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Influences of Land Use on Water Quality of a Diverse New England Watershed

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Analysis of variations in major ion chemistry in the Mill River watershed reveals the importance of anthropogenic activities in controlling streamwater chemistry. Average concentrations of NO_3^- and SO_4^{2-} show a positive correlation with percent catchment area altered by human land uses, and concentrations of Cl^- increase with road density. Water removal from municipal reservoirs increases the downstream concentration of NO_3^- and SO_4^{2-} over that predicted by land use changes, showing that removal of high quality upstream water concentrates pollutants downstream. In salt-impacted streams, Cl^- exceeds Na^+ by 10–15% due to cation exchange reactions that bind Na^+ to soil. The net effect of nonpoint source pollution is to elevate ANC in the most developed areas, which impacts the natural acidity of a large swamp. The sum of base cations (C_B) exceeds ANC for all samples. Plotting C_B against ANC and subtracting Cl^- quantifies the impact of road salt from the impact of the addition of strong acids.

Introduction

Population growth and land-use changes are strongly associated with degrading water quality and diminishing surface and groundwater supplies (*1*). As a result, many heavily populated New England communities have a long history of reconciling water demands with needs to preserve water quality for human consumption and ecological health. Although controls on rates of atmospheric emissions from combustion have improved chemical quality of precipitation in the northeastern U.S. (*2*), pollution of surface waters from diffuse sources, such as urban and agricultural runoff, may prevent achievement of national water-quality goals, even after minimizing point-sources of pollution (*1*). Sensitive systems in the northeastern U.S. are still impacted negatively by acid deposition, despite emission rate controls on SO_2 and NO_x from utility emissions (*2*), and nonpoint source pollution in runoff is difficult to control because its sources cannot be attributed to one particular discharge location but rather to a diffuse area (*3*). Therefore, degradation of water quality often results from multiple land use activities, and separating the impact of mixed sources of nonpoint source pollution is difficult. Understanding the consequences of multiple land uses on water quality and quantity is best achieved at a watershed scale, where the watershed is divided into subcatchments characterized by different human activities (*4*). Increasingly, studies of land use effects on water quality operate using a watershed framework (*3, 5–7*).

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Watersheds across New England typically occur within diverse physiographic and geologic settings and are subject to a wide variety of land uses associated with varied settlement patterns. For example, the expansive Connecticut River watershed extends from remote, sparsely populated upland regions in northern New England to densely populated, residential, agricultural, and industrial regions further downstream in Massachusetts and Connecticut. Over 2.5 million people live within its boundaries. Thus, evaluating land-use effects on watershed processes in New England environments requires a field area that encapsulates the diversity of landscape and human activity at a scale suitable for detailed study.

The Mill River watershed, Hatfield, Massachusetts (~13 000 hectares) is a fourth-order catchment within the Connecticut River basin (Figure 1). It contains the diversity found in larger New England watersheds (*4, 8*). Sharp differences in topography, geology, and human settlement patterns define its heterogeneity. Topography separates the landscape into two distinct, geomorphic regions with 420 m of relief. In the west, hilly terrain supports high gradient streams with dendritic drainage patterns, whereas meandering streams flow over flat, lowland areas in the east. Terrain differences are due to the differential erosion of rocks exposed on either side of a Mesozoic normal fault (*9*). The upland areas are underlain by Paleozoic metamorphic and igneous rock units, covered by a thin veneer of glacial till or localized, thick deposits of stratified drift. The low gradient streams flow over thick glaciolacustrine, varved clay, or aeolian sand sequences associated with Glacial Lake Hitchcock, a large glacial lake that existed in the region from ~16–14 000 years ago (Stone and Ashley, in ref *10*). Except for a cuesta in the northeastern part of the watershed that survived erosion, the glacial lake deposits prohibit the majority of surface and shallow groundwaters from interacting with buried Mesozoic basalt and arkose. Unlike the upland regions covered by till, rich soils and the absence of rocks in the lake deposits facilitate clearing for agriculture, transportation, and dense settlement. However, patches of contiguous, deciduous swamp forest (The Great Swamp) associated with low permeability soils still exist in the lowland regions. Descriptions of the geologic and land-use history of western Massachusetts are found in Robinson and Brady (*10*) and Foster (*11*).

Sections of six townships occupy the MRW. Approximately 11 000 people lived in the MRW in 1990 and ~32 000 vehicles per day crossed the watershed on Interstate-91 in 1999. Low-density suburban sprawl is the area's dominant form of growth over the past two decades, where agricultural land has been replaced by residential development. Anthropogenic cover types occupy 25% of the watershed acreage: 16% agricultural (pasture, dairy cow grazing, and row crops); 6.5% residential; 1.2% commercial, industrial, and urban land; and 1.3% highway. Human development is densest in the low elevation, eastern portion of the area. Forests (73%) and nonforested wetlands (2%) occupy the "nonanthropogenic" area, predominantly in the western uplands. The primary human impact in the upland region involves water removal from two tributaries by municipal surface reservoirs, which export in excess of 9500 m^3 of water per day from MRW (*12*).

The purpose of the MRW project is to investigate the processes that affect water chemistry in remote versus human-populated regions, as a way to assess the effects of land-use activity on water quality within a mixed land-use watershed. The disparity of land use—between heavily populated and remote areas—combined with the manageable size of the watershed provides an excellent opportunity to distinguish the natural processes that control water chemistry
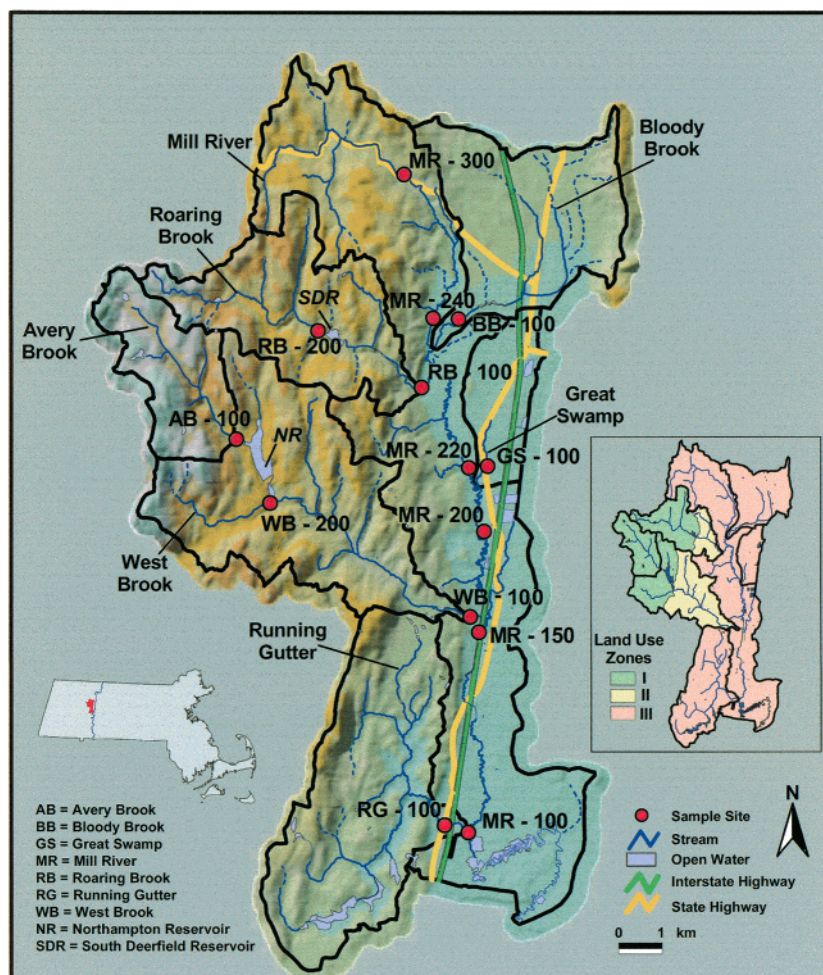
FIGURE 1. Land-use classification and sample locations of the MRW.

from anthropogenic influences. Other studies of New England watersheds center on small, remote catchments, such as the Hubbard Brook Experimental Forest, New Hampshire and Cadwell Creek, Massachusetts, or remote to rural catchments, such as Sleepers River, Vermont. Typically, studies of these watersheds investigate dynamics of biogeochemical processes of ecosystems (13–16), or they address impacts of specific anthropogenic effects on ecosystems, such as acidic atmospheric deposition (17) or effects of forest harvesting on soils and water chemistry (18). However, none have integrated directly geochemical knowledge to assess the dynamics of chemical loading from multiple land uses within a watershed. Likewise, studies of mixed land-use watersheds, such as the Fraser River, British Columbia, Canada (5), are too large to separate effects of chemical loads from different anthropogenic activities. This paper will present an overview that characterizes the parameters controlling water chemistry within the MRW. Specific analysis of processes within distinct subcatchments and hydrologic analysis will be the subject of subsequent papers.

Experimental Section

Watershed Study Design. We divided the MRW into six major subcatchments based on the drainage patterns of six dominant tributaries. Using a Geographic Information System (GIS), we calculated specific land-use areas and further classified the catchments into zones defined by different intensities of human activity (Figure 1), based on the MacConnell GIS land-use categories (19). Low impact zones (zone I) are regions where human activity is minimal to absent. The landscape is predominantly forested with some

wetlands associated with beaver impoundments. Dirt roads do exist; however, road density is lowest in zone I. We expect the dominant source of human pollution in zone I to be atmospherically derived. Therefore, sample sites within zone I serve as our baseline for assessing human influences on water quality further downstream. Low impact zones (zone II) are primarily affected by water withdrawal from drinking water reservoirs on two tributaries. Removal of water from these reservoirs potentially diminishes the quantity of water capable of diluting pollution derived within zone III. Zone III consists of highly impacted regions that receive runoff from agricultural, residential, and transportation areas. Road density is highest in zone III and includes interstate and state highways. Results presented in this paper aim to describe the relative impacts of human activities on water quality within each zone.

Water Analyses. Since June 1997, we have sampled waters bimonthly for major ion chemistry from 13 permanent sites distributed within the catchments of major tributaries, and we have sampled above and below major confluences of the Mill River to determine the relative chemical inputs and outputs of the system. Specific conductance and temperature were measured in the field. Waters were collected in acid-washed polyethylene bottles, after rinsing three times with the sample, and then refrigerated. Samples were analyzed in the laboratory for specific conductance, pH, acid neutralizing capacity (ANC), cation concentrations (Ca^{2+}, Mg^{2+}, Na^{2+}, K^+, NH_4^+), anion concentrations (F^-, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}), and dissolved silica. ANC was measured by Gran titration (20) on unfiltered samples within 5 days of collection. Samples then were vacuum filtered through a 0.45 micron Millipore

membrane. Cation concentrations of acidified splits and anion concentrations of unacidified splits were determined by ion chromatography (21), using a Dionex 500 ion chromatograph. However prior to September 1999 cation concentrations, except NH_4^+, were measured by atomic absorption and emission using a Perkin-Elmer 3030 atomic absorption spectrometer. Instruments were standardized to solutions of known concentrations; errors in accuracy were ≤ 0.07 mg/L for cation results and ≤ 0.16 mg/L for anions. Dissolved silica concentrations were determined by colorimetry (22) using a Bauch and Lomb Spectronic 21 spectrometer. For each sample, charge balances were calculated in equivalents as (Σcations−Σanions)/(Σcations+Σanions)*100%. Samples having imbalances greater than 5% were either reanalyzed or assessed for cause of the imbalance. Typically imbalances >5% resulted from poor ANC analyses, and ANC values from these samples were removed from the study. Almost all results reported here in molar (μmol/L) units; equivalents (μequiv/L) are used when data evaluation requires charge balances. F^-, PO_4^{3-} and NH_4^+ results will not be presented because concentrations were consistently negligible.

Results and Discussion

The Mill River watershed displays diverse water chemistry associated with differences in geologic substrate, geomorphology, population diversity and activity, and time of year. In this paper, we demonstrate ways to distinguish anthropogenic effects on water quality from natural processes. The extent of nonpoint source pollution is achieved through comparison with remote regions of the watershed.

Anion Characterization of MRW. As has been shown in other studies that characterize water quality with land use (1, 3, 7), concentrations of strong acid and salt anions (SO_4^{2-}, NO_3^-, and Cl^-), typically derived from anthropogenic sources, are greatest in more densely populated and nonforested regions of the MRW (zone III; Figure 2A). In contrast, concentrations of these anions are low and uniform in remote catchments (zone I). At WB-200, for example, SO_4^{2-} and NO_3^- average 62.5 and 4.4 μmol/L. In fact, SO_4^{2-} concentrations in AB (47 ± 4.7 μmol/L) and WB-200 are similar to other remote systems worldwide affected only by distant sources of air pollution (23, 24). Therefore the chemistry of stream segments in zone I serves as an appropriate baseline for the rest of the watershed and allows us to quantify the amount of SO_4^{2-} and NO_3^- pollution contributed from regional wet and dry deposition (25). Road salt is applied to the road near WB-200, and average Cl^- (82.2 μmol/L) is slightly higher than at AB-100 (28 μmol/L), where no roads occur. However, Cl^- concentrations at WB-200 are much lower than in zone III, where average concentrations of major anions are 2.5−20 times higher than the remote catchments. Highest average SO_4^{2-} (196 ± 120 μmol/L), NO_3^- (82.8 ± 76 μmol/L), and Cl^- (2596 ± 700 μmol/L) concentrations occur in the Great Swamp, which receives road runoff from interstate and state highways.

Throughout the watershed, average concentrations of NO_3^- and SO_4^{2-} correlate with percent catchment area classified for human use (agricultural, residential, commercial, industrial, urban open, and transportation areas; Figure 3). A linear, best-fit line demonstrates a positive correlation between NO_3^- (and SO_4^{2-}) and percent human land use at $R^2 = 0.68$ (and 0.69). Standard deviation from average values also increases with greater percent human land-use area. Similar to NO_3^- and SO_4^{2-}, Cl^- concentrations increase with greater road density with a positive linear correlation of $R^2 = 0.87$ and higher standard deviation from mean values with higher road density. These results are similar to those reported for first-order catchments of the Ipswich River, Massachusetts (26), where a positive relation-
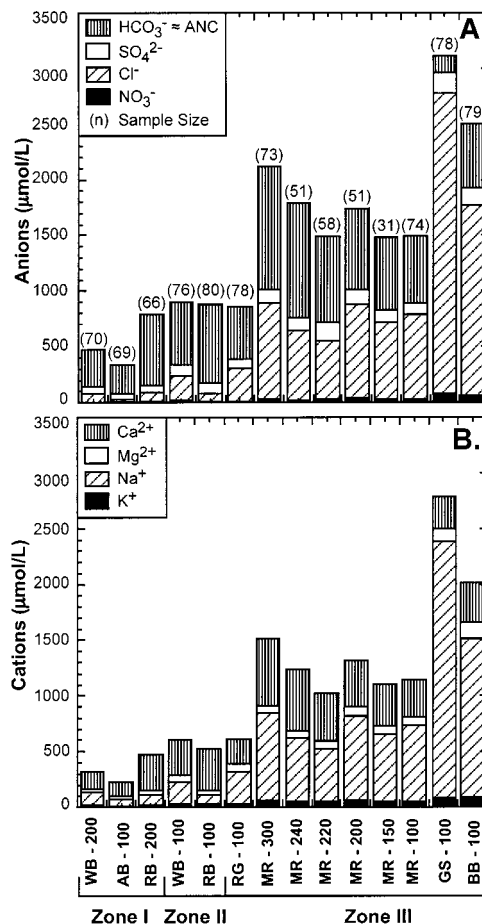

FIGURE 2. Major anion and cation concentrations for each land-use zone.

ship exists between SO_4^{2-}, NO_3^-, Cl^-, and Na^+ with percent urban area. Gubrek (7) also devised an algorithm to predict NO_3^- from percent forest and agricultural land uses in a 730 ha watershed. Similarly in this study, the positive correlation in Figure 3 can predict how NO_3^-, SO_4^{2-}, and Cl^- concentrations will increase with future development within the subcatchments of MRW.

In remote catchments, chemical variation from mean values is largely due to seasonal controls on concentration; highest concentrations occur during times of low precipitation such as the summer or fall. In impacted watersheds, multiple sources of chemical loading produce greater variations. Scatter of mean concentration values around the best-fit lines (Figure 3) is expected because of the large variation of environmental and land-use variables in the watershed. For example at GS-100, NO_3^-, SO_4^{2-}, and Cl^- plot above the best-fit line, showing that low-gradient wetlands are more susceptible to chemical loading than the high-gradient catchments. Shallow groundwater in Great Swamp showed greater NO_3^- and SO_4^{2-} concentrations within the vicinity of a local truck stop (27) having a history of environmental waste violations (28). Leaching from this point source combined with the low-gradient landscape and low permeability in the swamp greatly concentrates the pollution. Likewise, lower West Brook (WB-100) yields higher NO_3^- and SO_4^{2-} than predicted by the best-fit line. Higher concentrations here result from large water withdrawals from the Northampton Reservoir (~5700 m³/day) that prevent water upstream of the reservoir from reaching WB-100, except during large precipitation events (12). Recalculating percent area classified for human use downstream of the reservoir causes WB-100 to plot closer to the best-fit line, showing
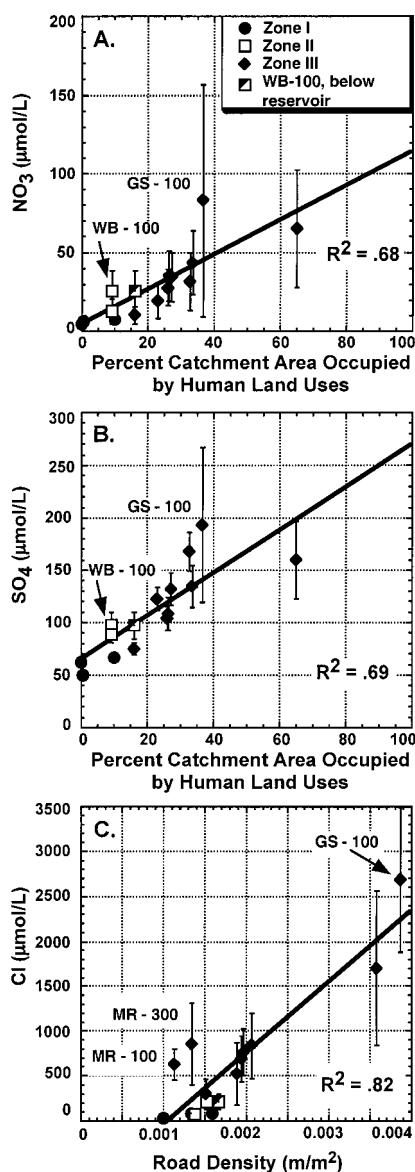
FIGURE 3. NO₃ and SO₄ show a positive relationship with percent catchment area classified for human use (A, B). GS plots above the best-fit line, showing the susceptibility of this wetland to chemical loading. High NO₃ and SO₄ values at WB-100 result from water withdrawals from a surface water reservoir. WB-100 plots closer to the best-fit line when only the area downstream of the reservoir is considered. (C) Chloride increases with greater road density, calculated as the total length of all roads in a catchment, divided by the catchment area. Error bars = 1 SD.

that water withdrawals from reservoirs concentrate chemical loads when land use increases downstream. This effect is not present on RB because land use below the South Deerfield Reservoir is similar to upstream. However, water withdrawals from both reservoirs do limit dilution of chemical loads in the Mill River (see below).

Cation Characterization of MRW. Calcium is the dominant base cation ($Ca^{2+} > Na^+ > Mg^{2+} > K^+$) in the high gradient streams (Figure 2B). Average values of calcium are highest in stream regions underlain in part by carbonate-bearing bedrock (e.g. 600 ± 99 μmol/L at MR-300 and 372 ± 52 μmol/L at RB-100). Sodium is the most abundant cation ($Na^+ > Ca^{2+} > Mg^{2+} > K^+$) in low gradient streams close to the interstate highway. In GS Brook, the mean sodium concentration (2242 ± 585 μmol/L) reaches the same order of magnitude as Cl^-. Potassium concentrations are consis-

tently low in zone I (<33 μmol/L) and increase in more populated areas, with highest values (up to 212 μmol/L) occurring where agriculture activity is greatest.

Bedrock weathering strongly controls the concentration of Ca^{2+} and Mg^{2+} in the upland regions of the watershed; this in turn affects the Ca/Mg ratio. Sample sites that receive water from tributaries flowing over marble-bearing schist units (e.g. MR-300 and RB-100) are characterized by the highest Ca/Mg ratios (~8.4), whereas Running Gutter, which drains tonalite absent of marble, has a low Ca/Mg ratio (3.1). Cation chemistry is so sensitive to the underlying geology that the Ca/Mg ratios change as streams flow over different rock types. For example, the ratio increases downstream along WB and RB, both of which contain more carbonate in their downstream reach. The zone III catchments, GS and BB, have the lowest Ca/Mg ratio (2.6). Both streams drain the lowland regions and are polluted by human activities. The high concentrations of Ca^{2+} and Mg^{2+} in these streams, despite the absence of carbonate minerals, suggest an anthropogenic source for these cations; however, separating natural sources from pollution (e.g. fertilizers or road salt) is difficult. Evaluation of variation in acid neutralizing capacity (ANC) and road salt impacts throughout the watershed helps make this distinction.

Variation in ANC. The competing influences on water chemistry—between natural processes and land use activities—are demonstrated by the remarkable variability of ANC throughout the MRW. In most natural systems, mineral weathering and soil cation exchange are the dominant sources of cations and ANC to surface waters, with high cation and ANC concentrations in streams dominated by base flow having a long residence time or in contact with geologic materials having high weathering rates (29, 30). ANC can also be produced by reduction of sulfate and nitrate driven by microbial activity (31). ANC can be added by human activities as well, such as through liming of agricultural fields. Streams having low (<100 μequiv/L) and even negative ANC values often contain high concentrations of organic acids and have little contribution from base flow.

The varying contributions of both natural and anthropogenic contributions to ANC should be observed at a watershed scale when diverse land uses are present. In fact, the entire range of ANC in the MRW extends from −90 to 1848 μequiv/L. The highest ANC values occur in the headwaters of the MR where marble-bearing bedrock is abundant. A large range in ANC values (from ~160−1050 μequiv/L) also occurs in BB (zone III), which encapsulates the greatest residential and agricultural acreage of any MRW catchment. The high mean ANC value (575 ± 248 μequiv/L) resembles streams underlain by marble-bearing bedrock, yet BB flows through quartz- and feldspar-dominated sands—materials that weather less readily—and over impermeable varve clay deposits. No calcite has been observed in surface sediments, and the strikingly different Ca:Mg ratio in BB and GS from the marble-bearing terrains indicates that detrital carbonate minerals from upland regions of MRW are not in the lake deposits. Although at BB we expected some cations and ANC from weathering, such high concentrations are inconsistent with the mineralogy of the catchment. Detailed sampling of ANC through the BB catchment shows that ANC is highest near crop fields. Therefore, the high ANC values in zone III appear to be anthropogenic in their source, most likely from lime in agricultural runoff.

Like BB, GS (zone III) receives alkaline pollution causing wide variation in ANC values throughout the year (−90 to 600 μequiv/L). Low ANC values are expected in GS because of high concentrations of organic acids leached from peat, and the mineralogy of sands below the peat are the same as in BB. As is expected for this environment, episodic acidification does occur at GS-100, where ANC falls below zero

with an associated decrease in pH from ~6.5 to 4.1. Remote systems that experience episodic acidification, such as lakes in the Adirondack Mountains of New York, have ANC values that typically are <100 μequiv/L (*32*). Yet at GS-100, ANC values are as high as 600 μequiv/L. In this case, the extreme variation results from mixing of two tributaries with different chemistries to GS Brook. An eastern tributary supplies alkaline runoff from the developed region of the swamp near I-91. Low to negative ANC values prevail when flow is dominated by a second tributary from a more remote region of the swamp that adds natural acidity from decaying organic matter (*33*).

Anthropogenic Salts. Road runoff containing deicing agents is common throughout the northern and especially northeastern United States and can result in contamination of water and soil resources (*34*). Rock salt (predominantly NaCl) is the most common deicing chemical, and the amount applied varies with climate and frequency of winter storms. Massachusetts used an average of 245 000 tons of salt/year, just on state roads during the mid-1980s (*35*), and more than 6500 tons of salt/year was applied to major roads within the MRW in 2000. In the MRW, road salt application is greatest on interstate and state highways that cross the lowland regions (zone III; Figure 1). Less than 1% of the salt is composed of $CaCl_2$; the remaining is NaCl (*36*). Both GS Brook and BB display elevated concentrations of sodium and chloride that persist throughout the year—even during summer months when no salt application occurs. The low gradient of the catchments allows for a long residence time for the road runoff. Persistence of Cl^- in a salt-impacted stream can be attributed to slow release of salt held in the micropores of soils or from groundwater, even during nonsalting periods (*34*).

High concentrations of Na^+ and Cl^- in soils can adversely affect plant growth and plant community richness. Intercellular growth of salt crystals desiccates many plants, and salt toxicity is greatest when soils are dry (*37*). Sodium added to soil solutions can exchange with other cations adsorbed onto soil exchange sites, releasing plant nutrients (K^+, Ca^{2+}, and Mg^{2+}) to runoff (*34*), while exchange of sodium for hydrogen in acidic soils can promote acidification of nearby surface waters.

Within the MRW, all zone III streams receiving road runoff display a strong positive correlation between Na^+ and Cl^- ($R^2 = 0.86-0.95$). The stoichiometry of the salt predicts a one-to-one (1:1) molar ratio between Cl^- and Na^+ concentrations. However, Cl^- exceeds Na^+ in intermediate and highly impacted streams, and the discrepancy in concentrations of Cl^- and Na^+ increases when chloride exceeds ~1200 μmol/L. In GS and BB, Cl^- exceeds Na^+ by ~15% (up to 500 and 700 μmol/L, respectively), whereas the discrepancy is ~10% (~70 μmol at MR-300) in streams moderately affected by road salt. These differences result from cation exchange between Na^+ and other base cations located in the soils. Measurements of exchangeable cations on soils neighboring the interstate in GS and BB exhibit high base saturation values (>90%) in organic horizons, where exchangeable Ca^{2+} is the dominant base cation, and exchangeable Na^+ increases with proximity to the highway (*38, 39*). In BB, these soils are agricultural and treated with fertilizers. High base saturation in GS near the highway, however, is surprising for swamp soils, since soils in more remote regions of GS are highly acidic (base saturation < 10%). Runoff from the interstate highway remarkably increased the base saturation of swamp soils with Ca^{2+} and Mg^{2+} being as abundant on the exchange complex as sodium. The net result of these cation exchange reactions is the binding Na^+ to soil and release of other base cations. Therefore, the higher the salt concentrations in a catchment, the more binding of Na^+ to soil exchange sites occurs. The high accompanying base saturation of the exchange sites results in release of base cations rather than acid cations.
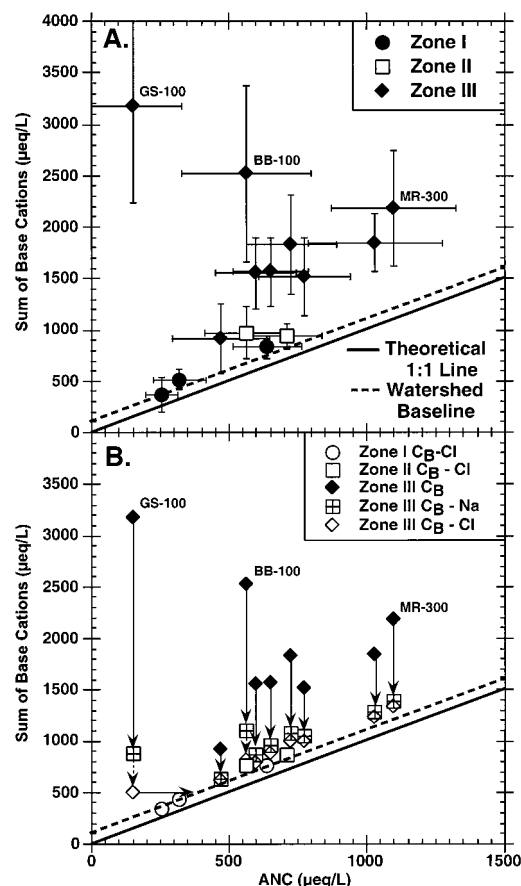
FIGURE 4. (A) C_B vs ANC for each land use zone. The salt-impacted sites (GS, BB, and MR-300) show the greatest number of excess C_B. Error bars = 1 SD. (B) C_B-Cl quantifies the number of cations added by road salt. Subtracting C_B-Na from C_B-Cl quantifies the sum of Ca + Mg + K derived from cation exchange due to binding of Na to soils. The difference between C_B-Cl and the watershed baseline represents the loss of ANC from local acidity.

Distinguishing Salt from Acid Impact. In stream systems where chemistry is controlled by mineral weathering, a 1:1 relationship will exist between ANC and the sum of base cations (where $C_B = Ca^{2+} + Mg^{2+} + K^+ + Na^+$). Addition of anthropogenic acids, such as acid rain, can remove ANC without changing C_B. Adding salts will increase C_B without changing ANC, except if cation exchange occurs with H^+.

In MRW, C_B is always greater than ANC. The relative impacts of nonpoint source pollution for each sample site is illustrated plotting C_B vs ANC (Figure 4A). The zone I sites plot closest to the theoretical 1:1 line and have a slope of one and x-intercept of −97 μequiv/L. This suggests a ~100 μequiv/L loss of ANC by regional acid inputs, consistent with results observed in other remote watersheds in the northeastern U.S. (e.g. ref *40*). Samples from the zone II and zone III sites deviate from the "watershed baseline" estimated by the zone I sites, indicating further impact by anthropogenic pollution derived from *within* the watershed; the lowland zone III tributaries, BB and GS, deviate the most. Although plotting a watershed baseline is based on three sample sites, these three points represent average values of ~200 samples, which cluster tightly around this baseline when plotted individually. For the zone II and III samples, deviation from the baseline shows that these samples were affected by (1) an addition of C_B from salts, which adds C_B without changing ANC and moves points up from the baseline; (2) a loss of ANC by acid addition from any source contributing H^+, which moves points left from the baseline; or (3) a combination of salt and acid impact.

We illustrate the relative impacts of salt and acid on water chemistry for the zone III sites in Figure 4B. C_B-Cl identifies the amount of base cations added from road salt application. Subtracting C_B-Na from C_B-Cl distinguishes the amount of other base cations ($Ca^{2+} + Mg^{2+} + K^+$) released from cation exchange sites by the exchange with Na^+. This difference represents the molar imbalance between Cl^- and Na^+, attributed to the binding of Na^+ to cation exchange sites in soils having high base saturation. Finally, the difference between C_B-Cl and the watershed baseline illustrates the loss of ANC from local acidic chemical loading. Should any C_B be balanced by SO_4^{2-}, such as agricultural gypsum, then the amount of ANC loss indicated by the diagram would be less; however, we have no indication of this gypsum use in the watershed.

For all the zone III sites, salt impacts are greater than local sources of acids. For the high salt impact areas (BB and GS), salts represent 92% of the deviation of C_B from ANC, with 14% of this excess C_B from cation exchange. In the intermediate salt impacted areas (e.g. MR-300), 87% of the deviation of C_B from ANC is due to salt, with 5% of this extra C_B from cation exchange. However, the greatest removal of ANC by acid addition does occur in GS, since C_B-Cl plots the furthest from the baseline of all the samples in the watershed. At WB-100, 32% of excess C_B is due to local acids, representing an average 100 μequiv/L loss of ANC downstream of the Northampton Reservoir.

Effect of Water Removal on Water Quality. The two municipal reservoirs in the MRW collect and export the highest quality water from the watershed. Once used and treated by regional towns, this water is discharged directly into the Connecticut River. In excess of 5700 m^3/day are removed from WB (10% of its potential discharge). Typically, no water escapes over the spillway of the reservoir. Water withdrawals from RB are capped at 2300 m^3/day, and population growth is pressuring an increased allowance to almost 3800 m^3/day. Under the current withdrawal amounts, RB contributes ∼48% of the water to the upstream portion of the MR, and its contribution drops by ∼5% during daily demand periods.

Removal of high quality water from the reservoir limits the effects of dilution on chemical loading to the watershed. We have shown that SO_4^{2-} and NO_3^- additions and ANC loss in the zone II region of WB rivals and even exceeds some zone III sites, despite lower land use intensity. Water removal from reservoirs also impacts water quality in the MR. Sulfate, NO_3^-, and Cl^- rise in MR (by 14%, 37%, and 60%, respectively) downstream of the confluence with GS. Although these effects are diluted by WB, concentrations of SO_4^{2-}, NO_3^-, and Cl^- do not drop below levels that occur at MR-300. Overall, RB does dilute pollution from BB. However, the amount of dilution may fluctuate with changes in streamflow. Further work by the authors will quantify the hydrologic effects of water removal on water quality of the Mill River.

Unlike the arid western United States, high precipitation rates in New England lessen public attitudes toward conservation of water. Yet as populations grow, development encroaches on the supply of water suitable for human consumption. In rural regions, removal of water from watersheds to meet drinking water demands increases the concentration of nonpoint source pollution. Therefore water conservation may hold more importance in temperate climates than otherwise might be anticipated. Continued work in the MRW will help determine the extent that its population can grow and still be sustained by the watershed.

Acknowledgments

Supporting Information Available

Figures describing the distribution of land uses in MRW, variation of Ca and Mg by sample site, and Na and Cl correlations for salt-impacted sites; additional discussion and a figure further illustrate the variation and temporal dynamics of SO_4 and ANC in zones I and III. This material is available free of charge via the Internet at http://pubs.acs.org.

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