

Aqueous geochemistry of Mill River watershed, Northampton, Massachusetts

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INTRODUCTION

The Mill River Watershed Project is a study of the impact of land use on water quality in a small tributary to the Connecticut River in western Massachusetts. The role of the Keck Geology Consortium in this project was to analyze the stream, soil, and shallow ground water geochemistry to first determine how the bedrock geology influences stream chemistry, and then assess how land uses alter the "background" stream water composition. Within the Mill River watershed, catchments were identified and allocated to individual researchers to study in more detail. This particular study focused on assessing the aqueous geochemistry of the headwaters catchment and analyzing the mainstem of Mill River for varying concentrations of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , SO_4^{2-} , silica, HCO_3^- /Acid Neutralizing Capacity (ANC), silica, specific conductivity (sc), and pH.

The 130 km² Mill River watershed is separated into two distinct geomorphic regions lying on either side of the mainstem of Mill River. To the west, tributaries drain a highland with 300' of relief mantled by a till of varying thickness, and to the east, streams flow through a lowland underlain by Glacial Lake Hitchcock sediments. Within the watershed, bedrock outcrops are dominated by granodiorite, tonalite, amphibolite, and phyllite-limestone-schist-marble units (Willard, 1956). Land uses include forests, and residential, commercial, and agricultural developments. Mill River's headwaters are located in the western upland region; the stream collects input from tributaries of various land uses, and ultimately drains into the Connecticut River.

METHODS

The analysis of water samples was conducted at Smith College's Aqueous Geochemistry Laboratory during summer research of 1998, and procedures followed Newton (1998). Bedrock mineralogy was assessed by hand specimen and thin section analysis. Land-use assessment was facilitated by air-photo analysis and field observations.

DATA

Geology. Bedrock underlying the western portion of the Mill River watershed has been lumped into carbonate-bearing and non-carbonate-bearing units. Thin section analysis supports this mineralogical division of the bedrock within the headwaters catchment. Thin sections show either $\geq 50\%$ carbonate, which is accompanied by biotite, muscovite, and quartz, or $\leq 10\%$ carbonate, in which case garnet, plagioclase, orthoclase, and quartz dominate the mineralogy. Roughly 70% of the western headlands drain carbonate-bearing rocks, while the eastern catchments contain no carbonate bedrock.

Aqueous Geochemistry. The eight ions quantitatively analyzed were chosen because they represent the major ions of natural surface waters (Langmuir, 1997). Fig. 1 illustrates sample sites from the headwaters and mainstem of Mill River, as well as catchment locations; sample sites where the main tributaries (Bloody Brook, Roaring Brook, West Brook, Great Swamp, and Running Gutter) drain into Mill River are labeled BB-100, RB-100, WB-100, GS-100, and RG-100, respectively. Fig. 2 displays the relative proportions of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , ANC (HCO_3^-), SO_4^{2-} , and NO_3^- represented at each water sampling locality. The histograms in Fig. 2 show that K^+ and Mg^{2+} play a relatively small role in the overall cation composition of Mill River, on average contributing 3.17% and 5.36%, respectively, to watershed cation composition. NO_3^- concentrations remain relatively low (<2%), as do sulfate values which also remain low throughout the watershed, comprising 11.7% on average of the anion values. Na^+ , Ca^{2+} , ANC and Cl^- dominate the stream chemistry, with these ions typically representing $\geq 85\%$ cation and anion composition. Bivariate plots show that ANC and Ca^{2+} , and Na^+ and Cl^- are strongly correlated ($r^2 = 0.94$ and 0.99 , respectively).

DISCUSSION

The concentrations of the ions analyzed in the Mill River watershed fall within "typical" values observed in surface waters (McCutcheon et al., 1993). Notable variation in cation or anion composition between sample sites

signals a change in stream input. Postulated explanations for these changes include differences in land use, bedrock, and tributary input/dilution between sample sites. Two distinct aqueous geochemical trends were observed; Ca^{2+} and ANC components of stream waters seem to be derived from the western highlands, and Na^+ and Cl^- values are most concentrated in eastern catchments, as well as along the mainstem of Mill River.

The concentrations of the less abundant ions in the watershed vary, but almost always fall within "standard" concentration ranges (Hem, 1985). Typical sources of NO_3^- in stream waters include agricultural runoff from fertilizers and manure (Hem, 1985). While some fluctuation in nitrate values was observed with respect to land use, values of NO_3^- did not exceed harmful concentrations (Hem, 1985). Likewise, SO_4^{2-} sources, which include acid rain and weathering of sulfide-bearing minerals, do not appear to have a dramatic or deleterious affect on the aqueous geochemistry of Mill River, because these concentrations were relatively consistent and within "typical" ranges throughout the watershed (McCutcheon et al., 1993). Finally, both Mg^{2+} and K^+ represent a small fraction of overall cation composition in stream waters, and are most likely a product of weathering of muscovite, biotite, and amphiboles present in rocks described in the bedrock map of Williamsburg (Willard, 1956). Values of both Mg^{2+} and K^+ fall well within typical ranges (McCutcheon et al., 1993).

The histograms in Fig. 2 show that Ca^{2+} and ANC represent higher percentages of cations and anions in catchments draining the western highlands than these ions in the tributaries from the east. The highest values for these ions were collected from sites that drained carbonate-bearing bedrock, and ion values correlate when plotted bivariately ($R^2 = 0.94$). The correlation of Ca^{2+} and ANC suggests that these ions have a common source, which has been attributed to the carbonate bedrock which underlies 70% of the western catchments, and none of the eastern catchments. The lack of carbonate bedrock in the east contributes to the "dilution effect", or the observed decrease in percentage of total cation and anion composition that Ca^{2+} and ANC represent downstream.

Conversely, concentrations of Na^+ and Cl^- represent the majority of cation and anion composition in eastern tributaries (Fig. 2). High values of Na^+ and Cl^- occur not only in Bloody Brook and Great Swamp tributaries, but also at sample site locations along the mainstem of Mill River which border major highways. The nearly perfect correlation of Na^+ and Cl^- , the peaks of concentrations of these ions in the summer and winter, the absence of evaporite deposits or other Cl^- bearing minerals in local lithologies, and the historical usage of road salt to de-ice Williamsburg roads after winter storms (60 tons of road salt applied during a single season), lead to the conclusion that road salt is the major source of these ions in Mill River (Storms, 1987).

CONCLUSIONS

Mill River stream chemistry is characterized by typical ranges of NO_3^- , SO_4^{2-} , K^+ , and Mg^{2+} . Extremely high and fluctuating values of Na^+ and Cl^- along the mainstem and in the east raise concerns regarding the amount of road salt applied to local roads during winter storms. While concentrations of both Ca^{2+} and ANC observed in western streams range beyond average values (Langmuir, 1997), increased values of these ions probably results from the natural weathering of carbonate bedrock. Mill River demonstrates acceptable values of major ions in pristine areas, and in most agriculturally and residentially developed areas of the watershed; highways appear to have the greatest seasonal and long-term impact on the aqueous geochemistry of the Mill River watershed.

REFERENCES CITED

- Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water: U. S. Geological Survey Water Supply Paper 2254, 264p.
- Hem, J.D., A. Demayo, and R.A. Smith, 1990, Hydrogeochemistry of rivers and lakes, *in* M.G. Wolman and H.C. Riggs, eds., Surface water hydrology: Geological Society of America, The Geology of North America v. O-1, p. 189-231.
- Langmuir, Donald, 1997, Aqueous environmental geochemistry: Upper Saddle River, Prentice Hall, Inc., 600p.
- McCutcheon, S. C., J. L. Martin, and T. O. Barnwell Jr., 1993; Water quality, *in* D. K. Maidment, ed., Handbook of hydrology: New York, McGraw Hill, p. 11.1-11.73.
- Newton, R.M., 1998, Aqueous geochemistry lab methods: Northampton, Smith College, 37p.
- Storms, Erik, and W. S. Motts, 1987, Hydrogeologic investigation of Williamsburg, Massachusetts, *in* Proceedings of the fourth annual Eastern Regional Ground Water Conference, 4: Dublin, National Water Well Association, p. 467-490.
- Willard, M. E., 1956, Bedrock geologic map of the Williamsburg Quadrangle, Massachusetts: U.S. Geological Survey Geological Quadrangle Map GQ-85.

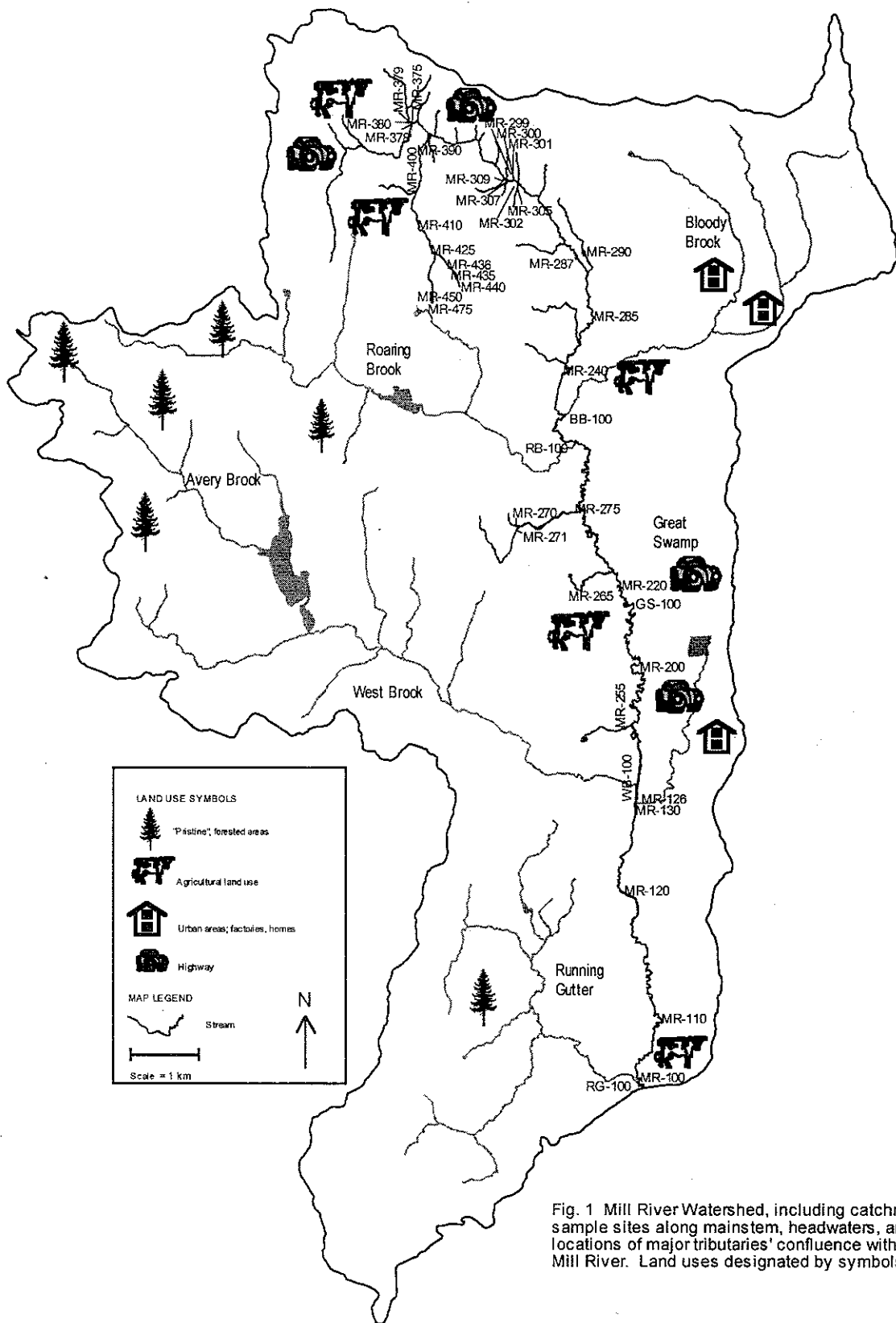


Fig. 1 Mill River Watershed, including catchments, sample sites along mainstem, headwaters, and locations of major tributaries' confluence with the Mill River. Land uses designated by symbols.

Figure 2: Relative percent of cations and anions at sample sites in the head waters and along the mainstem of the Mill River, as well as cation and anion input from each tributary, and mean composition of both anions and cations of all samples taken within the watershed. Sample sites with an "X" after number indicate multiple sample values have been averaged.

