

Hydrogeochemical Cycling and Chemical Denudation in the Fort River Watershed, Central Massachusetts: An Appraisal of Mass-Balance Studies

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The Fort River watershed in central Massachusetts receives precipitation with a composition similar to that in Hubbard Brook (New Hampshire), yet the average stream water chemistry is substantially different, showing higher pH and TDS. This is largely a function of bedrock and surficial geology, and chemical differences among small streams within the Fort River watershed are apparently controlled by the composition and thickness of the prevailing surficial cover. The surficial deposits determine groundwater and surface water flow paths, thereby affecting the resultant contact time with mineral matter and the chemistry of the runoff. Despite the rural setting, over 95% of the annual sodium and chloride in the streams comes from road salt; after correcting for this factor, cation denudation rates are about equal to those at Hubbard Brook. However, silica removal is occurring at a rate more than 30% greater in the Fort River. When climatic conditions in Hubbard Brook and Fort River are normalized, weathering rates appear consistently higher in the Fort River, reflecting differences in weathering processes (i.e., cation exchange and silicate breakdown) and hydrogeology. Because of uncertainties in mechanisms of cation removal from watersheds, the silica denudation rate may be a better index of weathering intensity.

INTRODUCTION

The determination of weathering rates and reaction mechanisms in watersheds has been a central focus of hydrogeochemistry for a number of years. Approaches to this problem have come under three broad fields: (1) laboratory investigations of mineral weathering [Busenberg and Clemency, 1976; Berner and Holdren, 1979; Chou and Wollast, 1984], (2) detailed studies of selected segments of watershed systems, usually soils [Hornbeck et al., 1977; Mollitor and Raynal, 1982; Lau and Mainwaring, 1985], and (3) chemical mass balances [Cleaves et al., 1970; Likens et al., 1977; Plummer and Back, 1980; Paçes, 1986]. The first two approaches are necessarily directed toward small-scale processes, whereas the third endeavors to obtain weathering or chemical denudation rates over a wide area. Numerous studies undertaken in various locations throughout North America and Europe have demonstrated that major regional differences exist for hydrochemical cycling rates, dependent upon topography, climate, soil, and geology [Johnson et al., 1968; Lewis and Grant, 1979; Dethier, 1979; Katz et al., 1985; Hornung et al., 1986]. Furthermore, increasing concern about the effects of acidic deposition upon soil development and weathering has also prompted quantitative analysis of mass-balance data to look for evidence of watershed acidification [Paçes, 1985, 1986].

Many of the fundamental field-based investigations of watershed geochemistry were conducted in remote, forested regions of moderate-to-high elevation, and often these have become the standard by which the geochemical cycling in a whole region is characterized. For example, the thoroughly documented watersheds of the Hubbard Brook Experimental Forest [Likens et al., 1977] are used routinely as the type locality for hydrogeochemistry in the northeastern United

States. However, it has become quite clear that such regional generalizations based on individual, small watersheds may not always be appropriate. In the Adirondack Mountains of New York, the Integrated Lake Watershed Acidification Study (ILWAS) found that adjacent lake basins of similar bedrock geology had very different hydrochemistries. This was attributed to a pronounced contrast in the surficial geology, soil development, and hydrogeology of the two basins [Newton and April, 1982; April and Newton, 1985; Cronan, 1985]. Similar effects have been observed in small watersheds in the United Kingdom [Hornung et al., 1986], and it is clear that the simple extrapolation of processes derived from mass-balance studies may not be possible, even over short distances, unless the hydrogeological characteristics of the region are also considered.

The optimal way of overcoming this problem is to document carefully the hydrochemical reaction processes at each stage in the hydrologic cycle, as realized in the ILWAS project, but such studies require an army of investigators with a budget to match! A more practical and efficient approach is to make reasonable estimates of mass-balance geochemistry with accurate reconnaissance information on surficial geology and hydrogeology. Accordingly, we have studied a representative watershed system in central Massachusetts in order to (1) determine if differences in surficial geology and hydrogeology within the drainage basin are reflected in stream water chemistry, (2) compare the results from a mass-balance study to the "type watersheds" (in this case primarily Hubbard Brook), and (3) make a preliminary assessment of weathering processes to account for observed differences in hydrochemical cycling between the two locations.

DESCRIPTION OF AREA

The headwaters of the Fort River watershed are located predominantly within the Shutesbury Quadrangle of west-central Massachusetts (Figure 1). This region encompasses some 54 km² and can be divided into nine smaller

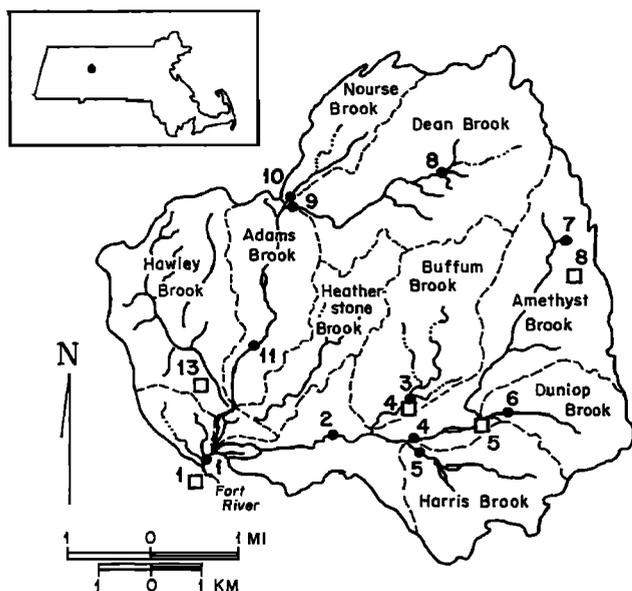


Fig. 1. Location map of the Fort River headwaters area, showing individual subwatersheds. Precipitation collectors are indicated by open squares; stream water sampling sites are represented by solid circles.

subwatersheds. Within this network lie three surface-water reservoirs which provide about half the drinking water supply to the town of Amherst, Massachusetts. Most of the watershed is forested, with some rural residential development along roadways. The terrain is very hilly, with elevations ranging from 46 to 380 m above sea level. Although details of the vegetative history are not known, the area belongs to the northern hardwood forest [Bormann and Likens, 1979] and has been undergoing a gradual reforestation since the early twentieth century, as agricultural land was abandoned and extensive logging terminated. Accordingly, we will start with the assumption that this area, like Hubbard Brook, is aggrading, an assumption which seems to be borne out by our later calculations.

The bedrock geology of the region is relatively homogeneous. The most abundant rock type is gneiss, consisting of the late Precambrian Dry Hill, Butter Hill, and Poplar Mountain formations. These are massive, coarse-to-medium grained, feldspar-biotite gneisses. In addition, the Pelham Quartzite crops out in the west-central part of the study area. This lithology consists of massive-to-well bedded, moderately foliated coarse-to-fine-grained quartzite, with minor biotite, feldspar, and actinolite. In any case, the bedrock is of a type often viewed as resistant to chemical weathering and, in this general respect, is superficially similar to Hubbard Brook.

The surficial deposits in the study area consist primarily of a sandy till (Figure 2) with a thickness of 0–5 m. This till is overlain locally and discontinuously by an aeolian mantle of silt and fine sand up to 1 m thick, with the greatest accumulations on west facing hill slopes. Localized stratified drift deposits occur as kame terraces, kame deltas, and valley-train deposits.

METHODS

Five precipitation collectors were placed at various elevations in the watershed (Figure 1) to ascertain topographic effects on both precipitation volume and composition. The

collectors were modeled after those used by Yuretich *et al.* [1981], were made of polyethylene, and open continuously to the atmosphere. Despite the popularity of wet-only collection in recent years, we feel that bulk precipitation gives a better estimate of the total geochemical input into the watershed and is also more directly comparable with the long-term data from Hubbard Brook. In any case, there are as yet no generally accepted methods for evaluating separately the impact of dry deposition on watersheds. Consequently, all samples represent bulk precipitation from the atmosphere. Collectors were sampled on a monthly basis for 18 months beginning in July 1981.

Stream waters were collected at 11 sites throughout the watershed (Figure 1). Sites were located in each subwatershed, with the exception of Hawley and Heatherstone brooks. Hawley Brook has significant suburban and agricultural development, and an accurate assessment of its normal chemical characteristics was deemed unlikely. The small Heatherstone Brook watershed was not easily accessible. Samples were collected monthly, coincident with precipitation collection, in acid-washed 500-mL polyethylene bottles which had been rinsed with distilled water and river water prior to collection. Water temperatures were recorded in the field, and pH measurements were made during several sampling excursions. The pH was measured on all precipitation and stream samples immediately after being returned to the laboratory. The waters were then filtered (Whatman 41) to remove particulates, and subsequent analyses (Ca^{2+} , Mg^{2+} , Na^{+} , K^{+} , SO_4^{2-} , SiO_2 , and alkalinity) were performed on filtered samples. Tests on samples that had been filtered through 0.45- and 0.1- μ filters showed no statistically significant differences among the major cations and silica for the various filtration methods.

Alkalinity was determined on river water samples by acidimetric titration according to the two endpoint low-level method [Greenberg *et al.*, 1981]. Sodium and potassium were analyzed by atomic emission; calcium and magnesium were determined by atomic absorption after addition of lanthanum as an ionization suppressant. Chloride was measured with a specific-ion electrode, and silica was analyzed spectrophotometrically using the heteropoly blue method. Sulfate was determined by adding a calibrated excess of BaCl_2 (5 mL of a 7.28×10^{-4} solution, dissolved in 5000 ppm KNO_3 to inhibit ionization) to 20 mL of sample in order to precipitate all sulfate as BaSO_4 . After heating to 60°C overnight, and subsequent cooling, the remaining barium was analyzed by atomic absorption, and the sulfate calculated. Based upon analysis of replicate samples, cation concentrations are accurate to $\pm 3\%$, alkalinity and silica to $\pm 5\%$, and sulfate to $\pm 10\%$. Nitrate was not included in the original analytical protocol but was analyzed at a later date (along with a rerun of sulfate and chloride) on a Wescan ion chromatograph. Consequently, nitrate values should be regarded as estimates only.

RESULTS AND DISCUSSION

Precipitation

Variations were observed in the volume of precipitation collected at different elevations during each sample interval. Site 8, situated near the top of the Pelham Hills, usually contained the largest volumes, whereas site 13, located near the margin of the Connecticut River Valley, frequently had

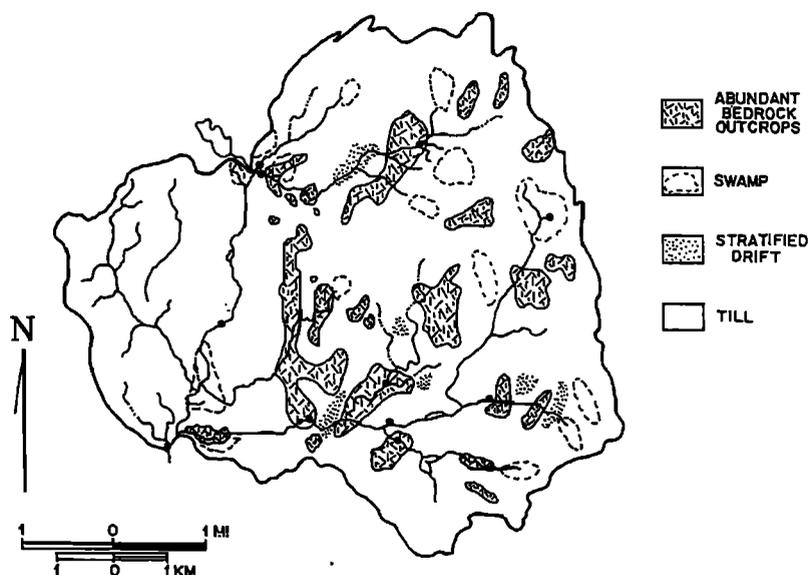


Fig. 2. Generalized map of the surficial geology of the Fort River headwaters. Underlying bedrock is dominated by gneiss and quartzite.

the least amount. The data for all five sites were averaged to obtain monthly rainfall amounts; these in turn were averaged to determine annual precipitation. Our data were compared with those collected in Amherst [Bradley *et al.*, 1987], and the results are similar. In both observations, 1250 mm of precipitation fell on the area during water year 1982 (October 1981 to September 1982). This contrasts with the long-term precipitation average of 1080 mm, based on approximately 100 years of record, and an average of 1140 mm from 1970 through 1981.

No apparent geographical or elevational effects were observed in the chemical composition of the precipitation. Accordingly, all five sites were averaged together on a monthly basis to determine the general composition of precipitation in this area (Table 1), which follows the regional patterns observed in other parts of the northeastern United States. The proximity of the headwaters of the Fort River to the Hubbard Brook Experimental Forest (about 200 km to the north) [Likens *et al.*, 1977; Martin, 1979] is consistent with the observed compositional similarity. Although it is difficult to evaluate the significance of differences in composition, given the dissimilarities in length of observation, the sodium content in the Fort River seems to be

much higher (almost twice). This results in an average Na:Cl ratio of 0.57 in Fort River precipitation, more than double that of Hubbard Brook (0.25) and close to that found in average seawater (0.56). We believe that this reflects a greater influence of marine aerosols in the Fort River area, which is approximately 125 km north of Long Island Sound. Similar effects were noticed in the precipitation chemistry in the southeastern United States [Gambell and Fisher, 1966] and in New Jersey [Yuretich *et al.*, 1981].

It is quite clear that the charge balance of the average rainwater is not as desirable as it could be (not an uncommon occurrence in a study of this nature), although the charges overlap within the standard deviation (Table 1). We feel that the greatest source of error is in the pH measurement: an average pH of 0.1 unit higher (a 3% measurement error) would decrease the H^+ concentration by about 18 $\mu\text{eq/L}$ and provide a much more agreeable balance.

Temporal changes in precipitation composition are substantial (Figure 3), with seasonal changes in pH and most ions. Low pH during the summer months is accompanied by low sodium and chloride and high sulfate values, with a general reversal of these patterns during the winter. Such variations have been observed in other parts of the eastern

TABLE 1. Composition of Precipitation

| | Fort River* | | | Hubbard Brook† | | |
|---------------|-------------|------------------|---------|----------------|----------------|--------|
| | ppm | $\mu\text{eq/L}$ | | ppm | μeq | |
| Sodium | 0.22 | 9.36 | (5.29) | 0.12 | 5.22 | (0.43) |
| Potassium | 0.08 | 22.13 | (1.18) | 0.07 | 1.79 | (0.51) |
| Calcium | 0.28 | 13.87 | (4.08) | 0.16 | 7.98 | (1.00) |
| Magnesium | 0.08 | 6.52 | (2.07) | 0.05 | 4.16 | (0.83) |
| Hydrogen (pH) | 4.06 | 87.13 | (26.16) | 4.13 | 73.9 | (0.30) |
| Total cations | | 118.37 | (38.78) | | 93.05 | (2.77) |
| Chloride | 0.36 | 10.33 | (2.45) | 0.51 | 14.4 | (2.55) |
| Sulfate | 2.65 | 52.91 | (24.89) | 2.87 | 60.3 | (1.14) |
| Nitrate | 1.63 | 26.3 | (25.2) | 1.43 | 23.1 | (1.77) |
| Total anions | | 89.54 | (52.54) | | 97.8 | (5.46) |

Numbers in parentheses are standard deviation (σ).

* This study, $n = 65$.

† Likens *et al.* [1977].

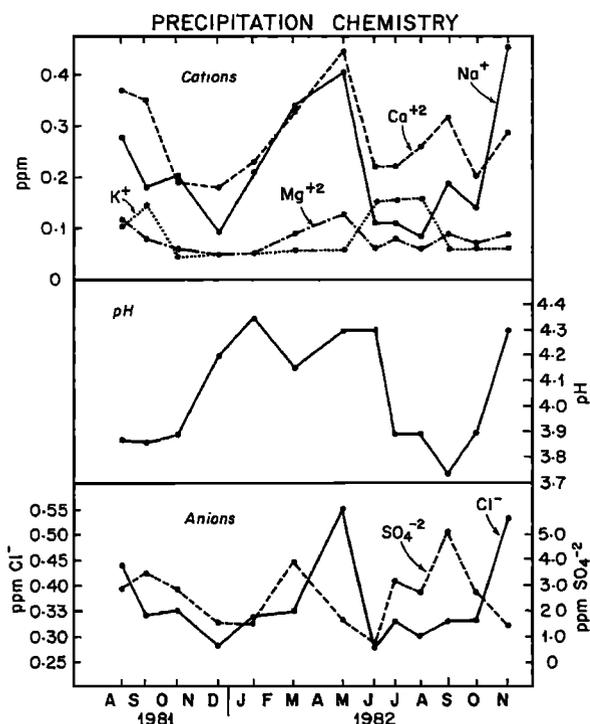


Fig. 3. Annual trends in precipitation chemistry.

seaboard and have been attributed to yearly shifts in storm tracks, with winter storms transporting a greater marine component into the region [Hornbeck *et al.*, 1977; Yuretich *et al.*, 1981]. We endorse this interpretation for central Massachusetts as well, since seasonal changes in storm paths are similar.

Stream Water

Despite the close similarities in precipitation composition between the Fort River and Hubbard Brook watersheds, there is a very large divergence in average stream water chemistry between the two areas (Table 2). The average values for the Fort River headwaters were based on the data from sampling sites 2 and 11 (Figure 1). These sites represent

the total composition of the two master streams in the headwaters, avoiding the developed areas around Hawley Brook and site 1. It was felt that any contamination from these areas would affect the overall water composition at site 1, the location farthest downstream. In spite of the exclusion of these suspect areas, the Fort River waters are still elevated in all measured constituents.

Drainage basinwide averages alone are insufficient for total comparison because of stream chemistry variations throughout the watershed. There are pronounced and progressive increases in concentration of all components in a downstream direction (Figure 4). This increase in concentration with stream length and order reflects the length of groundwater flow paths and therefore is related to the residence time of water in contact with surficial materials. The relatively impermeable bedrock of the area causes water to move predominantly in surficial materials as described for two Adirondack watersheds [Newton and April, 1982]. The nature of these surficial deposits will control the chemistry of the surface waters to a significant extent [Newton and April, 1982; Yuretich *et al.*, 1981].

The importance of surficial geology in the present study area is illustrated by examining land-use patterns and populations of two subcatchments of approximately the same size: Nourse Brook (site 10) has an area of 259 ha, and Dunlop Brook (site 6) contains 340 ha within its watershed. These small streams are both underlain by the Dry Hill Gneiss plus a small amount of Pelham Quartzite, yet Nourse Brook has consistently greater amounts of all dissolved components (Figure 4). Outcrop patterns and preliminary seismic refraction studies indicate that depth to bedrock is shallower in the Dunlop Brook watershed. In general, Dunlop Brook has up to 4–5 m of sandy till overlying bedrock, whereas Nourse Brook has an additional thickness of 5–8 m of a compact, clay-rich lower till underneath the sandy till. Furthermore, the surficial material of Dunlop Brook also contains large areas of stratified drift deposits (Figure 2).

Such geological differences will cause divergent patterns in runoff and groundwater flow patterns [Newton and April, 1982]. In the Dunlop Brook area, larger expanses of shallow

TABLE 2. Stream Water Chemistry

| | Fort River* (pH = 6.13) | | Hubbard Brook† (pH = 4.92) | | "Normalized" Fort River,‡ μeq/L |
|---------------|----------------------------|---------------|-------------------------------|-------|---------------------------------------|
| | ppm | μeq/L | ppm | μeq/L | |
| Sodium | 1.06 [3.99] | 45.7 (7.4) | 0.87 | 37.8 | 50.2 |
| Potassium | 0.55 | 14.1 (3.0) | 0.23 | 5.2 | 6.9 |
| Calcium | 2.89 [2.96] | 148.0 (25.0) | 1.65 | 82.3 | 109.5 |
| Magnesium | 0.72 | 58.8 (6.3) | 0.38 | 31.3 | 41.7 |
| Total cations | | 266.6 (41.7) | | 156.6 | 208.3 |
| Chloride | 0.74 [5.49] | 20.9 (2.5) | 0.55 | 15.5 | 20.6 |
| Sulfate | 6.41 | 133.5 (13.5) | 6.30 | 131.0 | 174.2 |
| Nitrate | 2.79 | 45.0 (2.3) | 2.01 | 32.4 | 43.4 |
| Alkalinity | | 50.6 (33.7) | | 15.1 | 20.2 |
| Total anions | | 250.0 (54.0) | | 194.0 | 258.4 |
| Silica | 9.37 | 156.2 (17.8)§ | 4.50 | 75.0§ | 100.5§ |

Numbers in parentheses are standard deviation (σ). Numbers in square brackets are values before correction for contribution from road salt. See text for details.

* This study, averages from sites 2 and 11, $n = 46$.

† Likens *et al.* [1977].

‡ Projected composition of Fort River if weathering processes were identical to those of Hubbard Brook. See text for details.

§ Values in $\mu\text{mol/L}$.

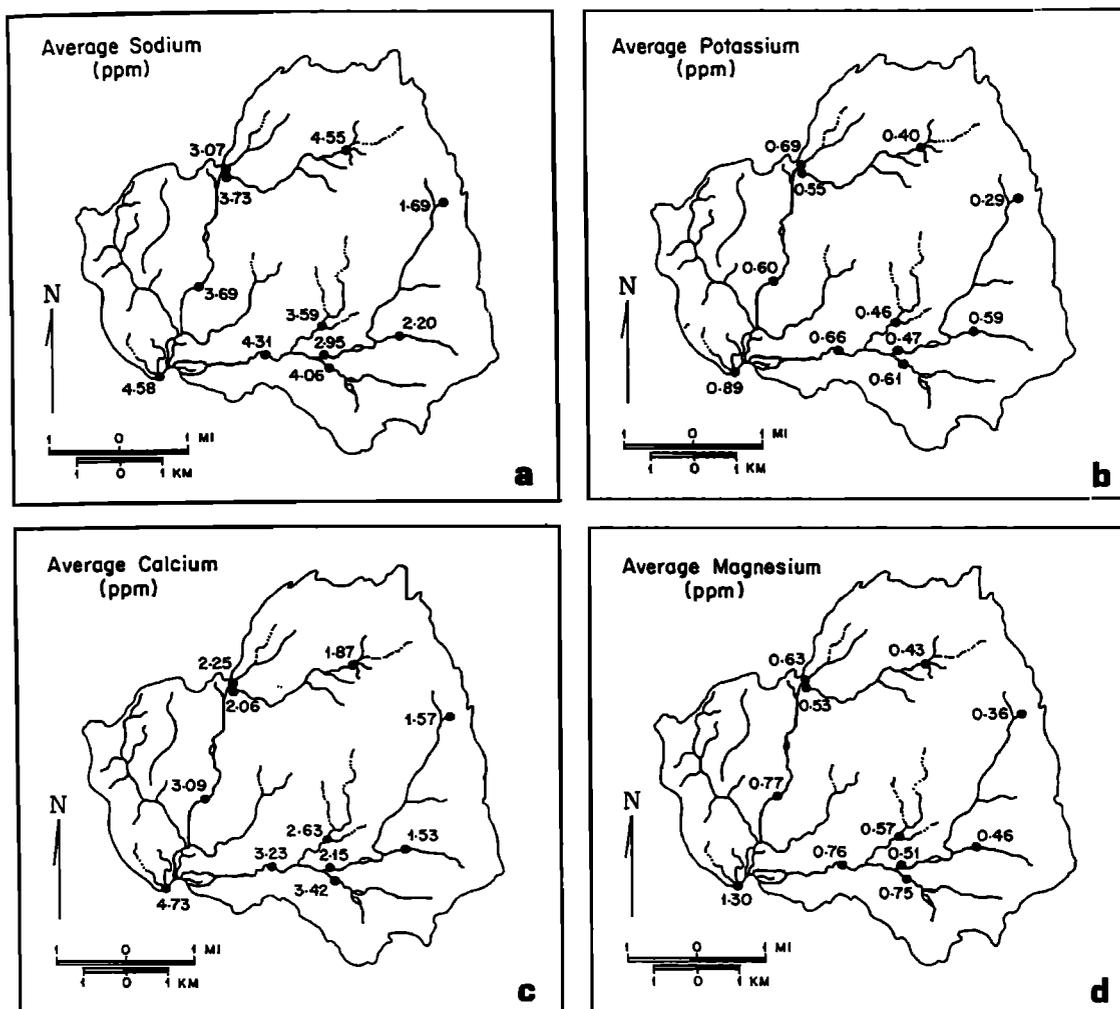


Fig. 4. Annual average values of stream water chemistry for major components at each sampling site.

bedrock will promote runoff and interflow, and greater permeability in the stratified drift should encourage a more rapid movement of groundwater despite a lower average topographic gradient (4.5% versus 6% in Nourse Brook). These characteristics will combine to give Dunlop Brook a comparatively low pH and total dissolved solids.

Temporal variations in stream water chemistry do not correspond to seasonal changes in precipitation composition. The dampened fluctuations in the concentrations of major cations seem to be an inverse function of discharge (Figure 5), as has been demonstrated convincingly in other areas, most notably the Rocky Mountains [Miller and Drever, 1977; Lewis and Grant, 1979; Feller and Kimmins, 1979].

The seasonal variability in composition of Nourse and Dunlop brooks reveals both the general behavior of the entire stream system as well as the likely hydrogeological differences between these two subwatersheds. Although a general concordant variation in chemical composition over the course of the year is apparent in these streams (Figure 6), some pronounced differences are clearly present. For example, during the low-flow months of May–September 1981, calcium and magnesium in Dunlop Brook decrease, whereas they increase in Nourse Brook (Figure 6). A more subdued version of the same pattern also occurred during the dry months August–October 1982. Since these periods represent

the time of maximum base flow, some fundamental differences in the paths of that base flow must be at work here. A detailed hydrologic investigation of the two watersheds will ultimately be necessary to substantiate all observations, but spot measurements of discharge confirm higher summer base flow in the Nourse Brook watershed.

Mass Balances and Chemical Denudation

The short-term compositional data from the Fort River watershed might be regarded as insufficient to calculate significant mass balances or denudation rates. However, Likens *et al.* [1977] have demonstrated that annual chemical concentrations in stream water are fairly constant and that ionic transfer rates are largely determined by changes in water budgets. It is therefore of greater importance to have long-term records of stream discharge and precipitation input. Yuretich *et al.* [1981] demonstrated this very effectively in examining the hydrochemical balance in the Pinelands of New Jersey. Using 2 years of chemical data coupled with water records of up to 46 years' duration, they computed an input-output balance in this region of quartz sand where mineral-water reactions are minimal.

In the present study, discharge data were available for a U.S. Geological Survey gaging station downstream from the study area. Because of differences in the size of the drainage

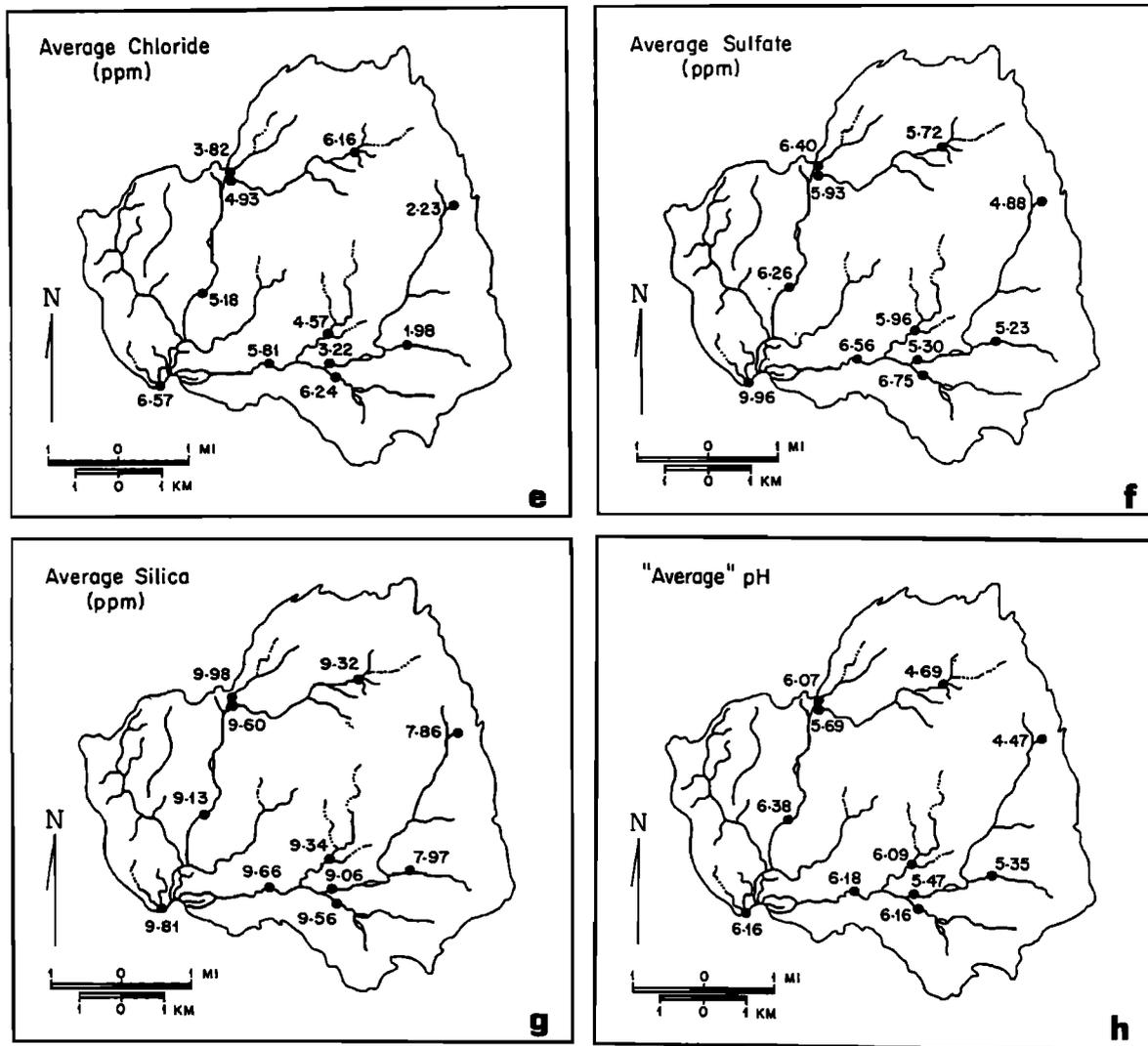


Fig. 4. (continued)

basin at the gaging site, the raw discharge measurements are not directly comparable. However, the long-term specific discharge of the Fort River is identical to that of other streams, both large and small, in the central Massachusetts area (Table 3). A similar relationship was observed for stream flow in the New Jersey Coastal Plain [Yuretich *et al.*, 1981]. Such consistency is reasonable: one would expect watersheds with similar soil, surficial and bedrock characteristics, topography, and vegetation to exhibit the same long-term average hydrological response. Accordingly, the most reliable mass-balance calculations will be realized from the use of long-term specific discharge coupled with the average precipitation input for the same period of record.

The chemical fluxes were calculated by multiplying the average chemistry determined for 1981–1982 by either the average 12-year precipitation volume (for input) or the average long-term specific discharge (for output). Unlike Hubbard Brook, these raw fluxes are not suitable for direct comparison because of additions to stream water load by road salt. The input-output data show that the amount of dissolved chloride leaving the watershed is almost 8 times as great as the amount entering in precipitation. Chloride contributions from the bedrock and tills in this area are likely insignificant, and in the absence of any groundwater leakage,

chloride can be considered as a conservative component in the central Massachusetts area. Accordingly, all chloride in the streams other than that contributed by precipitation has its ultimate source from the salt used to de-ice area roads. The road salt in use is a mixture of 95% NaCl and 5% CaCl₂ by weight, and the proper road-salt contribution to sodium and calcium in the streams must be subtracted from the total output. This has been done (Table 4) to provide the corrected figures derived from natural watershed sources.

The size of the road-salt component can be obtained from the annual evapotranspiration, which was calculated using two methods. First the long-term precipitation volumes and specific discharge were compared:

$$(\text{average discharge})/(\text{average precipitation}) =$$

$$(5.36 \times 10^8 \text{ L/km}^2/\text{yr}) (11.4 \times 10^8 \text{ L/km}^2/\text{yr}) = 0.47$$

Thus a 53% evapotranspiration rate is computed from these data. As an independent evaluation of these values, we also calculated evapotranspiration using the method of Thornthwaite and Mather [1957], which determines evapotranspiration as a function of geographical location and soil qualities together with precipitation and air temperature. During the 12-year time span for which we have both precipitation and

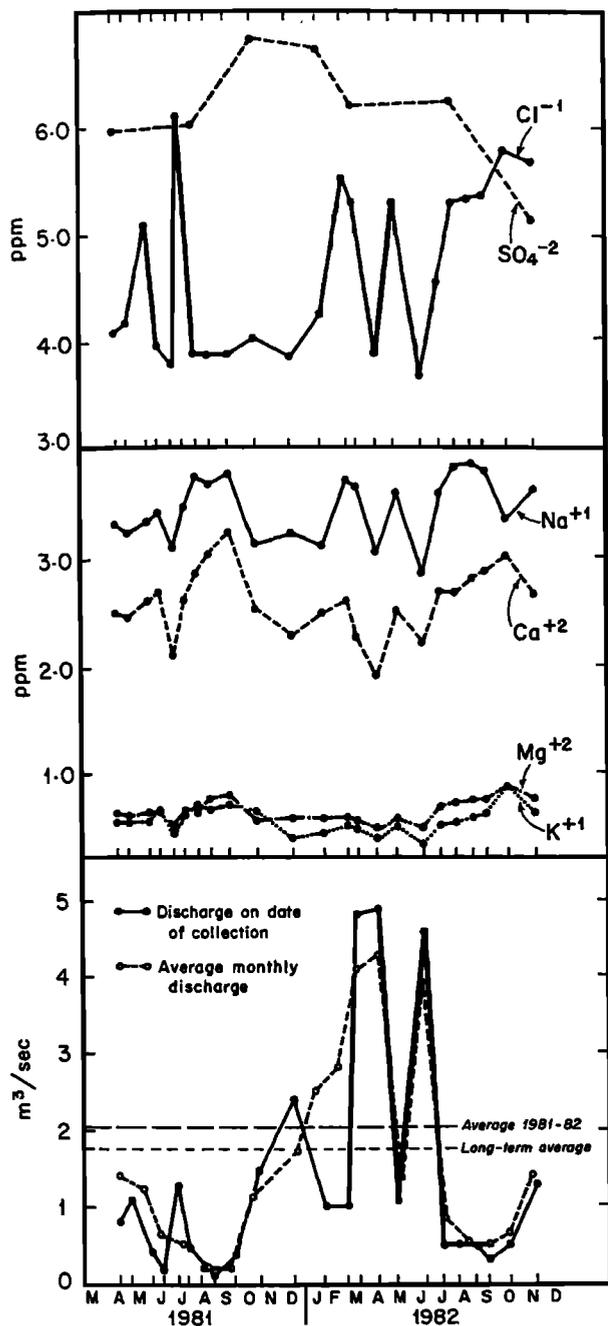


Fig. 5. Temporal changes in stream chemistry and discharge. Seasonality is muted, but cations have an apparent correlation with discharge.

discharge records, this method yields an average evapotranspiration of 55%. The average of these two evapotranspiration values, or 54%, produces a natural chloride concentration of 0.75 ppm in the Fort River; the remainder (95%) comes from road salt.

Cation Denudation Rates

It is clear from the data in Table 4 that hydrogen ion is being neutralized effectively in the Fort River soils and surficial materials and this is accompanied by a substantial change in water chemistry. After adjustment is made for evapotranspiration, 75% of the incoming cations are H^+ ; yet these constitute only 0.3% of cations in stream water.

Concomitant with the depletion of H^+ in stream water is the enrichment of other major cations. The cations released from the watershed are about 10% higher than the precipitation acidity (988 eq/ha H^+ lost; 1069 eq/ha cations added), in this respect similar to Hubbard Brook; the remaining base cations are presumably balanced by internally generated hydrogen ions produced in the soil profile [Van Breemen *et al.*, 1984]. Compared with many other studies, this cation excess is small [Hornung *et al.*, 1986] and suggests that mineral weathering and cation exchange are the most important controls on water chemistry.

When the road-salt effect has been subtracted, calcium is being removed at the greatest rate, followed in order by magnesium, sodium, and potassium. The total cation denudation rate is identical to that of the Hubbard Brook area, although there are some differences in individual ion removal rates, particularly for sodium and potassium. These are probably attributable to differences in the mineralogy and chemical composition of the surficial and bedrock materials at each location. The Dry Hill Gneiss, for example, is particularly rich in K-bearing minerals, and till derived from this bedrock might be expected to yield more potassium to the drainage water.

Much large differences exist in the sulfate and silica denudation rates. The behavior of sulfate and sulfur cycling in watershed systems is currently a topic of major research interest [Mollitor and Raynal, 1982], and the cause of the difference is still quite speculative. Bedrock control could enter into the equation here as well; there may be more sulfide-bearing minerals in the Littleton Schist of Hubbard Brook compared with the Dry Hill Gneiss. These sulfides would not only produce more sulfate, but would contribute to the elevated acidity levels observed in Hubbard Brook stream waters. There may also be some differences in the ability of the Fort River and Hubbard Brook soils to absorb sulfate. Additionally, sulfate levels in the watershed may be related to the input from dry deposition. Katz *et al.* [1985] have postulated that excess sulfate in the watersheds of the

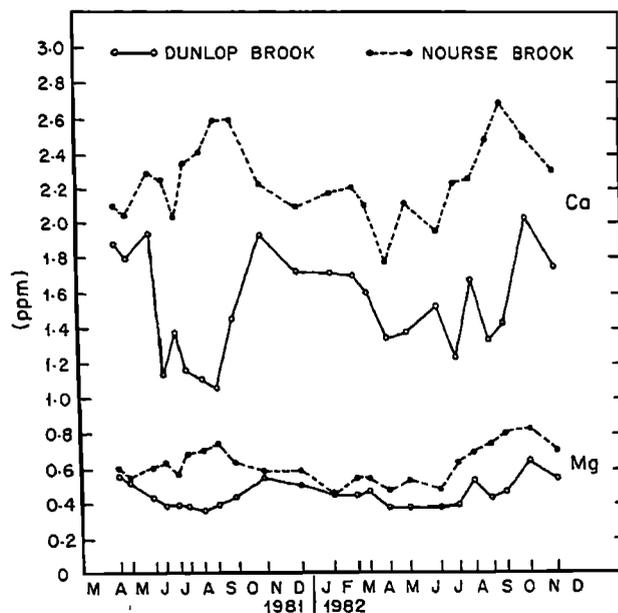


Fig. 6. Differences in the composition of Dunlop and Nourse brooks, as indicated by calcium and magnesium concentrations, are maintained all year long.

TABLE 3. Streamflow Records

| | Years of Record | Drainage Area, ha | Average Discharge, m ³ /s | Specific Discharge, × 10 ⁻³ m ³ /s/ha |
|----------------------------|-----------------|-------------------|--------------------------------------|---|
| Fort River | 16 | 1052 | 1.784 | 1.70 |
| Cadwell Creek | | | | |
| Main weir | 12 | 728 | 0.125 | 1.71 |
| Upper weir | 12 | 163 | 0.030 | 1.84 |
| East Swift River | 42 | 1132 | 1.954 | 1.73 |
| Average specific discharge | | | | 1.74 |
| Standard deviation | | | | 0.06 |
| % standard deviation | | | | 3.7% |

Catoctin Mountains in Maryland (Table 4) comes from this source. If this is the case in the Fort River, then the dry deposition of sulfate must be of lesser importance, although this seems unlikely.

Of possibly greater significance is the very high silica denudation rate in the Fort River watershed, which approaches that of Hauver Branch in the Catoctin Mountains [Katz *et al.*, 1985]. The silica denudation rate is 30% greater in the Fort River than in Hubbard Brook. This indicates that the concordance of cation denudation between the watersheds may not tell the entire story of chemical weathering.

Differences in the cation/silica ratio in stream water could result from a number of factors, among them, differences in sample handling procedures, variability in drainage basin area, balance between cation exchange and silicate weathering in the soils, the types of secondary minerals produced in the weathering zone, and water flow paths and resulting contact time with soil minerals.

With regard to the first item, the principal difference between our techniques and those of the other studies was method of filtration. The Hubbard Brook samples were filtered through a 0.45- μ filter [Likens *et al.*, 1977], and the Hauver Branch samples were filtered 0.1 μ [Katz *et al.*, 1985] prior to analysis. However, our tests on the Fort River samples showed that filtration had no influence on the molybdate-reactive silica or cations.

The differences in watershed size could have some effect on stream chemistry as well. The very small size of the Hubbard Brook watersheds (12–43 ha) might limit the contact time between interflow or groundwater and surficial

materials, thereby reducing the amount of chemical reaction. Arguing against this, the chemical differences between small headwaters and the larger areas in the Fort River Basin are relatively small, and silica, in particular, is quite constant (Figure 4). Moreover, even in the most extreme headwater sites (site 7), the SiO₂ is still much higher than in Hubbard Brook, pointing toward some fundamental differences between the two locations. Additional evidence comes from more detailed hydrogeological studies we have recently conducted at nearby locations. Leonard *et al.* [1984] and Yuretich *et al.* [1986] report a groundwater residence time of about 1 year for watersheds of 73 and 52 ha. Blum [1986] studied the larger river basin (1132 ha) which contained these small watersheds and found no difference in the average groundwater residence time, nor for that matter, in the baseflow-runoff relationships. In general, watersheds with similar geological characteristics will display similar hydrological behavior, regardless of size, and the hydrogeochemical processes should also be the same.

One way of sorting out the remaining weathering processes is to normalize the water budgets in the two areas. Because of the lower precipitation (1140 mm) and greater evapotranspiration (54%) compared with Hubbard Brook (1320 mm and 37%, respectively), the total net water flux per square meter through the Fort River watershed is only 64% of Hubbard Brook (536 L versus 832 L; Figure 7). For example, 100 mm of precipitation in Hubbard Brook produces 63 mm of runoff; in the Fort River, only 47 mm of runoff results. Each square meter of the Hubbard Brook watershed receives 1320 L of water as precipitation (Figure

TABLE 4. Mass Balance and Chemical Denudation Rates, eq/ha/yr

| | Fort River* | | | Hubbard Brook | Hauver Branch |
|----------------------|-------------|--------------|------------|---------------|---------------|
| | Input | Total Output | Net Output | Net Output† | Net Output‡ |
| Hydrogen | 992 | 4 | -988 | -980 | -812 |
| Sodium | 97 | 245§ | 148§ | 245 | 316§ |
| Potassium | 25 | 76 | 51 | 25 | 141 |
| Calcium | 149 | 771§ | 623§ | 579 | 592§ |
| Magnesium | 68 | 315 | 247 | 210 | 1286 |
| Total cation removal | | | 1069 | 1059 | 2335 |
| Chloride | 118 | 118§ | 0§ | 57 | 0§ |
| Sulfate | 584 | 716 | 132 | 319 | 648 |
| Alkalinity | | 271 | 271 | 125 | 1280 |
| Total anion removal | | | 403 | 501 | 1928 |
| Silica | | 837 | 837 | 640 | 930 |

* This study.

† Likens *et al.* [1977].

‡ Katz *et al.* [1985].

§ Corrected for road-salt contribution.

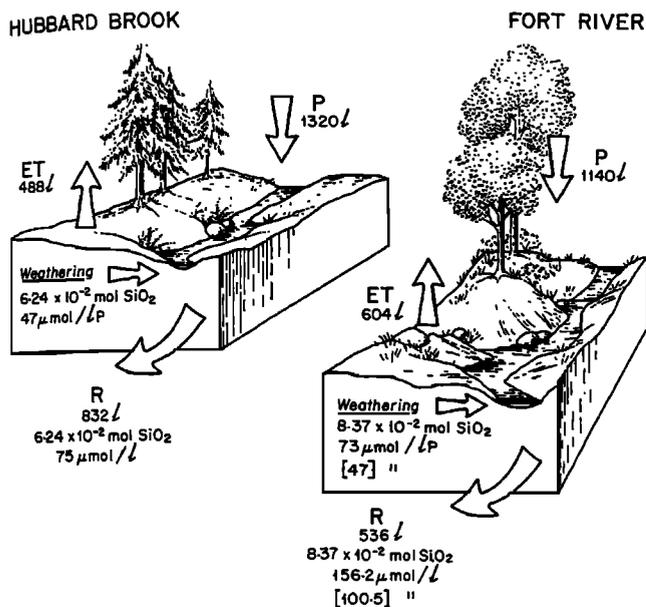


Fig. 7. Comparison of water flux and silica removal in the Fort River and Hubbard Brook watersheds. A greater amount of silica per liter of incident precipitation is removed from the Fort River watershed. Numbers in brackets show amount of silica that would be removed under Hubbard Brook water-flux conditions.

7, left) and loses 6.24×10^{-2} mol SiO_2 from the soils and surficial materials annually. This translates into an effective silica removal rate of $47 \mu\text{mol/L}$ of incident precipitation. If weathering processes are identical in the Fort River watershed, then a similar silica removal rate would produce a concentration of $100 \mu\text{mol/L}$ SiO_2 in the river water (Figure 7, right). This is lower than the observed concentration (Table 2). Applying this reasoning to all other dissolved components, after adjusting for the precipitation and evaporation differences between the two locations, the Fort River should be concentrated by a factor of

$$63 \text{ mm}/47 \text{ mm} = 1.34$$

compared with Hubbard Brook if chemical weathering processes were identical. Table 2 shows that, with the exception of sodium and sulfate, all dissolved substances are more concentrated in the Fort River than predicted by simple extrapolation of the Hubbard Brook system. The conservative nature of chloride is confirmed by this analysis, since the predicted value is virtually identical to the measured chloride in Fort River water.

The differences in silica and cation removal between Hubbard Brook and Fort River are therefore likely related to water-flow paths, cation exchange versus silica weathering, and the types of secondary minerals formed within the soils. The presence within the Fort River watershed of a thicker surficial cover over much of the area may allow a relatively large annual groundwater base flow. In watersheds adjacent to the Fort River basin, we have calculated base flow values of 42–48% of total runoff [Leonard *et al.*, 1984; Yuretich *et al.*, 1986]. Although precise data for Hubbard Brook are not at our disposal, estimates from published information [Likens *et al.*, 1977] and comparisons with British watersheds of similar characteristics [Hornung *et al.*, 1986] suggest a base flow of 20–30%. As a consequence, the waters of Fort River

are more effectively neutralized (higher concentrations of cations and silica) than Hubbard Brook.

The cation/silica ratio in the waters should be a direct function of mineral weathering processes. Bricker [1986] has shown that various ratios will occur in streams dependent upon the bedrock being weathered. Moreover, the cation export from a watershed is known to be influenced by a variety of additional processes [Fölster, 1985]. Differences in vegetation will affect the rate of uptake and retention time in the biosphere. The thickness of the weathering mantle (i.e., the degree of soil development) will determine the balance between ion exchange and silicate-weathering reactions. Available data indicate that ion exchange may be more important in Hubbard Brook than in Fort River. Mineral soils in this region of New Hampshire tend to have base saturation in the range of 30–50% [Federer and Hornbeck, 1985]. Our own measurements on soils near the Fort River watershed show base saturations of 1–12% in the mineral horizons [Leonard *et al.*, 1984]. At present, it is not possible to reasonably quantify all the processes that could augment or retard cation removal from watersheds. However, silica is much less prone to recycling and retention in the watershed [Smith and Dunne, 1977], is derived exclusively from mineral weathering [Reid *et al.*, 1981], and therefore should be more reliable than cations as an indicator of total chemical denudation.

CONCLUSIONS

The chemistry of precipitation in central Massachusetts follows patterns similar to those observed for other locations in the northeastern United States, in particular, Hubbard Brook in New Hampshire. However, stream water chemistry exhibits some notable differences. In the Fort River watershed, concentrations of all constituents are greater than those in Hubbard Brook. In addition, there is a marked influence of surficial geology upon stream water characteristics. Streams in areas of thick till cover have higher pH and total dissolved solids than streams with large areas of shallow bedrock. The total cation denudation rate is similar to that reported from other regions in New England (specifically Hubbard Brook), but a much higher silica removal rate together with a greater net water flux indicate that effective chemical erosion in the central Massachusetts area may be higher. When the water flux for the Fort River is normalized to that in Hubbard Brook, the weathering rate for the Fort River averages 30% greater, a finding consistent with the presumed weathering processes and hydrogeological conditions in central Massachusetts. Field-based studies of stream geochemistry should, in the future, pay more attention to silica export as a weathering-rate indicator.

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