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**The effect of hydrologic pathways and runoff episodes on
aluminum and major cations in two northern Michigan streams**

Fegan, Nancy Ellen, Ph.D.

Michigan State University, 1993

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THE EFFECT OF HYDROLOGIC PATHWAYS AND
RUNOFF EPISODES ON ALUMINUM AND MAJOR CATIONS
IN TWO NORTHERN MICHIGAN STREAMS

By

Nancy Ellen Fegan

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ABSTRACT

THE EFFECT OF HYDROLOGIC PATHWAYS AND RUNOFF EPISODES ON ALUMINUM AND MAJOR CATIONS IN TWO NORTHERN MICHIGAN STREAMS

By

Nancy Ellen Fegan

Researchers concerned with understanding acid precipitation effects have identified many processes that control stream chemical variations, such as episodic discharge, controls on aluminum (Al), and mineral weathering. To represent these processes in predictive models, an understanding of how water evolves as it travels through specific hydrologic pathways is needed. Currently, detailed knowledge of specific flowpaths in watersheds is extremely limited.

In this investigation, individual source water inputs traveling through specific hydrologic pathways are identified in two rivers receiving the same acidic deposition. Since input is the same, differences in chemical variations are directly linked to geological differences. Samples were obtained weekly from rivers, springs, and precipitation for one year to compare seasonal variations. Samples of runoff and regional groundwater were also analyzed. Results from chemical analyses were compared to weathering petrology to derive mineral weathering reactions to account for observed aqueous chemical trends.

Significant chemical episodes occurred in response to

snow melt and major storms. Increased discharge caused lower pH, decreased cations, and increased total Al in both rivers. Aluminum behaved as expected based on gibbsite solubility control, but in the Peshekee where there are numerous swamps, organic-Al is inversely proportional to dissolved organic carbon (DOC). In the same river, polymeric Al corresponds directly to DOC. Input of complex Al-organic compounds from swamps during high discharge appears to be an important aspect of Al behavior not previously identified.

In the Peshekee, high cation flux is correlated with large storms flushing vadose water through mafic dikes, while in the Yellow Dog, high cation fluxes occur weeks or months after large storms as a result of deeper infiltration and flushing of thick glacial sediment. Mass balance calculations from weathering reactions for different input waters show that water chemistry is highly dependent on local geology. Based on results from this study, models of watershed acidification would be improved by considering polymeric Al, swamp overflow, and detailed geological and structural influences on input sources to surface waters.

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TABLE OF CONTENTS

LIST OF TABLES	vii
LIST OF FIGURES	ix
INTRODUCTION	1
Previous Research	3
STUDY AREA	13
Location	13
Geology	14
Hydrologic Setting and Climate	17
METHODS	19
Water Sampling and Analysis	19
Discharge Measurements	25
Rock, Sediment and Soil Sampling and Analysis	26
RESULTS AND DISCUSSION	27
Hydrology	27
Water Chemistry	31
1. Precipitation	31
2. River waters	35
3. Springs, groundwater and other inputs	54
Cation Release Rates	57
Thermodynamic Mineral Relationships	60
Elemental Mass Balance from Weathering Reactions	68
1. Weathering petrology	68
2. Mass balance reactions	73
SUMMARY AND CONCLUSIONS	83
BIBLIOGRAPHY	90
APPENDICES	100
Appendix A. Reverse mineral weathering reactions used in Table 6 to reconstruct source minerals for dissolved solutes	100
Appendix B. Complete aqueous chemical data for all water samples	104

LIST OF TABLES

Table 1. Studies that have identified watershed processes that affect Al concentrations in streams .	11
Table 2. Methods of aqueous chemical analysis	22
Table 3. Concentrations of major solutes in precipitation (in mg/l)	32
Table 4. Concentrations (in mg/l) of major solutes in the Peshekee and Yellow Dog Rivers	36
Table 5. Solute concentrations (in mg/l) in different ground and surface water types in the Peshekee and Yellow Dog vicinity	55
Table 6. Reconstruction of source minerals for Northern Michigan waters (in mol/l*10 ⁴); equations shown in Appendix A	74
Table 7. Correlation coefficients of molar concentrations for river and source waters	82
Table 8. Aqueous chemical data for Peshekee River, Site 1 (1988-1989)	104
Table 9. Aqueous chemical data for Peshekee River, Site 3 (1988-1989)	106
Table 10. Aqueous chemical data for Peshekee River, Site 4 (1988-1989)	108
Table 11. Aqueous chemical data for Peshekee Spring (1988-1989)	109
Table 12. Aqueous chemical data for Yellow Dog River, Site 1 (1988-1989)	110
Table 13. Aqueous chemical data for Yellow Dog River, Site 3 (1988-1989)	112
Table 14. Aqueous chemical data for Yellow Dog River, Site 4 (1988-1989)	113

Table 15. Aqueous chemical data for Yellow Dog Upper Spring (1988-1989)	114
Table 16. Aqueous chemical data for Yellow Dog Lower Spring (1989)	114
Table 17. Aqueous chemical data for Precipitation (1988-1989)	115
Table 18. Aqueous chemical data for groundwater, lakes and runoff	117

LIST OF FIGURES

Figure 1. Location of the Peshekee and Yellow Dog Rivers showing schematically the main geological features of the area; actual dike thicknesses 2-25 meters (after Sims, 1992)	15
Figure 2. Location of precipitation, stream, spring and ground water samples (S1=Peshekee Spring; S2=Yellow Dog Upper Spring; S3=Yellow Dog Lower Spring)	20
Figure 3. Precipitation and discharge records for Peshekee and Yellow Dog Rivers (Van Riper=Peshekee area; Big Bay=Yellow Dog area)	29
Figure 4. Typical storm event hydrograph showing the more rapid response of the Peshekee River	30
Figure 5. Weekly anion and cation variation in western Marquette County precipitation, 1988-1989	34
Figure 6. Weekly pH variation for three sites on each river, 1988-1989	38
Figure 7a. Weekly ion concentrations, Peshekee River Site 1, 1988-1989	41
Figure 7b. Weekly ion concentrations, Peshekee River Site 3, 1988-1989	42
Figure 7c. Weekly ion concentrations, Peshekee River Site 4, 1988-1989	43
Figure 8a. Weekly ion concentrations, Yellow Dog River Site 1, 1988-1989	44
Figure 8b. Weekly ion concentrations, Yellow Dog River Site 3, 1988-1989	45
Figure 8c. Weekly ion concentrations, Yellow Dog River Site 4, 1988-1989	46
Figure 9. Weekly variation in Al species for downstream sites in both rivers, 1988-1989	49

Figure 10. Relationship of individual Al species to pH for downstreams sites of both rivers	50
Figure 11. Relationship of individual Al species to DOC for downstream sites of both rivers	52
Figure 12. Release rates of major cations out of the Peshekee and Yellow Dog watersheds	58
Figure 13a. Plot of pAl (-log[inorganic monomeric Al]) versus pH for river water samples (squares=downstream sites, circles=midstream sites, triangles=upstream sites in both rivers)	62
Figure 13b. Plot of pAl (-log[inorganic monomeric Al]) versus pH for groundwater and spring samples	63
Figure 14. Activity diagram for river and ground water samples (including springs), showing mineral stability fields for 0° and 25°C in the system HCl-H ₂ O-Al ₂ O ₃ -K ₂ O-SiO ₂	65
Figure 15. Activity diagram for river and ground water samples (including springs), showing line of quartz saturation at 0° and 25°C in the system HCl-H ₂ O-Al ₂ O ₃ -K ₂ O-SiO ₂ at 25°C	66
Figure 16. Activity diagram for river and ground water samples (including springs), showing line of quartz saturation at 0° and 25°C for the system HCl-H ₂ O-Al ₂ O ₃ -CaO-SiO ₂ at 25°C	67
Figure 17. Representative x-ray diffraction patterns for clays from Peshekee and Yellow Dog soils	71

INTRODUCTION

Concerns about the environmental effects of acid precipitation have prompted numerous studies in the past 20 years aimed at understanding processes that cause toxic biological effects in surface waters. Many geological, chemical, climatic, and environmental factors that may affect ionic concentrations in streams have been identified by past research (Krug and Frink, 1983; Likens, 1988). One major area of investigation encompasses the study of major ion balances and changes in response to acid deposition (Neal et al., 1986; Ryan et al., 1989; Kress et al., 1990), including episodic events (Seip et al., 1989; Schaefer et al., 1990). Other lines of research focus on the study of Al behavior and the causes of toxic Al increases (Johnson et al., 1981; Driscoll et al., 1980, 1984, 1985; Hooper and Shoemaker, 1985; Cronan et al., 1986; Lawrence et al., 1986; Nordstrom and Ball, 1986; Manley et al., 1987; Neal et al., 1989). Rock and soil weathering processes are major sources of ions to streams, and have also received attention (Cronan, 1985; Velbel, 1985, 1992; Wright, 1988).

Problems with previous approaches that need to be addressed are: 1) developing ways of identifying specific

hydrologic pathways and geochemical reactions within a particular watershed, including those controlled by geologic features; 2) identifying end member source water types and determining how each water attains its chemical signature; 3) determining how the contribution from each different water source changes with changing hydrologic conditions. To address these problems, rigorous geochemical studies of water types within a watershed must be conducted in conjunction with hydrogeologic survey to distinguish likely flowpaths, and petrologic study to identify specific minerals involved in chemical reactions in water as it flows through hydrologic conduits.

In this investigation, individual water types flowing through specific hydrologic pathways that control the release of aluminum (Al) and major cations (calcium, Ca; magnesium, Mg; sodium, Na; potassium, K) to two streams are identified. These water types and flowpaths are identified by correlating episodic changes in stream chemistry to discrete climatic events, distinct geological characteristics and petrologic make-up of the watersheds studied. The two watersheds in this investigation are geographically adjacent to each other, and located in an area of exposed granitic rock in northern Michigan, a region that receives acid precipitation but has undergone little study. Since the initial precipitation input to each river system is the same, differences in water chemistry between rivers in the down-gradient direction must be directly linked to compositional and physical differences

in watershed materials.

Individual sources of water to the streams, including runoff, overflow from lakes and swamps, shallow groundwater and deep groundwater, are recognized in this study based on correlations of hydrology, geology and water chemistry. The relative importance of each input in contributing ions during major discharge episodes is also discerned by evaluating how closely connected the source water is to the stream hydrologically. Finally, specific mineral reactions are derived from weathering petrologic study that account for nearly all of the geochemical variability in each system.

Previous Research

The basic question addressed by the research considered here is how do solutes get into stream water? To answer this question, one needs to consider what happens after rain water of a particular composition contacts earth materials inducing mineral weathering reactions, how ions released from reactions are transported to streams, and how reactions that occur in streams affect solute concentrations. Few studies have attempted to examine all conceivable aspects of geochemical and hydrological processes in a particular system, but many have encompassed a number of integrated facets in one watershed.

By the mid-1970's, it became clear that large areas of

North America and Europe were being affected by potentially harmful acidic precipitation caused by industrial emissions (Hörnberger et al., 1989; Baker et al., 1991). This knowledge led to numerous surveys of precipitation chemistry across many industrialized nations (e.g., USEPA, 1979; Paces, 1985; Galloway et al., 1987; Wright, 1987; NAPAP, 1990). To understand the influence of acid rain and snowfall input on surface water chemistry, knowledge of specific mineral weathering processes in rocks and soils was required, as well as information on surface and groundwater hydrologic processes.

Much of the work completed in past years by other workers has been stimulated by a need to predict potential acidification problems of the future. This work has led to the advancement of computer models that incorporate chemical and hydrologic parameters to simulate predictions (Christophersen et al., 1982; Chen et al., 1984b; Schnoor, 1984; Wright, 1984; Cosby et al., 1985; Kamari et al., 1989). Proposed models have been applied to numerous watershed systems (e.g., Schnoor et al., 1984; Whitehead et al., 1988), with varying levels of success. Many of the more well known watershed models (BIRKENES, Christophersen et al., 1982; ILWAS, Chen et al., 1984b; MAGIC, Cosby et al., 1985; Ruess and Johnson, 1986) are based on key chemical reactions that are linked to submodels of soil properties and their control on water chemistry (Hendershot et al., 1992). These models treat the watershed as two or three homogeneous layers, not

generally realistic for geologically complex regions. Other workers have put forth a mixing model, conceptualizing that stream waters are generated by the mixing of chemically and spatially distinct water types (Christophersen et al., 1990; Hooper et al., 1990; Wels et al., 1990; Hendershot et al., 1992). This approach also has inadequacies, in that it does not address the question of water flowpath identification and the chemical changes of water as it passes through specific flowpaths (Hendershot et al., 1992).

In recent literature, some researchers have been trying to incorporate geochemical models with mixing models, notably Christophersen and Neal (1990), Robson et al. (1991), and Hooper and Christophersen (1992). All of these authors have underscored the need to assess hydrologic flow paths in order to fully understand and model watershed chemical processes and episodic responses, since hydrologic pathways ultimately control any mechanism which results in changes in stream chemistry. Many watershed studies have expressed this result (e.g., Chen et al., 1984a; Cozzarelli et al., 1987; Peters and Driscoll, 1987; Hendershot et al., 1992). Schaefer et al. (1990) concluded that hydrologic flow paths were critical factors in controlling the sensitivity of Adirondack lakes to acidification. Rochelle et al. (1989) also determined that hydrologic parameters were a major control on surface water chemistry in 144 watersheds studied in the northeast U.S.

Current thinking is that stream water can be considered as a mixture of specific chemical water types from within a

watershed, with contributions from each depending on the hydrological conditions. Accordingly, a complete interpretation of chemical changes in stream water requires an understanding of how geochemical changes occur within watershed materials, and also how hydrologic pathways that lead to the stream influence stream chemistry. More detailed field studies must be completed in order to understand how waters evolve as they progress through the hydrologic cycle to enter streams, and in particular, studies are needed that delineate the sources of waters of different composition and how they mix before entering the stream (Neal et al., 1992).

However, the problem is that in most watersheds knowledge of specific flowpaths is extremely limited (Hooper and Christophersen, 1992). The individual flow paths in a particular setting could depend on a large number of geologic, climatic and ecological factors, all of which may not be entirely discernable until after a large-scale study has been instituted. Most research thus far has concentrated on flowpaths within soil layers, but other kinds of hydrologic controls, such as structural features, may be important. In addition, while large scale hydrologic parameters like discharge or recharge may be measurable, some mechanisms operate on scales as small as the sub-microscopic level, and may not even be quantifiable. Because of these difficulties, researchers have tried to determine water sources and flow paths by using aqueous chemical information.

One important area of study with regard to understanding

the geochemical evolution of dilute water as it travels through flowpaths in soils and rocks concerns mineral weathering reaction rates and mechanisms. Chemical weathering is basically the only process by which incoming acidity can be neutralized over geologic time (Galloway et al., 1983). While cation exchange can also cause neutralization, the supply of base cations must be continually resupplied by weathering or neutralization will no longer take place. Surface water acidification occurs primarily in areas with much exposed bedrock that is chemically resistant, particularly granite, granitic gneiss or quartzite.

While it is not clear whether acid deposition actually changes the rate of chemical weathering (Folster, 1985; Wright, 1988), it is apparent that reaction mechanisms are complex and poorly understood, and that reaction rates observed in laboratory studies are not reflected by natural weathering processes (Wollast and Chou, 1988; Velbel, 1990). Many authors have used mass balance calculations to establish natural rates of weathering and cation release in watersheds in an effort to understand how specific cations are liberated and delivered to streams, and which minerals are the source for specific cations. Drever and Hurcomb (1986), for example, found the principle mineral reactions occurring in an area of the North Cascade Mountains of Washington to be calcite dissolution and alteration of biotite to vermiculite, based on mass balance calculations. Cronan (1985) and Folster (1985) calculated similar cation release rates for systems in

different parts of the world, but each found broad differences between different soil types and soil horizons. Clayton (1986) found a differential weathering rate for albite and anorthite in the Idaho Batholith based in Na and Ca flux in streams. Velbel (1985, 1992) was able to relate differences in cation releases from forested watersheds of the Southern Blue Ridge to hydrologic processes and textural differences, using mass balance models. Further evaluation of weathering rates calculated from Southern Blue Ridge and Minnesota watersheds allowed Velbel (1993) to show that the magnitude of discrepancy between laboratory-derived weathering rates and those calculated from field data is similar for different minerals within one watershed. In other words, the same weathering rate "correction factor" can be calculated and applied to each mineral in a data set, a coefficient independent of composition but likely highly dependent on hydrologic factors (Velbel, 1993).

In trying to elucidate weathering rate information from ion budgets in streams, workers studying watershed geochemical balances have underscored the need to consider individual sources of input water and specific hydrologic pathways to fully explain stream water variability. The link between chemical episodes in streams and large-scale hydrologic events like high runoff following major rain storms or snow melt have been recognized in numerous past studies (e.g., Neal et al., 1986; Seip et al., 1989; Ryan et al., 1989; Schaefer et al., 1990). However, the relationship between small- or even

microscopic-scale hydrologic processes and mineral weathering reactions that occur on scales as small or smaller than one mineral grain has not been studied. The importance of local chemical equilibria to the formation of secondary weathering products can be seen in alteration halos and rims in tiny fractures and pores observed through petrographic and electron microscopes (Meunier and Velde, 1979; Nahon, 1991). To fully explain cation release from watershed materials, chemical weathering reactions specific to the individual macro- and microscopic weathering sites within the system must be coupled to interpretations of macro- and micro-scale hydrologic mechanisms.

Another major geochemical problem that has prompted many stream acidification studies relates to Al chemistry. Numerous studies have shown that high Al levels in surface waters are toxic to fish, resulting in respiratory problems and clogging of gill structures (Baker and Schofield, 1982; Muniz and Leivestad, 1980; Rosseland et al., 1986). Al toxicity has also been documented in aquatic invertebrates (Havas, 1986; Hall et al., 1987). In most cases, the chemical form, molar ratio, and the timing of release to waters are important factors in determining biological effects or toxicity of Al and other cations in the environment.

Understanding Al chemistry in streams is also necessary for discerning mineral weathering processes. While some cationic weathering products like Ca, Mg, Na and K may be delivered directly to streams and carried out of the watershed

upon release, other cations are less soluble than others at normal pH, notably Fe and Al, and are often redeposited in the soil column as oxides, clays, or organic compounds (Johnson et al., 1981; Bloom et al., 1979; Arp and Ouimet, 1986; Cronan et al., 1986). Thus, amorphous Al hydroxides, Al (clay) silicates, and Al-organic matter complexes precipitated in soils may be the primary source of Al to ground and surface waters. Dissolution of or leaching from these compounds is highly pH dependent, consequently elevated Al concentrations in soil and surface waters in regions affected by acid deposition are common. One of the major controls on Al concentrations in natural waters is pH. Aluminum becomes much more soluble with lower than normal pH (Hem and Roberson, 1967; May, et al., 1979), such as occurs in precipitation and in surface waters in much of the northeastern U.S. (Johannes et al., 1985).

A partial compilation of research papers dealing with Al in surface water systems is presented in Table 1, which shows major observations and locations of studies. Centered mostly in watersheds in Norway and the northeast U.S., these studies and others have identified numerous processes that affect Al in streams, rivers and lakes. Some of these include release of Al from minerals by weathering, interactions with mineral and organic matter in soils and in solution, hydrologic variability, changes in precipitation chemistry, and seasonal climatic variability. In many of these watersheds, large increases in stream acidity occur in spring due to rapid

Table 1. Studies that have identified watershed processes that affect Al concentrations in streams.

Site	Author(s)	Major Observations	Comments
Northeast U.S. (Hubbard Brook, New Hampshire)	Johnson et al., 1981; Lawrence, et al., 1986, 1988; Lawrence & Driscoll, 1988;	Stream cations increase, SO_4 decrease after clear cutting forests; dilution of Al; Al speciation is flowpath dependent, upper soil releases organic Al, lower gives inorganic Al, equilibrium w/gibbsite	a series of studies that address changes in stream chemistry due to acidification, forestry practices, soil nitrification and vegetative uptake, hydrology
	Hooper & Shoemaker, 1985	Al not in equilibrium w/ $\text{Al}(\text{OH})_3$ or any readily formed mineral; high Al not during snowmelt (low pH)	contrary to other Hubbard Brook studies; kinetic or hydrologic control; samples only for high flow
Northeast U.S. (Massachusetts)	MacAvoy, 1989	Ion exchange regulates stream Al, organic acids control Al in wetlands	samples taken only during autumn rain storms
Eastern U.S. (Virginia)	Cozzarelli, Herman & Parnell, 1987	Soil Al decreases w/depth, controlled by mineral solubility in lower soil, organics in upper soil	lysimeter study of soil water
soils, Netherlands & Hubbard Brook (U.S)	Mulder, van Breeman & Eijck, 1989	Most soil Al is organically complexed	soil leaching experiments
soils, Northeast U.S. & Southeast Canada	Cronan, Walker & Bloom, 1986	Al explained by $\text{Al}(\text{OH})_3$ and humic phase complexes	lab experiments, thermodynamic modeling
Southeast Canada (Ontario)	Manley, Chesworth & Evans, 1987	Organic Al in upper soil, lower soil has inorganic Al; supersat. w/respect to several Al-SiO ₂ phases	soil extractions
Northeast Australia (Queensland)	Little, 1986	Al transported through soils via organic complexes	soil leaching experiments
Scotland	Bache & Sharpe, 1986	Polymeric Al compounds readily leached from soils	soil leaching experiments
Southern Norway (Birkenes)	Seip, et al., 1989	Al controlled by variable hydrologic pathways, not mineral solubility	stressed the importance of developing more complex (realistic) hydrologic models
Wales (Afon Hafren, Afon Hore)	Neal, Smith, Walls & Dunn, 1986; Neal, 1988; Neal et al., 1989	Stream chemistry determined by mixing of soil organic component and products of deeper bedrock weathering; stream Al not controlled by simple kaolin or $\text{Al}(\text{OH})_3$	stressed reappraisal of conventional stability diagrams to determine stream Al controls

melting of accumulated snow or after major rain storms (Seip, 1980; Seip et al., 1989; Schaefer et al., 1990), causing a corresponding increase in Al concentrations.

Since the development of laboratory and field techniques to measure various chemical forms of Al in natural waters (Barnes, 1976; Driscoll, 1984), detailed studies of Al behavior in stream waters has been possible. Chemical equilibrium with gibbsite or some other easily formed Al-OH compound appears to control Al in certain stream systems, such as in the Hubbard Brook Experimental Watershed in New Hampshire (Johnson et al., 1981; Driscoll et al., 1984, 1985; Lawrence et al., 1988). Other studies have not found gibbsite solubility to be a satisfactory explanation for observed Al behavior. Hooper and Shoemaker (1985) reported gibbsite disequilibrium during high discharge events in a small watershed in Hubbard Brook, only a few kilometers away from areas in which other workers considered to exhibit gibbsite control over stream Al concentrations (Johnson et al., 1981). Higher than expected Al in streams during spring melt was attributed to flushing of soil-accumulated Al in the Hooper and Shoemaker (1985) study.

Other researchers have given additional explanations for observed Al behavior in streams that does not coincide with gibbsite solubility control. Arp and Ouimet (1986), Bache (1986) and Mulder et al. (1989) considered organically bound Al as a primary controlling mechanism for surface water Al concentrations. Cation exchange has also been invoked to

explain Al behavior in certain systems (McAvoy, 1989). Some studies have indicated equilibrium with Al-SO₄ minerals such as jurbanite as major controlling factors on Al concentrations (Eriksson, 1981; Arp and Ouiment, 1986). Numerous studies have considered aluminosilicate mineral weathering as most important in understanding Al (Manley et al., 1987; Neal and Williams, 1988; Neal et al., 1989, 1992). Adsorption of Al by clay minerals in soils has also been considered important (Walker et al., 1988).

In light of these many studies, it seems clear that no single mechanism controls Al chemistry in all watersheds. It appears that in order to understand fully the relationships between weathering processes, soil and in-stream reactions, and hydrologic factors and their effect on stream chemistry, it is necessary to evaluate each watershed individually, at least until models more adaptable to specific watershed conditions become available.

STUDY AREA

Location

The two watersheds in this study are located in Marquette County in the Upper Peninsula of Michigan, shown in Figure 1. The Peshekee River begins near the highest elevation in the state (Mt. Curwood, 1980 feet) in the extreme eastern portion

of Baraga County, and flows to the southeast for approximately 30 miles through western Marquette County, draining into Lake Michigamme at its mouth. The Yellow Dog River also has its source in the highlands on the border of Baraga and Marquette Counties, but flows northeasterly for about 33 miles before draining into man-made Lake Independence near the town of Big Bay. Both rivers drain nearly uninhabited forested areas. The two rivers carry approximately the same quantity of water, but one noticeable difference between them is the color of the water. The Peshekee River, like many in northern Michigan, is colored tea brown by tannins leached from organic debris on the forest floor and the numerous bogs and swampy areas found throughout the watershed. The Yellow Dog is similarly, albeit more lightly, colored in its upper and middle reaches, but is remarkably clear by the time it reaches downstream stretches.

Geology

The geology of the region drained by the Peshekee and Yellow Dog rivers consists of Precambrian igneous and metamorphic bedrock, covered in places by varying thicknesses of Pleistocene glacial sediments. The majority of the rocks, mostly granitic gneiss, are considered to be at least 2.5 billion years old by Rb-Sr dating (Cannon and Simmons, 1973), a stratigraphic division known regionally as Precambrian W age (Cannon and Gair, 1970). These older rocks are overlain

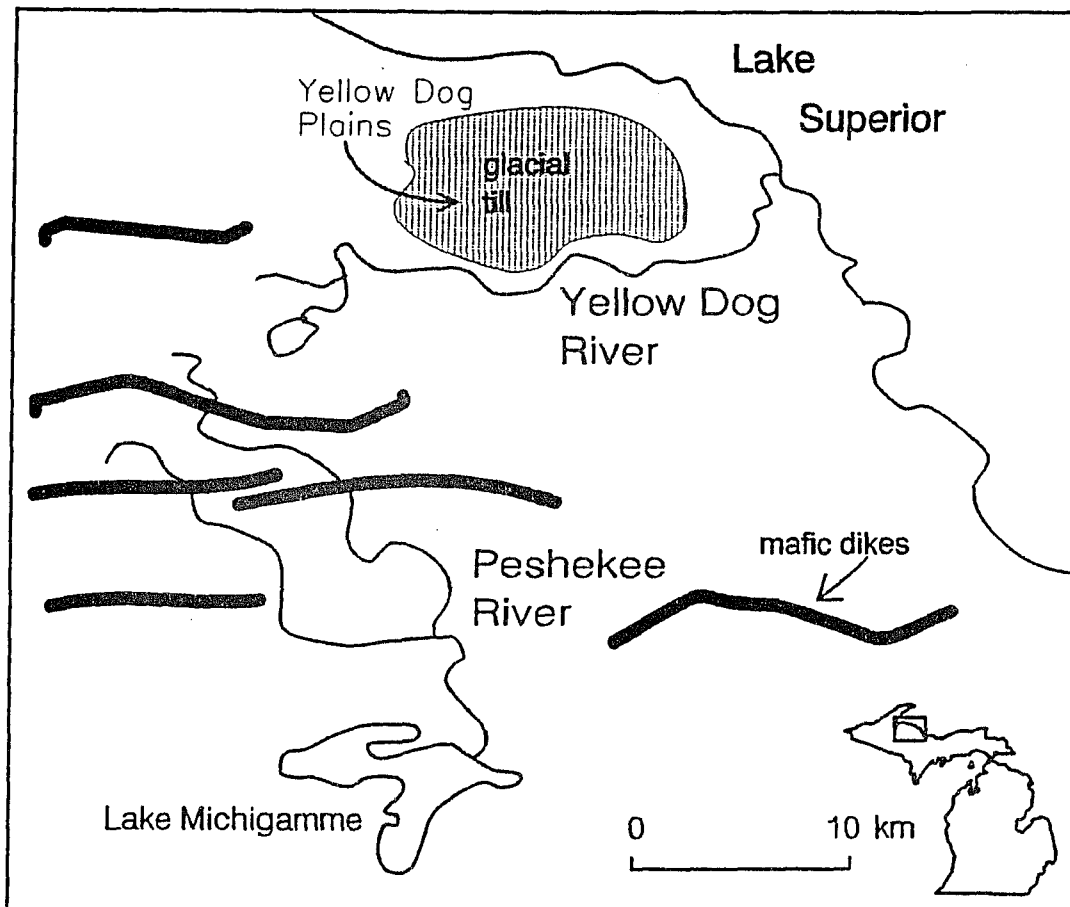


Figure 1. Location of the Peshekee and Yellow Dog Rivers showing schematically the main geological features of the area; actual dike thicknesses 2-25 meters (after Sims, 1992).

unconformably by Precambrian X rocks of Early Proterozoic age, composed of metamorphosed sedimentary and, less commonly, metavolcanic rocks. Numerous diabase dikes trending nearly east-west and a few small scattered mafic plutons intrude all rocks in the region, and are believed to be of Middle Proterozoic age, or Precambrian Y (Cannon and Gair, 1970; Sims, 1992). The mineralogy and chemical composition of the dikes and plutons has been studied in detail by Wood (1962), Morris (1977), and Shanabrook (1978), who have shown that they contain large amounts of pyroxene, plagioclase, olivine, and in places, pyrite. These intrusive bodies have been interpreted to be related to the well known Keweenawan tholeiitic basalts and andesites which host native copper deposits in the western Upper Peninsula of Michigan, and are believed by some to have been feeders for Keweenawan lavas (Wood, 1962; Hubbard, 1975; Morris, 1977). Middle Proterozoic magmatism is associated with the opening of a continental rift system that is thought to have resulted in the positive linear gravity anomaly extending 1300 km from Lake Superior to Kansas (Chase and Gilmer, 1973).

The Peshekee watershed contains numerous large Precambrian W outcrops of granitic, granodioritic and tonalitic gneiss, occurring as rounded elongate ridges with moderate foliation. Thin layers (generally less than 1.5 meters) of glacial till fill the interr ridge areas, which also contain extensive bogs and swamps. In several places along roadcuts, locations of mafic dikes can be identified by

seeping or dripping water that freezes into icicles in winter. The headwaters of the Yellow Dog River originate in similar terrain. However, the middle and lower reaches of the Yellow Dog flow through extensive glacial till and outwash, which attains a thickness of 300 feet or more in the area known as the Yellow Dog Plains in the central part of the watershed.

Figure 1 shows the main geologic features of the region and the orientation of the rivers with respect to the mafic dikes and glacial outwash. For the most part, dikes run east-west across the entire area, intersecting the Peshekee River at nearly right angles and parallelling the Yellow Dog. A few small plutons of peridotite and gabbro are present in the middle portion of the Yellow Dog watershed. The locations of dikes shown in Figure 1 are schematic, but are based on the geologic map of the area by Sims (1992) who mapped the dikes from geophysical evidence. Wood (1962) and Shanabrook (1978) report dike thicknesses of 2 to 30 meters.

Hydrologic Setting and Climate

Although the Peshekee and Yellow Dog rivers are of similar length and transport more or less equivalent amounts of water, the nature of drainage within each watershed is not the same. The main trunk of the Peshekee drains numerous 1st through 5th order tributaries separated by rounded ridges of granitic bedrock, and morphologically represents a rather

typical dendritic drainage pattern. More than 50% of the low-lying areas of the Peshekee drainage basin are covered by swamps, which are drained by tributaries during high flow periods, but are not connected to the surface hydrologic system during low flow. The Yellow Dog River begins as two separate branches; each drains a small lake within the same rocky terrain as the Peshekee. However, there are very few additional tributaries that join the main trunk of the Yellow Dog for the rest of its course. The drainage basin overall is asymmetric. The river flows from west to east across the southernmost part of the sandy Yellow Dog Plains, paralleling an extensive ridge that forms a drainage divide marking the southern boundary of the basin. Few swampy areas exist within the Yellow Dog watershed.

Springs are a common feature in both watersheds, and can be seen flowing into each river at many places along the banks. Some of these springs flow year-round at approximately constant discharge, while flow from others subsides during extended dry periods. These springs appear to be related to fracture systems in the bedrock.

Annual rainfall in the Peshekee and Yellow Dog watersheds averages about 90 cm per year, with up to half of this amount occurring as winter snowfall. The winter season in northern Michigan is quite long and cold, and midwinter snowpack depths are typically 1.2 meters or more. Runoff is therefore generally highest during spring snow melt, especially early in the season before soils have had a chance to thaw. Rainfall

acidity has been monitored at several sites in Michigan over the past 15 years, and has been previously measured to average pH 4.1 to 4.6 in northern Michigan (DeGuire, 1988; Doonan and VanAlstine, 1982).

METHODS

Water Sampling and Analysis

To monitor these watersheds, samples of water from three sites on each river were taken weekly over the course of one year (summer, 1988 through summer, 1989). Sampling sites are shown on Figure 2, labeled Sites 1, 3, and 4 on each stream. Samples were also taken daily from Site 1 on each stream during the initial three days of the first major spring runoff in late March. The uppermost site on the Yellow Dog River (Site Y4), and occasionally other sites, were inaccessible during winter and major rain storms and were not sampled during those times. Hydrologic measurements were taken periodically at each sampling site, while Site 2 on each river was set up for continuous recording of hydrologic data. Precipitation was collected on a weekly basis, in an Aerochem-Metrics[™] wet/dry precipitation collector placed in an open area between the two watersheds, away from tall trees (location in Figure 2). Because high snowfall prevented operation of the wet/dry collector during winter, weekly snow

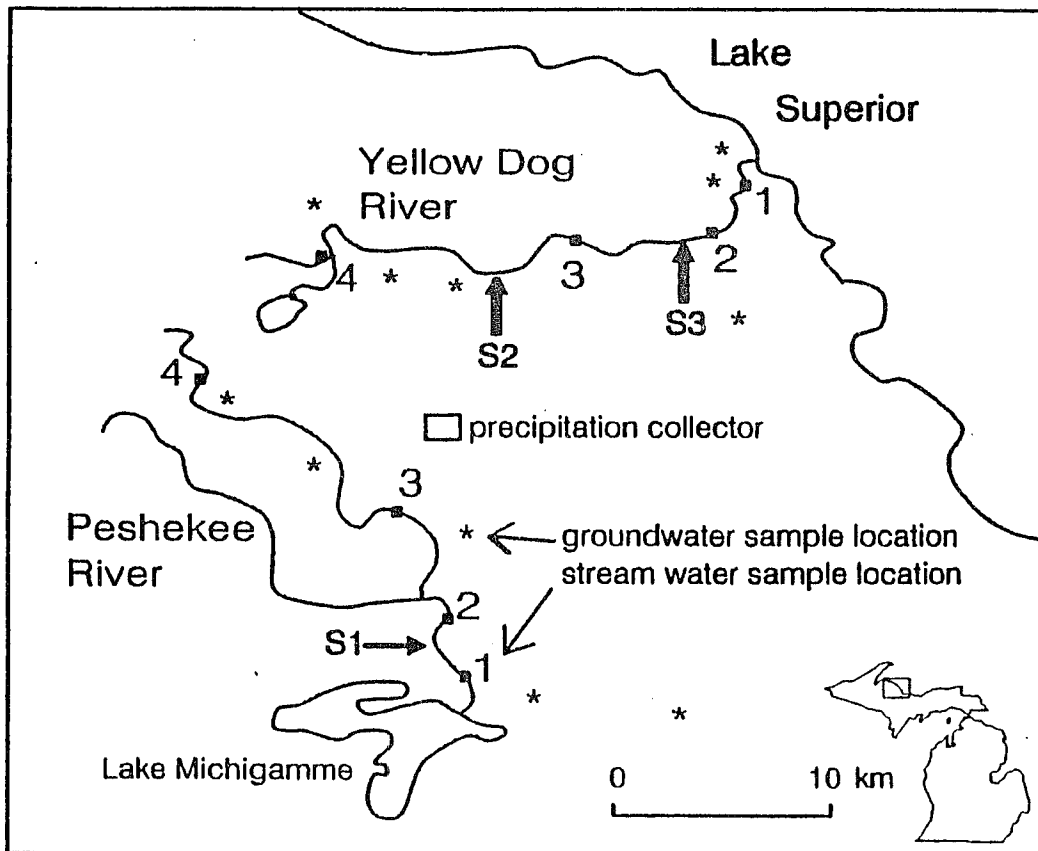


Figure 2. Location of precipitation, stream, spring and ground water samples (S1=Peshekee Spring; S2=Yellow Dog Upper Spring; S3=Yellow Dog Lower Spring).

samples including dry precipitation were collected from the same location in clean, open buckets from December through April.

In addition to stream water and precipitation, groundwater from various depths and locations within the two watersheds was sampled from shallow domestic wells. The locations of groundwater samples are noted on Figure 2. Three perennial springs, one near the Peshekee and two within the Yellow Dog watershed, were sampled on a weekly to monthly basis to further define the nature of the regional groundwater.

Analytical methods used to measure ion concentrations are listed in Table 2. Field methods, sample preparation techniques and further analytical details are discussed in the following paragraphs.

Measurement of temperature, pH, alkalinity, and fluorine was done in the field for all water samples, which were then field processed and preserved for transport to the laboratory for storage and further analysis. Samples for major and minor elements and dissolved organic carbon (DOC) were filtered through 0.45 micron Millipore[™] mixed cellulose filters, then subsamples taken and preserved for later analyses as follows: for Ca, Mg, Na, K, Fe and Mn, 100 ml subsamples were placed in 125 ml pre-cleaned polypropylene bottles with 1 ml reagent grade concentrated nitric acid; 125 ml subsamples for SO₄ analysis were preserved in plastic bottles by adding 1 ml formaldehyde; 100 ml subsamples for Cl and SiO₂ were placed in

Table 2. Methods of aqueous chemical analysis.

<i>Species</i>	<i>Method</i>	<i>Reference</i>
pH	in field, combination electrode	Orion instrument manual
alkalinity	in field, Gran titration	
Ca, Mg, Na, K, Fe,	samples preserved w/HNO ₃ ; analysis by atomic absorption spectrophotometry (AAS)	Slavin, 1968
F	in field, specific ion electrode with buffer solution	Orion, 1984
Al species	separated in field by hydroxyquinoline/MIBK/ion exchange; analysis by AAS w/graphite furnace	Barnes, 1976; Driscoll, 1984
SiO ₂	automated colorimetry, molybdate blue method	APHA, 1976
DOC	optical absorbance measured in field, analysis in lab by catalytic oxidation	Sugimura and Suzuki, 1988; Martin, pers. comm., 1991
Cl	automated colorimetry, mercuric thiocyanate method	APHA, 1984
SO ₄	turbidimetric	APHA, 1971
NO ₂ , NO ₃	automated colorimetry, sulfanilamide method with Cu-Cd reduction for nitrite	APHA, 1984
NH ₄	automated colorimetry, indophenol blue method	APHA, 1976
PO ₄	automated colorimetry, phosphomolybdenum blue method	APHA, 1976

bottles with no treatment; subsamples for nutrients (PO_4 and N species) were placed in 125 ml plastic bottles and frozen within a few hours; DOC subsamples were also frozen, but placed in glass bottles. All samples (except those frozen) were immediately cooled and kept refrigerated until analysis.

Field processing of samples for Al speciation study followed methods to prevent contamination suggested by Barnes (1976), Driscoll (1984), and R. Aller (personal communication, 1987). To pre-clean, all bottles for storage of Al subsamples were filled with 10% HCl and heated to 95° C in a water bath for 12 hours, rinsed twice with distilled, deionized water, then filled with purified water and allowed to stand for 24 hours before final rinsing and drying. Samples were filtered through 0.2 or 0.4 μm Nucleopore[™] polycarbonate filters which were pre-cleaned by soaking in 50% reagent grade nitric acid for 24 hours, rinsed, then soaked in purified water for 24 hours before thorough rinsing and storage in purified water. All labware was soaked in an acid bath of 10% nitric acid and thoroughly rinsed with purified water before use. Except for transfer pipettes and volumetric flasks, no glass was used in processing Al samples.

To separate Al into component species, methods of Driscoll (1984) and Barnes (1976) were modified for use in the field. For the monomeric fraction, 50 ml samples filtered through 0.2 μm filters were placed in 250 ml volumetric flasks with 50 ml purified water and 2 ml 5% 8-Hydroxyquinoline solution, and shaken vigorously for exactly 10 seconds. Ten

ml of methyl isobutyl ketone (MIBK) were immediately added and the mixture was again shaken vigorously, then allowed to separate into organic and hydrous layers. The organic portion, theoretically that containing reacted singly-complexed Al molecules, was collected using a micropipette and transferred into a 30 ml cleaned storage bottle. To separate the simple organically complexed Al portion, an aliquot of 0.2 μm filtered sample was passed through a teflon column filled with Amberlite IR-120 exchange resin. The column was prepared to the specifications given by Driscoll (1984). A 50 ml portion of exchanged sample was then treated using the method described above to extract the easily reactable Al. Total Al was determined from a sample prepared by passing water through a 0.4 μm filter, collecting 50 ml in a clean bottle and adding 0.1 ml double-distilled Ultrextm nitric acid. Blanks were processed using each of the Al speciation techniques on a monthly basis. Measurement of Al in all cases was accomplished using AAS with a graphite furnace.

Dissolved organic carbon was estimated within hours of sample collection by measuring the optical absorbance of filtered water. A representative suite of samples were then analyzed for DOC at Woods Hole Oceanographic Institute using a technique developed by B. Martin and others (personal communication, 1991), modified from Sugimura and Suzuki (1988). Absorption readings were correlated (correlation coefficient = .95) with DOC measurements for a final

approximation of concentrations. A strong correlation between color and DOC is not always detected in studies of surface waters, such as reported by Henriksen et al. (1988) for lakes in southern Norway. In this study, however, stream water color appeared to relate directly to the amount of dissolved organic carbon, a finding also reported by Merna and Alexander (1983) in previous studies of streams in northern Michigan. Estimates of DOC concentrations made in this way represent good quantitative approximations for these streams, but should not be viewed as precise measurements.

Discharge Measurements

To measure discharge, a Stevens continuous water level recorder was installed at one site on each river to monitor stage. Instruments were located under bridges on each river, labeled Site 2 in Figure 2, approximately midway between sampling Sites 1 and 3. Sites chosen for monitoring flow were fairly symmetric, and provided security and relative ease of access to instruments. Measurements of flow velocity were made once weekly at these sites using a Teledyne-Gurley flowmeter. A manual depth measurement was also made weekly to check the stage recorder readings. In winter, the clock mechanism of the water level recorders could not be coerced into operation, therefore manual measurements were made through holes drilled through the ice layer that covered each

river. Water depth and velocity were combined with cross-sectional area to calculate stream discharge, representative of flow conditions at time of sampling for each week.

Rock, Sediment and Soil Sampling and Analysis

Soil, sediment and rock samples were obtained from each watershed for overall mineralogical analysis. Samples from floodplain material of the Peshekee River were taken from a mid-stream location, from a depth of approximately 0.5 meter. Several samples were taken of the near-surface glacial outwash material from approximately the center of the Yellow Dog Plains. Samples of Yellow Dog outwash were also obtained at various elevations from the slope of a steep valley where the river has eroded through the glacial material to a depth of at least 75 meters.

Samples of granular material were studied in two ways. First, fine material was separated from coarse by gravity settling, then the clay-sized portion prepared for X-ray diffraction analysis. Organic material was removed from dark colored clays by pre-treating with 10% hydrogen peroxide with gentle heating until reaction subsided, then clays were oriented in a thin layer on cellulose filters under moderate suction. Oriented clay layers were transferred from filters to glass slides by gently rolling a glass rod over the back of

a filter pressed against a slide. X-ray diffraction patterns were obtained for untreated, K-saturated, Mg-saturated, and Mg-ethylene-glycol saturated clay samples, as well as samples heated to 500° C.

The second method used to determine mineralogy of watershed materials was to make thin sections of rocks and grain mounts of the coarse granular material. Numerous thin sections from each watershed were studied using standard petrographic techniques to identify microscopic weathering features. Coarse grain mineralogy was then compared to clays and previously determined bedrock compositions.

RESULTS AND DISCUSSION

Hydrology

During the year of weekly sampling of these watersheds, a number of major hydrologic events affected stream flow and chemistry. Sampling began in late July, 1988, after approximately three months of unusually dry, warm weather. Samples from the first week of the study therefore reflect baseflow conditions. Heavy rain storms occurred during the second and fourth weeks (Aug. 3 and 17), and also between weeks 10 and 20 (Sept. 28 - Dec. 8), resulting in significant and rapid increases in discharge in both rivers. Precipitation and hydrograph records depicting these events

are shown in Figure 3. Precipitation records were collected from weather stations located within each watershed, the Van Riper station near the mouth of the Peshekee River, and Big Bay station by the Yellow Dog outflow.

For the most part, flow in the Peshekee and Yellow Dog rivers were similar in total flow amount and quickness of response to rainfall events, with discharge from the Yellow Dog averaging about 80% of that from the Peshekee. Differences in response to rainfall events are due in part to small differences in actual rainfall amounts within each watershed, and also to higher infiltration within the Yellow Dog watershed compared to the Peshekee. Hydrograph records from each watershed for an individual rain event are shown in Figure 4. Although discharge in both rivers increases rapidly with the onset of heavy rain, the recession of the hydrograph for the Peshekee is steeper than that for the Yellow Dog, indicating that the Peshekee returns more quickly to baseflow conditions, while the Yellow Dog collects water from surface runoff and interflow for a longer period of time after heavy rain.

The winter season in northern Michigan was quite long and cold during 1988-89, and gave rise to a thick layer of ice (>20 cm) which covered all of the Peshekee and most of the Yellow Dog. During this period, flow in both rivers was stable, and consisted mainly of baseflow inputs flowing through the closed tube of the stream channel capped with ice.

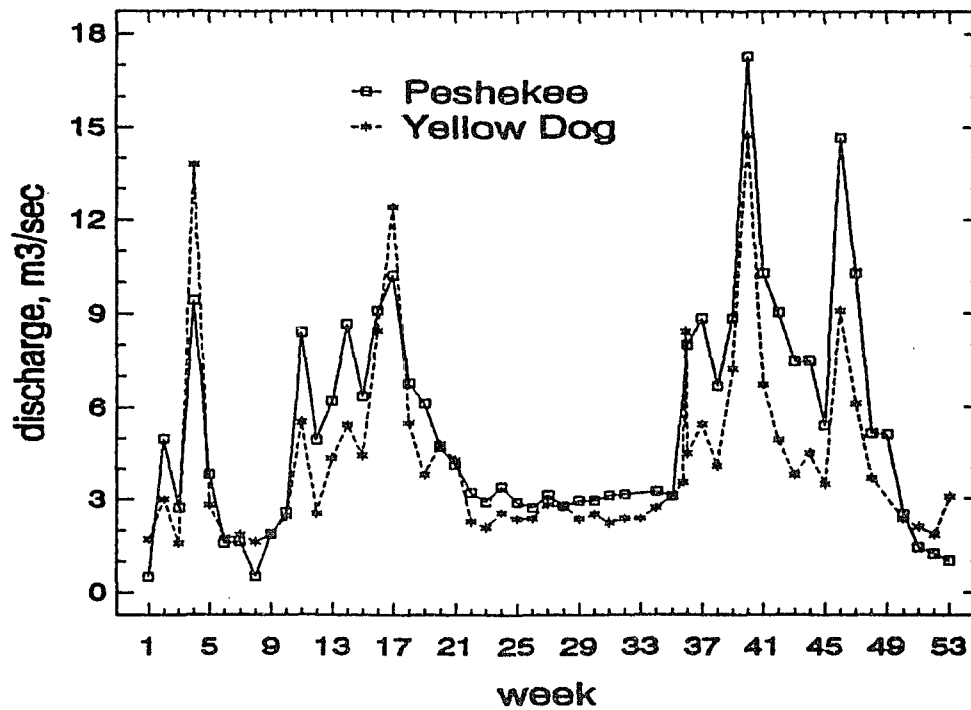
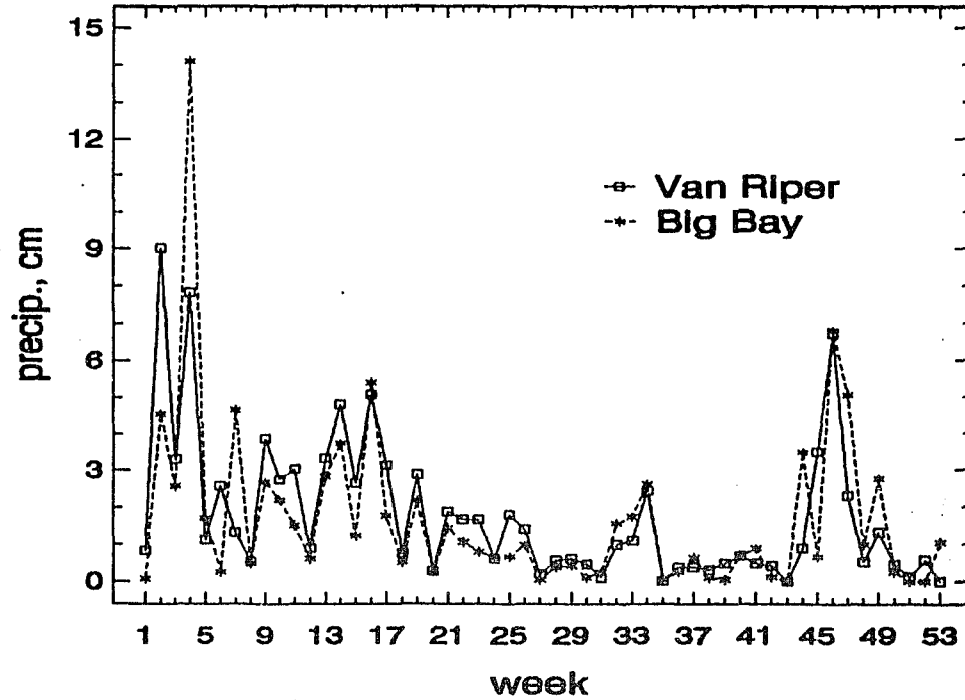


Figure 3. Precipitation and discharge records for Peshekee and Yellow Dog Rivers (Van Riper=Peshekee area; Big Bay=Yellow Dog area).

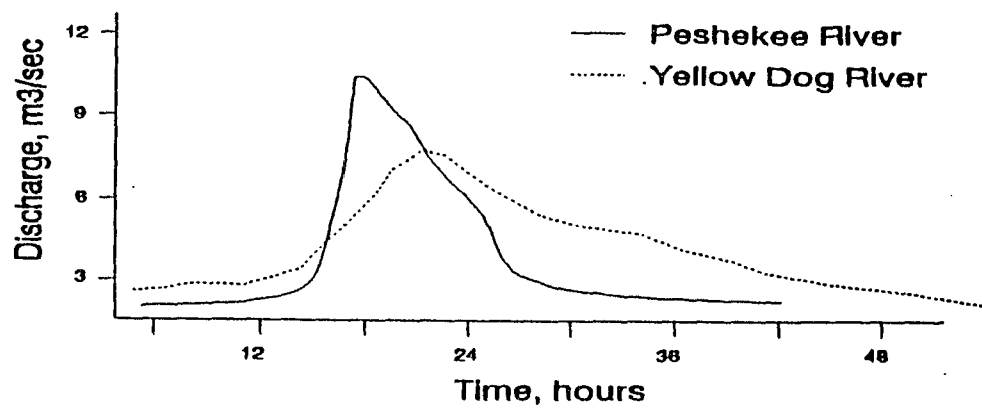


Figure 4. Typical storm event hydrograph showing the more rapid response of the Peshekee River.

Some portion of the winter stream flow was also occasionally from melted snow and ice, as the thickness of the ice layer varied from week to week.

Spring snow melt and runoff occurred mainly between week numbers 35 and 45 (March 25 - June 1), resulting in an abrupt increase in discharge initially, followed by several more pulses of high runoff. Runoff and high discharge from snow melt was slightly more sustained in the Peshekee watershed, reflecting the higher infiltration rates of the Yellow Dog. Another large rainstorm occurred during week number 46 (June 9), causing the major peak furthest to the right in both the precipitation and hydrograph records (Figure 3).

Water Chemistry

Results from aqueous chemical analyses of all waters in this study are tabulated in Appendix B, and are discussed in detail in the following sections.

1. Precipitation

Weekly precipitation chemistry was quite variable. Data tabulated in Table 3 and plotted over one year's time in Figure 5 represent filtered ($0.45\ \mu\text{m}$) bulk samples of wet fall during spring, summer and autumn, and wet plus dry fall during winter (December through April) when bulk snow samples were

Table 3. Concentrations of major solutes in precipitation (in mg/l) .

	<i>Mean</i>	<i>WM*</i>	<i>Range</i>
pH	4.38	4.34	4.0-5.5
Ca	0.46	0.39	0.0-2.0
Mg	0.07	0.06	0.0-0.3
Na	0.11	0.06	0.0-0.7
K	0.23	0.27	0.01-3.2

	<i>Mean</i>	<i>WM*</i>	<i>Range</i>
SiO ₂	0.005	0.01	0.0-0.1
NO ₃	2.94	4.66	0.03-26.1
Cl	1.57	1.43	0.20-18.6
SO ₄	0.20	0.18	0.09-0.59
Al	0.006	.005	0.00-0.03

*Volume weighted mean

collected. Although no distinct differences between summer and winter samples in the data are attributable to sampling methods, these data should be considered as overall estimates rather than exact representations of specific wet or dry chemistry. Mean values for precipitation chemistry are reported in Table 3 as arithmetic means as well as volume weighted means, although for most solutes there is little difference between the two values. The pH of precipitation varied between 4.0 and 5.5, and tended to be slightly higher during winter. Of the acidic anions associated with acid precipitation, NO_3 concentrations were high during the first large rain events after sampling commenced, events that were acidic, but also during a winter event when low pH's were measured. On the other hand, SO_4 concentrations in precipitation do appear to be related to pH, with higher amounts generally found in samples with low pH.

Rain and snow were quite dilute with respect to major cations, as expected. No discernable correlation among all components exists, although the variability of Ca and Mg appears somewhat similar when plotted as in Figure 5. Higher concentrations of cations occur during low volume rain events, probably related to the fact that the earlier precipitation in an event "washes" most of the particles out of the atmosphere. Longer (larger) rain events are thus generally less concentrated because continued rainfall is "cleaner" and dilutes the bulk sample.

Two other processes which have affected concentrations

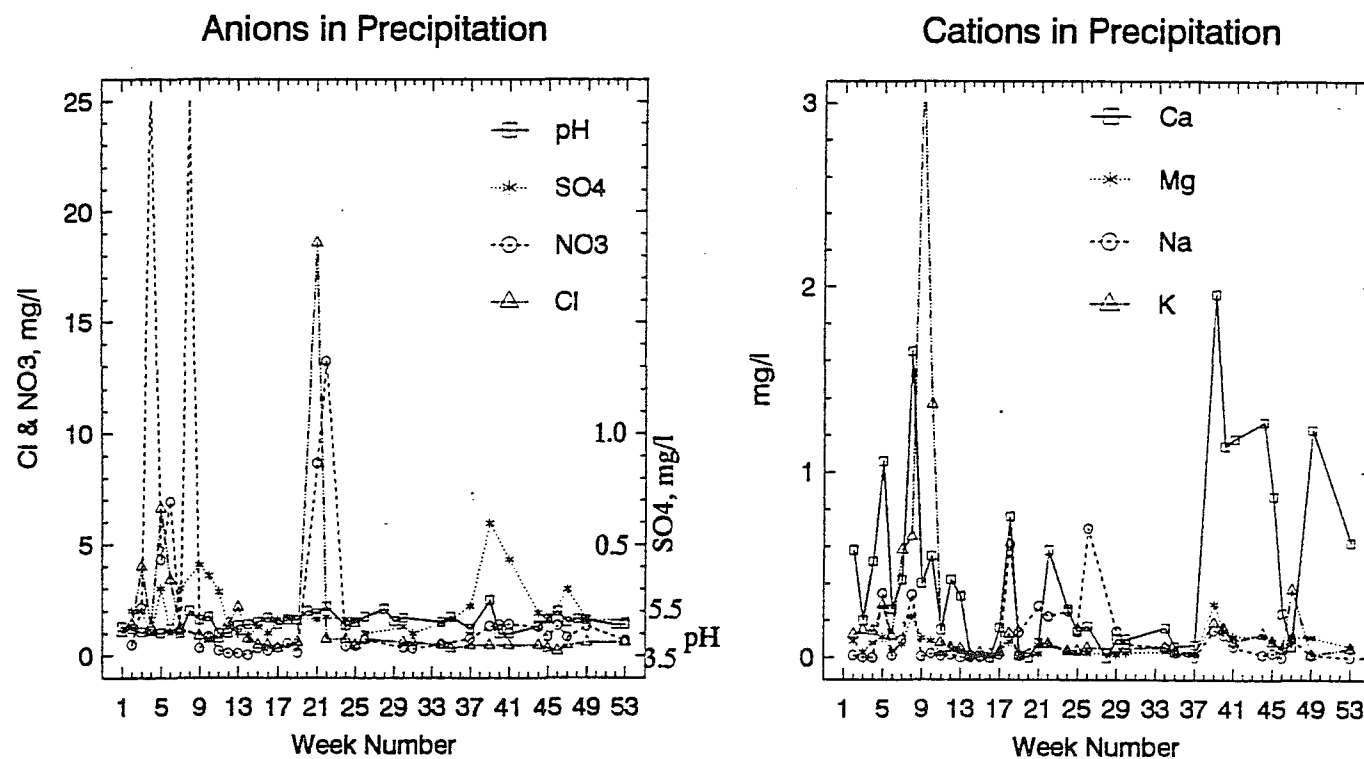


Figure 5. Weekly anion and cation variation in western Marquette County precipitation, 1988-1989.

are also reflected in the data. One of these relates to the use of rock salt for de-icing of roads in the winter. Although no salt is used on the access roads in the study area, dust in the air during winter must contain a significant amount of NaCl, as both of these ions were found in highest quantities during the winter months. Another chemical event is apparently related to the huge forest fires that consumed much of Yellowstone National Park in Wyoming during the dry summer in which this study commenced. A large plume of smoke and ash from the fires reached Michigan by the middle of September. The first major rain after the arrival of the plume (week 9, Sept. 20) contained an unusually high concentration of K, probably of biogenic origin, released to the atmosphere during burning. This K increase was accompanied by a corresponding increase in SO_4 , as well as a decrease in other major cations.

2. River waters

With certain exceptions, the major element chemistry of the Peshekee and Yellow Dog Rivers is rather similar in terms of average concentrations and overall seasonal variations. Results of chemical analyses of the most abundant solutes for 3 sites on each river are compiled in Table 4; a complete tabulation of all chemical data from river samples is given in Appendix B. Average solute concentration values reported in

Table 4. Concentrations (in mg/l) of major solutes in the Peshekee and Yellow Dog Rivers.

	Peshekee River		Yellow Dog River	
	range	mean	range	mean
pH	site 1: 4.80 - 7.3 3: 5.65 - 7.4 4: 5.25 - 7.1	6.12 6.31 6.12	site 1: 5.7 - 7.8 3: 5.8 - 7.4 4: 5.7 - 7.2	6.93 6.45 6.63
Ca	site 1: 2.01 - 8.51 3: 2.00 - 11.36 4: 2.32 - 19.73	4.34 5.61 6.37	site 1: 4.59 - 21.61 3: 2.71 - 21.99 4: 5.65 - 12.46	12.04 7.13 8.60
Mg	site 1: 0.52 - 2.14 3: 0.51 - 2.31 4: 0.51 - 3.87	1.08 1.23 1.31	site 1: 0.97 - 3.94 3: 0.63 - 3.78 4: 1.33 - 2.44	2.36 1.50 1.89
Na	site 1: 0.41 - 1.18 3: 0.30 - 1.08 4: 0.34 - 2.34	0.68 0.57 0.60	site 1: 0.49 - 1.74 3: 0.37 - 1.04 4: 0.58 - 0.93	0.86 0.65 0.76
K	site 1: 0.17 - 0.82 3: 0.06 - 0.64 4: 0.04 - 0.58	0.34 0.28 0.28	site 1: 0.28 - 0.81 3: 0.13 - 0.53 4: 0.38 - 0.55	0.48 0.35 0.46
Al _i	site 1: .018 - .178 3: .018 - .176 4: .012 - .175	.122 .115 .118	site 1: .022 - .137 3: .022 - .154 4: .028 - .125	.066 .085 .060
Fe	site 1: 0.17 - 0.83 3: 0.10 - 0.72 4: 0.13 - 0.67	0.41 0.38 0.38	site 1: 0.10 - 0.39 3: 0.16 - 1.10 4: 0.12 - 0.51	0.20 0.44 0.29
SiO ₂	site 1: 1.39 - 8.27 3: 0.85 - 8.90 4: 0.60 - 8.76	4.72 4.64 4.29	site 1: 3.67 - 9.35 3: 3.00 - 7.78 4: 3.77 - 7.97	6.29 5.32 6.23
HCO ₃	site 1: 3.00 - 32.0 3: 5.00 - 40.0 4: 4.00 - 40.0	11.6 16.0 15.4	site 1: 14.35 - 84.08 3: 6.00 - 48.00 4: 20.00 - 40.00	43.2 21.8 27.4
Cl	site 1: 0.93 - 5.25 3: 0.49 - 2.04 4: 0.63 - 3.30	1.97 0.97 1.00	site 1: 0.32 - 2.99 3: 0.49 - 2.32 4: 0.49 - 1.60	1.12 0.81 0.84
SO ₄	site 1: 1.62 - 11.52 3: 0.67 - 5.64 4: 1.00 - 5.95	4.18 3.73 3.69	site 1: 1.00 - 6.19 3: 1.80 - 6.01 4: 1.31 - 6.83	4.32 3.83 5.01
NO ₃	site 1: .005 - 2.47 3: .016 - 5.96 4: .001 - 3.03	0.39 0.46 0.42	site 1: .018 - 2.12 3: .001 - 0.07 4: .018 - 0.77	0.29 0.03 0.29
DOC	site 1: 6.48 - 18.88 3: not measured 4: not measured	11.8 - -	site 1: 0.06 - 22.08 3: not measured 4: not measured	9.48 - -

Table 4 are simple arithmetic means. Volume weighted averages were not calculated because of the difficulty of estimating 'average' discharge and the lack of information about discharge at individual sampling sites. While average amounts of particular solutes are not greatly different between rivers, certain elements are more concentrated in the Yellow Dog River, and the Yellow Dog also displays more spatial variability. For the purpose of identifying and comparing seasonal and spatial variability, annual data from both rivers were plotted and are presented in Figures 6 through 9, and are discussed in the following sections.

pH: The pH range measured at river sites, shown in Figure 6, varies from 4.8 to 7.4 in the Peshekee and from 5.7 to 7.8 in the Yellow Dog. Spatial variability in pH from the headwaters to the outflow differs between the two rivers. In the Peshekee, pH does not vary dramatically from one site to another, but does decrease slightly in the downstream direction. In contrast, the Yellow Dog midstream location (Site 3) is typically the most acidic, while the pH of downstream waters (Site 1) is consistently 0.1 - 0.5 pH units higher than Sites 3 or 4. The low pH at Site 3 can be attributed to the extensive outwash plains covered with jack pine forests which are cultivated for lumber. As shown by Lawrence and Driscoll (1988), low pH runoff is typical from areas that have been clear cut. The lowest pH's were measured in each stream during initial spring snow melt and runoff; low pH episodes also occurred in response to large rainstorms in

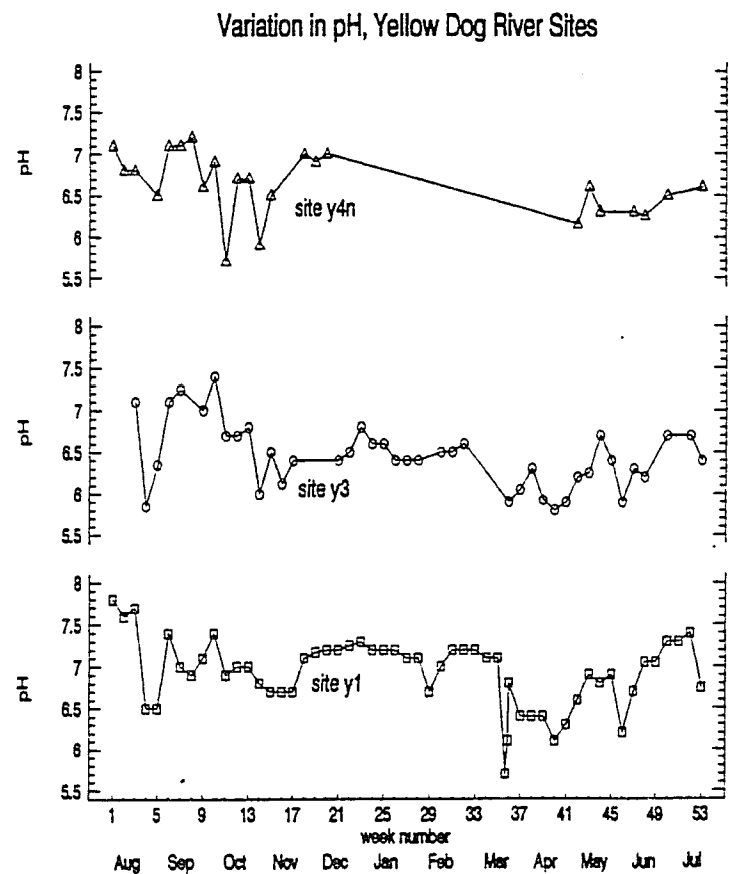
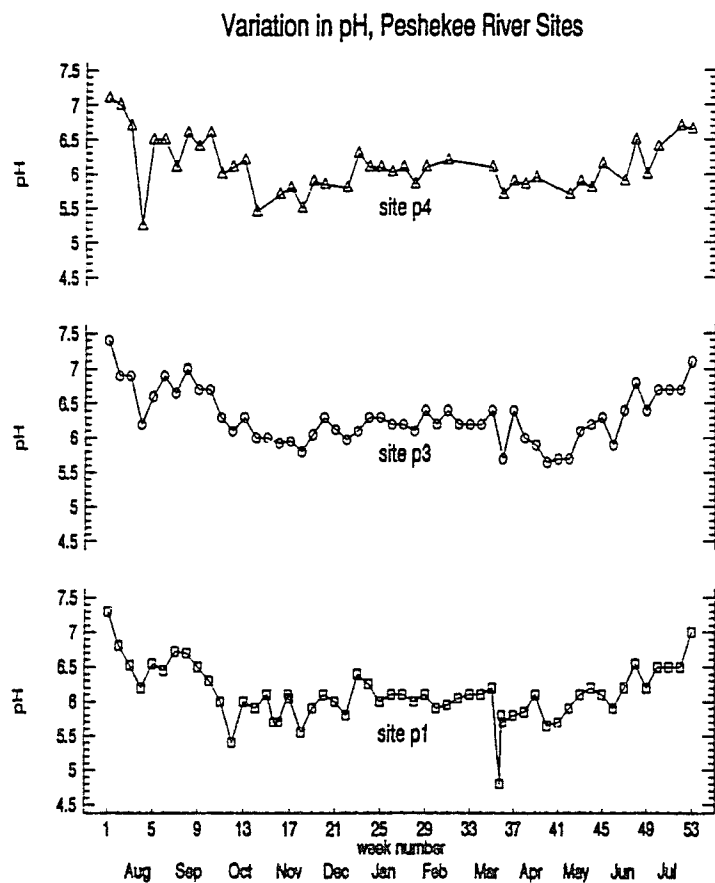


Figure 6. Weekly pH variation for three sites on each river, 1988-1989.

autumn and spring.

Cations: Weekly variations in cation concentrations and SiO_2 are plotted for the two rivers in Figures 7a-c and 8a-c. The concentrations of Ca, Mg, Na, K and SiO_2 in both rivers vary in direct response to the proportion of baseflow component present in total stream flow. Waters are relatively concentrated during dry periods and during winter, and become diluted when there are large inputs of precipitation or melted snow. Direct precipitation contributes an insignificant amount of Ca, Mg and SiO_2 to stream water, as it is less concentrated than the stream water by 1 to 2 orders of magnitude. For Na and K, a few precipitation events contain the same order of magnitude concentrations as stream water and results in noticeable peaks in stream water concentrations, but for the most part rain is still much more dilute than the streams. Cations appear to be incorporated into the streams from groundwater, interflow, or runoff that has picked up solutes as throughfall or from surfaces within the forest floor debris.

As in the case of downstream changes in pH, the two rivers behave differently in terms of spatial variability. In the Peshekee River, cation concentrations stay nearly the same as water travels downstream, and similar weekly or seasonal changes are reflected at all sites. In the Yellow Dog River, however, there is more variability between sites with respect to weekly or seasonal changes. Concentrations of Ca, Mg, Na and K are lowest in midstream locations, whereas by the time

waters have reached the mouth of the stream, cations have been concentrated by 50% or more.

Anions: Both rivers exhibit similar mean concentrations of Cl, NO₃ and SO₄, but seasonal patterns of variability are inconsistent between species as well as between river systems. Data from measurement of anionic species are shown graphically in Figures 7a-c and 8a-c. It is unclear from the data if differences between the sites on individual rivers are correlated to precipitation or discharge patterns, but it appears that aside from the major discrepancies, the same overall pattern persists at sites in each river for a particular species. Large individual peaks in stream NO₃ are probably a direct result of input from acid precipitation, as concentrations in precipitation even from large events can be more than ten times that of river water. Sulfate concentrations, like NO₃ associated with acid deposition, tend to be quite similar between sites and rivers. However, even though the pattern of SO₄ seasonal variation is similar between precipitation and stream water, the absolute concentrations of SO₄ in rain and snow is much less (<10%) than that of the streams, implying that stream SO₄ is derived in large part from watershed materials during high runoff episodes. High stream Cl also appears to be partially due to large rain events. While F was measured in all samples, concentrations were quite low, near the detection limit of the analytical method used (0.02 mg/l), and little weekly variation was observed.

Ionic concentrations, Peshekee River site 1
(mMol/L)

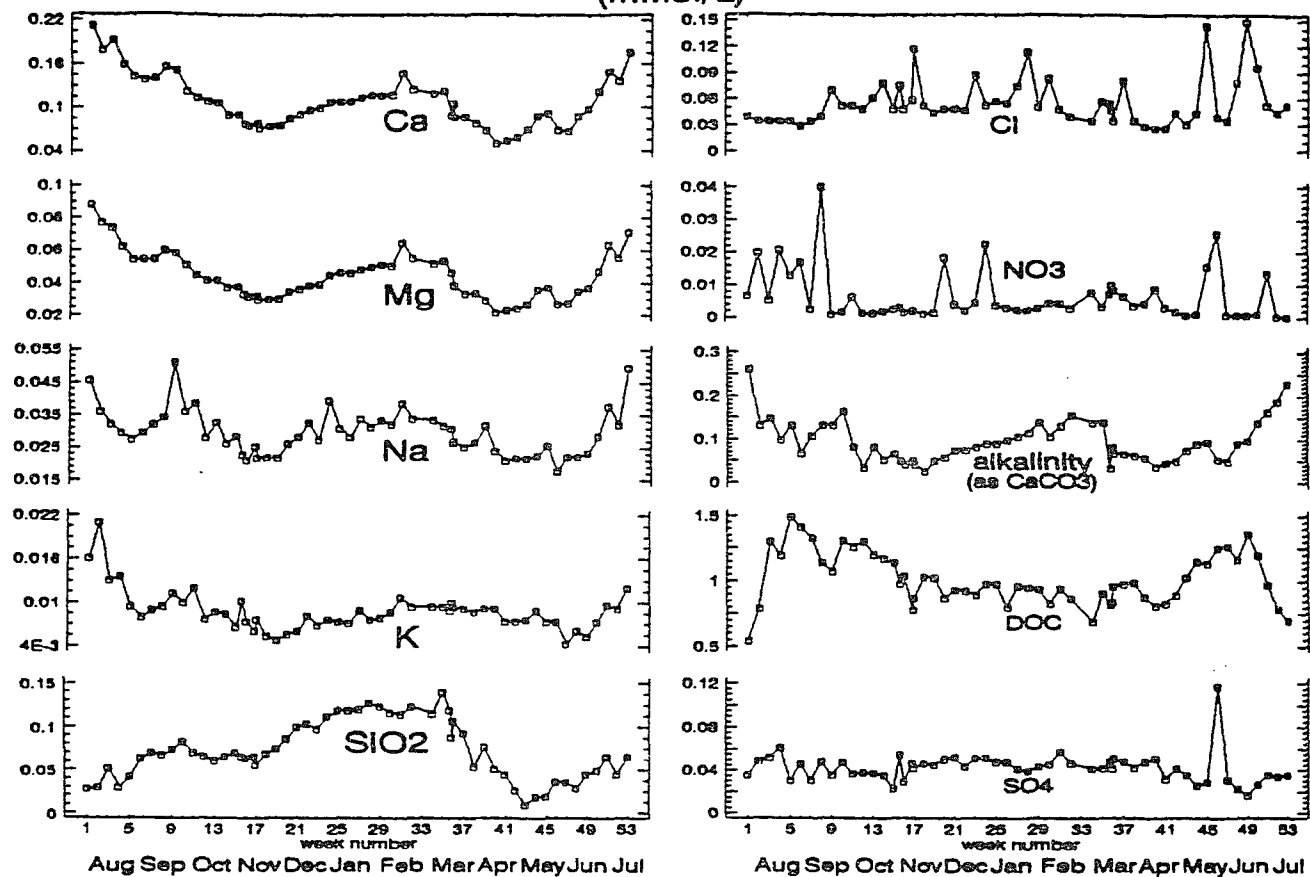


Figure 7a. Weekly ion concentrations, Peshekee River Site 1, 1988-1989.

Ionic concentrations, Peshekee River site 3
(mMol/L)

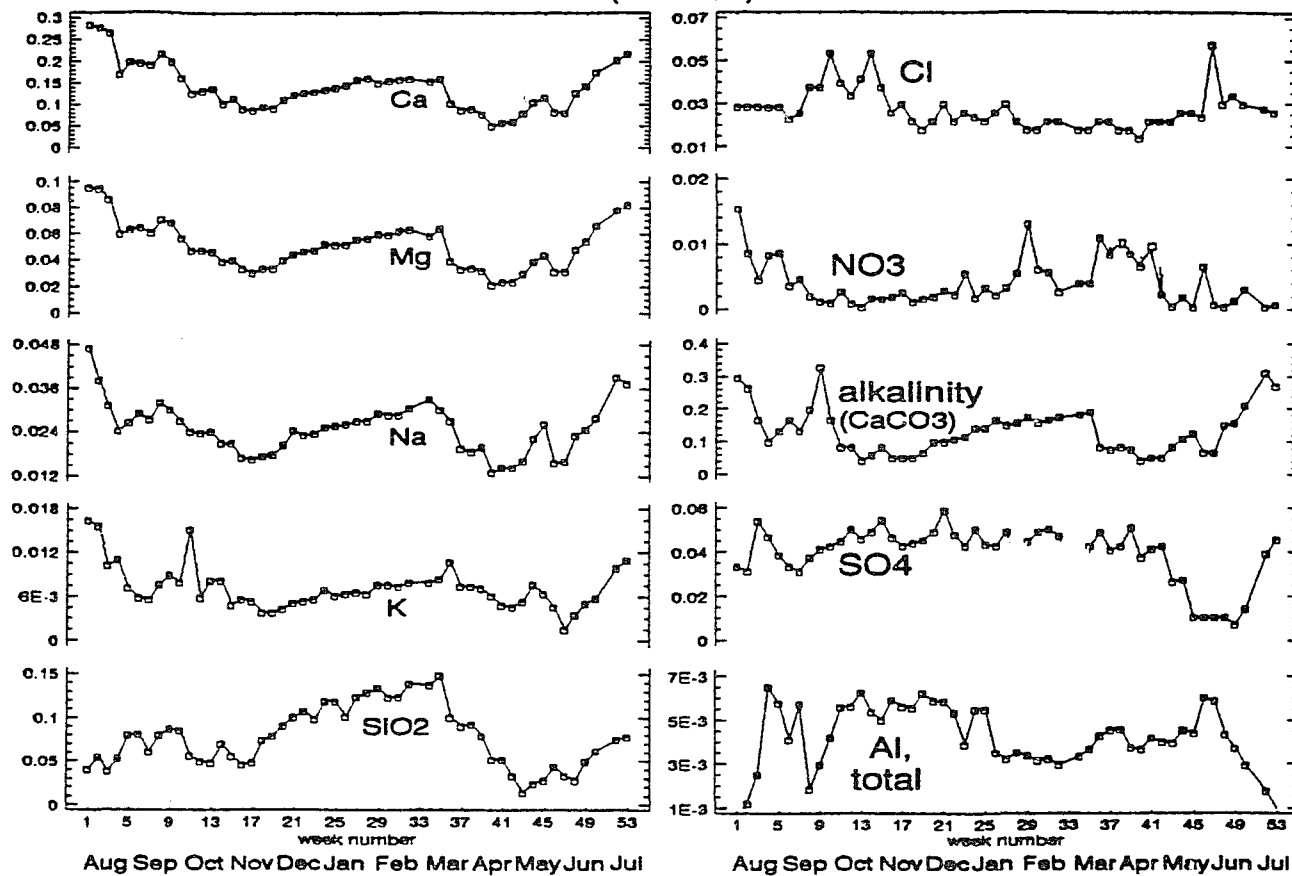


Figure 7b. Weekly ion concentrations, Peshekee River Site 3, 1988-1989.

Ionic Concentrations, Peshekee River, site 4
(mMol/L)

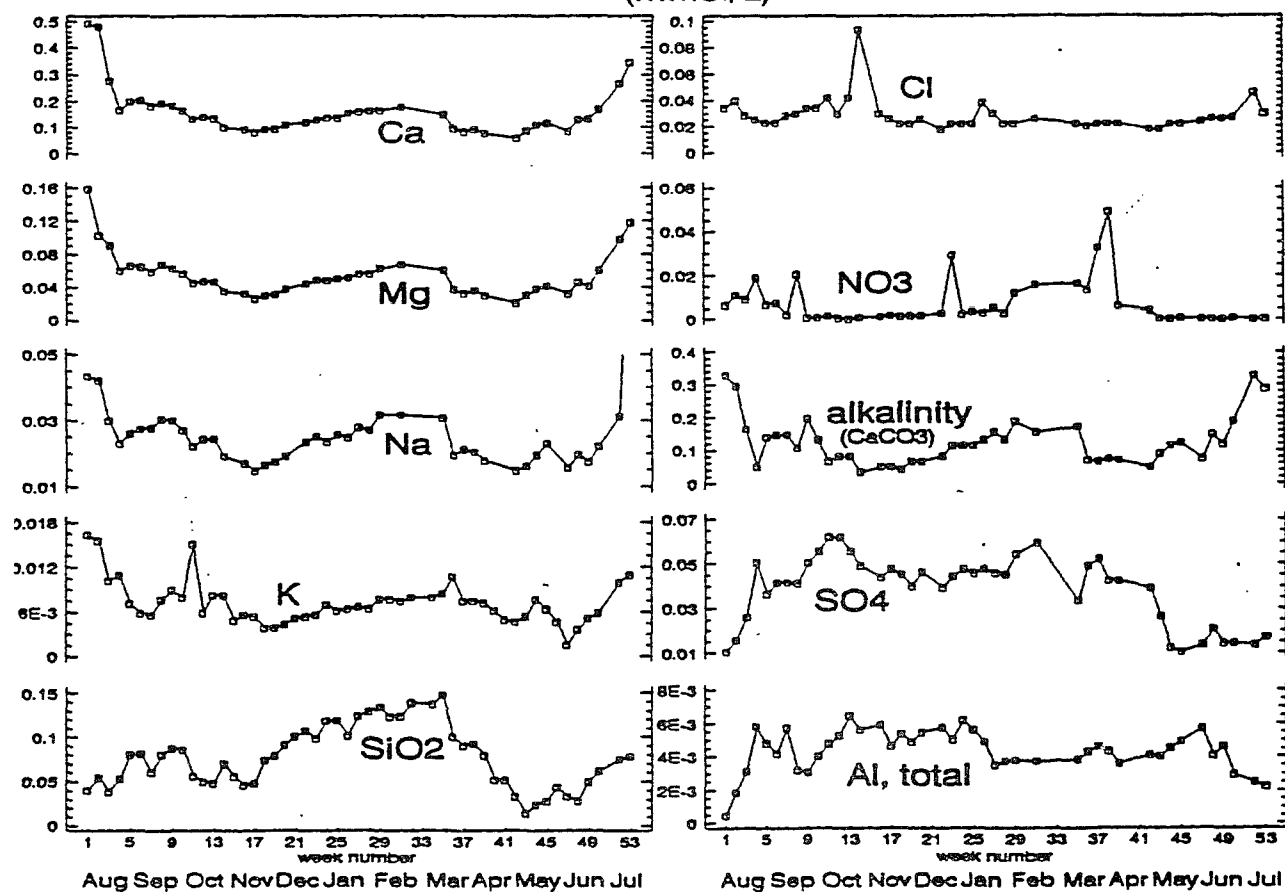


Figure 7c. Weekly ion concentrations, Peshekee River Site 4, 1988-1989.

Ionic Concentrations, Yellow Dog River, site 1
(mMol/L)

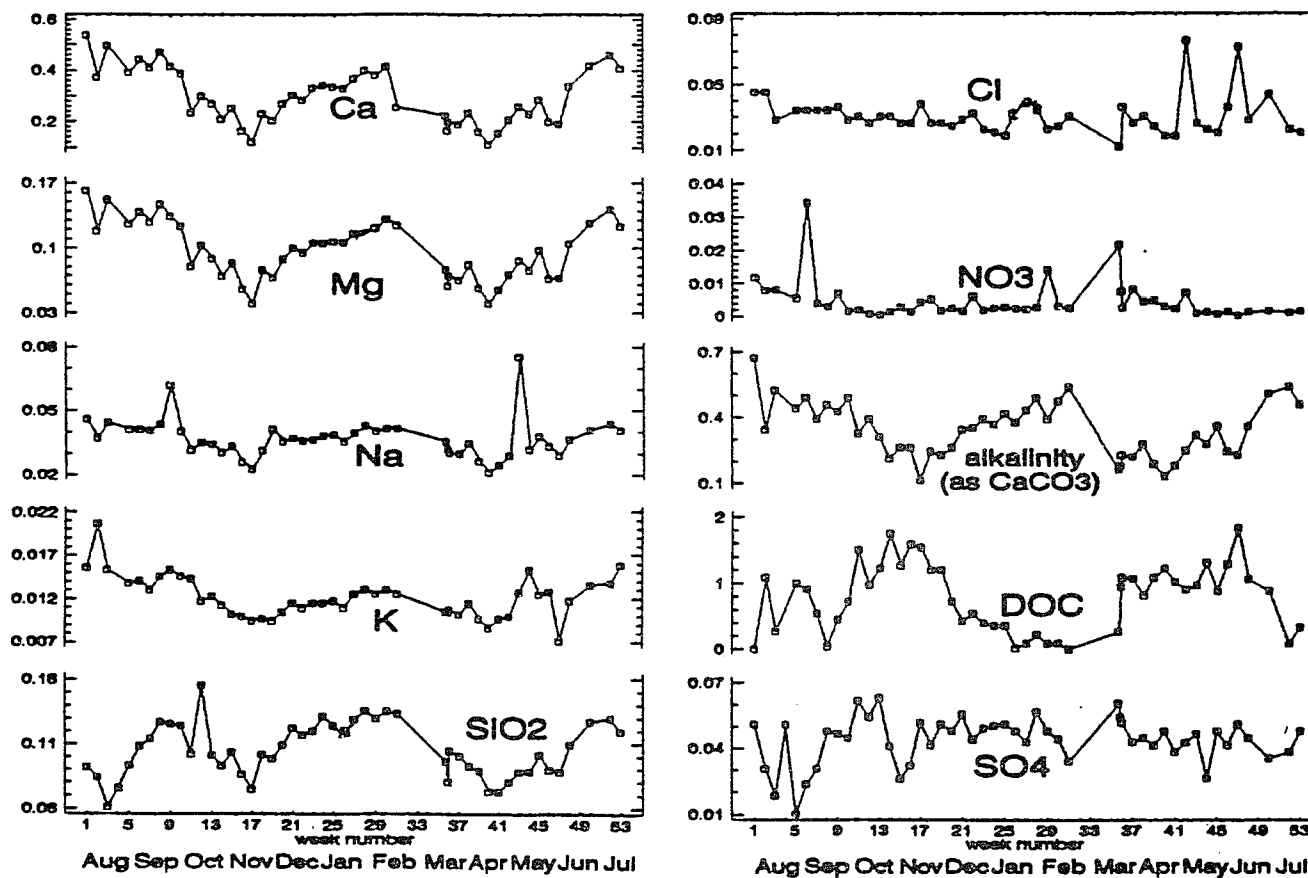


Figure 8a. Weekly ion concentrations, Yellow Dog River Site 1, 1988-1989.

Ionic Concentrations, Yellow Dog River, site 3
(mMol/L)

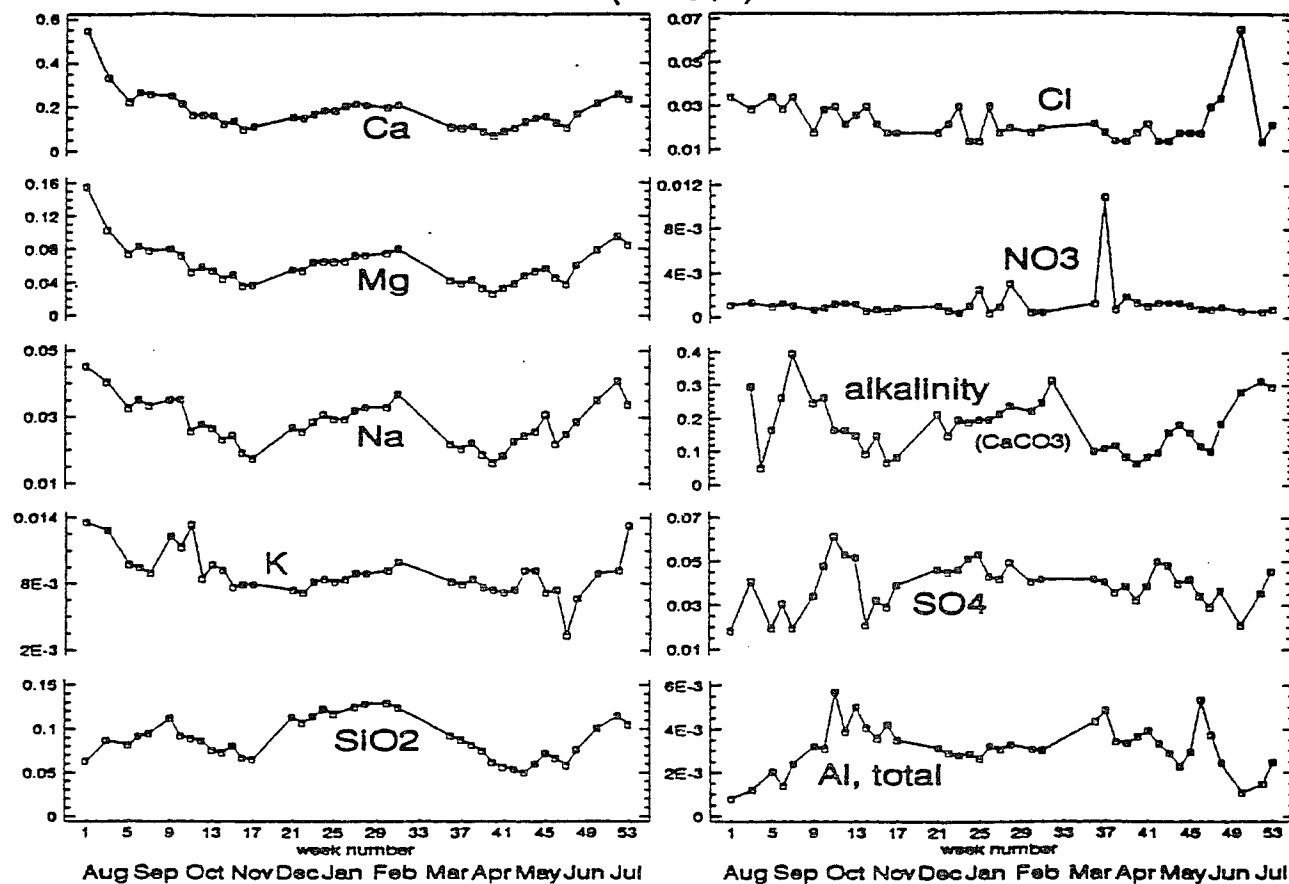


Figure 8b. Weekly ion concentrations, Yellow Dog River Site 3, 1988-1989.

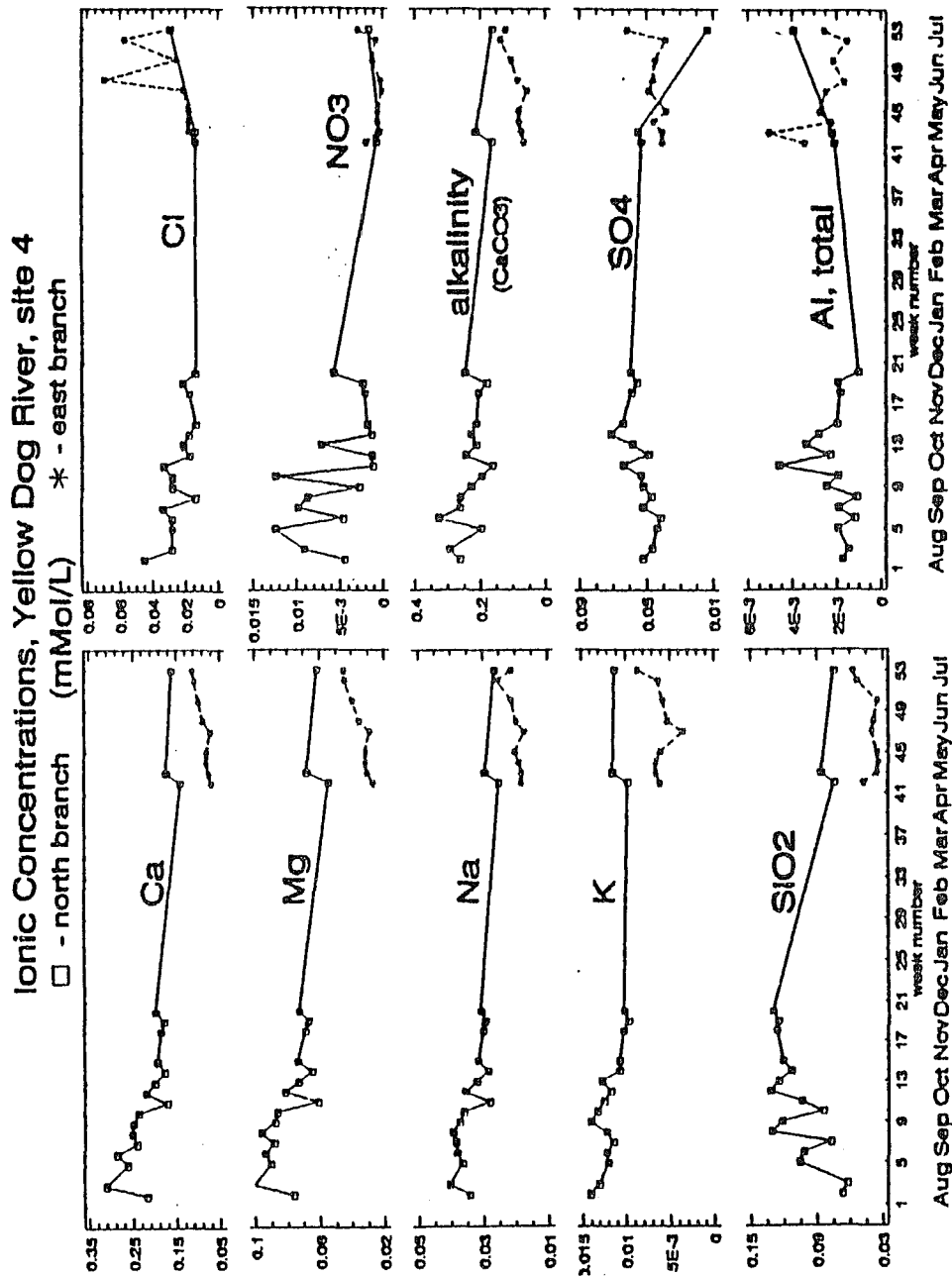


Figure 8c. Weekly ion concentrations, Yellow Dog River Site 4, 1988-1989.

The relative changes in alkalinity from week to week are quite consistent between individual sites and between rivers, and correlate well with variations in discharge and pH. Differences in results from this measurement have to do with downstream chemical changes characteristic of each river. Site 1 on the Peshekee River, furthest downstream, has lower alkalinity than up-gradient sites, while Site 1 on the Yellow Dog is significantly more alkaline than Y3 or Y4.

DOC: Dissolved organic carbon was measured only in samples from Sites 1 of each river. From Figures 7a and 8a, it can be seen that DOC behaved quite similarly in the downstream portions of each river. Generally, DOC was higher during times of high discharge, and low during low discharge periods. Concentrations were initially higher in the Peshekee than in the Yellow Dog during the first big rains in autumn just after the long dry summer, but were higher in the Yellow Dog for other episodes of high discharge. This result is somewhat surprising considering that the coloration from tannins and other organic acids is always greater in the Peshekee, even when DOC is higher in the Yellow Dog. Winter DOC concentrations were higher in the Peshekee.

Al species: From the three Al species separated from samples in the field, total dissolved Al (Alt), total monomeric (Alm), and organically complexed monomeric (Alo), two other species were calculated. Inorganically complexed monomeric Al (Ali) is equal to the difference of Alm and Alo, and polymeric forms of Al (Alp) equals Alt minus Alm. While

Alt and Alm were measured from all stream samples, Alo was measured only from Site 1 of each river. Weekly variability of Al species from Sites P1 and Y1 are presented in Figure 9.

It is evident from Figure 9 that Al behavior is not the same in the two rivers. After the dry summer, autumn rains resulted in relatively large amounts of Alt being released into the Peshekee during weeks 3-9, while Yellow Dog Al concentrations stayed about the same. It is not until late in autumn that there is a major influx of Al into the Yellow Dog from a smaller but still significant storm (week 17), during which time Al in the Peshekee stays consistently high. In spring, both streams respond to meltwaters and storms with distinct increases in total and monomeric Al species. Overall, the Peshekee River contains more of each Al species than does the Yellow Dog.

A limited correlation between Al and pH exists in both rivers, but only for some of the Al fractions, as indicated by the graphs in Figure 10 showing Al species against pH. Total Al in both streams is higher at low pH, an expected relationship based on Al-hydroxide solubility. The relationship between pH and organically complexed Al is less clear, but a similar trend with pH is present. On the other hand, no definite correlation is apparent between Ali or Alp and pH. This implies that pH is not the dominant control on inorganic monomeric Al species nor polymeric forms of Al in these streams. Other processes that may influence Ali and Alp could be complexation reactions that take place within the

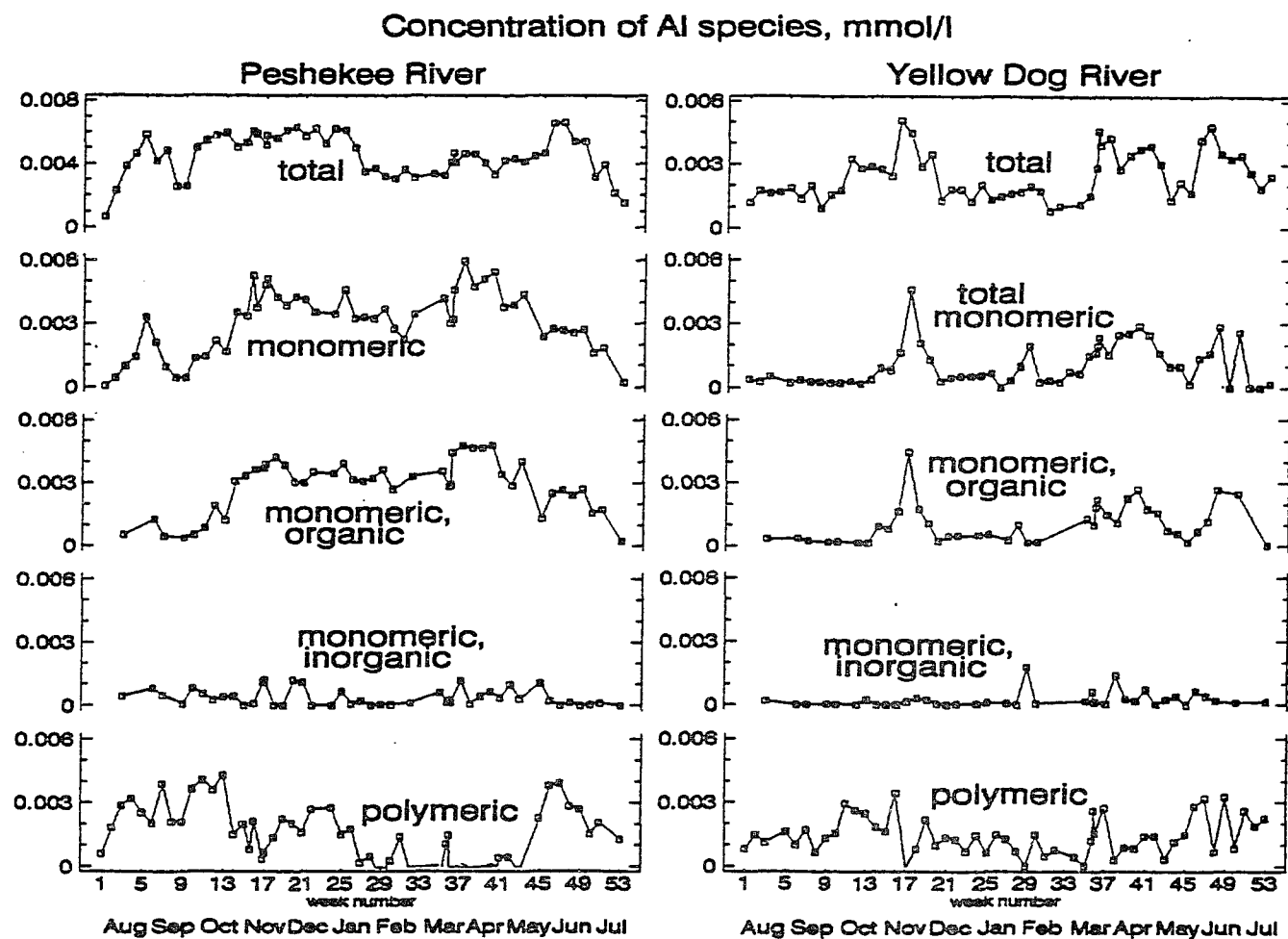


Figure 9. Weekly variation in Al species for downstream sites in both rivers, 1988-1989.

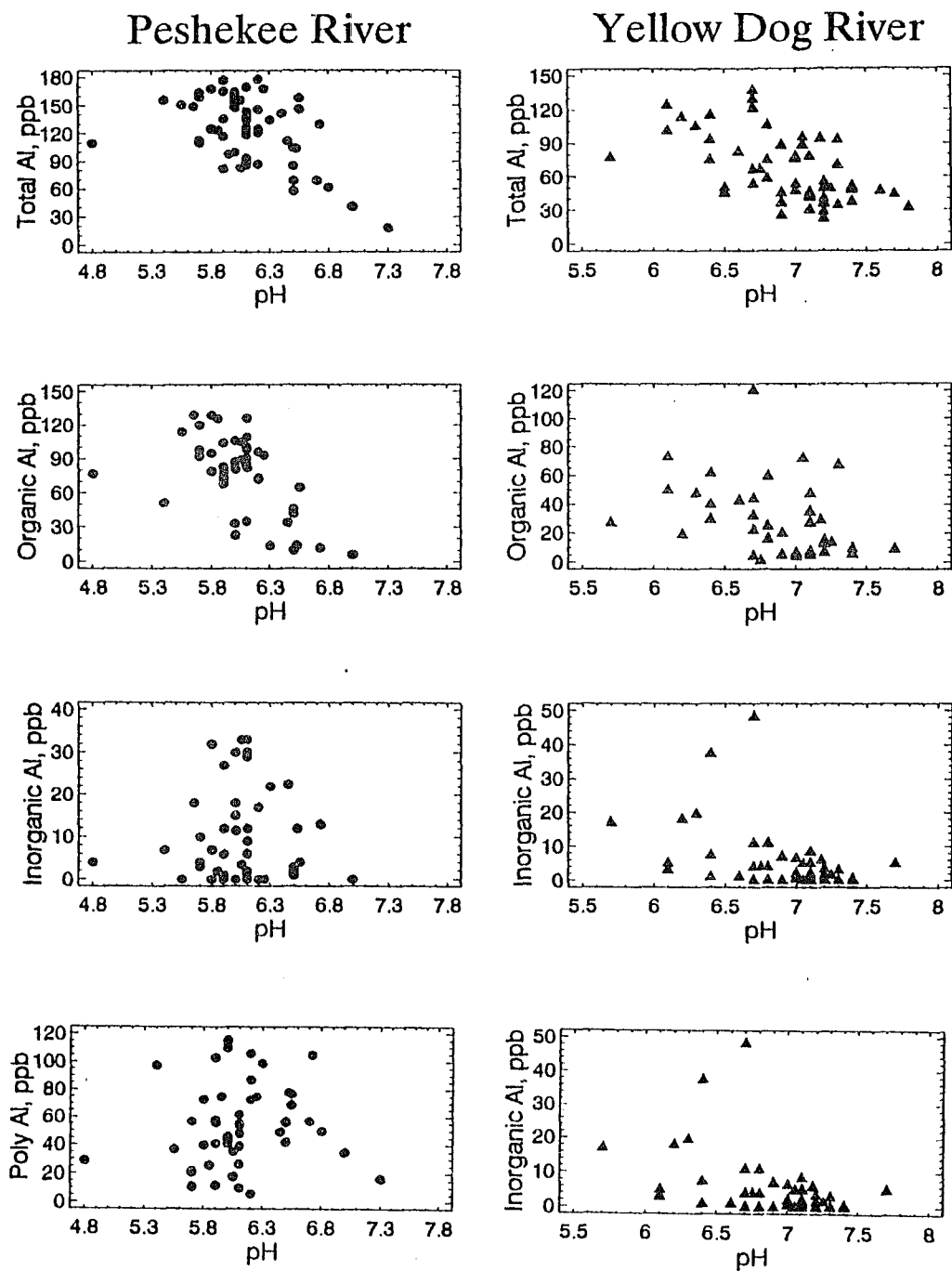


Figure 10. Relationship of individual Al species to pH for downstream sites of both rivers.

stream after Al is released from watershed materials, since solubility of Al at low pH does appear to control the total amount of Al available. Exactly how all of the Al molecules are complexed at different levels of acidity is not obvious; apparently Al is partitioned amongst organic, inorganic and polymeric compounds in varying proportions in ways that are not necessarily related to proton interactions.

To examine the nature of Al complexing further, Al species were plotted against DOC. The relationship of individual Al species to DOC in river waters is not the same in these two systems, as can be seen in Figure 11. Although data points are rather scattered in these plots, there appears to be a direct correlation between Al_t and DOC in each river, and no clear dependency of Al_m or Al_i on DOC. As for other Al species, data for Al_o versus DOC are not tightly constrained, but there is an apparent inverse relationship between Al_o and DOC in the Peshekee River. In other words, as DOC increases in concentration with greater discharge, the added carbon compounds in the water do not appear to be forming monomeric organic-Al complexes. Instead, Al_p and DOC are positively correlated, suggesting a relationship between these solutes. The same is not true for the Yellow Dog Al_o and Al_p data, which tend to follow Al_t and appears to be directly correlated to DOC.

One explanation for the dissimilarity in the behavior of organically complexed Al in these rivers may be that the type of organic compounds supplied to the Peshekee during high flow

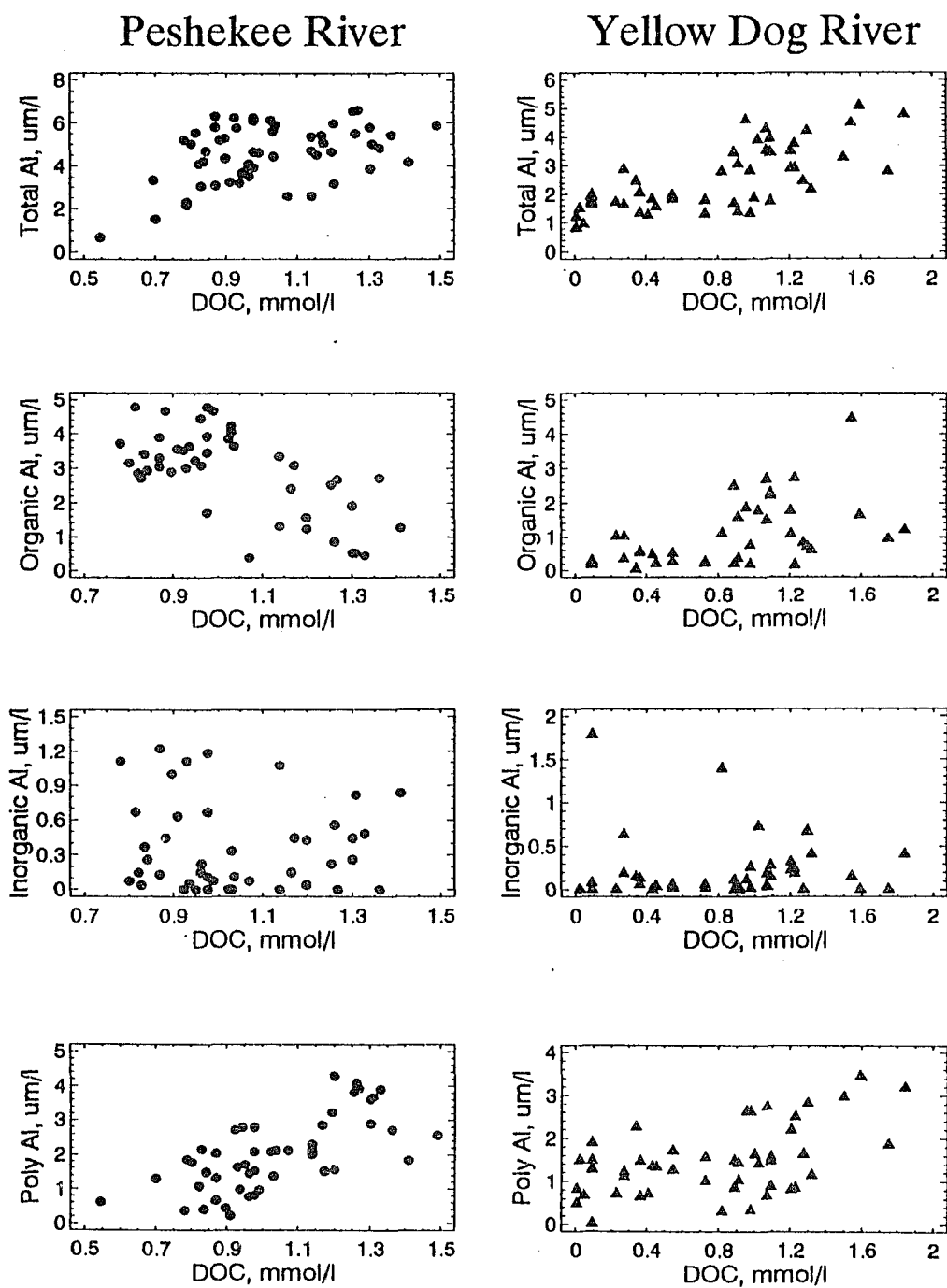


Figure 11. Relationship of individual Al species to DOC for downstream sites of both rivers.

are unlike and are from a different source than those delivered to the Yellow Dog. The Peshekee watershed comprises a high percentage of land covered with swamp compared to the Yellow Dog, and these swamps and bogs spill their organic load into the Peshekee as they fill during periods of high runoff. The source of organic carbon to the Yellow Dog during high runoff is not swamps but overland flow and throughflow, water recently in contact with upper soil horizons which may therefore reflect interaction with secondary minerals in the soil. Since the method used to extract organic-Al specifically targets monomeric complexes (Driscoll, 1984) with easily extractable Al, the correlation between Al_o and DOC in the Yellow Dog may represent cation exchange reactions that took place as organics preferentially exchanged other cations for Al while being flushed through the upper soil materials. On the other hand, easily extractable Al is inversely related to DOC in the Peshekee, but overall total Al shows a positive correlation, as does polymeric Al. This suggests that organic-Al compounds in the swampy Peshekee waters are of more complicated forms, possibly containing polymeric Al chains. It may be that in stagnant swamps and bogs, the Al present has enough time to combine with organic molecules into a variety of forms. These organic-Al_p compounds must remain somewhat stable when stagnant swamp water is flushed out of the swamps by up-gradient runoff to become part of the river load.

3. Springs, groundwater and other inputs

There is a good deal of contrast in chemical species in the groundwater and springs sampled within the study area; the differences are a function of location and depth. This is apparent in Table 5, where average values are shown for components in waters from artesian springs, shallow (<15 meters) and deep (30 meters or more) groundwater, spring runoff, swamps, and lakes from both watersheds. Complete chemical data for all ground and surface water samples are given in Appendix B.

For springs, each was sampled numerous times over the course of the year (generally bi-monthly) with very little chemical variation observed. Discharge did vary seasonally for the Peshekee Spring and the Yellow Dog Upper Spring, which tapered off in winter, but the Yellow Dog Lower Spring flowed at a constant rate of more than 1 liter per second throughout the year. Locations of samples are indicated in Figure 2.

Deep groundwater from all locations sampled and the Yellow Dog Lower Spring are more alkaline and contain higher dissolved solids compared to all other water sampled in this study. The similarity of Yellow Dog Lower Spring to deeper Yellow Dog groundwater suggests a similar source, possibly an older groundwater body that has been in contact with a different rock type, or more likely the same rock type as other waters but for a much longer time. The chemical make-up and location of Yellow Dog Lower Spring explains the striking

Table 5. Solute concentrations (in mg/l) in different ground and surface water types in the Peshekee and Yellow Dog vicinity.

Source	pH	Ca	Mg	Na	K	SiO ₂	Al _i	Cl	SO ₄	HCO ₃
Springs										
Peshekee	6.24	6.05	1.98	0.76	0.91	7.56	0.024	0.65	6.12	23.8
YD Upper	6.64	7.14	1.41	0.62	0.80	7.26	0.038	0.54	4.14	26.8
YD Lower	7.50	31.20	6.04	1.34	0.68	10.83	0.009	0.63	7.60	110.0
Shallow gw										
Peshekee	6.01	8.02	1.76	0.89	0.56	8.92	0.078	2.39	9.19	48.8
Yellow Dog	6.07	8.33	1.59	1.05	0.71	6.91	0.051	2.07	2.53	33.2
Deep gw										
Peshekee	6.95	24.78	7.44	2.59	1.44	19.21	0.003	11.33	17.0	71.0
Yellow Dog	7.25	10.27	4.16	1.15	0.56	3.12	0.001	0.98	2.23	55.0
Surface runoff										
Peshekee	5.70	2.20	0.60	0.35	0.15	4.48	0.160	0.77	4.09	7.0
Yellow Dog	6.00	3.97	1.00	0.46	0.45	3.58	0.155	0.59	2.85	12.3
Lakes	6.21	3.71	0.82	0.44	0.24	2.01	0.065	0.35	4.71	26.5
Swamps	5.80	5.14	1.04	0.57	0.30	4.59	0.162	1.33	4.59	12.0

increase in pH, alkalinity and cations in going from Sites 1 to 3 in the Yellow Dog River, as Yellow Dog Lower Spring drains into the river between those two locations. A significant portion of the water being carried by that river in its lowest reaches is apparently either from deeper groundwater sources or groundwater that has, at least, been in contact with rocks for a longer time than other water. The deep groundwaters in the Peshekee system appear to be from a different source than deep Yellow Dog waters, or may represent older water, as the Peshekee deep groundwater samples are significantly more concentrated than those from the Yellow Dog region. Deep groundwater does not appear to be an important input for Peshekee River waters. For shallow groundwater, samples from both systems are more acidic and dilute than deep samples, and there is a wider range in solute concentrations even among samples taken from locations near each other within the same watershed. Peshekee Spring and Yellow Dog Upper Spring closely resemble shallow groundwater samples, but are more dilute with respect to all solutes except K. This suggests that these springs represent water that has not infiltrated deeply enough or into the necessary material to acquire the dissolved load seen in the shallow groundwater samples.

Some similarity exists between water from runoff, lakes and swamps sampled in each watershed. In general, these represent the most dilute terrestrial waters in this study, demonstrated by a comparison of runoff, lake and swamp data to

other entries in Table 5 and to river water in Table 4. A comparison to other data also shows that the relative distribution of elemental species is rather similar in all surface waters measured, the dominant ions being Ca, Mg, HCO_3 , and SO_4 .

Cation Release Rates

To compare the timing of releases of particular solutes to the streams, fluxes to the streams were calculated in moles per second by multiplying concentrations by discharge. Although these calculations represent only one point in time per week, distinct events are apparent seasonally and spatially. The variation over the course of the year of these fluxes, or release rates, of specific elements are shown in Figure 12 for the most downstream site on each river. While the general pattern of release is similar for individual cations, notable differences exist in the timing of releases of Ca and Mg compared to Na and K in the Peshekee River. The greatest rate of delivery of Ca and Mg occurs in August from storms following a long dry summer, while the fastest delivery rate of Na and K occurs in April during spring snowmelt. This difference can be readily explained from the geology of the Peshekee watershed. Mafic dikes containing pyroxene, labradorite, pyrite and other opaque minerals (Wood, 1962) cross the Peshekee river at high angles (see Figure 1),

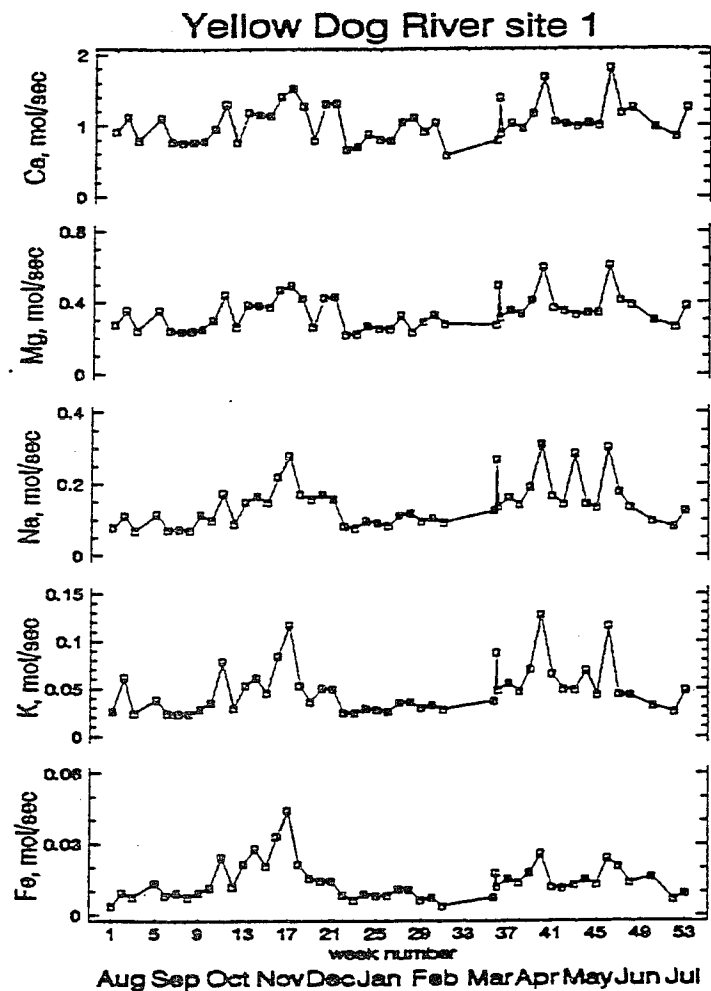
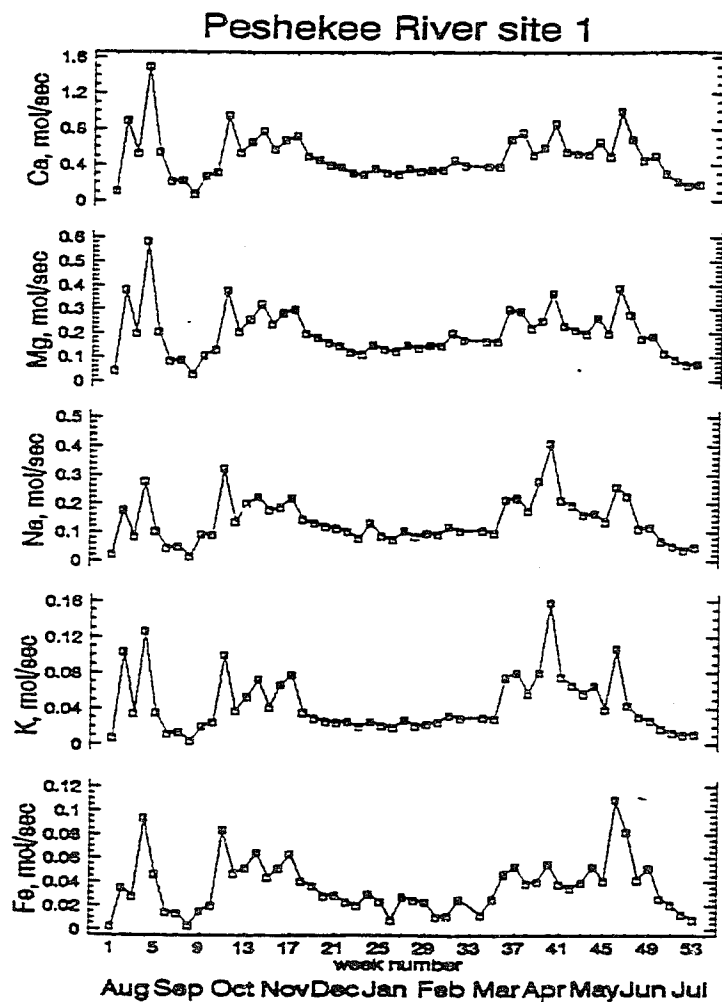


Figure 12. Release rates of major cations out of the Peshekee and Yellow Dog watersheds.

creating direct hydrologic pathways for water draining to the river. Probably, pore waters clinging to mafic grains in the unsaturated zone in these dikes become more concentrated in Mg and Ca as mineral weathering continues during times of little rain (Meunier and Velde, 1979; Nahon, 1991). The first large rain to fall after extended dryness would then quickly flush vadose water high in Mg and Ca through to the stream along the hydrologic pathways created by dike orientation. Large runoff events that occur when there has not been an extended dry period would not contain above average concentrations of dissolved solutes from weathering, as periodic rains would keep the vadose water well-flushed. This interpretation is supported by fluxes for Fe being similar to Mg and Ca, shown in Figure 12; Fe occurs with Mg and Ca in the diabase dikes. Rocks and sediments that contain minerals with weatherable Na and K do not occur with hydrologic features that intersect the Peshekee River, therefore these cations are not released in the same manner as those from mafic minerals. Instead, the highest flux of Na and K to the river appears in the spring, slightly after the initial snowmelt, and is probably related to deeper flushing of fractures in granitic domes and to breakdown of feldspars in the thin sediments and soils of the watershed.

The pattern of cation release to the Yellow Dog River can also be interpreted as flushing of deeper water that has been in contact with minerals for some time. For all cations, the fastest rates of release occur in late fall just before the

ground is frozen, and in spring during snowmelt, but after the initial surge of melting. The longer time it takes for cations to be flushed out of the Yellow Dog watershed materials and into the stream follows from the nature of the geology in the area. A much greater percentage of precipitation that falls in the Yellow Dog drainage infiltrates the ground compared to the Peshekee, because of the great thicknesses of glacial outwash in the Yellow Dog basin. Runoff that did reach the stream immediately after the major rain events during weeks 2-5 (August) did not contribute large amounts of cations, so apparently water traveling over surface materials does not interact significantly with minerals or other soil particles. A steady increase in cation flux from August to a high in late November suggests that the August rains finally did cause flushing of dissolved weathering products to the stream, but that a much longer pathway was taken.

Thermodynamic Mineral Relationships

Activities calculated using thermodynamic modeling (WATEQ4F, Plummer et al., 1978) were used to plot stability diagrams showing various mineral relationships in the dissolved fraction of the waters analyzed in this study. All chemical species measured (reported in Appendix B) were used in chemical modeling, including trace elements of F, Al, Mn

and PO_4 . When data from rivers, groundwater and springs are plotted showing pAl (pAl_i) against pH , as in Figure 13a and b, it is clear that at least for waters with a pH of 5.5 or greater, data plots along linear curves defined by equilibrium of the waters with natural gibbsite or some other form of $\text{Al}(\text{OH})_3$. At lower pH , which occurs only in the river waters during high discharge, activities of Al are less than predicted for gibbsite equilibrium. Low pH coincides with high dissolved organic carbon in the streams, suggesting that Al -organic complexing is one important control on monomeric Al concentrations. However, from comparisons of Al_i , Al_o and DOC , Al ions are not being combined with organic molecules in a simple way; it may be that polymerization of Al occurs in addition to organic complexing.

The data plotted in Figures 13a and b also suggest that $\text{Al}(\text{OH})_3$ does not control Al_i at pH above 7. For both river water and the most alkaline groundwater, less Al_i is present than predicted by gibbsite equilibrium. These high pH waters are from Yellow Dog River Site 1 and from the deepest groundwater samples in the Yellow Dog hydrologic system, and are apparently quite distinctive from other waters in this study, as described in the sections on aqueous chemistry and mass balance.

Other mineral stability diagrams were plotted using activities of major ionic species to examine the state of various mineral species with respect to water chemistry. In all diagrams, data plot either within the kaolinite field, or

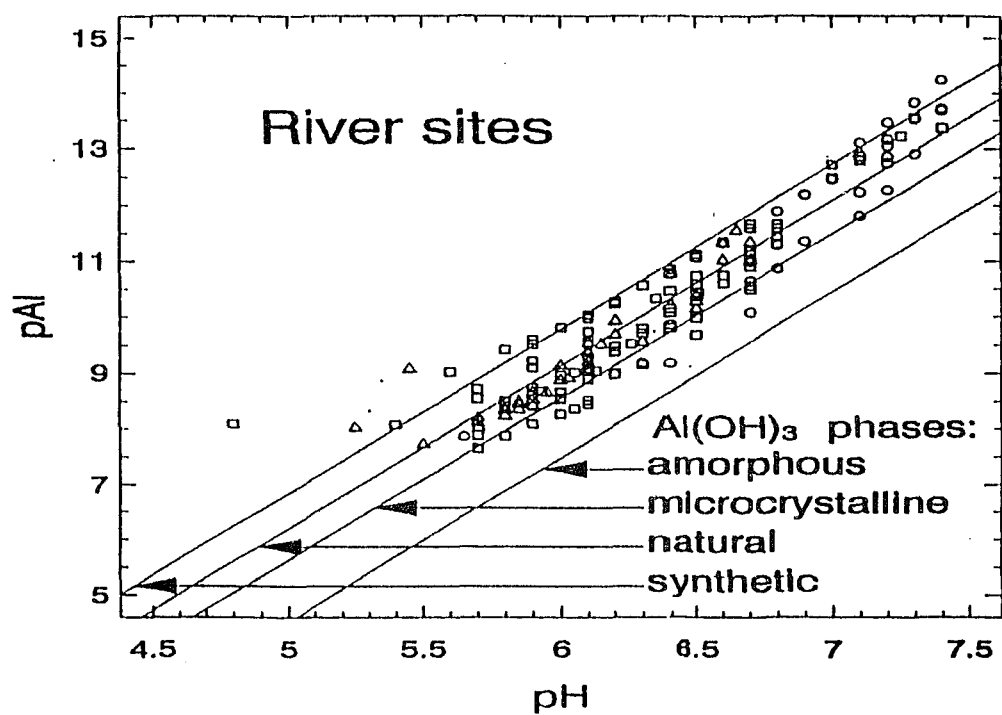


Figure 13a. Plot of pAl ($-\log[\text{inorganic monomeric Al}]$) versus pH for river water samples (squares=downstream sites, circles=midstream sites, triangles=upstream sites in both rivers).

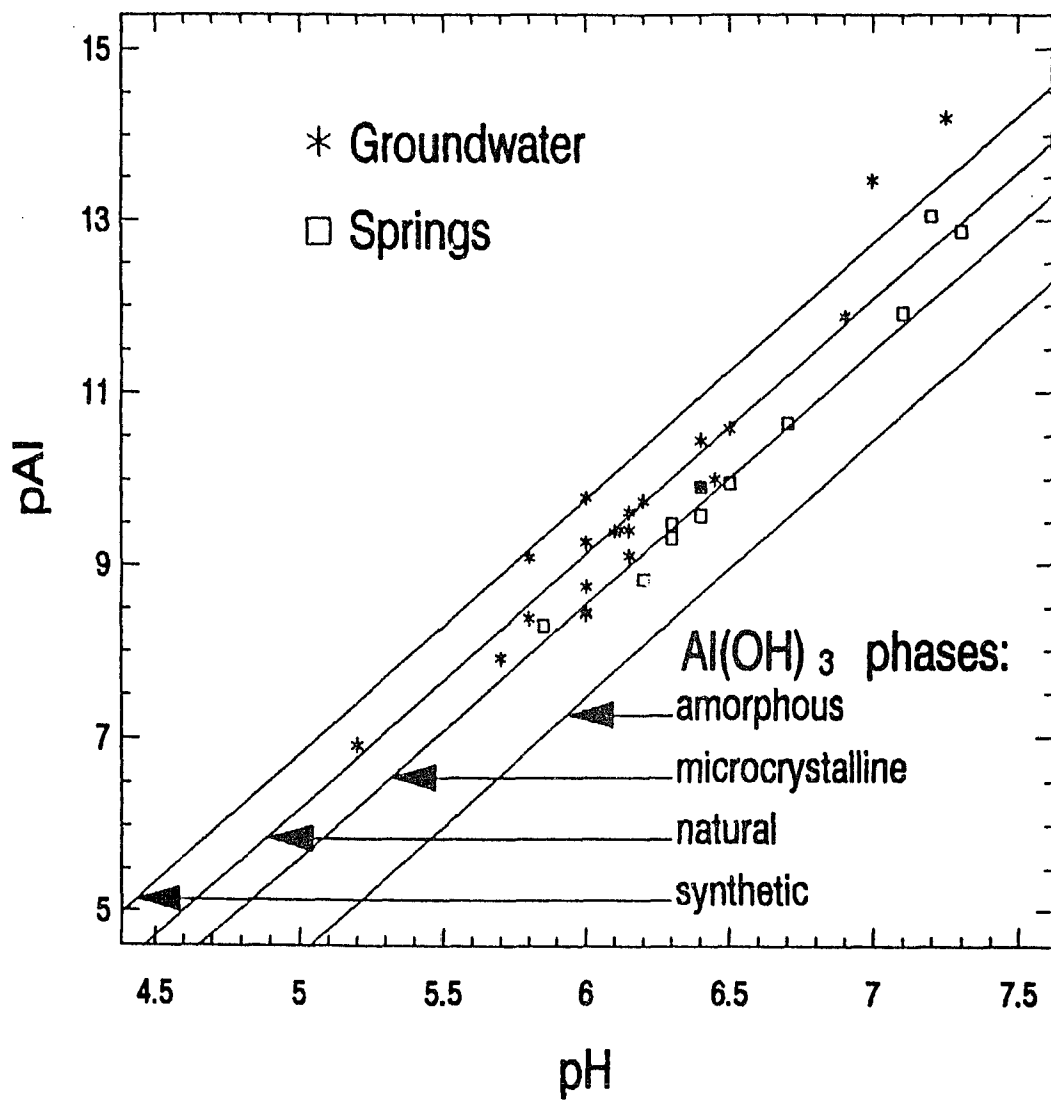


Figure 13b. Plot of pAl ($-\log[\text{inorganic monomeric Al}]$) versus pH for groundwater and spring samples.

along a line suggesting quartz equilibrium. Two of these plots are shown in Figures 14 and 15. In Figure 14, activities of K, Al, and H are combined to relate quartz and the main K-bearing aluminosilicates considered in this study. Two different fields are shown for each mineral, based on thermodynamic data from Bowers, et al. (1984) representing 0° and 25° C. All river water, spring, and groundwater samples plot within the kaolinite field, and data do not imply an equilibrium between kaolinite and either muscovite or K-feldspar. More specifically, the data plot almost entirely on and between the lines for the two temperatures considered, which may indicate a relationship between quartz and kaolinite that appears diffuse rather than linear because samples represent a range of temperatures. Some of the data points do appear to plot linearly in Figure 14, possibly implying quartz-kaolinite equilibrium at a temperature of around 15° C, although further analysis of those points did not show any correlation with respect to temperature.

In Figure 15, activities of K, H and silica are combined. Again, nearly all data plot within the kaolinite field, implying that waters are stable with respect to that mineral. However, most of the data, especially the river water data, also fall on or between lines of quartz saturation at 0° and 25°C, implying that rather than equilibrium between gibbsite and kaolinite, quartz saturation dictates where points fall on the diagram.

The relationship between kaolinite stability and quartz

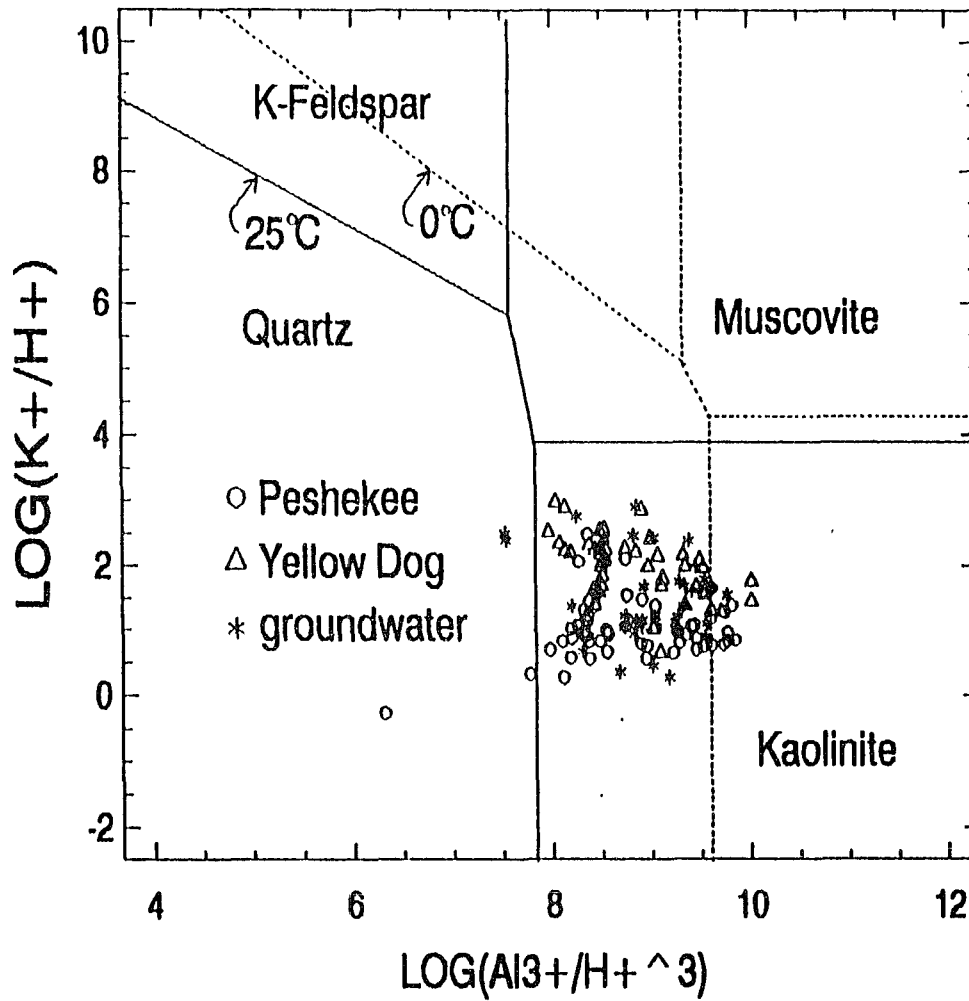


Figure 14. Activity diagram for river and ground water samples (including springs), showing mineral stability fields for 0° and 25°C in the system $\text{HCl-H}_2\text{O-Al}_2\text{O}_3\text{-K}_2\text{O-SiO}_2$.

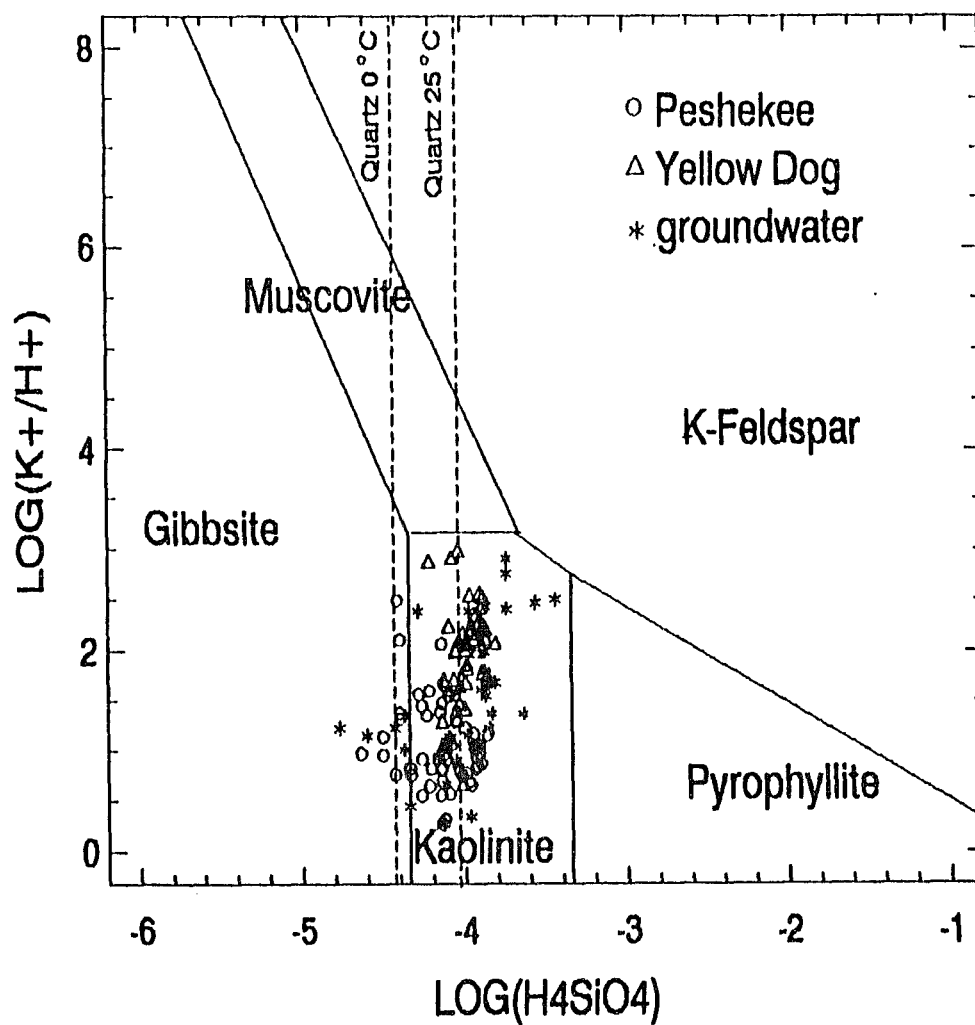


Figure 15. Activity diagram for river and ground water samples (including springs), showing line of quartz saturation at 0° and 25°C in the system $\text{HCl-H}_2\text{O-Al}_2\text{O}_3\text{-K}_2\text{O-SiO}_2$ at 25°C .

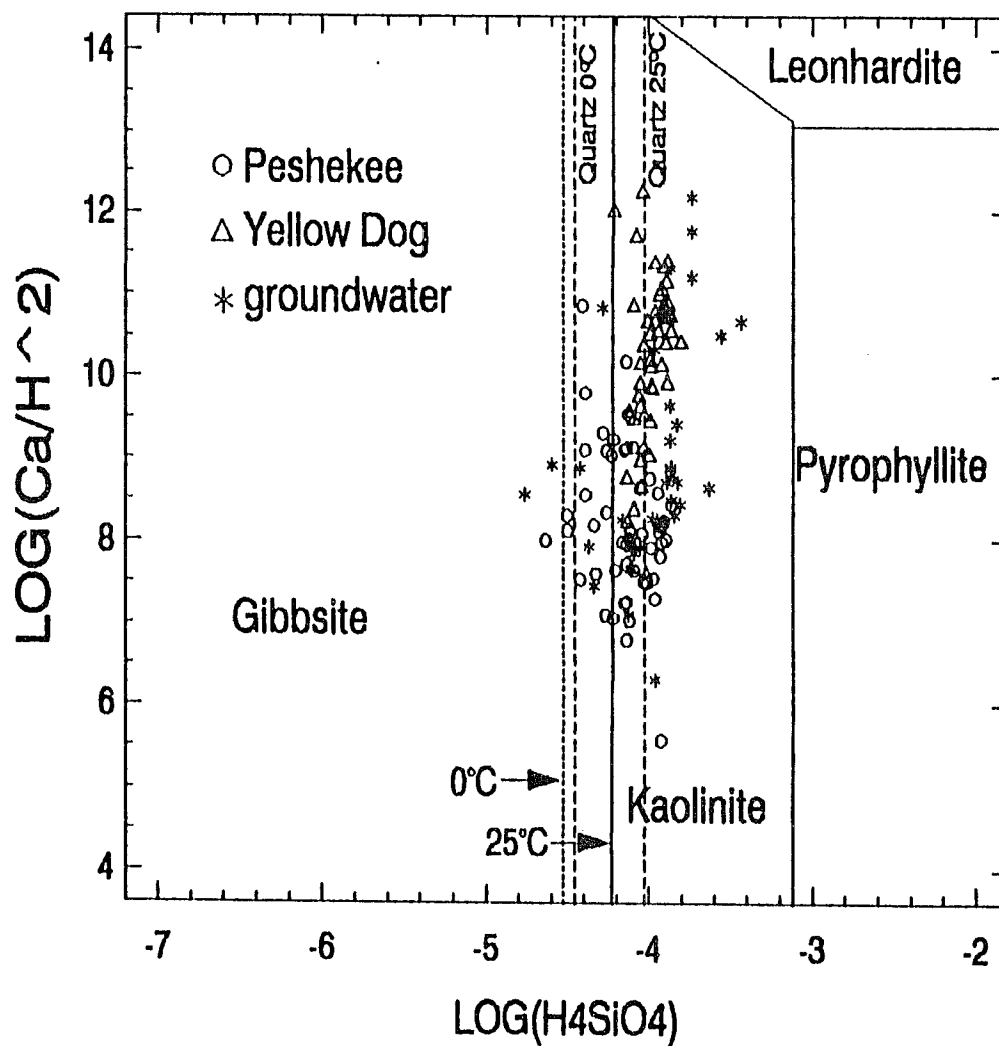


Figure 16. Activity diagram for river and ground water samples (including springs), showing line of quartz saturation at 0° and 25°C for the system $\text{HCl-H}_2\text{O-Al}_2\text{O}_3\text{-CaO-SiO}_2$ at 25°C.

saturation is repeated in Figure 16, which shows activities of Ca, H and silica. While data again plot mainly within the kaolinite field, it appears to be more related to quartz saturation from 0° to 25°C rather than an equilibrium reaction between gibbsite and kaolinite over the same temperature range.

Elemental Mass Balance from Weathering Reactions

1. Weathering petrology

To develop a set of reactions that relates the dissolved solute chemistry of water to primary and secondary minerals in the watersheds, mineralogical study of weathered rocks, sediments and clay soil particles was performed. Wood (1962), Morris (1977) and Shanabrook (1978) have studied the minerals in Peshekee and Yellow Dog rocks in considerable detail, and their work has been used here as the basis for specific compositions of olivine, pyroxene and plagioclase applied in weathering reactions. Morris (1977) and Wood (1962) do report a limited number of weathering features associated with mafic minerals, the most pronounced being the distinctive rusty brown color of the surface of mafic outcrops. Morris (1977) also found pyroxene not as weathered as olivine in thin section, with secondary mineral products forming along fractures or cleavages, and plagioclase fresh to totally

weathered. Wood (1962) and Shanabrook give mineralogies of mafic dikes from across the study area, but provide no observations of weathering except that much of the plagioclase and pyroxene appear rather fresh.

To augment previous work, six hand samples and three thin sections of rocks from each stream area were studied for evidence of primary mineral decay. Olivine was not observed in the few samples chosen for inspection, but pyroxene and amphibole show signs of transformation to chlorite. Weathering textures observed in thin section appear as feathery or fibrous clumps in patches and along grain edges. Generally there is no discernible boundary between the altered zones and the original pyroxene or amphibole in plane polarized light. Some rocks that display moderate foliation also contain chlorite of metamorphic origin, identified as such from obvious boundaries around clumps of fibrous masses oriented in line with foliation. Other metamorphic minerals present are Ca-rich, including calcite, epidote, clinozoisite and sphene. Clusters of opaque minerals are commonly found along rims of mafic minerals and red oxide staining is present in fractures and cleavages. Plagioclase is partly weathered to clay, even in the most siliceous rocks. Not surprisingly, quartz appears quite fresh in all thin sections along with most of the potassium feldspar.

Five thin sections were made from coarse grained sediments sifted out of samples from river channels and soil profiles. In unconsolidated grains, hornblende and pyroxene

grains are mostly decayed to fibrous clay-like material, but relict cleavages and grain outlines give evidence of the original mineral. The most obvious weathering feature seen in grain mounts compared to rocks is the increased amount of reddish staining from oxidation. Quartz appears fresh, potassium feldspars are fresh to sericitized, and plagioclase feldspars range from partly to mostly weathered.

Diffraction patterns from clay separates ($< 2\mu$) from representative soil samples are given in Figure 17, showing the major mineralogical features of Yellow Dog and Peshekee clays. Based on x-ray diffraction, clays from Peshekee soils consist of mainly chlorite and smectite with a small amount of vermiculite and possibly kaolinite. The strong peaks at 7.13 and 14.24 Å are persistent in all clay treatments, indicating the presence of plentiful chlorite. In the untreated (air dried) clay samples, the specific peaks at 7.13 and 14.24 Å, together with the distinct peak at 4.77 Å, indicate the particular chlorite mineral present is clinocllore, a Mg-rich chlorite containing varying amounts of Al and Fe. No shift in the position of the 14.2 Å peak was observed upon Mg-saturation of the Peshekee clays, indicating an Mg-rich 2:1 clay. A discrete shift from 14.2 to 16.98 Å after treating Peshekee clays with ethylene glycol confirms the presence of expandable Mg-smectite. Upon treatment with K there is a small amount of clay in Peshekee samples that shows collapse from 14 to 10 Å, which is evidence for vermiculite. The existence of kaolinite in this soil cannot be verified from

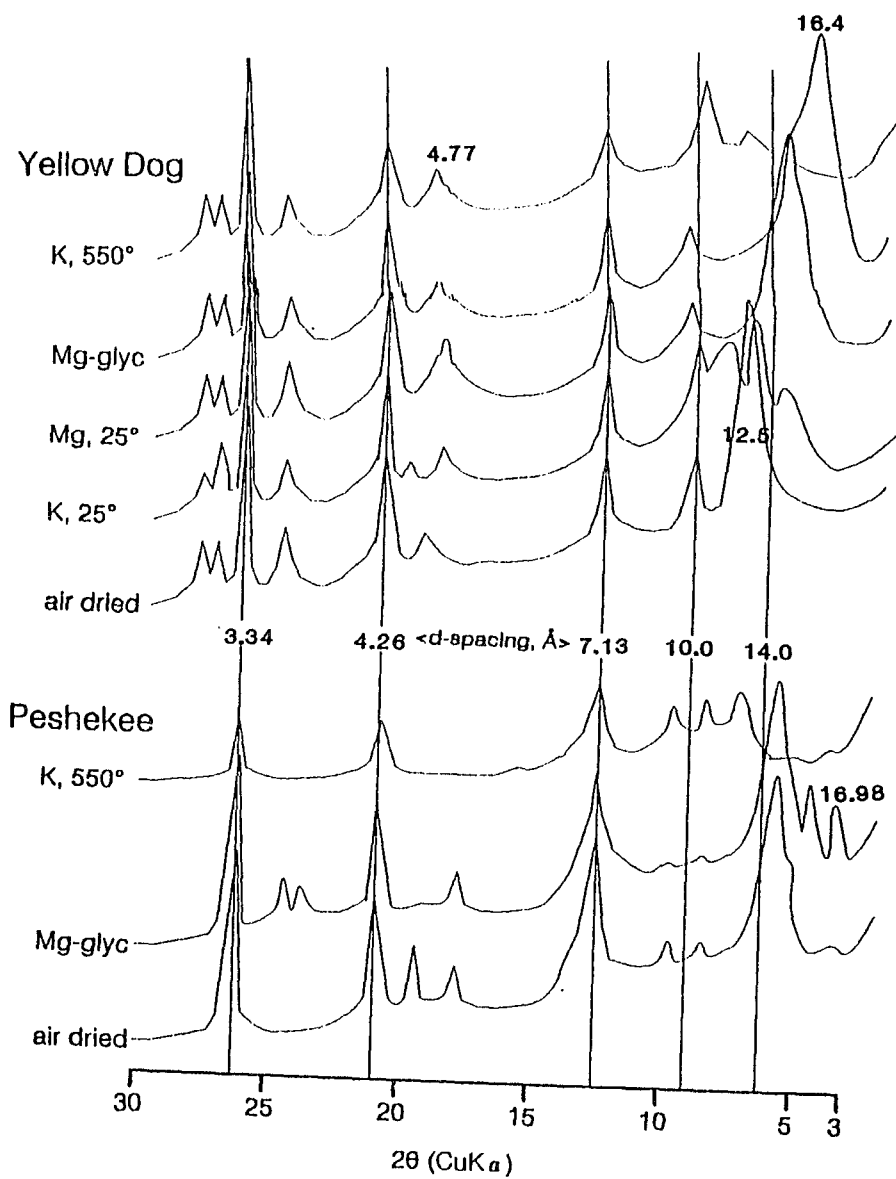


Figure 17. Representative x-ray diffraction patterns for clays from Peshekee and Yellow Dog soils.

these data, nor can it be judged absent since the 7.13 Å peak from chlorite would regardless be present.

The Yellow Dog clays are similar to the Peshekee but show specific mineralogical differences. They appear to contain a large percentage of smectite as there is a distinct and almost complete shift from a peak of 12.5 to 16.4 Å after Mg and ethylene glycol saturation in most samples, as shown in Figure 17. The smectite present in Yellow Dog soils is at least partly Na-rich, as the air-dried sample exhibits a peak marking a 12.5 Å d-spacing which expands to 14.5 upon Mg saturation. The most well-defined peak in all the x-ray data occur around 7.13 Å, and does not shift or decline with any of the clay treatments including heat, indicating a chlorite mineral is present. There is also evidence for vermiculite in Yellow Dog soils since the 12.5 Å peak partially collapses to near 10 with K saturation. Most samples contain small amounts of illite as well, but the 10 Å peak indicative of illite is always small and indistinct.

In addition to petrographic analysis of solid particles, a number of samples of suspended particles collected from each stream were examined by SEM. While detailed examination was not conducted on these samples one significant observation made was that all samples contained an abundance of fresh water diatoms, an important consideration in establishing a SiO₂ budget. From chemical modeling it appears that most water in this study is near equilibrium with quartz, implying that free silica is readily available for any weathering

reactions, assuming that the dissolution of silica from diatoms or other crystalline sources is not regulated kinetically.

2. Mass balance reactions

Tabulated results of mass balance calculations derived from mineral weathering reconstructions are shown in Table 6. In developing this table, primary inputs to streams quantified by this study were considered to be groundwater from springs, direct precipitation, and overland flow. Each of these inputs follows a distinct hydrologic pathway before reaching the stream. While other inputs to the streams like overflowing swamps and interflow are most definitely present in the two systems, they are not included in the reconstruction because they were not considered quantifiable by the data obtained in this study. Instead, known information was used to gain insight about such inputs; where groundwater and soil runoff do not appear to fully account for observed river chemistry, other inputs are considered to be important. Chemical reactions used are based on observed primary and secondary minerals or products identified from chemical modeling. These reactions are numbered sequentially and listed in Appendix A. For each type of water considered in Table 6, the first row of values represents the average solute concentrations of that water (arithmetic average calculated from all samples; data

Table 6. Reconstruction of source minerals for Northern Michigan waters (in mol/l*10⁴); equations shown in Appendix A.**Peshekee Spring**

Reaction	Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺	HCO ₃ ⁻	SO ₄ ²⁻	SiO ₂	Products
Subtract precipitation	.283	1.395	.786	.174	4.730	.043	.125	
Kaolinite-->An ₅₅ ¹	.000	1.049	.786	.174	3.755	.043	.000	.629 An ₅₅
Saponite-->biotite ²	.000	1.049	.786	.000	3.581	.043	.000	.174 Biot
Clinochlore-->pyx ³	.000	.044	.000	.000	.000	.043	.000	2.0W ₂₅ E ₇₅
Form pyrite ⁴	.000	.044	.000	.000	.000	.000	.000	.02 Pyrite

Yellow Dog Upper Spring

Reaction	Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺	HCO ₃ ⁻	SO ₄ ²⁻	SiO ₂	Products
Subtract precipitation	.222	1.666	.551	.146	4.392	.205	1.207	
Kaolinite-->plagioclase ⁵	.000	1.333	.551	.146	3.504	.205	.763	.555 An ₆₀
Vermiculite-->biotite ⁶	.000	1.333	.551	.000	3.358	.205	.643	.146 Biot
Clinochlore-->pyx ⁷	.000	.000	.481	.000	.552	.205	.000	3.6W ₄ E ₃ F ₁
Form olivine ⁸	.000	.000	.260	.000	.000	.205	.000	.14 Fa ₂ Fe ₈
Form pyrite ⁹	.000	.000	.260	.000	.000	.000	.000	.10 Pyrite

Yellow Dog Lower Spring

Reaction	Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺	HCO ₃ ⁻	SO ₄ ²⁻	SiO ₂	Products
Subtract precipitation	.535	7.669	2.456	.115	19.53	.770	1.264	
Kaol-->plagioclase ¹⁰	.000	7.461	2.456	.115	18.58	.770	.195	.743 An ₂₈
Kaolinite-->biotite ¹¹	.000	7.461	2.226	.000	17.77	.770	.000	.115 Biot
Talc-->clinocllore ¹²	.000	7.461	.000	.000	13.32	.770	.000	2.2 Chlor
Form calcite ¹³	.000	.798	.000	.000	.000	.770	.000	6.7 Calcite
Form pyrite ¹⁴	.000	.798	.000	.000	.000	.000	.000	.385 Pyrite

Peshekee runoff

Reaction	Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺	HCO ₃ ⁻	SO ₄ ²⁻	SiO ₂	Products
Subtract precipitation	.104	.434	.218	.000	1.147	.188	.746	
Kaol-->plagioclase ¹⁵	.000	.394	.218	.000	.963	.188	.538	.144 An ₂₈
Form saponite ¹⁶	.000	.394	.000	.000	.527	.188	.285	.07 Sapon

Yellow Dog runoff

Reaction	Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺	HCO ₃ ⁻	SO ₄ ²⁻	SiO ₂	Products
Subtract precipitation	.152	.876	.382	.056	2.016	.276	.595	
Kaolinite-->biotite ¹⁷	.152	.876	.270	.000	1.736	.276	.483	.056 Biot
Kaolinite-->saponite ¹⁸	.000	.876	.000	.000	1.044	.276	.427	.46 Sapon

from Appendix B) minus mean precipitation values. Because Cl and NO₃ were not considered in mineral reactions, they are not included in Table 6. However, this exclusion causes an imbalance in the positive versus negative charges in starting values for Table 6 entries. For this reason, initial excess positive charge was balanced by arbitrarily adjusting bicarbonate values. While this approach is not the only way this data could be handled, the discrepancies in charge balances are small, and do not significantly affect the final results.

In the Peshekee watershed where soils are quite thin, springs must follow the most fractured or weathered regions in the rocks, the mafic dikes. The rationale to account for the chemical signature of the Peshekee Spring in Table 6 starts by first assuming all Na and some of the Ca is derived from the breakdown of labradorite (An₅₅), the predominant plagioclase in the dikes (Shanabrook, 1978), to kaolinite. While kaolinite was not conclusively identified by mineralogical study of Peshekee watershed materials, chemical modeling does show that the water is thermodynamically stable with respect to kaolinite. Second, dissolved K in the Peshekee Spring has been attributed to the release of cations from biotite weathering to saponite, chosen based on x-ray data. Clinocllore could have also been used as a weathering product of biotite, giving essentially the same result. Application of these two quite reasonable assumptions leaves Ca, Mg and bicarbonate in almost exactly the proportions required by the

reaction of pyroxene weathering to clinocllore, the third reaction shown in Table 6 for the Peshekee Spring. Shanabrook (1978) reports the composition of pyroxene in the Peshekee dikes as diopsidic augite, and the chlorite composition is taken from x-ray analysis of Peshekee clays. Reactions of other mafic silicates like olivine or hornblende could also produce the cation concentrations seen in the spring even though direct observation supports the combinations chosen here.

Finally, a small amount of pyrite dissolution is invoked to explain the SO_4 concentrations in the spring, not unreasonable as trace amounts to several modal percent of pyrite have been reported in both mafic dikes and in granitic gneisses (Shanabrook, 1978; Taylor, 1972; Wood, 1962). Alternately, SO_4 could be derived from SO_4 absorbed in soils from precipitation inputs, a process known to occur in regions receiving acid precipitation (Drever, 1988; Krug, 1991). For the Peshekee Spring weathering reactions (and other water types in Table 6), there is some remaining positive charge, which could be ascribed to Ca or Mg depending on how the reactions are written. Since there is no way to balance the cationic charge in this spring or in any of the waters in this study without using SO_4 , it may be that SO_4 and Ca or Mg are involved in the same reaction. No empirical evidence suggests, however, that a Ca or Mg sulfate mineral is present in the system. Another problem with balancing the cationic charge in Table 6 is that NO_3 and Cl are not considered

because they do not typically participate in mineral reactions. Possibly excess Ca is involved in interactions with organic anions.

Chemical modeling data show that waters in this study are near saturation or supersaturation with quartz. In the reactions derived for Table 6, silica is presumed to precipitate or stay in the solid state except for the small amount of aqueous SiO_2 found in water samples. Another possibility is that excess dissolved SiO_2 is utilized through uptake by diatoms.

The sequence of weathering reactions inferred for the Peshekee Spring accounts quite well for the observed major element concentrations, with only a little Ca left over. Another possible source for the excess Ca may be the breakdown of small amounts of epidote or other Ca-bearing metamorphic minerals present in the Peshekee rocks, like calcite, but this should produce corresponding acid anions.

A similar approach was used to develop weathering reactions that lead to the composition of the Yellow Dog Upper Spring. The geology in the region of this spring is similar to that of the Peshekee, and comprises several small plutons of peridotite and gabbro; congruent dissolution of olivine (Fa_{20}), and incongruent weathering of labradorite (An_{60}), and diopside ($\text{Wo}_{38}\text{En}_{50}\text{Fs}_{12}$) from these rocks was presumed to release much of the Mg, Ca, and Na to the spring. Specific chemical compositions of primary mafic minerals were taken from the work of Morris (1977), and the compositions of secondary

minerals were derived from x-ray and petrographic analyses. All Na and some Ca were assumed to be derived from the breakdown of labradorite, and transformation of biotite to vermiculite was considered the source of K. Potassium feldspar weathering would have also been an appropriate choice; probably both reactions occur in this system, although much of the microcline seen in thin section appeared fresh. The formation of clinocllore from pyroxene is used to rationalize the remaining Ca and a portion of the Mg, while the dissolution of olivine is presumed for the balance of Mg. Since x-ray data indicates Na smectite is present in soils, an alternate reaction such as



could also explain solute concentrations in water, and provides that more of the Ca comes from plagioclase. Also, the amount of pyroxene called for by this reconstruction is rather high compared to the amount of olivine or plagioclase used. Because previous work implies that olivine is more weathered than pyroxene in the Yellow Dog rocks, it would also be appropriate to allow that more of the Mg is from olivine. As in the case of the Peshekee Spring sulfate is attributed to pyrite oxidation, based on Morris' (1977) notes of sulfide patches up to 1 cm in diameter in these rocks.

For the Yellow Dog Lower Spring, weathering reactions developed are distinctly different than for other springs.

This is because the Lower Spring emanates from glacial outwash, material that contains few unweathered mafic minerals. The main source of ions from the glacial sediments are primary minerals of moderate weatherability, andesine and biotite. Another reaction that is used in Table 6 for the Yellow Dog Lower Spring is the breakdown of clinocllore to release Mg. While chlorite is relatively stable under surface conditions in soils, it may begin to break down if exposed to dilute aqueous solutions for long periods of time such as would occur if the path traveled by the spring water was quite long. The chemistry of the Lower Spring is markedly more alkaline than other water in this study, and contains comparatively high amounts of Ca and bicarbonate. Carbonate rocks are known to occur in regions immediately south and west of the Yellow Dog study area (Boyum, 1975), and have been referred to by Sims (1992) as occurring northwest of the Yellow Dog drainage. It is likely that the Lower Spring originates in similar rocks. Discharge from this spring is two to three times greater than the Upper Spring, and unlike other springs in this study is constant year round, suggesting that waters follow a long flowpath through a regional flow system, one that is not affected by local flow patterns and near surface processes like freezing.

In addition to, but less important than, groundwater input, runoff was considered a major although episodic contribution to streams. To account for ions present in spring runoff samples, reactions describing alterations of

secondary minerals that were determined by mineralogic study to be present in soils were applied to mass balance calculations. For Peshekee runoff, the specific smectite formed by pyroxene weathering described above (see Peshekee Spring, Table 6), was assumed to break down into kaolinite in the upper soil, releasing Ca and Mg to water. Andesine weathering was used to explain Na in Peshekee runoff. Very limited amounts of K were found in Peshekee runoff, but biotite alteration to kaolinite was used to justify the K in Yellow Dog runoff. Since Na-rich smectite was indicated by x-ray study of Yellow Dog soils, a reaction between Na-rich smectite and kaolinite was employed to account for all of the Na and some of the Ca and Mg present in runoff. Rather than invoking other chemical reactions to completely balance ions in runoff samples, examination of concentrations remaining after considering the above reactions shows quite similar results for both the Peshekee and Yellow Dog. This suggests similar processes may be acting in both systems to result in much of the Ca, Mg, HCO_3 , SiO_2 and SO_4 in runoff. It appears that these ions are being leached from upper soil particles and organic debris as water runs over and through the top few inches of surface material, either by cation exchange or simple dissolution of uncharacterized mineral matter.

Direct comparison of molar concentrations from each river location with chemistry from individual input sources shows that for the Peshekee River, the middle and upper portions are similar to water from springs and shallow groundwater flowing

through rocks from which mafic minerals are weathering, while the downstream stream water is more dilute and possibly influenced by overland flow which gains its chemical character from interactions mainly from soil minerals. This result can also be explained by considering the lakes and swamps drained within the Peshekee watershed that contribute proportionally more water downstream. Lake contributions would tend to dilute stream water while swamp input is rich in Al and would increase Al in the stream; both of these characteristics are seen in low elevation Peshekee water.

The Yellow Dog River, for the most part, appears to receive its water predominantly from groundwater sources. The upper and middle stretches also reflect a runoff source, in addition to groundwater. Two major types of groundwater contribute to the river at different elevations. In mid to upstream areas, shallower groundwater flowing through glacial till containing mafic minerals and rocks is most important. In the downstream portion of the river, water has the chemical signature, in part, of springs that emanate from bedrock rich in carbonate. Such rocks occur at some distance away from the river; water entering the Yellow Dog River at low elevation therefore must follow the longest flowpaths of any sampled in this study.

These interpretations of source waters are supported by simple statistical correlation of source and river waters within each watershed. Correlation coefficients calculated by performing multivariate statistical analyses of river water

chemical data and data from runoff and springs are tabulated in Table 7.

Table 7. Correlation coefficients of molar concentrations for river and source waters.

PESHEKEE	P1	P3	P4
Runoff	.931	.909	.883
Spring	.903	.953	.945

YELLOW DOG	Y1	Y3	Y4
Runoff	.993	.999	.999
Upper Spring	.990	.993	.994
Lower Spring	.997	.989	.991

Correlation analysis shows all waters sampled in this study are chemically quite similar, an inference made previously based on chemical modeling data. However, minor but noticable variations in correlation coefficients do exist in Table 7, and point to the same conclusions reached earlier about the nature of source water to each river location.

SUMMARY AND CONCLUSIONS

The purpose of this research was to identify the processes controlling concentrations of Al species and major cations in two Northern Michigan streams. Hydrogeochemical processes were identified by determining local geology, hydrologic pathways and source water inputs in conjunction with weekly monitoring of rivers, springs and precipitation. The major findings and conclusions of this study are summarized in the following paragraphs.

The most significant chemical episodes measured in the Peshekee and Yellow Dog Rivers during the one year study period occurred in response to input from 1) spring snow melt, which greatly reduced stream pH and increased total Al concentrations; and 2) large autumn rain storms that followed an extended dry period that flushed certain cations from specific watershed locations.

Precipitation pH ranged from 4.0 to 5.5; values for river water pH ranged from 4.8 during spring snowmelt to 7.8 during dry periods in summer and when rivers were frozen over in the winter. River water acidity showed distinct seasonal and spatial variation. The Peshekee River becomes slightly more acidic and dilute downstream as input from lakes and swamps increases, while the Yellow Dog is most acidic in mid-stream location, becoming alkaline downstream due to the input of deep groundwater.

Aluminum speciation behavior is not the same for each

river, and apparently is related to the composition of source waters as well as chemical interactions within the streams. Aluminum is partitioned amongst organic, inorganic and polymeric compounds in varying proportions in ways that are not necessarily related to proton interactions. Total dissolved Al (Alt) in both streams increases with acidity, as does monomeric organically complexed Al (Alo). However, inorganic monomeric Al (Ali) and polymeric Al (Alp) do not correlate with pH. Concentration levels of dissolved organic carbon are also directly correlated with Alt in both streams, but with Alo only for the Yellow Dog. In the Peshekee, Alo is inversely proportional to DOC but Alp correlates directly. Since the Peshekee receives a larger percentage of its water from swamps compared to the Yellow Dog, it is likely that polymeric organically complexed Al, a species not directly quantified in this study, is responsible for the relationship between Alp and DOC. Contradiction from expected Alo and DOC behavior may also be attributable to the analytical methods used to determine Alo, which are designed to detect simple organic molecules complexed to single Al ions (Driscoll, 1984). In the Yellow Dog system, simpler Alo compounds from soil water that interacts with organic debris may explain the association of DOC and Alo. Alternately, problems may exist in interpreting reactive organic carbon based on measuring total DOC, which does not discern organics that complex cations or those that may contribute to acidity (Krug, 1991). Other processes that may influence Ali and Alp could be

complexation reactions that take place within the stream after Al is released from watershed materials to form inorganic compounds of Al chains (inorganic Alp), since increased solubility of $\text{Al}(\text{OH})_3$ with lower pH does appear to control the total amount of Al available.

Equilibrium reactions with certain mineral phases also control Al concentrations to some extent. For all groundwater, surface water and river water in this study, activities of Al_i and H are as expected for equilibrium with gibbsite. For river waters with pH less than 5.5, however, gibbsite does not control Al_i activity. Instead, when pH is low during high discharge, there is less Al_i than predicted by gibbsite equilibrium, probably because Al ions are being preferentially sequestered by organic molecules or are forming polymeric Al compounds. The alteration of kaolinite to gibbsite may also control Al_i activities to some degree, but this relationship is not readily discernable from saturation with quartz. In any case, specific aqueous ionic concentrations resulting from both reactions are definitely temperature dependent, as the observed range of ion activities plotted on mineral stability diagrams can be explained largely by considering the range of water temperatures measured throughout the year.

While base cations are, in general, diluted by runoff during high runoff events, there are distinct increases in release rates of certain cations in the Peshekee watershed when large rains follow long dry spells. This occurs because

pore fluids clinging to surfaces of mafic minerals throughout dry periods become increasingly concentrated with cations leached from minerals. In the Peshekee watershed, numerous pyroxene dikes intersect the main trunk of the stream at nearly right angles, and it is pore waters flushed from these dikes that are responsible for increased fluxes of Ca, Mg and Fe during such storms. Weathering of mafic dikes as a major contributor of solutes to streams has been identified in other similar systems, such as in the study by Rochette et al. (1988). These authors found that weathering of mafic minerals in dikes cross-cutting quartzite was the most important terrestrial ionic input to West Glacier Lake in Wyoming. This effect is not observed in the Yellow Dog, where dikes and other mafic intrusive bodies exist but do not intersect the river, and therefore do not provide direct hydrologic pathways for storm runoff. In fact, once regular precipitation resumed after the summer dry spell, cation release rates progressively increased with time in the Yellow Dog watershed because of infiltration and flushing of groundwaters through deeper soil and sediment zones. A similar mechanism for cation release to streams has been proposed in other similar studies (Velbel, 1985). The same pattern of progressively increasing cation flux with time was also observed in spring after the ground had thawed and meltwaters had a chance to infiltrate to the water table.

Evaluation of elemental mass balance from mineral weathering reactions for five different kinds of waters that

are input sources to the rivers shows that the chemical nature of the input water is highly dependent on geology. Reaction sequences developed from specific chemical compositions of primary and secondary minerals in the watershed account quite well for the observed water chemistry. The Peshekee Spring composition is directly related to the mafic minerals in the diabase dikes that it passes through, and surface runoff chemistry is produced from weathering of minerals in the upper soil zones. Runoff chemistry in the Yellow Dog basin is also from soil mineral weathering, but is the result of reactions of different mineral phases specific to the Yellow Dog soils. The two groundwater types identified in the Yellow Dog system are distinctly different from each other; the chemical signature of springs in higher elevations reflect weathering of minerals in bedrock, whereas the water of low elevation springs is of an alkaline Ca-Mg type from groundwater flowing through regional systems that pass through carbonate rocks.

Discrete sources of water to each stream at different locations can be identified by direct comparison of waters and by statistical correlation of chemical data. The major sources of input water to the Peshekee River are shallow groundwater at the middle and higher elevations, and shallow groundwater plus overland flow and overflow of lakes and swamps at downstream location. These distinct inputs result in lower pH, lower cation concentrations and higher Al concentrations at low elevation in the Peshekee. In addition to accounting for higher overall Al concentrations, the input

from swamp overflow also explains the peculiar DOC/Al_o relationship observed in the Peshekee. Overflow from swamps during high discharge has not been emphasized in previous watershed studies, but is probably important in other regions that have experienced continental glaciation.

Sources of water to the Yellow Dog River are from two different groundwater types; shallow groundwater draining granitic bedrock containing infrequent mafic intrusions feeds the middle and upper portion of the Yellow Dog, while deeper groundwater from regional hydrologic circulation through carbonate rocks is the major source to the lower elevation areas. In addition, during heavy rains and spring melt, overland flow and interflow flush soil water enriched in Al to the Yellow Dog, causing decreased pH and higher Al_t.

Conclusions reached in this study point to the need to delineate specific sources of water to streams in order to understand how solute concentrations vary with season and with distance downstream in any watershed under investigation. Although the Peshekee and Yellow Dog Rivers receive the same initial precipitation input, broad differences in chemical behavior exist between and even within each river. The chemical nature and "hydrologic connectedness" of specific input sources dictates the chemical variability observed at different locations in each river.

The pairing of watersheds receiving the same input, as in the work presented here, can be a useful method of determining specific hydrogeochemical interactions that are unique to an

individual watershed. Distinct differences in Al behavior between the streams in this study could be interpreted as a function of geology and drainage characteristics mainly because a direct comparison was available. That fact that polymeric Al appears to be associated with organic inputs, especially from swamp overflow, suggests that more attention needs to be given to understanding Al-organic complexation in relation to drainage patterns in future research. It is likely that reactions involving polymeric Al forms also affect simple Al complexes and thus potential Al toxicity. Studying paired watersheds also allowed identification of specific geochemical interactions and hydrologic pathways that are a direct function of watershed geology and structural features. The dependence of stream chemistry on the geology of watershed materials is not a new idea (Bricker and Rice, 1989), but one that is not currently emphasized in predictive models of acidification effects. Improved models must be capable of reflecting localized geologic features if they are to be useful for a wide range of watershed systems.

BIBLIOGRAPHY

BIBLIOGRAPHY

- APHA, 1971, 1976, 1984, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association.
- Arp, P.A., and R. Ouimet, 1986, Aluminum speciation in soil solutions: equilibrium calculations, *Water, Air, and Soil Pollution*, 31, 359-366.
- Bache, B.W., 1986, Aluminum mobilization in soils and waters, *Jour. Geological Society*, 143, 699-706.
- Bache, B.W., and G.S. Sharp, 1976, Soluble polymeric hydroxy-aluminum ions in acid soils, *Jour. Soil Science*, 27, 167-74.
- Baker, J.P., and C.L. Schofield, 1982, Aluminum toxicity to fish in acidic waters. *Water, Air, and Soil Pollution*, 18, 289-309.
- Baker, L.A., A.T. Herlihy, P.R. Kaufmann, and J.M. Eilers, 1991, Acidic lakes and streams in the United States: the role of acidic deposition, *Science*, 252, 1151-1154.
- Barnes, R. B., 1976, The determination of specific forms of aluminum in natural water, *Chemical Geology*, 15, 177-191.
- Bloom, P. R., M. B. McBride, and R. M. Weaver, 1979, Aluminum organic matter in acid soils; buffering and solution aluminum activity. *Soil Sci. Amer. Jour.*, 43, 488-493.
- Bowers, T.S, K.J. Jackson, and H.C. Helgeson, 1984, *Equilibrium Activity Diagrams for Coexisting Minerals and Aqueous Solutions at Pressures and Temperatures to 5 kb and 600° C*, Springer-Verlag.
- Boyum, B.H., 1975, *The Marquette Mineral District of Michigan*, 2nd ed., Cleveland Cliffs Iron Company, Ishpeming, Michigan, 62 p.
- Bricker, O.P., and K.R. Rice, 1989, Acidic deposition to streams--a geology-based method predicts their sensitivity, *Environ. Sci. Technol.*, 23, 379-385.

- Cannon, W.F., and J.E. Gair, 1970, A revision of stratigraphic nomenclature for middle Precambrian rocks in northern Michigan, *Geol. Soc. Amer. Bull.*, 81, 2843-2846.
- Cannon, W.F., and G.C. Simmons, 1973, Geology of part of the southern complex, Marquette district, Michigan, *U.S. Geol. Survey Jour. Res.*, 1, 165-172.
- Chase, C.G., and T.H. Gilmer, 1973, Precambrian plate tectonics: the Mid-continent Gravity High, *Earth Planet. Sci. Lett.*, 21, 70-78.
- Chen, C.W., S.A. Gherini, N.E. Peters, P.S. Murdoch, R.M. Newton and R.A. Goldstein, 1984a, Hydrologic analyses of acidic and alkaline lakes, *Water Resour. Res.*, 20, 1875-1882.
- Chen, C.W., S.A. Gherini, J.D. Dean, R.J.M. Hudson and R.A. Goldstein, 1984b, Development and calibration of the Integrated Lake-Watershed Acidification study model, in *Modeling of Total Acid Precipitation Impacts*, J. Schnoor, ed., Ann Arbor Science, p. 175-203.
- Christophersen, N., H.M. Seip and R.F. Wright, 1982, A model for streamwater chemistry at Birkenes, Norway, *Water Resources Research*, 18, 977-996.
- Christophersen, N., and C. Neal, 1990, Linking hydrological, geochemical, and soil chemical processes on the catchment scale: an interplay between modeling and field work, *Water Resources Research*, 26, 3077-3086.
- Christophersen, N., C. Neal and R.P. Hooper, 1990, Modelling streamwater chemistry as a mixture of soil-water end-members--a step towards second generation acidification models, *Journal of Hydrology*, 116, 307-320.
- Clayton, J.L., 1986, An estimate of plagioclase weathering rate in the Idaho Batholith based upon geochemical transport rates, in S.M. Colman and D.P. Dethier (eds.), *Rates of Chemical Weathering of Rocks and Minerals*, Academic Press, Orlando, 453-466.
- Cosby, B. J., G. M. Hornberger, J. N. Galloway and R. F. Wright, 1985, Modeling the effects of acid deposition: Assessment of a lumped parameter model of soil water and streamwater chemistry, *Water Resources Research*, 21, 51-63.
- Cozzarelli, I.M., J.S. Herman and R.A. Parnell, Jr., 1987, The mobilization of aluminum in a natural soil system: effects of hydrologic pathways, *Water Resources Research*, 23, 859-874.

- Cronan, C.S., 1985, Chemical weathering and solution chemistry in acid forest soils: differential influence of soil type, biotic processes and H^+ deposition, in J. I. Drever (ed.), *The Chemistry of Weathering*, Reidel Publishing, 175-195.
- Cronan, C.S., W.J. Walker and P.R. Bloom, 1986, Predicting aqueous aluminium concentrations in natural waters, *Nature*, 324, 140-143.
- DeGuire, L.J., 1988, *The Great Lakes Atmospheric Deposition Program in Michigan*, Air Quality Division, Michigan Department of Natural Resources, Lansing, Michigan.
- Doonan, C.J., and J.L. VanAlstine, 1982, Ground water and geology of Marquette County, Michigan. *USGS Open File Report 82-501*.
- Drever, J.I., 1988, *The Geochemistry of Natural Waters*, 2nd ed., Prentice-Hall, New Jersey.
- Drever, J.I., and D.R. Hurcomb, 1986, Neutralization of atmospheric acidity by chemical weathering in an alpine drainage basin in the North Cascade Mountains, *Geology*, 14, 221-224.
- Driscoll, C.T., 1980, Aqueous speciation of aluminum in the Adirondack Region of New York State, USA, in *Proceedings of the International Conference on Ecological Impacts of Acid Precipitation*, D. Drablos and A. Tollan, eds., SNSF Project, Oslo, Norway, 214-215.
- Driscoll, C.T., 1984, A procedure for the fractionation of aqueous aluminum in dilute acidic waters, *Int. J. Environ. Anal. Chem.*, 16, 267-284.
- Driscoll, C.T., J.P. Baker, J.J. Bisogni and C.L. Schofield, 1984, Aluminum speciation and equilibria in dilute acidic surface waters of the Adirondack region of New York State, in *Geologic Aspects of Acid Deposition*, O. P. Bricker, ed., Ann Arbor Science, p. 55-76.
- Driscoll, C.T., N. van Breemen, and J. Mulder, 1985, Aluminum chemistry in a forested spodosol, *Soil Sci. Soc. Amer. Jour.*, 49, 437-444.
- Durand, P., C. Neal and F. Lelong, 1992, Anthropogenic and natural contributions to the rainfall chemistry of a mountainous area in the Cevennes National Park (Mont-Lozere, southern France), *Journal of Hydrology*, 130, 71-85.
- Eriksson, E., 1981, Aluminum in groundwater--possible solution

equilibria, *Nordic Hydrology*, 12, 43-50.

- Folster, H., 1985, Proton consumption rates in Holocene and present-day weathering of acid forest soils, in J.I. Drever (ed.), *The Chemistry of Weathering*, Reidel Publishing, 197-209.
- Galloway, J.N., S.A. Norton and M.R. Church, 1983, Freshwater acidification from atmospheric deposition of sulfuric acid: a conceptual model, *Environ. Sci. Technol.*, 17, 541A-545A.
- Galloway, J.N., Z. Dianwu, X. Jiling, and G.E. Likens, 1987, Acid rain: China, United States, and a remote area, *Science*, 236, 1559-1562.
- Hall, R.J., C.T. Driscoll, and G.E. Likens, 1987, Importance of hydrogen ion and aluminum in regulating the structure and function of stream ecosystems: an experimental test, *Freshwater Biology*, 18, 17-43.
- Havas, M., 1986, A hematoxylin staining technique to locate sites of aluminum binding in aquatic plants and animals, *Water, Air, Soil Pollut.*, 30, 735-741.
- Hem, J.D., and C.E. Roberson, 1967, Form and stability of aluminum hydroxide complexes in dilute solution, *USGS Water Supply Paper 1827-A*, 55 p.
- Hendershot, W.H., S. Savoie and F. Courchesne, 1992, Simulation of stream-water chemistry with soil solution and groundwater flow contributions, *Journal of Hydrology*, 136, 237-252.
- Henriksen, A., D.F. Brakke and S.A. Norton, 1988, Total organic carbon concentrations in acidic lakes in southern Norway, *Environ. Sci. Technol.*, 22, 1103-1105.
- Hooper, R.P., and C.A. Shoemaker, 1985, Aluminum mobilization in an acidic headwater stream: temporal variation and mineral dissolution disequilibria, *Science*, 229, 463-465.
- Hooper, R.P., N. Christophersen, and N.E. Peters, 1990, Modelling streamwater chemistry as a mixture of soilwater end members--an application to the Panola Mountain catchments, Georgia U.S.A., *Journal of Hydrology*, 116, 321-343.
- Hooper, R.P., and N. Christophersen, 1992, Predicting episodic stream acidification in the southeastern United States: combining a long-term acidification model and the end-member mixing concept, *Water Resources Research*, 28, 1983-1990.

- Hornberger, G.M., B.J. Cosby and R.F. Wright, 1989, Historical reconstructions and future forecasts of regional surface water acidification in Southernmost Norway, *Water Resources Research*, 25, 2009-2018.
- Hubbard, H.A., 1975, Lower Keweenawan volcanic rocks of Michigan and Wisconsin, *U.S. Geol. Surv. Jour. Res.*, 3, 529-541.
- Johannes, A.H., E.R. Altwicker and N.L. Clesceri, 1985, The integrated lake-watershed acidification study: Atmospheric inputs, *Water Air Soil Pollut.*, 26, 339-353.
- Johannessen, M., T. Dales, E.T. Gjessing, A. Henricksen and R.F. Wright, 1977, Acid precipitation in Norway: the regional distribution of contaminants in snow and the chemical concentration processes during snowmelt, *Proceedings of Isotopes and Impurities in Snow and Ice Symposium*, Int. Assoc. Hydrol. Sci. Publ., 118, 116-120.
- Johnson, N.M., C.T. Driscoll, J.S. Eaton, G.E. Likens and W.H. McDowell, 1981, 'Acid rain', dissolved aluminum and chemical weathering at the Hubbard Brook Experimental Forest, New Hampshire, *Geochim. Cosmochim. Acta*, 45, 1421-1437.
- Kamari, J., D.F. Brakke, A. Jenkins, S.A. Norton and R.F. Wright (eds.), 1989, *Regional Acidification Models*, Springer, Berlin.
- Krug, E.C., and C.R. Frink, 1983, Acid rain on acid soil: A new perspective. *Science*, 221, 520-525.
- Krug, E.C., 1991, Review of acid-deposition-catchment interaction and comments on future reseach needs, *Journal of Hydrology*, 128, 1-27.
- Kress, M.W., R. Baker and S.J. Ursic, 1990, Chemistry response of two forested watersheds to acid atmospheric deposition, *Water Resources Bulletin*, 26, 747-755.
- Lawrence, G.B., Fuller, R.D. and Driscoll, C.T., 1986, Spatial relationships of aluminum chemistry in streams of the Hubbard Brook Experimental Forest, New Hampshire, *Biogeochemistry*, 2, 115-135.
- Lawrence, G.B., and C.T. Driscoll, 1988, Aluminum chemistry downstream of a whole-tree-harvested watershed, *Environ. Sci. Technol.*, 22, 1293-1299.
- Lawrence, G.B., C.T. Driscoll, and R.D. Fuller, 1988, Hydrologic control of aluminum chemistry in an acidic headwater stream, *Water Resources Research*, 24, 659-669.

- Likens, G.E., 1988, Information needs--aquatic, in J.C. White (ed.), *Acid Rain, the relationship between source and receptors*, Elsevier, p. 101-119.
- Little, I.P., 1986, Mobile iron, aluminium, and carbon in sandy coastal podzols of Fraser Island, Australia: a quantitative analysis, *Jour. Soil Science*, 37, 439-454.
- Manley, E.P., W. Chesworth, and L.J. Evans, 1987, The solution chemistry of podzolic soils from eastern Canadian shield: a thermodynamic interpretation of the mineral phases controlling soluble Al^{3+} and H_4SiO_4 , *Jour. Soil Science*, 38, 39-51.
- May, H.M., P.A. Helmke and M.L. Jackson, 1979, Gibbsite solubility and thermodynamic properties of hydroxy-aluminum ions in aqueous solution at 25° C, *Geochim. Cosmochim. Acta*, 43, 861-868.
- McAvoy, D.C., 1989, Episodic response of aluminum chemistry in an acid-sensitive Massachusetts catchment, *Water Resources Research*, 25, 233-240.
- Merna, J.W. and G.R. Alexander, 1983, Effects of snowmelt runoff on pH and alkalinity of trout streams in northern Michigan, *Fisheries Technical Report No. 83-2*, Michigan Department of Natural Resources, 14 p.
- Meunier, A., and B. Velde, 1979, Weathering mineral facies in altered granites: the importance of local small-scale equilibria, *Mineral. Mag.*, 43, 261-268.
- Morris, W.J., 1977, *Geochemistry and Origin of the Yellow Dog Plains Peridotite*, Marquette County, Northern Michigan, M.Sc. Thesis, Michigan State University, East Lansing, Michigan.
- Mulder, J., N van Breemen and H.C. Eijck, 1989, Depletion of soil aluminum by acid deposition and implications for acid neutralization, *Nature*, 337, 247-249.
- Muniz, I.P., and H. Leivestad, 1980, Toxic effects of aluminum on the brown trout, in K. Drablos and A. Tollan (eds.), *Ecological Impact of Acid Precipitation*, SNSF Project, Norway, p. 320-321.
- Nahon, D.B., 1991, *Introduction to the Petrology of Soils and Chemical Weathering*, Wiley-Interscience, 313 pp.
- NAPAP, 1990, Acidic Deposition: State of Science and Technology, *National Acid Precipitation Assessment Program Report #10*, Washington, D.C.

- Neal, C., 1988, Aluminium solubility relationships in acid waters--a practical example of the need for a radical reappraisal, *Journal of Hydrology*, 104, 141-159.
- Neal, C., C.J. Smith, J. Walls and C.S. Dunn, 1986, Major, minor and trace element mobility in the acidic upland forested catchment of the upper River Severn, Mid Wales, *Journal Geological Soc.*, 143, 635-648.
- Neal, C., and R.J. Williams, 1988, Towards establishing aluminum hydroxy silicate solubility relationships for natural waters, *Journal of Hydrology*, 97, 347-352.
- Neal, C., B. Reynolds, P. Stevens and M. Hornung, 1989, Hydrogeochemical controls for inorganic aluminium in acidic stream and soil waters at two upland catchments in Wales, *Journal of Hydrology*, 106, 155-175.
- Neal, C., A. Robson, B. Reynolds, and A. Jenkins, 1992, Prediction of future short-term stream chemistry--a modelling approach, *Journal of Hydrology*, 130, 87-103.
- Nordstrom, D. K., and J. W. Ball, 1986, The geochemical behavior of aluminum in acidified surface waters, *Science*, 232, 54-56.
- Orion Research Incorporated, 1984, Orion instruction manual, fluoride electrodes, 35 p., Cambridge, Mass.
- Paces, T., 1985, Sources of acidification in Central Europe basins, *Nature*, 315, 31-36.
- Peters, N.E., and Driscoll, C.T., 1987, Hydrogeologic controls of surface-water chemistry in the Adirondack region of New York State, *Biogeochemistry*, 3, 163-180.
- Plummer, L.N., B.F. Jones and A.J. Truesdell, 1978, WATEQF-a Fortran IV version of WATEQ, a computer program for calculating chemical equilibrium of natural waters. *U.S. Geol. Surv. Wat.-Res. Invest.* 76-13, 63p.
- Reuss, J. O., and D. W. Johnson, 1986, *Acid Deposition and the Acidification of Soils and Waters*, Springer Verlag, 119 p.
- Robson, A., A. Jenkins and C. Neal, 1991, Towards predicting future episodic changes in stream chemistry, *Journal of Hydrology*, 125, 161-174.
- Rochelle, B.P., C.I. Liff, W.G. Campbell, D.L. Cassell, M.R. Church and R.A. Nusz, 1989, Regional relationships between geomorphic/hydrologic parameters and surface water chemistry relative to acidic deposition, *Journal of*

Hydrology, 112, 103-120.

- Rochette, E.A., J.I. Drever and F.S. Sanders, Chemical weathering in the West Glacier Lake drainage basin, Snowy Range, Wyoming: implications for future acid deposition, *Contributions to Geology, University of Wyoming*, 26, 29-44.
- Rosseland, B.O., O.K. Skogheim, F. Kroglund and E. Hoell, 1986, Mortality and physiological stress of year-classes of landlocked and migratory Atlantic salmon, brown trout and brook trout in acid aluminum-rich soft water, *Water, Air, Soil Pollution*, 30, 751-756.
- Ryan, P.F., G.M. Hornberger, B.J. Cosby, J.N. Galloway, F.R. Webb and E.B. Rastetter, 1989, Changes in the chemical composition of stream water in two catchments in the Shenandoah National Park, Virginia, in response to atmospheric deposition of sulfur, *Water Resources Research*, 25, 2091-2099.
- Schaefer, D.A., C.T. Driscoll, R. Van Dreason, and C.P. Yatsko, 1990, The episodic acidification of Adirondack lakes during snowmelt, *Water Resources Research*, 26, 1639-1647.
- Schnoor, J.L. (ed.), 1984, *Modeling of Total Acid Precipitation Impacts*, Ann Arbor Science.
- Schnoor, J.L., W.D. Palmer and G.E. Glass, 1984, Modeling impacts of acid precipitation for northeastern Minnesota, in *Modeling of Total Acid Precipitation Impacts*, J. L. Schnoor, ed., Ann Arbor Science, p. 121-154.
- Seip, H.M., 1980, Acid snow-snowpack chemistry and snowmelt, in *Effects of Acid Precipitation of Terrestrial Ecosystems*, T. C. Hutchinson and M. Havas, eds., Plenum Press, 77-94.
- Seip, H.M., D.O. Andersen, N. Christophersen, T.J. Sullivan and R.D. Vogt, 1989, Variations in concentrations of aqueous aluminium and other chemical species during hydrological episodes at Birkenes, southernmost Norway, *Journal of Hydrology*, 108, 387-405.
- Shanabrook, D.C., 1978, *A Geophysical and Geological Study of the Basement Complex Along the Peshekee River, Marquette County, Northern Michigan*, M.Sc. Thesis, Michigan State University, East Lansing, Michigan.
- Sims, P.K., 1992, Geologic map of Precambrian rocks, Southern Lake Superior Region, Wisconsin and Northern Michigan, *U.S. Geol. Surv. Map I-2185*.

- Slavin, W., 1968, *Atomic Absorption Spectroscopy*, Wiley Interscience, New York.
- Sugimura, Y. and Y. Suzuki, 1988, A high-temperature catalytic oxidation method for the determination of non-volatile dissolved organic carbon in seawater by direct injection of a liquid sample, *Marine Chemistry*, 24, 105-131.
- Taylor, L.G., 1972, *Stratigraphy, Sedimentology and Sulfide Mineralization of the Kona Dolomite*, Ph.D. Dissertation, Michigan Technological University, Houghton, Michigan.
- USEPA, 1979, *Acid Rain Research Summary*, U.S. EPA Office of Research and Development, U.S. EPA-600/8-79-028, 23 pp.
- Velbel, M.A., 1985, Hydrogeochemical constraints on mass balances in forested watersheds of the Southern Appalachians, in J. I. Drever (ed.), *The Chemistry of Weathering*, Reidel Publishing, 231-247.
- Velbel, M.A., 1990, Influence of temperature and mineral surface characteristics on feldspar weathering rates in natural and artificial systems: a first approximation, *Water Resources Research*, 26, 3049-3053.
- Velbel, M.A., 1992, Geochemical mass balances and weathering rates in forested watersheds of the Southern Blue Ridge. III. Cation budgets and the weathering rate of amphibole, *American Journal of Science*, 292, 58-78.
- Velbel, M.A., 1993, Constancy of silicate-mineral weathering-rate ratios between natural and experimental weathering: implications for hydrologic control of differences in absolute rates, *Chemical Geology*, 105, 89-99.
- Walker, W.J., C.S. Cronan and H.H. Patterson, 1988, A kinetic study of aluminum adsorption by aluminosilicate clay minerals, *Geochim. Cosmochim. Acta*, 52, 55-62.
- Wels, C., R.J. Cornett, and B.D. LaZerte, 1990, Groundwater and wetland contributions to stream acidification: an isotopic analysis, *Water Resources Research*, 26, 2933-3003.
- Whitehead, P.G., S. Bird, M. Hornung, J. Cosby, C. Neal, and P. Paricos, 1988, Stream acidification trends in the Welsh Uplands--a modelling study of the Llyn Brianne Catchments, *Journal of Hydrology*, 101, 191-212.
- Wollast, R., and L. Chou, 1988, Rate control of weathering of silicate minerals at room temperature and pressure, in A. Lerman and M. Meybeck (eds.), *Physical and Chemical Weathering in Geochemical Cycles*, Kluwer Academic

Publishers, 11-32.

- Wood, W.W., 1962, *Distribution and Stratigraphic Position of Late Precambrian Diabase Dikes in Parts of Northern Michigan*, M.Sc. Thesis, Michigan State University, East Lansing, Michigan.
- Wright, R.F., 1984, Norwegian models for surface water chemistry: An overview, in *Modeling of Total Acid Precipitation Impacts*, J. L. Schnoor, Ed., Ann Arbor Science, p. 73-87.
- Wright, R.F., 1987, RAIN Project, Annual report for 1986, *Acid Rain Res. Rep 13*, Norwegian Institute for Water Research, Oslo, 89 pp.
- Wright, R.F., 1988, Influence of acid rain on weathering rates, in Lerman and Meybeck (eds.), *Physical and Chemical Weathering in Geochemical Cycles*, Kluwer Academic Publishers, 181-196.

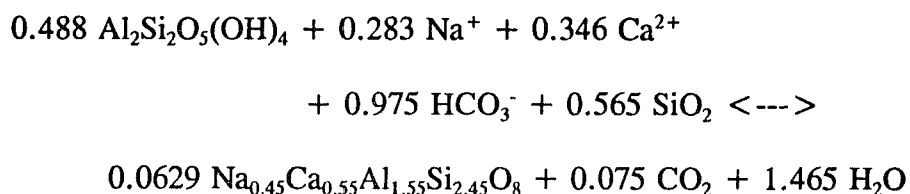
APPENDICES

Appendix A

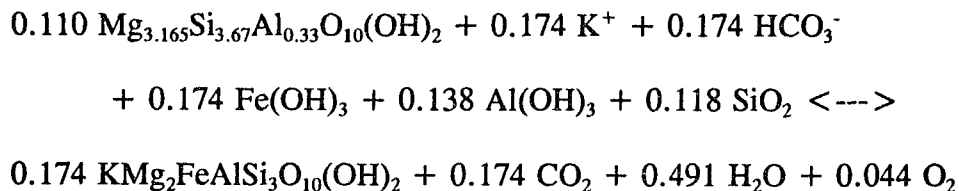
Reverse mineral weathering reactions used in Table 6 to reconstruct source minerals for dissolved solutes.

Peshekee Spring:

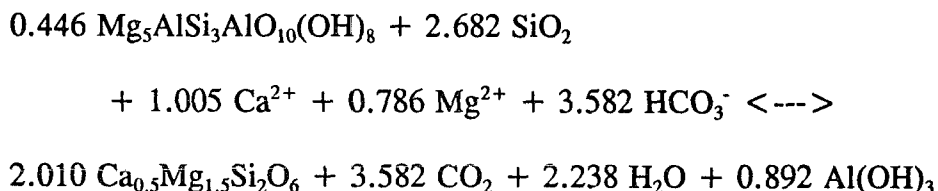
1. Kaolinite --> Plagioclase:



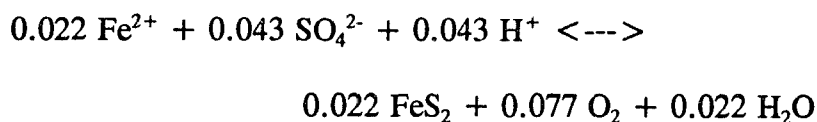
2. Saponite --> Biotite:



3. Clinocllore --> Pyroxene:

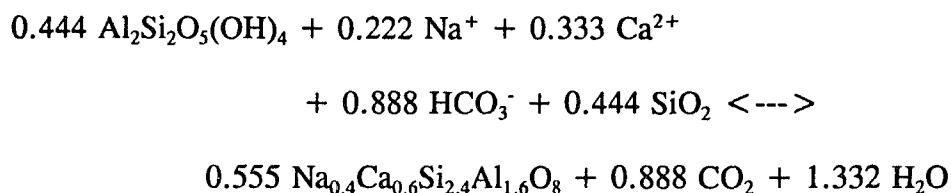


4. Form Pyrite:

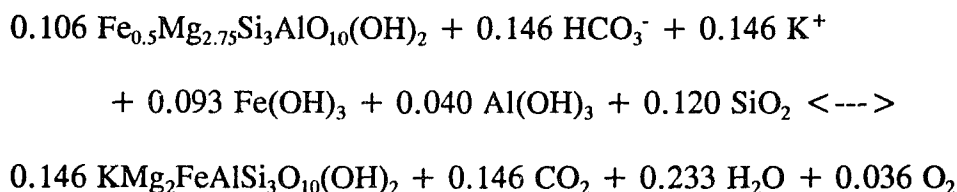


Yellow Dog Upper Spring:

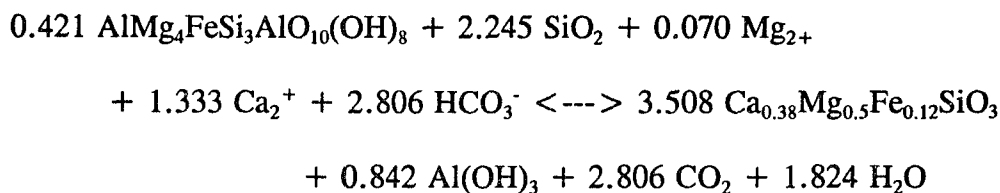
5. Kaolinite --> Plagioclase:



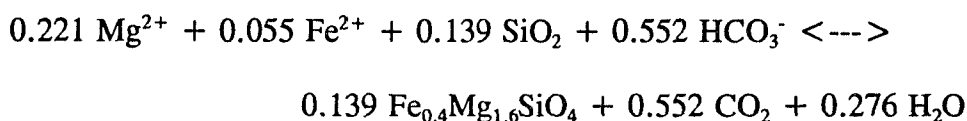
6. Vermiculite --> Biotite:



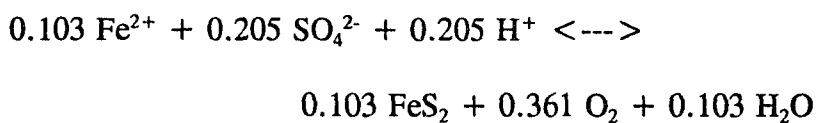
7. Clinocllore --> Pyroxene:



8. Form Olivine:

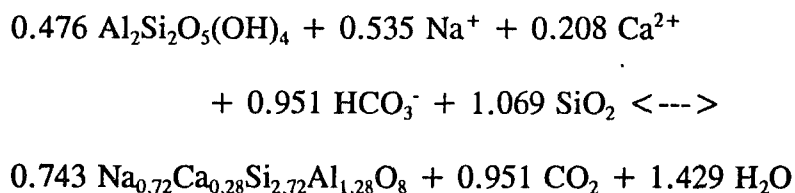


9. Form Pyrite:

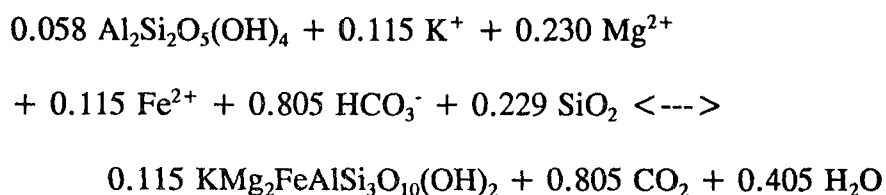


Yellow Dog Lower Spring:

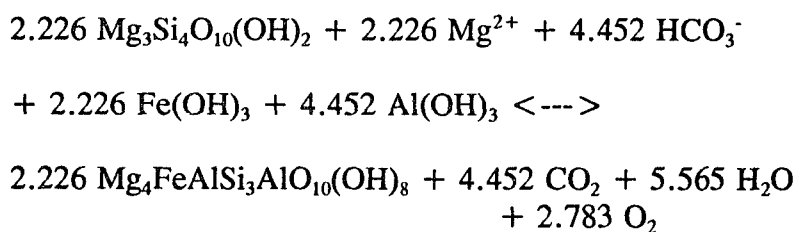
10. Kaolinite --> Plagioclase:



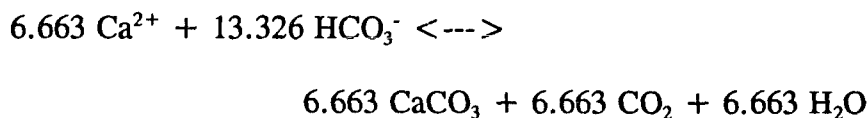
11. Kaolinite --> Biotite:



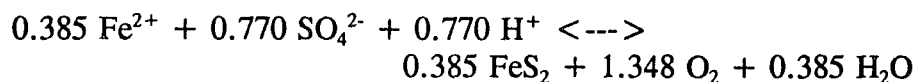
12. Talc --> Clinocllore:



13. Form Calcite:

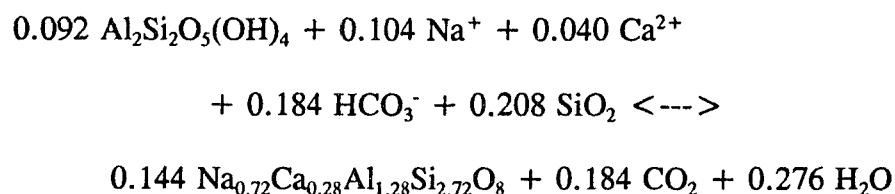


14. Form Pyrite:

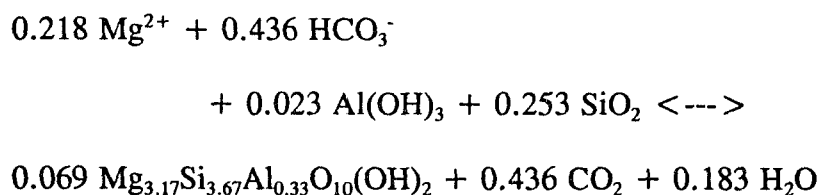


Peshekee Runoff:

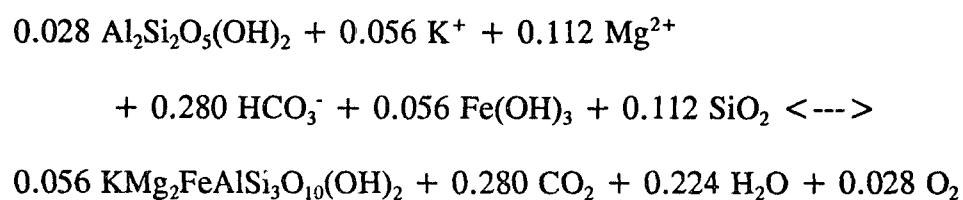
15. Kaolinite --> Plagioclase



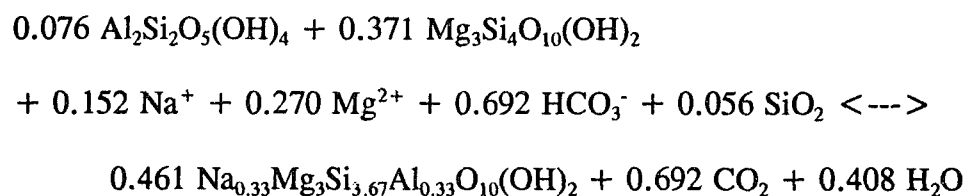
16. Form Saponite:

Yellow Dog Runoff:

17. Kaolinite --> Biotite:



18. Kaolinite + Talc --> Na-Saponite:



Appendix B

Complete aqueous chemical data for all water samples.

Table 8. Aqueous chemical data for Peshekee River, Site 1 (1988-1989).

Units: all solutes in mg/l, except DOC is mmol/l; temperature in ° C.

Date	pH	Alt	Alm	Alo	SiO2	Ali	Alp	Ca	Mg	K	Na	Temp	F	Cl	SO4	HCO3	PO4	NH3	NO3	Fe	Mn	DOC
7/27	7.3	0.018	0.0015		2.34		0.0165	8.51	2.14	0.63	1.05	20.0	0.03	1.400	3.50	26.246	0.008	0.043	0.414	0.33	0.027	0.544
8/3	6.8	0.062	0.0120		2.44		0.0500	7.20	1.87	0.82	0.83	20.5	0.04	1.200	4.80	13.122	0.019	0.038	1.217	0.40	0.066	0.787
8/10	6.5	0.104	0.0260	0.014	3.62	0.012	0.0780	7.75	1.79	0.51	0.74	18.0	0.05	1.200	5.10	14.736	0.023	0.043	0.318	0.58	0.032	1.301
8/17	6.2	0.125	0.0380		2.44		0.0870	6.39	1.51	0.53	0.68	20.0	0.06	1.200	6.00	9.842	0.031	0.065	1.273	0.56	0.034	1.192
8/23	6.6	0.158	0.0890		3.12		0.0690	5.69	1.32	0.37	0.63	19.5	0.04	1.200	3.00	13.123	0.030	0.049	0.796	0.69	0.038	1.490
8/31	6.5	0.112	0.0565	0.034	4.23	0.023	0.0495	5.52	1.33	0.31	0.68	13.3	0.03	1.000	4.50	6.561	0.025	0.043	1.037	0.54	0.018	1.409
9/7	6.7	0.130	0.0250	0.012	4.59	0.013	0.1050	5.62	1.34	0.35	0.74	10.0	0.05	1.200	3.00	10.662	0.025	0.046	0.148	0.49	0.010	1.328
9/14	6.7	0.069	0.0120		4.43		0.0570	6.25	1.47	0.37	0.79	12.0	0.05	1.400	4.71	13.123	0.013	0.043	2.472	0.42	0.011	1.138
9/20	6.5	0.069	0.0120	0.010	4.77	0.002	0.0570	6.08	1.43	0.44	1.18	15.0	0.05	2.475	3.47	13.123	0.016	0.043	0.046	0.49	0.010	1.071
9/28	6.3	0.135	0.0360	0.014	5.25	0.022	0.0990	4.96	1.26	0.39	0.83	10.5	0.06	1.858	4.65	16.404	0.013	0.041	0.097	0.45	0.008	1.307
10/5	6.0	0.148	0.0380	0.023	4.59	0.015	0.1100	4.59	1.10	0.47	0.89	6.0	0.03	1.858	3.60	8.202	0.012	0.049	0.392	0.56	0.022	1.260
10/12	5.4	0.156	0.0585	0.052	4.35	0.007	0.0975	4.39	1.02	0.30	0.64	4.5	0.04	1.704	3.72	3.280	0.011	0.049	0.079	0.54	0.017	1.301
10/19	6.0	0.161	0.0445	0.033	4.10	0.012	0.1155	4.30	1.02	0.34	0.75	6.0	0.03	2.167	3.65	8.202	0.011	0.049	0.073	0.47	0.011	1.199
10/26	5.9	0.136	0.0950	0.083	4.35	0.012	0.0410	3.65	0.91	0.33	0.60	2.0	0.02	2.784	3.47	5.249	0.010	0.043	0.109	0.42	0.015	1.172
11/2	6.1	0.144	0.0900	0.090	4.59	0.000	0.0540	3.65	0.92	0.26	0.65	0.5	0.03	1.704	2.23	6.561	0.009	0.054	0.148	0.39	0.017	1.138
11/6	5.7	0.164	0.1420		4.35		0.0220	3.15	0.81	0.40	0.52	0.5	0.03	2.670	5.33	4.921	0.012	0.049	0.190	0.34	0.025	0.976
11/9	5.7	0.159	0.1010	0.098	4.26	0.003	0.0570	3.03	0.77	0.29	0.48	1.3	0.04	1.704	2.85	4.101	0.011	0.051	0.089	0.32	0.025	1.037
11/15	6.1	0.140	0.1300	0.100	4.36	0.030	0.0100	3.18	0.78	0.24	0.58	1.5	0.03	2.090	4.59	4.921	0.011	0.049	0.109	0.38	0.018	0.780
11/16	6.1	0.156	0.1380	0.105	3.86	0.033	0.0180	2.88	0.72	0.30	0.50	2.5	0.03	4.173	4.15	4.101	0.012	0.046	0.125	0.35	0.018	0.868
11/23	5.6	0.151	0.1140	0.114	4.53	0.000	0.0370	2.97	0.72	0.21	0.50	1.0	0.03	1.858	4.59	2.460	0.013	0.049	0.064	0.34	0.021	1.030
11/30	5.9	0.165	0.1040	0.104	4.84	0.000	0.0560	3.03	0.73	0.19	0.50	0.6	0.03	1.549	4.40	4.921	0.011	0.049	0.083	0.34	0.019	1.024
12/7	6.1	0.170	0.1150	0.082	5.45	0.033	0.0550	3.42	0.84	0.22	0.60	0.3	0.03	1.704	4.96	5.741	0.010	0.049	1.140	0.34	0.019	0.868
12/15	6.0	0.155	0.1110	0.081	6.19	0.030	0.0440	3.66	0.88	0.24	0.65	0.3	0.04	1.704	5.14	7.381	0.013	0.043	0.240	0.40	0.018	0.929
12/21	5.8	0.168	0.0950	0.095	6.37	0.000	0.0730	3.89	0.93	0.32	0.75	0.0	0.03	1.627	4.28	7.381	0.015	0.043	0.120	0.41	0.019	0.922
12/31	6.4	0.142			6.06			4.00	0.95	0.27	0.63	0.0	0.02	3.093	5.02	8.202	0.012	0.041	0.280	0.39	0.015	0.895
1/5	6.3	0.168	0.0930	0.093	6.80	0.000	0.0750	4.31	1.09	0.30	0.91	0.0	0.03	1.858	5.08	9.022	0.012	0.049	1.391	0.50	0.013	0.976
1/11	6.0	0.165	0.1240	0.106	7.17	0.018	0.0410	4.31	1.13	0.29	0.71	0.0	0.03	2.012	4.71	9.022	0.012	0.054	0.232	0.46	0.012	0.976
1/19	6.1	0.135	0.0870	0.085	7.17	0.002	0.0480	4.34	1.12	0.28	0.65	0.0	0.03	1.935	4.71	9.842	0.012	0.054	0.180	0.17	0.011	0.801
1/25	6.1	0.094	0.0890	0.083	7.23	0.006	0.0390	4.54	1.17	0.35	0.78	0.0	0.03	2.630	4.09	10.662	0.010	0.049	0.140	0.50	0.012	0.963
2/1	6.0	0.100	0.0870	0.087	7.63	0.000	0.0460	4.68	1.21	0.30	0.72	0.0	0.03	4.019	3.84	11.482	0.010	0.049	0.129	0.50	0.013	0.949

Table 8 (cont'd).

2/10	6.1	0.086	0.0995	0.098	7.41	0.002	0.0265	4.65	1.25	0.31	0.77	0.0	0.04	1.781	4.28	13.943	0.015	0.076	0.170	0.45	0.010	0.936
2/15	5.9	0.082	0.0740	0.073	7.05	0.001	0.0580	4.70	1.23	0.34	0.74	0.0	0.03	2.938	4.46	10.662	0.009	0.070	0.261	0.21	0.006	0.828
2/22	6.0	0.098	0.0600		6.95		0.0750	5.90	1.57	0.42	0.89	0.0	0.03	1.704	5.64	13.123	0.009	0.070	0.256	0.22	0.008	0.942
3/2	6.1	0.083	0.0925	0.089	7.40	0.003	0.0355	4.98	1.34	0.37	0.78	0.0	0.03	1.395	4.59	15.583	0.013	0.065	0.169	0.46	0.009	0.868
3/16	6.1	0.090			6.98			4.74	1.26	0.37	0.77	0.0	0.03	1.241	4.09	13.943	0.010	0.054	0.473	0.22	0.003	0.692
3/22	6.2	0.087	0.1130	0.096	8.27	0.017	0.0060	4.90	1.30	0.37	0.73	0.3	0.03	2.012	4.09	13.943	0.010	0.059	0.191	0.47	0.010	0.909
3/27	4.8	0.110	0.0810	0.077	7.18	0.004	0.0290	3.55	1.13	0.35	0.71	0.5	0.03	1.940	4.71	13.280	0.013	0.081	0.443	0.38	0.021	0.821
3/29	5.8	0.126	0.0860	0.079	5.57	0.007	0.0400	4.20	0.94	0.39	0.61	0.5	0.04	1.650	4.09	8.202	0.011	0.076	0.604	0.31	0.031	0.841
3/30	5.7	0.110	0.1240	0.120	6.55	0.004	0.0210	3.47	0.92	0.37	0.62	0.5	0.03	1.241	5.02	6.725	0.010	0.059	0.524	0.33	0.028	0.961
4/5	5.8	0.125	0.1610	0.129	5.82	0.032		3.48	0.81	0.36	0.58	0.0	0.03	2.861	4.71	6.561	0.011	0.054	0.392	0.34	0.027	0.976
4/12	5.9	0.124	0.1280	0.126	3.73	0.002	0.0260	3.10	0.81	0.34	0.61	0.8	0.03	1.241	4.15	6.151	0.012	0.049	0.211	0.33	0.024	0.990
4/19	6.1	0.140	0.1380	0.126	4.97	0.012		2.73	0.70	0.36	0.73	1.8	0.03	1.009	4.71	5.741	0.013	0.043	0.261	0.26	0.024	0.882
4/26	5.7	0.149	0.1470	0.129	3.61	0.018		2.01	0.52	0.36	0.55	2.5	0.03	0.932	5.02	3.690	0.013	0.043	0.544	0.18	0.025	0.814
5/3	5.7	0.113	0.1020	0.092	3.24	0.010	0.0110	2.15	0.55	0.29	0.48	7.8	0.03	0.932	3.16	4.511	0.012	0.038	0.186	0.21	0.012	0.834
5/10	5.9	0.117	0.1050	0.078	2.26	0.027	0.0120	2.35	0.58	0.29	0.50	11.5	0.03	1.549	4.09	4.921	0.012	0.038	0.100	0.22	0.014	0.895
5/17	6.1	0.119	0.1180	0.109	1.39	0.009		2.80	0.65	0.30	0.50	15.0	0.03	1.086	3.47	7.381	0.010	0.038	0.028	0.30	0.014	1.030
5/24	6.2	0.121			1.89			3.55	0.87	0.35	0.52	16.5	0.03	1.549	2.54	9.022	0.013	0.038	0.064	0.40	0.020	1.152
6/1	6.1	0.126	0.0640	0.035	1.90	0.029	0.0620	3.70	0.90	0.29	0.59	15.3	0.03	5.099	2.85	9.432	0.024	0.043	0.967	0.43	0.018	1.138
6/9	5.9	0.177	0.0740	0.068	2.81	0.006	0.1030	2.76	0.65	0.29	0.41	9.0	0.03	1.395	1.52	5.331	0.013	0.049	1.594	0.42	0.026	1.253
6/14	6.2	0.178	0.0720	0.072	2.76	0.000	0.1060	2.69	0.66	0.17	0.51	11.0	0.03	1.241	3.04	4.921	0.009	0.043	0.044	0.45	0.019	1.267
6/22	6.6	0.146	0.0690	0.065	2.42	0.004	0.0770	3.52	0.84	0.24	0.51	20.3	0.05	2.784	2.23	9.022	0.009	0.038	0.032	0.46	0.021	1.165
6/28	6.2	0.146	0.0730	0.073	3.27	0.000	0.0730	3.93	0.90	0.21	0.54	17.8	0.04	5.253	1.62	9.842	0.010	0.043	0.032	0.57	0.019	1.361
7/5	6.5	0.085	0.0430	0.042	3.51	0.001	0.0420	4.88	1.15	0.29	0.66	20.5	0.03	3.401	2.61	13.943	0.010	0.038	0.059	0.59	0.021	1.199
7/14	6.5	0.105	0.0490	0.046	4.35	0.003	0.0560	5.98	1.54	0.38	0.87	20.0	0.05	1.858	3.47	16.404	0.009	0.038	0.837	0.83	0.018	0.976
7/20	6.5	0.058			3.27			5.48	1.35	0.36	0.74	24.5	0.04	1.549	3.35	18.864	0.008	0.030	0.015	0.59	0.016	0.787
7/26	7.0	0.041	0.0060	0.006	4.35	0.000	0.0350	7.07	1.73	0.47	1.14	24.4	0.04	1.858	3.47	22.965	0.005	0.027	0.005	0.49	0.021	0.699

Table 9. Aqueous chemical data for Peshekee River, Site 3 (1988-1989).

Units: all solutes in mg/l; temperature °C.

pH	Date	Temp	Alt	Alm	F	Ca	Mg	Na	K	SO4	Cl	Si	PO4	NH3	NO3	Fe	Mn	HCO3
7.40	7/27	24.0	0.018	0.007	0.040	11.36	2.31	1.08	0.64	3.200	1.000	2.44	0.010	0.032	0.949	0.25	0.028	29.5
6.90	8/3	22.0	0.033	0.014	0.061	11.11	2.29	0.88	0.61	3.000	1.000	3.31	0.010	0.048	0.532	0.27	0.020	26.2
6.90	8/10	21.5	0.068	0.034	0.045	10.62	2.09	0.72	0.40	5.200	1.000	2.34	0.014	0.043	0.277	0.54	0.020	16.4
6.20	8/17	19.0	0.176	0.074	0.038	6.79	1.45	0.56	0.43	4.500	0.990	3.21	0.023	0.053	0.512	0.56	0.032	9.8
6.60	8/23	16.0	0.156	0.078	0.038	7.91	1.54	0.61	0.28	3.700	1.000	4.84	0.019	0.048	0.531	0.65	0.014	13.1
6.90	8/31	15.0	0.111	0.035	0.030	7.79	1.58	0.67	0.23	3.200	0.800	4.89	0.022	0.043	0.224	0.39	0.013	16.4
6.65	9/7	12.0	0.155	0.051	0.060	7.64	1.49	0.63	0.22	3.000	0.900	3.67	0.024	0.053	0.288	0.57	0.007	13.1
7.00	9/14	12.0	0.050	0.021	0.045	8.68	1.74	0.74	0.30	3.595	1.335	4.83	0.010	0.053	0.123	0.43	0.010	19.7
6.70	9/20	13.0	0.080	0.019	0.040	7.98	1.68	0.69	0.35	3.966	1.335	5.26	0.012	0.048	0.074	0.60	0.010	32.8
6.70	9/28	10.5	0.114	0.006	0.040	6.53	1.39	0.62	0.31	4.090	1.896	5.14	0.011	0.048	0.062	0.44	0.005	16.4
6.30	10/5	5.5	0.151	0.036	0.030	5.11	1.16	0.55	0.59	4.300	1.408	3.40	0.010	0.053	0.169	0.51	0.025	8.2
6.10	10/12	4.0	0.152	0.037	0.040	5.33	1.16	0.54	0.23	4.832	1.190	2.99	0.012	0.059	0.055	0.49	0.009	8.2
6.30	10/19	5.8	0.169	0.039	0.030	5.53	1.13	0.55	0.32	4.399	1.471	2.88	0.015	0.059	0.021	0.39	0.010	4.1
6.00	10/26	1.0	0.145	0.092	0.025	4.14	0.95	0.48	0.32	4.720	1.896	4.22	0.014	0.051	0.104	0.36	0.011	5.7
6.00	11/2	0.5	0.135	0.087	0.030	4.59	0.97	0.48	0.19	5.220	1.335	3.36	0.014	0.048	0.098	0.37	0.012	8.2
5.93	11/9	1.3	0.160	0.107	0.030	3.61	0.81	0.39	0.22	4.466	0.900	2.76	0.014	0.048	0.119	0.32	0.015	4.9
5.95	11/16	2.0	0.152	0.118	0.040	3.48	0.73	0.38	0.21	4.090	1.045	2.93	0.012	0.048	0.160	0.29	0.014	4.9
5.80	11/23	0.5	0.150	0.117	0.030	3.78	0.81	0.40	0.15	4.214	0.765	4.46	0.009	0.048	0.068	0.33	0.009	4.9
6.05	11/30	0.5	0.168	0.131	0.030	3.67	0.81	0.41	0.15	4.337	0.620	4.77	0.009	0.048	0.100	0.29	0.011	6.6
6.30	12/7	0.3	0.159	0.094	0.030	4.48	0.96	0.47	0.17	4.709	0.765	5.48	0.010	0.043	0.120	0.35	0.016	9.8
6.13	12/15	0.3	0.158	0.093	0.040	4.89	1.07	0.56	0.20	5.637	1.045	6.06	0.011	0.048	0.178	0.37	0.017	9.8
5.98	12/21	0.0	0.144	0.107	0.025	5.08	1.12	0.53	0.21	4.585	0.765	6.48	0.010	0.048	0.140	0.40	0.015	10.7
6.10	12/31	0.0	0.105		0.020	5.16	1.14	0.54	0.22	4.090	0.900	5.94	0.013	0.048	0.342	0.26	0.012	11.5
6.30	1/5	0.0	0.148	0.048	0.025	5.37	1.26	0.58	0.27	4.832	0.832	5.16	0.014	0.048	0.108	0.40	0.015	13.9
6.30	1/11	0.0	0.148	0.118	0.030	5.56	1.25	0.59	0.24	4.152	0.767	7.15	0.009	0.059	0.200	0.35	0.013	13.9
6.20	1/19	0.0	0.095	0.054	0.030	5.81	1.26	0.60	0.25	4.090	0.908	6.12	0.009	0.053	0.134	0.12	0.011	16.4
6.20	1/25	0.0	0.087	0.081	0.030	6.33	1.35	0.62	0.26	4.709	1.049	7.47	0.009	0.037	0.100	0.36	0.015	14.8
6.10	2/1	0.0	0.095	0.071	0.030	6.46	1.37	0.62	0.25	2.605	0.767	7.78	0.013	0.048	0.339	0.40	0.014	15.6
6.40	2/10	0.0	0.091	0.082	0.030	6.00	1.45	0.67	0.30	4.275	0.626	8.08	0.015	0.048	0.804	0.34	0.014	17.2
6.20	2/15	0.0	0.085	0.038	0.030	6.22	1.44	0.66	0.30	4.709	0.626	7.43	0.010	0.037	0.373	0.15	0.011	15.6
6.40	2/22	0.0	0.087	0.025	0.030	6.31	1.51	0.66	0.29	4.832	0.767	7.47	0.008	0.032	0.343	0.13	0.009	16.4
6.20	3/2	0.0	0.080	0.071	0.025	6.37	1.53	0.70	0.31	4.523	0.767	8.36	0.009	0.037	0.161	0.37	0.011	17.2
6.20	3/16	0.0	0.090		0.025	6.13	1.41	0.76	0.31	1.924	0.626	8.29	0.012	0.037	0.242	0.10	0.011	18.0
6.40	3/22	0.0	0.099		0.035	6.38	1.55	0.69	0.33	4.090	0.626	8.89	0.014	0.059	0.242	0.37	0.011	18.9
5.70	3/30	0.5	0.116	0.100	0.050	4.10	0.95	0.62	0.42	4.709	0.767	6.06	0.013	0.048	0.675	0.34	0.030	8.2
6.40	4/5	0.5	0.123	0.110	0.045	3.47	0.80	0.45	0.29	3.904	0.767	5.44	0.014	0.043	0.514	0.35	0.021	7.4
6.00	4/12	1.0	0.124	0.115	0.025	3.57	0.82	0.43	0.29	4.090	0.626	5.57	0.010	0.037	5.961	0.42	0.019	8.2
5.90	4/19	1.8	0.101	0.098	0.025	3.06	0.77	0.46	0.28	4.894	0.626	4.77	0.011	0.043	0.524	0.26	0.015	7.4
5.65	4/26	2.8	0.099	0.092	0.030	2.00	0.51	0.30	0.24	3.595	0.485	3.13	0.011	0.048	0.403	0.18	0.012	4.1
5.70	5/3	7.5	0.113	0.096	0.025	2.31	0.57	0.33	0.19	3.966	0.767	3.11	0.010	0.048	5.659	0.20	0.005	4.9
5.70	5/10	9.0	0.108	0.097	0.023	2.40	0.57	0.33	0.18	4.090	0.767	2.00	0.010	0.043	0.139	0.15	0.003	4.9

Table 9 (cont'd).

6.10	5/17	15.0	0.107	0.100	0.030	3.17	0.71	0.37	0.21	2.543	0.767	0.84	0.012	0.045	0.021	0.39	0.012	8.2
6.20	5/24	16.3	0.123	0.087	0.025	4.20	0.94	0.51	0.30	2.620	0.908	1.46	0.017	0.048	0.109	0.44	0.005	10.7
6.30	6/1	15.3	0.119	0.040	0.030	4.65	1.06	0.60	0.25	0.996	0.908	1.70	0.010	0.043	0.016	0.42	0.005	12.3
5.90	6/9	8.5	0.163	0.064	0.030	3.28	0.75	0.36	0.18	0.996	0.838	2.62	0.016	0.048	0.400	0.44	0.009	6.6
6.40	6/14	9.8	0.159	0.077	0.030	3.22	0.76	0.37	0.06	0.996	2.035	2.01	0.006	0.043	0.039	0.44	0.007	6.6
6.80	6/22	19.5	0.117	0.035	0.044	5.10	1.17	0.53	0.14	0.996	1.049	1.70	0.009	0.043	0.017	0.42	0.012	14.8
6.40	6/28	18.0	0.100	0.047	0.030	5.74	1.33	0.57	0.20	0.686	1.190	2.99	0.012	0.043	0.077	0.56	0.007	15.6
6.70	7/5	21.5	0.079	0.013	0.040	7.01	1.61	0.64	0.23	1.373	1.049	3.73	0.015	0.032	0.188	0.72	0.006	20.9
6.70	7/14																	
6.70	7/20	25.5	0.048	0.010	0.042	8.13	1.90	0.90	0.39	3.780	0.978	4.52	0.010	0.032	0.020	0.45	0.003	31.2
7.10	7/26	24.4	0.025	0.004	0.042	8.68	2.00	0.86	0.43	4.399	0.908	4.71	0.007	0.032	0.044	0.47	0.017	27.1

Table 10. Aqueous chemical data for Peshekee River, Site 4 (1988-1989).

Units: all solutes in mg/l; temperature °C.

pH	Date	Temp	Ca	Mg	Na	K	Cl	SO4	Fe	SiO2	NH4	PO4	Alm	F	NO3	Mn	Alt
7.10	7/28	21.0	19.78	3.87	1.00	0.30	1.200	1.000	0.17	4.120	0.021	0.005	0.005	0.03	0.393	0.061	0.012
7.00	8/3	19.5	19.29	2.51	0.97	0.42	1.400	1.500	0.33	3.310	0.021	0.009	0.020	0.06	0.664	0.029	0.050
6.70	8/10	23.0	11.10	2.21	0.69	0.29	1.000	2.500	0.42	2.650	0.024	0.015	0.047	0.05	0.554	0.030	0.085
5.25	8/17	18.0	6.68	1.46	0.53	0.50	0.880	4.850	0.44	2.140	0.032	0.021	0.084	0.04	1.169	0.041	0.157
6.50	8/24	16.3	7.95	1.61	0.60	0.26	0.800	3.500	0.48	4.170	0.029	0.018	0.078	0.03	0.410	0.042	0.130
6.50	8/31	17.5	8.17	1.58	0.63	0.15	0.800	4.000	0.40	3.060	0.027	0.019	0.055	0.03	0.462	0.010	0.113
6.10	9/7	14.0	7.33	1.43	0.64	0.12	1.000	4.000	0.35	3.820	0.027	0.017	0.059	0.03	0.116	0.004	0.155
6.60	9/14	13.0	7.75	1.65	0.70	0.21	1.049	3.966	0.25	4.406	0.027	0.006	0.022	0.08	1.270	0.004	0.087
6.40	9/21	12.0	7.34	1.52	0.69	0.35	1.190	4.832	0.32	4.222	0.027	0.006	0.010	0.04	0.036	0.003	0.083
6.60	9/28	10.8	6.61	1.37	0.62	0.27	1.200	5.327	0.32	4.280	0.021	0.007	0.006	0.03	0.038	0.008	0.109
6.00	10/5	5.5	5.26	1.10	0.51	0.58	1.471	5.946	0.36	3.854	0.027	0.012	0.040	0.03	0.092	0.010	0.129
6.10	10/1	3.8	5.59	1.14	0.56	0.29	1.049	5.946	0.35	3.732	0.027	0.014	0.044	0.03	0.038	0.008	0.143
6.20	10/19	5.3	5.30	1.12	0.56	0.40	1.471	5.327	0.29	3.842	0.021	0.013	0.021	0.03	0.007	0.004	0.175
5.45	10/26	1.0	3.92	0.84	0.44	0.30	3.302	4.709	0.40	3.351	0.027	0.012	0.092	0.03	0.058	0.009	0.152
5.70	11/9	1.0	3.67	0.78	0.39	0.23	1.049	4.220	0.40	3.891	0.021	0.012	0.130	0.03	0.069	0.014	0.160
5.80	11/16	2.0	3.25	0.64	0.34	0.15	0.908	4.585	0.36	3.719	0.027	0.012	0.120	0.03	0.119	0.013	0.125
5.50	11/23	0.5	3.67	0.72	0.38	0.15	0.767	4.337	0.39	4.014	0.027	0.014	0.142	0.03	0.079	0.012	0.145
5.90	11/30	0.3	3.71	0.75	0.40	0.14	0.767	3.842	0.38	4.468	0.027	0.014	0.120	0.03	0.094	0.011	0.132
5.85	12/7	0.3	4.30	0.91	0.44	0.17	0.908	4.461	0.40	4.959	0.027	0.013	0.087	0.03	0.110	0.018	0.148
5.80	12/21	0.0	4.76	1.07	0.54	0.25	0.626	3.780	0.43	5.879	0.032	0.012	0.111	0.03	0.161	0.034	0.156
6.30	12/31	0.0	5.15	1.18	0.58	0.28	0.767	4.275	0.44	6.369	0.048	0.017		0.02	1.808	0.044	0.136
6.10	1/5	0.0	5.49	1.17	0.54	0.23	0.767	4.585	0.48	6.829	0.032	0.014	0.098	0.03	0.139	0.024	0.168
6.10	1/11	0.0	5.40	1.22	0.59	0.28	0.767	4.399	0.48	7.020	0.027	0.012	0.101	0.03	0.211	0.040	0.152
6.03	1/19	0.0	6.16	1.25	0.57	0.27	1.330	4.585	0.26	6.860	0.032	0.011	0.085	0.03	0.171	0.032	0.132
6.10	1/25	0.0	6.36	1.35	0.64	0.30	1.049	4.399	0.52	6.443	0.037	0.012	0.088	0.03	0.317	0.039	0.094
5.85	2/1	0.0	6.49	1.35	0.62	0.29	0.767	4.337	0.51	7.780	0.037	0.014	0.097	0.03	0.166	0.039	0.100
6.10	2/10	0.0	6.56	1.52	0.73	0.36	0.767	5.204	0.53	8.302	0.027	0.015	0.100	0.03	0.731	0.040	0.102
6.20	2/22	0.0	7.11	1.65	0.73	0.39	0.908	5.705	0.42	7.657	0.048	0.013	0.039	0.03	0.978	0.023	0.100
6.10	3/22	0.0	5.95	1.47	0.71	0.42	0.767	3.230	0.52	8.762	0.032	0.014	0.080		1.009	0.023	0.103
5.70	3/30	0.5	3.79	0.91	0.45	0.37	0.697	4.709	0.35	5.695	0.027	0.014	0.112	0.03	0.827	0.044	0.116
5.90	4/5	0.3	3.34	0.79	0.49	0.39	0.767	5.018	0.35	5.940	0.027	0.013	0.119	0.03	2.019	0.026	0.125
5.85	4/12	0.3	3.67	0.87	0.47	0.34	0.767	4.090	0.39	6.185	0.027	0.014	0.111	0.03	3.028	0.017	0.117
5.95	4/19	1.0	3.05	0.72	0.41	0.30	0.767	4.090	0.30	4.713	0.021	0.015	0.090	0.03	0.372	0.016	0.097
5.70	5/10	8.5	2.32	0.51	0.34	0.26	0.626	3.780	0.13	1.646	0.021	0.014	0.082	0.02	0.241	0.002	0.111
5.90	5/17	16.5	3.45	0.73	0.37	0.30	0.626	2.543	0.31	0.603	0.021	0.015	0.102	0.03	0.013	0.026	0.109
5.80	5/24	17.5	4.41	0.93	0.45	0.35	0.767	1.181	0.34	0.665	0.027	0.016	0.098	0.03	0.007	0.047	0.122
6.15	6/1	15.5	4.67	1.01	0.53	0.24	0.767	0.996	0.32	1.033	0.027	0.014	0.035	0.03	0.038	0.030	0.133
5.90	6/15	10.0	3.38	0.77	0.36	0.04	0.838	1.305	0.25	1.707	0.032	0.007	0.067	0.03	0.007	0.011	0.154
6.50	6/22	21.0	5.14	1.11	0.45	0.13	0.908	1.992	0.35	0.922	0.021	0.009	0.050	0.04	0.001	0.046	0.110
6.00	6/28	18.5	5.31	1.00	0.40	0.11	0.908	1.373	0.45	2.137	0.024	0.008	0.076	0.04	0.007	0.036	0.125
6.40	7/5	22.0	6.76	1.47	0.51	0.18	0.943	1.373	0.41	2.260	0.021	0.007	0.037	0.03	0.041	0.050	0.079
6.70	7/20	24.5	10.71	2.39	0.72	0.23	1.612	1.305	0.67	2.763	0.021	0.015		0.04	0.004	0.052	0.067
6.65	7/26	22.5	13.80	2.86	2.34	0.33	1.049	1.615	0.51	4.357	0.024	0.013	0.005	0.04	0.009	0.097	0.060

Table 11. Aqueous chemical data, Peshekee Spring (1988-1989).

Units: all solutes in mg/l; temperature °C.

Date	Temp	pH	Ca	Mg	Na	K	Cl	SO4	Fe	SiO2	HCO3	NH4	PO4	Alm	F	NO3	Alt
8/10	11.	5.20	5.64	1.99	0.80	0.73	1.000	6.200	0.025	6.520	20.0	0.037	0.01	0.008	0.040	2.112	0.03
8/17	10.	5.55	6.00	2.03	0.81	0.83	0.990	6.200	0.023	4.480	32.0	0.027	0.01	0.010	0.032	0.949	0.03
8/31	10.	5.85	6.53	2.01	0.81	0.77	1.100	6.200	0.024	4.840	26.0	0.037	0.01	0.014	0.035	0.109	0.03
9/14	8.	6.75	6.57	2.03	0.81	0.82	1.000	6.256	0.028	6.420	20.0	0.027	0.01	0.004	0.035	0.135	0.01
9/28	9.	6.30	6.25	2.07	0.81	0.93	1.400	5.946	0.023	7.950	24.0	0.027	0.01	0.002	0.040	0.050	0.01
10/5	8.	6.30	6.29	2.02	0.81	0.93	0.274	5.946	0.024	8.886	24.0	0.027	0.01	0.001	0.030	0.122	0.01
10/12	7.	6.20	6.65	2.07	0.80	0.93	0.345	6.441	0.028	8.886	24.0	0.032	0.01	0.004	0.030	0.035	0.01
10/19	7.	6.20	6.65	2.07	0.82	0.96	0.485	5.637	0.034	9.131	24.0	0.029	0.01	0.002	0.040	0.030	0.03
10/26	7.	6.20	6.34	2.07	0.80	0.96	0.908	4.709	0.033	8.640	26.0	0.027	0.01	0.005	0.025	0.038	0.03
11/2	7.	6.30	6.39	2.08	0.78	0.95	0.485	6.256	0.022	8.702	30.0	0.027	0.01	0.010	0.020	0.042	0.04
11/9	7.	6.60	6.60	2.09	0.82	0.96	0.485	5.327	0.030	8.640	26.0	0.029	0.01	0.014	0.050	0.030	0.03
11/16	6.	6.30	6.38	2.05	0.77	0.94	0.345	6.813	0.022	8.456	24.0	0.032	0.01	0.015	0.030	0.023	0.03
11/23	6.	6.00	6.49	2.03	0.79	0.98	0.345	6.256	0.022	8.370	24.0	0.037	0.01	0.016	0.035	0.027	0.03
11/30	6.	6.40	6.27	2.02	0.72	0.92	0.274	6.565	0.020	8.610	24.0	0.037	0.01	0.013	0.025	0.031	0.05
12/7	6.	6.40	6.33	2.01	0.71	0.91	0.485	6.256	0.019	8.395	22.0	0.035	0.01	0.007	0.025	0.013	0.03
12/15	4.	6.40	6.08	1.95	0.73	0.91	0.767	6.256	0.014	8.333	22.0	0.035	0.01	0.008	0.030	0.035	0.03
12/21	5.	6.10	6.01	1.92	0.71	0.91	0.485	6.070	0.010	8.333	26.0	0.037	0.01	0.008	0.030	0.030	0.03
12/31	5.	6.40	5.41	1.84	0.67	0.87	0.626	5.637	0.010	7.192	24.0	0.037	0.01		0.020	0.038	0.02
1/5	4.	6.40	5.74	1.88	0.76	0.94	0.626	6.070	0.011	8.211	24.0	0.035	0.00	0.009	0.025	0.020	0.02
1/11	4.	6.40	5.73	1.94	0.71	0.92	0.485	6.256	0.018	8.333	22.0	0.037	0.01	0.007	0.020	0.023	0.02
1/19	4.	6.40	6.09	1.90	0.71	0.96	1.330	5.637	0.002	2.137	24.0	0.032	0.01	0.001	0.025	0.601	0.02
1/25	4.	6.20	6.07	1.94	0.71	0.91	1.049	5.699	0.016	8.211	22.0	0.027	0.01	0.007	0.025	0.038	0.02
2/1	4.	6.20	5.92	1.93	0.72	0.92	1.612	6.194	0.017	8.149	24.0	0.027	0.01	0.019	0.030	0.037	0.03
2/10	3.	6.20	5.53	1.94	0.77	0.90	0.485	5.946	0.018	8.149	24.0	0.027	0.01	0.025	0.030	0.045	0.03
2/15	3.	6.30	5.64	1.90	0.78	1.02	0.345	6.565	0.005	8.192	22.0	0.037	0.01	0.001	0.025	0.125	0.01
4/5	3.	6.30	5.93	1.95	0.75	0.96	0.415	6.256	0.019	8.162	24.0	0.037	0.01	0.017	0.025	0.085	0.02
4/19	4.	6.40	5.69	1.94	0.72	0.91	0.345	6.256	0.019	8.162	22.0	0.037	0.01		0.020	0.099	0.02
5/3	6.	6.20	5.59	1.98	0.70	0.88	0.345	5.327	0.007	8.272	24.0	0.032	0.01		0.030	0.102	0.01
5/17	6.	6.20	5.52	1.95	0.72	0.90	0.345	9.040	0.018	8.211	24.0	0.032	0.01	0.022	0.015	0.052	0.03
6/22	6.	6.40	5.22	1.79	0.67	0.73	0.274	5.327	0.019	8.137	22.0	0.035	0.01		0.035	0.045	0.04

Table 12. Aqueous chemical data, Yellow Dog River, Site 1 (1988-1989).

Units: all solutes in mg/l, except DOC in mmol/l; temperature °C.

pH	Alt	Date	SiO2	Alm	AlO	Ali	Ca	Mg	K	Na	Cl	SO4	F	HCO3	PO4	NH3	NO3	Fe	Mn	DOC	Alp
7.8	0.032	7/28	5.540	0.010			21.61	3.94	0.61	1.06	1.600	5.000	0.04	67.256	0.012	0.016	0.726	0.13	0.01	0.005	0.022
7.6	0.047	8/4	5.050	0.007			15.00	2.89	0.81	0.86	1.600	3.000	0.04	34.448	0.016	0.027	0.483	0.18	0.01	1.090	0.040
7.7	0.044	8/11	3.670	0.014	0.01	0.005	19.92	3.70	0.60	1.02	1.000	1.800	0.05	52.492	0.012	0.032	0.494	0.27	0.01	0.272	0.030
6.5	0.045	8/17	4.560																		
6.5	0.050	8/25	5.610	0.006			15.74	3.07	0.54	0.95	1.200	1.000	0.04	44.290	0.016	0.037	0.341	0.27	0.01	1.000	0.044
7.4	0.037	9/1	6.520	0.010	0.01	0.0000	17.76	3.38	0.55	0.95	1.200	2.300	0.05	49.212	0.014	0.037	0.287	0.27	0.01	0.909	0.027
7.0	0.053	9/8	6.880	0.007	0.01	0.0005	16.52	3.13	0.51	0.94	1.200	3.000	0.06	39.369	0.012	0.032	0.246	0.29	0.01	0.545	0.046
6.9	0.025	9/15	7.657	0.007			18.93	3.59	0.57	1.01	1.206	4.709	0.02	45.931	0.007	0.027	0.191	0.27	0.01	0.045	0.018
7.1	0.042	9/22	7.559	0.006	0.01	0.0010	16.74	3.28	0.60	1.43	1.275	4.585	0.04	42.650	0.007	0.027	0.429	0.29	0.01	0.454	0.036
7.4	0.048	9/29	7.473	0.006	0.01	0.0005	15.61	3.01	0.57	0.93	1.001	4.399	0.04	49.212	0.007	0.029	0.100	0.27	0.01	0.727	0.042
6.9	0.088	10/5	6.155	0.008			9.43	1.95	0.56	0.73	1.069	6.070	0.03	32.808	0.010	0.032	0.116	0.25	0.01	1.500	0.080
7.0	0.076	10/13	9.344	0.005	0.00	0.0005	12.07	2.51	0.46	0.81	0.932	5.328	0.04	39.369	0.010	0.037	0.049	0.27	0.01	0.977	0.071
7.0	0.078	10/20	6.093	0.011	0.00	0.0065	10.85	2.16	0.48	0.79	1.069	6.194	0.02	31.167	0.012	0.032	0.028	0.28	0.01	1.227	0.068
6.8	0.075	10/27	5.584	0.025	0.03	0.0000	8.45	1.70	0.44	0.70	1.069	4.028	0.03	21.325	0.012	0.037	0.089	0.29	0.01	1.750	0.050
6.7	0.066	11/3	6.247	0.022	0.02	0.0000	10.18	2.04	0.40	0.77	0.932	2.543	0.05	26.246	0.010	0.032	0.181	0.26	0.01	1.272	0.044
6.7	0.137	11/10	5.204	0.044	0.04	0.0000	6.65	1.35	0.39	0.60	0.932	3.162	0.02	26.246	0.010	0.032	0.089	0.22	0.01	1.590	0.093
6.7	0.121	11/17	4.492	0.124	0.12	0.0040	4.91	0.97	0.37	0.52	1.343	5.080	0.01	11.482	0.008	0.032	0.269	0.20	0.01	1.545	0.003
7.1	0.078	11/24	6.124	0.056	0.05	0.0085	9.27	1.86	0.38	0.72	0.932	4.090	0.05	24.606	0.008	0.037	0.321	0.22	0.01	1.204	0.022
7.2	0.094	12/1	5.928	0.035	0.03	0.0060	8.28	1.66	0.37	0.95	0.932	5.018	0.03	22.965	0.007	0.032	0.109	0.23	0.01	1.204	0.059
7.2	0.035	12/8	6.566	0.008	0.01	0.0015	10.84	2.14	0.41	0.82	0.864	4.709	0.03	26.246	0.010	0.032	0.152	0.17	0.02	0.727	0.027
7.2	0.049	12/16	7.351	0.013	0.01	0.0000	12.22	2.44	0.45	0.85	1.001	5.451	0.03	34.448	0.012	0.027	0.100	0.19	0.01	0.431	0.037
7.3	0.049	12/22	7.044	0.015	0.01	0.0015	11.46	2.32	0.43	0.83	1.138	4.337	0.04	35.268	0.010	0.037	0.383	0.21	0.01	0.545	0.034
7.3	0.034	1/1	7.228	0.015			13.33	2.58	0.45	0.84	0.795	4.832	0.03	39.369	0.014	0.032	0.117	0.17	0.01	0.409	0.019
7.2	0.055	1/6	7.903	0.016	0.01	0.0015	13.75	2.56	0.45	0.88	0.727	4.956	0.05	36.909	0.007	0.043	0.161	0.20	0.01	0.363	0.040
7.2	0.036	1/12	7.473	0.019	0.02	0.0035	13.52	2.61	0.46	0.89	0.658	5.018	0.03	41.830	0.007	0.032	0.182	0.20	0.01	0.363	0.017
7.2	0.040	1/20	6.836			0.0000	13.28	2.58	0.43	0.82	1.823	4.709	0.03	37.729	0.008	0.027	0.151	0.20	0.01	0.022	0.040
7.1	0.044	1/27	7.749	0.010	0.01	0.0020	14.80	2.81	0.49	0.91	2.987	4.214	0.04	43.470	0.008	0.037	0.141	0.22	0.01	0.090	0.035
7.1	0.046	2/2	8.160	0.027	0.03	0.0000	16.03	2.03	0.51	0.99	1.206	5.575	0.04	49.212	0.008	0.048	0.182	0.22	0.02	0.227	0.019
6.7	0.053	2/11	7.792	0.053	0.00	0.0481	15.35	2.97	0.49	0.93	0.795	4.709	0.05	39.369	0.008	0.037	0.877	0.15	0.01	0.090	0.001
7.0	0.047	2/16	8.148	0.007	0.01	0.0020	16.62	3.19	0.51	0.96	0.864	4.337	0.04	47.571	0.009	0.037	0.200	0.17	0.02	0.090	0.040
7.2	0.022	2/23	8.026	0.009			10.23	3.03	0.49	0.96	1.069	3.347	0.03	54.133	0.007	0.037	0.161	0.10	0.02	0.005	0.013
7.2	0.028	3/2		0.007																	
7.2		3/9		0.020																	
7.1	0.030	3/16		0.018																	
7.1	0.041	3/22		0.040	0.03	0.0050															
5.7	0.077	3/27	5.790	0.044	0.03	0.0170	8.90	1.87	0.41	0.82	0.440	5.950	0.03	16.400	0.010	0.027	0.353	0.12	0.01	0.272	0.033
6.1	0.124	3/29	4.840	0.053	0.05	0.0030	6.63	1.44	0.41	0.74	0.320	5.330	0.04	18.040	0.008	0.027	0.469	0.12	0.01	0.954	0.071
6.8	0.106	4/1	6.308	0.064	0.06	0.0040	7.93	1.70	0.42	0.70	1.275	5.080	0.04	22.965	0.008	0.037	0.171	0.15	0.01	1.090	0.043
6.4	0.115	4/7	6.063	0.041	0.04	0.0010	7.58	1.59	0.40	0.69	0.932	4.214	0.03	22.145	0.005	0.032	0.514	0.16	0.01	1.068	0.074
6.4	0.075	4/13	5.572	0.067	0.03	0.0375	9.43	2.00	0.45	0.80	1.069	4.399	0.03	27.886	0.007	0.035	0.281	0.19	0.02	0.818	0.008
6.4	0.093	4/20	5.339	0.069	0.06	0.0075	6.47	1.38	0.38	0.61	0.864	4.090	0.03	18.864	0.009	0.029	0.301	0.14	0.00	1.090	0.024

Table 12 (cont'd).

6.1	0.101	4/27	4.394	0.078	0.07	0.0050	4.59	0.99	0.34	0.49	0.658	4.709	0.03	13.123	0.009	0.035	0.190	0.10	0.00	1.227	0.023
6.3	0.105	5/4	4.370	0.067	0.05	0.0195	6.30	1.34	0.38	0.57	0.658	3.780	0.03	18.044	0.009	0.032	0.150	0.10	0.01	1.022	0.038
6.6	0.082	5/12	4.836	0.044	0.04	0.0010	8.34	1.74	0.39	0.67	2.713	4.214	0.03	25.016	0.005	0.027	0.443	0.13	0.01	0.909	0.038
6.9	0.036	5/18	5.302	0.027	0.02	0.0070	10.47	2.12	0.50	1.74	0.932	4.585	0.03	31.987	0.007	0.037	0.060	0.19	0.01	0.977	0.009
6.8	0.058	5/25	5.327	0.027	0.02	0.0110	9.24	1.86	0.60	0.74	0.795	2.605	0.03	27.886	0.007	0.037	0.084	0.19	0.01	1.318	0.031
6.9	0.045	6/1	6.124	0.005	0.01	0.0000	11.54	2.40	0.49	0.88	0.727	4.709	0.04	36.088	0.006	0.043	0.039	0.21	0.01	0.886	0.040
6.2	0.113	6/8	5.388	0.037	0.02	0.0180	8.00	1.63	0.50	0.77	1.275	4.090	0.05	24.606	0.008	0.048	0.089	0.15	0.02	1.295	0.076
6.7	0.129	6/16	5.290	0.043	0.03	0.0110	7.67	1.64	0.28	0.67	2.576	5.018	0.03	22.965	0.008	0.048	0.017	0.19	0.01	1.840	0.086
7.1	0.095	6/23	6.578	0.077	0.07	0.0050	13.61	2.55	0.46	0.84	1.001	4.399	0.04	36.088	0.009	0.043	0.090	0.21	0.01	1.068	0.018
7.1	0.088	6/28				0.0000															0.088
7.3	0.093	7/6	7.657	0.070	0.07	0.0030	16.76	3.09	0.53	0.94	1.549	3.471	0.03	50.852	0.005	0.037	0.100	0.39	0.01	0.886	0.023
7.3	0.070	7/14				0.0000															0.070
7.4	0.051	7/19	7.805			0.0000	18.47	3.46	0.54	1.01	0.795	3.780	0.04	54.133	0.005	0.037	0.070	0.20	0.01	0.090	0.051
6.8	0.066	7/27	7.191	0.005	0.00	0.0040	16.39	3.01	0.62	0.94	0.727	4.709	0.03	45.931	0.004	0.037	0.099	0.17	0.01	0.340	0.061

Table 13. Aqueous chemical data, Yellow Dog River, Site 3 (1988-1989).

Units: all solutes in mg/l; temperature °C.

Date	Temp	pH	Ca	Mg	Na	K	Cl	SO4	Fe	SiO2	NH4	PO4	Alm	F	NO3	Mn	NO2	Alt
7/28			21.99	3.78	1.04	0.53	1.200	1.800	0.16	3.800	0.032	0.004	0.007		0.001	0.012	0.049	0.022
8/11	19.0	7.1	13.30	2.48	0.93	0.50	1.000	4.000	0.67	5.210	0.048	0.010	0.009	0.05	0.001	0.031	0.058	0.033
8/17	16.0	5.9																
8/25	14.0	6.4	8.83	1.79	0.75	0.38	1.200	1.900	0.48	4.890	0.037	0.009	0.014	0.05	0.035	0.032	0.015	0.055
9/1	15.0	7.1	10.60	2.02	0.81	0.37	1.000	3.000	0.33	5.500	0.048	0.009	0.008	0.03	0.018	0.029	0.042	0.038
9/8	12.0	7.3	10.29	1.90	0.77	0.35	1.200	1.900	0.56	5.710	0.037	0.009	0.004	0.05	0.056	0.029	0.004	0.065
9/22	13.0	7.0	10.02	1.96	0.81	0.48	0.626	3.347	0.56	6.737	0.048	0.007	0.010	0.05	0.004	0.011	0.025	0.087
9/29	10.5	7.4	8.71	1.77	0.81	0.44	1.000	4.709	0.45	5.500	0.043	0.008	0.013	0.03	0.047	0.010	0.003	0.084
10/5	5.5	6.7	6.73	1.29	0.59	0.52	1.049	6.008	0.42	5.351	0.043	0.009	0.027	0.03	0.064	0.020	0.006	0.154
10/13	4.3	6.7	6.74	1.44	0.64	0.33	0.767	5.204	0.50	5.179	0.043	0.009	0.012	0.03	0.070	0.019	0.005	0.105
10/20	5.0	6.8	6.61	1.33	0.61	0.38	0.908	5.080	0.45	4.529	0.043	0.012	0.019	0.02	0.068	0.017	0.002	0.136
10/27	2.0	6.0	5.08	1.09	0.53	0.36	1.049	2.048	0.40	4.370	0.037	0.010	0.056	0.03	0.023	0.012	0.007	0.110
11/3	2.0	6.5	5.58	1.21	0.56	0.30	0.767	3.162	0.39	4.836	0.043	0.010	0.040	0.03	0.024	0.011	0.015	0.097
11/10	1.5	6.1	4.02	0.87	0.44	0.31	0.626	2.852	0.34	4.038	0.048	0.012	0.096	0.03	0.015	0.016	0.015	0.114
11/17	1.5	6.4	4.51	0.90	0.40	0.31	0.626	3.842	0.25	3.916	0.032	0.010	0.090	0.02	0.040	0.010	0.010	0.095
12/16	0.0	6.4	6.15	1.34	0.62	0.29	0.626	4.523	0.41	6.836	0.035	0.012	0.049	0.03	0.050	0.012	0.010	0.085
12/22	0.0	6.5	5.99	1.32	0.59	0.28	0.767	4.399	0.41	6.431	0.037	0.010	0.060	0.03	0.010	0.019	0.020	0.079
1/1	0.0	6.8	6.72	1.56	0.66	0.32	1.049	4.523	0.46	6.860	0.027	0.013		0.03	0.007	0.021	0.013	0.076
1/6	0.0	6.6	7.34	1.58	0.71	0.33	0.485	5.018	0.51	7.381	0.021	0.012	0.070	0.04	0.008	0.026	0.042	0.078
1/12	0.0	6.6	7.30	1.58	0.68	0.32	0.485	5.204	0.50	7.069	0.037	0.010	0.065	0.04	0.001	0.031	0.116	0.072
1/20	0.0	6.4	8.19	1.60	0.68	0.33	1.049	4.214	0.50		0.048	0.009	0.060	0.04	0.012	0.023	0.008	0.087
1/27	0.0	6.4	8.51	1.75	0.74	0.35	0.626	4.090	0.49	7.535	0.053	0.009	0.051	0.03	0.015	0.027	0.025	0.083
2/2	0.0	6.4	8.20	1.76	0.76	0.35	0.697	4.832	0.52	7.719	0.059	0.012	0.056	0.04	0.001	0.029	0.138	0.089
2/16	0.0	6.5	7.79	1.83	0.76	0.36	0.626	3.966	0.51	7.780	0.048	0.010	0.055	0.03	0.009	0.020	0.010	0.083
2/23	0.0	6.5	8.25	1.95	0.85	0.39	0.697	4.090	0.45	7.473	0.037	0.009	0.046	0.04	0.007	0.019	0.013	0.082
4/1	0.8	5.9	4.27	1.03	0.50	0.32	0.767	4.090	0.32	5.535	0.048	0.009	0.076	0.03	0.001	0.025	0.053	0.117
4/7	3.0	6.1	4.07	0.94	0.47	0.31	0.626	3.966	0.32	5.265	0.048	0.009	0.074	0.03	0.001	0.014	0.497	0.131
4/13	1.0	6.3	4.41	1.06	0.51	0.33	0.485	3.471	0.41	4.897	0.048	0.009	0.060	0.03	0.006	0.018	0.024	0.092
4/20	4.0	5.9	3.43	0.79	0.43	0.30	0.485	3.780	0.27	4.505	0.048	0.012	0.079	0.03	0.001	0.011	0.081	0.091
4/27	5.8	5.8	2.71	0.63	0.37	0.29	0.626	3.162	0.18	3.707	0.043	0.013	0.080	0.03	0.001	0.007	0.056	0.099
5/4	7.5	5.9	3.48	0.80	0.42	0.28	0.767	3.780	0.18	3.364	0.048	0.010	0.076	0.03	0.036	0.007	0.014	0.106
5/12	10.3	6.2	4.12	0.93	0.52	0.29	0.485	4.894	0.24	3.216	0.048	0.009	0.074	0.03	0.017	0.011	0.043	0.090
5/18	17.0	6.3	5.32	1.17	0.56	0.36	0.485	4.709	0.31	2.996	0.043	0.010	0.068	0.03	0.056	0.007	0.014	0.078
5/25	15.3	6.7	5.90	1.30	0.59	0.36	0.626	3.904	0.47	3.609	0.037	0.009	0.047	0.03	0.059	0.020	0.011	0.062
6/1	14.0	6.4	6.26	1.39	0.71	0.28	0.626	4.090	0.46	4.345	0.043	0.010	0.017	0.04	0.059	0.013	0.001	0.080
6/8	9.0	5.9	5.00	1.10	0.50	0.29	0.626	3.347	0.42	3.977	0.037	0.009	0.030	0.05	0.035	0.027	0.005	0.144
6/16	9.8	6.3	4.12	0.92	0.57	0.13	1.049	2.852	0.41	3.486	0.037	0.009	0.047	0.03	0.037	0.011	0.003	0.101
6/23	20.5	6.2	6.69	1.48	0.66	0.26	1.190	3.595	0.51	4.590	0.037	0.011	0.060	0.03	0.054	0.016	0.001	0.066
7/6	21.0	6.7	8.58	1.92	0.81	0.35	2.316	2.048	1.10	6.063	0.037	0.012	0.026	0.04	0.023	0.017	0.006	0.029
7/19	21.5	6.7	10.27	2.32	0.94	0.36	0.485	3.471	0.77	6.921	0.043	0.008	0.003	0.04	0.028	0.009	0.001	0.040
7/27	21.0	6.4	9.25	2.06	0.78	0.52	0.767	4.461	0.62	6.308	0.037	0.009	0.003	0.03	0.025	0.014	0.015	0.067

Table 14. Aqueous chemical data, Yellow Dog River, Site 4, (1988-1989).

Units: all solutes in mg/l; temperature °C.

North Branch:

Date	Temp	pH	Ca	Mg	Na	K	Cl	SO4	Fe	SiO2	NH4	PO4	Alm	F	NO3	Mn	Alt	HCO3
7/28	20.00	7.1																
8/4	19.00	6.8	8.73	1.86	0.79	0.55	1.600	5.000	0.51	4.030	0.043	0.014	0.034	0.042	0.267	0.009	0.047	26.2
8/11	17.50	6.8	12.46	2.44	0.93	0.51	1.000	4.500	0.48	3.770	0.032	0.010	0.006	0.045	0.563	0.005	0.040	29.5
8/25	14.00	6.5	10.53	2.20	0.84	0.47	1.000	4.200	0.37	6.370	0.032	0.007	0.011	0.062	0.765	0.005	0.053	19.7
9/1	15.00	7.1	11.48	2.29	0.88	0.48	1.000	4.000	0.37	6.170	0.027	0.007	0.003	0.048	0.280	0.004	0.032	32.8
9/8	11.00	7.1	9.74	2.16	0.89	0.45	1.200	5.000	0.27	4.690	0.032	0.007	0.004	0.050	0.603	0.005	0.052	26.2
9/15	12.00	7.2	10.15	2.35	0.91	0.48	0.485	4.523	0.29	7.903	0.032	0.005	0.003	0.040	0.538	0.007	0.030	26.2
9/22	12.00	6.6	10.03	2.14	0.86	0.55	1.000	5.018	0.20	7.340	0.037	0.007	0.007	0.040	0.169	0.003	0.067	23.0
9/29	10.50	6.9	9.55	2.11	0.83	0.52	1.000	5.142	0.29	5.100	0.037	0.007	0.010	0.030	0.765	0.005	0.053	19.7
10/5	5.50	5.7	6.96	1.50	0.65	0.49	1.190	6.132	0.26	6.277	0.048	0.007	0.010	0.040	0.068	0.012	0.125	16.4
10/13	5.00	6.7	8.85	1.99	0.82	0.46	0.626	4.709	0.39	7.964	0.037	0.010	0.009	0.040	0.077	0.010	0.063	24.6
10/20	4.75	6.7	8.07	1.79	0.74	0.50	0.767	5.637	0.25	7.523	0.027	0.010	0.006	0.020	0.442	0.004	0.092	21.3
10/27	1.50	5.9	7.17	1.59	0.66	0.42	0.626	6.832	0.26	6.823	0.032	0.010	0.029	0.050	0.079	0.004	0.076	23.0
11/3	1.00	6.5	7.82	1.80	0.73	0.42	0.485	6.162	0.19	7.289	0.043	0.007	0.029	0.030	0.109	0.006	0.054	21.3
11/24	2.00	7.0	7.47	1.68	0.69	0.40	0.626	5.637	0.17	7.608	0.048	0.007	0.036	0.055	0.130	0.006	0.050	20.5
12/1	0.25	6.9	7.19	1.64	0.68	0.38	0.767	5.327	0.17	7.565	0.037	0.007	0.043	0.030	0.139	0.005	0.053	18.0
12/8	0.25	7.0	8.02	1.78	0.71	0.40	0.485	5.699	0.12	7.841	0.037	0.007	0.010	0.030	0.346	0.004	0.028	24.6
5/12	7.50	6.2	5.65	1.33	0.58	0.38	0.485	5.080	0.15	4.468	0.043	0.011	0.035	0.030	0.036	0.005	0.057	16.4
5/18	14.00	6.6	7.01	1.66	0.68	0.45	0.485	5.266	0.21	5.204	0.048	0.012	0.029	0.035	0.017	0.007	0.060	21.3
7/27	18.25	6.6	6.47	1.50	0.61	0.44	1.049	1.305	0.51	4.500	0.029	0.014	0.038	0.028	0.097	0.031	0.107	16.4

East Branch:

Date	Temp	pH	Ca	Mg	Na	K	Cl	SO4	Fe	SiO2	NH4	PO4	Alm	F	NO3	Mn	Alt	HCO3
5/12	7.50	6.2	2.78	0.66	0.42	0.24	0.485	3.904	0.14	2.873	0.070	0.010	0.071	0.030	0.119	0.006	0.093	6.56
5/18	15.50	6.3	3.10	0.75	0.42	0.26	0.626	3.904	0.12	2.137	0.016	0.010	0.058	0.031	0.017	0.007	0.136	
5/25	16.00	6.2	3.29	0.78	0.44	0.26	0.626	4.399	0.16	2.076	0.024	0.012	0.052	0.030	0.033	0.006	0.061	8.20
6/1	14.50	6.3	3.30	0.78	0.47	0.24	0.626	3.657	0.11	2.161	0.024	0.012	0.019	0.040	0.033	0.005	0.075	8.20
6/15	10.00	6.2	2.89	0.71	0.40	0.14	0.767	4.709	0.14	2.444	0.010	0.012	0.044	0.030	0.006	0.006	0.068	5.74
6/23	21.00	6.1	3.59	0.87	0.46	0.21	2.457	4.461	0.18	2.321	0.016	0.012	0.036	0.030	0.017	0.006	0.046	8.61
6/28																		
7/6	21.75	6.3	4.02	0.97	0.49	0.23	0.908	4.337	0.27	2.137	0.045	0.012	0.015	0.035	0.073	0.013	0.059	10.66
7/14																		
7/20	19.75	6.7	4.36	1.09	0.59	0.25	2.035	3.719	0.22	3.241	0.032	0.011	0.020	0.030	0.048	0.010	0.042	13.94
7/27	21.00	6.4	4.58	1.10	0.49	0.34	1.049	5.946	0.26	3.486	0.102	0.010	0.013	0.028	0.178	0.007	0.070	12.30

Table 15. Aqueous chemical data, Yellow Dog Upper Spring (1988-1989).

Units: all solutes in mg/l; temperature °C.

Date	Temp	pH	Ca	Mg	Na	K	Cl	SO4	HCO3	SiO2	Alm	NO3	Alt
9/7	8.	6.8	7.40	1.43	0.65	0.83	0.20	3.50	42.0	5.15	0.02	0.09	0.067
9/14	10.	6.2	7.87	1.49	0.64	0.77	1.00	3.47	16.0	4.08	0.01	0.42	0.035
9/20	10.	6.7	7.90	1.47	0.63	0.79	0.50	4.09	24.0	8.03	0.01	0.01	0.045
9/28	8.	6.8	8.13	1.53	0.63	0.77	0.50	3.84	40.0	8.00	0.01	0.09	0.029
10/5	7.	7.0	7.39	1.43	0.63	0.81	0.50	4.83	30.0	7.72	0.00	0.01	0.055
10/12	6.	6.8	7.40	1.50	0.64	0.79	0.50	4.09	28.0	8.03	0.00	0.02	0.040
10/19	7.	6.8	7.53	1.47	0.62	0.82	0.50	4.09	24.0	7.90	0.01	0.01	0.048
10/26	6.	6.4	6.52	1.31	0.56	0.84	0.50	5.95	22.0	6.89	0.01	0.04	0.046
11/2	6.	6.5	7.55	1.44	0.62	0.79	0.40	4.21	26.0	8.06	0.01	0.02	0.027
11/23	6.	6.9	7.56	1.42	0.60	0.79	0.50	4.21	26.0	8.01	0.02	0.03	0.020
11/30	5.	6.5	6.84	1.33	0.61	0.80	0.50	3.97	26.0	7.90	0.01	0.02	0.028
12/7	5.	7.1	6.14	1.25	0.65	0.79	1.19	4.09	26.0	6.46	0.01	0.13	0.015
5/17	7.	6.3	5.79	1.28	0.61	0.85	0.40	3.78	24.0	7.72	0.01	0.39	0.022
6/22	9.	6.3	5.89	1.30	0.61	0.82	0.30	3.78	26.0	7.66	0.01	0.54	0.048

Table 16. Aqueous chemical data, Yellow Dog Lower Spring (1989).

Units: all solutes in mg/l; temperature °C.

Date	Temp	pH	Ca	Mg	Na	K	Cl	SO4	HCO3	SiO2	F	NO3	Alt
1/27	6.50	7.5	32.00	6.10	1.34	0.69	1.190	8.11	116.0	10.97	0.055	0.290	0.01
2/2	6.00	7.5	32.07	6.12	1.37	0.69	1.331	8.42	118.0	10.97	0.056	0.268	0.01
2/11	6.25	7.2	31.92	6.10	1.36	0.68	0.500	7.68	102.0	10.97	0.070	0.331	0.01
2/16	6.25	7.5	31.78	6.06	1.32	0.67	0.500	8.42	101.0	10.79	0.060	0.268	0.01
2/23	6.00	7.3	31.80	6.05	1.32	0.65	0.500	5.95	114.0	10.24	0.060	0.268	0.02
4/7	5.75	7.7	30.74	6.06	1.34	0.68	0.400	8.11	115.0	10.97	0.052	0.670	0.02
4/20	5.75	7.5	30.45	6.03	1.34	0.69	0.400	8.05	112.0	10.85	0.050	0.355	0.01
5/25	6.00	7.5	30.66	5.94	1.33	0.66	0.400	5.95	109.0	10.73	0.050	0.333	0.00
6/23	6.50	7.5	29.46	5.88	1.36	0.75	0.400	7.68	102.0	10.97	0.025	0.866	

Table 17. Aqueous chemical data, Precipitation (1988-1989).

Units: all solutes in mg/l; precipitation amounts in inches.

Date	amount,Y	amount,P	pH	Ca	Mg	Na	K	SiO2	NO3	Cl	SO4	Alt
7/27	0.03	0.33	4.3							1.032		0.013
8/3	1.79	3.55	4.2	0.58	0.090	0.012	0.126	0.033	0.485	1.400	0.200	0.008
8/10	1.01	1.30	4.1	0.20	0.028	0.000	0.151	0.000	2.159	4.000	0.200	0.005
8/17	5.55	3.08	4.1	0.52	0.080	0.000	0.143	0.000	26.050	1.320	0.100	0.004
8/23	0.67	0.44	4.0	1.06	0.111	0.345	0.284	0.000	4.311	6.600	0.300	0.010
8/31	0.10	1.01	4.2	0.26	0.035	0.012	0.117	0.000	6.920	3.400	0.100	0.002
9/7	1.83	0.52	4.0	0.42	0.074	0.095	0.584	0.000	1.137	1.200	0.300	0.006
9/14	0.19	0.21	5.0	1.65	0.220	0.340	0.652	0.001	25.581			0.023
9/20	1.05	1.52	4.6	0.40	0.105	0.008	3.220	0.072	0.333	0.890	0.408	0.004
9/28	0.86	1.08	4.8	0.55	0.091	0.023	1.370	0.000	0.855	0.749	0.358	0.005
10/5	0.59	1.19	4.0	0.15	0.018	0.011	0.081	0.000	0.224	0.749	0.284	0.008
10/12	0.24	0.35	4.0	0.42	0.045	0.015	0.052	0.000	0.105	1.457	0.129	0.002
10/19	1.11	1.31	4.4	0.33	0.037	0.000	0.048	0.000	0.094	2.165	0.099	0.001
10/26	1.47	1.89	4.4	0.01	0.003	0.000	0.014	0.000	0.029	0.749	0.086	0.000
11/2	0.48	1.04	4.5	0.01	0.005	0.000	0.027	0.000	0.322	0.466	0.129	0.001
11/9	2.12	1.99	4.7	0.00	0.002	0.000	0.017	0.077	0.224	0.466	0.099	0.007
11/16	0.69	1.23	4.4	0.16	0.024	0.017	0.028	0.000	0.333	0.324	0.160	0.000
11/23	0.20	0.29	4.6	0.76	0.087	0.610	0.130	0.000	0.550		0.173	0.004
11/30	0.85	1.13	4.6	0.01	0.004	0.137	0.015	0.000	0.126	0.607		0.000
12/7	0.10	0.11	5.0	0.00								
12/15	0.56	0.73	4.9	0.08	0.021	0.278	0.072	0.000	8.659	18.600	0.160	0.005
12/21	0.41	0.65	5.2	0.58	0.066	0.222	0.075	0.000	13.224	0.749	0.173	
12/31	0.31	0.65										
1/5	0.25	0.24	4.4	0.26	0.029	0.249	0.035	0.000	0.420	0.749	0.160	0.001
1/11	0.26	0.70	4.5	0.14	0.021	0.150	0.038	0.000	0.431	0.466	0.160	0.012
1/19	0.38	0.55	4.8	0.17	0.025	0.697	0.052	0.000	0.735	0.749	0.099	0.003
1/25	0.02	0.08										
2/1	0.15	0.22	5.1									
2/10	0.17	0.24	4.6	0.10	0.015	0.144	0.050	0.000				
2/15	0.04	0.18	4.7	0.10	0.026	0.073	0.050	0.000	0.355	0.607	0.129	0.003
2/22	0.10	0.04						0.000	0.311	0.607	0.099	0.002
3/2	0.61	0.39										
3/9	0.68	0.43										
3/16	1.03	0.96	4.5	0.16	0.033	0.055	0.057	0.000	0.529	0.466	0.148	0.002
3/22	0.02	0.01	4.8	0.06	0.015	0.026	0.026	0.000		0.324	0.160	
3/30	0.10	0.15										
4/5	0.25	0.15	4.2	0.07	0.019	0.000	0.031	0.000	0.768	0.466	0.222	0.003
4/12	0.04	0.12										
4/19	0.02	0.19	5.5	1.96	0.289	0.149	0.187	0.002	1.322	0.466	0.594	0.004
4/26	0.27	0.27	4.0	1.14	0.146	0.122	0.157	0.000	1.398			0.026

Table 17 (cont'd).

5/3	0.35	0.19	4.0	1.18	0.115	0.059	0.086	0.000	1.420	0.466	0.433	0.010
5/10	0.05	0.17										
5/17	0.00	0.00										
5/24	1.37	0.35	4.4	1.27	0.113	0.016	0.130	0.000	1.290	0.466	0.191	0.006
6/1	0.26	1.38	4.7	0.87	0.091	0.024	0.086	0.000	0.855	0.324	0.160	0.004
6/9	2.68	2.64	5.0	0.24	0.045	0.000	0.047	0.000	1.344	0.218		0.000
6/14	1.99	0.91	4.5	0.06	0.117	0.102	0.368	0.016	0.822	0.466	0.297	0.010
6/22	0.39	0.21	4.7									
6/28	1.09	0.52	4.6	1.23	0.109	0.013	0.015	0.000	1.333	0.607	0.160	0.003
7/5	0.10	0.18										
7/14	0.00	0.05										
7/20	0.00	0.23	4.4									
7/26	0.41	0.00	4.4	0.62	0.056	0.000	0.050	0.000	0.681	0.607	0.160	0.001

Table 18. Aqueous chemical data for groundwater, lakes and runoff.

Units: all solutes in mg/l; temperature °C. GW=groundwater from well, L=lake, RO=runoff, SW=swamp.

Site type	Temp	pH	Ca	Mg	Na	K	Cl	SO4	HCO3	Fe	SiO2	NH4	Alm	F	NO3	Mn	Alt
mgw8/3 GW	15.	6.450	16.12	3.190	1.160	0.700	2.400	12.753	84.0	40.	8.870	1.132	0.008	0.050	0.937	0.360	0.064
cgw8/4 GW	15.	6.000	2.09	0.580	0.530	0.440	2.000	4.090	12.0	0.	4.670	0.074	0.003	0.025	2.007	0.015	0.016
hlgw8/23 GW	12.	6.100	5.30	1.070	0.720	0.360	3.000	18.941	44.0	0.	6.730	0.113	0.004	0.042	2.449	0.043	0.022
bgw8/25 GW	9.	6.000	25.41	4.200	1.520	0.970	1.800	2.852	90.0	6.	8.970	0.035	0.001	0.054	0.355	0.380	0.002
kgw8/31 GW	11.	5.200	3.54	0.630	0.710	0.570	0.700	1.615	12.0	0.	6.520	0.035	0.038	0.030	0.094	0.017	0.083
vrgw9/20 GW	11.	6.900	26.12	8.910	2.470	1.560	14.288	30.327	60.0	0.	16.518	0.055	0.002	0.026	0.485	0.465	0.003
wdl9/21 L	13.	6.400	5.44	1.170	0.520	0.270	0.626	7.184	12.0	0.	2.260	0.035	0.007	0.050	0.155	0.002	0.021
blsw9/21 SW	14.	5.800	5.14	1.040	0.570	0.300	1.330	4.585	12.0	1.	4.591	0.035	0.021	0.040	0.046	0.034	0.162
lsg10/5 L	10.	7.000	23.43	5.970	2.700	1.320	8.373	3.595	82.0	5.	21.892	0.035	0.000	0.040	0.010	0.460	0.002
4il10/12 L	6.	6.400	2.56	0.630	0.470	0.270	0.485	3.780	60.0	0.	1.033	0.035	0.012	0.025	0.874	0.006	0.056
sgw11/10 GW	10.	6.125	7.19	1.750	2.180	1.470	2.176	4.709	20.0	0.	9.254	0.035	0.004	0.025	1.006	0.002	0.009
yro4/26 RO	6.	6.000	3.80	0.950	0.450	0.410	0.415	4.090	12.0	0.	2.567	0.038		0.035	0.677	0.001	0.122
yro6/8 RO	10.	6.000	4.14	1.050	0.470	0.500	0.767	1.615	12.0	0.	4.591	0.030		0.023	0.427	0.006	0.187
pro5/3 RO	6.	5.700	2.20	0.600	0.350	0.150	0.767	4.090	8.0	0.	4.481	0.043		0.020	0.191	0.001	0.160
cl5/18 L	15.	5.800	3.13	0.660	0.330	0.180	0.767	3.162	8.0	0.	2.751	0.035		0.040	0.025	0.039	0.117
sqg7/20 GW	6.	6.000	3.72	0.850	0.590	0.320	3.302	0.501	24.0	16.	5.327	0.074		0.040		0.075	0.141
smgw8/4 GW	7.	7.250	10.27	4.160	1.150	0.560	0.908	2.233	56.0	0.	3.119	0.035		0.050	0.010	0.210	0.001
ksgw10/7 GW	7.	6.150	4.55	1.110	0.840	0.480	0.626	3.595	22.0	1.	8.579	0.094		0.040	0.015	0.050	0.072
bugw10/7 GW	8.	6.150	10.58	2.790	1.010	0.680	1.471	9.040	82.0	68.	13.916	1.367		0.040	0.005	0.348	0.151
frg10/8 GW	8.	6.200	3.22	0.580	0.410	0.360	1.049	0.501	20.0	25.	6.309	0.231		0.030	0.000	0.033	0.087