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ECOSYSTEMS

Rainfall-Driven Amplification of Seasonal Acidification in Poorly Buffered Tropical Streams

Gaston E. Small,[1]* Marcelo Ardón,[2] Alan P. Jackman,[3] John H. Duff,[3] Frank J. Triska,[3] Alonso Ramírez,[4] Marcía Snyder,[5] and Catherine M. Pringle[5]

[1]*Department of Ecology, Evolution, and Behavior, University of Minnesota, St. Paul, Minnesota 55108, USA;* [2]*Department of Biology, East Carolina University, Greenville, North Carolina 27858, USA;* [3]*Water Resources Division, U.S. Geological Survey, Menlo Park, California 94025, USA;* [4]*Institute for Tropical Ecosystem Studies, University of Puerto Rico, San Juan, Puerto Rico 00931, USA;* [5]*Odum School of Ecology, University of Georgia, Athens, Georgia 30602, USA*

Abstract

Acidification in freshwater ecosystems has important ecological and biogeochemical effects. Temperate streams affected by anthropogenic acidification have been extensively studied, but our understanding of natural acidification in tropical streams has been constrained by the lack of long-term datasets. Here, we analyze 14 years of monthly observations from 13 sampling stations in eight tropical streams in lowland Costa Rica. Stream pH increased during the 4-month dry season and declined throughout the wet season. The magnitude of the seasonal pH decline was greatest following the driest dry seasons, including the historically large El Niño Southern Oscillation event in 1998 when pH values dropped below 4.0 in some streams. Dissolved CO_2 accounts for the low baseline pH in the poorly buffered study streams, and we hypothesize that an influx of soil-derived CO_2 via subsurface flow paths contributes to the observed seasonal pH declines. Our results show tight coupling between rainfall, terrestrial, and aquatic ecosystems in the tropics. Predicted decreases in dry season rainfall for the tropics may lead to an increased magnitude of seasonal acidification.

Key words: acidification; carbonic acid; climate; CO_2; El Niño; stream; tropical.

Introduction

The causes and consequences of acidification in aquatic ecosystems have been the focus of extensive study in recent decades (for example, Likens and others 1972; Doney and others 2009). Many aquatic species are highly sensitive to declines in pH, and acidification can lead to decreased species richness and simplified food webs (Sutcliffe and Carrick 1973; Hall and others 1980; Fabry and others 2008). Besides its direct effect on organisms, pH is also a master variable for biogeochemical reactions, potentially altering ecosystem nutrient dynamics by controlling interactions between dissolved nutrients and mineral surfaces (Stumm and Morgan 1996). Potential drivers of acidification in aquatic ecosystems include dilution of acid neutralizing capacity (ANC), inputs of mineral acids (as in acid precipitation), oxidation–reduction (redox)

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*Corresponding author; e-mail: gesmall@umn.edu

reactions (as in acid mine drainage), organic acid inputs (such as in streams draining peat bogs), and elevated concentrations of dissolved carbon dioxide (CO_2) (such as ocean acidification).

Acidification in temperate streams has been intensively studied and may be driven by direct anthropogenic influences such as acid precipitation (Galloway and others 1976) and acid mine drainage (Nordstrom and others 2000), or may occur naturally due to ANC dilution or sulfate oxidation (Erlandsson and others 2010). In contrast, data from tropical streams are rare, and primary causes of stream acidification are poorly understood. In addition to the mechanisms described above, CO_2 may be an important contributor to episodic acidification in tropical streams. The warm, wet climate in much of the tropics creates the potential for high rates of CO_2 production in tropical soils. When combined with subsurface water flows that dissolve this CO_2 and transport it to streams, natural acidification may occur in relatively pristine areas. In a study of a small watershed in the Amazon basin, Johnson and others (2008) found that high soil CO_2 concentrations contribute to groundwater springs with a pH of 4.65 although excess CO_2 is rapidly evaded with distance downstream and stream pH climbs above 6.0 in first order streams. Another study in the same watershed demonstrated that the magnitude and frequency of precipitation events affected CO_2 pulses as drier antecedent conditions corresponded to larger CO_2 pulses from subsurface flowpaths (Johnson and others 2007).

The link between the frequency and intensity of rain events and stream pH is likely to be strong in lowland tropical wet forests, and predicted changes in tropical precipitation regimes as a result of climate change (Milly and others 2005; Min and others 2011), which may have important consequences for these stream ecosystems. However, the lack of long-term studies of tropical stream chemistry has precluded an understanding of relationships between these variables. In this paper, we use one of the few long-term datasets of stream chemistry in the tropics to evaluate the potential contribution of dissolved CO_2 in local groundwater, along with other potential mechanisms, in determining the response of stream pH to interannual variation in precipitation. We present an analysis of 14 years of monthly pH data from thirteen sampling stations in eight streams (ranging from 1st to 4th order) in lowland Costa Rica, and use hourly pH measurements from a focal stream to evaluate pH dynamics during seasonal transitions. We also evaluated how differences in stream chemistry due to interbasin groundwater flow (IGF) mediate these seasonal and climate-driven trends.

Methods

Site Description

La Selva Biological Station (LSBS) is a 1,536-ha reserve situated on the Caribbean Slope of Costa Rica at the gradient break between the central mountain range and coastal plain (10°26′N, 84°01′W). LSBS is drained by two major watersheds, the Sura and Salto. Geomorphological features of this landscape result in natural interbasin transfers of solute-rich groundwater entering some streams, emerging in seeps at the base of Pleistocene lava flows (Pringle and Triska 1991; Pringle and others 1993; Genereux and others 2009). These regional groundwater inputs are characterized by high-solute concentrations (for example P, Na^+, Cl^-, and HCO_3^-) (Pringle and others 1993) ranging from 13 to 29 times more concentrated than corresponding solute concentrations in low-solute local groundwater (Genereux and others 2002). These solutes are derived from magmatic outgassing or weathering of volcanic rock beneath nearby Volcan Barva (Pringle and others 1993; Genereux and others 2009). Similar high-solute streams are found in volcanically active areas throughout Central America (Pringle and Triska 2000).

Average annual temperature at LSBS is 25.8°C with monthly mean daily temperatures ranging from an average of 24.7°C in January to 27.2°C in August (Sanford and others 1994). Annual precipitation averaged 4367 ± 99 mm (mean ± SE) from 1963 to 2009 (Organization for Tropical Studies, La Selva Meteorological Data, http://www.ots.ac.cr/meteoro). Approximately 64% of annual precipitation is exported as runoff (Genereux and others 2005). Average monthly rainfall values for May–December exceed 320 mm. February–April is relatively dry with average rainfall below 200 mm per month, and January is intermediate with an average rainfall of 274 mm (Sanford and others 1994). However, the timing and precipitation totals during the dry season vary across years. Rainfall at LSBS has a volume-weighted mean pH of 5.4 (Eklund and others 1997).

The small watersheds that were the focus of this study are characterized by strongly weathered residual soils originating from andesitic lava flows. These soils were originally classified as Ultisols (Sollins and others 1994), but have been reclassi-

fied as Oxisols (Kleber and others 2007), which are common in tropical latitudes.

Long-Term Sampling

As part of a long-term stream monitoring program at LSBS (described in Pringle and Triska 1991; Triska and others 2006), monthly in situ pH and conductivity measurements, along with other physical and chemical measurements, have been recorded for 13 streams sites (Figure 1) beginning in April 1997. Discharge is measured monthly based on staff gage readings. Long-term data from this project are archived at http://streamslaselva.net.

These study streams vary in the contribution of regional groundwater, as reflected by base flow conductivity levels (Table 1). Stream sites are named according to the watershed and approximate elevation (in m above sea level). The same technician has collected all measurements over 14 years. We measured pH values at these 13 sites during the first week of each month using a Hannah Instruments 9025 handheld pH meter. The pH probe was calibrated in pH 4 and 7 buffer on the days when the measurements were taken. For two of the 13 sites (Arboleda-30 and Taconazo-30), pH measurements were not collected from October 1998 to September 1999, while weirs were being installed in these streams.

Daily precipitation data have been collected since 1992 at LSBS using an automated tipping-bucket rain gauge. Manual rain gauge measurements collected at the same site, as well as measurements from additional tipping-bucket gauges installed on above-canopy towers, were used for quality-control and gap-filling (Clark and others 2010).

Additional Measurements at Focal Site

The low-solute Taconazo-30 stream site was selected for more intensive analysis (Table 2) due to its accessibility and a history of previous research focusing on this watershed (Genereux and Pringle 1997; Genereux and Jordan 2006; Genereux and others 2009). Beginning in August 2003, monthly measurements of shallow groundwater pH were made from a well adjacent to the Taconazo-30 site. The well, located 2.5 m from the stream, consists of a 1-m PVC pipe with slits along the length for water exchange. Water is pumped out of the well using a peristaltic pump and after the well immediately refills, water is collected and the pH is measured. Because of the historical sampling schedule, stream measurements are made during the first week of each month and well measurements are conducted approximately 2 weeks later. For the purpose of analysis in this study, well pH measurements in a given month were paired with stream pH measurements from the following month (that is, an approximate 2-week time lag). The actual travel time of local groundwater from the well to the stream is unknown and potentially varies by season, but this analysis allows us to capture seasonal dynamics in local groundwater chemistry.

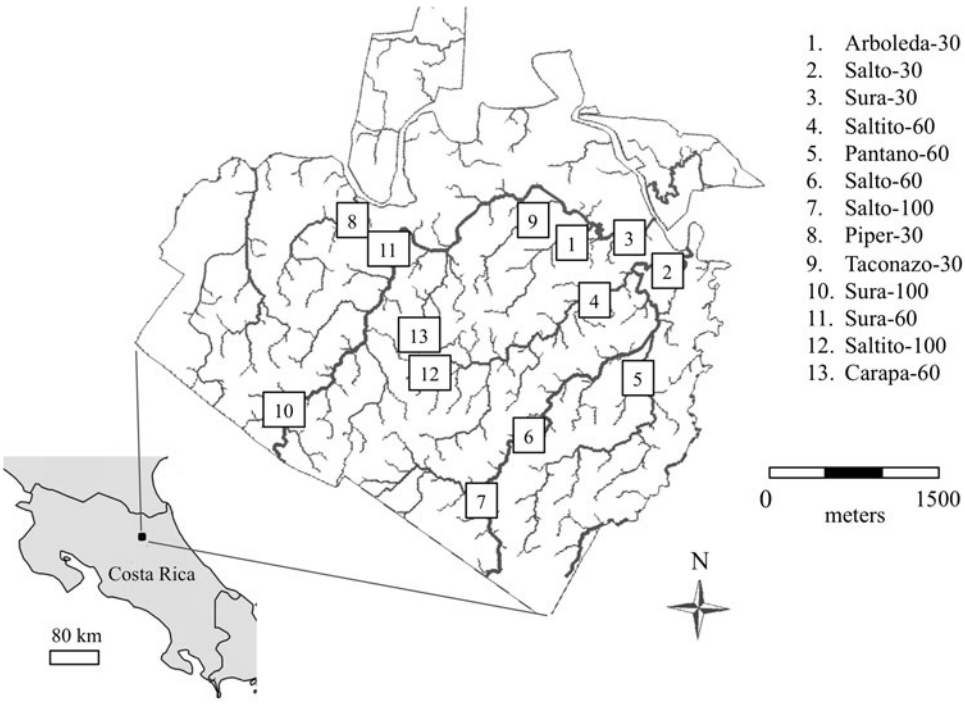

Figure 1. Location of the 13 stream monitoring sites at LSBS, Costa Rica.

Table 1. Chemical Characteristics of the 13 Study Sites (8 Streams)

Stream	EC (μS cm^{-1})	Na^+ (mg l^{-1})	K^+ (mg l^{-1})	Mg^{2+} (mg l^{-1})	Ca^{2+} (mg l^{-1})	pH	Discharge (l s^{-1})
Arboleda-30	279.2	20.28	4.41	15.13	17.18	6.20	170
Salto-30	175.8	11.10	3.62	7.36	9.33	6.34	434
Sura-30	164.1	10.29	3.76	6.25	10.51	6.23	568
Saltito-60	109.6	6.41	2.23	3.78	5.37	6.21	242
Pantano-60	70.0	4.26	1.17	2.60	2.78	6.03	274
Salto-60	32.5	2.33	0.98	0.90	1.36	5.77	298
Salto-100	29.2	2.07	0.99	0.69	1.49	5.69	270
Piper-30	25.4	1.67	0.49	0.59	1.22	5.33	100
Taconazo-30	22.3	1.48	0.53	0.86	0.92	5.44	23
Sura-100	22.2	1.83	0.69	0.54	0.70	5.46	99
Sura-60	20.6	1.78	0.58	0.54	0.80	5.64	190
Saltito-100	20.4	1.55	0.46	0.45	0.72	5.36	3
Carapa-60	17.7	1.54	0.52	0.38	0.36	5.40	2

Numbers following stream name represent approximate elevation (m above sea level). Values for electrical conductivity (EC), pH, and discharge are means from monthly observations recorded from 1997 to 2010. Concentrations of Na^+, K^+, Mg^{2+}, and Ca^{2+} are means from monthly observations from 1999 to 2001 (not flow-weighted, as a constant record of discharge is not available for most sites). Streams with mean conductivity values exceeding 35 μS cm^{-1} receive inputs of high-solute interbasin groundwater.

Table 2. Summary of Data Presented in this Paper

Measurement	Frequency	Years	Number of sites
Stream pH	Monthly	1997–2010	13
Well pH	Monthly	2003–2010	1
Stream pH	Hourly	2007–2010	1
Total DIC	Weekly	2009–2010	1
Equilibrated pH	Weekly	2009–2010	1

Well pH, hourly stream pH, DIC, and equilibrated pH measurements are from the focal site, Taconazo-30.

Beginning in March 2007, a YSI 600xlm data sonde (YSI, Yellow Springs, OH, USA) was deployed in Taconazo-30 to record pH at hourly intervals. These probes were initially cleaned and calibrated every 3 weeks, but then weekly after October 2008. During calibration, the mV span of the pH probes was monitored with pH 4 and 7 buffers to assess the probe performance.

Between March 2009 and April 2011, weekly water samples were collected from Taconazo-30 for analysis of total dissolved inorganic carbon (DIC). Water samples were withdrawn approximately 10–15 cm below the water surface in a 10-ml plastic syringe. A 25-mm diameter, 0.45-μM syringe filter with a 22-gauge needle was attached to the syringe and 6 ml of water was gently expelled through the filter and needle to purge the ambient air. The remaining 4 ml of water was gently injected through the filter into a 10-ml glass serum bottle sealed with gray butyl rubber stoppers at ambient pressure. The syringe and serum bottles were inverted during this process to minimize loss of the overpressure as the needle was removed from the bottle. Serum bottles were pre-charged with 40 μl of 6 N HCl before they were sealed to achieve a final pH below 2 (so that essentially all DIC is converted to CO_2). Following equilibration on a shaker table at 24°C, typically 250 μl of gas from the headspace was analyzed for CO_2 on an SRI Instruments (Las Vegas, Nevada) gas chromatograph equipped with a thermal conductivity detector and 3-foot silica gel column (He carrier flow rate 10 ml/min; oven 90°C; detector 150°C). Carbon dioxide (aq) was calculated from the partial pressure of CO_2 (pCO_2) in the headspace by a form of Henry's Law (Flett and others 1976) after the ambient quantity of CO_2 in the bottle was subtracted. Using these DIC values and corresponding in situ pH values, we estimated pCO_2 by means of the freshwater setting for the program CO2SYS (Carbon Dioxide Information Analysis Center, Oak Ridge, Tennessee, USA).

In addition, beginning in May 2009, water samples were collected weekly from the Taconazo-30 and allowed to equilibrate with the atmosphere for 48 h. Following equilibration, pH was measured using the Hanna Instruments 9025 pH probe. The difference in pH between in situ and equilibrated measurements was taken to indicate the contribution of excess CO_2 to stream pH.

Statistical Analysis

We tested for seasonal differences in pH by comparing mean monthly pH (n = 14 in most cases) for each of the 13 study sites by means of analysis of covariance. We accounted for the potential effects

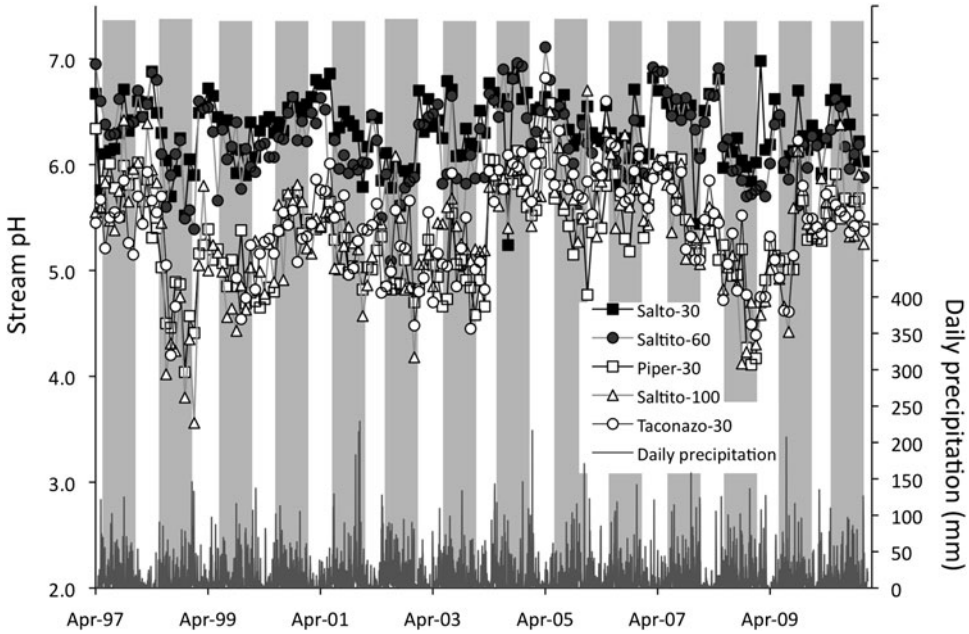

Figure 2. Fourteen-year time series (April 1997–December 2010) of monthly pH observations for five representative sites. Salto-30 and Saltito-60 are well buffered as a result of inputs of solute-rich inter-basin groundwater, whereas Piper-30, Saltito-100, and Taconazo-30 are low-solute, poorly buffered streams. Daily precipitation is shown on the *right axis*. *Shaded regions* identify the annual wet season.

of temporal autocorrelation by including the previous month's pH value as a factor in the model. Although sites are not truly independent due to hydrologic connectivity (Figure 1), chemically, upstream influence is minimal as solute concentrations typically increase greater than 5-fold between upstream and downstream sites on the same stream due to inputs of high-solute groundwater (Table 1). To investigate the effects of this assumption, we also ran models using stream (that is, combining sites along the same stream) or watershed instead of sites. In each case, the same focal variables remained significant. There were insufficient degrees of freedom to have both stream (or watershed) and site in the same model as some streams (or watersheds) are represented only by a single sampling site.

To test for the effects of seasonal precipitation on seasonal change in pH, another analysis of covariance was used in which the annual average difference between dry season (January–April) and wet season (May–December) pH for each site in a given year was predicted as a function of that year's total dry season rainfall and total wet season rainfall with site identity as a covariate. Because the onset of the wet season can occur as early as mid-April (Appendix S1), for this analysis, we defined dry season rainfall as occurring between Julian days 1–100 with wet season rainfall corresponding to the remainder of the year. All statistical analyses were conducted by means of Statistica software (version 9, StatSoft), with alpha set at 0.05.

Results

The long-term record of monthly stream pH readings shows differences among types of streams, as well as seasonal and interannual variability. Over 14 years of observations, low-solute streams (which receive no regional groundwater) have shown periods of extended pH declines (multiple months below pH 5.0) during the wet seasons of 1998, 1999, 2002, 2003, and 2008 (Figure 2). The most pronounced extended pH drops (below pH 4.5) in low-solute streams occurred in 1998 and 2008, following the two driest dry seasons on record. During other years, low-solute study streams had pH values near 6.0. Mean pH values for low-solute streams were typically below pH 5.5, whereas streams which received contributions of high-solute, interbasin groundwater had mean pH values above 6.2 (Figure 3A).

Analysis of seasonal trends from the long-term monthly pH data shows significant differences among months ($P < 0.0001$) after accounting for site identity and the previous month's pH (Table 3) with pH increasing during the dry season (January–April) and declining throughout the wet season (May–December) (Figure 3B). A site × month interaction term was not significant.

Dry season rainfall (defined as Julian day 1–100) varies greatly among years, ranging from 288 mm in 1998 to 1,274 mm in 2009 (Appendix S1). The magnitude of pH change following the onset of the wet season is positively related to the precipitation

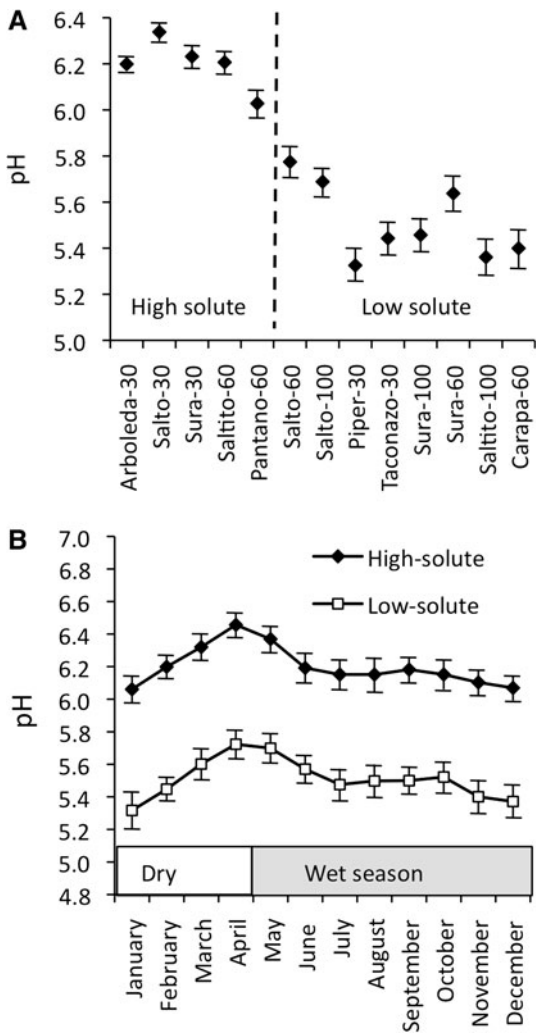

Figure 3. **A** Mean pH (and 95% CI) for the 13 study sites over 14 years of monthly observations. Streams sites are ranked in the order of decreasing average conductivity, representing contribution of solute-rich IGF. Low-solute stream sites to the right of the dashed line are not influenced by IGF contributions. **B** Mean pH (and 95% CI) for high-solute and low-solute study sites by month over the 14-year study period.

Table 3. Results for ANCOVA Characterizing Long-Term Monthly pH Observations as a Function of Site and Month, After Accounting for Effects of pH Observed in the Previous Month

Effect	SS	DF	MS	F	*P*
Prev. month pH	120.0	1	120.0	917.8	<0.00001
Site	12.6	11	1.1	8.7	<0.00001
Month	30.9	12	2.6	19.7	<0.00001
Site × month	9.5	132	0.1	0.6	0.999
Error	258.3	1976	0.1		

Adjusted r^2 = 0.60.

Table 4. Results from ANCOVA Characterizing Mean Decline in pH as a Function of Cumulative Dry Season Rainfall and Site

Effect	SS	DF	MS	F	*P*
Dry season precipitation	14.5	1	14.5	178.5	<0.0001
Wet season precipitation	1.3	1	1.3	15.5	0.0001
Site	0.5	12	0.0	0.5	0.91
Error	27.9	150	0.1	0.2	

Adjusted r^2 = 0.52.

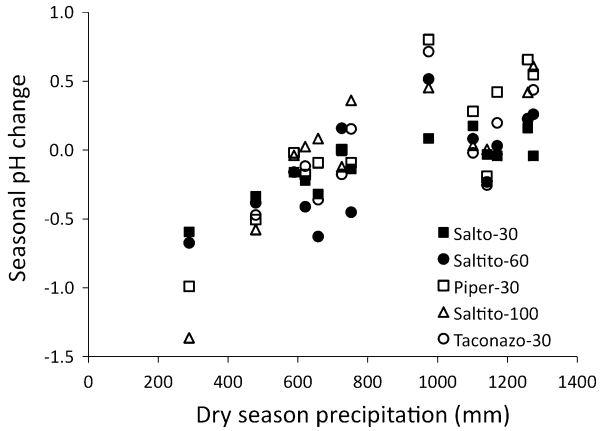

Figure 4. Mean seasonal change in pH between dry season (January–April) and wet season (May–December) over 14 years of monthly observations. For illustration, data are shown from two representative high-solute sites (Salto-30 and Saltito-60) and two low-solute sites (Piper-30 and Saltito-100). See Table 4 for results of ANCOVA.

totals for both the dry season and the wet season (adjusted r^2 = 0.52; $P < 0.0001$; Table 4). In other words, drought years result in an amplification of seasonal pH patterns, with larger pH drops accompanying the ensuing wet season. Although both dry season and wet season rainfall totals were significant factors, the parameter estimate for dry season rainfall was around 5-fold greater, indicating the greater sensitivity of the model to this parameter (Figure 4). Site identity was not a significant factor in the model.

Monthly samples from the focal stream, Taconazo-30, illustrate the relationship between pH of shallow (local) groundwater and stream water pH. From August 2003-December 2010, mean pH from well water samples was 4.78, compared to 5.55 from the stream. Well water pH was positively related to corresponding stream water pH measurements (R^2 = 0.44, $F_{1,81}$ = 64.01, $P < 0.001$; Figure 5).

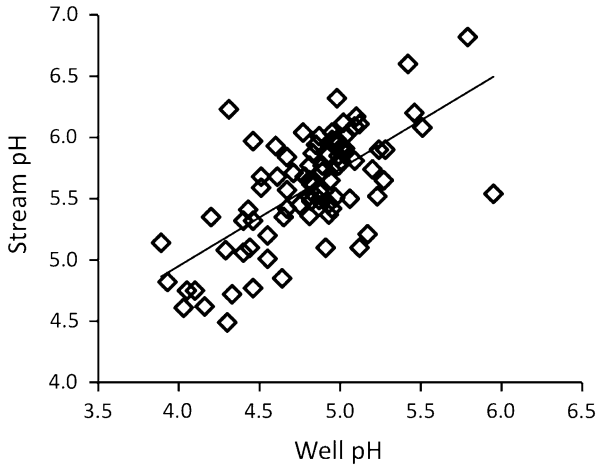

Figure 5. Relationship between monthly observations of well pH and stream pH over 8 years of monthly observations for the Taconazo-30 site. Well pH observations preceded corresponding stream pH measurements by 2 weeks. Result of least-squared regression is shown ($R^2 = 0.44$, $P < 0.0001$).

High temporal resolution pH measurements from the data sonde in the Taconazo-30 generally agree with the long-term monthly record and show pH drops of approximately 0.5 units associated with individual precipitation events (Figure 6). The high-resolution pH record for 2008, which had the second driest dry season in this 14-year record, illustrates the dynamics associated with seasonal transitions. Following the end of the rainy season in early January, stream pH gradually increased from 5.2 to 5.8 over a period of 2 months. Stream pH remained at or above 5.8 throughout the remainder of the dry season except for a brief drop to 4.9 following a 100-mm rain event on April 17. The wet season began in earnest on May 21 with an immediate pH drop and continued gradual decline over the following months (Figure 6).

Weekly DIC measurements from the Taconazo-30 from March 2009 to April 2011 ranged from 1.37 to 4.73 mg C l^{-1} and showed evidence of seasonal variability (Figure 7). The highest observations corresponded to the first measurements taken at the onset of the 2009 dry season following heavy rains in early March. DIC values declined over the following 6 months to 2.2 mg C l^{-1} and remained between 2 and 3 mg C l^{-1} throughout the 2010 dry season. DIC gradually increased throughout the 2010 wet season to 3.7 mg C l^{-1} then dropped below 2 mg C l^{-1} with the onset of the 2011 dry season. At ambient pH, these DIC values correspond to pCO_2 values ranging from 3,800 to 10,400 µatm or approximately 10–25× greater than atmospheric concentrations.

Weekly measurements of air-equilibrated stream water from May 2009 to November 2010 ($n = 73$) had an average pH of 5.98 ± 0.06, 0.5 pH units higher than in situ stream water during this period (5.43 ± 0.04). Assuming pure water at 25°C, these values would correspond to a mean original (in situ) DIC concentration of 2.13 mg C l^{-1}, a mean final DIC concentration of 0.19 mg C l^{-1} (equivalent to the DIC concentration of pure water equilibrated at 380 ppm CO_2), and a mean excess DIC concentration of 1.94 mg C l^{-1}.

Discussion

This 14-year dataset of tropical stream chemistry shows clear seasonal trends in stream pH with pH increasing through the dry season and decreasing through the wet season (Figures 2, 3). This seasonal pattern is amplified during drier years with

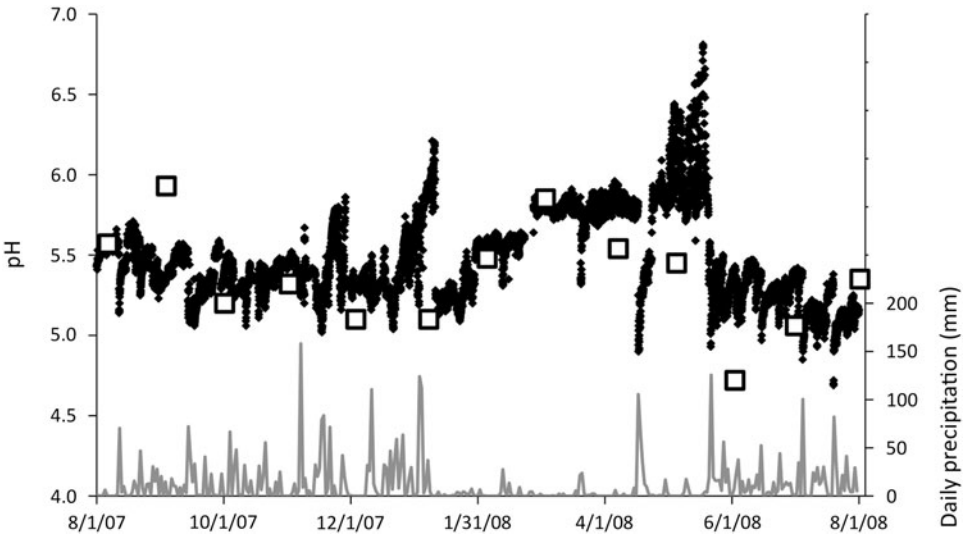

Figure 6. Twelve months of hourly pH observations from the Taconazo-30 site, beginning August 2007, shown on the *left axis*. Long-term monthly pH measurements are shown as *open squares*. Daily precipitation is shown in *gray* on the *right axis*.

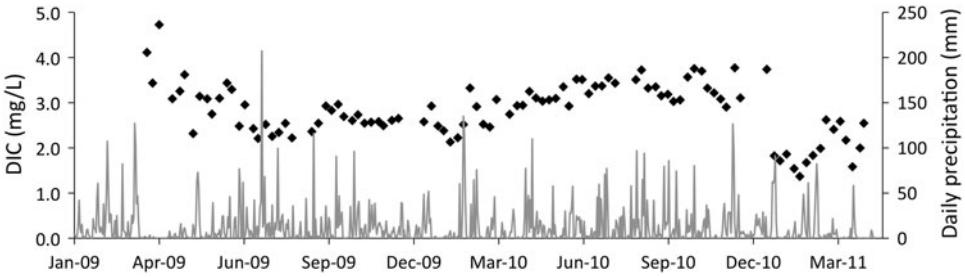

Figure 7. Thirteen months of weekly measurements of total DIC, shown on the *left axis*. Daily precipitation in shown in *gray* on the *right axis*.

more acidic conditions sustained throughout the wet season (Figures 2, 4). Seasonal acidification was most pronounced in low-solute streams, whereas streams which received solute-rich inter-basin groundwater were well buffered and maintained their more characteristic pH (Figure 3). Previous studies in temperate systems have found episodic acidification associated with preceding drought conditions (Laudon and others 2004; Clark and others 2005; Eimers and others 2008), but the absence of long-term datasets has precluded similar analyses for tropical streams.

Although several different mechanisms, including ANC dilution, mineral acidity, organic acid inputs, and redox reactions may contribute to seasonal pH patterns, our data suggest that CO_2 may be an important contributor to seasonal acidification in the low-solute study sites. Direct measurements of DIC and pH of in situ and air-equilibrated stream water samples from the Taconazo-30 indicate that dissolved CO_2 is the major component of the DIC and contributes to the low baseline pH in the low-solute streams. Measured values of DIC are sufficiently high to account for the pH associated with the DIC samples between March 2009 and April 2011. For example, the highest recorded DIC value (4.73 mg C l^{-1}) would produce a pH of 4.89 in pure water at 25°C. The corresponding in situ pH was 5.39, suggesting that some buffering was present despite the very low-solute levels in this stream. Similarly, the lowest DIC value recorded (1.37 mg C l^{-1}) would produce a pH of 5.16 in pure water, compared to an in situ pH of 5.46. Calculated pCO_2 concentrations from the Taconazo-30 in 2009–2011 (3,800–10,400 μatm) were similar to concentrations measured in first-order Amazonian streams by Johnson and others (2008). The seasonal DIC patterns further support the hypothesis that dissolved CO_2 is influencing stream pH. The highest observed DIC values occurred in March 2009, at the end of an extended wet season, and also at the end of the 2010 wet season. We observed DIC declines of approximately 2 mg C l^{-1} during the dry seasons of 2009 and 2011. Although variation in DIC was not related to variation in pH during this 2-year period, we note that 2009 and 2010 were both among the wettest ''dry seasons'' in our 14-year dataset, and streams showed little seasonal change in pH during this period. We speculate that in years with larger contrast between dry and wet seasons, larger CO_2 fluxes may contribute to the observed seasonal pH declines. Ongoing measurements will test this hypothesis.

Several lines of evidence from the long-term observations are consistent with the hypothesis that local subsurface water flows transport dissolved CO_2 to the streams, contributing to acidification. The pH of shallow groundwater is about 0.5 pH units lower than stream pH, exhibits the same seasonal patterns, and is positively related to corresponding stream pH measurements made 2 weeks later. In addition, recent measurements of DIC concentrations of shallow groundwater sampled in the Taconazo well are double that of stream water (JH Duff, U.S. Geological Survey, unpublished data) with CO_2 comprising nearly 100% of the DIC. Finally, stream pH drops associated with individual rain events and the seasonal declines at the onset of the wet season are consistent with the findings of Johnson and others (2007), who found that subsurface storm flows dissolve high concentrations of CO_2 derived from soil respiration, and that drier antecedent conditions correspond to larger CO_2 pulses. A similar influx of pCO_2 from groundwater, following periods of high rainfall, has been shown to cause seasonal pH declines in coastal lakes in Brazil (Marotta and others 2010).

Our results suggest that biogenic DIC is an important component of the pH chemistry in the low-solute study streams. Because every mole of HCO_3^- derived from dissolved CO_2 is accompanied by a mole of H^+ ions, the contribution of this HCO_3^- to alkalinity is effectively negated. The extremely low concentrations of Na^+, Ca^{2+}, Mg^{2+}, and K^+ in the low-solute streams (Table 1) indicate that H^+ ions generated from the dissociation of H_2CO_3

have not been replaced by these base cations (residual soils at LSBS have % base saturation of ~30%; Sollins and others 1994). The seasonal pH decline observed in our study streams differs from the response observed by Markewitz and others (2001) in a pasture stream in the Amazon basin, where CO_2-derived acidity was manifested as a net increase in alkalinity during the wet season. This difference can be attributed to the nutrient-rich soil in the Amazonian pasture, which contained ash from historic forest burning and had calcium levels of 2.68 $cmol_c\ kg^{-1}$ (0–10 cm) more than four times higher than the residual soils typical of LSBS headwaters which have calcium concentrations of 0.59 $cmol_c\ kg^{-1}$ (Sollins and others 1994). Although inputs of biogenic DIC from local groundwater also occur in the high-solute study streams, high concentrations of magmatic HCO_3^- account for most of the DIC pool in these streams (Genereux and others 2009), and the resultant alkalinity leads to pH values nearly one unit higher throughout the year relative to the low-solute study streams (Figure 3B). The observed pH seasonality of the high-solute sites is likely caused by dilution of base cations. These sites are located lower in the watershed (Figure 1); although they receive water from runoff throughout the watershed, a significant fraction of their discharge and an even greater fraction of their solute load is derived from IGF (Genereux and others 2005). During the dry season when local runoff is relatively low, the high-solute regional groundwater constitutes a larger fraction of discharge in these streams. For example, at the moderately high-solute Saltito-60 site, at the end of the driest dry season of record (May 1998), total base cation concentration (Na^+, Ca^{2+}, Mg^{2+}, and K^+) was approximately 2500 $\mu Eq\ l^{-1}$ and stream pH was 6.8. Two months later, after the onset of the wet season, total base cation concentration fell below 1000 $\mu Eq\ l^{-1}$ and stream pH fell to 5.6 (Appendix S2).

The sustained period of acidification in 1998 followed the historically large 1997–1998 El Niño Southern Oscillation (ENSO), which was characterized at LSBS by an extended drought (Clark and others 2003). Increased labile carbon in the soil following this ENSO event may have contributed to higher levels of dissolved CO_2 in shallow groundwater upon the return of the 1998 wet season. The unusually warm and dry conditions in early 1998 caused significant stress on the tree community at LSBS, contributing to decreased tree growth (Clark and others 2003, 2010) and increased root mortality (Espeleta and Clark 2007), potentially increasing stocks of labile organic carbon in the soil. With the onset of the wet season, increased soil moisture may have accelerated the decomposition of this additional organic matter, elevating soil CO_2 concentrations. During the 1998 wet season, Schwendenmann and Veldkamp (2006) documented elevated rates of soil CO_2 production at LSBS at depths of 2–3 m and elevated concentrations of CO_2 near the surface at a depth of 0.05 m (the highest in their >5 year record). The water table rise at the beginning of the wet season would have likely resulted in higher soil CO_2 concentrations due to decomposition and root respiration, as documented in other tropical watersheds (Johnson and others 2007), thereby increasing carbonic acid (H_2CO_3) concentrations. The low pKa (that is, high acid dissociation constant) of molecular H_2CO_3 (3.76 at 25°C) causes this compound to be a potent acidifying agent in soil porewater (Oh and Richter 2004), and potentially also in headwater streams fed by this shallow groundwater. Soil porewater in equilibrium with the soil CO_2 concentrations reported by Schwendenmann and Veldkamp (2006) at 0.05 m (~2% CO_2) would have a pH of approximately 4.76. Soil porewater in equilibrium with higher CO_2 levels from deeper soil layers (~3% at 2.5 m) would have a pH of approximately 4.67.

In addition to the potential effects of variation in precipitation on the dissolved CO_2 levels in soil porewater, the residence times of this groundwater likely vary with precipitation patterns. There are no data available from LSBS on residence times of shallow groundwater, but it is likely that extended residence times during the dry season allow for the buildup of dissolved CO_2, which is then flushed into streams once the wet season begins, as documented in other tropical wet forests (Johnson and others 2007).

The magnitude of pH drops in some years suggests that additional mechanisms are also contributing to acidification, as pCO_2 levels exceeding 100,000 µatm (12-fold greater than mean values for Taconazo-30 in 2010) would be required to fully account for the multiple observations below 4.5 in some low-solute streams during 1998 and 2008. Mineral acidity appears to be an unlikely contributor because long-term stream chemistry observations showed no increases in the anions of strong acids (that is, Cl^-, SO_4^{2-}, NO_3^-) corresponding to pH drops ($R^2 < 0.15$; Appendix S2). Organic acids are another potential contributor (for example, Buffam and others 2007). Assuming a charge density of 10 $\mu Eq\ mg^{-1}$ (Oliver and others 1983), dissolved organic carbon (DOC)

concentrations of approximately 10 mg l^{-1} would be required to completely account for observed pH declines. In contrast, DOC concentrations across these study streams are low and relatively constant (1.3 ± 0.05 mg l^{-1}) and are not associated with seasonal pH fluctuations (Appendix S2). Higher DOC values (5–15 mg C l^{-1}) have been measured underneath leaf litter at La Selva (Schwendenmann and Veldkamp 2005), which could represent an important source of organic acids during overland flow although it is unclear whether this flux would be sufficient to support the sustained acidification events observed here. Redox reactions, including oxidation of iron or sulfur, may also be important contributors to observed pH patterns although charge balances during the extended pH drop in 1998 do not support this mechanism (Appendix S2). Although we do not have comprehensive records of atmospheric, terrestrial, and aquatic data across multiple decades from LSBS that would allow for a definitive understanding of biogeochemical mechanisms influencing stream chemistry, as do some long-term temperate study sites (for example, Likens and Bormann 1995; Norton and others 2010), our record of long-term stream chemistry data, short-term stream experiments, and complementary terrestrial datasets makes this study unique among tropical stream ecosystems. Ongoing research will help elucidate the combination of mechanisms responsible for these seasonal and interannual patterns.

The biological effects of seasonal stream acidification in tropical streams are largely unknown, but potentially significant. Other low pH streams have been associated with decreased algal diversity (Niyogi and others 2002) and reduced density and diversity of invertebrate taxa (Rosemond and others 1992; Courtney and Clements 1998). There is some indication that the naturally low pH in low-solute streams at LSBS can determine algal and invertebrate community composition. Diatom communities in the low-solute streams are dominated by acidophilic taxa, whereas diatoms in the high-solute streams are predominantly estuarine taxa (R. Bixby, Univ. of New Mexico, unpublished data). Ramírez and others (2006) found no trend in invertebrate assemblages across streams at LSBS, but did detect decreases in insect density and biomass over the course of the year in 1998, concurrent with sustained declines in pH. Understanding how stream acidification shapes biotic interactions in these streams will be a fruitful area for future research.

Conclusions and Implications

Although stream acidification has received extensive attention in temperate ecosystems, the lack of long-term datasets has limited our understanding of acidification in tropical streams. Here, we use one of the few long-term stream chemistry datasets from the tropics to show that drought conditions amplify seasonal pH declines. Our findings illustrate a tight coupling between rainfall, terrestrial ecosystems, and aquatic ecosystems. Whether through altering stocks of labile C in soil, altering hydrologic flowpaths and soil water residence times, or other as yet unknown mechanisms, interannual variability in rainfall affects stream pH and potentially alters biotic communities. Changes in precipitation regimes are an expected consequence of global climate change with diminished rainfall and runoff expected in drier tropical regions and increased precipitation likely in wetter areas of the tropics (Milly and others 2005). Seasonal rainfall patterns are also predicted to intensify, leading to increased frequency of drought conditions (Rauscher and others 2008; Min and others 2011). The hydrologic and meteorological effects of climate change at high latitudes are expected to increase episodic acidification in northern boreal streams (Erlandsson and others 2010), and our results suggest that the expected intensification of seasonal rainfall patterns in the Mesoamerican tropics appears likely to increase the magnitude of seasonal acidification in these study streams and in weakly buffered streams of other lowland tropical wet forests in the region.

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