

# Biological versus geochemical control and environmental change drivers of the base metal budgets of a tropical montane forest in Ecuador during 15 years

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**Abstract** To assess the susceptibility of the base metal budget of a remote tropical montane forest in Ecuador to environmental change, we determined the extent of biological control of base metal fluxes and explored the impact of atmospheric inputs and precipitation, considered as potential drivers of ecosystem change, on the base metal fluxes. We quantified all major base metal fluxes in a ca. 9.1 ha forested catchment from 1998 to 2013. Mean ( $\pm$ s.d.) annual flux to the soil via throughfall + stemflow + litterfall

was  $13800 \pm 1500 \text{ mg m}^{-2}$  Ca,  $19000 \pm 1510 \text{ mg m}^{-2}$  K,  $4690 \pm 619 \text{ mg m}^{-2}$  Mg and  $846 \pm 592 \text{ mg m}^{-2}$  Na of which 22  $\pm$  6, 45  $\pm$  16, 39  $\pm$  10 and 84  $\pm$  33%, respectively, were leached to below the organic layer. The mineral soil retained 79–94% of this Ca, K and Mg, while Na was released. Weathering rates estimated with three different approaches ranged from not detected (ND) to  $504 \text{ mg m}^{-2} \text{ year}^{-1}$  Ca, ND– $1770 \text{ mg m}^{-2} \text{ year}^{-1}$  K,  $287\text{--}597 \text{ mg m}^{-2} \text{ year}^{-1}$  Mg and  $403\text{--}540 \text{ mg m}^{-2} \text{ year}^{-1}$  Na. The size of mainly biologically controlled aboveground fluxes of Ca, K and Mg was 1–2 orders of magnitude larger than that of mainly geochemically controlled fluxes (sorption to soil and weathering). The elemental catchment budgets (total deposition – streamflow) were positive for Ca ( $574 \pm 893 \text{ mg m}^{-2}$ ) and K ( $1330 \pm 773 \text{ mg m}^{-2}$ ), negative for Na ( $-370 \pm 1300 \text{ mg m}^{-2}$ ) and neutral for Mg ( $1.89 \pm 304 \text{ mg m}^{-2}$ ). Our results demonstrate that biological processes controlled element retention for Ca, K and Mg in the biological part of the ecosystem. This was different for Na, which was mainly released by weathering from the study catchment, while the biological part of the ecosystem was Na-poor. The deposition of base metals was the strongest driver of their budgets suggesting that the base metal cycling of the study ecosystem is susceptible to changing deposition.

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## Introduction

Catchment budgets of elements in forested ecosystems inform about the response of the ecosystem to external influences, usually long before the changes become visible in the vegetation or soil (Bormann and Likens 1967; Bruijnzeel 1991; Likens 2013). Therefore, catchment budgets are helpful in detecting the response of ecosystems to environmental changes. Among the currently strongest environmental changes are climate change and changing atmospheric inputs (Boy and Wilcke 2008; Galloway et al. 2008; IPCC 2013).

The response of terrestrial ecosystems to environmental change depends on the interplay between biological and geochemical processes. The biota of terrestrial ecosystems, including plants, animals and microorganisms tighten element cycles to minimize water-bound nutrient losses (Jordan et al. 1980; Jordan 1982; Ulrich 1983; Jobbagy and Jackson 2001, 2004; Riotte et al. 2014). For growth-limiting nutrients, this internal cycling has been shown to be particularly tight (Jobbagy and Jackson 2001, 2004). There is increasing evidence that the essential plant nutrients K, Ca and Mg can limit biological functioning (Wright et al. 2011; Baribault et al. 2012; Wullaert et al. 2013; Fay et al. 2015), although the dominating limitation is frequently attributed to N and/or P (Elser et al. 2007; LeBauer and Treseder 2008; Fisher et al. 2013; Velescu et al. 2016).

Mineral weathering in soils and parent rocks can be a major source of base metal supply (which also includes the plant-beneficial Na) to the vegetation of tropical montane forests on young, little-weathered soils such as in the erosion-prone tropical mountains. Therefore, the functioning of these ecosystems is closely linked with geochemical processes in soil and bedrock (Bruijnzeel 1991; Braun et al. 2005; Meunier et al. 2010). However, the weathering rates are also influenced by the biota of the ecosystem (Bormann et al. 1998; Moulton et al. 2000; Brantley et al. 2011). Consequently, the element export via headwater streams is driven by the interplay of geochemical and biological processes (Dunne 1978; Gaillardet et al. 1997; Johnson et al. 2014; Porder et al. 2015). In native ecosystems with low surface erosion, the element export via headwater streams represents the chemical denudation. Therefore, fluxes of base metals in stream water can be used to draw conclusions on

local weathering rates and the nutritional status of the vegetation in the catchment drained by the stream under study (Dunne 1978; Bruijnzeel 1991; Likens 2013).

To predict the response of forested catchments to environmental change, we need to disentangle biological and geochemical contributions to the element cycles, because it can be expected that biological and geochemical processes respond differently to changing environmental conditions. We furthermore need to understand the relative importance of external drivers of the elemental budgets of the ecosystems. In the north Andes, changing climate (rainfall and temperature) and changing atmospheric inputs (alkaline dust and acids) are expected to impact the tropical montane forests (Boy and Wilcke 2008; Boy et al. 2008a; Peters et al. 2013; Wilcke et al. 2013b). For temperate ecosystems, for instance, it has been shown that the bulk deposition of  $H^+$  and water fluxes via rainfall or streamflow can have an important impact on the base metal budgets of forest ecosystems (Matzner et al. 2004; Likens 2013). In temperate ecosystems in the northeastern USA and Germany, the acid rain of the 1970s and early 1980s caused pronounced base metals losses from the catchment. Similarly, at both locations streamflow (responding to rainfall) was a major driver of base metal losses from catchments. There are much fewer studies in tropical than in temperate forests (Bruijnzeel et al. 1991), including the earlier work of Boy and Wilcke (2008) on the 5-year catchment budget of base metals at the same study site.

The tropical montane rain forests on the eastern slope of the eastern cordillera of The Andes in Ecuador receive considerable Ca and Mg inputs via episodic deposition of alkaline dusts causing elevated pH values in rainfall (Boy and Wilcke 2008; Wilcke et al. 2013a). Boy and Wilcke (2008) have presented inferential evidence that at least part of this alkaline dust originates in the Sahara by considering back trajectories of the wind and climatic conditions in the Amazon basin. The dust seems to be transported by the northeasterly trade winds from north Africa over the Atlantic and the Amazon basin to the forests on the rim of the basin. However, a direct dust mineralogical proof of this hypothesis is still lacking. Dust inputs cause the accumulation of base metals in topsoils, like it was observed in the Caribbean (Prospero et al. 1981; Muhs et al. 1990; Pett-Ridge et al. 2009) and suspected in Panama for Ca and K (Messmer et al. 2014). Dust-

related base metal input into the Ecuadorian tropical montane forests is reflected by decreasing concentrations of Ca and Mg with increasing depth in the thick organic layers of the soils, while the elements mainly originating from the bedrock weathering (e.g., Al, Fe, K, Na) show increasing concentrations with depth (Wilcke et al. 2002). On the other hand, outside the episodic dust deposition periods, nitric acid and  $\text{NH}_4^+$  originating from forest fires in the Amazon basin reach the east Andean cordillera and produce acid rain, which is buffered by the release of base metals from the forest canopy and the soils (Boy et al. 2008a; Wilcke et al. 2013b).

Currently, the long-term effect of alternating base metal deposition via alkaline dust and acidification periods on the base metal budget of the Andean headwater catchments is unknown. Both forest fires in the Amazon basin and alkaline dust inputs are related with climatic conditions, which are currently changing globally (IPCC 2013) and locally in Ecuador (Peters et al. 2013; Wilcke et al. 2013b). Envisaging the future of the Andean tropical montane forests therefore requires the understanding of the long-term effect of alternating acid and alkaline dust deposition.

To improve our understanding of the susceptibility of tropical montane forests to environmental change, we (i) quantified the biological and geochemical contributions to base metal fluxes in a native old-growth tropical montane forest in Ecuador. We hypothesized that the base metal fluxes were more strongly controlled by biological than by geochemical processes. Furthermore, we (ii) identified which of the three external drivers (total deposition of base metals, rainfall water fluxes or bulk deposition of  $\text{H}^+$ ) influenced the base metal budgets of the forest canopy and the entire catchment most strongly and how the same external drivers influenced the base metal budgets of the organic layer after modification by the canopy. We expected a strong influence of acid deposition and of rainfall volume on the base metal budgets. Finally, we (iii) determined the effect of the alternating dust and acid inputs on the base metal budget of the catchment over a period of 15 years (1998–2013). We suspected that the deposited base metals were retained in the catchment, because of biological demand, except for Na. To reach our objectives, we quantified bulk and dry deposition, internal cycling in the biological compartment of vegetation and organic layer, weathering rates, net

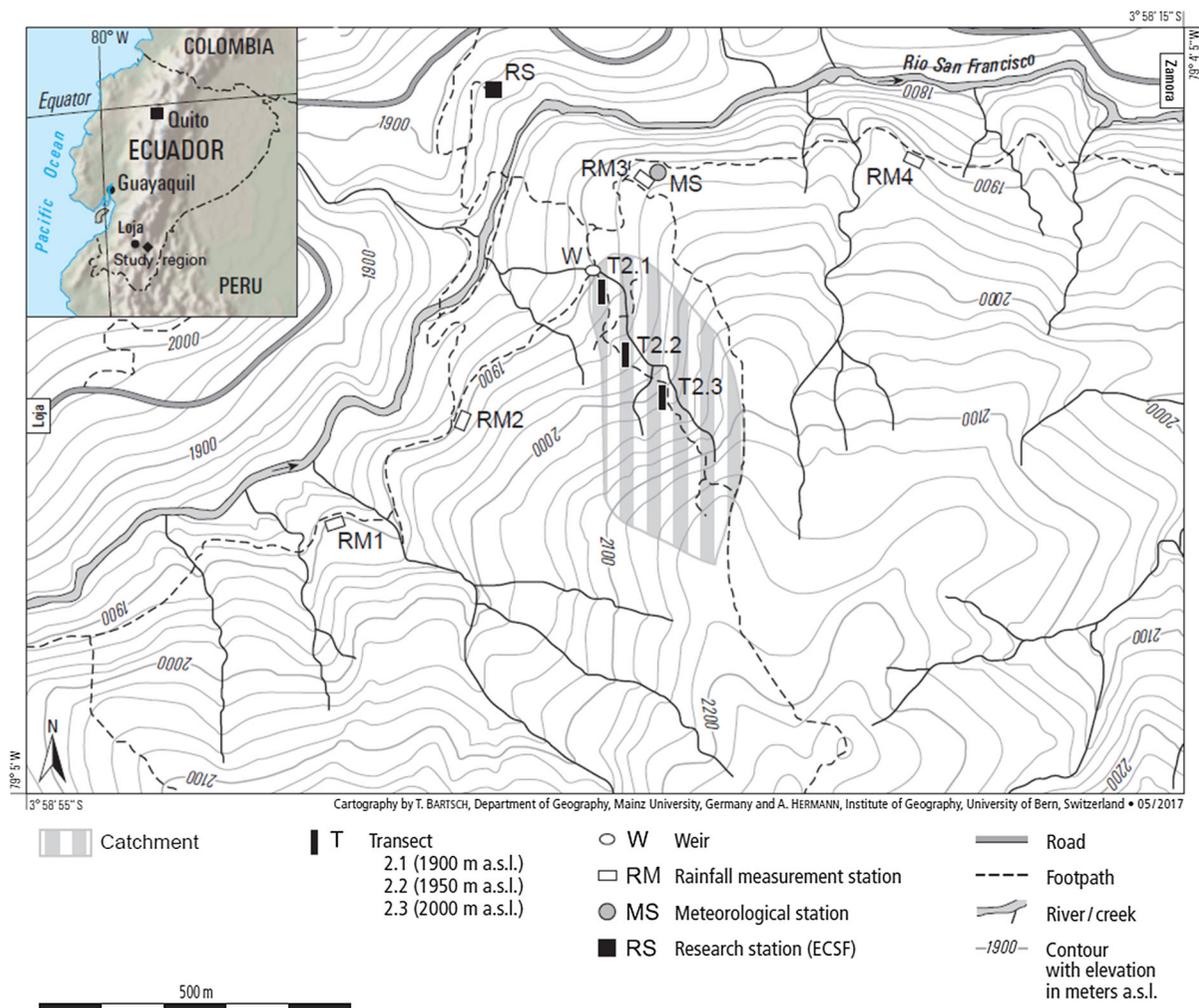
hydrological fluxes and the elemental catchment budget. We set up annual budgets of Ca, K, Mg and Na by aggregating data from weekly to monthly measurements following common practice in ecosystem research (e.g., Matzner et al. 2004; Likens 2013).

## Materials and methods

### Study site

We studied a ca. 9.1 ha catchment under old-growth montane rainforest on a  $30^\circ$ – $50^\circ$  steep slope between 1850 and 2200 m above sea level (a.s.l., Fig. 1; Wilcke et al. 2001; Boy et al. 2008b). The mean annual precipitation ranged between 2000 and 2500 mm and mean annual temperature was  $14.9^\circ\text{C}$  during 1999–2010 (Wilcke et al. 2013b). Soils are mainly shallow Dystric Cambisols developed from metamorphic rock (phyllite and quartzite) (IUSS Working Group WRB 2014). The dominating clay mineral was an illite-vermiculite mixed layer mineral (40–80% of the total peak area in the diffractograms in the topsoils and 20–40% in the subsoils) followed by kaolinite (10–40% in topsoils and 20–60% in subsoils; Schrupf et al. 2001). Schrupf et al. (2001) detected up to 20–40% illite in topsoils. The illite concentrations decreased with increasing elevation and soil depth. In two soils, up to 40% hydroxyl-interlayered vermiculite or pedogenic chlorite were found. In one soil, there were also low concentrations of vermiculite (< 10%). In 20 ca. 0.5–1 m deep soil profiles along two transects near the stream and near the ridge, we only found phyllite up to an elevation of ca. 2000 m a.s.l. In the soils above this elevation there were always both phyllite and quartzite present in the subsoil, which we attribute to the mixing of the two parent rocks by ancient landslides. Mean soil thickness we could dig with a spade was  $0.57 \pm 0.24$  m. Horizon thicknesses are given in Table 1. The chemical composition of the parent materials is given in Table S1 (Supplementary Materials).

The studied forest can be classified as evergreen montane forest (Balslev and Øllgaard 2002) or as Lower Montane Forest (Bruijnzeel and Hamilton 2000). More information on the composition of the forest can be found in the work of Homeier (2004).



**Fig. 1** Map of the location of the studied catchment (MC) including the weir, the measurement transects (T), rainfall measurement stations, meteorological station and research station. The elevation given after the transects refers to the lowermost point of the transects covering ca. 10 m in elevation (transect symbols are not exactly to scale to be clearly visible). The catchment in this study is the same as Microcatchment 2 in

### Sampling and field measurements

In the year 1998, we sampled Oi, Oe, Oa, A, B and C horizons of 29 soils, covering all topographic positions in the catchment including lower slope (13 soils), midslope (6 soils) and ridge (10 soils) between 1880 to 2100 m a.s.l. We estimated the volumetric rock fragment content visually in the field. Samples were collected from the walls of a soil pit to be representative of each horizon. Soil pits were hand-dug with a spade as deep as it was possible. Soil samples were air-

previous studies (e.g., Boy et al. 2008b) and therefore the transects are designated T2.1 to T2.3 as in previous publications. Rainfall measurement station 1 was operational from May 2000 to December 2005, station 2 from April 1998 to March 2013, station 3 from May 2000 to March 2013, and station 4 from June 2004 to June 2009. The weir and the meteorological station operated from April 1998 to March 2013

dried and mineral soil samples sieved to < 2 mm. Samples of the O horizon and aliquots of the mineral soil horizon samples were finely ground with a ball mill. All samples were stored in closed plastic bags at room temperature until analysis.

We used frequency domain reflectometry (FDR) probes to measure soil water contents as the basis for calculating changes in water storage in the organic layer (O horizon) and the mineral soil (A and B horizon). FDR probes were installed in January 2000 at 0.10, 0.20, 0.30 and 0.40 m depth, spanning the

**Table 1** Means and standard deviations of selected soil properties of 29 soils of the study catchment (13 from the lower slope, 6 from the midslope and 10 from the ridges)

Horizon	O <sup>f</sup>	A	B <sup>h</sup>	C <sup>i</sup>
Thickness (cm)	13 ± 6.9 (29)	20 ± 13 (29)	19 ± 6.8 (22)	26 ± 15 (29)
Sand (%)	NA <sup>g</sup>	46 ± 8.8 (21)	44 ± 10 (12)	46 ± 6.3 (19)
Silt (%)	NA <sup>g</sup>	37 ± 6.5 (21)	37 ± 10 (12)	35 ± 6.0 (19)
Clay (%)	NA <sup>g</sup>	17 ± 5.8 (21)	20 ± 7.5 (12)	19 ± 5.3 (19)
Rock fragments <sup>a</sup> (Vol. %)	NA <sup>g</sup>	21 ± 12 (21)	22 ± 15 (13)	42 ± 16 (20)
pH <sup>b</sup> (–)	4.3	4.4 (29)	4.7 (22)	4.9 (29)
Organic C (g kg <sup>-1</sup> )	377 ± 66 (29)	32 ± 19 (29)	21 ± 12 (22)	13 ± 8.6 (29)
C/N (–)	18 ± 5.0 (29)	11 ± 2.8 (24)	11 ± 2.5 (17)	10 ± 2.9 (20)
ECEC <sup>c</sup> (mmol <sub>c</sub> )	NA <sup>g</sup>	63 ± 26 (29)	64 ± 37 (22)	44 ± 31 (29)
Ca (mmol <sub>c</sub> )	NA <sup>g</sup>	5.6 ± 5.8 (29)	2.0 ± 2.7 (22)	2.6 ± 5.0 (29)
K (mmol <sub>c</sub> )	NA <sup>g</sup>	1.6 ± 0.76 (29)	0.77 ± 0.47 (22)	0.76 ± 0.46 (29)
Mg (mmol <sub>c</sub> )	NA <sup>g</sup>	8.5 ± 7.6 (29)	3.8 ± 4.0 (22)	4.9 ± 9.7 (29)
Na (mmol <sub>c</sub> )	NA <sup>g</sup>	2.9 ± 0.78 (29)	3.1 ± 0.34 (22)	3.1 ± 0.53 (29)
Al (mmol <sub>c</sub> )	NA <sup>g</sup>	44 ± 34 (29)	54 ± 40 (22)	32 ± 31 (29)
BS <sup>d</sup> (%)	NA <sup>g</sup>	13 ± 16 (29)	23 ± 24 (22)	35 ± 29 (29)
Ca total (g kg <sup>-1</sup> )	6.7 ± 4.0 (29)	0.50 ± 0.22 (29)	0.49 ± 0.54 (22)	0.54 ± 0.72 (29)
K total (g kg <sup>-1</sup> )	3.9 ± 2.0 (29)	18 ± 3.5 (29)	17 ± 3.4 (22)	19 ± 4.8 (29)
Mg total (g kg <sup>-1</sup> )	2.2 ± 1.0 (29)	0.76 ± 0.24 (29)	0.73 ± 0.17 (22)	0.98 ± 0.55 (29)
Na total (g kg <sup>-1</sup> )	0.11 ± 0.05 (29)	1.5 ± 0.93 (29)	1.5 ± 0.85 (22)	1.6 ± 1.0 (29)
Ca exch. stock <sup>e</sup> [g m <sup>-2</sup> (0.3 m) <sup>-1</sup> ]		24 ± 25 (29)		
K exch. stock <sup>e</sup> [g m <sup>-2</sup> (0.3 m) <sup>-1</sup> ]		15 ± 10 (29)		
Mg exch. stock <sup>e</sup> [g m <sup>-2</sup> (0.3 m) <sup>-1</sup> ]		8.5 ± 10 (29)		
Na exch. stock <sup>e</sup> [g m <sup>-2</sup> (0.3 m) <sup>-1</sup> ]		21 ± 4.6 (29)		

The number of horizons, for which data are available, is given in brackets

<sup>a</sup>Estimated in the field

<sup>b</sup>Measured in H<sub>2</sub>O, soil:solution ratio 1:10 for O and 1:2.5 for mineral soil horizons, mean pH was calculated as  $-\log(\text{mean H}^+ \text{ activity})$

<sup>c</sup>ECEC effective cation-exchange capacity

<sup>d</sup>BS base saturation

<sup>e</sup>Stock of exchangeable cations to a mineral soil depth of 30 cm

<sup>f</sup>Thickness-weighted mean of Oi, Oe and Oa horizons

<sup>g</sup>NA not available

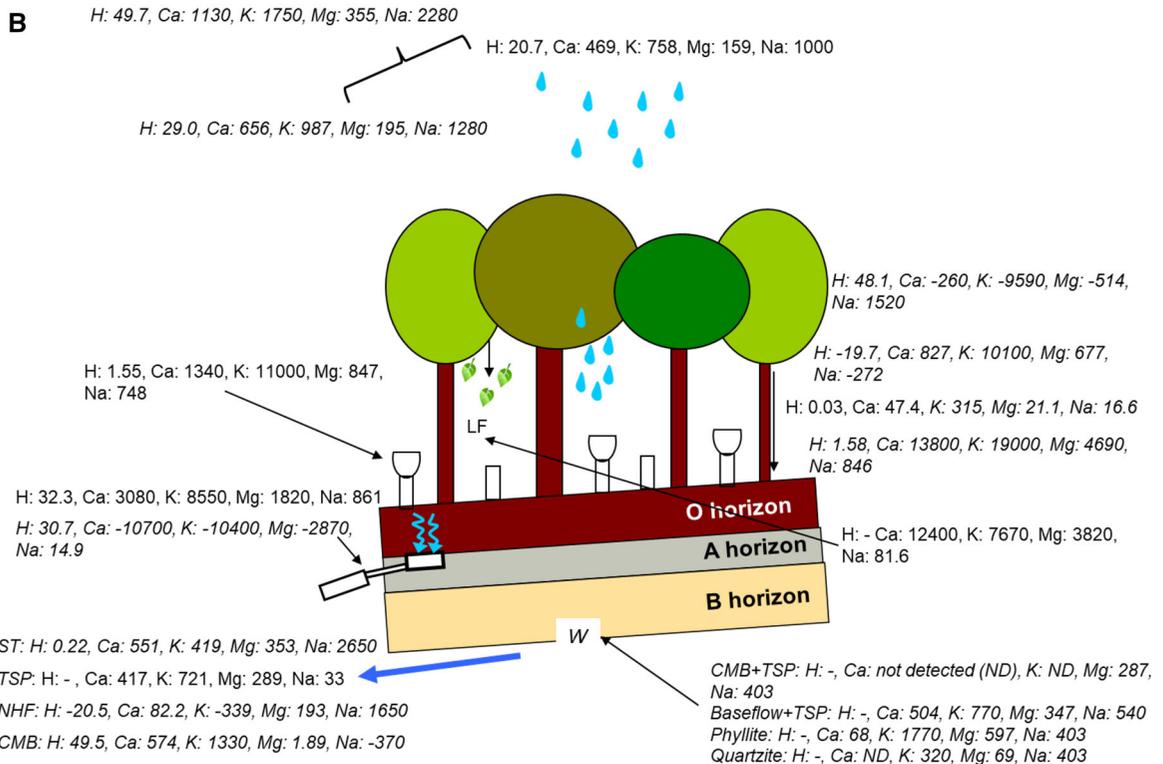
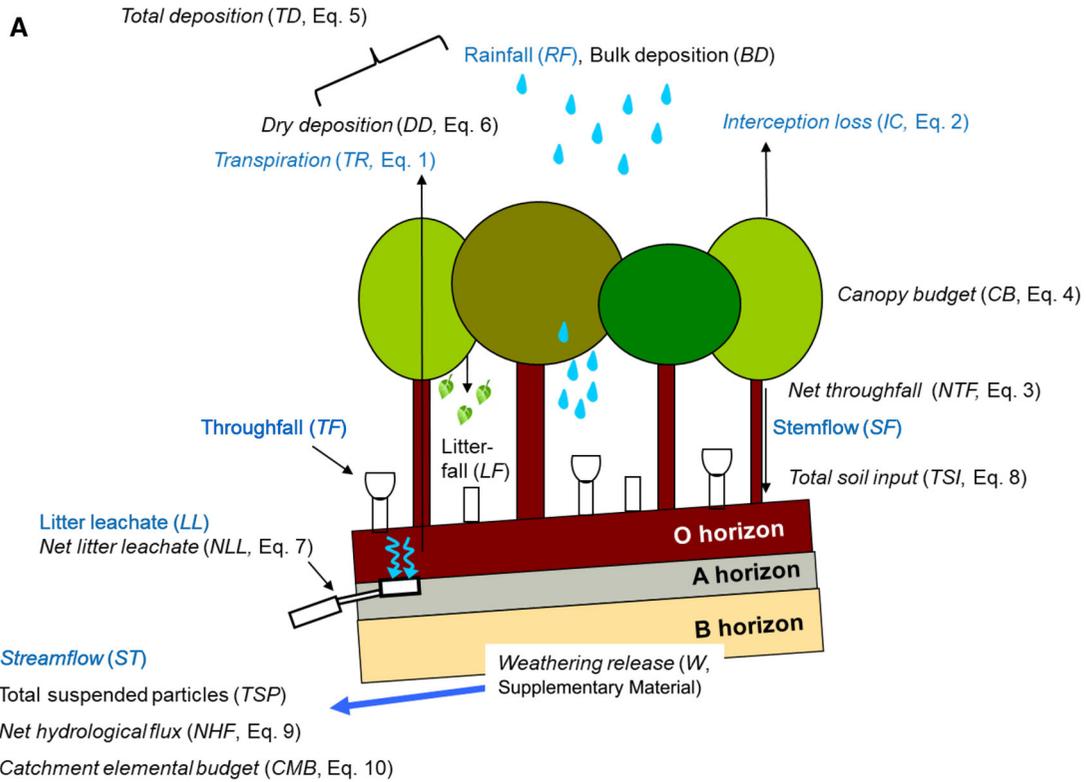
<sup>h</sup>B horizons did not occur in all soils

<sup>i</sup>Soil profiles were hand-dug with a spade as deep as it was possible, C horizons may have been deeper than given here (but unaccessible)

entire thickness that was suitable for the installation of FDR probes (i.e., with sufficiently low stone content), and one in the organic layer (0.05 m above the mineral soil surface in the Oa horizon) at a central position of Transect 2.1 (Fig. 1). Data were recorded hourly with a data logger since January 2000. We considered this depth profile measurements as representative of the

entire catchment, because differences in soil water content can be expected to be minor as a consequence of the overall wet environment of the study site (Fleischbein et al. 2006).

Setting up catchment budgets of elements requires a complete assessment of all major hydrological fluxes including rainfall, throughfall, stemflow, soil water



◀ **Fig. 2 a** Overview of the measured and calculated/modeled ecosystem fluxes, their abbreviations, and the equation number used to estimate them. Water fluxes are shown in blue and summarized in Fig. 3. **b** The mean of the measured and calculated H, Ca, K, Mg and Na fluxes in  $\text{mg m}^{-2} \text{ year}^{-1}$ . The data is shown at the same position as their explanation in subfigure **a**. In subfigures **a** and **b**, calculated/modeled data are shown in italics. A positive sign of the budgets means accumulation and a negative sign loss

flow and streamflow. Furthermore, the potentially important contribution of dry particulate deposition of base metals needs to be quantified for a complete budget (Ulrich 1983; Likens 2013). Because dry particulate deposition cannot be measured directly, Ulrich (1983) suggested a canopy budget model based on the assumption that  $\text{Na}^+$  or  $\text{Cl}^-$  can be considered as inert tracers, which is widely used (Draaijers et al. 1996; Staelens et al. 2008; Talkner et al. 2010). This suggestion is based on the low  $\text{Na}^+$  or  $\text{Cl}^-$  concentrations in plant tissues relative to the deposition fluxes. Figure 2 summarizes all considered fluxes.

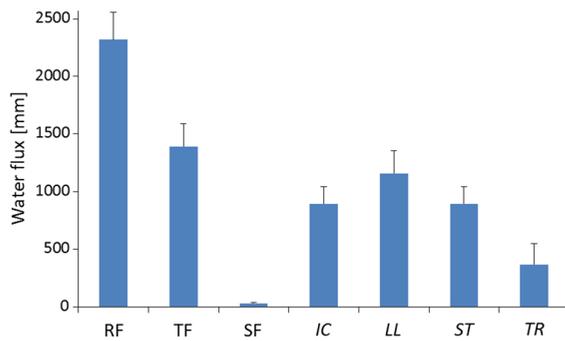
Rainfall (*RF*, see Fig. 2a for an overview of all fluxes and their abbreviations) was collected weekly at 2–4 gauging stations each consisting of five Hellmann-type collectors, placed on clear-cut areas (Fig. 1). As the collectors were permanently open, collected samples represent bulk deposition (*BD*, i.e. rainfall and soluble coarse particulate dry deposition [*DD*], which can drop into the open collectors). The error of the rainfall measurement was < 5%, because in a comparison of five different measurement methods for rainfall, our samplers measured during a ca. 3-year period 3.7% more rainfall than an adjacent tipping bucket instrument (Rollenbeck et al. 2007).

To determine the internal element cycling, we set up three ca. 20 m-long measurement transects on the 38°–70° steep lower to mid slope aligned downhill across about 10 m in elevation (starting at 1900, 1950 and 2000 m a.s.l., respectively, Fig. 1). We chose the placement of our transects because the lower to mid slope represented the largest part of the catchment. The elevational gradient of 100 m, we covered, was a compromise between reasonable accessibility and representativeness of the ca. 200 m gradient of the entire catchment. At each measurement transect, we collected throughfall (*TF*), litter leachate (*LL*), and fine litterfall (*LF*, Fig. 2a). Throughfall was collected with 5–20 fixed-position funnel collectors per

transect. We started with five collectors in 1998 and increased the number of collectors to eight in 2000 and to 20 in 2002. Litter leachate was collected with three zero-tension lysimeters per transect made of plastic boxes covered with a polyethylene net. The lysimeters had a collecting surface area of 0.15 m × 0.15 m and were installed below the organic layer. Fine litterfall was collected with three litter traps per transect. We started with 0.3 × 0.3 m traps used from April 1998 to October 2005 and switched to 0.5 × 0.5 m large traps thereafter. All throughfall, litter leachate and litterfall samplers were spread evenly along the transects. Stemflow (*SF*) was collected with polyurethane collars at five trees in the lower part of the catchment near Transect 2.1. Streamflow (*ST*) was sampled above a weir, which was used to gauge streamflow (Fleischbein et al. 2006; Boy et al. 2008b). Between August 2000 and January 2003, we additionally collected weekly 100-mL aliquots of stream water to measure the concentrations of total suspended particles (*TSP*). The total suspended particles were accumulated on ashless filters with a pore size of 4–7  $\mu\text{m}$  (folded filter type 392; Sartorius-Stedim GmbH, Göttingen, Germany) for ten 3-month intervals and ashed at 450 °C.

Water level at the weir was measured hourly with a pressure transducer in the first five years. However, there were periods during which the pressure transducer did not work properly (Fleischbein et al. 2006). After 2003, water levels were recorded weekly by manual measurement. According to the work of Wullaert et al. (2009) our water flux measurement in throughfall with 20 samplers had an error of approximately 12% (with a 95% confidence interval). There was no indication of unaccounted water fluxes into or out of the study catchment so that the catchment can be considered as watertight (Goller et al. 2005; Fleischbein et al. 2006).

All solution (rainfall, throughfall, stemflow, litter leachate, streamflow) and litterfall samples were collected weekly between April 1998 and March 2013 (Fig. 2a). For rainfall, throughfall, stemflow and litter leachate, each sample was cumulative for the whole week, while for streamflow it was an instantaneous sample. Rainfall, throughfall and stemflow volumes were measured with a graduated cylinder in the field and bulked volume-weighted to result in one composite sample per sample type, measurement site and collection date. Litter leachate was directly bulked into one collection vessel per measurement transect to



**Fig. 3** Mean water budget of the hydrological years April 1998–March 1999 to April 2012–March 2013. *RF* rainfall, *TF* throughfall, *SF* stemflow, *IC* interceptions loss, *LL* litter leachate (water flow below the organic layer), *ST* streamflow, *TR* transpiration. *RF*, *TF* and *SF* were directly measured. *IC* was calculated with Eq. (2). *LL* was modelled from April 1998 to March 2003 with the Soil Water Balance model (DVWK 1996) and taken from Boy et al. (2008b) and from April 2003 to March 2013 by regression of the 1998–2003 *LL* fluxes on simultaneous *TF* fluxes. *ST* was modeled with the distributed catchment model TOPMODEL (Beven et al. 1995) from April 1998 to March 2003 and taken from Fleischbein et al. (2006) and Boy et al. (2008b) and estimated from April 2003 to March 2013 by assuming a constant water level per week measured manually at a weir and converted to flow by a hand-calibrated water level-flow function. *TR* was calculated by budgeting all fluxes of the catchment (Eq. 1). Calculated/modeled fluxes are shown in italics in the figure. Error bars represent standard deviations among the study years ( $n = 15$ ). See also Fig. 2a for a visualization of the fluxes

yield one individual sample per measurement site and collecting date. Litterfall was combined to one sample per measurement transect and sampling date, air-dried, ground with a ball mill and composited to monthly samples (including four or five weekly samples) prior to chemical analysis. Our hydrological year lasted from 01 April to 31 March of the following year because the experiment was established in March 1998.

#### Chemical analyses

Soil pH was measured in water (soil:solution ratio 1:2.5 v/v for the mineral soil and 1:10 for the organic horizons) with a glass electrode (Orion U402-S7, Thermo Fisher Scientific, Waltham, MA, USA), total C and N concentrations with an Elemental Analyzer (vario EL, Elementar Analysensysteme, Hanau, Germany) on finely ground samples and effective cation-exchange capacity (*ECEC*) by extraction with 1 M  $\text{NH}_4\text{NO}_3$ . Base saturation (*BS*) was calculated by

summing up the proportion of charge equivalents of extractable Ca, K, Mg and Na and dividing the sum by the *ECEC*. Total base metal concentrations in the mineral soil samples were determined by digestion with concentrated  $\text{HNO}_3/\text{HF}$  (4:1 v/v) and O horizons, litterfall and total suspended particles by digestion with concentrated  $\text{HNO}_3$  and 2 mL  $\text{H}_2\text{O}_2$  under pressure in a microwave oven (MARS5Xpress, CEM, Matthews, USA). Texture of the mineral soil samples was determined with the Boyoucus method after treatment of the < 2 mm-sieved mineral soil samples with Na-oxalate and NaOH (Tan 1996).

The pH value of the solution samples was measured in an unfiltered aliquot of each sample within < 24 h with a glass electrode. Another aliquot was filtered with ashless filters with a pore size of 4–7  $\mu\text{m}$  (folded filter type 392; Sartorius-Stedim GmbH, Göttingen, Germany). After export of the filtered 100-mL aliquots from Ecuador to Germany or Switzerland in frozen state, we determined  $\text{Cl}^-$  concentrations in rainfall, throughfall and stemflow with an ion-selective electrode (Thermo Fisher, Beverly, USA) in a continuous flow analyzer (CFA, Seal Analytical, Norderstedt, Germany). Because of the low ionic strength in all samples (usually < 0.001 mol  $\text{L}^{-1}$ ), we adjusted the ionic strength with a solution of 1.13 g  $\text{L}^{-1}$   $\text{NaNO}_3$  + 2 mL  $\text{L}^{-1}$  surfactant (Triton X-100, 50% solution) so that all samples had a similar ionic strength prior to ion-sensitive electrode measurement. Concentrations of Al, Ca, K, Mg and Na in the extracts, digests and ecosystem solutions were determined with a flame Atomic Absorption Spectrometer (AAS, Varian, Darmstadt, Germany and Analytik Jena, Jena, Germany).

#### Calculations and statistical analyses

For annual flux and budget calculations, weekly data were aggregated to monthly values. This reduced the influence of outliers and the number of missing values. Monthly mean concentrations were calculated by arithmetically averaging weekly concentrations. Monthly fluxes were calculated by multiplying monthly mean concentrations by monthly water fluxes. Water fluxes with rainfall, throughfall and stemflow were directly measured (Fig. 2a).

Because the zero-tension lysimeters did not collect water fluxes quantitatively (Jemison and Fox 1992), we modelled water fluxes in soil by modifying the Soil

Water Balance model (DVWK 1996). The Soil Water Balance model determines water fluxes out of predefined soil layers (in our case the organic layer) as the sum of throughfall + stemflow (input) minus independently determined transpiration ( $TR$ , output) minus (or plus) change in stored water in the soil layers. The change in stored water was calculated by the difference in water contents of the respective soil layer between two soil water measurements with FDR probes at Transect 2.1 (Fig. 1). We assumed direct evaporation from the soil as negligible and derived weekly transpiration rates by partitioning the annual difference between throughfall and streamflow proportionally to the weekly evapotranspiration rates as modeled by REF-ET (Allen 1991, described in Fleischbein et al. 2006). Weekly transpiration rates were furthermore split between the soil layers according to the root length densities of the respective soil layer taken from Soethe et al. (2006), assuming a linear relationship between water uptake of the vegetation and fine root abundance.

Data gaps of soil water fluxes were substituted with the help of a regression of modeled weekly litter leachate on measured weekly throughfall including all available data from 1998 to 2003 ( $LL = 0.86 \times TF - 0.71$ ,  $R^2 = 0.85$ ). This regression equation was also used to calculate litter leachate from 2004 to 2013. The litter leachate data from 1998 to 2003 were taken from Boy et al. (2008b).

In the first five years (1998–2003) we used streamflow modeled with the distributed catchment model TOPMODEL (Beven et al. 1995) taken from Fleischbein et al. (2006) and Boy et al. (2008b). For the later years (2004–2013) we used weekly measurements of the water level at the weir which was transformed to streamflow by a calibrated streamflow function of water level determined with a bucket and stop watch at different water levels (Fleischbein et al. 2006; Boy et al. 2008b). From 2004 to 2013, we assumed that the water level was constant during the measurement week.

To calculate transpiration we used the catchment-scale hydrological mass-balance (Eq. 1).

$$RF = IC + TR + E + ST + \Delta S \quad (1)$$

where  $IC$  is interception loss (evaporation from the forest canopy),  $E$  is direct evaporation from soil and  $\Delta S$  is change in water storage. We neglected direct evaporation ( $E$ ) from soil, because the sites were under

dense forest canopy with a relative humidity of nearly 100%, and we assumed no change of the water storage ( $\Delta S$ ) at our annual budgeting scale. Then, the only remaining variable in Eq. (1),  $IC$ , was calculated according to Eq. (2).

$$IC = RF - TF - SF \quad (2)$$

To set up complete budgets of the forest canopy, the organic layer and the entire catchment, a number of calculations were necessary (Fig. 2a). The net throughfall flux ( $NTF$ ) of an element  $i$  is defined in Eq. (3).

$$NTF_i = TF_i - BD_i \quad (3)$$

where  $BD$  is bulk deposition (i.e., element flux with incident rainfall).

To set up the canopy budget ( $CB$ ) of an element  $i$ , we used the model of Ulrich (1983), where the canopy budget is calculated as the difference between throughfall + stemflow fluxes and total deposition ( $TD$ , Eq. (4)).

$$CB_i = (TF_i + SF_i) - TD_i \quad (4)$$

Positive values of the canopy budget indicate leaching, negative ones uptake of an element  $i$  by the canopy (including plants, phyllosphere organisms and soil-like accumulations). Total deposition ( $TD$ ) for any given element  $i$  was calculated with Eq. (5).

$$TD_i = BD_i + DD_i \quad (5)$$

where  $DD$  is the fine particulate part of dry deposition estimated with Eq. (6).

$$DD_i = [(TF_{Cl} + SF_{Cl})/BD_{Cl}] \times BD_i - BD_i \quad (6)$$

Here  $TF_{Cl}$  represents the throughfall flux,  $SF_{Cl}$  the stemflow flux, and  $BD_{Cl}$  the bulk deposition of  $Cl^-$ , considered as inert tracer. The quotient  $(TF_{Cl} + SF_{Cl})/BD_{Cl}$  is called deposition ratio (Ulrich 1983); it gives an indication of the contribution of dry deposition to total deposition.

The gaseous part of dry deposition, which is only relevant for  $H^+$ , cannot be estimated with Eq. (6). We relied on previous work at the same study site which demonstrated that  $Cl^-$  can be considered as a non-reactive tracer and therefore can successfully be used to calculate canopy budgets (Boy and Wilcke 2008; Boy et al. 2008a; Wilcke et al. 2008). Because our budgeting interval was annual, we needed a deposition

ratio of  $\text{Cl}^-$  which was unaffected by lag effects between dry deposition and leaching with throughfall and stemflow. Therefore, we calculated one deposition ratio of  $\text{Cl}^-$  per hydrological year and used this annual  $\text{Cl}^-$  deposition ratio for our canopy budget calculations.

Net litter leachate (*NLL*) is a measure of the retention of base metals in the biotic compartment and thus the closeness of base metal cycling between soil and vegetation, because most roots are restricted to the densely rooted organic layer (Soethe et al. 2006). Only few, mainly larger roots reached into the mineral soil at our study site. Net litter leachate was calculated with Eq. (7).

$$NLL_i = LL_i - TSI_i \quad (7)$$

where *TSI* is total soil input according to Eq. (8).

$$TSI_i = (TF_i + SF_i + LF_i) \quad (8)$$

To estimate weathering rates, we used three approaches. The first approach was based on a budget assuming that the input of elements into the ecosystem by total deposition and weathering equals the losses with streamflow and changes in the stocks of various soil pools (Likens 2013). The second approach assumed that weathering can be approximated by the sum of dissolved element losses with baseflow plus the losses with total suspended particles. The third approach attributed the entire loss of Na with streamflow to weathering and assumed that the other base metals were released in the same ratio to Na as they occurred in the parent rocks. Details of the methods are shown in Table S2 in the Supplementary Materials.

To assess accumulation or loss of elements in the study catchment, net hydrological fluxes (*NHF*—excluding dry deposition) and the catchment elemental budget (*CMB*—including dry deposition) were used as defined in Eqs. (9) and (10).

$$NHF_i = ST_i - BD_i \quad (9)$$

$$CMB_i = ST_i - TD_i = ST_i - BD_i - DD_i \quad (10)$$

To test for relationships between data sets, we used Pearson product-moment correlation analysis if data were normally distributed (expressed with the correlation coefficient *r*) and Spearman's sign rank test for not normally distributed data (expressed with the correlation coefficient *ρ*).

## Uncertainty of the flux estimates

Fleischbein et al. (2006) have quantified the errors of most water fluxes in our study catchment (as standard errors in % of the mean). According to their work, the rainfall measurement had an error of < 2% and the throughfall measurement had an error of 12% in the first five years of our study period (15–24 samplers), which decreased to < 10% after the number of samplers had been increased to 60 (i.e., 20 per measurement transect) in the year 2002 (Wullaert et al. 2009). The error of the streamflow measurement was 5.6% in the first four years (Fleischbein et al. 2006), which can be extrapolated to the fifth year (Boy et al. 2008b). We cannot quantify the error of our later streamflow measurement because we lack a true value for comparison. We also cannot quantify the error of the litter leachate because of the lack of a true value for comparison and because we cannot test the representativeness of our water content measurements at Transect 1 (Fig. 1). However, the close correlation of litter leachate with throughfall suggests a similar error of litter leachate than that of throughfall (i.e., < 12%).

## Results

### Water cycle

The hydrological budget of the study catchment is characterized by a high annual interception loss of 587–1190 mm representing 28–50% (mean 39%) of rainfall (Fig. 3). Rainfall ranged from 1910 to 2790 mm year<sup>-1</sup> and streamflow from 780 to 1350 mm year<sup>-1</sup>, representing 38–58% (45%) of rainfall. Mean annual streamflow was similar in the periods 1998–2003 (1111 mm, modeled) and 2004–2013 (1028 mm, estimated from weekly water levels). The same was true for the mean annual runoff coefficient (i.e., streamflow/rainfall), 0.46 from 1998 to 2003 vs. 0.45 from 2004 to 2013), which quantifies the fraction of rainfall that leaves the catchment with streamflow. The annual runoff coefficient varied in a narrow range during the entire period (0.38–0.48) except for the last year (2012/13, 0.58).

Water flow below the organic layer (litter leachate) ranged from 932 to 1650 mm year<sup>-1</sup> and was on average 103 mm higher than streamflow, suggesting

**Table 2** Means  $\pm$  standard deviations (SD,  $n = 15$  hydrological years) of  $H^+$  and base metal fluxes through the ecosystem

	Mean $\pm$ SD ( $mg\ m^{-2}\ year^{-1}$ )				
	$H^+$	Ca	K	Mg	Na
Bulk deposition	20.7 $\pm$ 12.2	469 $\pm$ 356	758 $\pm$ 367	159 $\pm$ 162	1000 $\pm$ 702
<i>Dry deposition</i>	<i>29.0 <math>\pm</math> 20.9</i>	<i>656 <math>\pm</math> 642</i>	<i>987 <math>\pm</math> 498</i>	<i>195 <math>\pm</math> 171</i>	<i>1280 <math>\pm</math> 852</i>
<i>Total deposition</i>	<i>49.7 <math>\pm</math> 30.3</i>	<i>1130 <math>\pm</math> 943</i>	<i>1750 <math>\pm</math> 772</i>	<i>355 <math>\pm</math> 326</i>	<i>2280 <math>\pm</math> 1460</i>
Throughfall	1.55 $\pm$ 1.03	1340 $\pm$ 409	11000 $\pm$ 1200	847 $\pm$ 122	748 $\pm$ 609
<i>Net throughfall</i>	<i>-19.1 <math>\pm</math> 12.7</i>	<i>827 <math>\pm</math> 205</i>	<i>10100 <math>\pm</math> 1200</i>	<i>677 <math>\pm</math> 126</i>	<i>-272 <math>\pm</math> 247</i>
Stemflow	0.03 $\pm$ 0.02	47.4 $\pm$ 445.4	315 $\pm$ 94.4	21.1 $\pm$ 11.2	16.6 $\pm$ 94.4
<i>Canopy budget<sup>a</sup></i>	<i>48.1 <math>\pm</math> 30.6</i>	<i>-260 <math>\pm</math> 785</i>	<i>-9590 <math>\pm</math> 1410</i>	<i>-514 <math>\pm</math> 220</i>	<i>1520 <math>\pm</math> 1000</i>
Litterfall		12400 $\pm$ 1320	7670 $\pm$ 1190	3820 $\pm$ 532	81.6 $\pm$ 65.2
<i>Total soil input</i>	<i>1.58 <math>\pm</math> 1.03</i>	<i>13800 <math>\pm</math> 1500</i>	<i>19000 <math>\pm</math> 1510</i>	<i>4690 <math>\pm</math> 619</i>	<i>846 <math>\pm</math> 592</i>
Litter leachate	32.3 $\pm$ 15.6	3080 $\pm$ 899	8550 $\pm$ 3220	1820 $\pm$ 579	861 $\pm$ 944
<i>Net litter leachate</i>	<i>30.7 <math>\pm</math> 15.8</i>	<i>-10700 <math>\pm</math> 1340</i>	<i>-10400 <math>\pm</math> 3210</i>	<i>-2870 <math>\pm</math> 576</i>	<i>14.9 <math>\pm</math> 413</i>
<i>Weathering rates<sup>b</sup></i>					
<i>Method 1</i>		<i>ND</i>	<i>ND</i>	<i>287</i>	<i>403</i>
<i>Method 2</i>		<i>504</i>	<i>770</i>	<i>347</i>	<i>540</i>
<i>Method 3 Phyllite</i>		<i>68</i>	<i>1770</i>	<i>597</i>	<i>403</i>
<i>Method 3 Quartzite</i>		<i>ND</i>	<i>320</i>	<i>69</i>	<i>403</i>
Streamflow	0.22 $\pm$ 0.15	551 $\pm$ 206	419 $\pm$ 217	353 $\pm$ 127	2650 $\pm$ 463
Total suspended matter		417	721	289	33
<i>Net hydrological fluxes<sup>a</sup></i>	<i>-20.5 <math>\pm</math> 12.2</i>	<i>82.2 <math>\pm</math> 275</i>	<i>-339 <math>\pm</math> 414</i>	<i>193 <math>\pm</math> 154</i>	<i>1650 <math>\pm</math> 591</i>
<i>Catchment elemental budget<sup>a</sup></i>	<i>49.5 <math>\pm</math> 30.4</i>	<i>574 <math>\pm</math> 893</i>	<i>1330 <math>\pm</math> 773</i>	<i>1.89 <math>\pm</math> 304</i>	<i>-370 <math>\pm</math> 1300</i>

Calculated values are italicized, see methods section, Fig. 2a and Supplementary Material for the used equations. All numbers were rounded to a maximum of three valid figures

<sup>a</sup>A positive sign means net accumulation and a negative sign net loss

<sup>b</sup>The used methods are described in detail in the Supplementary Material

<sup>c</sup>ND is not detected

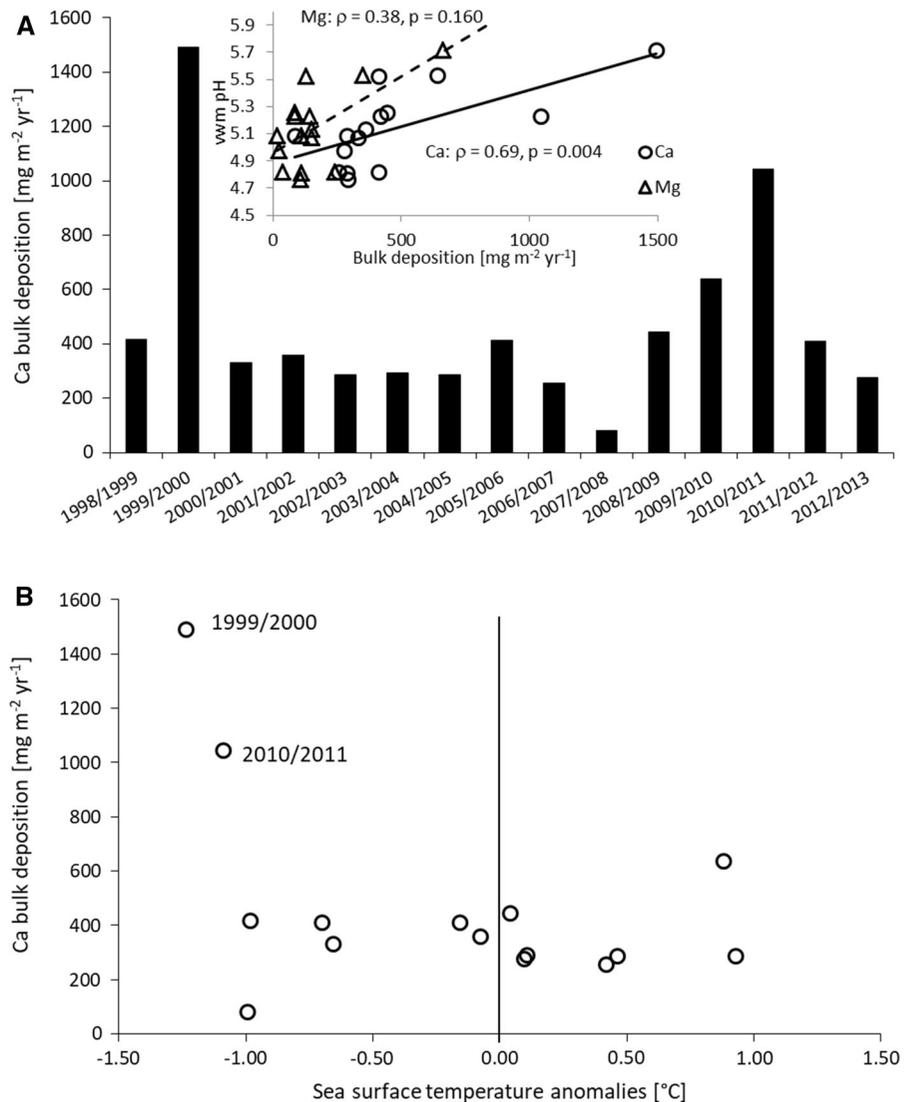
that the vegetation took up some of its transpiration water from the mineral soils, while we considered direct evaporation from the soil as negligible. In the period April 1998 to March 2012, calculated transpiration based on the catchment-scale hydrological mass-balance (Eqs. 1, 2) ranged from 132 to 637 mm. In 2012/2013, however, our calculated annual transpiration was -30 mm, which is a physically impossible value and mainly attributable to the highest estimated streamflow value (1350 mm) of the entire observation period. Mean annual transpiration increased by 8% to  $396 \pm 151$  mm, while mean annual streamflow decreased by 1% to  $1056 \pm 156$  mm if we calculated the annual means of the components of our catchment-scale

hydrological mass-balance for the period May 1998–April 2012 only, omitting the last study year.

#### $H^+$ and base metal fluxes

The understanding of the base metal budget of the catchment requires knowledge of the mean soil properties of the study area, which are presented in Table 1. The pH value of the soils was consistently in the Al oxide buffer range (pH 3.0–5.0). The effective cation-exchange capacity reflected the presence of three-layer clay minerals such as illite-vermiculite mixed layer minerals and some vermiculites (Schrumpp et al. 2001). The base saturation was highly variable, partly because of systematic

**Fig. 4 a** The course of annual bulk deposition of Ca from 1998 to 2013; the inset figure shows the relationships between annual bulk depositions of Ca and Mg and the volume-weighted mean (vwm) pH of rainfall. **b** The relationship between mean annual sea surface temperature anomalies in the Pacific 3 + 4 regions taken from NOAA (<http://www.cpc.ncep.noaa.gov/data/indices/sstoi.indices>, 07/10/2015) and bulk deposition of Ca



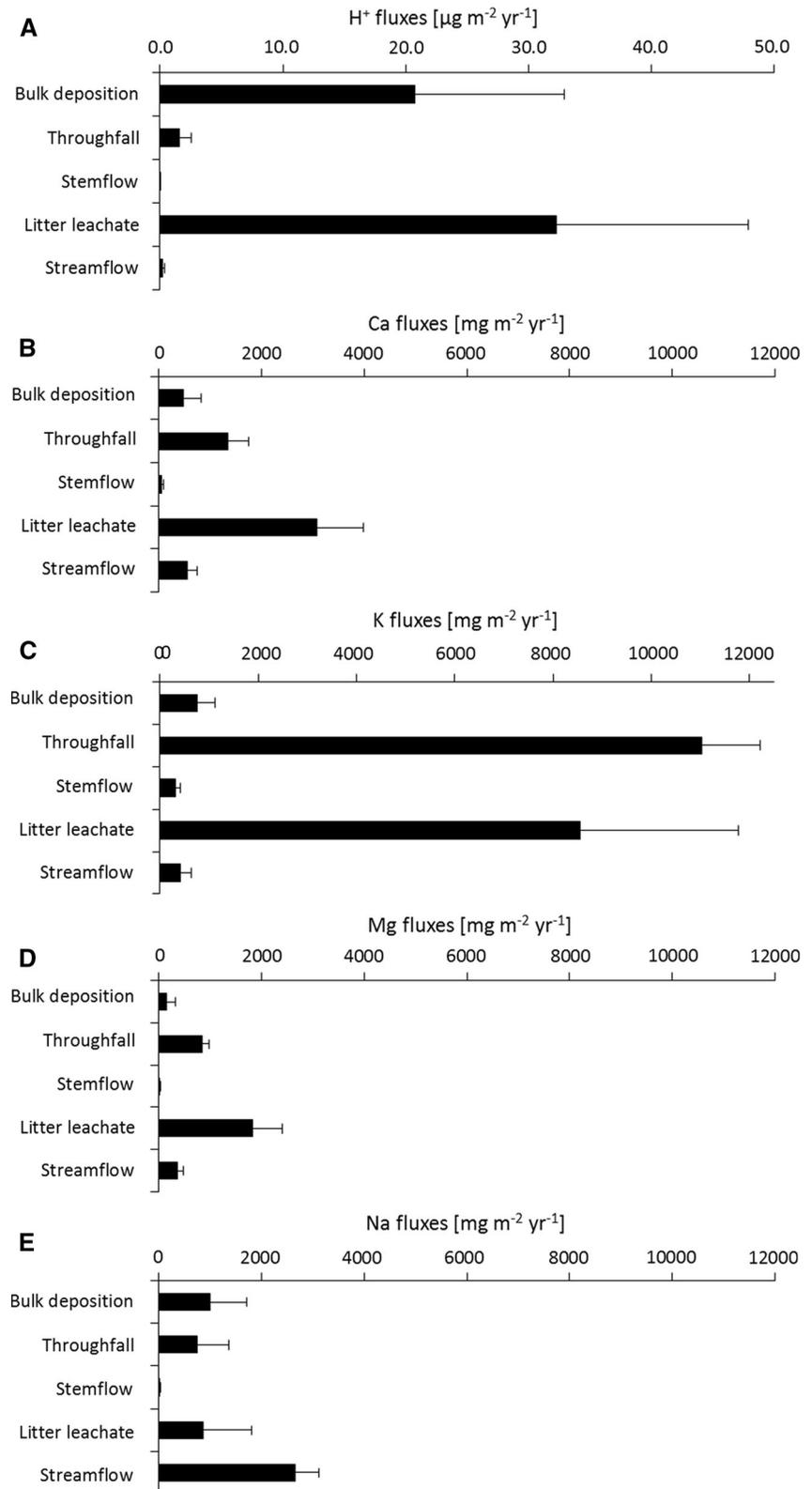
differences between the nutrient-poorer and more acidic soils on the ridges and the nutrient-richer, less acidic soils in the valleys (Wilcke et al. 2010). Previous work has shown that the base saturation was also influenced by the episodic alkaline dust deposition, which is unevenly distributed in the study area as a consequence of the highly heterogeneous water and element fluxes with throughfall and stem-flow (Wilcke et al. 2002; Wullaert et al. 2009).

Annual bulk deposition of Ca showed a considerable variation (Table 2, Fig. 4a). The highest annual bulk deposition in the hydrological years 1999/2000 and 2010/2011 were related with pronounced La Niña events. This is shown by the fact that excessive Ca

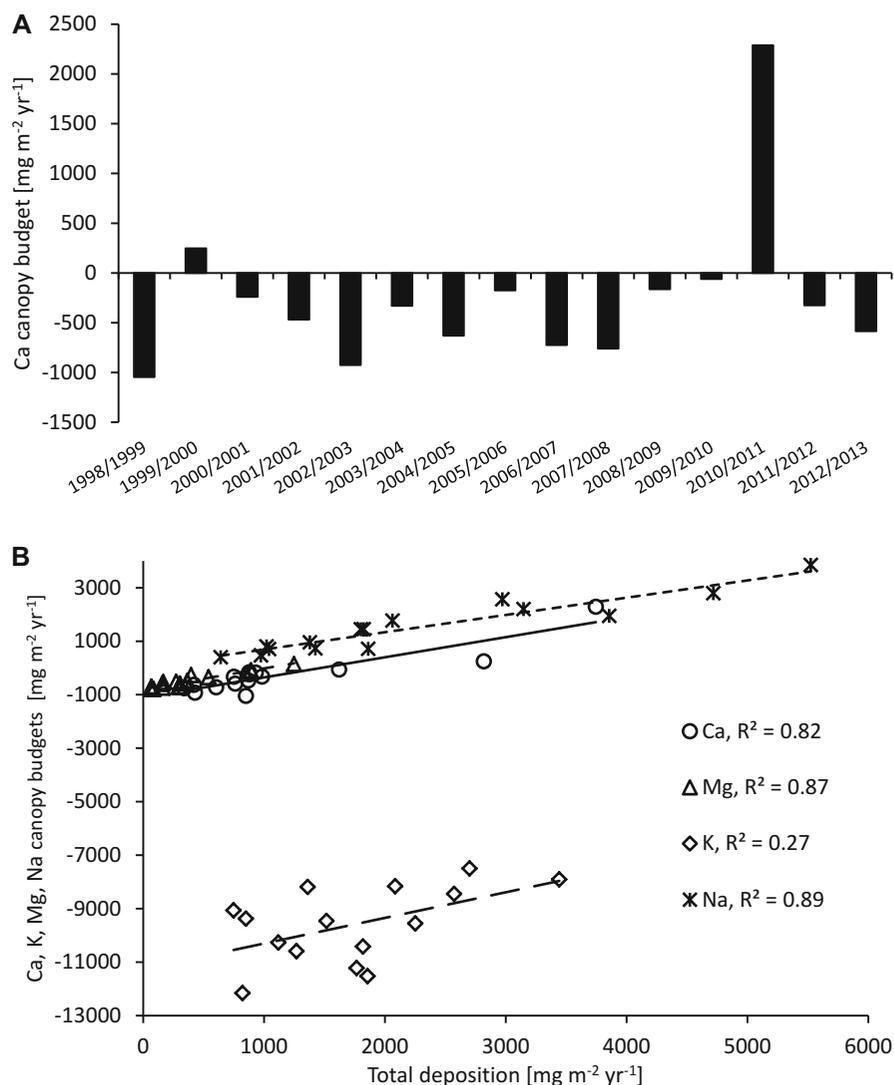
deposition occurred only during the periods of most negative anomalies of the mean annual sea surface temperature in the Pacific region 3 + 4 (Fig. 4b), while during all other conditions Ca deposition varied only little (Fig. 4a). The annual bulk deposition of Ca correlated significantly with that of Mg ( $\rho = 0.63, p = 0.013$ ) and annual volume-weighted mean pH of bulk deposition (Fig. 4a, inset) but not with the annual bulk deposition of K and Na. The annual deposition of K and Na were significantly correlated with each other ( $\rho = 0.52, p = 0.048$ ) but not with pH.

The aqueous  $\text{H}^+$  and base metal (Ca, K, Mg, Na) fluxes through the forest ecosystem along the water path from rainfall to streamflow showed element-

**Fig. 5** The vertical variation of the mean fluxes of **a** H<sup>+</sup>, **b** Ca, **c** K, **d** Mg and **e** Na through the forest ecosystem during 1998–2013. Error bars represent standard deviations among the study years (n = 15)



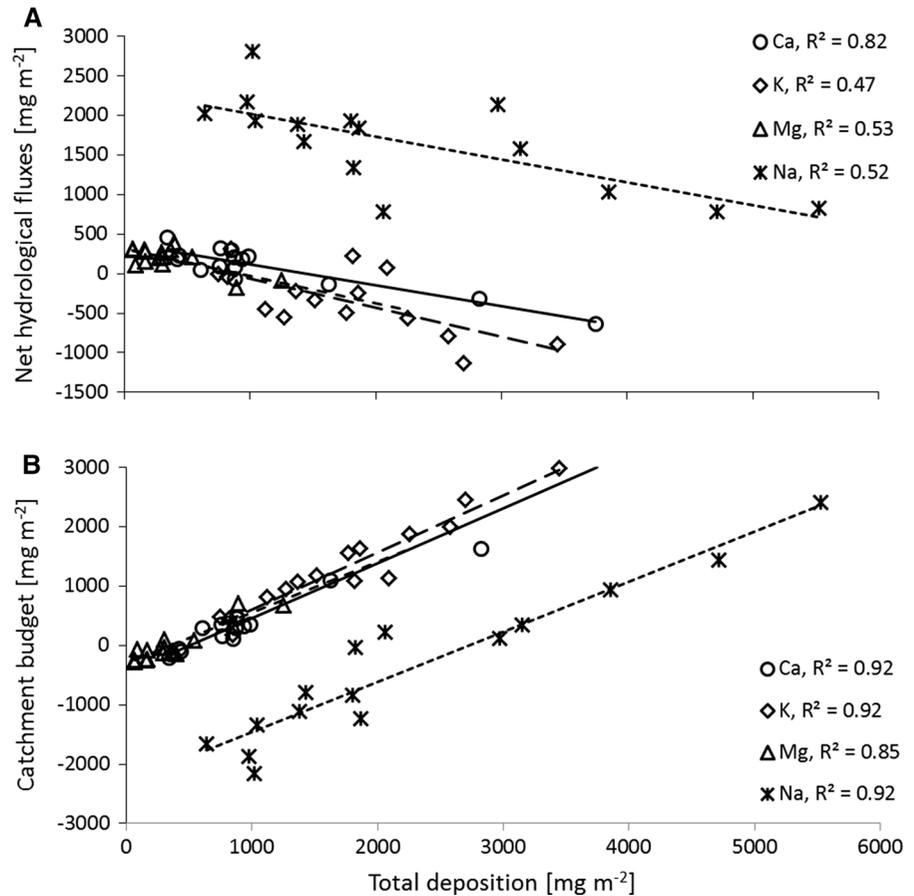
**Fig. 6 a** The course of the annual canopy budgets of Ca from 1998 to 2013. The inlet figure shows the relationship between the annual canopy budgets ( $CB$ , Eq. 4) of Ca and Mg; for the correlation analysis the outlier marked as a triangle (the 2010/11 value) was excluded. **b** The relationship between the mean annual total deposition (Eq. 5) and the mean annual canopy budgets of Ca, K, Mg and Na. Because total deposition and canopy budgets are not statistically independent from each other, we only calculated coefficients of determination for the relationships but did not conduct an inference test



specific patterns, although all five considered elements had in common that stemflow represented consistently the smallest flux (Table 2, Figs. 2b, 5). The Ca and Mg fluxes through the ecosystem showed a similar vertical distribution (Fig. 5b, d). Aqueous Ca and Mg fluxes increased from rainfall to throughfall and litter leachate and strongly decreased in the mineral soil, so that the export of Ca and Mg with streamflow was only slightly larger than the fluxes of these elements with bulk deposition. Of the Ca and Mg leached from the organic layer,  $82 \pm 5.0$  and  $79 \pm 10\%$  were retained in the mineral soil, respectively. The mean annual input of Ca and Mg into the mineral soil represented  $13 \pm 3.8$  and  $22 \pm 6.8\%$ , respectively, of

the stock of exchangeable Ca and Mg in the uppermost 0.3 m (Table 1). The K flux increased on average by a factor of 14.5 in throughfall relative to bulk deposition, because K was strongly leached from the canopy (Fig. 5c). On its further way through the ecosystem, K was partly retained in the organic layer and strongly in the mineral soil, which stored  $94 \pm 3.6\%$  of the K leaving the organic layer. The mean annual input of K from the organic layer into the mineral soil via litter leachate represented  $57 \pm 22\%$  of the stock of exchangeable K in the uppermost 0.3 m of the mineral soil (Table 1). Organic layer and mineral soil together reduced the aqueous fluxes of K reaching the soil surface (via throughfall + stemflow) by  $96 \pm 2.1\%$ .

**Fig. 7** The relationship between total deposition (bulk deposition + dry deposition using  $\text{Cl}^-$  as tracer, Eq. 5) and **a** the net hydrological fluxes (element export from the catchment with streamflow—bulk deposition, Eq. 9) and **b** the catchment budget (total deposition—element export from the catchment with streamflow, Eq. 10)



Finally, the vertical pattern of Na fluxes was distinct from that of all other elements (Fig. 5e). Na was retained in the canopy as reflected by lower Na fluxes in throughfall + stemflow than in bulk deposition. The dissolved Na flux that reached the soil surface with throughfall + stemflow had a similar size as the Na flux leached from the organic layer with litter leachate. The mean annual input of Na into the mineral soil with litter leachate represented  $4.1 \pm 4.5\%$  of the stock of exchangeable Na in the uppermost 0.3 m of the mineral soil (Table 1).

It was not possible to quantify weathering rates of Ca and K with our first approach (Table S2), because Ca and K fluxes with streamflow and total suspended particles were lower than total deposition of Ca and K (Table 2, Fig. 2b). The weathering rates of Mg and Na estimated with our second approach were slightly higher than those estimated with our first approach. The weathering rates calculated with our third approach resulted in lower estimates of Ca weathering

for both parent rocks, while the weathering rates of K and Mg according to the second approach were between those of the release from phyllite and quartzite as can be expected because of the mixed lithology of our study catchment.

The mean annual deposition ratios of  $\text{Cl}^-$  were  $2.43 \pm 0.68$  suggesting that dry deposition (Eq. 6) amounted to  $143 \pm 68\%$  of bulk deposition. Consequently, dry deposition of base metals contributed in most years more to total deposition than bulk deposition (Table 2, Fig. 2b), while dry deposition of  $\text{H}^+$ , which likely occurs mainly in gaseous form, remains unknown.

Litterfall was the most important vector of Ca and Mg to the soil carrying  $90 \pm 2.3\%$  of the Ca and  $81 \pm 1.8\%$  of the Mg reaching the soil via throughfall + stemflow + litterfall. Litterfall carried less K ( $40 \pm 5.0\%$ ) to the soil than throughfall + stemflow and much less Na ( $15 \pm 13\%$ ). Total soil input (Eq. 8) represented, on average, 56 times the K export with

streamflow, 27 times that of Ca, 16 times that of Mg and 0.31 times that of Na. This sequence roughly matched the plant requirements of the elements (Marschner 1995).

### H<sup>+</sup> and base metal budgets

We budgeted the canopy (net throughfall, Eq. 3; canopy budget, Eq. 4), the biotic part of the catchment (net litter leachate, Eq. 7), and the entire catchment (net hydrological fluxes, Eq. 9; catchment elemental budget, Eq. 10) to identify sinks and sources of the considered elements and to quantify the biological influence on the element cycle and losses in the study catchment. Net throughfall was consistently positive for Ca, K and Mg and the throughfall enhancement increased in the order,  $K > Ca > Mg$  (Table 2, Fig. 2b). In contrast, net throughfall was negative for H<sup>+</sup> and Na in 14 of the 15 observation years. The exceptional year for H<sup>+</sup> was 1999/2000, the first strong La Niña year (Fig. 4b), when net throughfall of H<sup>+</sup> equaled bulk deposition. The exceptional year for Na was 2000/2001 when net throughfall was positive (+149 mg m<sup>-2</sup> year<sup>-1</sup>). In line with these findings, the canopy budget of Ca was in most years negative with exception of the two strongest La Niña years when Ca was retained in the canopy (Fig. 6a), while the canopy budgets of H<sup>+</sup> and of Na were consistently positive indicating retention of these elements in the canopy (Fig. 6b). The canopy budgets of Ca and Mg were closely correlated (Fig. 6a, inlet) but there was no relationship between the canopy budgets of any other of the considered elements. The canopy budget of K was consistently and most pronouncedly negative (Fig. 6b).

Mean net litter leachate of H<sup>+</sup> (not including litterfall) was positive coinciding with the finding that the organic layer was a source of H<sup>+</sup> for the mineral soil (Figs. 2b, 5a). In contrast, mean net litter leachate (including litterfall) of Ca, K and Mg was negative, indicating that the three nutrient metals are to a large part retained in the organic layer (Table 2, Fig. 2b). The organic layer retained on average  $78 \pm 5.7$ ,  $55 \pm 16$  and  $61 \pm 10\%$  of the Ca, K and Mg arriving with throughfall + stemflow + litterfall at the soil surface, respectively, and kept these nutrients in the biotic part of the catchment. The mean net litter leachate of Na was slightly positive. However, the mean of the 15-year observation period was strongly

influenced by the pronounced Na release in 1999/2000 (1280 mg m<sup>-2</sup> year<sup>-1</sup>) when we recorded the highest alkaline dust inputs (Fig. 4a). When the net litter leachate of 1999/2000 was removed, the mean net litter leachate of Na was negative (-76 mg m<sup>-2</sup> year<sup>-1</sup>) indicating retention of Na in the organic layer similar to the canopy. The latter was true in 12 of the 15 observation years. In the early part of the observation period, Na was leached from the organic layer (in the hydrological years 1998/1999, 1999/2000, and 2001/2002; 250–1280 mg m<sup>-2</sup> year<sup>-1</sup>), the three years with the highest total deposition of Na (3900–5500 mg m<sup>-2</sup> year<sup>-1</sup>).

Net hydrological fluxes were consistently positive for H<sup>+</sup> demonstrating that the study catchment is well buffered (Table 2, Fig. 2b). Net hydrological fluxes of Ca and Mg were mostly (i.e., in 11 and 13 of the 15 observation years for Ca and Mg, respectively) and on average negative. Net hydrological fluxes of Na were consistently negative, while net hydrological fluxes of K were mostly (i.e., in 12 of 15 years) and on average positive (Figs. 2b, 7a). Thus, K was more strongly retained than Ca and Mg in line with the specific plant requirements of these elements (Marschner 1995).

The catchment elemental budgets, which besides the net hydrological fluxes additionally included our estimates of dry deposition, revealed a mean retention of H<sup>+</sup>, Ca and K, while Mg showed a nearly balanced mean budget and Na was mostly (i.e., in 9 of 15 years) and on average released from the catchment (Table 2, Figs. 2b, 7b).

### External drivers of base metal budgets

For net throughfall ( $R^2 = 0.04$  to  $0.41$ ) and the canopy budget (Fig. 6b), the total deposition of the respective base metal showed the highest  $R^2$  value, while both rainfall (water flux,  $R^2 \leq 0.28$ ) and bulk deposition of H<sup>+</sup> ( $R^2 \leq 0.10$ ) had a minor influence. The relationships between total deposition and canopy budgets of Ca, Mg and Na were closer than that of K (Fig. 6b). These relationships were negative for net throughfall (not shown) and positive for the canopy budgets (Fig. 6b) showing that a higher base metal input resulted in an even stronger retention (or reduced leaching) in the canopy.

The total deposition of the respective base metals influenced both their net hydrological fluxes and canopy elemental budgets consistently most strongly

(Fig. 7). Rainfall influenced net hydrological fluxes of Ca ( $R^2 = 0.40$ ) and Mg ( $R^2 = 0.37$ ) positively and catchment elemental budgets of Ca ( $R^2 = 0.39$ ) and Mg ( $R^2 = 0.21$ ) negatively. However, rainfall did not have an influence on net hydrological fluxes and catchment elemental budgets of K and Na ( $R^2 < 0.06$ ). The bulk deposition of  $H^+$  had little influence on any net hydrological flux or catchment elemental budget of all four base metals ( $R^2 < 0.14$ ).

The relationships between the three considered external drivers after their modification by the forest canopy (total soil input of the respective base metals, Eq. (8), water flux with throughfall + stemflow and throughfall + stemflow of  $H^+$ ) and the net litter leachate were generally weak ( $R^2 < 0.40$ ) and varied. The only closer relationship existed between the total soil input of Na and net litter leachate of Na ( $R^2 = 0.55$ ).

## Discussion

### Biological versus geochemical control over elemental fluxes

A similarly high interception loss at our study site was already reported in earlier work for shorter observation periods (Fleischbein et al. 2005; Wullaert et al. 2009; Breuer et al. 2013). Our transpiration estimate based on the catchment hydrological budget (Eqs. 1 and 2) was similar to those of other tropical montane forests, for which Bruijnzeel (2001) reported a range of 170–845 mm. We cannot explain the physically impossible *TR* estimate of the last year of the observation period.

Protons from atmospheric deposition were almost entirely buffered in the forest canopy presumably mainly by exchange with base metals which were leached (Fig. 5a, Matzner et al. 2004; Likens 2013). The organic layer was a second ecosystem-internal source of  $H^+$  (Fig. 5a). We attribute this to the dissolution of organic acids from the accumulated organic matter and additional release of acids by organisms for nutrient mining and uptake. Furthermore, it can be assumed that the biological activity in the organic layer produces  $CO_2$  which forms carbonic acid. The  $H^+$  produced in the organic layer was again buffered in the mineral soil likely mainly by

dissolution of Al oxides, the main buffer compound at the pH of the study soils (Table 1).

The biological control of base metal fluxes is manifested by plant uptake of base metals as nutrients (Ca, Mg, K) or as plant-beneficial elements (Na) via roots, mycorrhiza and plant surfaces (i.e., of the leaves, branches and stems) and their release via plant tissue leaching and litterfall (Marschner 1995). Part of the element uptake of the ecosystem can also be attributed to microorganisms, particularly on the surface of the plants (above- and belowground), and to animals (Likens 2013). The latter flux is difficult to measure directly, but can be approximated as retention of an element in the biologically most active parts of the system (i.e., the aboveground biomass and the soil organic layer, Jobbagy and Jackson 2004).

The uppermost compartment, in which biological flux control occurs, is the forest canopy. The forest canopy consists of the branches and leaves of the trees, epiphytes, the microorganism community on the plant surfaces and in the soil-like, strongly organic accumulations in and around epiphytes or crutches (Ulrich 1983; Nadkarni et al. 2002; Matson et al. 2014). The bulk and fine particulate dry deposition reaching the canopy can either be retained by uptake into organisms or passed on to throughfall and stemflow, which can be further enhanced by element leaching mainly out of the plant tissues. Leaching out of the plant tissues is known to be particularly pronounced for K followed by Mg and Ca (Parker 1983). The studied base metals showed differential interactions with the canopy. While K was consistently leached from the canopy, Ca and Mg were retained in years with particularly high total deposition (Eq. 5) and Na was consistently retained (Figs. 2b, 6). The apparently paradoxical retention of Ca and Mg during times with high total deposition of these elements was already observed by Boy and Wilcke (2008) and explained by the effects of elements which are deposited together with Ca and Mg in the alkaline dust and which might stimulate plant growth. Alternatively, the alkalization of soil by the dust inputs might have stimulated the release of nutrients from the organic layer thereby improving growth conditions. As a consequence, the demand of Ca and Mg increased because of the additional growth.

The retention of Na in the canopy is unexpected because Na is no essential plant nutrient and Na fluxes with litterfall were small (Table 2, Fig. 2b). However,

Na is essential for animals (Hill et al. 2016) and it has been shown to play a role for  $N_2$ -fixing cyanobacteria (Thomas and Apte 1984). Furthermore, N influenced litter decomposition in Na-poor (sub)tropical forests (Kaspari et al. 2009, 2014; Clay et al. 2014, 2015; Jia et al. 2015) but not in Na-rich forests close to the ocean like in Panama (Clay et al. 2015). Because total deposition of Na is low at our study site as a consequence of the easterly winds and the long downwind distance to the ocean (the Atlantic, Wilcke et al. 2001), we suggest that the consistent Na retention in the canopy can be explained by the Na demand of animals and possibly also microorganisms living in the canopy.

Further important vectors of element fluxes to the soil are coarse and fine litterfall, which can be considered as purely biologically controlled fluxes. While coarse litterfall is only a minor contribution to annual element fluxes (Wilcke et al. 2005), fine litterfall accounted for > 80% of the total soil input (Eq. 8) of Ca and Mg, about one third of that of K and around 15% of that of Na, in line with reports from other forests (Table 2, Fig. 2b; Vogt et al. 1986; Likens 2013).

The mean contribution of total deposition to total soil input was < 9.3% for Ca, K and Mg. Consequently, the aboveground fluxes of these elements were up to > 90% biologically controlled. For Na, total deposition was about three times higher than the total soil input. Thus, Na was retained in the canopy, likely because it was needed by the organism community of the canopy. The extent to which the total soil input is retained in the biological part, i.e. cycled internally, can be described by the percentage of the total soil input that leaves the organic layer to the mineral soil with litter leachate and thus the main root zone (Soethe et al. 2006). Consistently more than half and up to three quarters of the Ca, K and Mg fluxes are cycled internally (compare total soil input with litter leachate in Table 2 and Fig. 2b). Sodium was on average and in most individual years retained in the organic layer indicating that it was used by the organism community, albeit to a lesser extent than in the canopy (Table 2, Fig. 2b). However, when Na was delivered at high rates by deposition such as in three years of the early part of the observation period (1998/1999, 1999/2000, 2001/2002), Na was leached from the organic layer, suggesting that the Na availability surpassed the need of the organisms.

The pronounced retention of Ca and Mg in the mineral soil (compare litter leachate with streamflow in Table 2 and Fig. 2b) can mainly be explained by adsorption to the cation-exchange sites (Table 1). For K, fixation by illites and illite-vermiculite mixed layer minerals (Schrumpf et al. 2001) likely also played a role in its retention in the mineral soil. Sodium is the only element showing higher fluxes in streamflow than in litter leachate by a factor of ca. 5, indicating that Na was released by weathering in the mineral soil. Although it cannot be ruled out that some of the Na leached from the organic layer into the mineral soil was retained on the cation-exchange sites, the release of Na from the mineral soil by weathering was much larger than its retention (compare litter leachate with streamflow in Table 2 and Fig. 2b).

We compared our estimated weathering rate (Table 2, Fig. 2b) with results from some other subtropical and tropical catchments under forest, for which near steady-state conditions could be assumed. The weathering rate of Ca, Mg and Na estimated with all of our three approaches are lower than those of various catchments in Puerto Rico on Quartz diorite and Andesite for which 3000–16900  $\text{mg m}^{-2} \text{ year}^{-1}$  Ca, 590–2100  $\text{mg m}^{-2} \text{ year}^{-1}$  K, 1900–5700  $\text{mg m}^{-2} \text{ year}^{-1}$  Mg and 2200–9100  $\text{mg m}^{-2} \text{ year}^{-1}$  Na were reported (McDowell and Asbury 1994; Stallard 2012). Only our estimates of K fall in the range of the values from Puerto Rico. Our weathering rate of Ca was also lower than that reported from the Taï tropical rainforest in Côte d'Ivoire on strongly weathered granite and metamorphite of 2010  $\text{mg m}^{-2} \text{ year}^{-1}$  Ca, while our weathering rates of K and Mg are similar to those reported from the Taï forest of 1520  $\text{mg m}^{-2} \text{ year}^{-1}$  K and 710  $\text{mg m}^{-2} \text{ year}^{-1}$  Mg (Stoorvogel et al. 1997). Finally the sum of weathering-sourced cations (Ca + K + Mg + Na: 690–2840  $\text{mg m}^{-2} \text{ year}^{-1}$ ) at our study catchment was consistently lower than that reported from a range of three catchments in Panama on Andesite to Gabbro of 21300–30900  $\text{mg m}^{-2} \text{ year}^{-1}$  (Harmon et al. 2009). This comparison with the literature reveals that except for K, all base metals are released at a lower rate than in other tropical catchments on igneous rocks under warmer and partly wetter climatic conditions (McDowell and Asbury 1994; Harmon et al. 2009; Stallard 2012). Our weathering rates resemble more those reported from strongly weathered lowland tropical forests. The comparatively high weathering rates of K are

attributable to the K richness of the parent rock and the K retention in the mineral soil by the illites and illite-vermiculite mixed layer minerals at our study site (Schrumpf et al. 2001).

The biologically controlled fluxes of the three nutrient elements Ca, K and Mg are on average at least one order of magnitude larger than the total deposition and the physico-chemical weathering rates, while for Na the reverse is true (Table 2, Fig. 2b). Therefore, we conclude that in the studied tropical montane forest catchment on metamorphic rock, the biological control of the nutrient fluxes by the vegetation, microorganisms and animals is more important than the control by either the atmospheric deposition or the physico-chemical weathering, resulting in at least one order of magnitude larger biologically than geochemically controlled fluxes of Ca, K and Mg. The high importance of biological flux control in our study supports the hypotheses of Brantley et al. (2011) and Taylor et al. (2012), who stated that biological flux control is far stronger than the geochemical flux control, because the nutrient demand of the vegetation is actively driving nutrient budgets at the stand level.

#### External drivers of base metal budgets

We considered the total deposition of base metals, rainfall water fluxes and bulk deposition of  $H^+$  into the canopy and the entire catchment and their modification after the passage through the canopy, i.e., the total soil input of base metals, throughfall + stemflow water fluxes and throughfall + stemflow of  $H^+$  into the organic layer (see Fig. 2 for a visualization of these fluxes) as potential drivers of the base metal budgets of the considered compartments, because all of these fluxes might change in the near future in our study area (Boy and Wilcke 2008; Boy et al. 2008a; Wilcke et al. 2013a, b; Peters et al. 2013). Because water and base metal fluxes were components of the budgets, we refrained from conducting inferential tests and instead visualized the relationships and calculated coefficients of determination ( $R^2$ ).

Among the three considered potential drivers (total deposition, rainfall water fluxes and bulk deposition of  $H^+$ ) of the canopy budget, net hydrological fluxes and catchment elemental budget, total deposition was the most influential (Figs. 6, 7). We suggest that leaching from the canopy or losses from the catchment would only occur if total deposition exceeded the biological

demand, reflecting the strong biological control of the base metal fluxes. The little influence of the rainfall water fluxes on the variation in canopy budgets and catchment elemental budgets of base metals may also be related with the small temporal variation of these fluxes, reflected by the small error bar in Fig. 3. Alternatively, rainfall could have little influence on solute concentrations in stream water, because release and immobilization of base metals respond contrarily to varying rainfall. Little changing solute concentrations were reported by Torres et al. (2015) for rivers draining Andean catchments despite large changes in runoff. A similar chemostatic behavior of Ca, Mg and Na was observed by Godsey et al. (2009) and for Mg and Na also by Herndon et al. (2015) in various catchments in the USA. Boy et al. (2008b) suggested that one reason for this response of base metal concentrations to water fluxes is the depth of water flow in the soils of our study catchment, which depends on rainfall volume and intensity.

The small impact of the  $H^+$  deposition on element budgets is unexpected, because acid deposition may result in substantial base metal depletion from the forest canopy or entire catchments in temperate sites (Lovett 1994; Likens 2013). This small impact may be attributable to the fact that the mean bulk deposition of  $H^+$  was 5–15 times lower than in temperate sites such as the Hubbard Brook Experimental Forest, USA, and the Fichtelgebirge, Germany, during roughly the same time (Matzner et al. 2004). Furthermore, periods with increased acid deposition were several times followed by the deposition of alkaline dust as reflected in the varying pH value of rainfall and bulk deposition of Ca and Mg (e.g., in the hydrological years 1999/2000 and 2010/2011, Boy and Wilcke 2008; Wilcke et al. 2013a), so that the effect of acidification was likely regularly reversed.

#### Long-term effect of alternating base metal and acid deposition

The 15-year catchment budget was positive for Ca and K, nearly neutral for Mg, while Na was overall lost (Table 2, Fig. 2b). Thus, the deposition from the atmosphere contributed to satisfying the nutrition needs of the ecosystem with the two essential nutrients Ca and K, while fixation in illites and illite-vermiculite mixed layer minerals also might play a role for K retention. The Mg deposition only compensated for

hydrological losses. The Na loss from the catchment is attributable to weathering losses from the soil and the bedrock.

Against our expectations based on the literature from temperate climates (Lovett 1994; Matzner et al. 2004; Likens 2013), the continuous acidification because of increasing bulk deposition of  $H^+$  between 1999 and 2007 reported by Wilcke et al. (2013a) did not substantially affect the base metal budgets (net throughfall, canopy budget, net hydrological fluxes, catchment elemental budget) of the study catchment. Instead, the base metal budgets were most strongly driven by the total deposition of base metals (Fig. 7b).

Except for Na, the arithmetic sign of the budget (i.e., negative for loss or positive for accumulation) depended on our estimate of dry deposition. Without consideration of dry deposition, all base metals were apparently lost. This emphasizes the importance of an appropriate estimate of dry deposition for constructing accurate catchment elemental budgets. Unfortunately, the estimation of dry deposition is difficult and has a high uncertainty. We used the canopy budget model proposed by Ulrich (1983) which is based on the assumption that  $Cl^-$  acts as an inert tracer (i.e., is neither significantly retained nor leached in the canopy). If this assumption holds true, the  $Cl^-$  deposition ratio should be  $> 1$ , which was indeed consistently the case. The deposition ratio of  $Cl^-$  is then considered to represent the ratio of total deposition to bulk deposition of all elements, implying that dry deposition accounted on average for 140% of bulk deposition (50–410%) in our study. These findings compare well with the estimates compiled in Lovett (1994) for N deposition in a range of North American forests, particularly if it is considered that some cloud water deposition might contribute to this value (Bruijnzeel 2001). In the hydrological year 2010/2011, high  $Cl^-$  deposition ratios (3.6) were probably linked to high dust input. The high  $Cl^-$  deposition ratio (4.1) in 2007/2008 coincided with the end of a 9-year long period of continuous acid deposition, which was followed by increasing pH values in rainfall, suggesting deposition of alkaline dust that buffered the rainfall to higher pH values.

## Conclusions

Our results demonstrate that for the essential plant nutrients Ca, K and Mg, biologically controlled fluxes, which are up to ca. 90% internally cycled, are one magnitude larger than sorption to the mineral soil and soil and rock weathering fluxes. Only if total deposition of a nutrient element surpassed the biological demand, this element would not be retained in the biological compartment of the catchment.

Beyond the strong biological control, the base metal budgets (canopy budget, net hydrological fluxes and catchment elemental budget), are strongly influenced by the total deposition of base metals, but little by rainfall water fluxes and bulk deposition of  $H^+$ . Water fluxes are less important drivers, possibly because annual water fluxes vary little under the continuously humid conditions of the study site and because element release rates from the soil and bedrock respond to the water fluxes via the depth of water flow in soil. The variation in  $H^+$  deposition has little importance, demonstrating that the studied ecosystem is well buffered and base metals are closely cycled between soil and vegetation. Furthermore,  $H^+$  bulk deposition was low compared to that reported for temperate forest ecosystems suffering from acid rain.

In the long run, a considerable accumulation of the two essential nutrients Ca and K occurred driven by biological retention. Furthermore, the cation-exchange capacity and the illites and illite-vermiculite mixed layer minerals in the soil retained the base metals which escaped the organic layer by providing cation-exchange sites and fixation of K. For Mg, we observed a neutral budget which indicates that Mg fluxes are in steady-state conditions and Mg stocks in the study system remain constant.

The findings for Na deviated from those of the other base metals, because Na was retained in the above-ground biotic part of the catchment but net lost from the weathering front. The retention of Na in the above-ground biotic part can be attributed to the scarcity of Na, which is needed by some organisms in the forest canopy and organic layer. The loss of Na from the subsoil to the stream can be explained by the fact that it can hardly be taken up by the mainly shallow plant roots and the low microbial activity in the subsoil.

Our results emphasize that the understanding of chemical denudation requires consideration of the

biological element cycling, which dominates the flux regime of base metals in headwater catchments of tropical montane forests. Furthermore, dry deposition had a similar size as bulk deposition and therefore needs to be quantified for complete budgets.

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