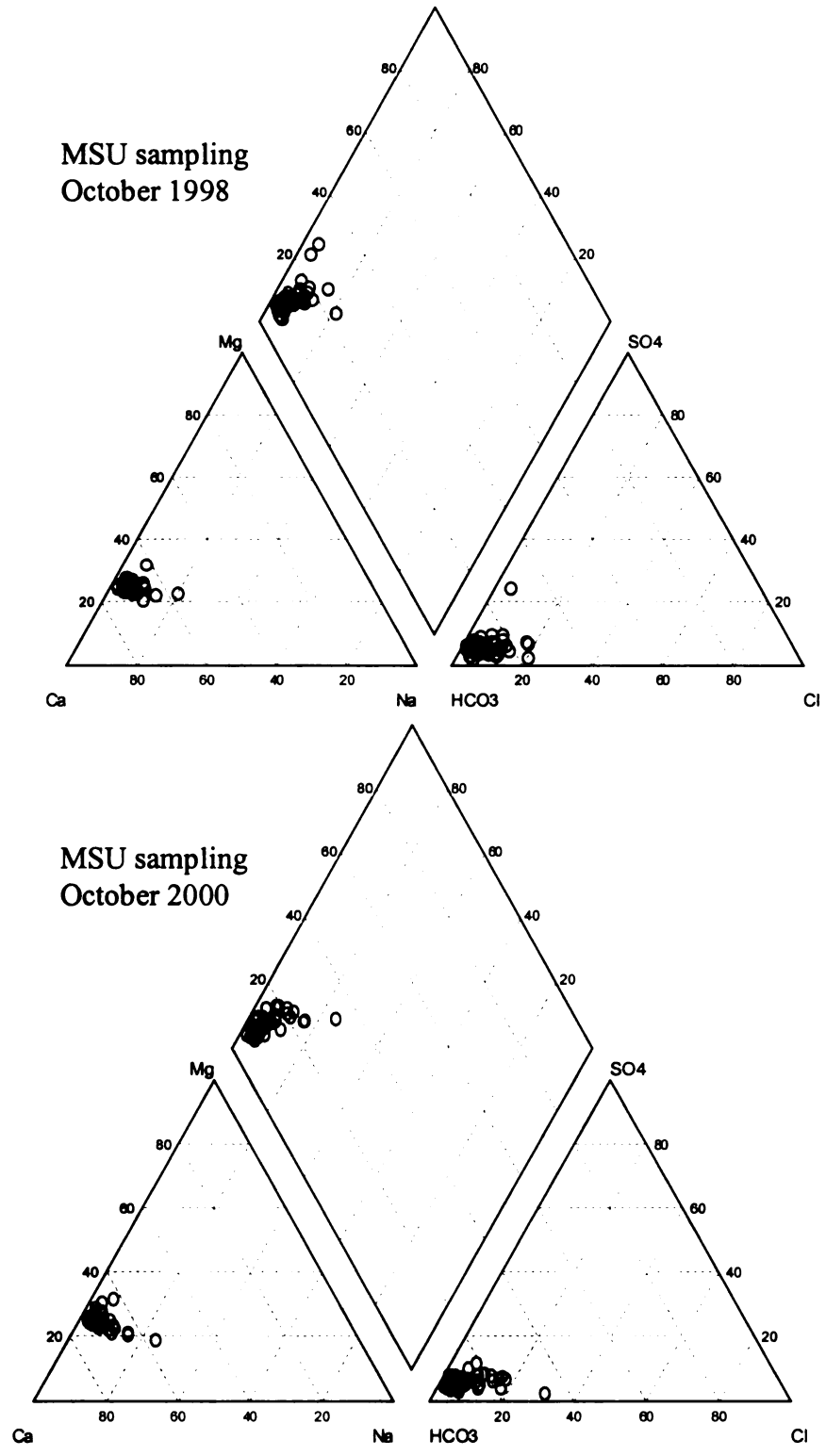

Figure 2.4b. Piper diagrams for streams in Grand Traverse Bay Watershed, October 1998 and October 2000.

Table 2.3. Median and mean concentrations for 13 stream sampling sites common to USGS and MSU studies.

	June 1986		May 1998		October 1998		October 2000	
	Median	Mean	Median	Mean	Median	Mean	Median	Mean
pH	8.3	8.25	8.17	8.20	7.99	8.07	8.04	8.06
DO	10.05	9.82	9.53	9.40	10.59	11.37	10.00	9.84
Ca (mg/l)	50	54	52.5	55.29	52.3	56.5	61.3	66.05
Mg (mg/l)	12	12	11.80	12.44	12.05	12.89	13.66	14.45
Na (mg/l)	3.95	4.68	5.00	5.86	4.53	5.35	6.08	7.30
K (mg/l)	0.9	0.9	0.75	0.80	0.85	0.88	0.96	1.02
Alkalinity (as mg HCO_3/l)	198	215	211	217	214	229	231	231
Cl (mg/l)	6.3	6.8	8.29	8.70	7.35	8.83	9.67	11.33
SO_4 (mg/l)	11	11.69	8.66	8.85	10.34	10.91	11.13	11.79
NO_3-N (mg/l)	0.25	0.31	0.23	0.36	0.20	0.36	0.30	0.40
F (mg/l)	0.10	0.15	0.16	0.20	0.11	0.15	0.16	0.18
SiO_2 (mg/l)	7.7	7.55	7.85	7.66	10.47	11.14	10.33	10.70

Table 2.4. Results of Kruskal-Wallis tests comparing USGS and MSU stream sites and all MSU sites.

	MSU-USGS			MSU, all sites		
Variable	X^2	Prob > X^2	n[a]	X^2	Prob >X^2	n[b]
pH	10.14	0.0174	13, 13, 11, 10	13.63	<0.0001	71, 56, 62
Ca	6.18	0.1031	13, 13, 11, 10	15.69	0.0004	71, 56, 63
Mg	3.53	0.3166	13, 13, 11, 10	16.93	0.0002	71, 56, 63
Na	5.79	0.1224	13, 13, 11, 10	1.24	0.5362	71, 56, 63
K	3.39	0.3350	13, 13, 11, 10	23.26	<0.0001	71, 56, 63
SiO_2	32.03	<0.0001	13, 13, 11, 10	80.76	<0.0001	71, 56, 63
Alkalinity (as HCO_3)	2.72	0.4317	13, 13, 11, 10	0.01	0.9960	71, 56, 61
Cl	0.98	0.8072	11, 13, 11, 10	1.49	0.4749	68, 56, 63
SO_4	6.05	0.1094	12, 13, 11, 10	16.57	0.0003	68, 56, 63
NO_3-N	1.56	0.6678	12, 13, 11, 10	2.72	0.2567	68, 56, 63
F	6.60	0.0857	13, 13, 11, 10	26.16	<0.0001	68, 56, 63

n[a]: number of samples for June 1986, May 1998, October 1998 and October 2000

n[b]: number of samples for May 1998, October 1998 and October 2000

Table 2.5. Results of Tukey's studentized range test for differences among sampling dates for the 13 stream sites common to the USGS and MSU studies. Only variables that were identified as having significant differences by the Kruskal-Wallis test were included in this analysis.

	June 1986	May 1998	October 1998	October 2000
June 1986	----			
May 1998		----		
October 1998	pH, SiO_2	SiO_2	----	
October 2000	SiO_2	SiO_2		----

The median and mean values for all MSU stream sites in the GTBW are listed in Table 2.6. Streams are of high quality, with DO concentrations often exceeding 10 mg/l. In contrast to the previous analysis in which only 13 sites were included, stream chemistry varies significantly ($p < 0.05$) from date to date for most parameters when data from

Table 2.6. Median and mean concentrations of all sampling sites from MSU study.

	May 1998		October 1998		October 2000	
	Median	Mean	Median	Mean	Median	Mean
pH	8.17	8.15	8.1	8.12	8.05	8.03
DO	9.18	9.02	10.7	11.2	10.05	9.65
Ca (mg/l)	60	62.56	53.55	58.7	64.45	65.31
Mg (mg/l)	13.5	14.17	11.95	12.97	14.8	15.13
Na (mg/l)	4.4	5.91	4.17	5.51	4.27	6.54
K (mg/l)	0.8	0.8	0.8	0.9	0.9	1.1
Alkalinity (as mg HCO_3/l)	227	235	224	236	232	236
Cl (mg/l)	6.9	10	7.3	11	8.1	12
SO_4 (mg/l)	8.65	9.31	10.4	12.8	11.4	12.9
NO_3-N (mg/l)	0.33	0.57	0.35	0.60	0.49	0.70
F (mg/l)	0.19	0.23	0.10	0.17	0.13	0.16
SiO_2 (mg/l)	7.60	7.40	9.75	9.84	10.10	9.71

across the watershed are compared over the three MSU sampling events (Table 2.4).

Only Na^+, alkalinity, Cl^-, and NO_3^-N concentrations show no significant difference for the three dates. The results of the Tukey test to distinguish differences between pairs of dates are given in Table 2.7. Four parameters (Mg^{2+}, SiO_2, F^-, and SO_4^{2-}) show differences from May 1998 to October 1998, while five parameters (pH, Ca^{2+}, K^+, SiO_2, and SO_4^{2-}) differ from May 1998 to October 2000. Only Ca^{2+}, Mg^{2+}, and K^+ concentrations differ from October 1998 to October 2000.

Table 2.7. Results of Tukey's studentized range test for differences among sampling dates for all sampling sites in the MSU study. Only variables that were identified as having significant differences by the Kruskal-Wallis test were included in this analysis.

	May 1998	October 1998	October 2000
May 1998	----		
October 1998	Mg, SiO_2, F, SO_4	----	
October 2000	pH, Ca, K, SiO_2, SO_4	Ca, K, Mg	----

Spatial Differences in Groundwater Geochemistry

In general, the lowest concentrations of all parameters sampled by MSU in 1998 were measured in wells located in the Pere Marquette State Forest (see Figure 2.1), except for Cl^-. At most wells, Cl^- concentrations were below 15 mg/l, but one well within the forest and one well in the Mitchell Creek subwatershed had concentrations of 55.3 and 51.6 mg/l, respectively. The highest concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, and HCO_3^- were measured in the Mitchell Creek well, and the well also had one of the three highest concentrations of SiO_2. The highest concentrations of NO_3^--N were observed in the two wells on the eastern shore of the bay, while the highest SO_4^{2-} concentration was measured in a well on Old Mission Peninsula. Again, SO_4^{2-} in the Mitchell Creek well was higher than in most other wells. In contrast, the USGS data show that the Mitchell

Creek well has some of the lowest concentrations of solutes during the 1985-86 sampling. The highest concentrations of solutes from the 1985-86 sampling were consistently measured in a well on Old Mission Peninsula that was not sampled by MSU in 1998.

Spatial Differences in Surface Water Geochemistry

The large size of the surface water database makes generalizations about spatial distributions of solutes difficult without further data manipulation. Cluster analysis was used to identify surface water sample sites with similar chemistry in the GTBW. To determine which parameters were responsible for cluster membership, the log of the ratio of the median cluster value to the median value for all MSU stream data was graphed for each parameter. These graphs represent the geochemical fingerprint of each cluster. Cluster dendograms and the geochemical fingerprint graphs for the May 1998, October 1998, and October 2000 MSU sampling events are shown in Figures 2.5, 2.6, and 2.7, respectively. Clusters were also mapped to show the spatial distribution of clusters within the watershed and to surmise relationships between geochemical fingerprints and land use (Figures 2.8, 2.9, and 2.10). Symbols in the left corner of each fingerprint graph correspond to symbols on the maps of cluster distributions. For May 1998 and October 1998, the symbols are intended only to show the general locations of similar clusters in Figure 2.8, since maps for these dates are not presented. Note that the cluster number is arbitrary and is simply used for identification purposes; a similar cluster number does not indicate that the membership in the cluster (sample sites) remains constant from date to date, nor does it imply that the geochemical fingerprint for a cluster is the same from date to date.

While both cluster membership and geochemical fingerprints vary from date to date, some similarities can be observed. Geochemical fingerprints that are similar among dates are indicated on the graphs (Figures 2.5-7) and spatial distribution maps (Figures 2.8-10) with identical symbols. For all dates, most sample sites fall into two-three larger clusters, while one outlier site does not fit into any cluster. This outlier is identified as Cluster 2 in May 1998, as Cluster 3 in October 1998 and October 2000 (Figures 2.5-7), but on all maps (Figures 2.8-10) is identified by a cross mark. This sample is characterized by extremely high concentrations of Cl^- and F^- for all dates compared to the median of other clusters, and by low DO and SO_4^{2-}, and high Na^+ and K^+ in May 1998 and October 2000. This site is always located in the Mitchell Creek subwatershed (see inset in Figures 2.8-10) but is not always the same location.

For all dates, Cluster 4 contains the highest number of sample sites and has the geochemical fingerprint closest to the median value for all GTBW surface water samples. The median concentration of virtually all chemical parameters is lowest in this cluster, with the exception of Na^+ and Cl^- in May 1998; on this date, median Na^+ and Cl^- value is slightly higher than in Cluster 3. Cluster 4 is denoted by a triangle in the spatial distribution maps (Figures 2.8-10), and sample sites in this cluster are consistently located within forested lands in the watershed.

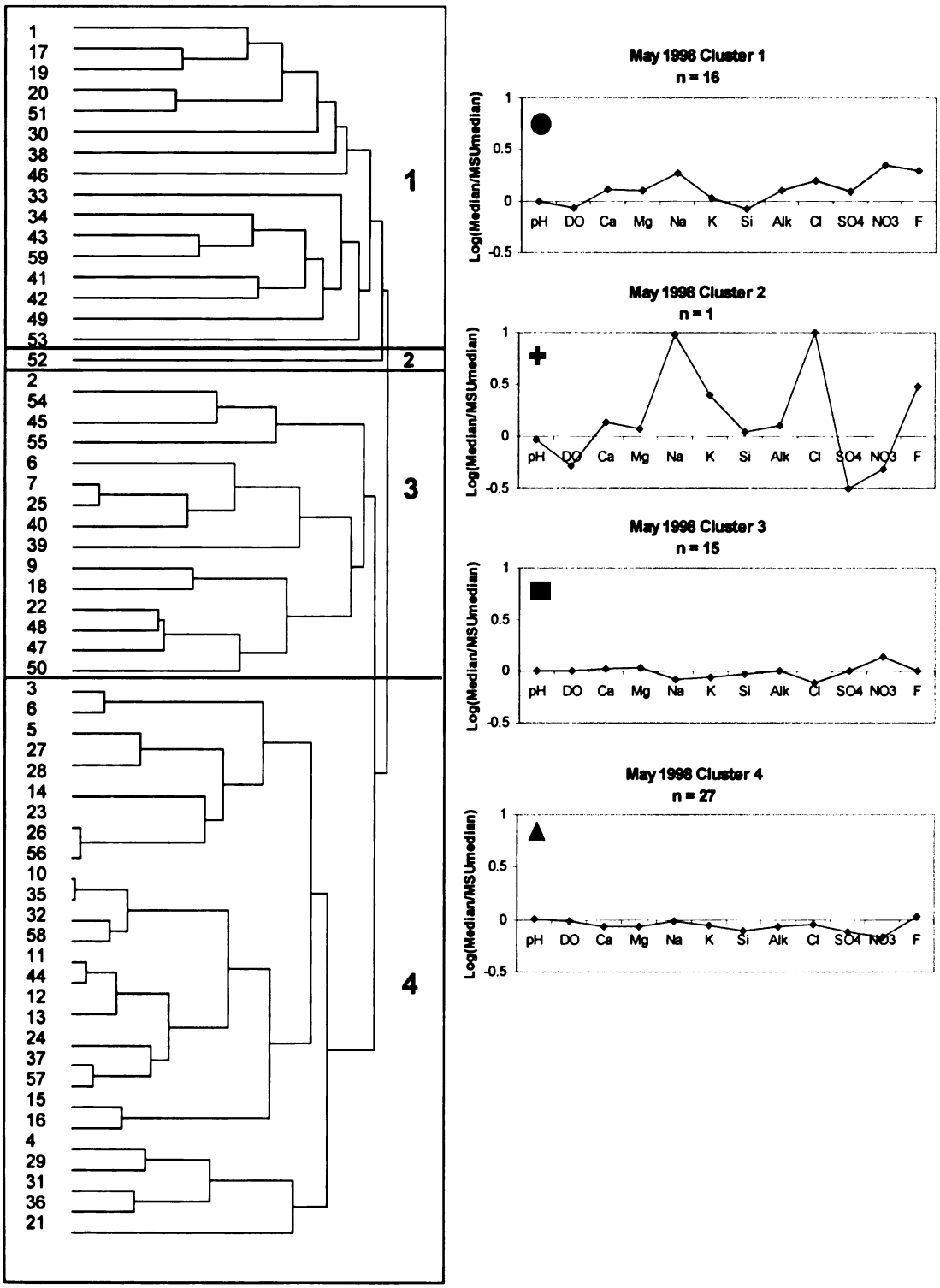

Figure 2.5. May 1998 dendrogram and fingerprint of each cluster, MSU medians.

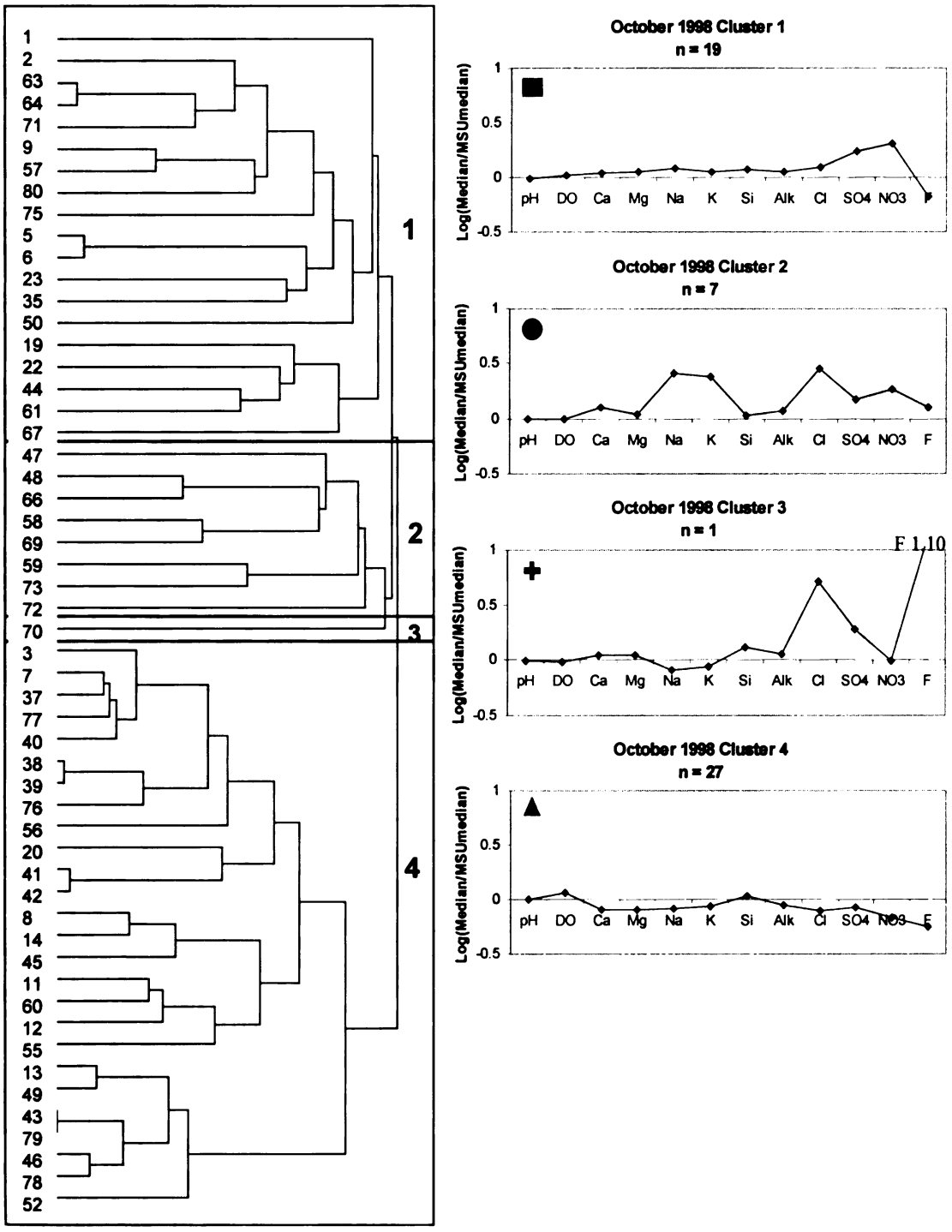

Figure 2.6. October 1998 dendrogram and fingerprint of each cluster, MSU median.

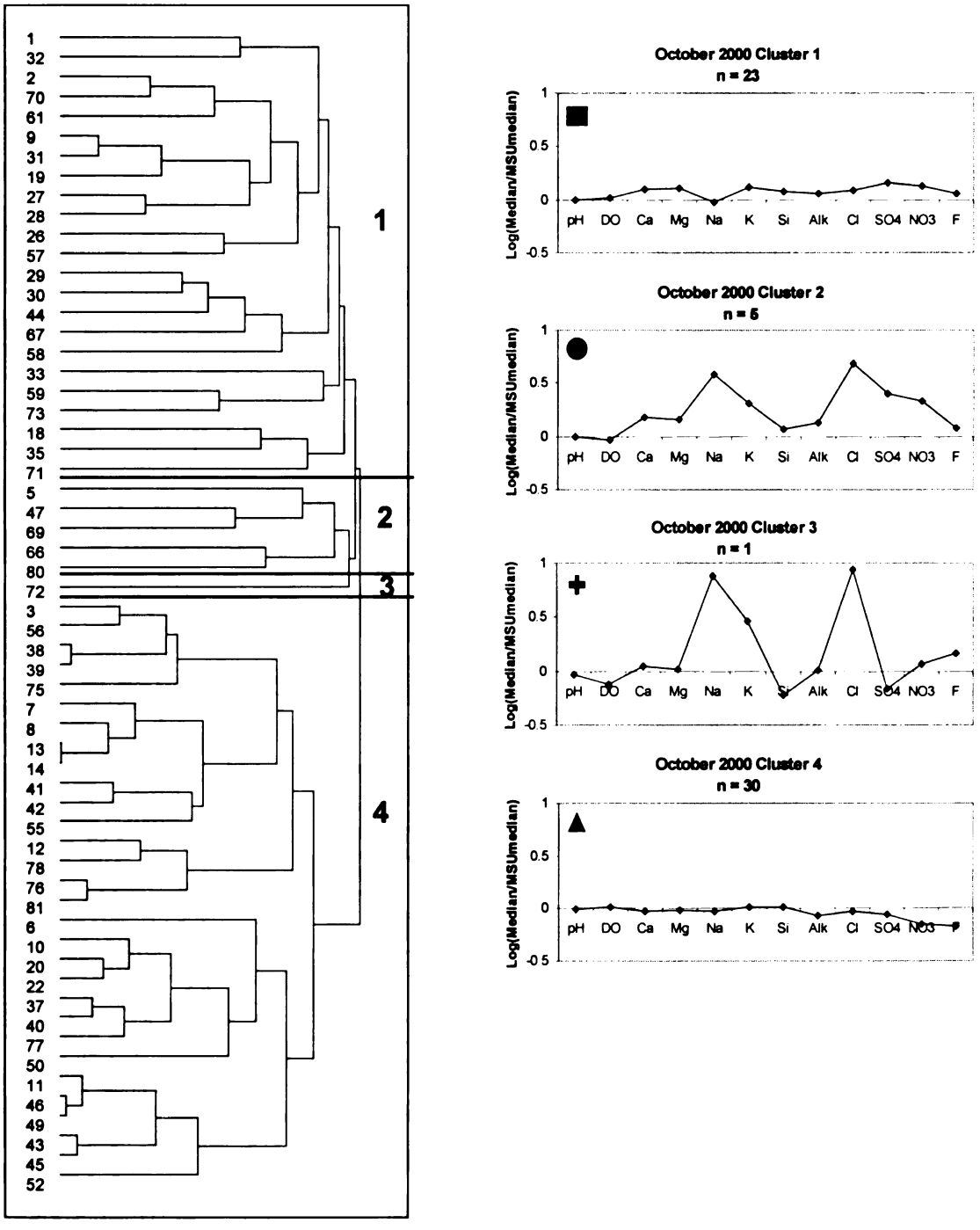

Figure 2. 7. October 2000 dendrogram and fingerprint of each cluster, using MSU median.

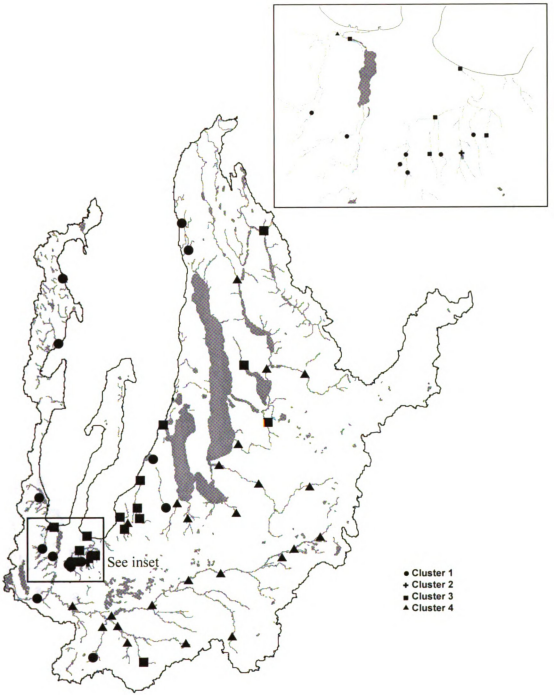

Figure 2.8. Map of May 1998 clusters.

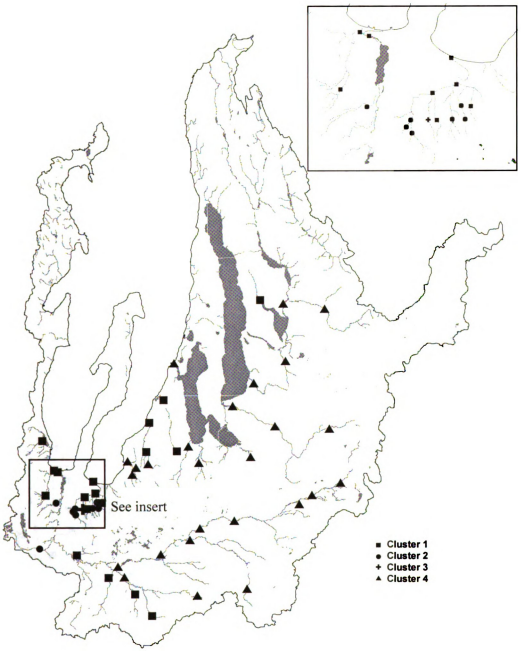

Figure 2.9. Map of October 1998 clusters.

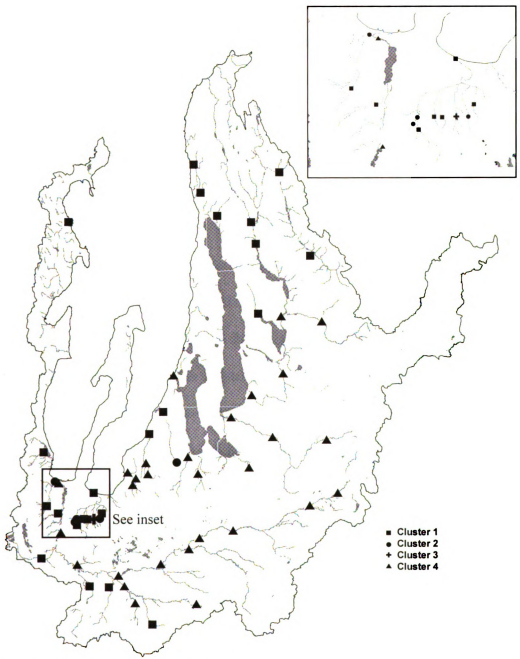

Figure 2.10. Map of October 2000 clusters.

Another similar cluster among sampling dates is characterized by slightly less dilute waters than Cluster 4. This cluster is identified in the dendograms as Cluster 3 in May 1998, and as Cluster 1 in October 1998 and October 2000, but on all maps is denoted by a square. In general, the median concentrations of all parameters in this cluster are higher than those of Cluster 4 but do not exhibit marked variation from the median of all MSU stream data combined. The exception is NO_3^- N in May 1998 and October 1998, when the median concentration was relatively high. The sample sites in this cluster are scattered throughout the watershed but are generally outside forested areas.

The last set of clusters is characterized by lower median DO and higher median cation and anion concentrations than Cluster 4 of all dates and the less dilute clusters described in the previous paragraph. This cluster is identified by a circle on the spatial distribution maps, but is identified as Cluster 1 in May 1998 and Cluster 2 in October 1998 and October 2000. The geochemical fingerprints of this cluster all show spikes in Na^+ and Cl^-, although the median concentrations are less than the outlier sample sites' fingerprints. Median values for K^+, SO_4^{2-}, and NO_3^- N are also higher than most other clusters. Most of the sample sites in this cluster are located in the Mitchell Creek subwatershed, with a few sites in other locations primarily near Traverse City.

The cluster analysis was conducted to identify sites with similar surface water chemistry. The three distinct biogeochemical fingerprints groupings and the outlier site showed fairly consistent spatial distributions across the watershed. Because the surface water samples were collected at baseflow conditions, the stream should be representative of shallow groundwater. The geochemical processes and sources of solutes responsible

for stream chemistry can be interpreted by exploring the evolution of water from wells to stream and as water flows downstream in surface waters.

Evolution of Water from Wells to Streams

The chemical evolution of water as it moves from the groundwater aquifer to discharge as stream baseflow can be described with saturation indices (SI) and solute-solute diagrams. Saturation indices were calculated for all surface and groundwater samples from both the MSU and USGS studies. The SI is the log of the ratio of the activity coefficient for the solution to the solubility product and will equal zero at when the solution is at equilibrium with a mineral phase. We consider a solution to be at equilibrium if the SI falls within a tolerance interval of +/- 5% of the log of the solubility product (Long et al. 1988). Saturation indices and the equilibrium range for minerals that may affect water chemistry in the GTBW are shown in Table 2.8. Ground and surface waters are at equilibrium or supersaturated with calcite, dolomite, and quartz. Based on the high saturation indices in both media for the aforementioned minerals, Ca^{2+}, Mg^{2+}, alkalinity, and SiO_2 concentrations appear to be controlled by equilibrium or steady state reactions rather than other processes that can affect their fate and transport (Pionke and DeWalle, 1994; Exner, 1979). Ground and surface waters are undersaturated with respect to gypsum, anhydrite, fluorite, and chalcedony.

Solute-solute diagrams for ground and surface waters are shown in Figure 2.11. Fifteen possible diagrams are possible for six solutes, but only the most revealing plots are included. The solute-solute diagrams enhance our ability to interpret process from a

Table 2.8. Median and mean saturation indices for groundwater and streams in USGS and MSU studies.

	Study and Sampling Date		Saturation Indices						
			Calcite	Dolomite	Gypsum	Anhydrite	Fluorite	Chalcedony	Quartz
Groundwater	USGS 1985-86	Mean	0.130	-0.273	-2.580	-2.835	-2.093	-0.254	0.227
		Median	0.163	-0.211	-2.479	-2.735	-2.070	-0.262	0.215
	MSU August 1998	Mean	0.006	-0.531	-2.323	-2.690	-3.022	-0.281	0.264
		Median	0.029	-0.535	-2.323	-2.690	-2.964	-0.301	0.243
Streams	USGS June 1986	Mean	0.696	0.956	-2.550	-2.798	-2.692	-0.351	0.111
		Median	0.688	0.972	-2.602	-2.847	-2.932	-0.328	0.139
	MSU May 1998	Mean	0.691	0.896	-2.385	-2.699	-2.366	-0.398	0.126
		Median	0.690	0.921	-2.409	-2.714	-2.369	-0.383	0.139
	MSU October 1998	Mean	0.566	0.556	-2.276	-2.645	-2.708	-0.211	0.335
		Median	0.519	0.478	-2.324	-2.674	-2.772	-0.204	0.341
	MSU October 2000	Mean	0.523	0.517	-2.480	-2.735	-2.519	-0.166	0.312
		Median	0.567	0.570	-2.512	-2.768	-2.580	-0.152	0.324
Equilibrium Range (+/-5% of Log(K_{sp}))			0.424	0.855	0.229	0.275	0.530	0.136	0.199

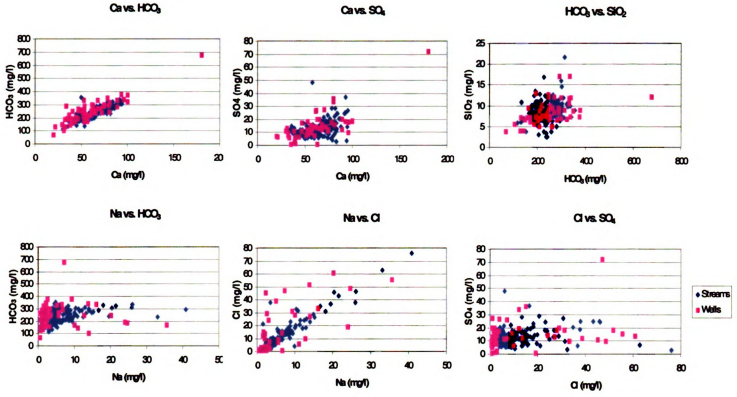

Figure 2.11. Solute-solute plots for selected ion pairs. Plots include all Grand Traverse Bay Watershed streams and ground water samples collected in USGS and MSU studies.

large dataset. A linear relationship between two solutes implies that the same process or source is acting on both solutes. A more dispersed distribution is indicative of multiple sources or processes. Furthermore, if stream data is plotted together with well data, the solute-solute diagrams can show how the relationship between solutes changes as groundwater evolves to surface waters. Comparison of the relative concentrations of solutes in groundwater and stream samples may indicate that a process or source is adding or removing a solute from the system, leading to enrichment or depletion of stream chemistry relative to groundwater. For brevity, the use of the term "source" in the following discussion refers both to an actual input of a solute to the system, such as from atmospheric deposition, or to a process that affects the relative concentrations of solutes, such as adsorption/desorption.

The consistency of the relationship between Ca^{2+} and HCO_3^- at all concentration levels suggests a single source for the two solutes (Kleissen et al., 1990), most likely the dissolution of calcite and dolomite. The more dispersed plots for Ca^{2+} vs. SO_4^{2-} and HCO_3^- vs. SiO_2, in which there is no direct relationship between concentrations of the two solutes, suggests multiple sources in the watershed, such as atmospheric deposition of SO_4^{2-}, dissolution of gypsum, oxidation of pyrite, SO_4^{2-} reduction, exchangeable pools of SO_4^{2-} and SiO_2, and diatom productivity within the stream. However, the clumping of groundwater and stream samples together in the Ca^{2+}-SO_4^{2-} and HCO_3^--SiO_2 plots implies that there is no shift in the relative concentrations of these solutes as groundwater moves through the watershed and discharges as streamflow. The solute-solute diagram for Na^+ vs. HCO_3^- suggests multiple sources of at least one solute as well as enrichment of Na^+ in stream water relative to groundwater. These sources may include dissolution of feldspars

and plagioclase in the glacial till, anthropogenic sources of Na^+, and addition of HCO_3^- through mineral dissolution and respiration of organic matter in the soil. The Na^+ vs. Cl^- plot shows that there may be multiple sources of the solutes in groundwater, such as oil field brines, wastewater, and road salt, but that by the time water reaches streams, the relationship between the two solutes is more linear, suggesting that a single source controls the concentration of these two solutes in surface waters. Surface water appears to be slightly enriched in both Na^+ and Cl^- compared to many of the groundwater samples. The mixing diagram for Cl^- vs. SO_4^{2-} implies multiple sources for at least one of the solutes and a slight enrichment in Cl^- in stream water compared to the majority of groundwater samples, however both waters show a skewed distribution with a number of samples with extreme Cl^- concentrations.

Evolution of Water from Upstream to Downstream

Further characterization of the cumulative effects of natural and human-induced processes (Sidle and Hornbeck, 1991) can be achieved by describing the evolution of surface water from upstream sites to downstream sites using saturation indices (SI) and plots of concentrations over distance along a stream. Maps of SI across the GTBW stream samples illustrate the influence of the mineral-water interactions in controlling the chemistry of stream water (Figure 2.12). Because concentrations vary with date, saturation indices vary temporally as well. However, in general, the patterns shown in Figure 2.12 were similar for all dates and therefore only May 1998 is shown. Most stream samples were supersaturated with respect to calcite, but small streams in the headwaters of some subwatersheds were at equilibrium. In contrast, many headwaters sites were

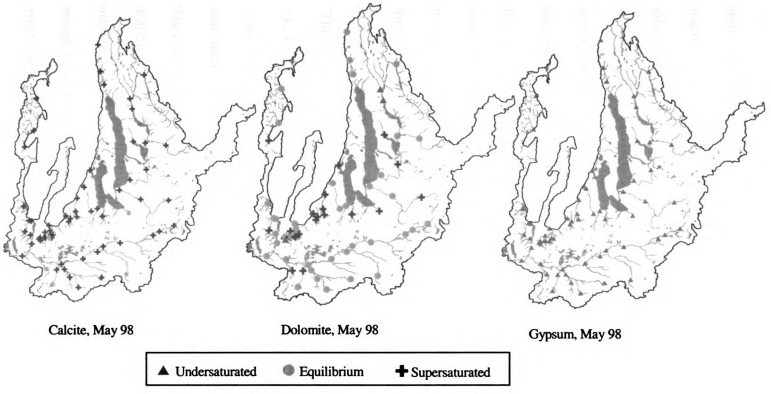

Figure 2.12. Saturation indices for calcite, dolomite, and gypsum at stream sites sampled in May 1998.

supersaturated with respect to dolomite, while most sites on higher order streams were at equilibrium. The change in SI is probably related to dilution by water with lower Mg^{2+} concentrations in higher order streams, since the kinetics of dolomite preclude precipitation (Drever 1997). Baseflow in shallow, upland streams may have a different chemistry than deeper groundwater that discharges in larger streams, explaining why headwaters show different thermodynamic conditions than higher-order streams. Two processes, evaporation and mixing of stream water with groundwater of a different concentration, will change the thermodynamics of the system as water moves downstream. All sites in the watershed were undersaturated with respect to gypsum, anhydrite, and fluorite, while saturation indices ranged near equilibrium or were supersaturated for quartz. Most sites were undersaturated with respect to chalcedony although a few sites were at equilibrium.

The cumulative effects of natural and human-induced processes (Sidle and Hornbeck, 1991) are illustrated by plots of concentration changes with distance downstream. The Boardman River has the greatest number (8) of sampling sites in series in the watershed, so upstream-downstream changes for this river system are shown in relation to land use change in Figure 2.13. Solutes are graphed as the ratio of the concentration at a site divided by the maximum concentration measured in all Boardman River sites on the corresponding date. The headwaters of the north branch of the river flow through a wetland and the village of Kalkaska before passing into the Pere Marquette State Forest. The river merges with its south branch just above the 29-km sampling site. After the state forest, the Boardman River passes through a series of small ponds on the outskirts of Traverse City before flowing into the Boardman Lake, a

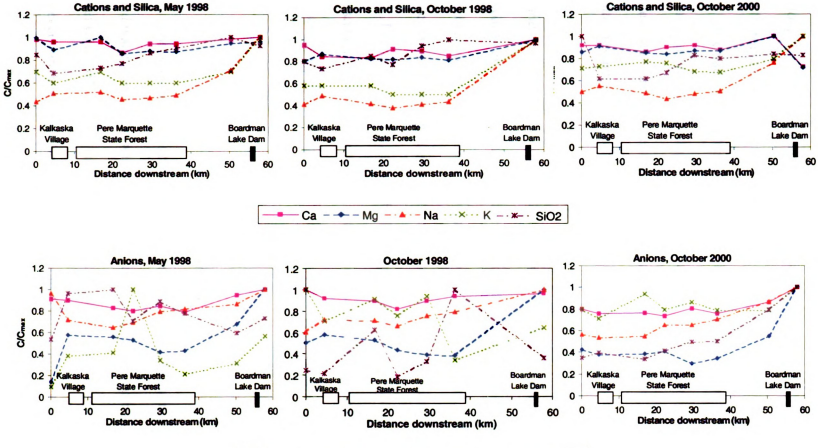

Figure 2.13. Changes in solute concentration along the Boardman River. Solutes are graphed as the ratio of the concentration at a site divided by the maximum concentration of all Boardman River sites on the corresponding date.

dammed impoundment within the urban center. The last sampling site on the river (at 58 km along the river from the most upstream site) is located just below the dam along a main thoroughfare in the city.

The pattern of changes in cation concentrations moving downstream is fairly consistent from date to date, while anion behavior is more variable. Concentrations of Ca^{2+} and Mg^{2+} are relatively constant for all sample sites; Na^{+} and K^{+} concentrations remain constant along much of the river but exhibit a sharp increase in concentration below the 50-km sampling site (MSU site ID 10), probably related to the transition from the rural-urban fringe to downtown Traverse City. In addition, enhanced evaporation in the Boardman Lake may increase concentrations from the 50-km site to the 58-km site. Silica behavior varies with date, which is to be expected given the seasonality of diatom productivity, but generally increase moving downstream, particularly after of the state forest. The anions HCO_3^-, SO_4^-, and Cl^- also generally increase in concentration moving downstream and show less variability from date to date than NO_3^- and F^-, which show sharp spikes in concentration in the upstream reaches, particularly in May and October 1998.

Discussion

The Kruskal-Wallis test for differences among the USGS and MSU surface and ground water sampling results showed changes for only a few parameters (pH and Cl^- in groundwater, pH and SiO_2 in surface waters). While statistically significant, these differences are based on a small dataset from only two sampling events over a 14-year period. Long-term trends in solute concentrations may be occurring in the watershed but

were not apparent in comparisons of a small number of sites and data points. The GTBW groundwater flow and transport model for Cl^- (Boutt et al., 2001) suggests that other conservative species would exhibit similar increases in stream concentrations over time. More robust temporal variability in the geochemistry of the GTBW is revealed by comparing data from the three MSU sampling events.

The higher number of solutes that showed significant temporal variability when all MSU surface water data were considered can be attributed in part to flow-related differences in sample sites. The 13 sites in the MSU-USGS comparison were dominated by a high-volume system, the Boardman River, while the additional sites added to the MSU study are predominantly smaller streams in the headwaters of the GTBW. The chemistry of the lower reaches of the Boardman River may be controlled by deeper groundwater with more constant solute concentrations, while small variations of the water table in headwater areas may result in vastly different chemical contributions from different subsurface layers (Rice and Bricker 1995; Pionke and DeWalle, 1994; Hooper et al., 1990; Christophersen et al., 1990). Seasonal differences may also explain differences among sampling dates, particularly for the biologically active solutes K^+, SiO_2, and NO_3^-, which will undergo transformations in the subsurface zone and surface water during the growing season. The solute-solute diagrams for most solute pairs imply multiple sources or processes affecting concentrations, and therefore a better understanding of the spatial and temporal variability in shallow groundwater chemistry would enhance interpretation of differences among surface water sampling sites and sampling dates.

The cluster analyses show that the most dilute stream water is associated with forested land, while higher concentrations of solutes, particularly of Na^+, K^+, SO_4^-, NO_3^- N, and Cl^-, are associated in or near rapidly developing areas. These solutes appear to be indicators of human activities associated with rural and urban areas outside forested regions. Potential watershed sources include direct anthropogenic loading from human and animal waste, agricultural and residential use of fertilizers, road deicing, and atmospheric deposition, in addition to indirect effects of human activities, such as the increased weathering of soil minerals from tillage operations (Collins and Jenkins, 1996) and leaching of previously sorbed species as the composition of the soil solution changes (i.e., K^+; see Puckett and Bricker, 1992). A smaller number of heavily impacted sites have both higher concentrations of these solutes and lower concentrations of DO than the majority of sites in the watershed. The Mitchell Creek subwatershed appears to be a hotspot in the GTBW, with higher concentrations of most solutes. This area, which lies outside the Traverse City storm sewer and wastewater systems, includes intensive agriculture in close proximity to newly urbanized parcels. The outlier site identified in cluster analysis always occurs in the Mitchell Creek headwaters; its fingerprint of low DO, NO_3^--N, and SO_4^{2-} concentrations and Na^+-Cl^- spike in May 1998 and October 2000 may indicate reducing conditions associated with a contamination site or the influence of septic systems. The October 1998 outlier site does not have a similar fingerprint, and its extreme concentrations of Cl^- and F^- are not balanced by higher values of any cation, which implies analytical error. However, we have retained this data point because laboratory analyses were performed with standard quality assurance protocols, and therefore the point may reflect actual conditions at the site.

The solute-solute diagrams show that for solutes derived from mineral weathering, e.g., Ca^{2+} and HCO_3^-, groundwater and streams have roughly the same concentration distribution. This suggests that our synoptic sampling events captured true baseflow conditions. Other researchers (Rice and Bricker, 1995; Cameron 1996; Evans et al., 1996) have observed dilution of mineral-derived solutes in streams relative to groundwater as flow increased above baseflow. The solute-solute diagrams also show that concentrations of Na^+ and Cl^- in streams are strongly correlated and are probably dominated by a single source relative to ground water sampled in wells away from the streams, which appears to be affected by multiple sources. This effect could be explained by the widespread regional use of road salt (halite), which could potentially affect all sites in the study area, in contrast to localized sources of contamination, such as septic tanks and oil drilling activities, which would not exert a dominant influence on stream chemistry across the watershed but might affect individual sites and wells.

The concentration profiles for the Boardman River show that some solutes (Na^+, K^+, and Cl^-) consistently increased as the river flows through suburban and finally urban land uses, while mineral-derived solutes (Ca^{2+} and HCO_3^-) remained relatively constant. (Gburek and Folmar 1999) reported that with the exception of HCO_3^-, anion concentrations had greater variability in relative concentrations moving downstream than cation concentrations. The presence of impoundments along the Boardman River raises the issue of evaporation and its potential role in increasing concentrations from upstream to downstream sampling sites. The difference in behavior between the two groups of solutes (anthropogenically influenced vs. mineral derived) suggests that evaporation in the Boardman Lake is not a significant process influencing the increased concentrations

of Na^+, K^+, and Cl^-; more likely, the increases result from anthropogenic sources. The association of Na^+, K^+, and Cl^- with human-impacted areas of watersheds has been noted by other researchers, including our past work in this watershed (Wayland et al., in press; Bolstad and Swank 1997; Cameron, 1996; Katz et al. 1985). Nitrate and fluoride are also probably anthropogenic in origin but behave less conservatively in the Boardman River than other human-derived solutes, as well as showing more variability from date to date. The drop in mineral-derived solutes below the Boardman Lake Dam during the October 2000 sampling may be a result of storage of overland flow enriched in anthropogenic solutes in the lake behind the dam. Although we sampled streams during low flow, the watershed experienced brief rainstorms one week prior to sampling. Overland flow would have lower concentrations of mineral-derived solutes and would therefore cause those solutes to be diluted below the dam relative to the rest of the river, which had returned to baseflow conditions. We observed a similar decrease in concentrations of mineral-derived trace elements below the dam relative to trace elements with anthropogenic sources (Chapter 4).

The concentration profile for SO_4^{2-} along the Boardman River exhibited increasing trends moving downstream, except in May 1998, when one of the highest concentrations was observed in the most upstream sampling site. The solute-solute diagrams suggest that there are multiple sources or processes affecting SO_4^{2-} in the watershed, and both natural and anthropogenic sources could contribute to the general increase in this solute moving downstream. These diagrams also suggested that the streams were not enriched or depleted in SO_4^{2-} relative to groundwater, which implies that SO_4^{2-} -related processes occur in the aquifer or upland areas rather than in surface

waters. Other researchers have noted that SO_4^{2-} that accumulates on the watershed surface during low flow periods associated with the growing season is flushed out when the water table rises as evapotranspiration ceases (Miller and Hirst, 1998; Puckett and Bricker 1992). Sulfate concentrations should therefore exhibit strong seasonality, and we observed significant differences in SO_4^- concentrations in surface water with date. However, the pattern of SO_4^{2-} transport from upstream to downstream sites along the Boardman River is fairly constant from date to date, indicating that in-stream processes do not change with date. In contrast, the Kruskal-Wallis test for surface water sites revealed significant differences in SiO_2 concentrations with date, and the concentration profiles along the Boardman River also show slight variations in SiO_2 behavior with date, while the solute-solute diagrams indicated behavior similar to mineral-derived solutes. These results suggest that that in-stream processes, such as seasonal diatom productivity, exerts a strong control on SiO_2 in GTBW surface waters. This would explain why SiO_2 concentrations varied moving downstream with no apparent relationship to land use or position along the river. Gburek and Folmar (1999) observed similar dissolved SiO_2 behavior in a Pennsylvania watershed, but did not hypothesize a cause for the variability.

Conclusions

The approach described in this paper leads to a detailed characterization of the spatial and temporal variability in the geochemistry of a watershed. Through three synoptic sampling events, the use of data from a previous study in the mid-1980's, and a variety of graphical and statistical methods, we were able to describe the distribution of solutes across a watershed in the context of geochemical processes and land use. The results suggest that the concentrations of some solutes are strongly influenced by human

activities and seasonality. Statistical tests showed significant differences for most solutes over two-year period. Cluster analysis revealed four distinct geochemical fingerprints for surface waters in the watershed; these fingerprints show the imprints of the land uses with which sample sites in each cluster are associated. Solute-solute diagrams show that to fully explain the evolution of water as it moves from the groundwater system to the surface water network, more information is needed, such as detailed aquifer mineralogy and an understanding of the relative contributions of solutes from soil solution, subsurface flow, and deeper groundwater. Concentrations of anthropogenically-derived solutes generally increase as water moves towards the outlet of the Boardman River. In the GTBW, Na^+, K^+, SO_4^-, NO_3^-N, and Cl^- appear to be important response variables to human disturbance. As the population in the GTBW continues to grow, and the imprint of land use in upland areas reaches the stream through groundwater flow, more dramatic changes in stream chemistry may be evident. Because the effects of land transformation on surface water chemistry are subtle and may not be visible over short time periods, the data presented in this paper can provide comparative information for future evaluations of geochemical conditions in the GTBW.

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CHAPTER 3
IDENTIFYING BIOGEOCHEMICAL FINGERPRINTS OF LAND USE WITH BASEFLOW SYNOPTIC SAMPLING AND FACTOR ANALYSIS

Abstract

Land use may cause changes in the abundance of major and minor ions in surface waters. Associations between land use and groups of chemical species are termed "biogeochemical fingerprints." Most previous research reported fingerprints from a single land use; few studies have explored the cumulative effects of multiple land uses on stream chemistry. GIS-derived land use distributions were paired with biogeochemical data from three synoptic sampling events to identify biogeochemical fingerprints of land use with R-mode factor analysis. The results identified consistent associations between agricultural activity and Ca^{2+}, Mg^{2+}, alkalinity and frequently K^{+}, SO_4^{2-}, and NO_3^{-}. Urban areas were associated with Na^{+}, K^{+}, and Cl^{-}. Associations of Mg^{2+}, alkalinity, and F^{-} with urban areas and shrub/brush were revealed when all data were combined. Wetlands were inversely related to nitrate concentrations. Barren lands were associated with elevated levels of SO_4^{2-}. Factor analysis identified biogeochemical processes not associated with unique land uses, specifically the influence of pH and diatom productivity on stream chemistry. Solute concentrations in baseflow varied over three sampling events, except for sodium and chloride, yet the agricultural activity and halite dissolution factors were consistent for all sampling events individually and when data were combined. Other factors were not consistent among sampling events. These results suggest that an individual sampling event may not adequately characterize the processes controlling interactions between land use and stream chemistry. The use of data collected over two

years appears to enhance our ability to understand the relationship between land use and stream chemistry.

Introduction

Geology, land use, land cover, and climate control the geochemistry of surface waters in pristine watersheds. Natural patterns of stream chemistry can be altered by human activities, such as agriculture, road construction, urbanization, and deforestation, and these land use changes can result in the degradation of water quality and aquatic ecosystems. The U.S. EPA estimates that 35% of the country's rivers and streams are impaired by pollution from agriculture, hydromodification, and runoff from urban areas (EPA, 2000). The effects of this pollution range from eutrophication to siltation of riverbed habitat to the bioaccumulation of persistent toxins in fish. Land use impacts are often obvious and dramatic; for example, anoxia caused by polluted runoff in the Black River in Washington State resulted in massive fish kills (Pickett, 1997).

In watersheds that are beginning to undergo land use intensification (i.e., rapid population growth or shifts to more intensive farming practices), concentrations of potential pollutants in surface waters may be low and impacts on ecosystem integrity may not be evident. However, the effects of land use change may be expressed through changes in the relative abundance of major and minor ions. For example, nutrient cycles, such as for nitrogen and phosphorus, are highly influenced by agricultural practices (Goss and Goorahoo, 1995; Richards et al., 1993; Stone et al., 1998; Withers and Jarvis, 1998; Tufford et al., 1998). Some studies indicate that agriculture can also affect calcium, magnesium, and alkalinity cycles (e.g., Collins and Jenkins, 1996; Hamilton and Helsel,

1995). Urban environments have been associated with increased levels of Na and Cl (e.g., Long and Saleem, 1974; Vengosh and Pankratov, 1998). We have termed such consistent associations between land use and groups of chemical species in surface waters "biogeochemical fingerprints." Most fingerprints reported in the literature resulted from studies of the environmental effects of a single land use; few studies have explored the cumulative effects of multiple land uses on stream chemistry (Sidle and Hornbeck, 1991). This work links landscape patterns to stream chemistry on a watershed scale, addressing a basic research need for more information on how complex landscapes affect geochemical processes (Sidle and Hornbeck, 1991). The driving hypothesis is that land use categories exhibit characteristic biogeochemical fingerprints and that the relationship between a land use and the group of chemical species comprising its unique fingerprint can be quantified.

The relationship between land use and stream chemistry is 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). As long as flow remains relatively constant during the sampling period, thus eliminating discharge-related variability in chemical concentrations, synoptic sampling can be used to study the spatial component of stream chemistry variability (Grayson et al., 1997). Most synoptic studies are conducted during baseflow conditions when groundwater dominates streamflow. The chemistry of baseflow thus represents an integrated signal of the climate, geology, and historical land use patterns throughout the watershed.

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 groundwater discharge to streams. Rose (1996) suggested that during cooler or wetter months vadose zone drainage may contribute to baseflow in addition to discharge of deeper groundwater, even in regions with thick soils and a shallow water table. These hydrologic studies may explain why baseflow chemistry can be highly variable over time in some watersheds (Clow et al., 1996), while remaining relatively constant in others (Pionke et al., 1999).

Given the possibility that baseflow chemistry varies temporally as well as spatially, it is necessary to further examine 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 biogeochemical fingerprints of land use 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). However, 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 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. The results support our hypothesis that synoptic sampling can be used to produce consistent, quantifiable associations between land use and biogeochemical parameters.

Study Site

The Grand Traverse Bay Watershed (GTBW, Figure 3.1) was chosen as the research site because the region is undergoing rapid land use change, primarily urbanization. Grand Traverse Bay and its watershed, located in the northwestern portion of Michigan's Lower Peninsula, are important natural and economic resources for the Great Lakes Region for their great scenic beauty, quality of waters, and recreational opportunities. Grand Traverse is one of the last remaining oligotrophic bays in Lake Michigan, and more than 55 of the over 250 miles of stream are highly prized for trout fishing. Superimposed on this relatively healthy ecosystem is some of the most intense population growth and land use change of any region in the United States (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).

Land use/land cover in GTBW is predominantly forest (49%) and agriculture (20%). The agricultural landscape is diverse, with a large number of orchards and vineyards, as well as row crops and livestock production. Urban land use comprises about 6% of the total area of the watershed, with the Traverse City urban region located on the shores of Grand Traverse Bay. The other main land cover categories are shrub/brush

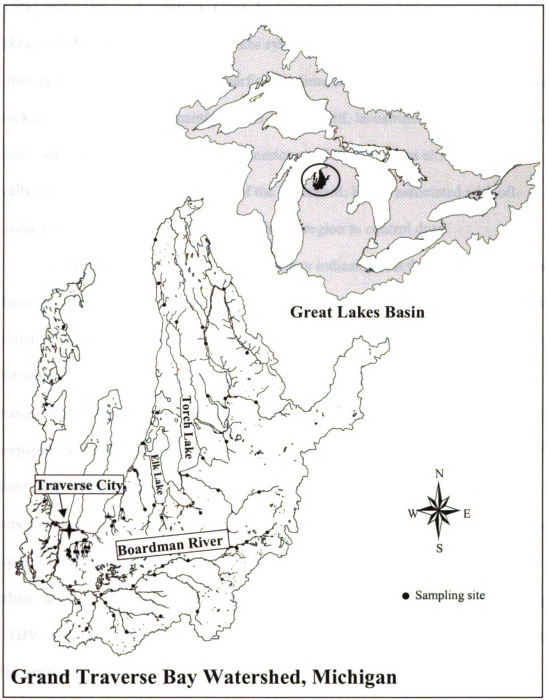

Figure 3.1. Location of the Grand Traverse Bay Watershed, Michigan.

(15%), water (9%), and wetlands (1%). This 2600-km^2 watershed contains over 100 lakes, including the Torch and Elk Lakes systems. The Boardman River is the main tributary draining the GTBW. The surficial sediments of the watershed, which can be as thick as 290 m, are predominantly glacial outwash, till, lacustrine sand and gravel, and dunes, all of which overlay 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.

A 1998 summary of conditions in the bay indicated that the water quality in near-shore areas has deteriorated as a result of nutrient loading (GTBWI, 1998). The GTBW Initiative has identified three major areas of concern for the health of the bay: inputs of nutrients, sediment, and toxic substances; the effects of land use and land use management decisions on those inputs; and exotic species (GTBWI, 1998). A report prepared for the International Joint Commission (International Joint Commission, 1996) identified five key stresses affecting the Great Lakes Basin Ecosystem: nutrients, persistent toxic substances, physical alterations (e.g., sedimentation, infiltration, runoff, water levels); human activities as manifested in land-use change, population growth, urbanization, etc.; and non-native exotic species. Therefore, the problems confronting the GTBW are a microcosm of those confronting the entire Great Lakes Basin Ecosystem. The approach presented in this paper is highly transferable to other parts of the Great Lakes region, and any humid region where groundwater is a major source of surface water flow, to explore links between land use and water quality.

Limited research has been conducted in GTBW to examine the relationship between land use and water quality on a watershed scale. Cherry orchards have been

linked to high nitrate concentrations in wells in some areas of the watershed (Rajagopal, 1978). From 1984-86, the USGS sampled streams and wells in Grand Traverse County and documented potential correlations between nitrate concentrations in groundwater and nitrogen loading from precipitation, animal waste, septic tanks, and fertilizers (Cummings et al., 1990). Beginning in 1998, surface water sites from the earlier USGS study have been resampled at least annually; preliminary analysis of the two datasets suggests that only minor changes in the biogeochemistry of the watershed have occurred (Woodhams et al., 1998). A regional groundwater flow and solute transport model has been developed for the GTBW to simulate the flux of Cl^- from roads into Lake Michigan (Boutt et al., 2001). An important conclusion of this model is that the dissolution of road salt (halite) appears to be the most significant source of Cl^- to surface waters. However, road salt alone cannot account for observed Cl^- concentrations at many stream sites, thus wastewater and oilfield brines likely also contribute Cl^- to surface waters.

Methods

Synoptic Sampling and Laboratory Analyses

Biogeochemical data were collected during three baseflow synoptic sampling events in September of 1997, and May and October of 1998. The sampling events occurred during low flow conditions on the recession limb of the hydrograph; flow during each sampling event and two weeks prior are shown in Figure 3.2. In this study, we consider baseflow to be the period between storms when the hydrograph is in the later stages of the recession limb, similar to the classification used by (Pionke et al., 1999). Baseflow conditions varied for each sampling event. Discharge at the USGS Boardman

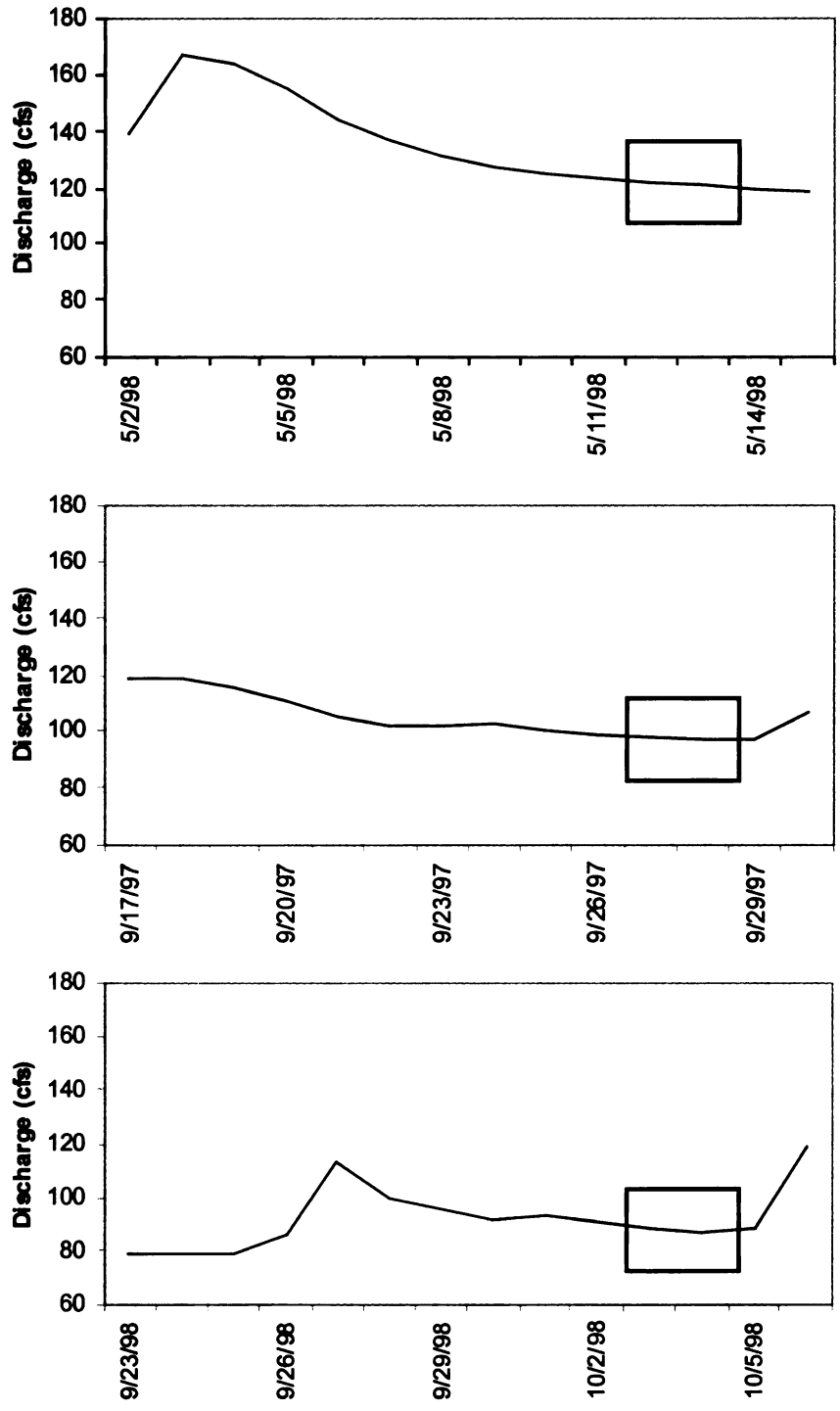

Figure 3.2. Flow at USGS Boardman River gaging station for three synoptic sampling events and two-week period prior to sampling. The sampling dates are enclosed in shaded boxes.

River gaging station (Figure 3.2) on the first day of the September 1997, May 1998 and October 1998 sampling events was 98 cfs, 122 cfs, and 89 cfs, respectively.

The sampling sites are shown in Figure 3.1 and were located at bridges or other easily accessible locations to facilitate rapid sample collection. Three crews of two-to-four people each were necessary to visit the approximately 75 sites across the watershed in 2.5 days. Although we identified approximately 80 potential sampling sites, some streams were dry during at least one of the sampling events and could not be sampled.

At each site, samples were taken from the thalwag portion of the river using a plastic bucket or bottle. Sampes were taken from the upstream side of bridges. Buckets and bottles were rinsed three times with river water before samples were taken. Dissolved oxygen, temperature, redox potential, and pH were measured at each site with a YSI or HydroLab multi-parameter probe. Specific conductance and redox potential are not included in this analysis because of the number of missing values. Alkalinity was determined at each sample site by potentiometric titration. As necessary, samples were filtered (0.45 μm acid-washed filters), acidified with nitric acid to a pH near 2 (cations), preserved with formaldehyde (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.

In addition to the field measurements described above, samples were analyzed for Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SiO_2, Cl^{-}, F^{-}, NO_3^{-}, and SO_4^{2-}. Cations were analyzed by flame atomic adsorption (Perkin-Elmer 5100 PC). Chloride and fluoride were analyzed by specific ion electrode or capillary electrophoresis (Hewlett Packard 3DCE). Nitrate and

sulfate were determined by capillary electrophoresis. Silica was determined by colorimetry (Milton Roy Spectronic 1001 uv-vis).

Sourcesheds and Land Use Distributions

Land use and sampling points were related through the development of surface water sourcesheds. A sourceshed is defined as the total area that contributes to a selected drainage point, or sampling site (Figure 3.3). Total sourcesheds were created within Arc/INFO GRID using the WATERSHED command. A raster drainage network was generated in GRID using the FLOWDIRECTION and FLOWACCUMULATION commands. Each sampling point was then assigned to a grid cell within the drainage network. The WATERSHED process requires a set of one or more seed points for which a drainage area will be delineated. To delineate the total sourcesheds, an Arc Macro Language script was used to iteratively select the 78 sample sites and seed the DEM using only one site at a time. Following delineation, each set of sourcesheds was converted to polygons.

The polygon layer was then intersected with a gridded Level 1 Anderson land use/land cover data from the 1980 Michigan Resource Information System (MIRIS). Proportions of each land-use type (urban, agriculture, shrub/brush, forest, water, wetland, and barren) were calculated for the sourcesheds and exported to Excel spreadsheets for use in statistical analyses. Brief descriptions of each land use category are listed in 3.1. A more in-depth description of the land use classification scheme used in this study can be found in Anderson et al., 1976. Land use distributions for all sourcesheds are shown in Table 3.2 to illustrate the range of land use types within the GTBW. It is

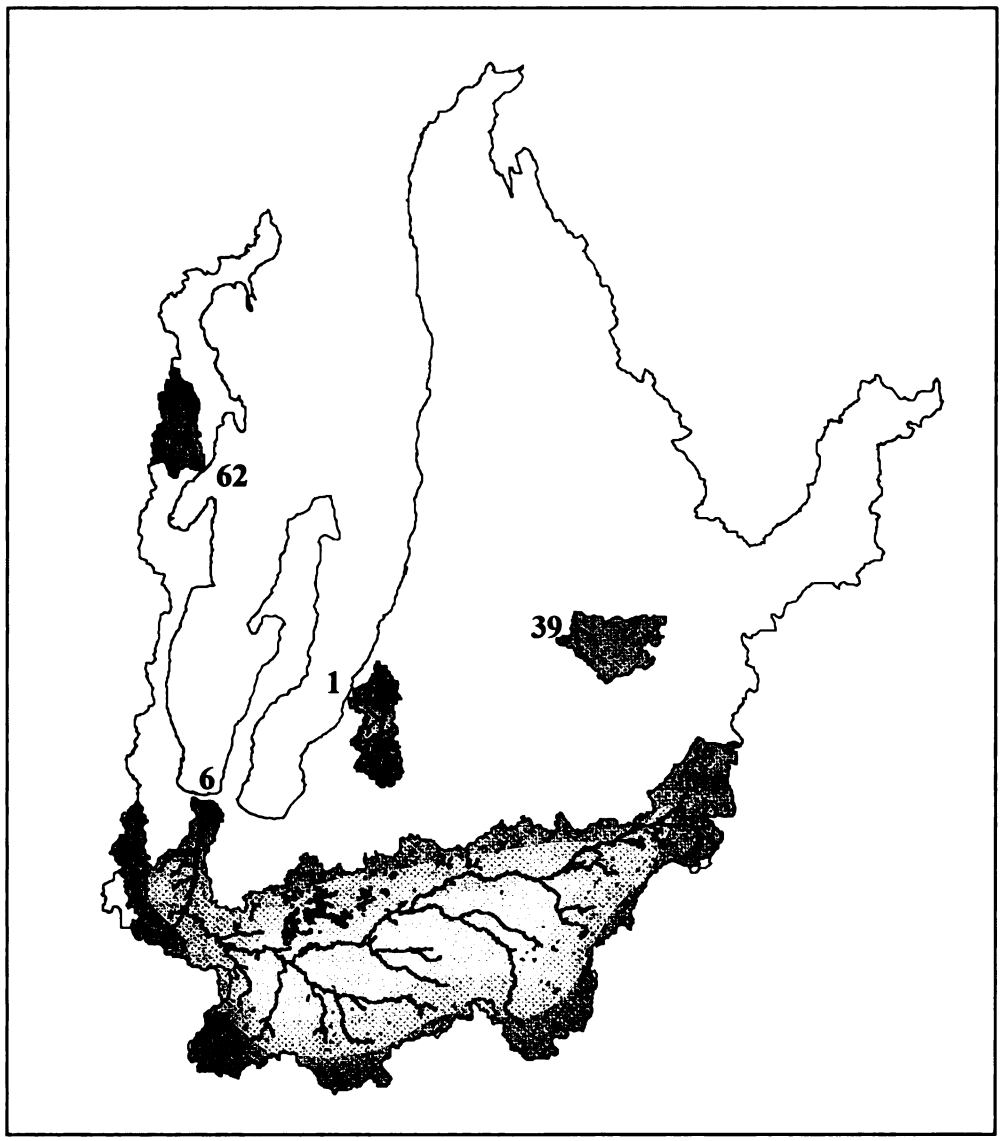

Figure 3. 3. Sourcesheds for sample sites 1, 6, 39 and 62. A sourceshed is defined as the total area that contributes to a selected drainage point, or sampling site. Sourcesheds were generated using the GIS software package Arc/INFO (ESRI).

Table 3.1. 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	Includes 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	Includes 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

Table 3.2. Land use distributions in sourcesheds of twenty sampling sites in Grand Traverse Bay Watershed. Sourcesheds were chosen to show the range of land use distributions in the contributing area above sampling sites.

Sourceshed	% Urban	% Ag.	% Shrub	% Forest	% Water	% Wetlands	% Barren
2	1.52	48.50	21.65	21.58	0.00	6.61	0.14
3	3.17	6.51	19.80	65.93	0.00	0.26	4.33
4	1.97	7.59	27.47	59.21	0.00	1.60	2.16
5	38.77	25.89	20.66	13.59	0.00	1.08	0.00
19	5.43	15.21	23.54	54.75	0.23	0.85	0.00
20	0.59	23.32	18.28	55.35	0.15	2.07	0.23
21	7.22	10.32	14.72	48.37	13.99	5.39	0.00
23	0.00	33.71	12.24	50.00	0.00	4.04	0.00
34	3.16	35.94	26.15	20.75	0.10	13.90	0.00
36	0.02	71.61	12.68	15.08	0.00	0.61	0.00
38	5.95	5.76	16.09	70.80	0.04	1.36	0.00
39	0.17	8.75	24.16	65.99	0.87	0.06	0.00
50	3.79	25.70	34.41	34.77	0.00	1.34	0.00
52	0.00	22.44	28.64	43.01	0.00	3.16	2.75
53	0.73	24.93	41.90	30.11	0.00	2.33	0.00
67	2.13	13.83	64.43	17.35	0.63	1.63	0.00
69	2.42	63.22	19.92	14.12	0.11	0.20	0.00
77	0.05	99.95	0.00	0.00	0.00	0.00	0.00
78	0.90	23.73	5.30	67.23	0.00	2.84	0.00
79	5.07	0.00	18.64	76.29	0.00	0.00	0.00

important to note that the sourcesheds are nested, so the sourceshed for a downstream sampling site includes the sourcesheds for all sites upstream.

Statistical Procedures

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., 1992; Long et al., 1988). A previous analysis of the GTBW data using 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 structured 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 one. This is the default procedure in SAS System (Cody and Smith, 1997).

The 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 ± 1). Oblique rotations, such as the Promax algorithm, 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 ± 1 indicates strong correlation between a variable and the factor, while a loading close to zero 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. A value of 0.4 for the lower end of moderate loading has been used in previous research (Evans et al., 1996; Miller et al., 1997), while other researchers have used the more conservative cutoff value of 0.5 (Puckett and Bricker, 1992).

Factor analysis does not require normalized data sets as long as data are not excessively skewed (Child, 1990), but transformation of data may result in an improved ability to interpret the factors (Gorsuch, 1974). Data can be log-transformed (Schot,

1992; Cameron, 1996), rank-ordered (see Miller et al., 1997), or converted to z-scores with a mean of zero and variance of one (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). Raw GTBW data were not normally distributed; preliminary analyses showed that log-transformation did not noticeably improve the interpretability of factors from GTBW data, nor were data normalized by this procedure. 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 run 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 the database, factor analysis was also run 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.

All statistical procedures were run using SAS System software (SAS Institute). The non-parametric Kruskal-Wallis test was used to test the hypothesis that the biogeochemical data from the three synoptic sampling events are equivalent.

Results and Discussion

Variability of Baseflow Chemistry

The surface waters of GTBW are well buffered, with alkalinity values ranging from 98 to 310 mg HCO_3^- mg/l and pH values from 7.44 to 8.72 (Table 3.3) over the three sampling events. The dominant cations are Ca^{2+} and Mg^{2+}, and the dominant anion is HCO_3^-. The concentration of other chemical species indicates that the waters in this area are of high quality. Dissolved oxygen levels are high, in some cases exceeding 100% saturation, and the mean nitrate concentration for each sampling event ranges from 0.25-0.59 mg/l. The maximum, minimum, median, and mean concentrations for all parameters over the three sampling events are shown in Table 3.3. Some common ions are graphed for each sampling event in Figure 3.4. A cursory comparison of the concentration information in Table 3.3 and Figure 3.4 suggests that baseflow chemistry varies with sampling event for most parameters. The mean and median values exhibit small fluctuations, but the high values show more dramatic differences among sampling events. This variability may be related to differences in flow (see Figure 3.2) and local inputs during each sampling event, and also seasonal effects (Clow et al., 1996; Puckett and Bricker, 1992).

The non-parametric Kruskal-Wallis test was used to test the hypothesis that the populations from which the three datasets were drawn have equivalent means

Table 3.3: Minimum, maximum, and mean concentrations and bioconcentration factors for Kendall Wetlands

Table 3.3. Minimum, maximum, and mean concentrations and chi-squared values from Kruskal-Wallis test.

	Sept. 1998				May 1998				Oct. 1998					
Variable	Min.	Mean	Median	Max.	Min.	Mean	Median	Max.	Min.	Mean	Median	Max.	χ^2	Prob > χ^2
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
DO	6.89	9.42	9.57	10.82	5.18	9.04	9.18	11.6	7.4	11.17	10.63	16.18	53.3642	<0.0001
Temp.	8.5	12.12	12.71	17.89	9.53	14.96	14.6	23.85	6.78	9.92	9.52	15.23	77.4813	<0.0001
Ca^{2+}	49.25	71.47	68.38	101.25	41	62.59	60	94	36.3	58.7	53.55	84.1	21.3048	<0.0001
Mg^{2+}	8.5	12.94	12.38	20.5	10.2	14.02	13.7	20.3	8.6	12.97	12	19.2	8.4402	0.0147
Na^{+}	1.5	5.37	4.87	13.7	1.2	5.94	4.3	40.72	1.03	5.5	4.23	21.5	0.3439	0.842
K^{+}	0.5	0.96	0.90	1.67	0.5	0.82	0.8	2	0.5	0.91	0.8	2.6	11.1779	0.0037
SiO_2	4.2	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
Alkalinity	98	199	192	323	163	236	232	310	172	235	215	355	17.402	0.0002
Cl^{-}	0	13.07	9.96	45.43	0.68	10.52	6.87	75.99	0.54	10.67	7.32	43.13	1.8611	0.3943
SO_4^{2-}	0	18.23	17.06	73.43	2.93	9.36	8.65	24.7	4.86	12.79	10.39	48.06	8.0646	0.0177
NO_3^{-}	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^{-}	N/A	N/A	N/A	N/A	0.001	0.229	0.194	0.775	0	0.168	0.099	1.89	16.5708	<0.0001

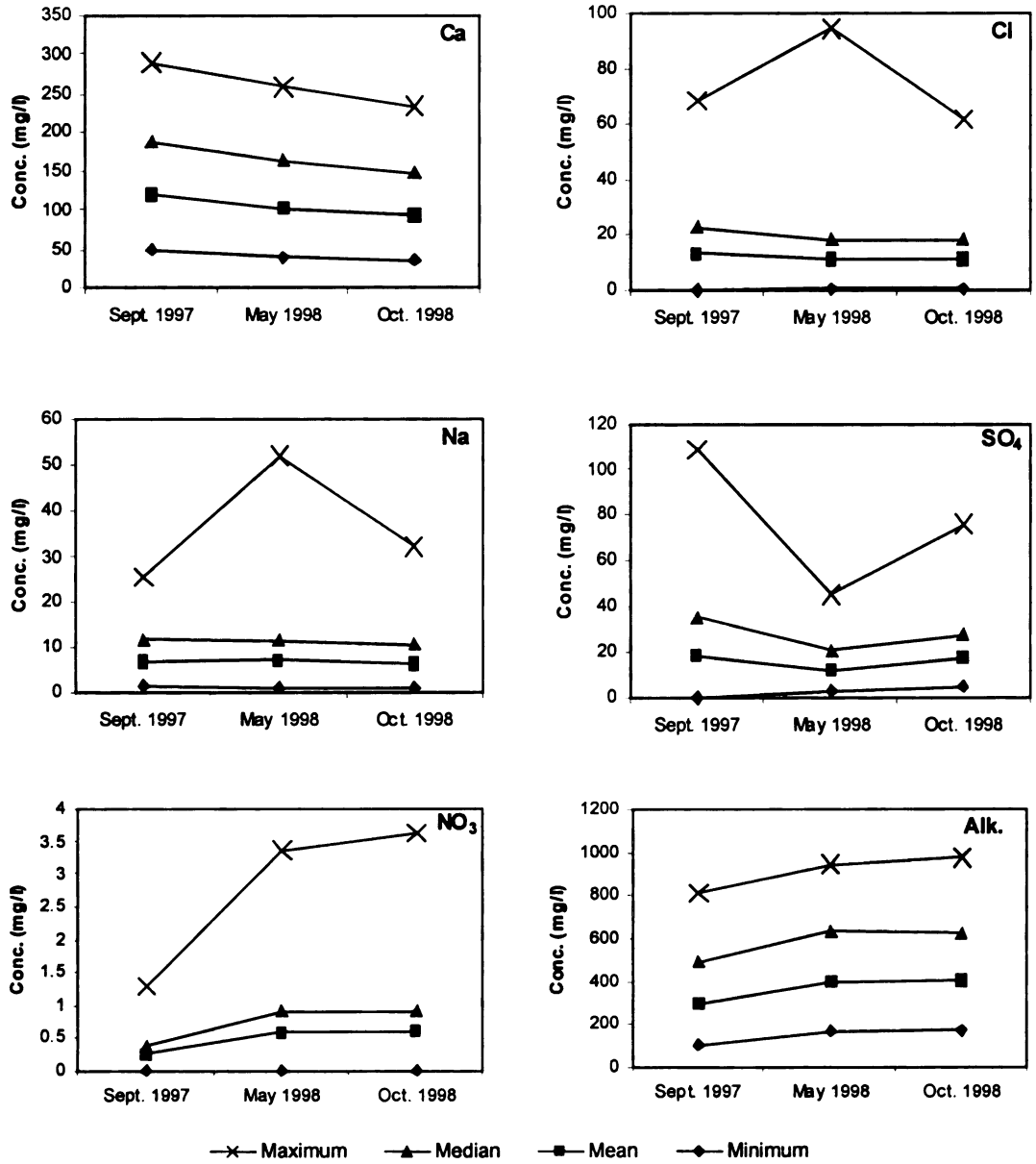

Figure 3.4. Mininum, mean, median, and maximum concentrations for some common ion concentrations over three sampling events.

(Gilbert, 1987). The χ^2 values and probabilities of exceeding χ^2 are listed in Table 3.3. A probability < 0.05 indicates that the chemical parameter is significantly different over the three sampling events. Only Na^+ and Cl^- concentrations were not significantly different at the 95% confidence limit, probably because these elements are least likely to be affected by changes in vegetative uptake over the course of the study period (Drever, 1997). These results show that baseflow chemistry varied significantly for most parameters over the three sampling events, potentially affecting our ability to develop consistent biogeochemical fingerprints for land use.

Factor Analysis

Comparison of Factors from Three Sampling Events

Factors for rank-ordered data from sampling events in September 1997, May 1998, and October 1998 are shown in Tables 3.4, 3.5, and 3.6, respectively. September 1997 samples were not analyzed for F^-, and DO measurements were not taken during this synoptic sampling event. Six factors had eigenvalues > 1 for the September 1997 dataset and seven factors for May 1998. The models explained approximately 91% and 85%, respectively, of the variability in the land-use/biogeochemistry databases. The six October 1998 factors explained approximately 100% of variability in the data, as shown in Table 3.6. The high percentage is probably 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^{2+}, Mg^{2+}, 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

Table 3.4. Factors for September 1997 data. Numbers in bold indicate strong loading on a factor (loading > 0.75). Only loadings > 0.5 are shown. F^- was not measured, and DO was excluded because of missing values. The cumulative percentage of variability in the data explained by factors is shown in the last line.

	Factors					
Variable	I	II	III	IV	V	VI
Urban		0.5985				
Agriculture	0.5748		0.5461	-0.5428	0.6336	
Shrub/brush						**0.8334**
Forest			-0.5679	0.5378		
Water	-0.6649				-0.5516	
Wetlands			**0.8403**			
Barren				**0.7790**		
pH						0.6672
DO						
Temp					-0.5550	
Ca^{2+}	**0.8860**				0.5048	
Mg^{2+}	**0.8433**					
Na^+		**0.8990**				
K^+		0.6718	0.7214			
SiO_2	**0.7646**					
Alkalinity	**0.8094**					
Cl^-		**0.9120**				
SO_4^{2-}				**0.8214**		
NO_3^-					0.7242	
Cumulative % Variance	21.8	39.7	54.5	67.2	80.3	91.1

Table 3.5. Factors for May 1998 data. Numbers in bold indicate strong loading on a factor (loading > 0.75). Only loadings > 0.5 are shown. The cumulative percentage of variability in the data explained by factors is shown in the last line.

	Factors						
Variable	I	II	III	IV	V	VI	VII
Urban		0.7197					
Agriculture	0.6701				0.5859		
Shrub/brush	0.6722						
Forest	**-0.7596**						
Water	-0.5529						-0.5256
Wetlands			**0.7738**				
Barren							**0.8183**
pH				0.7220			
DO				**0.8625**			
Temp			0.6975				
Ca^{2+}	**0.9244**						
Mg^{2+}	**0.9033**						
Na^{+}		**0.9063**					
K^{+}		0.6570			0.5949		
SiO_2			-0.5122				
Alkalinity	**0.8975**						
Cl^{-}		0.7346					
SO_4^{2-}						**0.8402**	
NO_3^{-}					**0.8448**		
F^{-}			0.5177				
Cumlative % Variance	26.5	42.4	56.5	70.4	78.0	85.4	85.4

Table 3.6. Factors for October 1998 data. Numbers in bold indicate strong loading on a factor (loading > 0.75). Only loadings > 0.5 are shown. The cumulative percentage of variability in the data explained by factors is shown in the last line.

	Factors					
Variable	I	II	III	IV	V	VI
Urban			**0.7643**			
Agriculture	0.6440	0.7088				
Shrub/brush	0.6305					
Forest	-0.5764	**-0.7663**				
Water	-0.6526					
Wetlands						**0.7951**
Barren						0.6530
pH				**0.7528**		
DO				**0.8114**		
Temp		**0.7574**				
Ca^{2+}	**0.8799**					
Mg^{2+}	**0.8326**			-0.6447		
Na^{+}		0.6492	**0.8704**			
K^{+}		**0.9141**	0.5044			
SiO_2				-0.5723	0.5622	
Alkalinity	**0.7996**					
Cl^{-}		0.6445	**0.8414**			
SO_4^{2-}	**0.8032**					
NO_3^{-}	0.6371					
F^{-}					**0.7830**	
Cumulative % Variance	27.7	50.1	67.3	83.8	94.5	~100

shrub/brush, K^+, SiO_2, SO_4^{2-}, and NO_3^-; 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^+, K^+, and Cl^-. 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 that appear in this comparison of sampling events 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. The researchers combined their data from different seasons into a larger database for factor analysis. This approach has the advantage of increasing the ratio of variables to observations, which can improve the interpretability of factors (Child, 1990). In fact, Evans et al. (1996) were able to include two additional 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 one-to-one to ten-to-

one (Child, 1990). In the case of our 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 was increased to 176, but 26 observations were omitted because of missing values. Factor analysis on the remaining150 observations is reported in Table 3.7. The seven factors explain approximately 88% of the variability of the data. Proportion agriculture exhibited strong loadings on Factor I, along with Ca^{2+}, Mg^{2+}, and alkalinity. Proportion forest had a strong negative loading on Factor I, and K^+ and NO_3^- had moderate loadings. Alkalinity, Ca, Mg, and K loadings on Factor 1 can be explained by the increased dissolution of soil minerals, such as calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and potassium feldspar (KAl_2SiO_8), 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 Wal, 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 attributed this effect to higher weathering rates of soil overturned during tillage. Other variables that load on Factor I in this analysis (K^+

Table 3.7. Factors for data from all sampling events combined. Numbers in bold indicate strong loading on a factor (loading > 0.75). Only loadings > 0.5 are shown. The cumulative percentage of variability in the data explained by factors is shown in the last line.

	Factors						
Variable	**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**
Urban		0.5936		0.5387			
Agriculture	**0.8793**						
Shrub/brush				**0.7509**			
Forest	**-0.7906**						
Water							
Wetlands					0.7455		
Barren							0.7433
pH						**0.8877**	
DO			**0.7827**				
Temp			**-0.8693**				
Ca^{2+}	**0.7746**						
Mg^{2+}	**0.7794**			0.6158			
Na^{+}		**0.8892**					
K^{+}	0.5955	0.7224					
SiO_2			**0.8244**				
Alkalinity	**0.7109**			0.6148			
Cl^{-}		**0.8498**					
SO_4^{2-}							0.6400
NO_3^{-}	0.5027				-0.6296		
F^{-}				0.5252			
Cumulative % Variance	23.1	30.0	51.7	64.5	72.0	80.7	87.8

and NO_3^-) are frequently associated with agricultural activities, such as land applications of fertilizer and animal wastes.

Factor II had strong loadings of Na^+ and Cl^- and moderate loadings of proportion urban and K^+. 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. There are other sources of Na^+, K^+, and Cl^- 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 watershed. The molar ratio of Na^+ to Cl^- in halite is 1:1; Figure 3.5 shows that the majority of samples collected during the three sampling events fall along a line with a slope of 1:1, as would be expected if halite

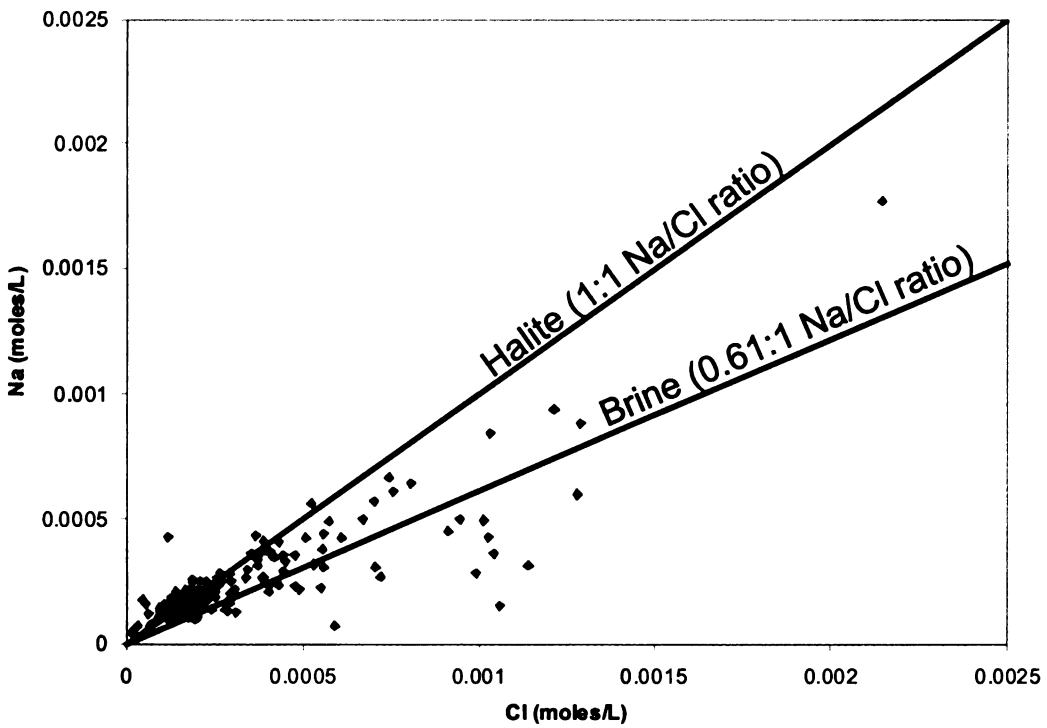

Figure 3.5. Ratio Na+ to Cl- (moles/L) in all samples for three sampling events. Halinte line represents 1:1 molar ratio that would result from halite dissolution. Brine line represents typical Na:Cl ratio in Michigan brines (from Wilson, 1989).

were the dominant source of these ions. Wastewater is enriched in Na^+ relative to Cl^- (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^-, 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:Cl molar ratio towards Cl, as well as the association of potassium concentrations on this factor. A reduction in the Na: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 (Shanley, 1994, Driscoll et al., 1991) and wastewater (Vengosh and Keren, 1996). Shanley (1994) summarized a series of studies reporting Na: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^- all occur outside Traverse City, and therefore may also be influenced by the application of brines to dirt roads. The typical Na:Cl ratio in brines from the GTBW region is approximately 0.61 (Wilson, 1989); a line representing this ratio is plotted on Figure 3.5. This ratio should also decrease due to cation exchange of Na^+ as brines move through the aquifer, which would explain Cl^- enriched samples that fall below the brine line.

Temperature was inversely related to DO and SiO_2 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_2 (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_2 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 may reflect daily cycles in SiO_2 and DO concentrations in the streams.

Factor IV included proportion urban, proportion shrub/brush, Mg^{2+}, alkalinity, and F^-, with only shrub/brush exhibiting strong loadings. Weathering of disturbed soils in urban regions and shrub/brush may account for the associations of Mg^{2+} and alkalinity with these land uses. The presence of fluoride is more difficult to explain. There is no major source of F^- 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. Non-sewered residential areas in GTBW include urban areas outside the Traverse City sewer system, pasture/shrubland that has been developed since the MIRIS database, and forested land that has recreational housing.

Proportion wetlands and NO_3^- had moderate but opposite loadings on Factor V. This inverse relationship between wetlands and NO_3^- concentrations may indicate that wetlands play a role in reducing nitrate concentrations, probably through denitrification, in sourcesheds with a higher proportion of wetlands than in other sourcesheds with fewer wetlands.

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 barren and SO_4^{2-} have moderate loadings on Factor VII. Atmospheric deposition is a major source of SO_4^{2-} to watersheds of the midwestern United States (Drever, 1997). Other sources in the GTBW may include sulfate-bearing fertilizers, sediments, and bacterial reduction 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 (see Table 3.1), since there is very little exposed bedrock or quarries in the watershed. These areas most likely have sandy soils with few exchange sites and little vegetation, and hence SO_4^{2-} should be more mobile in this environment, leading to higher concentrations of SO_4^{2-} associated with the barren land use category.

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 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 3.8). The inclusion of chemical parameters only for factor analysis is the standard approach for most studies of stream chemistry that utilize 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 (see Table 3.7). The first factor (Table 3.8) has strong loadings of Ca^{2+}, Mg^{2+}, and alkalinity, and a moderate loading of F^-. This factor reflects mineral weathering, similar to the first factor in all the previous analyses. The association of 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 Na^+, K^+, and 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 SiO_2 and a strong negative loading of temperature, which is identical to Factor III in the previous analysis. As described above, this factor likely 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.

Table 3.8. Factors for data from all sampling events combined but land use variables excluded. Numbers in bold indicate strong loading on a factor (loading > 0.75). Only loadings > 0.5 are shown. The cumulative percentage of variability in the data explained by factors is shown in the last line.

	Factors			
Variable	I	II	III	IV
pH				**0.7805**
DO			**0.7509**	
Temp			**-0.8656**	
Ca^{2+}	**0.8065**			
Mg^{2+}	**0.8986**			
Na^{+}		**0.8644**		
K^{+}		**0.8536**		
SiO_2			**0.8192**	
Alkalinity	**0.8685**			
Cl^{-}		**0.8678**		
SO_4^{2-}				
NO_3^{-}				
F^{-}	0.5653			
Cumulative % Variance	26.6	49.9	68.8	81.1

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 environmental 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 sampling event individually 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 Ca^{2+}, Mg^{2+}, alkalinity, and frequently K^+, SO_4^{2-}, and NO_3^-. Urban areas are associated with higher concentrations of Na^+, K^+, and Cl^-, most likely as a result of road salting. These two relationships were apparent even within individual sampling events. When all data were combined, associations of Mg^{2+}, alkalinity, and 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 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 identified some biogeochemical processes controlling variability in our data that are not associated with a unique land use, specifically the influence of pH and diatom productivity on stream chemistry.

The results of this research suggest that an individual sampling event cannot adequately characterize the complexity of processes controlling the interactions between land use and stream chemistry. The pathway of water to the stream may differ seasonally or with more short-term variations in antecedent moisture conditions, and thus the water-

rock, microbial, and dilution processes that influence baseflow biogeochemistry may vary as well. Variability in baseflow chemistry may be a potential limitation for the usefulness of one-time synoptic sampling to characterize 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 Anderson Level II land use classifications. Our analyses may also be improved by the use of groundwater sourcesheds that better reflect flowpaths of groundwater moving through a watershed. Riparian sourcesheds comprised 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 groundwater within a watershed must be considered in order to account for the effects of land use legacy on baseflow chemistry.

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CHAPTER 4
TRACE ELEMENT CONCENTRATIONS IN SURFACE WATERS OF A MIXED USE WATERSHED DRAINING TO LAKE MICHIGAN

Abstract

Improved data on the spatial variability of trace elements in surface waters are needed to determine the influence of natural and anthropogenic sources. This paper describes the results of a synoptic sampling of dissolved trace elements in a watershed draining to Lake Michigan. Data were collected using clean techniques to reduce sample contamination, and a multi-element analysis with ICP-MS allowed for reliable quantification of V, As, Mo, Sr, Mn, Ba, U, Fe, and Rb. Scandium data are consistent but less reliable. Correlations, cluster analysis, and factor analysis were used to explore dominant controls on stream chemistry, geochemical fingerprints for sample sites in similar clusters, and associations among chemical parameters and land use distributions. Sample sites with predominantly forested drainage areas clustered together. Geochemical fingerprints for other clusters with similar but mixed land use distributions were different, suggesting that land use distributions alone are unable to explain spatial variability in trace element concentrations. Only Ba and Rb were strongly correlated to land use. Factor analysis showed that redox processes may be important controls on the distribution of dissolved trace elements. The interaction of natural and anthropogenic processes complicates interpretation of trace element behavior the study site. However, concentration profiles along the largest river in the watershed showed that Mn, V, Rb, and Ba behave like solutes of anthropogenic origin, while Sc, Sr, Fe, U, As, and Mo behave like mineral-derived solutes. The Rb/Sr ratio was used to identify areas of the

watershed influenced by wastewater from septic systems or wastewater treatment facilities.

Introduction

Trace metals contamination is a growing concern in the Great Lakes (Nriagu et al. 1996); (Colburn et al. 1990), and improved data on the spatial variability of trace element inputs to the lakes will shed light on the relative importance of natural and anthropogenic sources. Reliable characterizations of trace element concentrations in surface waters draining to the Great Lakes are rare, and thus the influence of human activities on the geochemical cycling of these elements is poorly understood (Markich and Brown 1998; Sherrell and Ross 1999; Shafer et al. 1997; Shafer et al. 1999; Hurley et al. 1996). Recent studies have shown that conventional sampling protocols can be significant sources of trace element contamination to dilute freshwater samples (Benoit et al. 1997; Creasy and Flegal 1999), calling into question much of the data collected before ultraclean techniques were adopted for trace element studies (Benoit 1994; Hunt 1998). In essence, the study of trace elements in Great Lakes waters and their tributaries is a relatively new field due to the development of clean techniques, with the recognition that actual levels may be much lower than previously reported in the literature.

In the Great Lakes region, studies that employed clean techniques to sample streams and rivers have tended to emphasize the suite of heavy metals Pb, Cu, Cr, Cd, and Zn (i.e., Hurley et al. 1996; Nriagu et al. 1996; Shafer et al. 1999) because they are some of the most common elements associated with human activities (Moore 1990). Little is known about the distribution, chemical behavior and effects of other trace elements, such as V, Sc, Ti, Mo, U, Rb, and Sr, in the Great Lakes or their drainage

basin. Some of these elements can be highly toxic and/or persistent, but whether they pose an immediate or impending threat to the Great Lakes ecosystem cannot be gauged without a basic understanding of their sources and concentration levels.

New instruments for measuring pollutants in the environment, particularly inductively coupled plasma-mass spectroscopy (ICP-MS), have enabled detection of trace elements at the parts per billion to parts per trillion level. The ICP-MS technology also allows for multiple elements to be measured simultaneously, thereby increasing the amount of information that a single sample can provide. This multi-element approach for studying trace elements may reveal new insights into the interactions between natural and human-induced processes in the environment, which Sidle and Hornbeck have called "cumulative effects" (Sidle and Hornbeck 1991).

In this paper, we present the results of a synoptic sampling of dissolved trace elements in the surface waters of a watershed that drains to Lake Michigan. The primary goal of this research is to document concentration levels of some less abundant trace elements using a multi-element analysis to provide basic generalizations of terrestrial contributions to the Great Lakes. Trace element concentrations are evaluated in the context of land use distributions to identify possible relationships between the behavior of elements and human activities in the watershed.

Methods

The Grand Traverse Bay watershed (GTBW) is located in the northwest region of Michigan's lower peninsula (Figure 4.1). The Grand Traverse Bay is one of the last remaining oligotrophic bays in Lake Michigan. Aquatic ecosystems in the watershed are

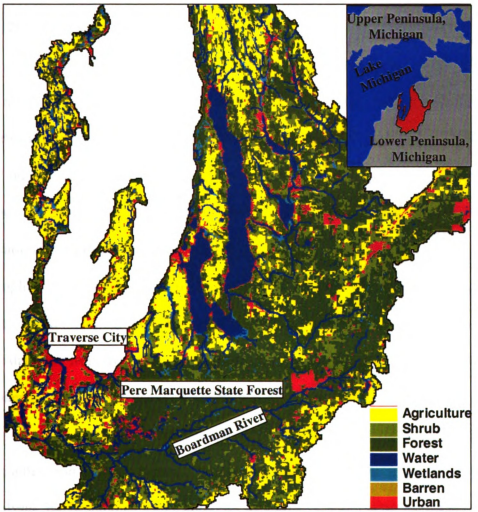

Figure 4. 1. Location of Grand Traverse Bay Watershed, Michigan and land use distribution.

still relatively healthy, but the region is undergoing some of the most rapid population growth in the state of Michigan (Michigan Information Center, 1997). Land use is diverse, with approximately 49% forested area, 20% agriculture, 15% shrub, 9% open water, and 1% wetlands. Urban areas comprise 6% of the watershed. The watershed's main urban center, Traverse City, is located at the mouth of the Boardman River, the major river draining to Grand Traverse Bay. The surficial geology of the watershed is

primarily glacial till and outwash of calcareous origin (Cummings et al., 1990; Boutt et al., 2001).

Surface water samples were collected over a three-day period in October 2000 at 63 sites along streams and rivers in the GTBW during baseflow conditions. Although parts of the watershed experienced light precipitation one week before the sampling period, the Boardman River hydrograph for the two weeks prior to sampling did not show a peak for storm flow. Sampling sites were located at bridges or other easily accessible locations to facilitate the rapid collection of samples. Land use distributions for each sampling site were generated by using GIS software to delineate surface water drainage areas based on topography. The resulting drainage areas were then merged with a land use database from the Michigan Resource Information System to calculate the percent of Anderson Level I land uses (Anderson et al. 1976) for each drainage area.

Clean sampling techniques were used to prevent the introduction of trace element contamination during equipment preparation, sample collection, storage, and subsequent analysis. We based the clean techniques used in this research on procedures reported in the literature (Benoit 1994; Horowitz et al. 1994; Nriagu et al. 1996; Benoit et al. 1997; Creasy and Flegal 1999), with modifications reflecting cost, time, and space constraints of the project. All equipment for trace element sampling was prepared in a Class 100 lab by personnel wearing booties, gloves, and full-length plastic lab coats. HDPE bottles and syringes were soaked in 15% trace metal grade HCl for 24 hours, followed by a 24-hour soak in 40% trace metal grade HNO_3. Syringes were disassembled, and the rubber cover to the plunger was removed because the rubber disintegrated in the acid baths. Bottles and syringes then soaked in hot HNO_3 (45° C) for 24 hours, rinsed, and soaked in

Nanopure cleaned water (NCW) water for 24 hours. The HCl bath was dumped and refilled three times during the bottle-washing period of the project to prevent build-up of trace elements. The HNO_3 bath was replenished each time bottles were removed with fresh acid and NCW water, and the entire bath was discarded twice over the preparation period. Bottles were filled with a 0.5% solution of Optima HNO_3 for transport to the field. Syringes were dried and reassembled.

Equipment that was intended only for one-time field use (syringe and 250-ml bottle for taking samples), rather than long-term sample transport and storage, was inserted in a single plastic bag, while 60-ml sample bottles were double-bagged. The plastic bags were prepared by turning them inside-out, then soaking them for several days in consecutive baths of 15% trace metal grade HCl and NCW water. The bags were then rinsed with NCW water, turned right side out, and dried. Field bottle kits were comprised of the afore-mentioned bottles and syringe, two bottles for anions, and a trace metal grade individually wrapped disposable 0.45-μm filter (Gelman AquaPrep) in a large plastic bag. One anion bottle was pre-preserved with 250 ml formaldehyde for SO_4 samples. Some bottle kits contained an extra bag with a clean-washed 60-ml bottle, syringe, and filter for field blanks.

At each sample site, a collapsible PVC cage was assembled and covered with two large, clear plastic bags to isolate the sample and sampling equipment from potential sources of contamination outside the clean cage. Slits were cut in one plastic bag for access, and the other bag was slid over the slits when the cage was not in use. The 250-ml sampling bottle was emptied of its storage solution and inserted into a plastic sampler before being dropped into the thalwag of the river. A sample was taken after the bottle

had been rinsed three times with river water. The bottle was then bagged and inserted into the clean cage. The filter was removed from its factory packaging and attached to the syringe. The storage solution in the 60-ml bottle was discarded, and after rinsing three times with the sample, water was poured into the syringe. The sample was filtered into the sample bottle by depressing the syringe plunger slowly, taking care that the rubber end of the plunger did not contact the sample. The sample was then acidified with Optima HNO_3 to a pH<2. The trace element sample bottle was double-bagged and the rest of the sample was filtered for alkalinity, anions, and SO_4. Field blanks were taken whenever a randomly chosen bottle kit contained the extra bag of field blank equipment. Blanks were processed with a fresh filter and syringe inside the cage using NCW water from 250-ml double-bagged bottles. Samples were taken using a standard "clean-hands, dirty-hands" protocol in which the "clean" person touched only the sample bottle and the "dirty" person touched all other sampling equipment. If this was not possible because of the layout of the sample site (usually if the stream was too shallow for the plastic sampler), the sampling person changed gloves before processing the sample in the clean cage.

Dissolved oxygen, temperature, and pH were measured at each site with a multi-parameter probe. Alkalinity was determined at each site with the Gran titration method. Anion samples were flash-frozen on dry ice. Bottles for cations and SO_4 samples were stored on ice until return to the laboratory.

Trace elements were measured using inductively coupled plasma-mass spectroscopy (ICP-MS; Micromass Platform ICP with concentric nebulizer) in a Class 100 facility. The Platform ICP is fitted with a hexapole lens that removes argon-based molecular interferences and allows lower detection limits for K, Ca, Fe, As, and Se than

earlier ICP-MS technologies. Samples were also analyzed for Ca, Mg, Na, K, SiO_2, Cl, F, NO_3-N, and SO_4. Major cations were analyzed by flame atomic adsorption (Perkin-Elmer 5100 PC) after the ICP-MS analyses had been completed. Fluoride was analyzed by specific ion electrode. Chloride, bromide, nitrate, and sulfate were determined by capillary electrophoresis (Hewlett Packard 3DCE). Silica was determined as silicon by ICP-MS.

Results and Discussion

Multi-Element ICP-MS Analysis

Standards for the ICP-MS analysis included Ti, Cr, Ag, Sc, V, Co, Ni, Cu, As, Sn, Se, Cd, Pb, U, Mo, Se, Rb, Fe, Sr, Ba, Mn, Zn, Al, K, and P. A solution of 20 µg/l In and Bi was added in a 1:1 ratio to standards and samples as an internal standard to test instrument stability. The data files generated from the ICP-MS runs therefore included counts and concentrations for all of these elements. However, this raw data must be censored to account for ICP-MS sensitivities for particular elements and concentrations above or below standards in the calibration curves. While the ICP-MS can be tuned to return high sensitivity to single elements, the instrument shows reduced sensitivity if used for multi-element analyses. Sample data must be further censored if analysis of field blanks indicates potential contamination.

Indium and bismuth are not considered analytes because they are used to test ICP-MS consistency between samples. The elements Cu and Ni were immediately eliminated from the data files because the ICP-MS cone is made of Ni and the coils contain Cu, and results indicated that the instrument cannot return accurate results for these elements in

the low-concentration range of the GTBW samples. Similarly, Al was eliminated because it is used as a substitute for other metals in the clean lab, and background levels are high compared to the concentrations in GTBW samples. The ICP-MS shows low sensitivity for K and P at concentrations in the GTBW samples, so these elements were also eliminated. Potassium was measured using atomic adsorption and is not considered a trace element but was included to see how the ICP-MS responded. The machine also produces unreliable estimates of Zn at low concentrations, so this element was eliminated. Silver results were disregarded because background silver levels in the ICP-MS are near or above concentrations in GTBW samples. Silver is an impurity in the Au solution used to preserve sediment samples for Hg analysis, and Hg-contaminated sediments are frequently run through the instrument. Titanium results were initially viewed as acceptable because the calibration curves were reasonable, but concentrations in the NCW rinses following each set of standards had high concentrations of Ti, indicating contamination between samples within the ICP-MS system or that the instrument is not sensitive to Ti at concentrations in the μg/l range. Scandium has not been eliminated from the data file, but results should be viewed with caution, because the element behaves similarly to Ti. Rinse concentrations for Sc were not as high as for Ti, but some were higher than the quantification limit.

Most of the elements discussed in the previous paragraph were eliminated solely on the known performance of the ICP-MS and its ability to produce reliable results for samples with extremely low concentrations. Other elements were eliminated from the data files because most samples had concentrations below the quantification limits determined by the calibration curves. The 63 samples and 13 blanks were analyzed in

four runs. Each run of approximately 20 samples included a set of seven standards before and after the samples. Calibration curves were calculated with a regression line that included standards with measured concentrations that fell within 15 percent of the expected value; points outside this range were not included in the calibration curves. The quantification limit for the run is considered the lowest standard in the final calibration curve. Concentrations below the quantification limit are typically reported as non-detects. However, if the blank (considered to represent a concentration of zero) was included in the calibration curve, values lower than the quantification limit were accepted without censure. The elements Se, Sn, Co, Pb, Cr, and Cd were eliminated from data files because concentrations for most samples were zero, which implies that the actual concentrations were much lower than quantification limit for each run (Table 4.1). The quantification limit was between 0.1 and 0.5 ppb for all elements except Se, which had quantification limits from 0.1 to 5 ppb. Almost all samples had higher concentrations for the remaining elements (V, As, Mo, Sr, Mn, Ba, U, Fe, and Rb) than the quantification limit for each run, so the data should be considered reliable. As mentioned previously, Sc was retained in the data file but the results are less reliable than for other elements.

Field Blanks

Thirteen field blanks were taken to ensure that the clean techniques eliminated potential sources of trace element contamination. With the exception of Sc and one V measurements, all concentrations in blanks were below the quantification limit for the run (Table 4.1). While the mean Sc concentration for blanks was 0.22 μg/l, the mean of all samples was six times this level (Table 4.2), and therefore, while the absolute values of Sc in samples are not reliable, the data may show general trends across the watershed.

The V concentration of one blank was slightly above the quantification limit of 0.10 μg/l (0.11), but since the concentrations of samples were on average three times the quantification limit, this blank does not indicate systematic V contamination from our clean techniques.

Table 4.1. Mean concentration and standard deviation for trace elements in 13 blanks for October 2000 synoptic sampling. Quantification limits are defined as the lowest standard included in the calibration curve. Quantification limits in bold indicate that the calibration curve included the zero concentration standard. All concentrations in μg/l.

Element	Mean and Standard deviation	Quantification limit
Sc	0.22 ± 0.04	**0.10**
V	0.04 ± 0.03	**0.10**
Cr	0.63 ± 0.22	0.25
Co	0.10 ± 0.05	**0.10**
As	0.06 ± 0.05	0.25
Mo	0.00 ± 0.01	**0.10**
Cd	0.00 ± 0	**0.50**
Pb	0.03 ± 0.10	**1.0**
Se	0.00 ± 0	0.10
Sr	0.00 ± 0	**1.00**
Mn	0.00 ± 0.01	**25.00**[a]
Ba	0.07 ± 0.08	**1.00**
U	0.00 ± 0	**0.10**
Fe	0.00 ± 0	25.00[b]
Sn	0.02 ± 0.02	0.50[c]
Rb	0.14 ± 0.02	0.25[d]

[a] Three of four runs had a quantification limit for Mn of 1.0 μg/l.
[b] Three of four runs had a calibration curve that included the zero concentration standard.
[c] Three of four runs had a quantification limit for Sn of 0.10 μg/l; these runs also had a calibration curve that included the zero concentration standard.
[d] Two of four runs had a quantification limit for Rb of 0.10 μg/l. The three runs not represented in this table had a calibration curve for Rb that included the zero concentration standard.

The field blanks did show potential Cr and Co contamination. The mean blank concentrations for Cr and Co were 0.63 μg/l and 0.10 μg/l, respectively, with

quantification limits of 0.25 μg/l and 0.10 μg/l, respectively. However, sample concentrations were almost all below the quantification limit, so our clean techniques do not appear to have contributed Cr and Co contamination. More likely, the bottles in which the NCW was stored contaminated the blanks. All sample bottles and syringes were new and were never opened outside the clean lab. Although none of the bottles used to transport NCW to the field had been used prior to this project, some had been acid-washed in a lab in which sediment samples from a heavily contaminated tannery site were processed. Both Cr and Co are used as pigments in the leather tanning process, and Cr was of particular concern at the tannery facility. The bottles were washed again in the Class 100 lab using the clean techniques described in the Methods section, but some residual Cr and Co may have remained in the bottles. While the potential contamination did not appear to have compromised our sample data, it implies that if equipment cannot be isolated to a Class 100 lab, a more rigorous washing procedure must be developed.

Trace Element Concentrations

Mean, median, minimum and maximum concentrations for major ions and dissolved trace elements are shown in Table 4.2. In general, the lowest concentrations of trace elements were measured in forested regions in the eastern and southern regions of the watershed, while sampling sites near Traverse City and the eastern shore of the bay had the highest concentrations. The eastern coast is highly developed, and sampling sites were located near a busy county road. The distribution of As did not follow this pattern: concentrations varied across the watershed with no apparent pattern, but some of the highest concentrations occurred in forested areas. High concentrations of As in streambed sediments and caddisfly larvae were correlated with forests in western Lake Michigan

drainages (Scudder et al. 1997). The cause of this association was not clear and may have been related to the use of arsenic-based defoliants during forestry operations or to contributions from igneous/metamorphic bedrock. The GTBW, including the Pere Marquette State Forest, was heavily logged prior to the early 1900's (Colby 1971), but it is unknown whether arsenic-based chemicals were used. Arsenic-based pesticides were used from the late 1800's to the mid-1900's in the United States, and old orchard soils and other agricultural land under long-term cultivation may be associated with high levels of arsenic (Azcue and Nriagu 1994; Bhumbla and Keefer 1994). Farmers moved in to deforested regions of the GTBW and planted potatoes, orchards, and other crops (Colby 1971). Again, it is not known if contemporary forests in the GTBW received As-based chemical inputs in the past, but the distribution of As in the watershed suggests that an understanding of historical land uses may be important in explaining current stream chemistry.

Median dissolved trace element concentrations in the streams and rivers of the GTBW are compared to concentrations in larger rivers in Table 4.3. Concentrations in the GTBW are generally lower than in larger rivers, with the exception of Fe and Mn, although there are not enough data to draw conclusions about the effects of scale on trace element concentrations. The comparison does show that trace elements in the GTBW are within one order of magnitude of values reported in recent studies that utilized clean techniques.

Table 4.2. Mean, median, minimum and maximum concentrations of geochemical parameters measured in 63 GTBW samples from October 2000.

	Mean	Median	Minimum	Maximum
DO (mg/l)	9.66	10.08	1.41	13.84
pH	8.03	8.05	7.48	8.35
Temp (°C)	10.03	9.82	5.60	17.65
Ca (mg/l)	68.31	64.45	42.15	95.10
Mg (mg/l)	15.13	14.80	9.69	20.62
Na (mg/l)	6.54	4.27	1.78	33.00
K (mg/l)	1.05	0.94	0.60	2.33
Cl (mg/l)	11.77	8.14	2.39	62.60
Alkalinity (as mg HCO_3/l)	236	232	133	336
SO_4 (mg/l)	12.90	11.44	5.54	36.70
NO_3-N (mg/l)	0.61	0.42	0.15	2.99
SiO_2 (mg/l)	10.17	10.26	5.38	16.86
F (mg/l)	0.16	0.13	0.06	0.53
Sc (μg/l)	1.22	0.98	0.42	4.24
V (μg/l)	0.30	0.30	0.08	1.14
As (μg/l)	0.32	0.26	0.00	1.19
Mo (μg/l)	1.16	0.96	0.27	3.53
Sr (μg/l)	56.89	54.30	24.08	108.06
Mn (μg/l)	11.55	5.14	0.00	302.82
Ba (μg/l)	18.47	14.69	7.31	68.85
U (μg/l)	0.38	0.32	0.07	1.61
Fe (μg/l)	33.40	11.04	0.00	1021.72
Rb (μg/l)	0.66	0.62	0.35	1.28

Table 4.3. Comparison of the median dissolved trace element concentrations in GTBW samples with other multi-element studies of U.S. rivers. Concentrations in µg/l.

	GTBW (median value)	Mississippi River[a]	Upper Mississippi[b]	Missouri River[b]	Ohio River[b]	Fraser River at Fitzwilliam[c]	Fraser River at Alexander Bridge[c]
Sc	0.98						
V	0.3	<3	1.4	1.8	0.5		
As	0.26	1.1				0.1	0.25
Mo	0.96	1.8	1.9	3.3	3.7		
Sr	54.3					39	85
Mn	5.14	1.8	0.7	2.7	1.3		
Ba	14.69	56	50.5	92.2	32.4	7.6	12.5
U	0.32		2.2	3.3	0.3	0.25	0.31
Fe	11.04	6.7					
Rb	0.62		1.3	1.4	1.6	0.12	0.83

[a]Horowitz, et al. (2001)
[b]Shiller (1997)
[c](Cameron et al. 1995)

Cluster Analysis and Trace Element Fingerprints

To better understand the spatial distribution of trace elements and their interrelationships, cluster analysis was performed on the trace element data. Cluster analysis of the major ions was discussed in Chapter 2. Before running the cluster analysis, the data were checked for correlations with the non-parametric Spearman's rho (Table 4.4). Sets of strongly correlated variables bias the identification of clusters within the data (Tatsuoka 1988); because Ba was correlated with so many variables (trace elements, or major ions that were then correlated to trace elements), Ba was excluded from the cluster analysis. Geochemical fingerprints for each cluster were developed by graphing the log of the cluster median divided by the median concentration for all samples for each element, including Ba. The cluster dendogram and geochemical fingerprints for each cluster are shown in Figure 4.2. Each sample site was also assigned

Table 4.4. Spearman's rho for correlations between geochemical variables. All geochemical variables were tested for correlations, but only rows containing correlations with rho>0.5 are shown in the matrix below. All correlations are significant at $p < 0.0001$.

	Ca	Mg	Na	K	Cl	HCO_3	SO_4	NO_3-N	F	Mo	Sr	Mn	Ba
Ca	1												
Mg	0.9256	1											
Na			1										
K	0.6523	0.5935	0.5420	1									
Cl			0.8457	0.6189	1								
HCO_3	0.8918	0.8809		0.5913		1							
SO_4	0.7177	0.7426		0.5212		0.7559	1						
NO_3-N							0.5032	1					
F	0.5833	0.5743				0.6498	0.6324		1				
Mo	0.5108					0.5014	0.7038		0.6197	1			
Sr			0.5412						0.5394		1		
Ba	0.6805	0.5374	0.5757	0.6536	0.6004	0.5625	0.6008		0.6633	0.5853	0.5506		1
U	0.6540	0.6958				0.6447	0.7541	0.5912		0.6538			
Fe												0.7515	
Rb	0.5580	0.5367		0.7281									0.5192

a number representing the cluster into which it fell; cluster membership could then be mapped across the watershed using GIS software (Figure 4.3).

The trace element data was separated into three groups with one outlier sample remaining after the clustering. Cluster 1 contained the majority of sampling sites (47) and therefore its cluster most closely represents the median values of each element for the entire watershed. Sample sites in Cluster 1 are located on streams that drain predominantly shrub and forested land with some agriculture (Table 4.5). Cluster 2 is comprised of seven sites; its geochemical fingerprint is characterized by lower V and As, and higher Mo, Mn, Ba, U, Fe and Rb than Cluster 1. The watersheds for cluster 2 sites are predominantly agriculture and shrub, although one site is heavily urbanized (40% of drainage area). The eight sites in Cluster 3 are also located in drainage areas with high

Table 4.5. Mean percentage of land use for sample sites in Clusters 1, 2, and 3. Cluster 4 is a single site, so table shows actual percentage land use in the drainage area for the site.

Cluster	% Urban	% Agriculture	% Forest + Shrub	% Water + Wetlands
1	3.6	26.2	66.8	3.2
2	4.9	44.9	47.7	2.4
3	11.9	31.2	56.1	0.8
4	13.1	36.3	46.7	3.9

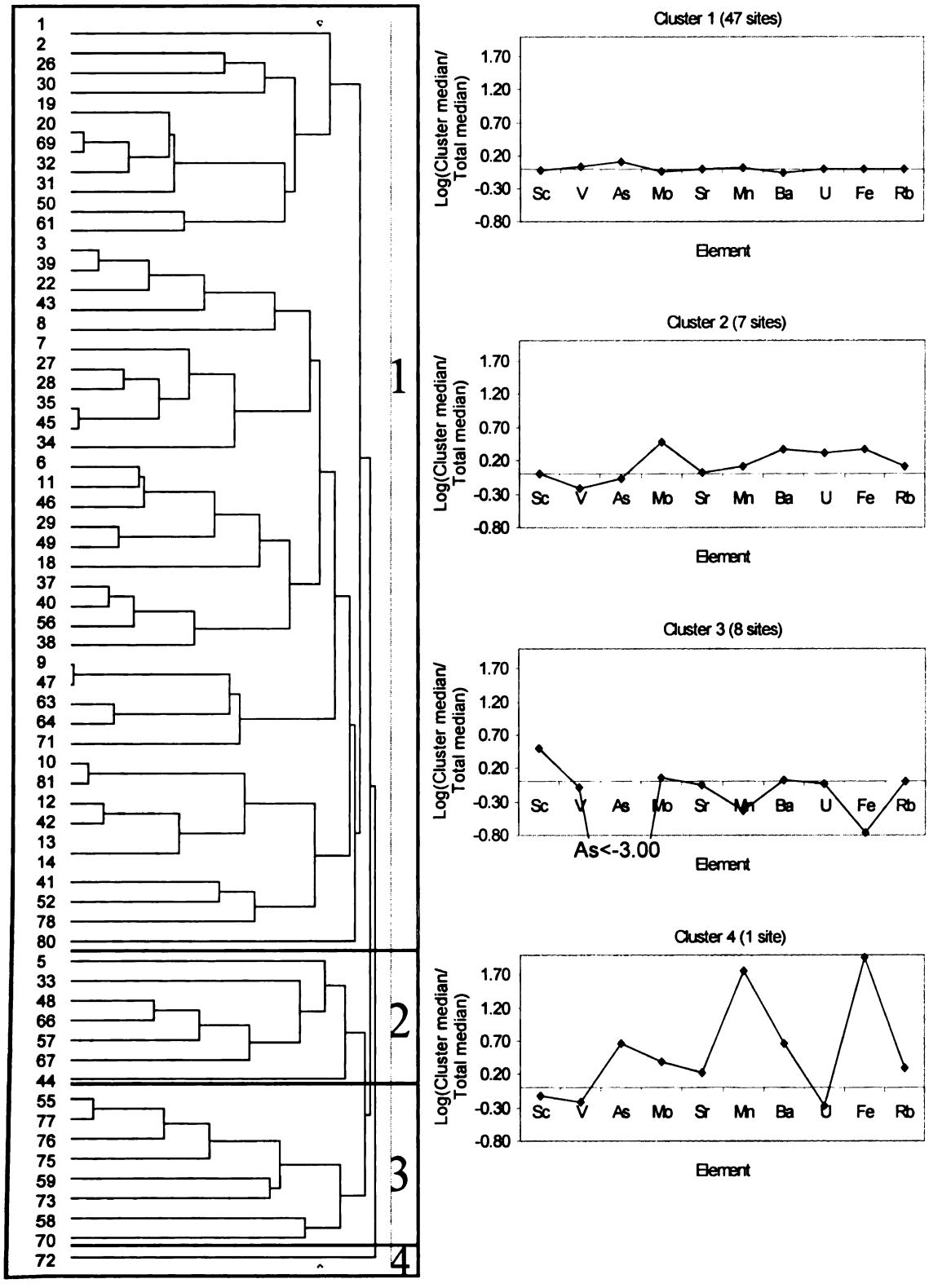

Figure 4.2. Cluster dendogram and geochemical fingerprints for trace elements.

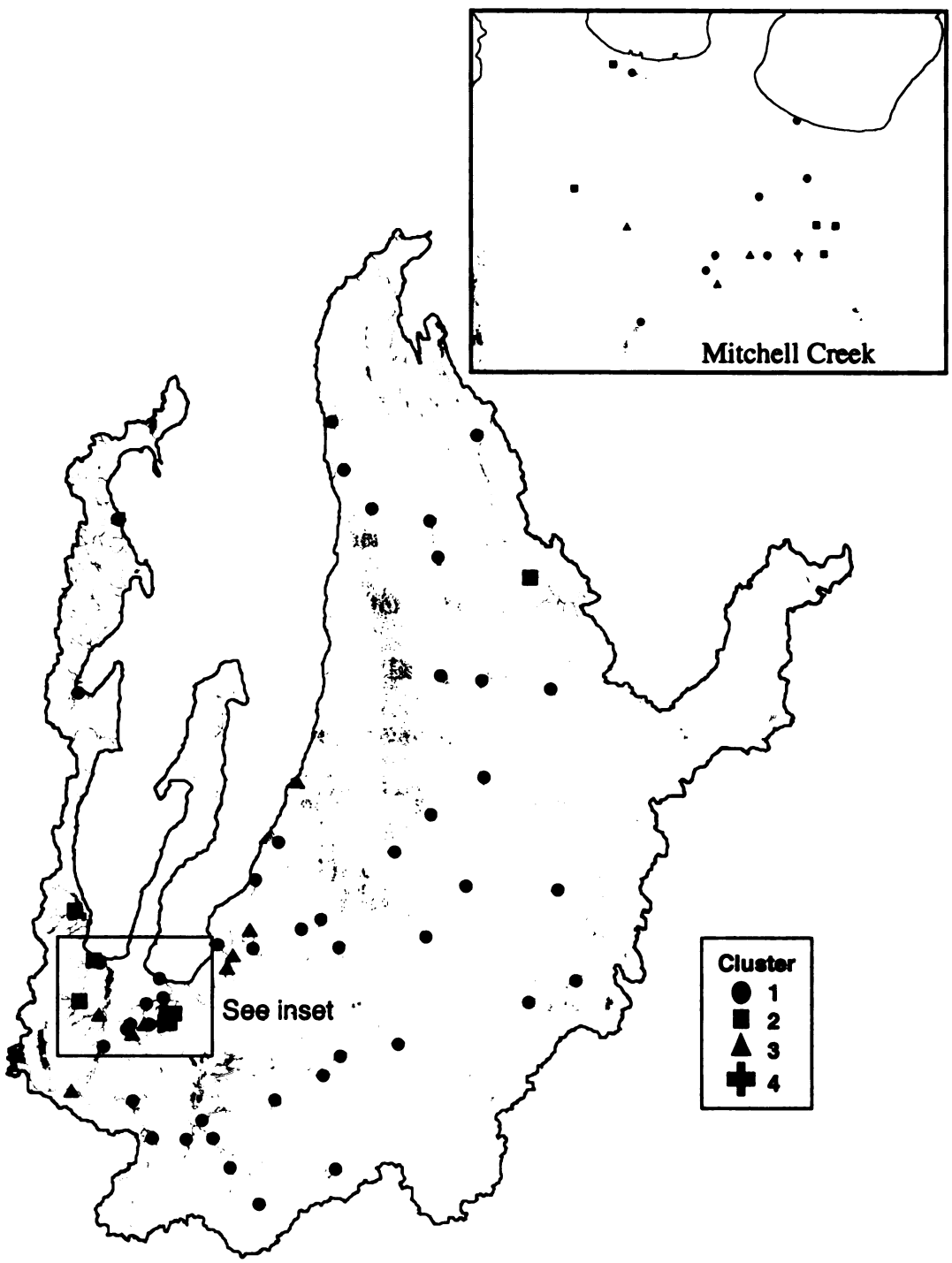

Figure 4.3 Distribution of trace element clusters in the Grand Traverse Bay Watershed.

percentages of agriculture and shrub, although one site drains a forested area, and the cluster has a higher mean percent urban than Clusters 1 and 2. The geochemical fingerprint for Cluster 3 is much different from that of either Cluster 1 or 2, with high Sc, and very low As, Mn, and Fe. The final site, which is labeled Cluster 4, has low concentrations of Sc, V, and U compared to the median values, and high concentrations of As, Mo, Sr, Mn, Ba, Fe, and Rb. This site was an outlier in the major ion cluster analysis (Chapter 2), too, and the high concentrations of redox-sensitive elements may indicate a localized contamination problem causing reducing conditions.

The similarity of land uses in the watersheds of sites in Clusters 2 and 3 contrasts sharply with their different geochemical fingerprints. This implies that the relationship between land use and trace element concentrations in the GTBW is complex, and that it may not be possible to develop a unique trace element fingerprint for individual land uses with our sampling approach. Only Ba and Rb concentrations were correlated with land use (Table 4.6). Barium was positively correlated to percent urban and agricultural land and inversely correlated to percent forested land, while Rb was positively correlated to percent agriculture ($p<0.0001$). Our previous work (Chapter 3) confirms associations shown in Table 4.3 between Ca, Mg, K, and HCO_3, and percent agriculture. These associations were attributed to enhanced soil mineral weathering from soil cultivation and

Table 4.6. Spearman's rho for correlations between land use and geochemical parameters. All land use and geochemical variables were tested for correlations, but only rows containing correlations with rho>0.5 are shown in the matrix below. All correlations are significant at $p<0.0001$.

	Ca	Mg	Na	K	Cl	HCO_3	SO_4	Ba	Rb
Urban			0.5281					0.5141	
Ag	0.5853	0.5201		0.7425		0.5844		0.5722	0.5253
Forest	-0.5868	-0.5558		-0.7428	-0.5032	-0.5909	-0.5819	-0.6953	

the use of fertilizers and animal waste. The link between percent agriculture and Rb and Ba is consistent with this explanation because these elements are naturally associated with K (Reimann and Caritat 1998). Wastewater from agricultural areas may also be responsible for elevated levels of Rb (Nirel and Revaclier 1999). The positive association between Ba and percent urban may be explained by other anthropogenic sources. Barium is released during fossil fuel combustion (WHO 1990), is found in brake linings (Hopke et al. 1980) and water softeners, and is used in a wide variety of industrial processes (WHO 1990). Barium can be used in sewage treatment plants (Reimann and Caritat 1998), and the cities of Kalkaska and Traverse City have treatment facilities along the Boardman River.

The inverse relationship of Ba and percent forested areas is more difficult to explain. The primary use of Ba is for drilling fluids (Reimann and Caritat 1998; WHO 1990; Moore 1990). There are oil and gas wells in the Grand Traverse Bay watershed, but sample sites with high Ba do not correspond to locations of oil and gas wells. In fact, most production wells are located in forested regions, and Ba concentrations are negatively correlated to percent forest.

Factor Analysis

For most of the trace elements in this study, natural sources (e.g., windblown dust and aquifer/soil minerals) may outweigh anthropogenic sources in the GTBW (Moore 1990; Reimann and Caritat 1998). Therefore, geochemical fingerprints may reflect differences in conditions affecting the mobility of each element, rather than direct anthropogenic inputs of these elements to the environment. Exploratory R-mode factor analysis was performed on rank-ordered trace element data to identify factors that may

explain the dominant controls on stream chemistry. Factors were rotated using the Varimax procedure. The interpretation of factors can form the basis of hypotheses for future research into trace element cycling in surface waters. Barium was excluded from the analysis because of its correlation with other elements. Factor analysis was run on data from all 63 sampling sites, and also on headwaters sites that were the first sampling site on a stream to test if serial correlation from sampling points on the same stream affected results. There was little difference in the factors returned by the two analyses, so the results from the total dataset are presented here. Four factors explained approximately 77% of the variance in the data. Factor loadings for each factor are listed in Table 4.7. Only loadings >0.5000 are shown; loadings between 0.5000 and 0.7500 are considered moderate, and those >0.7500 are considered strong.

Table 4.7. Results of R-mode factor analysis of rank-ordered trace element data. Only factor loadings <0.50 are shown. Factors from 0.50-0.75 are considered moderate loadings. Strong loadings (>0.75) are indicated by bold type.

Element	Factor 1	Factor 2	Factor 2	Factor 3
Sc				0.6261
V			**0.8020**	
As	0.5289		0.5067	
Mo		**0.8308**		
Sr				**0.8756**
Mn	**0.8834**			
U		**0.9332**		
Fe	**0.8697**			
Rb	0.5827		-0.5261	
% variance	25.7	20.0	16.6	14.4
Cumulative % variance	25.7	45.7	62.3	76.7

Manganese and iron have strong loadings on Factor 1, and arsenic and rubidium have moderate loadings. This factor reflects their similar behavior in response to redox conditions; these elements are more soluble under reducing conditions. Factor 2 has strong loadings for Mo and U, reflecting the tendency for these elements to form insoluble compounds in reducing conditions (Colodner et al. 1993; Crusius et al. 1996). Factor 3 has a strong positive loading for V, a moderate positive loading for As, and a moderate negative loading for Rb. Factor 4 has a strong loading for Sr and a moderate loading for Sc. Differences in response to redox conditions among elements, affinities for particulate and organic matter, dissolution of host minerals, and complexes with other solutes may explain Factors 3 and 4.

The results of the factor analysis imply that redox processes are important controls on dissolved trace element concentrations, which is consistent with the findings of a study of the temporal variability of the Mississippi River (Shiller 1997). The interpretation of factors is subjective, particularly without data on DOC, particulate concentrations, or speciation, and is made more difficult by the lack of information on the mobility of some elements (e.g., Sc; see Reimann and Caritat 1998). For example, Mn and Fe are predominantly associated with the particulate phase (Dekov et al. 1997; Shiller 1997; Horowitz et al. 2001), whereas the transport of Mo and U is dominated by the dissolved phase (Shiller 1997), and therefore, data on suspended particulate matter would provide more information for interpreting factors. Furthermore, the factors identified in this analysis can be interrelated, such as when Mo and U are scavenged by Fe- and Mn-oxides (Crusius et al. 1996; Andersson et al. 2001). We have also observed increased interpretability of factors as the number of observations increases (Chapter 3). These

factors are therefore suggestive of processes that may control trace element concentrations in surface waters of the GTBW, but more data are needed to fully explain these relationships.

Boardman River Concentration Profiles

The cumulative effects of human activities and natural processes (Sidle and Hornbeck 1991) are seen by plotting concentration changes along the Boardman River; differences in behavior along the length of the river may provide insight into the extent to which elements are affected by anthropogenic sources. Our analyses of major ion data from four synoptic sampling events in the GTBW (Chapters 2 and 3) indicate that trends for mineral-derived solutes (e.g., Ca, Mg, and HCO_3) are different from solutes that may be more directly affected by human activities. Chloride appears to be a strong indicator of anthropogenic influence in the GTBW and other watersheds (Herlihy et al. 1998); sources include road salt, agriculture, oil field brines, and domestic wastewater. While Ca concentrations and agricultural land distributions are correlated, Ca is a predominantly a mineral-derived solute in this calcareous region and is insensitive to pollution (Roy et al. 1999). We can use the behavior of Ca and Cl in the watershed's major river to predict which trace elements may be affected by anthropogenic inputs. As water flows from upstream to downstream sample sites along the Boardman River, solutes of anthropogenic origin tend to show fluctuations in concentration in the upper reaches but a generally increasing trend moving downstream, especially in the Traverse City region, while the concentrations of mineral-derived solutes remain relatively constant (Figure 4.4). However, the decrease in Ca concentrations below the Boardman Lake Dam observed in October 2000 was probably the result of baseflow dilution by overland flow

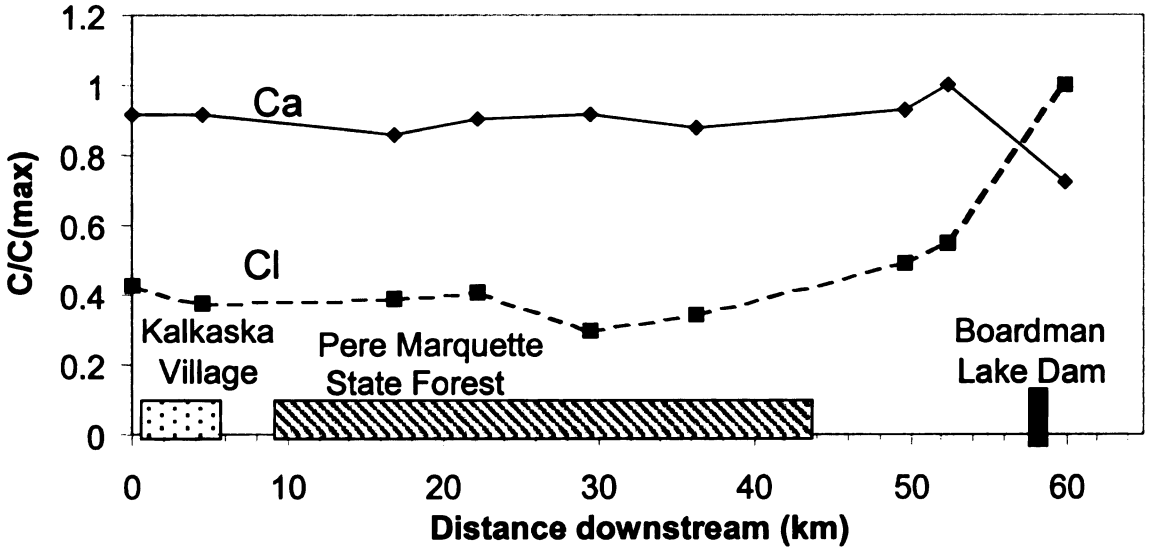

Figure 4.4. Concentration profiles from upstream sampling sites to downstream sampling sites along the Boardman River for Ca (a primarily mineral-derived solute) and Cl (a solute strongly influenced by anthropogenic inputs.)

from rainstorms one week before our sampling. Streams had returned to baseflow conditions during our sampling event, but the lake above the dam retained an overland flow signature because of its longer flush time relative to flowing streams.

The profiles for trace elements along the Boardman River are not conclusive as to the dominant controls (natural vs. anthropogenic) on concentrations, but they do suggest that Mn, V, Rb, and Ba behave like solutes of anthropogenic origin (Figure 4.5). These elements show increasing concentrations in downstream sampling sites of the river similar to Cl. Combustion of fossil fuels is the dominant anthropogenic source of V to surface waters (Moore, 1990). Fertilizers, agriculture and traffic can contribute Mn to the environment. The Boardman profiles further support the link between human activities and the elements Rb and Ba discussed previously.

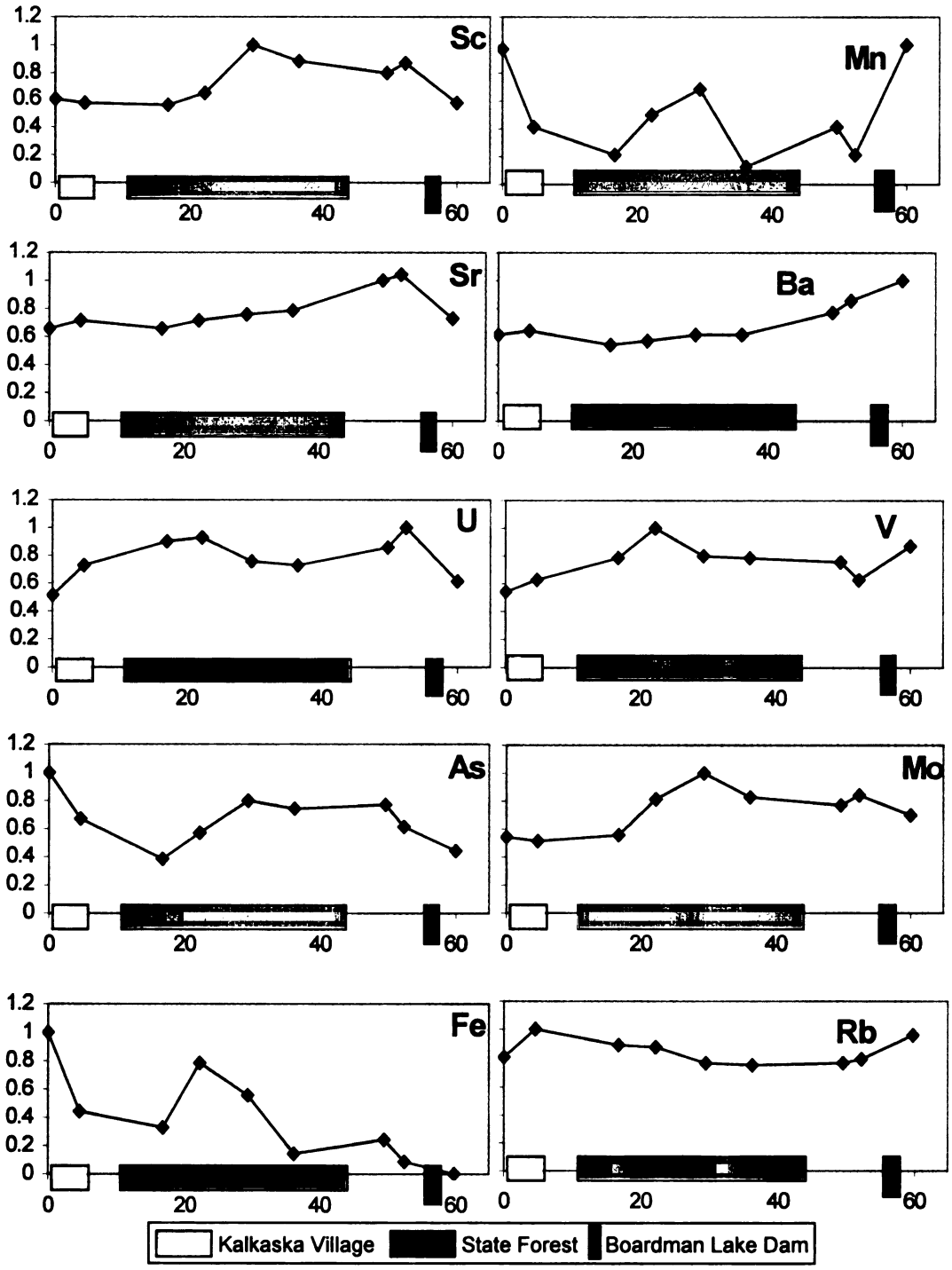

Figure 4.5. Concentration profiles of trace elements along the Boardman River from upstream sampling sites to downstream sites.

The elements Sc, Sr, Fe, U, As, and Mo show concentration decreases below the Boardman Lake dam, behaving similarly to Ca. With the exception of As and Fe, concentrations of these elements decrease between the last two sites on the Boardman River and are probably mineral-derived. Research in larger river basins has shown that while uranium has potential anthropogenic sources, such as fertilizers, most U in rivers is from the dissolution of carbonates. In contrast to Sc, Sr, U and Mo, the concentrations of As and Fe begin to decrease several sites above the Boardman Lake. Both of these elements have widespread anthropogenic sources, but their concentration profiles in the Boardman River are evidence that spatial patterns of anthropogenic sources overlay spatial variability in geochemical processes. For example, Mn and Fe concentrations are highly correlated (Table 4.4) and their behavior should be roughly similar, however their profiles differ sharply in the lower reaches of the river. Other research has shown tha anthropogenic sources of Mn can be significantly larger than natural sources, in contrast to Fe (Markich and Brown 1998). However, although Mn and Fe occur predominantly in the particulate phase in rivers, most Mn is in a less stable form as coatings on particles, while a significant fraction of Fe can be present in the particulate phase (Dekov et al. 1997; Prahl et al. 1998). The Boardman Lake dam may trap particles, reducing Fe concentrations, while Mn may be released from particles in the suboxic zone of the reservoir. The divergent behavior of Fe and Mn may be the result of interactions between natural processes and anthropogenic disturbances in the Boardman River watershed, illustrating the importance of considering the cumulative effects of land use on ecosystems.

Rb/Sr Ratio as an Indicator of Wastewater

Multivariate analysis of the trace element data collected in this study, as well as concentration profiles along the Boardman River, show that stream chemistry is affected by both anthropogenic and natural sources of solutes. The data can also be used to show the influence of a specific anthropogenic source, wastewater, on surface waters in the GTBW. The population of the GTBW has grown dramatically over the last two decades, and therefore, domestic wastewater may be a significant source of solutes to surface waters. Element ratios, particularly Cl/Br, have been used to track wastewater plumes (Vengosh and Pankratov 1998), but Br concentrations are below detection limits in the surface waters of the GTBW. Recent research has introduced the Rb/Sr ratio as an indicator of areas influenced by wastewater in calcareous regions (Nirel and Revaclier 1999), because biological material is enriched in Rb relative to Sr. Wastewater treatment plant effluent can have a Rb/Sr ratio of 0.10, while the ratio in limestone is 0.0050 (Nirel and Revaclier 1999). The spatial distribution of the Rb/Sr ratio in the GTBW is shown in Figure 4.4. Sites with higher Rb/Sr ratios are generally located in agricultural or mixed use drainage areas; the lowest Rb/Sr ratios are found within forested areas. Septic systems may account for high Rb/Sr in non-agricultural areas or predominantly agricultural watersheds in which animal waste is not produced or land-applied, such as orchards. The effects of wastewater can also be seen along the Boardman River. The Rb/Sr ratio increases near the city of Kalkaska, then decreases as relatively dilute water discharges to

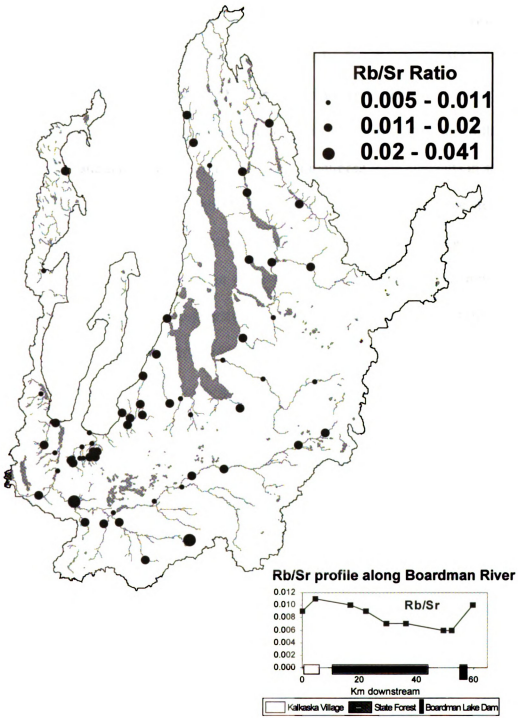

Figure 4.6. Rb/Sr ratios in the Grand Traverse Bay Watershed and along the Boardman River.

the river through the Pere Marquette State Forest. As the river flows through Traverse City below the wastewater treatment plant outflow, the Rb/Sr ratio rises again.

Research Questions for Future Work

The multi-element approach described in this paper has produced one of the first watershed-scale datasets of the occurrence of rarely monitored trace elements in surface waters. The data provide basic generalizations about associations among trace elements, as well as suggesting some intriguing relationships of element distributions with land use. Clearly, this work is only the first step in understanding linkages between natural and anthropogenically-influenced processes that control the fate and transport of trace elements in this watershed. A number of research questions arise from the results:

(1) The effects of regional atmospheric deposition must be distinguished from local sources of trace elements. Shafer et al. (1997) surmised that atmospheric deposition delivered similar fluxes of trace elements to two proximal watersheds in the western Lake Michigan drainage area. Differences in surface water concentrations were a result of watershed disturbances and resulting differences in export rates, rather than watershed inputs of trace elements. Our results imply that some elements may have sources within the watershed, but targeted sampling of potential sources, including wet and dry precipitation, would address this issue.

(2) Trace element geochemical fingerprints can be further refined by sampling drainage areas under a single land use to provide greater insight into the processes and sources that give rise to land use fingerprints. Scudder et al. (1997) sampled three types of sites: those with minimal anthropogenic influence, indicator sites with all land under a single use, and integrator sites

(3) Non-conservative processes that would obscure the dissolved trace element signatures of land use should be identified. The extent to which DOC, suspended particulate matter, and redox conditions affect the mobility of trace elements in this study should be further investigated through laboratory and field studies at both the watershed and molecular scales.

(4) Temporal variability of concentrations should be examined by periodic synoptic sampling throughout the year, or by continuous monitoring at some representative sites within the watershed. Even diel variations in trace elements related to changes in redox conditions, hydrology, and suspended particle concentrations have been observed in streams (Brick and Moore 1996) and may affect the results of synoptic sampling;

(5) The lag time between anthropogenic inputs in the watershed and arrival of solutes to surface waters should be quantified to understand how historical land use affects current geochemical conditions.

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CHAPTER 5
MODELING THE IMPACT OF HISTORICAL LAND USES ON SURFACE WATER QUALITY USING GROUND WATER FLOW AND SOLUTE TRANSPORT MODELS

Abstract

Groundwater age, and its influence on contemporary water chemistry, needs to be accurately described to quantify the temporally varying impacts of land use on water quality. The time lags between solute inputs at the land surface and impacts on stream chemistry can be an important factor for managing land use in regional watersheds. Our approach uses MT3D and a modified MODFLOW code to simulate reverse groundwater flow regional flow and solute transport model; flow distributions can then coupled with GIS analysis to examine the relationship between water quality and land use patterns in each sampling site's drainage area. The reverse flow and solute modeling produced a reasonable distribution of groundwater travel times across the watershed given the hydrology of the system. These groundwater flow paths would be unexpected if surface topography or even surface hydrology were used to predict groundwater movement. Approximately 70 percent of the watershed has a groundwater lag of 30 years or less. When the temporal lags for individual drainage areas within the watershed are compared, flush times vary dramatically; the variability is related both to the size of the sourceshed and its geology. The influence of a particular land use on stream chemistry changes depending on the time scale considered, and also depending on the sourceshed in question as a result of landscape diversity. The results suggest that land use management practices to reduce solute loading to a watershed may not result in water quality improvements for many years, especially if implemented on land far from streams. The

influence of long groundwater flow paths that integrate past with current land uses must be considered in the interpretation of land use effects on surface water quality.

Introduction

The biogeochemistry of surface water and groundwater are related to land use and land cover as well as to the geology of a region. One of the most common approaches to examine these relations is to develop statistical correlations between water chemistry and current land use in the drainage basins of surface water sampling points. Although this provides a good initial assessment, it does not account for the temporal lag for solutes to travel from the land surface to discharge points at streams or lakes. This time lag is commonly a period of decades for the groundwater inputs that supply the baseflow component of stream flow. Evaluating the distribution of time lags between source input and the impact on the stream chemistry can be an important factor for managing land use in regional watersheds.

The environmental impacts of land use/cover are not static in time or space. Variations in natural processes, such as microbial activity or plant growth, or seasonal variation in land use intensity can cause seasonal variations in stream chemistry. Temporal effects also occur on longer time scales. Recent research indicates that watershed land use in the 1950's was the best predictor of present-day aquatic invertebrate and fish diversity in three North Carolina rivers (Harding et al. 1998). Surface water quality samples taken at low flow are known to be representative of the groundwater chemistry in humid regions (Modica et. al., 1997). However, it is rarely considered that each stream-water sample taken at low flow represents a wide variety of groundwater ages, and thus reflects a time-weighted average of anthropogenic inputs

from the land surface. Therefore, groundwater age, and its influence on contemporary water chemistry, needs to be accurately described to quantify the temporally varying impacts of land use on water quality.

Ultimately, our research will explore whether a dynamic land use database that incorporates temporal changes can better explain current stream chemistry than static databases of land use at a single point in time. This paper describes the first step of our work, which is the development of a groundwater flow and transport modeling method that will allow us to link current stream chemistry measured at baseflow with historical land use distributions. Groundwater age distributions will be coupled with GIS-derived land use patterns to improve our understanding of the time lag between watershed-scale landscape changes and observed effects in surface waters. The approach presented in this work provides critical input for watershed planners on the potential delay between implementing land use management strategies and observing improvements in surface water quality.

Study Site

The Grand Traverse Bay Watershed (GTBW) in the Northern Lower Peninsula of Michigan (Figure 5.1) was chosen for this research because of the rapid population growth and land use intensification occurring in the region over the last several decades. The region was a relatively pristine watershed and has had increased urban and agricultural development over the last 50 years. As a result, there is increased concern over the impacts of these changes on the high quality surface and ground water resources.

Grand Traverse Bay is one of the last remaining oligotrophic bays in Lake Michigan. However, a 1998 summary of conditions in the bay indicated that the water quality in near-shore areas has deteriorated as a result of nutrient loading (GTBWI, 1998). Previous work in the watershed has documented potential correlations between high nitrate concentrations in groundwater and cherry orchards (Rajagopal, 1978). Nitrogen loading in the watershed has also been linked to atmospheric deposition, animal

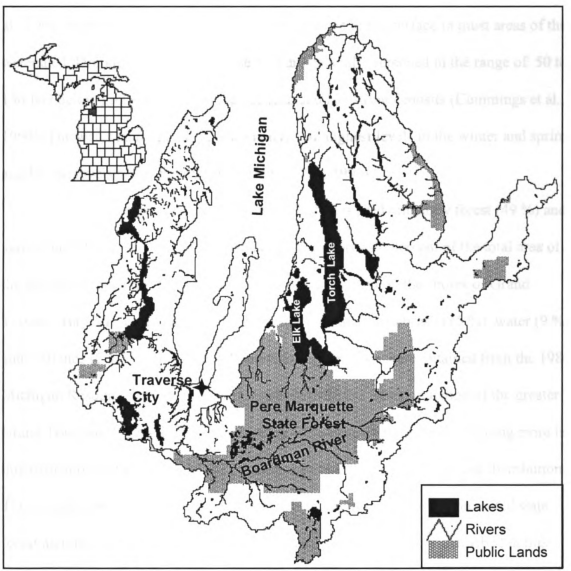

Figure 5.1. Grand Traverse Bay Watershed, Michigan.

waste, septic tanks, and fertilizers (Cummings et al., 1990).

The 2600-km^2 watershed contains over 100 lakes, including the Torch and Elk Lakes systems. The Boardman River is the main tributary draining the GTBW and exerts a strong influence on groundwater flow and gradient in the southern half of the watershed (Boutt et al., 2001; Cummings et al., 1990). The surficial sediments of the watershed, which can be as thick as 900 feet, are predominantly glacial outwash, till, lacustrine sand and gravel, and dunes, all of which overlay shale and limestone bedrock (Cummings et al., 1990; Boutt et al., 2001). The water table is close to the surface in most areas of the watershed. Drinking water wells in the area are generally screened in the range of 50 to 150 feet below ground surface in the outwash and lacustrine deposits (Cummings et al., 1990). The water table fluctuates seasonally, with highest levels in the winter and spring and lowest levels in the summer (Cummings et al., 1990).

Land use/land cover in the watershed is predominantly forest (49 %) and agriculture (20 %) (Figure 5.2). Urban land use comprises 6 percent of the total area of the watershed, with the Traverse City urban region located on the shores of Grand Traverse Bay. The other main land cover categories are shrub/brush (15 %), water (9 %), and wetlands (1 %). Land use distributions for our analysis were obtained from the 1980 Michigan Resource Inventory System database (MIRIS). The population of the greater Grand Traverse Bay region has increased by 42 % from 1980 to 2000, resulting more in intensification of the 1980 land uses than in significant changes in land use distributions. This is largely because almost all the forested land in the watershed is protected state forest and thus cannot be converted to any other land use. The work described in this paper is part of a larger research effort in the GTBW to study the

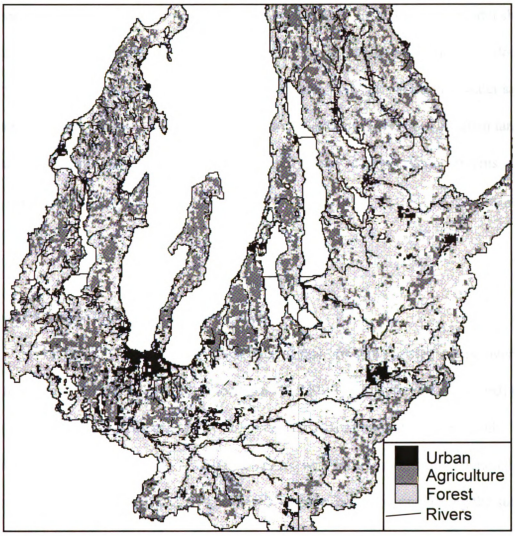

Figure 5.2. Distribution of urban, agriculture, and forested land in the Grand Traverse Bay Watershed.

relationship between land use and water quality indicators. Other components of this project include the development of geochemical fingerprints of land use through synoptic sampling of approximately 80 surface water sampling sites in the watershed, modeling land use change based on socio-economic drivers, and fingerprinting *E. coli* DNA to identify bacterial sources to streams and beaches. We previously developed and calibrated a groundwater flow model for this region and simulated the transport of

chloride from road salt to surface water bodies (Boutt et al., 2001). This model showed that although road salt is not the only source of chloride to this watershed, it is does appear to be the most significant on a regional scale. Through our surface water sampling program, we have also found strong associations between the amount of urban land in a drainage area and elevated levels of sodium, potassium, and chloride in streams (Wayland et al., in press).

Methods

Grand Traverse Bay Watershed Flow Model

The groundwater model that was used in this research has two layers, over one million grid 100x100 m cells, and more than 34,000 river cells (Boutt et al., 2001). Aquifer properties were obtained by compiling records of oil and gas wells and residential drinking wells in the watershed along with information from a detailed map of surficial geology (Farrand and Bell, 1984). The shale formation underlying the surficial aquifer, or the overlying thick clay layer present in some areas of the watershed, was identified in regional well logs and geostatistically interpolated to provide the bottom of the simulated aquifer. This shale/clay unit is assumed to be a confining layer impeding vertical flow. Six zones of similar glacial units were identified and assigned unique hydraulic conductivity values based on pump tests (Cummings et al., 1990) or published values for similar materials (Freeze and Cherry, 1979). Both layers were assigned the same value except where lacustrine sand and gravel overlie low conductivity clays. Head distributions simulated by the flow model accurately represented observed heads across the watershed, thus the model was used to produce the reverse vectors necessary to

simulate groundwater age distributions.

The hydrologic boundary of the groundwater system is shown in Figure 5.3 overlain by the watershed boundary as determined by surface topography. The surface boundary is typically used to delineate the area of watershed for management purposes, but groundwater inputs to the corresponding surface water body may not coincide with areas generating overland flow. Subwatersheds, or sourcesheds, also have different boundaries when determined by surface topography and groundwater flow.

Reverse Groundwater Flow Modeling Approach

Direct methods for dating groundwater age, such as isotopes and environmental tracers, rely on decay constants (isotopes) or time of introduction into the environment (environmental tracers such as CFCs and tritium). These methods are primarily useful for determining recent groundwater from older water (Domenico and Schwartz, 1990). Direct methods cannot delineate specific areas within a sourceshed that have contributed groundwater to a stream over a specific time period due to limitations caused by mixing of waters of different age and uncertainty of production, deposition, and decay. Groundwater age distributions can be developed using a relatively new modeling technique introduced by Goode (1996). Goode's direct simulation method uses a modified solute transport equation with age substituted for concentration and a unit aging term that increases by one for each day of the simulation (Goode, 1996; Varni and Carrera, 1998). An alternative modeling technique that has received little attention in the literature is reverse flow modeling, which will be used in this project to generate ground water age distributions for each sourceshed.

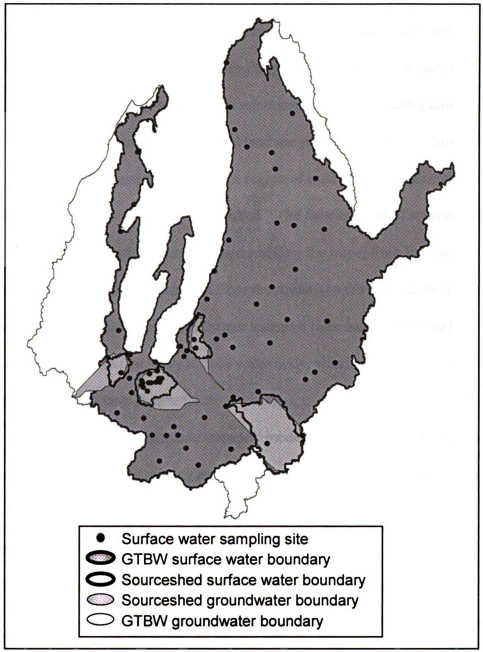

Figure 5.3. Groundwater and surface water boundaries for the Grand Traverse Bay Watershed and sourcesheds.

Our approach involves modifying the regional flow and solute transport model to simulate reverse groundwater flow; the resulting flow distributions at each time step are coupled with GIS analysis to examine the relationship between water quality measured at surface water sampling sites and historical land use patterns in each sampling site's drainage area. We first estimate the source region of water to each stream reach between sampling points, which we call a "sourceshed." The development of sourcesheds will be explained in greater depth below. We then simulate the travel time for water to reach the stream by tracking particles backward from the streams to the water table along simulated groundwater flow paths. This groundwater transport time map depicts the time for groundwater to flow to reach any surface water body, which will range from current ages near streams to decades-old ages far from streams.

The regional flow and solute transport model (Boutt et al., 2001) was used to simulate groundwater flow moving away from perennial streams instead of flowing to these discharge points. A similar approach was used to estimate historical nitrogen loading from the Waquoit Bay watershed (Brawley et al., 2000). Brawley et al. (2000) used reverse particle tracking to establish flow paths and groundwater travel times from streams, bay shoreline, and ponds. Our approach differs in two respects. First, reverse flow is achieved by modifications to the MODFLOW code so that water flows from surface water discharge points backwards to recharge points. Forward flow vectors are multiplied by –1 to produce reverse flow vectors, and the recharge flux becomes evapotranspiration loss. Secondly, solute transport modeling with MT3D produces advective fronts that represent contour lines of travel time. Rather than tracking specific

particles to establish travel times as was done by Brawley et al. (2000), all surface water bodies become sources of an unreactive species with a constant concentration of 1. As the solute transport simulation progresses, a concentration front moves from discharge to recharge along groundwater flowpaths. Areas within the concentration front are expected to contribute recharge water to surface water bodies over the specified timeframe.

The model was run for 150 years and output was saved at annual time steps. Output files for annual time steps were processed by converting all cells with concentrations > 0.5 to 1 and concentrations <0.5 as 0, since the advective front is represented by the 50% arrival location in advection dispersion simulations. All processed output files were then summed together to provide the number of years that an advective front was present. The final groundwater legacy map was then produced by subtracting this sum by one less than the maximum number of years (149). For ease of data manipulation, cell information was aggregated into 10-year intervals. This groundwater transport time database depicts the time for groundwater to flow to reach any surface water body, which will range from current ages near streams to decades-old ages far from streams.

Sourcesheds

The resulting flow distributions at each time step are coupled with GIS analysis to examine the relationship between water quality and historical land use patterns. We have developed both groundwater and surface water sourcesheds for each sample point. Surface water sourcesheds are based on DEM data, and groundwater sourcesheds were developed from the groundwater model. Although development of a groundwater flow

model is the most accurate method of determining groundwater sourcesheds, they can also be developed using an interpolated map of measured head data, provided enough data are available to approximate the location of the water table. Thus, an assessment of regional land use impacts on stream water quality can be developed without the expense of model development.

Sourcesheds were created within Arc/INFO GRID using the WATERSHED command. A raster drainage network was generated in GRID using the FLOWDIRECTION and FLOWACCUMULATION commands. Each sampling point was then assigned to a grid cell within the drainage network. The WATERSHED process requires a set of one or more seed points for which a drainage area will be delineated. To delineate the total sourcesheds, an Arc Macro Language script was used to iteratively select the 80 sample sites and seed the DEM using only one site at a time. Following delineation, each set of sourcesheds was converted to polygons. The polygon layer was then intersected with a gridded Level 1 Anderson land use/land cover data from the 1980 Michigan Resource Information System (MIRIS).

The travel time contour files for each decadal interval were clipped with the boundaries of each groundwater sourceshed using Arc/INFO. Data were organized by an integer code (001 – 147) containing information about decade and land use. Each line of data was assigned a code representing the decade (0 – 14) and the appropriate Anderson Level I land use category (1 – 7) from the MIRIS database. For example, the value 21 represents the period 20 - 30 years before present and the land use category urban (1). The value 103 indicates years 100 – 110 before present and forested land (3). The resulting grids were then stored as individual raster grids for future analysis. The portion

of each sourceshed polygon in a particular land use for each decade was calculated by summing cells in that land use. The 3-digit combined code was then separated back into two sets of codes representing decade and land use. The resulting table was exported to a spreadsheet program and used to examine changes in the contributing area of a sourceshed over time, and also how land use distributions within contributing areas changes with decade.

Surface Water Sampling

The sourcesheds discussed in the following section were chosen based on a comparison of estimated annual mass loadings of nitrate, sodium and chloride at different sites in the watershed. Surface water samples and flow measurements were taken during baseflow synoptic sampling in October 2000 at approximately 63 sites within the watershed. Sites 2, 5, 9, and 12 consistently had some of the highest mass loadings of solutes (see Figure 5.3 for locations of sites). These sites were also located in different regions of the watershed, and currently have a wide range of land use types. Sites 2, 5, and 9 are mixed-use sourcesheds undergoing rapid urbanization, particularly in the downstream regions near the GTBW shore. Site 12 is located at the mouth of the south branch of the Boardman River and drains forested and agricultural land. In a typical watershed planning scenario, these drainage areas would receive high priority for management activities because of their contributions to total pollutant loads from the watershed, and we therefore chose to illustrate the relationship between land use and groundwater age in these four sourcesheds.

Results and Discussion

Groundwater Flow and Age Distribution

The reverse flow and solute modeling produced a distribution of groundwater travel times across the watershed that appears to be reasonable given the hydrology of the system (Figure 5.4). Most of the watershed has travel times less than 150 years for water moving from recharge at the water table to discharge in a surface water body. Coastal regions discharge directly to the bay rather than streams and therefore have no specified travel time in this map since the bay was not considered as a solute source in the reverse flow simulation. The forward flow model estimated that roughly 7% of all water discharging to Grand Traverse Bay was direct groundwater flux, with the remainder coming from rivers and streams (Boutt, 2001). The longest travel times are found along the outermost edges of the watershed, although a slim band of longer travel times (indicated by dark cells) passes under the Boardman River. The map shows two distinct hydrologic regimes in the southern half of the watershed: one controlled by the Torch and Elk Lake systems and the other controlled by the lower reaches of the Boardman. In the eastern portion of the watershed in the headwaters of the Boardman River, it appears that only shallow groundwater feeds the river, while deeper groundwater flows under the river and discharges in the lakes region. In the western portion of the watershed, groundwater flows towards the Boardman River or smaller streams that discharge directly to the bay. These groundwater flow paths would be unexpected if surface topography or even surface hydrology were used to predict groundwater movement. The groundwater sourcesheds of sampling sites north of the Boardman River in the vicinity of Torch and

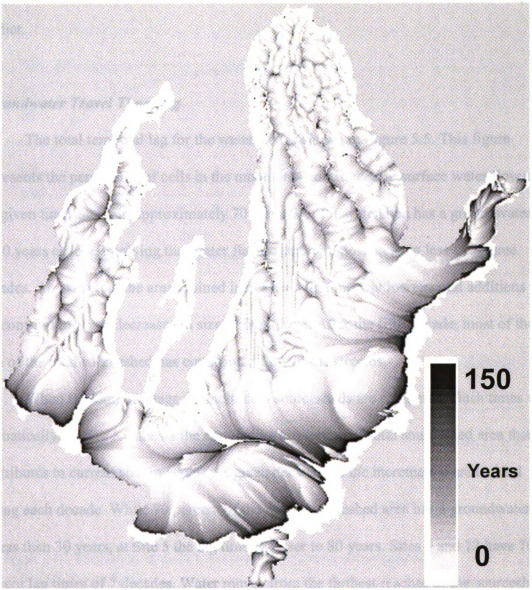

Figure 5.4. Land use legacy map for Grand Traverse Bay Watershed.

Elk Lake therefore encompass a far greater land area than surface sourcesheds would predict.

Groundwater Travel Time Lag

The total temporal lag for the watershed is shown in Figure 5.5. This figure represents the percentage of cells in the model that contributed to surface water flow over the given time interval. Approximately 70 percent of the watershed has a groundwater lag of 30 years or less, implying that water flushes through most areas in less than three decades. As expected, the area drained increases with time, but incremental additions to the contributing area decreases in size through time. After the fifth decade, most of the area of the total sourceshed has contributed flow to the streams.

When the temporal lags for individual sourcesheds are compared, flush times vary dramatically. Figure 5.6 shows the cumulative proportion of total sourceshed area that contributes to current stream water in a given decade and the incremental area added during each decade. While 70 percent of the Site 2 sourceshed area has a groundwater lag of less than 30 years, at Site 5 the lag time is closer to 80 years. Sites 9 and 12 have 70 percent lag times of 7 decades. Water moves from the farthest reaches of the sourceshed to the outlet in 70, 120, 140, and 120 years for Sites 2, 5, 9, and 12, respectively, based on 95 percent of the total area of each sourceshed.

Variability in flush times is related both to the size of the sourceshed and its geology. Site 2 is the smallest sourceshed with an area of approximately 18 km^2; sites 5, 9, and 12 are 95, 110, and 212 km^2, respectively. The effects of geology are reflected in the slope in the cumulative area curves. The slopes of the curves are shallower as water

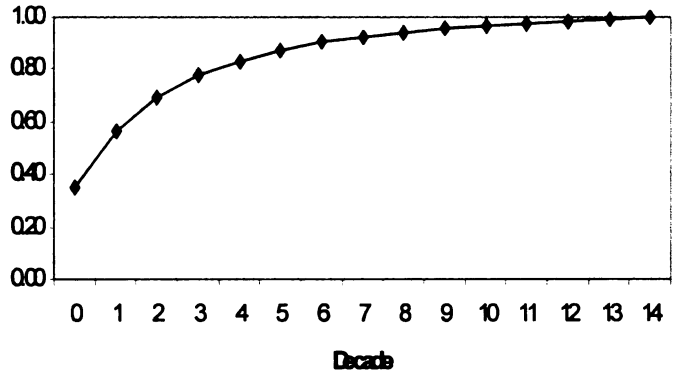

Figure 5.5 Proportion of total watershed flushed at a given time interval.

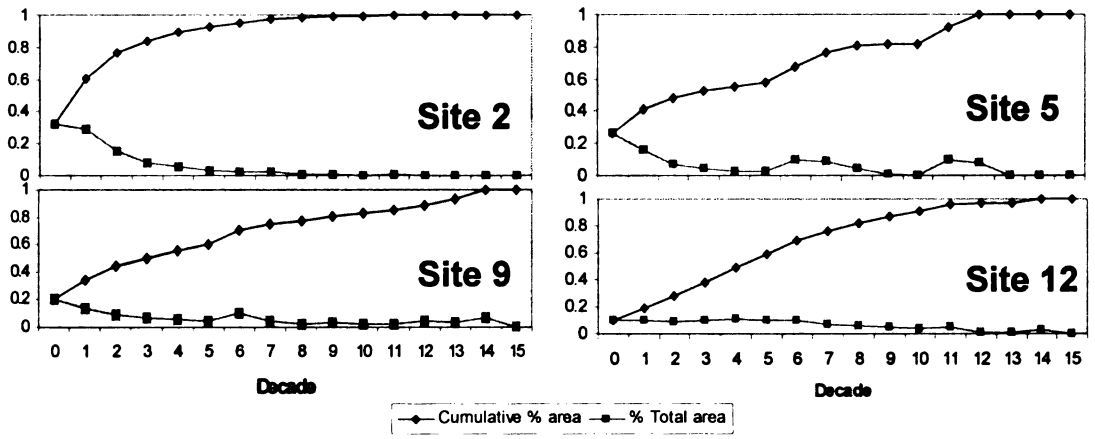

Figure 5.6. Variations in flush times and incremental area/decade for individual sourcesheds.

moves through areas of lower hydraulic conductivity, such as tills (3 m/day) and dune sands (10 m/day). Water moves faster through lacustrine sand and gravel deposits (21 m/day) and outwash plains (24 m/day), and therefore more area per decade is added to the contributing area of the sourceshed in higher conductivity zones. The best example of this effect can be seen at Site 5: the cumulative percent curve shows pronounced steps as the geology changes from sand and gravel to end moraine to outwash moving from the mouth of the sourceshed to its headwaters. The bottom curve representing the incremental addition of area per decade has two peaks during which a greater percentage of area is added to the sourceshed; these peaks likely correspond to high conductivity zones within the sourceshed.

There are several implications of differences in flush times across a watershed for land use planners and environmental managers. The reverse flow model shows that the time period for groundwater to move through 90 percent of the area of a sourceshed fluctuates spatially in the GTBW (Figure 5.7). The shortest flush times (20-50 years) occur in small coastal sourcesheds, while larger coastal sourcesheds and the downstream reaches of large streams can have 90 percent flush times exceeding 80 years. Watershed management strategies applied uniformly across the landscape to reduce solute loading will therefore have variable influence on stream chemistry related to the flush time of individual sourcesheds. An understanding of flush time distributions can help target priority drainage areas and also create realistic expectations for the short-term effectiveness of management activities.

A second and related implication of our results is that regardless of the size or geology of a sourceshed, the lag time between groundwater recharge at the landscape

surface and discharge in surface waters is significantly longer than the life of most management plans. Land use plans are typically developed for relatively short time periods compared to groundwater travel times. County master plans in Michigan are redrawn at five-year intervals; state environmental grants rarely exceed the same time period. Therefore, twenty years may be considered long-term planning. The effects of management practices may not result in water quality improvements for many years, especially if implemented on land far from streams. In the GTBW, 60-80 percent of many smaller sourcesheds are drained in 20 years, while in some of the large sourcesheds, groundwater moves through less than 20 percent of the area during the same time period (Figure 5.8). Furthermore, management strategies to improve surface water quality frequently focus on infiltration enhancement to reduce overland flow, because runoff is often the greatest source of nonpoint source pollution in a watershed. Cassell and Clausen (1993) modeled a shift in phosphorus export from a field after runoff controls were implemented to increased loading through infiltration. Thus, some management strategies may initially improve water quality while resulting in continued loading to the groundwater system that will eventually discharge to surface waters. This is particularly a concern for conservative species, such as chloride and to lesser extent, sodium.

The Changing Influence of Land Use on Stream Chemistry

Land uses are not evenly spread across landscapes, and therefore the land use distribution in the contributing area of a sourceshed will change as travel time front moves through the sourceshed. The patchiness of landscapes is reflected in Figure 5.9.

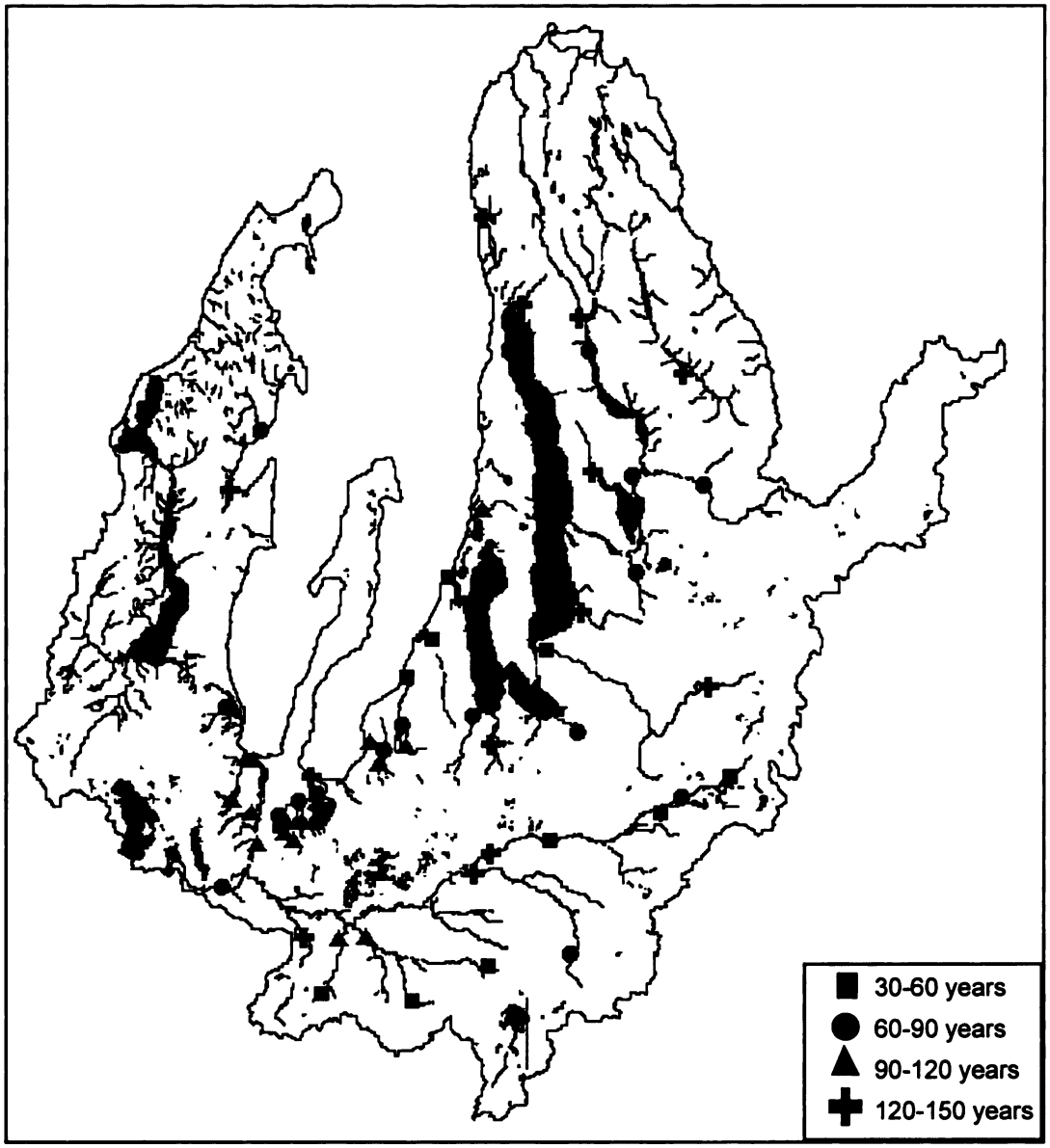

Figure 5.7. Flush time for 90% of total sourceshed area.

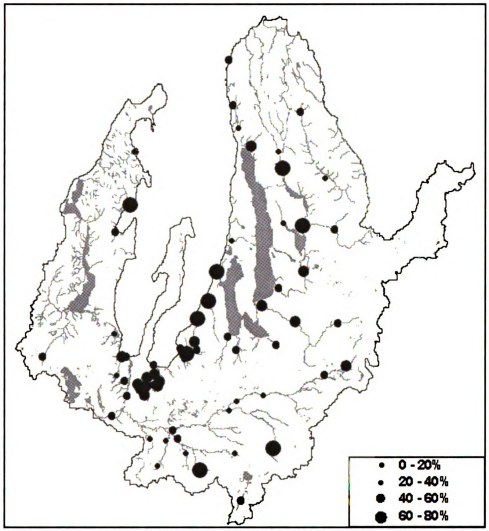

Figure 5.8. Percentage of groundwater sourceshed flushed in a 20-year period.

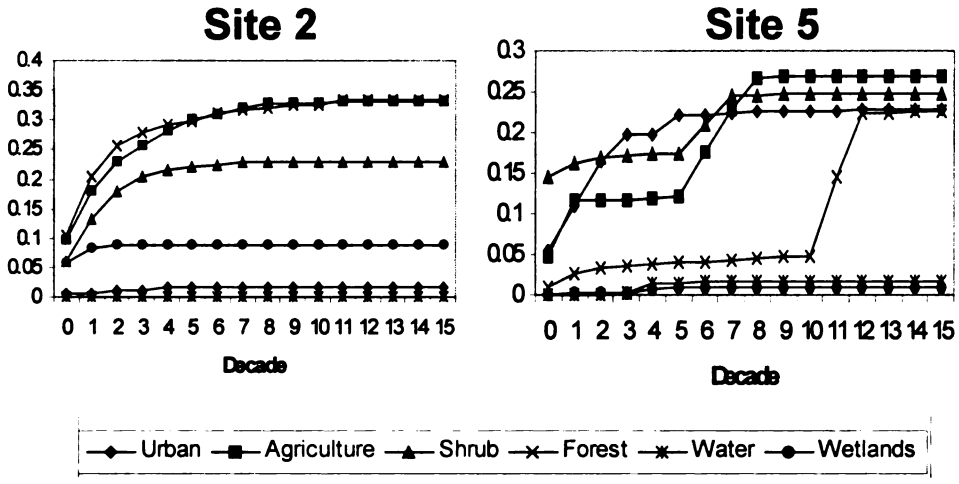

Figure 5.9. Changes in proportion of land use in contributing area relative to the total sourceshed area over time.

Each curve represents the cumulative total of a land use within the contributing area for the time step divided by the total sourceshed area. In other words, the influence of a particular land use on stream chemistry changes depending on the time scale considered, and also depending on the sourceshed in question as a result of landscape diversity. Site 2 does not exhibit much landscape diversity, while Site 5 has patches of different land uses that variably influence stream chemistry with time. Within the 50-year travel interval, urban land comprises a larger percent of the contributing area than other land uses, but after the 60-year contour, agriculture, shrub, and forest become important. Land management strategies will clearly have the most immediate effect on water quality if implemented in the near-stream zones, since the lag time between reductions in solutes and groundwater movement to streams will be lowest in this zone. Our model suggests that buffer zones should be based not on some arbitrary distance from streams but on

groundwater travel times, and that management plans must consider the land use distributions within the contributing area that corresponds to the desired planning horizon.

Landscapes exhibit not only spatial variability but also temporal variability; the incorporation of land use changes over time adds another layer of complexity to the development of an accurate model of the influence of land use on water quality. GIS coverages of recent land use may not reflect conditions in the watershed during most of the transport period. More robust chemical signatures for individual land uses may appear if the legacy of land use is considered instead of a static distribution of land uses based on a single year, as is shown in Figure 5.9. The next step in our research is to merge the areas for each decadal time step with a land use database corresponding to the appropriate time interval.

Conclusions

The approach presented in this paper provides a groundwater transport time distribution that can be coupled with GIS-based land use data to improve our understanding of linkages between land use and surface water chemistry. We recognize that the impacts of overland flow and near-surface groundwater flow during storm events represents a significant source of anthropogenic solutes to a watershed. However, our approach addresses the impact of land use on stream chemistry through groundwater inputs, both spatially and temporally, which is rarely given weight in management plans. The results from preliminary work with this approach illustrate the importance of considering the time lag between management activities in upland regions and effects in

surface waters. Regions that have rapid transport to surface water can be quickly identified on the map of predicted travel times. Thus, rather than developing stream buffer zones based on some arbitrary distance, they can be determined based on the simulated travel time to surface water bodies. The groundwater flow model also emphasizes that surface topography does not always coincide with groundwater flow patterns, and therefore groundwater sourcesheds should be delineated along with surface sourcesheds to accurately target land uses contributing solutes to streams. In addition, the degree to which constituents measured in surface water samples actually arise from groundwater inputs, and the influence of long groundwater flow paths that integrate past with current land uses must be considered in the interpretation of land use effects on surface water quality.

Groundwater travel time from recharge to discharge can be on the order of 100 or more years in some watersheds, and therefore baseflow is a mixture of groundwater ages. Baseflow geochemistry is thus an integration of land use both spatially and temporally. Effective watershed modeling and management efforts must address the imprint of past land uses on groundwater, or the land use legacy. More robust relationships between stream chemistry and land uses may appear if a dynamic database of land uses is considered instead of a static distribution of land uses based on a single year. Future work with the reverse groundwater flow and solute transport model will include the incorporation of multiple databases on land use distributions in the watershed as far back as 1938. The model will also be used to predict the sensitivity of water quality at individual sampling sites to different land uses.

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CHAPTER 6
CONCLUSIONS

The overall hypothesis of this research was that the effects of land use on the biogeochemistry of streams can be quantified and that a unique biogeochemical fingerprint can be identified for an individual land use. The quantification of unique biogeochemical fingerprints for land use was difficult in the GTBW because sample sites were not specifically located in drainage areas with unique land uses. However, cluster analyses of major ions and trace elements showed similar patterns of low concentrations in forested areas and higher concentrations near Traverse City and the Mitchell Creek watershed. Correlations and factor analysis showed strong associations between some solutes (Na, Cl, K, SO_4, NO_3-N, Ba, and Rb) and areas in the watershed that are undergoing land disturbance from development or agriculture. The Rb:Sr ratios and the weak association of F with shrub/brush suggests that domestic and agricultural wastewater has influenced surface waters. The microbial data collected by the USGS in conjunction with this biogeochemical work may confirm the impacts of wastewater on the watershed.

The results show that even in a watershed that is still relatively pristine and has excellent water quality, the approach used in this research can identify associations between specific land uses and solutes in surface waters. These relationships may become more robust if the following factors are considered in the analysis of GTBW data:

(1) The use of land use intensity factors in addition to land use percentages in statistical analyses: Because nearly half the watershed is in state forest that cannot undergo land use transformation, any land use change must occur in the other half of the watershed. In the GTBW,

the rapid population growth may be expressed as intensification of land uses, rather than in land use changes. For example, seasonal homes could be converted to year-round homes, or apartment complexes could be built in areas already considered urban. In addition, the use of land use percentages may not reflect true impacts on the landscape. From 1980 to 1995 in the Mitchell Creek watershed, plots of land changed from shrub to agriculture, but other plots changed from agriculture to shrub (Figure 6.1). The extent of landscape disturbance may therefore be better expressed by other indicators, such as population or housing density, number of septic systems, road density, and proximity to water bodies.

(2) The use of historical land use distributions coupled with the ground water travel time data described in Chapter 5: All analyses in this dissertation used the 1980 MIRIS land use database. Ultimately, a GIS-based Land Transformation Model (Pijanowski et al., 2000) will predict a land use for each cell based on the exact travel time predicted by the ground water model. Until the Land Transformation Model has been fully calibrated, the land use legacy concept can be incorporated into this analysis by merging land use distributions from other years with the travel time contours produced by groundwater modeling (Chapter 5) to produce a dynamic land use database (Figure 6.2). The statistical and graphical analyses described in Chapters 2-4 can be redone with the new land

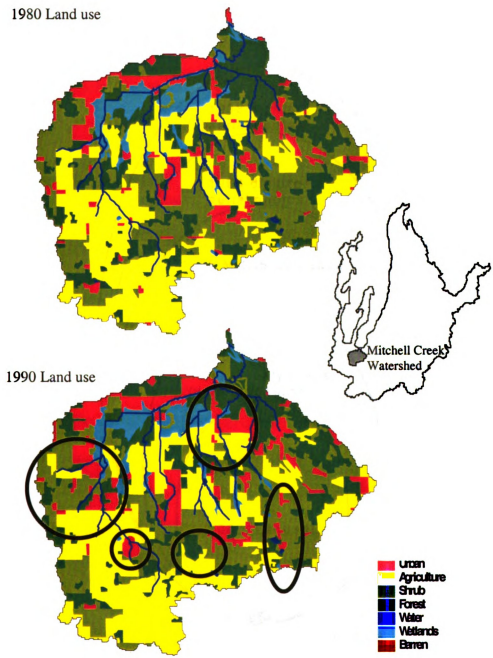


Figure 6.1. Land use change in the Mitchell Creek watershed from 1980 to 1990. Some major areas of land use change are circled in the 1990 map.

use distributions to see if stronger associations between specific land use types become apparent.

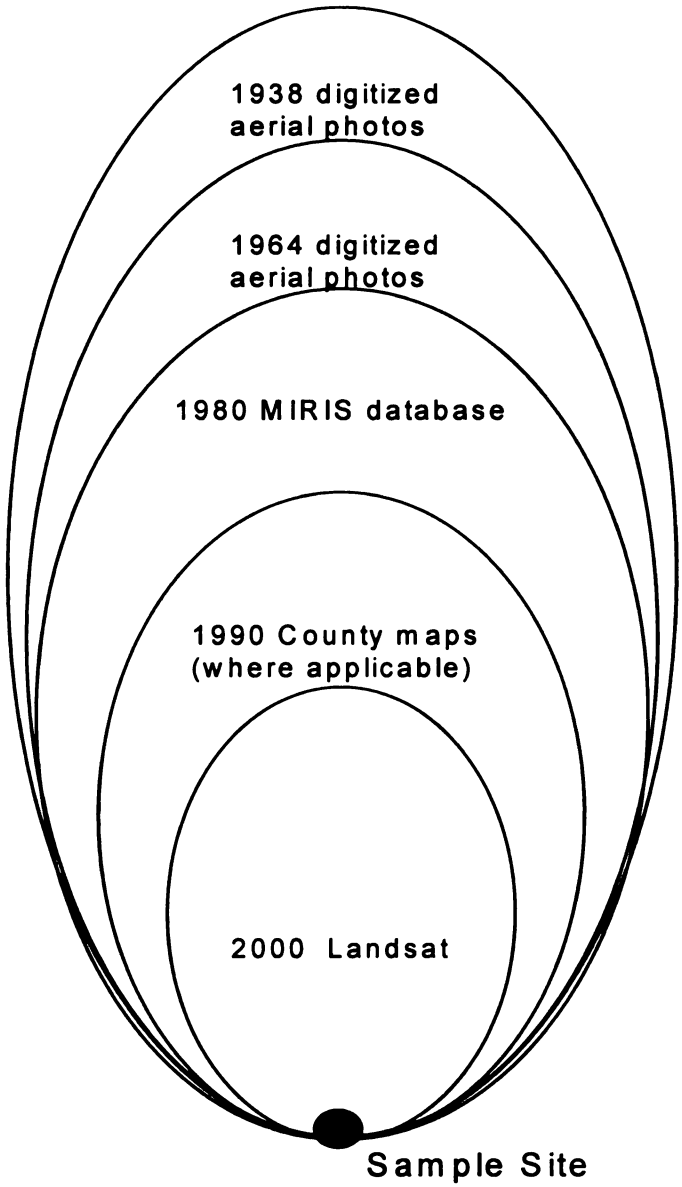


Figure 6.2. Available land use distributions for land use legacy analysis. Travel time contours from the ground water simulations described in Chapter 5 can be used to determine which land use distribution is assigned to each cell in a sourceshed.

The approach used in this research is highly transferable to other watersheds and can be modified to reflect time, personnel, and budget levels of the organization that undertakes the work. The major components of the research approach are (a) multiple synoptic sampling events of baseflow, (b) GIS analyses with land use distributions, and (c) statistical and graphical analyses. The results of this research show that major ions can reveal links between human activities in a watershed and surface water quality; these links may suggest areas of the watershed that are vulnerable to degradation of aquatic ecosystems. It is therefore unnecessary to collect trace element data if the goal of the work is only to monitor where land use change affects surface waters. Clearly, monitoring for trace elements or other contaminants increases both the budget, effort, and personnel required to collect these data. If a monitoring program is intended to document whether water bodies are meeting designated uses, then concentrations of other solutes that affect either environmental integrity or human health should be monitored. A single synoptic sampling event may provide significant information on the relationship between land use and surface water quality. However, this approach is strengthened by multiple sampling events that account for flow-related variability in solute concentrations in baseflow and the improved reliability of statistical analyses as the number of observations increases.

The approach can be improved by designating two types of sampling sites: indicator sites that are located in drainage areas with a single land use (including undisturbed land), and integrator sites with mixed land uses (Scudder et al., 1997). Relationships between solutes and land use may be dampened in mixed-used landscapes, but cumulative effects cannot studied in single-use landscapes. Depending on the level of

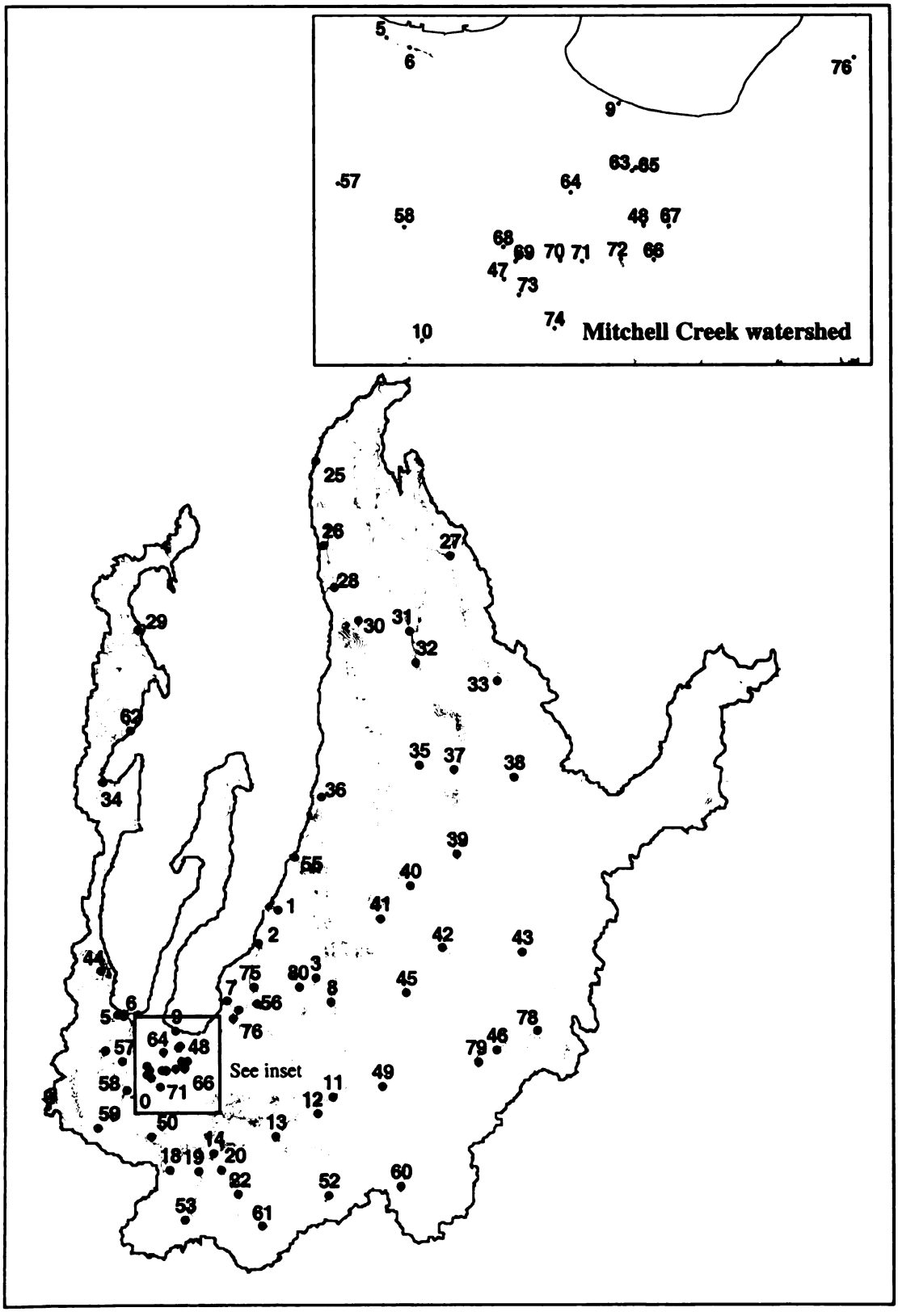
information desired from this approach, samples for total chemistry (dissolved plus filterable) and dissolved organic carbon can be taken with minimal additional effort. Efforts at collecting flow data during one synoptic sampling event of this research met with mixed success, but the collection of flow data for comparisons among sampling events may be useful if budget allows.

It is the author's experience that water quality monitoring projects most often lack adequate data analysis and reporting. In other words, a local watershed organization or consulting firm could easily implement the synoptic sampling approach described in this dissertation. Even if the organization did not have laboratory facilities, field sampling for major ions could be accomplished with a contract laboratory completing the chemical analyses. However, without training in GIS software and statistics, the transformation of a multivariate dataset into useful information would be difficult. The level of training necessary to conduct the data analysis component of this approach may become less of a limitation as GIS and statistical software packages become more user-friendly. More importantly, in order for this information to be useful to decision-makers and scientists alike, it must be disseminated in well-crafted and timely reports that are accessible to both the scientific community and general public.

APPENDICES

APPENDIX A

LOCATION OF SAMPLING SITES


Mitchell Creek watershed
See inset

MSU ID	Site Name	Latitude	Longitude
1	Tobeco Creek	4451110	8525590
2	Yuba Creek	4449370	8527300
3	Williamsburgh Creek	4447651	8523322
4	Cedar Run	4446050	8548410
5	Kids Creek	4445510	8537390
6	Boardman @ Union St. Bridge	4445510	8537240
7	Acme Creek	4446320	8530590
8	Battle Creek	4447651	8523234
9	Mitchell Creek	4444440	8533310
10	Boardman River @ Cass Rd	4723010	9436540
11	North Branch Boardman	4441380	8522077
12	South Branch Boardman	4440537	8523216
13	Ranch Rudolf		
14	Brown Bridge Dam	4438491	8530939
15	Bridge Lake Outlet	4438090	8546580
16	near Mud Lake, Interlochen	4438300	8546110
17	Mason Creek	4437530	8543170
18	Jaxson Creek	4437713	8539634
19	Swainston Creek	4437662	8530324
20	East Creek	4437664	8539324
21	Betsie River at Green Lake		
22	Jackson Creek	4436366	8529185
23	Anderson Creek	4430731	8537363
24	Fife Lake Outlet	4431635	8521480
25	Whiskey Creek	4515909	8522270
26	Antrim Creek	4510365	8528330
27	St. Clair Creek	4509770	8512910
28	Guyer Creek	4508232	8521600
29	Ennis Creek		
30	Wilkinson Creek	4506462	8519830
31	Ogletro Creek	4506485	8516340
32	near Central Lake	4504201	8515580
33	Spence Creek	4503544	8509390
34	Leo Creek, Suttons Bay		
35	Gries Creek	4450394	8515710
36	Paradine Creek	4457465	8522350
37	Intermediate River near Bellaire	4458555	8512750
38	Cedar River	4458132	8508320
39	Finch Creek	4454171	8512650
40	Spencer Creek	4452086	8516050
41	Torch River	4450073	8518040
42	Rapid River	4449069	8513909
43	Rapid River, East Branch	4448967	8507984
44	Cedar Creek		

(cont.)

MSU ID	Site Name	Latitude	Longitude
45	Desmond Creek	4446843	8516529
46	N. Branch Boardman, Kalkaska	4443863	8509889
47	Mitchell Creek	4442670	8535710
48	Vanderli Creek	4443400	8533180
50	Tributary to Boardman on River Rd.		
52	Twenty-two Creek	4437401	8522404
53	Swainston Creek near Kingsley		
55	Elk River	4453580	8524420
56	Yuba Creek	4446230	8527350
57	Kids Creek	4443580	8538470
58	Miller Creek	4443230	8537290
59	Tributary. to Boardman, Chums Corner	4439590	8539230
60	Albright Swamp	4445925	8530345
61	Bancroft Creek	4434719	8527289
62	Belangers Creek		
63	Mitchell Creek		
64	Mitchell Creek		
66	Mitchell Creek		
67	Mitchell Creek		
69	Mitchell Creek		
70	Mitchell Creek		
71	Mitchell Creek		
72	Mitchell Creek		
73	Mitchell Creek		
75	Yuba Creek		
76	Acme Creek		
77	Acme Creek		
78	Havenstein Creek		
79	Boardman on US131		
80	Tobeco Creek Swamp		
81	Boardman River below wastewater treatment plant		

Sites common to this research and study conducted by USGS (Cummings et al., 1990).

MSU Site ID	USGS Site ID	USGS Station #	Station name
1	21	04127550	Tobeco Creek near Elk Rapids
2	20	04127535	Yuba Creek near Acme
3	23	04127620	Williamsburg Creek near Williamsburg
4	24	04126845	Cedar Run near Cedar
6	16	04127490	Boardman River at Traverse City
7	19	04127528	Acme Creek at Acme
8	22	04127600	Battle Creek near Williamsburg
9	18	04127520	Mitchell Creek at Traverse City
10	15	04127250	Boardman River near Traverse City
11	7	04126958	N. Branch Boardman River near S. Boardman Rd.
12	8	04126950	S. Branch Boardman River near S. Boardman Rd.
13	9	04126970	Boardman River at Brown Bridge Rd. near Mayfield
14	12	04126991	Boardman River below Brown Bridge Pond
15	5	04126546	Green Lake Inlet near Interlochen
16	4	04126532	Duck Lake Outlet near Interlochen
17	3	04126525	Mason Creek near Grawn
18	14	04127019	West Branch Jaxon Creek near Mayfield
19	13	04127008	Swainston Creek at Mayfield
20	11	04126997	East Creek near Mayfield
21	6	04126550	Betsie River near Karlin
22	10	04126995	Jackson Creek near Kingsley
23	2	04123910	Anderson Creek near Buckley
24	1	04123706	Fife Lake Outlet near Fife Lake

APPENDIX B

DATASETS FOR MAJOR ION CONCENTRATIONS

MSU ID	USGS ID	Date	pH	Temp (C)	DO (mg/l)	Cond (uS)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	Alkalinity (mg HCO_3/l)	SiO_2 (mg/l)	Cl (mg/l)	SO_4 (mg/l)	NO_3-N (mg/l)	F (mg/l)
1	4127550	June 1986	7.9	18	7.9	445	68	15	3.3	1.2	278	4.9	6.1	12		0.2
		May 1998	8.1	19	7.7	762	70	15.5	5.0	1.4	291	6.9	7.82	6.92	0.009	0.192
		October 1998	7.7	11	9.7	523	77.8	18	5.2	1.2	313	21.6	8.96	4.86	0.021	0.077
		October 2000	7.9	12	7.5	315	87.8	19.2	6.4	1.6	298	15.9	11.14	14.04	0.768	0.156
2	4127535	June 1986	8.0	17	7.8	441	66	16	3.2	1.2	260	5.4	5.3	16	0.172	0.1
		May 1998	8.2	14	10.3	735	68	16	3.7	0.7	249	8.5	5.94	12.07	1.554	0.134
		October 1998	7.9	8	11.0	476	69.8	16.5	3.5	0.8	258	11.2	5.76	21.37	1.607	0.046
		October 2000	8.0	9	8.9	273	75.7	17.54	4.0	1.0	270	8.6	6.12	13.81	4.286	0.158
3	4127620	June 1986	8.2	15	10.2	336	46	12	3.3	0.7	199	7.8	4.2	10	0.117	0.1
		May 1998	8.4	17	9.7	592	52	12.5	5.0	0.6	240	8.1	6.35	7.77	0.119	0.133
		October 1998	8.0	8	10.6	332	50.8	12.4	4.1	0.7	233	8.4	5.44	9.32	0.139	0.000
		October 2000	8.2	12	11.1	306	60.25	13.66	4.9	0.9	246	9.6	6.95	9.66	1.016	0.146
5	4127498	June 1986	8.2	12	9.9	533	74	17	12.0	1.2	289	9.9	18	23	0.463	0.4
		May 1998	8.1	17	10.0	372	53	11.6	9.4	1.1	212	7.8	13.83	8.29	0.404	0.156
		October 1998	8.0	15	9.5	404	52.6	11.9	8.7	1.3	207	9.0	14.22	10.29	0.203	0.100
		October 2000	8.0	10	10.1	585	92.95	19.37	25.9	1.7	308	11.8	37.94	24.73	1.898	0.498
6	4127490	June 1986	8.3	17	9.2	360	52	11	6.7	1.0	196	7.4	12	11	0.288	0.1
		May 1998	8.1	17	9.5	365	51	11.4	8.5	1.0	219	7.3	13.44	9.06	0.404	0.150
		October 1998	8.0	15	9.5	405	52.7	12.2	8.4	1.2	205	10.6	14.40	10.39	0.199	0.123
		October 2000	8.0	12	9.7	374	44.65	9.69	8.0	1.1	231	10.4	17.74	11.67	1.542	0.224
7	4127528	June 1986	8.3	12	10.9	329	47	11	2.8	0.7	196	8.2	3.4	12	0.133	0.1
		May 1998	8.4	13	10.7	565	50	11.9	3.6	0.6	184	8.3	4.26	9.62	0.104	0.104
		October 1998	8.0	7	11.0	315	49.8	11.6	3.1	0.6	213	9.8	3.47	10.49	0.116	0.009
		October 2000	8.2	8	10.0	203	58.05	12.95	3.4	0.7	193	8.6	4.26	10.65	0.714	0.181
8	4127600	June 1986	8.2	10	11.1	331	47	11	3.2	0.6	201	8.7	3.8	< .6	0.189	0.2
		May 1998	8.3	12	10.8	569	53	11.6	3.7	0.5	222	9.1	3.79	5.69	0.152	0.129
		October 1998	8.1	9	10.6	326	49.5	11.9	4.3	0.6	215	11.2	4.54	5.83	0.091	0.416
		October 2000	8.2	12	10.7	329	58.3	12.98	4.5	0.8	213	11.3	5.12	6.59	0.655	0.117

MSU ID	USGS ID	Date	pH	Temp (C)	DO (mg/l)	Cond (uS)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	Alkalinity (mg HCO_3/l)	SiO_2 (mg/l)	Cl (mg/l)	SO_4 (mg/l)	NO_3-N (mg/l)	F (mg/l)
9	4127520	June 1986	8.4	12	10.5	421	62	14	4.7	0.9	250	8.4	7	14	0.781	0.2
		May 1998	8.4	18	8.4	744	67	14.7	8.3	0.9	256	8.3	12.47	11.76	0.576	0.199
		October 1998	8.0	10	10.5	482	69.1	15.6	6.8	1.0	248	11.3	12.05	17.91	0.551	0.126
		October 2000	8.0	7	10.5	457	76.9	16.91	8.6	1.2	258	10.3	10.55	11.13	2.442	0.182
10	4127250	June 1986	8.3	19	9.7	347	52	12	4.8	0.9	196	7.6	8.8	10	0.252	0.1
		May 1998	8.3	17			50	11.3	6.0	0.7	207	7.9	9.11	7.83	0.221	0.122
		October 2000	8.0	11	9.4	361	61.6	13.45	6.1	0.9	199	10.5	9.67	10.16	1.214	0.177
11		May 1998	8.1	17	8.9	306	44	10.2	3.9	0.6	175	6.1	7.12	6.30	0.714	0.146
		October 1998	8.2	7	10.4		48.1	10	3.2	0.6	174	8.5	6.23	6.85	0.233	0.062
		October 2000	7.9	9	9.7	314	55.5	11.29	3.5	0.8	170	8.4	7.21	7.63	1.220	0.093
12		May 1998	8.2	16	9.2	300	47	10.5	3.9	0.6	172	8.2	4.38	9.06	0.395	0.202
		October 1998	8.3	7	11.9		46	10.3	3.5	0.6	176	10.0	4.37	9.01	0.389	0.000
		October 2000	8.1	8	10.8	308	53.5	11.93	3.8	0.7	133	10.8	4.65	8.66	1.547	0.086
13	4126970	June 1986	8.2	12	10.1	322	46	10	3.8	0.6	182	7.3	< .6	8.8	0.283	0.1
		May 1998	8.2	15	9.4	306	48	10.5	4.0	0.6	185	6.8	5.64	7.20	0.242	0.183
		October 1998	8.4	7	15.1		47.1	10.2	3.5	0.6	191	10.3	5.64	7.84	0.289	0.113
		October 2000	8.1	9	10.0	312	56.45	11.68	3.8	0.7	186	10.3	5.23	7.64	1.329	0.111
14	4126991	June 1986	8.4	16	10.0	316	45	10	3.9	0.7	178	7.0	< .1	8.5	0.180	0.1
		May 1998	8.1	15	9.4	300	48	10.4	4.2	0.6	172	7.2	5.74	7.42	0.150	0.160
		October 1998	8.3	12	10.1		45	9.9	3.7	0.6	200	11.0	5.56	8.23	0.105	0.343
		October 2000	8.2	11	10.2	309	54.1	11.73	4.0	0.7	175	10.0	6.12	8.26	1.215	0.112
18		May 1998	7.7	12	7.1	380	64	12.8	4.5	0.7	246	8.7	6.90	5.53	0.059	0.206
		October 1998	8.0	9	8.8		58.4	11.9	4.4	0.8	238	8.9	6.86	10.97	0.104	0.000
		October 2000	7.6	8	5.5	315	62.2	12.93	3.0	0.8	201	8.5	6.42	7.28	0.663	0.127
19	4127008	June 1986	8.4	14	10.5	386	58	12	5.5	0.9	216	8.5	11	16	0.269	0.1
		May 1998	8.0	13	9.8	412	64	13.1	9.3	0.9	200	8.1	15.29	12.05	0.253	0.229
		October 1998	8.3	10	16.2		62.2	12.7	8.2	1.0	254	9.3	16.97	13.23	0.260	0.113
		October 2000	8.1	8	10.1	395	70.65	14.8	8.8	1.1	231	12.4	15.94	13.78	2.492	0.134

MSU ID	USGS ID	Date	pH	Temp (C)	DO (mg/l)	Cond (uS)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	Alkalinity (mg HCO_3/l)	SiO_2 (mg/l)	Cl (mg/l)	SO_4 (mg/l)	NO_3-N (mg/l)	F (mg/l)
20	4126997	June 1986	8.3	13	10.3	341	48	12	4.3	0.9	190	8.0	8.2	11	0.759	0.1
		May 1998	8.1	16	9.1	332	53	11.7	4.8	0.8	188	6.6	8.76	9.02	0.759	0.294
		October 1998	8.3	8	12.7		52	11.8	4.8	0.9	205	10.0	8.93	11.19	0.752	0.290
		October 2000	8.0	7	9.8	340	61.3	13.9	6.4	1.0	193	9.6	10.45	11.20	3.223	0.117
22		May 1998	8.4	15	9.5	320	50	11	4.8	0.8	185	6.4	6.93	11.03	1.009	0.321
		October 1998	8.4	10	14.4		51.4	11.3	4.5	0.9	342	7.2	7.32	14.79	1.141	0.080
		October 2000	8.0	6	10.5	330	57.55	12.28	4.8	1.0	191	11.0	5.12	8.10	3.960	0.133
23		May 1998	7.9	15	7.4	760	71	14.5	5.4	1.1	256	3.7	15.30	11.85	0.996	0.225
		October 1998	7.7	12	9.9	475	68.9	13.8	5.3	1.2	238	7.1	16.90	18.96	0.956	0.053
26		May 1998	8.2	14	9.0	457	80	15.3	3.8	0.8	293	6.4	6.81	7.54	0.616	0.217
		October 2000	8.1	10	10.4	535	94.5	20.52	5.9	1.7	327	10.7	9.53	14.20	2.491	0.231
27		May 1998	8.1	14	8.8	421	73	15	2.5	0.6	278	7.7	4.91	9.84	0.361	0.212
		October 2000	7.8	6	10.9	452	81.65	17.18	2.7	0.8	301	9.8	5.75	13.03	2.873	0.146
28		May 1998	8.0	14	8.1	484	81	17.8	4.4	0.5	293	8.0	8.15	8.59	0.182	0.167
		October 2000	8.0	8	10.6	502	87.75	19.69	4.0	0.9	303	10.5	9.39	14.09	1.370	0.173
29		May 1998	8.1	15	8.4	416	75	15.7	2.1	0.7	296	7.7	3.17	8.70	0.896	0.487
		October 2000	8.2	10	10.6		82.8	18.17	2.5	1.1	265	12.5	2.81	10.60	3.731	0.223
30		October 2000	8.1	9	11.1	489	83.85	20.62	4.6	1.2	275	10.7	9.36	12.41	1.484	0.354
31		May 1998	8.1	18	8.0	366	60	13.5	3.2	0.9	236	3.4	8.50	5.55	0.214	0.163
		October 2000	8.0	10	10.9	425	73.1	18.07	3.5	1.2	260	10.8	6.76	12.71	1.754	0.173
32		May 1998	8.1	18	8.5	374	59	13.2	4.9	1.1	225	3.7	7.11	9.59	0.522	0.107
		October 2000	8.1	12	9.2	390	64.45	16.14	5.1	1.1	227	16.9	8.78	12.43	1.155	0.125
33		October 2000	8.1	8	11.0	424	72.2	18.59	2.8	1.0	270	10.7	2.68	18.55	13.223	0.106
34		May 1998	8.1	11	9.6	403	70	15.4	2.9	0.6	273	10.2				
		October 2000	8.1	10	11.0	282	48.3	9.74	4.3	0.9		13.2	10.14	17.05	5.266	0.269
35		May 1998	8.3	14	9.3	396	66	15.6	2.2	0.7	246	8.7	4.42	13.58	0.314	0.150
		October 1998	7.7	9	10.2	427	61.6	15.2	2.7	0.8	260	11.0	2.27	11.43	0.106	0.074
		October 2000	7.7	11	4.5	324	68.6	19.5	3.8	0.8	262	11.4	3.29	13.70	1.420	0.152

MSU ID	USGS ID	Date	pH	Temp (C)	DO (mg/l)	Cond (uS)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	Alkalinity (mg HCO_3/l)	SiO_2 (mg/l)	Cl (mg/l)	SO_4 (mg/l)	NO_3-N (mg/l)	F (mg/l)
		May 1998	8.2	17	9.4	357	56	13.3	4.9	0.8	217	6.6	6.52	8.51	0.413	0.103
37		October 1998	8.1	11	11.2	361	49.7	12	4.4	0.7	203	9.3	6.67	9.37	0.427	0.055
		October 2000	8.1	11	9.6	279	58.75	14.76	4.9	0.9	210	7.9	8.14	10.73	3.040	0.113
		May 1998	8.3	14	9.6	344	56	12.3	4.3	0.5	192	7.1	5.51	6.54	0.817	0.108
38		October 1998	8.2	8	12.0	369	52.8	11.3	3.7	0.5	210	9.8	5.72	7.63	0.759	0.060
		October 2000	8.2	9	10.9	279	61.25	13.22	4.0	0.6	227	8.4	5.55	7.40	2.966	0.086
		May 1998	8.3	11	9.9	334	54	12.4	3.0	0.6	191	8.0	5.39	8.20	0.648	0.172
39		October 1998	8.1	9	11.4	359	51.5	11.3	2.6	0.5	206	10.2	4.96	8.58	0.612	0.036
		October 2000	8.1	10	10.5	274	60.35	13.4	2.9	0.7	212	9.0	4.86	7.80	2.760	0.098
		May 1998	8.2	15	8.9	366	57	14.5	2.9	0.7	208	7.6	6.44	8.87	0.332	0.116
40		October 1998	8.2	9	11.4	384	53.4	13.1	2.5	0.6	214	9.9	7.11	11.03	0.282	0.029
		October 2000	8.1	12	9.2	297	62.05	15.25	3.4	0.9	197	9.2	9.50	11.44	1.311	0.090
		May 1998	8.3	16	9.6	360	57	11.6	7.2	0.8	208	7.1	13.20	6.13	0.266	0.109
41		October 1998	8.1	8	12.1	379	53.7	10.8	6.2	0.8	202	8.9	13.79	7.01	0.307	0.038
		October 2000	8.2	11	10.2		49.8	10.27	6.0	0.7	203	8.1	15.51	7.80	1.848	0.077
		May 1998	8.3	13	10.1	632	57	11.3	7.6	0.8	209	7.0	15.90	7.09	0.334	0.115
42		October 1998	8.2	9	11.7	387	53.8	10.6	6.7	0.8	204	8.2	15.70	7.02	0.278	0.065
		October 2000	8.2	11	10.1	288	62.3	12.41	6.5	0.9	199	8.1	15.57	7.50	1.299	0.074
		May 1998	8.1	11	9.6	597	57	11.7	4.1	0.6	218	7.8	10.45	6.34	0.291	0.333
43		October 1998	8.4	8	13.9		51	10.9	3.8	0.7	175	8.1	9.90	5.46	0.296	0.136
		October 2000	7.9	8	9.4	272	59.1	12.44	3.9	0.8	199	9.1	8.28	5.54	1.307	0.101
		May 1998	7.9	15	6.5	529	94	15.5	10.3	0.5	303	7.0	32.30	3.21	0.000	0.313
44		October 1998	8.2	9	15.1		67.1	15.8	3.3	0.6	264	10.3	3.36	18.80	0.856	0.071
		October 2000	8.2	9	11.5	270	76.2	17.55	3.9	0.8	284	11.0	4.08	20.29	4.018	0.356
		May 1998	7.9	10	8.7	600	58	12.7	2.7	0.5	227	8.5	5.20	8.38	0.137	0.195
45		October 1998	8.1	9	12.6		53	11.9	2.5	0.5	211	10.3	5.21	7.79	0.096	0.253
		October 2000	7.9	10	9.2	350	60.95	13.48	2.7	0.7	211	9.2	6.04	8.81	0.672	0.100

MSU ID	USGS ID	Date	pH	Temp (C)	DO (mg/l)	Cond (uS)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	Alkalinity (mg HCO_3/l)	SiO_2 (mg/l)	Cl (mg/l)	SO_4 (mg/l)	NO_3-N (mg/l)	F (mg/l)
		May 1998	8.3	18	9.2	524	49	10.6	4.3	0.6	197	5.4	7.78	6.49	0.273	0.199
46		October 1998	8.4	10	15.0		44.6	10.6	4.1	0.7	196	8.1	8.32	7.41	0.218	0.073
		October 2000	8.0	10	10.5	321	56.4	12.25	4.4	0.8	175	7.7	6.69	6.25	1.091	0.088
		May 1998	7.9	12	7.9	645	92	18.4	20.3	1.3	303	8.9	45.74	24.70	1.705	0.428
47		October 1998	7.6	11	7.4	603	84.1	18	21.5	1.6	322	10.5	43.13	24.57	1.378	0.182
		October 2000	7.9	13	9.4	475	91.55	18.4	26.0	1.9	336	9.9	46.04	24.50	5.172	0.198
		May 1998	8.4	17	9.0	8.67	82	16	12.9	1.0	310	7.1	18.51	13.95	0.506	0.140
48		October 1998	8.2	10	9.4	511	77.9	19.2	11.2	0.9	296	10.3	20.39	28.51	0.459	0.179
		October 2000					95.1	18.16	18.0	1.2	327	9.8	30.71	26.83	1.500	0.146
		May 1998	8.2	17	8.8	302	49	11.9	4.4	0.7	182	5.8	7.50	5.88	0.294	0.206
49		October 1998	8.5	9	14.8		43.9	10.1	3.5	0.7	191	9.3	7.56	7.39	0.282	0.214
		October 2000	8.0	8	10.0	301	52.8	11.46	3.9	0.8	176	7.7	6.85	6.38	1.441	0.076
		May 1998	7.9	12	8.2	335	57	13.2	4.3	0.5	205	6.4	5.27	6.72	0.137	0.215
50		October 1998	8.0	10	10.8	398	57.6	11.7	3.6	1.2	176	9.8	6.04	48.06	0.112	0.057
		October 2000	7.8	10	8.5	364	64.95	13.4	3.6	1.5	211	9.0	6.64	8.63	2.384	0.090
		May 1998	8.2	13	10.0	447	41	10.8	1.9	0.8	166	7.0	2.66	7.96	0.481	0.117
52		October 1998	8.4	10	14.4		38.7	8.6	1.6	0.8	193	8.3	2.37	7.81	0.402	0.094
		October 2000	7.9	7	10.2	234	44.9	9.75	1.8	0.9	142	6.8	2.39	8.25	1.836	0.060
53		May 1998	7.4	21	5.3	358	62	13.7	1.6	0.7	239	9.5	1.16	7.81	0.016	0.279
		May 1998	8.3	12	11.6	510	43	13.8	4.7	0.8	163	8.1	6.38	8.13	0.255	0.080
55		October 1998	8.3	15	9.4	299	36.3	11.5	4.3	0.8	172	8.7	6.84	9.46	0.164	0.085
		October 2000	8.4	13	9.0	176	42.15	13.12	4.7	0.9	165	9.1	7.94	10.21	1.043	0.095
		May 1998	8.2	12	10.3	614	60	14.6	2.9	0.8	211	9.6	4.55	9.58	0.664	0.075
56		October 1998	7.8	7	11.4	387	56.3	12.1	2.7	0.8	190	10.6	4.96	12.74	0.716	0.063
		October 2000	8.1	11	10.6	358	62.55	13.6	3.3	1.0	284	9.2	4.91	10.40	2.169	0.112
		May 1998	7.9	13	10.1	498	83	18.6	8.2	0.8	296	8.8	14.57	17.11	0.576	0.347
57		October 1998	8.0	11	10.8	527	76	15.7	8.1	1.2	275	10.8	15.70	19.36	0.533	0.269
		October 2000	7.9	10	9.1	501	85.9	17.6	10.1	1.5	270	10.7	18.01	20.69	2.784	0.250

MSU ID	USGS ID	Date	pH	Temp (C)	DO (mg/l)	Cond (uS)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	Alkalinity (mg HCO_3/l)	SiO_2 (mg/l)	Cl (mg/l)	SO_4 (mg/l)	NO_3-N (mg/l)	F (mg/l)
		May 1998	8.2	16	8.6	537	81	18.3	14.8	1.3	266	7.9	28.67	13.58	0.978	0.443
58		October 1998	8.1	11	10.4	539	79.9	14.8	15.2	1.5	272	9.5	26.42	12.77	0.777	0.251
		October 2000	8.2	10	10.3	467	78.95	17.21	8.8	1.1	258	12.3	14.90	15.03	1.388	0.535
		May 1998	8.5	12	7.6	512	77	16.2	13.1	1.0	262	6.4	24.93	11.15	1.813	0.178
59		October 1998	7.8	10	9.8	523	72.4	14.8	10.1	1.9	256	10.1	19.78	14.43	1.903	0.104
		October 2000	7.8	10	9.1	495	77.65	15.29	12.4	1.2	232	7.0	23.97	14.79	7.239	0.120
		May 1998	8.1	13	8.7	478	47	12	1.2	0.5	179	7.6	0.68	7.91	0.285	0.141
60		October 1998	8.1	9	11.3		45.5	9.6	1.0	0.5	172	9.2	0.54	9.61	0.260	0.181
		May 1998	8.2	16	9.4	654	65	14.7	2.4	1.0	236	7.6	6.18	10.00	2.025	0.001
61		October 1998	8.4	10	13.2		66.5	13.6	2.3	1.1	289	10.3	6.84	12.36	1.559	0.089
		October 2000	8.0	6	10.4	400	73.2	16.18	2.5	1.4	241	10.9	8.84	14.88	7.913	0.081
62		May 1998	8.1	14	8.8	400	71	16.9	2.7	0.7	232	6.9	5.28	11.40	1.759	0.775
		May 1998	8.6	18	9.9	758	71	17.7	7.3	1.0	262	8.3				
63		October 1998	8.1	9	9.3	435	70.7	15.7	5.8	0.9	264	11.3	9.46	17.17	0.922	0.351
		October 2000	8.3	10	12.2	289	79.75	17.64	8.8	1.2		10.0	14.40	14.69	3.190	0.150
		May 1998	8.4	15	9.6	765	74	18.1	5.8	0.9	276	8.6	7.94	12.74	0.908	0.222
64		October 1998	8.0	9	9.7	438	72	15.8	5.8	0.9	275	11.4	9.13	17.63	1.204	0.269
		October 2000	8.3	10		0.25	79.05	17.75	7.5	1.2	284	10.5	13.03	16.08	3.527	0.146
		May 1998	8.1	14	8.5	457	80	19.2	4.9	0.9	293	8.0				
66		October 1998	8.2	11	8.9	471	81.7	16.6	7.7	0.9	303	9.4	13.19	28.31	0.639	0.309
		October 2000	7.9	11	9.1	433	92.95	19.26	8.2	1.1	322	10.4	16.47	36.70	2.955	0.184
		May 1998	8.3	13	10.0	757	76	17.9	3.8	0.8	287	9.3	5.39	12.86	0.177	0.232
67		October 1998	9.5	10	10.3	428	72.9	15.7	3.2	0.7	276	11.0	5.34	18.10	0.019	0.164
		October 2000	8.1	10	13.8	286	81.25	17.33	3.8	0.9	233	10.6	8.74	21.92	1.063	0.198
		May 1998	8.4	14	8.9	544	81	19.7	14.0	2.0	299	7.6	26.81	17.91	1.289	0.345
69		October 1998	8.2	11	10.1	522	77.9	16.4	11.4	1.9	283	10.3	23.79	17.31	1.180	0.301
		October 2000	8.2	12	9.0	422	87.6	18.19	16.7	2.2	289	11.4	34.68	20.27	6.088	0.160

MSU ID	USGS ID	Date	pH	Temp (C)	DO (mg/l)	Cond (uS)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	Alkalinity (mg HCO_3/l)	SiO_2 (mg/l)	Cl (mg/l)	SO_4 (mg/l)	NO_3-N (mg/l)	F (mg/l)
		May 1998	8.2	10	9.8	435	74	18.5	3.8	0.7	274	10.2	4.93	5.83	0.049	0.199
70		October 1998	8.0	9	9.5	403	67.4	15.1	3.5	0.7	265	11.6	37.54	18.85	0.418	1.890
		October 2000	8.0	10	9.3	326	71.75	17.17	4.1	0.8	265	11.7	5.63	16.77	5.882	0.188
		May 1998	8.0	14	8.5	410	72	18.5	2.8	0.7	274	7.3	3.94	13.11	1.170	0.323
71		October 1998	8.1	11	9.6	393	66.8	14.9	2.5	0.7	278	9.4	3.36	14.56	1.236	0.331
		October 2000	8.2	11	1.4	320	74.45	16.73	2.8	1.0	239	12.0	4.84	17.33	6.949	0.169
		May 1998	7.5	11	5.2	636	83	16.1	40.7	2.0	293	9.9	75.99	2.93	0.206	0.448
72		October 1998	7.7	14	7.5	400	48.2	11.9	19.5	1.9	241	2.5	36.59	6.17	0.008	0.139
		October 2000	7.5	13	7.4	380	68.3	14.03	33.0	2.3	233	5.4	62.60	6.76	2.163	0.216
		May 1998	7.9	19	9.3	452	64	17.3	9.9	2.0	236	2.5	4.14	12.90	1.251	0.194
73		October 1998	7.7	14	10.1	457	66.8	14.2	8.7	2.6	264	7.5	19.63	7.88	2.700	0.189
		October 2000	8.0	15	9.7	365	72.9	16.69	10.8	2.0	241	5.9	31.41	9.50	6.718	0.071
		May 1998	8.2	11	10.3	652	64	15.9	3.4	0.7	233	8.7	5.53	12.08	1.235	0.200
75		October 1998	8.0	7	10.9	368	59.7	13.4	3.3	0.8	235	9.7	6.20	14.75	2.605	0.080
		October 2000	8.2	12	10.8	3.76	63.8	14.8	4.2	0.9	213	10.2	7.41	14.28	4.132	0.126
		May 1998	8.2	10	10.8	533	53	13.2	1.6	0.5	209	7.9	20.88	6.19	2.450	0.120
76		October 1998	8.0	9	9.8	308	49.9	10.9	3.6	0.5	205	9.5	3.94	9.49	0.597	0.071
		October 2000	8.1	9	9.5	198	55.65	12.65	4.3	0.7	208	12.8	5.04	11.64	1.249	0.113
		May 1998	8.1	12	9.8	563	55	13.5	2.7	0.9	209	7.8	3.32	8.79	0.285	0.151
77		October 1998	8.1	10	11.0	314	50.2	11.4	2.4	0.9	212	9.8	3.13	9.79	0.213	0.086
		October 2000	8.0	10	9.3	207	57.55	13.29	2.9	1.1	232	9.1	3.30	8.82	1.253	0.103

MSU ID	USGS ID	Date	pH	Temp (C)	DO (mg/l)	Cond (uS)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	Alkalinity (mg HCO_3/l)	SiO_2 (mg/l)	Cl (mg/l)	SO_4 (mg/l)	NO_3-N (mg/l)	F (mg/l)
78		May 1998	8.3	14	9.8	531	50	11.8	3.7	0.7	200	6.7	1.86	8.72	0.067	0.110
		October 1998	8.3	8	14.4		50.1	9.8	3.5	0.7	213	8.8	7.22	6.26	0.310	0.084
		October 2000	7.9	8	10.6	317	56.35	11.54	4.0	0.8	185	12.5	7.53	6.60	1.226	0.078
79		May 1998	8.4	19	9.3	539	50	12.3	4.8	0.7	191	5.5	6.45	5.06	0.305	0.117
		October 1998	8.4	10	13.9		47.4	10.5	4.2	0.7	179	8.5	8.89	7.26	0.301	0.099
80		May 1998	8.4	24	8.0	824	79	20.3	7.9	0.9	274	7.5	14.87	13.03	1.664	0.193
		October 1998	7.8	8	10.2	489	77.6	18	6.1	0.8	301	14.6	13.57	17.05	1.098	0.287
		October 2000	8.0	18	4.1	509	83.8	19.47	8.8	1.1	289	9.5	23.07	24.36	3.975	0.131
81		October 1998	8.5	13	10.2		49.6	11	4.7	0.7	355	8.8	8.18	8.64	0.168	0.093
		October 2000	8.2	11	10.6	339	57.15	12.85	5.3	0.8	189	13.4	8.72	9.18	1.006	0.117

APPENDIX C

UNCENSORED TRACE ELEMENT DATA

Uncensored trace element data.

Sample	Analysis Date	Sc	Ti	V	Cr	Co	Ni	Cu	As	Mo	Cd	In	Pb	Bi
1	3/4/01	2.18	2.04	0.09	0	0.25	4.49	0.12	0.33	0.27	0	0.98	0	0.93
2	3/4/01	1.34	1.46	0.4	0	0.13	2.23	0.24	0.34	0.87	0	0.96	0	0.95
3	3/4/01	0.82	0.86	0.35	0	0.01	0.44	0.21	0.21	0.91	0	1	0	1
5	3/4/01	1.41	1.22	0.21	0	0.03	0	0.08	0.22	3.53	0	1.05	0	1.03
6	3/4/01	0.67	0.93	0.36	0	0	0	0.11	0.39	0.99	0	1.04	0	1.04
7	3/4/01	1.06	0.98	0.19	0	0	0	0.04	0.39	1.21	0	1.05	0	1.05
8	3/4/01	1.08	1.08	0.08	0	0	0	0	0.24	0.75	0	1.08	0	1.07
9	3/4/01	1.08	1.18	0.35	0	0	0	0.07	0.23	1.59	0	1.07	0	1.04
10	3/4/01	1	1.12	0.26	0	0	0	0.13	0.54	1.2	0	1.04	0	1.03
11	3/4/01	0.75	1.07	0.41	0	0	0	0.13	0.5	0.43	0	1.05	0	1.04
12	3/4/01	1.01	1.17	0.4	0	0	0	0.06	0.62	0.67	0	1.03	0	1.02
13	3/5/01(A)	1.16	1.32	0.33	0	0	7.37	0.2	0.7	0.73	0	1.03	1	1.02
14	3/5/01(A)	1.03	1.09	0.32	0	0	7.1	0.42	0.65	0.76	0	1.04	0	1.05
18	3/5/01(A)	1.05	1.17	0.41	0	0	3.82	0.05	0.21	0.7	0	1.04	0	1.03
19	3/5/01(A)	0.75	0.58	0.21	0	0	3.37	0.09	0.49	1.51	0	1.05	0	1.05
20	3/5/01(A)	1.06	0.98	0.32	0	0	3.66	0.1	0.37	1.11	0	1.04	0	1.04
22	3/5/01(A)	1.22	1.13	0.37	0	0	3.1	0.08	0.36	0.92	0	1.05	0	1.06
26	3/5/01(A)	1.3	1.24	0.18	0	0	0.92	0.38	0.23	1.23	0	1.05	0	1.04
27	3/5/01(A)	0.99	0.95	0.2	0	0	1.99	0.15	0.26	1.01	0	1.06	0	1.08
28	3/5/01(A)	1.04	0.78	0.18	0	0	0.69	0.08	0.17	1.33	0	1.08	3.29	1.09
29	3/5/01(A)	0.84	0.64	0.32	0	0	0.03	0.2	0.18	0.28	0	1.11	0	1.12

Uncensored trace element data.

Sample	Analysis Date	Sc	Ti	V	Cr	Co	Ni	Cu	As	Mo	Cd	In	Pb	Bi
30	3/5/01(A)	1.07	0.95	0.16	0	0	1.35	0.2	0.61	0.59	0	1.04	0	1.05
31	3/5/01(A)	0.94	0.94	0.15	0	0	2.11	0.1	0.33	0.86	0	1.03	0	1.05
32	3/5/01(A)	0.81	0.42	0.23	0	0	0	0.14	0.31	0.98	0	1.12	0	1.14
33	3/5/01(A)	0.96	0.76	0.18	0	0	0.59	0	0.19	3.26	0	1.07	0	1.1
34	3/5/01(A)	0.42	0.35	0.16	0	0	1.62	0.02	0.1	1.14	0	1.05	0	1.08
35	3/5/01(A)	0.98	1.06	0.22	0	0	2.76	0	0.12	1.03	0	1.04	0	1.06
37	3/5/01(A)	0.55	0.46	0.38	0	0	0.63	0.1	0.26	0.82	0	1.05	0	1.07
38	3/5/01(A)	0.53	0.58	0.48	0	0	1.18	0.05	0.13	0.61	0	1.04	0	1.06
39	3/5/01(A)	0.81	0.97	0.35	0	0	1.13	0	0.11	0.8	0	1.04	0	1.05
40	3/5/01(A)	0.86	0.89	0.38	0	0	0.6	0	0.23	0.69	0	1.07	0	1.08
41	3/5/01(A)	0.58	0.75	0.31	0	0	1.98	0.03	0.42	0.35	0	1.03	0	1.05
42	3/5/01(A)	0.79	0.88	0.5	0	0	1.69	0	0.57	0.45	0	1.04	0	1.05
43	3/5/01(A)	0.62	0.59	0.39	0	0	0.85	0	0.24	0.33	0	1.04	0	1.04
44	3/5/01(B)	1.25	1.41	0.26	0.23	0.04	5.33	0.09	0.53	3	0	1.04	0	1.04
45	3/5/01(B)	0.84	0.86	0.15	0	0	4	0	0.18	0.93	0	1.01	0	1.03
46	3/5/01(B)	0.67	0.68	0.26	0.22	0	2.04	0	0.58	0.57	0	1.05	1.19	1.07
47	3/5/01(B)	1.01	1.19	0.34	0.2	0.01	2.58	0.07	0.26	1.27	0	1.06	0	1.07
48	3/5/01(B)	0.94	0.88	0.16	0.2	0	0	0.18	0.23	1.75	0	1.08	0.12	1.07
49	3/5/01(B)	0.65	0.74	0.32	0.29	0	0.02	0	0.34	0.38	0	1.06	0	1.08
50	3/5/01(B)	0.82	0.78	0.24	0.01	0	0	0.15	0.37	1.37	0	1.06	0	1.09
52	3/5/01(B)	0.75	0.86	0.39	0.18	0	0	0.02	0.64	0.34	0	1.05	0	1.07

Uncensored trace element data.

Sample	Analysis Date	Sc	Ti	V	Cr	Co	Ni	Cu	As	Mo	Cd	In	Pb	Bi
55	5/25/01	2.52	0.99	0.31	0	0	0	0	0	0.84	0	1.1	0	1.12
56	3/5/01(B)	0.96	0.79	0.41	0.07	0	0	0	0.25	0.65	0	1.05	0	1.06
57	3/5/01(B)	0.98	0.9	0.1	0	0	0	0	0.09	2.84	0	1.05	0	1.06
58	5/25/01	3.86	1.68	0.09	0	0	0	0	0	2	0	1.16	0.31	1.13
59	5/25/01	2.86	1.29	0.2	0	0	0	0	0	1.94	0	1.06	0	1.03
61	3/5/01(B)	0.95	1.07	0.26	0	0	0	0.13	0.41	0.88	0	1.03	0	1.04
63	3/5/01(B)	1	0.9	0.43	0	0	0	0.03	0.33	1.69	0	1.05	0	1.05
64	3/5/01(B)	1.06	1.02	0.56	0	0	0	0.01	0.28	1.68	0	1.03	0	1.03
66	3/5/01(B)	0.85	1.36	0.18	0	0.09	2.61	0.07	0.31	2.28	0	0.96	0	0.96
67	3/5/01(B)	0.99	1.04	0.08	0	0	0	0	0.18	2.37	0	1.05	0	1.06
69	3/5/01(B)	0.93	0.91	0.25	0	0	0	0.17	0.33	1.23	0	1.01	0	1.02
70	5/25/01	4.24	1.93	0.52	0.05	0	0	0	0	1.7	0	1.07	0	1.07
71	3/5/01(B)	0.73	0.64	0.46	0	0	0	0.02	0.12	1.44	0	1.01	0	1.02
72	3/5/01(B)	0.74	1.55	0.18	0	0.17	4.49	0.13	1.19	2.32	0	0.93	0	0.93
73	5/25/01	2.17	0.82	0.13	0	0	0	0	0	0.32	0	1.09	0	1.08
75	5/25/01	3.57	1.53	0.43	0	0	0	0	0	0.83	0	1.1	0	1.1
76	5/25/01	3.05	1.31	0.16	0	0	0	0	0	1.22	0	1.09	0	1.11
77	5/25/01	3.02	1.34	0.3	0	0	0	0	0	0.94	0	1.09	0	1.11
78	3/5/01(B)	0.7	0.71	0.22	0	0	0	0.01	0.87	0.5	0	0.99	0	1
80	3/5/01(B)	0.92	1.41	1.14	0	0	0	0.09	0.59	1.19	0	0.97	0	0.97
81	3/5/01(B)	0.92	1.01	0.31	0	0	0	0	0.67	0.96	0	0.99	0	1

Uncensored trace element data.

Sample	Analysis Date	Al	Zn	Se	Sr	K	Mn	Ba	U	P	^{54}Fe	^{56}Fe	Ag	Sn	Rb
1	3/4/01	48.97	47.84	0	90.68	831.6	7.08	28.45	0.08	52.84	9.38	9.89	0.44	0	1.28
2	3/4/01	53	41.94	0	65.82	550.6	6.27	19.13	0.48	33.92	16.31	17.49	0.46	0	0.93
3	3/4/01	42.9	70.79	0	54.98	459.8	10.26	11.82	0.32	10.7	36.51	36.68	0.45	0.13	0.58
5	3/4/01	27.86	17.45	0	108.1	742.4	11.03	48.47	0.49	17.01	23.51	25.02	0.45	0	0.86
6	3/4/01	50.96	139	0	52.84	521.7	15.51	19	0.18	0.81	0	0	0.45	0	0.68
7	3/4/01	38.5	1.08	0	41.6	366	1.89	11.57	0.27	2.82	4.36	6.45	0.45	0	0.52
8	3/4/01	35.9	0	0	69.48	337.9	2.28	14.64	0.11	0	0.51	3.01	0.45	0	0.48
9	3/4/01	30.99	31.42	0	64.58	501.7	3.73	22.07	0.49	20.03	11.61	13.87	0.45	0	0.66
10	3/4/01	43	13.79	0	75.73	409.6	3.4	16.42	0.29	0	1	3.53	0.45	0	0.56
11	3/4/01	46.56	66.67	0	51.86	371	7.72	10.96	0.27	0	33.61	34.97	0.46	0	0.62
12	3/4/01	55.49	3.29	0	63.36	355.8	6.9	11.05	0.24	0	4.56	6.74	0.46	0	0.43
13	3/5/01(A)	39.35	12.17	0	55.17	347.1	10.7	11.77	0.22	3.52	24.08	24.82	0.46	0	0.54
14	3/5/01(A)	36.76	23.3	0	56.95	333.5	2.09	11.69	0.21	0	4.74	6.34	0.46	0	0.53
18	3/5/01(A)	25.88	9.99	0	39.98	358.1	24.95	17.56	0.07	0	133.5	136.3	0.47	0	0.8
19	3/5/01(A)	11.09	91.57	0	58.95	479.2	25.59	22.18	0.35	0	36.59	37.01	0.45	0	0.8
20	3/5/01(A)	27.33	6.5	0	62.33	481.5	11.03	14.65	0.29	0	18.75	19.72	0.46	0	0.77
22	3/5/01(A)	30.87	65.84	0	59.71	420	4.32	10.61	0.32	0	7.26	8.61	0.45	0	0.52
26	3/5/01(A)	10.24	340.3	0	74.03	741.7	3.06	19.3	0.64	0	14.87	16.55	0.45	0.01	1.02
27	3/5/01(A)	6.88	17.4	0	47.61	373.6	12.14	10.39	0.5	0	84.64	87.16	0.46	0	0.58
28	3/5/01(A)	3.36	9.55	0	48.23	377.8	1.95	14.69	0.56	0	8.21	10.39	0.45	0	0.66
29	3/5/01(A)	0	11.21	0	50.68	413	1.88	16.78	0.25	0	0.67	3.33	0.45	0	0.74

Uncensored trace element data.

Sample	Analysis Date	Al	Zn	Se	Sr	K	Mn	Ba	U	P	^{54}Fe	^{56}Fe	Ag	Sn	Rb
30	3/5/01(A)	16.86	15.84	0	86.54	516.9	6.86	16.85	0.49	0	26.66	28.5	0.46	0	0.88
31	3/5/01(A)	26.29	30.84	0	63.23	537.5	5.89	12.83	0.31	0	18.54	20.23	0.44	0	0.9
32	3/5/01(A)	0	37.28	0	54.25	451.8	3.65	10.25	0.36	0	0.7	2.83	0.45	0	0.71
33	3/5/01(A)	6.96	22.88	0	50.9	430.6	1.67	7.31	1.06	0	10.17	12.1	0.45	0	0.61
34	3/5/01(A)	25.73	4.94	0	54.3	288.9	1.84	12.53	0.41	0	7.07	8.95	0.45	0	0.38
35	3/5/01(A)	30.05	73.9	0	39.94	376.4	5.14	10.19	0.4	0	8.75	10.75	0.45	0	0.63
37	3/5/01(A)	3.28	1.49	0	44.34	404.8	5.28	9.37	0.42	0	12.26	13.56	0.46	0	0.6
38	3/5/01(A)	11.33	22.22	0	32.44	266	0.88	8.09	0.39	0	0.8	2.1	0.46	0	0.42
39	3/5/01(A)	24.45	2.87	0	50.11	303.3	1.06	11.34	0.29	0	0	1.2	0.46	0	0.49
40	3/5/01(A)	14.85	25.43	0	35.68	360	1.22	11.4	0.37	0	2.4	3.94	0.46	0	0.69
41	3/5/01(A)	41.51	46.3	0	42.6	312.1	6.63	10.18	0.17	0	2.71	4.51	0.46	0	0.36
42	3/5/01(A)	27.08	135	0	64.13	391	3.4	12.51	0.22	0	4.36	6.01	0.45	0	0.48
43	3/5/01(A)	6.36	0	0	69.3	326.6	3.49	8.07	0.22	0	3.7	4.89	0.45	0	0.43
44	3/5/01(B)	35.26	6.27	0	69.92	315.7	4.91	30.2	1.61	22.75	5.89	8.63	0.48	0	0.35
45	3/5/01(B)	44.44	18.49	0	41.35	287.8	4.41	8.48	0.33	8	5.68	7.72	0.47	0	0.57
46	3/5/01(B)	34.18	0	0	52.33	347.3	6.39	12.3	0.21	0	18.61	19.33	0.47	0	0.71
47	3/5/01(B)	36.81	19.96	0	61	775.7	9.37	31.97	0.45	0.44	7.49	10.19	0.48	0	0.71
48	3/5/01(B)	16.52	31.31	0	56.77	488.7	3.7	33.93	0.55	8.2	8.13	11.01	0.47	0	0.83
49	3/5/01(B)	24.33	19.54	0	47.56	354.7	3.25	10.36	0.26	0	12.2	14.3	0.47	0	0.63
50	3/5/01(B)	19.79	70.46	0	37.8	630.9	4.19	16.44	0.44	0.29	17.76	18.89	0.47	0	1.07
52	3/5/01(B)	19.03	0	0	24.08	382.1	0.66	9.47	0.14	1.7	3.26	5.49	0.48	0	0.51

Uncensored trace element data.

Sample	Analysis Date	Al	Zn	Se	Sr	K	Mn	Ba	U	P	^{54}Fe	^{56}Fe	Ag	Sn	Rb
55	5/25/01	0	72.93	0	49.97	374.7	0	11	0.29	0	0	0	0.18	0	0.62
56	3/5/01(B)	11.57	0	0	35.99	402.5	2.11	9.93	0.25	5.97	0.67	2.66	0.47	0	0.53
57	3/5/01(B)	10.36	13.98	0	55.81	615.7	15.41	40.91	0.65	1.3	28.96	30.41	0.4	0	0.81
58	5/25/01	0	52.44	0	96.72	432	2.16	53.78	0.32	0	24.21	28.66	0.19	0	0.64
59	5/25/01	0	61.13	0	45.17	495.1	0.24	20.78	0.44	0	0	0	0.19	0.02	0.86
61	3/5/01(B)	28.81	6.35	0	46.9	571	7.26	18.72	0.65	6.41	21.8	23.18	0.47	0	0.88
63	3/5/01(B)	10.61	25.94	0	69.27	516.4	7.91	21.37	0.59	8.93	17.14	19.12	0.47	0	0.6
64	3/5/01(B)	17.61	248.5	0	71.42	495.7	10.62	21.29	0.6	14.05	20.64	22.53	0.47	0	0.53
66	3/5/01(B)	40.22	6.32	0	55.17	500	22.09	35.09	0.75	5.51	46.68	49.56	0.47	0	0.81
67	3/5/01(B)	17.54	32.92	0	50.01	369.4	6.54	32.03	0.31	18.25	23.71	26.47	0.48	0	0.64
69	3/5/01(B)	27.84	18.48	0	66.96	951.3	7.41	27.22	0.36	9.64	9.61	11.59	0.48	0	0.71
70	5/25/01	0	8.74	0	70.87	344.4	1.69	18.89	0.54	0	0	0.65	0.18	0.02	0.4
71	3/5/01(B)	18.68	13.05	0	49.09	431	2.17	20.73	0.54	0	1.33	3.66	0.48	0	0.47
72	3/5/01(B)	64.44	11.37	0	90.53	1074	302.8	68.85	0.17	4.58	1006	1022	0.47	0	1.21
73	5/25/01	0	0	0	45.75	806.4	12.57	15.58	0.26	0	33.02	35.21	0.19	0	0.88
75	5/25/01	0	67.19	0	49.51	386.9	1.42	14.85	0.31	0	0	0	0.18	0	0.58
76	5/25/01	0	2.43	0	43.44	295.7	2.43	10.98	0.23	0	2.29	3.81	0.19	0	0.52
77	5/25/01	0	181.7	0	45.47	445.1	12.2	13.14	0.24	0	18.54	20.66	0.18	0.01	0.61
78	3/5/01(B)	25.74	0	0	47.43	335.8	15.15	11.66	0.15	5.42	43.02	44.36	0.47	0	0.57
80	3/5/01(B)	42.69	2.27	0	54.88	498.3	31.31	25.12	0.61	18.09	25.46	26.09	0.47	0	0.86
81	3/5/01(B)	29.8	2.78	0	72.61	369.5	6.39	14.73	0.25	6.57	9.79	11.04	0.47	0	0.54

APPENDIX D

STANDARDS FOR TRACE ELEMENT ANALYSIS USING ICP-MS

ICP-MS Standards
Grand Traverse Bay Watershed Project

Group 1
Standards: 0, 0.1, 0.25, 0.5, 1, 5, 10, 20 ppb
Ti, Cr, Sc, V, Co, Ni, Cu, As, Ag, Sn, Se, Cd, Pb, U, Mo, Rb

Group 2
Standards: 0, 1, 25, 50, 100, 500, 1000, 2000 ppb
Fe, Sr, Ba, Mn, Zn, Al, K, P

Stock Solutions
Internal Standard (1 ppm In and Ba, 2.5% HNO_3)

Solution 1: 1 ppm Group A
0.1 ml of each 1000 ppm standard solution in 100 ml volumetric

Solution 2: 0.1 ppm Group A
10 ml of Solution 1 in 100 ml volumetric

Solution 3: 1 ppm Group B
0.1 ml of each 1000 ppm standard solution in 100 ml volumetric

Standards

Std. 1: 0.1 ppb Group A, 1 ppb Group B
a) 0.1 ml Solution 2 in 100 ml volumetric
b) 0.1 ml Solution 3

Std. 2: 0.25 ppb Group A, 25 ppb Group B
a) 0.25 ml Solution 2 in 100 ml volumetric
b) 2.5 ml Solution 3

Std. 3: 0.5 ppb Group A, 50 ppb Group B
a) 0.5 ml Solution 2 in 100 ml volumetric
b) 5 ml Solution 3

Std. 4: 1 ppb Group A, 100 ppb Group B
a) 1 ml Solution 2 in 100 ml volumetric
b) 10 ml Solution 3

Std. 5: 5 ppb Group A, 500 ppb Group B
a) 0.5 ml Solution 1 in 100 ml volumetric
b) 0.05 ml of each Group B 1000 ppm stock standard

Std. 6: 10 ppb Group A, 1000 ppb Group B

a) 1 ml Solution 1
b) 0.1 ml of each Group B 1000 ppm stock standard

Std. 7: 20 ppb Group A, 2000 ppb Group B

a) 2 ml Solution 1
b) 0.2 ml of each Group B 1000 ppm stock standard

Matrix matching: 75 ppm Ca—Add 7.5 ml 1000 ppm Ca standard to each 100 ml standard
Add 1 ml Optima HNO_3 to each 100 ml standard

APPENDIX E

CENSORED TRACE ELEMENT DATA

Criteria for Censoring Trace Element Data

Standards for the ICP-MS included Ti, Cr, Ag, Sc, V, Co, Ni, Cu, As, Sn, Se, Cd, Pb, U, Mo, Se, Rb, Fe, Sr, Ba, Mn, Zn, Al, K, and P. A solution of 20 μg/l In and Bi was added in a 1:1 ratio to standards and samples as an internal reference to test instrument stability . The data files generated from the ICP-MS runs therefore included counts and concentrations for each of these elements. However, this raw data must be censored to account for ICP-MS sensitivities for particular elements and concentrations below or above standards in the calibration curves. While the ICP-MS can be tuned to return high sensitivity to single elements, the instrument shows reduced sensitivity if used for multi-element analyses. Sample data must be further censored if analysis of field blanks indicates potential contamination.

Indium and Bi are not considered analytes because they are used to test ICP-MS consistency between samples. The elements Cu and Ni were immediately eliminated from the data files because the ICP-MS cone is made of Ni and the coils contain Cu, and the machine cannot return accurate results for these elements in low-concentration samples. Similarly, Al was eliminated because it is used as a substitute for other metals in the clean lab, and background levels are high compared to the concentrations in GTBW samples. The ICP-MS shows low sensitivity for K and P, so these elements were also eliminated. Potassium was measured using atomic adsorption and is not considered a trace element but was included to see how the ICP-MS responded. The machine also produces unreliable estimates of Zn at low concentrations, so this element was also eliminated. Silver results were disregarded because background Ag levels in the ICP-MS are near or above concentrations in GTBW samples. Silver is an impurity in the Au

solution used to preserve sediment samples for Hg analysis, and Hg-contaminated sediments are frequently run through the machine. Titanium results were initially viewed as acceptable because the calibration curves were reasonable, but concentrations in the Nanopure rinses following each set of standards had high concentrations of Ti, suggesting contamination between samples within the ICP-MS system or that the machine is not sensitive to Ti at concentrations in the μg/l range. Scandium has not been eliminated from the data file, but results should be viewed with caution, because the element behaves similarly to Ti. Rinse concentrations for Sc were not as high as for Ti, but could be higher than the low standard.

Most of the elements discussed in the previous paragraph were eliminated solely on the known performance of the ICP-MS and its ability to produce reliable results for samples with extremely low concentrations. Other elements were eliminated from the data files because most samples had concentrations below the quantification limits determined by the calibration curves. Each run of approximately 20 samples included a set of seven standards before and after the samples. Calibration curves were calculated by adding or deleting samples until a best-fit line was obtained. The lowest standard in the final calibration curve is considered the quantification limit for the run. Concentrations below the quantification limit are typically reported as non-detects. However, if the blank (considered to represent a concentration of zero) was included in the calibration curve, values lower than the quantification limit were accepted without censure. The elements Se, Sn, Co, Pb, Cr, and Cd were eliminated from data files because concentrations for most samples were zero, which implies that the actual concentrations were much lower than quantification limit for each run. The quantification limit was between 0.1 and 0.5

ppb for all elements except Se, which had quantification limits from 0.1 to 5 ppb. Almost all samples had higher concentrations for the remaining elements (V, As, Mo, Sr, Mn, Ba, U, Fe, and Rb) than the quantification limit for each run, so the data should be considered reliable. As mentioned previously, Sc was retained in the data file but the results are less reliable than for other elements.

Thirteen field blanks were taken to ensure that the clean techniques eliminated potential sources of trace element contamination. With the exception of Sc and one V measurements, all concentrations in blanks were below the quantification limit for the run. While the mean Sc concentration for blanks was 0.22 μg/l, the mean of all samples was six times this level, and therefore, while the absolute values of Sc in samples is not reliable, the data may be used to show general trends across the watershed. The V concentration of one blank was slightly above the quantification limit of 0.10 μg/l (0.11), but since the concentrations of samples were on average three times the quantification limit, this blank does not indicate V contamination.

The field blanks did show potential Cr and Co contamination. The mean blank concentrations for Cr and Co were 0.63 μg/l and 0.10 μg/l, respectively, with quantification limits of 0.25 μg/l and 0.10 μg/l, respectively. However, sample concentrations were almost all below the quantification limit, so our clean techniques do not appear to have contributed Cr and Co contamination. More likely, the blanks were contaminated by the bottles in which the NCW was stored. All sample bottles and syringes were new and were never opened outside the clean lab. Although none of the bottles used to transport NCW to the field had been used prior to this project, some had been acid-washed in a lab in which sediment samples from a heavily Cr-contaminated

tannery site were processed. Both Cr and Co are used as pigments in the leather tanning process. The bottles were washed again in the Class 100 lab using the clean techniques described in the Methods section, but some residual Cr may have remained in the bottles. While the potential Cr contamination did not appear to have compromised our sample data, it does suggest that if sample bottles are not new, a more rigorous washing procedure must be developed.

Site ID	Sc	V	As	Mo	Sr	Mn	Ba	U	^{56}Fe	Rb
1	2.18	0.09	0.33	0.27	90.68	7.08	28.45	0.08	9.89	1.28
2	1.34	0.40	0.34	0.87	65.82	6.27	19.13	0.48	17.49	0.93
3	0.82	0.35	0.21	0.91	54.98	10.26	11.82	0.32	36.68	0.58
5	1.41	0.21	0.22	3.53	108.06	11.03	48.47	0.49	25.02	0.86
6	0.67	0.36	0.39	0.99	52.84	15.51	19.00	0.18	<1.00	0.68
7	1.06	0.19	0.39	1.21	41.60	1.89	11.57	0.27	6.45	0.52
8	1.08	0.08	0.24	0.75	69.48	2.28	14.64	0.11	3.01	0.48
9	1.08	0.35	0.23	1.59	64.58	3.73	22.07	0.49	13.87	0.66
10	1.00	0.26	0.54	1.20	75.73	3.40	16.42	0.29	3.53	0.56
11	0.75	0.41	0.50	0.43	51.86	7.72	10.96	0.27	34.97	0.62
12	1.01	0.40	0.62	0.67	63.36	6.90	11.05	0.24	6.74	0.43
13	1.16	0.33	0.70	0.73	55.17	10.70	11.77	0.22	24.82	0.54
14	1.03	0.32	0.65	0.76	56.95	2.09	11.69	0.21	6.34	0.53
18	1.05	0.41	0.21	0.70	39.98	24.95	17.56	0.07	136.25	0.80
19	0.75	0.21	0.49	1.51	58.95	25.59	22.18	0.35	37.01	0.80
20	1.06	0.32	0.37	1.11	62.33	11.03	14.65	0.29	19.72	0.77
22	1.22	0.37	0.36	0.92	59.71	4.32	10.61	0.32	8.61	0.52
26	1.30	0.18	0.23	1.23	74.03	3.06	19.30	0.64	16.55	1.02
27	0.99	0.20	0.26	1.01	47.61	12.14	10.39	0.50	87.16	0.58
28	1.04	0.18	0.17	1.33	48.23	1.95	14.69	0.56	10.39	0.66
29	0.84	0.32	0.18	0.28	50.68	1.88	16.78	0.25	3.33	0.74
30	1.07	0.16	0.61	0.59	86.54	6.86	16.85	0.49	28.50	0.88
31	0.94	0.15	0.33	0.86	63.23	5.89	12.83	0.31	20.23	0.90
32	0.81	0.23	0.31	0.98	54.25	3.65	10.25	0.36	2.83	0.71
33	0.96	0.18	0.19	3.26	50.90	1.67	7.31	1.06	12.10	0.61
34	0.42	0.16	0.10	1.14	54.30	1.84	12.53	0.41	8.95	0.38
35	0.98	0.22	0.12	1.03	39.94	5.14	10.19	0.40	10.75	0.63
37	0.55	0.38	0.26	0.82	44.34	5.28	9.37	0.42	13.56	0.60
38	0.53	0.48	0.13	0.61	32.44	0.88	8.09	0.39	2.10	0.42
39	0.81	0.35	0.11	0.80	50.11	1.06	11.34	0.29	1.20	0.49
40	0.86	0.38	0.23	0.69	35.68	1.22	11.40	0.37	3.94	0.69

Site ID	Sc	V	As	Mo	Sr	Mn	Ba	U	^{56}Fe	Rb
41	0.58	0.31	0.42	0.35	42.60	6.63	10.18	0.17	4.51	0.36
42	0.79	0.50	0.57	0.45	64.13	3.40	12.51	0.22	6.01	0.48
43	0.62	0.39	0.24	0.33	69.30	3.49	8.07	0.22	4.89	0.43
44	1.25	0.26	0.53	3.00	69.92	4.91	30.20	1.61	8.63	0.35
45	0.84	0.15	0.18	0.93	41.35	4.41	8.48	0.33	7.72	0.57
46	0.67	0.26	0.58	0.57	52.33	6.39	12.30	0.21	19.33	0.71
47	1.01	0.34	0.26	1.27	61.00	9.37	31.97	0.45	10.19	0.71
48	0.94	0.16	0.23	1.75	56.77	3.70	33.93	0.55	11.01	0.83
49	0.65	0.32	0.34	0.38	47.56	3.25	10.36	0.26	14.30	0.63
50	0.82	0.24	0.37	1.37	37.80	4.19	16.44	0.44	18.89	1.07
52	0.75	0.39	0.64	0.34	24.08	0.66	9.47	0.14	5.49	0.51
55	2.52	0.31	0.00	0.84	49.97	0.00	11.00	0.29	<1.00	0.62
56	0.96	0.41	0.25	0.65	35.99	2.11	9.93	0.25	2.66	0.53
57	0.98	0.10	0.09	2.84	55.81	15.41	40.91	0.65	30.41	0.81
58	3.86	0.09	0.00	2.00	96.72	2.16	53.78	0.32	28.66	0.64
59	2.86	0.20	0.00	1.94	45.17	0.24	20.78	0.44	<1.00	0.86
61	0.95	0.26	0.41	0.88	46.90	7.26	18.72	0.65	23.18	0.88
63	1.00	0.43	0.33	1.69	69.27	7.91	21.37	0.59	19.12	0.60
64	1.06	0.56	0.28	1.68	71.42	10.62	21.29	0.60	22.53	0.53
66	0.85	0.18	0.31	2.28	55.17	22.09	35.09	0.75	49.56	0.81
67	0.99	0.08	0.18	2.37	50.01	6.54	32.03	0.31	26.47	0.64
69	0.93	0.25	0.33	1.23	66.96	7.41	27.22	0.36	11.59	0.71
70	4.24	0.52	0.00	1.70	70.87	1.69	18.89	0.54	<1.00	0.40
71	0.73	0.46	0.12	1.44	49.09	2.17	20.73	0.54	3.66	0.47
72	0.74	0.18	1.19	2.32	90.53	302.82	68.85	0.17	1021.72	1.21
73	2.17	0.13	0.00	0.32	45.75	12.57	15.58	0.26	35.21	0.88
75	3.57	0.43	0.00	0.83	49.51	1.42	14.85	0.31	<1.00	0.58
76	3.05	0.16	0.00	1.22	43.44	2.43	10.98	0.23	3.81	0.52
77	3.02	0.30	0.00	0.94	45.47	12.20	13.14	0.24	20.66	0.61
78	0.70	0.22	0.87	0.50	47.43	15.15	11.66	0.15	44.36	0.57
80	0.92	1.14	0.59	1.19	54.88	31.31	25.12	0.61	26.09	0.86
81	0.92	0.31	0.67	0.96	72.61	6.39	14.73	0.25	11.04	0.54

APPENDIX F

THE USE OF FACTOR ANALYSIS TO EXPLORE THE RELATIONSHIP BETWEEN LAND USE AND WATER QUALITY: EFFECTS OF DATA TRANSFORMATION

THE USE OF FACTOR ANALYSIS TO EXPLORE THE RELATIONSHIP BETWEEN LAND USE AND WATER QUALITY: EFFECTS OF DATA TRANSFORMATION

Introduction

Complex, multivariate water quality datasets reveal little information about the underlying biogeochemical processes and patterns without mathematical and statistical manipulation. Statistical modeling (regression) of stream chemistry and land cover does not fully explain relations between variables (Herlihy et al., 1998; Battaglin and Goolsby, 1997). Various factors, such as microbial processes, geology, and climate, may mask relationships between land uses and environmental biogeochemistry. Exploratory factor analysis is a powerful tool for examining and quantifying land use-water quality relationships and the factors that control biogeochemical distributions across a watershed (Gupta and Subramanian, 1998; Ramanathan et al., 1996; Cameron, 1996; Abu-Jaber et al., 1997; Eyre and Pepperell, 1999; Miller et al., 1997; Evans et al., 1996).

Factor analysis has been used extensively in this dissertation to study the linkages between land use and water quality. This section describes the effects of data transformation (log and ranked vs. raw) on the interpretability of factors using a single data set.

Statistical Methods

R-mode factor analysis was used to study associations between land use distributions and chemical variables. Factor analysis reduces a multivariate data set into a smaller number of factors that may simplify interpretation of processes controlling variability in the data. Because the factors controlling surface water chemistry in GTBW

were unknown, the analysis was exploratory in nature, with the objective being to uncover empirical relationships between land use and biogeochemistry.

Factor analysis includes a number of related procedures, including principal components analysis (PCA), R-mode and Q-mode factor analysis, and principal coordinates analysis (Davis, 1986). PCA and R-mode factor analysis are the two most commonly used procedures cited in the water quality literature. Both methods return 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). Each variable in the dataset is described as "loading" on the factors identified by the analysis. A loading close to ± 1 indicates strong correlation between a variable and the factor; a loading close to zero indicates weak correlation (Davis, 1986; Evans et al., 1996).

Unlike PCA, R-mode factor analysis is considered a statistical method with assumptions about the population from which samples are drawn (Davis, 1986). 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). The most common method for retaining factors when the actual number is unknown is to consider only those factors whose eigenvalues are greater than one. This is the default procedure in SAS System (Cody and Smith,1997), the computer software package used in this research. The interpretation of factors can be difficult and may 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 (zero

and ± 1). Oblique rotations, such as the Promax, result in correlated factors and may improve the ability to interpret factors (Davis, 1986).

For this research, R-mode factor analysis was run on a data set that included land use percentages for the sourceshed associated with each sampling point and the biogeochemical data for the corresponding sample. Columns contained variables, and rows contained sample locations (reversing this structure results in cluster analysis, not factor analysis). Factors were retained if their eigenvalues were greater than one, and the factor structure from a Promax rotation are reported below.

Factor analysis does not require normalized data sets (Child, 1990; Gorsuch, 1974), but transformation of data may result in an improved ability to interpret the factors (Gorsuch, 1974). Data can be log-transformed (see Schot and van der Wal, 1992; Cameron, 1996), ranked (see Miller et al., 1997), or converted to z-scores with a mean of zero and variance of one (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). To examine the effects of data transformation on the ability to interpret factors controlling the variability of the GTBW data, factor analysis was run on raw, log-transformed, and ranked data. Two columns of data (water and barren) were removed from the log-transformed data set; the percentage of these land use categories in a sourceshed is frequently zero and thus cannot be log-transformed.

Results and Discussion

R-mode factor analysis was run on raw, log-transformed and ranked data, and each model identified six factors with eigenvalues greater than one. The factors were then rotated using the Promax algorithm and the resulting factors are reported in Tables 1, 2,

and 3. Loadings of a variable on a factor are considered high if the loading is greater than 0.75 and moderate if the loading falls between 0.40 and 0.75. This division is somewhat arbitrary but has been used by other researchers (Evans et al., 1996). The three models explained between 73% and 78% of the variability of the data.

The first factor for all runs shows a strong positive association between Ca, Mg, and alkalinity; sulfate loads high when data is log-transformed or ranked. Associations with agriculture, range, NO_3, K, Na, and Cl were more variable among the three runs, but generally showed moderate loadings on Factor 1. Forest exhibited a high negative loading on Factor 1 for all runs. Factors 2-6 for the three cases are not similar enough to compare on a factor-by-factor basis. For example, even if two runs returned a factor that had similar variables with high loadings, these factors did not occur in the same order. However, it is possible to make some generalizations about factors controlling the variability of surface water chemistry in GTBW by grouping factors, because fairly consistent relationships among indicators are found. These generalizations will be referred to as signals instead of factors to avoid confusion.

Table 1. Factor loadings for raw data. High associations between a factor and variable occur if factor loading is > 0.75 and are listed in bold type. Moderate associations are those with factor loadings between 0.40 and 0.75. The last number in each column represents the cumulative percentage of variance explained by each additional factor.

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Urban						
Agriculture	0.72604	0.50620				
Range	0.49129		**0.79984**			
Forest	**-0.79022**	-0.52401				
Water					**0.82326**	
Wetlands				0.68874		
Barren						**0.89704**
PH		-0.67168				
DO		-0.61189				
Temperature		0.60163			0.67935	
Ca	**0.89962**	0.44008				
Mg	**0.86980**					
Na	0.44763	**0.85972**				
K	0.55578	**0.84375**				
Si				**0.84976**		
Alkalinity	**0.83803**					
Cl	0.42575	**0.80611**				
SO_4	0.64518					
NO_3	0.60651					
F			0.71303			
Cumulative %	32.9	45.3	54.4	61.6	67.5	72.7

Table 2. Factor loadings for log-transformed data. High associations between a factor and variable occur if factor loading is > 0.75 and are listed in bold type. Moderate associations are those with factor loadings between 0.40 and 0.75. The last number in each column represents the cumulative percentage of variance explained by each additional factor.

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Urban		0.54179				
Agriculture	0.54495	0.51230				-0.53381
Range	**0.79391**					
Forest	**-0.73612**	0.74646		0.45940		
Wetlands					**0.74422**	
PH				**0.86191**		
DO	-0.53439			**0.77328**		
Temperature		0.66006	-0.40788			
Ca	**0.89602**	0.41930			0.45891	
Mg	**0.90946**				0.47785	
Na		**0.91162**				
K	0.49106	**0.87806**				
Si		-0.40640	0.56014		0.64632	
Alkalinity	**0.78946**	0.44229			0.42458	
Cl		**0.84890**				
SO_4	**0.74401**					
NO_3			**0.82519**			
F						0.61070
Cumulative %	36.2	50.2	57.9	65.0	71.6	77.7

Table 3. Factor loadings for rank-transformed data. High associations between a factor and variable occur if factor loading is > 0.75 and are listed in bold type. Moderate associations are those with factor loadings between 0.40 and 0.75. The last number in each column represents the cumulative percentage of variance explained by each additional factor.

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Urban			**0.76427**			
Agriculture	0.64398	**0.70877**				
Range	0.63050					
Forest	-0.57636	**-0.76626**				
Water	-0.65257					
Wetlands						**0.79514**
Barren						0.65301
PH				**0.75277**		
DO				**0.81138**		
Temperature		**0.75741**				
Ca	**0.87993**					
Mg	**0.83256**			-0.64469		
Na		0.64922	**0.87043**			
K		**0.91405**				
Si				-0.57232	0.56223	
Alkalinity	**0.79960**					
Cl		0.64447	**0.84137**			
SO_4	**0.80317**					
NO_3	0.63710					
F					**0.78304**	
Cumulative %	36.7	49.4	56.8	63.3	69.6	74.8

The first signal has been described above and may be related to agricultural activity. The associations of agriculture, range, Ca, Mg, K, and alkalinity can be explained by the increased dissolution of soil minerals, such as calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and potassium feldspar (KAl_2SiO_8), during soil cultivation This signal can include NO_3, SO_4, Na, and Cl, which is consistent with the use of fertilizers and animal wastes in agricultural areas. The land use category "range" is shrub and grassland, and in the GTBW, can be both abandoned farmland and fallow land. For all three runs, this signal includes a negative association with forest, which is to be expected, since as the percentage of agriculture or rangeland increases, the percentage of land in forest must decrease.

The second signal that can be generalized from the factor analysis is that of the dissolution of halite (NaCl), which is probably related to road salt. Na and Cl show high factor loadings in all three runs (Raw, Factor 2; Log, Factor 2; Rank, Factor 3). The ranked data set returns a high loading of Na, Cl and percentage urban land, while this signal includes moderate associations with other land uses and chemicals when data are log-transformed or raw. While the density of roads may be higher in urban areas, roads are present in all land use categories, and thus a road salt signature may not be uniquely associated with urban areas. Other sources of Na and Cl in GTBW include septic systems and brines from oil and gas operations. However, the Na:Cl ratio in surface water samples closely matches that of natural halite (0.65 in mg/L, or 1 in a molar scale) rather than the Na:Cl ratio of Michigan brines (<0.5). Figure 1 is a plot of molar Na vs. molar Cl for each sample. If the source for chloride is from the dissolution of halite, then the cluster of data should plot along a trajectory with a slope of 1. The plot shows that the

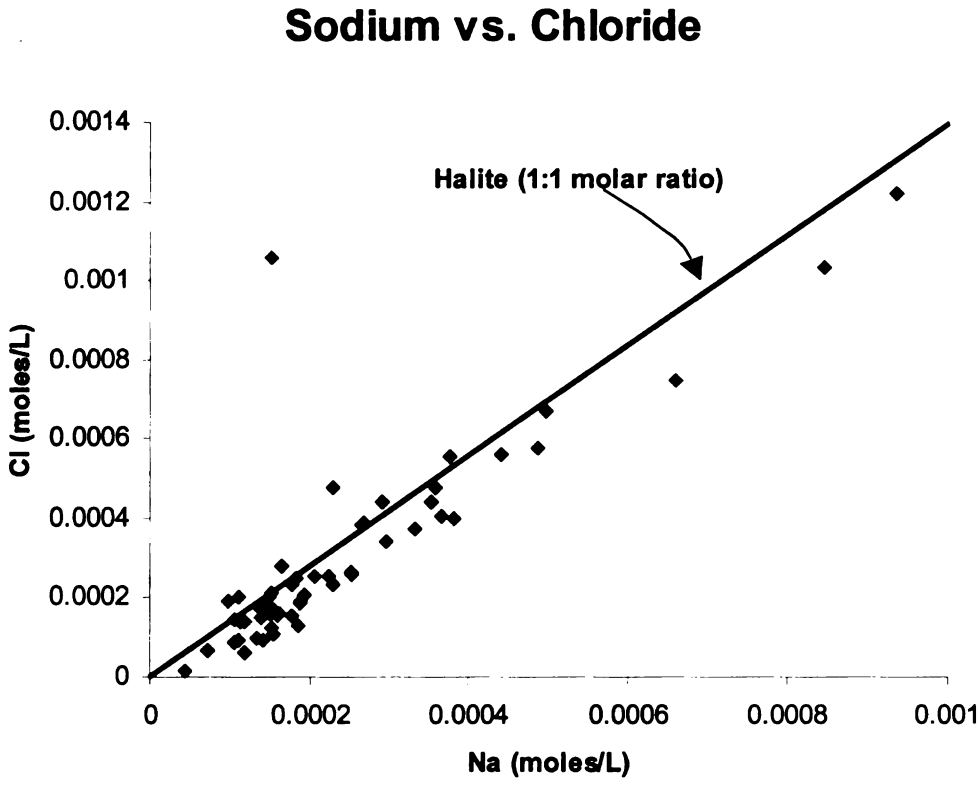


Figure 1. Sodium vs. Chloride Concentrations. If the source for chloride is from the dissolution of halite, then the cluster of data should plot along a trajectory with a slope of 1. The plot shows that the samples fall near the trajectory for halite, with a few samples falling above or below the halite line. Subsurface brines, leakage from septic systems or animal feed lots could account for variations from the halite line.

samples fall near the trajectory for halite, with a few samples falling above or below the halite line. The presence of K in this factor can be attributed to the inclusion of K-salts in road salt mixtures. Na and Cl appear in two factors for the ranked data set, one with a moderate correlation with agriculture and the other with a strong correlation with urban. Oblique rotations create factors that are no longer independent, and therefore these factors are probably interrelated. Again, roads are linear landscape features that cross land uses, so the road salt signature may not have a strong association with a single land use.

The third signal that can be generalized from the factors is related to fluoride. Fluoride is strongly associated with range (Raw, Factor 3), has a negative association with the percentage of agricultural land (Log, Factor 6), and loads positively but moderately with silica (Rank, Factor 5). There is no natural source of fluoride in GTBW, but a significant anthropogenic source could be fluoridated toothpaste. In areas without sewers, septic systems are probably the principal source of fluoride to surface waters. Non-sewered areas in GTBW include urban areas outside the Traverse City sewer system, rangeland that has been developed since the MiRIS database, and forested land that has recreational housing. The relationship between F and silica is not clear and may indicate a spurious correlation.

Other signals are more difficult to interpret from the three factor analysis runs. Dissolved oxygen and pH comprise a fourth signal (Log, Factor 4; Rank, Factor 4). The two variables show high loadings for both runs in which this signal is present. Forest is moderately loaded with this factor in the log-transformed data set, and Mg and Si are negatively loaded with this factor in the ranked data. Wetlands and alkalinity show an association (Raw, Factor 4; Log, Factor 5). Temperature appears in several factors (Raw, Factors 2 and 5; Log, Factors 2 and 3; Rank, Factor 2). These factors represent processes that influence surface water chemistry, but the models are not able to adequately suggest quantifiable relationships among the variables in these factors. The interpretation of these factors and their effects on surface water chemistry may be improved by increasing the number of samples used in the analysis.

Conclusions

R-mode factor analysis was used to explore the relationship between land use and surface water chemistry. The results of the factor analysis suggest that certain groups of chemicals may be more likely to be associated with specific land uses. For example, agriculture may have a biogeochemical fingerprint characterized by elevated levels of elements that dissolve out of the dominant soils of a region and by nutrients added as fertlizers. Urban areas or areas with high road densities may have a biogeochemical fingerprint dominated by Na and Cl resulting from de-icing activities. The presence of flouride in surface waters may be indicative of wastewater from septic systems and may be a component of non-sewered residential land use fingerprint.

Increasing the sample size may improve the models described in this paper two ways. The ability of the models to explain the variability in the original data may increase as the sample size increases. Perhaps more importantly, a larger sample size may improve the interpretability of the factors and/or reduce the number of factors. Child (1990) defines a small sample size as less than 30 members; in these data sets, a small change in the number of samples can have a large effect on the factors. The ratio of samples to variables needed to produce factors with significant meaning is debated, with rules varying from one-to-one to ten-to-one (Child, 1990). In the case of the GTBW data, while the use of 53 samples and 20 variables (seven land use variables and 13 chemical variables) does not violate any rules of factor analysis, a larger number of samples would probably produce clearer factors with better explanatory power.

Data transformation did not significantly improve the interpretability of the factors. Rank order has the greatest influence on the correlation coefficients upon which

factors are based (Gorsuch, 1974). Because log-transformation does not change rank order, this normalization procedure has little effect on correlation coefficients. The fact that ranking the GTBW data did not improve interpretability of factors cannot be separated out from the influence of sample size; a larger, ranked data set may produce more easily understood factors than those discussed in this paper. For future analyses, this data set will be combined with data from other sampling dates to investigate the effects of sample size on factor analysis.

The factor analysis described in this section is a preliminary, exploratory step in a study of the relationship between land use and water chemistry. Factors do not confirm any causal processes that link land uses and biogeochemical fingerprints. Rather, factor analysis helps to search for quantitative relationships among variables that serve as the basis for further research. For example, without factor analysis, the association of rangeland with fluoride would have gone undetected and may be indicative of significant development in this land use category. This relationship will now be considered in a spatial analysis of land use intensity variables within the rangeland category. The results of the factor analyses presented here will shape hypotheses about what chemicals may be associated with particular land uses, with the ultimate goal being the prediction of biogeochemical fingerprints for land uses in Michigan.

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