# Selected Achievements, Science Directions, and New Opportunities for the WEBB Small Watershed Research Program

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## Abstract

Over nearly two decades, the Water, Energy, and Biogeochemical Budgets (WEBB) small watershed research program of the U.S. Geological Survey (USGS) has documented how water and solute fluxes, nutrient, carbon, and mercury dynamics, and weathering and sediment transport respond to natural and humancaused drivers, including climate, climate change, and atmospheric deposition. Together with a continued and increasing focus on the effects of climate change, more investigations are needed that examine ecological effects (e.g., evapotranspiration, nutrient uptake) and responses (e.g., species abundances, biodiversity) that are coupled with the physical and chemical processes

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historically observed in the WEBB program. Greater use of remote sensing, geographic modeling, and habitat/watershed modeling tools is needed, as is closer integration with the USGS-led National Phenology Network. Better understanding of process and system response times is needed. The analysis and observation of land-use and climate change effects over time should be improved by pooling data obtained by the WEBB program during the last two decades with data obtained earlier and (or) concurrently from other research and monitoring studies conducted at or near the five WEBB watershed sites. These data can be supplemented with historical and paleo-environmental information, such as could be obtained from tree rings and lake cores. Because of the relatively pristine nature and small size of its watersheds, the WEBB program could provide process understanding and basic data to better characterize and quantify ecosystem services and to develop and apply indicators of ecosystem health. In collaboration with other Federal and State watershed research programs, the WEBB program has an opportunity to contribute to tracking the short-term dynamics and long-term evolution of ecosystem services and health indicators at a multiplicity of scales across the landscape.

**Keywords:** biogeochemistry, climate, ecohydrology, ecosystem indicators, ecosystem services, experimental forests, experimental watersheds, LTER, WEBB

### **Program Background and Achievements**

Scientists in the <u>WEBB</u> (Water, Energy, and Biogeochemical Budgets) program of the U.S. Geological Survey (USGS) have been monitoring and conducting hydrologic-process research at five small watershed sites across the United States since 1991: Luquillo, PR; Panola Mountain, GA; Sleepers River, VT; Trout Lake, WI; and Loch Vale, CO (Baedecker and Friedman 2000, Baedecker 2003). The cumulative database now contains 18 years of observations of hydrology (streamflow, groundwater levels, and soil moisture), meteorology (precipitation, temperature, humidity, and wind speed and direction), and water quality (including major solutes, nutrients, stable environmental isotopes, mercury and methylmercury, and organic carbon). This long-term effort has successfully explained and quantified many of the hydrological and biogeochemical processes in these watersheds, which have very different soils, relief, and climate. The WEBB program provides an excellent example of the importance of long-term environmental monitoring (such as argued by Lovett et al. 2007). Important differences in water and solute fluxes and in mercury deposition and cycling have been revealed through comparisons of monitoring and modeling results. Although not the sole research focus when initiated, the WEBB watersheds also have served as sentinels of global change, providing a record of climatic and anthropogenic effects on hydrologic and biogeochemical processes. Examples of global change effects considered by the WEBB program include:

- Timing of streamflow and snowmelt (D. Clow, 2008, "Changes in the timing of snowmelt and streamflow in Colorado: A response to recent warming," USGS, written commun.);
- Loss of alpine permafrost (Clow et al. 2003a) and the relation between snowpack and solute chemistry;
- Wetland carbon gas exchanges (Wickland et al. 2001) and snowpack and tundra carbon gas fluxes (Mast et al. 1998);
- Carbon sequestration (Huntington 1995);
- Dissolved organic carbon fluxes (Schuster et al. 2004) and implications for methylmercury fate and transport;
- Water fluxes and chemical trends (Aulenbach et al. 1996, Peters et al. 2002);
- Response of watershed hydrology (Hunt, Walker, et al. 2008a; Walker et al., this volume) and ecology (Hunt, Walker, et al. 2008b);
- Soil-calcium depletion (Huntington 2000, Huntington et al. 2000, Peters and Aulenbach, this volume); and

• Rock-weathering rates (White and Blum 1995 a and b; White et al. 1999) and mass-wasting and landslides (Carter et al. 2001).

USGS Fact Sheets for each of the five WEBB sites and a synthesis paper for the entire WEBB program provide a retrospective on some of the processes listed above and their trends over the last two decades (D. Clow, USGS, oral commun.). Information about the WEBB program is available at the program's website, <u>http://water.usgs.gov/webb</u>.

The small size of the WEBB program watersheds (ranging from 41 to 12,000 ha) has allowed detailed investigation of hydrological and biogeochemical processes that would not have been possible in larger watersheds. Because of its montane and alpine environments, limited forest cover (5 percent), and extensive tundra, talus, and rock and snow glaciers, the Loch Vale site is exceptionally sensitive and responsive (i.e. not resilient) to atmospheric anthropogenic contamination and to climate change. Research at the Loch Vale site has taken advantage of this sensitivity by investigating, for example, (1) the effects of climate on weathering rates (Clow and Drever 1996), and (2) the effects of nitrogen deposition, much of it of anthropogenic origin, on the diatom community in the lake (Baron et al. 2005). Clow et al. (2003a) also found that warming climate and melting permafrost are affecting groundwater flow and solute fluxes at the site and are exposing soils that have a surprising amount of microbial activity. Atmospheric inputs and the changing chemistry of Loch Vale have been compared with deposition and changes in other high-elevation glacial lakes (Clow et al. 2003b, Ingersoll et al. 2008). As part of Rocky Mountain National Park, the Loch Vale site is a UNESCO\* International Biosphere Reserve and is also one of the sites monitored under the National Acidic Precipitation Assessment Program (NAPAP), a cooperative Federal program authorized in 1980.

The Sleepers River watershed in Vermont, a research site that was established in 1958 by the Agricultural Research Service (ARS), has been the focus of detailed hydrological and biogeochemical investigations in a mixed land-use setting (forests, agricultural lands, and low-density residential). Dunne and Black (1970)

<sup>\*</sup> United Nations Educational, Scientific, and Cultural Organization

developed the variable source-area concept at the Sleepers River watershed and studied dynamic subsurface and surface flow processes that control the movement of water from the landscape to a stream. Subsequent studies have quantified how preferential flow paths control stream hydrochemical responses during stormflow (Kendall et al. 1999, McGlynn et al. 1999, Shanley et al. 2003, Sebestyen et al. 2008). Studies have traced variable sources and biogeochemical transformations that control the chemical speciation and concentrations of a wide range of stream solutes including nitrogen (Sebestyen et al. 2008), carbon (Doctor et al. 2008, Sebestyen et al. 2008), mercury (Shanley, Mast, et al. 2008), sulfur (Shanley et al. 2005; Shanley, Mayer, et al. 2008), and weathering products (Bullen and Kendall, 1998, Shanley et al. 2002). In addition, the timing, intensity, and character of organic carbon transport at the site has been studied (Sebestyen et al. 2008, Schuster et al. 2008) and contrasted to carbon transport processes in the Yukon River Basin (Schuster et al. 2004). Acidic deposition effects at the site have also been studied extensively and have been contrasted with those occurring in other watersheds. For example, Shanley et al. (2004) compared acid deposition effects in the Sleepers River watershed with those in a watershed in the Czech Republic. The long-term data from Sleepers River have frequently been included in regional assessments of northeastern United States watersheds to quantify nutrient budgets and understand sources and sinks of biogeochemically active solutes (Hornbeck et al. 1997; Campbell et al. 2000, 2004).

The Trout Lake site in northern Wisconsin is part of the North Temperate Lakes Long-Term Ecological Research (LTER) site, one of 26 LTER sites established in 1980 that are funded by the National Science Foundation (NSF). Because of the relatively flat topography and northern temperate climate, this watershed ecosystem is dominated by groundwater flow. Research at the site has focused on surface/groundwater interaction at local to watershed scales. Hydrologic modeling tools were used to: (1) better delineate the groundwater watershed (Hunt et al. 1998), (2) simulate surface/groundwater interactions (Hunt et al. 2003, Hunt 2003), and (3) evaluate the utility of different types of field data for model calibration and prediction (Hunt et al. 2005, Hunt and Doherty 2006, Doherty and Hunt 2009). Novel applications of isotope and ion chemistry were used to investigate lake/groundwater interactions (Krabbenhoft

et al. 1994, Walker et al. 2007) and groundwater flow paths (Walker and Krabbenhoft 1998; Pint et al. 2003; Walker et al. 2003; Fienen et al., in press). Flow-path processes were characterized from the unsaturated zone starting points (Hunt, Prudic, et al. 2008), through the saturated aquifer (Bullen et al. 1996), to hyporheic discharge locations (Schindler and Krabbenhoft 1998, Lowry et al. 2007). This understanding of surface/groundwater interactions provided the foundation for site-scale evaluations of temperature modulation, nutrient concentrations, and invertebrate populations (Hunt et al. 2006), as well as response of the watershed hydrology (Hunt, Walker, et al. 2008a; Walker et al., this volume) and ecology (Hunt, Walker, et al. 2008b) to climatic change.

The Panola Mountain watershed in Georgia is located 25 km southeast of Atlanta in the Panola Mountain State Conservation Park. The watershed has a large impervious area (greater than 10 percent of the watershed) that is provided by granitic bedrock outcrops. This feature has led to a comparison with urbanized watersheds in the Atlanta area (N.E. Peters, 2008, USGS, written commun.). Since 1985, research at the Panola Mountain Research Watershed (PMRW) has improved the conceptual understanding of the watershed's response to precipitation over a range of temporal and spatial scales (McDonnell et al. 1996, Freer, McDonnell, et al. 2002, Peters et al. 2003a, Tromp-Van Meerveld et al. 2007) and has investigated the impact of different hydrologic pathways on solute transport (Peters 1989, 1994; Hooper et al. 1990, 1998; Shanley 1992; Shanley and Peters 1993; Huntington et al. 1994; Aulenbach et al. 1996; Burns et al. 1998, 2001, 2003; Peters et al. 1998; Peters and Ratcliffe 1998; Aulenbach and Hooper 2001, 2006; Hooper 2003; Webb et al. 2003; Peters and Aulenbach, this volume). Research at PMRW has investigated biogeochemical cycling, mercury and sulfur dynamics, dry deposition processes and vegetation transpiration effects on soil moisture content. Hillslope studies quantified the importance of bedrock topography in controlling subsurface stormflow (Freer et al. 1997; Freer, Beven, et al. 2002) and of bedrock leakage in dominating the hillslope water balance (Tromp-van Meerveld et al. 2007). In addition to the development of a detailed hydrologic and biogeochemical conceptual model, the availability of detailed long-term hydrologic measurements is a prerequisite for deterministic hydrologic modeling (Freer, McDonnell, et al. 2002; Peters et al. 2003b; Clark et al. 2008) and detailed

assessments of hillslope and catchment hydrologic behavior (Tromp-van Meerveld and McDonnell 2006c), in particular during rainstorms (Peters et al. 2003a, Tromp-van Meerveld and McDonnell 2006 a and b). Climate impacts are expected because watershed and hillslope stormflow water yields at PMRW are nonlinearly related to soil moisture content, rainfall, and water-table elevation, and the relations vary on a seasonal basis.

The Luquillo WEBB project has evaluated hydrologic, chemical, and sediment processes and budgets in four watersheds of differing geology (granitic versus volcanic) and land use (mature rainforest versus agricultural legacy). The forested catchments are located in the U.S. Forest Service (FS) Luquillo Experimental Forest, part of which has been designated a UNESCO International Biosphere Reserve and belongs to the NSF LTER network. The Luquillo WEBB watersheds are undergoing rapid change, both locally induced (including landcover change, species introductions, water resource management) and externally driven (including climate change and longrange advection of pollutants). The Luquillo WEBB program has investigated the effects of hurricanes, atmospheric pollution, drought, climate change, precipitation patterns, and land use on hydrology and water quality (Scatena and Larsen 1991; Zack and Larsen 1994; Larsen 2000; Stallard 2001; Shanley et al. 2008 a and b; Murphy and Stallard, this volume). Research at the Luquillo site has investigated the possible causes of amphibian decline (Stallard 2001) and has contributed to an understanding of the dynamics of cloud forest hydrology, extending previous work conducted on Hawaii (Scholl et al., in press) and detailing the relative importance of orographic and convective precipitation regimes to forested mountain watersheds (M. Scholl (USGS), J.B. Shanley (USGS), J.P. Zegarra (University of Puerto Rico in Mayaguez), and T.B. Coplen (USGS), 2008, "A new explanation for the stable isotope amount effect using NEXRAD echo tops: Luquillo Mountains, Puerto Rico,"written commun.). Extensive work on mass wasting has teased out the importance of several factors affecting landslides, including rainfall intensity and duration, historical land use, and road construction (Larsen and Simon 1993, Larsen and Parks 1997, Larsen and Torres-Sanchez 1998, Larsen et al. 1999, Larsen and Santiago-Román 2001, Gellis et al. 2006). Studies of weathering and solute fluxes have been performed in the Icacos watershed, which has one of the highest

documented chemical weathering rates of granitic rocks in the world (Brown et al. 1995, 1998; White and Blum 1995 a and b; Dong et al. 1998; Murphy et al. 1998; White et al. 1998; Schulz and White 1999; Turner et al. 2003; Buss et al. 2004, 2005, 2008; Fletcher et al. 2006; Chabaux et al. 2008). Analyses of sediment and solute concentrations in the Luquillo WEBB rivers and soil porewaters have revealed that fluxes are dominated by storm effects (Peters et al. 2006, Kurtz et al. 2004), indicating that climate change-related perturbations in storm patterns would seriously affect sediment and solute fluxes from the Luquillo WEBB watersheds. Luquillo WEBB studies have also evaluated methane emissions from reservoirs (Joyce and Jewell 2003) and mercury and methylmercury deposition (Shanley, Mast, et al. 2008).

In addition to funding research at individual sites, projects in the WEBB program have developed models, tools, and theories to help understand and quantify hydrologic and biogeochemical processes in small watersheds. For example, the program has spurred the development and application of watershed models such as the Precipitation Runoff Modeling System (PRMS; Leavesley et al. 2005), the Water, Energy, and Biogeochemical Model (WEBMOD; Webb et al. 2006), and GSFLOW (Markstrom et al. 2008), which is the new USGS surface/groundwater interactions model that couples the USGS groundwater flow model MODFLOW with PRMS. The program also has provided a forum for development and testing of methods, such as flux computations (Aulenbach and Hooper 2001, 2006), water-quality sampling (Peters 1994), and dry deposition (Cappellato and Peters 1995). The WEBB program also has stressed the need for watershed comparison studies, especially amongst the five WEBB watersheds. Some of the key comparative studies published include: (1) a principal-component analysis used to identify the statistical relations between hydrologic conditions and the net exports of major cations, anions, and silica at the five sites (Webb et al. 2003); (2) a mass-balance comparison of water and major-solute fluxes monitored at the five watersheds between 1992 and 1997 (Peters et al. 2006); and (3) a comparison of mercury and methylmercury deposition, cycling, and transport in the WEBB watersheds (Shanley, Mast, et al. 2008).

## What Are Some of the Future Directions for the WEBB Program?

Federal science priorities in general, and USGS science priorities in particular, have become refocused on climate change issues, in part because of the recent release of the <u>Intergovernmental Panel on Climate</u> <u>Change (IPCC) 4th Assessment Report</u>. A wealth of data has been collected in the last 18 years at the WEBB watersheds, and historical data are available for many of the sites prior to the establishment of the WEBB program. The data are being analyzed through an intersite comparison study to examine the effects of climatic trends and variations in temperature and precipitation, in water storage and fluxes, and in nutrient and major solute cycling in the five watersheds.

During the next 5 years, WEBB research plans to take advantage of the gradients in climate, land use, and basin physical characteristics inherent to the five WEBB sites. Water availability under changing climate is a key issue, with potential effects on agriculture, industry, and quality of drinking water. To study the effects on water availability, plans are to evaluate the response of runoff, groundwater flow, and evapotranspiration to variations in climate, and to conduct hydrologic modeling under various climate change scenarios, thereby putting site results in a regional context. The hydrologic and chemical responsiveness of catchments to climate change and atmospheric deposition of pollutants are strongly influenced by water residence times. Residence times could be quantified through a multi-tracer (CFCs, tritium, water isotopes) approach that permits characterization of slow, medium, and fast flow pathways through the catchments; the temporal variability of stream-water residence times can also be assessed with respect to climate change/variability and compared among sites. Trends in climate, runoff, and streamwater chemistry will be evaluated with the objective of establishing the response of runoff and chemistry to climate. However, climate variability often is large and can obscure climate change signals, so developing models that account for short-term variability will be important for detection of long-term trends. Carbon and nitrogen cycles can exert strong feedbacks on climate (positive and negative), and quantification of carbon and nitrogen fluxes and associated processes is planned as an important component of WEBB research in the future.

Complementing the hydrologic and biogeochemical data obtained from the WEBB sites since 1991 is an important priority for the program, helping put the WEBB record of environmental change in an extended historical context. There are several ways to extend the WEBB records of environmental change. The first is to make full use of the data available from other, earlier and concurrent, Federal (or State/local) agency investigations (e.g. ARS, LTER, and FS data). In addition to extending our temporal knowledge of the WEBB sites, this would also add richness to the data available. It would be most useful to have all the Federal program data for the WEBB watersheds easily accessible through the Internet, preferably from some common web interface. Secondly, dendrochronological studies could be conducted to further extend the historical records of hydrologic and biotic response to climatic effects. These studies might also provide information on historical pest infestations and other environmental changes. Similarly, lake/pond sediment cores could be obtained, dated, and analyzed to also obtain a record of environmental change at least over the last century, documenting the temporal variations in flow and sediment transport, in chemical fluxes, and in biotic abundances (e.g. pollen, diatom species, and individual counts).

Indeed, the study of climatic effects in the WEBB program could be further strengthened by increasing the monitoring of biota and biological processes in the WEBB watersheds. One avenue of future research, mentioned in the statement provided above by the WEBB site coordinators, could be to provide a better understanding of the effects and feedbacks of changing vegetative-cover distribution on evapotranspiration and water/sediment budgets, as well as on nutrient and solute cycling. Another avenue could be to examine the climatic effects of changing water/sediment budgets and nutrient cycling on aquatic invertebrate distributions and (or) on amphibian distributions. Because of their sensitivity to climate and water quality effects, and their limited ability to migrate, these populations (along with plant distributions) could be of value in assessing climatic effects and general ecosystem health in the WEBB watersheds. Monitoring and research on evapotranspiration and water availability for ecological needs are two of the key monitoring and research components (along with streamgaging and groundwater depletion) often mentioned for the National water census envisaged in the 2008 USGS Science Strategy plan. Because of their potential scope, however, these

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efforts to link biological, hydrological, and geochemical process research and monitoring will require increased interdisciplinary collaboration in the USGS as well as continued partnering with Federal and State agencies, university researchers, and NSF programs. The increased use of remote sensing technologies, geographic information system (GIS) modeling, habitat modeling, and watershed modeling can provide valuable help in developing a monitoring program for the WEBB watersheds.

In assessing ecosystem health, trends, and natural variability in its watersheds, the WEBB program has an opportunity to utilize and develop further the series of ecosystem indicators advanced by the Heinz Center in its recent 2008 report "The State of the Nation's Ecosystems" (Heinz Center 2008). The 108 indicators outlined by the Heinz Center can be grouped into four categories: (1) extent and pattern indicators, such as area of wetlands, length of streams, and proximity to residential areas; (2) chemical and physical characteristics, such as nutrient loads delivered, soil erosion, dissolved oxygen, and contaminant levels; (3) biological component indicators, such as threatened and endangered species, biodiversity, and percentage of non-native species; and (4) ecosystem goods and services, such as amount of timber harvested, water withdrawals, pollination services, and outdoor recreation services. The Heinz Center indicators are also grouped into a set of core national indicators and six sets of ecosystem-specific indicators (coast and oceans, farmlands, forests, freshwaters, grasslands and shrublands, and urban and suburban landscapes). The WEBB program could focus on a few of the Heinz Center indicators and might benefit from adding other indicators that may better characterize the WEBB watersheds.

The need for ecohydrology studies was described several years ago by Hunt and Wilcox (2003 a and b), who wrote in the context of coupled ecological– groundwater–surface-water processes: "There are few studies that have linked the abiotic effects that hydrologists know well to the ecological community that the public holds dear. Without understanding the ecohydrology, we will never truly answer these important societal questions" (2003 a, p. 289). The authors were referring to the need to understand ecohydrologic processes so as to better protect the biota (including humans) that depend on water to survive; they were also referring to the need to better understand and quantify the role of biotic processes on water quality and quantity. The need to holistically integrate our understanding of biological and hydrological processes has long been at the core of USGS researcher Tom Winter's "aquatic continuum concept" (Winter 2004) and its variants (e.g., the "Wetland Continuum." Euliss et al. 2004). The need continues today, and few programs within the USGS have tried to address it.

Monitoring the seasonal timing of key ecosystem functions in the WEBB watersheds can be expected to be highly relevant in helping to understand climate effects and feedbacks on biota and water resources. The National Phenology Network, a recently established, collaborative, interagency, and citizenscientist network (Betancourt et al. 2007, 2005), could provide some help in this effort and could also benefit from some of the climate effects research and monitoring conducted in the WEBB program. In general, a better understanding of process response times and system lags in the watersheds could be developed that would allow improved adaptive management for these and other small watersheds in the face of climate and land-use change. These lags and response times occur on a wide variety of time scales, not just on seasonal scales, but often across yearly and decadal time scales and longer, affecting biologic and hydrologic responses and landscape evolution. Improved understanding and modeling of processes and response times in small research watersheds could lead to important advances in managing our larger National landscape. The small size of the WEBB watersheds uniquely lends itself to the elucidation of system processes and response times.

New and developing watershed-modeling tools, such as the USGS integrated groundwater and surface-water modeling code GSFLOW and related advances in temperature modeling of watershed biotic habitats, have great promise for helping foster an improved understanding of the biologic, hydrologic, and geochemical processes controlling water, sediment, and nutrient transport. Coupled modeling of physiochemical, hydrological, and biological processes and the development of forecasting and scenario analysis tools based on such coupling have been suggested as among the highest priorities in a recent (December 3-4, 2008) USGS-sponsored multipartner workshop that focused on the science priorities for a proposed National Climate Change and Wildlife Science Center (Haseltine and Jones 2008). The

development of modeling, geographic information system, and remote sensing tools that not only help couple a variety of biologic, hydrologic, and physicochemical processes, but also help translate process-research findings from small watershed studies into larger regional contexts and assessments will be invaluable in helping forecast the effects of climate change and changing land use. Implementing a strengthened monitoring and research plan for the WEBB watersheds in a nationally consistent framework would be a step towards this goal.

Establishing new indicators for ecosystem health in the WEBB watersheds and continuing current efforts in process research, monitoring, and modeling will contribute to a better understanding and quantification of ecosystem services (e.g., as defined in the 2005 <u>Millenium Ecosystem Assessment</u> synthesis report) in the watersheds. This work will help build scenario analyses to forecast the effects of climate change and land-use change on these and similar watersheds around the Nation. Most importantly, the WEBB program can help communicate to the public the importance of small watershed research programs and their relevance in preserving and managing ecosystem health and services for society.

Although some of the science directions and next steps described in our paper can be initiated with existing resources in the WEBB program, additional resources would be required to adequately implement our science vision. Close collaborations with other Federal watershed research and monitoring efforts, such as the U.S. Forest Service Experimental Forest program (e.g. Lugo et al. 2006), the Agricultural Research Service experimental watershed program (e.g. Moran et al. 2008), and the National Science Foundation LTER program (e.g. <u>Hobbie et al. 2003</u>), are also key to implementation of this vision.

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#### References

Aulenbach, B.T., and R.P. Hooper. 2001. Removing climatic effects from trends in streamwater load estimates. In J.J. Warwick, ed., Proceedings of the AWRA Conference on Water Quality Monitoring and Modeling, San Antonio, TX, 30 April–2 May 2001, pp. 47–52. American Water Resources Association.

Aulenbach, B.T., and R.P. Hooper. 2006. The composite method: An improved method for streamwater solute load estimation. Hydrological Processes 20(14):3,028–3,047.

Aulenbach, B.T., R.P. Hooper, and O.P. Bricker. 1996. Trends in precipitation and surface-water chemistry in a national network of small watersheds. Hydrological Processes 10(2):151–181.

Baedecker, M.J. 2003. <u>Overview of the Water, Energy</u>, <u>Biogeochemical Budgets Program of the U.S.</u> <u>Geological Survey</u>. In K.G. Renard, S.A. McElroy, W.J. Gburek, H.E. Canfield, and R.L. Scott, eds., Proceedings of the First Interagency Conference on Research in the Watersheds, Benson, AZ, 27–30 October 2003, pp. 30–35. U.S. Department of Agriculture, Agricultural Research Service.

Baedecker, M.J., and L.C. Friedman. 2000. <u>Water</u>, energy, and biogeochemical budgets: A watershed research program. U.S. Geological Survey Fact Sheet 165-99.

Baron, J.S., K.R. Nydick, H.M. Rueth, B.M. Lafrancois, and A.P. Wolfe. 2005. High Elevation Ecosystem Responses to Atmospheric Deposition of Nitrogen in the Colorado Rocky Mountains, USA. In U.M. Huber, H.K.M. Bugmann, and M.A. Reasoner, eds., Global Change and Mountain Regions: A State of Knowledge Overview, pp. 429–436. Springer, Dordrecht, The Netherlands.

Betancourt, J.L., M.D. Schwartz, D.D. Breshears, C.A. Brewer, G. Frazer, J.E. Gross, S.J. Mazer, B.C. Reed, and B.E. Wilson. 2007. Evolving plans for a USA national phenology network. Eos, Transactions American Geophysical Union 88:211.

Betancourt, J.L., M.D. Schwartz, D.D. Breshears, D.R. Cayan, M.D. Dettinger, D.W. Inouye, E. Post, and B.C. Reed. 2005. <u>Implementing a U.S. national phenology</u> <u>network</u>. Eos, Transactions American Geophysical Union 86:539, 542.

Brown, E.T., R.F. Stallard, M.C. Larsen, D.L. Bourlès, G.M. Raisbeck, and F. Yiou. 1998. Determination of predevelopment denudation rates of an agricultural watershed (Cayaguás River, Puerto Rico) using in situproduced <sup>10</sup>Be in river-borne quartz. Earth and Planetary Sciences Letters 160:723–728.

Brown, E.T., R.F. Stallard, M.C. Larsen, G.M Raisbeck, and F. Yiou. 1995. Denudation rates based on accumulation of in situ produced <sup>10</sup>Be compared with watershed mass balance results in the Luquillo Experimental Forest, Puerto Rico. Earth and Planetary Science Letters 129:193–202.

Bullen, T.D., and C. Kendall. 1998. Tracing of Weathering Reactions and Flowpaths: A Multi-Isotope Approach. In C. Kendall and J.J. McDonnell, eds., Isotopes Tracers in Catchment Hydrology, pp. 611–646. Elsevier, New York.

Bullen, T.D., D.P. Krabbenhoft, and C. Kendall. 1996. Kinetic and mineralogic controls on the evolution of groundwater chemistry and <sup>87</sup>Sr/<sup>86</sup>Sr in a sandy silicate aquifer, northern Wisconsin, U.S.A. Geochimica et Cosmochimica Acta 60(10):1,807–1,821.

Burns, D.A., R.P. Hooper, J.J. McDonnell, J.E. Freer, C. Kendall, and K. Beven. 1998. Base cation concentrations in subsurface flow from a forested hillslope: The role of flushing frequency. Water Resources Research 34(12):3,535–3,544.

Burns, D.A., J.J. McDonnell, R.P. Hooper, N.E. Peters, J.E. Freer, C. Kendall, and K. Beven. 2001. Quantifying contributions to storm runoff through endmember mixing analysis and hydrologic measurements at the Panola Mountain Research Watershed (Georgia, USA). Hydrological Processes 15(10):1,903–1,924.

Burns, D.A., N. Plummer, J.J. McDonnell, E. Busenberg, G.C. Casile, C. Kendall, R.P. Hooper, J.E. Freer, N.E. Peters, K. Beven, and P. Schlosser. 2003. The geochemical evolution of riparian groundwater in a forested piedmont catchment. Ground Water 41(7):913–925.

Buss, H.L., M.A. Bruns, M.J. Schultz, J. Moore, C.F. Mathur, and S.L. Brantley. 2005. The coupling of biological iron cycling and mineral weathering during saprolite formation, Luquillo Mountains, Puerto Rico. Geobiology 3:247–260.

Buss, H.L., P.B. Sak, S.M. Webb, and S.L. Brantley. 2008. Weathering of the Rio Blanco quartz diorite, Luquillo Mountains, Puerto Rico: Coupling oxidation, dissolution, and fracturing. Geochimica et Cosmochimica Acta 72:4,488–4,507.

Buss, H.L., P.B. Sak, A.F. White, and S.L. Brantley. 2004. Mineral dissolution at the granite–saprolite interface. In R.B. Wanty and R.R. Seal, eds., Water– Rock Interaction (WRI-11): Proceedings of the Eleventh International Symposium on Water–Rock Interaction, Saratoga Springs, NY, 27 June–2 July 2004, p. 819–823. Taylor and Francis, London.

Campbell, J.L., J.W. Hornbeck, W.H. McDowell, D.C. Buso, J.B. Shanley, and G.E. Likens. 2000. Dissolved organic nitrogen budgets for upland, forested ecosystem in New England. Biogeochemistry 49:123–142.

Campbell, J.L., J.W. Hornbeck, M.J. Mitchell, M.B. Adams, M.S. Castro, C.T. Driscoll, J.S. Kahl, J.N. Kochenderfer, G.E. Likens, J.A. Lynch, P.S. Murdoch, S.J. Nelson, and J.B. Shanley. 2004. Input-output budgets of inorganic nitrogen for 24 forest watersheds in the northeastern United States: A review. Water, Air, and Soil Pollution 151:373–396.

Cappellato, R., and N.E. Peters. 1995. Dry deposition and canopy leaching rates in deciduous and coniferous forests of the Georgia Piedmont: An assessment of a regression model. Journal of Hydrology 169:131–150.

Carter, L.M., E. Shea, M. Hamnett, C. Anderson, G. Dolcemascolo, C. Guard, M. Taylor, T. Barnston, Y. He, M.C. Larsen, L. Loope, L. Malone, and M. Meehl. 2001. <u>Potential Consequences of Climate Variability</u> and Change for the US-Affiliated Islands of the Pacific and Caribbean. In The Potential Consequences of Climate Variability and Change: Foundation Report, pp. 315–349. Report by the National Assessment Synthesis Team for the U.S. Global Change Research Program. Cambridge University Press, Cambridge.

Chabaux, F., E. Blaes, E. Pelt, A. Dosseto, H. Buss, A. White, and S. Brantley. 2008. Rate of spheroidal weathering determined by U-series nuclides (Rio Icacos basin, Puerto Rico). Geochimica et Cosmochimica Acta 72:A145.

Clark, M., D. Rupp, R. Woods, H.J. Tromp-van Meerveld, N.E. Peters, and J. Freer. 2008. Consistency between hydrological models and field observations: Linking processes at the hillslope scale to hydrological responses at the watershed scale. Hydrological Processes 23(2):311–319.

Clow, D.W., and J.I. Drever. 1996. Weathering rates as a function of flow through an alpine soil. Chemical Geology 132:131–141. Clow, D.W., L. Schrott, R.M. Webb, D.H. Campbell, and M.M. Dornblaser. 2003a. Groundwater occurrence and contributions to streamflow in an alpine catchment, Colorado Front Range, USA. Ground Water 41(7):937– 950.

Clow, D.W., J.O. Sickman, R.G. Striegl, D.P. Krabbenhoft, J.G. Elliott, M.M. Dornblaser, D.A. Roth, and D.H. Campbell. 2003b. Changes in the chemistry of lakes and precipitation in high-elevation National Parks in the western United States, 1985–99. Water Resources Research 39(6):1,171.

Doctor, D.H., C. Kendall, S.D. Sebestyen, J.B. Shanley, N. Ohte, and E.W. Boyer. 2008. Carbon isotope fractionation of dissolved inorganic carbon (DIC) due to outgassing of carbon dioxide from a headwater stream. Hydrological Processes 22:2,410–2,423.

Doherty, J., and R.J. Hunt. 2009. Two statistics for evaluating parameter identifiability and error reduction. Journal of Hydrology 366:119–127.

Dong, H., D.R. Peacor, and S.F. Murphy. 1998. TEM study of progressive alteration of igneous biotite to kaolinite throughout a weathered soil profile. Geochimica et Cosmochimica Acta 62:1,881–1,887.

Dunne, T., and R.D. Black. 1970. Partial area contributions to storm runoff in a small New England watershed. Water Resources Research 6:1,296–1,311.

Euliss, N.H., Jr., J.W. LaBaugh, L.H. Fredrickson, D.M. Mushet, K.L. Murray, G.A. Swanson, T.C. Winter, D.O. Rosenberry, and R.D. Nelson. 2004. The wetland continuum: A conceptual framework for interpreting biological studies. Wetlands 24(2):448– 458.

Fienen, M.F., R.J. Hunt, D.P. Krabbenhoft, and T. Clemo. In press. Obtaining parsimonious hydraulic conductivity fields using head and transport observations: A Bayesian geostatistical parameter estimation approach. Water Resources Research.

Fletcher, R.C., H.L. Buss, and S.L. Brantley. 2006. A spheroidal weathering model coupling porewater chemistry to soil thickness during steady-state denudation. Earth and Planetary Science Letters 244(1–2):444–457.

Freer, J., K.J. Beven, and N. Peters. 2002. Multivariate Seasonal and Sub-Period Model Rejection within the Generalised Likelihood Uncertainty Estimation Procedure. In Q. Duan, S. Sorooshian, H. Gupta, A.N. Rousseau, and R. Turcotte, eds., Calibration of Watershed Models, AGU Monograph—Water Science and Applications, v. 6, pp. 69–87. American Geophysical Union.

Freer, J., J. McDonnell, K.J. Beven, D. Brammer, D.A. Burns, R.P. Hooper, and C. Kendall. 1997. Topographic controls on subsurface storm flow at the hillslope-scale for two hydrologically distinct small catchment. Hydrological Processes 11(9):1,347–1,352.

Freer, J., J.J. McDonnell, K.J. Beven, N.E. Peters, D.A. Burns, R.P. Hooper, B.T. Aulenbach, and C. Kendall. 2002. The role of bedrock topography on subsurface storm flow. Water Resources Research 38(12):1,269.

Gellis, A.G., R.M.T. Webb, S. McIntyre, and W.J. Wolfe. 2006. Land-use effects on erosion, sediment yields, and reservoir sedimentation: A case study in the Lago Loiza basin, Puerto Rico. Physical Geography 27:39–69.

Haseltine, S., and K.B. Jones. 2008. National Climate Change and Wildlife Science Center. U.S. Geological Survey fact sheet. [online] URL: <u>http://nccw.usgs.gov/documents/NCCWSC\_factsheet.p</u> df. Accessed 5 June 2009.

Heinz Center. 2008. The State of the Nation's Ecosystems 2008: Measuring the Land, Waters, and Living Resources of The United States. Island Press, Washington DC. [online] URL: http://www.heinzctr.org/ecosystems. Accessed 5 June

<u>nttp://www.heinzetr.org/ecosystems</u>. Accessed 5 June 2009.

Hobbie, J.E., S.R. Carpenter, N.B. Grimm, J.R. Gosz, and T.R. Seastedt. 2003. <u>The US long term ecological</u> research program. Bioscience 53(1):21–32.

Hooper, R.P. 2003. Diagnostic tools for mixing models of stream chemistry. Water Resources Research 39(3):1,055.

Hooper, R.P., B.T. Aulenbach, D.A. Burns, J. McDonnell, J. Freer, C. Kendall, and K. Beven. 1998. Riparian control of streamwater chemistry: Implications for hydrochemical basin models. In K. Kovar, U. Tappeiner, N.E. Peters, and R.G. Craig, eds., Hydrology, Water Resources and Ecology in Headwaters, Proceedings of the Headwater '98 Conference, Merano, Italy, 20–23 April 1998, pp. 451– 458. International Association of Hydrological Sciences Proceeding and Reports 248.

Hooper, R.P., N. Christophersen, and N.E. Peters. 1990. Modelling streamwater chemistry as a mixture of soilwater end members: An application to the Panola Mountain watershed, Georgia, USA. Journal of Hydrology 116:321–343.

Hornbeck, J.W., S.W. Bailey, D.C. Buso, and J.B. Shanley. 1997. Streamwater chemistry and nutrient budgets for forested watersheds in New England: Variability and management implications. Forest Ecology and Management 93:73–89.

Hunt, R.J. 2003. Ground water/lake interaction modeling using the LAK3 Package for MODFLOW2000. Ground Water 41(2):114–118.

Hunt, R.J., M.P. Anderson, and V.A. Kelson. 1998. Improving a complex finite-difference ground water flow model through the use of an analytic element screening model. Ground Water 36(6):1,011–1,017.

Hunt, R.J., and J. Doherty. 2006. A strategy of constructing models to minimize prediction uncertainty. In MODFLOW and More 2006: Managing Ground Water Systems, Proceedings of the 7th International Conference of the International Ground Water Modeling Center, Golden, CO, 21–24 May 2006, pp. 56–60. Colorado School of Mines, International Ground Water Modeling Center.

Hunt, R.J., D.T. Feinstein, C.D. Pint, and M.P. Anderson. 2005. The importance of diverse data types to calibrate a watershed model of the Trout Lake Basin, northern Wisconsin, USA. Journal of Hydrology, 321(1–4):286–296.

Hunt, R.J., H.M. Haitjema, J.T. Krohelski, and D.T. Feinstein. 2003. Simulating ground water-lake interactions: Approaches and insights. Ground Water 41(2):227–237.

Hunt, R.J., D.E. Prudic, J.F. Walker, and M.P. Anderson. 2008. Importance of unsaturated zone flow for simulating recharge in a humid climate. Ground Water 46(4):551–560.

Hunt, R.J., R.M. Strand, and J.F. Walker. 2006. Measuring groundwater-surface water interaction and its effect on wetland stream benthic productivity, Trout Lake watershed, northern Wisconsin, USA. Journal of Hydrology 320:370–384.

Hunt, R.J., J.F. Walker, and J. Doherty. 2008a. Using GSFLOW to simulate climate change in a northern temperate climate. In MODFLOW and More 2008: Ground Water and Public Policy, Proceedings of the 9<sup>th</sup> International Conference of the International Ground Water Modeling Center, Golden, CO, 18–21 May 2008, pp. 109–113. Colorado School of Mines, International Ground Water Modeling Center.

Hunt, R.J., J.F. Walker, and M. Strand. 2008b. Simulating sensitivity to climate change in the Trout Lake Watershed, northern Wisconsin, USA. In Integrating Groundwater Science and Human Well-Being, Proceedings from the IAH 36<sup>th</sup> International Congress, Toyama, Japan, 26 October–1 November 2008, 7 p. International Association of Hydrogeologists.

Hunt, R.J., and D.A. Wilcox. 2003a. Ecohydrology: Why hydrologists should care. Ground Water 41(3):289.

Hunt, R.J., and D.A. Wilcox. 2003b. Response to comment of Ecohydrology: Why hydrologists should care. Ground Water 41(5):562–563.

Huntington, T.G. 1995. Carbon sequestration in an aggrading forest ecosystem. Soil Science Society of America Journal 59:1,459–1,467.

Huntington, T.G. 2000. The potential for calcium depletion in forest ecosystems of southeastern United States: Review and analysis. Global Biogeochemical Cycles 14(2):623–638.

Huntington, T.G., R.P. Hooper, and B.T. Aulenbach. 1994. Hydrologic processes controlling sulfate mobility in a small forested watershed. Water Resources Research 30(2):283–295.

Huntington, T.G., R.P. Hooper, C.E. Johnson, B.T. Aulenbach, R. Cappellato, and A.E. Blum. 2000. Calcium depletion in a southeastern United States forest ecosystem. Soil Science Society of America Journal 64(5):1,845–1,858.

Ingersoll, G.P., M.A. Mast, D.H. Campbell, D.W. Clow, L. Nanus, and J.T. Turk. 2008. Trends in snowpack chemistry and comparison to National Atmospheric Deposition Program results for the Rocky Mountains, US, 1993–2004. Atmospheric Environment 42(24):6,098–6,113.

Joyce, J., and P.W. Jewell. 2003. Physical controls on methane ebullition from reservoirs and lakes. Environmental and Engineering Geoscience 9:167–178.

Kendall, K.A., J.B. Shanley, and J.J. McDonnell. 1999. A hydrometric and geochemical approach to test the transmissivity feedback hypothesis during snowmelt. Journal of Hydrology 219:188–205.

Krabbenhoft, D.P., C.J. Bowser, C. Kendall, and J.R. Gat. 1994. Use of Oxygen-18 and Deuterium To Assess

the Hydrology of Groundwater-Lake Systems. In L.A. Baker, ed., Environmental Chemistry of Lakes and Reservoirs, pp. 67–90. American Chemical Society, Washington DC.

Kurtz, A.C., and L.A. Derry. 2004. Tracing silicate weathering and terrestrial silica cycling with Ge/Si ratios. In R.B. Wanty and R.R.I. Seal, eds., Water–Rock Interaction (WRI-11): Proceedings of the Eleventh International Symposium on Water–Rock Interaction, Saratoga Springs, NY, 27 June–2 July, 2004, pp. 833– 840. Taylor and Francis, London.

Larsen, M.C. 2000. Analysis of 20th century rainfall and streamflow to characterize drought and water resources in Puerto Rico. Physical Geography 21:494– 521.

Larsen, M.C., P.D. Collar, and R.F. Stallard. 1993. Research plan for the investigation of water, energy, and biogeochemical budgets in the Luquillo mountains, Puerto Rico. U.S. Geological Survey Open-File Report 92-150.

Larsen, M.C., and J.E. Parks. 1997. How wide is a road? The association of roads and mass-wasting disturbance in a forested montane environment. Earth Surface Processes and Landforms 22:835–848.

Larsen, M.C., and A. Santiago-Román. 2001. Mass Wasting and Sediment Storage in a Small Montane Watershed: An Extreme Case of Anthropogenic Disturbance in the Humid Tropics. In J.M. Dorava, B.B. Palcsak, F. Fitzpatrick, and D. Montgomery, eds., Geomorphic Processes and Riverine Habitat, AGU Monograph—Water Science and Applications, v. 4, pp. 119–138. American Geophysical Union.

Larsen, M.C., and A. Simon. 1993. A rainfall intensityduration threshold for landslides in a humid-tropical environment, Puerto Rico. Geografiska Annaler 75A:13–23.

Larsen, M.C., and A.J. Torres Sánchez. 1998. <u>The</u> frequency and distribution of recent landslides in three montane tropical regions of Puerto Rico. Geomorphology 24(4):309–331.

Larsen, M.C., A.J. Torres-Sánchez, and I.M. Concepción. 1999. Slopewash, surface runoff, and fine litter transport in forest and landslide scars in humid tropical steeplands, Luquillo Experimental Forest, Puerto Rico. Earth Surface Processes and Landforms 24:481–506. Leavesley, G.H., S.L. Markstrom, R.J. Viger, and L.E. Hay. 2005. USGS Modular Modeling System (MMS)– Precipitation-Runoff Modeling System (PRMS) MMS-PRMS. In V. Singh and D. Frevert, eds., Watershed Models, pp. 159–177. CRC Press, Boca Raton, FL.

Lovett, G.M., D.A. Burns, C.T. Driscoll, J.C. Jenkins, M.J. Mitchell, L. Rustad, J.B. Shanley, G.E. Likens, and R. Haeuber. 2007. Who needs environmental monitoring?. Frontiers in Ecology and the Environment 5(5):253–260.

Lowry, C.S., J.F. Walker, R.J. Hunt, and M.P. Anderson. 2007. Identifying spatial variability of groundwater discharge in a wetland stream using a distributed temperature sensor. Water Resources Research 43: W10408. [online] URL: <u>http://www.agu.org/pubs/crossref/2007/2007WR00614</u> <u>5.shtml</u>. Accessed 5 June 2009.

Lugo, A.E., F.J. Swanson, O. Ramos Gonzalez, M.B. Adams, B. Palik, R.E. Thill, D.G. Brockway, C. Kern, R. Woodsmith, and R. Musselman. 2006. <u>Long-term</u> research at the USDA Forest Service's Experimental <u>Forests and Ranges</u>. Bioscience 56(1):39–48.

Markstrom, S.L., R.G. Niswonger, R.S. Regan, D.E. Prudic, and P.M. Barlow. 2008. <u>GSFLOW—Coupled</u> ground-water and surface-water flow model based on the integration of the Precipitation-Runoff Modeling System (PRMS) and the Modular Ground-Water Flow <u>Model (MODFLOW-2005)</u>. U.S. Geological Survey Techniques and Methods 6-D1.

Mast, M.A., K.P. Wickland, R.G. Striegl, and D.W. Clow. 1998. Winter fluxes of  $CO_2$  and  $CH_4$  from subalpine soils in Rocky Mountain National Park, Colorado. Global Biogeochemical Cycles 12(4):607–620.

McDonnell, J., J. Freer, R. Hooper, C. Kendall, D. Burns, K. Beven, and J. Peters. 1996. New method developed for studying flow on hillslopes. EOS, Transactions American Geophysical Union 77(47):465–472.

McGlynn, B.L., J.J. McDonnell, J.B. Shanley, and C. Kendall. 1999. Riparian zone flowpath dynamics during snowmelt in a small headwater catchment. Journal of Hydrology 222:75–92.

Millennium Ecosystem Assessment. 2005. <u>Ecosystems</u> and <u>Human Well-Being: Synthesis</u>. Island Press, Washington DC. Moran, M.S., D.P.C. Peters, M.P McClaran, M.H. Nichols, and M.B. Adams. 2008. Long-term data collection at USDA experimental sites for studies of ecohydrology. Ecohydrology 1:377–393.

Murphy, S.F., S.L. Brantley, A.E. Blum, A.F. White, and H. Dong. 1998. Chemical weathering in a tropical watershed, Luquillo Mountains, Puerto Rico: II. Rate and mechanism of biotite weathering. Geochimica et Cosmochimica Acta 62:227–243.

Peters, N.E. 1989. Atmospheric Deposition of Sulfur to a Granite Outcrop in the Piedmont of Georgia, U.S.A. In D.J. Delleur, ed., Atmospheric Deposition, pp. 173– 181. International Association of Hydrological Sciences, no. 179.

Peters, N.E. 1994. Water-quality variations in a forested piedmont catchment, Georgia, USA. Journal of Hydrology 156:73–90.

Peters, N.E., J. Freer, and B.T. Aulenbach. 2003a. Hydrologic dynamics of the Panola Mountain Research Watershed, Georgia, USA. Ground Water 41(7):973– 988.

Peters, N.E., J. Freer, and K.J. Beven. 2003b. Modeling hydrologic responses in a small forested catchment (Panola Mountain, Georgia, USA): A comparison of the original and a new dynamic TOPMODEL. Hydrological Processes 17(2):345–362.

Peters, N.E., T.P. Meyers, and B.T. Aulenbach. 2002. Status and trends in atmospheric deposition and emissions near Atlanta, Georgia, 1986–99. Atmospheric Environment 13(10):1,577–1,588.

Peters, N.E., and E.B. Ratcliffe. 1998. Tracing hydrologic pathways using chloride at the Panola Mountain Research Watershed, Georgia, USA. Water, Air and Soil Pollution 105(1/2):263–275.

Peters, N.E., E.B. Ratcliffe, and M. Tranter. 1998. Tracing Solute Mobility at the Panola Mountain Research Watershed, Georgia, USA: Variations in Na<sup>+</sup>, Cl<sup>-</sup>, and H<sub>4</sub>SiO<sub>4</sub> Concentrations. In K. Kovar, U. Tappeiner, N.E. Peters, and R.G. Craig, eds., Hydrology, Water Resources and Ecology in Headwaters, pp. 483–490. International Association of Hydrological Sciences, no. 248.

Peters N.E., J.B. Shanley, B.T. Aulenbach, R.M. Webb, D.H. Campbell, R. Hunt, M.C. Larsen, R.F. Stallard, J. Troester, and J.F. Walker. 2006. <u>Water and solute mass</u> <u>balance of five small</u>, relatively undisturbed watersheds in the U.S. Science of the Total Environment 358(1–3):221–242.

Pint, C.D., R.J. Hunt, and M.P. Anderson. 2003. Flow path delineation and ground water age, Allequash Basin, Wisconsin. Ground Water 41(7):895–902.

Scatena, F.N., and M.C. Larsen. 1991. Physical aspects of Hurricane Hugo in Puerto Rico. Biotropica 23(4A):317–323.

Schindler, J.E., and D.P. Krabbenhoft. 1998. The hyporheic zone as a source of dissolved organic carbon and carbon gases to a temperate forested stream. Biogeochemistry 43:157–174.

Scholl, M.A., W. Eugster, and R. Burkard. In press. Understanding the Role of Fog in Forest Hydrology: Stable Isotopes as Tools for Determining Input and Partitioning of Cloud Water in Montane Forests. In L.A. Bruijnzeel, F.N. Scatena, and L.S. Hamilton, eds., Mountains in the Mist: Science for Conserving and Managing Tropical Montane Cloud Forests. Cambridge University Press, Cambridge.

Schulz, M.S., and A.F. White. 1999. Chemical weathering in a tropical watershed, Luquillo Mountains, Puerto Rico: III. Quartz dissolution rates. Geochimica et Cosmochimica Acta 63:337–350.

Schuster, P.F., M.M. Reddy, G.R. Aiken, and J.B. Shanley. 2004. What effect does permafrost have on dissolved organic carbon transport to streams during snowmelt. In R.B. Wanty, and R.R. Seal, eds., Water– Rock Interaction (WRI-11), v. 2: Proceedings of the Eleventh International Symposium on Water–Rock Interaction, Saratoga Springs, NY, 27 June–2 July 2004, pp. 1,385–1,389. Taylor and Francis, London.

Schuster, P.F., J.B. Shanley, M. Marvin-Dipasquale, M.M. Reddy, G.R. Aiken, D.A. Roth, H.E. Taylor, D.P. Krabbenhoft, and J.F. DeWild. 2008. Mercury and organic carbon dynamics during runoff episodes from a northeastern USA watershed. Water, Air, and Soil Pollution 187:89–108.

Sebestyen, S.D., E.W. Boyer, J.B. Shanley, C. Kendall, D.H. Doctor, G.R. Aiken, and N. Ohte. 2008. Sources, transformations, and hydrological processes that control stream nitrate and dissolved organic matter concentrations during snowmelt in an upland forest. Water Resources Research 44:W12410.

Shanley, J.B. 1992. Sulfur retention and release in soils at Panola Mountain, Georgia. Soil Science 153(6):499–508.

Shanley, J.B., K.N. Hjerdt, J.J. McDonnell, and C. Kendall. 2003. Shallow water table fluctuations in relation to soil penetration resistance. Ground Water 41:964–972.

Shanley, J.B., C. Kendall, T.E. Smith, D.M. Wolock, and J.J. McDonnell. 2002. Controls on old and new water contributions to stream flow at some nested catchments in Vermont, USA. Hydrological Processes 16:589–609.

Shanley, J.B., P. Krám, J. Hruska, and T.D. Bullen. 2004. <u>A biogeochemical comparison of two wellbuffered catchments with contrasting histories of acid</u> <u>deposition</u>. Water, Air, and Soil Pollution: Focus 4:325–342.

Shanley, J.B., and N.E. Peters. 1993. Variations in aqueous sulfate concentrations at Panola Mountain, Georgia. Journal of Hydrology 146:361–382.

Shanley, J.B., A. Mast, D.H. Campbell, G.R. Aiken, D.P. Krabbenhoft, R.J. Hunt, J.F. Walker, P.F. Schuster, A. Chalmers, B.T. Aulenbach, N.E. Peters, M. Marvin-DiPasquale, D.W. Clow, and M.M. Shafer. 2008. Comparison of total mercury and methylmercury cycling at five sites using the small watershed approach. Environmental Pollution 154(1):143–154.

Shanley, J.B., B. Mayer, M.J. Mitchell, and S.W. Bailey. 2008. Seasonal and event variations in  $\delta^{34}$ S values of stream sulfate in a Vermont forested catchment: Implications for sulfur sources and cycling. Science of the Total Environment 404:262–268.

Shanley, J.B., B. Mayer, M.J. Mitchell, R.L. Michel, S.W. Bailey, and C. Kendall. 2005. Tracing sources of streamwater sulfate during snowmelt using S and O isotope ratios of sulfate and 35S activity. Biogeochemistry 76:161–185.

Stallard, R.F. 2001. Possible environmental factors underlying amphibian decline in eastern Puerto Rico: Analysis of U.S. Government data archives. Conservation Biology 15(4):943–953.

Tromp-van Meerveld, H.J., and J.J. McDonnell. 2006a. Threshold relations in subsurface stormflow: 1. A 147storm analysis of the Panola hillslope. Water Resources Research 42:W02410.

Tromp-van Meerveld, H.J., and J.J. McDonnell. 2006b. Threshold relations in subsurface stormflow: 2. The fill and spill hypothesis. Water Resources Research 42:W02411. Tromp-van Meerveld, H.J., and J.J. McDonnell. 2006c. On the interrelations between topography, soil depth, soil moisture, transpiration rates and species distribution at the hillslope scale. Advances in Water Resources 29:293–310.

Tromp-van Meerveld, H.J., N.E. Peters, J.J. McDonnell. 2007. <u>Effect of bedrock permeability on</u> <u>subsurface stormflow and the water balance of a</u> <u>trenched hillslope at the Panola Mountain Research</u> <u>Watershed, Georgia, USA</u>. Hydrological Processes 21(6):750–769.

Turner, B.F., R.F. Stallard, and S.L. Brantley. 2003. Investigation of in situ weathering of quartz diorite bedrock in the Río Icacos basin, Luquillo Experimental Forest, Puerto Rico. Chemical Geology 202:313–341.

Walker, J.F., R.J. Hunt, T.D. Bullen, D.P. Krabbenhoft, and C. Kendall. 2003. Spatial and temporal variability of isotope and major ion chemistry in the Allequash Creek basin, northern Wisconsin. Ground Water 41(7):883–894.

Walker, J.F., and D.P. Krabbenhoft. 1998. Groundwater and Surface-Water Interactions in Riparian and Lake-Dominated Systems. In J.J. McDonnell, and C. Kendall, eds., Isotope Tracers in Catchment Hydrology, pp. 467– 488. Elsevier, Amsterdam, The Netherlands.

Walker, J.F., D.A. Saad, and R.J. Hunt. 2007. Dynamics of CFCs in northern temperate lakes and adjacent groundwater. Water Resources Research 43:W04423.

Webb, R.M.T., J.I. Linard, and M.E. Wieczorek. 2006. <u>The Water, Energy, and Biogeochemical Model</u> (WEBMOD): A TOPMODEL application developed within the modular modeling system. In Proceedings of the 3rd Federal Interagency Hydrologic Modeling Conference, Reno, NV, 2–6 April 2006. Advisory Committee on Water Information, Subcommittee on Hydrology.

Webb, R.M.T., N.J. Peters, B.T. Aulenbach, and J.B.
Shanley. 2003. <u>Relations between hydrology and solute</u> fluxes at the five water, energy, and biogeochemical budget (WEBB) watersheds of the United States
<u>Geological Survey</u>. In K.G. Renard, S.A. McElroy, W.J.
Gburek, H.E. Canfield, and R.L. Scott, eds.,
Proceedings of the First Interagency Conference on Research in the Watersheds, Benson, AZ, 27–30
October 2003, pp. 332–339. U.S. Department of Agriculture, Agricultural Research Service. White, A.F., and A.E. Blum. 1995a. Effects of climate on chemical weathering in watersheds. Geochimica et Cosmochimica Acta 59:1,729–1,747.

White, A.F., and A.E. Blum. 1995b. Climatic Effects on Chemical Weathering in Watersheds: Applications of Mass Balance Approaches. In S.T. Trudgill, ed., Solute Modeling in Catchment Systems, pp. 101–131. John Wiley and Sons, New York.

White, A.F., A.E. Blum, T.D. Bullen, D.V. Vivit, M.S. Schulz, and J. Fitzpatrick. 1999. The effect of temperature on experimental and natural weathering of granitoid rocks. Geochimica et Cosmochimica Acta 63:3,277–3,291.

White, A.F., A.E. Blum, M.S. Schulz, D.V. Vivit, M. Larsen, and S.F. Murphy. 1998. Chemical weathering in a tropical watershed, Luquillo Mountains, Puerto Rico: I. Long-term versus short-term weathering fluxes. Geochimica et Cosmochimica Acta 62:209–226.

Wickland, K.P., R.G. Striegl, M.A. Mast, and D.W. Clow. 2001. Carbon gas exchange at a southern Rocky Mountain wetland, 1996–1998. Global Biogeochemical Cycles 15(2):321–335.

Winter, T.C. 2004. The aquatic systems continuum. American Geophysical Union, Fall Meeting 2004, abstract #H31F-01.

Zack, A., and M.C. Larsen. 1994. Island hydrology: Puerto Rico and the U.S. Virgin Islands. National Geographic Research and Exploration Water Issue, pp. 126–134.