

Geochemical analysis of the Running Gutter subcatchment of the Mill River Watershed, Hatfield, Massachusetts

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INTRODUCTION

The Mill River is located in the Connecticut Valley of west-central Massachusetts. The Mill River Watershed (MRW) covers an area of 130 square kilometers (31,000 acres) and lies within the towns of Conway, Deerfield, Hatfield, Whately and Williamsburg. MRW drains into the Connecticut River at Hatfield, and is host to a variety of ecosystems that range from undeveloped forests to residential and agricultural areas.

Land-use practices may be threatening the water quality of the Mill River and its associated watershed. This is an extremely important area because it is the home of the federally endangered Dwarf Wedged Mussel (*Alasmidonta heterodon*), which was previously thought to be extirpated from Massachusetts. The small population found in the lower stem of the Mill River was the only extant population in Massachusetts when the study began in 1997. Understanding the controls that affect water quality is essential for the survival of this mussel. The specific goals of the project are to assess the hydrological and chemical impacts of land-use on the Mill River and its associated wetlands and aquifers.

This study focuses on the Running Gutter (RG) subcatchment, located in the southern-most portion of the MRW (see Newton, et al., the volume for map). The main purpose of the study is to determine how and why the water chemistry changes as it flows through the system and compare it to other subcatchments. Studying the RG subcatchment provides an opportunity to compare different land use impacts. The subcatchment can be further divided into two areas: the main stem of Running Gutter and a tributary named Broad Brook. The main stem drains a forested area with few residential influences. Conversely Broad Brook drains a forested area but also has more residential and agricultural areas. Comparison of Broad Brook and the main stem provides a means to assess effects of varying land-use on water chemistry.

METHODS

Field Work. Samples were taken biweekly at RG-100 (see Newton, et al., the volume) from June 1997. Thirty additional sites were sampled, some sampled twice, during the summer of 1998 throughout the RG subcatchment. Water samples were also taken from two municipal wells. In fall 1998, five soil pits, approximately one cubic meter in size, were dug and sampled at approximate 10 cm intervals. Rocks characteristic to the soil pits were also collected to be examined petrographically. Five tonalite bedrock samples were collected later in the fall. A staff gauge was installed at RG-100 during the summer. Due to flooding associated with beaver activity, the staff gauge became useless and another one was installed further downstream.

Laboratory work. Water samples were analyzed in the Smith College Aqueous Geochemistry Lab for pH, air-equilibrated pH, specific conductance (SC), dissolved silica, major cations and anions, and acid neutralizing capacity (ANC). pH was measured using a Fisher Scientific Accumet 1002 Model pH meter. Air-equilibrated pH was measured after air was bubbled through the sample for at least 15 minutes. The SC was measured by a temperature-compensated YSI model 34 Conductance-Resistance Meter in $\mu\text{mhos/cm}$. Dissolved silica was analyzed by the molybdate blue method; the amount of silica present was a function of the color measured by a spectrophotometer at a wavelength of 700 nm. Major base cations (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) were analyzed from acidified samples by flame atomic absorption spectrometry. Major acid anions (SO_4^{2-} , NO_3^- , and Cl^-) were analyzed from unacidified samples by ion chromatography. ANC was measured using the Gran Plot method from Gran titrations with a strong acid. For the soil analyses, exchangeable base cations were determined by soaking soil samples in ammonium chloride then analyzing by flame atomic absorption spectrometry. Soil samples were also soaked in potassium chloride then titrated to a phenolphthalein endpoint to determine exchangeable aluminum and hydrogen.

RESULTS

Data from the sample sites throughout the subcatchment show two different trends for specific conductance (SC) as the water flows downstream. On the main stem of Running Gutter (RG), the SC tends to increase as the distance downstream increases while in Broad Brook the SC tends to decrease as the distance downstream increases. There is an overall greater chemical load in the Broad Brook tributary than in the main stem of RG, with calcium being the most abundant in both. Anion concentrations should give a good indication of human impact on the water chemistry because such anions would not naturally occur here in large quantities. However, chloride, sulfate and nitrate concentrations in Broad Brook tend to decrease downstream while in the main stem of RG the concentrations initially rise then fall as distance increases downstream. Even though the average concentration of chloride in summer precipitation in central Massachusetts is about $3.74 \mu\text{eq/L}$ (NADP, 1999), chloride in the Broad Brook tributary is unusually high at almost $320 \mu\text{eq/L}$ near the headwaters compared to almost $30 \mu\text{eq/L}$ at the headwaters of Running Gutter.

The analyzed data from the soil pits show that different locations within the subcatchment vary greatly in total cation exchange capacity. In all five pits, the highest total cation exchange capacity occurs in the top organic layers. Soil pits that contain very sandy material are dominated by exchangeable total acidity. Where till is thick, the cation exchange capacity tends to depend on the total base cations. In areas of thin till, the cation exchange capacity tends to be determined by the total acidity and exchangeable aluminum rather than base cations. Calcium is the most dominant cation in the organic layers of all five soil pits and is also the most dominant cation in the water samples taken throughout the watershed.

Figure 1 shows how the ANC concentrations change with time. Calcium, sodium, magnesium, chloride and sulfate concentrations fluctuate over time while potassium and nitrate concentrations remain rather steady at values of approximately $25 \mu\text{eq/L}$ and $10 \mu\text{eq/L}$, respectively. Calcium, sodium and chloride concentrations are most variable, and generally rise and fall in synch with ANC.

Figure 1. ANC varies seasonally with the highs corresponding to the summer months.

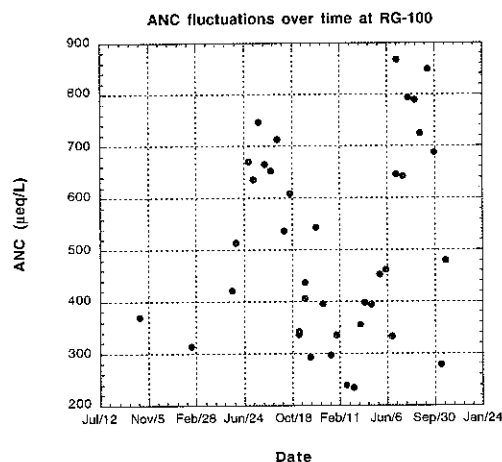
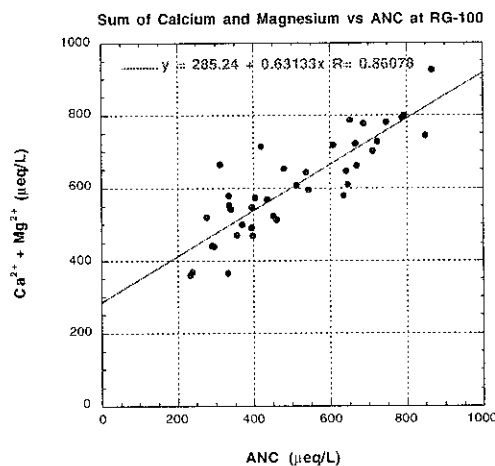


Figure 2. Calcium and magnesium concentrations account for 63% of the total acid neutralizing capacity.



The ANC of water can be calculated by the sum of the base cations minus the sum of the acid anions. Therefore, when base cations are added to the system or acid anions are removed, the acid neutralizing capacity will increase. Calcium accounts for 50% of the acid neutralizing capacity while magnesium accounts for 12% of the acid neutralizing capacity (Figure 2). The figure also shows that when the acid neutralizing capacity is zero there can be up to $285 \mu\text{eq/L}$ of calcium and magnesium.

The sum of the total base cations (Figure 3) account for more that 98% of the ANC. When the sum of the acid anions is subtracted from the sum of the base cations and plotted against the acid neutralizing capacity, the resulting relationship should theoretically be a 1:1 ratio. However, there is no significant correlation between the sum of the total acid anions and ANC which suggests that base cations have a greater impact on ANC than acid anions.

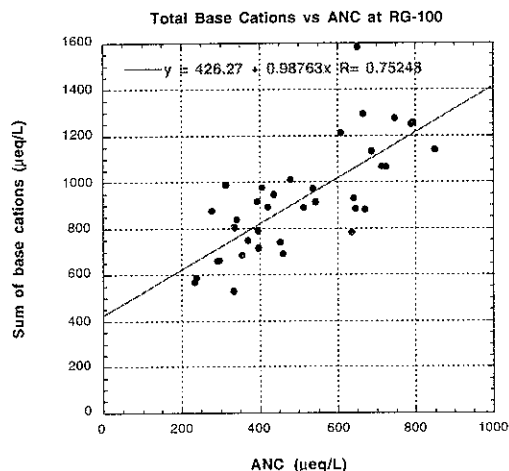


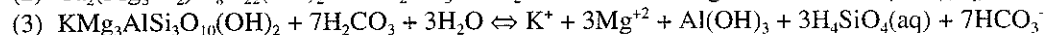
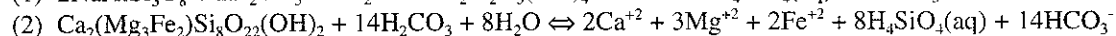
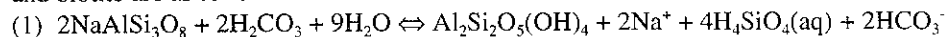
Figure 3. The sum of the total base cations account for almost 99% of the total acid neutralizing capacity at RG-100.

DISCUSSION

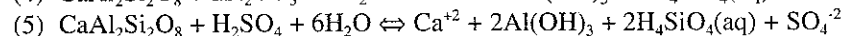
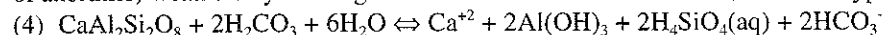
The difference in anion concentrations in the main stem of RG and in Broad Brook are consistent with population distribution in the watershed. The highest population and greatest number of major roads occur close to the headwaters of Broad Brook. In the mainstem of RG, the headwaters are heavily forested and have few residential influences while the number of roads and residences increase downstream. Between the inlet and outlet of Fitzgerald Lake on Broad Brook (see Newton, et al., this volume), the concentrations of chloride, sulfate and nitrates decrease. The lake may dilute the chloride, reduce the sulfate under anoxic conditions at depth, or serve as a sink for nitrates by the aquatic vegetation.

The Running Gutter subcatchment is almost entirely underlain by tonalite. Tonalite contains relatively few reactive minerals; therefore, one would expect to find surface waters with relatively low pH values due to the inputs from acid deposition. Preliminary observations show that the ANC is relatively high despite the abundance of tonalite and the lack of apparent calcium carbonate-bearing rocks in the area.

The major minerals in tonalite are plagioclase feldspar (mainly in the form of albite), quartz, biotite and hornblende. Tonalite weathering is not expected to have a strong influence on the water chemistry but can serve as sources of sodium, calcium, magnesium and potassium. Weathering reactions for albite, hornblende (Bricker, 1986) and biotite are as follows:



When the minerals weather as shown, they produce bicarbonate which contributes to ANC. As discussed earlier and demonstrated in Figures 2 and 3, there must be additional sources of these cations that do not also contribute to the ANC. The concentrations of base cations from precipitation are too small to have any significant impact on the total cations in the water. For example, in 1997, the sum of the base cations deposited by precipitation in central Massachusetts was only about 10.15 µeq/L while calcium concentrations were only 2.81 µeq/L (NADP, 1999). Other types of weathering must be taking place. When plagioclase feldspar (in the form of anorthite) weathers by reacting with carbonic acid or sulfuric acid, different byproducts result:



The weathering of anorthite with carbonic acid produces calcium ions and bicarbonate (Equation 4). If anorthite is weathered by sulfuric acid, calcium ions and sulfate are produced (Equation 5). Therefore, if sulfuric acid weathers plagioclase rather than carbonic acid, the ANC of the water will not increase.

Weathering by sulfuric acid releases cations and sulfate but no bicarbonate. Figure 4 shows that as sulfate concentrations increase, the ANC decreases. The strong relationship between sulfate and ANC suggests that sulfuric acid is a major acid for mineral weathering in the subcatchment.

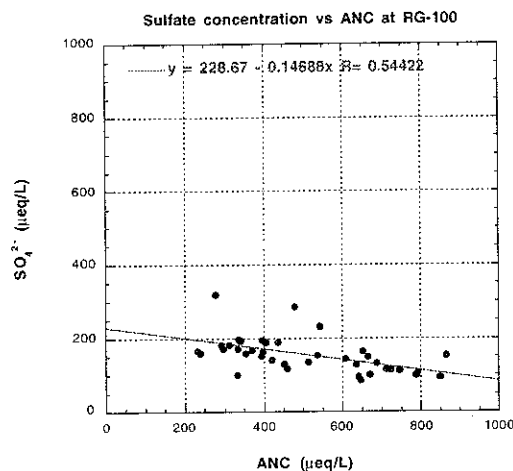


Figure 4. Sulfate, the major acid anion in the RG subcatchment, is inversely proportional to the acid neutralizing capacity.

Of all the cations and anions in precipitation, sulfate has the highest concentration at about 31.78 µeq/L in 1997 (NADP, 1999), making atmospheric deposition a reasonable source of it in Running Gutter.

Finally, understanding the water chemistry is compounded by the presence of till. Except for some patches of exposed bedrock, the entire area is covered by till that ranges from thin to thick. According to Yuretich et al. (1996), watersheds with thick glacial till deposits or large proportions of reactive minerals tend to show little impact on the water chemistry from acid precipitation. The RG

subcatchment does not contain large proportions of reactive minerals but till is abundant and widespread. The till may be one of the sources of a rather high ANC by introducing carbonate-bearing rocks.

Observations have shown a cyclic pattern to the ANC over time not only at the RG-100 sample site, but throughout the RG and other subcatchments of the MRW. The high peaks at RG-100 correlate to the late summer and may suggest that evaporation affects the water chemistry. The ratios between potassium and magnesium differ for each subcatchment, but also oscillate over time within the RG subcatchment which suggests that some other factor besides evaporation is the cause for the fluctuating ANC values. More precipitation in the spring and summer may result in a higher rate of mineral weathering. The summer is also the time when sulfate concentrations in the precipitation is the highest (NADP, 1999). An influx of cations caused from increased weathering of the bedrock may cause the oscillating ANC values throughout the year.

The majority of the RG subcatchment is covered by till of varying thickness. As the soil analyses show, the upper parts of the soil are typically rich in cations, especially calcium. If the soil is thin and underlain by sand and gravel, then the cations will leave the soil and enter nearby streams. Soils derived from thick till have higher total base cation concentrations and therefore have a greater ability to buffer acidity from rain. Therefore, soils derived from the till have high cation exchange capacities and will contribute cations, especially calcium, to the water from the uppermost layers.

CONCLUSIONS

The mainstem of Running Gutter and the Broad Brook tributary show impacts of population based on the concentration and distribution of anions in the water. The ANC of Running Gutter fluctuates greatly throughout the year. Such changes are attributed to base cations that enter the water from the soil and the weathering of bedrock. Bedrock weathering cannot be due solely to carbonic acid. Sulfuric acid, input by atmospheric deposition, causes weathering without introducing bicarbonate into the system.

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