Relations between Hydrology and Solute Fluxes at the Five Water, Energy, and Biogeochemical Budget (WEBB) Watersheds of the United States Geological Survey

Richard M.T. Webb, Norman J. Peters, Brent T. Aulenbach, James B. Shanley

Abstract

A clear understanding of how natural watersheds receive, transform, and export solutes can lead to improved environmental management. With this background, decision makers can better anticipate how natural and anthropogenic stressors will alter the existing equilibrium.

A principal component analysis was used to identify statistical relations between hydrologic conditions and net exports of cations (H^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+), anions (HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-) and silica (H_4SiO_4) for the five U.S. Geological Survey (USGS) Water Energy and Biogeochemical Budget (WEBB) sites. The input data consisted of six years of monthly averages of daily simulated precipitation, snow melt, evapotranspiration, saturated overland flow, infiltration excess overland flow, macropore flow, recharge of the root zone from the saturated zone, soil moisture content, groundwater discharge, and net solute fluxes.

Five principal components account for 83 percent of the variance in observed in net fluxes of water and solutes at the WEBB watersheds. The components appear related to basic hydrologic controls on the net exports of major ions common to these five hydroclimatologically distinct sites. Each component describes two diametrically opposed conditions: (1) Wet (storm or melt)/Dry (drought or freeze) (50 percent of variance). All solutes, with the exception of ammonia, were correlated with this component; (2) Dry periods (with cool, wet soils) /Wet periods (with warm soils with available root zone storage) (14 percent of variance). Nutrients and sulfate were correlated with this component; (3) Dry soils (during warm, dry periods)/Wet soils (during cool, wet periods) (8 percent of variance). Nitrate and chloride were weakly correlated with this component; (4) Low base flows with limited recharge /Moderate baseflows with some recharge (7 percent of variance). Weathering products were positively correlated and nutrients and sulfate negatively correlated with this component; and (5) Spring melts or rains on dry soils/late summer rains on wet soils (4 percent of variance). Ammonium was negatively correlated with this component.

These results describe generic relations observed at all sites. Statistical models exist that better describe the variance at any single site.

Keywords:

watersheds, geochemistry, hydrology, surface water model, principal component analysis, elemental fluxes

Introduction

To clarify first-order processes governing the quantity and quality of water flowing from the headlands of small, forested watersheds (less than 100 km²), the U.S. Geological Survey initiated the Water, Energy, and Biogeochemical Budget (WEBB) project in 1992

Webb, Peters, Aulenbach, and Shanley are hydrologists with the United States Geological Survey. Richard Webb, Box 25046, MS412, DFC, Bldg.53, Denver, CO 80215. Email: rmwebb@usgs.gov. Norman Peters, 3039 Amwiler Road, Atlanta, GA 30360. Email: npeters@usgs.gov. Brent Aulenbach, 3039 Amwiler Road, Atlanta, GA 30360. Email: btaulenb@usgs.gov. Jamie Shanley, Box 628, Montpelier, VT 05602. Email: jshanley@usgs.gov.

(Baedecker and Friedman 2000). Five forested upland sites were chosen for long term study: Loch Vale, Colorado; Trout Lake, Wisconsin; Sleepers River, Vermont; Panola Mountain, Georgia; and Luquillo Forest, Puerto Rico. Each site is unique in its climate, geology, soils, and vegetation (Table 1).

A key objective of the WEBB program is to understand how basic hydrologic and biogeochemical processes active at each site may respond to changes in precipitation chemistry (acid rain) and temperature (global warming). The objective of this study was to identify the dominant linkages between the hydrology and biogeochemistry for developing physical and geochemical models. Principal component analysis (PCA) of variables describing the hydrology and net solute exports was used to identify common linkages across the diverse hydroclimatic regimes occupied by the WEBB sites.

Methods

The PCA variables consisted of six years of monthly averages of daily precipitation, snow melt, evapotranspiration, saturated overland flow, infiltration excess overland flow, macropore flow, recharge of the root zone from the saturated zone, soil moisture content, and groundwater discharge, each derived from a hydrologic simulation, and net solute fluxes derived from a mass balance of precipitation inputs and streamwater outputs from each watershed.

XTOP_PRMS

Hydrologic fluxes and average soil moisture content deficit were simulated using XTOP_PRMS, a hydrologic model built in the USGS Modular Modeling System (MMS)(Leavesley et al. 1998) using modules built from the Precipitation Runoff Modeling System (PRMS) (Leavesley et al. 1983), the National Weather Service's HYDRO-17 snowpack model (Anderson 1973); and a multi-catchment version of TOPMODEL (Beven and Kirkby 1979, Beven 1997) modified and coupled with the other MMS modules. The TOPMODEL module in XTOP_PRMS differs from the original TOPMODEL in three ways: A fraction of recharge can be routed directly to the stream to simulate interception by macropores such as worm borrows or roots (Piñol and others, 1997); negative saturation deficits (artesian conditions) are used to replenish root zone deficits with any excess accounted for as exfiltration; and vertical hydraulic conductivities are modeled as having a log-normal distribution described by a median and a coefficient of variation.

Spatial parameters were derived using the GIS Weasel (Viger, 1998). The Weasel is a GIS interface used to delineate, characterize, and parameterize basin features. It is composed of ArcInfo∗ (ESRI, 1992) GIS software, C language programs, and shell scripts. Spatial parameters needed by XTOP_PRMS include elevation, slope, aspect, topographic index, soil type, available water-holding capacity of the soil, vegetation type and cover density, the dominant radiation planes (zone receiving similar radiation loadings), interception-storage capacity, and stream topology.

Daily precipitation totals, and minimum and maximum temperatures provide the temporal data needed to drive the model. Intrinsic parameters affecting processes such as snowmelt and fluxes within the hillslope were manually calibrated to obtain a good match between the observed hydrograph and the simulated one. The Nash-Sutcliffe efficiency (Nash and Sutcliffe 1970) values for the manually-calibrated models were 0.71, 0.24, 0.79, 0.68, and 0.60 for Loch Vale, Allequash, Sleepers River, Panola Mountain, and Icacos respectively. The poor calibration for the Allequash is probably because beavers dam the stream at times, resulting in extreme fluctuations unrelated to precipitation or snowmelt. The overall affect of the beavers on the hydrologic model results is mitigated by monthly averaging of daily flows.

Hydrologic variables

Fluxes between hydrologic compartments and the soil moisture in the root zone were normalized by the basin areas to obtain depths per unit area. Monthly total (or average in the case of soil moisture content) fluxes of the daily values were then standardized to yield a distribution with a mean of zero and unit variance. This step was necessary to avoid principal components from

∗ Use of trade names is for identification purposes only and does not imply endorsement by the U.S. Government.

Table 1. Characteristics of the five U.S. Geological Survey Water, Energy, and Biogeochemical Budget sites.

WEBB site	Loch Vale[1]	Trout Lake[2]	Sleepers River[3]	Panola Mountain[4]	Luquillo[4]
Geographic Province	Southern Rocky Mountains	Northern Highland	New England piedmont	Southern piedmont	Caribbean island arc
Catchment used for water quality model	Andrews Brook	Allequash	W-9	Lower Gage	Icacos
National Acid Deposition Site used for solute inputs	Loch Vale - CO98	Trout Lake – WI36	none	none	El Verde - PR20
Catchment area for hydrologic model (ha)	690	4000	41	41	326
Outlet elevation (m)	3215	494	524	222	616
Highest elevation (m)	3850	555	679	279	844
Climate Type	Cold continental	Humid continental	Humid continental	Humid continental / subtropical	Humid tropical
Mean Annual Temperature (°C)	0	4.5	6	16	21
Mean Annual Precipitation (mm)	1230	760	1100	1245	4320
Percentage of Mean Annual Precipitation as snow (percent)	85	15	25	<1	0
Ecosystem type	Taiga - boreal forest / alpine tundra	Northern lakes and forests	Northern hardwood forest	Southern hardwoods	Subtropical lower montane wet forest
Percent forest cover	2	84	100	91	99
Surficial geology	Thin soil / talus	Glacial drift	Calcareous silty glacial till	Weathered colluvium / alluvium	Colluvium, frequent landslides
Average depth to bedrock (m)	0 to 5	30 to 50	1 to 4	0 to 5	4 to 15
Bedrock Type(s) and areal percentage	Biotite schist	Granite/ amphibolite	Phyllite / calcareous granulite	Granodiorite/ amphibolite	Quartz diorite

1 (Baron 1992, Campbell et al. 1995, Clow et al. 2000)
2 (Walker and Bullen 2000)
3 (Shanley 2000)
4 (Peters et al. 2000)
5 (Larsen and Stallard, 2000)

identifying individual site processes rather than common intersite processes. Eight hydrologic flux variables and one state variable (root-zone soil moisture content) were evaluated with respect to 10 solute fluxes using principal component analysis. The hydrologic variables were selected because of their anticipated explanatory power for describing biogeochemical fluxes.

- Net precipitation (NP) – is the amount of precipitation reaching the land surface after subtracting the amount that is intercepted by the forest canopy and evaporated back to the atmosphere.
- Snowmelt (Melt) – is calculated using a temperature index method during days with no rain (Anderson 1973). On days with rain, a more complete energy balance is computed. Energy transfers are scaled according to the estimated percent snow-covered area.
- Actual evapotranspiration (ET) – is equal to 100 percent of the potential evapotranspiration (Hamon 1961) during periods of active transpiration when the root zone is at field capacity; ET reduces linearly to zero at the wilting point.
- Overland flow from infiltration-excess (OFInfex) – occurs when the precipitation rate exceeds the capacity of the soils to absorb it (Green and Ampt 1911, Horton 1939). This results in a perched water table.

- Saturated overland flow (OFSat) – occurs when precipitation falls on areas where the water table is at the surface (Dunne and Black 1970).
- Root zone moisture (SMCont) – increases with recharge from rain or melt and decreases during active evapotranspiration or by recharge by exfiltrated waters.
- Flux of water from the saturated zone to the root zone (RZWet) – occurs during dry periods in areas of the catchment where exfiltration is predicted to occur.
- Macropore flow (MF) – Recharge in excess of field capacity infiltrates through the unsaturated zone if storage is available. A fraction of the recharge is routed directly to the stream as macropore flow.
- Baseflow and exfiltration (BF) – Following the standard TOPMODEL concept, baseflow increases exponentially as the water table nears the surface.

Where the model predicts zero flux for the entire time period, such as melt at Luquillo or infiltration excess at Allequash, the time series of standardized variables was set to zero.

Deposition and export of solutes

The deposition and export of major cations (H^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+), anions (HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-) and silica (H_4SiO_4) are routinely measured for each WEBB site. In the absence of any internal chloride sources, any chloride leaving a watershed must have arrived through atmospheric deposition. At the other extreme is silica, the most common element, other than oxygen, in the crystal lattices of the bedrock minerals. The other species vary in that they are found both in the atmosphere and in bedrock minerals or vegetation.

Input chemical fluxes were computed using methods developed for the National Acid Deposition Program (NADP) (Dossett and Bowersox 1999). NADP maintains collection sties at or near Loch Vale (CO98), Allequash (WI36), and Icacos (PR20). At Sleepers River and Panola Mountain precipitation samples were collected and analyzed using NADP protocols. Concentrations of major solutes were multiplied by the volume of precipitation to arrive at spatially averaged input fluxes.

Output fluxes were estimated using charge-balanced flux models created for each solute. Terms include a hyperbolic fit of the concentration and discharge relations and annual and semiannual sine and cosine terms. Fluxes were normalized by basin area to describe output fluxes in units of millimoles or milliequivalents per square meter. Modeled concentrations were adjusted to observations through linear interpolation of residuals between observations (Aulenbach and Hooper 2001).

Monthly input fluxes were subtracted from monthly output fluxes to obtain net fluxes. Wherever output chemistry was unavailable for a site during water years 1992 through 1997, the mean monthly export from the remainder of the series was inserted. Ammonia concentrations never exceeded detection levels for stream samples collected at Loch Vale, Trout Lake, and Sleepers River; net exports were equal to the negative of the input flux at these sites. The net values for each solute flux for each site were then standardized to mean zero and unit variance.

Principal Component Analysis

Principal Component Analysis (PCA) is a linear dimensionality reduction technique, which identifies orthogonal directions of maximum variance in the original data, and projects the data into a lower-dimensionality space formed of a subset of the highest-variance components (Bishop 1995).

Input for the all-site PCA described here consists of 360 observations of 19 variables (9 hydrologic and 10 chemical variables); The 360 observations consist of 72 months (October 1991 through September 1997 - water years 1992-97) of observations for each of the five WEBB sites. Individual PCA models were also run for each site to compare the complexity of the individual hydrobiochemical systems. The data for each of these was 72 observations by 19 variables for Loch Vale, Sleepers River, and Panola Mountain. The Icacos PCA included 18 variables (no snow melt), and the Allequash PCA included 17 variables (highly permeable soils results in no infiltration excess or root zone wetting).

Results

The number of components needed to explain the variance in all observations in a dataset reflects the complexity of the overall system. In general, strong seasonality of hydrologic fluxes and associated solute fluxes corresponds to simpler systems that can be described with fewer components. Only two components account for more than 80 percent of the variance for the Loch Vale PCA model. Three components are required to account for a similar amount of variance at Panola Mountain and Sleepers River, and four for Allequash and Icacos. To explain 80 percent of the variance for the combined data set of all sites, five components are needed (Table 2). Each of these five can be related to general processes present to some degree at all sites, but would not necessarily be an optimal descriptor at any given site.

Table 2. Component loads for the all-site PCA. Loads less than 0.1 are not shown. [Abbreviations: Comp; component; BF, baseflow and exfiltration; ET, evapotranspiration; Melt, snowmelt; MF, macropore flow; NP, net precipitation; OFInfex, overland flow from infiltration excess; OFSat, saturated overland flow; RZwet, flux from the saturated zone to the root zone; SoilM, root-zone soil moisture; ANC, acid-neutralizing capacity; Ca, calcium; Cl, chloride; H2SiO4, silicic acid; K, potassium; Mg, magnesium; Na, sodium; NH4, ammonium; NO3, nitrate; SO4, sulfate]

	Comp.1	Comp.2	Comp.3	Comp.4	Comp.5
Proportion of Variance (in percent)	50	14	8	7	4
BF	0.26			-0.12	0.25
ET		-0.35	0.53		-0.11
Melt	0.23				0.59
MF	0.25	-0.16	-0.19	-0.23	0.26
NP		-0.41	-0.40		-0.36
OFInfex	0.17	-0.33		-0.19	-0.40
OFSat	0.24	-0.23		-0.35	
RZwet	0.23	-0.24	0.20	-0.24	
SoilM	0.10	0.14	-0.63		
ANC	0.28			0.30	
Ca	0.30			0.20	
Cl	0.26	0.13	0.15	0.18	-0.13
H2SiO4	0.29			0.13	
K	0.29				-0.10
Mg	0.29			0.31	-0.11
Na	0.29			0.27	-0.13
NH4		0.45		-0.37	-0.38
NO3	0.15	0.37	0.20	-0.39	
SO4	0.25	0.25		-0.25	

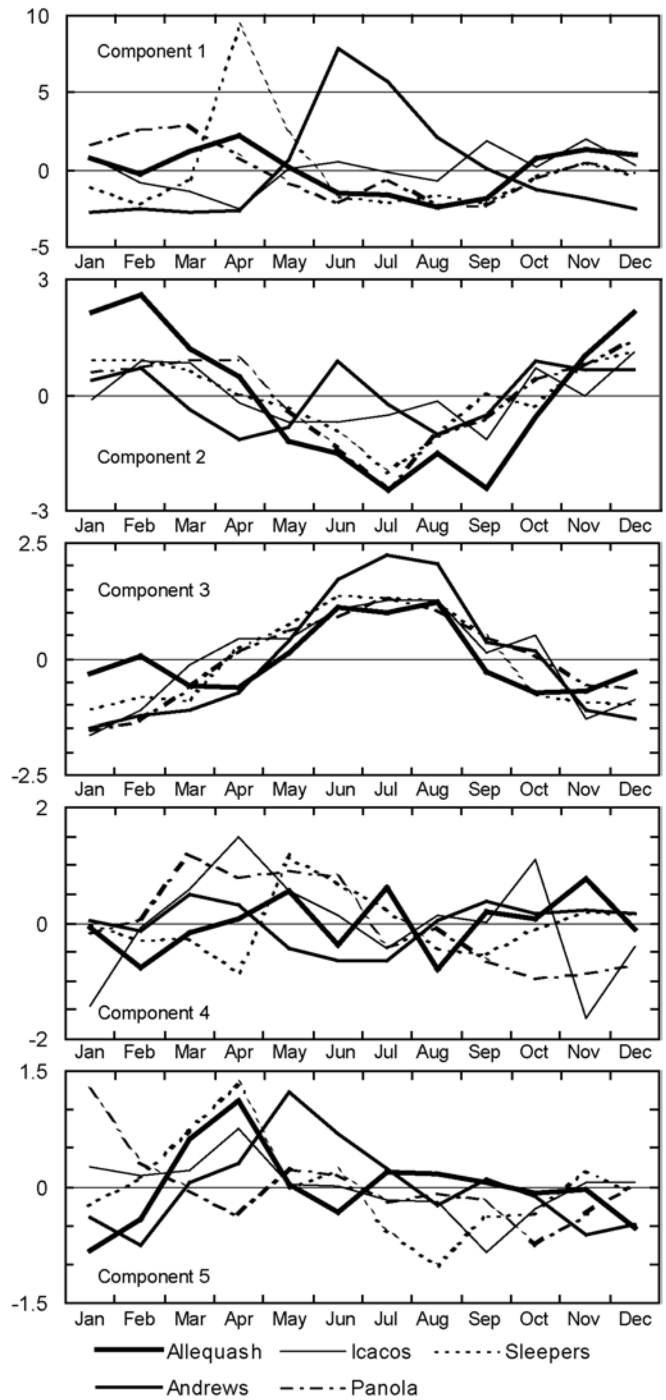

Figure 1. Mean monthly scores for the first five principal components of the combined hydrologic- geochemical WEBB data set.

Hydrologic and biogeochemical significance of the first five principal components

A component consists of a combination of the original variables. The loading of each variable in Table 2 describes how heavily weighted that variable is on the component. The loadings are the coefficients of the principal component transformation. For each observation (month) in the original data set, a score for each component was also computed. A score indicates the relative presence and sign for each component for each observation. The sign indicates which of the two diametrically-opposite hydrologic conditions is present during a given month. Seasonal patterns can be discerned by plotting mean monthly scores (Figure 1).

Component 1 - Flushing/freezing (50 percent of variance): Accumulated solutes are flushed from the watershed by intense rain or snow melt or alternately retained when precipitation and solutes are locked up when the basins freeze or enter a drought.

Component 2 – Dry periods (with cool, wet soils) /Wet periods (with warm soils with available root zone storage) (14 percent of variance): Retention of ammonia, nitrate, and sulfate is less during dry and cool periods with saturated soils than it is during wet warm periods with available root zone storage.

Component 3 - Dry soils (during warm, dry periods)/Wet soils (during cool, wet periods) (8 percent of variance): This component describes the upward flux of water from the saturated zone into drying riparian soils during periods of high evapotranspiration. Exfiltration through desiccating surfaces increases the net export of nitrate and chloride; during wet and cool periods, the nitrate and chloride in the precipitation may move from the base of wet soils down to mix with ground water as might occur during ground water ridging.

Component 4 - Low base flows (with limited recharge) /Moderate baseflows (with some recharge) (7 percent of variance): During very low flows, ions from deep in the soil profile are released; nutrients and sulfate are tightly retained near the surface. During moderate recharge events the nutrients and sulfate exports are rinsed into a more saturated soil profile to be released in the base flow as the contribution of base cations diminishes.

Component 5 - Spring melts or rains on dry soils/late summer rains on wet soils (4 percent of variance): Ammonia is taken up by growing vegetation in the spring. Mineralization of organic debris reintroduces the ammonia into the system to be released during late summer rains when transpiration begins shutting down.

Conclusions

The route that water from rain and snowmelt takes on its way to the stream or back to the atmosphere affects the stream chemistry. Upcoming modeling efforts directed at simulating the hydrologic and biogeochemical processes active in this diverse set of watersheds should be able to incorporate the following:

- Precipitation chemistry and dry deposition
- Weathering of bedrock and subsequent release of cations and alkalinity
- Soil processes including ion exchange and redox variations in the root zone resulting from different ET rates.
- Energy balances for accurate estimates of evapotranspiration and rates of chemical and biological reactions in the soils.
- Biologic uptake

The water coursing through the nation's rivers carries with it a myriad of constituents, some innocuous, some toxic. Truly pristine waters are scarcer every day as development continues into once remote headwaters. By evaluating the present hydrologic state of a watershed and the forecasted climatology, the fate of solutes deposited in precipitation and those applied to or naturally existing in the watershed can be reasonably predicted.

Acknowledgments

WEBB project personnel were critical in the collection of the hydrologic and water quality data and in providing reviews of the draft manuscript: Don Campbell, Dave Clow, and Alisa Mast at Loch Vale, Colorado; John Walker at Trout Lake, Wisconsin; Jamie Shanley at Sleepers River, Vermont; Jake Peters and Brent Aulenbach at Panola Mountain, Georgia; and Joe Troester, Matt Larsen, Angel Torres, and Iris Concepcion at Luquillo Mountain, Puerto Rico. The manuscript also benefited from reviews by George Leavesley, Jill Baron, Alex Blum, and Pierre Glynn.

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