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Total organic carbon concentrations in ecosystem solutions of a remote tropical montane forest respond to global environmental change

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Abstract

The response of organic carbon (C) concentrations in ecosystem solutions to environmental change affects the release of dissolved organic matter (DOM) from forests to surface and groundwaters. We determined the total organic C (TOC) concentrations (filtered <1–7 μm) and the ratios of TOC/dissolved organic nitrogen (DON) concentrations, electrical conductivity (EC), and pH in all major ecosystem solutions of a tropical montane forest from 1998 to 2013. The forest was located on the rim of the Amazon basin in Ecuador and experienced increasing numbers of days with >25°C, decreasing soil moisture, and rising nitrogen (N) deposition from the atmosphere during the study period. In rainfall, throughfall, mineral soil solutions (at the 0.15- and 0.30-m depths), and streamflow, TOC concentrations and fluxes decreased significantly from 1998 to 2013, while they increased in stemflow. TOC/DON ratios decreased significantly in rainfall, throughfall, soil solution at the 0.15-m depth, and streamflow. Based on $\Delta^{14}C$ values, the TOC in rainfall and mineral soil solutions was 1 year old and that of litter leachate was 10 years old. The pH in litter leachate decreased with time, that in mineral soil solutions increased, while those in the other ecosystem solutions did not change. Thus, reduced TOC solubility because of lower pH values cannot explain the negative trends in TOC concentrations in most ecosystem solutions. The increasing TOC concentrations and EC in stemflow pointed at an increased leaching of TOC and other ions from the bark. Our results suggest an accelerated degradation of DOM, particularly of young DOM, associated with the production of N-rich compounds simultaneously to changing climatic conditions and increasing N availability. Thus, environmental change increased the CO_2 release to the atmosphere but reduced DOM export to surface and groundwater.

KEYWORDS
carbon:nitrogen ratio, carbon-14 dating, dissolved organic matter, rainfall, soil solution, stemflow, streamflow, throughfall

1 | INTRODUCTION

Dissolved organic matter (DOM) pouring out of forest ecosystems into surface and groundwaters contributes about 20% to the C input via rivers to the ocean and thus links the terrestrial and aquatic carbon (C) cycles (Camino-Serrano et al., 2014; Dai et al., 2012; Regnier et al., 2013). The contribution of montane tropical forests to DOM fluxes in rivers might even be larger, because organic C in three tropical montane forest watersheds in Puerto Rico was primarily exported in dissolved form (McDowell & Asbury, 1994). While there is ample literature about DOM concentrations and fluxes in rivers and in temperate and boreal ecosystems, tropical ecosystems are still understudied (Camino-Serrano et al., 2014). Although Camino-Serrano et al. (2014) reported in their review that DOC concentrations in soils of lower latitudes (<35°) were generally lower than at higher latitudes at all soil depths, data from a tropical forest in Kalimantan suggest that the subsoil fluxes of DOM were comparable to those in temperate and boreal ecosystems (Fujii et al., 2009).

Origins of DOM in ecosystem fluxes are multiple and concentrations typically increase along their flow path through the aboveground part of the ecosystem (Likens et al., 1983; Möller et al., 2005; Qualls & Haines, 1991). DOM is a generic term for a large variety of organic molecules from simple low molecular weight organic acids and sugars to complex macromolecules. Its persistence in the environment depends largely on the type of molecules present. Hydrophilic DOM including carbohydrates, proteins, and organic acids is readily degradable, hydrophobic, and aromatic fractions less so (Marschner & Kalbitz, 2003). Frequently, DOM is approximated as dissolved organic C (DOC, filtered <0.20–0.45 μm) or total organic carbon (TOC, filtered with a larger pore size). As a mobile and partly bioavailable component of soil organic matter, DOM is susceptible to environmental change (Evans et al., 2008; Michalzik et al., 2001). A detailed study of the molecular structure of DOM requires considerable technical effort, but first insights into the chemical DOM composition can be gained by stoichiometric indicators such as the C/N ratio. Hydrophilic DOM is usually richer in nitrogen (N) than hydrophobic DOM (Möller et al., 2005).

One source of DOM is wet and dry deposition from the atmosphere. In South America, wet deposition of C was the globally third highest after Africa and Central America (Iavorivska et al., 2016). Atmospheric C inputs are biogenic or anthropogenic and hence are susceptible to global environmental change (Iavorivska et al., 2016; Likens et al., 1983; Willey et al., 2000). Major sources of atmospheric C in the Amazon region are vegetation fires and the emission of volatile organic C (VOC, Bauwens et al., 2016; Sindelarova et al., 2014). The majority of atmospheric C input occurs as DOM and is biologically available, although humified macromolecules are also present (Iavorivska et al., 2016; Likens et al., 1983; Willey et al., 2000).

The major source of DOM in ecosystem-internal solutions after the passage through the forest canopy is plant-derived organic matter. Leaching of organic matter from the canopy exceeded atmospheric input in three of four Amazonian lowland forests (Tobón et al., 2004). A recent review suggested that DOM concentrations in throughfall and stemflow are in the same order of magnitude as DOM concentrations in continental rivers (Van Stan & Stubbins, 2018). Stemflow DOM concentrations are generally higher than throughfall DOM concentrations but both vary with vegetation type, climate zone, and tree age (Hofhansl et al., 2012; Van Stan & Stubbins, 2018). The molecular structure of DOM leached from the vegetation varies considerably but it was reported that the majority (50%–75%) is readily degraded by microorganisms (Bischoff et al., 2015; Qualls & Haines, 1992; Van Stan & Stubbins, 2018). Highest DOM concentrations in forest ecosystems typically occur in organic layers (Camino-Serrano et al., 2014; Dantas da Costa et al., 2017; McDowell & Likens, 1988; Möller et al., 2005). The DOM in soil solutions can originate from fresh sources such as fine litter, coarse woody debris, root litter, or root exudates or humified sources via leaching and microbial processing of solid phase soil organic matter (Guggenberger et al., 1998; Kalbitz et al., 2000). Cleveland et al. (2010) reported that DOM concentrations increased with increasing soil respiration rates. However, there are also indications that microorganisms can use part of DOM as C source, thereby decreasing DOM concentrations (Kalbitz et al., 2000).

In the mineral soil, DOM concentrations are about 75% lower than that in corresponding organic layers across various climate zones and soil types, mainly because of DOM sorption to the minerals rendering the soil the first DOM sink along the water flow path through a forest ecosystem (Camino-Serrano et al., 2014; Möller et al., 2005). The chemical DOM composition in the mineral soil appeared not to depend on the tree species, suggesting that it mainly consists of microbial degradation products (Thieme et al., 2019). Aged soil organic matter may also contribute to DOM concentrations in soil solutions, particularly at low soil moisture as detected by dating DOM with the help of the ^{14}C released to the atmosphere in the 1950s by nuclear weapon tests (Sanderman et al., 2008). Mineral soil DOM dynamics appear to correlate well with inorganic properties that control sorption and desorption of organic matter on soil particles such as pH, Al and Fe concentrations, and C/N ratios of solid soil or Al, Fe, and NH_4^+ concentrations, and ionic strength of soil solution (Camino-Serrano et al., 2014; Kalbitz, et al., 2000; Michalzik & Matzner, 1999). A further control of DOM concentrations in the mineral soil are hydrological conditions (Kalbitz, et al., 2000). Localized areas of high throughfall and especially stemflow water flux can initiate preferential flow paths, along which DOM is flushed into the subsoil. Moreover, preferential infiltration along roots could lead to in-depth penetration of stemflow DOM (Van Stan & Stubbins, 2018).

Most DOC sources and transformation pathways are affected by the current pronounced changes in environmental conditions at the global scale. These include changed climatic conditions, which can modify water budgets of forest soils and involve more favorable temperatures for biological turnover (IPCC, 2014) and N deposition (Galloway et al., 2004, 2008). In the south Ecuadorian tropical montane forests on the rim of the Amazon basin, the number of dry days and the frequency of longer lasting dry periods (up to 14 days) as well as the regional temperatures increased since 1964 (Peters et al., 2013)

in line with model predictions by Vuille et al. (2003). Increasing temperatures and stronger soil drying during dry spells, which reduces waterlogging in a perhumid environment, will stimulate microbial activity with unclear consequences for DOM concentrations in soil solutions (Marschner & Kalbitz, 2003). Because highest soil respiration rates are generally observed during rewetting, an increased number of drying–wetting cycles might enhance DOM mineralization (Borken et al., 1999; Ishikura et al., 2017; Lundquist et al., 1999).

On the Amazon-exposed eastern slope of the north Andes, deposition of NH_4^+ and NO_3^- increased (Wilcke, Leimer, et al., 2013). This corroborates previous expectations that particularly in tropical developing countries the deposition of the frequently most growth-limiting nutrient N will increase (Galloway et al., 2004, 2008). The reasons include increasing biomass burning (Da Rocha et al., 2005), and use of N fertilizers and fossil fuels (Galloway et al., 2004, 2008). Deposition of N can fertilize N-limited forests and contribute to soil acidification if occurring as NH_4^+, because of subsequent nitrification and NO_3^- leaching with accompanying base metal cations (Lohse & Matson, 2005; Matson et al., 1999; Vitousek & Matson, 1988). On the eastern slopes of the north Andes, soil acidification is further enhanced by the deposition of mineral acids (mainly HNO_3) released from forest fires in Amazonia (Boy et al., 2008). Wilcke, Boy, et al. (2013) observed decreasing dissolved organic N (DON) concentrations in many ecosystem solutions of an Andean tropical montane forest in south Ecuador from 1998 to 2010. The authors attributed this finding to enhanced microbial degradation because of reduced periods of waterlogging and in the litter leachate also to decreasing DON solubility in response to decreasing solution pH in the acidifying organic layer. Based on observations in a long-term N-fertilizing experiment in Colorado, USA, Neff et al. (2002) suggested that N input accelerates the degradation of reactive soil organic matter pools, which likely include DOM, while recalcitrant pools are stabilized. A positive correlation of the C/N ratios of the soil solid phase with DOC concentrations in soil solutions suggests that increasing N availability (reflected by decreasing C/N ratios) decreases DOM concentrations (Borken et al., 2011; Camino-Serrano et al., 2014), although this does not seem to be generally true (Michalzik et al., 2001). In a fertilizer experiment in the south Ecuadorian Andes, TOC and DON concentrations decreased significantly if P and N + P were added, but did not change if only N was added, pointing at a P or N + P co-limitation of the microorganisms at the study site (Velescu et al., 2016).

In the literature, we only found a few reports on temporal trends in DOM concentrations in forest ecosystem solutions covering at least a decade (Borken et al., 2011; Wu et al., 2010). In these studies, which were restricted to temperate ecosystems, DOM concentrations in mineral soil solutions mostly decreased. This was mainly explained by increased DOM sorption to the soil solid phase in response to decreasing acid rain. In contrast, the DOM concentrations in litter leachate of south German forests sites increased, likely because of decreasing SO_4^{2-} concentration as a consequence of flue gas desulfurization (Borken et al., 2011). The DOM concentrations in throughfall of Norwegian forests did not show a temporal trend

(Wu et al., 2010). We are not aware of any study about temporal trends in DOM concentrations and fluxes in tropical forests, which do not have the same history of industrial development and associated formation of acid rain until the 1990s and later recovery.

To contribute to filling this gap, we collected DOM concentration and flux data over 15 years from a tropical montane rain forest in Ecuador. We determined temporal trends and linked them with current environmental change. We hypothesized that (a) TOC concentrations and fluxes decreased during the past 15 years, because of enhanced degradation favored by reduced soil waterlogging and increasing N availability. (b) Increasing degradation is reflected by increasing TOC/DON ratios, because the more polar N-rich compounds are preferentially degraded as reflected by the reported decreasing DON concentrations in ecosystem solutions. (c) We furthermore expected that the DOM was mainly derived from fresh C sources in the dense forest canopy and the thick soil organic layer, and that the young age of the DOM allowed for its fast response to environmental change.

2 | MATERIALS AND METHODS

2.1 | Study area

We studied a ca. 9.1-ha watershed under old-growth montane rain forest on a 38°–70° steep slope between 1,850 and 2,200 m above sea level (a.s.l.; Boy et al., 2008; Wilcke et al., 2001, 2017; Figure 1).

During the observation period from April 1998 to March 2013, mean ($\pm SD$) annual precipitation was 2,320 $\pm$ 238 mm of which 39 $\pm$ 4.9% was lost from the catchment as interception evaporation, 16 $\pm$ 7.7% as transpiration, and 45 $\pm$ 4.3% as surface runoff in the stream. Mean annual temperature was 15°C (Peters et al., 2013; Wilcke, Leimer, et al., 2013; Wilcke et al., 2017). Soils are mainly shallow Folic Dystric Cambisols developed from metamorphic rock (phyllite and quartzite) with thick organic layers (IUSS Working Group WRB, 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 ca. 0.5–1 m deep soil profiles along two transects near the stream and near the ridge, we found only phyllite up to an elevation of ca. 2,000 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. The A horizons of 29 study soils, assumed to representatively cover the catchment area, contained 46 $\pm$ 28% sand, 37 $\pm$ 6.5%, silt and 17 $\pm$ 5.8% clay, had a mean pH of 4.4, a mean effective cation-exchange capacity of 63 $\pm$ 26 mmol$_c$/kg, a mean soil organic C concentration of 32 $\pm$ 19 g/kg, and a mean C/N ratio of 11 $\pm$ 2.8 (Wilcke et al., 2017). More details about the location of the study soils and their properties can be found in the work of Wilcke et al. (2017). The studied forest can be classified as evergreen
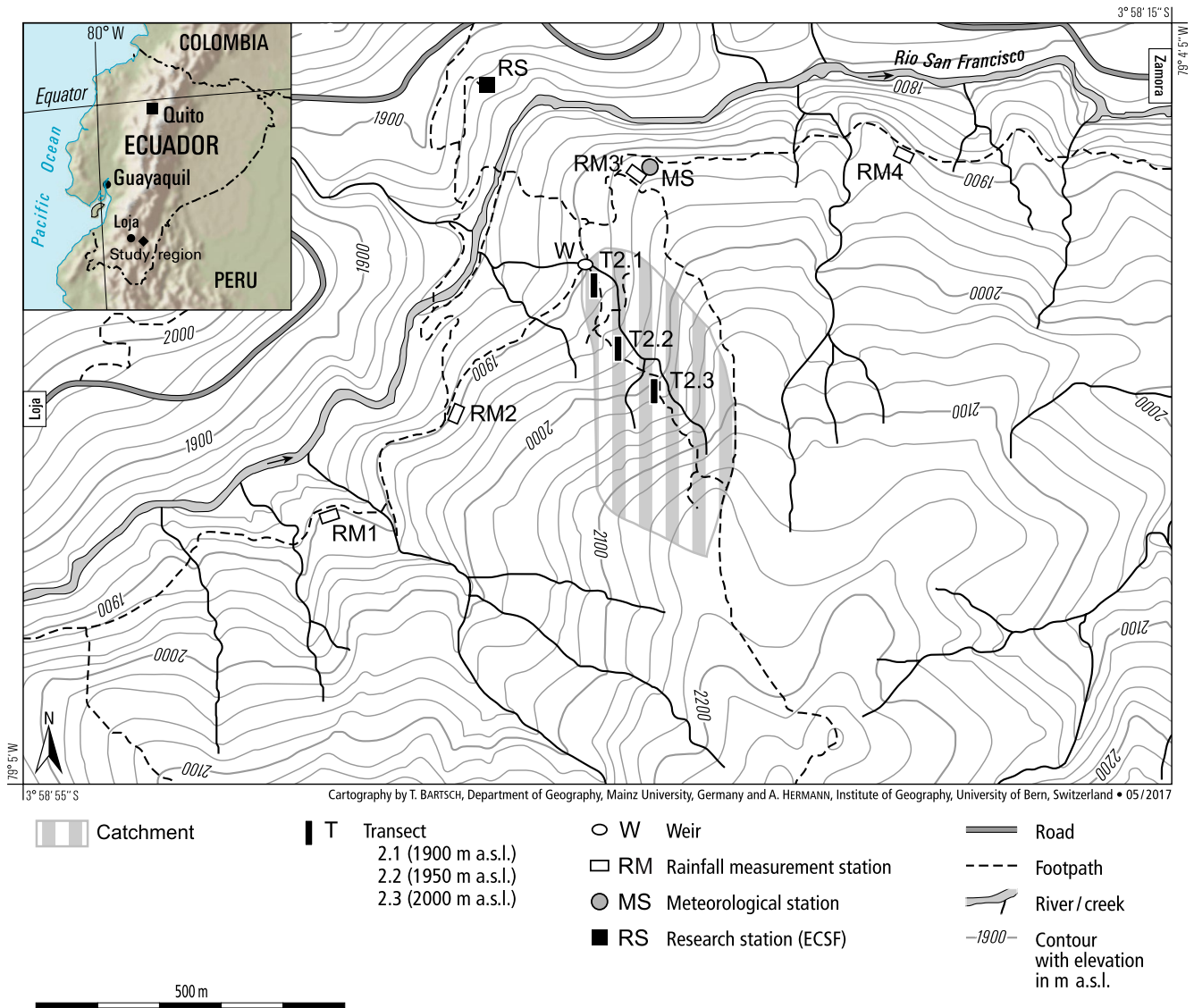
FIGURE 1 Map of the location of the studied catchment including the weir, the measurement transects, rainfall measurement stations, meteorological station, and research station. The elevation given after the transects refers to the lowermost point of the transects which were 20 m long and covered an elevational range of 10 m (transect symbols are not exactly to scale to be clearly visible). The catchment in this study is the same as Microcatchment 2 in previous studies (e.g., Wilcke et al., 2001, 2017, 2019) 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

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 | Field sampling

Rainfall was collected at two to four gauging stations (Figure 1), each consisting of five Hellmann-type collectors, placed on clear-cut areas. As the collectors were permanently open, collected samples represent bulk deposition (i.e., rainfall and soluble coarse particulate dry deposition).

To measure TOC and DON concentrations in ecosystem solutions, 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 1,900, 1,950, and 2,000 m a.s.l., respectively; Figure 1). We considered our transects to be representatives for the largest part of the catchment. The covered elevational gradient of 100 m 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, litter leachate, and soil solution at the 0.15- and 0.30-m mineral soil depths. 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 laterally installed below the organic layer from a small soil pit. Mineral soil solution was sampled with three ceramic suction cups (mullite, 1 ± 0.1 μm pore size) at each of the two soil depths. Vacuum was held permanently and pressure was manually adjusted to the matric potential once per week. The free-draining lysimeters only collect solution during comparatively wet conditions. In the mineral soil, we applied a vacuum to overcome the matrix potential, which is usually higher than in the organic layer. However, even suction cups with vacuum only collect soil solution if the soil is sufficiently moist. The upper limit of suctions cups is a matric potential of 60–80 kPa. Therefore, we thought that we collected a similar portion of the soil solution from the wetter end with both instruments. Throughfall and litter leachate samplers were spread evenly along the transects, while suction cups were concentrated at a central position. Stemflow was collected with polyurethane collars at five trees in the lower part of the catchment. Streamflow was sampled above a weir, which was used to gauge streamflow (Fleischbein et al., 2006).

All solution samples were collected weekly between April 1998 and March 2013. For rainfall, throughfall, stemflow, litter leachate, and mineral soil solutions, 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 to result in one volume-weighted, composite sample per sample type, measurement site, and collection date. Litter leachate and mineral soil solutions were bulked into one collection vessel per measurement transect to yield one individual sample per measurement site and collecting date.

In the year 1998, we collected 29 representatively distributed soil samples from the A horizons to determine pedogenic Fe concentrations. In the year 2007, we collected representative bulk soil samples of the Oi, Oe, Oa, A (0–0.2 m) and B horizons (0.2–0.6 m) from the wall of a soil pit in the center of the transect T2/2 (Figure 1) and accumulated DOM from rainfall, litter leachate, mineral soil solutions at the 0.15- and 0.30-m depths, and streamflow for ^{14}C dating.

2.3 | Chemical analyses

Immediately after sampling, we determined electrical conductivity and then pH with a glass electrode (Sentix HWS; WTW GmbH) in an aliquot of the sample which was discarded afterward. Another aliquot of the rainfall, throughfall, stemflow, and litter leachate samples, but not of the mineral soil solution samples, was filtered (ashless filters with pore size 4–7 μm, folded filter type 389; Munktell & Filtrak GmbH). After export of the filtered 100-mL aliquots from Ecuador to Europe in frozen state, TOC concentrations were determined with an automatic TOC analyzer (TOC 5050; Shimadzu Corp., until 2004 and thereafter with a TOC Analyzer, Elementar Analysensysteme GmbH) as non-purgeable organic carbon.

Furthermore, water samples were analyzed with a continuous flow analyzer using high-resolution colorimetry and photometric detection (AutoAnalyzer 3 HR; Seal GmbH) for concentrations of dissolved NH_4-N and NO_3-N + NO_2-N, and total dissolved N (TDN, after UV oxidation to NO_3). DON concentrations were calculated as difference between TDN and DIN. The DON measurements started in the hydrological year 1999/2000. Measurement values below the detection limits were set to 0.

Selected soil and DOM samples were ^{14}C-dated in the Leibniz laboratory of the University of Kiel, Germany with accelerated mass spectrometry (AMS). Prior to ^{14}C measurement, samples were checked for contaminations under the microscope and only processed further if no contamination was detected. Subsequently, the samples were treated with 0.1% HCl, freeze-dried, and combusted at 900°C in a quartz tube filled with CuO and silver wool. The produced CO_2 was reduced to graphite with H_2 at 600°C with the help of a Fe catalyzer to reduce all C to graphite. A mixture of Fe and graphite was pressed for AMS. The ^{14}C concentration of the samples resulted from the comparison of the simultaneously determined ^{14}C, ^{13}C, and ^{12}C concentrations with those of a CO_2 measurement standard (oxalic acid II) and appropriate blanks (hard coal). The conventional ^{14}C age was calculated according to Stuiver and Polach (1977) correcting for AMS-related isotope fractionation with the help of the simultaneously measured ^{13}C/^{12}C ratios. The uncertainty of the ^{14}C result includes the count statistics, the stability of the AMS device and the uncertainty of the subtracted blank. The ^{14}C concentrations were translated into calibrated age with CALIB rev 4.3 (Stuiver et al., 1998) or into Δ^{14}C values according to Trumbore (2009).

Pedogenic Fe oxides were extracted from the mineral soil samples with the dithionite-citrate-buffer method of Mehra and Jackson (1960). Extracted Fe concentrations were determined with atomic absorption spectrometry (Varian).

2.4 | Calculations and statistical evaluation

To reduce the influence of outliers, data of element concentrations in four to five weekly samples were aggregated to monthly values for annual flux calculations. 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 and throughfall were directly measured. Stemflow water fluxes were extrapolated from the individually monitored trees via the stem number per area. Based on the work of Homeier (2004), we estimated that there were 1,000 stems with a diameter at breast height (dbh) > 0.1 m and 4,000 trees with a dbh < 0.1 m on 1 ha. We assumed that the mean stemflow volume of the five monitored trees (all with a dbh > 0.1 m) was representative of all trees with a dbh > 0.1 m, while the trees with a dbh < 0.1 m were assumed to contribute half of this volume. As a consequence, the measured mean stemflow volume was multiplied with 3,000 to arrive at the stemflow flux on 1 ha, which was then converted to

L/m² (mm). Litter leachate fluxes, which cannot be directly quantified by zero-tension lysimeters, were modeled with the soil water balance equations as given in DVWK (1996) and described in Boy et al. (2008). 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 1999 to 2003 (litter leachate = 0.86·throughfall − 0.71, R^2 = .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. (2008) and those from 2004 to 2013 were from Wilcke et al. (2017, 2019).

For the first four hydrological years (April 1998–March 2001/2002) we took streamflow data from Fleischbein et al. (2006) and for 2002/2003 from Boy et al. (2008) modeled with the distributed catchment model TOPMODEL (Beven et al., 1995) to calculate streamflow fluxes of DOM. For the later years (2003–2013) we used weekly measurements of the water level at the weir and calculated streamflow by a calibrated streamflow function of water level determined with a bucket and stop watch at different water levels (Boy et al., 2008; Fleischbein et al., 2006; Wilcke et al., 2017, 2019).

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). To test differences in the mean annual pH, electrical conductivity (EC), TOC and DON concentrations, and TOC/DON ratios, we performed hierarchical (Type 1) ANOVAs with the function *aov()* and subsequently post hoc Tukey's honest significant difference tests with the function

TukeyHSD() in the statistical software R (R Core Team, 2017). In the ANOVA, year was fit before sample type. Normal and random distribution of the residuals was checked graphically.

3 | RESULTS

The mean Fe concentrations in pedogenic oxides of the 29 A horizons was 14 ± 6.7 g/kg, which is typical of non-desilified temperate and tropical mountain soils implying a moderate sorption capacity for DOM. The mean pH in rainfall was acidic and increased significantly after the passage through the forest canopy because of buffering. The mean pH of all three soil solutions was similar, although the soil solution at the 0.30-m depth had a slightly but significantly higher pH than that at the 0.15-m depth, and significantly lower than in throughfall, stemflow, and streamflow (Table 1). The mean EC increased significantly along the water flow path in the aboveground part of the ecosystem from rainfall to litter leachate and decreased in the belowground part of the ecosystem. The EC in mineral soil solutions and streamflow was not significantly different but significantly higher than in rainfall (Table 1). The mean TOC and DON concentrations were significantly highest in litter leachate and lowest in streamflow. (Table 1). They increased continuously in the aboveground part of the ecosystem from rainfall to litter leachate and decreased continuously in the belowground part of the ecosystem from litter leachate to the stream. Most of the differences between subsequent ecosystem solutions along the water path were significant. The mean TOC and DON concentrations in streamflow were not significantly different from those in rainfall. The mean TOC/DON ratios were similar in most ecosystem-internal solutions but significantly lowest in rainfall and significantly highest in streamflow (Table 1).

The pH did not show significant temporal trends in rainfall, throughfall, stemflow, and streamflow but decreased in litter leachate and increased in the mineral soil solutions at the 0.15- and

TABLE 1 Means and ranges of the volume-weighted annual pH, electrical conductivity (EC), total organic carbon (TOC), and dissolved organic nitrogen (DON) concentrations in all solutions except the mineral soil solutions at the 0.15- and 0.30-m depths, for which arithmetic means are shown (n = 15 year, 1998–2013). Lower case letters behind the numbers indicate significant differences (p < .05) among the ecosystem solutions according to a Tukey's HSD post hoc test following bifactorial (year before ecosystem solution) ANOVA. Year was significant for all solution properties except TOC. Means of the pH were calculated based on H⁺ activities, which were then back-transformed to pH. The ANOVA and post hoc test were also run on H⁺ activities

|	pH	EC μS/cm	TOC mg/L	DON mg/L	TOC/DON
Rainfall	5.1 (4.8–5.7) b	7.7 (4.5–12) e	4.0 (2.2–5.5) e	0.25 (0.15–0.35) de	17 (7.4–34) c
Throughfall	6.0 (5.5–6.3) a	43 (33–55) c	14 (12–17) c	0.72 (0.50–1.0) bc	20 (12–33) bc
Stemflow	6.3 (6.0–6.6) a	50 (32–67) b	22 (11–35) b	0.93 (0.53–1.3) b	24 (12–38)bc
Litter leachate	4.6 (4.4–5.2) cd	60 (46–78) a	41 (31–53) a	1.7 (1.1–2.5) a	25 (15–34) abc
Soil solution at the 0.15-m depth	4.5 (4.3–4.8) d	23 (18–30) d	13 (8.5–16) cd	0.51 (0.39–0.69) cd	26 (15–37) ab
Soil solution at the 0.30-m depth	4.7 (4.6–4.8) c	19 (12–29) d	8.7 (6.6.–11) d	0.37 (0.24–0.45) cd	24 (16–34) abc
Streamflow	6.0 (5.1–6.7) a	20 (18–22) d	3.7 (2.2–5.4) e	0.13 (0.05–0.20) e	32 (15–54) a
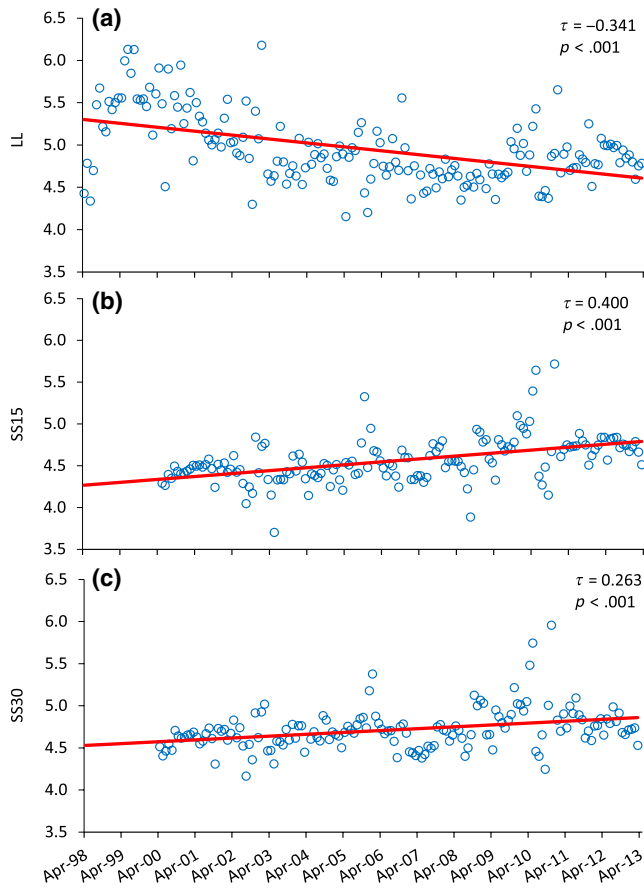
FIGURE 2 Course of the pH in soil solutions from April 1998 to March 2013. (a) Litter leachate (LL), (b) soil solution at the 0.15-m depth (SS15), and (c) soil solution at the 0.30-m depth (SS30). Temporal trends in monthly data were statistically evaluated with the Seasonal Mann-Kendall test (Hirsch et al., 1982)

FIGURE 3 Course of the electrical conductivity in stemflow (SF) from April 1998 to March 2013. Temporal trends in monthly data were statistically evaluated with the Seasonal Mann-Kendall test (Hirsch et al., 1982)

0.30-m depths (Figure 2). Thus, the solubility of DOM decreased in the litter leachate but increased in the mineral soil, because of the change in its protonation. The only significant temporal trend in the EC occurred in stemflow, where the EC increased during the observation period (Figure 3). Consequently, the ionic strength remained unchanged in all ecosystem solutions except for stemflow assuming that there were no major changes in the ionic charge distribution. Increasing ionic strength in stemflow should reduce DOM solubility, although the literature is not fully consistent (Kalbitz, et al., 2000).

During the observation period, TOC concentrations decreased significantly in most ecosystem solutions (Figure 4). The TOC concentrations in litter leachate did not change significantly and those in stemflow showed a significant positive trend. The positive temporal trend in the TOC concentrations in stemflow was observed although the increasing ionic strength (Figure 3) without changes in pH should decrease TOC solubility. The strongest negative temporal trends in the TOC concentrations as assessed with the help of Kendall's τ value occurred in the mineral soil solutions (Figure 4) in spite of the simultaneously increasing pH values (Figure 2), which should favor DOM solubility. The TOC concentrations in rainfall did also show
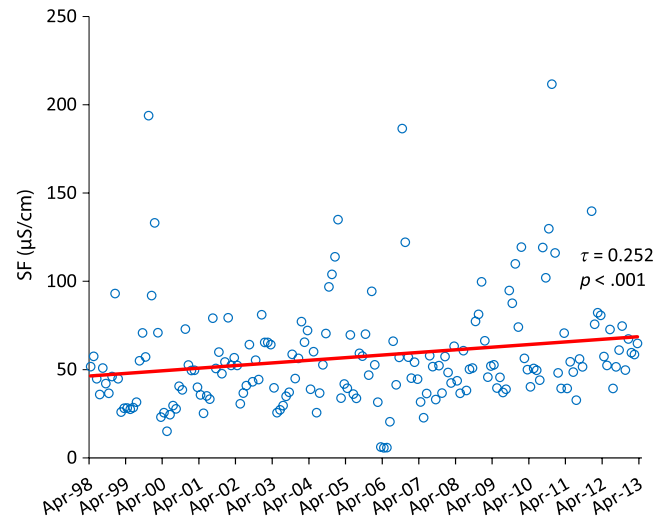
a negative trend indicating that the bulk deposition of DOM decreased during the observation period.

In our bifactorial ANOVA, year had a significant effect on all considered solution properties except for TOC. Thus, there were significant interannual variations in the solution properties among the 15 study years, likely related with occasional strong dust inputs in some years (Boy & Wilcke, 2008) or particularly strong vegetation fires in the Amazon region in other years (Boy et al., 2008).

The DOM input with rainfall was a smaller source of DOM than the canopy and the organic layer, as reflected by the decreasing mean TOC and DON fluxes in the order, litter leachate (TOC: 47,700 ± 11,100; DON: 1,920 ± 466 mg m^{-2} year^{-1}) > throughfall (19,200 ± 3,330; 981 ± 215) > rainfall (9,130 ± 2,920, 583 ± 120), while stemflow only contributed 689 ± 314 and 29.2 ± 9.82 mg m^{-2} year^{-1} to the soil input of TOC and DON, respectively. However, the TOC and DON fluxes with rainfall were more than double the TOC and DON fluxes with streamflow (3,920 ± 1,150; 138 ± 43.7 mg m^{-2} year^{-1}), respectively. The TOC fluxes showed similar trends as the concentrations. The TOC fluxes with rainfall ($\tau = -0.301$, $p < .001$), throughfall ($\tau = -0.252$, $p < .001$), and streamflow ($\tau = -0.113$, $p = .051$) decreased significantly, albeit with streamflow only marginally (with $p < .1$), while the TOC fluxes with stemflow increased significantly ($\tau = 0.394$, $p < .001$) and those with litter leachate did not show a temporal trend. The only DON flux with a significant trend, which was positive, was that with streamflow ($\tau = 0.161$, $p = .008$).

During the observation period, the TOC/DON ratios decreased significantly in most ecosystem solutions, although this trend was only marginally significant in the soil solution at the 0.30-m depth (Figure 5). Stemflow showed a marginally significant positive trend in the TOC/DON ratios, while the TOC/DON ratios did not change in the litter leachate. The strongest trend in TOC/DON ratios was
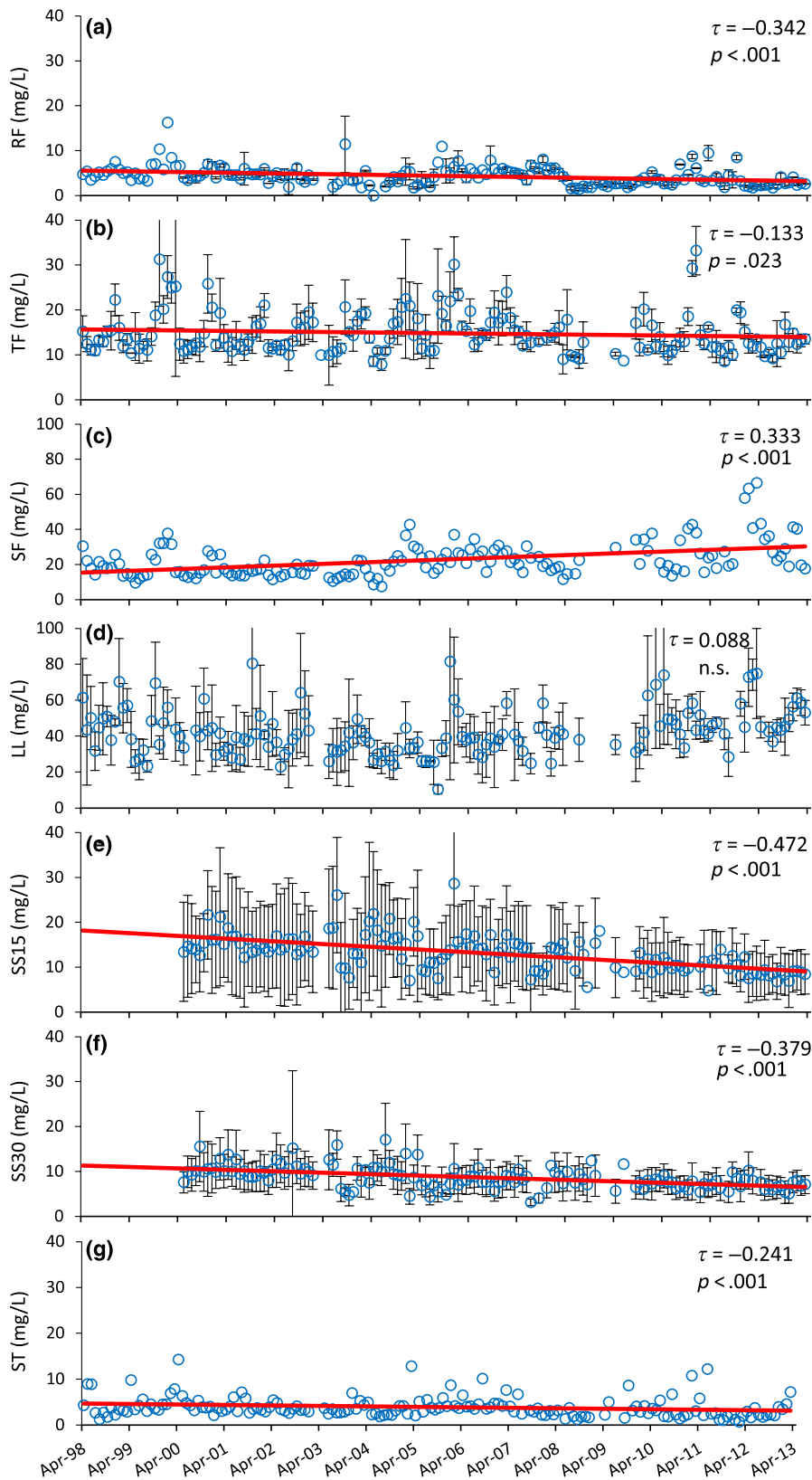
FIGURE 4 Course of the mean monthly total organic carbon concentrations in ecosystem solutions from April 1998 to March 2013. (a) Rainfall (RF), (b) throughfall (TF), (c) stemflow (SF), (d) litter leachate (LL), (e) soil solution at the 0.15-m depth (SS15), (f) soil solution at the 0.30-m depth (SS30), and (g) streamflow (ST). Error bars indicate standard deviations among the two to four gauging stations (a) or three study transects (b, d–f). Temporal trends in monthly data were statistically evaluated with the Seasonal Mann-Kendall test (Hirsch et al., 1982). n.s., not significant. Mind the different Y axis scalings

observed in the streamflow followed by the soil solution at the 0.15-m depth, rainfall, and throughfall.

The organic matter in the three horizons of the organic layer was younger than 12 years, while in the mineral soil (A and B horizons) it was ca. 42–115 years old (Table 2). For the A horizon, this age is true if the measured $\Delta^{14}C$ value is assigned to the date when the corresponding atmospheric conditions occurred for the first time. We did this, because we assumed that this is more likely

FIGURE 5 Course of the mean monthly TOC/DON ratios in ecosystem solutions from April 1998 to March 2013. (a) Rainfall (RF), (b) throughfall (TF), (c) stemflow (SF), (d) litter leachate (LL), (e) soil solution at the 0.15-m depth (SS15), (f) soil solution at the 0.30-m depth (SS30), and (g) streamflow (ST). Error bars indicate standard deviations among the two to four gauging stations (a) or the three study transects (b, d–f). Temporal trends in monthly data were statistically evaluated with the Seasonal Mann-Kendall test (Hirsch et al., 1982). Values in italics and dashed regression lines indicate marginally significant trends ($p < .1$)
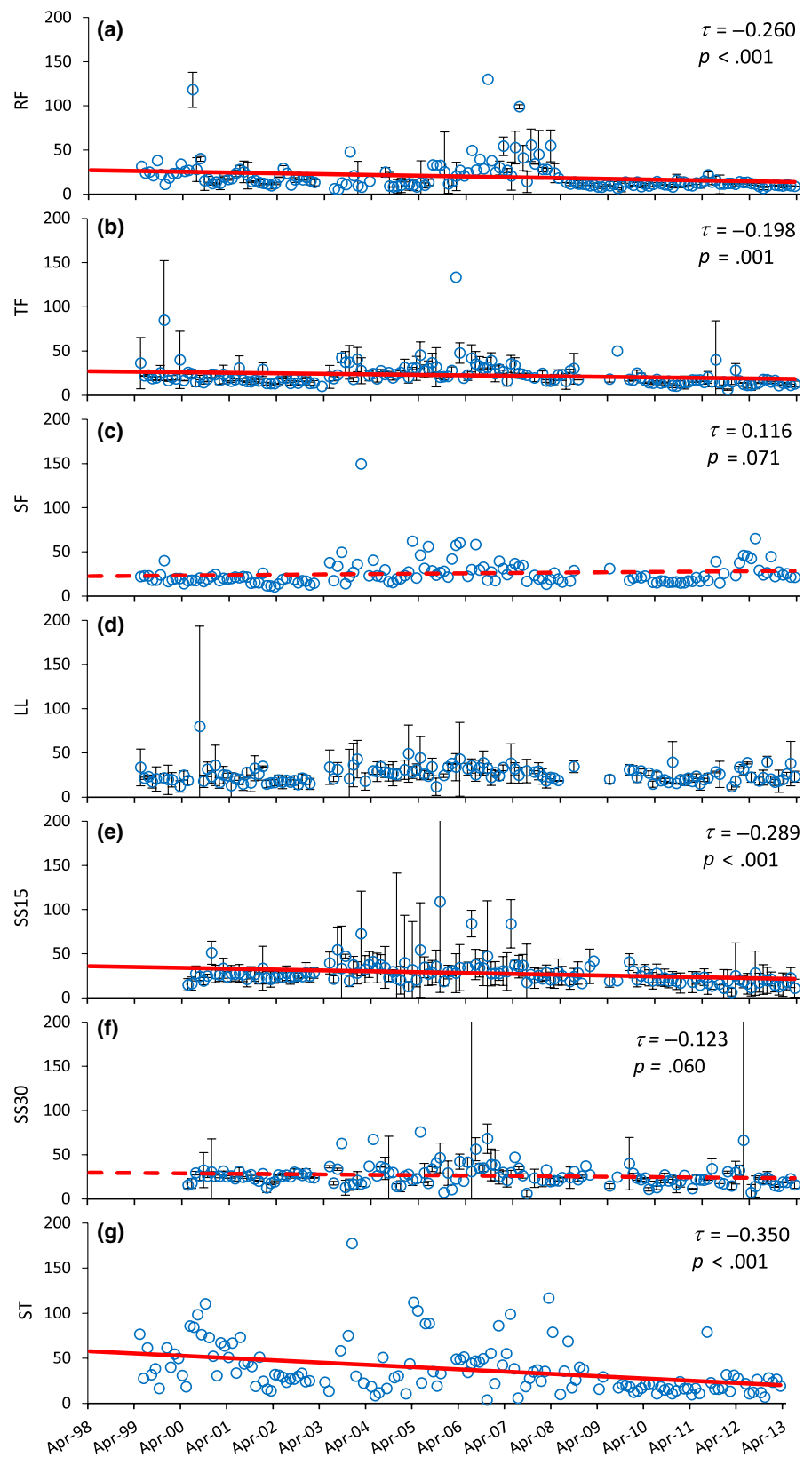
than the alternative young age of only 3 years (i.e., even younger than the organic layer, which is a major source of the organic matter in the A horizon). However, we cannot entirely rule out that the young age is true, which would then potentially be attributable to

the sorption of a young fraction of DOM introduced to the mineral soil via leaching or as root exudates as major source of soil organic matter. The age of DOM in the litter leachate was similar to the age of DOM in the organic horizons. The age of DOM in rainfall and

	Δ^{14}C (‰)	Atmospheric condition of ca. (year)	Calibrated age before present (year)
Organic matter in bulk soil horizons			
Oi	76.0	1998	
Oe	86.3	2000	
Oa	135.1	1996	
A (0–0.2 m)	52.4	1965/2004	
B (0.2–0.6 m)	−21.3		115 ± 25
TOC in ecosystem solutions			
Rainfall	105.4	2006	
Litter leachate	130.8	1996	
Mineral soil solution at the 0.15-m depth	40.4	2006	
Mineral soil solution at the 0.30-m depth	49.4	2006	
Stream flow	8.5	1955	

TABLE 3 Comparison values from the literature of total organic carbon concentrations (mg/L) in ecosystem solutions of tropical and temperate forests

	Puerto Rico[a]	Brazilian Cerrado[b]	Mexico[c]	Peru[d]	South America[e]	Thailand[f]	Indonesia[g]	Temperate[h]
Rainfall	ca. 1	2.6			3.0	1.7		2.6
Throughfall	6.2	2.6–6.7				3.9–4.9	4.7–9.0	3–35
Stemflow	9.2 (palms)							18–90
Litter leachate		17–35 (pine)					25–35	13–90
Soil solution	2.6	1.4–15		13		11–14	6.0–19	1.2–75
Streamflow	1.4–2.1		0.88–7.1			2		2.4–19

[a]McDowell and Asbury (1994), McDowell (1998).
[b]Ciglasch et al. (2004).
[c]Soria-Reinoso et al. (2019).
[d]Lao (2017).
[e]Iavorivska et al. (2016).
[f]Möller et al. (2005).
[g]Fujii et al. (2009).
[h]Borken et al. (2011), Evans et al. (2008), Iavorivska et al. (2016), Michalzik et al. (2001), Thieme et al. (2019).

mineral soil solutions was young, while that in streamflow was the oldest of all ecosystem solutions.

4 | DISCUSSION

4.1 | Temporal trends in TOC concentrations and fluxes

The comparison of our TOC concentrations (Table 1) with the literature (Table 3) illustrates that TOC concentrations in the aboveground ecosystem solutions (rainfall, throughfall, stemflow, and litter leachate) were higher than all available comparison values from other tropical forests but in the range of temperate forests. We suggest that the reason for the elevated TOC concentrations in the aboveground ecosystem solutions are the high productivity as reflected by high litterfall rates of 8.5–9.7 Mg ha^{-1} year^{-1} (Wilcke et al., 2002) in the upper half of old-growth tropical forests in South America of 5.19–12.5 Mg ha^{-1} year^{-1} (Chave et al., 2010) and the widespread thick organic layers (30–713 Mg/ha; Wilcke et al., 2002). In contrast, the TOC concentrations in the mineral soil solutions and streamflow were similar to those at other tropical sites and at the lower end of the temperate sites illustrating a strong sorption of DOM in the mineral soil.

The significant negative trends in TOC concentrations in and fluxes with rainfall indicate that there were decreasing sources of TOC along the mainly northeasterly trade wind trajectories carrying most of the rainfall to our study site (Figure 4). These

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sources include vegetation fires and emissions of VOC from the canopy of the Amazon rain forest. The decreasing TOC concentrations in rainfall are in line with Bauwens et al. (2016) who reported an overall strong decrease in pyrogenic emissions from 2005 to 2013, and a simultaneous slight decrease in isoprene emissions, a representative of the VOCs, in the Amazon region. However, they are not in line with findings of Wilcke, Leimer, et al. (2013) who reported that fire intensity, based on fire pixel counts along the wind trajectories, increased in the Amazon basin from 1998 to 2010. The significantly decreasing TOC concentrations in and fluxes with throughfall might be attributable to the changing rainfall distribution in the study area with increasing dry spells during the observation period (Peters et al., 2013), resulting in less leaching of TOC from the canopy. The increasing dry spells are reflected by an increasing number of hours with a temperature >25°C (Figure S1; Rollenbeck et al., 2015) and decreasing soil moisture in the organic layer (Figure S2). As a consequence of these climatic changes, Wilcke, Leimer, et al. (2013) have shown that throughfall decreased and canopy interception loss increased significantly from 1998 to 2010. The positive trends in TOC concentrations and fluxes in stemflow coincided with the increasing EC (Figure 3). This suggests a general increase in ion concentrations including organic anions contained in DOM. At the same time, an increasing proportion of rainfall reached the soil via stemflow ($\tau = 0.391$, $p < .01$). Because rainfall did not show a significant temporal trend, increasing dry spells (Peters et al. 2013) resulted in more concentrated rainfall and thus stronger events producing more stemflow. If such a rain event followed a dry spell, during which soluble TOC and other ions accumulated on the canopy surfaces, more stemflow could result in a higher TOC concentration and EC.

While the TOC concentrations and fluxes in litter leachate did not change significantly during the observation period (Figure 4d), the TOC concentrations in soil solutions at the two mineral soil depths and in streamflow decreased significantly (Figure 4e–g). However the negative trend in the TOC fluxes with streamflow was only marginally significant. We do not avail TOC fluxes in the mineral soil. There may be several reasons for decreasing DOM concentrations in soil solutions. (a) The production of DOM is reduced because of decreased microbial activity in the organic layer and decreased soil–water exchange. Wilcke, Boy, et al. (2013) and Wilcke, Leimer, et al. (2013) indeed reported reduced soil moisture from 1998 to 2010, which continued to 2013 (Figure S2). However, an increasing number of dry/moist changes would on the contrary increase TOC release (Kalbitz, et al., 2000; Lilienfein et al., 2000). Because the thick organic layer of tropical montane forests is attributed to prolonged waterlogging (Schuur & Matson, 2001), a reduction in soil moisture caused by increasing soil dryness might even be favorable for the microbial activity in the organic layer. This would again increase the release of DOM. Thus, reason (a) seems unlikely. (b) Soil acidification may have decreased the solubility of DOM and increased its retention in the mineral soil because of a less negative surface charge of the organic molecules (Kaiser et al., 1996). However, a negative trend in pH was only observed in litter leachate (Figure 2a), which did not

show a significant trend in TOC concentrations and fluxes, while the trends in pH in the mineral soil solutions were even significantly positive (Figure 2b,c). Therefore, acidification can also not explain the decreasing TOC concentrations in the mineral soil. (c) Decreasing TOC concentrations in mineral soil solutions and streamflow might be attributable to increased degradation. There is a significantly increasing dissolved inorganic N input into the mineral soil (both, the NH_4^+ and the NO_3^- concentrations increase highly significantly in the litter leachate, Figure S3a,b). In the mineral soil, this N seems to be increasingly used, because the concentrations of NH_4^+ showed a negative temporal trend in the mineral soil solutions (Figure S3c,e), while those of NO_3^- increased (Figure S3f,g) pointing at increasing microbial nitrification, which could have resulted in a simultaneous degradation of DOM. An increasing sorption of NH_4^+ to negatively charged mineral surfaces during the observation period as explanation for decreasing NH_4^+ concentrations in mineral soil solutions was unlikely, because of the dominance of bivalent and trivalent cations in the studied acid soils (pH < 5; Wilcke et al., 2017), which are more competitive for cation-exchange sites than the monovalent NH_4^+. In line with our suggestion, Corre et al. (2010) reported increased biological activity in a tropical montane forest in Panama already after 1 year of the addition of 125 kg urea-N and decreased DOC concentrations in soil solution after 9 years of addition of the same amount of urea-N in a tropical lowland forest. However, Velescu et al. (2016) have shown in a fertilization experiment near to our study site that TOC concentrations decreased if P alone or N + P but not N alone was added. While the P availability in the mineral soil solutions even slightly decreased at the 0.15-m mineral soil depth possibly in response to increasing pH values (Figure 2) or did not change significantly at the 0.30-m depth from 1998 to 2013 (Figure S4), the P availability in the whole ecosystem increased, because the constant P deposition from the atmosphere was entirely retained (Wilcke et al., 2019), particularly in the organic layer and the mineral soil (Wilcke et al., 2020). Microbial activity might also have been favored by increasing temperatures (Peters et al., 2013; Figure S1) and reduced waterlogging (Wilcke, Boy, et al., 2013; Wilcke, Leimer, et al. 2013; Figure S2). Increased microbial activity might have increased mineralization of DOM and released CO_2 to the atmosphere (Bragazza et al., 2006; Neff et al., 2002). The same had already been suggested to explain decreasing DON concentrations in ecosystem solutions of the same study site by Wilcke, Leimer, et al. (2013).

4.2 | Temporal trends in the TOC/DON ratios of DOM

The mean TOC/DON ratio of throughfall was lower than the mean value of 28 ± 14 in the compilation of Michalzik et al. (2001) for temperate forest ecosystems, but still in the range of the reported values, indicating N-rich DOM, similar to a study site in North Thailand where C/N ratios in DOM of 18–22 were found (Möller et al., 2005). The TOC/DON ratios in the litter leachate and soil solutions (Table 1) compared well with the mean C/N ratio in

temperate forest soil solutions of 26 ± 9.8 reported by Michalzik et al. (2001) and those at the 0.15-m mineral soil depth in North Thailand of 24–27 (Möller et al., 2005), but were higher than at the 0.05-m depth (10–11) and in subsoils and streams (18–20) of the study of Möller et al. (2005). In contrast to the TOC and DON concentrations, the mean TOC/DON ratios were not significantly different among the litter leachate and the two mineral soil solutions (Table 1). This suggests that there was no significant change in DOM quality once it had left the organic layer. The streamflow had the significantly highest TOC/DON ratio illustrating that the stream water contained the N-poorest DOM. Simultaneously, the streamflow contained the oldest DOM of all ecosystem fluxes (Table 2). This either indicated that DOM in streamflow originated from N-poor organic matter sources such as root litter or that the hydrophilic N-rich components of DOM were preferentially sorbed in the subsoil or more strongly degraded than in the other ecosystem solutions. Root litter with a high C/N ratio is a major source of subsoil organic matter (Rumpel & Kögel-Knabner, 2011). Chabbi et al. (2009) also mention deep-reaching plant roots as contributors to carbon transfer into deep soil horizons. Because tree roots in tropical forests can live for decades (Trumbore et al., 2006), root-derived organic matter in the mineral soil could be older than litter-fall-derived organic matter in the organic layer at the soil surface, but still considerably younger than organic matter in the soil matrix, which can be >100 to thousands of years old (Paul et al., 1997; Scharpenseel et al., 1989; Table 2). Accumulations of organic matter with modern age and C/N ratios above those typically found in more processed soil humus commonly occur in the soil matrix (Chabbi et al., 2009; Rumpel & Kögel-Knabner, 2011). The quality of DOM in streamflow and its age suggest that it originates from accumulations of mainly root-derived organic matter (Tables 1 and 2). Because in the study area most fine roots are constrained to the organic layer and the A horizons (Soethe et al., 2006), this root-derived organic matter must have originated from the few deeper reaching coarse roots of larger trees.

The significant decrease in the TOC/DON ratios in rainfall during the observation period illustrated that not only the size of the sources of DOM along the wind trajectories to our study area changed but also the chemical quality (Figure 5). The bulk deposition of DOM with rainfall became N richer, because of the negative trend in TOC concentrations, while the DON concentrations did not change significantly from 1998 to 2013, although they had significantly decreased from 1998 to 2010 (Wilcke, Leimer, et al., 2013). We speculate that this originates from increasing N concentrations in the vegetation of Amazonia in response to increasing N deposition (Galloway et al., 2004, 2008). A N-richer vegetation would also emit N-richer organic compounds during forest fires or as VOCs, although the total emission of DOM-generating organic compounds decreased from 1998 to 2013 in the Amazon basin (Bauwens et al., 2016).

The significantly negative trends in the TOC/DON ratios in throughfall, soil solution at the 0.15-m depth, and streamflow from 1998 to 2013 indicated that the DOM in these solutions became also N richer and thus likely more polar, in contrast to our hypothesis

(Figure 5). Because the pH of the throughfall did not change with time, a change in DOM solubility cannot explain the increasing TOC/DON ratios. In the mineral soil solutions, there was a significant increase in pH from 1998 to 2013 which should increase the solubility of TOC and is not in line with the observation of decreasing TOC concentrations (Figure 4). Moreover, the pH effect should reduce the solubility of the more polar DON more strongly than of the TOC resulting in increasing TOC/DON ratios while the reverse was observed. We can therefore rule out a pH effect as explanation for changing TOC/DON ratios. The reason for the negative trend in the TOC/DON ratios in throughfall might be the increasing leaching of more polar and N-richer organic compounds from the canopy. This could be caused by increased N concentrations in plant tissue and a higher microbial activity resulting in more N-containing metabolites as source of leaching in response to increasing N availability (Figure S3). This might also be true for the decreasing TOC/DON ratios in soil solution at the 0.15-m depth in spite of the fact that the TOC/DON ratios of litter leachate did not change significantly (Figure 5), because its DOM was younger than that of the litter leachate (Table 2). This illustrates that the DOM in the mineral soil solution at the 0.15-m depth originated either from a reactive subpool in the organic layer or directly from throughfall. The increasing leaching of organic compounds with lower TOC/DON ratios through the mineral soil into the stream might also explain the decreasing TOC/DON ratios in the stream. Alternatively, the increasing NO_3^- availability in the deeper mineral soil (Figure S3f) might have stimulated denitrifying microorganisms (Rivett et al., 2008), which produced N-rich microbial compounds that were increasingly leached into the stream. Wolf et al. (2011) estimated N_2O-N + NO-N emissions of 60 mg m^{-2} year^{-1} and Schwarz et al. (2011) interpreted changes in the δ^{15}N value of NO_3^- in ecosystem solutions as an indication of denitrification at our study site.

4.3 | Sources and age of DOM

The vertical distribution of TOC concentrations along the water path indicates that the organic layer was the major source of TOC and that during the percolation through the mineral soil, TOC concentrations decreased because of TOC sorption to the soil solid phase (Table 1; Dantas da Costa et al., 2017; Goller et al., 2006; Guggenberger et al., 1998, Möller et al., 2005). The largest part of the sorption already occurred in the topsoil above a depth of 0.15 m, while the TOC concentrations only changed little between 0.15- and 0.30-m mineral soil depth. This distinct drop in DOM concentrations between the organic layer and the topsoil is different from observations in the temperate zone where organic layers and topsoils frequently have similar DOM concentrations (Cronan & Aiken, 1985; Guggenberger et al., 1998). In line with this, the studies of Dantas da Costa et al. (2017) and Möller et al. (2005) in Brazil and Thailand, which did not include litter leachate, reported the highest DOC concentrations in soil solutions of the upper mineral soil. Similar findings as in our study were reported by Ciglasch et al. (2004) and

Lilienfein et al. (2001) for a pine plantation in the Brazilian Cerrado. The latter authors attributed the strong DOM retention already in the uppermost few centimeters of the mineral soil to the high Al and Fe oxide concentrations (29–32 g/kg of dithionite-extractable Fe) in the strongly weathered Ferralsols of the Brazilian Cerrado. However, the soils in our study area are less developed and contain lower Fe oxide concentrations. Interestingly, the DOM in litter leachate had a similar age as the organic layer, while the DOM in the mineral soil solutions was considerably younger (Table 2). This illustrates that some fresh, soluble, and likely recalcitrant compounds were leached to the deeper mineral soil, while the bulk of the older organic matter was retained in the upper 0.15 m of the mineral soil above our uppermost suction cup. Alternatively, the young DOM in the mineral soil might also originate from fresh root exudates. Tückmantel et al. (2017) reported that root exudation in the mineral soil of a European beech (*Fagus sylvatica* L.) stand could produce as much DOC as we observed in our mineral soil solutions. However, if root exudates were the major sources of DOM in the mineral soil, the increasing dryness at our study should have resulted in increasing DOM concentrations because of the positive response of root exudation to drought (Preece et al., 2018), which was, however, not the case. Perhaps the increasing release of root exudates was overcompensated by even more stimulated microbial DOM degradation, because of the increased supply of C sources and the decreased waterlogging. The same young age of the DOM as in the mineral soil solution was found for the DOM in rainfall. Given that on average 45% of the rainfall reached the stream water during the observation period (Wilcke et al., 2017, 2019), it is also feasible that the DOM of rainfall was leached through the soil without being retained or degraded.

The dating of the DOM in the various ecosystem solutions supports our hypothesis that DOM in rainfall originated from fresh plant tissue in the forest canopies and in the mineral soil solutions from canopy leachates, aboveground and belowground litter, or root exudates. This would be in line with Godin et al. (2017), Kalbitz et al. (2000), and Raymond and Hopkinson (2003) who also found that DOM contains mainly young components by ^{14}C dating. However, the litter leachate had a greater age of about one decade which coincided with the age of the organic layer (Table 2). This illustrates that the DOM in litter leachate contained mineralization products of more processed organic matter from the organic layer. This more processed DOM seemed to be completely retained by sorption processes in the uppermost few centimeters of the mineral soil, because it apparently did not reach the 0.15-m mineral soil depth. We suggest that the young fraction of DOM released from the canopy or fresh litter during rain events is not sorbed by the mineral soil because of fast percolation through the organic layer and the mineral topsoils possibly along preferential flow paths in the mineral soil (Hagedorn & Bundt, 2002) and therefore passes through the 0.15- and 0.30-m soil depths with little change in concentration and composition. This assumption is supported by the close correlation between throughfall and modeled litter leachate water fluxes. It is also in line with the finding of high saturated water conductivities in the whole soil profiles in the order of 1×10^{-7} m/s measured with a Guelph permeameter by Fleischbein et al. (2006). The mean saturated water conductivity in near-surface soil horizons was in the order of 1×10^{-4} and in the subsoil still 1×10^{-3} m/s, because of the high stone content resulting in a large number of macropores (Fleischbein et al., 2006).

The Δ^{14}C-dated ages of DOC in litter leachate and mineral soil solutions were at the younger end of those in streams of the part of the Amazon basin above 1,000 m a.s.l. near the Andes (Mayorga et al., 2005) and in litter leachates of south German forest soils (Schulze et al., 2011). The latter finding is in line with the usually longer turnover times of temperate than tropical montane organic layers (Vogt et al., 1986). The ^{14}C-derived age of the organic layer (<11 years) fits well to the estimated turnover time of the organic layers in the study area of 8.8–16 years (Wilcke et al., 2002).

The fact that the DOM of both mineral soil solutions was much younger than the solid phase organic matter illustrates that decomposition of solid phase organic matter in the topsoil is not the main source of DOM in the mineral soil solutions (Table 2). Instead, DOM in mineral soil solutions likely consists of recent DOM compounds from the canopy, a reactive subpool of the organic layer transported into deeper soil horizons via preferential flow paths (Hagedorn & Bundt, 2002), or from fresh root exudates (Preece et al., 2018; Tückmantel et al., 2017). However, the dating of the soil organic matter in the A horizon is not unambiguous, although we are confident that this is not attributable to a measurement error because the dating of an archived A horizon sample from 1998 gave a similar Δ^{14}C value (48.2‰). A possible explanation could be that the ^{14}C signal corresponded to the rising branch of the atomic bomb signal in the 1960s and thus that the organic matter in the A horizon had an age of 42 years, which seems plausible (Trumbore, 2009). The higher age of DOM in streamflow indicated that it has partly been released from solid phase organic matter in the deeper mineral soil. We therefore suggest that the DOM in streamflow consists of a mixture of a large contribution of organic matter from sources with high C/N ratios such as deep-reaching roots, which would have a young age and a small contribution of solid- phase organic matter of the subsoil with an age >100 years (Table 2), but a mean C/N ratio of 10 ± 2.9 (Wilcke et al., 2017).

5 | CONCLUSIONS

Our results demonstrate that the TOC concentrations and fluxes in throughfall, mineral soil solutions, and streamflow of a tropical montane forest in Ecuador decreased significantly during the past 15 years. This coincided with decreasing water logging in response to increasing dry spells and a higher frequency of temperatures >25°C and increasing N availability because of increasing N deposition. Overall, the results support our first hypothesis. The most likely explanation for the decrease in the TOC concentrations is the enhanced microbial decomposition. This was, however, not true for stemflow, where TOC concentrations and fluxes increased

significantly, likely because of a changing rainfall distribution and the associated enhanced leaching of soluble organic compounds during dry spells followed by rain events.

In contrast to our second hypothesis, the assumed microbial decomposition did not result in increasing TOC/DON ratios from 1998 to 2013. Instead, in throughfall, soil solution at the 0.15-m depth, and streamflow the reverse was true. We explain this as the consequence of the enhanced leaching of N-containing plant and microbial metabolites. We suggest that the concentrations of these metabolites increased because of increasing N concentrations in plant tissue and microbial activity in response to increasing N availability and more favorable soil moisture conditions.

Our third hypothesis was only partly confirmed, because litter leachate and stream water contained older DOM originating from the microbial decomposition of the about a decade-old organic layer and the >100-year-old organic matter in the deeper mineral soil, respectively. The youngest DOM in rainfall and the mineral soil solutions showed the most pronounced temporal trends.

If our finding that DOM is increasingly degraded in response to environmental change also applied to the solid organic matter in the organic layer and the mineral soil, it would seem possible that this ecosystem with its enormous stocks of organic matter in soil, particularly in the organic layer, becomes a C source because of enhanced CO_2 release, which might result in a positive feedback to the climate system.

DATA AVAILABILITY STATEMENT

The data will be uploaded to the database of the Research Unit FOR 2730: Environmental changes in biodiversity hotspot ecosystems of South Ecuador: RESPonse and feedback effECTs (RESPECT) which will become public after an embargo period.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.