AGU100 ADVANCING EARTH AND SPACE SCIENCE

JGR Biogeosciences

RESEARCH ARTICLE
10.1029/2018JG004942

Temporal Trends of Phosphorus Cycling in a Tropical Montane Forest in Ecuador During 14 Years

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Key Points:

- A remote tropical montane forest accumulated P during 14 years
- The main sink of the accumulated P was the soil organic layer
- The P accumulation increased the P fluxes with litterfall and stemflow

Supporting Information:

- Data Set S1

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Citation:
Wilcke, W., Velescu, A., Leimer, S., Bigalke, M., Boy, J., & Valarezo, C. (2019). Temporal trends of phosphorus cycling in a tropical montane forest in Ecuador during 14 years. *Journal of Geophysical Research: Biogeosciences*, *124*. https://doi.org/10.1029/2018JG004942

Received 19 NOV 2018
Accepted 8 APR 2019
Accepted article online 25 APR 2019

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Funding acquisition: Wolfgang Wilcke
Investigation: Wolfgang Wilcke, Andre Velescu, Jens Boy, Carlos Valarezo
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Abstract

Increased bioavailability of P can have a negative impact on plant biodiversity. In an approximately 9-ha catchment under N + P-limited megadiverse tropical montane forest in Ecuador, we budgeted all major P fluxes and determined whether the P fluxes changed from 1999 to 2013. Furthermore, we assessed which external drivers (rainfall, total P and acid deposition) caused this potential change. Mean (±*SD*) annual P deposition (bulk+dry) was 240 ± 270 mg/m^2, with the *SD* reflecting the interannual variation. The annual P flux to the soil via throughfall+stemflow+litterfall was 1,400 ± 170 mg/m^2 of which 18 ± 9.2% was leached to below the organic layer. The mineral soil retained 80 ± 12% of the P leached from the organic layer. The mean annual P weathering rate was 79 ± 63 mg/m^2. The sum of P fluxes was approximately 5 times larger above than below the mineral soil surface, illustrating that P was tightly cycled in the biological part of the forest. The mean annual canopy budget was negative (−120 ± 280 mg/m^2); that is, P was leached from the canopy. Throughfall was the largest source of dissolved P. The P catchment budget (total deposition-streamflow) was positive (200 ± 270 mg/m^2); that is, P was retained, mainly in the soil organic layer. From 1999 to 2013, P fluxes with throughfall, stemflow, and streamflow increased significantly. The strongest driver of the P budgets of the canopy and the catchment was total P deposition. Our results demonstrate that mainly biological processes retained deposited P in the vegetation and the organic layer enhancing the internal P cycle.

Plain Language Summary

Phosphorus is quantitatively the second most important essential plant nutrient. In the tropics, the growth of many ecosystems is limited by this nutrient. This is also the case in the studied tropical montane forest in Ecuador, where phosphorus limits growth together with nitrogen. We assessed whether the cycling of phosphorus changed in a period of 14 years from 1999 to 2013. We found that the total storage of phosphorus in the whole ecosystem increased, because some phosphorus was introduced from the atmosphere and retained by the organisms. As a consequence, more phosphorus was forest-internally cycled, mainly with throughfall, the water that passes the forest canopy, and stemflow, the water running down the tree trunks. We found that the phosphorus concentrations in throughfall and stemflow increased from 1999 to 2013 providing directly usable phosphorus to the organisms of the ecosystem. The main reason for this increasing phosphorus supply was the incorporation of the phosphorus input from the atmosphere into the internal phosphorus cycling.

1. Introduction

A common view of the P cycle in tropical ecosystems implies that P availability depends on ecosystem age and associated stage of soil development with a low P availability in young and old soils and a maximum P availability in intermediately aged soils (around a few 100.000 years old; Chadwick et al., 1999; Walker & Syers, 1976). With increasing soil age and associated depletion of rock-derived P, dust-derived P increasingly contributes to plant nutrition. As a consequence, the growth limitation changes from N via N + P to P with increasing soil age (Chadwick et al., 1999). This concept has been confirmed for some tropical lowland forests but cannot be directly transferred to tropical montane forest soils, because of tectonic uplift and associated erosion and the frequent landslides, which rejuvenate the soils (Frei, 1958; Wilcke et al., 2003).

The soils of the tropical Andes are little developed and therefore shallow and rich in stones (Frei, 1958; Schrumpf et al., 2001). The mineralogy reflects their young age with moderate Fe and Al concentrations and the presence of primary minerals such as mica and three-layer clay minerals (Schrumpf et al., 2001). Consequently, the bioavailability of P in forests on these acidic young soils strongly depends on mineralization of the thick organic layers and the cycling of P between the soil and the biomass and less on the mineral soils (Dietrich et al., 2017; Grubb, 1995; Wilcke et al., 2002). Thick organic layers are typical for tropical montane forests and frequently host a large part of the plant roots (Soethe et al., 2006; Tanner et al., 1998; Wilcke et al., 2002). In the humid tropical montane forests, soil organic matter mineralization is usually limited by episodic waterlogging contributing to the accumulation of thick organic layers (Roman et al., 2010; Schuur & Matson, 2001).

The strongest driver of P availability in the mineral soil is the pH, which limits P availability because of the precipitation of little soluble P minerals, that is, Ca phosphates at $\mathrm{pH} \geq 7$ and Al and Fe phosphates at $\mathrm{pH} \leq 5$ (Alt et al., 2011; Goller et al., 2006; Hinsinger, 2001). In the acidic mineral soils of the tropical Andes, P can therefore be strongly bound in little soluble Al phosphates because of the release of Al^{3+} by H^{+} buffering or sequestered at the surface and in the interior of Fe oxides (Hinsinger, 2001). However, Rehmus et al. (2017) have shown that >80% of the dissolved Al in acidic soils under tropical montane forest with thick organic layers is organically complexed and thus not available for precipitation as Al phosphate.

The biomass production of many terrestrial ecosystems is P- or N + P-limited (Elser et al., 2007; LeBauer & Treseder, 2008). This is also true for some of the humid tropical montane forests of the east-exposed slope of the eastern Andean Cordillera in South America, such as in Ecuador and Peru (Fisher et al., 2013; Homeier et al., 2012; Velescu et al., 2016), which consist of megadiverse plant communities (Barthlott et al., 2007). It has been shown that an increase in the bioavailability of P can be more detrimental for biodiversity than that of N (Wassen et al., 2005). Therefore, it is important to detect possible changes of the P bioavailability in the Andean tropical montane forests in response to environmental changes in the region in order to determine if the biodiversity may be threatened by P eutrophication.

Bol et al. (2017) reported that there is a scarcity of complete ecosystem-based assessments of dissolved P fluxes in temperate forest ecosystems and attributed this to the difficulty of measuring the low dissolved P concentrations and possibly also to a stronger focus on C and N than on P cycling in the literature. In the compilation of catchment budgets of tropical lowland forests of Bruijnzeel (1991), P accumulated in most studied systems, while also some negative budgets, that is, P losses were reported. In tropical montane forests in the Venezuelan Andes (Steinhardt, 1979), Jamaica (Hafkenscheid, 2000), and Ecuador (Wilcke et al., 2008) whole ecosystem budgets of dissolved $\mathrm{PO_4}$-P (Venezuela and Jamaica) and total P (Ecuador) for periods of 1–5 years were generally positive. On the contrary, Bruijnzeel (1991) reported one example of a negative P budget for a tropical montane forest on fertile, quickly weathering andesitic tuff in Costa Rica. These results suggest that P accumulates in most tropical montane forests on acidic rocks. However, in the few studies reporting P accumulation in tropical montane forests at the catchment level, it remained unclear where in the forest the accumulated P was stored and if it increased the bioavailability of P.

In the north Andes, several simultaneously occurring environmental changes affecting the native forests have been observed. For the eastern part of the north Andes, a warmer climate and locally variable positive and negative changes of rainfall have been predicted by model projections (Urrutia & Vuille, 2009; Vuille et al., 2003). Increasing temperatures on the eastern Andean slope in Ecuador in the last few decades have been confirmed by the evaluation of the available climate data of the past four decades (Peters et al., 2013). Changing rainfall might influence catchment budgets of P, because it has been shown for temperate forest catchments that the water input plays a major role for canopy and catchment budgets of dissolved nutrients (Lischeid et al., 2004; Matzner et al., 2004). Increasing temperatures and resulting locally drier conditions could enhance mineralization of soil organic matter by decreasing the duration of high moisture contents or waterlogging of the soils. More mineralization might increase the P availability by release from the large P stock in organic matter (Wilcke et al., 2002). Furthermore, increasing temperatures and atmospheric $\mathrm{CO_2}$ concentrations might also accelerate weathering, thereby releasing P into the ecosystems (Qafoku, 2014). However, Boy, Valarezo, and Wilcke (2008) have shown for a tropical montane forest in Ecuador that the weathering front, in which P was released, was largely below the root zone so that the additionally weathered P would be more likely released into the streams draining the catchments than included into internal ecosystem cycling.

Furthermore, N deposition increases strongly in the tropical montane forests of Ecuador, possibly enhancing P limitation (Wilcke, Leimer, et al., 2013). A stronger P limitation might result in even tighter P cycling, which enhances P accumulation at the catchment level and in the biological part of the forest ecosystem (Jobbagy & Jackson, 2001, 2004; Zhou, Lu, et al., 2018). Finally, episodic alkaline dust deposition and seasonal acid deposition originating from Amazonian forest fires reach the east Andes by long-range transport (Boy, Rollenbeck, et al., 2008; Boy & Wilcke, 2008). Changing soil acidity likely influences the P availability. Alkaline input has a positive effect on P availability in acidic soils, because of the stimulation of soil organic matter mineralization and reduced Al release from Al oxides. Increasing acidification in contrast might further impede mineralization and increase Al solubility and thus enhance the precipitation of little soluble Al phosphates.

To detect ecosystem responses of forests to environmental changes early, internal element fluxes and catchment budgets of elements are helpful, because they change usually long before the vegetation or soil (Bormann & Likens, 1967; Bruijnzeel, 1991; Likens, 2013). In forest ecosystems, P is cycled in inorganic forms ($H_2PO_4^{-}$ and HPO_4^{2-}), which are directly bioavailable, and as dissolved organic P (DOP, a complex mixture of low-molecular weight P-containing organic compounds), which is not directly bioavailable but may become bioavailable after mineralization. Furthermore, litterfall (LF) cycles organically bound P from plants to the soil, where it is mineralized in the organic layer (Vogt et al., 1986; Wilcke et al., 2002). Goller et al. (2006) reported mean contributions of DOP to total P of 39–77% in ecosystem-internal fluxes (throughfall [TF], stemflow [SF], lateral flow, and litter leachate [LL]) from five study sites in a tropical montane forest in Ecuador during one hydrological year, while no DOP was detected in rainfall, soil solution, and stream water.

To determine whether a remote native old-growth tropical montane forest accumulated P and whether its P cycling changed from 1999 to 2013 in response to climate change and deposition from the atmosphere, we (i) quantified all major P fluxes and set up canopy and catchment budgets of P in annual resolution. We hypothesized that deposited P was retained, mainly in the biologically controlled vegetation and organic layer with their associated organism communities. Furthermore, (ii) we determined if there were temporal trends in monthly time series of all major ecosystem fluxes of P. We expected increasing internal dissolved P fluxes mainly between the aboveground biomass and the soil organic layer and upper mineral soil with time because of the retained P. Finally, we (iii) identified which of the three external drivers, total P deposition, rainfall water fluxes, and bulk deposition (BD) of H^+, influenced the P budgets of the forest canopy and the entire catchment most strongly. We suspected a strong influence of P and acid deposition on the P budgets.

2. Materials and Methods

2.1. Study Site

We studied an approximately 9.1-ha catchment under old-growth montane rainforest on a 30–50° steep slope between 1,850 and 2,200 m above sea level (asl; Boy, Rollenbeck, et al., 2008, Boy, Valarezo, & Wilcke, 2008; Wilcke et al., 2001, 2017). During the observation period from April 1999 to March 2013, mean (±*SD*, reflecting interannual variation) annual precipitation was 2,330 ± 244 mm of which 40 ± 4.0% was lost from the catchment as interception evaporation, 15 ± 7.2% as transpiration, and 46 ± 4.4% as surface runoff in the stream. Mean annual temperature was 14.9 °C (Wilcke et al., 2017; Wilcke, Leimer, et al., 2013). Soils are mainly shallow Folic Dystric Cambisols developed from metamorphic rock (phyllite and quartzite) with thick organic layers (IUSS Working Group WRB, 2014) or Humic and Lithic Dystrudepts (Soil Survey Staff, 2014). The soils are dominated by three-layer clay minerals (illite-vermiculate interlayer minerals, illites, and vermiculites) but also contain considerable kaolinite concentrations (10–60% of the clay fraction), and some soils contain pedogenic chlorite (Schrumpf et al., 2001). In 20 approximately 0.5- to 1-m-deep soil profiles along two transects near the stream and near the ridge, we found only phyllite up to an elevation of approximately 2,000 m asl. 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 ± 0.24 m. The A horizons of 29 study soils, assumed to representatively cover the catchment area, contained on average 46 ± 28% sand, 37 ± 6.5% silt, and 17 ± 5.8% clay, had a pH of 4.4, an effective cation-exchange capacity of 63 ± 26 $mmol_c$/kg, a mean soil organic C concentration of 32 ± 19 g/kg, and a mean C/N ratio of 11 ± 2.8. More details about the location of the study soils and their properties can be found in Wilcke et al. (2017). The studied forest can be classified as evergreen montane forest (Balslev & Øllgaard, 2002) or as Lower Montane Forest (Bruijnzeel & Hamilton, 2000). More information on the composition of the forest can be found in the work of Homeier (2004).

2.2. Sampling and Field Measurements

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 horizons). FDR probes were installed in January 2000 at 0.10-, 0.20-, 0.30-, and 0.40-m soil depth, spanning the 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 1,905 m asl. 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, TF, SF, soil water flow, and streamflow (ST). Furthermore, the potentially important contribution of dry particulate deposition of P needs to be quantified for a complete budget (Likens, 2013; Ulrich, 1983). Because dry particulate deposition cannot be measured directly, Ulrich (1983) suggested a widely used canopy budget (CB) model (Draaijers et al., 1996; Staelens et al., 2008; Talkner et al., 2010) based on the assumption that Na^+ or Cl^- can be considered as inert tracers. This suggestion is based on the low Na^+ or Cl^- concentrations in plant tissues relative to the deposition fluxes.

Rainfall was collected at 2–4 gauging stations, each consisting of five Hellmann-type collectors, placed on clear-cut areas. As the collectors were permanently open, collected samples represent BD (i.e., rainfall and soluble coarse particulate dry deposition [DD]), which can drop into the open collectors (Figure 1). In a comparison of five different measurement methods for rainfall, our samplers measured during an approximately 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 approximately 20-m-long measurement transects on the 38–70° steep lower to midslope aligned downhill across about 10 m in elevation (starting at 1,900, 1,950, and 2,000 m asl, respectively). We chose the placement of our transects because the lower slope to midslope represented the largest part of the catchment. The covered elevational gradient of 100 m was a compromise between reasonable accessibility and representativeness of the approximately 200-m gradient of the entire catchment. At each measurement transect, we collected TF, *LL*, and fine LF (Figure 1). TF 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. LL 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 LF was collected with three litter traps per transect. We started with a 0.3 × 0.3 m trap used from April 1998 to October 2005 and switched to 0.5 × 0.5 m large traps thereafter. All TF, LL, and LF samplers were spread evenly along the transects. SF was collected with polyurethane collars at five trees in the lower part of the catchment. *ST* was sampled above a weir, which was used to gauge ST (Boy, Valarezo, & Wilcke, 2008; Fleischbein et al., 2006). From August 2000 to January 2003, we additionally collected weekly 100-mL aliquots of stream water to measure the concentrations of total suspended particles (*TSPs*). The TSPs were accumulated on ashless filters with a pore size of 4–7 μm (folded filter type 392; Sartorius-Stedim GmbH, Göttingen, Germany) for ten 3-month intervals, dried at 40 °C in a drying oven, and weighed. The filter dry weight was subtracted from the total weight of the dried *TSP* sample and filter to determine the *TSP* mass. Prior to digestion, the *TSP* sample and filter were ashed at 450 °C to remove organic matter and destroy the filter.

Water level at the weir was measured hourly with a pressure transducer in the first 5 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 TF 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 (Fleischbein et al., 2006; Goller et al., 2005).

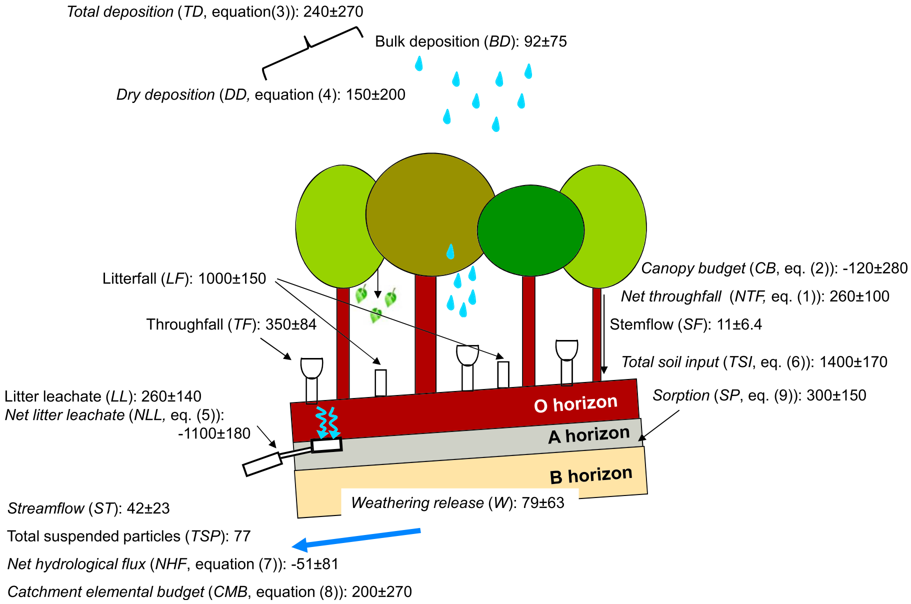

Figure 1. Overview of the measured and calculated/modeled ecosystem fluxes of P, their abbreviations, the equation (eq.) number used to estimate them, and the mean and standard deviation (n = 14 years) of the measured and calculated total dissolved P fluxes in mg/(m^2 year). Calculated/modeled data are shown in italics. A positive sign of the budgets means accumulation and a negative sign loss. Mind that for the net fluxes the reverse is true. The standard deviation is a reflection of the interannual variation of the P fluxes.

All solution (rainfall, TF, SF, LL, and ST) and LF samples were collected weekly between April 1999 and March 2013. For rainfall, TF, SF, and LL, each sample was cumulative for the whole week, while for ST it was an instantaneous sample. Rainfall, TF, and SF 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. LL was bulked into one collection vessel per measurement transect to yield one individual sample per measurement site and collecting date. LF 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 1 April to 31 March of the following year because the experiment was established in March 1998. However, the measurement of total P concentrations in the ecosystem solutions only started in May 1999.

2.3. Chemical Analyses

Total P concentrations in the mineral soil samples were determined by digestion with concentrated HNO_3/HF (4:1 v/v) in open teflon vessels on a sand bath, and the samples of O horizons, LF, and ashed TSPs were digested in 8-mL suprapure concentrated HNO_3 (Carl Roth GmbH, Karlsruhe, Germany) and 2-mL H_2O_2 (Merck KGaA, Darmstadt, Germany) in a microwave oven.

The pH value of the solution samples was measured in an unfiltered aliquot of each sample within <24 hr after sampling with a glass electrode. Another aliquot was filtered with ashless filters with a pore size of 4–7 μm (folded filter type 392; Sartorius-Stedim GmbH, Göttingen, Germany). After export of the filtered 100-mL aliquots from Ecuador to Europe in frozen state, we determined Cl^- concentrations in all ecosystem solutions 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/L), we adjusted the ionic strength with a solution of 1.13 g/L $NaNO_3$ and added 2 mL/L surfactant (Triton X-100, 50% solution) so that all samples had a similar ionic strength prior to ion-sensitive electrode measurement. Total P concentrations were determined with inductively coupled plasma - optical emission spectrometry (ICP-OES; Integra XMP, GBC Scientific Equipment Pty. Ltd., Australia) in the first 4 years of the experiment and thereafter with an automated colorimetric analyzer (CFA, Skalar, Breda, The Netherlands or Bran & Lübbe, Norderstedt, Germany) by irradiation with UV and oxidation with

$K_2S_2O_8$ followed by reaction with ammonium molybdate. Ammonium molybdate catalyzed by antimony tartrate reacts in an acidic medium with phosphate and forms a phospho-molybdic acid complex. Ascorbic acid reduces this complex to an intensely blue-colored complex. We measured 255 samples with both methods (CFA and ICP-OES) and found a close correlation ($P_{CFA} = 1.08 \cdot P_{ICP\text{-}OES} - 0.01$, $R^2 = 0.91$).

2.4. 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, TF, and SF were directly measured (Figure 1).

Because the zero-tension lysimeters did not collect water fluxes quantitatively (Jemison & Fox, 1992), we modeled water fluxes in soil with the soil water balance equations as given in 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 TF + SF (input) minus independently determined transpiration (output) minus (or plus) change in stored water in the soil layers. The change in stored water was calculated by the difference in water storage (derived from soil water contents) of the respective soil layer between two soil water measurements with the FDR probes. We assumed direct evaporation from the soil as negligible and derived weekly transpiration rates by partitioning the annual difference between TF + SF and ST proportionally to the weekly evapotranspiration rates as modeled by REF-ET (Allen, 2000; 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 LL on measured weekly TF including all available data from 1999 to 2003 ($LL = 0.86 \cdot \mathrm{TF} - 0.71$, $R^2 = 0.85$). This regression equation was also used to calculate LL from 2004 to 2013. The LL data from 1999 to 2003 were taken from Boy, Valarezo, and Wilcke (2008).

In the first 4 years (1999–2003), we used ST modeled with the distributed catchment model TOPMODEL (Beven et al., 1995) taken from Fleischbein et al. (2006) and Boy, Valarezo, and Wilcke (2008). For the later years (2004–2013) we used weekly measurements of the water level at the weir which was transformed to ST by a calibrated ST function of water level determined with a bucket and stop watch at different water levels (Boy, Valarezo, & Wilcke, 2008; Fleischbein et al., 2006). From 2004 to 2013, we assumed that the water level was constant during the measurement week.

To set up budgets of the forest canopy, the organic layer, and the entire catchment, a number of calculations were necessary. The net TF flux (*NTF*) of P is defined in equation (1).

$$\mathrm{NTF_P} = \mathrm{TF_P} - \mathrm{BD_P} \tag{1}$$

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

To set up the *CB* of P, we used the model of Ulrich (1983) to estimate the particulate DD of P scavenged out of the atmosphere by the canopy, that is, the space created by the crowns of the trees in the two forest stories at the study sites and all organisms living in this space (epiphyts, epiphylls, biological crusts, etc.). It considers fine particulate dry and bulk deposition, TF, and SF but not plant nutrient uptake from the soil via the roots and LF. The CB is calculated as the difference between TF + SF fluxes and total deposition (*TD*, equation (2)).

$$\mathrm{CB_P} = \mathrm{TD_P} - (\mathrm{TF_P} + \mathrm{SF_P}) \tag{2}$$

Negative values of the CB indicate leaching, positive ones retention of P by the canopy (including plants, phyllosphere organisms, and soil-like accumulations). *TD* of P was calculated with equation (3):

$$\mathrm{TD_P} = \mathrm{BD_P} + \mathrm{DD_P} \tag{3}$$

where DD is the fine particulate part of dry deposition estimated with equation (4).

$$DD_P = [[[TF_{Cl} + SF_{Cl}]/BD_{Cl}] \text{ x } BD_P]–BD_P \tag{4}$$

here TF_{Cl} represents the TF flux, SF_{Cl} represents the SF flux, and BD_{Cl} represents the BD 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 DD to TD. The deposition ratio of Cl^- can be used to estimate the DD if it is assumed that the ratio of dry to BD is the same for all elements (Ulrich, 1983). We relied on previous work at the same study site, which demonstrated that Cl^- can be considered as a nonreactive tracer (i.e., uptake and leaching by the canopy can be neglected) and therefore can successfully be used to calculate CBs (Boy, Rollenbeck, et al., 2008; Boy & Wilcke, 2008; Wilcke et al., 2008). Because our budgeting interval was annual, we needed a deposition ratio of Cl^- which was unaffected by lag effects between DD and leaching with TF and SF. Therefore, we calculated one deposition ratio of Cl^- per hydrological year and used this annual Cl^- deposition ratio for our CB calculations.

Net LL (*NLL*) is a measure of the retention of P in the biotic compartment and thus the closeness of P cycling between soil and vegetation, because a large part of the roots is restricted to the densely rooted organic layer (Soethe et al., 2006). NLL was calculated with equation (5).

$$NLL_P = LL_P - TSI_P \tag{5}$$

where *TSI* is total soil input according to equation (6).

$$TSI_P = TF_P + SF_P + LF_P \tag{6}$$

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 TD and weathering equals the losses with ST 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 TSPs. The third approach attributed the entire loss of Na with ST to weathering and assumed that P was released in the same ratio to Na as it occurred in the parent rocks. The three approaches are summarized in Table 1.

To assess accumulation or loss of P in the study catchment, net hydrological fluxes (*NHFs*—excluding DD, which is frequently not determined in other studies) and the catchment elemental budget (*CMB*—including DD) are used as defined in equations (7) and (8).

$$NHF_P = ST_P–BD_P \tag{7}$$

$$CMB_P = TD_P–ST_P = (BD_P + DD_P)–ST_P \tag{8}$$

Like for the CB, a negative sign of the CMB means P loss and a positive one P gain in the catchment. Mind that the NHF is defined differently, so that a positive sign means that P fluxes with ST were higher than with BD and a negative sign the reverse.

Finally, we calculated the sorption in the mineral soil (*SP*) with equation (9) neglecting the P uptake by plants from the mineral soil, because of the high root density in the organic layer, where P concentrations were much higher than in the mineral soil.

$$SP_P = LL_P + W_P–ST_P \tag{9}$$

where W is the weathering rate. The monthly time series data sets were tested for significant temporal trends with the Seasonal Mann-Kendall test (Hirsch et al., 1982) as implemented in the function *SeasonalMannKendall()* from the package *Kendall* (McLeod, 2011) in the statistical software R (R Core Team, 2017). The Seasonal Mann-Kendall test is a nonparametric trend test considering the most important autocorrelation (i.e., seasonal) which we detected. The test is not sensitive to a small number of outliers. The application of the test does not necessarily require a linear trend (Helsel & Hirsch, 2002). The seasonal Sen's slope (trend) per unit time (Hirsch et al., 1982) was calculated with the function *sea.sens.slope()* from the package *trend* (Pohlert, 2018), which requires complete time series without data gaps. Therefore, data gaps were filled with the package *mice* (van Buuren & Groothuis-Oudshoorn, 2011) using the method of

Table 1
Overview of the Methods Used to Determine Weathering Rates

Method number	Equation used to calculate weathering rates
1a	$TD_i + W_i = ST_i + \Delta B_i \pm \Delta OM_i \pm \Delta X_i \pm \Delta M_i$[a]
1b	$W_i = ST_i + TSP_i - TD_i$[b]
2	Wi = element export during baseflow + TSP_i [c]
3	$Wi = (C_i/C_{Na})_{rock} \times (ST_{Na} + TSP_{Na})$[d]

[a] *W* is weathering release from primary minerals, Δ is change, *B* is storage in biomass, OM is long-term storage in soil organic matter, *X* is the exchangeable pool, and *M* is the secondary mineral pool. Equation taken from Likens (2013) [b] Simplification of equation (1a) based on the assumptions that ΔB_i, ΔOM_i, and ΔX_i equaled zero and ΔM_i total suspended particles (TSP_i).

Justifications:

1. ΔB_i does not change, because the studied forest is an old growth native forest in steady state.
2. ΔOM_i does not change because we did not find significant differences (*t* test, $p < 0.05$) in (i) the thickness of the organic layer, (ii) the C concentrations, and (iii) the C/N ratios of A and B horizons did not change between our two surveys in 1998 and 2007 (organic layer thickness: 12 ± 8.2 cm; C concentrations: 29 ± 16 and 10 ± 7.1 g/kg and C/N ratios: 14 ± 2.9 and 10 ± 3.3 in the A and B horizons, respectively; $n = 20$ soils of which 10 were in slope and 10 in valley bottom position, Wilcke et al., 2017).
3. ΔX_i does not change because soil development (ΔM) was assumed to equal the erosional loss of secondary minerals, which is measured as *TSP*. This assumption is based on the observation that the study soils were all shallow (usually hardly deeper than 0.5 m and rich in stones; Wilcke et al., 2017) and did not show a further development than to the state of a Cambisol (IUSS Working Group WRB, 2014) in spite of the tropical perhumid climate. We therefore assumed that continuous erosion kept the soils at a steady-state young development stage

[c] Element export during baseflow (including superdry flow) was 87 mg/(m^2 year) Ca, 49 mg/(m^2 year) K, 58 mg/(m^2 year) Mg, and 507 mg/(m^2 year) Na (Boy, Valarezo, & Wilcke, 2008). Approach 2 is based on a suggestion of Stoorvogel et al. (1997) [d] $(C_i/C_{Na})_{rock}$ is the concentration ratio of element *i* to Na in the parent rocks. For the third approach, we assumed that the loss of Na can be entirely attributed to weathering, because Na is not an essential plant nutrient and because our study site is far away from the ocean in downwind (i.e., western) direction and that weathering resulted in a homogeneous complete dissolution of the parent rock (i.e., a stoichiometric release of Na and the other base metals). The third approach was used separately for phyllite and quartzite.

predictive mean matching prior to calculation of the Sen's slope. The linear regression lines in our graphs are meant to facilitate a fast recognition of significant trends.

3. Results

3.1. P Fluxes and Budgets

The P concentrations in the organic layers were 1,000 ± 290 mg/kg, the A horizons 590 ± 200 mg/kg, the B horizons 500 ± 180 mg/kg, and the C horizons 570 ± 330 mg/kg. The phyllite contained 780 ± 10 and the quartzite 80 ± 0.0 g/kg P, and the P:Na mass ratios were 0.079 and 0.006, respectively.

Annual TD of P varied from 40 to 1,100 mg/m^2 by a factor of 28 (Figures 1 and 2). The two hydrological years with the highest TD of P were 2001/2002 (460 mg/m^2) and 2007/2008 (1,100 mg/m^2). The mean annual deposition ratios of Cl^- were 2.43 ± 0.68 suggesting that DD (equation (4)) amounted on average to 143 ± 68% of BD. Consequently, DD of P contributed in most years more to TD than BD (Figure 1).

The by far largest individual P flux was LF, which had a mean mass flux of 1.1 kg/(m^2 year) during the observation period. LF carried 73 ± 11% of the total P arriving at the soil surface (TSI; equation (6)), followed by TF, the largest aqueous P flux (Figure 3). Of the P arriving at the soil surface, 18 ± 9.2% was leached to below the organic layer. Of the P leached from the organic layer, 80 ± 12% remained in the mineral soil or was recycled to the vegetation by plant uptake. The sorption to soil calculated by ignoring plant uptake from the mineral soil (equation (9); Figure 3) accounted for only 0.0015% of the P stock of 100 g/m^2 in the on average 0.2-m-thick A horizons. The SF was the smallest P flux followed by the ST. TF and LL provided the most dissolved and thus directly bioavailable P, because 41 ± 27% of the dissolved P was inorganic in TF and 35 ± 17% in LL (Goller et al., 2006).

It was not possible to quantify weathering rates of P with our first approach based on the catchment P budget (Table 1), because P fluxes with ST and TSPs were lower than TD of P (Figure 1). The weathering rate of P estimated with our second approach was 95 mg/m^2, assuming that the sum of superdry flow and baseflow of the stream taken from Boy, Valarezo, and Wilcke (2008) plus TSPs approximated the P release by

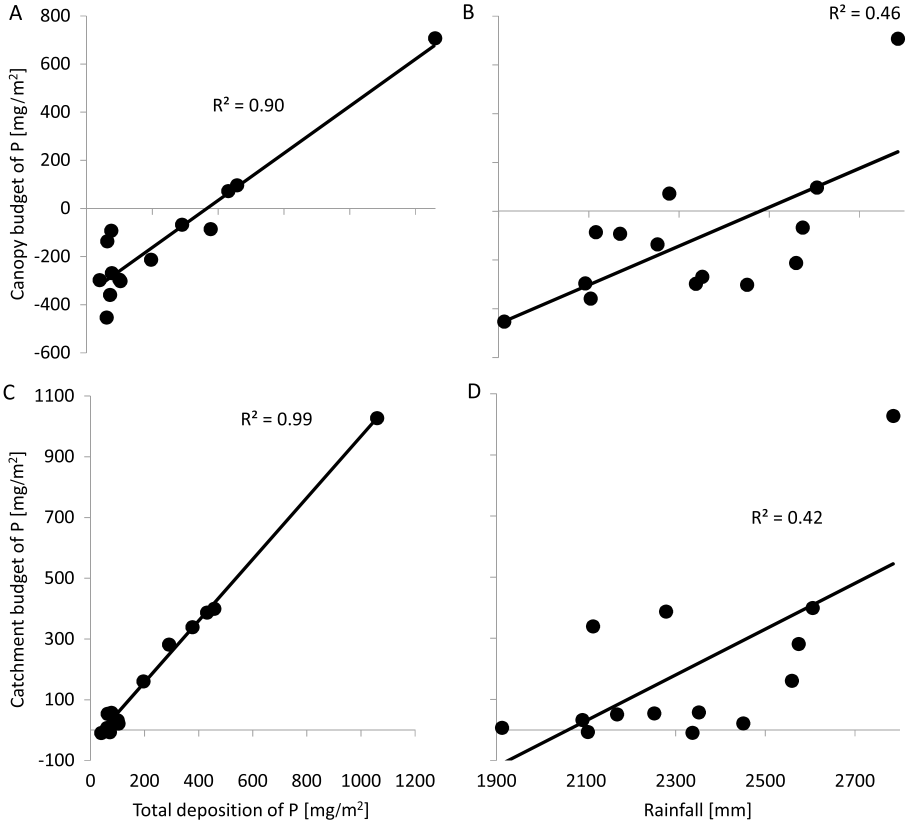

Figure 2. The relationship between total deposition of P (bulk deposition + dry deposition using Cl^{-} as tracer; equation (3)) and (a) the canopy (equation (2)) and (c) the catchment elemental budgets of P (equation (8)) and between rainfall and (b) the canopy and (d) the catchment elemental budgets of P during 1999–2013. Because water and P fluxes were components of the canopy and catchment budgets, we refrained from statistical inference tests. Instead, we visualized the relationships and calculated the coefficients of determination (R^2).

weathering. This value fell in between the weathering releases of P estimated with the third approach. In our third approach we assumed that the ratio of P release by weathering to the Na release by weathering was the same as the ratio of the concentrations of P and Na in the bedrock. Consequently, phyllite weathering released 130 mg/m^2 P and quartzite 10 mg/m^2 P. The mean value for weathering shown in Figure 1 was derived by averaging the three weathering release rates estimated with the second method and those estimated for phyllite and quartzite with the third method.

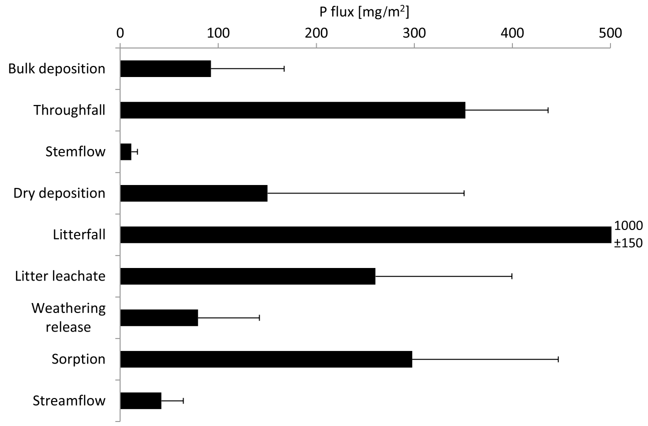

Figure 3. The vertical variation of the mean fluxes of P through the forest ecosystem during 1999–2013. The error bars represent standard deviations among the study years ($n = 14$).

The size of the mainly biologically controlled sum of P fluxes above the surface of the mineral soil was approximately 5 times larger than that of mainly geochemically controlled fluxes below the surface of the mineral soil (sorption to soil and weathering; Figures 1 and 3). The annual TSI of P was 55 ± 54 times larger than the dissolved P output with ST in the same year. This illustrates that P was tightly cycled in the biological part of the forest, resulting in only minor P losses from the study catchment.

We budgeted the canopy (net TF, equation (1); CB, equation (2)), the biotic part of the catchment (NLL, equation (5)), and the entire catchment (NHFs, equation (7); CMB, equation (8)) to identify sinks and sources of P and to quantify the biological influence on the P cycle and losses in the study catchment. Net TF of P was consistently positive (140–750 mg/(m^2 year)), and the CB of P was negative in all but the three hydrological years with the highest TD (2001/2002, 2003/2004, and

2010/2011; Figure 3) illustrating that P was considerably leached from the canopy (i.e., from the leaves and twigs and the biota living in the canopy; Figure 1). Mind that—following the common definition in the literature (e.g., Likens, 2013; Parker, 1983)—a positive net flux (net TF, NLL, and NHF) means that the incoming P flux (BD or TSI) was smaller than the outgoing P flux (TF, LL, and ST) implying that gains of dissolved P along the water path through the ecosystem and a negative sign indicate the reverse. For the budgets (CB and CMB), in contrast, a positive sign means a gain and a negative sign a loss of P in the whole catchment considering all fluxes (i.e., including DD) again following usual definitions of budgets (e.g., Bruijnzeel, 1991). The canopy was the largest source of dissolved P in the ecosystem providing immediately bioavailable P, when the TF and SF reached the forest floor.

The NLL was strongly negative; that is, most of the TSI (LF + TF + SF) remained in the organic layer and was recycled by the vegetation and organisms in the organic layer (Figure 1). On average, only 18 ± 9.2% of the P arriving at the forest floor was leached from the organic layer into the mineral soil. Even of this P, likely some was recycled to the vegetation by uptake of the roots reaching into the mineral soil. However, we were unable to measure this flux. Thus, by far most of the P was closely cycled in the biotically dominated part of the catchment.

The NHFs were on average negative but in five of the 14 studied years positive (11 to 49 mg/m^2). The catchment P budget was on average positive, and there were only 2 years with a slightly negative budget (2009/2010: −5.8 mg/m^2 and 2012/2013: −8.4 mg/m^2; Figure 2). During the 14-year period, the whole catchment cumulatively accumulated 2.8 g/m^2 P, which accounted for 14% of the mean P stock in the organic layer of 20 ± 11 g/m^2 (Wilcke et al., 2002) and 2.8% of the mean P stock in the mineral A horizons of 100 ± 26 g/m^2.

3.2. Temporal Trends of Phosphorus Fluxes

There was no temporal trend in the BD of P. The total dissolved P fluxes increased from 1999 to 2013 significantly in TF, SF, and ST (Figure 4). The seasonal Sen's slope of the trends increased in the order, SF < ST < TF. The annual increase rates of the P flux with TF, SF, and ST were much lower than the annual accumulation rate of P in the whole catchment (Figure 1). It can therefore be inferred that most of the accumulated P was stored in the soil. The annual increase rate of the P flux with ST was also much lower than the weathering release, indicating that most of the P released by weathering remained in the study catchment.

3.3. External Drivers of the Canopy and Catchment Elemental Budgets of Phosphorus

The strongest external driver of the canopy and the CMBs of P was total P deposition (Figure 2). The influence of the water input with rainfall was much smaller. In the hydrological year 2007/2008, we recorded the highest annual rainfall of 2,790 mm, which was 460 mm or 20% above the 14-year average of 2,330 mm and therefore also showed the highest BD. If the year 2007/2008 was removed, the coefficients of determination (R^2) decreased to 0.68 for the correlation between TD and the CB of P and to 0.98 for that between TD and the CMB of P. For rainfall, it decreased to 0.24 and 0.18, respectively. Thus, the TD was still the strongest driver of the canopy and catchment budgets after the highest recorded annual rainfall was removed as an outlier. The BD of H^+ only had a minor influence on the canopy and CMBs of P ($R^2 \leq 0.10$).

4. Discussion

4.1. Phosphorus Fluxes and Budgets

The BD of P in the study area was higher than reported for a small number of forest sites in Bol et al. (2017) of 7–33 mg/(m^2 year), the mean values for coniferous and deciduous forests of the temperate zone of 38 ± 51 and 57 ± 107 mg/(m^2 year), respectively, compiled in Sohrt et al. (2017), and two sites in Central and South America of 19 mg/(m^2 year) (Tipping et al., 2014), illustrating that considerable P inputs reached the study ecosystem (Figure 1). Our estimated DD of P was higher than the 88 mg/(m^2 year) reported from the Taï tropical rainforest in Côte d'Ivoire attributed to Harmattan dust (Stoorvogel et al., 1997). Possible sources of the P deposited at our study site include transport of dust or combustion exhaust from the dry, partly densely settled intra-Andean depressions or sea salt from the Pacific Ocean during the rare periods of westerly wind directions, occasional Sahara dust input (Boy & Wilcke, 2008), volcanic exhausts, or Amazonian forest fires.

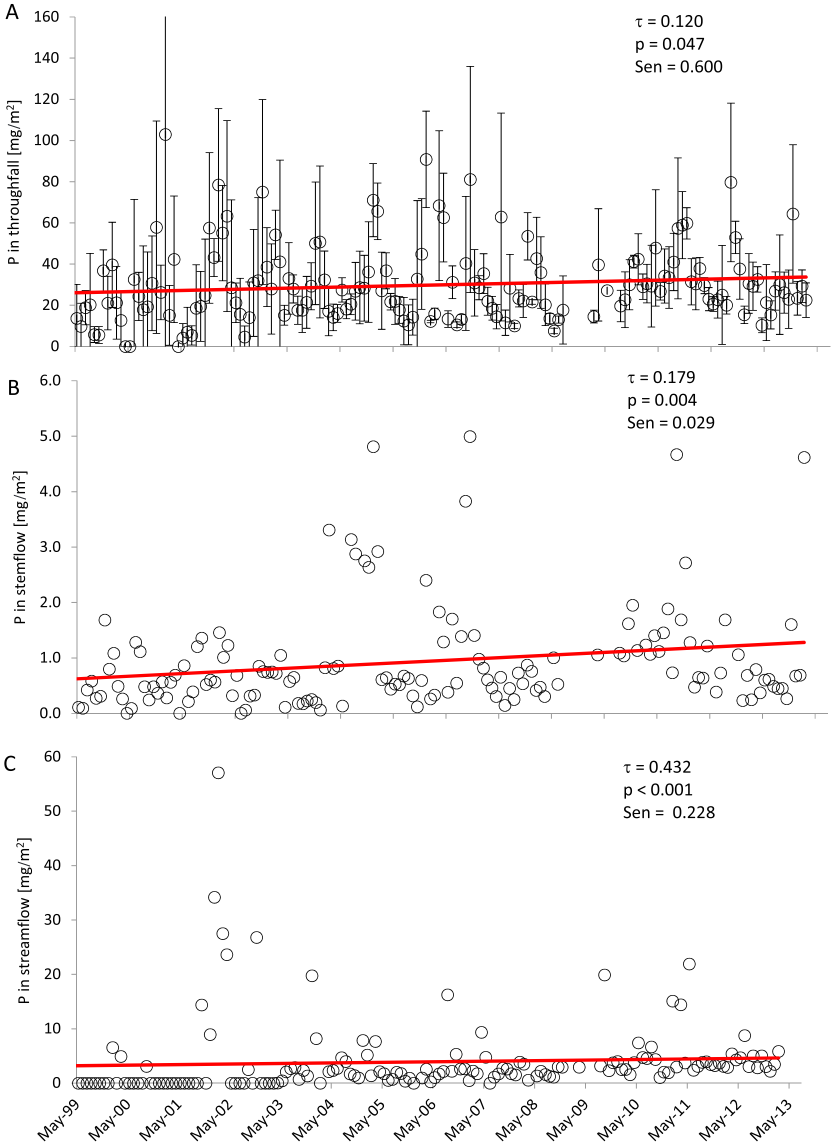

Figure 4. Temporal course of dissolved P concentrations in (a) throughfall, (b) stemflow, and (c) streamflow. The error bars in (a) show the standard deviations between three measurement stations. Temporal trends of monthly data were statistically evaluated with the Seasonal Mann-Kendall test and Kendall's τ values, and Seasonal Sen's slopes (Sen) were calculated (Hirsch et al., 1982). Regression lines are shown to illustrate significant trends. Mind the different *y* axis scaling.

The mean monthly P deposition (3.5 mg/m^2) during December/January, when westerly winds usually prevailed, was lower than during the rest of the year (8.7 mg/m^2). This rendered a P source in the west of our study area little likely. The lack of a correlation between the BD of Ca and P ($r = 0.014$) ruled Sahara dusts out (Ca data taken from Wilcke et al., 2017). The two volcanic eruptions of the Guagua Pichincha in October 1999 and the El Reventador in November 2002 evaluated by Boy and Wilcke (2008) with respect to their function as a source of base metals were not related with elevated P deposition. A higher, albeit nonsignificantly, DD of P during fire than during nonfire periods reported by Boy, Rollenbeck, et al. (2008) pointed at the Amazonian forest fires, which are to a large part anthropogenic (Kauffman et al., 1995), as potential P sources.

The by far largest individual P flux was LF (Figures 1 and 3), because of the low water solubility of P and the high P demand of the vegetation at our study site, which is likely N + P-limited (Homeier et al., 2012; Velescu et al., 2016; Wullaert et al., 2010). The P fluxes with LF in our study forest were at the upper end of the range of P fluxes with LF in global forests of 200–1100 mg/(m^2 year) with the higher values in tropical forests (Vogt et al., 1986). This is attributable to the high biomass productivity of the study forest (Wilcke et al., 2002). The retention of >80% of the P fluxes reaching the soil by LF + TF+ SF in the biological part of the forest (vegetation+organic layer and their associated organism communities), illustrated a tight P cycling (Figures 1 and 3). The finding that of the little P that leached from the organic layer into the mineral soil, again 80% was retained together with the P released by weathering, emphasized the important role of adsorption of P in the study soils to Fe and Al oxyhydroxides, occlusion into Fe and Mn concretions, and precipitation as little soluble Al phosphates together termed "sorption" (Figure 3). Part of the P leached from the organic layer and released by weathering might, however, still be recycled into the vegetation, because at 1,900 m asl (the lower end of our study catchment), Soethe et al. (2006) found 49% of the fine roots in the mineral soil. This percentage decreased with increasing elevation and was 39% at 2,400 m asl, which is higher than the upper end of our study catchment at 2,170 m asl. Soethe et al. (2006) also have shown that the fine root distribution correlated with the plant uptake of a ^{15}N label so that it is likely that some of the P leached from the organic layer into the mineral soil was taken up and recycled into the vegetation and the organic layer. Consequently, the P cycle of the study forest was to a large part controlled by plants, animals, and microorganisms mainly living in the part of the ecosystem above the mineral soil.

Our estimated weathering release of P (Figure 1) was at the lower end of the rates compiled by Zhou, Bing, et al. (2018) of 9.3–796 mg/(m^2 year) for a number of soils worldwide and much lower than that reported from some other subtropical and tropical catchments including various catchments in Puerto Rico on Quartz diorite and Andesite (5,600–29,000 mg/(m^2 year), "annual net yield"; Stallard, 2012) and on migmatite in Côte d'Ivoire (15,000 mg/(m^2 year), "inorganic baseflow plus sediment" Stoorvogel et al., 1997). Because particularly the phyllite in our study catchment did not show much lower P concentrations (0.78 g/kg) than the parent rocks in the Puerto Rican catchments (0.11–1.35 g/kg) and in Côte d'Ivoire (1.13 g/kg), we attribute this difference to the higher temperature and humidity at the locations used for comparison. However, the weathering release at our study site was still higher than the estimates of 4.41 mg/(m^2 year) for metamorphic rocks and 8.53 mg/(m^2 year) for the global mean weathering release (Hartmann et al., 2014). Generally low weathering rates were also found for base metals (Ca, K, Mg, and Na) at our study site (Wilcke et al., 2017). Low weathering rates at our study site were also reflected by the finding that the export of dissolved P with ST (Figure 1) was at the lower end of the range of 1–1,300 mg/(m^2 year) reported for several temperate and tropical forested catchments (Figure 1; Bol et al., 2017). When the extreme value of 1,300 mg/(m^2 year) $\cdot$ m^{-2} $\cdot$ year^{-1} in Bol et al. (2017) was disregarded, our export of dissolved P with ST fell in the middle of the reported range of 1–60 mg/(m^2 year) and it was slightly higher than the mean export rates of P with ST from temperate catchments under coniferous (11 ± 20 mg/(m^2 year) and deciduous forest (12 ± 20 mg/(m^2 year) ; Sohrt et al., 2017). The export of P with TSPs (Figure 1) was much lower than in a study of Meyer and Likens (1979) in a temperate forest, where 800 mg/(m^2 year) P were exported with fine particles.

The weathering rates of P were more than 1 order of magnitude lower than the TSI via LF + TF + SF (Figure 1), further emphasizing the important role of the tight P cycling in the vegetation and the organic layer in providing bioavailable P. Moreover, Boy, Valarezo, and Wilcke (2008) have shown that the P release by weathering occurs mainly in the subsoil as reflected by the highest P concentrations in ST during baseflow conditions. This P is hardly reached by plant roots and thus is likely little included in the biological P cycling, but instead mainly sorbed to the mineral soil or to a small extent exported with ST.

Deposited P comes first into contact with the forest canopy consisting 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 (Matson et al., 2014; Nadkarni et al., 2002; Ulrich, 1983). The bulk and fine particulate DD reaching the canopy can either be retained by uptake into organisms or passed on to TF and SF, which can be further enhanced by element leaching mainly out of the plant tissues (Parker, 1983). The consistently positive net TF and the negative CB in most years indicated that P was mainly leached from the canopy (Figures 1 and 2). The result that the canopy was the largest internal source of dissolved P in the ecosystem was in line with previous findings of Goller et al. (2006).

The positive CMB in most years indicates the accumulation of P in the study forest supporting our first hypothesis that the forest became P-richer during the observation period (Figures 1 and 2). Assuming a constant accumulation, it would take only 100 years to accumulate the P stock of the organic layer from the atmosphere. The P stock in the organic layer constitutes the most important P pool for plant supply (Wilcke et al., 2002). This emphasizes that the atmosphere is a considerable external source of P for the vegetation. We speculate that the accumulation of P in the study ecosystem might affect the species richness of the megadiverse study forest negatively at centennial scale, because it has been shown that an increase in bioavailable P can threaten the presence of rare species even more strongly than the deposition of N (Wassen et al., 2005). Moreover, the mineralization of P from the organic layer might be enhanced by increasingly longer periods of dry conditions, as observed in the recent past and attributed to the rising temperatures (Peters et al., 2013; Wilcke, Leimer, et al., 2013). The potentially detrimental effect of P will also be influenced by the development of the N deposition, which has been shown to increase in the study period (Wilcke, Leimer, et al., 2013). Should a continued elevated N deposition shift the current likely N + P co-limitation to a pure P limitation, the ecosystem could become even more sensitive to an increasing bioavailability of P.

4.2. Temporal Trends of Phosphorus Fluxes

The increasing P fluxes with TF and SF reflect the accumulation of P in the biological part of the study catchment (Figure 4) and indicate that the bioavailability of P increased. However, the annual increase in the P cycling with TF and SF was much lower than the annual TD of P, which was almost entirely retained in the catchment (Figures 1 and 4). Because the studied forest had reached the mature old-growth stage, there should be no net annual P accretion in wood. This suggests that most of the deposited P retained in the catchment was stored in the soil. Because only a small part of the TSI of P was leached into the mineral soil, the soil organic layer was likely the most important storage compartment of deposited P in the studied forest.

The TF showed the highest annual increase rate of all ecosystem fluxes, for which we detected a significant temporal trend (Figure 4). Together with the smaller significant increase rate of the P fluxes with SF, this indicates that the bioavailable P pool tightly cycled between soils and plants increased from 1999 to 2013. The result supports our second hypothesis and emphasizes the risk of P eutrophication in the long run. Especially luxurious supply by easily accessible P forms might reduce nutritional niches and potentially destabilizes community composition (Taylor, 2009). The increasing P fluxes with ST might indicate that a small part (approximately 3.3%) of the external P inputs into the system (i.e., TD and weathering release, assuming that primary minerals do not belong to the ecosystem as is commonly done in ecosystem science; Likens, 2013) was lost from the system. Alternatively, the increasing P fluxes with ST might be indicative of increasing weathering rates in response to the increasing temperatures and CO_2 concentrations in the study area. However, the warming is probably only slightly more than 0.13 K per decade (Peters et al., 2013). Therefore, the mean annual temperature might have increased roughly by 0.2 K during the observation period, which is unlikely to accelerate weathering to a measurable extent. An increase in atmospheric CO_2 concentrations would result in the formation of more carbonic acid and thus increase the H^+ input into the mineral soil. From 1999 to 2013, the atmospheric CO_2 concentrations at Mauna Loa Hawaii grew by cumulative 29.5 ppm from approximately 365 ppm, that is, by approximately 12% (Global Monitoring Division, 2018). Although we cannot rule out that this resulted in a slight acceleration of weathering, we suggest that this increase is small relative to the much higher CO_2 concentrations in the soil atmosphere, which varies strongly but can reach up to >50,000 ppm and is frequently >1,000 ppm (Brady, 1990). Finally, for the Amazon basin an increasing number of rainstorm events have been reported (e.g., Marengo & Espinoza, 2016), which might accelerate weathering because of enhanced denudation (Dixon & von Blanckenburg, 2012).

4.3. External Drivers of the Canopy and Catchment Elemental Budgets of Phosphorus

We considered the TD of base metals, rainfall water fluxes, and BD of H^+ into the canopy and the entire catchment as potential drivers of the P budgets of the canopy and the entire catchment, because all of these fluxes might change in the near future in our study area (Boy, Rollenbeck, et al., 2008; Boy & Wilcke, 2008; Peters et al., 2013; Wilcke, Boy, et al., 2013; Wilcke, Leimer, et al., 2013). Because water and P fluxes were components of the budgets, we refrained from conducting inferential tests and instead visualized the relationships and calculated coefficients of determination (R^2; Figure 2).

Among the three considered potential drivers (TD, rainfall water fluxes, and BD of H^+) of the CB and CMB, TD was by far the most influential (Figures 2a and 2b). Even if the extreme deposition of the year 2007/2008 was eliminated as an outlier, the R^2 value of the relationship between total P deposition and the CB was still high. The high R^2 values reflect that the deposition of P was almost entirely retained in the study catchment (Figure 1). Interestingly, the relationship between total P deposition and the CB was positive; that is, the more P was deposited, the more was retained in the canopy. We suggest that this can be attributed to the fact that a high DD of P was associated with that of other nutrients providing generally improved conditions for the growth of the canopy organisms. Unfortunately, biomass productivity data to support generally better growth conditions in years of high P deposition are not available. A similar hypothesis was postulated by Boy, Rollenbeck, et al. (2008), who found a relationship between the deposition of Mn and the retention of N in the canopy of the same study forest.

The weaker and again positive relationship between rainfall and the canopy and CMB of P (Figures 2b and 2d) is counterintuitive, because increasing rainfall should enhance P leaching. We attribute the finding to the fact that a higher rainfall was related with a higher TD of P (and possibly also other nutrients), because of the close correlation between rainfall and TD of P ($r = 0.64$, $p = 0.014$), which overwhelmed the leaching effect.

The almost negligible impact of the H^+ deposition on the canopy and catchment budgets is unexpected, because Alt et al. (2011) and Goller et al. (2006) have shown that the pH of soil is an important driver of dissolved P concentrations and P partitioning in soils. The little influence of the H^+ deposition on the canopy and the elemental catchment budgets of P might have three reasons. (i) The BD of H^+ was 5–15 times lower than at temperate sites such as the Hubbard Brook Experimental Forest, USA, and the Fichtelgebirge, Germany, during roughly the same time (Likens, 2013; Matzner et al., 2004). (ii) Periods with increased acid deposition were several times followed by the deposition of alkaline dust (Boy & Wilcke, 2008; Wilcke, Boy, et al., 2013), so that the effect of acidification was likely regularly reversed. (iii) The H^+ deposition was almost completely buffered in the canopy by the release of base metals without influencing the CB of P so that the water reaching the soil carried an even lower H^+ input into the soil than into the canopy preventing any measurable effects on P solubility in the soil (Wilcke et al., 2017). Consequently, our results supported the important role of TD for the P budgets assumed in our third hypothesis but it did not support an important role of H^+ deposition.

5. Conclusions

Our results demonstrate that the deposited P was almost completely retained in the vegetation and organic layer and their associated organism communities. The P that leached to below the organic layer into the mineral soil and was released by weathering in the mineral soil was again to a large extent retained in the mineral soil, presumably by adsorption to Fe and Al oxyhdroxides, occlusion in Fe and Mn concretions, and precipitation of little soluble Al phosphates. Because a part of the roots reached into the mineral soil, it is likely that some of this P was recycled into the vegetation by plant uptake. Thus, P was tightly cycled above the surface of the mineral soil by biological control with minor losses, which were even further reduced by geochemical retention mechanisms in the mineral soil.

The almost complete retention of deposited P in the study catchment resulted in increasing P fluxes with TF and SF illustrating an enhanced cycling of bioavailable P. The largest part of the deposited P was stored in the organic layer. In spite of the almost complete retention of the P inputs in the ecosystem (TD and weathering release), P output fluxes with ST significantly increased during the 14 observation years, mainly because a minor part (approximately 3.3%) of the inputs was lost from the catchment and to a smaller degree because of accelerated weathering.

The most influential driver of the canopy and CMBs of P was TD of P, while rainfall and particularly H^+ deposition had little influence. Interestingly, we found a positive relationship between the TD of P and the canopy and CMBs indicating that at a higher deposition more P was retained in the canopy and the catchment. We attribute this to the accompanying deposition of other nutrients, which improved living conditions of the organisms in the system and therefore caused increased growth and uptake of P, at least of part of the organism community.

Acknowledgments

We thank E. Beck, K. Müller-Hohenstein, M. Richter, and W. Zech for coinitiating the long-term study; K. Fleischbein, R. Goller, M. Meyer-Grünefeldt, M. Sequeira, H. Wullaert, S. Yasin, and numerous undergraduate students for data acquisition during parts of the observation period; W. Schädler for providing RFA data of rock macro element concentrations; the Ecuadorian Environmental Ministry for the research permits; and Naturaleza y Cultura Internacional (NCI) in Loja for providing the study area and the research station and the Deutsche Forschungsgemeinschaft (DFG) for funding (FOR402 and FOR816). The original data are included in the supporting information.

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