Aluminum cycling in a tropical montane forest ecosystem in southern Ecuador

Agnes Rehmus[a], Moritz Bigalke[a*], Jens Boy[b], Carlos Valarezo[c], Wolfgang Wilcke[a,b]

*Corresponding author: moritz.bigalke@giub.unibe.ch Tel: +41-31-6314055

[a]Geographic Institute, University of Bern, Hallerstr. 12, 3012 Bern, Switzerland, agnes.rehmus@giub.unibe.ch

[b] Institute of Soil Science, Leibniz Universität Hannover, Herrenhäuser Str. 2, 30419 Hannover, boy@ifbk.uni-hannover.de

[c]Dirección General de Investigaciones, Universidad Nacional de Loja, Ciudadela Universitaria Guillermo Falconí, sector La Argelia, Loja, Ecuador, cvalarezom@gmail.com

[d]Institute of Geography and Geoecology, Karlsruhe Institute of Technology (KIT), Reinhard-Baumeister-Platz 1, 76131 Karlsruhe, Germany, mailto:wolfgang.wilcke@kit.edu

Abstract

Growth limitation induced by Al toxicity is believed to commonly occur in tropical forests, although a direct proof is frequently lacking. To test for the general assumption of Al toxicity, Al, Ca, and Mg concentrations in precipitation, throughfall, stemflow, organic layer leachate, mineral soil solutions, stream water, and the leaves of 17 native tree species were analyzed. We calculated Al fluxes, analyzed temporal trends and modeled Al speciation in the litter leachate and mineral soil solutions. We assessed potential Al toxicity based on soil base saturation, Al concentrations, Ca:Al and Mg:Al molar ratios and Al speciation in soil solution as well as Al concentrations and Ca:Al and Mg:Al molar ratios in tree leaves. High Al fluxes in litterfall (8.77 ± 1.3 to 14.2 ± 1.9 kg ha^{-1} yr^{-1}, mean±SE) indicate a high Al circulation through the ecosystem. The fraction of exchangeable and potentially plant-available Al in mineral soils was high, being a likely reason for a low root length density in the mineral soil. However, Al concentrations in all solutions were consistently below critical values and Ca:Al molar and the Ca^{2+}:Al$_{inorganic}$ molar ratios in the organic layer leachate and soil solutions were above 1, the suggested threshold for

28 Al toxicity. Except for two Al-accumulating and one non-accumulating tree species, the Ca:Al

29 molar ratios in tree leaves were above the Al toxicity threshold of 12.5. Our results demonstrate

30 a high Al cycling through the vegetation partly because of the presence of some Al accumulator

31 plants. However, there was little indication of an Al toxicity risk in soil and of acute Al toxicity in

32 plants likely reflecting that tree species are well adapted to the environmental conditions at our

33 study site and thus hardly prone to Al toxicity.

34 **Keywords**

35 tropical forest ecosystems, aluminum fluxes, aluminum toxicity, Al speciation, molar Ca:Al ratios

1   Introduction

37   Many plant species are sensitive to high concentrations of the phytotoxic Al^{3+}, $AlOH^{2+}$, or

38 $AlOH_2^+$ and various other inorganic Al complexes which can occur in soil solutions at pH values <

39 5.5 (Alleoni et al., 2010; Delhaize and Ryan, 1995; Kabata-Pendias and Pendias, 2001; Macdonald

40 and Martin, 1988). Aluminum phytotoxicity contributes to forest decline in temperate forests

41 (Cronan, 1989; Farr et al., 2009; Godbold et al., 1988). In tropical montane forests, pH usually

42 ranges betwen 4 and 5 and Al toxicity was suggested to contribute to low biomass production and

43 slow nutrient-cycling rates (Bruijnzeel, 2001; Bruijnzeel and Veneklaas, 1998; Hafkenscheid,

44 2000).

45   The Al fluxes in an ecosystem vary strongly depending on tree species (coniferous,

46 deciduous), the climate conditions (temperate, tropical) and soil properties like texture, organic

47 C concentrations and pH (Table 1). Aluminum inputs depend on dust deposition and amount of

48 precipitation. Our literature review revealed that the highest Al fluxes with litterfall occur in

49 tropical environments while the highest Al fluxes in soil solution were reported in acidified

50 temperate forests, because of locally low soil pH (Table 1).

51   The pH is the most important control of Al concentrations in soil solution and acid

52 deposition is a main driver of Al fluxes in a forest (Mulder, 1988). Thus, seasonal acid deposition

53 originating from Amazonian forest fires (Boy et al., 2008a) and the increasing NH_4^+ deposition

54 with subsequent nitrification already in the forest canopy and nitrate leaching through the

55 ecosystem resulted in acidification of the organic layer leachate at our study site (Wilcke et al.,

56   2013), which will probably also couple back to Al fluxes in the system.

57   A hydroponic experiment with saplings of three different tree species typical for the south

58   Ecuadorian montane forests has shown that Al toxicity thresholds (EC10 values) are between 126

59   and 376 μM Al in solution (Rehmus et al., 2014). However, knowledge of Al concentrations in soil

60   solutions alone is not sufficient to judge the threat of Al toxicity, because Al speciation is crucial

61   for toxic effects (Alleoni et al., 2010). If the solid Al pool is limited, which is particularly the case

62   in the organic layer compared to the mineral soil, ligand complexation in the solid and dissolved

63   phases leads to detoxification of Al^{3+}. Several studies demonstrated an alleviation of Al toxicity by

64   the formation of organo-Al complexes with dissolved organic matter in solution (Alleoni et al.,

65   2010; Drabek et al., 2005; Hernandez-Soriano et al., 2013; Vieira et al., 2009) and in the solid

66   organic matter (Álvarez et al., 2012; Eimil-Fraga et al., 2015). At our study site, most nutrients are

67   stored in the thick organic layers (Wilcke et al., 2002) where also 51 to 76 % of the fine root length

68   is located (Soethe et al., 2006). Previous studies showed that depending on dissolved organic

69   matter concentrations, 97 % to almost 100 % of the Al in organic layer solution is organically

70   bound in complexes and nontoxic (Wullaert et al., 2013).

71   A variety of indices based on chemical composition of the soil solid phase, soil solution,

72   and plant tissue can be used to estimate Al stress of an ecosystem (Álvarez et al., 2005). One

73   commonly used approach to estimate the threat of Al stress to plants is the Ca:Al molar ratio in

74   plant tissue and soil solution and the base saturation of the soil (Cronan and Grigal, 1995),

75   because the Ca-Al antagonism may disturb the Ca nutrition at high Al concentrations (Rengel,

76   1992). According to Cronan and Grigal (1995), indices for a 50 % risk of adverse impacts on tree

77   growth induced by Al stress are a $Ca^{2+}:Al_{inorganic}$ (sum of inorganic Al species) molar ratio of ≤ 1.0

78   in soil solution, a Ca:Al molar ratio of ≤ 12.5 in the foliar tissue, and a soil base saturation ≤ 15 %

79   of the effective cation-exchange capacity (ECEC). Aluminum can also affect the Mg nutrition of

80   plants (Kidd and Proctor, 2000; Kinraide, 2003). Reduced Mg concentrations in needles of *Picea*

81   *abies* (L.) H.Karst. in an in-situ experiment with elevated Al concentrations (up to 500 μM) in soil

82   solution were revealed by De Wit et al. (2010). In a previous hydroponic experiment, impaired

83   Mg translocation to the leaves and possibly reduced photosynthesis was suggested as a reason

84   for reduced shoot biomass production under Al stress (Rehmus et al., 2015).

85   We analyzed Al fluxes and cycling in a tropical mountain forest in southern Ecuador and

86 tested soil, soil solution and plant leaves for indications of Al toxicity to answer the following

87 questions:

1. Is Al cycling enhanced in tropical montane forests because of acid soils and
   elevated litterfall production?

2. Do toxicity indicators point at negative effects of Al on plant growth?

2 Materials & Methods

2.1 Study site and sampling procedures

93 The study site is an approx. 9 ha-large microcatchment (MC 2) between 1900 and 2010

94 m a.s.l. (above sea level) on 30–50° steep slopes on the north-facing part of the Rio San Francisco

95 valley (Boy and Wilcke, 2008). The ecosystem flux measurements in the forest are concentrated

96 along three ca. 20 m-long transects covering about 10 m in elevational difference at 1900 – 1910,

97 1950 – 1960 and 2000 – 2010 m a.s.l. (MC 2.1, MC 2.2, and MC 2.3, Figure 1). We considered the

98 three measurement transects as replicates to account for the spatial variation in the study

99 catchment.

100 Incident precipitation and throughfall were collected with Hellmann-type collectors on a

101 clearing and at the three transects in the forest, respectively. Stemflow was collected on five

102 representative large trees in MC 2.1 and surface flow was measured with a V-shaped weir at the

103 outlet of the stream draining MC 2. Further instrumentation (to collect litter leachate, soil

104 solutions, and litterfall) was placed along three measurement transects (MC 2.1 – 2.3). The

105 following equipment was established at each of the three replicate transects: Three litter

106 collectors with the dimension 0.3 m x 0.3 m and 0.5 mm mesh size, three zero-tension lysimeters

107 below the organic layer to collect organic layer leachate from below the Oi, Oe, and Oa horizons

108 (LL), and three suction cups at each of the 0.15 and 0.3 m depths of the mineral soil to collect

109 mineral soil solution (SS15 and SS30, respectively). Weekly sample replicates were bulked to a

110 composite sample per sample type (solution or litterfall) and measurement site prior to chemical

111 characterization. Solution samples were analyzed in weekly resolution while litterfall samples

112 were bulked to monthly samples before chemical analysis. Soil water content was measured with

113 FDR (frequency domain reflectometry) probes at transect MC 2.1 at the 0.1, 0.2, 0.3, and 0.4 m

depths. We calculated monthly element concentration means of incident precipitation, throughfall precipitation, stemflow, and surface flow from April 1998 to March 2003, of soil solutions from May 2000 to April 2003, and of the organic layer leachate from April 1998 to December 2007 and September 2009 to April 2010. Our time series included smaller gaps (6 % of time) because of missing samples. Samples of fresh tree leaves representing the most abundant tree species in the highly biodiverse study area (Homeier et al., 2002) were collected in two sampling campaigns between October 2005 and February 2006 and in October 2011 from 21 and 9 individual trees, respectively (17 tree species in total, Table 2). Young leaves were sampled randomly from the tree crown. The base and Al saturation of the effective cation exchange capacities of the mineral soils were determined as the sum of the charge equivalents of Ca, Mg, Na and K or Al, respectively, divided by sum of the charge equivalents of Ca, K, Mg, Na, Mn and Al extracted with 1 M NH_4NO_3 (soil:solution ratio 1:25) from the A horizons of 23 soils. Three of the soil samples were collected at our measurement transects (each composited from three sampling sites, Wilcke et al., 2001), 10 soils were located along an elevational transect near the stream draining the watershed between 1880 and 2100 m a.s.l. (valley bottom) and further 10 soils were located along an elevational transect near the ridge between 1890 and 2110 m a.s.l. (Wilcke et al., 2010). The latter two transects were considered to represent a large part of the soil variation in the study catchment. More detailed information about the study site and sampling is given in the Supporting Material (SM).

2.2 Chemical analyses

Within 24 h of collection of the precipitation, throughfall, stemflow, soil solution, and stream water samples were analyzed first for electric conductivity (EC) (ProfiLine Cond 3110, WTW GmbH, Weilheim, Germany) and then for pH (Sentix HWS, WTW GmbH, Weilheim, Germany), filtered (ashless filters with pore size 4-7 µm, folded filter type 389; Munktell & Filtrak GmbH, Bärenstein, Germany) and frozen at the day of sampling until analysis. To ensure that the time gap between sampling and analysis had no effect on pH, selected samples were analyzed immediately and after 24 and 48 hours and showed no change in pH (Table S1). The samples were kept frozen until further chemical analyses. Aluminum concentrations were determined with inductively-coupled plasma mass spectrometry (ICP-MS, VG PlasmaQuad PG2 Turbo Plus, Thermo

143 Fisher Scientific, Waltham, USA and 7700x Agilent Technologies, Frankfurt am Main, Germany).

144 The Ca, Mg, K, Na and Al concentrations in leaves and extracts of soils and suspended particulate

145 matter of stream water were analyzed with atomic absorption spectroscopy (AAS, SpectraAA400,

146 Varian, Darmstadt, Germany and Zeenit700P, Analytik Jena, Jena, Germany). Fluoride

147 concentrations were determined with an ion-sensitive electrode (WTW Inolab pH/Ion 735 with a

148 WTW F800 electrode, WTW, Weilheim, Germany) after addition of TISAB III (Fluka Analytical) by

149 standard addition. Concentrations of Cl^- were determined with a Cl^--specific ion electrode (Orion

150 9617 BN, Thermo Fisher Scientific, Waltham, USA) after adjustment of the ionic strength with a

151 solution of 1.13 g L^{-1} $NaNO_3$+2 mL L^{-1} surfactant (Triton X-100, 50% solution) during the first 3

152 years on a segmented Continuous Flow Analyzer (CFA, AutoAnalyzer 3 HR, SEAL Analytical,

153 Germany). Concentrations of, NH_4^+, NO_3^-, and PO_4^{3-} were determined photometrically with a CFA

154 (initially a San plus, Skalar, Breda, Netherlands device was used and later the AutoAnalyzer 3 HR).

155 Sulfate was determined by ion chromatography (Dionex ICS-900, Thermo Scientific, Waltham,

156 MA, USA). Total organic carbon (TOC) concentrations were analyzed with a TOC-5050 (Shimadzu,

157 Düsseldorf, Germany).

158 The litter and leaf samples were digested in a closed vessel microwave system (MARS

159 Xpress, Kamp-Lintfort, Germany and MLS Ethos, Leutkirch, Germany, respectively) after drying

160 and homogenization with an agate ball mill. The litter and leaf samples of 2005/2006 were

161 digested with 65 % HNO_3 and leaf samples of 2011 with 69 % HNO_3/30 % H_2O_2/48 % HF and

162 subsequently with 5 % H_3BO_3 to complex residual HF (16 HNO_3:6 H_2O_2:1 HF:10 H_3BO_3 v/v/v/v).

163 Concentrates of particulate matter in stream water were digested with 65 % HNO_3/48 % HF (4:1

164 v/v). The quality of digestions and measurements of Al, Ca and Mg concentrations was controlled

165 with the help of the certified reference material (CRM) BCR-100 (beech leaves IRMM, Geel,

166 Belgium). The accuracy of Ca and Al measurement in both types of digests was within ± 5% and

167 that of Mg within ±10% deviation of the certified value. The pH values of the solid soil samples

168 were determined in 0.01 M $CaCl_2$ (soil:solution ratio 1:2.5). The detection limits of our chemical

169 analyses are given in Table S2.

170

2.3 Calculations and Al speciation modeling

The base saturation and saturation of exchangeable Al was calculated as the proportion of charge equivalent of extractable Ca + K + Mg + Na and Al of the ECEC. The Al fluxes were calculated for 5 consecutive hydrological years from April 1998 to March 2003 (in the case of soil solutions 3 years from May 2000 to April 2003). More details about the calculation of fluxes are given in the supporting material. Surface flow was modeled with the hydrological catchment model TOPMODEL (Beven et al. 1995). Details about the parameterization and validation of the model are given in Fleischbein et al. (2006). Soil water fluxes were calculated from climate data and soil moisture measurements with a soil water budget model as described by Boy et al. (2008b). Data gaps of soil water fluxes (because of lacking soil water contents) were substituted with the help of a regression model of modeled weekly soil water fluxes on measured weekly throughfall volumes ($R^2 = 0.85$). The Al canopy budget and total Al deposition was estimated with the canopy budget model of Ulrich (1983) assuming Cl^- as inert tracer (Boy and Wilcke, 2008) as described in the SM.

Potential drivers of Al concentrations are soil acidity and concentrations of complexing agents including TOC, F^-, and SO_4^{-2}. Wullaert et al. (2013) showed that only TOC occurred in relevant concentrations for Al complexation. Complexes of other ligands (Cl^-, F^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) hardly contributed to total Al concentrations. Furthermore, total Al concentrations are influenced by dilution/concentration effects which we addressed by including soil moisture contents in our analysis. Multiple regressions were calculated among monthly Al concentrations and Ca:Al molar ratios, respectively, with pH, TOC concentrations and soil moisture (only in the organic layer leachate (see SM for more details).

The Al speciation was calculated using Visual MINTEQ (VMINTEQ, Version 3.0 beta, J.P. Gustafsson) for LL (n=176), SS15 (n=41), and SS30 (n=50) samples, for which a complete data set was available. The F^- concentrations were determined for a subset of 176 samples from all three solution types and were in all cases below the limit of quantification ($1.16\,\mu M$) and in 89 % of the cases even below the limit of detection ($0.37\,\mu M$). Thus, for the calculation we set F^- concentrations of all samples to half of the detection limit ($0.18\,\mu M$). In the model, SO_4^{2-} concentrations were set to $6.35\,\mu M$ (i.e. the mean sulfate concentration of 31 measured samples of all three solution types). Ionic strength was estimated from EC according to Griffin and Jurinak

201 (1973). Within VMINTEQ, the NICA-Donnan model was used to assess complexation of Al with
202 humic substances. Details of the NICA-Donnan model are given in Kinniburgh et al. (1996). NICA-
203 Donnan properties of metal complexation by organic acids were taken from the literature (Milne
204 et al., 2003). An active DOM/DOC ratio of 2 was assumed and the dissolved organic acids were
205 adjusted to be 100 % fulvic acids (Tipping and Carter, 2011).

3   Results

3.1   Al fluxes

208   Mean annual Al fluxes at each of the three measurement transects were lowest in bulk,
209 dry, and throughfall deposition (< 0.6 kg ha^{-1} yr^{-1}, Figure 1). Stemflow contributed negligibly to the
210 Al fluxes reaching the soil (< 0.05 – 5.4 %). Soil deposition by litterfall was 9 to 18 times higher
211 than that of the sum of all dissolved aboveground Al fluxes. The mean annual litter input at MC 2
212 from April 1998 to March 2003 was 10.0±0.3 t ha^{-1} yr^{-1}. The mean annual canopy budget was
213 positive at each of the three measurement transects. The Al fluxes in organic layer leachate were
214 lower than in mineral soil solutions except at transect MC 2.3, where lowest Al fluxes occurred in
215 SS30. The multiple regression among Al concentrations (C_{Al}) and pH values, soil moisture content,
216 and TOC concentrations (C_{TOC}) in organic layer leachate (Eq. 1) shows the highest partial
217 regression coefficient for the pH, highlighting the importance of pH for Al concentrations in soil
218 solutions (Figure S1).
219   Eq. 1 $C_{Al} = 7.88 - 0.88 \cdot pH - 0.03 \cdot$ soil moisture (vol.%) $+ 0.02 \cdot C_{TOC}$ (mgL^{-1})
220   ($R^2 = 0.31$, $p < 0.001$, n = 75)
221 The net hydrological export of Al (i.e. SW-BD, Table 1) was slightly negative, indicating a net
222 accumulation of Al, which was even more pronounced when the total catchment budget (i.e.
223 SW-[BD+DD]) was considered. Yet, the loss of Al as suspended particulate matter in stream
224 water averaged 28.8 kg ha^{-1} yr^{-1} (August 2000 – January 2003). From the sum of the net
225 hydrological export and the Al export in suspended particulate matter in stream water, the
226 weathering rate of Al can be estimated as 28.7 kg ha^{-1} yr^{-1} (Likens, 2013). This approach is based
227 on the assumption that the soil thickness is in steady state and that superficial erosion equals
228 soil formation at the subsoil-parent material border (Likens, 2013).

3.2 Al toxicity indicators

The total Al concentrations in LL, SS15 and SS30 were usually higher in mineral soil solutions than in LL (Table 2). The total Al concentrations in precipitation, stemflow and stream water were below 1 μM. The sum of the concentrations of inorganic Al species (Al$_{inorg}$) in LL, SS15 and SS30 ranged 0.00 - 30.9 μM (Table S3). The fraction of organically bound Al was highest in LL (mean: 96 %) and decreased with soil depth (83 % in SS30).

Aluminum concentrations in leaves of the tree species in the study area were generally in the range of 0.05 – 0.14 (mg g^{-1}, Table 2). Two tree species, *Graffenrieda emarginata* (Ruiz & Pav.) Triana and *Miconia sp*, belonging to the family of Melastomataceae are Al accumulators (Jansen et al., 2002) and therefore had distinctly higher Al concentrations than the Al non-accumulating tree species.

The Ca^{2+}:Al$_{inorganic}$ and Mg^{2+}:Al$_{inorganic}$ molar ratios were distinctly higher in LL than in SS15 and SS30 solutions (Table S3). The Ca and Mg concentrations in the leaves ranged 1.7 – 12.5 and 1.2 – 5.3 (mg g^{-1}), respectively (Table 2). The Ca:Al molar ratios were consistently higher than 12.5 and ranged up to 144. Only the two Melastomataceae species and *Ocotea bentamiana* Mez. (Lauraceae) had Ca:Al molar ratios of 0.5 – 9.2, indicating potential Al toxicity.

The pH in soil A horizons ranged 3.2 – 5.2 (mean 3.7). The base saturation ranged 4.77 – 97.1 % (mean 41.4 %) and the Al saturation ranged 2.65 – 95.2 % (mean 57.7 %). Seven of the 23 soil A horizons had a base saturation of ECEC below 15 % and two soil A horizons had a base saturation between 15 and 16 % (Figure 2). Soils with low base saturation mainly occurred on the ridges (mean±SE base saturation on the ridges: 22.2±5.2 % and in the valley: 65.2±9.1 %) (Wilcke et al., 2010).

4 Discussion

4.1 Al fluxes

The Al fluxes with bulk and dry deposition were well in the range reported from other forests. They were higher than in the Hubbard Brook experimental forest (Likens, 2013) and a humid tropical ecosystem in Fiji (excluding cyclone events, Waterloo et al., 1997), similar to that of a temperate forest in the USA (Rustad and Cronan, 1995, Table 1) but low compared to other

257 tropical rain forests in Brazil (Mayer et al., 2000; Cornu et al., 1998) and a temperate forest in

258 Germany, which was affected by acid deposition (Matzner, 1989; Figure 1 and Table 1). The Al

259 bulk and dry deposition mostly derives from mineral dust, because Al is an ubiquitous element in

260 soils (Macdonald and Martin, 1988), but is also affected by the total amount of precipitation,

261 which is high compared to temperate but medium to low compared to other tropical forests. The

262 positive canopy budget indicates leaching of Al from the canopy. The leaching of cations is a result

263 of proton buffering in the canopy and release of cations to achieve electroneutrality (Matzner,

264 1989). The lowest Al fluxes occurred in stemflow, which were also lower than in other studies

265 (Figure 1). However, the input of Al and H^+ ions by the stemflow to the soil is restricted to a small

266 area around the stem basis which might have a considerable impact on the local soil chemistry,

267 but minor importance for the total Al fluxes in the ecosystem (Koch and Matzner, 1993; Levia and

268 Frost, 2003).

269   The Al fluxes with litterfall were high compared to temperate forest ecosystems and most

270 study sites in the tropics (Table 1) and attributable to both, the overall high quantity of litterfall

271 and high Al concentrations in litterfall (Table 2 and Figure 1). Compared with a temperate forest

272 in Bavaria, Germany, mean annual litterfall was two and approximately five times that of a

273 deciduous and a coniferous forest, respectively, while Al concentrations in litterfall were around

274 10 times higher (Berg and Gerstberger, 2004). Litterfall and associated Al fluxes were lower at

275 some tropical montane forest (Jamaica, Table 1, Hafkenscheid, 2000) but similar to others

276 (Bolivia, Table 1; Gerold, 2008). The Al concentrations in litterfall were three times higher than

277 the Al concentrations in fresh foliage (Table 1), which is in agreement with Hafkenscheid (2000)

278 who reported enriched Al concentrations in litterfall compared to fresh leaves of the same species

279 in a tropical montane forest in Jamaica. They explained the Al enrichment as an attempt of the

280 trees to dispose excess Al via litterfall. Another reason is the withdrawal of mobile essential

281 nutrients prior to leaf fall, which will relatively enrich Al. However, another major explanation for

282 high Al concentrations in leaf litter is the wide distribution of Al-accumulating tree species. The

283 two families Melastomataceae and Rubiaceae, which are known to include Al-accumulating

284 species, belong to the most frequent families and *G. emarginata* is the most frequent tree species

285 in the studied forest (Homeier et al. 2002). However a quantification of the contribution of Al

286 accumulators to Al fluxes in litterfall would require samples in which leaf litter is differentiated

287 according to the species which could not be realized in our study.

288   The Al fluxes with organic layer leachate and soil solutions had a wide range, covering
289 most of the span reported by other studies from similar soil depths (Figure 1 and Table 1). The Al
290 fluxes with the organic layer leachate and the soil solution are coupled to their pH (Eq. 1). In
291 stream water, the dissolved Al fluxes were low compared to two temperate forest ecosystems in
292 the USA (Likens, 2013; Rustad and Cronan, 1995), which is probably attributable to the high pH
293 of the stream water (Table 3), causing precipitation of Al e.g., as Al hydroxide. However, Al in
294 suspended particulate matter in stream water and thus also the Al weathering rate was 20 times
295 higher than e.g., that of the Hubbard Brook experimental forest (Likens 2013) in line with the
296 more pronounced tropical weathering regime at our study site than at Hubbard Brook.

297 4.2   Al toxicity indicators

298   The mean base saturation in the soil A horizons was low and the mean Al saturation high,
299 which implies reduced supply with base cations. The base saturation would even be lower if
300 exchangeable protons had been included to calculate the ECEC as it is done in part of the literature
301 (e.g., Cronan and Schofield, 1990). Because of the higher pH values in the valley bottom soils and
302 lateral addition of leached base metals from above-lying soils, the mean base saturation was
303 significantly higher in the valley bottom than the ridge top soils (Wilcke et al., 2010; Figure 2). The
304 ranges of base and Al saturation are complementary at respective pH values and show that the
305 fraction of exchangeable Al can be high (up to 95 %). In mineral soils, Al might have an indirect
306 negative effect on plant nutrition via Al-P precipitation. However, the soil P status can be
307 improved by chelation of Al in organic complexes (Haynes and Mokolobate, 2001). The resulting
308 nutrient scarcity and high Al concentrations might be the reason for the low root length density
309 in the mineral soils and high root length density in the organic layers (Soethe et al., 2006).
310 Applying the critical base saturation of ≤ 15 % proposed by Cronan and Grigal (1995), out of the
311 23 analyzed soils in our study approximately 30 % might pose a potential risk of Al toxicity,
312 particularly on the ridges, where 4 of the 7 soils with a BS < 15 % and two soils with marginally
313 higher BS (< 16 %) were located (Figure 2). The percentage of soils with critical base saturation
314 would even increase if exchangeable protons had been included in the ECEC.

315   The mean pH values in organic layer leachate and soil solutions were consistently < 5.5

316 and thus favorable for high Al concentrations (Table 3). The total Al concentrations which caused

317 a 10 % reduction in shoot biomass of saplings of three tree species from the same forest (EC10

318 values: 126 to 376 μM Al, Rehmus et al., 2014) were not approached in any ecosystem solution.

319 To reach the EC10 values, an approximately 8 to 23-fold increase of the mean total Al

320 concentrations in organic layer leachate would be necessary. The lowest Al concentrations at

321 which a negative response of sensitive species was observed ranged from 35 to 170 μM (Schaedle

322 et al., 1989). Thus the present total Al concentrations in the organic layer leachate can be

323 considered as nontoxic. In addition, the Al speciation modeling confirmed that up to 97 % of the

324 Al in the organic layer leachate is organically bound (Table S3). The remaining free Al_{inorg}

325 concentration in the organic layer leachate of approximately 0.5 μM is unproblematic even for

326 Al-sensitive plant species (Wheeler et al., 1992). The mineral soil solutions had higher total Al and

327 lower DOC and thus highest concentrations of inorganic Al species. The mean $Al_{inorganic}$

328 concentrations were above 0.5 μM in 30 cm depth at transect MC 2.1 and at both soil depths at

329 transects MC2.2 and 2.3 (Table S3) and thus Al toxicity might occur for sensitive plants. However,

330 high $Al_{inorganic}$ concentrations in in the mineral horizons will have a limited Al toxicity effect to local

331 tree species, because 51 to 76 % of the fine root length is concentrated in the organic layer

332 (Soethe et al., 2006). On the other hand, this distribution of root length density may be a reaction

333 to the higher Al concentrations in mineral soil solution compared to organic layer leachate.

334 Applying the $Ca^{2+}:Al_{inorganic}$ molar ratios in the organic layer leachate and the mineral soil

335 solutions as an indicator for a negative impact on the tree growth (Cronan and Grigal, 1995), only

336 few solutions might pose a 50 % and higher risk of Al stress (Table S3). Because Al has a higher

337 affinity for dissolved organic matter than Ca, the majority of the organic layer leachates and even

338 the mineral soil solutions had a Ca:total Al and even $Ca^{2+}:Al_{inorganic}$ molar ratios far higher than the

339 suggested threshold of 1 (mean $Ca^{2+}:Al_{inorganic}$ molar ratios 1.17 - > 10^{36}, Table S3), which renders

340 an Al effect on plant Ca uptake unlikely. Jorns and Hecht-Buchholz (1985) reported Mg deficiency

341 symptoms in Norway spruce (*P. abies*) at Mg:Al molar ratios of < 0.2. In the hydroponic

342 experiment with species from our study site, Al-induced toxicity symptoms occurred at > 300 μM

343 Al and Mg:total Al molar ratios in nutrient solution were < 0.2 at treatments ≥ 600 μM Al (Rehmus

344 et al., 2014). Thus, Mg deficiency might be a reason for reduced biomass production and Mg:Al

345 molar ratios might be a suitable indicator for Al stress. The Mg:Al molar ratios of SS15 and SS30

346 were < 0.2 but distinctly higher in all other ecosystem solutions, suggesting problematic Mg:Al

347 molar ratios again only in the mineral soil (Table S2). However, calculating $Mg^{2+}:Al_{inorganic}$ molar

348 ratios resulted in far higher values also in the mineral soil solutions (Table S3).

349   The Ca concentrations in tree leaves were all in the range required for optimal plant

350 growth ($1 - > 50$ mg g^{-1}; Marschner, 2012). The Mg concentrations in the leaves (Table 2) are

351 comparable to Mg concentrations in leaves of Brazilian Cerrado trees ($0.71 - 2.1$ mg g^{-1}; Lilienfein

352 et al., 2001) and in tree leaves of a tropical seasonal rain forest in southwest China ($3.2 - 5.4$ mg

353 g^{-1}; Shanmughavel et al., 2001). In leaves of 4 and 8 of the 17 analyzed tree species in our study,

354 Mg concentrations were below the limiting values required for optimal growth of crop plants

355 reported by Amberger (1996) ($2 - 50$ mg g^{-1}) and Marschner (2012) ($1.5 - 3.5$ mg g^{-1}), respectively.

356 Thus, Mg deficiency might affect growth of some of the tree species. However, low Mg

357 concentrations in trees might primarily result from Mg-poor bedrock and only secondarily from

358 the Mg-Al antagonism. According to Cronan and Grigal (1995), the Ca:Al molar ratios of the two

359 Melastomataceae species and the Lauraceae species which were < 12.5 (Table 2) would mean a

360 50 % and higher risk of Al stress. However, beneficial effects of Al on plant growth in hydroponic

361 experiments with Al-accumulating tree species, adapted to acid soils, have been reported (Osaki

362 et al. 1997, Watanabe and Okada 2005). Only *O. bentamiana*, which is Al non-accumulating, might

363 suffer immediate Al stress.

364 **5 Conclusions**

365 We conclude that

366   1. Al fluxes in the ecosystem are mainly controled by high precipitation, biomass production,

367   presence of Al-accumulating plant species and soil pH. Partly high Al fluxes, particularly in

368   litterfall, illustrate a high Al circulation through the ecosystem possibly influenced by the

369   abundance of Al-accumulating plants.

370   2. The fraction of exchangeable Al on cation exchanger surfaces and the concentrations of

371   dissolved $Al_{inorganic}$ were high in mineral soils. Together with the problematic Mg:Al ratios,

372   Al toxicity is a likely reason for a low root length density in the mineral soil. The

373   concentrations of inorganic Al species in the organic layer leachate were low and most

374   probably below toxicity levels for trees and Ca:Al and Mg:Al molar ratios were

375 unproblematic. As plants have their main rooting zone in the organic layers, Al toxicity
376 might be of minor importance. The Al concentrations in tree leaves were high in Al-
377 accumulating, but in a normal range for non-accumulating species. The Ca:Al molar ratios
378 in leaves of most Al non-accumulating tree species were unproblematic. Hence, the trees
379 of our study ecosystem seems to be well adapted to the given Al concentrations.
380

Supplementary Material

382 More information about the study site, sampling procedures, calculations, one figure and 3
383 tables can be found in the Supplementary Material.

Acknowledgments

Conflict of interest

395 The authors declare no competing financial or personal interests.

References

Alleoni, L.R.F., Cambri, M.A., Caires, E.F., Garbuio, F.J., 2010. Acidity and aluminum speciation as affected by surface liming in tropical no-till soils. Soil Sci. Soc. Am. J. 74, 1010–1017.

Álvarez, E., Fernández-Marcos, M.L., Monterroso, C., Fernández-Sanjurjo, M.J., 2005. Application of aluminium toxicity indices to soils under various forest species. For. Ecol. Manage. 211, 227–239.

Álvarez, E., Fernández-Sanjurjo, M.J., Núñez, A., Seco, N., Cort,i G., 2012. Aluminium fractionation and speciation in bulk and rhizosphere of a grass soil amended with mussel shells or lime. Geoderma 173-174, 322–329.

Amberger, A., 1996. Pflanzenernährung, 4th edn. Stuttgart: Ulmer. 319p.

Berg, B., Gerstberger, P., 2004. Element fluxes with litterfall in mature stands of norway spruce and european beech in Bavaria, south Germany. Matzner E, editor. Biogeochemistry of forested catchments in a changing environment. Ecological Studies, vol 172. Berlin Heidelberg, Springer. p271–278.

Bergamini, Scheer, M., Gatti, G., Wisniewski, C., 2011. Nutrient fluxes in litterfall of a secondary successional alluvial rain forest in southern Brazil. Revista de Biologia Tropical 59, 1869–1882.

Beven, K., Lamb, R., Quinn, P., Romanowicz, R., 1995. TOPMODEL. Singh V, editor. Computer models of watershed hydrology. Highlands Ranch, Colorado, Water Resource Publications. p627–668.

Boy, J., Valarezo, C., Wilcke, W., 2008. Water flow paths in soil control element exports in an Andean tropical montane forest. European Journal of Soil Science 59, 1209–1227.

Boy, J., Wilcke, W., 2008. Tropical Andean forest derives calcium and magnesium from Saharan dust. Global Biogeochem. Cycles 22(1), 1–11

Bruijnzeel, L., Veneklaas, E., 1998. Climatic conditions and tropical, montane forest productivity: The fog has not lifted yet. Ecology 79(1): 3–9. DOI 10.2307/176859

Bruijnzeel LA. 2001. Hydrology of tropical montane cloud forests: A reassessment. Water Resour. Res. 1, 1–18.

Cornu, S., Lucas, Y., Ambrosi, J., Desjardins, T., 1998. Transfer of dissolved Al, Fe and Si in two

425   Amazonian forest environments in Brazil. Eur. J. Soil Sci. 49(3), 377–384.

426   Cronan, C.S., 1989. Aluminum toxicity in forests exposed to acidic deposition: the Albios

427   results. Water Air Soil Poll. 48, 181–192.

428   Cronan, C.S., Schofield, C.L., 1990. Relationships between aqueous aluminum and acidic

429   deposition in forested watersheds of North America and Northern Europe. Environ. Sci.

430   Technol. 24, 1100-1 105

431   Cronan, C.S., Grigal, D.F., 1995. Use of calcium/aluminum ratios as indicators of stress in forest

432   ecosystems. J. Environ. Qual. 24(2), 209–226.

433   Delhaize, E., Ryan, P.R., 1995. Aluminum toxicity and tolerance in plants. Plant Physiol. 107(2),

434   315–321. DOI 10.1104/pp.107.2.315

435   De Wit, H.A., Eldhuset, T.D., Mulder, J., 2010. Dissolved Al reduces Mg uptake in Norway

436   spruce forest: results from a long-term field manipulation experiment in Norway. For.

437   Ecol. Manage. 259(10), 2072–2082.

438   Dijkstra, F.A. and Fitzhugh, R.D. 2003. Aluminum solubility and mobility in relation to organic

439   carbon in surface soils affected by six tree species of the northeastern United States.

440   Geoderma 114, 33-47.

441   Drabek, O., Mladkova, L., Boruvka, L., Szakova, J., Nikodem, A., Nemecek, K., 2005. Comparison

442   of water-soluble and exchangeable forms of Al in acid forest soils. J. Inorg. Biochem. 99(9),

443   1788–1795.

444   Eimil-Fraga, C., Álvarez-Rodríguez, E., Rodríguez-Soalleiro, R., Fernández-Sanjurjo, M.J., 2015.

445   Influence of parent material on the aluminium fractions in acidic soils under *Pinus pinaster*

446   in Galicia (NW Spain). Geoderma 255-256, 50–57.

447   Farr, C., Skousen, J., Edwards, P., Connolly, S., Sencindiver, J., 2009. Acid soil indicators in

448   forest soils of the Cherry River Watershed, West Virginia. Environ. Monit. Assess. 158,

449   343–353.

450   Fleischbein, K., Wilcke, W., Valarezo, C., Zech, W., Knoblich, K., 2006. Water budgets of three

451   small catchments under montane forest in Ecuador: experimental and modelling

452   approach. Hydrol. Process. 20(12), 2491–2507.

453   Gerold, G., 2008. The tropical mountain forest – patterns and processes in a biodiversity

454   hotspot. Gradstein SR, Homeier J, Ganser D, editors. Biodiversity and Ecology Series, vol 2.

455   Göttingen, Universitätsverlag Göttingen. p137–162.

456   Godbold, D., Fritz, E., Hüttermann, A., 1988. Aluminum toxicity and forest decline. Proc. Nat.

457   Acad. Sci. U. S. A. 85, 3888–3892.

458   Griffin, B., Jurinak, J.. 1973. Estimation of activity-coefficients from electrical conductivity of

459   natural aquatic systems and soil extracts. Soil Sci. 116(1), 26–30.

460   Hafkenscheid, R.L., 2000. Hydrology and biogeochemistry of tropical montane rain forests of

461   contrasting stature in the Blue Mountains, Jamaica. Dissertation. Enschede, Print Partners

462   Ipskamp. 315p.

463   Haynes, R., Mokolobate, M., 2001. Amelioration of Al toxicity and P deficiency in acid soils by

464   additions of organic residues: a critical review of the phenomenon and the mechanisms

465   involved. Nutr. Cycling in Agroecosyst. 59(1), 47–63.

466   Hernandez-Soriano, M.C., Peña, A., Mingorance, M.D., 2013. Soluble metal pool as affected by

467   soil addition with organic inputs. Environ. Toxicol. Chem. 32(5), 1027–1032.

468   Hirsch, R.M., Slack, J.R., Smitz, R.A., 1982. Techniques of trend analysis for monthly water

469   quality data. Water Resour. Res. 18: 170–121.

470   Homeier, J., Dalitz, H., Breckle, S.W., 2002. Waldstruktur und Baumartendiversität im

471   montanen Regenwald der Estación Científica San Franscisco in Südecuador. Bericht der

472   Reinhold-Tüxen Gesellschaft 14, 109–118.

473   Jansen, S., Watanabe, T., Smets, E., 2002. Aluminium accumulation in leaves of 127 species in

474   Melastomataceae, with comments on the order myrtales. Ann. Bot. 90(1), 53–64.

475   Jorns, A., Hecht-Buchholz, C., 1985. Aluminiuminduzierter Magnesium- und Calciummangel im

476   Laborversuch bei Fichtensämlingen. Allg. Forstzeitschrift 46, 1248–1252.

477   Kabata-Pendias, A., Pendias, H., 2001. Trace elements in soils and plants, 3rd edn. Boca Raton:

478   CRC Press. 548p.

479   Kidd, P.S., Proctor, J., 2000. Effects of aluminium on the growth and mineral composition of

480   *Betula pendula* Roth. J. Experim. Bot. 51(347), 1057–1066.

481   Kinniburgh, D.G., Milne, C.J., Benedetti, M.F., Pinheiro, J.P., Filius, J., Koopal, L.K., Van

482   Riemsdijk, W.H., 1996. Metal ion binding by humic acid: application of the NICA-Donnan

483   model. Environ. Sci. Technol. 30(5), 1687–1698. .

484   Kinraide, T.B., 2003. Toxicity factors in acidic forest soils: attempts to evaluate separately the

485   toxic effects of excessive Al^{3+} and H^+ and insufficient Ca^{2+} and Mg^{2+} upon root elongation.

486   Eur. J. Soil Sci. 54(2), 323–333.

487   Koch, A., Matzner, E., 1993. Heterogeneity of soil and soil solution chemistry under Norway

488   spruce (*Picea abies* Karst.) and European beech (*Fagus silvatica* L.) as influenced by

489   distance from the stem basis. Plant Soil 151(2), 227–237.

490   Levia, D.F.J., Frost, E.E., 2003. A review and evaluation of stemflow literature in the hydrologic

491   and biogeochemical cycles of forested and agricultural ecosystems. J. Hydrol. 274(1–4), 1–

492   29.

493   Likens, G., 2013. Biogeochemistry of a forested ecosystem. New York: Springer-Verlag New

494   York. 159p.

495   Lilienfein, J., Wilcke, W., Zimmermann, R., Gerstberger, P., Araújo, G.M., Zech, W., 2001.

496   Nutrient storage in soil and biomass of native Brazilian Cerrado. J. Plant Nut. Soil Sci.

497   164(5), 487–495.

498   Macdonald, T., Martin, R., 1988. Aluminum ion in biological systems. Trends Biochem. Sci.

499   13(1), 15–19.

500   Marschner, P., editor. 2012. Marschner's mineral nutrition of higher plants, 3rd edn. London:

501   Academic Press.

502   Matzner, E., 1989. Acidic precipitation: Case study Solling. Adriano D, Havas M, editors. Acidic

503   precipitation: Case studies, Advances in environmental science, vol 1. New York, Springer-

504   Verlag New York. p39–83.

505   Mayer, R., Liess, S., Lopes, M.I.M.S., Kreutzer, K., 2000. Atmospheric pollution in a tropical rain

506   forest: effects of deposition upon biosphere and hydrosphere II. Fluxes of chemicals and

507   element budgets. Water Air Soil Poll. 121(1–4), 79–92.

508   Milne, C., Kinniburgh, D., Van Riemsdijk, W., Tipping, E., 2003. Generic NICA-Donnan model

509   parameters for metal-ion binding by humic substances. Environ. Sci. Technol. 37(5), 958–

510   971.

511   Moraes, R.M., Delitti, W.B.C., Struffaldi-De Vuono ,Y., 1999. Litterfall and litter nutrient

512   content in two Brazilian tropical forests. Brazil. J. Bot. 22, 09–16.

513   Osaki, M., Watanabe, T., Tadano, T., 1997. Beneficial effect of aluminum on growth of plants

514   adapted to low pH soils. J. Soil Sci.Plant Nutr. 43(3), 551–563.

515 Rehmus, A., Bigalke, M., Valarezo, C., Mora Castillo, J., Wilcke, W., 2014. Aluminum toxicity to

516 tropical montane forest tree seedlings in southern Ecuador: response of biomass and

517 plant morphology to elevated Al concentrations. Plant Soil 382, 301–315.

518 Rehmus, A., Bigalke, M., Valarezo, C., Mora Castillo, J., Wilcke, W., 2015. Aluminum toxicity to

519 tropical montane forest tree seedlings in southern Ecuador: response of nutrient status to

520 elevated Al concentrations. Plant Soil 388, 87–97.

521 Rengel, Z., 1992. Role of calcium in aluminium toxicity. New Phytology 121, 499–513.

522 Rustad, L.E., Cronan, C.S., 1995. Biogeochemical controls on aluminum chemistry in the O

523 horizon of a red spruce (*Picea rubens* Sarg.) stand in central Maine, USA. Biogeochem.

524 29(2), 107–129.

525 Schaedle, M., Thornton, F., Raynal, D., Tepper, H., 1989. Response of tree seedlings to

526 aluminum. Tree Phys. 5, 337–356.

527 Shanmughavel, P., Liqing, S., Zheng, Z., Min, C., 2001. Nutrient cycling in a tropical seasonal

528 rain forest of Xishuangbanna, Southwest China. Part 1: tree species: nutrient distribution

529 and uptake. Bioresour. Technol. 80(3), 163–170.

530 Soethe, N., Lehmann,J., Engels, C., 2006. The vertical pattern of rooting and nutrient uptake at

531 different altitudes of a south Ecuadorian montane forest. Plant Soil 286, 287–299.

532 Tipping, E., Carter, H.T., 2011. Aluminium speciation in streams and lakes of the UK Acid

533 Waters Monitoring Network, modelled with WHAM. Sci. Tot. Environ. 409, 1550–1558.

534 Ulrich, B., 1983. Interaction of forest canopies with atmospheric constituents: SO_2, alkali and

535 earth alkali cations and chloride. Ulrich B, Pankrath J, editors. Effects of accumulation of

536 air pollutants in forest ecosystems. Dordrecht, D Reidel Publishing. p33–45.

537 Vieira, F.C.B., Bayer, C., Zanatta, J., Ernani, P.R., 2009. Organic matter kept Al toxicity low in a

538 subtropical no-tillage soil under long-term (21-year) legume-based crop systems and N

539 fertilisation. Austral. J. Soil Res. 47(7), 707–714.

540 Watanabe, T., Okada, K., 2005. Interactive effects of Al, Ca and other cations on root

541 elongation of rice cultivars under low pH. Ann. Bot.any 95(2), 379–385.

542 Waterloo, M., Schelleken, J., Bruijnzeel, L., Vugts, H.F., Assenberg, P., Rawaqa, T., 1997.

543 Chemistry of bulk precipitation in southwestern Viti Levu, Fiji. J. Tropic. Ecol. 13, 427–447.

544 Wheeler, D., Edmeades, D., Christie, R., Gardner, R.. 1992. Effect of aluminum on the growth of

545   34 plant species: a summary of results obtained in low ionic strength solution culture.

546   Plant Soil 146, 61–66.

547 Wilcke, W., Yasin, S., Valarezo, C., Zech, W., 2001. Change in water quality during the passage

548   through a tropical montane rain forest in Ecuador. Biogeochem. 55, 45-72.

549 Wilcke, W., Yasin, S., Abramowski, U., Valarezo, .C, Zech, W., 2002. Nutrient storage and

550   turnover in organic layers under tropical montane rain forest in Ecuador. Eur. J. Soil Sci.

551   53(1), 15–27.

552 Wilcke, W., Boy, J., Goller, R., Fleischbein, K., Valarezo, C., Zech, W., 2010. Chapter 43. Effect of

553   topography on soil fertility and water flow in an Ecuadorian lower montane forest. In

554   Bruijnzeel, L.A., F.N. Scatena & L.S. Hamilton (eds.): Tropical Montane Cloud Forests:

555   Science for Conservation and Management. Cambridge University Press, Cambridge, UK,

556   402-409.

557 Wullaert, H., Bigalke, M., Homeier, J., Cumbicus, N., Valarezo, C., Wilcke, W., 2013. Short-term

558   response of the Ca cycle of a montane forest in Ecuador to low experimental $CaCl_2$

559   additions. J. Plant Nutr. Soil Sci. 176(6), 892–903.

Table 1

Aluminum fluxes (kg ha^{-1} yr^{-1}) of bulk (BD) and dry deposition (DD), throughfall (TF), stemflow (SF), litterfall (LF*), organic layer leachate (LL), mineral soil solution (SS**), stream water (SW), and suspended particulate matter loss with stream water (PL) from the literature. * total litterfall (t ha^{-1} yr^{-1}) in parentheses, ** soil depth (m) in parentheses

Reference	Ecosystem	Al fluxes (kg ha^{-1} yr^{-1})								
		BD	DD	TF	SF	LF*	LL	SS**	SW	PL
Current study	tropical montane forest, Ecuador	0.2	0.2	0.5	0.01	11.4 (10.0)	5.0	10.19 (0.15), 6.02 (0.30)	0.18	28.8
Likens (2013)	northern hardwood forest, USA	< 0.01							2.79	1.38
Rustad and Cronan (1995)	northern red spruce forest, USA	0.2		0.06	0.03	0.65	2.1		2.6	
Berg and Gerstberger (2004)	deciduous forest, Germany					0.98 (5.45)				
Matzner et al. (2004)	deciduous forest, Germany							2.4 (0.6)		
Berg and Gerstberger (2004)	coniferous forest, Germany					1.2 (2.14)				
Matzner et al. (2004)	coniferous forest, Germany							17.2 – 26.9 (0.2 – 0.9)		
Matzner (1989)	temperate forest, Germany	1.2	0.9 – 1.3	1.6 – 2.9				17.6 – 52.7 (0.9)		
Cornu et al. (1998)	tropical lowland rainforest, Brazil	1.4		0.6	0.03	2.62		3.7 (0.4)		
Mayer et al. (2000)	rain forest, Brazil	5.2		3.2				26.5 – 43.5 (0.1 – 1)		
Hafkenscheid (2000)	tropical montane forest, Jamaica					1.50 – 5.22 (6.47 – 6.16)	1.9 – 4.9	16.1 – 35.1 (0.05 – 0.14)		
Gerold (2008)	tropical montane forest, Bolivia					15.5 (12.2)				
Bergamini Scheer et al. (2011)	Atlantic rain forest, Brazil					11.2 – 9.69 (6.37 – 3.01)				
Moraes et al. (1999)	Atlantic rain forest, Brazil					5.3 (6.31)				

Table 2

Al, Ca and Mg concentrations and molar Ca:Al ratios in fresh leaves sampled between October 2005 and February 2006 and in October 2011 and in litterfall from April 1998 to March 2003. N is number of individual replicates, values represent mean ± standard error.

Species	Family	N	Ca	Mg	Al	Ca:Al
				$(mg\,g^{-1})$		molar ratio
Sampling October 2005 to February 2006						
Purdiaea nutans Planch.	Cyrilliaceae	3	9.8 ± 0.8	2.6 ± 0.3	0.1 ± 0.0	53.7 ± 7.2
Alchornea pearcei Britton.	Euphorbiaceae	3	6.6 ± 1.9	1.9 ± 0.3	0.1 ± 0.0	64.0 ± 16.5
Graffenrieda emarginata (Ruiz & Pav.)	Melastomataceae	3	2.4 ± 0.2	1.6 ± 0.2	3.4 ± 0.4	0.5 ± 0.1
Podocarpus oleifolius (Donex Lamb.)	Podocarpaceae	3	4.3 ± 0.7	1.4 ± 0.2	0.1 ± 0.0	37.1 ± 1.3
Alazatea verticilata (Ruiz & Pav.)	Lythraceae	1	4.7	1.8	0.07	47.9
Clusia ducoides (Engl.)	Clusiaceae	1	10.9	2.0	0.05	144
Hyeronima moritziana (Mull. Arg.)	Euphorbiaceae	1	3.9	1.5	0.09	30.2
Ocotea aciphylla (Nees) Mez.	Lauraceae	1	2.5	1.2	0.1	19.8
Ocotea bentamiana Mez.	Lauraceae	1	1.7	1.2	0.12	9.2
Miconia sp	Melastomataceae	1	7.7	3.3	1.64	3.2
Elaeagia sp	Rubiaceae	1	3.7	1.6	0.10	25.4
Matayba inelegans Spruce ex Radlk.	Sapindaceae	1	3.2	2.7	0.06	34.8
Prunus opaca (Benth.) Walp.	Rosaceae	1	12.5	2.6	0.09	99.0
Sampling October 2011						
Cedrela odorata L.	Meliaceae	1	6.5	2.3	0.10	42.9
Cedrela sp	Meliaceae	2	9.1 ± 2.8	3.3 ± 0.3	0.12 ± 0.02	47.6 ± 9.5
Heliocarpus americanus L.	Tiliaceae	3	7.6 ± 1.4	5.3 ± 0.7	0.14 ± 0.04	42.9 ± 13.3
Tabebuia chrysantha (Jacq.) G. Nicholson	Bignoniaceae	3	5.8 ± 1.3	3.2 ± 0.4	0.07 ± 0.01	53.4 ± 11.5
Litterfall 1998-2003						
litterfall		59	12.1 ± 0.2	4.0 ± 0.1	1.2 ± 0.1	8.5 ± 0.6

Table 3

Range and mean of pH, mean (± SE) of Ca, Mg, Al, and TOC concentrations in bulk precipitation, throughfall, stemflow, organic layer leachate (LL), soil solutions in the 0.15 and 0.3 m soil depths (SS15 and SS30, respectively), and stream water at the three measurement transect in Microcatchment 2 (MC2.1 – 2.3) from April 1998 to March 2003 (LL April 1998 to April 2010) and in soil solutions from May 2000 to April 2003.
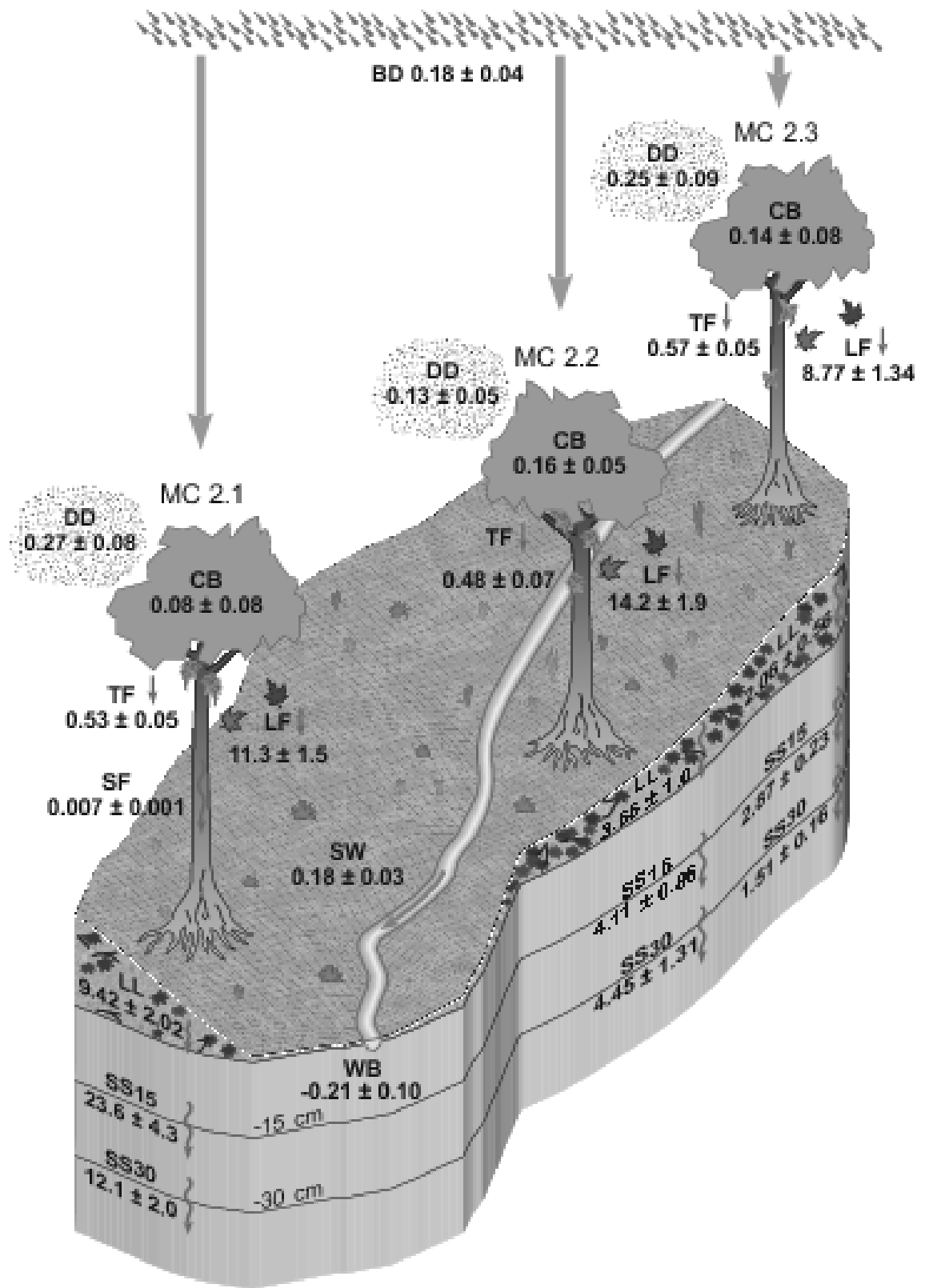
solution	pH		Ca	Mg	Al	TOC
	range	mean		(μM)		(mg L^{-1})
precipitation MC 2	3.9 – 7.8	5.1	6.44 ± 0.62	4.44 ± 0.47	0.33 ± 0.04	5.28 ± 0.18
throughfall MC 2.1	4.5 – 8.2	6.2	25.1 ± 1.7	20.7 ± 1.3	1.39 ± 0.08	13.5 ± 0.4
throughfall MC 2.2	4.9 – 7.5	6.2	22.9 ± 1.2	20.4 ± 1.1	1.30 ± 0.08	14.3 ± 0.4
throughfall MC 2.3	4.2 – 8.0	6.0	41.9 ± 1.7	43.1 ± 2.0	1.47 ± 0.09	17.4 ± 0.8
stemflow MC 2.1	4.2 – 7.7	6.1	26.3 ± 1.4	22.0 ± 1.2	0.99 ± 0.07	18.3 ± 0.5
stream water MC 2	5.5 – 9.1	6.7	16.6 ± 0.7	18.2 ± 0.6	0.47 ± 0.07	4.48 ± 0.28
LL MC 2.1	3.8 – 6.6	4.4	31.9 ± 1.6	45.5 ± 1.9	27.18 ± 0.8	40.8 ± 0.9
LL MC 2.2	3.6 – 7.5	4.6	48.8 ± 2.5	58.2 ± 3.0	14.3 ± 0.9	33.0 ± 0.9
LL MC 2.3	3.3 – 6.9	5.0	111 ± 5.2	89.7 ± 4.8	4.42 ± 0.36	46.5 ± 1.9
SS15 MC 2.1	3.8 – 4.6	4.2	7.99 ± 1.20	7.14 ± 0.92	73.0 ± 3.02	27.0 ± 0.6
SS15 MC 2.2	4.0 – 5.6	4.4	6.19 ± 0.77	24.3 ± 1.9	12.4 ± 0.94	7.80 ± 0.23
SS15 MC 2.3	4.4 – 5.2	4.9	31.6 ± 1.9	16.6 ± 1.4	9.35 ± 0.32	10.7 ± 0.3
SS30 MC 2.1	4.1 – 4.9	4.4	3.53 ± 0.50	3.70 ± 0.55	36.8 ± 1.9	15.5 ± 0.4
SS30 MC 2.2	4.2 – 5.6	4.5	8.71 ± 1.08	24.7 ± 3.5	13.3 ± 1.4	7.77 ± 0.44
SS30 MC 2.3	4.4 – 5.6	5.2	40.6 ± 11.4	21.2 ± 5.0	4.86 ± 0.28	7.59 ± 0.36

Figure 1. Schematic illustration of Al fluxes (kg ha^{-1} yr^{-1}) in bulk (BD) and dry deposition (DD), throughfall (TF), litterfall (LF), stemflow (SF), organic layer leachate (LL), soil solution in the 0.15 (SS15) and 0.3 (SS30) m soil depths, and stream water (SW), and the Al canopy (CB) and dissolved Al catchment budgets (WB) for an approximately 9-ha large water catchment under tropical montane rain forest in southern Ecuador. Shown are arithmetic means of annual values (± SE) from 1998 to 2003 ($n = 5$), in case of soil solutions from 2000 to 2003 ($n = 3$).

Figure 2. Frequency histogram of base saturation (% of ECEC) of 23 A horizons (a), of selected 10 A horizons in the valley bottom (b), and selected 10 A horizons on the ridge top of a 9-ha large catchment (MC 2).

Figure 1

Figure 2