Dissolved organic carbon dynamics through Atlantic rainforest compartments in Southeast Brazil

Felipe Miranda¹ and André Avelar¹

¹Federal University of Rio de Janeiro

May 5, 2020

Abstract

Considering the importance of dissolved organic carbon (DOC) flows for the carbon biogeochemical cycle, and a set of organic matter (OM) ecosystem services, our work aimed to analyze and discuss water DOC concentrations from different forest compartments: bulk precipitation, throughfall, soil solution, and stream water, in a mountainous rainforest in southeastern Brazil (Atlantic Forest). A hillslope-scale spatial design aimed to add to the discussion an analysis linked to the litter decomposition heterogeneity observed between different hillslope positions for DOC leaching. A temporal analysis was carried out by comparing rainfall events, which are different about their rainfall characteristics and antecedent humidity context. A dilution effect associated with rainfall intensity was observed in wet and dry depositions, being more pronounced on the dry deposition, which also showed a pre-wash effect linked to the previous rainfall-volume, with the time range of 15-days of previous rainfall as more relevant. Under-litter DOC concentrations showed no dilution or pre-wash effects. While in the throughfall there was no spatial difference in a hillslope-scale, the litter leaching showed great spatial variation, so that the intermediate stocks (and decomposition rates) of the mid-hillslope areas presented higher concentrations, which it is due to a balance between accumulation of material on the soil (little loss by microbiota respiration) and chemical rework on the material (new solubles) that favors the DOC leaching. In the soil solution, there is a tendency to decrease concentrations in depth. However, in events with greater rainfall intensity, soil packages with a higher OM incorporated can change from an adsorption environment to a desorption environment. The stream water showed, under baseflow condition, lower concentrations of DOC than observed in the bulk precipitation, highlighting the soil role for the organic carbon retention, where a high water infiltration capacity and OM decomposition efficiency may have key-role.

INTRODUCTION

Spatial flows of dissolved organic carbon (COD) are an important component of the carbon (C) balance in ecosystems and the global cycle of this element (Cole et al., 2007). Rainwater permeates terrestrial environments, transporting considerable amounts of organic carbon (OC) to waterbodies, which can affect limnic ecosystems and water resources quality (Graeber et al., 2018).

The development of models that can synthesize the dynamics of DOC in river basins, aimed to assist the management of water resources and meet the growing demand for information about the C cycle, demands an increasing knowledge about the production and migration dynamics of OC in the terrestrial environment and the rainfall action on these process (Neff & Asner, 2001). The watershed is the spatial matrix of capitation, production, storage, decomposition, and export of OC.

In line with the relevance of this theme, some researchers have directed their efforts towards the study of the balance of DOC in hydrographic basins, as well as towards the flows between forest compartments and to aquatic ecosystems (Hongve, 1999; Jiang et al., 2014; Meyer et al., 1988). The modulation of DOC concentrations in streams has been evaluated in their capacity to indicate the rates of surface runoff in the basin area using the hydrogeochemical signature idea (Chaplot e Ribolzi, 2014; Figueiredo et al., 2014).

In forest environments, litter above the ground is the main source of OC for deep soil horizons and aquatic environments (Camino-Serrano et al., 2014; Hafner, Groffman, & Mitchell, 2005; Moyer, Powell, Gordon, Long & Bliss, 2015). In the soil, complex chemical interactions between water, microorganisms and organic matter (OM) are manifested (Kaiser, Peake, Willey, & Brooks, 1996; Singh et al., 2017;). Leaching of litter and sorption to mineral particles are the main processes in the DOC dynamics of terrestrial environments and their flow into aquatic environments. These processes have equally important local features, such as primary productivity, decomposition rates, pluviometric dynamics, and soil water infiltration capacity.

The pluviometric dynamics given by the conditions of antecedent humidity and characteristics of the rainfall events are variables that act directly on the effects of DOC dilution and environments pre-washing (Li et al., 2016; Michalzik, Kalbitz, Park, Solinger, & Matzner, 2001). In addition, it acts in conjunction with the soil water infiltration capacity to define the water flow pathways in terrestrial environments and, consequently, regulate the sorption opportunities of DOC to soil particles and arrival rates to waterbodies (Graeber et al., 2018).

Concentrated in temperate and boreal forests, studies on DOC leaching has given attention to the control exercised by litter decomposition rates. Several studies have compared coniferous and hardwood forests about DOC flows including leaching of their leaves, discussing aspects such as material lability (Fröberg, Hansson, Kleja, & Alavi, 2011; Lee et al., 2018; Liu & Sheu, 2003). In tropical environments, DOC studies that enter the universe of litter leachate and soil solution are still scarce (e.g. Zhou et al., 2015), and studies on the balance of DOC in hydrographic basins are a little more common, addressing DOC inputs by rainfall (e.g. Godoy-Silva, Nogueira, & Campos, 2017) and/or outputs through the drainage channel (e.g. Costa et al., 2017).

Our study area is a tropical rainforest environment with primary productivity and litter decomposition rates different from temperate and boreal forests. Previous studies confirmed that the rugged relief of the area differentiated litter decomposition rates on the hillshope-scale (Miranda & Avelar, 2019), a representative situation of the forested mountains of the Brazilian coast and with a singular potential for research about DOC litter leaching.

In this way, our work aimed to analyze and discuss the water DOC concentrations from different forest compartments, in a hillslope-scale, to contribute with a general panorama about the leaching and balance of DOC in tropical rain forests, coupling an approach about the decomposition rates influence for DOC leaching from litter provided by a favorable laboratory-situation (decomposition rates heterogeneity). Analysis of the rainfall characteristics allowed us to infer its influence on the DOC concentrations in the different forest compartments. Thus, the comparison between hillslope positions as environmental spatial heterogeneity and the comparison between rainfall events based on the potential control exercised by the precipitation dynamics conform, respectively, the spatio-temporal scope of the present paper.

MATERIALS AND METHODS

Study area

The study was conducted in the Tijuca Forest, an Atlantic Forest fragment that covers the Tijuca Massif (22°55 'and 23°00'S - 43°20' and 43°10'W), one of the three mountainous physiographic units of the city of Rio de Janeiro and representative of the Coastal Massifs of southeastern Brazil. The Tijuca Massif a rugged relief environment, marked by the presence of rocky outcrops and abrupt slopes, reaching a maximum altitude of 1021m (Tijuca peak). The Tijuca Massif relief is the basis of the upper and middle courses of the Cachoeira River, which drains the flows from the massif to a coastal lagoon system (Tijuca Lagoon).

The local climate is Tropical Altitude (Cfa), with an annual average temperature of 22 ° C and monthly averages that vary from 25 to 19 ° C in February and June, respectively (Negreiros & Coelho Netto, 2011). The average annual rainfall varies from 2000 to 2500 mm, being able to register up to 3,300 mm in wettest and 1600 mm in the driest years.

The lithological basis is mainly formed by several gneisses and some granite intrusions which dates from

the Upper Proterozoic. Latosols predominate, especially Red-Yellow ones. The soil texture on horizon A is sandy, ranging from sandy loam to loamy sand (Negreiros e Coelho Netto, 2009).

The vegetation is a typical late secondary succession of Atlantic Forest, with the presence of exotic tree species and inherent anthropic interference. The forest that is currently protected by the Tijuca National Park (3,972 ha) was recovered by reforestation actions (5.2% of the area) and the natural regeneration process (94.8%), after being almost totally deforested for coffee production until the middle of the XIX century (Drummond, 1996). Today the area has over 140 years of natural succession for the most part. The south-facing hillslopes have more lushier vegetation and less grassland due to both natural (sunny and Norwegian slopes) and land-use reasons (Dias e Coelho Netto, 2011; Oliveira et al., 1995).

We chose the southern slope of Archer Hill for the research, located at the Cachoeira River upper course and completely inserted in Tijuca National Park, where the data were collected in 04 different positions (hillslope-scale): Summit (SMT); Upper Hillslope (UHS); Lower Hillslope (LHS); and Valley Bottom (VBT) (Figure 1). The natural heterogeneity of litter accumulation and decomposition rates on the hillslope positions, exposed in (Miranda & Avelar, 2019), represented an interesting "laboratory situation" for the discussion about the DOC leaching, which led us to adopt this sample design for spatial analysis.

Litter Dynamics and its spatial heterogeneity on the hillslope

According to the study by Miranda and Avelar (2019) conducted at the same hillslope positions, there are small spatial variations in vegetation structure linked to the topographic gradient. The main variant elements are the lower density of tree individuals in the downhill direction and the higher presence of dead trees and palm trees at the SMT, as well as lower and more open canopy vegetation at this hillslope position. In short, the SMT exhibits a less wet and more slightly lighted forested environment compared to the other positions (figure 2).

The spatial variation observed in the vegetation structure does not materialize in a significant difference in the annual litterfall between the different hillslope positions. At the time of litter-fall, debris can be spatially redistributed by downhill movement on steeper areas without the need for water-carrying action. Additionally, leaves (or leaf fragments) and seeds already deposited above ground can be moved downhill through the possible influence of overland flows. However, the occurrence of surface runoffs is sporadic in the area and the redistribution of debris by water is non-massive. The infiltration capacity is enough for the occurrence of hortonian flows to be uncommon. Saturation-excess overland flows caused by heavy rainfall may occur confined to small ephemeral drainage channels.

The litter moisture increases in the downhill direction and controls the efficiency of decomposition on the hillslope, with the differentiated decomposition rates being the main driver for the heterogeneity of litter accumulation above ground. The SMT area stands out with its thick litter stock as a result of a less favorable environment for decomposition, considering that the lower moisture content is combined with the higher presence of palm trees (more recalcitrant leaves), where a large accumulation of semi-composed material is observed. In contrast, the VBT exhibits a thin litter stock as a reflex of the most efficient decomposing action, where there is very little accumulation of semi-composed material. The two mid-hillslope positions (HHS and LHS) have similar litter stocks, with intermediate accumulation between that observed in SMT and VBT, while SMT has a 3x higher stocked mass than VBT. Lastly, SMT exhibits topsoil (20 cm) richer in OM, while VBT has the lowest content, given the OM mineralization efficiency.

Water samples and DOC analysis

Water samples from 08 rainfall events in 2016 and 2017 were analyzed. In each rainfall event, we collected samples from bulk precipitation (BP) (n=1 for the hillslope) and different forest hydrological compartments: throughfall (TF) (n=5); under-litter (UL) (n=5) from each hillslope position. In the SMT and VBT areas, soil solution (SS) samples were collected at two depths: 50 cm (n=1) and 100 cm (n=1). The stream water (SW) from Archer River (n=3) complete the each-event collection.

Thus, a total of 384 water samples were analyzed about their DOC concentrations, distributed as follows

among the forest compartments: BP (n=8); TF (n=160); UL (n=144 – because in EV5 little water was obtained in each collector and the analyzes were made with samples composed by the 05 collectors of each area); SS (n=32 – 16 in each depth); and from the Archer River (n=24).

The BP samples were collected with a handcrafted PVC (polyvinyl chloride) rain gauge, placed in the nocanopy area: administrative office of the Tijuca National Park. This rain gauge had a funnel positioned at the upper opening of the PVC duct, where a "ping-pong" ball was positioned to allow water to enter and make evaporation losses difficult (figure 3).

The TF samples were collected with rain gauges identical to the cited, positioned below the forest canopy (\pm 1.4 m above ground) and one in each corner and one in the center, in a previously delimited 300 m² rectangular (12 x 25 m) plot in each area. With the same distribution in each hillslope position, the minicular collectors were installed between the litter stock and the soil mineral horizon for UL samples. The mini-chute was handcrafted using a PP (polypropylene) plastic dustpan, which drained water flows into an LDPE (Low-density polyethylene) bottle through a PVC drainage tube (\emptyset 6 mm).

Soil solution samples were collected with handcrafted suction lysimeters consisting of a PVC pipe (1/2") with a porous ceramic capsule glued to the lower tip (positioned inside the soil) and the upper opening sealed with a pierced rubber stopper through which a PVC tube (\emptyset 4 mm) passed connecting the inside-bottom of the lysimeter to the outside environment. At the time of collection in the other compartments, a -68 kPa pressure was applied inside the lysimeters with a manual vacuum pump connected with the PVC tube. The tube was closed by a clip for keeping the vacuum within the lysimeter. Approximately 24 hours later, new tension was applied to remove accumulated water within the lysimeter.

Water samples from Archer River were always collected between 24 and 48 hours after rainfall ended, with it has already returned to baseflow. The Archer River flow level was monitored by the Alert-Rio System website (spate risk monitoring) where real-time water level data is exposed, acquired by automated equipment positioned 650 m downstream of the collecting areas (Mayrink Chapel Station), maintained by the Environmental State Institute (INEA-RJ).

Except for lysimeters, all sampling instruments were washed with deionized water after each collection and did not remain in the field at all times. The field positioning of the collectors was based on rainfall forecasts to reduce organic dust or debris accumulation. In the laboratory, all samples were filtered with Macharey-Nagel 0.45 µm pore size PES (Polyethersulfone) syringe-filters, kept refrigerated (05° C) and analyzed within 5 days from the collection, using a Shimadzu TOC-L equipment, which uses the acid oxidation method.

Intended to approach the leaching from each forest compartment, a second data set for TF and UL was presented (alternative to field-values), obtained by subtracting the mean values of previous compartment DOC concentration from field-values and denominated: canopy leachate (CL) and litter leachate (LL), respectively. From each TF field sample values, the same value (BP DOC) was subtracted to all hillslope positions at each event (CL obtained), while from each UL field sample values, the mean values of TF from each respective hillslope position was subtracted (LL obtained).

The study was based on a spatial analysis given on a comparison between the different hillslope positions and a temporal analysis based on the comparison between the rainfall events. For the temporal analysis, the hillslope compartment DOC data (TF mean between hillslope positions, n = 20 per event for TF-CL and UL-LL) obtained in the different events were tested as a dependent variable against characteristics of rainfall events and the antecedent rainfall context. The (independent) variables used were: rainfall volume (RfV, mm); Rainfall intensity (RfI, mm.hour⁻¹); previous drought days (PdD, number of days); and antecedent rainfall (AcR, mm) for three time-ranges (10, 15 and 30 days). These data were obtained from the Mayrink Chapel Weather Station.

Statistical analysis

The mean values were compared by a two-factorial ANOVA delineated in blocks and treatments, where the rainfall events represented the different treatments replicated at the hillslope positions. The non-parametric

Kruskal-Wallis test was used to compare hillslope positions at each rainfall event. In both cases, the Dunn's test was used for variant group differentiation in a posteriori analysis.

To analyze the rainfall event characteristics influence on the DOC leaching in each compartment, individual linear regressions were performed against each independent variable, with the calculation of respective coefficients of determination ($\rm r^2$) and model significance (P-value). Some best-adjusted independent variables were tested by multiple linear regressions to analyze the combined influence of rainfall event characteristics with previous rainfall conditions. For all significance analyses (variance and regressions) they were considered significant when P <0.05.

RESULTS

The analyzed rainfall events

The rainfall during the analyzed period presented atypical seasonality for the area, with the autumn/winter (dry session) more rainy than usual (figure 4). The spring marked the start of the traditionally rainy session, but the summer, usually the wettest season, did not reach the usual rainfall levels, with less accumulated rain volume than the winter, which was the wettest season of this hydrological year.

The analyzed events presented distinct characteristics concerning the rainfall volume, the previous humidity conditions, and the intensity of precipitation (Table 1). Five of the eight events analyzed presented precipitation equal or greater than 30 mm accumulated during 24 hours, which characterizes intense precipitation as established by Dereczynski et al. (2009) for the city of Rio de Janeiro. The rainfall volumes presented better adjustment to the duration of events ($r^2 = 0.892$; P < 0.001) than to the intensities ($r^2 = 0.209$; P = 0.011).

The high rainfall volume observed during winter is more associated with the cold fronts strength than with a higher occurrence of these, with higher rainfall volumes at each occurrence compared to what usually occurs in other years. Thus, the autumn-winter session was characterized by a smaller number of rainy days compared to the spring-summer session, reflecting a trend towards a larger number of days of drought preceding the analyzed events that occurred in autumn and winter.

DOC in bulk precipitation

The average BP DOC concentration was $5.17 (\pm 4.25) \text{ mg.L}^{-1}$, presenting considerable variation between the events. Highlights were the highest concentrations in EV3 and EV7, respectively in winter and spring (figure 5). Apart from these two occurrences, the DOC concentration was always below the level of 04 mg.L^{-1} , with the lowest concentration occurring at the end of winter (EV4).

Rainfall intensity was the only variable to present a significant linear model in an inversely proportional relationship to BP DOC concentrations (table 2). Regarding the previous rainfall variables, the time-interval of better adjustment was the previous 15-days, but the significance value did not corroborate the model (P > 0.05).

When analyzed by multiple regression the two variables of best individual adjustments (RfI and AcR 15-day), there increased the coefficient of determination, but the model was non-significant. When analyzing all variables combined (excluding the accumulated 10 and 30 days), there was a considerable increase in the determination coefficient, but remaining a non-significant model.

DOC in Throughfall and Canopy leachate

The mean DOC concentration in TF was 13.96 (\pm 8.12) mg.L⁻¹ for the studied hillslope. The observed variation between events substantially reflects the variations found in the BP (r = 0.9434) (figure 5). For CL data, there is a reduction in the correlation to BP DOC (r = 0.6332) and the significance of variation between events, with a posteriori variant group alteration.

BP DOC exerted a strong influence on field-values (TF) since its start-value for through-canopy increases. The TF DOC showed a moderate and significant linear model in inversely proportional relationship to the

precipitation intensity (Table 3). The time range of antecedent rainfall which on showed best explanatory capacity was 15-days, followed by the 10-days range, both presenting significant linear models with an inversely proportional relationship.

Combined by multiple regression, the two independent variables with best individual adjustments (RfI and 15-days AcR) showed a high explanatory capacity of TF DOC concentration through a significant linear model, which increase considerably when the concentration of the previous compartment (BP DOC) was added to the model.

For the CL data, the modulation of the values increased the similarity inversely proportional to the 15-days AcR and the rainfall intensity, demonstrating a more pronounced pre-wash and dilution effects (respectively) for the dry deposition than was observed in wet deposition (BP DOC). The 30-days range for antecedent rain proved not to be relevant, as observed for TF.

Spatial analysis indicated that variability remains high within each slope position, resulting in similar averages and a non-significant variation between areas in a hillslope-scale analysis for both TF and CL data (figure 6). The spatial heterogeneity is extremely punctual, reflecting local details of rain interception, washing and crossing processes.

DOC Under-litter and Litter leachate

The mean UL DOC concentration was $44.26~(\pm 15.99)~{\rm mg.L^{-1}}$ for the studied hillslope. The variation between the events was significant. However, there was a large reduction in the determination coefficients compared to that observed under-canopy (TF and CL), with a total loss of model significances related to the variables on antecedent humidity and characteristics of the rainfall events (table 4). The 10-days AcR was the variable that most approached the significance of the linear model for UL, maintaining the inverse proportionality trend.

About UL data, there is an even bigger reduction in the coefficients of determination for the variables of antecedent humidity and characteristics of rainfall events. Such observation indicates no influence of the dilution and pre-wash effects on DOC leaching from litter.

The proximity to a significant correlation observed between UL data and 10-days AcR should be residual, reflecting part of the correlation observed in TF, once the TF concentrations are start-values for the DOC through-litter increase. However, it is noteworthy that litter is the main DOC source in the forest leaching process and, thus, the UL field values show less anterior compartment dependence (TF DOC) than was observed in the BP-TF transition.

The vBT presented the lowest mean DOC concentration for UL and LL for all events, except for LL at EV7 (figure 7). The SMT tended to intermediate concentrations and both mid-hillslope areas (UHS and LHS) achieved the highest concentrations. The similarity in the spatial variation between the results obtained at the different events reinforces the confidence in the average result obtained.

Analyzing the DOC results in view of the spatial variability of litter stocks, it is evident that both midhillslope areas (UHS and LHS), which with the highest DOC concentrations, have similar litter stocks between itself and intermediate litter mass compared to SMT and VBT. In VBT rainwater percolates thin stocks with little accumulated organic matter, resulting in lower DOC concentrations in the leachate. On the other hand, the thicker litter stock at SMT did not materialize in higher DOC concentrations, demonstrating some limiting factor to leaching compared to what occurs in mid-hillslope areas.

Since the areas (hillslope positions) produce similar litterfall, the difference between the litter stocks reflects differentiated decomposition rates. Therefore, DOC concentrations are related to decomposition rates analogously to that observed for litter stocks, with more intense leaching in areas with intermediate decomposition rates. This observation indicates the nonlinearity of the relationship between DOC concentrations with litter stocks and their decomposition rates, suggesting a curve trend (Second Degree Polynomial) that

best demonstrates an "optimal" condition for DOC leaching in this environment under moderate stocks and decomposition rates (figure 8).

It's important to state that we do not intend to expose a standard curve representing a probabilistic model, as it would require a larger range of positions to be significant. Our intention is only to emphasize the nonlinearity trend under the conditions of the analyzed environment, believing that such a general idea may contribute to analyzes in similar environments. The high coefficient of determination value found for the curve in DOC related to the litter stocks, besides being favored by the low number of areas, reflects the fact that the stocks have similar accumulated litter mass in UHS and LHS that produced similar DOC concentrations, which was an interesting result.

DOC in soil solution and stream water

The mean DOC concentration in the soil solution was $25.56 (\pm 12.06) \text{ mg.L}^{-1}$ at 50 cm depth and $21.76 (\pm 7.71) \text{ mg.L}^{-1}$ at 100 cm depth for the studied hillslope. There was significant spatial variation so that SMT showed higher values for both depths compared to VBT, and that difference was less significant for 100 cm (P = 0.021) compared to 50 cm depth (P < 0.001) (table 5).

Soil solution DOC concentrations tended to decrease with increasing depth, and this reduction was smaller (P = 0.0356) at the SMT topsoil (0-50 cm) in comparison to VBT. However, there is an additional behavior associated with increased precipitation intensity which results in a reduction in this trend and causes the concentration to increase in depth sometimes.

Such behavior occurred in the richest OM-incorporated compartments: soil top (0-50 cm) in the SMT; and at higher depth (50-100 cm) in the VBT, where the typical local colluvial dynamics of relief evolution usually bury OM. In the VBT case, this behavior was observed in five of the eight events analyzed, resulting in no significant difference (P > 0.05) between their two depths about the mean DOC concentrations (eight-events mean). In contrast, that difference was quite significant in SMT (P < 0.001).

In this context, the regression analyses showed significant linear models inversely proportional to the precipitation intensity and: the difference between the DOC concentrations at 0 (UL data) - 50 cm in the SMT; the difference between DOC concentrations at 50-100 cm in the VBT (table 6). In general, our results indicate that the decrease tendency of DOC concentrations in the deep soil solution is reduced in events of higher precipitation intensity, so that part of the incorporated rich mineral OM compartment may behave as a DOC source (desorption) rather than an adsorption trend.

The SW showed similar DOC concentrations (P > 0.05) in post-event baseflow conditions. The SW DOC was lower (P = 0.0117) than that found in the BP, which demonstrates the soil efficiency as OM sorption and mineralization environment. Even with sandy and relatively shallow soils, it can efficiently retain the OM originated by the high primary productivity of the area.

A significant inversely proportional trend was observed between the SW DOC concentrations and the rainfall intensity. This result indicates that the OM desorption behavior in higher rainfall intensity occasions does not materialize in an increase in the SW DOC concentration when it returns to the base level. On the contrary, there was a tendency for a slight reduction in concentrations.

DISCUSSION

Comparison to other environments

Some DOC content can be observed in BP due to the dissolution/carriage of volatile organic compounds found in the atmosphere. There is a wide variety of organic molecules in the atmosphere such as light hydrocarbons, aldehydes, and ketones, as these molecules can vaporize under natural environmental conditions. In addition, a large amount of organic soot is released into the atmosphere by industrial activities and the burning of fossil fuels (Siudek, Frankowski, & Siepak, 2015).

DOC concentrations up to 2 mg.L⁻¹ may only have biogenic origin due to volatile exudates from natural

environments, so values above this level usually represent some anthropogenic influence (Liu & Sheu, 2003). In the case of the present study, the forest fragment is totally inserted in the second-largest metropolis of Brazil, the Rio de Janeiro, which explains the fact that only one of the rainfall events analyzed presented value below the mentioned level.

The average BP DOC found in the present study is close to that reported by Siudek et al. (2015) in an urban environment in Poland and by Coelho et al. (2008) in an urban-rural transition area in Brazil, occasions where some anthropogenic influence was cited as an important explanatory factor. Lower values were reported by Costa et al. (2016) in an area away from urban centers in Brazil, by Kieber, Peake, Willey, & Brooks (2002) under the influence of sea breezes in the coastal zone of New Zealand and by Roig-Planasdemunt, Llorens, and Latron (2016) in a forested area in Spain, locations with lower anthropogenic influence. Higher values were reported under more extreme conditions of pollutant emissions, as by Godoy-Silva, Nogueira, and Campos (2017) in an agricultural area influenced by sugarcane burning in southeastern Brazil.

Our results of TF DOC seem slightly higher than those reported by Bäumler and Zech (1997) in temperate forests in Germany, Liu & Sheu (2003) in Taiwan, and Chen, Yoshitake, Iimura, Asai, and Ohtsuka (2017) in Japan, as well as in the intertropical zone (Brazil) by Costa et al. (2016). The DOC concentrations in this compartment correspond to the bulk precipitation DOC contents increased by canopies leaching, in turn, controlled by dry deposition de OM from the atmosphere. Thus, the proximity relationship to urban centers tends to be the most important factor controlling the increases in through-canopy water, so that, like as for bulk precipitation, the urban context must answer for the slightly higher values in the forest fragment studied.

The under-litter DOC concentration in our area was similar to the reported in coniferous forests by Park and Matzner (2003) in the Czech Republic, and by Fröberg, Berggren, Bergkvist, Bryant, and Mulder (2006), and Fröberg et al. (2011) in coniferous and silver birch forests in Sweden. The higher litterfall mass combined with the efficiency of microbial activity, both typical features of tropical forests, should explain the maintenance of similar values to those reports in higher-latitudes, where litter accumulation above ground tends to be as higher as the organic carbon source-stock (Pregitzer & Euskirchen, 2004). The fast chemical transformations on the litter by microbiota constantly making new available solubles should play a key role.

The soil solution DOC concentrations have similar values (surface) and tendency to decrease with increasing depth as observed in studies in different areas and ecosystems, as by Richter and Markewitz (1996) in the United States (conifers), by Liu and Sheu (2003) in China (Conifers and Hardwoods), by Leinemann et al. (2016) in Germany (hardwoods) and by Roig-Planasdemunt et al. (2016) in Spain (grasses). The sandy texture of the A and B soil horizons should be the main reason for the decrease rates to be lower than that reported in most cited studies, considering the clay performance as a favorer the OM adsorption (Kaiser et al., 1996; Kaiser & Guggenberger, 2007; Singh, Sarkar, Biswas, Churchman, & Boland, 2016; Singh et al., 2017).

The Archer River, under baseflow conditions, has low DOC concentrations, closely to the reported by Hale and Godsey (2019) in the United States (coniferous and grasses) and by Figueiredo et al. (2014) in Spain (agricultural and forest). Slightly higher values, but close to those exposed here, were reported by Liu and Sheu (2003) (leafy and coniferous forests). The efficiency of OM mineralization and the rare occurrence of hortonian surface flows (high water soil infiltration capacity) should be the most relevant explanatory factors for the occurrence of DOC concentrations below those reported in some temperate (Chaplot & Ribolzi, 2014) and boreal (Ledesma et al., 2016) environments. There are no wetlands or peatlands in our study area, which are usually, along with overland flows, significant sources of DOC in streams or lakes in steppe vegetation and boreal or temperate forests (Hongve, 1998; Chaplot & Ribolzi, 2014; Oni, Futter, Molot, & Dillon, 2014).

Temporal analysis

Since our study area is located in the inter-tropical zone, with mild winter, the bulk precipitations not show seasonal variation for DOC concentrations caused by pollution emissions from domestic heating, as reported in the studies in higher latitudes as by Inagaki, Sakai, and Ohnuki (1995) in Japan, Pan et al.

(2003) in China, and Siudek et al. (2015) in Poland. However, one of two rainfall events with higher DOC concentrations occurred in winter (EV3). The tendency of less precipitation - drier vegetation and litter - coupled with the practice of balloon release typical of the São João festivities that occur at this time in Brazil (June to August), makes winter the highest occurrence time of forest fires in the Atlantic Forest, in particular in the Tijuca Forest. It seems that DOC concentrations in BP tend to be close to 3 mg.L⁻¹ in our study area, however, they may present higher values linked to stochastic causes.

Storms formed over the ocean usually have lower DOC concentrations than those originated over the continent (Kieber et al., 2002). However, according to reports from the Rio de Janeiro State Meteorological Monitoring System, only EV5 was not caused by cold fronts. This indicates similar origins between events in relation to rainfall formation including the DOC-peak events (EV3 and EV7), considering that these cold fronts that usually reach Rio de Janeiro by sea winds from the southwest (Dereczynski et al., 2009), this is not an explanatory factor for our DOC peaks

There was a dilution effect, but not associated with rainfall volume as reported by Li et al. (2016), being such an effect linked to the rainfall intensity. Iavorivska et al. (2017) reported the trend of decreasing DOC concentrations during rainfall events which seems to be an important factor for the occurrence of a dilution effect linked to rainfall volume. These authors also mention an interactive set of factors that can contain the downward trend or even generate increases in DOC concentrations over the course of rainfall events that may help explain our weak correlation between DOC concentrations and rainfall volumes. In particular, the low-temperature reduction from the rainfall beginning (maintenance of the dilution capacity) and the maintenance of atmospheric OM sources (urban spatial context) are factors, among those mentioned by the authors, which may be key elements in this matter.

The TF DOC showed a bigger dilution effect relative to the rainfall intensity and the maintenance of the absence of correlation with the total rainfall volumes, in comparison to occurs in BP. The rainfall intensity protagonism for the dilution effect in detriment of the total rainfall volume infers the idea of some temporal continuity about the OM sources to be considered for both wet and dry deposition.

The two events with the highest wet deposition (BP data) lost prominence in comparison to the dry deposition (CL data), demonstrating that the factors behind the wet deposition "peaks" did not conduce the same increase in dry deposition. Similarly to that observed by Kieber et al. (2002), this difference can be explained by the constant action of sea breezes pushing the air laden with organic components into inland areas, which adds to the fact that rainfall is often caused by cold fronts that reach the sea (Dereczynski, 2009).

The arise of the pre-wash effect in TF, not observed in BP, is evidenced by the statistical correlation of concentrations and some antecedent humidity parameters. That is, the pre-wash effect occurs similarly to the reported by Turgeon and Courchesne (2008), which found greater DOC flows in a dry climatic context. However, here, this effect was manifested statistically related to the previous rainfall volume and not to the number of previous drought days, indicating that small rainfall volumes may not be effective for washing. In this context, the previous time range that stood out as the most relevant for this rainfall accumulated volume was 15-days.

About litter leaching, authors such as Dawson et al. (2008) and Jiang et al. (2014) found higher DOC concentrations from the temperate forest floor in the summer, when litter decomposition rates and DOC solubility are highest. The low thermal amplitude typical of the area reduces the temperature effect (freezing and solubility) relevance on litter leaching described by Zhou et al. (2015).

The evergreen character of the forest in question results in a strong temporal correlation between litterfall and rainfall since stormy winds mechanically act for the fall of senile leaves (constantly produced). Therefore, the occurrence of rainfall tends to be accompanied by fresh leaves with high leaching potential, which helps to explain the pre-wash absence in this compartment. That is, the small variance in temperature, with the absence of litter freezing at the winter, and the poor seasonality of litterfall with constant new leaves replacement throughout the year result in no seasonal-tendency for litter DOC leaching in our study area.

The absence of a dilution effect on litter leachate indicates that the DOC available on the forest floor does not deplete easily (Schmidt, Wang, Chang, & Matzner, 2010). Michalzik, Kalbitz, Park, Solinger, and Matzner (2001) also found no dilution effect in litter leachate in a temperate forest. In this situation, higher amounts of rainfall result in more DOC infiltration into the soil or export through the drainage channel (dependent on the soil DOC retention). The continuity and efficiency of biochemical action on litter can be an important factor for the maintenance of leaching rates. No dilution or prewash effects were observed for soil solution.

The stream water DOC concentration is largely given by the balance between atmospheric deposition, biomass leaching, soil sorption, and biodegradation processes on the OM in the terrestrial environment (Nosrati, Govers, & Smolders, 2012; Jiang et al., 2014; Oni et al., 2014). In the post-event baseflow condition, the SW DOC concentrations were similar between the analyzed events, which highlights the soil capacity to dampen the oscillation in DOC flows from the other compartments.

DOC modulations correlated to variations in canal discharge, as observed by Turgeon and Courchesne (2008) and Roig-Planasdemunt et al. (2016), were not contemplated in the present study since water in stormflow condition was not collected. However, hortonians runoffs, the main sources of DOC to the canal during rainfall events according to these authors, are uncommon in our area due to the high water infiltration capacity in the soil (Coelho Netto, 1987).

A study of variations of inorganic compounds chemistry of stream water in association with stream water discharge modulation was carried out in the same (our) area by Ovalle (1985). This author reported the tendency of stream water, in the first moment of increased discharge, to be chemically close to the soil solution on the influence of more intense rainfalls ("piston" effect pushing edaphic water), and that the water started to return to the chemical condition of the baseflow even before the water discharge reduction. When the rainfall was intense enough to generate overland flows, either Hortonian or saturation flows, a large amount of OM was transported to the stream in addition to typical inorganic solubilization of elements of rocky outcrops.

Spatial analysis

Because it is a multi-diverse forest with low species dominance, the small differences in vegetation structure and composition observed between hillslope positions were not sufficient to configure significant variations for the TF DOC concentrations, without effects arising from allometric variations between tree-species as observed between conifers and hardwoods (Liu & Sheu, 2003; Inagaki et al., 1995). The spatial heterogeneity of canopy leaching is high, but it occurs on a small spatial scale (punctual) and the means obtained from 300 m^2 area were very similar when comparing to the hillslope positions. The variance of the TF DOC data within each hillslope position reflects that the local minutiae in the dry deposition, canopy washing, and rainwater interception control the DOC enrichment process in this compartment.

The slightly larger canopy opening in the SMT did not materialize lower DOC values as expected. Probably, the canopy opening variation between the SMT and the other hillside positions is not sufficient to generate differences as observed by Costa et al (2016) between native forests and cacao agroforestry, since the largest native forest biomass would manifest in less canopy opening (unmeasured).

An apparent duality regarding the relationship between litter decomposition rates and DOC leaching seems to manifest itself prominently on the studied hillslope. Lower DOC concentrations from birch forest floor compared to conifers were reported by Froberg et al (2011) and argued for the higher biological activity on birch litter (lower C / N ratio), resulting in thin soil litter stocks above ground. Similarly, lower DOC concentrations have also been reported for Mull humus form compared to the adjacent area with Moder humus (the difference between humus forms is due to the greater accumulation of the sub-horizon H for Moder type) by McDowell and Wood (1984). The key issue is the maintenance or not of a MO source stock above ground and the greater leaching probability when percolating thicker litter stocks. However, it is noteworthy that the non-observation of the litterfall rates can be a large error source factor when relating the litter accumulation above ground and DOC leaching in the comparison between areas.

On the other hand, some studies showed the positive effect of decomposition for the DOC leaching in a comparison between broadleaved forest areas (Camino-Serrano et al., 2014; Guggenberger & Zech, 1993; Zhou et al., 2015), as well as by experiments with controlled leaching and/or decomposition. (Don & Kalbitz, 2005; Lee et al., 2018). According to Zhou et al. (2015), at the first moment, the DOC leaching is high due to the great solubles availability in fresh leaves, with subsequent rate decreases. Continuity of DOC leaching depends on the availability of new solubles, which is greater in situations where biochemical activity in material degradation is more intense. The key issue here is the availability of new solubles by chemical rework on the material, mobilizing C for leaching. However, laboratory-controlled experiments may not consider the effect of constant accumulation of semi-degraded material in topsoil that occurs under natural field conditions. Additionally, the positive relation between decomposition and leaching of DOC may be affected by considering losing massive C by microbiota respiration (mineralization) in environments where decomposition is more intense (e.g., tropical forests).

Camino-Serrano et al. (2014) comment about this duality from the idea of concurrent pathways to C: being breathed by the microbiota or being leached by water. Efforts to modeling the DOC leaching behavior from the conferous forest floor also face this duality, represented by the challenge to combine the leaching of semi-decomposed material accumulated in topsoil to the large contribute by fresh leaves (gren, Kleja, & Bosatta, 2018).

In this way, by analyzing our data, it not surprising to us that the lower DOC concentrations in the VBT litter leachate, where decomposition is faster and there is little accumulation of OM material as DOC source, with a high loss of C by microbiota respiration. It is also not surprising that the largest litter accumulation in the SMT did not materialize in higher DOC concentrations, as the availability of new solubles is slower. Both mid-hillslope positions, with similar litter stock between themselves and intermediates compared to the summit and bottom valley, showed very close DOC concentrations between themselves and higher compared to geomorphological extremes.

Our inference, considering the fact that hillslope positions have similar litterfall, is that the mid-hillslope conditions, with intermediate decomposition rate, presents a balance between source material accumulation and availability of new solubles that favors DOC leaching. The leaching is lower at the valley bottom due to the little material accumulation (less C available) but is also limited at the summit by the lower biochemical work over the material (fewer solubles available).

The second-degree polynomial tendency presented in figure 9 does not represent a proposed mathematical model of this relation, being only a tool to emphasize the nonlinear character of the behavior for the studied area. Given the studied area representativeness to the Atlantic forest domains of the mountainous environment (Miranda & Avelar, 2019), we believe such nonlinear behavior may be a standard to be considered for the large extension of the forested domains of the Serra do Mar and Mantiqueira, main actual Atlantic Forest strongholds.

Higher soil solution DOC concentrations at 50 cm depth in summit compared to the VBT result from the joint action of higher inputs (UL DOC) and lower adsorption rates once the higher MO content incorporated into the soil results in higher occupation of sorption sites (kaiser et al., 1996; Singh et al., 2016). At higher depth (100 cm) the difference between hillslope positions reduces its significance due to the soil acting as a sorption environment, a similar observation as reported by Park and Matzner (2003). In both cases (50 and 100 cm) the reported differences (SMT vs VBT) are further influenced by occasional increases in-depth concentration that has been treated as an interaction of spatio-temporal factors.

Spatio-temporal interactions

A set of spatio-temporal interactions was considered from variations between events related to the rainfall intensity that were associated with singular conditions of the evaluated spatial heterogeneity. In soil solution, we observed situations where the DOC adsorption rates to the soil decrease when the rainfall intensity increases, such behavior spatially is limited to areas where there is a large amount of OM incorporated in the soil: the top of the soil (0-50 cm) in the summit; and in-depth (50-100 cm) in the bottom valley (OM

buried by colluvial dynamics).

As intense manifestations of this behavior, in these compartments and at times of higher rainfall intensities, the DOC concentration increased in depth indicating the change of soil behavior from an adsorption compartment to a desorption compartment (DOC source compartment) for the transport by water. This should be due to increased water elution capacity for OM desorption by increased soil pore pressure under stormy conditions (Stone and O'Shaughnessy, 2005).

CONCLUSIONS

The urban matrix character where forest fragments (Tijuca Forest) are inserted conditions anthropogenic DOC inputs by wet and dry depositions and stochastic causes. These can generate some input peaks, mainly due to wet deposition. Temporal variations (between-event) in rainfall and throughfall DOC concentrations are controlled by precipitation intensity and antecedent rainfall (15-days) producing dilution and prewash effects, respectively. The rainfall canopy-through percolate presented DOC increases with very spatially punctual control so that spatial variations in the hillslope-scale (between hillslope positions) are not significant.

Litter above ground is the main source compartment of DOC to inside soil and its DOC leaching reflects the balance between synthesis and decomposition of OM in the local ecosystem in a non-linear tendency. In an increasing litter decomposition rates gradient on the downhill way, typical of these mountainous rainforests, mid-hillslope areas stand out with higher DOC leaching due to a favorable balance between OM accumulation above ground (DOC source) and OM degradation (new solubles). Our results demonstrated the absence of dilution and prewash effects litter leaching so that the DOC concentrations in this compartment were independent of the antecedent rainfall and the rainfall intensity and volume.

A high soil-water infiltration capacity is responsible for maintaining low DOC concentrations in the stream water, given the opportunities of MO sorption to soil particles. Even under a high productivity environment with shallow and sandy soils, in baseflow condition (after stormflow), the stream water presented lower values compared to the bulk precipitation, which highlights the role of soils in the retention of OM and maintenance of the quality of water resources. In this sense, the efficiency of OM mineralization by providing new sorption sites seems to be a prominent factor in this ecosystem service provided by soils concerning the water quality.

REFERENCES

gren, G., Kleja, D., & Bosatta, E. (2018). Modeling Dissolved Organic Carbon Production in Coniferous Forest Soils. *Soil Science Society of America Journal*, 82 (1), 392-1403. https://doi.org/10.2136/sssaj2017.11.0407

Bäumler, R. & Zech, W. (1997). Atmospheric deposition and impact of forest thinning on the throughfall of mountain forest ecosystems in the Bavarian Alps. Forest Ecology and Management, 95 (3), 243-251. https://doi.org/10.1016/S0378-1127(97)00039-X

Camino-Serrano, M., Gielen, B., Luyssaert, S., Ciais, P., Vicca, S., Guenet, B., ... & Janssens, I. (2014). Linking variability in soil solution dissolved organic carbon to climate, soil type, and vegetation type. *Global Biogeochemical Cycles*, 28 (5), 497-509. https://doi.org/10.1002/2013GB004726

Chaplot, V. & Ribolzi, O. (2014). Hydrograph separation to improve understanding of Dissolved Organic Carbon Dynamics in Headwater catchments. *Hydrological Processes*, 28 (21), 5354-5366. https://doi.org/10.1002/hyp.10010

Chen, S., Yoshitake, S., Iimura, Y., Asai, C., & Ohtsuka, T., 2017. Dissolved organic carbon (DOC) input to the soil: DOC fluxes and their partitions during the growing season in a cool-temperate broad-leaved deciduous forest, central Japan. *Ecological Research*, 32 (5), 713–724. https://doi.org/10.1007/s11284-017-1488-6

Coelho, C. H., Francisco, J. G., Nogueira, R. F. P., & Campos, M. L. A. M., (2008). Dissolved organic

- carbon in rainwater from areas heavily impacted by sugar cane burning. Atmospheric Environment ,42 (30), 7115–7121. https://doi.org/10.1016/j.atmosenv.2008.05.072
- Coelho Netto, A. L. (1987) Overlandfl ow production in a tropical rainforest catchment: the role of litter cover. *Catena*, 14 (1-3), 213-231, https://doi.org/10.1016/S0341-8162(87)80019-X
- Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., ... Melack, J. (2007). Plumbing the Global Carbon Cycle: Integrating Inland Waters into the Terrestrial Carbon Budget. *Ecosystems*, 10 (1), 172–185. https://doi.org/10.1007/s10021-006-9013-8
- Costa, E. N. D., Souza, J. C., Pereira, M. A., Souza, M. F. L., Souza, W. F. L., & Silva, D. M. L., (2016). Influence of hydrological pathways on dissolved organic carbon fluxes in tropical streams. *Ecology and Evolution*, 7, 228-239. https://doi.org/10.1002/ece3.2543
- Dawson, J. C., Soulsby, C., Tetzlaff, D., Hrachowitz, M., Dunn, S. M., & Malcolm, I. A. (2008). Influence of hydrology and seasonality on DOC exports from three contrasting upland catchments. *Biogeochemistry*, 90 (1), 93-113. https://doi.org/10.1007/s10533-008-9234-3
- Dereczynski, C. P., Oliveira, J. S., & Machado, C. O. (2009). Precipitation climatology of the city of Rio de Janeiro. Brazilian Journal of Meteorology, 24 (1), 24-38. http://dx.doi.org/10.1590/S0102-77862009000100003
- Dias, M. A. & Coelho Netto, A. N. (2011). A influência da topografia na distribuição de gramíneas em um fragmento de Floresta Atlântica urbana montanhosa Maciço da Tijuca/RJ. Revista Brasileira de Geomorfologia, 12 (2) 03-14. http://dx.doi.org/10.20502/rbg.v12i2.230
- Don, A., & Kalbitz, K. (2005). Amounts and degradability of dissolved organic carbon from foliar litter at different decomposition stages. *Soil Biology and Biochemistry*, 37 (12), 2171–2179. https://doi.org/10.1016/j.soilbio.2005.03.019
- Drummond, J. (1996) The Garden in the Machine: An Environmental History of Brazil's Tijuca. *Environmental History*, 1 (1) 83-104.
- Figueiredo, J. A., Menor, E. A., Taboada-Castro, M. T., Taboada-Castro, M. M., Rodríguez-Blanco, M. L., Braga, E. S., (2014). Using hydrogeochemical signatures of stream water to assess pathways for rainfall events: toward a predictive model. *Hydrological Processes*, 28 (4), 2301-2311. https://doi.org/10.1002/hyp.9801
- Fröberg, M., Berggren, D., Bergkvist, B., Bryant, C., Mulder, J. (2006). Concentration and fluxes of dissolved organic carbon (DOC) in three Norway spruce stands along a climatic gradient in Sweden. Biogeochemistry, 77, 1-23. https://doi.org/10.1007/s10533-004-0564-5
- Fröberg, M., Hansson, K., Kleja, D.B., & Alavi, G. (2011). Dissolved organic carbon and nitrogen leaching from Scots pine, Norway spruce, and silver birch stands in southern Sweden. *Forest ecology and management*, 262 (9), 1742-1747. https://doi.org/10.1016/j.foreco.2011.07.033
- Godoy-Silva, D., Nogueira, R. F. P., & Campos, M. L. A. M., 2017. A 13-year study of dissolved organic carbon in rainwater of an agro-industrial region of São Paulo state (Brazil) heavily impacted by biomass burning. *Science of the Total Environment*, 609, 476-483. Disponível: https://doi.org/10.1016/j.scitotenv.2017.07.145
- Guggenberger, G., & Zech, W. (1993). Dissolved organic carbon control in acid forest soils of the Fichtelgebirge (Germany) as revealed by distribution patterns and structural composition analyses. Geoderma, 59 (1-4), 109-129. https://doi.org/10.1016/0016-7061(93)90065-S
- Graeber, D., Poulsen, J. R., Heinz, M., Rasmussen, J. J., Zak, D., Gücker, B., ... Kamjunke, N. (2018). Going with the flow: Planktonic processing of dissolved organic carbon in streams. *Science of The Total Environment*, 625, 519–530. https://doi.org/10.1016/j.scitotenv.2017.12.285
- Hafner, S. D., Groffman, P. M., & Mitchell, M. J. (2005). Leaching of dissolved organic carbon, dissolved organic nitrogen, and other solutes from coarse woody debris and litter in a mixed forest in New York

- State. Biogeochemistry, 74(2), 257-282. http://www.jstor.org/stable/20055238
- Hale, R. L. & Godsey, S. E. (2019). Dynamic stream network intermittence explains emergent dissolved organic carbon chemostasis in headwaters. *Hydrological Processes*, 33 (13), 1926-1936. https://doi.org/10.1002/hyp.13455
- Hongve, D., (1999). Production of dissolved organic carbon in forested catchments. Journal of Hydrology, 224 (3-4) 91-99. https://doi.org/10.1016/S0022-1694(99)00132-8
- Iavorivska, L., Boyer, E. W., Grimm, J. W., Miller, M. P., DeWalle, D. R., Davis, K. J., Kaye, M.W. (2017). Variability of dissolved organic carbon in precipitation during storms at the Shale Hills Critical Zone Observatory. *Hydrological Processes*, 31 (16), 2935-2950. https://doi.org/10.1002/hyp.11235
- Inagaki, M., Sakai, M., & Ohnuki, Y. (1995). The effects of organic carbon on acid rain in a temperate forest in Japan. Water, Air, and Soil Pollution, 85 (4), 2345-2350. https://doi.org/10.1007/BF01186184
- Jiang, R., Hatano, R., Zhao, Y., Kuramochi, K., Hayakawa, A., Woli, K. P., & Shimizu, M. (2014). Factors controlling nitrogen and dissolved organic carbon exports across timescales in two watersheds with different land uses. *Hydrological Processes*, 28 (19), 5105-5121. https://doi.org/10.1002/hyp.9996
- Kaiser, K., Guggenberger, G., & Zech, W. (1996). Sorption of DOM and DOM fractions to forest soils. Geoderma, 74 (3-4), 281-303. https://doi.org/10.1016/S0016-061(96)00071-7
- Kaiser, K. & Guggenberger, G., (2007). Sorptive stabilization of organic matter by microporous goethite: sorption into small pores vs. surface complexation. *European Journal of Soil Science*, 58 (1): 45-59. https://doi.org/10.1111/j.1365-2389.2006.00799.x
- Kieber R. J., Peake B., Willey J. D., & Brooks A. G., (2002). Dissolved organic carbon and organic acids in coastal New Zealand rainwater. $Atmos\ Environment$, 36 (21). 3557–3563. https://doi.org/10.1016/S1352-2310(02)00273-X
- Leinemann, T., Preusserb, S., Mikuttac, R., Kalbitzd, K., Cerlie, C., Höschenf, C., ... Guggenbergera, G. (2018). Multiple exchange processes on mineral surfaces control the transport of dissolved organic matter through soil profiles. *Soil Biology and Biochemistry*, 118, 79–90. https://doi.org/10.1016/j.soilbio.2017.12.006
- Ledesmaa, J., Futtera, M., Laudonb, H., Evans, C., & Köhler, S. (2016). Boreal forest riparian zones regulate stream sulfate and dissolved organic carbon. *Science of the Total Environment*, 560-561, 110–122. https://doi.org/10.1016/j.scitotenv.2016.03.230
- Lee, M. H., Park, J. H., & Matzner, E. (2018). Sustained production of dissolved organic carbon and nitrogen in forest floors during continuous leaching. Geoderma, 310, 163-169. https://doi.org/10.1016/j.geoderma.2017.07.027
- Li, C., Yan, F., Kang, S., Chen, P., Qu, B., Hu, Z., & Sillanpää, M. (2016). Concentration, sources, and flux of dissolved organic carbon of precipitation at Lhasa city, the Tibetan Plateau. *Environmental Science and Pollution Research*, 23 (13), 12915-12921. https://doi.org/10.1007/s11356-016-6455-1
- Liu, C. P. & Sheu, B. H., (2003). Dissolved organic carbon in precipitation, throughfall, stemflow, soil solution, and stream water at the Guandaushi subtropical forest in Taiwan. Forest Ecology and Management, 173, 315-325. https://doi.org/10.1016/S0378-1127(01)00793-9
- Meyer, J. L., Mcdowell, W. H., Bott, T. L., Elwood, J. W., Ishizaki, C., Melack, J. M., . . . Rublee, P. A. (1988). Elemental dynamics in streams. *Journal of the North American Benthological Society*, 7, 410-432. http://www.jstor.org/stable/1467299
- Mcdowell, W. H. & Wood, T. (1984). Podzolization: soil processes control dissolved organic carbon concentrations in stream water. Soil Science, 137 (1), 23-32.

- Michalzik, B., Kalbitz, K., Park, J.-H., Solinger, S., & Matzner, E. (2001). Fluxes and concentrations of dissolved organic carbon and nitrogen a synthesis for temperate forests. *Biogeochemistry*, 52 (2), 173–205. https://doi.org/10.1023/a:1006441620810
- Miranda, F. S. M. & Avelar, A., S. (2019). Dynamics of surface organic matter conditioned by topography in the Atlantic Forest of the coastal massif, PARNA-Tijuca, RJ. Revista Brasileira de Geomorfologia, 20 (3), 641-661. https://doi.org/10.20502/rbg.v20i3.1544
- Moyer, R. P., Powell, C. E., Gordon, D. J., Long, J. S., & Bliss, C. M. (2015). Abundance, distribution, and fluxes of dissolved organic carbon (DOC) in four small sub-tropical rivers of the Tampa Bay Estuary (Florida, USA). *Applied Geochemistry*, 63, 550–562. https://doi.org/10.1016/j.apgeochem.2015.05.004
- Neff, J. C.; & Asner, G. P. (2001). Dissolved Organic Carbon in Terrestrial Ecosystems: Synthesis and a Model. *Ecosystems*, 4 (1), 29-48. https://doi.org/10.1007/s100210000058
- Negreiros, A. B. & Coelho Netto, A. N. (2009). Reabilitação funcional de clareira de deslizamento em encosta íngreme no domínio da Floresta Atlântica, Rio de Janeiro (RJ). Revista Brasileira de Geomorfologia, 10 (1), 85-93. https://doi.org/10.20502/rbg.v10i1.120
- Nosrati, K., Govers, G., & Smolders, E. (2012). Dissolved organic carbon concentrations and fluxes correlate with land use and catchment characteristics in a semi-arid drainage basin of Iran. Catena, 95 , 177-183. https://doi.org/10.1016/j.catena.2012.02.019
- Oni, S. K., Futter, M. N., Molot, L. A., Dillon, P. J., (2014). Adjacents catchments with similar patterns of land use and climate have markedly different dissolved organic carbon concentration and runoff dynamics. *Hydrological Processes*, 28 (3), 1436-1449. https://doi.org/10.1002/hyp.9681
- Oliveira, R. R., Záu, A. S, Lima, D. F., Silva, M. B. R., Viana, M. C., Sodré, D. O. & Sampaio, P. D. (1995). Ecological significance of slope orientation in the Tijuca Forest ecosystem (Rio de Janeiro, Brazil). *Oecologia Brasiliensis*, 1 (1), 523-542. https://doi.org/10.4257/oeco.1995.0101.28
- Ovalle, A. R. C. (1985). Geochemical study of fluvial waters of the Upper Rio Cachoeira Basin, Tijuca National Park. Master Thesis in Geochemistry, Fluminense Federal University (UFF).
- Pan, Y., Wang, Y., Xin, J., Tang, G., Song, T., Wang, Y., ... Wu, F. (2010). Study on dissolved organic carbon in precipitation in Northern China. *Atmospheric Environment*, 44, 2350-2357. https://doi.org/10.1016/j.atmosenv.2010.03.033
- Park, J. & Matzner, E. (2003). Controls on the release of dissolved organic carbon and nitrogen from a deciduous forest floor investigated by manipulations of aboveground litter inputs and water flux. *Biogeochemistry*, 66 (3), 265-286. https://doi.org/10.1023/B:BIOG.0000005341.19412.7b
- Pregitzer, K. S. & Euskirchen, E. S. (2004) Carbon cycling and storage in world forests: Biome patterns related to forest age. $Global\ Change\ Biology$, 10, 2052–2077. https://doi.org/10.1111/j.1365-2486.2004.00866.x
- Richter, D. D. & Markewitz, D. (1996). Carbon changes during the growth of loblolly pine on formerly cultivated soil. The Calhoun Experimental Forest, U.S.A. *Advanced Science Institutes Series*, 38, 397-407. https://doi.org/10.1007/978-3-642-61094-3_38
- Roig-Planasdemunt, M., Llorens, P., & Latron, J., (2016). Seasonal and stormflow dynamics of dissolved organic carbon in a Mediterranean mountain catchment (Vallcebre, eastern Pyrenees). *Hydrological Sciences Journal*, 62 (1), 50-63. https://doi.org/10.1080/02626667.2016.1170942
- Schmidt, B.H.M., Wang, C., Chang, S, Matzner, E. (2010). High precipitation causes large fluxes of dissolved organic carbon and nitrogen in a subtropical montane Chamaecyparis forest in Taiwan. Biogeochemistry, 101 (1-3), 243-256. https://doi.org/10.1007/s10533-010-9470-1
- Seekell, D.A., Lapierre, J.F., Ask, J., Bergström, A.K., Deininger, A., Rodríguez, P., Karlsson, J. (2015). The influence of dissolved organic carbon on primary production in northern lakes. *Limnology and Oceanography*

, 60 (4), 1276–1285. https://doi.org/10.1002/lno.10096

Singh, M., Sarkar, B., Biswas, B., Churchman, J., Boland, N. S. (2016). Adsorption-desorption behavior of dissolved organic carbon by soil clay fractions of varying mineralogy. *Geoderma*, 280, 47-56. https://doi.org/10.1016/j.geoderma.2016.06.005

Singh, M., Sarkar, B., Hussain, S., Ok, Y.S., Nanthi S. Bolan, N.S., Churchman, G.J., 2017. Influence of physico-chemical properties of soil clay fractions on the retention of dissolved organic carbon. *Environmental Geochemistry and Health*, 39, 1335–1350. https://doi.org/10.1007/s10653-017-9939-0

Siudek, P., Frankowski, M., & Siepak, J. (2015). Seasonal variations of dissolved organic carbon in precipitation over urban and forest sites in central Poland. *Environment Science Pollution Research*, 22, 11087-11096. https://doi.org/10.1007/s11356-015-4356-3

Toming, K., Kutser, T., Tuvikene, L., Viik, M., & Nõges, T. (2016). Dissolved organic carbon and its potential predictors in eutrophic lakes. *Water Research*, 102, 32–40. https://doi.org/10.1016/j.watres.2016.06.012

Turgeon, J. M. L., Courchesne, F., (2008). Hydrochemical behaviour of dissolved nitrogen and carbon in a headwater stream of the Canadian Shield: relevance of antecedent soil moisture conditions. *Hydrological Processes*, 22 (3), 327-339. https://doi.org/10.1002/hyp.6613

Zhou, W.-J., Sha, L.-Q., Schaefer, D. A., Zhang, Y.-P., Song, Q.-H., Tan, Z.-H., ... Guan, H.-L. (2015). Direct effects of litter decomposition on soil dissolved organic carbon and nitrogen in a tropical rainforest. *Soil Biology and Biochemistry*, 81, 255–258. https://doi.org/10.1016/j.soilbio.2014.11.019

Table 1: Characteristics and antecedent humidity conditions of the analyzed rainfall events

	Rainfall event characteristics	Rainfall event characteristics	Rainfall event characteristics	Rainfa
	Date	volume (mm)	intensity (mm.h ⁻¹)	drough
EV1	27-30/04/16	48.8	0.64	23
EV2	12-20/05/16	176.0	0.94	11
EV3	18-22/07/16	58.4	0.49	22
EV4	31/08-02/09/16	49.7	1.16	05
EV5	12/10/2016	4.9	0.31	01
EV6	12-18/12/2016	100.8	0.84	01
EV7	8-10/02/17	7.2	0.14	04
EV8	14-15/03/17	40.8	1.27	05
Mean	-	60.8	0.72	9.00
SD	-	55.5	0.40	8.90

Table 2: Coefficients of determination (r^2) of the linear regressions between the DOC data in bulk precipitation (dependent variable) against the characteristics and antecedent humidity conditions of the rainfall events (independent variables).

Bulk precipitation DOC concentrations (mg.L ⁻¹)	Bulk precipitation DOC concentrations (mg.L ⁻¹)	Bulk j
Variables	r^2	$\mathbf{r^2}$
Rainfall Volume	0.095	0.095
Rainfall Intensity	0.515^{*}	0.515^{*}
Previous Drought Days	0.034	0.034
AcR 10 days	0.293	0.293
AcR 15 days	0.352	0.352
AcR 30 days	0.143	0.143
RfI x AcR 15 days	0.514	0.514

Bulk precipitation DOC concentrations (mg.L ⁻¹)	Bulk precipitation DOC concentrations (mg.L ⁻¹)	Bulk j
RfV x RfI. x PdD x AcR 15 days	0.760	

Note. AcR: antecedent rainfall; RfI: rainfall intensity; RfV: rainfall volume; PdD: previous drought days.

Regression model significance: absent (non-significant); * (P<0.05); c^{**} (P<0.01); *** (P<0.001).

Table 3: Coefficients of determination (r2) of the linear regressions between the DOC content in throughfall and canopy leachate (dependent variables) against the characteristics and antecedent humidity conditions of the rainfall events (independent variables).

Throughfall	Throughfall	Throughfall	Canopy leachate	Canopy leachate
Variables	r^2	r^2	r^2	$ ightharpoonup^2$
BP DOC	BP DOC	0.890 ***	0.890 ***	0.401
Rainfall Volume	Rainfall Volume	0.087	0.087	0.042
Rainfall Intensity	Rainfall Intensity	0.658 *	0.658 *	0.705 **
Previous Drought Days	Previous Drought Days	0.109	0.109	0.231
AcR 10 days	AcR 10 days	0.510 *	0.510 *	0.670 *
AcR 15 days	AcR 15 days	0.585 *	0.585 *	0.728 **
AcR 30 days	AcR 30 days	0.186	0.186	0.172
RfI x AcR 15d	RfI x AcR 15d	$0.787\ ^*$	0.787 *	0.905 **
BP DOC x RfI x AcR 15d	BP DOC x RfI x AcR 15d	0.983 ***	0.983 ***	-

Note. BP: bulk precipitation; DOC: dissolved organic carbon; AcR: antecedent rainfall; RfI: rainfall intensity; RfV: rainfall volume; PdD: previous drought days.

Regression model significance: absent (non-significant: P>0.05); * (P<0.05); ** (P<0.01); *** (P<0.001).

Table 4: Coefficients of determination (r^2) of the linear regressions between the DOC content in under-litter and litter leachate (dependent variables) against the characteristics and antecedent humidity conditions of the rainfall events (independent variables).

	Under-litter	${\bf Under\text{-}litter}$	Litter leachate	Litter leachate
Variables	Variables	$\mathbf{r^2}$	r^2	$ ightharpoonup^2$
TF DOC	TF DOC	0.414	0.414	0.011
Rainfall Volume	Rainfall Volume	0.004	0.004	0.089
Rainfall Intensity	Rainfall Intensity	0.324	0.324	0.021
Previous Drought Days	Previous Drought Days	0.010	0.010	0.012
AcR 10 days	AcR 10 days	0.451	0.451	0.122
AcR 15 days	AcR 15 days	0.283	0.283	0.017
AcR 30 days	AcR 30 days	0.125	0.125	0.021
RfI x AcR10 days	RfI x AcR10 days	0.499	0.499	0.127

Note. TF: throughfall; DOC: dissolved organic carbon; AcR: antecedent rainfall; RfI: rainfall intesity. Regression model significance: absent (non-significant); * (P<0.05); *** (P<0.01); **** (P<0.001).

Table 5: Soil solution and stream water DOC concentrations at each rainfall event and values of difference between depths at different hillslope positions for the soil solution values.

		DOC con-	DOC con-	DOC con-	DOC con-	DOC con-	DOC con-	DOC con-	DOC con-
		cen- tra- tion (mg.L ⁻¹)	cen- tra- tion $(mg.L^{-1})$	cen- tra- tion $(mg.L^{-1})$	cen- tra- tion $(mg.L^{-1})$	cen- tra- tion $(mg.L^{-1})$	cen- tra- tion $(mg.L^{-1})$	cen- tra- tion $(mg.L^{-1})$	cen- tra- tion (mg.L ⁻¹)
Hillslope posi- tion	Soil depth	EV1	EV2	EV3	EV4	${ m EV5}$	EV6	EV7	EV8
Summit	$50~\mathrm{cm}$	37.42	44.49	32.16	42.26	30.21	28.64	40.21	35.05
	$100~\mathrm{cm}$	29.11	32.02	19.35	34.53	25.19	24.32	28.62	18.94
	Δ 0-50 cm	4.70	13.06	8.57	-11.09	13.04	7.12	19.64	-9.04
	Δ 50-100 cm	8.30	12.47	12.81	7.73	5.02	4.32	11.59	16.11
Valley	50 cm	14.83	17.74	19.06	13.01	11.82	11.80	23.13	7.44
Bottom	$100~\mathrm{cm}$	19.32	19.80	9.72	31.35	7.41	18.09	12.61	18.04
	Δ 0-50 cm	17.54	21.06	11.40	9.50	18.60	17.54	38.79	11.14
	Δ 50-100 cm	-4.49	-2.06	9.34	-18.34	4.41	-6.29	10.52	-10.60
Stream water		1.96 ± 0.2	1.66 ± 0.4	2.05 ± 0.4	1.68 ± 0.4	1.7 ± 0.3	1.82 ± 0.4	2.16 ± 0.7	1.45 ± 0.5

Note. DOC: dissolved organic carbon.

Table 6: Coefficients of determination (r^2) of the linear regressions between the DOC content in stream water and difference between depths for the soil solution (dependent variables) against the precipitation intensity (independent variable).

		Hillslope positions	Hillslope positions	Hillslope positions	Hills
Variable Precipitation intensity	Soil depth	Summit r ²	Summit r ²	Valley Bottom r ²	$ \begin{array}{c} \text{Valle} \\ \text{r}^2 \end{array} $
	$\begin{array}{c} \Delta \text{ DOC 0-50 cm} \\ \Delta \text{ DOC 50-100 cm} \end{array}$	Δ DOC 0-50 cm Δ DOC 50-100 cm	0.703** 0.062	0.703** 0.062	0.454 0.786

Note. DOC: dissolved organic carbon.

Regression model significance: absent (non-significant: P>0.05); * (P<0.05); ** (P<0.01); *** (P<0.001).

Figure 1: Location and Digital Terrain Model (DTM - from LiDAR mapping) of the southern hillslope of Archer Hill and sample areas: Summit (SMT); Upper Hillslope (UHS); Lower Hillslope (LHS); Valley Bottom (VBT).

Figure 2: Mean values of annual litterfall (n = 5) and litter stock above ground (n = 6) for each slope position. Significant difference: non-significant (ns); *** (P <0.001). The letters indicate variant groups by the Dunn's test. Decomposition coefficient (k') of Olson (1963). Adapted from Miranda and Avelar (2019).

Figure 3: Instruments for water sampling from different forest compartments.

Figure 4: Average monthly precipitation over 18-years and for 2016-2017 hydrological year (a); and daily precipitation for 2016-2017 hydrological year showing the eight sampled rainfall events (b).

Figure 5: Dissolved organic carbon (DOC) content in above-ground compartments in each rainfall event (n = 20). Bi-factorial ANOVA (temporal variation) for each compartment: ns (non-significant); * (p<0.05); *** (P<0.01); **** (P<0.001). Letters indicate the variant data-groups by the Dunn's test (P < 0.05): lowercase for the field-values (throughfall and under-litter); uppercase for leaching-values (canopy and litter leachates).

Figure 6: Content of dissolved organic carbon (DOC) in each compartment at different hillslope positions (n = 40, except for UL and LL, which had n = 36). Bi-factorial ANOVA (spatial variation) for each compartment: ns (non-significant); * (p<0.05); *** (P<0.01); **** (P<0.001). Letters indicate the variant data-groups by the Dunn's test (P < 0.05): lowercase for the field-values (throughfall and under-litter); uppercase for the leaching-values (canopy and litter leachates). DOC: dissolved organic carbon. TF: throughfall. CL: canopy leachate. UL: under-litter. LL: litter leachate.

Figure 7: DOC concentrations (under-litter and litter leachate) in the different hillslope positions in each event analyzed. Kurskal-Wallis variance analysis: ns (non-significant); * (p <0.05); *** (P <0.01); *** (P <0.001). Letters indicate the variant data-groups by the Dunn's test (P < 0.05): lowercase for the field-values (under-litter); uppercase for the leaching-values (litter leachate).

Figure 8: Scatter plots and second-degree regression of dissolved organic carbon (DOC) under-litter and litter leachate against litter stocks and decomposition coefficients (k') of each hillslope position.















