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Water and solute mass balance of five small, relatively undisturbed watersheds in the U.S.

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Abstract

Geochemical mass balances were computed for water years 1992–1997 (October 1991 through September 1997) for the five watersheds of the U.S. Geological Survey Water, Energy, and Biogeochemical Budgets (WEBB) Program to determine the primary regional controls on yields of the major dissolved inorganic solutes. The sites, which vary markedly with respect to climate, geology, physiography, and ecology, are: Allequash Creek, Wisconsin (low-relief, humid continental forest); Andrews Creek, Colorado (cold alpine, taiga/tundra, and subalpine boreal forest); Río Icacos, Puerto Rico (lower montane, wet tropical forest); Panola Mountain, Georgia (humid subtropical piedmont forest); and Sleepers River, Vermont (humid northern hardwood forest). Streamwater output fluxes were determined by constructing empirical multivariate concentration models including discharge and seasonal components. Input fluxes were computed from weekly wet-only or bulk precipitation sampling. Despite uncertainties in input fluxes arising from poorly defined elevation gradients, lack of dry-deposition and occult-deposition measurements, and uncertain sea-salt contributions, the following was concluded: (1) for solutes derived primarily from rock weathering (Ca, Mg, Na, K, and H_4SiO_4), net fluxes (outputs in streamflow minus inputs in deposition) varied by two orders of magnitude, which is attributed to a large gradient in rock weathering rates controlled by climate and geologic parent material; (2) the net flux of atmospherically derived solutes (NH_4, NO_3, SO_4, and Cl) was similar among sites, with SO_4 being the most variable and NH_4 and NO_3 generally retained (except for NO_3 at Andrews); and (3) relations among

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monthly solute fluxes and differences among solute concentration model parameters yielded additional insights into comparative biogeochemical processes at the sites.

Keywords: Atmospheric deposition; Biogeochemistry; Runoff; Water budgets; Watersheds; Weathering

1. Introduction

The estimation of a watershed mass balance is a fundamental technique for assessing effects of a variety of factors on watershed system function, and in particular the hydrologic and hydrochemical cycling of typically mobile solutes such as major ions and nutrients (Likens et al., 1977; Cerny et al., 1994; Likens, 2001). Furthermore, the knowledge of how the composition of water evolves under natural or at least minimally impacted conditions is important for establishing a baseline against which to compare the effects of human activities. The mass balance approach provides a mechanism for tracking changes of mass of water and specific elements or compounds in a watershed (Paces, 1986; Cerny et al., 1994). Water passing through a watershed interacts with vegetation, soils, regolith, and bedrock and reflects these interactions by changes in chemical composition and other characteristics. The flux of water and accompanying dissolved and suspended materials into and out of the watershed provides a frame of reference within which biotic and abiotic information can be combined to understand watershed ecosystem processes and how they affect water quality. The comparison of mass balance among watersheds with varying climate, geology, and vegetation provides a framework for establishing the relative controls on biogeochemical cycling. Additionally, it is important to evaluate the limitations in data collection and analysis techniques used to compute the mass balances across a broad range of environmental conditions.

Across geologic time scales, natural variations in climate and vegetation succession are dominant in changing the watershed mass balance. However, human activities either through physical alteration of the landscape or through emissions from industrial or municipal sources, fertilizer application, and liquid- and solid-waste disposal can significantly alter the mass balance. It is important to establish the processes controlling water-quality evolution under natural conditions and to identify human-induced changes. Water-quality degradation may threaten human and ecosystem health. Consequently, there is a need to assess mass transfers to provide not only an index of water-resource degradation, but also to provide knowledge of causal relationships to effectively manage these resources.

The objective of this paper is to evaluate the monthly and annual watershed mass balance of water and major solutes from five small relatively undisturbed watersheds in the U.S. with respect to the major factors controlling the cycling of these solutes. The watersheds, as described below, span a wide range of climatic, hydrological, physical, and geological conditions and were analyzed for a 6-year data-collection period from water year (WY) 1992 through WY1997 (October 1, 1991, to September 30, 1997).

1.1. Study sites

Water and solute mass balances were computed for each of the five watersheds studied as part of the U.S. Geological Survey's (USGS) Water, Energy, and Biogeochemical Budgets (WEBB) Program (Lins, 1994; Baedecker and Friedman, 2000) (Fig. 1 and Table 1). The watersheds include Andrews Creek (called Andrews herein) an alpine to subalpine watershed in the Loch Vale watershed, west-central Colorado (Clow et al., 2000); Río Icacos (Icacos) a lower montane wet tropical forest watershed in the Luquillo Experimental Forest, eastern Puerto Rico (Larsen and Stallard, 2000); Panola Mountain (Panola), a humid continental to subtropical forested watershed in north-central Georgia (Peters et al., 2000); watershed 9 at Sleepers Rivers (Sleepers), a temperate forested watershed in northeastern Vermont (Shanley, 2000); and Allequash Creek (Allequash) at Trout Lake, a forested temperate watershed in north-central Wisconsin (Walker and Bullen, 2000).

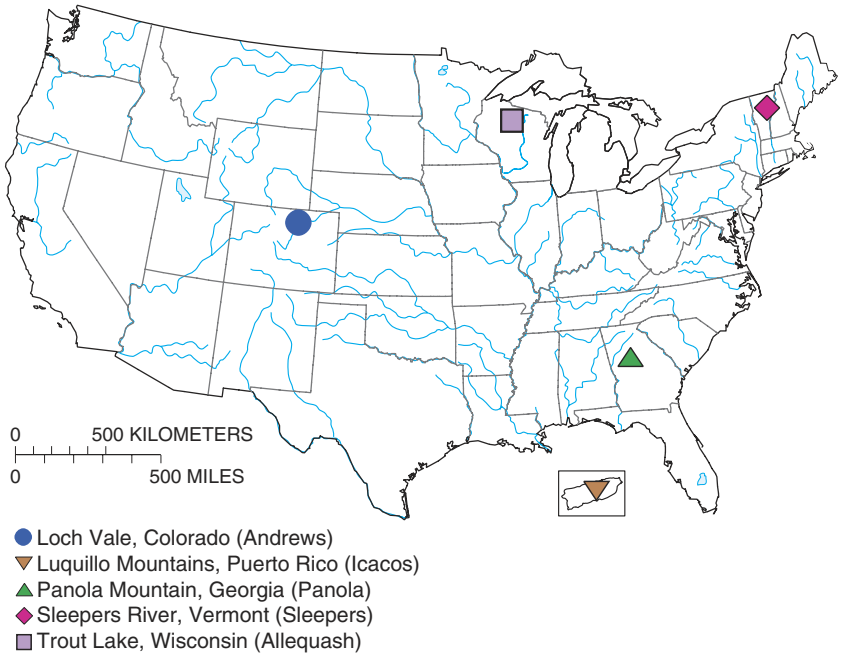

Fig. 1. Location map of the WEBB watersheds.

The five WEBB sites represent watersheds along a continuum of annual precipitation and temperature—from Luquillo in the tropics, where conditions are warm and wet, to the alpine Loch Vale site in Colorado. The range of climatic conditions (tropical, subtropical, temperate, subalpine, alpine) provides a gradient along which to study and contrast processes, such as weathering, within and across watersheds.

2. Methods

The wet-only deposition (input) and streamwater fluxes (output) of the major dissolved ions were evaluated from WY1992 to WY1997. Wet-only deposition was collected weekly at sites adjacent to each watershed. Precipitation (wet-only deposition, which includes rain, sleet, hail and snow) was monitored weekly using an Aerochem Metrics Model 301 wetfall collector at each site except Sleepers following NADP/NTN protocols (Dossett and Bowersox, 1999). The collector at Sleepers was a "Hubbard Brook type" bulk collector (Likens et al., 1977), which is always open to the atmosphere, but the sample collection and processing followed NADP/NTN protocols. Three sites used NADP/NTN network stations: CO98 for Andrews Creek, Colorado; PR20 for the Luquillo Experimental Forest, Puerto Rico (the NADP station was a few km outside of the Icacos watershed); and WI36 for Allequash Creek, Wisconsin; the remaining two sites were operated by researchers at the sites. The precipitation samples were analysed for major ion concentrations using standard methods (Fishman and Friedman, 1989). The solutes analyzed include hydrogen (H, from pH), calcium (Ca), magnesium (Mg) sodium (Na), potassium (K), ammonium (NH_4), chloride (Cl), nitrate (NO_3), sulfate (SO_4), acid neutralizing capacity (ANC, from Gran titration), and dissolved silica (H_4SiO_4). Deposition was calculated as the product of weekly sample concentration and weekly precipitation quantity. Weekly precipitation quantity was determined by a combination of the sample volume and the collector area, tipping bucket rain gages, weighing bucket rain gages, and standard rain gages. The weekly solute deposition was summed by month, and monthly concentrations were determined by dividing the deposition by the monthly precipitation depth. Annual solute deposition and concentrations were calculated similarly. The NADP/NTN network conducts an ongoing external audit program consisting

Table 1
Site characteristics

Characteristic	Watershed				
	Allequash	Andrews	Icacos	Panola	Sleepers
Topographic characteristics					
Geographic province	Northern highland	Southern rocky mountains	Caribbean island arc	Southern Piedmont	New England Piedmont
Catchment area (ha)	2290	183	3260	41	41
Minimum elevation (m)	494	3215	616	222	524
Maximum elevation (m)	555	3850	844	279	679
Drainage pattern	Dendritic	U-shaped glacial valley	Dendritic w/ some structural control	Dendritic w/ some structural control	Dendritic
Mean topographic index [$\ln(\alpha/\tan\beta)$]	8.9	2.4	3.4	4.3	3.6
Mean slope (%)	0.28	66	21	18	22
Climate/streamflow (WY1992–97)					
Climate type	Humid continental	Cold continental	Humid tropical	Humid continental, subtropical	Humid continental
Mean annual precipitation (mm)	790	1230	4280	1300	1320
Mean annual temperature (°C)	4.5	0	21	16	4.6
% Snow	15	75	0	<1	25
Mean annual runoff (mm)	430	950	3610	490	740
Geology					
Bedrock type	Amphibolite	Biotite schist	Quartz diorite (99%); tuff, tuff-breccia (1%)	Granodiorite, amphibolite	Quartz-mica-sulfidic phyllite, calcareous granulite
Suficial geology	Glacial drift	Thin soil, talus	Colluvium	Colluvium	Silty till
Glacial history	Yes	Yes	No	No	Yes
Regolith thickness (m)	30 to 50	0 to 5	4 to 15	0 to 5	1 to 4
Soil category	Spodozols	Spodozols	Inceptisols, ultisols	Inceptisols, ultisols	Inceptisols, spodosols
Ecology and land cover					
Ecosystem type	Northern lakes and forests	Alpine tundra	Subtropical lower montane wet forest	Southern hardwood forest	Northern hardwood forest
Forest cover (%)	84	2	99	91	100
Wetland (%)	5	1	2 to 5	1	3
Lakes (%)	11	0	0	0	0
Exposed bedrock w/ talus (%)	<1	93	1	9	<1
Anthropogenic influences					
Nearest population center (Direction, distance in km)	Minneapolis (SW 250 km)	Denver (SE 120 km)	San Juan (NW 35 km)	Atlanta (NW 25 km)	Montreal (NW 150 km)
Regional economic activity	Lake-based tourism, logging	Mountain-based tourism, logging	Agriculture	Commercial, light industry	Dairy farming, logging
Air quality	Excellent	Good	Good/excellent	Fair	Fair/good
Land-use history	Logged in the early 1900s	Undisturbed	Undisturbed	Woodland pasture until the 1970s	Logged in the early 1900s

of inter-site comparison, blind audit, inter-laboratory comparison, and collocated sampler programs. Although small biases were observed from the first three programs, these have extremely minor effects on calculated fluxes and are overshadowed by precipitation collection efficiencies and relative standard errors for sample collections for the collocated collectors, which can be as large as 20% for any given weekly collection. However, even with large week-to-week variations in flux, the median bias for collocated samples was less than 5% for any given solute and attributed to differences in the rate of lid opening to precipitation of the co-located collectors (Gordon, 1999).

Streamwater discharge was monitored continuously at each stream water-quality sampling site following standard USGS gauging procedures (Rantz, 1982). At each site, routine streamwater samples were collected manually from the centroid of flow following standard USGS protocols (Wilde et al., 1998). Samples also were collected during stormflow at several sites using manual techniques at Allequash, and automatic samplers triggered by changes in stage and time at Andrews, Icacos, Panola, and Sleepers (Table 2). Streamwater samples were analyzed for major ion concentrations similar to precipitation. For most streamwater, samples, solute concentrations were within the operating range of the analytical procedures, for which standard reference, replicate, and split samples indicate that the precision and accuracy of the individual major solutes are within 10% (± 1 standard deviation), except for the inorganic N species. Also, the precision varies among solutes, but it is much less than the temporal (monthly/annual) and spatial (among site) variations. Streamwater NH_4 concentration was only determined on samples at Icacos and Panola, and 47% and 20% of those samples were below the analytical detection limit (0.01 mg l^{-1}), respectively. Streamwater NO_3 concentration was determined on samples at each site, and was were within the operating range of the analytical procedures of almost all of the samples, except at Allequash and Panola where more than 69% and 65% of the samples were below the detection limit (0.02 mg l^{-1}), respectively. These low concentrations increase the uncertainty of the streamwater solute flux calculation, but you will see that the stream transport of N species is extremely small at most sites compared to the wet N deposition, even if the streamwater N flux was doubled or tripled.

A composite method was used to estimate streamwater solute fluxes. The composite method combines elements of the typically used regression-model method and period-weighting approach (Aulenbach and Hooper, in press). The total flux (Φ_T) is made up of two components:

$$\Phi_T = \Phi_M - \Phi_\varepsilon \quad (1)$$

where the model flux (Φ_M) is the flux from a regression model, and the residual flux ($\Phi\varepsilon$) is the flux from the residual concentrations to the regression model that is determined in a manner similar to a period-weighted approach. The regression-model component estimates short-term variations in solute concentrations between sample observations based on known relations with continuous variables such as discharge and season. The residual flux portion of the flux uses a period-

Table 2
Streamwater sampling characteristics

Site	Number of samples	Data collection period	Sampling frequency
Allequash Creek	58	Oct 1991–Sept 1997, except H_4SiO_4 and NH_4 missing in WY92	Monthly
Andrews Creek	406	May 1991–Sept 1997	Daily and more frequently during snowmelt, and infrequently (only 1–4 samples) from October through March
Río Icacos	239	Oct 1991–Sept 1997	Monthly and more frequently during several rainstorms
Panola Mountain	1255	Oct 1991–Sept 1997	Weekly and more frequently during rainstorms
Sleepers River	600	Oct 1991–Sept 1997	Weekly and more frequently during snowmelt and rainstorms

weighted approach to correct the regression model to the actual sample concentration by adjusting the model concentration by the residual concentration at the time of sampling and applying the error between sampling times in a piecewise linear fashion. The residual flux represents the portion of the flux unexplained by the regression model including changes in the model relation over time (trend) and measurement errors.

The concentration–discharge relation is modeled using a hyperbolic function (Johnson et al., 1969). This functional form fits the data in this study well. For some solutes, average discharge for a certain period immediately preceding the time of sample collection is used instead of instantaneous discharge in the hyperbolic model. Using average discharge instead of instantaneous discharge reduces hysteresis in the concentration-discharge relation. In addition to instantaneous discharge, average discharge with periods of 15 and 30 min, 1, 2, 4, 6, 8, and 12 h, and 1, 2, 7, 15, and 30 days were fit, with the best model chosen based on the proportion of variance explained and the distribution of residuals. Seasonal variations in concentration are modeled using sine and cosine functions. One year and half-year periods are used for sine and cosine terms to fit asymmetrical annual cycles.

A combination of the variance explained by the concentration regression relation and the frequency of sample collection affects the uncertainty in the flux estimation, particularly for short-time intervals. The precision and accuracy of the fluxes improves (smaller error) with increasing the frequency of sample collection, decreasing the coefficent of variation of the residual concentrations estimated from the regression relation, and the time interval of the load estimate, e.g., monthly and annual as evaluated herein (Aulenbach and Hooper, in press). According to Aulenbach and Hooper (in press), the load estimates are more precise and less biased using the composite method compared to the period-weighting approach and are more precise with increasing summation time and increasing sampling frequency. For example, for alkalinity load estimate for WY1994–WY2001 at Panola, the precision of period-weighted method improved from 7% to 2% annually and 30% to 6% monthly as the percentage of the large storms included in the computation increased from 0% to 77%, whereas the precision for the composite method improved from 1.9% to 0.2% annually and from 5.6% to 0.8% monthly (Aulenbach and Hooper, in press).

The general form of the mass balance assuming negligible groundwater losses of water and solutes modified from Paces (1986) is:

$$F_i^R + F_i^S = F_i^P + F_i^D + F_i^W + F_i^B + F_i^H \quad (2)$$

where F_i is the flux of an element (i) with respect to the superscripts, which include outputs:

R, dissolved phase in streamwater runoff
S, solid phase primarily in bedload and suspended sediment; inputs:
P, wet deposition (precipitation); and
D, dry deposition including particles, aerosols and gases internal changes, i.e., sources or sinks:
W, weathering contribution;
B, biological uptake or release; and
H, human activities resulting in removal or addition of elements.

Dry deposition, biomass accumulation, and changes in the storage pool were evaluated at some, but not all sites. For those sites where these components were evaluated, the methods differed among sites. These later components have been excluded from the mass balance computations. However, the potential effect of excluding these components has been discussed where other studies on a particular component indicate that the component may have a substantive impact on the interpretation of results. The mass balance therefore is simplified as:

$$F_i^N = F_i^R - F_i^P \quad (3)$$

where N denotes the net change, which will be associated with all of the remaining components of Eq. (2).

3. Results

3.1. Water budgets

Annual precipitation varied markedly among the sites; the lowest annual average was 790 mm at Allequash, the highest was 4360 mm at Icacos (Larsen and Concepción, 1998), and annual averages at

Andrews, Panola, and Sleepers were similar ranging from 1200 to 1300 mm. Patterns of monthly precipitation and runoff (total streamflow divided by basin area) varied markedly among and within sites during the 6 water years (Fig. 2). At each site, precipitation had a relatively uniform seasonal distribution, except for relatively high precipitation seasons at Allequash (April through November) and Andrews (November through May). The study period coincided with an extremely dry period in Puerto Rico with respect to 20th-century precipitation (Larsen, 2000).

Snowfall is an important component of the annual precipitation at Andrews, Sleepers, and Allequash (Table 1). Runoff was highest during snowmelt from May through September at Andrews and during April and May at Sleepers. The snowmelt runoff pattern at Andrews results in a pronounced skew in monthly runoff distribution (Fig. 2); Andrews receives more than 75% of the annual precipitation as snow, and more than 80% of the runoff occurs during one to two months in any given year. In contrast, snowfall accounts for only 25% of the precipitation at Sleepers,

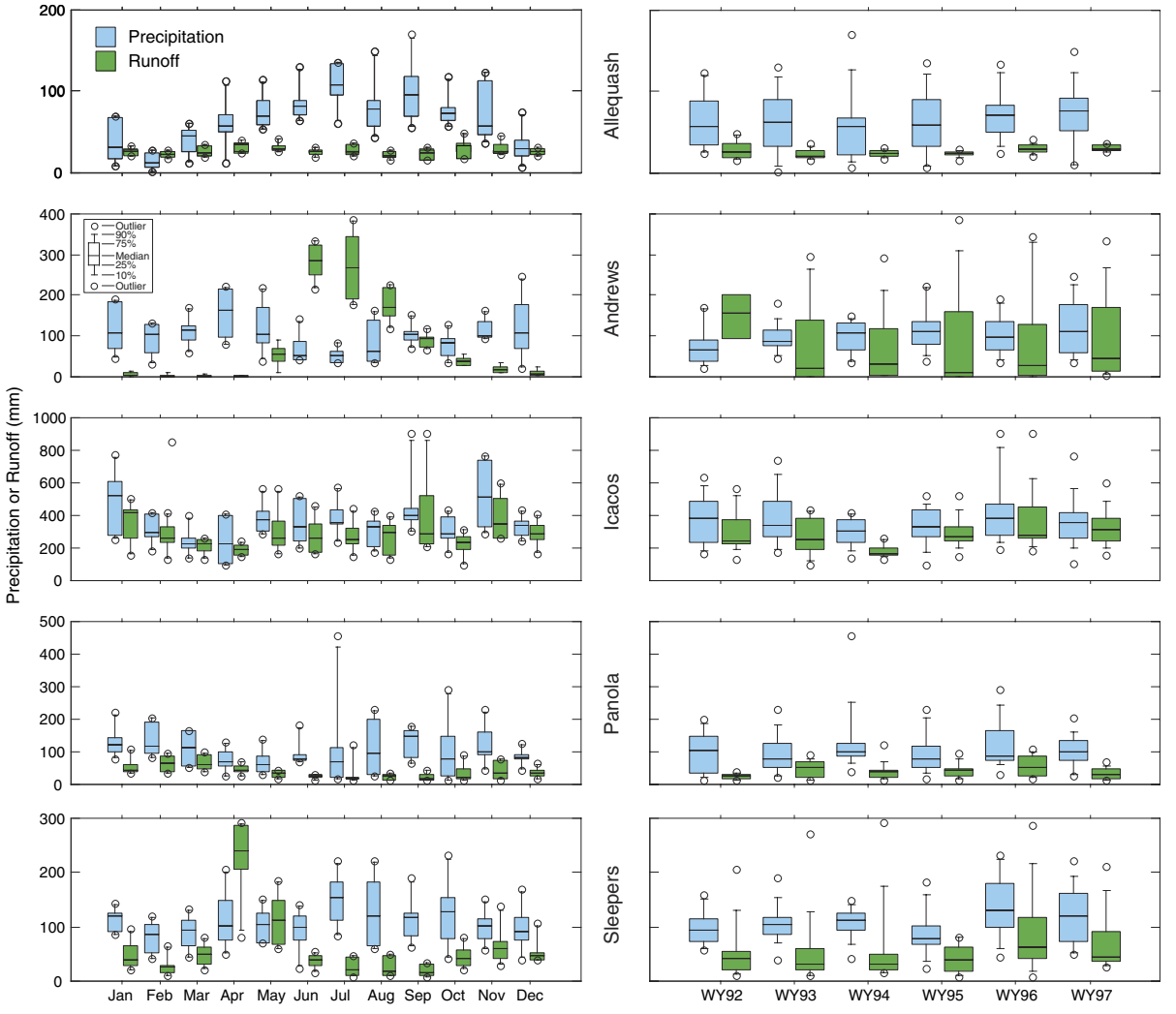

Fig. 2. Monthly precipitation and runoff for the five WEBB watersheds during WY92–WY97. The box plots on the left show the distribution of monthly values by month and the box plots on the right show the distribution of the monthly values by water year. Note that streamflow measurements did not begin until May of 1992 for Andrews Creek, hence the odd distribution compared to other years.

but monthly runoff at Sleepers also is skewed due to the few high monthly values during the relatively short snowmelt period. Although snowmelt occurs at Allequash, its influence is comparatively minor (Fig. 2) due to low snowfall amounts and high infiltration capacity. Additionally, the monthly runoff at Allequash is the least variable of that at any of the sites. Snowfall and snowmelt rarely occur at Panola, and runoff generally is much higher during the dormant winter season than during the growing season because of much lower evapotranspiration demand. Rainfall (no snowfall) and runoff were considerably higher at Icacos than at any other site, but no seasonal patterns were observed except that the rainfall and runoff at Icacos were the lowest and least variable during April (the end of the dry season). Icacos and Panola are sometimes affected by tropical storms and hurricanes. A tropical storm *Alberto*, and subsequent thunderstorms affected rainfall and runoff at Panola during July and August 1994; note the outlier in monthly rainfall and runoff during July at Panola (Fig. 2). Hurricanes *Luis* and *Marilyn* in September 1995 and Hurricane *Hortense* in September 1996 affected rainfall and runoff at Icacos; note the monthly outliers during September at Icacos (Fig. 2).

3.2. Biogeochemical budgets

3.2.1. Concentration models

Concentrations of most solutes at most of the sites vary systematically with flow and season (Table 3). The best concentration models, i.e., those with the highest R^2, at most sites are ANC, Ca, Mg, Na, and H_4SiO_4; these are weathering products whose concentrations decrease with increasing streamflow. The concentration models generally are the poorest (least amount of variance in concentration explained) for Allequash, which had the least variability in streamflow (Fig. 2) and fewest samples (Table 2). The concentration models are the best for most solutes at Andrews followed by Sleepers, where the largest contributions of annual runoff are from snowmelt (Table 1).

3.2.2. Annual budgets

Annual solute fluxes vary markedly among the sites (Fig. 3), as observed for annual precipitation and runoff (Fig. 2). The dominant difference among sites is the extremely high deposition of most solutes at Icacos, which also occurs concurrently with high rainfall and runoff. For example, Na and Cl deposition at Icacos exceeds that at the other sites by 50 to 300 times. Furthermore, the net flux of Na, K, and Cl is much higher at Icacos than at the other sites. In contrast, annual wet deposition of most of the major solutes is very low and generally comparable between Andrews and Allequash. The annual average precipitation solute concentrations at Andrews (lowest of all sites) are about 50% of those at Allequash, but annual precipitation is nearly double at Andrews. The average pH of rainfall at each site is acidic pH < ~5.0 (H^+ concentration ≥ 10 μeq l^{-1}). Deposition of the primary acid rain components, H^+, SO_4 and NO_3, is highest in the eastern U.S. sites (Fig. 3). The lowest average annual precipitation pH (determined by averaging the H concentration) is at Sleepers in the northeastern U.S. (4.40) followed by Panola (4.56) in the southeastern U.S. At each site the dominant acid anion is SO_4.

For base cations, deposition flux is small relative to stream flux, resulting in high positive net fluxes (Fig. 3). At Icacos, the net flux of base cations (and Cl) is generally greater than at the other sites (except for Ca at Sleepers), despite much greater precipitation inputs. For example, the net Na flux is similar among Allequash, Andrews, and Sleepers ranging from ~13 to 20 meq m^{-2}, and that at Panola is about 2 times these fluxes, whereas the net flux at Icacos is 15 times

Table 3
Variance, in percent, of the streamwater solute concentrations explained by the discharge and seasonality models

Solute	Site				
	Allequash	Andrews	Icacos	Panola	Sleepers
ANC	15	72	82	94	91
Ca	58	88	80	81	82
Mg	42	88	81	84	89
Na	52	80	63	93	86
K	47	69	49	31	69
NO_3	NS	80	35	NS	**62**
Cl	8	93	51	80	15
SO_4	77	84	**27**	**79**	75
H_4SiO_4	55	71	85	91	77

NS indicates that the relation was not statistically significant at $p < 0.05$.
For these relations, solute concentrations decreased with increasing discharge except for those values in bold, which increased with increasing discharge.

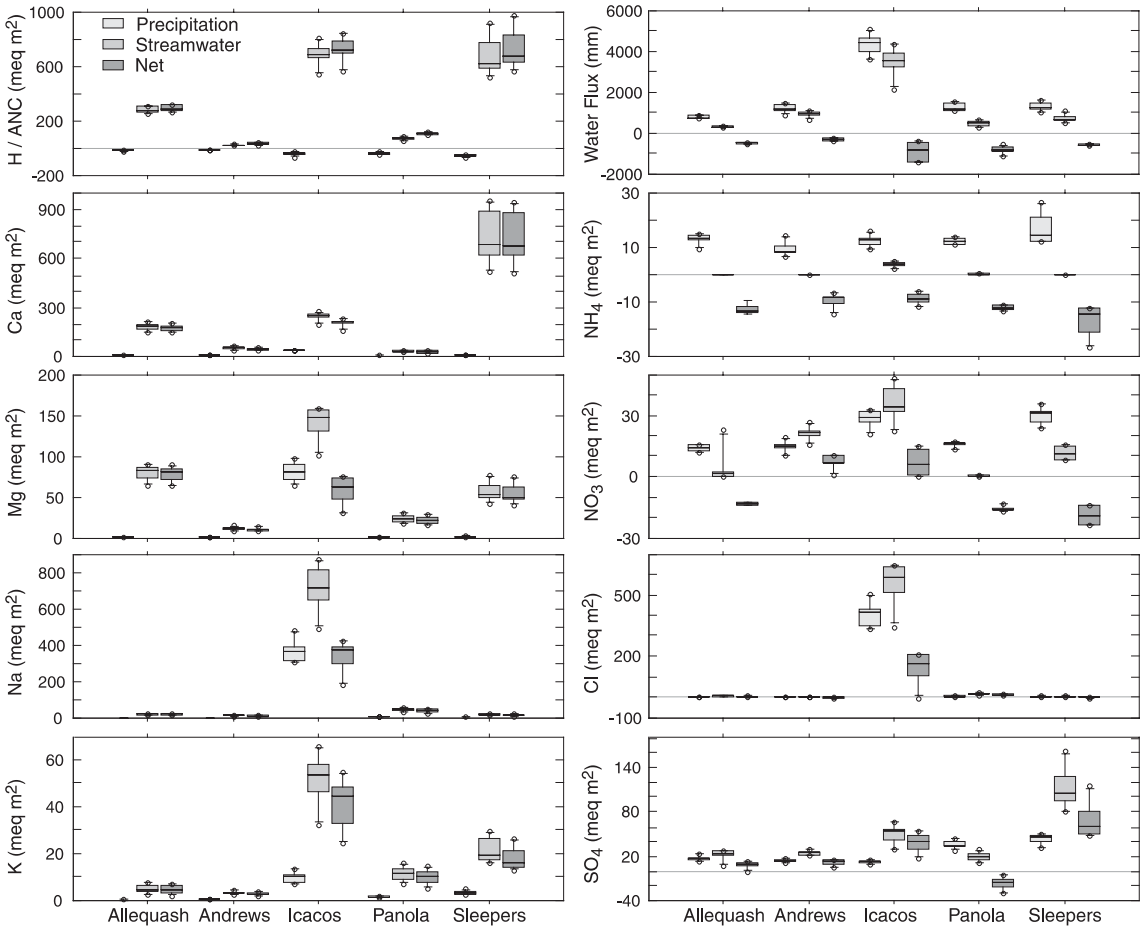

Fig. 3. Annual fluxes of water and major solutes for wet atmospheric deposition (input), runoff in streamflow (output), and net (output minus input), for the five WEBB watersheds (WY92–WY97).

higher. The net Mg flux is similar (~60 meq m^{-2}) at Allequash, Icacos, and Sleepers, and these net fluxes are at least ~3 times higher than at Allequash or Panola. The net NH_4 flux ranges only from −17 to −9 meq m^{-2} among the sites and is comparable to the atmospheric deposition flux because of the negligible stream transport. In contrast, net NO_3 flux is positive at Andrews and Icacos (~50% and ~26% more than the precipitation flux, respectively) and negative (retention) but similar (−13 to −18 meq m^{-2}) at Allequash, Panola, and Sleepers. Net ANC flux is very high and comparable at Icacos and Sleepers. The net Ca flux is comparable at Allequash and Icacos but higher by a factor of 3 at Sleepers. The net SO_4 flux is negative (retention) at Panola, low and comparable at Allequash and Andrews, double the Allequash amount at Icacos, and much higher at Sleepers.

3.2.3. Monthly budgets

Box plots of monthly solute fluxes and associated concentrations for each site were constructed for precipitation input (Fig. 4), streamwater output (Fig. 5), and net flux (Fig. 6) computed as streamwater minus precipitation. The monthly precipitation flux and concentration of most solutes, with the exception of Mg, Na, K, and Cl at Icacos, are similar within and among sites (Fig. 4). Precipitation Ca, NH_4, NO_3, and SO_4 flux and concentration vary seasonally at most sites, although the variability in flux for any given month at

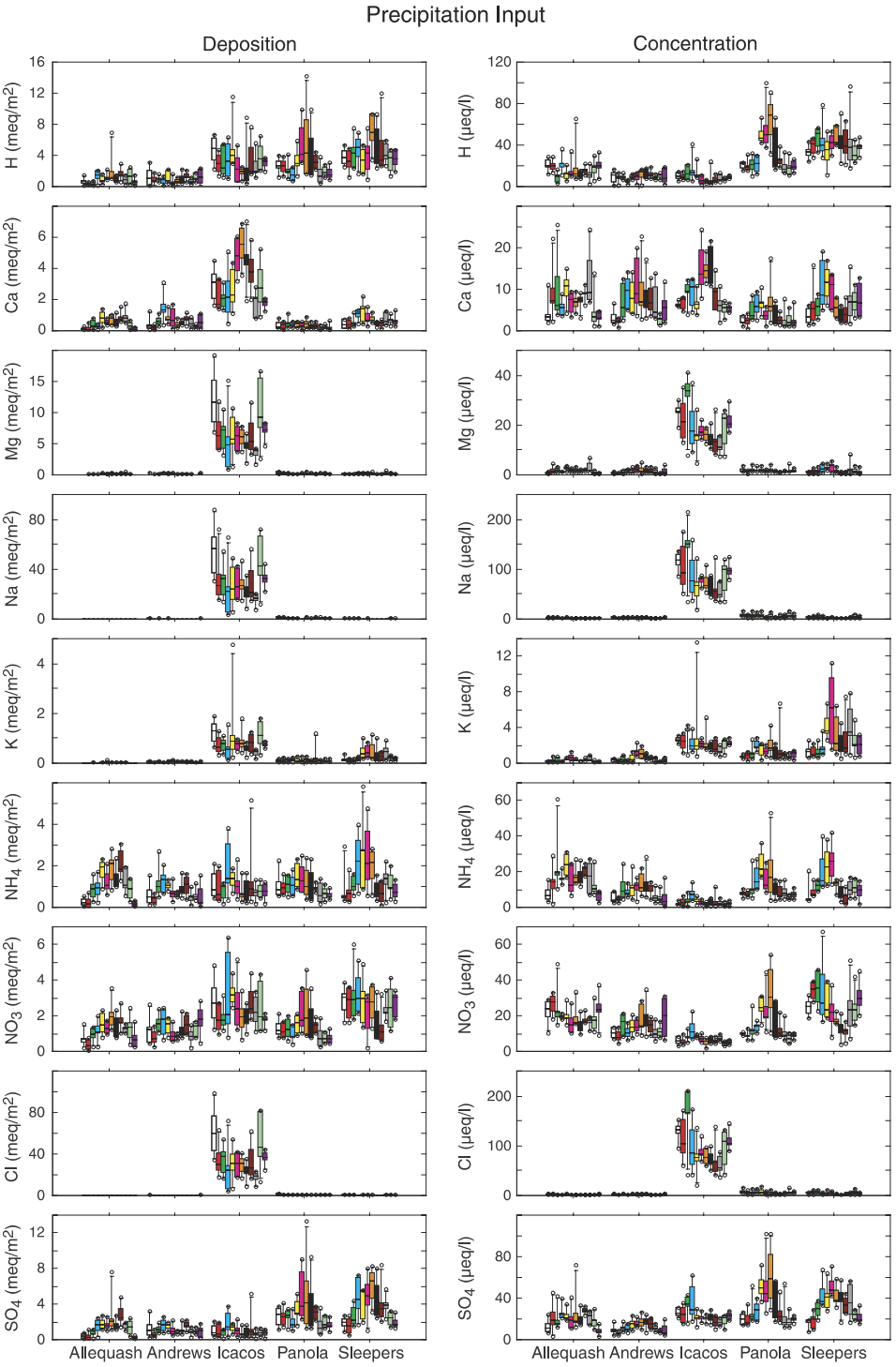

Fig. 4. Variation of monthly fluxes and concentrations of major solutes in precipitation among the WEBB watersheds (WY92–WY97).

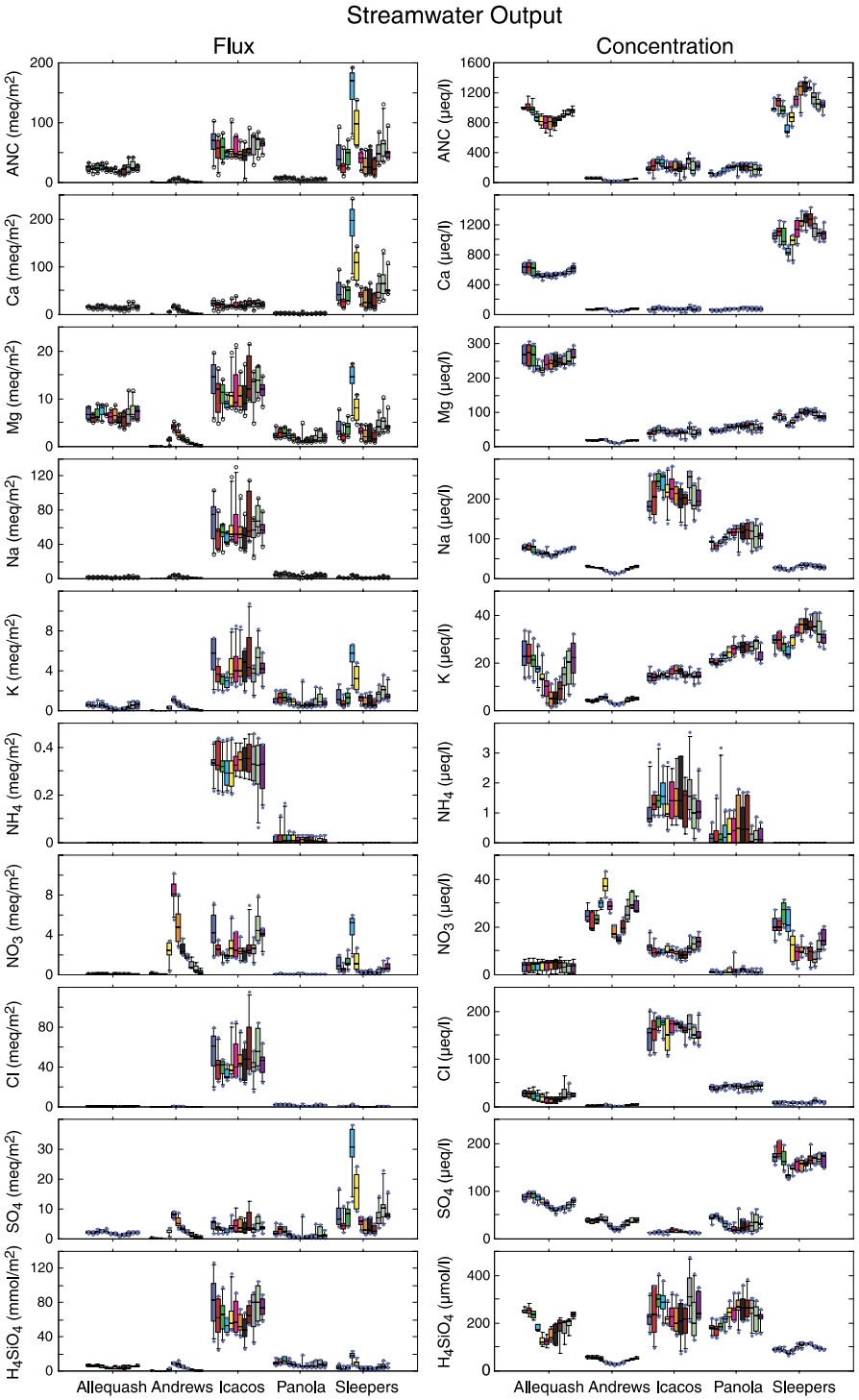

Fig. 5. Variation of monthly fluxes and concentrations of major solutes in streamwater among the WEBB watersheds (WY92–WY97).

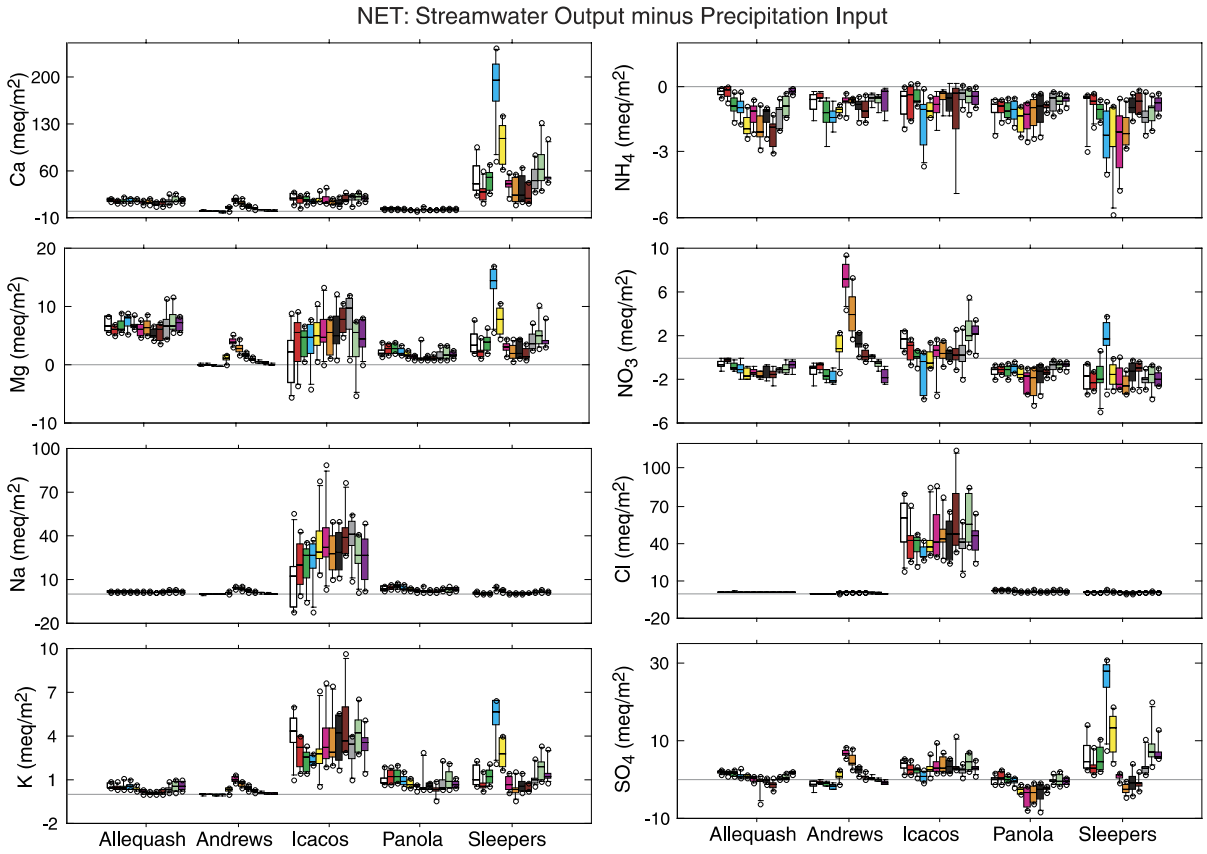

Fig. 6. Variation of monthly net fluxes (streamwater outputs minus precipitation inputs) among the WEBB watersheds (WY92–WY97).

each site was generally high during the 6-year study period. Precipitation Ca flux and concentration is high during summer and low during winter at Icacos. Ca concentration is high during spring and summer at Andrews, Panola and Sleepers, and low during late summer and fall at Sleepers and during winter at Allequash, Andrews, Panola, and Sleepers. The seasonal patterns of precipitation H, NH_4, NO_3 and SO_4 fluxes and concentrations are similar at Panola with the highest values occurring during June and July and the lowest during the dormant season from October through March (Fig. 4). Seasonally high concentrations of NH_4 and SO_4 also occur during early summer at Allequash, Andrews, and Sleepers, and low concentrations occur during winter.

The pattern of monthly streamwater flux and concentrations of major cations (Ca, Mg, Na, and K), H_4SiO_4, and ANC are similar at each site, but magnitudes differ among sites (Fig. 5). These fluxes and concentrations are similarly low and the least variable within a given month at Andrews compared to the other sites, with the maximum flux and minimum concentration coinciding with high runoff during the snowmelt period (Figs. 2 and 5). Furthermore, the streamwater H_4SiO_4 flux is similar at Allequash, Andrews, Panola, and Sleepers, but the associated monthly concentrations are the lowest and least variable at Andrews and Sleepers, and higher and more comparable among Allequash, Icacos, and Panola. Despite the low H_4SiO_4 flux and concentration at Sleepers, streamwater ANC flux and concentration at Sleepers are much higher than at Andrews and Panola. The seasonal variations of the monthly streamwater fluxes are similar for ANC, Ca, Mg, Na, K, NO_3, SO_4, and H_4SiO_4 at Sleepers, and concentration patterns also are similar (except for NO_3 and SO_4), with the lowest concentrations coinciding with high runoff during snowmelt in April and the

highest coinciding with summer baseflow (Fig. 5). Streamwater SO_4 concentrations are highest during winter low flow in February, then decrease to a minimum during high snowmelt runoff and subsequently recover to higher concentrations through the summer.

The snowmelt dominated catchments of Andrews and Sleepers display the most dynamic seasonal variations in NO_3 (Fig. 5). Nitrate flux is positively correlated with discharge. Consequently, most of the annual NO_3 export occurs during snowmelt. At Sleepers, streamwater NO_3 concentration is highest at the onset of snowmelt and remains high during high snowmelt runoff in April, then decreases and stays low through the summer. Furthermore, the NO_3 concentration at Sleepers is positively correlated with discharge, which accentuates the flux during snowmelt. At Andrews, the highest NO_3 concentration occurs during early snowmelt in May prior to maximum runoff, and NO_3 flux, therefore, is controlled primarily by the discharge. After a minimum in summer, NO_3 concentrations increase from late summer to fall, while runoff and NO_3 fluxes are still systematically decreasing, and reach another and slightly lower maximum in November (Fig. 5).

Net fluxes of most solutes are strikingly similar (within an order of magnitude) among sites (Fig. 6). For example, monthly net NH_4 fluxes are comparable (within a factor of 2) within and among sites. Despite the net transport of NO_3 from Andrews and Icacos (Fig. 3) and distinct seasonal transport at Andrews and Sleepers during snowmelt, monthly net NO_3 flux also is comparable within and among sites. Most of the atmospherically derived inorganic *N* is retained or at least likely transformed into organic forms within each of the watersheds. The NH_4 fluxes for Icacos and Panola, the only sites where measurable NH_4 concentrations were observed, were extremely low compared to the other solutes. In contrast, streamwater NO_3 concentrations typically were above the analytical detection limit at Andrews, Icacos, and Sleepers, with the highest monthly concentration and flux occurring at Andrews during snowmelt runoff and the lowest monthly concentrations (<10 μeq l^{-1}) and fluxes (<1 meq m^{-2}) at Allequash and Panola.

Despite the large precipitation and streamwater fluxes for some solutes at Icacos, the precipitation, streamwater, and net SO_4 fluxes at Icacos generally overlap the range of associated SO_4 fluxes of the other sites (Fig. 6). Also, the streamwater SO_4 concentrations at Icacos were the lowest and the least variable of any site.

4. Discussion

4.1. Atmospheric deposition

The extremely high deposition of solutes at Icacos is due its close proximity to the ocean and associated washout of marine aerosols in precipitation (e.g., Keene et al., 1986; McDowell et al., 1990). In contrast, Andrews and Allequash are farthest from a marine source (Fig. 1), and have the lowest fluxes and concentrations of solutes typically associated with a marine source. All sites were similarly affected by solutes derived from human activities, such as H, NH_4, NO_3, and SO_4, particularly with respect to precipitation acidity.

Unmeasured inputs of dry deposition associated with marine aerosols at Icacos tend to mask the contribution of other sources to streamwater output. For example, there are no known significant internal sources for Cl at Icacos, i.e., weathering of bedrock or human activities, but there is a net Cl flux (Fig. 3) probably due to dry Cl deposition, which was not measured. The exclusion of dry deposition from the input is a major factor affecting not only process interpretation at Icacos but potentially at other sites as well.

In many studies, sea-salt corrections have been applied to precipitation and streamwater to evaluate the non-sea-salt component and its effects on watershed biogeochemical processes (e.g., Stallard and Edmond, 1981; Meybeck, 1987). In the extreme, sea-salt deposition may cause episodic streamwater acidification (e.g., Wright et al., 1988; Heath et al., 1992). Sea-salt correction of precipitation is one technique to determine the non-sea-salt component (Granat, 1972; Stallard and Edmond, 1981). A reference element, typically Na or Mg, is used to adjust or correct the composition of precipitation for sea-salt contributions, with the following assumptions: (1) the reference is exclusively of sea-salt origin; (2) fractionation does not occur during aerosol formation; and (3) fractionation does not occur during aerosol transport and precipitation scavenging (Keene et al., 1986).

Small variations in the ratio of the element of interest to the reference can result in large differences in the computed sea-salt contribution.

A difficulty in applying corrections to streamwater is that marine reference solutes in atmospheric deposition may be enriched from other local sources, thereby violating the first assumption. Element ratios using Na as a reference derived from reduced-major axis (RMA) regression slopes of the NADP precipitation at Icacos are compared in Table 4 to the average ratios of seawater from Wilson (1975) consistent with the analysis of Keene et al. (1986). Comparing the RMA slopes to the seawater ratios indicates enrichment of all the constituents except Cl, which usually is used as the reference element for streamwater because weathering in the watershed produces Na and Mg, but this assumes no internal sources of Cl. In addition, the Cl in streamwater does not maintain the same ratio with other marine elements due to ion exchange and biological processes, which will likely affect interpretation of the results. For these reasons, the simple mass balance using wet-only precipitation inputs and streamwater outputs clearly has limitations with respect to interpreting results from coastal areas or other sites that are affected by large inputs from dry atmospheric deposition.

The problems of measuring dry deposition have been discussed at length elsewhere (Wesely and Hicks, 2000), but the dry deposition contribution to total deposition can be large. For example, the measured and modeled dry deposition of SO_4 at Panola varies from 30% to 50% (e.g., Peters, 1989; Cappellato et al., 1998; Peters and Ratcliffe, 1998). Estimates of dry *S* deposition for the northeastern U.S. using a watershed mass balance suggest that dry *S* deposition is 30% to 40% of the total deposition (Rochelle et al., 1987; Likens et al., 1990).

Table 4
Summary of reduced major axis regression results and tests of significance between concentrations (in μeq l^{-1}) of sea-salt constituents and Na, a reference element, in samples of precipitation collected at NADP site PR20 in Puerto Rico from 1985 to 2003

Constituent	Seawater (Wilson, 1975)	PR20 Slope ± std. error (r^2)
Mg versus Na	0.227	0.232 ± 0.002[a] (0.95)
Cl versus Na	1.16	1.15 ± 0.01 (0.97)
Ca versus Na	0.0439	0.146 ± 0.005[a] (0.14)
K versus Na	0.0218	0.0244 ± 0.0004[a] (0.82)
SO_4 versus Na	0.121	0.210 ± 0.005[a] (0.63)

[a] Differences significant at 95% confidence.

Assuming that SO_4 and Cl are relatively conservative over the long term and there are no internal *S* sources or transformations that retain *S* (or that the latter are at steady state), the net export of SO_4 relative to input gives a measure of the relative contribution of dry S deposition to the total S deposition, $F_i^P + F_i^D$ in Eq. (2). If SO_4 and Cl are conservative and mobile, and have no internal watershed source, then the dry deposition contribution should equal 100% minus the I/O percentages (Fig. 3). Sulfate is not conservative or mobile at Icacos or Panola where long-term weathering has produced Al and Fe oxides and hydroxides that immobilize SO_4 (Shanley, 1992; Shanley and Peters, 1993).

Dry deposition estimates using the median values from Fig. 3 suggests that this method may be applicable for SO_4 at Allequash, but deicing salts used during the winter on roads in the watershed is a known and variable, but unquantifiable, internal Cl source. For Andrews, computed dry deposition is only 10% for Cl, but >40% for SO_4 suggesting possible contributions from internal S sources consistent with results of other studies in the Loch Vale watershed (e.g., Mast et al., 1990; Michel et al., 2000). Michel et al. (2000) also indicate that the time scale for SO_4 retention is relatively short; 60% to 80% of the wet SO_4 deposition is transported out of the watershed within one year. For Icacos, the mass balance suggests that dry deposition can account for 25% of the Cl, which if corrected will likewise affect many other solutes of marine origin. For Sleepers, dry deposition can account for 20% of the Cl and ~60% of the SO_4, but the SO_4 value is overestimated because of weathering (Hornbeck et al., 1997; Bailey et al., 2004).

The mass balance suggests that dry deposition can account for ~75% of the Cl at Panola. Previous studies of Cl behavior at Panola, however, indicate that dry Cl deposition to the watershed is 50% (Peters and Ratcliffe, 1998), which also is comparable to an estimate of dry *S* deposition (Cappellato et al., 1998). However, the net Cl flux is positively correlated with water yield (Peters and Ratcliffe, 1998). This analysis has some major ramifications with respect to the interpretations of the mass balance herein, because it suggests that the solute fluxes are partly determined by climate and hydrologic conditions, which con-

found interpretation of short-term records because the fluxes operate on longer cycles. Furthermore, the effect will vary depending on the size of the basin and the hydrologic characteristics affecting the water and solute residence times. At Panola, the average groundwater residence times in the surficial aquifer range from less than 1 year in the headwaters to a decade in a lowland floodplain (Burns et al., 2003). This result also underscores the importance of establishing long-term records not only of climate and watershed hydrology, but of chemical concentrations and budgets as well.

4.2. Weathering

The fluxes of the major weathering products (Ca, Mg, Na, K, H_4SiO_4 and ANC) generally are low in precipitation, except for marine aerosol-derived Na, Mg, and K at Icacos and are substantially higher in streamwater. If watershed biogeochemical processes are in steady state, then on longer time scales, i.e., years to decades, streamwater transport primarily reflects mineral weathering contributions (Likens et al., 1977; Meybeck, 1983; Meybeck, 1987). Furthermore, when atmospheric deposition of these solutes is low relative to the streamwater output, the net flux is essentially equal to the streamwater flux and consequently, the flux of weathering products (Meybeck, 1987). The major differences in net fluxes of the weathering products among the sites, therefore, can be attributed to different bedrock types and mineral assemblages. For example, the net flux of Ca, Mg, and ANC (primarily HCO_3) at Sleepers is much higher than at the other sites and is consistent with carbonate-mineral weathering from the bedrock (Hornbeck et al., 1997; Shanley, 2000) and with the relatively lower H_4SiO_4 flux at Sleepers. Carbonate mineral weathering can increase chemical weathering rates by a factor of 12 compared to granitoid rocks (Meybeck, 1987), which is approximately the bedrock composition of each of the other watersheds (Table 1). Additionally, weathering is more intense in warmer climates; fluxes of the weathering products from Andrews, Panola, and Icacos, the basins underlain by similar granitoid bedrock, increase with increasing temperature consistent with the analysis of White and Blum (1995).

There are subtle differences in the relations among cations, ANC (primarily HCO_3), and H_4SiO_4, reflecting differences in the weathering history and bedrock composition (Fig. 7). The slope of the relation between H_4SiO_4 and ANC is much steeper for Sleepers than the other sites due to the production of alkalinity from carbonate mineral dissolution. The slopes of the relations for the other watersheds are similar and consistent with aluminosilicate mineral weathering. Likewise, the difference in the relation for Ca versus Mg at Sleepers shows the importance of calcite dissolution over other carbonates and the similarities in ratios of Ca to Mg in the bedrock weathering at the other watersheds. The Ca versus ANC relation, however, indicates that at Andrews, more Ca is produced per unit ANC than at any other site and may likely be due to calcite mineral weathering as reported elsewhere (Mast et al., 1990).

The slopes of the relation between Ca and H_4SiO_4 also vary among watersheds, suggesting differences in composition of the bedrock mineralogy and in physical weathering rates. Ca tends to weather preferentially from fresh mineral surfaces. At Andrews, fresh mineral surfaces are continually exposed due to steep slopes and freeze-thaw cycles that promote physical weathering. Therefore, despite similar mineral assemblages, relatively more Ca is weathered at the younger glaciated Andrews watershed than at either Panola or Icacos, where minerals are Ca-depleted due to weathering. In fact, the net Ca flux at Andrews is higher than at Panola. Furthermore, calcite, which occurs in varying amounts in all unweathered granitoid rocks (White et al., 1999), is likely a dominant source for Ca at Andrews (Mast et al., 1990), as also reflected by the net flux relations of Ca–ANC and Ca–H_4SiO_4 (Fig. 7).

4.3. Biochemical processes

Given the lack of data on biomass pools and accumulation at each of the watersheds, it was not possible to incorporate these estimates in the mass balance. Changes in inorganic *N* species fluxes, however, indicate some patterns and watershed responses with respect to biological processes. The highest atmospheric deposition of NH_4 and NO_3 occurs during the summer (dry season at Icacos), but the lowest streamwater concentrations and fluxes also occur during summer, which indicates the watersheds retain or at least convert the inorganic *N* to organic forms

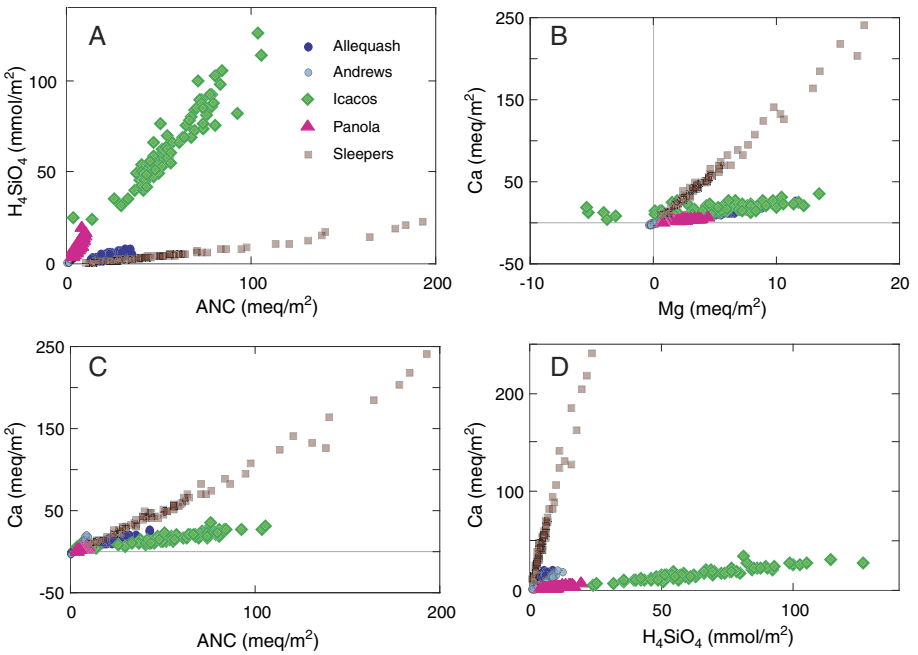

Fig. 7. Relations among monthly net fluxes of weathering products (streamwater outputs minus precipitation inputs) among the WEBB watersheds (WY92–WY97): (A) H_4SiO_4 versus ANC; (B) Ca versus Mg; (C) Ca versus ANC; and (D) Ca versus H_4SiO_4.

probably through biological uptake during the warmer and generally wetter growing season. The high streamwater NO_3 concentrations at Andrews and Sleepers, which occur at the onset of snowmelt, are attributed primarily to the flushing of NO_3 that accumulates in the soils under snowcover rather than from the preferential elution of NO_3 from the snowpack (Kendall et al., 1995; Campbell et al., 2000).

4.4. What do the concentration models tell us?

The solute concentration model parameters offer insights on factors controlling the various solute fluxes among sites. At Allequash, a long averaging period (1–4 weeks) was optimum for the Ca, Mg, and H_4SiO_4 models, indicating that groundwater not only dominates the source of these weathering solutes but that event water has little effect in diluting the streamwater solute concentrations on the short term. In contrast, the SO_4 model optimized with the 2-h average discharge, suggesting more rapid response than for the weathering solutes, or more rapid mobility, possibly associated with an atmospheric or a near-stream source that is more sensitive to short-term variations in flow. An instantaneous to very short discharge averaging period (15–30 min) was optimum for all solutes at Panola and Sleepers, except Cl (10 day) at Sleepers. Groundwater may still be a dominant source of streamwater solutes at Panola and Sleepers, but the short averaging period for the discharge term suggests that mixing of more dilute event water (precipitation or snowmelt) is rapid. The reason for the longer averaging period for Cl at Sleepers is unclear, but it may reflect high variability of the Cl concentration in soils and groundwater. The Cl is derived from atmospheric deposition, but Cl concentrations in soils and groundwater are controlled by the timing of recharge relative to the effects of evapotranspiration, which increases Cl concentrations in soil water, and flushing of the soil water during snowmelt, the primary groundwater recharge period. The discharge averaging period also is short for each solute at Icacos (≤6 h), suggesting relatively quick mixing there as well. At Andrews, the discharge averaging period is either instantaneous or 15-day (Ca, Mg, K, and NO_3). The longer discharge-averaging period in the models of some solutes are likely related to attenuation of runoff and corresponding long solute residence times in the talus slopes (Clow et al., 2003), as well as by the gradual changes in discharge during the broad snowmelt hydrograph.

Differences in the β term of the Johnson hyperbolic discharge model among solutes and among sites provide additional insight about factors affecting stream-water solute concentrations (Johnson et al., 1969). The β terms among the solute models at Sleepers, and to a lesser extent Andrews, are similar. For Sleepers, the similarity in the β terms is consistent with 2-component mixing, as suggested by other research (Kendall et al., 1999). Note that the β term for NO_3 is similar to the other solutes, although NO_3 concentrations increase rather than decrease (dilute) with increasing discharge. At the three other sites, the β term varies by 2 or more orders of magnitude among the solute models. The large ranges indicate fundamentally different processes or hydrologic pathways controlling transport among solutes at a site, although the β term is not highly significant in each model. The β term was normalized for area to compare models among sites because the original models were derived for discharge in l s^{-1}. The β term for any particular solute model generally decreases in the order Panola > Sleepers > Allequash = Andrews = Icacos. This order approximately follows a gradient of increasing watershed size (Panola = Sleepers < Andrews < Icacos < Allequash) and decreasing hydrologic flashiness. A comparison of the flow duration curves for each site (Fig. 8) indicates that flashiness (magnitude of stormflow relative to baseflow) is more important in the order(Andrews > Sleepers > Panola = Icacos > Allequash). Clearly, the groundwater contribution tends to dominate streamflow at Allequash with stormflow contributing less than 5% of the time, whereas stormflow is important about 15–20% of the time at Icacos and Panola, The flashiness associated with the smaller watersheds generally lends more weight (higher β) to the discharge term in controlling solute concentrations.

An additional process diagnostic is the magnitude and day-of-peak of the seasonal component of the models. At Panola and Sleepers, the seasonal peak for most solutes is late summer through early fall, a pattern attributed to the seasonal wetting and drying cycle at each site, with a wet winter/spring minimum and dry summer/fall maximum. The importance of this seasonal flushing is illustrated by the fact that some models have seasonal components that explain more variance in solute concentrations than the discharge component. At Sleepers, the maximum NO_3 concentrations occur during early March; the NO_3 concentration model has the most statistically significant seasonal component of all solutes. Furthermore,

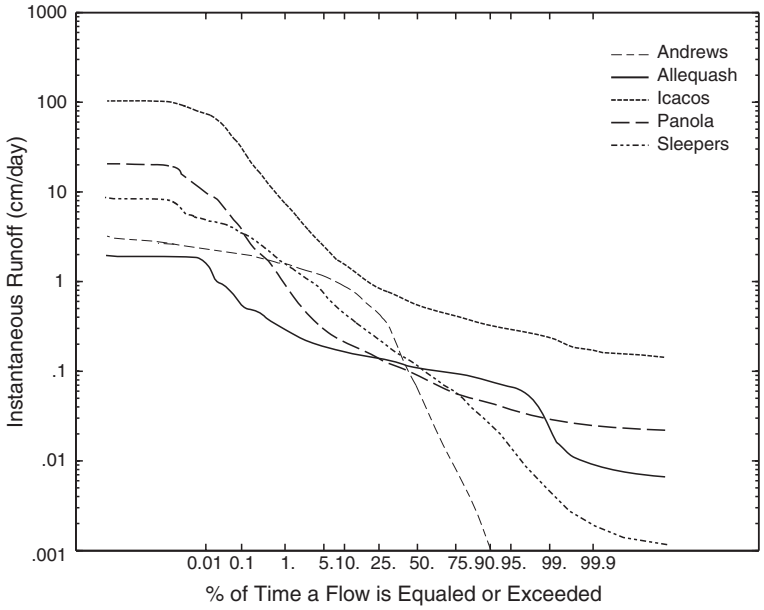

Fig. 8. Flow-duration curve of each site displaying the percentage of the time a given runoff (cm/day) is equaled or exceeded for the study period.

the late winter NO_3 concentration maximum is clearly related to initial flushing (and subsequent depletion and dilution) during the 6-week snowmelt period. At Allequash and Andrews, all seasonal solute peaks occur during winter or spring. At Andrews, flushing of soils during early snowmelt followed by dilution during peak snowmelt in early to mid summer controls seasonal solute variations.

4.5. Limitations of the mass balance

The sampling and measurements needed for computing precipitation input and streamwater output fluxes are relatively straightforward. For precipitation, an important consideration is the location of collectors, which can be affected by local variation in precipitation and sources of contamination. Accurate streamflow measurement is important because discharge typically varies more with time than solute concentrations. One assumption of this simplistic mass balance is that groundwater flow at the watershed outlet is negligible (Likens et al., 1977; Cerny et al., 1994), which is not the case for Allequash (Walker and Krabbenhoft, 1998; Walker and Bullen, 2000). In some cases, particularly when a solute concentration systematically increases with increasing discharge, streamwater sampling during stormflow is critical for accurate determination of the concentration–discharge relation. A major limitation in the mass balance approach used for the sites in this study is the uncertainty and lack of accounting of dry deposition, which may be a significant input term and a large percentage of the overall mass balance for Cl, SO_4, NO_3, and NH_4.

Andrews and Icacos illustrate some of the difficulties in obtaining accurate estimates of even wet deposition. At the high relief Andrews site, the only collector is at a low elevation (635 m). Furthermore, the Aerochem wetfall collector tends to underestimate snowfall inputs, particularly during windy conditions (Graham et al., 1988; Sevruk, 1989). The wet deposition estimates for snowfall at Andrews were increased by 20% based on comparison of the weekly wetfall deposition with snowcourse data, thus accounting for the underestimation associated with blowing snow at the collector.

The single collector near the Icacos site is located at an elevation of only 107 m above mean sea level, whereas the basin ranges from 616 to 844 m above mean sea level and has higher winds, higher rainfall, and cloudwater deposition at high elevation compared to the site of the rainfall collector (Weaver, 1972; Garcia-Martino et al., 1996). The cloudwater contribution was incorporated in the precipitation inputs to Icacos by evaluating rain gauge data at different elevations, the typical cloud base-level elevation (600 to 800 m), the elevation area relations for the watershed, the relative enrichment of solutes in cloudwater, and some throughfall estimates of cloudwater deposition at high elevations (F.N. Scatena and W. Eugster, personal communication; Weaver, 1972; Garcia-Martino et al., 1996). The estimated cloudwater contribution was 3% for water and ≤5% for the major solutes, which is relatively minor when compared to the spatial uncertainty in rainfall and lack of dry deposition measurements. For the evaluation of weathering contributions to streamwater, the atmospheric deposition of cations is relatively minor compared to the streamwater fluxes, except at Icacos as indicated by the relatively low percentage that precipitation contributes to net fluxes of most of the weathering components listed in Table 3.

When applying a particular method for mass balance computation, primary consideration should be given to the characteristics of the solute, the size of the watershed, the magnitude of input and output fluxes, and perhaps most importantly, the hydrologic residence time and related importance of hydrologic pathways contributing to streamwater (Cerny et al., 1994). Dry deposition is an important additional input of some solutes to some watersheds as discussed previously, but there are no simple or inexpensive methods available to quantify this input.

The method of mass balance computation applied herein, i.e. by use of wet-only deposition as the input and streamwater as the output, is typical of those reported in the literature (e.g., Likens et al., 1977; Cerny et al., 1994). The challenge here is that the large range in the effects of sources and receptors with respect to precipitation due to the large geographic separation of the watersheds, and the large range of watershed characteristics affecting the transport and transformation of the solutes. Probably the most important individual characteristic affecting interpretation of the mass balance is the time scale during which the solute inputs are transported through the basin to be exported from the basin in

streamwater. This is not as problematic for assessing solute fluxes derived from weathering as it is for those that are derived primarily from atmospheric deposition or from human activities in a watershed. The residence time is not known for each watershed, although estimates are available for the transport of some constituents. For example, most of the atmospherically derived S is transported rapidly (within 1 year) from Andrews (Michel et al., 2000), whereas it takes several years under average hydrologic conditions to transport Cl from Panola (Peters and Ratcliffe, 1998). Shallow groundwater in the floodplain upstream of the outlet of the Panola watershed, on average, is a decade old whereas groundwater from a deeper bore-hole drilled to 17 m in granodiorite near the basin outlet was 27 years old (Burns et al., 2003). The Cl transport at Panola appears to be associated more with short-term responses associated with flushing the shallower aquifer as is the S transport at Andrews. Simulation results from the model, MODPATH, for the Allequash basin indicate that the average travel time is ~30 years, the median travel time is 18 years (R. Hunt, personal communication) and some flowpaths in the Allequash basin exceed 200 years (Pint et al., 2003). In contrast, the residence times for most constituents in the Icacos watershed are likely to be relatively short because of the high annual precipitation and frequent high-magnitude storms. Evaluating factors affecting solute concentrations and fluxes thus poses a challenge to interpretation of solute mass balances in the short term. Despite its limitations, the mass balance is a fundamental requirement for assessing the status and trends of watershed processes because it provides constraints on the processes controlling element mobility.

5. Conclusions

Geochemical mass balances were computed using consistent methodologies at each of the five diverse watersheds of the U.S. Geological Survey's Water, Energy and Biogeochemical Budgets Program. The two snowmelt-dominated sites, Sleepers and Andrews, displayed the most seasonal pattern of streamwater output and net flux, largely in response to the high monthly variation in runoff. Sleepers had the highest Ca net export of the five sites as a result of calcite weathering. Net export of weathering solutes at the other 4 watersheds, all underlain by granitoid lithologies, generally increased with increasing annual temperature; Andrews < Allequash < Panola < Icacos. Andrews had relatively high runoff due to low evapotransporation, but low concentrations due to cold temperatures and rapid runoff having a short residence time. Allequash had higher concentrations due to long residence times in this groundwater-dominated system, but low runoff. Although runoff was low at Panola residence time was intermediate between Andrews and Allequash. Icacos had much higher weathering rates and runoff, though there is much uncertainy in the input term due to the low elevation of the collector and unmeasured dry deposition, particularly of marine aerosols.

For solutes derived primarily from the atmosphere (NH_4, NO_3, SO_4, and Cl), net fluxes are more similar across sites than for the other solutes. All sites show a similar magnitude of NH_4 retention. NO_3 is largely retained at Allequash, Panola, and Sleepers, but the net NO_3 flux at Andrews and Icacos is only slightly less than the net NH_4 retention indicating little net retention of dissolved inorganic N. Approximately 50% of the precipitation SO_4 is retained at Panola, where SO_4 adsorption has been documented by other studies. In contrast, the highest net SO_4 flux occurred at Sleepers and is attributed to contributions from the weathering of sulfide minerals in the watershed.

Relations among monthly solute fluxes and differences among solute concentration model parameters yield further insights into comparative biogeochemical processes at the sites. For example, high slopes of the relation between monthly H_4SiO_4 and ANC flux at Icacos and Panola suggest ANC generation from aluminosilicate mineral weathering, and a low slope at Sleepers suggest ANC generation from carbonate weathering. Similarly, a high slope for the relation between Ca and ANC at Andrews suggests that the Ca is derived from calcite weathering, which is consistent with the existence of microcrystalline calcite at the site (Mast et al., 1990). In contrast, the slope of the same relation is intermediate at Allequash, suggesting a mixture of carbonate and aluminosilicate mineral weathering. At Allequash, a long discharge averaging period (1–4 weeks) was the optimum for the solute concentration models, alluding to a low sensitivity of the streamwater concentrations to changes in dis-

charge because of long hydrologic pathways and residence times typical of a groundwater-dominated watershed. At the smaller and hydrologically flashier watersheds, Panola and Sleepers, instantaneous to very short-term discharge average periods dominated, and β terms (a weighting of the discharge term) were highest for these sites.

Despite uncertainties in input fluxes due to sea-salt contributions and limited measurements of dry deposition, the geochemical mass balance in small watersheds remains a powerful tool for constraining biogeochemical processes. When applied using a consistent methodology and refined to a monthly time step across diverse sites, additional biogeochemical information can be gleaned from seasonal dynamics and empirical concentration model parameters that provide insights into the controls on solute concentrations.

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