Biogeochemistry (2013) 116:175–186
DOI 10.1007/s10533-013-9916-3

Interactions between lithology and biology drive the long-term response of stream chemistry to major hurricanes in a tropical landscape

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Received: 2 August 2012 / Accepted: 25 September 2013 / Published online: 17 October 2013

Abstract Humid tropical forests play a dominant role in many global biogeochemical cycles, yet long-term records of tropical stream chemistry and its response to disturbance events such as severe storms and droughts are rare. Here we document the long-term variability in chemistry of two streams in the Luquillo Mountains, Puerto Rico over a period of 27 years. Our two focal study watersheds, the Río Icacos and Quebrada Sonadora, both drain several hundred hectares of tropical wet forests, and each received direct hits from Hurricanes Hugo (1989) and Georges (1998). They differ primarily in lithology (granitic vs. volcaniclastic) and elevation. Changes in major cations, anions, silica, and dissolved organic carbon were minimal over the study period, but the concentrations of nitrate show a strong response to hurricane disturbance and the longest time to recovery. Potassium also showed a large, although less consistent, response to disturbance. In the granitic terrain, nitrate concentrations exceeded long-term pre-hurricane background levels for over a decade, but were elevated in the volcaniclastic terrain for only 1–2 years. Lithology appears to be the primary driver explaining the different response trajectories of the two watersheds. In the granitic terrain, which showed slow recovery to pre-hurricane conditions, the quartz diorite bedrock weathers to produce coarser soils, deeper groundwater flow paths, and riparian zones with sharp spatial variation in redox conditions and very high nitrogen levels immediately adjacent to the stream. Groundwater flow paths are shallow and the levels of N in streamside groundwater are much lower in the volcaniclastic terrain. The recovery of vegetation following hurricane disturbance appears similar in the two watersheds, suggesting that the extent of structural damage to canopy trees determines the

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Responsible Editor: Melanie A. Vile

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magnitude of NO_3 increases, but that the duration of elevated concentrations in stream water is a function of lithology.

Keywords Watershed · Hurricane · Disturbance · Tropics · Nitrate · Potassium · Riparian zone · Stream chemistry

Introduction

Tropical biomes play a disproportionately large role in the global cycling of carbon and nutrients (Lal et al. 2000; Schlesinger and Bernhardt 2013), and rivers of the humid tropics are important contributors of material to the global ocean (Stallard and Edmond 1983; Gaillardet et al. 1999). In the humid tropics, small mountainous coastal rivers can be particularly important, as they deliver materials from rapidly weathering landscapes to the ocean with minimal residence time in coastal floodplains (e.g. Lyons et al. 2002). Small, steep islands are common in the Caribbean, and thus understanding the drivers of temporal and spatial variability in their chemistry has important regional ramifications.

In much of the world, high-energy tropical storms such as hurricanes and typhoons can alter forest structure and productivity for decades (Scatena et al. 1996; Lugo 2008). The effects of this forest alteration on nutrient availability in soils and streams are typically short-lived (several years), because rapid regrowth of vegetation results in rates of nutrient uptake sufficient to return chemistry to pre-disturbance conditions (e.g. Herbert et al. 1999; Schaefer et al. 2000; McDowell 2011). Similar disturbance-response relationships that link stream chemistry to watershed conditions have been studied for decades in temperate forests, using both observations and experimental manipulations. At the Hubbard Brook Experimental Forest (New Hampshire, USA), for example, the response of stream chemistry to both manipulative experiments (forest felling) and natural disturbances (an ice storm) has shown that recovery to pre-disturbance conditions takes only a year or two in these nitrogen-limited forests (Houlton et al. 2003). The extent to which this well-documented disturbance-response relationship in temperate forests is applicable to tropical forests is unclear, due to the fundamental differences in nutrient limitation and nitrogen cycling that appear to characterize the two biomes (Matson et al. 1999; Cleveland et al. 1999). Short-term increases in stream nitrate during typhoons (e.g. Zhang et al. 2007; Tsai et al. 2009) and up to one year after a hurricane (Schaefer et al. 2000) have been shown, but long-term studies that document the entire trajectory of stream chemistry following disturbance are lacking in the literature on tropical forest nitrogen (N) cycling.

The response of stream chemistry to hurricane disturbance is likely to be regulated in part by riparian processes that control the flux of N from groundwater to the stream channel. Riparian zones have long been recognized as potential biogeochemical hotspots for N removal through denitrification, owing to high water tables, anoxic conditions, and the convergence of hydrologic flow paths that bring reactants (DOC and NO_3) together (Peterjohn and Correll 1984; McClain et al. 2003). Following hurricane disturbance, groundwater N concentrations can increase greatly due to the decomposition of large amounts of litter and leaching from upper soil layers. Different riparian zones are variably effective in the amount of groundwater N removal, depending on flow paths, redox conditions, the concentrations of NO_3 and DOC, and residence time. Of these factors, redox conditions and NO_3 levels have been shown to vary greatly between the two lithologies in the Luquillo Mountains (McDowell et al. 1992).

Because many natural disturbances are not easily replicated in whole-system experiments, long-term observations provide the only feasible approach to quantifying ecosystem responses to infrequent but severe events that can have effects lasting for years to decades. Although such long-term observations provide the power to discern true long-term responses, disentangling the multiple strands of cause and effect that may be driving the whole-watershed response to disturbance is challenging due to inherent variability among watersheds and the lack of true replication. In this paper, we describe the response of two well-studied tropical watersheds to multiple hurricane disturbances, examining the potential effects of lithology and forest recovery on stream water chemistry.

Study area

Both study watersheds are located in the Luquillo Experimental Forest (LEF) of northeastern Puerto Rico, which is known locally as the El Yunque

National Forest (previously the Caribbean National Forest) (Fig. 1). As an NSF-funded LTER and CZO site, as well as a USGS WEBB site, considerable data describing the biota, geology, and disturbance regime of the Luquillo Mountains are available (Brokaw et al. 2012; Murphy and Stallard 2012). The mountain massif is of volcanic origin, and lacks the carbonate minerals that are found in some other parts of Puerto Rico (Seiders 1971). Quebrada Sonadora, a major headwater of the Río Espíritu Santo, drains north into the Atlantic Ocean and is underlain by volcaniclastic materials (USGS gaging station 50063400; Fig. 1). Bedrock is largely andesitic to basaltic sandstone, siltstone and mudstone, which weathers to dense clays and soils classified as Ultisols (Boccheciamp 1977). Valley forms are steep, channels are filled with boulders that are relatively stable over decadal time scales, and stream gradient is high (24 %) (McDowell and Asbury 1994; Pike et al. 2010). A second important study site on volcaniclastic terrain is the Bisley Experimental Watersheds, where shallow wells were installed in 1988 7 km E of the Sonadora watershed (McDowell et al. 1992). We use Quebrada Sonadora stream chemistry and the Bisley well fields to characterize the biogeochemistry of volcaniclastic terrain. The Río Icacos, a major headwater of the Río Blanco, drains south into the Caribbean Sea and is underlain by quartz diorite that weathers to clays and sandy clays (Inceptisols; Boccheciamp 1977). The main stem of the Río Icacos is choked with sand, and contains some riffles with pebbles and protruding boulders as well as large areas of sand in which pools are scoured and filled frequently by high flow events. The basin above the USGS station (USGS 5007500) is relatively flat for over a km, although the flanks of the watershed are steep; the overall average grade is 1.4 % in the main stem (McDowell and Asbury 1994). The Icacos is the fastest weathering siliceous terrain in the world (White and Blum 1995), based on initial work on stream solute and suspended sediment export by McDowell and Asbury (1994) and studies of clay mineralogy and soil depth (White et al.1998).

Hydrologic characteristics differ in watersheds on the two bedrock types. Flow duration curves are distinctly truncated at low flow in the diorite lithology; extreme high flows occur with similar frequency in the volcaniclastic and quartz diorite terrain, but extreme low flows (lowest 0.5 % of flow duration) are ten times higher on a unit area basis (0.3 vs. 0.03 l/ha/s) in the Icacos than in the Sonadora (McDowell and Asbury 1994). Depth to groundwater, response to storms, and persistence of groundwater along riparian flow paths also differ dramatically as a result of the differences in lithology and soils, with very shallow interflow (20–40 cm) occurring through cracks and macropores characteristic of the volcaniclastic terrain (McDowell et al. 1992; Schellekens et al. 2004). Surface soils in the Icacos riparian zone have almost double the sand content of those on the volcaniclastic terrain (Table 1). At depth, soils of the Icacos are characterized by saprolite at the upslope edge of the riparian zone, and by very sandy soils (64 % sand) in soils 1 m from the stream channel. Deep flow paths (water tables at 1–2 m), and wider riparian zones with more extensive occurrence of shallow riparian groundwater are also found in the Icacos (McDowell et al. 1992). There is strong spatial zonation in redox in the Icacos

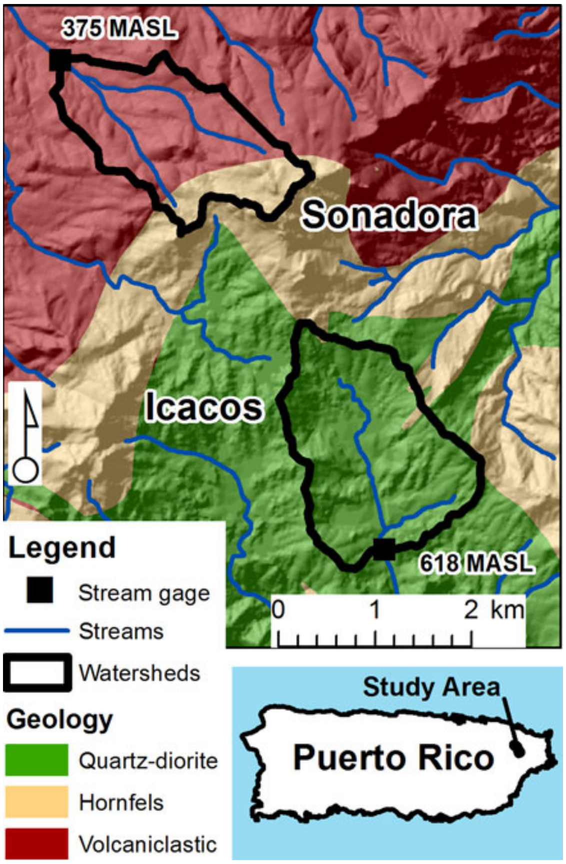

Fig. 1 Map of the study area in eastern Puerto Rico. The two study watersheds, Quebrada Sonadora and Río Icacos, are highlighted. Major lithologic units are shown (modified from Murphy and Stallard 2012)

well field, with oxic groundwater that is dominated by nitrate in upslope wells, and anoxic water in streamside wells with very high NH_4 and low NO_3 concentrations (McDowell et al. 1992). Although removal of N along the combined groundwater-hyporheic flow path is known to be quantitatively significant in reducing N concentrations in tributary streams of the Río Icacos (Chestnut and McDowell 2000), time series data of groundwater chemistry are available only for groundwater wells that are not influenced by hyporheic processes.

Past work in the Luquillo Mountains following Hurricane Hugo (September 1989) shows that across multiple watersheds on volcaniclastic terrain, nitrate had the largest and most consistent response to the hurricane, with a sharp peak in stream nitrate concentrations within 6 months, and a return to baseline concentrations and fluxes in about 1.5 years (Schaefer et al. 2000). Responses were similar for all the watersheds studied, including the Sonadora and Bisley watersheds. An additional major hurricane, hurricane Georges, hit the island of Puerto Rico in 1998, and had significant effects on the forest canopy as well as human infrastructure (Ayala-Silva and Twumasi 2004; Brokaw et al. 2012).

Table 1 Watershed and riparian zone characteristics in the two bedrock types, quartz diorite (Rio Icacos) and volcaniclastic (Quebarada Sonadora and the Bisley watershed well field)

Site characteristic	Watershed and bedrock type	
	Icacos (intrusive; quartz diorite)	Sonadora (volcaniclastic)
Lat., long. (NAD 27)	18°16′38″, 65°47′09″	18°19′24″, 65°49′03″
Elevation	618–846	375–1050
Watershed area (ha)	326	262
Average flow (m^3/s)	0.39	0.21
Vegetation (forest type)		
% Tabonuco	0	6
% Colorado	75	57
% Palm	24	25
% Elfin	1	12
Riparian Soils (0–10 cm)		
% sand	20	11
% silt	43	37
% clay	37	51
Depth to riparian groundwater (cm)	60–150	20–30

Data on watershed characteristics (elevation, runoff, vegetation) from McDowell and Asbury (1994); riparian zone characteristics from McDowell et al. (1992). Flow from annual USGS averages for 1983–2011

Materials and methods

For Quebrada Sonadora, samples were collected weekly from June 1983 to December 2011, with additional samples taken periodically during high flow events. Earlier publications include detailed descriptions of stream chemistry during the periods 1983–1987 (McDowell and Asbury 1994), and 1983–1994 (Schaefer et al. 2000). For Río Icacos, weekly sampling occurred from June 1983 to October 1987 (McDowell and Asbury 1994), which was followed by a period of intensive sampling of high flow events (1991–1997), and the resumption of weekly sampling in January 2000 (Shanley et al. 2011). Data reported here include an additional three years of sampling on the Icacos, 2009–2011, which were not included in Shanley et al. (2011). Shallow groundwater wells 1–2 m from the stream channel were sampled periodically as described in McDowell et al. (1992, 1996) and analyzed with the same methods as stream samples. For this study we report new data from well I-25, originally installed in October 1989 in a riparian zone strongly affected by Hurricane Hugo, which snapped the boles of many canopy trees above the well field (McDowell et al. 1996).

Samples were collected in the field, aliquots analyzed for pH and specific conductance, and filtered through a pre-combusted Whatman GF/F glass fiber filter (0.7 µm, combusted at 425 °C for 4 h) prior to analysis. Samples were held refrigerated prior to analysis through 1997 and analyzed within several weeks of collection. After 1997, samples were held frozen until analysis, with a refrigerated aliquot used for silica analysis.

Water samples were analyzed for SiO_2 and NH_4 by automated colorimetry (Technicon AA II, Lachat Quikchem AE, or Westco SmartChem). Major cations (Na, K, Ca, and Mg) were analyzed by atomic absorption spectrophotometry, ICP OES, or ion chromatography; major anions (Cl, NO_3, and SO_4) were analyzed by ion chromatography. Dissolved organic carbon was analyzed by manual wet oxidation (McDowell et al. 1987), automated persulfate

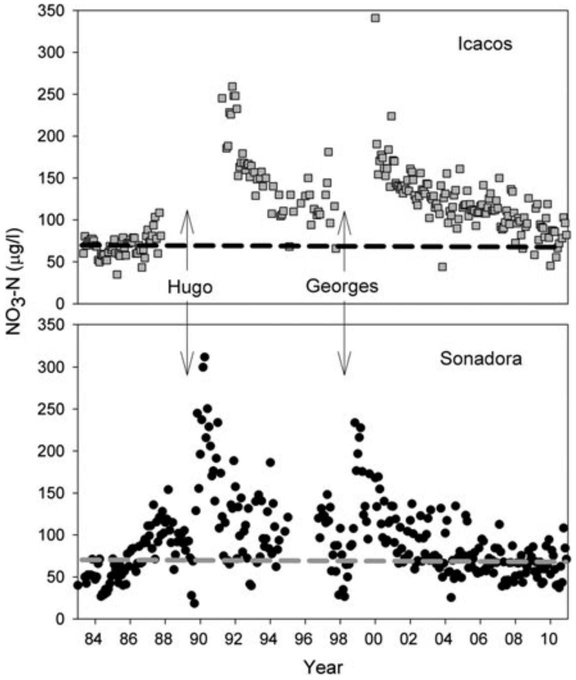

Fig. 2 Monthly average concentrations (µg/l) of stream water nitrate (as NO_3–N) from 1983 to 2011. *Upper panel* is the Río Icacos, and the *lower panel* is Quebrada Sonadora

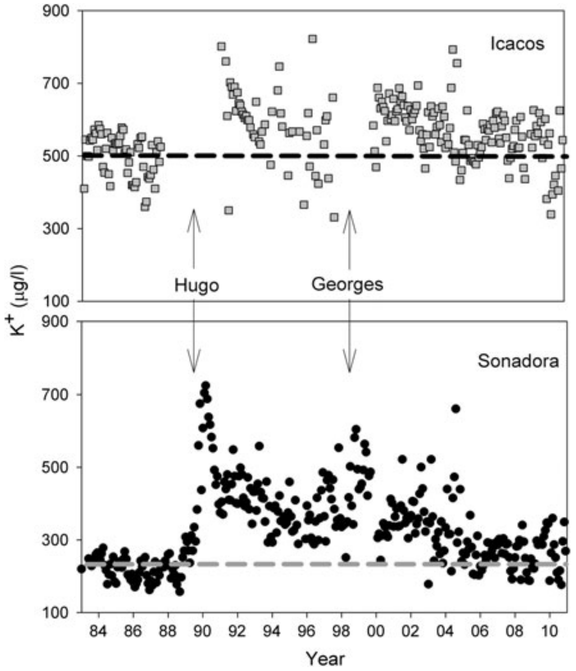

Fig. 3 Monthly average concentrations (µg/l) of stream water K^+ from 1983 to 2011. *Upper panel* is the Río Icacos, and the *lower panel* is Quebrada Sonadora

oxidation, or by high-temperature combustion (Shimadzu 5050 or Shimadzu TOC V). Details of analytical techniques used in different periods of the record and detection limits are described in McDowell and Asbury (1994), Schaefer et al. (2000), Shanley et al. (2011), and Murphy and Stallard (2012). Analytical techniques used for Icacos samples from 2000 to 2008 (Shanley et al. 2011) were continued for the most recent Icacos samples (2009–2011). Methods used for the Sonadora from 1997 to 2011 include ion chromatography for major cations, anions, and NO_3, colorimetric analysis of NH_4 and SiO_2, and high-temperature combustion for DOC and TDN. These methods are identical to those used for weekly samples on the Icacos after 2000.

Results

We assessed changes in stream chemistry following hurricane disturbance using two primary approaches. First, we examined changes in monthly average solute concentrations over time (Fig. 2), which showed that in both Icacos and Sonadora, NO_3 and K concentrations increased from long-term background levels following Hurricanes Hugo and Georges. Concentrations of both solutes then gradually returned to levels at or near background values within several years (Sonadora NO_3 and K, Icacos K). The temporal patterns in stream chemistry in the two watersheds were similar, with sharp increases in NO_3 following each of the two major hurricanes and similar changes in K (Figs. 2 and 3). No other solutes in either stream showed similar patterns over time. In contrast to the Sonadora, NO_3 levels in the Icacos took a decade or more to return to background levels following Hurricane Georges in 1998, but showed a very strong and consistent decline during this recovery period (Fig. 2).

Our second approach was to examine the average concentration of solutes in a period prior to major hurricanes (1983–1988), and compare that to post-hurricane values. Our summary of pre- and post-hurricane chemistry (Table 1) showed long-term (multi-year) effects of hurricanes on NO_3 and K in the Sonadora. Typically, for solutes other than NO_3 and K, concentrations varied by no more than 20–30 % when comparing pre-hurricane years to post-hurricane values in the Sonadora, with both increases and decreases observed (Table 1). Similar explicit comparisons were more difficult in the Icacos, due to a lack of data immediately before and after both large hurricanes. Comparison of weekly samples on Icacos prior to Hugo (1983–1987), and 18 months of weekly samples starting in late January 2000 (which represents a period of ~1.5–3 years after Hurricane Georges), shows large increases in NO_3 only (Table 2). No change was observed in concentration-flow relationships for solutes in Quebrada Sonadora or Río Icacos before and after hurricanes. Although many solutes in both watersheds showed a strong response to stream flow, the two solutes with the largest long-term response to hurricane disturbance, NO_3 and K (Figs. 2 and 3), were relatively insensitive to changes in stream flow and instead responded only to the longer-term effects of hurricane disturbance.

Within 2 months following Hurricane Hugo, groundwater NO_3–N concentrations in streamside well 2 of the Bisley well field increased from a baseline of 0.1 mg/l to a peak of 0.8 mg/l, then recovered to pre-Hugo levels in less than 2 years (Fig. 4); DON and TDN concentrations also showed similar peaks and rapid recoveries following hurricane disturbance across the study period. In contrast, concentrations of NH_4–N (the dominant form of N in streamside wells in the Icacos) were elevated to over 1.0 mg/l for two decades, similar to the time course of changes in stream nitrate (Fig. 5).

Table 2 Average concentrations (mg/l) of solutes in weekly samples collected from Quebrada Sonadora (volcaniclastic terrain) before Hurricane Hugo (1983–1989) and the first 1.5 years following Hugo (1989–1991)

Solute	Sonadora		Icacos	
	Pre-hurricane	Post-hurricane	Pre-hurricane	Post-hurricane
NO_3–N	0.072	0.20	0.069	0.189
K	0.23	0.55	0.51	0.60
Na	4.40	4.67	5.07	5.70
Ca	2.19	2.47	3.33	3.52
Mg	1.36	1.53	1.20	1.24
SiO_2	10.2	9.33	18.3	20.7
SO_4	2.37	2.31	2.28	1.35
Cl	6.96	8.89	6.24	6.33
DOC	2.05	2.84	1.58	1.10

For comparison, we include weekly samples (1983–1987) from Rio Icacos before Hurricane Hugo, and 1.5–3.0 years after Hurricane Georges (2000–2001). Weekly samples directly before and directly after hurricanes are not available for Icacos. All concentrations mg/l

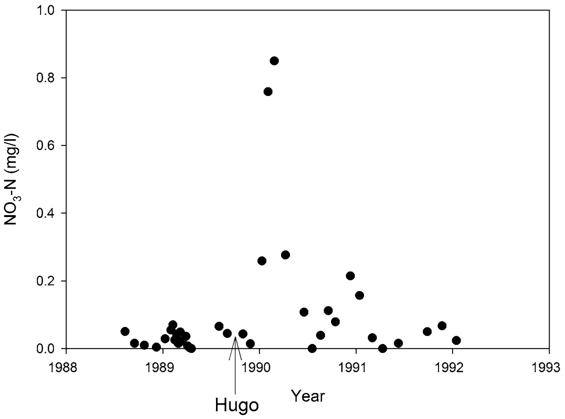

Fig. 4 Changes in concentration of NO_3 (the dominant form of N at this location) over time in riparian groundwater 2 m from Bisley stream, on volcaniclastic terrain (well B-2, redrawn from McDowell et al. 1996)

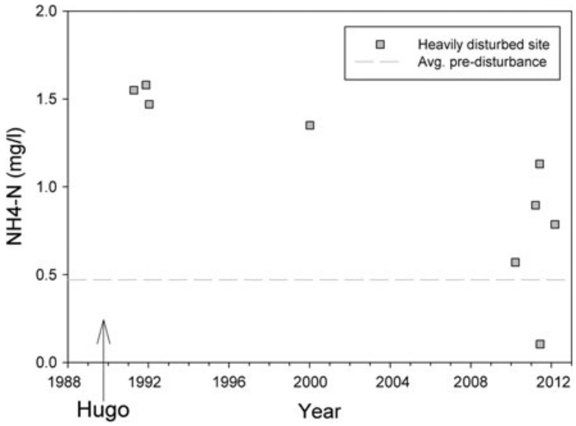

Fig. 5 Changes in concentration of NH_4 (the dominant form of N at this location) over time in riparian groundwater 1 m from an unnamed Icacos tributary, on quartz diorite terrain (well I-25; background pre-hurricane concentrations for streamside wells were originally reported in McDowell et al. (1996))

Discussion

Inferring causal drivers from long-term observations must always be done with caution, but multiple lines of evidence suggest that biota and lithology interact to drive the stream water response to disturbance that we have documented in our two long-term study watersheds. It is useful to differentiate between the response of ecosystem structure (e.g. condition of watershed vegetation) and overall ecosystem function, which is captured by the changes we have observed in stream chemistry over time. Because past work at the site shows that below-ground riparian structure and function differ with lithology in this landscape (McDowell et al. 1992), we assessed the working hypothesis that the long-term response of stream chemistry to disturbance is related to both vegetation dynamics following disturbance, as well as differences in riparian zone processes.

Differences in the trajectories of N, K, and other solutes in response to disturbance provide useful insight into the potential drivers of stream chemistry over the 27 years of sampling reported here. In an earlier paper, McDowell and Asbury (1994) observed that stream solutes fell into three classes based on their response to stream discharge. They proposed that the three classes of solutes represented elements under geochemical control (base cations and silica, which dilute at high flow), biotic control (N and K, which show no dependence on flow), and flow path control (DOC, which increases at high flow as water moves higher in the soil profile). Our long-term results support this earlier grouping of stream solutes. Both N and K showed sharp increases in concentration that persisted for months or more after major hurricanes had passed over the study sites, providing strong support for the suggestion that N and K are controlled by biotic processes in the watershed that were dramatically altered by hurricanes. In contrast, solutes thought to be under geochemical control did not show appreciable change in concentration following hurricanes (Table 1), nor did the concentration-discharge relationships change over the decades of this study (Shanley et al. 2011). The conundrum that remains is how to explain the long lag time in N but not K in the Río Icacos, given the synchrony between N and K response that was observed in the Sonadora. Increases in concentrations of both N and K in stream water are almost certainly the result of disruption of biotic processes such as uptake of nutrients by vegetation and decomposition of litter, as originally suggested by McDowell and Asbury (1994). This conclusion is supported by the fact that very large storm events that generate high runoff, but do so without the high winds that damage vegetation, are not followed by increases in NO_3 and K levels. As an example, the frontal storm of 17 April 2003, which produced the largest runoff in the Icacos from 1991 to 2004 (Murphy and Stallard 2012), had no discernible effect on the long-term trajectory of either K or NO_3 concentrations (Figs. 2 and 3).

Analysis of the internal cycling of various elements in the forest shows that N and K are distinctive in their biogeochemical cycles, and coupled in several ways to biotic structure in the forest. First, vegetation is the dominant (K) or an important (N) pool of these elements in the ecosystem; for the elements under geochemical control (e.g. Si, Ca and Mg), vegetation represents a very minor pool of these elements relative to what is available in the soils (McDowell 1998). Second, both N and K are actively cycled internally by biotic processes, with significant quantities of K released from leaves into throughfall and large amounts of N and K transferred from the forest canopy to the forest floor with litterfall and litter decomposition (McDowell 1998). The major differences between N and K cycling, however, are that K transport through watersheds is not subject to significant redox-sensitive reactions (in particular denitrification) that can result in its gaseous loss from the ecosystem, and that K is also very readily leached from vegetation (Tukey 1970), with very little K found in plant structural materials. Hurricanes disrupt N and K cycling by stripping leaves from trees, breaking limbs, snapping boles, and tipping up whole trees (Lugo 2008). Plant uptake of essential elements is reduced until foliar biomass is replaced and primary productivity reaches pre-disturbance levels; leaching and microbial decomposition of the large amounts of debris on the forest floor can release K and alter N dynamics (Lodge et al. 1991; Zimmerman et al.1995). We believe that the time course of vegetative response to disturbance is similar in the two watersheds, given the strong similarities in the trajectories of K concentration in stream water (Fig. 2). The decoupling of stream water N and K concentrations suggests that differences in the processing of N in the riparian zones of the two watersheds (which vary dramatically due to lithology) account for the elevation of N concentrations in the Icacos for over a decade. We address the evidence in support of this conclusion in the following sections.

Vegetation

Storms that snap boles or branches can disrupt watershed nitrogen cycling by reducing plant uptake, resulting in elevated losses of nitrate in stream water (Houlton et al. 2003). Differences in the level of hurricane damage to vegetation might thus provide a plausible explanation for differences between our two watersheds. All available evidence, however, suggests that vegetative response to hurricanes has been similar in the two watersheds. Although remote sensing images can be used to characterize vegetative cover at the watershed scale, Landsat data cannot be used to assess vegetation dynamics over time in our two study watersheds. Satellite imagery is available, but the images are of very limited utility due to heavy cloud cover and they cannot be used to provide information on spatial variation in either initial hurricane effects, or the trajectory of regrowth following hurricanes. Several sources of plot-scale data do provide some insight into the extent to which the recovery of vegetation following hurricanes was similar in the two basins.

Canopy height is one measure of the biotic condition of the forest and forest response to disturbance. Mean canopy height was measured in one plot in or near each of the two watersheds at one date before, and multiple dates after, Hurricane Hugo between 1989 and 2011 (Brokaw and Grear 1991; Brokaw et al. 2004; Brokaw unpublished). The plots are 1 ha grids with 451–475 grid points each, located at 350 m (in the Sonadora watershed below the gauging station) and 650 m (on quartz diorite, near the Río Icacos watershed). Presence or absence of vegetation is determined on a vertical line extending above each grid point. Due to differences in elevation and species composition, mean canopy height in the Sonadora plot was roughly double that of the Icacos plot before Hurricane Hugo. Despite this initial difference in canopy height in the two watersheds, however, canopy heights in both watersheds declined by similar proportions (55–60 %) following Hugo and recovered on similar trajectories (Fig. 6).

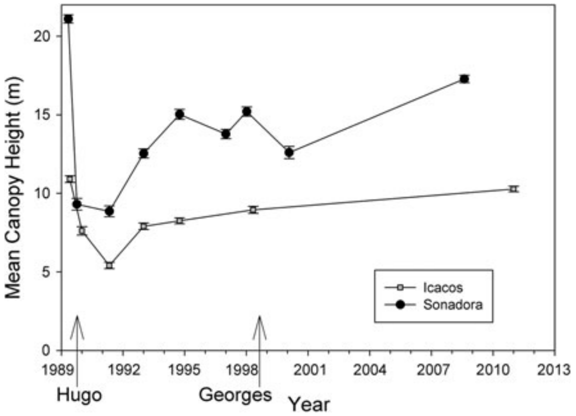

Fig. 6 Changes in canopy height following Hurricanes Hugo and Georges in plots located near the Icacos and Sonadora watersheds (mean and standard error of the mean; data from Brokaw and Grear 1991, Brokaw et al. 2004, and Brokaw unpublished)

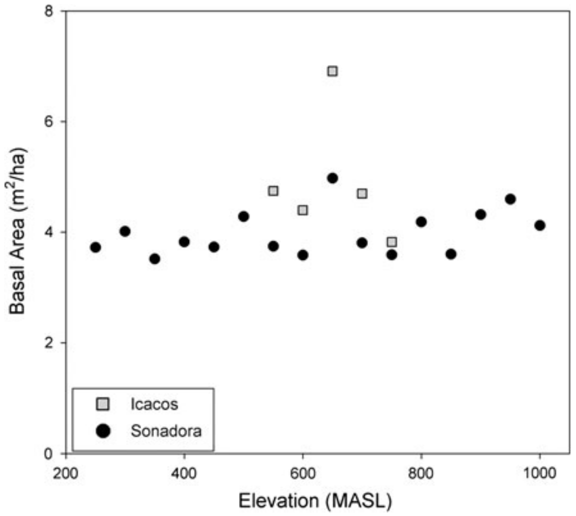

Fig. 7 Basal area of woody stems as a function of elevation in plots located in the Sonadora and Icacos watersheds, surveyed in 2001 (12 years after Hurricane Hugo and 3 years after Hurricane Georges; data from Barone et al. 2008)

Basal area is another measure of forest condition and regrowth following disturbance. Basal area was measured once along elevational transects in each watershed from September 2001 to July 2002. Plots were established at 50 m intervals in the Sonadora watershed from 250 to 1,000 m above sea level (MASL), and in the Icacos from 550 to 750 MASL (Barone et al. 2008). These data show that basal area of the plots was greater in the Icacos than the Sonadora watershed at each overlapping elevation (Fig. 7). Although pre-hurricane data are not available for these plots, the greater basal area in Icacos indicates that forest above-ground biomass was as large at a given elevation in the Icacos as it was in the Sonadora in 2001, when Sonadora stream NO_3 concentrations had returned to background levels but Icacos NO_3 concentrations were still at least double background levels. In short, there is no evidence of a more rapid recovery to pre-Hugo levels of tree biomass in the Sonadora watershed that could explain the more rapid return to background NO_3 levels in Quebrada Sonadora.

Based on the importance of pioneer tree species in ecological succession, we had expected that differences in tree species composition might be associated with the observed differences in the response of stream chemistry to disturbance. Plants that grow rapidly and colonize disturbed areas can capture mineralized N following a disturbance and accelerate the return to baseline of stream chemistry (Scatena et al. 1996; Silver et al. 1996). *Cecropia schreberiana* is the most important early successional pioneer tree species in the LEF, and data from the elevation gradient plots (Barone et al. 2008) indicate that *C. schreberiana* was actually more abundant (relative to other tree species) in the Icacos plots than in the Sonadora plots across all elevations (elevation 550–750 m: Icacos: 141 of 3001 stems; Sonadora: 50 of 2569 stems). Thus, differences in fast-growing early successional species cannot explain the differences between stream chemistry in the two watersheds.

Riparian controls on stream response

The long-term data on groundwater chemistry from both lithologies suggest that riparian zones in the volcaniclastic terrain are fundamentally more effective at retaining N than those in the quartz diorite, and this may play an important role in shaping the overall watershed response to hurricane disturbance. Nitrogen levels in riparian zones were altered only briefly after hurricane disturbance in the volcaniclastic terrain, and strong decreases in total N concentrations were observed as groundwater moved through the riparian zone and into the stream channel (McDowell et al. 1996; Fig. 4). In contrast, groundwater N concentrations were elevated for decades (Fig. 5) and are high along the entire riparian flow path in Icacos, declining only at the stream/groundwater interface (McDowell et al. 1992; Chestnut and McDowell 2000). From these observations we conclude that differences in riparian N dynamics play a major role in shaping the long-term response of stream chemistry to disturbance. Lithology, by structuring flow paths and biogeochemical conditions in the riparian zone, mediates the watershed response to disturbance and results in substantial differences in downstream export of nitrogen at a decadal time scale.

Other factors mediating the response to disturbance

The amount of N present in watershed soils cannot explain the elevated NO_3 concentrations in the Río Icacos. Riparian soils from the granitic terrain do have higher N concentrations than their counterparts on volcaniclastic terrain, which is consistent with the fact that levels of N in riparian groundwater are also higher on the granitic terrain (McDowell et al. 1992). In upland soils, however, the situation is reversed, with the high-N soils found in the watershed (Bisley) with lower N in riparian groundwater (Cusack et al. 2011). Thus, there is no consistent evidence of higher N availability in the terrain with higher N in shallow groundwater. We recognize the danger in extrapolating the response of individual watersheds to represent a class of watersheds. We note that many other watersheds on volcaniclastic terrain have been studied in the Luquillo Mountains (Schaefer et al. 2000) and none of them behaves as the Icacos does, with a long period of elevated NO_3 concentrations. Several tributaries of the Icacos have also been reported to have high concentrations of NO_3 following Hurricane Hugo (McDowell et al. 1996), and a comparison pairing land use and lithology in Puerto Rican streams also observed generally higher levels of NO_3 in quartz diorite than volcaniclastic terrains during the 1990s (Stallard and Murphy 2012). Finally, we note that landslides are twice as frequent in the quartz diorite lithology as in the volcaniclastic terrain (Larsen 2012), and they may be contributing to the long, slow decline in elevated NO_3 concentrations in the Icacos through their disruption of flow paths and forest vegetation.

Hydrologic residence time in our study watersheds may be an important factor in controlling the observed differences in response to disturbance, and it also varies by lithology. Residence time is a reflection of the relative speed and importance of various flow paths across the landscape, including deep flow paths that can bypass the riparian zone and discharge directly into the stream channel. Groundwater in the volcaniclastic Bisley watersheds mainly follows soil flow paths through macropores of less than 20 cm depth and infiltration to deeper soils is thought to be retarded by dense subsurface clay layers (McDowell et al. 1992; Schellekens et al. 2004). In contrast, shallow groundwater in the Icacos watershed appears to follow deeper flow paths (1–2 m) through layers of sandy or gravelly substrate, and deeper groundwater from bedrock is also a dominant source of stream base flow (McDowell et al. 1992; Shanley et al. 2011). McDowell and Asbury (1994) reported flow duration curves for Rio Icacos and Quebrada Sonadora that show a striking difference: Icacos has a shallower curve that indicates a larger, more persistent base flow per unit watershed area and a longer watershed residence time. Murphy and Stallard (2012) also found that residence time in two granitic watersheds (including Icacos) was roughly double that of two otherwise similar volcaniclastic watersheds, indicating that the pattern is robust with respect to lithology. Thus the effects of a nutrient pulse from hurricane disturbance may be more quickly flushed from the volcaniclastic terrains, and stored for slow release from the granitic terrains. This explanation is supported by higher NO_3–N concentrations (0.4 mg/l) in a deep well that samples the active weathering front above bedrock (20 m depth) in the Icacos watershed and lower NO_3–N concentrations (0.05 mg/l) in a similar deep well in the volcaniclastic terrain of the Bisley watershed (R. Brereton, unpublished data). Groundwater stored in granitic bedrock, with a higher residence time than in the volcaniclastic terrain, might also be contributing to the sustained high NO_3 concentrations in streams of the granitic terrain. A quantitative assessment of contributing areas (deep vs. shallow flow paths) would be necessary to address the role of deep groundwater in driving the patterns in stream chemistry that we have observed.

Understanding the role of lithology in driving watershed response to disturbance is important for predicting long-term changes in biogeochemistry across geologically variable tropical terrains. Because hurricane intensity is predicted to increase in the coming decades (Emanuel 2005), greater delivery of nitrogen to nitrogen-limited coastal ecosystems can be expected in the future, but the response to hurricanes may vary considerably with bedrock. With a higher frequency of intense hurricanes, the delivery of N from granitic terrains may be much larger than that from volcaniclastic terrains. The actual effect of these two major hurricanes on nitrogen export from the Icacos is probably underestimated, as we were not able to sample immediately after either hurricane, and instead only have data sets that begin about 1.5 years after each hurricane. Given the shape of the decline in NO_3 concentrations over time (Fig. 2), we suspect that concentrations in the months immediately after the hurricanes would have been considerably higher on the Icacos than what we have recorded, and much higher than those we observed with nearly continuous weekly sampling on the Sonadora.

Acknowledgments We thank John Bithorn, Carlos Estrada, Carlos Torrens, Mary Jean Sánchez, and Miriam Salgado for field sampling and sample processing. Alejo Estrada, Alonso Ramírez and Grizelle González provided site management and supervision that greatly facilitated long-term sampling. Jeff Merriam and Jody Potter provided critical assistance in sample analysis. Funding was provided by DOE and multiple grants from NSF: BSR-8718396, BSR-9007498, DEB-9981600, DEB-0087248, DEB-0108385, DEB-0620919, DEB-0816727, and EAR 0722476. This is a contribution of the LTER program in cooperation with the University of Puerto Rico and the USDA Forest Service International Institute of Tropical Forestry, Río Piedras, PR.

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