The geochemistry of the Avery Brook subcatchment in the Mill River watershed, Conway, MA

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INTRODUCTION

The Mill River watershed is a 125 km^2 area in western Massachusetts that lies just east of the low eastern slopes of the Berkshire Hills. The watershed drains into the Connecticut River in the southeast corner, just east of Interstate 91 in Hatfield. The Smith College Environmental Science Program has been involved in an interdisciplinary environmental study of the Mill River Watershed (MRW) incorporating the hydrology, geochemistry, biotoxicology, vegetation, and population and genetic variations in the MRW since the summer of 1997 (Internet Ref. 1). The Mill River is of particular interest due to the presence of the federally endangered Dwarf Wedge Mussel (*Alasmidonta heterodon*) that is the larger of only two known populations in Massachusetts. The focus of this environmental study is to assess the effects of human impact on the watershed ecosystem.

The MRW incorporates areas to the northwest that are more rural and forested, as well as areas to the east that have extensive human activity including agriculture, suburban residential regions, and Interstate 91. This range of human activity provides an excellent basis for comparing human impacted land with remote forested regions (Internet Ref. 2). Starting in June, 1997, nine sample sites on the major tributaries and the main branch of the Mill River were sampled biweekly. The geochemistry of water samples has been tested to assess the effects of human land-use on the quality of the water.

The Avery Brook subcatchment lies almost completely inside the Conway State Forest, a regrowth forest, and drains into the Northampton Reservoir which serves as the main drinking supply for Northampton. There is almost no recent human activity in the subcatchment, making it the most remote stream system in the MRW. The geochemistry and hydrology of this forested subcatchment could serve as a basis for comparison with the other more human impacted subcatchments in the MRW. My hypothesis is that Avery Brook system is a fairly natural watershed, and any ions in the water are present due to atmospheric deposition from air pollution, or natural inputs from trees, soils, glacial till, and bedrock. In order to identify the human impacts on the other subcatchments in the MRW we must distinguish between human and naturally occurring affects on water chemistry.

METHODS

Field Methods. Waters were sampled at 15 sites on the main stem and tributaries of Avery Brook. Three full transects of water samples were collected, two during the 1998 summer and one in November. Four soil pits were dug in the subcatchment in both thin and thick till, as well as both dominant bedrock types. The soil pits were generally 1.0 meter x 1.0 meter, and dug to a depth of 1.0 meter. Samples were collected at 10 cm. intervals. Bedrock composition was researched and roughly mapped with samples obtained from outcrops along the main stem of the brook and tributaries.

Lab Methods. Water samples were analyzed in the Smith College Aqueous Geochemistry Lab for specific conductivity (SC), pH, air equilibrated pH, acid neutralizing capacity (ANC), major cation concentrations, major anion concentrations, and dissolved silica content (Table 1); the cation exchange capacity of soils was determined (Table 2).

Table 1: Water Samples

Analyzed for:	Filtered/unfiltered:	Methods:
pH ANC	Unfiltered	Fisher Scientific Accumet 1002 model pH meter Gran titration
SC	Unfiltered	YSI model 34 Conductance/Resistance meter
Na^+, K^+, Mg^{2+}, Ca^{2+}	Filtered (0.45µm filter)	Atomic Emission and Absorption
SO_4^{2-}, NO_3^-, Cl^-	Filtered (0.45µm filter)	Ion Chromatography; Dionex Ion Chromatograph
Dissolved silica	Unfiltered	Molybdate Blue with Spectrophotometer

Table 2: Soil Samples

CEC Test:	Ions tested:	Chemical Method:	Methods:
Base cations	Na^+, K^+, Mg^{2+}, Ca^{2+}	Ammonium Chloride	Atomic Emission and Absorption
Exchangeable acidity	H^+, Al^{3+}	KCl, KF	Titration to colormetric endpoint

RESULTS

Geology of the Avery Brook Subcatchment. The bedrock geology in the Avery Brook subcatchment is approximately 80% Williamsburg granodiorite, primarily in the southwest regions, that intruded into undifferentiated Paleozoic quartz-schist and marble-schist member of the Conway formation (Willard, 1956). Surficial geology is dominated by glacial till. Thin till covers about 80% of the area. Other deposits include a few scattered drumlins, regions of thick till, and stratified drift at lower elevations near the reservoir (Sergerstrom, 1955).

Geochemical data. Avery Brook has low concentrations of desolved cations and anions relative to waters in the rest of the MRW (Figure 1). The acid neutralizing capacity (ANC) of Avery Brook (mean=235 μeq/L) is low relative to the other subcatchments in the watershed (mean=589 μeq/L). Figure 2 shows the relationship of the ANC with the pH for Avery Brook and the other MR tributaries. This graph is significant because it demonstrates the susceptibility of stream water to acidification by acid rain. The majority of the of the MRW has high ANC values relative to pH values. The buffering ability of the water is greater, so a higher quantity of acid can be deposited without acidification. When the ANC is low, less acid will cause rapid drops in pH levels; the position of the Avery Brook data on the ANC vs. pH curve display a higher susceptibility of Avery Brook to acidification, than many of the other MRW subcatchments.

Figure 3 demonstrates the dominant ion responsible for the ANC present in Avery Brook. The ANC vs. Ca^{2+} relationship yields a slope of 1, indicating weathering forms Ca^{2+} and HCO_3^- in a 1:1 μeq/L relationship.

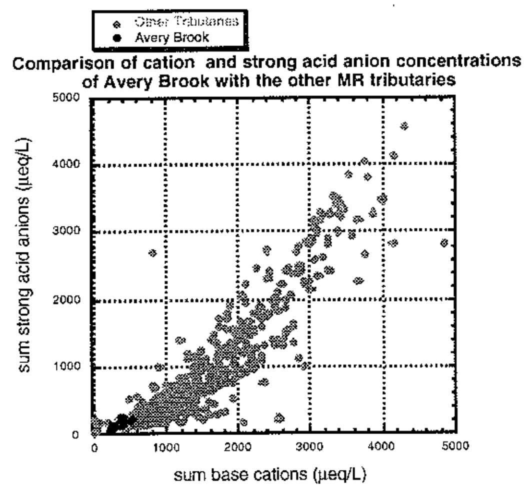

Figure 1: This graph demonstrates the relatively low cation and anion concentrations in Avery Brook relative to the other Mill River tributaries. This graph is not a straight line with slope = 1, because the HCO_3^- values, determined from ANC, are not included with the sum anions. Theoretically this would bring the values up to a 1:1 line.

One potential human impact on river geochemistry is road salt (NaCl), the influence of which can be determined by a 1:1 molar ratio of Na^+ to Cl^-. The Avery Brook concentrations of both Na^+ (mean=63.2 μeq/L) and Cl^- (mean= 32.8 μeq/L) are dramatically lower than concentrations in the other MR tributaries (Na^+ mean=623.5 μeq/L, Cl^- mean= 713.9 μeq/L). The Avery Brook data show a higher relative concentration of Na^+ to Cl^-; this suggests an additional source for Na^+ and does not indicate strong road salt influence (Figure 4). The other MR tributary data plot in a 1:1 molar relationship indicating road salt as the dominant influence.

The cation exchange capacity (CEC) of the soil pits show consistent results (Figure 5). Total acidity dominates the total cation exchange capacity (Figure 6). Exchangeable Al^{3+} is the main component in the exchangeable acidity. Overall the soil profiles demonstrate that the total CEC is highest in the top 10 cm of the pit, and the most exchangeable base cation of all pits is Ca^{2+}.

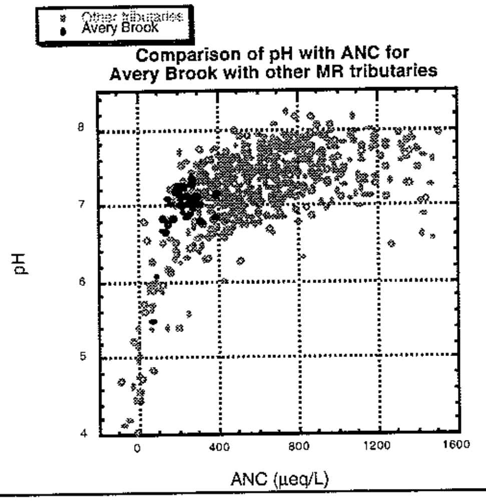

Figure 2: The pH vs. ANC for Avery Brook relative to the other tributaries in the MRW. Avery Brook has relatively low ANC values and the brook is susceptible to acidification.

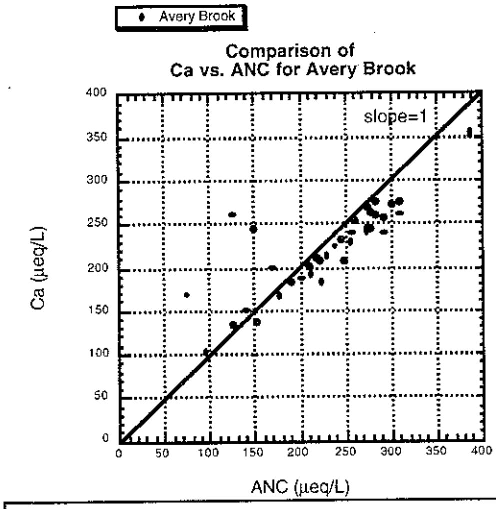

Figure 3: The 1:1 Ca:ANC μeq/L relationship in this graph indicates both that the dominant source of alkalinity in Avery Brook is Ca^{2+}. The same weathering source that forms ANC forms Ca^{2+} at a 1:1 ratio.

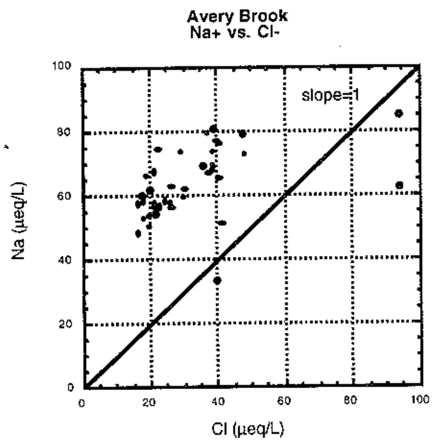

Figure 4: This graph shows the Na^+ and Cl^- data for Avery Brook. Note the lack of correlation with the 1:1 slope. This indicates that road salt is not a dominant factor in the presence of these ions in this stream system. Another possible source for the higher concentration of Na+ is the weathering of albite plagioclase in the granodiorite. A possible other source for Cl^- is atmospheric deposition.

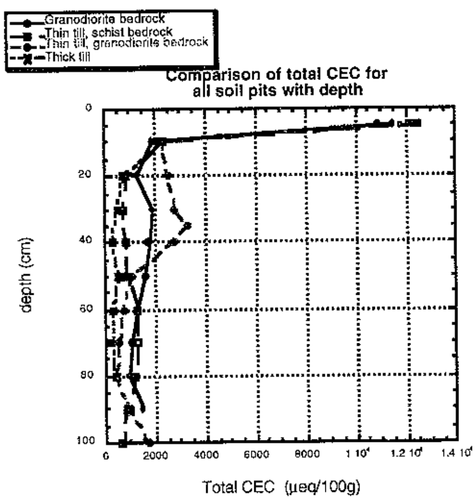

Figure 5: Compares the total CEC with depth of all soil pits.

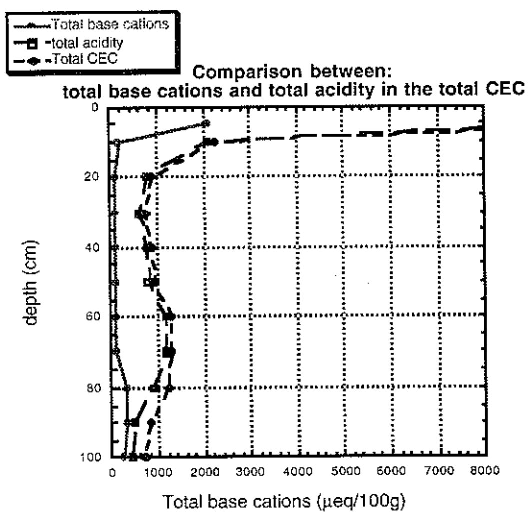

Figure 6: This is a representative soil pit demonstrating that total acidity is the major contributor in the total CEC.

DISCUSSION

Avery Brook is the most remote subcatchment in the MRW. Human activity is minimal and the catchment should contain the most pristine water chemistry in the watershed. This holds true for the low concentrations of cations, anions, and ANC. The most abundant cation in the stream is Ca^{2+}. Two possible sources for Ca^{2+} include the weathering of anorthite and calcite. Anorthite is present in the granodiorite bedrock; about 30% of the granodiorite in the subcatchment is plagioclase feldspar (Wilkerson, 1984). Calcite is present in the marble schist. Anorthite weathers to gibbsite with carbonic acid to produce Ca^{2+} according to the following reaction:

$$CaAl_2Si_2O_8+H_2CO_3+2H_2O\text{->}Ca^{2+}+2Al(OH)_3+2SiO_{2(aq)}+2HCO_3^-$$

Calcite weathers with carbonic acid to produce Ca^{2+} and $2HCO_3^-$ according to the following reaction:

$$CaCO_3+H_2CO_3\text{->}Ca^{2+}+2HCO_3^-$$

These equations explain the $Ca^{2+}:HCO_3^-$ charge balanced 1:1 µeq/L ratio shown in Figure 3.

The weathering of the minerals in the bedrock may account for other cations found in the stream; for example the weathering of albite to kaolinite may produce the Na^+ concentrations shown in Figure 4:

$$NaAlSi_3O_8+2H_2CO_3+9H_2O\text{->}Na^++Al_2Si_2O_5(OH)_4+4SiO_{2(aq)}+2HCO_3^-$$

Most anions, specifically nitrates, are present in watersheds due to human activity. Avery Brook shows almost no nitrates present. Sulfate (SO_4^{2-}) is the most abundant anion present, and is most likely derived from the atmosphere. Sulfuric acid reacts with minerals such as calcite to form sulfates according the following reaction:

$$2CaCO_3+H_2SO_4\text{->}2Ca^{2+}+2HCO_3^-+SO_4^{2-}$$

Many stream systems systematically change chemistry with position downstream. Avery Brook has no correlation between its relative stream position and geochemistry. However, the chemistry of an eastern tributary, Sinkpot Brook, differs from the rest of Avery Brook. Sinkpot Brook flows over marble-schist bedrock and yields the highest Ca^{2+} and ANC concentrations in the subcatchment. This demonstrates the partial control of bedrock type on the river chemistry. However, the low ANC values in the bulk of Avery Brook suggest that calcite is not abundant in the subcatchment and is concentrated in the Sinkpot Brook eastern region. Weathering of minerals in both schist and granodiorite also contribute to the surface water geochemistry. Low base saturation in the soils indicates little base cation contribution from soils to the stream, however high levels of total exchangeable acidity may contribute to lower ANC values (Figure 2). Atmospheric deposition and acid rain also influence surface runoff, but not nearly as much as bedrock influences.

CONCLUSION

Avery Brook is the most remote subcatchment in the Mill River watershed. Geochemistry of the river water indicates relatively low human contamination. Cation and anion concentrations are low relative to the other MRW water values. Those present may be accounted for by bedrock mineral weathering, cation exchange in soil and atmospheric deposition. The human influenced anion concentrations of NO_3^- and SO_4^{2-} are very low relative to the other subcatchments, and sulfate present is most likely from the atmosphere. By characterizing Avery Brook as a "pristine" subcatchment, the geochemistry of other more populated subcatchments may be compared and more thoroughly evaluated in terms of human impact on water quality.

ACKNOWLEDGMENTS

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1) http://www.science.smith.edu/mill_river/default.html 12/18/98
2) http://www.science.smith.edu/mill_river/project.html 12/18/98