Kinetics of element release by weathering in soils of southern Ecuador: A comparison among different climatic and land-use regimes

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ABSTRACT

To predict future changes in nutrient availability in the young soils of the tropical Andes, it is important to study the response of weathering rates to climate and land-use change. This is particularly true in highly biodiverse tropical forests, where increasing nutrient availability can threaten their biodiversity. Hence, our objectives were to compare the kinetics of element release by weathering along an elevation gradient and between forest and pasture in a tropical montane forest region in south Ecuador. We collected soil samples from three plots in both natural forest and pasture, at elevations of 1000, 2000, and 3000 m above sea level (a.s.l., i.e., 18 in total). The sites at 2000 and 3000 m a.s.l. had similar parent material and allowed for evaluating the climatic effect. To assess element mobilization from the soil, we conducted a weathering experiment at a constant pH value (pH$_{stat}$). During the experiment, ions were released from the soil into solution at pH 3 and removed from the solution using an ion-exchange resin. We described the release of base cations (Ca, Mg, K), Mn, Al, and Fe with a two-step first-order reaction, distinguishing a fast-reacting pool (FP) and a slow-reacting pool (SP), with their associated rate constants. The FP of Ca, Mg, K, and Mn closely correlated with and corresponded in size to the concentrations of the exchangeable cations of these elements ($r = 0.78 - 0.96$). The FP of Ca, Mg, K, and Mn was significantly larger in the soils under pasture than under forest vegetation, likely because of the input of alkaline ashes during slash-and-burn practices. The sizes of the FP and the SP of all studied elements under both land covers/uses were not significantly different between the sites at 2000 and 3000 m a.s.l., possibly because the opposing effects of increasing precipitation and decreasing temperature canceled each other out. Metal release kinetics differed markedly among sites with different parent materials, indicating that weathering is strongly influenced by the chemical composition of the parent rocks. Our study illustrates that element release by weathering in the soils of south Ecuador is strongly influenced by differences in land cover/use and chemical composition of parent rocks.

1. Introduction

Mineral weathering in soils provides plant-available nutrients which are essential for vegetation growth on the young soils of the steep slopes of the Ecuadorian Andes (Wilcke et al., 2019). The kinetics of element release by weathering is a driver of long-term nutrient availability and may respond to environmental change such as climate and land-use change (Alt et al., 2013; Banwart et al., 2009; Beaulieu et al., 2010; Brosens et al., 2021; Zeng et al., 2019). Since increasing soil fertility in

tropical forests can negatively influence biodiversity (Nadeau and Sullivan, 2015), understanding the response of weathering kinetics to environmental change is particularly important. Climate, land-use and land-cover change, particularly the conversion of natural forests to pastures, are among the most pronounced environmental changes in the highly biodiverse tropical montane forests of south Ecuador (Curatola Fernández et al., 2015; López et al., 2017; Peters et al., 2013).

From 1961 to 2008, a warming trend was observed in south Ecuador (Peters et al., 2013) as generally expected for the Andes because of

climate change (Urrutia and Vuille, 2009). Precipitation did not show a uniform trend. An increase in precipitation was measured in the Loja basin, while there was a non-significant decrease on the eastern Andean foothills (Peters et al., 2013).

According to Tapia-Armijos et al. (2015) approximately 46 % of the original forest cover in south Ecuador had been converted into pastures and other anthropogenic land cover types by the year 2008. The net loss of forest area in Ecuador decreased in the recent two decades from about 90 000 (1990–2000) to 53 000 ha year^{-1} (2010–2020; FAO, 2020). Land-use scenarios are expecting that deforestation continues and especially new pastures and urban areas are created (Knoke et al., 2020; Thies et al., 2014). With a business as usual scenario, Thies et al. (2014) expect grassland to cover a larger area than forest from 2030 onwards in south Ecuador. Pastures are mainly established by slash and burn and are later recurrently burnt, which releases nutrients stored in vegetation, while fertilization is uncommon (Beck et al., 2008a; Potthast et al., 2012a; Potthast et al., 2012b; Wilcke et al., 2013). The resulting alkaline ashes lead to an input of base cations and P into the soil and, as a consequence, alter soil chemical properties (Makeschin et al., 2008). An increase of the base saturation in combination with a higher pH, and subsequent faster organic matter decomposition rates increase soil fertility (Potthast et al., 2012a).

Because weathering is a slow process, laboratory experiments typically accelerate weathering by acidification of soil samples. One example is pH$_{stat}$ experiments, where the pH of the solution is lowered below the equilibrium pH of the soil and then held constant to maintain weathering through acid hydrolysis. The constant pH can be achieved by automatic titroprocessors that replace buffered protons by the addition of mineral acid (Süsser, 1987). In this approach, the released ions remain in the solution and can precipitate as secondary minerals, once solubility products are surpassed (Kaupenjohann and Wilcke, 1995a). In contrast, based on a method by Kaupenjohann and Wilcke (1995a), it is also possible to simulate an open system in which the products of weathering are removed. In the latter approach, an ion-exchange resin continuously removes released ions from the solution. Buffer reactions and element release during the experiment can be described as the sum of two independent, partly simultaneous reactions, both following first-order kinetics (Schwarz et al., 1999; Süsser, 1987). This leads to the identification of a fast-reacting (FP) and of a slow-reacting pool (SP) with their respective release rate constants kFP and kSP.

Our overall objective was to identify the effects of different climatic regimes and land covers/uses on the kinetics of element release by weathering. Climatic regimes were varied by selecting sites at different elevations. We hypothesized that (i) the FP can be attributed to the respective exchangeable element pool, which is larger in soils under pasture than under forest. (ii) With decreasing elevation and warmer climatic conditions, soil weathering should be more advanced, resulting in less remaining weatherable minerals. Hence, in our pH$_{stat}$ experiment, mineral weathering should occur faster with increasing elevation.

2. Materials and methods

2.1. Study area and sampling design

2.1.1. Study area

The study area is located between 1000 and 3000 m a.s.l. on the Amazon-exposed humid slope of the eastern Andean Cordillera in south Ecuador, which is a biodiversity hotspot of the Andes (Brehm et al., 2008; Myers et al., 2000). The parent material of the studied soils consisted of Paleozoic metamorphic and associated intrusive rocks formed probably during the Pan-African/Brasiliano orogeny and influenced by later orogenic events (Baldock, 1982). Our study sites were located on granodiorite (Zamora Batholith, 170–190 Ma, 1000 m a.s.l., Litherland et al., 1994) or interlayers of phyllite and metasandstone (Chigüinda unit, around 360 Ma, 2000 m, 3000 m a.s.l.; Chew et al., 2007; Table S1).

Because of the perennial easterlies and strong orographic lift, high precipitation occurs on the eastern slopes throughout the year (Beck et al., 2008b; Bendix et al., 2008). Mean annual precipitation varied between 2467 mm at 1000 m and 2267 mm at 2000 m, and increased to 2932 mm at 3000 m a.s.l. (Table S1). At 3000 m a.s.l., wind conditions make reliable precipitation measurements difficult while fog contribution becomes important. At this elevation, total annual precipitation may reach 4522 mm (Emck, 2007). Air temperatures show a low seasonal variability. The mean annual temperature (1999–2015) at the San Francisco meteorological station at 1957 m a.s.l. is 15.4 ± 0.3 °C (Velescu et al., 2016). Considering a regional air temperature gradient of 0.52 °C (100 m)$^{-1}$ (Bendix et al., 2008), this results in mean annual temperatures of approximately 20 °C at 1000 m, and 10 °C at 3000 m a.s.l. (Table S1).

Soils under forest in the research area are strongly acidic. Hydromorphic properties in some soils, indicating episodic waterlogging, increase in general with elevation with a high small-scale spatial heterogeneity (Table S1; Beck et al., 2008b; Liess et al., 2009; Schrumpf et al., 2001). Common reference soil units are Histosols, Stagnosols, Regosols, Cambisols, Umbrisols and Leptosols (Table S1; Liess et al., 2009; IUSS Working Group WRB, 2022). Landslides occur frequently due to the partly steep slopes (Bussmann et al., 2008). On similar parent material, the cation-exchange capacity in the A horizon decreases and the texture of the A horizon becomes coarser with increasing elevation (Schrumpf et al., 2001; Wilcke et al., 2008). While at 1000 m a.s.l. there is only a thin organic layer of <10 cm, its thickness increases with increasing elevation to a maximum of about 50 cm at 2000 m a.s.l. (Wilcke et al., 2008). Although at 3000 m a.s.l. the cool and moist climate slows down litter decomposition, the organic layers reach only a thickness of ca. 20 cm, likely because of the negative effect of the lower mean annual temperature on forest productivity (Homeier and Leuschner, 2021).

Chemical weathering dynamics in the research area are influenced by elevation. The presence of illite increases with increasing elevation, whereas the presence of kaolinite decreases (Schrumpf et al., 2001). This indicates that chemical weathering is more advanced in the soils of lower elevations (Fanning et al., 1989). Hence, the temperature decrease with elevation, slowing weathering down, seems to overrule the increase in precipitation, enhancing the chemical weathering (Rasmussen et al., 2011). Water availability and soil moisture are driving factors for chemical weathering (Schoonejans et al., 2016). While the increased episodic waterlogging in some of the soils can, potentially, lead to saturation of weathering products and, hence, decreased chemical weathering with elevation (Maher, 2011; Molina et al., 2019), there is no clear elevational pattern of soil moisture, and no indication of continuously saturated conditions in the topsoils (Fig. S2). Instead, the soil moisture shows episodic cycles caused by the temporal precipitation distribution (Fig. S2). The weathering products are removed from their source location and cycled between soil and vegetation or leached from the open system (Rehmus et al., 2017; Wilcke et al., 2017).

In general, soils under forest and pasture show a similar mineralogy in the study area (Makeschin et al., 2008). Soils under pasture show a higher pH and base saturation and contain increased concentrations of exchangeable base cations and more available P than soils under forest (Makeschin et al., 2008). Pastures generally lack an organic layer resulting in a decrease in the soil organic carbon stock of the root zone during the conversion from forest to pasture (Bahr et al., 2014; Makeschin et al., 2008). Faster decomposition rates and a higher CO_2 efflux have been reported for soils under pasture than under forest (Potthast et al., 2012a). Fertilization of the pastures is not common in the study area (Potthast et al., 2012a; Potthast et al., 2012b; Wilcke et al., 2013).

2.1.2. Sampling design and chemical analysis

This study was conducted within the framework of the DFG research unit 2730 – Environmental changes in biodiversity hotspot ecosystems of South Ecuador: response and feedback effects (RESPECT; Bendix

et al., 2021). Soil samples were collected from 54 soil profiles along an elevational gradient from 1000 to 3000 m a.s.l. at three sites: Bombuscaro at 1000 m, San Francisco at 2000 m and Cajanuma at 3000 m a.s. l. (Fig. S1). We could evaluate the climatic effect on the weathering kinetics between the sites with similar parent material (2000 and 3000 m a.s.l.). At each elevation, six statistically independent 1-ha large plots were established: three in undisturbed ecosystems which include evergreen premontane forest at 1000 m, lower montane forest at 2000 m and upper montane forest at 3000 m a.s.l. (Homeier et al., 2008), and three on managed pastures as anthropogenic replacement ecosystems (Bendix et al., 2021). On each plot, we collected representative samples from each A horizon of three profiles at upper, middle and lower slopes to account for topographic effects. The A horizons varied in thickness between 10 and 40 cm, with similar thicknesses among the different elevations and between forest and pastures, respectively.

Soil samples were dried at 40 °C in a drying oven, sieved to < 2 mm and an aliquot was milled in a planetary ball mill (Retsch PM400, Haan, Germany). We analyzed all samples individually to determine total element concentrations after microwave digestion with HNO_3, H_2O_2 and HF (4:1:2, v:v:v) and measurement by inductively-coupled plasma optical emission spectrometry (ICP-OES, 5100 VDV, Agilent, Waldbronn, Germany). Additionally, we measured exchangeable cation concentrations for all samples individually after unbuffered extraction with 1 M NH_4NO_3, using ICP-OES (Velescu et al., 2020a; Velescu et al., 2020b; Velescu et al., 2020c).

For the pH_{stat} experiment, we combined the <2 mm sieved aliquots of the samples from the three A horizons of the same plot in equal mass proportions into a single sample and homogenized it in order to obtain one representative sample per plot.

3. Experiment and modeling

3.1. pH_{stat} experiment

To determine the release kinetics of the target elements, we exposed the soil samples to a constant pH value of 3.0 in a pH_{stat} experiment, similar to that described by Schwarz et al. (1997). With this method, secondary mineral formation is prevented with ion-exchange resins, which remove the products of the buffer reactions from the reactor, thus mimicking an open system. The laboratory experiment uses disturbed soil samples and accelerates the weathering rates so that the obtained release kinetics reflect potential weathering rates that are likely to differ from those in the field but allow for direct comparisons among the different elevations and land covers/uses.

Two g of each sample were weighed into a 125 mL polyethylene (PE) bottle and 100 mL of deionized (DI) water (>18 MΩ cm^{-1}) were added. After 30 min of shaking to achieve a constant pH, we added 2.5 g of mixed-bed ion-exchange resin (Amberlite MB-20, Rohm and Haas, Philadelphia, USA) inside a self-made permeable 3 cm × 4 cm-large PE bag (100 μm mesh width). The resin was saturated with 1 M HNO_3 and rinsed with DI water, before it was placed inside the bag. Simultaneously, assuming that 1 mol of Ba^{2+} releases 2 mol of H^+ from the resin, we added as much $Ba(NO_3)_2$ as necessary to lower the pH from the equilibrium value to 3.0, depending on the initial sample pH (i.e., 0.97 mL to 1.00 mL 0.05 M $Ba(NO_3)_2$; Method S1) measured with a pH meter and a glass electrode (pH 3310 with Sentix 81 electrode, WTW, Weilheim, Germany). To determine the element release with time, the resin was removed from the bottle after 10 min, 30 min, 1 h, 2 h, 4 h, 24 h, 48 h and 96 h. For each time step, we prepared a separate aliquot of the same homogenized soil sample in an independent bottle. After the soil and the resin bag were separated, the bags were carefully rinsed with DI water and adsorbed ions were extracted from the resin using 3 × 30 mL of 2 M HNO_3, after shaking for 10 min in the first and second step, and 30 min in the third one. We processed 144 samples (3 elevations × 2 land covers/uses × 3 plots of each land cover/use × 8 aliquots for different times of shaking). Concentrations of Ca, Mg, K, Mn, Al and Fe

were measured with an ICP-OES (5100 VDV, Agilent, Waldbronn, Germany). Tests of element recovery from the resins with standard solutions containing a mixture of all elements yielded 101 ± 4 % (Ca, $n = 3$), 99 ± 3 % (Mg, $n = 6$), 106 ± 3 % (K, $n = 6$), 96 ± 2 % (Mn, $n = 6$), 117 ± 6 % (Al, $n = 6$), 94 ± 3 % (Fe, $n = 6$).

3.2. Kinetic model

Based on Süsser (1987) and Schwarz et al. (1999), the element release during pH_{stat} experiments is frequently described with a two-step first-order equation (Eq. (1); Method S2; e.g., Alt et al., 2013; Basdediós et al., 2022; Cappuyns and Swennen, 2008; Hacker et al., 2018):

$$Y(t) = FP(1 - exp(-kFP·t)) + SP(1 - exp(-kSP·t)) \quad (1)$$

Y(t) represents the release of elements from the soil (mg kg^{-1}) with time (t; h) with fast- and slow-reacting pools (FP and SP, respectively; mg kg^{-1}) and their associated release rate constants (kFP and kSP; h^{-1}).

We modeled and plotted the release of the elements per plot in *R* 4.4.1 (R Core Team, 2024) as nonlinear least squares regression using the Levenberg-Marquardt algorithm (Levenberg, 1944; Marquardt, 1963) in the *R* package Minpack.lm (Elzhov et al., 2023).

3.3. Statistical methods

In our modeled variables describing the release kinetics of the metal cations, i.e. values of FP, SP, kFP, kSP, we removed modeling artifacts by considering a value *v* as an outlier, if $v > (Q3 + 15 × IQR)$ or $v < (Q1 - 15 × IQR)$ with interquartile range (*IQR*), first quartile (*Q1*) and third quartile (*Q3*) of all values of this variable and element, independent of land cover/use and elevation (Method S3).

To infer information about the element speciation, particularly the size of the element pool that does not participate in our weathering experiment, we calculated the ratio of the SP to the total element concentration (c_{tot}) in soil that was not attributed to the FP (B_{rel}, Eq. (2)).

$$B_{rel} = \frac{SP}{c_{tot} - FP} × 100 \quad (2)$$

A low B_{rel} (%) indicates that a large part of strongly bound elements did not take part in our weathering experiment, while a high B_{rel} indicates that almost the entire element pool reacted during our weathering experiment.

To determine the influence of elevation and land cover/use on the properties of the soils or the kinetic parameters of the pH_{stat} experiment, and to test for significant differences of B_{rel} among the elements, we used a one-way (for B_{rel}) or two-way analysis of variance (ANOVA) followed by Tukey's HSD post-hoc test.

Normal distribution of the residuals was checked with the Shapiro-Wilk test. We tested for homoscedasticity visually by assessing scale-location plots or using Levene's test. Pearson correlation coefficient and linear regression, forced through the origin, were used to evaluate the relationships between the model variables and soil chemical properties. When necessary to approximate the prerequisites for ANOVA, correlation or regression, we transformed individual data differently with either natural logarithm, square root or Box-Cox (*R* package MASS; Venables and Ripley, 2002).

All statistical tests were carried out using *R* 4.4.1 (R Core Team, 2024). Significance was set to $p < 0.05$.

4. Results

4.1. Soil properties

We found significantly higher pH, exchangeable Ca, Mg, K, Mn concentrations, base saturation, and total Ca concentrations in the A horizons under pasture than under forest (Table 1). The exchangeable Al

Table 1

Means and standard deviations (to illustrate spatial variation; n = 6 plots for elevation and n = 9 plots for land cover/use) of selected chemical properties of the A horizons' fine earth (<2 mm): exchangeable and total element concentrations, pH (H$_2$O), effective cation-exchange capacity (ECEC), and base saturation. Different lower-case letters indicate significant differences among the elevations and different upper-case letters indicate significant differences between forest and pasture according to Tukey's HSD post-hoc test. Data was aggregated from Velescu et al. (2020a, b, c).

	Elevation			Land cover/use	
	1000 m	2000 m	3000 m	Forest	Pasture
Exchangeable Ca (mmol$_c$ Ca kg^{-1} soil)	18.9 ± 19.0	8.1 ± 9.2	8.4 ± 6.0	3.0 ± 3.7 B	20.6 ± 13.1 A
Exchangeable Mg (mmol$_c$ Mg kg^{-1} soil)	7.1 ± 5.6	3.8 ± 4.2	4.6 ± 1.6	2.8 ± 2.3 B	7.5 ± 4.4 A
Exchangeable K (mmol$_c$ K kg^{-1} soil)	2.8 ± 2.0	3.1 ± 3.3	3.9 ± 1.8	2.1 ± 1.5 B	4.4 ± 2.5 A
Exchangeable Mn (mmol$_c$ Mn kg^{-1} soil)	0.5 ± 0.3	0.2 ± 0.2	0.3 ± 0.2	0.2 ± 0.2 B	0.5 ± 0.3 A
Exchangeable Al (mmol$_c$ Al kg^{-1} soil)	21.2 ± 12.1 b	54.7 ± 27.7 a	37.0 ± 13.5 ab	48.5 ± 23.3 A	26.8 ± 17.3 B
Total Ca (g Ca kg^{-1} soil)	1.1 ± 0.9 a	0.2 ± 0.2 b	0.3 ± 0.1 b	0.4 ± 0.8 B	0.7 ± 0.4 A
Total Mg (g Mg kg^{-1} soil)	2.9 ± 1.9	2.3 ± 0.6	3.0 ± 1.6	2.4 ± 1.3	3.1 ± 1.4
Total K (g K kg^{-1} soil)	21.0 ± 9.5 a	12.2 ± 3.2 b	16.0 ± 7.2 ab	19.7 ± 8.7 A	13.2 ± 5.1 B
Total Mn (g Mn kg^{-1} soil)	0.3 ± 0.1	0.4 ± 0.3	0.3 ± 0.2	0.2 ± 0.1	0.4 ± 0.3
Total Al (g Al kg^{-1} soil)	86.4 ± 5.9 a	50.7 ± 13.8 b	51.6 ± 24.7	64.5 ± 23.9	61.3 ± 23.8
Total Fe (g Fe kg^{-1} soil)	28.8 ± 11.4	24.8 ± 7.6	21.0 ± 11.4	22.2 ± 7.9	27.5 ± 12.0
pH	4.7 ± 0.4 a	4.3 ± 0.3 ab	4.1 ± 0.3 b	4.1 ± 0.3 B	4.7 ± 0.4 A
ECEC (mmol$_c$ kg^{-1} soil)	51.7 ± 16.9	70.9 ± 15.7	55.5 ± 12.2	57.8 ± 19.6	60.9 ± 13.7
Base saturation (%)	47.0 ± 32.7	25.3 ± 27.1	33.7 ± 15.6	17.3 ± 16.2 B	53.4 ± 21.6 A

and total K concentrations were, in contrast, significantly higher under forest. The pH was significantly higher at 1000 than 3000 m a.s.l. At 1000 m a.s.l., total Ca and Al concentrations were significantly the highest. The exchangeable Al concentration was significantly higher, and the total K concentration significantly lower at 2000 than at 1000 m a.s.l.

4.2. Release models

In three of the 108 cases (18 plots × 6 elements) modeling the release was not possible with Eq. (1). All but 9 models showed $R^2 > 0.90$. The Fe release kinetics did not reach equilibrium conditions until the end of the experiment. Of the resulting 348 model variables (105 possible models − 18 Fe models = 87 models; 87 models × 4 variables FP, SP, kFP, kSP = 348) 13 were excluded from statistical analysis as modeling artifacts (Method S3). There were two cases in which the Mn release was completely described by a one-step first-order reaction instead of a two-step first-order reaction.

4.3. Release kinetics of Ca, Mg, K, Mn

The mean release kinetics of Ca, Mg, K and Mn showed an effect of elevation for Ca and Mn toward the end of the experiment and were for all elements strongly influenced by land cover/use from the beginning (Fig. 1).

There was no significant effect of elevation on any of the model variables FP, SP, kFP, kSP (Fig. S3–S6). Land cover/use had a significant effect on the FP of Ca, Mg, K and Mn (Fig. S3–S6). The mean FP of Ca, Mg, K and Mn was three to six times larger under pasture than under forest (Fig. S3–S6). Additionally, the SP of Ca was significantly larger and the kFP of Ca significantly smaller under pasture (Fig. S3).

The FP of Ca, Mg and K correlated significantly with the respective exchangeable cation concentration (Table S2). For Ca, Mg and K, the relationship between the FP and the respective exchangeable cation concentration was linear. The high R^2 values and slopes near to unity illustrated that the exchangeable cation pool constituted the FP of Ca, Mg and K (Fig. 2). The FP of Mn correlated significantly with the exchangeable Mn concentration (Table S2) and matched the size of the exchangeable Mn pool at all studied plots (Fig. S8).

4.4. Release kinetics of Al, Fe

In line with the findings of Cappuyns and Swennen (2008) and Kaupenjohann and Wilcke (1995b), the release kinetics of Fe were linear, in contrast to those of Al, which showed a decreasing element release over time (Fig. 3).

Neither land cover/use nor elevation had a significant effect on the model variables of Al (Fig. S7). Since the modeled Fe release was linear and did not reach equilibrium conditions till the end of the experiment, we did not evaluate the model parameters statistically.

The exchangeable Al concentration correlated significantly with the size of the FP of Al (Table S2). However, the FP of Al was in all cases larger than the exchangeable Al concentration (Fig. 4).

4.5. Size of the model variables and B_{rel}

The mean kFP values decreased in the order K > Ca ≈ Mg > Mn > Al (Fig. 5). Additionally, the FP and, especially, the SP of Al were much larger than those of the other elements (mean FP 4 to 72×, mean SP 79 to 174×; Fig. 5). Furthermore, the mean kSP of K was higher than that of the other elements (2 to 19×; Fig. 5). The B_{rel} values (Eq. (2)) showed significant differences among the elements and decreased in the order, Ca > Mn > Al ≫ Mg ≫ K (Table 2).

5. Discussion

### 5.1. Effect of land cover/use

We confirmed the first part of our Hypothesis (i) according to which the FP could be attributed to the respective exchangeable element pool, by showing that the exchangeable cation pool of Ca, Mg, K and Mn constituted the respective FP (Fig. 2). This conclusion was supported by the significant regressions (Fig. 2) and the direct comparisons of the size of the exchangeable cation concentration of Ca, Mg, K, Mn with that of their respective FP (Fig. S8).

The finding that the size of the FP of Al was consistently much larger than the exchangeable Al concentrations (Fig. 4) indicated that there must have been fast-reacting pools that were not extractable by 1 M NH$_4$NO$_3$. In line with findings of van de Sand and Fischer (1994), the additional fast-reacting pool might be organically complexed Al.

The fact that the order of the kFP values of the studied elements (K > Ca ≈ Mg > Mn > Al; Fig. 5) corresponds inversely to the order of their competitiveness for cation exchange further supported our Hypothesis (i). The ions with stronger exchange competitiveness usually have a slower kFP because of their stronger adsorption.

The FP of Ca, Mg, K and Mn was significantly larger under pasture (Fig. S3–S6), confirming the second part of Hypothesis (i), stating that the FP would be larger in soils under pasture compared to the soils under forest. However, the size of the FP of Al did not differ significantly between pasture and forest (Fig. S7). In the study area, native forest is usually converted to pasture by slash and burn practices (Beck et al.,
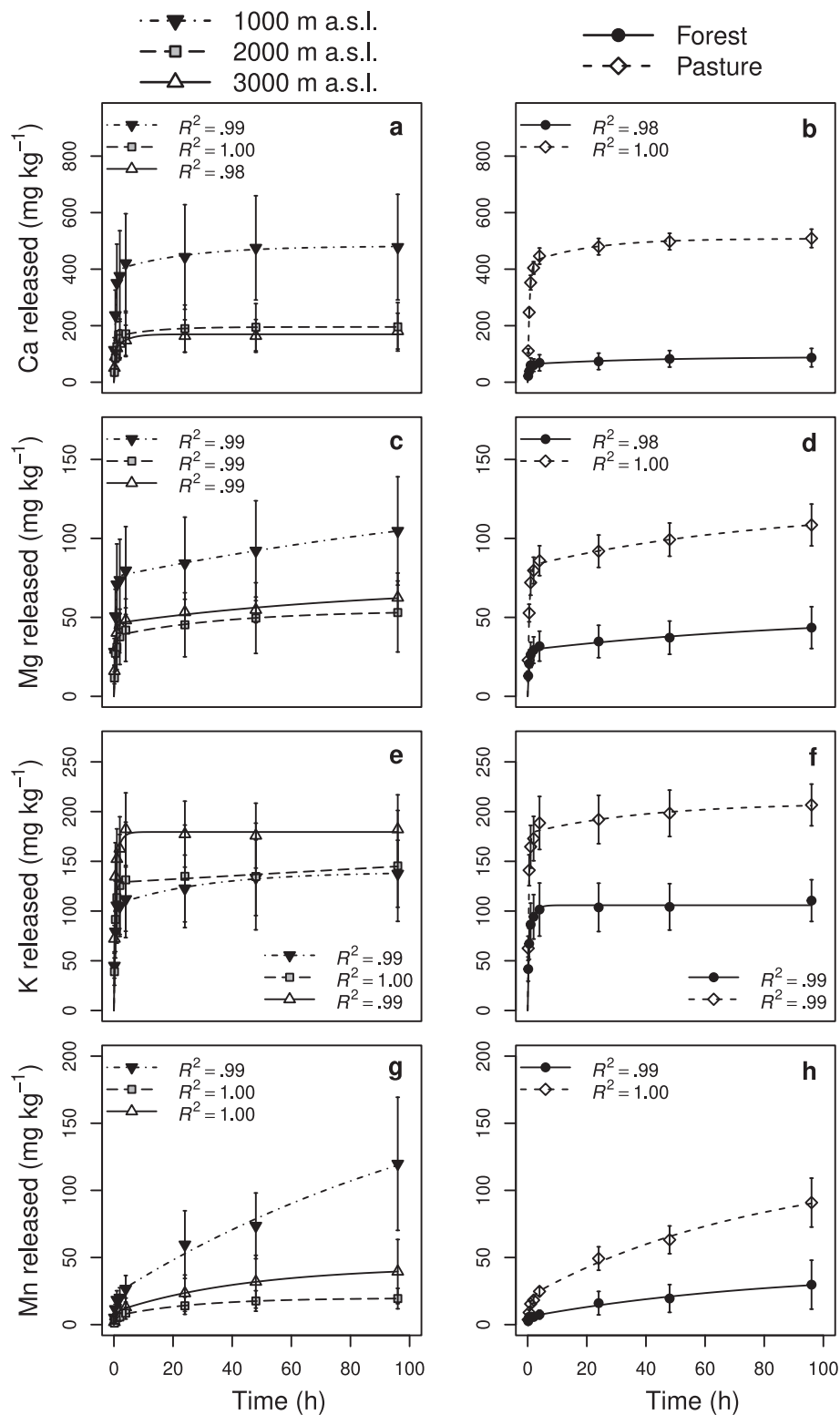
Fig. 1. Mean Ca, Mg, K and Mn release grouped according to elevation (left column, a, c, e, g) and land cover/use (right column, b, d, f, h), respectively. The lines illustrate the fit using Eq. (1). Error bars represent standard errors (to illustrate the error of the mean; n = 6 for elevation and n = 9 for land cover/use).

2008a), which release alkaline ashes (Makeschin et al., 2008). These ashes were reported to increase the exchangeable pool of base cations (Makeschin et al., 2008), and likely also of Mn (Sánchez-García et al., 2023). Additionally, repeated burning in an attempt to reduce the invasion of shrubs regularly causes new alkaline ash inputs (Beck et al., 2008a). As a consequence, the individual concentrations of

exchangeable base cations and of exchangeable Mn increased significantly in soils under pasture relative to forest (Table 1). Since the FP of Al includes substantial fast-reacting phases which could not be extracted by 1 M NH_4NO_3 (Fig. 4), it does not reflect the significantly higher exchangeable Al concentrations in the A horizons under forest than under pasture (Table 1).
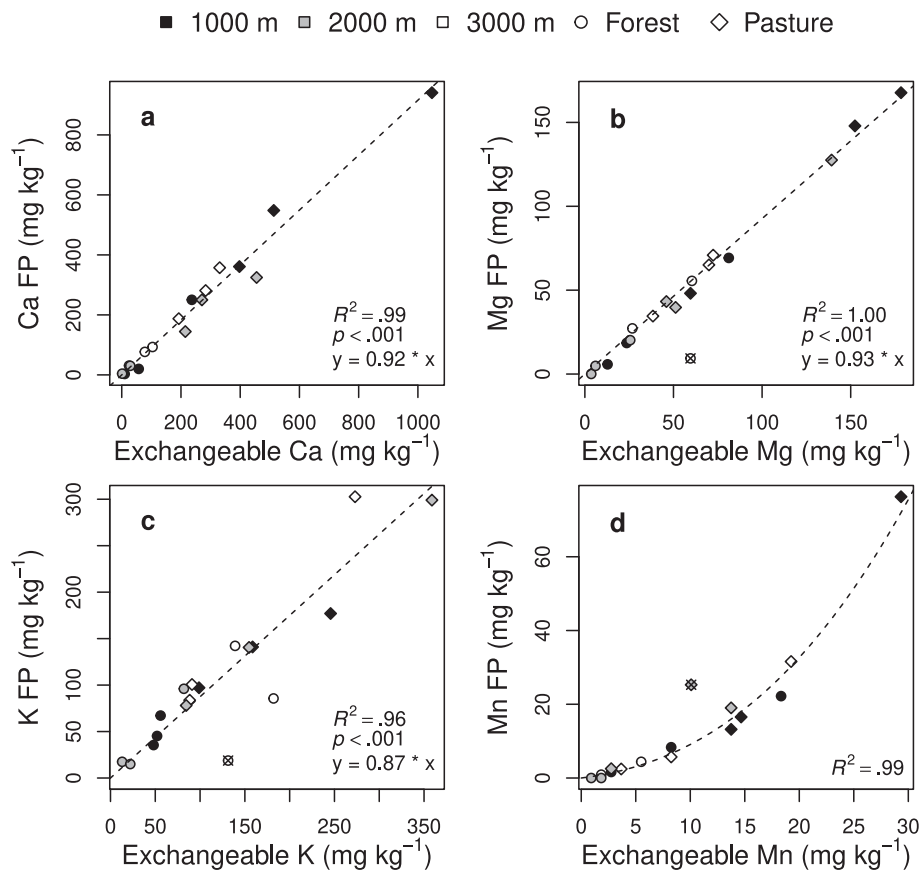
Fig. 2. Relationship between the exchangeable cation concentrations and the sizes of the fast-reacting pool (FP) for (a) Ca, (b) Mg, (c) K and (d) Mn. The different colors indicate the elevation and their shape the land cover/use. An exclusion of one outlier (crossed out dots) was necessary for each of Mg, K and Mn, because otherwise the residuals were not normally distributed. The R^2 values without the removal of outliers were 0.97 (Mg), 0.93 (K), 0.97 (Mn, Box-Cox transformed).

5.2. Effect of different climatic regimes along the elevational gradient

In contrast to our Hypothesis (ii), which expected an effect of elevation reflecting different climatic regimes on the element release by weathering, elevation did not have a significant effect on any of the model variables of all studied elements (Fig. S3–S7), even not between 2000 and 3000 m a.s.l. with the same parent materials. Moreover, there were no significant differences in the concentrations of exchangeable base cations and exchangeable Mn among the three elevations (Table 1).

Instead of a relationship of the element release kinetics with elevation, we identified a relationship of the SP of the studied elements with silicate or oxide weathering, indicating a connection between the SP and the parent material. The low B_{rel} values of Mg and K (Table 2) could indicate that a large part of silicates did hardly react at pH 3. The order of Mg > K fits to the weathering stability of common minerals. Mg was more easily released than K because, in general, mafic minerals such as pyroxenes and amphiboles are more easily weatherable than felsic minerals such as muscovite and orthoclase (Lasaga et al., 1994). The high kSP of K (Fig. 5) might be explained by the release of K from illites and vermiculites in which it was fixed or from micas, all occurring in the soils along the elevation gradient (Schrumpf et al., 2001; Table S1). Micas and illites/vermiculites are comparatively reactive pools containing silicate-bound K (Øgaard and Krogstad, 2005).

The higher B_{rel} of Al and Mn with about 20 % and 24 %, respectively (Table 2), compared to the values of Mg and K are likely attributable to the fact that Al and Mn do not only exist in silicates but also in oxides, which are more reactive than most silicates (Paterson et al., 1991; Rampazzo et al., 1999). This is consistent with the literature, which states that Al is released from oxides and hydroxides as part of the strong acid/Al oxide buffer system (pH 2.8 to 4.2; Ulrich 1981), because buffer

rates of the carbonic acid/silicate and strong acid/cation exchange buffers are exceeded (Schwarz et al., 1997; van de Sand and Fischer, 1994).

The element release of Ca (Fig. 1) as well as the corresponding FP and SP decreased in the order: 1000 m ≫ 3000 m ≈ 2000 m a.s.l. (Fig. S3), mirroring the exchangeable and total Ca concentrations (Table 1), which we attribute to differences in the parent material (Table S1). Hornblende-biotite granodiorites with Ca in hornblende and plagioclase occur in the Zamora granitoids at 1000 m a.s.l. Compared to 1000 m a.s.l, more muscovite/sericite, chlorite, and albite are present along with quartz in the phyllites and metasandstones at 2000 and 3000 m a.s.l. (Litherland et al., 1994). Thus, the chemical composition of the parent rock overruled a possible climatic effect. Moreover, even for the two sites with similar parent rocks (2000 and 3000 m a.s.l.) no differences were observed in spite of an elevation difference of 1000 m and associated climatic changes (Table S1). The opposing effects of the higher precipitation and the lower temperature on chemical weathering may have canceled each other out, although this would be in contrast to the observed mineralogical differences between 2000 and 3000 m a.s.l. Moreover, soil rejuvenation by landslides on the partly steep slopes at a temporal scale of decades to centuries may regularly expose fresh weatherable minerals at both elevations resulting in similar weathering states of the soils (Bussmann et al., 2008). Because it is unclear whether from 2000 to 3000 m a.s.l. pedogenic thresholds are crossed, sampling along a longer gradient would be beneficial to test for climatic effects (Chadwick et al., 2022).

6. Conclusions

The element release kinetics of base cations and Mn were strongly
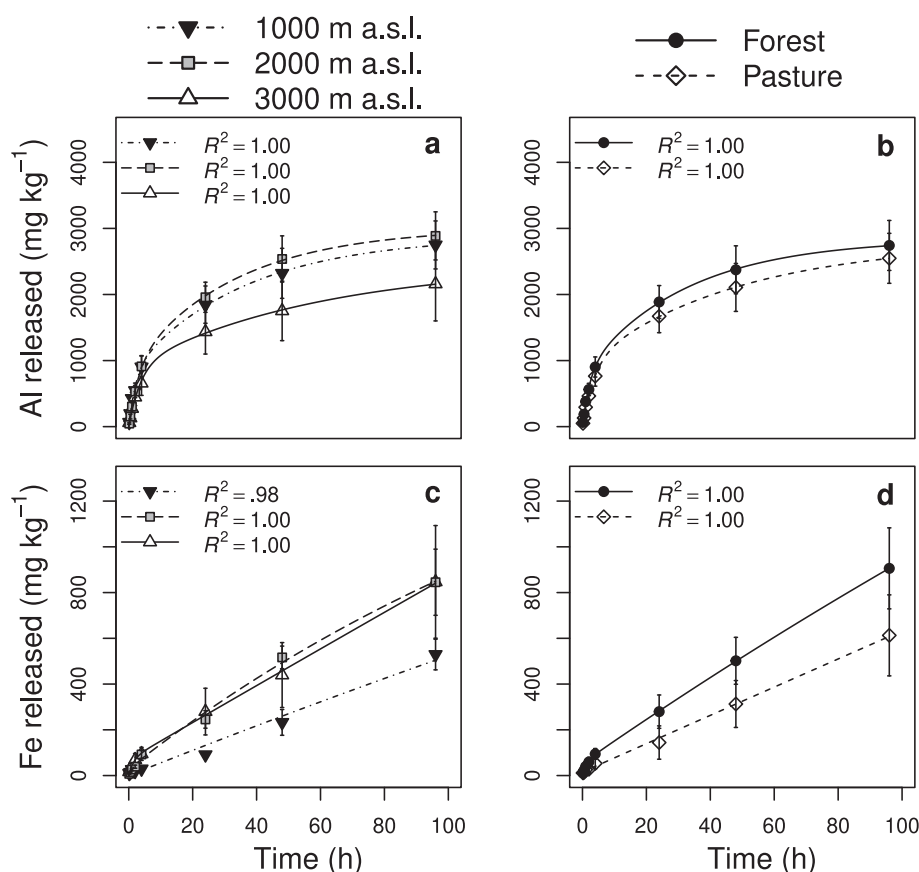
Fig. 3. Mean Al and Fe release grouped according to elevation (left column, a, c) and land cover/use (right column, b, d), respectively. The lines illustrate the fit using Eq. (1). Error bars represent standard errors (n = 6 for elevation and n = 9 for land cover/use).
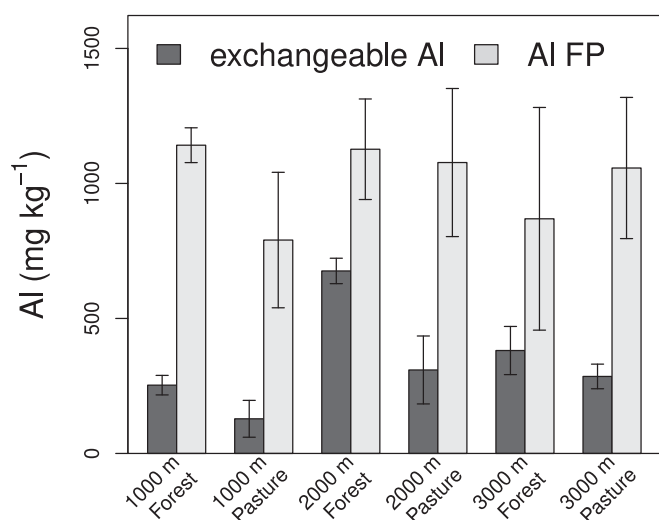
Fig. 4. Mean exchangeable Al concentrations and size of the fast-reacting pool (FP) depending on elevation and land cover/use. Error bars represent standard errors.

influenced by the land cover/use. Likely because of the established slash-and-burn practices and recurrent pasture fires to control shrub invasion, alkaline ashes may have increased the exchangeable cation pool of the pasture soils relative to the forest soils. As a consequence, pasture soils were more fertile than forest soils in the study area. Thus, our Hypothesis (i) is fully supported.

In contrast to our Hypothesis (ii), the climatic conditions approximated by elevation between the sites with similar parent material at 2000 and 3000 m a.s.l., did not have a significant influence on the metal release kinetics, possibly because the opposing effects of increasing precipitation and decreasing temperature canceled each other out, the continuous rejuvenation of the soils by landslides resulted in similar weathering state or pedogenetic thresholds were not crossed between the two sites. The chemically different parent material at the 1000 m site resulted in markedly different metal release kinetics compared to the 2000 m and 3000 m a.s.l. sites, which had similar parent material and exhibited similar metal release kinetics. Our results demonstrate that the local, low-intensity pasture use and the chemical composition of the parent rocks are important drivers of the soil fertility in the south Ecuadorian tropical montane rain forest region.

CRediT authorship contribution statement

Daniel Schöndorf: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation. **Nuria Basdediós:** Writing – review & editing, Validation, Supervision, Methodology, Investigation. **Andre Velescu:** Writing – review & editing, Resources, Project administration, Methodology, Investigation, Data curation. **Tobias Fabian:** Writing – review & editing, Methodology, Investigation. **Carlos Iván Espinosa:** Writing – review & editing, Supervision, Conceptualization. **Wolfgang Wilcke:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence
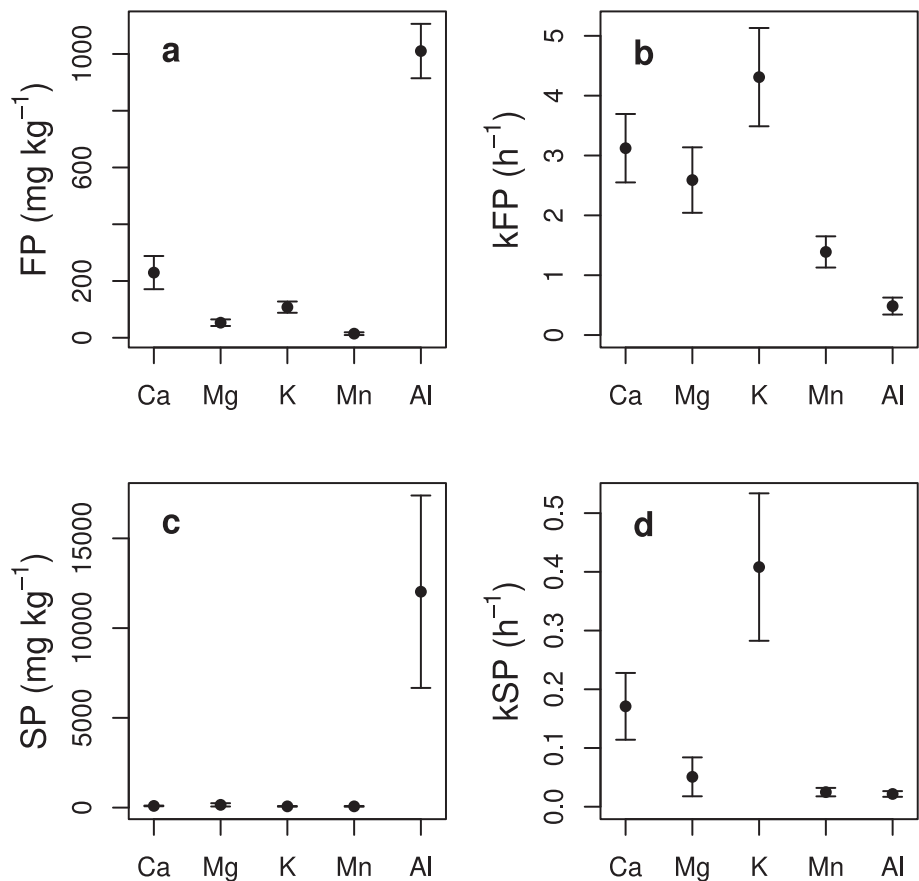
Fig. 5. Mean pool sizes and their release rate constants: (a) fast-reacting pool (FP), (b) fast-reacting pool release rate constant (kFP), (c) slow-reacting pool (SP) and (d) slow-reacting pool release rate constant (kSP) of the studied elements. Error bars represent standard errors.

Table 2
Means and standard deviations of the ratio of the slow-reacting pool to the total element concentration in soil not attributed to the fast-reacting pool (B_{rel}) according to Eq. (2) of Ca, Mg, K, Mn, Al. Different letters indicate significant differences according to Tukey's HSD post-hoc test.

		B_{rel}
Ca	(%)	45.9 ± 28.9 a
Mg	(%)	5.3 ± 11.6 c
K	(%)	0.5 ± 0.6 d
Mn	(%)	24.4 ± 23.9 ab
Al	(%)	19.7 ± 31.5 b

the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.geoderma.2025.117263.

Data availability

Data will be made available on request.

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