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Experimental acidification of two biogeochemically-distinct neotropical streams: Buffering mechanisms and macroinvertebrate drift

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HIGHLIGHTS

- We experimentally acidified a poorly and a well buffered stream in Costa Rica.
- The well buffered stream neutralized 745 μeq/L (96% of the acid added).
- The poorly buffered stream only neutralized 27.4 μeq/L (40% of the acid added).
- Protonation of HCO_3^- was the most important buffering mechanism in both streams.
- Macroinvertebrate drift increased in both streams in response to acidification.

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ABSTRACT

Research into the buffering mechanisms and ecological consequences of acidification in tropical streams is lacking. We have documented seasonal and episodic acidification events in streams draining La Selva Biological Station, Costa Rica. Across this forested landscape, the severity in seasonal and episodic acidification events varies due to interbasin groundwater flow (IGF). Streams that receive IGF have higher concentrations of solutes and more stable pH (~6) than streams that do not receive IGF (pH ~5). To examine the buffering capacity and vulnerability of macroinvertebrates to short-term acidification events, we added hydrochloric acid to acidify a low-solute, poorly buffered (without IGF) and a high-solute, well buffered stream (with IGF). We hypothesized that: 1) protonation of bicarbonate (HCO_3^-) would neutralize most of the acid added in the high-solute stream, while base cation release from the sediments would be the most important buffering mechanism in the low-solute stream; 2) pH declines would mobilize inorganic aluminum (Ali) from sediments in both streams; and 3) pH declines would increase macroinvertebrate drift in both streams. We found that the high-solute stream neutralized 745 μeq/L (96% of the acid added), while the solute poor stream only neutralized 27.4 μeq/L (40%). Protonation of HCO_3^- was an important buffering mechanism in both streams. Base cation, Fe^{2+}, and Ali release from sediments and protonation of organic acids also provided buffering in the low-solute stream. We measured low concentrations of Ali release in both streams (2-9 μeq/L) in response to acidification, but the low-solute stream released double the amount Ali per 100 μeq of acid added than the high solute stream. Macroinvertebrate drift increased in both streams in response to acidification and was dominated by Ephemeroptera and Chironomidae. Our results elucidate the different buffering mechanisms in tropical streams and suggest that low-solute poorly buffered streams might be particularly vulnerable to episodic acidification.

1. Introduction

Acidification is a major stressor to aquatic ecosystems (Driscoll et al., 2001). Recognizing the negative acidification effects of elevated sulfate (SO_4^{2-}) and nitrate (NO_3^-) deposition to watersheds led to passage of emission cap legislation in the US and Europe (Stoddard et al., 1999). While recovery has been observed, there are still episodic acidification events in many watersheds (Kowalik et al., 2007; Laudon, 2008; Lawrence et al., 2008; Wigington et al., 1996). Episodic acidification events are defined as periods of rapid and temporary (days to weeks) declines in stream water pH and acid neutralizing capacity (Laudon et

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al., 2004). Episodic acidification can be caused by base cation dilution from high discharge (due to snow melt or precipitation), flushing organic acids or oxidized nitrogen and sulfur from soils, and inputs of marine aerosols (Wigington et al., 1996). These low pH events can have detrimental effects on fish (Baker et al., 1996) and macroinvertebrates (Bernard et al., 1990). While much research has been conducted in North American and European streams on the causes and consequences of episodic acidification, tropical streams have received little attention (Kuylenstierna et al., 2001).

Mechanisms that buffer streams against pH changes include: 1) weathering of soil minerals, 2) dissolution of inorganic Al (Al_i), 3) ion exchange with sediments, and 4) changes in aqueous species such as the carbonate–bicarbonate system (Likens and Bormann, 1995). Understanding the relative role of these buffering mechanisms can help identify streams susceptible to episodic acidification (Norton et al., 2000). Experimental acidification has been used to examine the vulnerability of streams to, and the consequences of, acidification. A six month experimental addition of sulfuric acid (H_2SO_4) to a stream in the Hubbard Brook Experimental Forest increased export of Al_i, Ca^{2+}, Mg^{2+}, and K^{2+}, and decreased aquatic insect emergence (Hall et al., 1980). Short term (<24 h) acidification experiments report similar buffering mechanisms in response to inorganic acid addition: sediment release of base cations, release of Al_i, adsorption of SO_4^{2-}, and protonation of bicarbonate (HCO_3^-) and weak organic acids (Hedin et al., 1990; Hruska et al., 1999; Navratil et al., 2003; Norton et al., 1992; Norton et al., 2000). Environmental conditions and underlying geology determine the relative importance of these buffering mechanisms (Goss and Norton, 2008).

Much of the work on episodic acidification in temperate streams has focused on mineral acidity (NO_3^- and SO_4^{2-}, Laudon et al., 2004) and dissolved organic carbon (DOC, Hruska et al., 1999). The lack of long-term records and experimental data from tropical streams has limited our understanding of the buffering mechanisms in these systems. The pH of tropical streams is most likely affected by carbonate equilibrium, availability of base cations in soils, and organic acidity (Markewitz et al., 2001). Recent work on the supersaturation of carbon dioxide (CO_2) in tropical Amazonian rivers and streams (Johnson et al., 2008; Mayorga et al., 2005; Richey et al., 2002) suggests that carbonate equilibrium is important in determining the pH of tropical streams. Carbonate equilibrium might play an important role in buffering Central American streams, where deep geothermal activity and long subsurface flowpaths (2400–4000 years; Solomon et al., 2010) provide inputs of high HCO_3^- water emerging in springs and groundwater (Genereux et al., 2009; Pringle et al., 1993). The relative role that carbonate equilibrium, sediment release of base cations, and protonation of organic acids play in regulating the pH of Central American streams remains poorly understood.

We previously reported spatial variability in seasonal and episodic acidification events in streams draining a forested landscape in Costa Rica (Small et al., 2012). Spatial variability in seasonal and episodic acidification events is driven by interbasin groundwater flow (IGF): streams that do not receive IGF of bicarbonate-rich water had lower pH (pH of 5) and more pronounced seasonal and episodic pH drops compared to streams that receive IGF (pH of 6) (Small et al., 2012). Long-term data and short-term degassing experiments suggest that elevated dissolved CO_2 is primarily responsible for low baseline pH and seasonal acidification events in low-solute (no IGF) streams, though other mechanisms such as redox reactions of iron and sulfur compounds could also be contributing to pH drops (Small et al., 2012). Our current hypothesis is that an influx of soil-derived CO_2 via subsurface flow paths is causing pH shifts in low-solute streams (Small et al., 2012). In this study, our goal was to isolate the effects of stream water pH drops on stream buffering capacity and macroinvertebrate drift behavior from other environmental parameters that vary in our long-term dataset, such as discharge and temperature (Small et al., 2012). To do this, we experimentally acidified a low-solute, poorly buffered (no IGF) and a high-solute, well buffered stream (receives IGF). We used hydrochloric acid for the experimental acidification because (1) it is not biologically available, so it would not alter microbial and macroinvertebrate activity as other nitrogen and sulfur containing acids could (De Leeuw et al., 2003), (2) it was logistically more feasible, and (3) it achieved the goal of reducing pH to stimulate a geochemical response. We hypothesized that: 1) HCO_3^- equilibrium would provide the majority of the buffering capacity in the high-solute stream, while base cation exchange with the sediments would be the most important buffering mechanism in the low-solute stream; 2) pH declines would mobilize more Al_i from sediments in the low-solute stream than the high-solute stream; and 3) pH declines would increase macroinvertebrate drift in both streams.

2. Methods

2.1. Site description

We conducted this study at La Selva Biological Station, Costa Rica (10°26′ N, 84°01′ W). The 1536 ha reserve is the lowland end of the last protected biological corridor spanning an altitudinal gradient on the Caribbean slope of Central America. Annual precipitation averaged 4240 mm from 1958 to 2002 (Organization for Tropical Studies, La Selva Meteorological Data, www.ots.ac.cr/meteoro/default.php?pestacion=2). The dry season occurs from February through April with <200 mm of rain per month. The wet season is from May to December when average monthly rainfall is greater than 320 mm. January is usually intermediate with an average rainfall of 274 mm. Stream water temperature is relatively constant throughout the year (24–27 °C, http://streamslaselva.net).

Geology of La Selva consists of Quaternary volcanic rocks (mainly andesitic to basaltic lavas, ignimbrites, volcanic tuffs and breccias) embedded with mudflow deposits and ash (Alvarado-Induni, 1990). La Selva soils are highly weathered and derived from basaltic andesites, thought to be ~1.2 Ma (Alvarado-Induni, 1990; Porder et al., 2006). Major soil orders at La Selva were originally classified as Ultisols (covering 45% of the area, primarily Typic Tropohumults) and Inceptisols (55% of area, various suborders), (Sollins et al., 1994). Recently the soils at La Selva have been reclassified as Oxisols of different ages (Kleber et al., 2007). These soils have low cation exchange capacity and their mineralogy is dominated by iron and aluminum oxides (Kleber et al., 2007).

Streams at La Selva reflect the diversity of stream chemistry throughout Central America due to the influence of IGF (Pringle and Triska, 1991). This IGF emerges in seeps at the base of Pleistocene lava flows (Genereux et al., 2009; Pringle et al., 1993). Streams receiving IGF have high concentrations of cations (up to 900 μeq/L Ca^{2+}, 1900 μeq/L Na^+, 2000 μeq/L Mg^{2+}) and anions [up to 790 μeq/L Cl^-, 292 μeq/L SO_4^{2-}, 1000 μeq/L HCO_3^-, 11 μeq/L $H_2PO_4^-$, (Pringle et al., 1993)] and high alkalinity (3000 μeq/L). Nearby streams that do not receive IGF have low cation (<100 μeq/L Ca^{2+}, <87 μeq/L Na^+, <82 μeq/L Mg^{2+}) and anion (<80 μeq/L Cl^-, <40 μeq/L SO_4^{2-}, <30 μeq/L HCO_3^-, <1 μeq/L $H_2PO_4^-$) concentrations, and low alkalinity (5 μeq/L). Streams with and without IGF have relatively high inorganic nitrogen concentrations (>10 μeq/L NO_3^-, 1 μeq/L NH_4^+, Pringle et al., 1993).

2.2. Long-term pH measurements

In this study we focused on three streams at La Selva: Arboleda-30, Arboleda-Trib (a tributary of the Arboleda-30) and Taconazo-30 (Table 1). Arboleda-30 and Arboleda-Trib are high-solute well-buffered streams, while Taconazo-30 is low-solute, unbuffered stream (Table 1). Beginning in April 1997 we measured pH, conductivity and temperature during the first week of every month using a hand held pH meter (model 9025 Hanna Instruments, Woonsocket, Rhode Island, USA). All measurements and samples were collected by the same technician. The probe was calibrated at pH 4 and 7 the day measurements were taken. From October 1998 to September 1999 data were not collected from Taconazo-30 and Arboleda-30 while weirs were being installed. We started monitoring stream pH in Arboleda-Trib in 2004.

Table 1
Physical and chemical characteristics of the three streams examined in this study. Data for Arboleda-30 are long-term means (1997–2009), while Arboleda-Trib and Taconazo-30 data were before the acidification experiment in two stations (10 and 100 m downstream of the injection site). BDL — below detection limit.

	Arboleda-30	Arboleda-Trib		Taconazo-30	
		10 m	100 m	10 m	100 m
Discharge (L/s)	170	14	16.5	65	72
Temperature (°C)	25.2	23.7	23.8	23.1	23.4
pH	6.13	6.05	6.34	5.05	5.28
Conductivity (uS/cm)	277	39	94	15	15
DOC (μeq/L)	3.44	1.77	5.60	9.31	3.49
Ca^{2+} (μeq/L)	793.4	90.1	221.1	23.9	28.1
Cl^- (μeq/L)	395.0	86.5	154.1	66.3	61.6
H_2PO_4 (μeq/L)	6.37	0.83	1.11	BDL	BDL
K^+ (μeq/L)	102.3	17.5	27.4	8.4	8.2
Mg^{2+} (μeq/L)	1100.1	113.8	335.6	24.2	25.9
Na^+ (μeq/L)	813.5	119.1	278.3	68.0	60.5
NO_3^- (μeq/L)	12.1	18.0	11.9	7.1	9.9
NH_4^+ (μeq/L)	0.90	0.56	0.18	0.68	0.62
SO_4^{2-} (μeq/L)	91.1	12.3	25.1	8.1	8.3
Alkalinity (μeq/L)	3550.0	172.4	796.1	2.4	6.9

To examine short-term fluctuations in pH, in March 2007 we started monitoring pH hourly in the Arboleda-30 and the Taconazo-30 using YSI 600 XLM datasondes (YSI, Yellow Springs, Ohio, USA). These pH probes are cleaned and calibrated weekly to bi-monthly and the mV spread of all pH probes are scrutinized during calibration.

2.3. Acidification experiments

Our goal was to experimentally acidify 100-m reaches of a high-solute (buffered) and a low-solute (unbuffered) stream. However, the high-solute stream sites that we have been studying as part of the long-term research program were too large to make acidification feasible. The best site that received IGF and was small enough to acidify was a tributary to the Arboleda (Arboleda-Trib, Table 1). However, the only 100-m reach of stream available before Arboleda-Trib joined the Arboleda-30, included a 30-m section that was above the point where two major seeps with high solute IGF entered the tributary. Therefore, our experimental reach in the Arboleda-Trib included a 30-m section of stream with lower buffering capacity (alkalinity 172 μeq/L) and a 70-m section of high-solute well buffered stream (alkalinity 796 μeq/L, Table 1). Because our goal was to examine the immediate response to acidification, we restricted our acidification experiments to 3 h acid additions followed by 3 h recovery periods.

Based on stream water alkalinity we determined the volume and rate of acid addition required to drop the pH by at least one unit in each stream. On 10 March 2009 we added 5.04 L of HCl (12 N) to Taconazo-30 at a rate of 28 ml/min from 09:00 to 12:00. On 12 March 2009 we added 9.72 L of HCl (12 N) to the Arboleda-Trib at a rate of 54 mL/min from 09:00 to 12:00. During both injections we also added Rhodamine WT (RhWT) as a conservative tracer (target concentration = 100 μg/L) at a rate of 32 mL/min. We monitored pH, conductivity, dissolved oxygen, and temperature every 15 min using YSI 600 XLM datasondes.

During acidification (09:15–12:00) and recovery (12:15–14:45) we used ISCO automated samplers (Teledyne ISCO, Lincoln NE, USA) to collect water samples every 15 min for cation (Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+, Fe^{2+}, Mn^{2+}, Al^{n+}) and anion (NO_3^-, SO_4^{2-}, Cl^-, PO_4^{3-}) analyses. All samples were filtered in the laboratory (GFF, 0.7 μm pore size) immediately following the experiment. Samples analyzed for Ca^{2+}, Mg^{2+}, K^+, Na^+, Fe^{2+}, Mn^{2+}, and Al_i were acidified and analyzed using inductively coupled plasma atomic emission spectrometer (ICPMS, Perkin-Elmer Elan 6000, Waltham, MA). Samples analyzed for NH_4^+, H_2PO_4, NO_3^-, SO_4^{2-}, Cl^- and DOC were kept frozen until analyses. Samples were analyzed for SO_4^{2-} and Cl^- using ion chromatography (ICS-2000, Dionex Corporation, Sunnyvale, California, US). $H_2PO_4^-$, NO_3^- and NH_4^+ were analyzed on an automated flow injection analyzer (Rapid Flow Autoanalyzer-300, Alpkem corporation). DOC was measured on a Shimadzu TOC-VCPH high temperature, catalytic combustion infrared detector (Shimadzu Corp., Kyoto, Japan). We also collected samples for total dissolved inorganic C (DIC) hourly that were acidified to pH <2. Gas samples from the headspace of 14-mL serum bottles were analyzed for CO_2 using an SRI 310 C gas chromatograph with a 3-foot silica gel column (SRI Instruments, Las Vegas, NV).

We used Visual Minteq software (http://www.lwr.kth.se/English/OurSoftware/vminteq/) for charge balance and Al_i speciation calculations. To determine buffering mechanisms we looked at the average concentration changes (in μeq/L) between hourly samples during acid addition and the initial concentration of that ion before the acid injection (9:00 sample). We did the full charge balance for the hourly samples to match the hourly total DIC samples. To estimate the buffering potential of organic acids we used the following assumptions: 1) average charge density was 4.5 μeq/L per mg DOC over the entire pH range, 2) 55% of the DOC existed as organic acids that could be protonated, and 3) and weak organic acids were completely titrated (Goss and Norton, 2008).

2.4. Macroinvertebrate drift measurements

To determine ecological responses to acidification, we measured macroinvertebrate drift immediately before, during acidification, and during recovery in the two streams. Three stations were sampled: upstream, 10 m downstream, and 100 m downstream from the point of acid addition. Samples were collected using small drift nets (mouth: 0.06 m^2; length: 0.5 m; mesh size: 250 μm). Four nets were evenly distributed across the channel filtering the water column for 15 min. Current velocity was measured with a Marsh McBirney® current meter. Invertebrate drift density was calculated by dividing the number of invertebrates in a sample by the volume of water sampled. Water volume was calculated by multiplying net area (which was completely submerged), current velocity at the net mouth, and sampling time.

All samples were preserved in 80% ethanol. Aquatic insects were largely identified to genus or family level. Non-insect invertebrates were identified to class. Identifications were done by AquaBio Lab, San Jose, Costa Rica.

2.5. Statistical analyses

Comparisons of drift densities between sampling stations and times were conducted with a permutational multivariate analysis of variance (PerMANOVA, Anderson, 2001), because our data did not meet criteria for parametric tests. The Euclidean distance was used as the distance measure. Whenever significant differences were obtained among stations, times, or their interaction, we conducted pairwise comparisons. We used BetaDisper to assess homogeneity of dispersions to assess whether there was homogeneity of variances among stations and sampling times (Anderson, 2006). Analyses were completed using R version 2.15 and the vegan package.

3. Results

3.1. Long-term pH record

Taconazo-30 pH was consistently lower (~5) than the Arboleda-30 and the Arboleda-Trib (both ~6; Fig. 1). The lowest pH in Taconazo-30 was 4.20 in August 1998. In Taconazo-30 there were 27 pH measurements below 5.0, in the Arboleda-Trib there was only one (February 2006), and none in the Arboleda-30 (Fig. 1). Out of 14,000 measurements in the hourly dataset, there were 826 measurements of pH lower than 5.0 in the Taconazo-30, and none in the Arboleda-30 (Fig. 2 A–D). We also documented in 46 occasions in the Taconazo-30 in which pH dropped by more than 0.30 pH units (which corresponds to a doubling of H^+) in an hour (Fig. 2E and F provide examples).

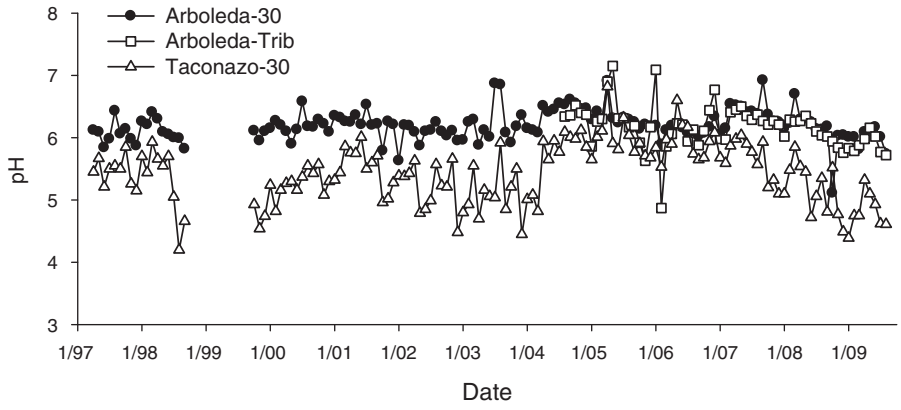

Fig. 1. Long-term monthly pH measurements in the Arboleda-30 (1997–2009), Arboleda-Trib (2004–2009) and Taconazo (1997–2009) at La Selva Biological Station, Costa Rica. No pH was measured from 1998 to 1999 due to weir construction.

The pH in the Taconazo-30 was lower during the rainy season (May–December) than during the dry season (February–April).

3.2. Experimental acidification

We measured an 18% discharge increase in Arboleda-Trib and an 11% increase in Taconazo-30 between 10 and 100 m stations using RhWT (Table 1); discharge did not change during the experiments (data not shown). There were differences in the water chemistry between 10 m and 100 m stations in the Arboleda-Trib before the acidification experiment. The 10 m station had low cation and anion concentrations, while the 100 m station had on average double the concentrations of cations and HCO_3^- (Table 1). The difference was due to inflow of two seeps that discharged high-solute, IGF 70-m above the 100 m station. Using a hydrological mixing model based on the Cl^- concentrations of the seeps and the 10 and 100 m stations before the

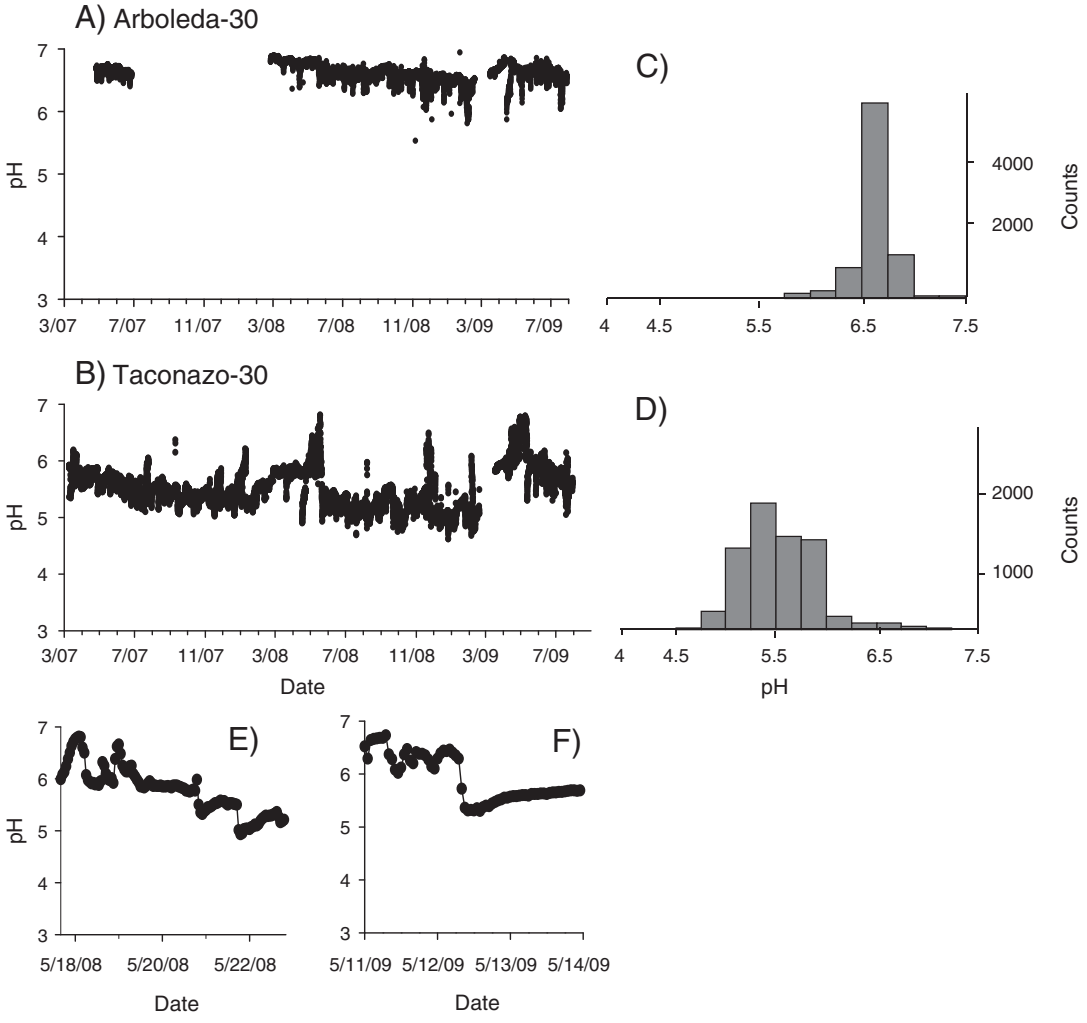

Fig. 2. Continuous pH measurements from the Arboleda-30 (A) and Taconazo (B) from March 2007 to July 2009, La Selva Biological Station, Costa Rica. Gap in Arboleda-30 data was due datasonde malfunction. Frequency distribution of pH measurements in Arboleda-30 (C) and Taconazo (D). Examples of natural acidification events in Taconazo (E, F).

addition, we estimated that 16–19% of the water at the 100 m station was lGF from the seeps (Genereux et al., 2002). This estimate agrees with the change in discharge measured using our conservative tracer. The discharge increase along the Taconazo-30 reach was largely due to overland surface water flow as the experiment was conducted following 10 days of rain.

3.2.1. Arboleda-Trib 10 m station

In the first 30 min of the experimental acidification we decreased the pH by 3.1 units, with the pH returning to background levels 45 min after stopping the injection (Fig. 3A). Due to a malfunction in the injection setup the pH at the 10 m station increased to 4.33 at 10:15. After the repair, pH dropped again to 2.71 (Fig. 3A). During the addition of HCl, Cl^- concentrations increased on average by 1174 μeq/L. H^+ concentrations increased by 833 μeq/L, indicating that 30% of the acid added was neutralized. The main buffering mechanism was protonation of HCO_3^- (192 μeq/L), followed by release of base cations (24 μeq/L), Fe^{2+} (11 μeq/L) and Al_i (9 μeq/L). Total Al_i increased from 1.18 to 9.51 μeq/L at the beginning of the injection, but then declined almost to background after stopping the injection (13:00, Table 2). During the acid addition, we measured rapid release of Fe^{2+} and Al_i accompanied by release of H_2PO_4 (Fig. 4A). There was an initial increase in Ca^{2+} concentration (from 90 to 97 μeq/L) at the beginning of the injection, followed by a decline and stabilizing below initial concentrations after stopping the acid injection (13:00, Table 2). Na^+ increased initially, and after some fluctuations slowly declined to below background at the end of the experiment (Table 2). There was a decline in DOC from the 9:00 sample and concentrations remained below background for the remainder of the experiment (Table 2). Both SO_4^{2-} and NO_3^- increased initially by 2 and 4 μeq/L respectively, and then fluctuated around background during the recovery (Table 2).

3.2.2. Arboleda-Trib 100 m station

During the experimental acidification pH decreased from 6.34 to 4.35 (Fig. 3A). On average, Cl^- concentrations increased by 776 μeq/L, while H^+ only increased by 30 μeq/L, indicating that 96% of the added acid was neutralized. Most of the buffering was through protonation of HCO_3^- (on average 64% of the acid added or 481 μeq/L, Fig. 4B) and release of base cations (13%, 100 μeq/L). Release of Fe^{2+} and Al_i, and protonation of organic acids each played minor roles in buffering (<5 μeq/L each). Ca^{2+} and Mg^{2+} increased during the first hour of the injection (from 221 to 283 μeq/L and 335 to 389 μeq/L, respectively), and then declined below background concentrations during the recovery (to 211.8 and 337.9 μeq/L, respectively; Table 2). DOC declined during the first hour of acid injection (from 5.6 to 1.6 μeq/L), remained low during the acid injection, and then increased to 3.45 μeq/L during the recovery period (Table 2). Both SO_4^{2-} and NO_3^- showed an initial increase and then remained fairly constant above background throughout the acidification and recovery (Table 2).

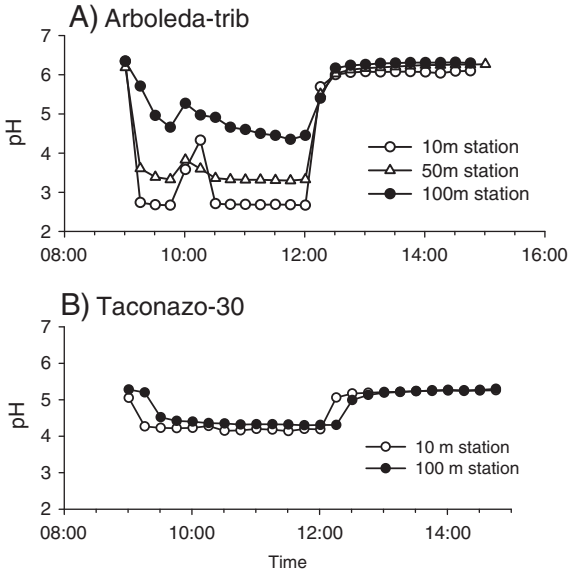

Fig. 3. pH in 3 and 2 stations in Arboleda-Trib (A) and Taconazo-30 (B) respectively, during the acidification experiments.

3.2.3. Taconazo-30 10 m station

Experimental acidification decreased the pH by 1.1 units (Fig. 3B). On average Cl^- concentrations increased by 69 μeq/L, while H^+ increased by 54.1 μeq/L, indicating the stream neutralized 21% of the added acid. Protonation of organic acids and HCO_3^- both contributed similar buffering (5.1 and 6.2 μeq/L). Release of base cations, Al_i, and Fe^{2+} all had similar buffering contributions (<2%, <2 μeq/L). DOC declined from 9.31 to 4.11 μeq/L during the first hour of the injection and continued to decline during the acidification and recovery (Fig. 4C). Ca^{2+} decreased slightly (from 23.9 to 23.5 μeq/L) during the experiment, and increased slowly during the recovery. Al_i increased from 2.6 to 4.6 μeq/L and then declined below background concentration during the recovery. Both SO_4^{2-} and NO_3^- increased during acidification and recovery (Table 2).

3.2.4. Taconazo-30 100 m station

Acidification decreased the pH by 1.1 units (Fig. 3B). Cl^- concentrations increased on average by 68 μeq/L, while H^+ concentrations increased by 40.6 μeq/L. The stream neutralized 40% of the added acid through protonation of HCO_3^- (12 μeq/L), followed by increases in base cations (8.3 μeq/L, Fig. 4D), release of Al (2 μeq/L) and protonation of organic acids (1.5 μeq/L). Ca^{2+} increased during the first hour of the acidification (28 to 33 μeq/L), decreased during the remainder of the acid addition (29 μeq/L), and declined below pre-injection concentrations (22 μeq/L) when the acid was stopped (Fig. 4D). Al_i increased during the acidification (from 1.79 to 4.5 μeq/L) and then declined to 2 μeq/L during the recovery period. DOC also declined (3.49 to 1.76 μeq/L) during the first hour of acidification and remained low for the rest of the sampling period (Table 2).

3.3. Macroinvertebrate drift

Drift composition was dominated by aquatic insects, mostly the families Leptophlebiidae, Baetidae, and Caenidae (Ephemeroptera) and Chironomidae (Diptera) (Table 3). Large numbers of cladocera and copepods were found in some samples. Other groups present in relatively low densities included Leptoceridae and Hydropsychidae (Trichoptera), water mites (Hydracarina), and polychaeta worms (Table 3). Drift species density ranged from 2 to 4 species/m^3 and total drift densities were higher in the Arboleda-Trib (up to 10.74 individuals/m^3) than in the Taconazo-30 (up to 0.70 individuals/m^3).

Total invertebrate drift densities remained low (<0.66 individuals/m^3) and constant over time above the site of acid addition in both streams (Table 4). At the upstream station, total drift densities remained similar over time in both streams (PerMANOVA comparisons $p > 0.05$; Fig. 5). At the 10 m station, total drift peaked at 12:00 and then decreased toward the end of the experiment at Arboleda-Trib (PerMANOVA comparisons $p = 0.06$) but remained unchanged at Taconazo (Fig. 5). At the 100 m station, total drift also peaked at 12:00, decreasing by 14:00 at Arboleda-Trib (Fig. 5). Taconazo had a similar significant increase in drift, but did not show signs of a decrease toward the end of the experiment (PerMANOVA comparisons $p > 0.05$; Fig. 5). Overall, drift responses to acidic addition were stronger in Arboleda-Trib than in Taconazo (Fig. 5).

Ephemeroptera drift responses to acidification were similar to those described for total drift densities (Table 4). Dipterans were less abundant in drift and their response to acidification was more variables, resulting in a lack of significant effects (Table 4). Species richness in drift was also similar among stations and times (Table 4).

Table 2
Ion concentrations during experimental acidification in Arboleda-Trib (12 March, 2009) and Taconazo-30 (10 March, 2009) in La Selva Biological Station, Costa Rica. Times in bold denote samples collected during acid addition. BDL — below detection limit.

Station	Ca^{2+}	K^+	Mg^{2+}	Na^+	NH_4^+	DOC	HCO_3^-	Al_i	Fe	Cl^-	H_2PO_4	SO_4^{-2}	NO_3^-
	(μeq/L)	(μeq/L)	(μeq/L)	(μeq/L)	(μeq/L)	(μeq/L)	(μeq/L)	(μeq/L)	(μeq/L)	(μeq/L)	(μeq/L)	(μeq/L)	(μeq/L)
Arboleda-Trib 10 m													
9:00	90.1	17.5	113.8	119.1	0.56	1.77	137.0	1.18	1.36	86.5	0.83	12.3	18.0
10:00	97.1	17.7	122.8	121.5	1.24	1.09	1.00	9.51	16.2	1304.0	2.33	14.6	22.0
11:00	73.1	13.2	94.9	97.6	0.26	1.10	0.12	8.20	11.3	1154.4	1.76	13.1	18.5
12:00	94.4	13.4	123.4	126.7	0.26	1.11	0.15	9.04	11.8	1324.1	1.18	13.1	12.1
13:00	82.7	13.4	117.4	125.0	0.11	1.14	234.0	1.87	2.54	133.5	0.06	18.1	16.0
14:00	82.7	13.0	117.7	123.7	0.17	1.30	256.0	1.59	1.79	46.7	0.08	6.2	17.7
14:45	73.4	11.4	102.9	114.8	0.17	0.97	205.0	1.67	2.15	97.8	0.26	12.9	18.1
Arboleda-Trib 100 m													
9:00	221.1	27.4	335.6	278.3	0.18	5.60	550.0	2.23	3.01	154.1	1.11	25.1	11.9
10:00	283.3	27.7	389.1	278.3	0.66	1.63	115.2	2.67	6.98	910.1	0.96	30.3	15.1
11:00	276.2	29.6	376.2	277.3	2.47	1.60	23.0	5.13	9.13	930.3	0.96	25.5	15.7
12:00	263.4	27.2	361.4	271.2	0.70	1.60	17.0	5.15	9.13	951.8	0.75	26.2	15.7
13:00	207.5	25.1	320.9	274.5	0.80	2.56	697.0	1.65	2.58	159.1	2.01	27.2	15.5
14:00	211.0	24.2	341.0	287.0	0.86	2.29	746.0	1.93	2.44	205.0	0.81	37.3	14.8
14:45	211.8	23.7	337.9	293.6	2.37	3.45	732.0	7.50	3.62	180.3	1.40	30.7	14.7
Taconazo-30 10 m													
9:00	23.9	8.44	24.2	68.0	0.68	9.31	1.41	2.66	1.93	66.3	BDL	8.06	7.12
10:00	23.5	7.67	23.4	66.4	0.41	4.11	1.41	3.54	1.90	128.7	BDL	8.45	9.84
11:00	24.3	8.24	24.9	69.5	1.63	3.58	2.83	4.66	1.29	142.1	BDL	8.22	10.5
12:00	23.8	8.08	24.4	69.8	0.77	3.18	2.18	4.11	1.68	135.9	0.23	8.86	9.72
13:00	19.6	8.26	22.6	68.7	0.94	3.46	26.2	1.59	0.82	71.8	0.01	8.42	11.3
14:00	20.5	7.98	22.5	68.6	1.28	2.86	28.8	1.48	0.54	70.0	BDL	7.76	10.4
14:45	36.0	8.06	26.0	66.9	1.71	2.81	23.5	1.88	1.25	68.4	BDL	9.44	16.0
Taconazo-30 100 m													
9:00	28.1	8.26	25.9	60.5	0.62	3.49	15.6	1.79	1.15	61.6	BDL	8.33	9.94
10:00	30.0	8.24	27.5	61.7	2.38	1.76	3.83	3.64	1.68	124.1	0.09	8.35	10.2
11:00	30.3	8.77	26.8	72.0	1.97	1.96	3.30	4.06	1.54	134.9	BDL	8.50	9.79
12:00	29.0	8.08	26.9	63.2	1.98	1.86	2.59	4.50	2.04	130.5	BDL	8.42	10.0
13:00	24.0	7.65	22.6	59.3	1.74	2.09	23.2	1.84	1.29	68.0	BDL	8.84	10.0
14:00	24.5	7.70	22.9	60.0	1.46	1.84	38.4	2.07	1.65	62.9	0.06	7.47	9.97
14:45	21.8	7.85	21.9	68.1	1.46	1.80	22.1	2.14	1.50	73.7	BDL	7.72	11.2

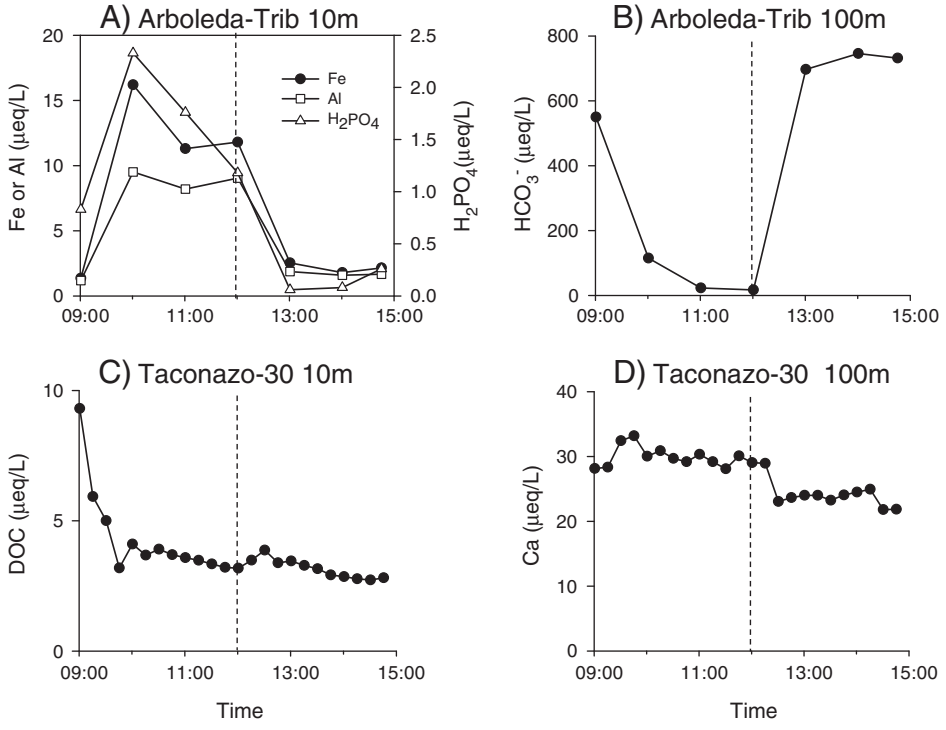

Fig. 4. Changes in ion concentrations during acidification experiments. Changes in Fe^{2+} and H_2PO_4 (μeq/L) at 10 m station in Arboleda-Trib (A). HCO_3^- (μeq/L) changes during acidification and recovery at 100 m in Arboleda-Trib (B). DOC (μeq/L) declines in response to acidification in Taconazo-30 10 m station (C). Changes in Ca^{2+} and Na^+ (μeq /L) during acidification in Taconazo-30 100 m station (D). Dashed line indicates end of acid addition.

Table 3
Dominant invertebrate taxa in both study streams during acidification experiments.

Group/orden	Family	Subfamily/genus	Taconazo-30	Arboleda-Trib
Non-insects				
Cladocera	Undetermined	Undetermined	x	x
Collembolla	Undetermined	Undetermined	x	x
Copepoda	Undetermined	Undetermined	x	x
Gastropoda	Undetermined	Undetermined		x
Hydracarina	Undetermined	Undetermined	x	x
Oligochaeta	Undetermined	Undetermined	x	x
Ostracoda	Undetermined	Undetermined	x	x
Polychaeta	Undetermined	Undetermined	x	x
Insects				
Coleoptera	Elmidae	*Hexacylloepus*	x	
	Hydrophilidae	Undetermined		x
	Staphylinidae	Undetermined	x	
Diptera	Ceratopogonidae	*Atrichopogon*	x	
		Ceratopogoninae		x
		Forcipomyiinae		x
		other	x	
	Chironomidae	Chironominae	x	
		Orthocladiinae	x	
		Tanypodinae	x	x
		other	x	x
	Empididae	Undetermined	x	
	Ephydridae	Undetermined		x
	Simuliidae	*Simulium*	x	
	Other	Undetermined		
Ephemeroptera	Baetidae	*Americabaetis*		x
		Indet	x	x
	Caenidae	Caenis		x
	Leptohyphidae	Tricorythodes		x
	Leptophlebiidae	Farrodes	x	x
		Undetermined	x	
	Other	Undetermined		x
Odonata	Anisoptera	Undetermined		x
	Zygoptera	Undetermined	x	x
Plecoptera	Perlidae	*Anacroneuria*		x
Trichoptera	Hydropsychidae	*Macronema*	x	
		Undetermined	x	
	Hydroptilidae	Undetermined	x	
	Leptoceridae	Undetermined	x	x
	Other	Undetermined		x

4. Discussion

Episodic acidification events were observed in both streams in our long-term monthly record and the 2.5-year record of continuous pH measurements, with the fluctuations being more pronounced in the low-solute Taconazo-30 stream (1.5 pH units, Figs. 1 and 2). The two streams responded differently to experimental acid addition. The solute-rich Arboleda-Trib neutralized more acid (746 μeq/L or 96% of the acid added) than the solute-poor Taconazo-30 stream (27.4 μeq/L or 40% of the acid added). As we had hypothesized, protonation of HCO_3^- was the most important buffering mechanism in the Arboleda-Trib. We expected release of base cations to be the main buffering mechanism in the Taconazo-30 because of its low pH and alkalinity (Fig. 2 and Table 1), but found that release of base cations provided slightly less buffering (8.3 μeq/L) than protonation of HCO_3^- (12 μeq/L). We observed modest increases in Al_i in response to acidification at all sites. The increase in Al_i was most significant in the Arboleda-Trib 10 m station, which had the lowest pH (Fig. 3). However, when normalized per μeq of acid added, Taconazo-30 released 83% more Al (4.2 μeq Al per 100 μeq of acid added) than Arboleda-Trib (2.3 μeq Al per 100 μeq of acid added, Table 5). Our results showed ecological consequences of acidification events as seen by increases in invertebrate drift in both streams (Fig. 5).

Even though this acidification experiment provides a valuable tool for assessing buffering mechanisms and potential consequences of pH declines, we acknowledge that it is not a perfect analog to the mechanisms driving natural episodic pH declines (Lepori and Ormerod, 2005). Our current hypothesis proposes that high dissolved CO_2 is contributing to seasonal and episodic pH declines in low solute streams (Small et al., 2012). The response of stream sediments and macroinvertebrates to addition of a strong mineral acid, like HCl, could be very different from the response due to pH changes driven by increases in CO_2. The rapid pH drop caused by the addition of HCl might induce a more pronounced response in both sediment ion exchange and macroinvertebrates than more gradual pH changes induced by increased CO_2 concentrations or other natural causes (Petrin et al., 2008). However, in our long-term dataset pH also varies with other variables such as discharge, making it difficult to isolate the effects of just pH on buffering and macroinvertebrate drift. This study provides an initial "worst-case" scenario of how two tropical streams respond to short-term pH declines. Our results are in line with previous studies that have shown that acidification experiments can provide valuable insights into the ecological (Bernard et al., 1990; Hall et al., 1980) and biogeochemical (Hedin et al., 1990; Hruska et al., 1999; Goss and Norton, 2008) responses to pH drops (Table 5).

4.1. Stream buffering mechanisms

As expected, we found differences in the buffering capacities between the two streams, and between the two stations at Arboleda-Trib (Fig. 4). At Arboleda-Trib 100 m station, which was downstream from 2 seeps that contributed interbasin groundwater transfer, 96% of the acid added was neutralized. In contrast, the Arboleda-Trib 10 m station only buffered 30% of the acid added, due to its lower buffering capacity because of the lack of IGF. The important role of HCO_3^- protonation in this stream is similar to the buffering mechanism reported for Hadlock Brook in Maine, a stream draining Cadillac Granite with sea salt deposition and similar initial pH (>6,Table 5, Goss and Norton, 2008). However, both the total and relative change in HCO_3^- was much higher in Arboleda-Trib than in Hadlock Brook (Table 5). We believe this was because IGF produces very high DIC concentrations in Arboleda-Trib ($HCO_3^- = 550$ μeq/L). The

Table 4
Average drift densities (n = 4) at three sampling stations in two streams Arboleda-Trib and Taconazo-30 over time. p values for PerMANOVA analyses. ns = not significant.

Site	Upstream			p	10 m			p	100 m			p
	9:00	12:00	14:00		9:00	12:00	14:00		9:00	12:00	14:00	
Arboleda-Trib												
Total	0.44	0.33	0.36	ns	1.12	2.57	0.90	0.06	0.33	10.74	2.06	<0.05
Ephemeroptera	0.03	0.12	0.03	ns	0.30	1.90	0.48	<0.05	0.21	10.44	1.75	<0.05
Diptera	0.30	0.18	0.00	ns	0.78	0.63	0.42	ns	0.06	0.36	0.27	ns
Richness	1.6	2.2	3	ns	3.7	6	3.5	ns	2.2	6	4.7	ns
Taconazo-30												
Total	0.60	0.39	0.66	ns	0.24	0.33	0.31	ns	0.42	0.70	0.61	<0.05
Ephemeroptera	0.12	0.03	0.00	ns	0.03	0.12	0.00	ns	0.00	0.18	0.21	<0.05
Diptera	0.36	0.30	0.18	ns	0.24	0.12	0.27	ns	0.33	0.54	0.18	ns
Richness	2.7	2	5	ns	2.2	2.7	2.6	ns	3	3	3	ns

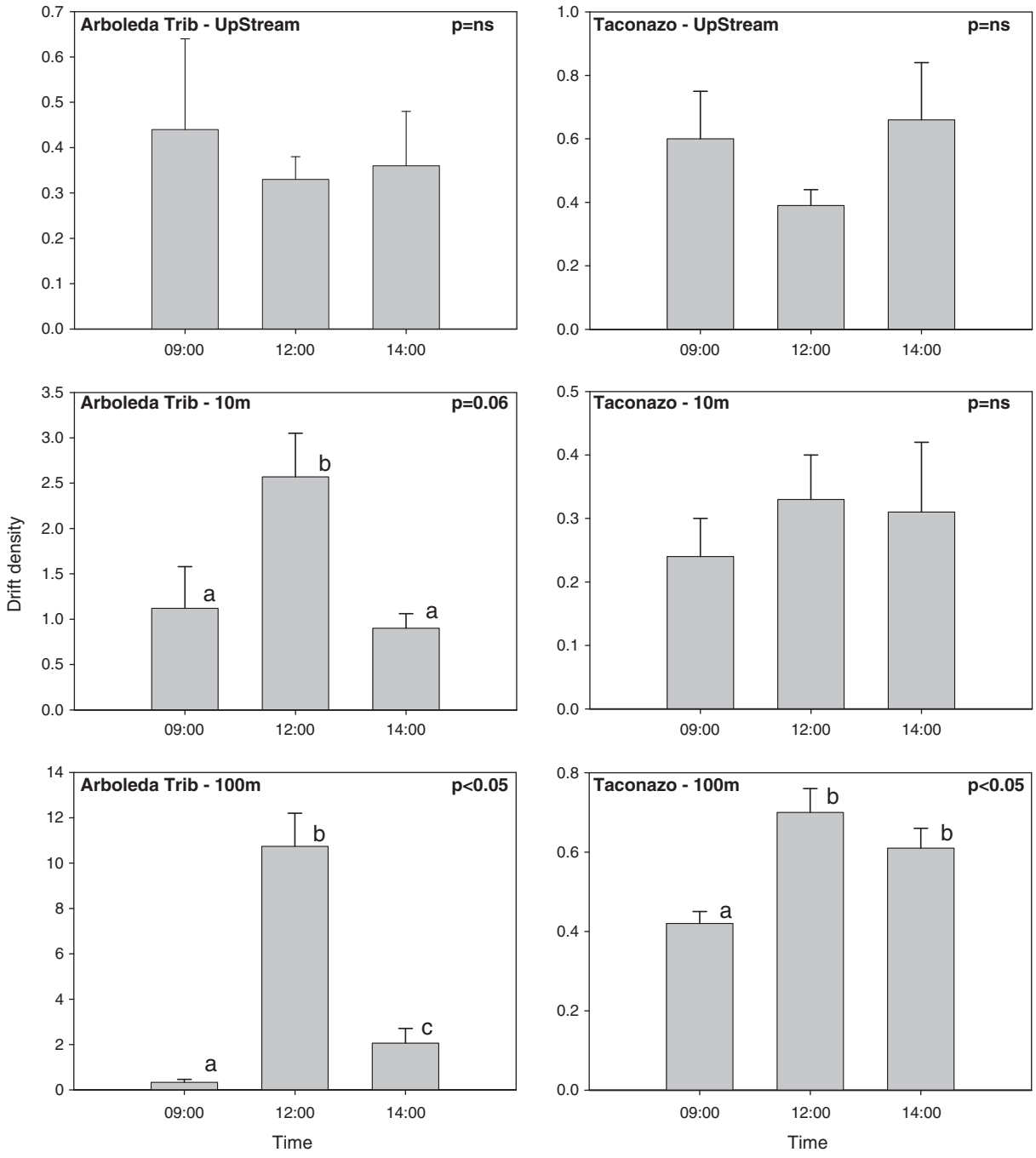

Fig. 5. Total invertebrate drift densities (number of individuals per m^3) in Arboleda-Trib and Taconazo-30 in response to experimental acidification.

Table 5
Comparison of buffering mechanisms during experimental acidification experiments using HCl. All Δ represent differences between acid addition and untreated stream water. We calculated the relative difference as change per 100 μeq/L of added HCl. All concentrations in μeq/L unless otherwise noted. BC = base cation. NR — not reported.

				ΔHCO_3		ΔBC		ΔAl_i		
Stream	Stream pH	Acid added (moles)	Time (min)	Total	Relative	Total	Relative	Total	Relative	Study
Taconazo-30	5.28	68	90	−13.08	−19.24	4.4	6.47	2.92	4.29	This study
Arboleda-Trib	6.34	114	90	−533	−467.54	60.91	53.43	2.71	2.38	This study
Hadlock Brook	6	60.5	254	−34.12	−56.40	9.16	15.14	2.06	3.40	Goss and Norton, 2008
Mud Pond inlet	4.3	60.5	80	0	0.00	6.46	10.68	5.38	8.89	Goss and Norton, 2008
East Bear Brook	5.4	20	1489	−2.43	−12.15	10.62	53.10	12.17	60.85	Goss and Norton, 2008
Beryllium stream	6.42	28	360	−15.5	−55.36	49.1	175.36	78.4	280.00	Norton et al., 2000
Lesni Potok	4.7	22	120	NR	NR	193.6	880.00	46.9	213.18	Navratil et al., 2003.

buffering response we observed at Arboleda-Trib 100 m station (~745 μeq/L) was 93% of the stream water alkalinity measured in the lab (796 μeq/L). On the other hand, the buffering response of Taconazo-30 was 20–29% higher in the stream (17–24 μeq/L) than stream water alkalinity measured in the lab (5 μeq/L), indicating the important role that sediments played in the buffering capacity of this low solute stream. Hedin et al. (1990) also found that alkalinity measurements of stream water in the laboratory underestimate the buffering capacity of streams because they ignore the role of cation exchange by sediments.

Our results from these short-term acidification experiments provide insights into the potential mechanisms driving long-term patterns in phosphorus concentrations in streams at La Selva. We have documented increased stream water P concentrations (Triska et al., 2006) and pH declines associated with ENSO events (Small et al., 2012). The increases in Fe^{2+}, Al_i, and H_2PO_4 in response to acidification at the Arboleda-Trib 10 m station (Fig. 4A) agree with the episodic increases in P concentrations observed in a long term record of three streams (Triska et al., 2006). Our results indicate that low pH in Arboleda-Trib 10 m led to the dissolution of ferric and aluminum phosphate compounds, leading to the release of P. Desorption of phosphorus in response to low pH has been observed in temperate streams and wetlands (Reddy et al., 1999).

Even though we observed increases in Al_i concentrations in all sites, we were surprised by the relatively low concentrations of Al_i released from the sediments during the acidification (Table 2, Table 5). The larger release of Al_i from Taconazo-30 than Arboleda-Trib (Table 5), suggests that the base cation exchange capacity of Taconazo-30 has decreased due to long-term lower pH and more frequent acidification events. This agrees with models of the evolution of acidification that have been proposed for temperate streams (Goss and Norton, 2008; Norton et al., 2000). Both the total and relative increases in Al_i in the streams in our study were some of the lowest reported in the literature (Table 5). The relatively low Al_i concentrations in stream water were surprising given the relatively high concentrations of Al in the soils in La Selva (4.8–7.7 $cmol \cdot kg^{-1}$ exchangeable Al^{3+}), (Kleber et al., 2007). It is possible that the acidification experiment was too short to cause large releases of Al_i, and that if we had run the experiment longer we would have seen more Al_i released from the sediments. It is also plausible that the sediments underlying these two streams have low concentrations of Fe and Al oxides, differing from upland soils in La Selva. Future work will examine the mineralogy of stream sediments across La Selva.

Rapid release of Al_i from stream sediments in response to both natural and experimental acidification has been reported in streams in North America and Europe (Cory et al., 2009; Goss and Norton, 2008; Hall et al., 1980; Hedin et al., 1990; Hruska et al., 1999; Lawrence et al., 2008; Navratil et al., 2003). Al_i has the potential to be toxic to fish (Baker et al., 1996) and macroinvertebrates (Baldigo et al., 2009; Hall et al., 1980). We observed total Al_i concentrations of 85 μg/L, which equals 2.8 μmol/L of monomeric inorganic Al. Toxic effects on biota have been reported above 100 μg/L or 3.7 μmol/L (Driscoll et al., 2001), suggesting the concentrations observed in the stream during the experiment were insufficient to cause direct toxic effects. The concentrations we observed exceed the threshold for sub-lethal effects (20–30 μg/L Al_i) that have been reported for temperate fish (Berntssen et al., 1997; Havas and Rosseland, 1995). However, the sensitivity of tropical fish to increased Al_i concentrations is currently unknown.

Weak organic acids only provided buffering at the Taconazo-30 10 m station (5.1 μeq/L), due to the low DOC concentrations (<10 μeq/L). Previous studies have shown the important role of DOC as a buffering mechanism of peat draining streams in Sweden (Buffam et al., 2007; Hruska et al., 1999). These streams tend to have higher DOC concentrations than our study streams (>60 μeq/L DOC, (Buffam et al., 2007; Hruska et al., 1999)), and DOC buffered 60% of added sulfuric acid (Hruska et al., 1999). The highest DOC that we measured (9.3 μeq/L) was in the 9 am sample from Taconazo-30 10 m station, which was located near an instream wetland. Long-term measurements from the Arboleda-30 and Taconazo-30 indicate that DOC in these two streams tends to be low, even during storms (<5 mg/L, McDowell et al. unpublished manuscript). Our results suggest that organic acids in stream water are likely to play a small role in the acid/base equilibrium of these streams.

4.2. Ecological responses to acidification

Benthic macroinvertebrates were clearly affected by the experimental whole-stream acidification. Entrance into drift is a well-known macroinvertebrate response to disturbances and increases in drift have been reported following episodic acidification (Bernard et al., 1990; Hall et al., 1980; Ormerod et al., 1987). Previous studies have shown that macroinvertebrates might show delayed responses to environmental stressors. Lowering stream pH in both of our study streams created adverse conditions that prompted invertebrates to move downstream. Given the small size of macroinvertebrates and the difficulty of processing drift samples in the field, it is difficult to assess if the increases in drift were caused by mortality or behavioral entrance into drift. We did not observe evidence of mass mortality of macroinvertebrates, but future studies will examine the physiological tolerance of macroinvertebrates to acidic conditions in La Selva streams. We did observe macroconsumers like fish and shrimp actively moving downstream to escape the low pH areas (Ardón personal observation). In addition, maximum drift densities during the experiment were similar in magnitude to peak night-time densities previously measured at La Selva in diel drift periodicity studies (Ramírez and Pringle, 1998; Ramírez and Pringle, 2001).

Previous studies at La Selva reported that changes in stream water pH can affect benthic invertebrate assemblages. Water pH and the number of days since the last rainstorm explain temporal changes in invertebrate assemblage density and composition at La Selva (Ramírez et al., 2006). Although we did not quantify benthic densities, drift response to our experimental manipulation corroborates those findings. Moreover, biomass and abundance of two of the major groups collected in drift, Ephemeroptera and Chironomidae, were also found to be positively related to stream water pH in several high- and low-solute streams at La Selva (Ramírez et al., 2006). Contrasting with previous studies, cladocerans and copepods were dominant in drift during acid addition. Although those two groups were not dominant in either benthic or drift samples at La Selva, they are known to occur in drift after acidification in temperate streams (Bernard et al., 1990).

Drift responses in Arboleda-Trib were stronger and less variable than those in Taconazo-30, however, two confounding factors make it challenging to compare the response of macroinvertebrates between the two streams. First the inputs of IGF within the experimental reach in the Arboleda-Trib meant that water chemistry differed between station before the experiment and that in order to decrease pH in the 100 m section by our target decline, the pH in the 10 m station declined much more (up to 3 pH units). We believe the differences in water chemistry were not a major factor affecting the macroinvertebrate community assemblage based on the similarities in richness and composition we measured before and after the experiment (Table 3 and 4). However, the lower pH in the 10 m station likely caused an increase in overall drift in the Arboleda-Trib compared to the Taconazo-30, where our acidification caused pH drop of 1 pH unit in both stations. Furthermore, the experiment in Taconazo-30 was conducted immediately after several days of high discharge due to rain. Although the stream is small, this period of high rainfall might have negatively impacted benthic invertebrate assemblages thus reducing responses to further disturbance created by acid addition. Our previous studies at La Selva Biological Station, as in studies elsewhere, have shown that invertebrate densities are negatively related to stream discharge and increase with time since the last storm (O'Hop and Wallace, 1983; Ramírez and Pringle, 1998; Ramírez et al., 2006). Taconazo-30 also had low densities of Ephemeroptera, one of the groups that are

known to respond strongly to changes in stream pH (Lepori and Ormerod, 2005). Despite these challenges to comparing the magnitude of the macroinvertebrate response between the two streams, it is clear that macroinvertebrate drift measured at the 100 m station of both streams increased in response to acidification (Fig. 5).

Similar to our findings, experimental acidification of temperate streams has resulted in increases in invertebrate drift densities (Bernard et al., 1990; Courtney and Clements, 1998; Hall et al., 1980). Also in accord with our findings, Ephemeroptera and Chironomidae were major groups responding promptly to decreases in pH and might have value as indicators of acidic conditions. While assessing the direct mechanisms affecting invertebrates was not the goal of our study, our results indicate that invertebrate responses appear to be related to direct effects of low pH and possibly toxic releases of metals. Studies along pH gradients suggest that aquatic invertebrates can adapt to acid conditions (Petrin et al., 2007). The strong response of benthic invertebrate assemblages to pH changes in La Selva streams, either experimental or natural, suggests lack of adaptation by benthic fauna. It could be expected that during high pH conditions, species from nearby buffered streams (e.g., those receiving IGF) could act as a source of colonizers. Thus, the episodic nature of changes in stream pH at La Selva could be a key factor in the dynamics of stream macroinvertebrate assemblages. As in temperate streams, episodic acidification in tropical lowland streams likely plays an important role in the ecology of invertebrate assemblages.

5. Conclusions

Our results illustrate similarities and differences in the buffering mechanisms of two biogeochemically-distinct streams. The prevalence of interbasin groundwater transfer across the Central American active volcanic landscape will play an active role in the response of streams to episodic acidification due to hydroclimatic and land use changes. We show that protonation of HCO_3^- was the dominant buffering mechanism in a high-solute stream. The buffering mechanisms in the low-solute stream included protonation of HCO_3^-, release of ions from stream sediments (base cations and Al_i) and to a lesser degree protonation of organic acids. We also observed an increase in macroinvertebrate drift in response to experimental acidification in both streams. Our results suggest that streams receiving inputs of highly buffered geothermally modified groundwater (of the sodium-chloride-bicarbonate type) might be capable of buffering increases in acidity due either to increases in terrestrially-derived CO_2 or to SO_4^{2-} and NO_3^- deposition as Central America continues to develop its urban centers (Hietz et al., 2011). For example, a recent paper reported high SO_4^{2-} deposition in Costa Rican cities associated with volcanic activity and high sulfur content of gasoline (Herrera et al., 2009). Many tropical streams are very poorly buffered (Pringle et al., 1993), and will be vulnerable to natural acidification.

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