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Journal of Geochemical Exploration 88 (2006) 214–219
JOURNAL OF GEOCHEMICAL EXPLORATION
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CO_2-driven cation leaching after tropical forest clearing

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Received 13 April 2005; accepted 19 August 2005
Available online 28 November 2005

Abstract

The objective of this study was to investigate the role of dissolved CO_2 (H_2CO_3*) as a mechanism of cation removal from surface soils under secondary land uses in the tropics. Soil leachate columns were prepared with 0–10 cm soils from mature and secondary forest, and managed pastures, and extracted with H_2CO_3* from deionized water equilibrated with 0%, 0.5%, 1%, and 10% CO_2 (g). Extraction of soil cations slowed over time following an exponential form for the cumulative data. The rate of cation concentration decline varied as a function of CO_2 concentration with the 10% solution resulting in a greater percent decline with extraction volume. Potassium removal from the exchange sites of all soils and for all solutions was nearly complete ranging from 85% to 97% while removals of Mg (31% to 71%) and Ca (12% to 42%) were lower. The asymptotic patterns of cation loss observed in this study suggest that H_2CO_3* acid-driven losses of cations may become self-limiting over time. Other stronger acids from atmospheric deposition or organic sources may serve to perpetuate cation removal, and re-forestation on these cleared lands would certainly re-distribute cations from soils to vegetation.

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Keywords: Amazon; Slash and burn; Exchangeable cations; Calcium; Magnesium; Potassium

1. Introduction

In tropical Amazonia, forest clearing through slash and burn has greatly accelerated over the last decades largely for cattle ranching (Houghton et al., 2000). Typical chemical responses to slash and burn include an increase in available soil N and P, an increase in exchangeable Ca, Mg, and K, and a concurrent increase in soil pH and base saturation (Sanchez, 1976). Improvements in crop growth that result from increased soil nutrient availability are generally limited to <5 years. The longevity of soil chemical changes, however, such as increased pH may be longer lived.

The re-acidification of soils, and removal of base cations, after slash and burn activities can be driven by a diversity of acid sources (Binkley and Richter, 1987). In tropical pastures of eastern Amazonia investigated in this study, re-accumulation of nutrients in woody vegetation and the associated soil acidification is small due to management activities such as fire, grazing, and hand weeding. Export of cations in cattle as meat is likely also small (Dias-Filho et al., 2001). Deposition of HNO_3 and H_2SO_4 in precipitation remains modest (~0.9 kg NO_3 and 2.4 kg SO_4 ha^{-1} $year^{-1}$) in this relatively undeveloped region (Markewitz et al., 2004). Consequently, H_2CO_3* and organic acids are likely the predominant acids available for base cation removal.

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0375-6742/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.gexplo.2005.08.042

Stream water chemistry in the 10,000 ha watershed of this study clearly indicated a predominance of HCO_3 over organic anions as the mobile anion balancing cation fluxes, particularly during high flow periods of the rainy season (Markewitz et al., 2001). The charge balance between HCO_3 and cation fluxes during high stream flow periods led us to hypothesize that surface soil re-acidification, after slash and burn activities, resulted primarily from elevated gaseous CO_2 in surface soils, and thus elevated dissolved H_2CO_3*.

The objective of this study was to demonstrate that surface soil under secondary forest or managed pasture would respond to elevated CO_2 with elevated fluxes of cationic elements compared to soil from mature forest.

2. Research site

Soils for this study were collected in Fazenda Vitoria, a cattle ranch 6 km north of the town of Paragominas (2°59′S, 47°31′W) in the Brazilian state of Pará, in Amazonia. Fazenda Vitoria has been the site of a number of studies during the last 18 years and much information is available (Nepstad et al., 1994; Uhl et al., 1988). At the time of soil sampling for this project, primary forest remnants (~200 ha) were still present on the ranch. The secondary forest areas utilized in this study were cleared, grazed by cattle for 6 to 8 years, and have been re-growing over the past 2 decades. The managed pastures, lands which tend to border streams, received management inputs such as disking, P fertilization (~50 kg ha^{-1}), and planting with an African grass (*Brachiaria brizantha*) in 1987 and have been actively grazed since. Row crop agricultural was not present at the time of sampling for this project.

All land uses within this study were situated in upper landscape positions on deeply weathered Oxisols (Haplustox or Latossolos Amarelos). In the undisturbed condition, soils of the mature forest have a clay-rich (~78%), shallow A horizon (0–20 cm) with pH in water <4.5.

3. Materials and methods

3.1. Soils

Upper 0 to 10 cm mineral soils were collected at five positions along three randomly located 200 m transects ($n=3$) in each land use (Markewitz et al., 2004). A subsample of the sieved, air-dried sample from each of the three transects within the mature forest, secondary forest, and managed pasture was composited by land use and homogenized. Prior to CO_2 extraction, soil from each land-use was analyzed in replicate for base cation contents. Samples were air-dried and extracted with Mehlich I double acid extract in a 1:10 soil mass to solution volume ratio. After leaching with CO_2, soils remaining in the columns were air-dried and re-measured for cation contents.

3.2. Extraction columns

Soil leachate columns were prepared with 10 g of soil in 15-mL centrifuge tubes. A total of 12 columns were run simultaneously; three land uses by four solution extracts. The solution extracts were comprised of CO_2 (g) equilibrated with deionized water (DI). Treatments were 0%, 0.5%, 1%, and 10% CO_2 (g) (i.e., equilibrated H_2CO_3* (aq)). The CO_2 concentrations utilized are characteristic of the soils at this research site (Davidson and Trumbore, 1995), although higher concentrations in bulk soil are only reached at >2 m. The measured pH values of 0%, 0.5%, 1%, and 10% CO_2-equilibrated water were 5.84, 5.12, 4.94, and 4.48, respectively.

The equilibrated waters were pulled from the bottom to the top of the column using a peristaltic pump. The flow rate was 0.035 mL min^{-1} which provided an average residence time of ~420 min inside the column. To further ensure interaction between soils and solutions, soils were leached for 1 week (7 days) and then incubated in the presence of CO_2-saturated solutions by stopping the peristaltic pump prior to further extraction. The period of incubation was 1, 2, 4, and 8 weeks followed by an additional week of leaching in each case; a total of 35 days of leaching over 140 days. Approximately 2 L of solution were collected per column over the experiment. Daily aliquots of leachate were collected during leaching (54 ± 16 ml; mean ± 1 S.D.) and later analyzed for Ca, Mg, and K by atomic absorption spectrophotometry.

3.3. Data analysis

In addition to comparative and mass balance approaches for the different extractions, we also used a non-linear regression model to estimate the potentially extractable cation pool and its rate of release. This approach follows the potentially mineralizable N assay of Stanford and Smith (1972). The non-linear model for cumulative data followed Cabrera and Kissel (1988):

$$M_t = M_0\left(1 - e^{kt}\right)$$

where M_t is cation release at time t, M_0 is total amount of cation available for release under the given extraction conditions, and k is rate of release under the given extraction conditions.

4. Results

4.1. Soil properties

Prior to soil leaching, exchangeable base cations totaled 227, 469, and 411 $\mu\text{mol}_c\ 10\ \text{g}^{-1}$ of soil for mature forest, secondary forest, and managed pasture, respectively (Table 1). These values are similar to those reported originally by Markewitz et al. (2001) and indicate an increase in base cation contents resulting from slash and burn activities. The secondary forest and managed pasture contain virtually twofold as many cations as the mature forest. The major exchangeable cation is Ca followed by Mg and K.

After soil leaching, total cation contents had been reduced on average to 162, 269, and 356 $\mu\text{mol}_c\ 10\ \text{g}^{-1}$ for mature and secondary forest, and managed pasture, respectively (Table 1). Cation declines varied as a function of CO_2 concentration with the 10% solution resulting in a greater percent decline. For example, in the mature forest, 10% CO_2 resulted in the removal of 42% of all cations while the 0% CO_2 only removed 21%. Cation loss was also element-specific. Exchangeable K removal was nearly complete ranging from 85% to 97% removal while that of Mg (31% to 71%) and Ca (12% to 42%) removal was lower (Table 1).

4.2. CO_2 leachates

Extraction of soil cations slowed over time following an exponential form for the cumulative data (Fig. 1). Extraction of K was more rapid than extraction of Ca and Mg in all cases. The 10% CO_2 clearly approached an asymptote more rapidly than the other solutions. Oddly, the extraction of cations by the 0% CO_2 in some cases exceeded that of the 0.5% and 1% CO_2. This greater leaching of cations by the 0% CO_2 is inconsistent with a purely pH-driven mechanism, although the results for the 0.5%, 1%, and 10% CO_2 suggest that pH is important (Stumm and Morgan, 1996). In some cases, the cumulative amount of cations recovered in solutions exceeded the estimated soil loses from above; however, in all cases, solution recovery was well correlated with the estimated soil losses (i.e., $r = 0.85$, 0.81, and 0.84 for Ca, Mg, and K, respectively).

The regression estimates with the exponential model generally provide good fits to the data (Fig. 1). It is clear, however, that in some cases (e.g., 0.5% CO_2), an asymptotic pattern has not yet been fully achieved. In the model estimates, M_0 for K actually exceeds the total amount of exchangeable K extracted with Mehlich I. For Ca and Mg, even with 10% CO_2, estimates of M_0 were below the total amount extracted. Potassium is sensitive to the extractant utilized and can also be released from micaceous interlayers (Richter and Markewitz, 2001). Estimates of k, the release rate, for K are steeper for the secondary forest and managed pasture, while similar differences in k are less apparent for Ca and Mg.

Table 1
Mehlich I exchangeable cations in 0–10 cm soils before and after extraction with deionized water equilibrated with 0%, 0.5%, 1%, or 10% CO_2

Land use	CO_2 (%)	Ca			Mg			K		
		Initial (μmol_c/10 g)	Final (μmol_c/10 g)	Removal (%)	Initial (μmol_c/10 g)	Final (μmol_c/10 g)	Removal (%)	Initial (μmol_c/10 g)	Final (μmol_c/10 g)	Removal (%)
Capoeira	10	350	263	24	103	42	59	15.7	0.7	95
	1		307	12		67	34		0.5	97
	0.5		296	15		71	31		0.7	96
	0[a]		305	13		70	31		0.8	95
Pasto	10	308	178	42	83	24	71	20.1	1.0	95
	1		238	22		48	42		3.0	85
	0.5		251	18		52	37		1.1	94
	0		233	23		45	44		1.6	92
Mata	10	154	109	29	65	23	64	8.4	1.0	88
	1		126	18		41	37		0.2	97
	0.5		130	15		39	39		0.5	94
	0		136	12		43	33		0.8	90

Soils were collected in 1996 from the Fazenda Vitoria ranch in eastern Amazonia under mature forest, secondary forest, and managed pasture. Mehlich extractions and leaching experiments were conducted in 2002.

[a] 0% CO_2 is N_2 gas.

5. Discussion

An increase in soil pH and cation contents is a relatively universal response to slash and burn activities (Sanchez, 1976) and was observed at Fazenda Vitoria (Table 1). The fate of these increased surface soil cations is less certain but where estimated indicates a potentially long-lived retention (McGrath et al., 2001).

Cationic losses to soil solutions or to stream waters after forest clearing and burning have also been measured in a few tropical forests of the Amazon region (Uhl and Jordon, 1984; Williams and Melack, 1997;

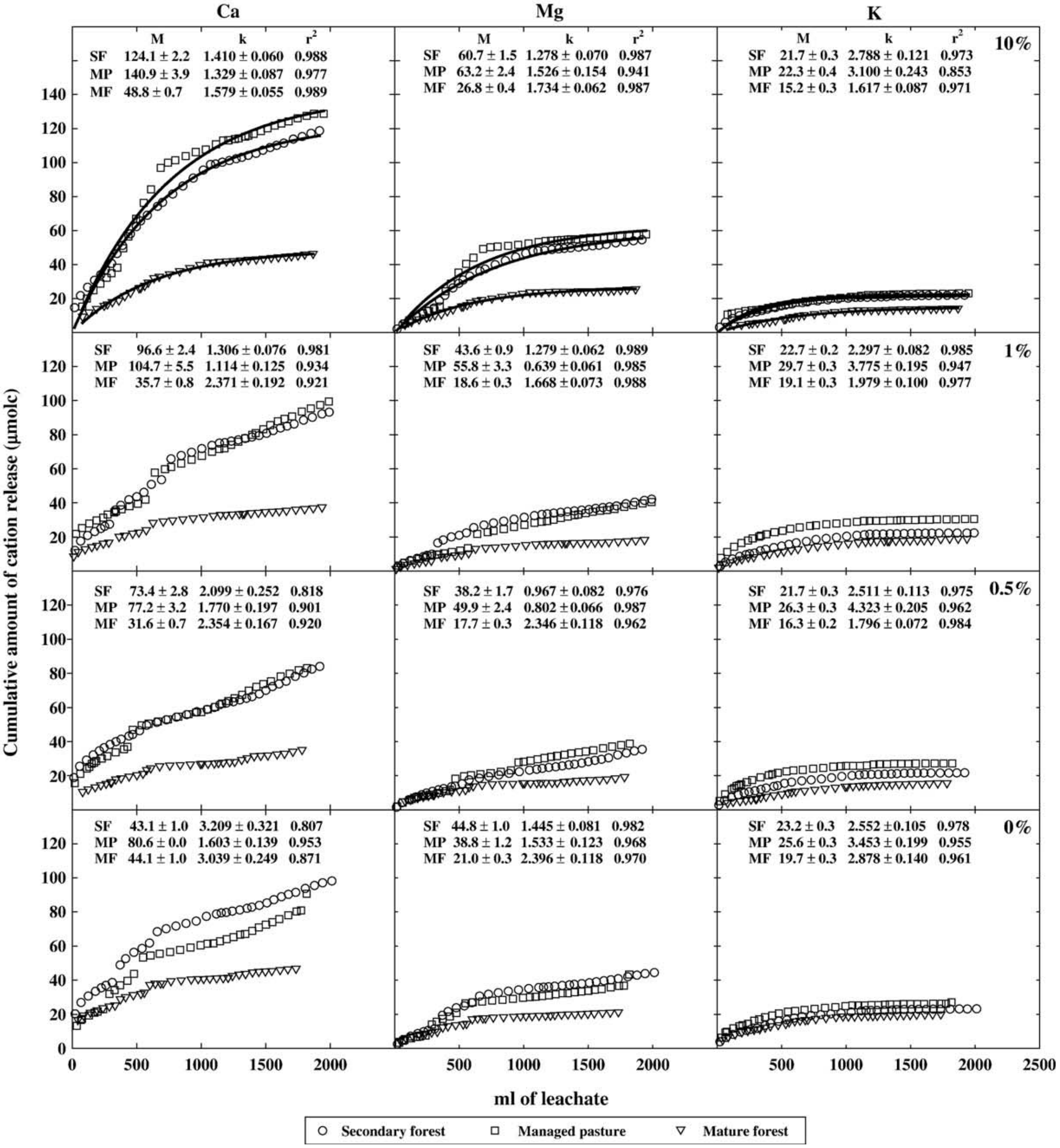

Fig. 1. Cumulative cation contents released from 0 to 10 cm soils during extraction with deionized water equilibrated with 0%, 0.5%, 1%, or 10% CO_2. Soils were collected in 1996 from the Fazenda Vitoria ranch in eastern Amazonia under mature forest (MF), secondary forest (SF), and managed pasture (MP). Extractions were performed in 2002. Regression coefficients (± 1 S.E.) and coefficient of determination (r^2) for cumulative cation release curves are estimated using the two-parameter, single-exponential model $M_t = M_0(1 - e^{kt})$. Units for M_0 are μmol_c and for k are μmol_c ml^{-1}. Regressions lines for 10% curves are included as examples.

Biggs et al., 2002; Markewitz et al., 2004). The longevity of these measured increases in solution concentrations is uncertain and, presently, no well-controlled studies exist in Amazonia to assess these long-term changes. In the well-monitored clearing experiments of the Hubbard Brook Experimental Forest (New Hampshire, USA), increases in stream water Ca and K concentrations have been sustained over three decades in clearcut watersheds relative to control watersheds (Likens and Bormann, 1995).

Despite a clear recognition that H_2CO_3* is a critical driver of soil acidification there have been only a few studies that experimentally manipulated CO_2 to test effects of carbonic acid on natural soils (Kohler and Hildebrand, 2003; McColl and Cole, 1968). Results of the current study are consistent with models of H_2CO_3* leaching (Ruess and Johnson, 1985) in demonstrating greater cation leaching with increasing CO_2 as well as greater cation leaching from soils under secondary land uses that have elevated exchangeable cations (Fig. 1).

Theoretically, the elevation in exchangeable soil cation contents, induced by tropical forest clearing and burning, would be expected to return to an equilibrium condition during forest re-growth (Vitousek and Reiners, 1975). In the long-term soil change studies of Richter and Markewitz (2001), elevated exchangeable Ca concentrations due to agricultural liming were demonstrated to decline over three decades of forest growth. Other perturbations to the environment such as increased acidic atmospheric deposition or increasing atmospheric CO_2 are also hypothesized to create a new equilibrium condition in soil exchangeable cation contents (Markewitz et al., 1998; Oh and Richter, 2004).

In the case of Fazenda Vitoria, a critical question is the extent to which the carbonic acid system can remove soil cations. H_2CO_3* is a weak acid (i.e., $pK_{a,1}$ of 6.36 at 25 °C) and is believed to be limited in its capacity to strongly acidify soils (Ruess and Johnson, 1985). Recently, however, Oh and Richter (2004) using a similar leaching experiment as the current study, but with a 100% CO_2 treatment, argue that the small portion of H_2CO_3* that is pure carbonic acid and a stronger acid (i.e., $pK_{a,1}$ of 3.76) can serve to strongly acidify soils. The current study, demonstrates an asymptotic relationship for both Ca and Mg with 10% CO_2 despite removal of <40% of the exchangeable pools (Fig. 1 and Table 1). These asymptotic patterns suggest that H_2CO_3*-driven losses of cations may become limited in these tropical soils. Conversely, other stronger acids from atmospheric deposition or organic sources may serve to re-acidify the soil, and re-forestation on these lands would re-distribute cations from soils to vegetation.

6. Conclusion

This experiment demonstrates that secondary lands in this tropical watershed, which have elevated exchangeable cation contents due to slash and burn activities, release more cations to solution relative to mature forest in response to leaching by H_2CO_3*. Furthermore, elevated H_2CO_3* concentrations accelerate cation release from these soils.

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