



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 $\mu\text{eq/L}$ (96% of the acid added).
- ▶ The poorly buffered stream only neutralized 27.4 $\mu\text{eq/L}$ (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.

ARTICLE INFO

Article history:

Received 26 June 2012

Received in revised form 17 September 2012

Accepted 17 October 2012

Available online 28 November 2012

Keywords:

Acidification

Bicarbonate

Macroinvertebrates

Drift

Costa Rica

La Selva

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 (Al) 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 $\mu\text{eq/L}$ (96% of the acid added), while the solute poor stream only neutralized 27.4 $\mu\text{eq/L}$ (40%). Protonation of HCO_3^- was an important buffering mechanism in both streams. Base cation, Fe^{2+} , and Al release from sediments and protonation of organic acids also provided buffering in the low-solute stream. We measured low concentrations of Al release in both streams (2–9 $\mu\text{eq/L}$) in response to acidification, but the low-solute stream released double the amount Al 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.

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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://streamslselva.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 $\mu\text{eq/L}$ Ca^{2+} , 1900 $\mu\text{eq/L}$ Na^+ , 2000 $\mu\text{eq/L}$ Mg^{2+}) and anions [up to 790 $\mu\text{eq/L}$ Cl^- , 292 $\mu\text{eq/L}$ SO_4^{2-} , 1000 $\mu\text{eq/L}$ HCO_3^- , 11 $\mu\text{eq/L}$ $H_2PO_4^-$, (Pringle et al., 1993)] and high alkalinity (3000 $\mu\text{eq/L}$). Nearby streams that do not receive IGF have low cation (<100 $\mu\text{eq/L}$ Ca^{2+} , <87 $\mu\text{eq/L}$ Na^+ , <82 $\mu\text{eq/L}$ Mg^{2+}) and anion (<80 $\mu\text{eq/L}$ Cl^- , <40 $\mu\text{eq/L}$ SO_4^{2-} , <30 $\mu\text{eq/L}$ HCO_3^- , <1 $\mu\text{eq/L}$ $H_2PO_4^-$) concentrations, and low alkalinity (5 $\mu\text{eq/L}$). Streams with and without IGF have relatively high inorganic nitrogen concentrations (>10 $\mu\text{eq/L}$ NO_3^- , 1 $\mu\text{eq/L}$ 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.

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