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Long-term patterns and short-term dynamics of stream solutes and suspended sediment in a rapidly weathering tropical watershed

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[1] The 326 ha Río Icacos watershed in the tropical wet forest of the Luquillo Mountains, northeastern Puerto Rico, is underlain by granodiorite bedrock with weathering rates among the highest in the world. We pooled stream chemistry and total suspended sediment (TSS) data sets from three discrete periods: 1983–1987, 1991–1997, and 2000–2008. During this period three major hurricanes crossed the site: Hugo in 1989, Hortense in 1996, and Georges in 1998. Stream chemistry reflects sea salt inputs (Na, Cl, and SO_4), and high weathering rates of the granodiorite (Ca, Mg, Si, and alkalinity). During rainfall, stream composition shifts toward that of precipitation, diluting 90% or more in the largest storms, but maintains a biogeochemical watershed signal marked by elevated K and dissolved organic carbon (DOC) concentration. DOC exhibits an unusual "boomerang" pattern, initially increasing with flow but then decreasing at the highest flows as it becomes depleted and/or vigorous overland flow minimizes contact with watershed surfaces. TSS increased markedly with discharge (power function slope 1.54), reflecting the erosive power of large storms in a landslide-prone landscape. The relations of TSS and most solute concentrations with stream discharge were stable through time, suggesting minimal long-term effects from repeated hurricane disturbance. Nitrate concentration, however, increased about threefold in response to hurricanes then returned to baseline over several years following a pseudo first-order decay pattern. The combined data sets provide insight about important hydrologic pathways, a long-term perspective to assess response to hurricanes, and a framework to evaluate future climate change in tropical ecosystems.

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1. Introduction

[2] Stream chemistry provides an integrated signal of the hydrologic and biogeochemical processes occurring in a watershed. Solutes provided by rainfall, forest canopy leaching, soil organic matter decomposition, ion exchange processes, weathering, and other watershed-scale processes vary in concentration in stream water as a function of source supply and hydrologic transport. Short- and long-term changes in stream chemistry provide valuable insight into solute sources, flow pathways, biogeochemical processes, and water residence time [*Huntington et al.*, 1994; *Buttle*, 1998; *Peters et al.*, 2006]. This understanding is key to projecting how stream chemistry and hydrology will respond to disturbance such as hurricanes [*McDowell et al.*, 1996; *Schaefer et al.*, 2000] and climate change [*Campbell et al.*, 2009; *Sebestyen et al.*, 2009].

[3] Tropical ecosystems with high rainfall can have high weathering rates relative to temperate systems [*Stallard and Edmond*, 1983]. Stream chemistry in these systems is a balance between solute supply from the landscape and dilution from rainfall of low ionic strength. Weathering solutes (Ca, Mg, Na, Si, and alkalinity) have high supply rates and tend to be diluted by stormflow, though watershed processes act to limit the amount of dilution [*Godsey et al.*, 2009; *Clow and Mast*, 2010]. Solutes with shallow sources, such as dissolved organic carbon (DOC), NO_3, and K, which are leached from vegetation and the forest floor, tend to have a tighter regulation by biogeochemical processes but are still subject to dilution at high flow. Significant dilution in wet tropical systems is favored by (1) soils maintaining a persistent near-saturated state from high and frequent rainfall that promotes fast shallow subsurface and surface pathways, often coupled with low-permeability subsoils that have a high residual clay content, and (2) low solute supply in the near-surface due to frequent flushing and a regolith of residual weathering products or slowly weathering primary minerals.

[4] High-flow hydrologic processes and solute dynamics have received less attention in tropical ecosystems than in their temperate counterparts. Studies that have examined high-flow hydrology in the high-rainfall tropics have documented the prevalence of fast flow paths [*Elsenbeer et al.*,

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Table 1. Data Sets Combined for This Paper

Years	Frequency	Who	Number of Samples	Publication
1983–1986	weekly	CEER[a,b]	185	*McDowell and Asbury* [1994]
1991–1997	events	USGS[c]	240	*Peters et al.* [2006]
2000–2008	weekly	LTER[b]	415	unpublished

[a]Center for Energy and Environment Research, now Institute for Tropical Ecosystem Studies at the University of Puerto Rico.

[b]The 1980s and 2000s data are available in a common file at http://luq.lternet.edu/data/lterdb20/data/RioIcacos.txt (accessed 11 February 2011).

[c]Data will be available in a forthcoming USGS publication [*Murphy and Stallard*, 2011].

1995a; *Elsenbeer and Lack*, 1996; *Godsey et al.*, 2004; *Kinner and Stallard*, 2004; *Schellekens et al.*, 2004; *Chappell*, 2010]. Of these studies, *Elsenbeer and Lack* [1996] and *Schellekens et al.* [2004] demonstrated significant stream water dilution. Tropical watershed studies that are long term (decades) provide the opportunity to observe ecosystem response to climatic (including catastrophic events) and anthropogenic forcings, but long-term watershed studies in the tropics are also rare. For this paper, by combining three separate stream chemistry data sets from a single site on Río Icacos, in the Puerto Rican montane wet forest, we have both a long-term 25 year record as well as a 7 year period of intensive event sampling. Integrating this record allows us to assess the dynamics of the system across a range of flows, the stability of concentration-discharge relations over time, and the response of the system to three hurricanes (and subsequent landslides) that crossed the site during the period of record.

2. Methods

[5] All stream samples were taken at the USGS gage on the Río Icacos near Naguabo, in northeastern Puerto Rico (18°15′N, 65°50′W). This gage operated from 1946 to 1963, and from 1980 to present. Río Icacos is within the El Yunque National Forest (formerly Caribbean National Forest), which is also designated for research as the Luquillo Experimental Forest (LEF) and hosts the Luquillo Long-Term Ecological Research (LTER) site. The watershed is 326 ha, with a relatively low-gradient stream channel (1.5%) but steep hillslopes (overall average watershed slope 21%). Elevation ranges from 616 to 844 m. Rainfall averages 4280 mm yr^{-1} and runoff averages 3610 mm yr^{-1} [*Peters et al.*, 2006]. Mean annual temperature is 21°C. The bedrock is a quartz diorite, and is deeply weathered with several meters of saprolite development and 1–2 m of weathered clayey and clay loam soils with a thin forest floor. The dominant vegetation is the colorado (*Cyrilla racemiflora*) forest type, with the low-canopy elfin forest found at the highest elevations (>750 m) [*McDowell and Asbury*, 1994]. Forest canopy is complete, except where openings persist from recent hurricanes and landslides. Human impact on the basin is minimal, with some small abandoned mines and two gated, lightly traveled roads.

[6] Three stream chemistry data sets from three consecutive decades were combined for this analysis (Table 1). The first data set derives from weekly samples and occasional storm event grab samples collected from 1983 to 1986 [*McDowell and Asbury*, 1994]. The second data set was developed by the USGS from 1991 to 1997 and includes mostly high-flow samples collected sequentially during rainfall events by automated samplers [*Peters et al.*, 2006; *Stallard and Murphy*, 2011]. The resulting data set contains 240 discrete samples with sufficient chemistry for this analysis, including 52 low-flow samples (<0.5 mm h^{-1}) and most of the remainder from 17 events (4 to 24 samples per event), 13 of which had flows exceeding 10 mm h^{-1}, in both wet and dry seasons. The third data set includes weekly samples from 2000 to 2008 collected through the LTER program. Río Icacos has high annual water yield and numerous high flow events in response to frequent and sometimes intense rainfall. The rainfall response is extremely flashy and the river returns quickly to base flow. Thus the weekly samples, collected on a fixed schedule (Tuesday mornings), usually represent base flow conditions. The flow ranges captured by the two weekly data sets and the event data set are almost mutually exclusive but highly complementary for evaluating overall system dynamics.

[7] An end-member mixing analysis (EMMA) was performed on the combined data sets to assess sources of streamflow [*Christophersen et al.*, 1990; *Burns et al.*, 2001; *Hooper*, 2003]. Compositions of waters from various hydrologic compartments in the watershed were evaluated as potential source water end-members. These waters included soil water from tension lysimeters on Guaba Ridge (Figure 1) [*Murphy et al.*, 1998; *White et al.*, 1998]; shallow groundwater from wells in riparian and hillslope settings [*McDowell et al.*, 1992], rainfall (annual average composition) from a nearby NADP station (PR20), and canopy throughfall (33 mostly weekly samples through most of a year) (W. H. McDowell and J. G. Macy, unpublished data, 2002). Surmising the importance of a deep groundwater source, but lacking the means to sample it, we equated deep groundwater to stream base flow composition. The extremely persistent base flow discharges between storms support this assumption. We represented the deep groundwater end-member by averaging solute concentrations for the 20 stream samples with the highest Si concentrations. Error in the EMMA was assessed by plots of observed versus predicted concentrations of the solutes used, and by assessing heteroscedasticity in individual solute residuals [*Inamdar and Mitchell*, 2006].

3. Results

3.1. Hydrology

[8] The Río Icacos is highly flashy. Response to rain inputs is large, rapid, and short lived. Historical maximum flows have approached 90 mm h^{-1}, about an order of magnitude greater than typical flows of record in humid temperate regions such as the northeastern USA. Despite rapid stream recession following events, Río Icacos maintains a remarkably stable and relatively high base flow of 0.1 to 0.2 mm h^{-1} that decreases little even during extended dry periods. Compared to two other streams on different lithologies within the LEF, Río Icacos has only slightly greater specific discharge at high flows, but a significantly greater and more sustained base flow [*McDowell and Asbury*, 1994].

3.2. Concentration-Discharge Relations

[9] At base flow, Río Icacos stream composition has high concentrations of Ca, Mg, Na, Si, and alkalinity, reflecting

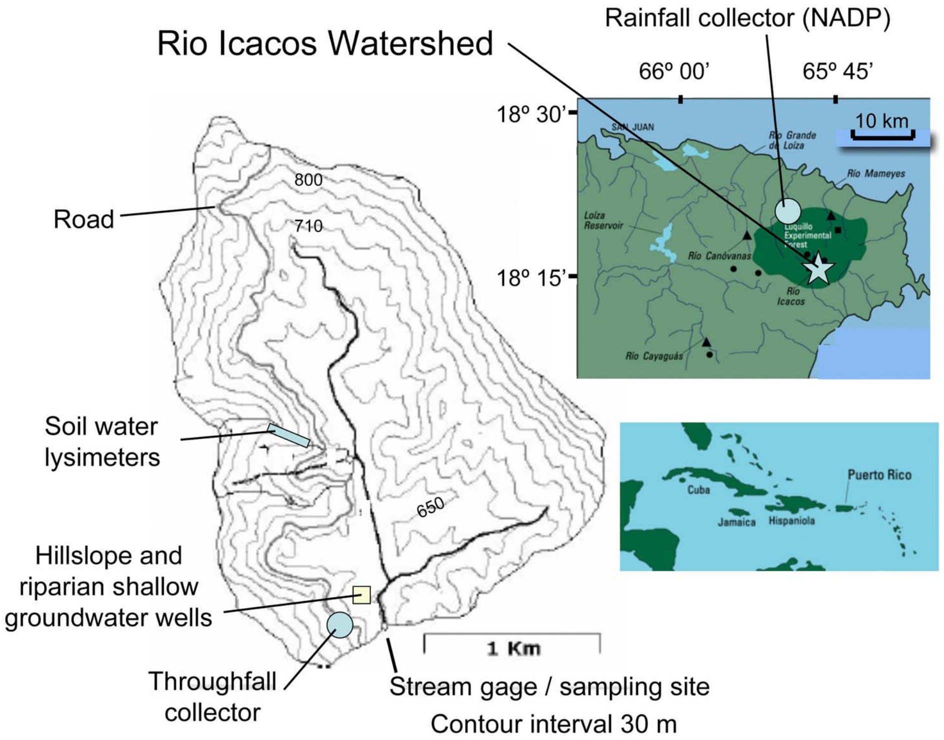

Figure 1. Map of Río Icacos watershed within the Luquillo Experimental Forest, Puerto Rico, showing sampling sites.

weathering of the granodiorite and high atmospheric loading of sea salts. During storms, base flow chemistry diluted by an order of magnitude or more for alkalinity, Ca, Mg, Na, and Si (Figure 2). For example, alkalinity decreased from near 500 μmol L^{-1} at base flow to −20 μmol L^{-1} at high flow (acidification); Si concentration decreased from near 450 μmol L^{-1} at base flow to as low as 2 μmol L^{-1} at high flow; and Ca diluted from 300 μeq L^{-1} at base flow to near 10 μeq L^{-1} at the highest flows. The pattern of dilution was log-log linear. Following *Godsey et al.* [2009], we plotted concentration and discharge with an equal number of log units (Figure 2) and computed power function slopes (Table 2) to assess each solute relative to ideal dilution (slope = −1) or chemostatic behavior (slope = 0). Si, Ca, and Mg, derived primarily from weathering, had the most negative slopes. Na and Cl, with significant sea salt components, had shallower slopes. K and NO_3 exhibited chemostatic behavior while SO_4 and DOC exhibited bimodal behavior.

[10] Analyses from the 1980s and 2000s weekly data sets, as well as the small number of low-flow samples from the 1990s data set, overlap strongly in the region representing flows less than 50 mm d^{-1}. This overlap suggests that little change has occurred in concentration-discharge relationships over the 25 years spanning those sampling efforts. There are few samples representing the intermediate flow range of 50 to 100 mm d^{-1}, but the event concentrations continue the trend from the weekly data sets, typically extending along the same power law slope. These relations are robust but do exhibit some scatter, possibly due to hysteresis, effects of antecedent moisture conditions, or seasonality. Si exhibited nonlinear behavior of excessive dilution at the highest flows, where its dilution paralleled the pure dilution line (Figure 2e).

[11] DOC concentration increased with increasing flow up to a threshold near 100 mm d^{-1}, then decreased abruptly with further flow increases (Figure 2j). This unusual "boomerang" trace suggests that at these very high flows, water contact with organic material diminishes due to the high water volume following surface flow paths, causing a dilution in DOC concentration. The sulfate concentration–flow relation paralleled that of DOC, but was muted; sulfate concentration increased slightly with flow for the fixed interval samples and decreased slightly with flow for the higher-flow event samples (Figure 2i).

[12] Nitrate concentration was not correlated with stream discharge at Icacos, suggesting apparent chemostatic behavior (Figure 2h). However, within the flat slope of the concentration-discharge relation, nitrate displays a broad range that reflects transient response to watershed disturbance (Figure 3). Pulses of nitrate released after hurricanes and landslides have been documented at Luquillo [*McDowell et al.*, 1996; *Schaefer et al.*, 2000], so the nitrate time trend denotes a record of ecosystem disturbance and recovery. Nitrate concentrations were quite stable near 5 μeq L^{-1} during the first sampling period in the 1980s, which followed a long period with no major hurricane since 1932. Hurricane Hugo struck in 1989 and nitrate concentrations at the start of USGS sampling in 1991 were three times higher than the 1980s values, declining to pre-Hugo values following a pseudo first-order decay pattern by 1995. Hurri-

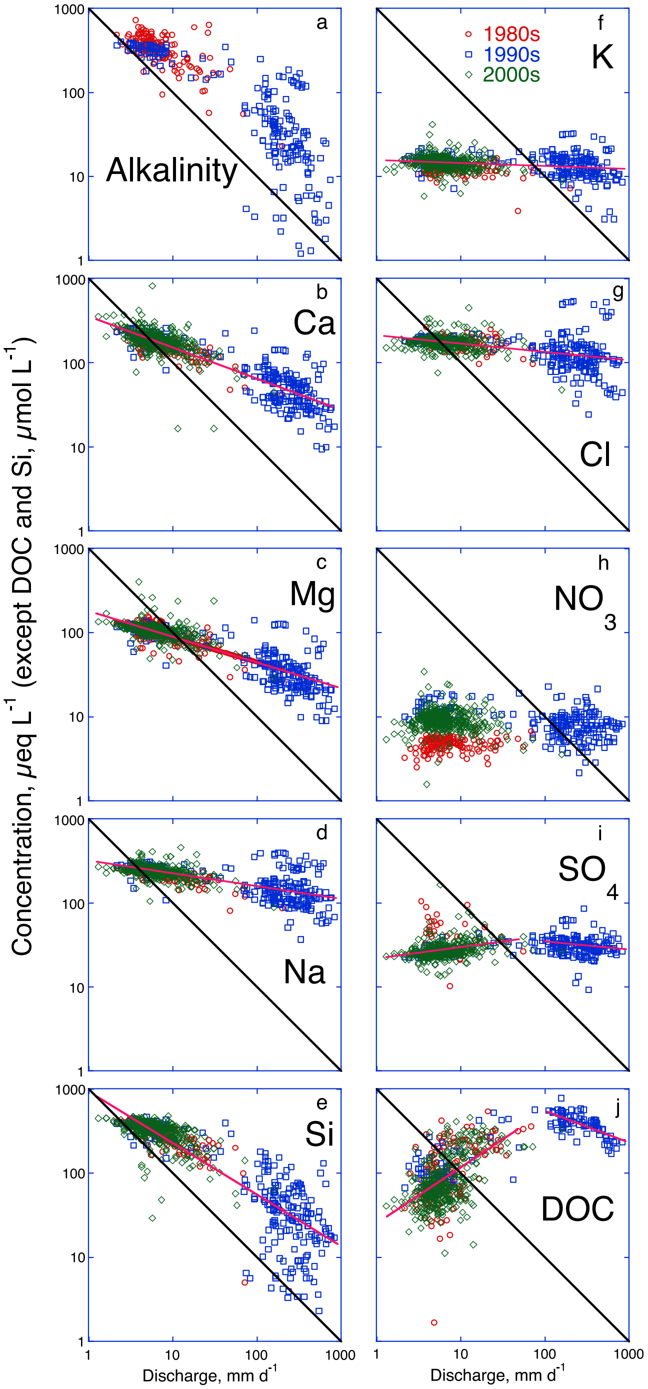

Figure 2. Concentration versus instantaneous discharge for the three data sets: (a) alkalinity (note that alkalinity was not determined in the 2000s data set), (b) Ca, (c) Mg, (d) Na, (e) Si, (f) K, (g) Cl, (h) NO_3, (i) SO_4, and (j) DOC. All concentration units are μeq L^{-1} except Si, which is μmol L^{-1}. Power function regression line fits shown here are presented in Table 2. The log-log plots with equal number of log units on each axis allow an assessment of solute behavior relative to pure dilution (diagonal black line with slope −1) or chemostasis (slope 0) SO_4 and DOC fitted separately for low- and high-flow regimes. Power function fit is not possible for alkalinity because of negative values (not shown).

Table 2. Power Function ($C = aQ^b$) Fits for Stream Solutes at Río Icacos[a]

Solute	a	b	r^2
Ca	110	−0.368	0.69
Mg	68	−0.310	0.62
Na	193	−0.148	0.44
Si	133	−0.616	0.76
K	15.3	−0.033	0.02
Cl	211	−0.100	0.25
$SO_4 < 50$ mm d^{-1}	22.3	0.122	0.03
$SO_4 > 100$ mm d^{-1}	50.4	−0.089	0.03
DOC < 50 mm d^{-1}	25.7	0.650	0.34
DOC > 100 mm d^{-1}	3145	−0.380	0.39
TSS	0.23	1.540	0.62

[a] See Figure 2. Concentrations are given in μeq L^{-1} and flow is given in mm d^{-1}. Separate fits were made for SO_4 and DOC for specified flow regimes.

canes Hortense in 1996 and Georges in 1998, and associated landslides, each caused subsequent upticks in nitrate. Nitrate concentration again slowly recovered to its 1980s values by 2008, 10 years after Hurricane Georges.

[13] Suspended sediment concentrations increased linearly with discharge, increasing 4 orders of magnitude over a nearly 3 order of magnitude increase in discharge (Figure 4). The total suspended sediment (TSS) flow pattern fit a power function with slope of 1.54 (Table 2). At the highest flows TSS concentrations exceeded 10,000 mg L^{-1}.

3.3. Hurricane Hortense: An Extreme Event

[14] While the concentration–discharge relations provide an overview of solute behavior in the Río Icacos system, it is instructive to examine the solute dynamics during a single large event. Hurricane Hortense dropped more than 600 mm of rain on the Icacos basin in just over 24 h in September 1996, producing one of the 10 highest flow peaks in the

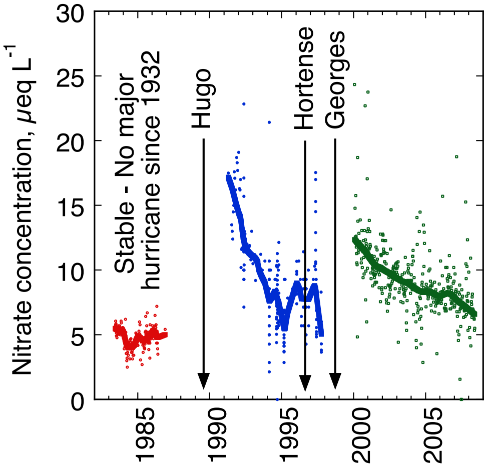

Figure 3. Time trend for nitrate in relation to major hurricanes at the site. Nitrate concentrations are independent of discharge, so the concentration pattern over time can be interpreted directly for trends. Weighted average trend line is fitted to each concentration series.

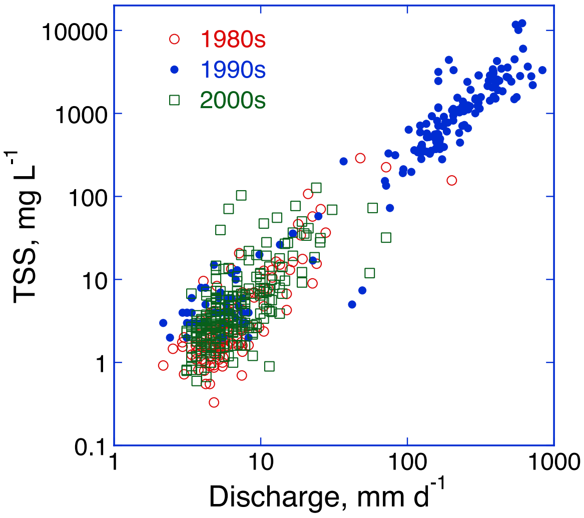

Figure 4. Total suspended sediment (TSS) concentration versus instantaneous discharge for the three data sets.

45 years of record. The USGS sampled before and after the peak stream response from Hurricane Hortense (Figure 5). The concentration range for base cations and DOC before and during this event spanned the entire range for all data sets. Base cations diluted to very low concentrations near the hydrograph peak. DOC peaked early on the rising limb of this large storm, then subsequently diluted by a factor of 3.

3.4. Mixing Analysis

[15] The solutes used in the EMMA were Ca, Mg, Na, Cl, DOC, and Si. A principal components analysis (PCA) resulted in two significant components, implying three end-members. The first principal component explained 67.0% of the variance and the second explained an additional 19.1%. The optimal set of end-members that bounded stream water composition was deep groundwater (stream base flow), throughfall, and rainfall (Figure 6). Soil water and shallow groundwater compositions (Table 3) generally fell within the mixing space (Figure 6), thus they are viable sources whose contribution to flow cannot be determined within this EMMA formulation. We lacked samples of a "quick flow", or shallow subsurface flow component that may be a dominant source during storms [*Elsenbeer et al.*, 1995a; *Kinner and Stallard*, 2004]. Overland flow water sampled at other wet tropical sites had the highest DOC concentrations of all water types (R. Stallard, unpublished data, 2004), and could account for the rising limb DOC increases at Icacos. Throughfall, which was enriched in all solutes relative to rainfall, due to foliar leaching, evaporative concentration, and wash off of sea salt aerosols, and had a notably higher DOC (Table 3), is probably similar in composition and thus a convenient proxy for this postulated but unsampled shallow or overland flow source. Note the large error bars on the throughfall end-member (Figure 6).

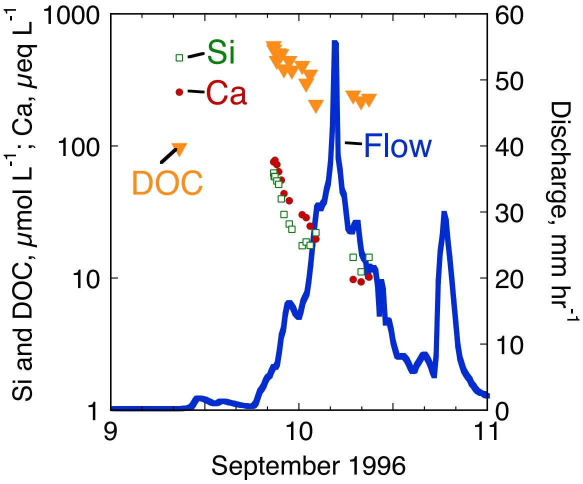

Figure 5. Hydrograph and solute concentrations during Hurricane Hortense in 1996. More than 600 mm of rain fell in just over 24 h. The prestorm values at the left of the plot were estimated from a base flow sample under similar hydrologic conditions and time of year, September 1992.

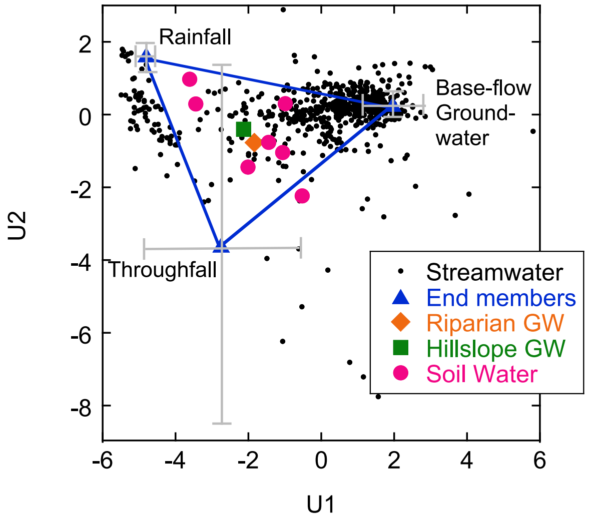

Figure 6. End-member mixing analysis (EMMA) diagram showing stream chemistry in relation to end-members of rainfall, throughfall, and deep groundwater. Gray bars represent uncertainty in end-members based on ±1 standard deviation for all six solutes used (Ca, Mg, Na, Cl, DOC, and Si). Uncertainty in the rainfall end-member is understated because it is based on variation in annual average composition rather than the storm-to-storm variation that directly affects stream composition.

[16] Regressions of EMMA-predicted versus observed concentrations for the six solutes had r^2 values that ranged from 0.70 to 0.88 (auxiliary material, Figure S1).[1] The linear fit was generally better than these values suggest, but was skewed by higher observed than predicted concentrations at the upper end of the range for all solutes except DOC and Si. These deviations were related to occasional high-Cl rainfall events caused by anomalously high sea salt entrain-

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[1] Auxiliary materials are available in the HTML. doi:10.1029/2010WR009788.

Table 3. Median End-Member Compositions Evaluated in EMMA

End-Member	Ca (μeq L^{-1})	Mg (μeq L^{-1})	Na (μeq L^{-1})	Cl (μeq L^{-1})	DOC (μmol L^{-1})	Si (μmol L^{-1})
Deep groundwater[a]	211.8	119.9	271.3	189.6	53.7	449.6
Standard deviation	54.0	15.2	27.3	14.6	34.5	12.6
Rainfall[b]	7.4	14.4	64.5	75.5	65.7	0.0
Standard deviation	0.9	2.7	11.9	12.6	34.6	0.0
Throughfall[c]	43.4	54.9	216.1	304.6	419.9	0.0
Standard deviation	23.6	39.8	138.8	228.9	240.3	0.0
Riparian shallow groundwater[d]	57.6	78.1	185.5	200.7	100.0	75.3
Standard deviation	25.2	24.8	38.9	41.3	75.7	161.5
Hillslope shallow groundwater[e]	11.0	74.9	146.2	206.0	36.6	129.1
Standard deviation	10.7	55.6	104.5	152.3	62.7	104.2
Guaba Ridge soil water[f]						
LG1_0.9	24.2	48.8	204.0	246.0	40.0	61.1
LG1_1.2	25.4	37.8	90.2	128.0	40.0	60.7
LG1_8.5	54.4	118.6	156.0	171.0	40.0	216.0
LG2_0.9	9.0	25.2	138.0	152.0	40.0	52.5
LG2_3.6	28.6	100.4	220.0	217.0	40.0	115.0
LG3_0.9	23.6	96.0	292.0	262.0	40.0	75.0
LG3_2.2	27.0	76.8	204.0	212.0	40.0	147.0

[a] Median from the 20 stream base flow samples with the highest Si concentrations.

[b] Median of annual weighted average concentrations at NADP site in El Verde, 15 km WNW. DOC not reported by NADP; values taken from precipitation samples at Icacos (W. H. McDowell and J. G. Macy, unpublished data, 2002). Si not reported by NADP; assumed to be zero.

[c] Based on 33 samples during 1 year (W. H. McDowell and J. G. Macy, unpublished data, 2002). Si not analyzed; assumed to be zero.

[d] Wells I-4 and I-7 from *McDowell et al.* [1992] (Figure 1).

[e] Wells I-9, I-10, and I-23 from *McDowell et al.* [1992] (Figure 1).

[f] Average composition from zero tension lysimeters, from *White et al.* [1998]. Standard deviation was not reported. Number after underscore is depth below land surface in m. DOC not analyzed; values assumed.

ment. Model residuals were thus heteroscedastic (auxiliary material, Figure S2), but most of the structure was attributed to these high-Cl events.

4. Discussion

4.1. Complementary Data Sets

[17] The weekly and event-based stream chemistry data sets were truly complementary in allowing us to interpret the hydrology and biogeochemistry of this tropical stream system. In combination they provided a continuum of the system response along the full gradient of hydrologic conditions. There was minimal overlap in the flow regimes represented by the two types of data, but there was clearly compatibility among the data sets when the relations defined by the low-flow regime extended seamlessly to the event data set. The consistent relations across data sets give confidence in the quality of the data, given that the three efforts were uncoordinated, separated in time, and undertaken by separate entities, and therefore no direct interlaboratory comparisons were made. Collectively, the three Río Icacos data sets span an unusually large range of flow conditions from which to assess the drivers of stream solute and sediment export.

4.2. Solute Sources

[18] Solutes in Icacos stream water derive from mineral weathering (base cations, alkalinity, and Si) [*Bhatt and McDowell*, 2007], atmospheric deposition of sea salts (Na, Cl, SO_4), and surface biogeochemical transformations (DOC, NO_3, K, SO_4). Based on throughfall enrichment, about 15% of sea salt input occurs as dry deposition [*McDowell*, 1998], which is readily dissolved and mobilized by subsequent rainfall. The granodiorite underlying the Río Icacos basin has one of the highest documented chemical weathering rates in the world for noncarbonate rock [*White and Blum*, 1995; *White et al.*, 1998], and plagioclase weathering controls base flow chemistry [*Pett-Ridge et al.*, 2009]. Base flow concentrations (Figure 2) are remarkably high given the high rainfall rates and high runoff available to transport weathering products off the landscape. Plagioclase has weathered out and is absent in the regolith, where biotite is the most readily weathered mineral remaining [*White et al.*, 1998]. Base flow had a Ca/Mg ratio near 1.8 (molar basis), due to high Ca supply from plagioclase weathering, in contrast to a mean ratio of 0.4 (range 0.25 to 0.70) in soil water, where weathering of Mg-rich biotite dominates [*White et al.*, 1998].

[19] Si is supplied by weathering, but nonweathering sources of Si have been documented at Icacos as well, including biogenic Si associated with organic matter [*Lugolobi et al.*, 2010] and Si from Sahara dust [*Pett-Ridge et al.*, 2009]. While the scatter in the Si discharge relation allows for some contribution from these sources, the extreme dilution during large events when surface flow paths are most active suggests that these sources are minor.

[20] Nitrate was independent of stream discharge but persistent at a low level in Río Icacos, despite evidence for ammonification in the riparian zone [*McDowell et al.*, 1996] and in-stream denitrification [*Mulholland et al.*, 2008; *Potter et al.*, 2010]. The base nitrate concentration (e.g., prior to Hurricane Hugo) was near the concentration in rain of ~5 μeq L^{-1} at that time, suggesting a steady state. Hurricanes and landslides cause a step input of organic N to the soil and disturbance to soil organic matter that induces a pulse of nitrification and nitrate release to stream water [*McDowell et al.*, 1996; *Schaefer et al.*, 2000]. The elevated nitrate concentrations in the 2000s period relative to the 1980s reflects continuing recovery from the late 1990s hurricanes, but may also reflect the increasing trend of nitrate in precipitation [*Ortiz-Zayas et al.*, 2006].

[21] DOC at base flow was near 50 μmol L^{-1}, suggesting riparian groundwater (average 100 μmol L^{-1}) as a possible

source, though autochthonous DOC production could also be responsible. During storms, DOC is supplied by the forest canopy and/or near-surface soil organic matter. Throughfall shows a twofold to sixfold enrichment of DOC in throughfall relative to rainfall in the Luquillo Mountains [*McDowell*, 1998; *Heartsill-Scalley et al.*, 2007]. From our sampling it was not possible to distinguish these two sources of DOC to stormflow, and they both probably contributed. However, the pattern of increasing DOC with flow is more suggestive of a shallow soil source, which should increase as the catchment wets up and hydrologically connects an ever greater source area. The reversal in the DOC discharge relation, or “boomerang” at the highest flows (>100 mm d^{-1}, Figure 2j) suggests that DOC is supply limited as sources become depleted.

[22] K and SO_4 present some parallels and some contrasts to NO_3 and DOC. Like DOC, K also has sources in throughfall and surface soil, and a minor weathering component. K flux in throughfall averaged 10 times that in precipitation at a nearby site [*Heartsill-Scalley et al.*, 2007]. However, K maintains a nearly constant stream concentration (only a slight dilution; Figure 2f) several fold greater than its mean concentration in precipitation of 1.6 μeq L^{-1}, indicating its sources do not become depleted. Sulfate increases with flow suggesting a shallow soil source, but like DOC it becomes depleted and concentrations tend to decline at the highest flows, but remain above concentrations in rain.

[23] We have discussed both deep and surface solute sources, but does the regolith (soil and saprolite) contribute? The EMMA is inconclusive in this regard, as subsurface waters from these source zones (shallow groundwater, soil water) plot intermediate to deep groundwater (base flow) and meteoric waters, so their possible contributions cannot be differentiated. However, riparian groundwater tables rise significantly during events [*McDowell et al.*, 1996], suggesting a shallow groundwater contribution. *Chestnut and McDowell* [2000] concluded from hydrometric and chemical evidence that shallow groundwater inputs contribute up to 10% of the flow in a 100 m reach of a Río Icacos tributary. Moreover, *Derry et al.* [2006] inferred from Ge/Si ratios in Icacos stream water that the source of Si shifted from bedrock minerals to soil minerals as stream Si concentration decreased during two moderate size storms. The nitrate pulse from disturbance associated with Hurricane Hugo appeared in shallow groundwater (i.e., from the near-surface aquifer in soil and saprolite) as well as a small tributary of the Icacos [*McDowell et al.*, 1996]. This poses the possibility that the sustained increases in stream nitrate following hurricanes (Figure 5) were contributed via shallow groundwater. *McDowell et al.* [1992] had previously noted the presence of a conductive layer of sand and gravel at 1–2 m depth in the riparian zone, which would promote such shallow groundwater inputs.

4.3. Flow Paths

[24] A bedrock source for base flow chemistry is supported by the sustained stable base flow rates exhibited by Río Icacos for up to weeks duration, with flow remaining always above 1.2 mm d^{-1} [*Peters et al.*, 2006], implying long, deep flow paths. During storms, Río Icacos stream chemistry undergoes profound dilution. Stream chemistry evolves toward the concentration of rainfall, and bears little resemblance to the original base flow chemistry. The dilution power law slope for Si of −0.62 is more negative than any of the 59 long-term stream data sets, including two tropical streams in Hawaii, analyzed by *Godsey et al.* [2009]. Slopes for Ca (−0.37) and Mg (−0.31) are within the most negative 10%.

[25] Major dilution has been documented in other tropical watersheds. *Schellekens et al.* [2004], working in a 6.4 ha volcaniclastic watershed on the opposite slope of the mountain from Río Icacos, observed that Si decreased to 10% and Ca and Mg to 20% of base flow values during a very large storm (227 mm) where flow reached 35 mm h^{-1}, matching the highest flow in our data set. *Elsenbeer et al.* [1995b], reported that stream alkalinity decreased to 20% of base flow during a 178 mm event at the Babinda catchment in tropical northeast Queensland, but persistent soil water contributions prevented further decreases even though saturation overland flow comprised nearly 80% of streamflow. Despite these reports of storm-induced dilution, we are not aware of any other stream system where stream chemistry is so thoroughly transformed during high flow events as at Río Icacos. The extent of dilution is all the more notable given that the Río Icacos basin is at least an order of magnitude greater in size than the research watersheds cited, a factor that promotes greater groundwater contributions, possible longer flow paths that foster greater modification of meteoric water, or simply longer channel travel times that would diffuse the dilution signal.

[26] The rapid and extensive dilution at Río Icacos requires a mechanism for rapid delivery of event water to the stream, calling for some combination of rapid shallow subsurface flow such as in natural soil pipes [*Chappell*, 2010], or overland flow. Overland flow has been documented as a significant and even dominant flow component during storms in other high-rainfall tropical systems, including Australia [*Elsenbeer et al.*, 1995b], Peru [*Elsenbeer and Lack*, 1996], and Panama [*Godsey et al.*, 2004]. *Larsen et al.* [1999] measured only a small fraction of precipitation running off as overland flow at Icacos, but numerous unchanneled surface rivulets are commonly observed in the field during storms, likely representing return flow from the focusing and discharge of shallow subsurface flow. *Schellekens et al.* [2004], in the small catchment near Icacos, performed pairwise solute mixing analyses and concluded that shallow subsurface flow (return flow) contributed about one third of the streamflow in each of two storms (one large and one small) analyzed. Likewise, *Elsenbeer et al.* [1994] sampled shallow subsurface flow (return flow) in a high-rainfall tropical Australian catchment and found its chemistry reflected in stream water. In order to simulate streamflow in a tropical watershed in Panama using TOPMODEL, *Kinner and Stallard* [2004] needed to incorporate a fast shallow flow component.

[27] Río Icacos contrasts to most stream systems, where groundwater remains a significant and usually the dominant component of flow even during large events. In most systems, meteoric water is thought to displace soil water and/or groundwater so that water preexisting in the catchment dominates the storm hydrograph [*Hooper and Shoemaker*, 1986; *Pearce et al.*, 1986; *Wels et al.*, 1991; *Buttle*, 1998]. Examples of new water dominance at high flow in the literature are far fewer [e.g., *McDonnell et al.*, 1990; *Brown et al.*, 1999; *Goller et al.*, 2005] and often represent special conditions,

Table 4. Stream Solute and TSS Export Fluxes[a]

	1980s		1990s	
	Precipitation	Stream	Precipitation	Stream
Water (mm yr^{-1})	4300	3680	4280	3610
Alkalinity		856	−35	720
Ca		475	30	254
Mg		292	75	146
Na		696	360	757
Si		800	0	780
K		44	10	55
Cl		592	400	575
SO_4		73	10	52
NO_3		18	30	35
DOC (mmol m^{-2} yr^{-1})		808		
TSS (g m^{-2} yr^{-1})		320		

[a]Values are calculated from the 1980s data set [*McDowell and Asbury*, 1994] and the 1990s data set [*Peters et al.*, 2006] as well as 1990s precipitation solute input fluxes reported by *Peters et al.* [2006]. All units in meq m^{-2} yr^{-1} unless otherwise noted.

such as snowmelt over frozen soil [*Shanley et al.*, 2002] or runoff over impervious urbanized areas [*Rijsdijk et al.*, 2007]. However, at Babinda in Queensland, *Bonell et al.* [1998] reported virtually 100% event water based on water isotopes at peak flow during intense monsoon rainfall and high antecedent moisture. We had no isotopic data, but the chemical signature of new water strongly suggested a meteoric source.

[28] The stream response at Icacos is consistent with the classification system of *Elsenbeer* [2001], whereby tropical acrisols generate lateral flow in surface soils. The high rainfall at Río Icacos, coupled with the high clay content and thus low permeability of upslope subsoils [*Simon et al.*, 1990; *McDowell et al.*, 1992], result in high water content of surface soils in both upslope and riparian positions [*McSwiney et al.*, 2001]. Water that infiltrates to greater depth at Icacos does so too slowly [*Simon et al.*, 1990] to contribute to the flashy storm hydrographs. Moreover, deeper soil water is depleted in DOC, which is strongly adsorbed in the mineral horizons at Icacos [*McDowell*, 1998]. Icacos may conform to the conceptual model recently advanced by *Brooks et al.* [2010], in which a reservoir of matrix-bound soil water supplies water for evapotranspiration but is relatively independent from sources of water that supply streamflow.

4.4. Conceptual Model

[29] Our conceptual model views base flow derived primarily from deep groundwater with a possible contribution from shallow riparian groundwater. As flow increases, streamflow composition evolves toward that of the sea salt–laden meteoric waters (throughfall and rainfall) driving the event, modified by contact with the forest floor and with possible additional contributions from shallow riparian groundwater and soil water. Meteoric waters acquire additional solutes from surface soils en route to the channel, but even these sources are diluted (or depleted) when vigorous overland flow minimizes contact with the soil surface.

[30] In the EMMA, deep groundwater and rainfall have a sound basis as end-members because it makes physical sense that they make up nearly 100% of flow at low and high flow, respectively. *Schellekens et al.* [2004], in the nearby volcaniclastic watershed, also determined rainfall to be an end-member, though it contributed only about 10% of streamflow in a small storm and 45% in a large storm. Having both rainfall and throughfall as end-members, however, raises questions. Most likely, throughfall in the EMMA proxies for a shallow soil water or overland flow component which we did not sample. The EMMA representation of the source of dilution shifting from throughfall to rainfall at progressively higher flows may be alternatively explained by progressive depletion of solutes, or progressively less soil contact as overland flow becomes more vigorous. Throughfall likely also contributes as it evolves along a parallel path of solute depletion [*McDowell*, 1998]. In this high-rainfall landscape, frequent flushing and lack of primary minerals in the shallow soil zone [*White et al.*, 1998] act to minimize the buildup and release of solutes. However, even during the largest events, stream K concentrations (Figure 2f) generally remain fivefold greater than the average rainfall K concentration (1.6 μeq L^{-1}), indicating that throughfall and/or surface soils persist as solute sources.

4.5. Sediment Dynamics

[31] TSS export at Río Icacos is quite high for a relatively pristine forested watershed with such a low channel gradient (1.4%). *McDowell and Asbury* [1994] attributed the high TSS export at Icacos to the high rainfall, steep hillslopes, and erodibility of watershed soils. The full data set with the high flow values in the current study reproduced the concentration-discharge relationship for TSS reported by *McDowell and Asbury* [1994] quite well (slope of log-log relation within 3%), confirming the high TSS export they reported for this basin. Despite the occurrence of 2 major hurricanes before and during the event sampling effort in the 1990s, the dynamics of sediment delivery from the landscape did not change appreciably compared to the prehurricane study period in the 1980s (Figure 4). This result suggests that in terms of erosion and sediment transport the landscape is in a quasi steady state from frequent disturbance by landslides [*Larsen and Torres-Sanchez*, 1998], or that the response to large disturbances like hurricanes [*Scatena and Larsen*, 1991] is gradual and long lived.

4.6. Mass Balance

[32] Stream solute export was computed independently for the 1980s period [*McDowell and Asbury*, 1994] and the 1990s period [*Peters et al.*, 2006] (Table 4). *Peters et al.* [2006] also computed solute input fluxes to construct a mass balance. The two periods had nearly identical precipitation and runoff, and all solute export fluxes agreed within a factor of 2, confirming the stability of the concentration discharge relations over a broad range of flows. For Ca, Mg, and Si, the high-flow sampling showed greater dilution than predicted from the 1980s weekly sampling, and these solutes had correspondingly lower fluxes. Na and Cl, contributed largely from sea salt, agreed within a few percent. The doubling of nitrate flux in the 1990s resulted from hurricanes and landslides. Stream fluxes of sea salts (Na, Cl), weathering products (Ca, Si, alkalinity), and internally generated DOC are of the same order of magnitude. The full mass balance for the 1990s [*Peters et al.*, 2006] underscores the high weathering contribution from plagioclase (net Ca, Na) in the bedrock versus biotite (net Mg) in soil and saprolite.

4.7. Implications and Transferability of Results

[33] We believe that this study is the first to present a combined long-term (~25 years) and high-frequency (event sampling) investigation of a tropical stream system. Comparable studies have been numerous in temperate latitudes but as noted by *Markewitz et al.* [2001], the tropics have received much less attention. One implication of our study is that a tropical catchment subject to high rainfall and frequent hurricanes and landslides demonstrated high resilience in the face of repeated disturbances. Stream chemistry before, during, and after a decade marked by hurricanes and landslides plotted in nearly identical concentration-discharge space for all solutes except nitrate. Even suspended sediment discharge patterns remained relatively stable throughout an active period of hurricanes and landslides. Landscape disturbance clearly perturbed the nitrogen cycle, and recovery as measured by nitrate in stream water took multiple years. Biogeochemically, this forested ecosystem appears to be well adapted to periodic, sometimes extreme disturbance. However, its resilience may be tested by possible future increases in hurricane frequency and intensity, as well as other aspects of climate change. A second implication of our study, based on the remarkable dilution at high flow, is that at high flows the ability of the ecosystem to process atmospheric inputs is compromised. If climate change brings more frequent and/or intense storms, even less atmospheric deposition, including pollutants, can be attenuated by the watershed, and groundwater recharge patterns could be altered.

[34] Do other tropical streams display the resiliency in concentration discharge relations found at Río Icacos? Though we know of no other long-term dedicated tropical watershed studies with intensive sampling for direct comparison, we examined concentration discharge relations for tropical rivers from the USGS NASQAN database [*Alexander et al.*, 1998]. Based on 4 sites in Hawaii and 6 sites in Puerto Rico, all on young geology, and all sampled at a wide range of runoff rates, Río Icacos was within the range of the other streams, though Ca showed a somewhat greater extent of dilution, and the TSS discharge relation had a somewhat greater slope relative to the other rivers.

5. Conclusions

[35] Pooling of three independent stream chemistry data sets from three consecutive decades at a stream gaging station on the Río Icacos in northeastern Puerto Rico has revealed both long-term patterns and short-term dynamics in this tropical ecosystem. Fixed-interval samples (weekly) from the 1980s and 2000s were assessed together with event-based samples from the 1990s. For most solutes, concentration-discharge relations overlapped for the weekly samples collected in the 1980s and 2000s, and the 1990s high flow samples plotted as smooth extensions of these relations. This continuity was present also for suspended solids, despite major hurricanes and associated landslides affecting the site in 1989, 1996, and 1998. Only nitrate responded to the hurricanes, exhibiting spikes in concentration of 2–3 times baseline that persisted up to years following each hurricane. The stability of solute-discharge and sediment-discharge relations during the 25 year span of the studies suggests that natural forest systems have considerable resilience, even under severe natural disturbance.

[36] In this rapidly weathering watershed, stream base flow sustains high concentrations of solutes from a deep groundwater source and from atmospheric sea salt deposition, with possible contributions from shallow riparian groundwater. As flow increases, stream chemistry shifts toward the composition of rainfall, with up to 90% or more dilution–more than any site reported in the literature–of weathering solutes (Si, Ca, Mg) and somewhat less dilution of sea salts (Na, Cl). As these solutes dilute, bioactive solutes (K, SO_4, NO_3, DOC) maintain or increase concentrations from canopy throughfall and/or from surface soils as source areas hydrologically connect. Even at maximum flow and extent of dilution, this watershed signature persists, as evidenced by K maintaining concentrations 5 times greater in the stream than in precipitation despite intense rainfall and vigorous overland flow that minimize surface reactions.

[37] DOC dynamics at Río Icacos are particularly noteworthy. The DOC concentration-discharge relation has a "boomerang" shape, initially increasing with flow, then decreasing with flow at higher discharge. This reversal during the largest events probably results from a combination of reduced interaction of overland flow with the soil surface and progressive depletion of organic carbon sources in the canopy and forest floor.

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