DOC Transport and Export in a Dynamic Tropical Catchment

Article *in* Journal of Geophysical Research: Biogeosciences · June 2019

DOI: 10.1029/2018JG004897

19 authors, including:

Ricardo Sánchez-Murillo
National University of Costa Rica

Luis G. Romero
Costa Rican Institute of Technology (ITCR)

Joaquín Jiménez Antillón
Costa Rican Institute of Technology (ITCR)

Germain Esquivel Hernández
National University of Costa Rica

JGR Biogeosciences

RESEARCH ARTICLE
10.1029/2018JG004897

Special Section:
Biogeochemistry of Natural Organic Matter

Key Points:
- Rapid (on average ~1.25 hr) allochthonous DOC transport during storm flows
- Storm flows contributed 62.2% to the annual DOC export in 14 events
- Novel data to validate global DOC models in climate sensitive hot spots

Supporting Information:
- Supporting Information S1
- Data Set S1
- Data Set S2
- Data Set S3

Correspondence to:
R. Sánchez-Murillo,
ricardo.sanchez.murillo@una.cr

Citation:
Sánchez-Murillo, R., Romero-Esquivel, L. G., Jiménez-Antillón, J., Salas-Navarro, J., Corrales-Salazar, L., Álvarez-Carvajal, J., et al. (2019). DOC transport and export in a dynamic tropical catchment. *Journal of Geophysical Research: Biogeosciences*, *124*. https://doi.org/10.1029/2018JG004897

Received 27 OCT 2018
Accepted 22 MAY 2019
Accepted article online 7 JUN 2019

Author Contributions:
Conceptualization: R. Sánchez-Murillo, J. Salas-Navarro, L. Corrales-Salazar
Data curation: R. Sánchez-Murillo, L. G. Romero-Esquivel, J. Jiménez-Antillón, J. Álvarez-Carvajal, S. Álvarez-McInerney, D. Bonilla-Barrantes, N. Gutiérrez-Sibaja, M. Martínez-Arroyo, E. Ortiz-Apuy, J. Salgado-Lobo, J. Villalobos-Morales, O. Vargas-Gutiérrez
Formal analysis: R. Sánchez-Murillo, L. G. Romero-Esquivel, J. Jiménez-Antillón, J. Salas-Navarro, L. Corrales-Salazar, J. Álvarez-Carvajal, S. Álvarez-McInerney, D. Bonilla-Barrantes, N.
(continued)

DOC Transport and Export in a Dynamic Tropical Catchment

R. Sánchez-Murillo[1,2], L. G. Romero-Esquivel[3], J. Jiménez-Antillón[3], J. Salas-Navarro[1,2], L. Corrales-Salazar[1], J. Álvarez-Carvajal[2], S. Álvarez-McInerney[2], D. Bonilla-Barrantes[2], N. Gutiérrez-Sibaja[2], M. Martínez-Arroyo[2], E. Ortiz-Apuy[2], J. Salgado-Lobo[2], J. Villalobos-Morales[2], G. Esquivel-Hernández[1,2], L. D. Rojas-Jiménez[4], C. Gómez-Castro[4], Q. Jiménez-Madrigal[4], O. Vargas-Gutiérrez[5], and C. Birkel[6]

[1]Stable Isotope Research Group, School of Chemistry, Universidad Nacional, Heredia, Costa Rica, [2]Chemistry School, Universidad Nacional, Heredia, Costa Rica, [3]Environmental Protection Research Center, School of Chemistry, Instituto Tecnológico, Cartago, Costa Rica, [4]Empresa de Servicios Públicos de Heredia (ESPH), Heredia, Costa Rica, [5]Natural Resources Laboratory, Agronomical Research Center, Universidad de Costa Rica, San Pedro, Costa Rica, [6]Department of Geography and Water and Global Change Observatory, University of Costa Rica, San José, Costa Rica

Abstract Dissolved organic carbon (DOC) transport and export from headwater forests into freshwaters in highly dynamic tropical catchments are still understudied. Here we present a DOC analysis (2017) in a pristine and small (~2.6 km^2) tropical catchment of Costa Rica. Storm flows governed a rapid surface and lateral allochthonous DOC transport (62.2% of the annual DOC export). Cross-correlation analysis of rainfall and stream discharge indicated that DOC transport occurred on average ~1.25 hr after the rainfall maxima, with large contributions of event water, ranging from 42.4±0.3% up to 98.2±0.3% of the total discharge. Carbon export flux (annual mean=6.7±0.1 g C · m^{-2} · year^{-1}) was greater than values reported in subtropical and temperate catchments. Specific ultraviolet absorbance indicated a mixture of hydrophobic humic and hydrophilic nonhumic matter during both baseflow and storm events. Our results highlight the rapid storm-driven DOC transport and export as well as low biogeochemical attenuation during baseflow episodes in a climate sensitive hot spot. By understanding the key factors controlling the amount of organic carbon transported to streams in dynamic tropical landscapes, better global- and catchment-scale model assessments, conservation practices, and water treatment innovations can be identified.

Plain Language Summary Humid tropical forests represent ~20% of the global soil organic matter reservoirs. Nutrient availability coupled with transport and export of dissolved organic carbon (DOC) from forests into freshwater ecosystems is still poorly understood in the tropics. Here we present a study of DOC dynamics in a humid tropical catchment of central Costa Rica. Overall, DOC was transported from the forest to the stream on average within ~1.25 hr after large rainfall events. Storm flows were dominated by event water (recent rainfall) in the catchment. Fluvial carbon flux exported from the catchment was estimated at 6.7±0.1 g C · m^{-2} · year^{-1}. Our results highlight the rapid DOC transport and export during storm flows as well as low biodegradation during baseflow episodes. These findings may contribute to improve model calibration and validation considering the limited high-resolution DOC data in dynamic tropical landscapes.

1. Introduction

Biogeochemical characteristics of soils coupled with climate conditions play a remarkable role in controlling hydrological responses (i.e., storage and release of water and solutes; McDowell & Asbury, 1994) in tropical forested ecosystems. Global carbon models (based on net primary productivity scenarios) posed humid tropical forests as hot spots of soil organic carbon (SOC) vulnerability considering the potential intensification of rainfall and temperature regimes, and consequently, acceleration of SOC degradation, transport, and export (Köchy et al., 2015; Schmidt et al., 2011). However, the mechanisms governing storage, transport, and export of organic matter from headwater forested ecosystems to lowlands remain poorly understudied in highly dynamic tropical regions (Butman et al., 2015; Masese et al., 2017; Pesántez et al., 2018). In particular, high-resolution sampling comprising storm and baseflow events is often scarce, which, in turn, limits fluvial carbon budget estimations worldwide.

Gutiérrez-Sibaja, M. Martínez-Arroyo, E. Ortiz-Apuy, J. Salgado-Lobo, J. Villalobos-Morales
Funding acquisition: R. Sánchez-Murillo
Investigation: R. Sánchez-Murillo, L. G. Romero-Esquivel, J. Salas-Navarro, L. Corrales-Salazar, G. Esquivel-Hernández
Methodology: R. Sánchez-Murillo, L. G. Romero-Esquivel, J. Jiménez-Antillón, J. Álvarez-Carvajal, S. Álvarez-McInerney, D. Bonilla-Barrantes, N. Gutiérrez-Sibaja, M. Martínez-Arroyo, E. Ortiz-Apuy, J. Salgado-Lobo, J. Villalobos-Morales
Project administration: R. Sánchez-Murillo
Resources: R. Sánchez-Murillo, L. G. Romero-Esquivel
Supervision: R. Sánchez-Murillo
Validation: J. Jiménez-Antillón
Visualization: R. Sánchez-Murillo
Writing - original draft: R. Sánchez-Murillo, L. G. Romero-Esquivel, J. Jiménez-Antillón, J. Salas-Navarro, L. Corrales-Salazar, J. Álvarez-Carvajal, S. Álvarez-McInerney, D. Bonilla-Barrantes, N. Gutiérrez-Sibaja, M. Martínez-Arroyo, E. Ortiz-Apuy, J. Salgado-Lobo, J. Villalobos-Morales, G. Esquivel-Hernández, L. D. Rojas-Jiménez, C. Gómez-Castro, Q. Jiménez-Madrigal, O. Vargas-Gutiérrez
Writing – review & editing: R. Sánchez-Murillo, L. G. Romero-Esquivel, J. Jiménez-Antillón, J. Salas-Navarro, L. Corrales-Salazar, J. Álvarez-Carvajal, S. Álvarez-McInerney, D. Bonilla-Barrantes, N. Gutiérrez-Sibaja, M. Martínez-Arroyo, E. Ortiz-Apuy, J. Salgado-Lobo, J. Villalobos-Morales, G. Esquivel-Hernández, L. D. Rojas-Jiménez, C. Gómez-Castro, Q. Jiménez-Madrigal, O. Vargas-Gutiérrez

Soils in the humid tropics are characterized by high concentrations of iron and aluminum oxides, low pH, and relatively large porosities and water contents. These factors have a great influence on the ability to store SOC (Dubinsky et al., 2010) and on the bioavailability of organic matter related-nutrients (i.e., N, P, and trace elements) in aquatic food webs (Brandão et al., 2018). In such ecosystems, rainfall seasonality has been identified as one of the main drivers of allochthonous carbon transport to aquatic environments (Osburn et al., 2018; Suhett et al., 2007). Exported DOC (ranging from ~1.1-2.7 Pg C/year from terrestrial ecosystems to inland waters and oceans; Aufdenkampe et al., 2011; Regnier et al., 2013¸ Khadka et al., 2014) is further decomposed (both biologically and photochemically) to CO_2 (~1.2 Pg C/year) downstream from the headwater forests and can be easily degassed within the surface water network before even reaching the coastal regions. A portion (~0.6 Pg C/year) is stored as sediments in inland waters, and finally ~0.9 Pg C/year is released to the oceans (Aufdenkampe et al., 2011). Hereby, wetlands play a remarkable role in controlling carbon sequestration (Aiken & Cotsaris, 1995; Cook et al., 2017; Dittmar et al., 2006; Moyer et al., 2015) from inland sources. Overall, half of the carbon exported from inland waters reaches the oceans as organic molecules (Aarnos et al., 2018; Battin et al., 2009). Therefore, quantification of riverine carbon fluxes from dynamic tropical forests may contribute to (a) validate global predictions and (b) reduce uncertainties of carbon sequestration estimates under different climate change scenarios (Shih et al., 2018; Tranvik et al., 2018).

SOC and DOC transport/export studies have been limited in Costa Rica, and in general, in the high elevation forests across the tropics. Grieve et al. (1990) in a pioneering work, reported an increased trend in the organic matter content from 18 to 49% in a transect from 100 to 2,600 m above sea level (asl), coupled with a decreased trend in clay content (from 80 to 10%) and free iron ratio (from 0.3 to 0.1) in central Costa Rica, indicating a clear potential of SOC reservoirs in high-elevation landscapes. More recently, Osburn et al. (2018) quantified the quality and fluxes of DOC during storm and base flows for two locations in a tropical rainforest in northeastern Costa Rica. The authors determined one of the largest DOC export fluxes in a forested tropical catchment (13.79 ± 2.07 g C · m^{-2} · year^{-1}). Contrary to the latter findings, Pesántez et al. (2018) reported that changes in land cover and use are the most important predictor of DOC concentrations in high-elevation ecosystems of Ecuador, with minimal influence of precipitation conditions. Table 1 shows a summary of DOC export fluxes in a wide range of tropical, temperate, arctic, and large river systems across the globe for comparison purposes. Commonly, headwater catchments in the tropics exhibited a large potential to export greater amounts of DOC when compared to less dynamic landscapes in temperate or artic regions, which emphasizes the need to improve DOC and fluvial carbon flux assessments in well-known sensitive ecosystems in the tropics under the premise of future rainfall/temperature spatio-temporal changes.

In this paper we focus on the seasonal changes (baseflow and storm events) of DOC in a pristine and small (~2.6 km^2) humid forested catchment of central Costa Rica to assess the governing mechanisms on DOC variability. High-resolution (15-30 min) hydro-meteorological data (i.e., stream discharge, rainfall, and soil conditions) were combined during a hydrological year with baseflow and stormflow DOC sampling, soil characterization, isotope hydrograph separation and mean transit times, and weekly physical and chemical stream water characteristics to evaluate two fundamental research questions for tropical regions: (1) to what extent does event or preevent water and biogeochemical processes govern DOC transport and export? and (2) what is the discharge-weighted carbon annual flux and how much is contributed by baseflow and storm events?

We hypothesize that (a) DOC is largely and rapidly transported during large rainfall events with minimal biogeochemical attenuation during intermittent baseflow episodes and (b) dynamic headwater tropical catchments may contribute large amounts of organic matter to lowland freshwater ecosystems during rapid pulses. Our results provide high-resolution evidence (from local to global) to validate coupled DOC-hydrological modeling at the catchment scale (Birkel et al., 2017) and may improve spatial distributions of global riverine DOC yields (Li et al., 2019) for the Mesoamerican region.

2. Materials and Methods

2.1. Study Area Description

This study was conducted at the Wildlife Refuge Cerro Dantas located within the Braulio Carrillo National Park, on the Caribbean slope of central Costa Rica (Figure 1a). Cerro Dantas is part of the Barva volcano

Table 1
Riverine DOC Export Flux Comparison Including Tropical, Temperate, Arctic, and Large River Systems

Site	DOC export flux (g C · m^{-2} · $year^{-1}$)	Reference
Tropics		
Awout River, Cameroon	7.93	Brunet et al. (2009)
Arboleda, Costa Rica	13.80	Osburn et al. (2018)
Taconazo, Costa Rica	2.62	Osburn et al. (2018)
R. Tempisquito, Costa Rica	3.70	Newbold et al. (1995)
Q. Toronja, Puerto Rico	3.30	Aitkenhead and McDowell (2000)
Río Isocacos, Puerto Rico	9.40	Aitkenhead and McDowell (2000)
Juruena headwaters, Brazil	3.15	Johnson et al. (2006)
Capesterra, French West Indies	5.70	Lloret et al. (2011)
Waikulu Stream, Hawaii, USA	0.83	Wiegner et al. (2009)
Waikulu River, Hawaii, USA	1.28	Wiegner et al. (2009)
Quebrada Grande, Costa Rica	6.7±0.1	*This study*
Temperate and Arctic		
Lena River, Russia (Arctic)	2,93	Raymond et al. (2007)
Yukon River, Canada and AK, USA (Arctic)	2,60	Raymond et al. (2007)
Deer Creek, CO, USA.	2.20	Brooks et al. (1999)
Wild River at Gilead, ME, USA	4.80	Raymond and Saiers (2010)
Satellite Branch, North Carolina, USA	0.74	Mulholland (1997)
Big Elk Creek, Maryland	1.80	Dhillon and Inamdar (2013)
Oberer Seebach, Austria	4.01	Fasching et al. (2015)
Large rivers		
Amazon	4.40	Raymond and Spencer (2015)
Congo	3.40	Raymond and Spencer (2015)
Essequibo	5.40	Raymond and Spencer (2015)
Mekong	1.40	Raymond and Spencer (2015)
Fly	8.60	Raymond and Spencer (2015)
Orinoco	4.50	Raymond and Saiers (2010)
Paraná	2.10	Raymond and Saiers (2010)
Global mean	1.08	Li et al. (2019)

Note. Global DOC export mean is also included as a reference (Li et al., 2019).

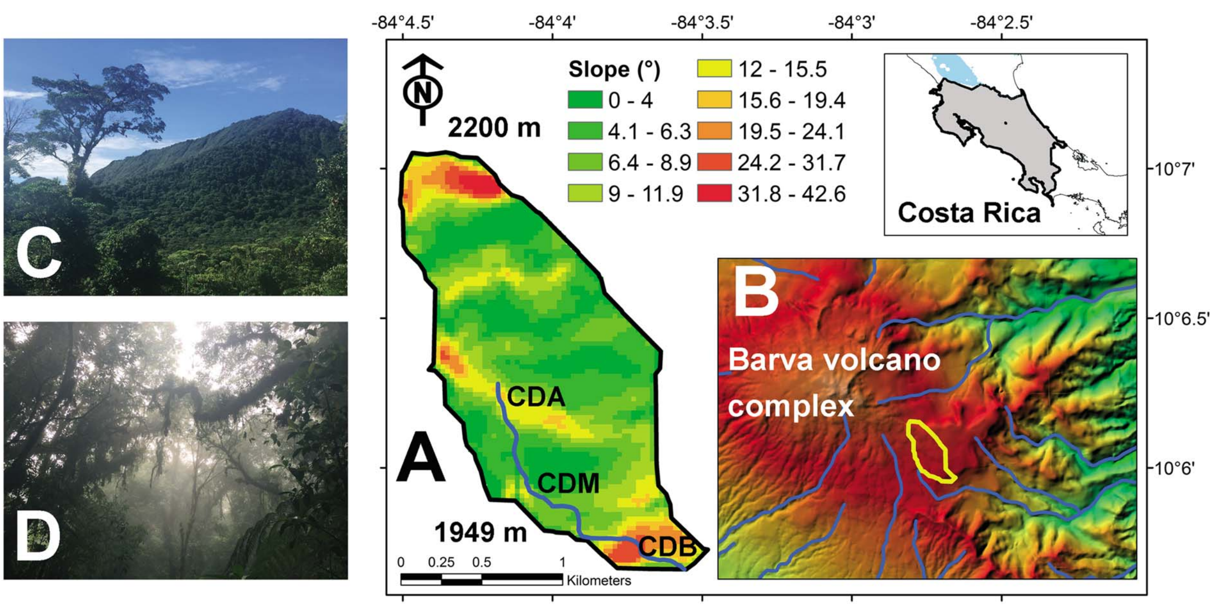

Figure 1. Study area. (a) Quebrada Grande (2.6 km^2) catchment including sampling site locations (CDA, CDM, and CDB); hydrometric data, dissolved organic carbon, and stable isotope samples were collected near CDB. Catchment slope (in degrees) is color-coded. The upper-left inset shows the location of study site in central Costa Rica. (b) Quebrada Grande is located within the Barva volcano edifice. The catchment (yellow bold line) drains to the Caribbean basin within a relative complex topography. (c and d) Photographs showing the typical aspect of this mixed primary and secondary forested catchment.

edifice, and the parental material is primordially basaltic and andesitic volcanic rocks (Figure 1b; Sánchez-Murillo et al., 2016). Quebrada Grande is a small (2.6 km^2) and mixed primary and secondary forested catchment with minimum anthropogenic activity in the last 100 years. Catchment elevation ranges from 1,949 up to 2,200 m asl with relative steep slopes (up to 43°; Figure 1a). The area is part of the Payment for Environmental Services (i.e., payment for forest conservation and ecosystem services) scheme of a local drinking water operator (Arriagada et al., 2015; Berbés-Blázquez et al., 2017; Wallbott et al., 2019).

2.2. Vegetation Characteristics

Quebrada Grande is categorized as a premontane rainforest catchment comprising mostly secondary forest (70-80 years old) with few reminiscences of relict primary forest (>100 years old) within the riparian zones and the highest portion of the catchment; Figure 1c). This type of forest is also under the influence of excessive humidity, partially due to the influence of the Caribbean trade winds rainfall regime (Sánchez-Murillo & Birkel, 2016) and strong orographic effects. The canopy reaches 25-30 m in height and intermingle with the middle stratum, which is the product of the large number of epiphytes of different groups (i.e., mosses, ferns, orchids, bromeliads, and ericaceae; Figure 1d). The understory is mostly dominated by palms and bamboo.

2.3. Hydrometeorological Data

Stream discharge and climate conditions were analyzed to better understand the biogeochemical response of the catchment during a hydrological year. Hydrometeorological and soil conditions (30-min resolution) were recorded with a Vantage Pro2 weather station (Davis Instruments, USA) installed since October 2015. Using the sudden salt injection method (volume used= 1-2 L; electrical conductivity [EC]~130,000 μS/cm; Moore, 2005; Richardson et al., 2017), weekly discharge measurements (i.e., during baseflow and storm events) were conducted for over 2 years to establish a robust rating curve. The mountainous nature of the stream (with abrupt channel and riparian slopes, large cobbles, high flow debris, and low EC) limits the use of digital or propelled flowmeters. Stream height (m) variations were measured every 15 min with a AS950 pressure transducer (Hach, USA). Stream heights were converted to discharge values (m^3/s) using a best fit exponential equation (y=1.77$e^{0.09x}$; r^2=0.87). Weekly instantaneous measurements of stream height were also conducted to calibrate the pressure transducer (±0.1 cm) if required. A cross-correlation analysis between rainfall and stream discharge was applied to determine the stream lag time response to rainfall events using the statistical programming language R (R Core Team, 2014).

2.4. Stream Monitoring

Stream chemistry was measured to analyze the effects of DOC inputs during baseflow and storm events to the aquatic chemistry. Weekly pH, EC (μS/cm), oxidation-reduction potential (ORP, mV), and stream temperature (°C) were measured during 2017 using a HI98194 multiparameter sonde (Hanna Instruments, USA). Routinely laboratory and filed electrode calibrations were carried out using certified standard solutions for pH (buffers: 4.0, 7.0, and 10.0), EC (84 and 1,413 μS/cm), and ORP (470 and 240 mV). Stream temperature (±0.01 °C) was also recorded continuously (15-min resolution) using a AS950 sensor (Hach, USA).

2.5. Rainfall and Stream Stable Isotope Sampling

Stable isotope hydrograph separation and mean transit times were computed to assess the role of preevent (old water) versus event water (new water) on DOC transport and export. Daily rainfall (N=242) was collected during 2017 using a passive collector (Palmex Ltd., Croatia; Gröning et al., 2012). Samples were filtered using a Midisart PTFE (polytetrafluorethylene) 0.45-μm syringe membrane (Sartorius AG, Germany), transferred to 30-ml HDPE (high-density polyethylene) vials, and stored at 5°C until analysis. Weekly stream samples (N=52) were collected using 30-ml HDPE (high-density polyethylene) bottles. Samples were filtered using a Midisart PTFE (polytetrafluorethylene) 0.45-μm syringe membrane (Sartorius AG, Germany) and stored at 5°C until analysis.

Stable isotope analysis was conducted at the Stable Isotope Research Group facilities of the Universidad Nacional of Costa Rica using a Cavity Ring Down Spectroscopy water isotope analyzer L2120-*i* (Picarro, USA) and a water isotope analyzer LWIA-45P (Los Gatos Research Inc., USA). The secondary standards were Moscow Tap Water, MTW (δ^2H = −131.4 ‰, $\delta^{18}O$ = −17.0 ‰), Deep Ocean Water, DOW (δ^2H = −1.7 ‰, $\delta^{18}O$ = −0.2 ‰), and Commercial Bottled Water, CAS (δ^2H = −64.3 ‰, $\delta^{18}O$ = −8.3 ‰). MTW and DOW standards were used to normalize the results to the VSMOW2-SLAP2 scale, while CAS was used as a quality control and drift control standard. The analytical long-term uncertainty was ± 0.5 (‰; 1σ) for δ^2H and ± 0.1 (‰; 1σ) for δ^{18}O (Ramírez-Leiva et al., 2017). Stable isotope compositions are presented in delta notation δ (‰, per mil), relating the ratios (R) of $^{18}O/^{16}O$ and $^2H/^1H$, relative to Vienna Standard Mean Ocean Water (V-SMOW).

The contribution of event water contributions to the total discharge was calculated as follows:

$$Q_n = \frac{Q_s(\delta_s - \delta_o)}{(\delta_n - \delta_o)}$$

where Q_n and Q_s are the new water and total discharge. δ_s, δ_o, and δ_n correspond to the isotopic composition of the stream, old water (baseflow), and rainfall (new water). Stream isotopic composition before each rainfall event was selected as baseflow (preevent water) based on the hydrograph. Nonstationary (Birkel et al., 2011) MTT reflects a proxy for the average water velocity in transit time distributions (McDonnell & Beven, 2014). The MTT was calculated using a lumped convolution integral and an exponential distribution as transfer function following Sánchez-Murillo et al. (2015).

2.6. DOC Sampling and DOC Quality

Stream samples for DOC and optical properties of the dissolved organic matter (DOM) analysis were collected during baseflow (N=22) and storm events (N=14) from the beginning of May 2017 to the end of November 2017. Stream samples were classified as baseflow or storm events based on the hydrograph and prevailing rainfall conditions in the catchment. Stream samples were collected in precleaned 1-L HDPE bottles. Bottles were rinsed at least two times with stream water before collection. Samples were filtered within 6 hr using 0.45-μm cellulose filter into 250-ml precleaned bottles and stored at -10°C until analysis. Prior to analysis, samples were thawed to room temperature and each sample was properly mixed with no significant precipitates observed.

Chromophoric dissolved organic matter (CDOM) absorbance at 254 nm (A_{254}, m^{-1}) was measured (Method 5910B; American Public Health Association (APHA), 2005) using a UV-1800 ENG120V spectrophotometer (Shimadzu Corp., Japan). After the optical measurements were performed, samples were transferred to precleaned glass vials and acidified with 85% phosphoric acid to a pH ~2 for DOC analysis. DOC concentration was measured using a Fusion Total Organic Carbon Analyzer (Teledyne Tekmar, USA). A standard curve for DOC was conducted using seven calibration solutions (i.e., stock solution of anhydrous primary-standard-grade potassium biphthalate, $C_8H_5KO_4$) ranging from 0 to 10 mg C/L (Method SM5310 C; APHA, 2005). The quantification and detection limits were 0.05 and 0.03 mg C/L. A certified standard of 2.0 mg C/L was used as a quality and drift control during the analysis. The standard deviation of the results varied from 0.02 up to 0.3 mg C/L. The A_{254}/DOC ratio (i.e., the specific UV absorption known as $SUVA_{254}$) was calculated to evaluate the presence of aromatic groups (Weishaar et al., 2003) in the DOM. Samples were analyzed at the Research Center of Environmental Protection (CIPA) of the Instituto Tecnológico de Costa Rica (Cartago, Costa Rica).

Mean annual carbon flux (g C · m^{-2} · year^{-1}) was calculated following Osburn et al. (2018). Here the annual export is calculated using the annual stream discharge and discharge-weighted mean DOC composition in the stream water. Empirical DOC and discharge relationship was simulated using a best fit parsimonious (3-parameter) hyperbola equation (r^2=0.49) as follows:

$$DOC_{sim} = DOC_o + \frac{aQ}{b + Q}$$

where DOC_{sim} corresponds to the simulated concentration, DOC_o represents baseflow DOC (2.93 mg/L), a (3.33) and b (0.11) are fitting parameters, and Q is the known stream discharge. Error propagation in MTT, event water contributions, and annual carbon flux was estimated using the root mean square method (Topping, 1972).

2.7. Soil Sampling and Analysis

Soil sampling sites were selected at top (CDA), middle (CDM), and bottom (CDB) catchment sites, across a hillslope transect from 1,949 up to 1,996 m asl. Approximately 2 kg of soil in sterile plastic bags and undisturbed triplicate soil core cylinders (diameter=5.18 cm and height=4.92 cm) were collected using small augers for chemical and physical analyses. Samples were transported within 8 hr to the laboratory facilities. Soil texture (ASTM: D 422-63), volumetric water content (ASTM: D 6780-02), and hydraulic conductivity (ASTM: D 5084-00) were measured at the Chemistry School of the Universidad Nacional (Heredia, Costa Rica), while soil pH (ASTM: D 4972-13), soil acidity (United States Department of Agriculture (USDA). Soil Survey Staff, 2014; in cmol/L), total soil carbon and nitrogen content (United States Department of Agriculture (USDA). Soil Survey Staff, 2014; in %), major cations (Ca, Mg, and K; United States Department of Agriculture (USDA). Soil Survey Staff, 2014; in cmol (+)/L), and other nutrients (P, Fe, Zn, Cu, Mn, Al; United States Department of Agriculture (USDA). Soil Survey Staff, 2014; in mg/L and g/kg) were analyzed at the Soil and Foliar Laboratory, Agronomical Research Center, Universidad de Costa Rica (San José, Costa Rica), and the Chemical Services Laboratory, Universidad Nacional (Heredia, Costa Rica). C/N ratios and the percentage of organic matter were also estimated.

3. Results

3.1. Hydro-meteorological Conditions

The rainfall regime in Quebrada Grande was characterized by heavy cumulative rainfall throughout the year (5,465 mm; Figure 2a). Monthly rainfall ranged from 178 mm (February) to 767 mm (December). Maximum daily rainfall ranged from 31.2 to 250.0 mm, with an average rainfall intensity of 2.42 mm/min. Ambient temperature ranged between 24.0 and 6.7 °C (Figure 2b), with a mean annual value of 15.2 °C. Relatively low temperatures denoted the influence of cold fronts between mid-November and February. Relative humidity was consistently high with a mean value of 97%. Overall, the abundant rainfall turns Quebrada Grande catchment in a highly dynamic system with recurrent high flows, near-saturated soils, and a shallow water table throughout the year.

Storm flows were characterized by large debris and cobbles transported along with a notable yellow/light brown pigmentation of the stream water. Stream temperature fluctuated between 10.4 and 16.8 °C, with a mean value of 14.1°C (Figure 2b). Quebrada Grande discharge ranged from 0.12 to 6.13 m^3/s (Figure 2c). A cross-correlation analysis between rainfall and stream discharge indicated that storm flows likely occurred on average within ~1.25 hr after the rainfall maxima (Figure 2d).

3.2. Isotope Hydrograph Separation and MTTs

The isotopic composition exhibited a bimodal pattern (W-mode type) throughout the year (Figure 2c). The latter is consistent with the pronounced intraseasonal oscillation modes of Central America rainfall that result in two or three depleted excursions during the wet season (May-November) and two enriched pulses during the Mid-summer drought (July-August) and the months of the strongest northeasterly trade winds (January-February; Sánchez-Murillo & Birkel, 2016). Rainfall isotope modes define the input composition into the catchment, whereas stream isotope pulses denote how the water and solutes are stored and released. The water isotope estimations and inferences provided knowledge on DOC water sources and potential transport flow paths.

Stream isotopic composition clearly depicted the isotopic variations in the rainfall modes (Figure 2c). Catchment processes such as infiltration and mixing with previous isotopic conditions resulted in a relative attenuation of the stream isotopic response. The event water contributions (catchment MTT=3.2±0.5 months) during storm flows ranged from 42.4±0.3% up to 98.2±0.3% (e.g., tropical storm Nate event; 4-5 October 2017; 314 mm in 48 hr). Consistent near-saturated soils promoted a rapid transport of a combined throughfall and soil DOC to the stream network.

3.3. Stream and Soil Chemistry Characteristics

Stream water commonly exhibited acidic (mean pH=5.96), low conductivity (mean EC=8.0 μS/cm), well oxygenated (mean DO=7.1 mg O_2/L), and oxic (mean OR212 mV) conditions (Figures 3a-3c). In summary, stream water revealed natural conditions of a headwater tropical catchment with turbulent mixing, whereby water-rock transit times are short, and soil and vegetation leachates mainly control the aquatic chemistry (da Costa et al., 2017).

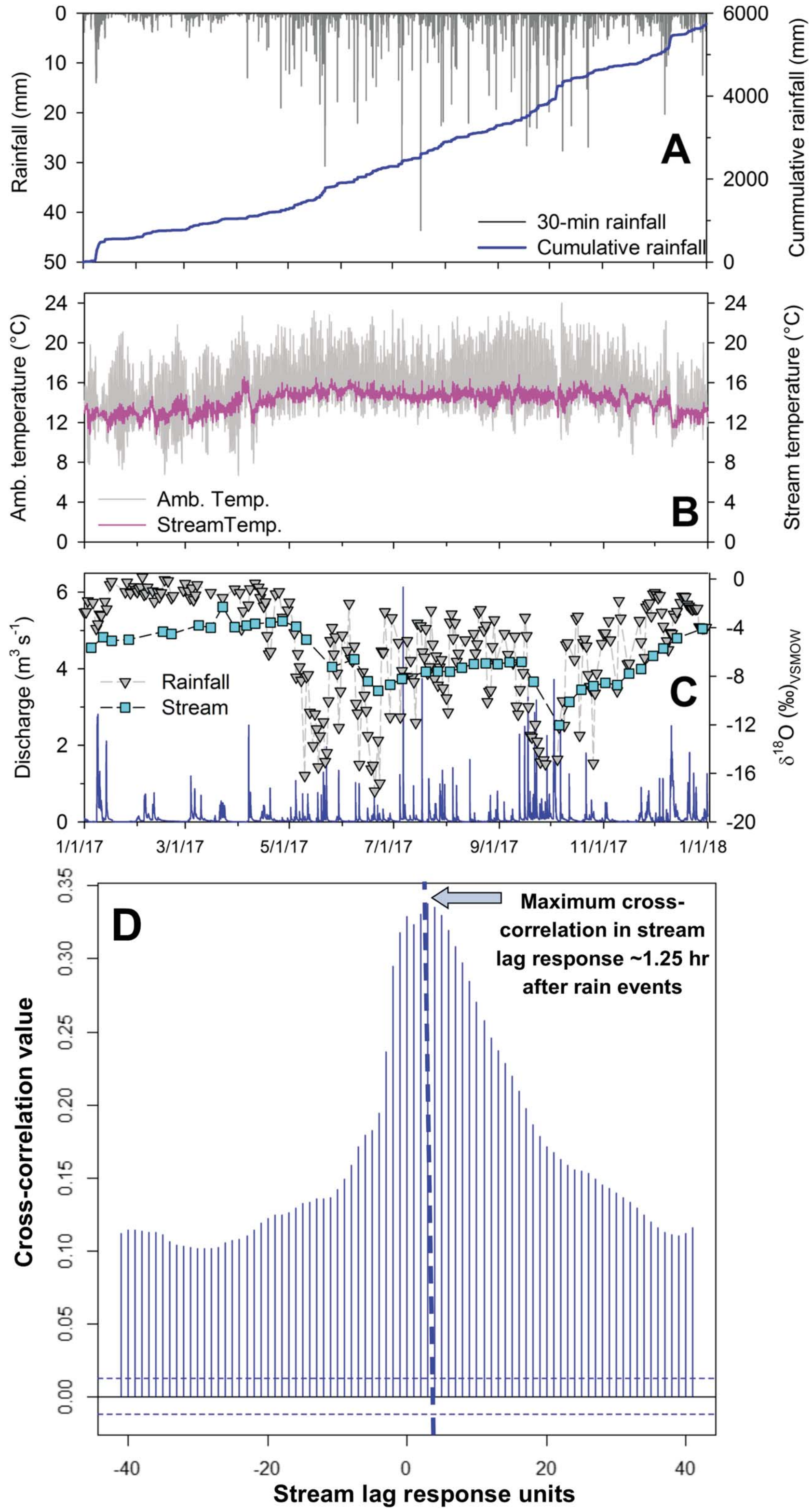

Figure 2. Time series during 2017 and rainfall and discharge cross-correlation. (a) Thirty-minute rainfall (mm) and cumulative rainfall (mm). (b) Ambient (30 min) and stream temperatures (15 min; °C). (c) Fifteen-minute stream discharge (m^3/s) and water stable isotope ($\delta^{18}O$ in ‰) variations in rainfall and stream water. (d) Maximum cross correlation in the stream lag response to rainfall events in Quebrada Grande catchment occurred on average ~1.25 hr after the rainfall maxima. Each vertical blue line presents a 15-min interval.

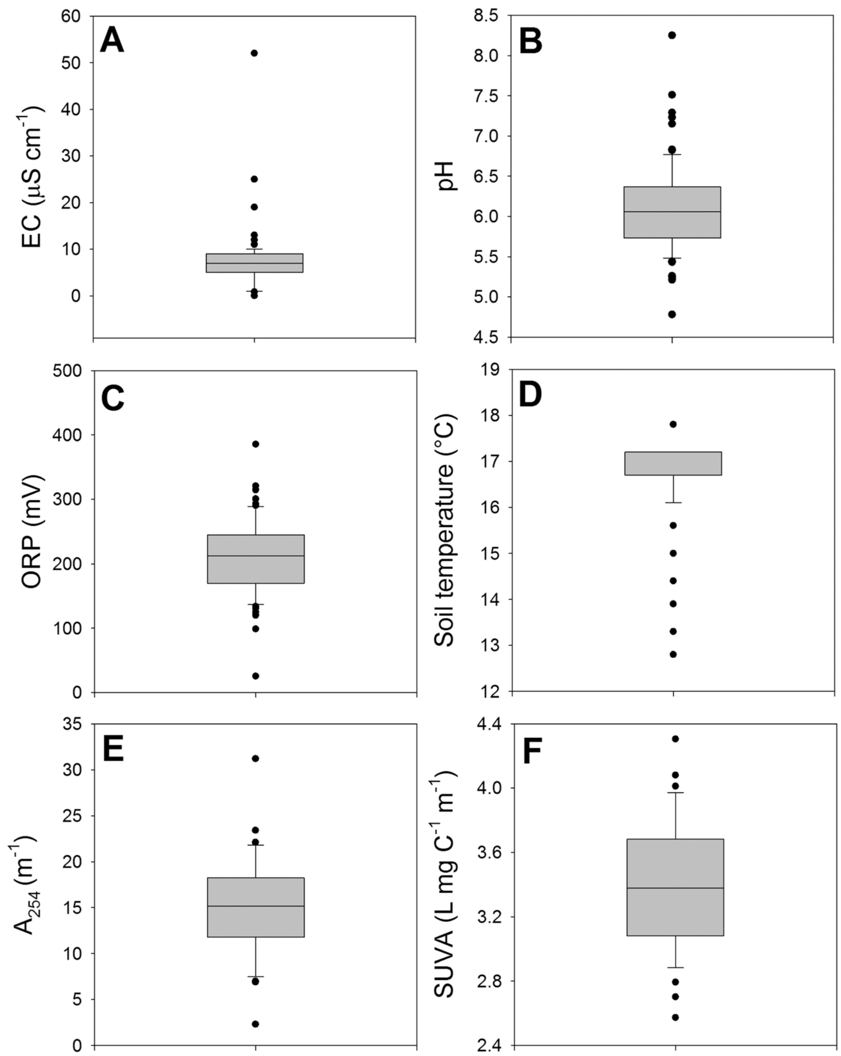

Figure 3. Box plots of physical, chemical, and optical dissolved organic matter properties at Quebrada Grande catchment. (a) Stream electrical conductivity (μS/cm), (b) stream pH, (c) stream ORP (mV), (d) soil temperature (°C), (e) Chromophoric dissolved organic matter absorbance at 254 nm (A_{254}, m^{-1}), and (f) specific UV absorption ($SUVA_{254}$ L mg · C^{-1} · m^{-1}). The black dots represent outliers.

CDOM (A_{254}, m^{-1}) and DOC concentration exhibited a significant linear correlation (r^2=0.88; Figure 4a); however, DOC varied throughout the year (Figure 4b). Storm DOC ranged from 3.74 to 7.65 mg/L, with a mean value of 5.51 ± 0.91 (1σ), reaching an asymptotic value near ~8 mg/L as discharge increases (Figure 4c). Intermittent baseflow conditions were characterized by variable DOC, ranging from 0.89 to 4.97 mg/L, with a mean value of 3.41 ± 0.97 (1σ). Mean annual carbon flux was 6.7±0.1 g C · m^{-2} · yr^{-1} in concordance with recent values reported by Osburn et al. (2018) in Costa Rica (1.9 – 13.79 6.7±0.1 g C · m^{-2} · $year^{-1}$) and with other tropical regions (Table 1). CDOM ranged from 2.3 up to 31.2 m^{-1}, while A_{254}/DOC ratio (i.e., the specific UV absorption known as $SUVA_{254}$) varied from 2.6 to 4.3 L mg · C^{-1} · m^{-1}.

The soils were classified as sandy-loam andosols with relatively high volumetric content (~70-83%) and a perennial and shallow water table (~80-cm depth) at the bottom of the catchment (CDB; Table 1). Hydraulic conductivity across the sampled hillslope transect ranged from 0.21 cm/hr (CDA) up to 2.06 cm/hr (CDB). Soil temperature seasonality was low, with a mean annual value of 16.9±0.3 °C (Figure 3d). Steady saturation and a moderate daily ambient temperature oscillation provided a nearly uniform soil thermal regime. Acidic conditions (soil pH range: 4.1-4.8; soil acidity range: 2.26-3.70 cmol/L) and high organic carbon content (up to 41.3%) were coupled with high iron and aluminum concentrations (Table 2). Total carbon content ranged from 15.8 % (CDB) and 28.9 % (CDA). Total nitrogen content ranged from 0.97 % (CDB)

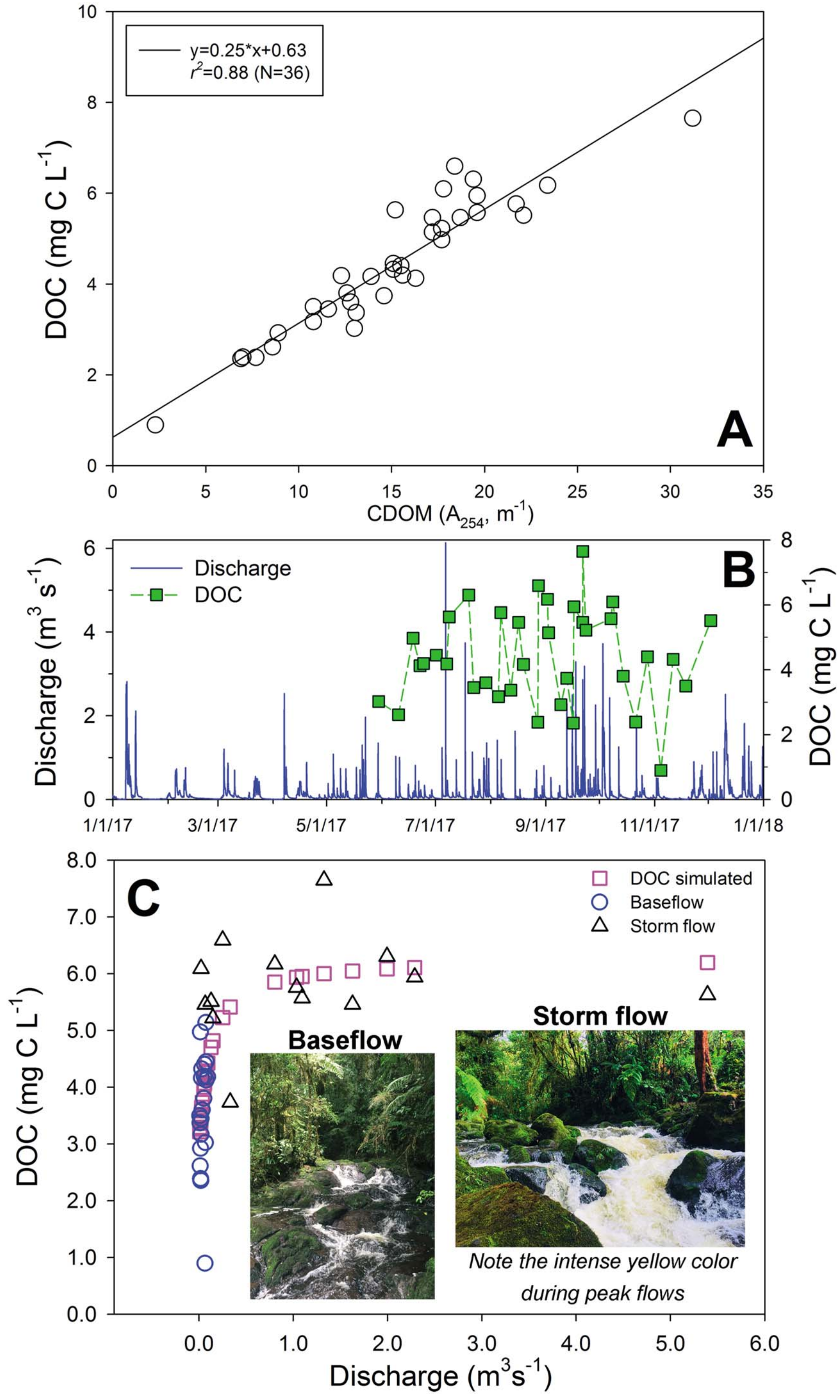

Figure 4. Stream discharge, dissolved organic carbon (DOC), and chromophoric dissolved organic matter (CDOM) relationships. (a) CDOM (A_{254}, m^{-1}) and DOC (mg C/L) linear regression. (b) Fifteen-minute stream discharge (m^3/s), baseflow, and storm-event DOC (mg/L) variations. (c) Baseflow (blue circles) and storm events (black triangles) DOC (mg C/L) variations from May through November 2017 in Quebrada Grande catchment. DOC (pink squares) was simulated using a best fit parsimonious (3-parameter) hyperbola equation (r^2=0.49). Inset pictures denote the distinct stream water pigmentation during baseflow or storm flow events.

and 1.93 % (CDA). The lower carbon/nitrogen and trace element content at the bottom of the hillslope (dynamic saturation area) denoted the large solute leaching during storm flows from this area in comparison with the larger concentrations measured at the top of the transect. An inverse situation was found in terms of total aluminum composition, whereby high Al content (Table 2) was measured at the

Table 2
Physical and Chemical Soil Characteristics Along a Representative Hillslope Transect in Quebrada Grande Catchment

Variable	CDA	CDM	CDB
Texture	Sandy loam	Sandy loam	Sandy loam
Volumetric water content (%)	82.6	78.9	78.1
Hydraulic Conductivity (cm/hr)	0.21	1.68	2.06
Acidity (cmol/L)	3.70	2.68	2.26
pH	4.1	4.7	4.8
Total Carbon content (%)	28.9	19.1	15.8
Total Nitrogen content (%)	1.93	1.24	0.97
C/N ratio	15.0	15.4	16.3
Organic matter content (%)	41.3	27.3	22.6
Trace elements (mg/L)			
Fe	520	283	498
P	9.0	2.0	2.0
Zn	2.7	1.0	1.2
Cu	2.0	7.0	6.0
Mn	4.0	5.0	2.0
Major cations (cmol/L)			
Ca	2.1	1.7	0.98
Mg	0.94	0.37	0.38
K	0.29	0.12	0.12
CEC (cmol/L)	7.0	4.9	3.7
Al (g/kg)	2.41	2.71	18.72

bottom of the hillslope, probably due to the large capacity of DOC to bind soluble Al in organic chelation forms (Cory et al., 2006). Likewise, the presence of organic acids lowering soil pH (Table 2) can inversely increase Al solubility. In addition, iron reduction conditions have also been correlated with DOC transport in small catchments (Knorr, 2013). Large soil iron concentrations and consistent saturated conditions favored a reduction scenario for rapid DOC mobilization.

4. Discussion

4.1. Key Drivers Controlling Tropical DOC Transport and Export

Riverine DOC (i.e., baseflow and storm events) is rarely documented in small headwater catchments across the tropics, whereby heavy rainfall, dynamic riparian areas, steep slopes, soil characteristics, low stream water pH, and high solar radiation exposure (Figure 1) are key features controlling SOC mobilization (Lee et al., 2019; Shih et al., 2018; Wymore et al., 2017). This study demonstrated that large daily rainfall up to 250 mm (a typical rainfall amount during tropical storm passages; Zhang et al., 2017) and sustained saturation within riparian areas (Figures 2a and 5) led to rapid allochthonous DOC transport to the stream network (Figure 4b). Quebrada Grande, as other humid tropical headwater catchments, was characterized by a fast runoff response (also known as wave celerity; McDonnell & Beven, 2014), which turns in, prompt solute transport (~1.25 hr; Figure 2d), reaching a DOC maximum near 8 mg C/L (Figure 4c).

This flushing hypothesis (Mei et al., 2014) explains the first-order mechanism of DOC transport at Quebrada Grande. Organic solutes are leached from near-surface horizons by a rising water table (~80-cm depth) followed by a rapid lateral transport of these materials to the stream via saturation excess runoff in the riparian areas, soils saturated throughout the catchment, and shallow groundwater discharge similar to another forested and steep mountainous catchment in northern Costa Rica as described by Dehaspe et al. (2018). The latter runoff generation is in contrast to other steep, tropical catchments with a dominating subsurface stormflow on volcanic substrate mainly due to different soil physical characteristics (Muñoz-Villers & McDonnell, 2012). Figure 5 illustrates a conceptual scheme of DOC transport and export in a typical tropical headwater catchment. DOC pools are denoted from S1 to S7. Although SOC (including litter leachate) near the riparian areas constitutes the main carbon pool in headwater tropical catchments, organic matter from throughfall (1-61 mg/L) and stemflow (7-482 mg/L; often stored and released from mosses, ferns, lichens, and bromeliads) may also contribute a significant DOC pulse during large rain events (Bischoff et al., 2015; da Costa et al., 2017; Van Stan & Stubbins, 2018) to the overall fluvial carbon budget.

Different DOC sources are often combined near the stream channel within a dynamic saturation area (CDB in Figure 1a), whereby a rapid rising water table intersects DOC-rich soil horizons (Table 2; up to 41.3% in organic matter content) similar to extratropical catchments as for example in the UK uplands (Birkel et al., 2014). The latter explained the high DOC concentrations measured during large storm events (Figure 4). DOC during baseflow exhibited large variations as a result of a potential low biogeochemical attenuation since water logging sustained soil temperature nearly constant at 16°C (Figure 3d). In addition, deep seepage to the bedrock may result in low DOC concentrations in regional groundwater flow within these humid and dynamic ecosystems (Osburn et al., 2018).

In contrast to most studies from forested catchments showing predominantly preevent water contributions to stormflow (Klaus & McDonnell, 2013), the high correlation between large rainfall events and runoff generation with high event water contributions (ranging from 42.4±0.3% up to 98.2±0.3% of the total discharge) indicated that surface and shallow lateral fluxes with more limited subsurface mixing governed DOC transport to the stream (Mei et al., 2014; Shih et al., 2018; Suhett et al., 2007; Wymore et al., 2017) with a relatively quick response time after the rainfall maxima. The latter coupled with moderate to steep slopes

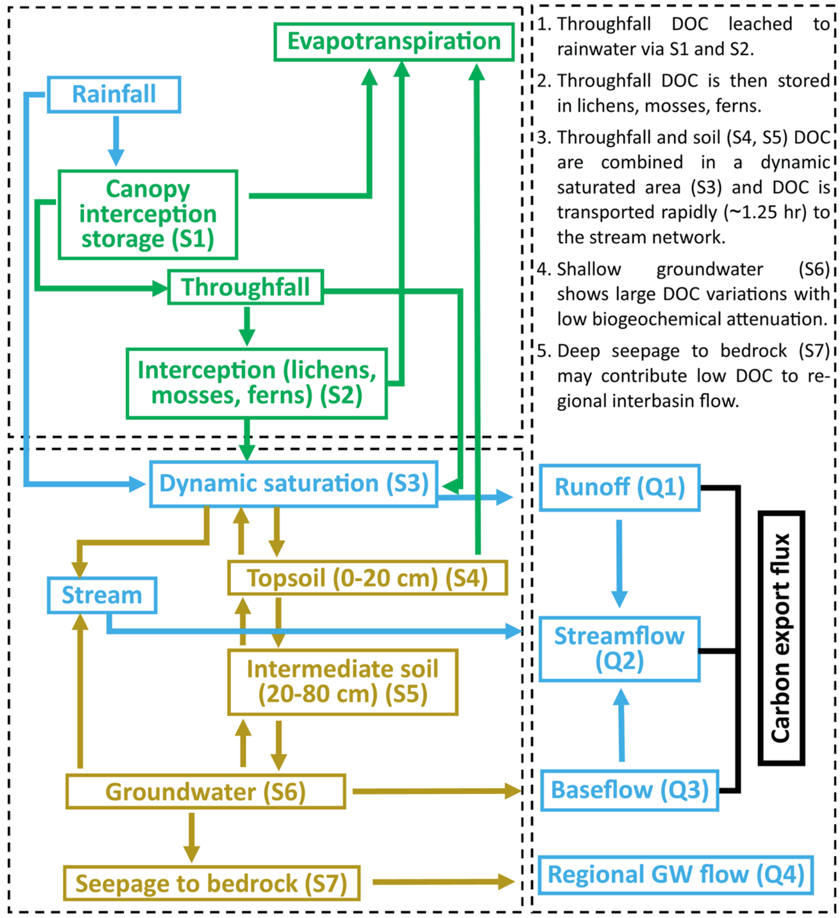

Figure 5. Conceptual model of dissolved organic carbon (DOC) transport and export in a dynamic headwater tropical catchment.

(Figure 1a) favored rapid DOC leaching from the canopy and understory providing fresh litter material (Figures 1c and 1d) as well as DOC from the rich organic soil surface toward Quebrada Grande.

Global DOC export usually ranges from 1 to 15 g C · m^2 · year^{-1} (Neff & Asner, 2001), with a mean annual value of 1.08 g C · m^2 · year^{-1} (Li et al., 2019; Table 1). While large tropical river systems (e.g., Amazon, Mekong, Orinoco, Parana; Table 1) exhibited DOC export values between ~2-5 g C · m^2 · year^{-1}, pristine and dynamic tropical forested catchments, such as Quebrada Grande, revealed a significant potential to export greater DOC amounts, in most cases, than temperate and arctic streams or large river systems (Lee et al., 2019). Baseflow and storm events contributed 37.8% and 62.2%, respectively, to the total discharge-weighted DOC export from Quebrada Grande (6.7±0.1 g C · m^{-2} · year^{-1}). Despite that stream water transit times are nonstationary (Birkel et al., 2011), MTT reflect a proxy for the average water velocity in transit time distributions (McDonnell & Beven, 2014) in first-order streams across tropical mountainous watersheds. The MTT of such tropical catchments are often shorter than large river systems; therefore, lower DOC degradation results in significant fluxes comparable to export in large riverine systems (Lloret et al., 2011).

Typically, $SUVA_{254}$ is strongly correlated with the hydrophobic organic acid fraction and constitutes a useful proxy of aromatic content and molecular weight DOM (Chowdhury, 2013; Hansen et al., 2016; Spencer et al., 2012; Weishaar et al., 2003). In general, the aromaticity content and molecular weight increase as $SUVA_{254}$ increases during the rising limb. In Quebrada Grande, baseflow periods exhibited a large $SUVA_{254}$ variability, suggesting a mixture of aliphatic and aromatic compounds and weak DOC subsurface biodegradation or sorption. The decreasing $SUVA_{254}$ trend during large storm flows indicated that these events were most likely dominated by a mixture of low- weight aliphatic compounds (Weishaar et al., 2003) during the falling limb. The highly significant linear relationship (r^2=0.88) between DOC and CDOM (Figure 4a) demonstrated that automated and systematic sampling during storm events and baseflow periods in a hydrological year can be used to estimate carbon fluxes when instrumental capabilities may limit DOC analysis on regular basis.

4.2. Tropical Storm DOC and Water Resources Implications Under a Changing Climate

The presence of natural SOC in drinking water sources is associated, among others, with color, taste and odors, metal complexation, higher disinfectant demand, bacterial regrowth in distribution systems, and disinfection by-product precursors. In tropical regions, El Niño-induced droughts (Vignola et al., 2018) have increased the exploration of high-elevation water sources such as forested headwater catchments, whereby spring flows are perennial (Salas-Navarro et al., 2018), and streams exhibit little anthropogenic influence. Our study explored, by first time, DOC transport and export with implications for large lowland urban areas in Central America, since previous studies (Osburn et al., 2018, and references therein) have been focused in regions with low population densities.

Quebrada Grande DOC variations with relatively high concentrations not only during storm flows but also during baseflow recession periods poses a challenge for drinking water operators. Low ambient and soil temperatures, reducing conditions due to consistent water logging (Figure 3), and high iron and aluminum oxide content (Table 2) limit SOC degradation, providing a carbon-rich reservoir (e.g., canopy, understory, and soil surface). The latter coupled with a large rainfall regime favors rapid DOC transport to the streams, and consequently, a significant carbon export to the lowland urban areas.

5. Conclusions

Our DOC data highlight the rapid surface and lateral DOC export in a humid tropical catchment and evidenced the governing control of large rainfall events and a rapid water table increase in such carbon transport, a common feature in most of the Caribbean slope of Central America. The short nonstationary MTT in the catchment reduced the expected DOC attenuation (i.e., sorption and microbial degradation) during baseflows (Neff & Asner, 2001; Schwendenmann & Veldkamp, 2005), resulting in large variability.

During large rainfall events, isotope hydrograph separation estimated up to 98.2% event water contributing to the total discharge. Such events mostly transported litter material from the canopy and understory as well as from the rich organic soil surface at Quebrada Grande within a dynamic saturation area, exemplified by high DOC concentrations and rapid yellow/brown stream pigmentation. $SUVA_{254}$ indicated a mixture of hydrophobic humic and hydrophilic nonhumic matter during both baseflow and storm events. Mean annual carbon flux (6.7 ± 0.1 g C · m^{-2} · yr^{-1}) highlights the importance of these headwater ecosystems on regulating riverine lowland carbon budgets.

CDOM appears to be a reliable proxy to estimate DOC variations, when systematic sampling throughout storm and baseflow events are conducted (Rochelle-Newall et al., 2014). Further carbon isotope and optical analyses (i.e., $\delta^{13}C$ in DIC and DOC and fluorescence emission-excitation spectrums; Chen et al., 2003) are required to distinguish between the different chemical structures (aliphatic and aromatic) contributing to the overall DOC in the stream. Temperature and rainfall intensity as well as land use changes may significantly alter carbon fluxes and consequently CO_2 emission to the atmosphere (Pesántez et al., 2018) under a changing climate; therefore, detailed DOC assessments are needed in climate sensitive hot-spots such as Central America.

Drinking water operators should pay careful attention to the exploration of new water sources in tropical forested catchments, whereby rapid solute transport coupled with high DOC concentrations may turn in a high chlorine demand and a potential formation of disinfection by-products in the resultant drinking water (Bower, 2014). However, this study may help to design and seek for better surface water treatment options. Likewise, our results highlight the importance of the Payment Environmental Services scheme of Costa Rica (Pagiola, 2008) as a conservation initiative that helps to protect carbon-rich forest degradation (since ~30 years ago), and ultimately, a large spectrum of ecohydrological services.

In developing tropical countries, the recurrent lack of (a) high-resolution hydrological networks (for water quality and related fluxes), (b) field optical and remote sensors, and (c) reliable analytical facilities limit the spatio-temporal assessment of traditional solutes (major ions, heavy metals, and trace elements) and emergent pollutants. Tetzlaff et al. (2017) highlighted the value of long-term monitoring networks to improve our understanding of the ecohydrological catchment functioning under a changing climate. However, in the tropics rapid and high-resolution assessments arise as a reliable solution to enhance the physically based processes governing water and solute transport (Riveros-Iregui et al., 2018). This study is an example of a 1-year assessment that can (a) provide useful information for water resources managers and (b) be transferred to other similar headwater catchments across the humid tropics.

Acknowledgments
This study was partially supported by International Atomic Energy Agency grant CRP-19747 to R. S. M. under the pan-tropical initiative “Stable isotopes in precipitation and paleoclimatic archives in tropical areas to improve regional hydrological and climatic impact models.” Partial support from the Empresa de Servicios Públicos de Heredia (ESPH, S.A), the Research Office of the Universidad Nacional de Costa Rica through grants SIA-0482-13, SIA-0378-14, and SIA-0101-14, was also fundamental. The authors thank various helping hands that contributed to rainfall and stream sampling during baseflow and storm events, particularly to the personnel of the Wildlife Refuge Cerro Dantas. Support from the Isotope Network for Tropical Ecosystem Studies (ISONet) funded by the University of Costa Rica Research Council, the Soil and Foliar Laboratory, Agronomical Research Center, Universidad de Costa Rica, the Research Center of Environmental Protection (CIPA) of Instituto Tecnológico de Costa Rica, and the Chemistry School of the Universidad Nacional is also acknowledged. All manuscript data are provided as supporting information. The authors thank the comments and suggestions from two anonymous reviewers.

References

Aarnos, H., Gélinas, Y., Kasurinen, V., Gu, Y., Puupponen, V. M., & Vähätalo, A. V. (2018). Photochemical mineralization of terrigenous DOC to dissolved inorganic carbon in ocean. *Global Biogeochemical Cycles*, *32*(2), 250–266. https://doi.org/10.1002/2017GB005698

Aiken, G., & Cotsaris, E. (1995). Soil and Hydrology: Their effect on NOM. *Journal - American Water Works Association*, *87*(1), 36–45. https://doi.org/10.1002/j.1551-8833.1995.tb06299.x

Aitkenhead, J. A., & McDowell, W. H. (2000). Soil C:N ratio as a predictor of annual riverine DOC flux at local and global scales. *Global Biogeochemical Cycles*, *14*(1), 127–138. https://doi.org/10.1029/1999GB900083

American Public Health Association (APHA) (2005). *Standard methods for the examination of water and wastewater*, (21a ed.). Washington, USA: American Public Health Association. https://www.apha.org/

Arriagada, R. A., Sills, E. O., Ferraro, P. J., & Pattanayak, S. K. (2015). Do payments payoff? Evidence from participation in Costa Rica's PESProgram. *PLoS ONE*, *10*(8), e0136809. https://doi.org/10.1371/journal.pone.0136809

Aufdenkampe, A. K., Mayorga, E., Raymond, P. A., Melack, J. M., Doney, S. C., Alin, S. R., et al. (2011). Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere. *Frontiers in Ecology and the Environment*, *9*(1), 53–60. https://doi.org/10.1890/100014

Battin, T., Luyssaert, S., Kaplan, L. A., Aufdenkampe, A. K., Richter, A., & Tranvik, L. J. (2009). The boundless carbon cycle. *Nature Geoscience*, *2*(9), 598–600. https://doi.org/10.1038/ngeo618

Berbés-Blázquez, M., Bunch, M. J., Mulvihill, P. R., Peterson, G. D., & de Joode, B. V. W. (2017). Understanding how access shapes the transformation of ecosystem services to human well-being with an example from Costa Rica. *Ecosystem Services*, *28*, 320–327. https://doi.org/10.1016/j.ecoser.2017.09.010

Birkel, C., Broder, T., & Biester, H. (2017). Nonlinear and threshold-dominated runoff generation controls DOC export in a small peat catchment. *Journal of Geophysical Research: Biogeosciences*, *122*, 498–513. https://doi.org/10.1002/2016JG003621

Birkel, C., Soulsby, C., & Tetzlaff, D. (2014). Integrating parsimonious models of hydrological connectivity and soil biogeochemistry to simulate stream DOC dynamics. *Journal of Geophysical Research: Biogeochemistry*, *119*(5), 1030–1047. https://doi.org/10.1002/2013JG002551

Birkel, C., Soulsby, C., Tetzlaff, D., Dunn, S. M., & Spezia, L. (2011). High-frequency storm event isotope sampling reveals time-variant transit time distributions and influence of diurnal cycles. *Hydrological Processes*. https://doi.org/10.1002/hyp8210

Bischoff, S., Schwarz, M. T., Siemens, J., Thieme, L., Wilcke, W., & Michalzik, B. (2015). Properties of dissolved and total organic matter in throughfall, stemflow and forest floor leachate of central European forests. *Biogeosciences*, *12*(9), 2695–2706. https://doi.org/10.5194/bg-12-2695-2015

Bower, K. M. (2014). Water supply and sanitation of Costa Rica. *Environmental Earth Sciences*, *71*(1), 107–123. https://doi.org/10.1007/s12665-013-2416-x

Brandão, L. P. M., Brighenti, L. S., Staehr, P. A., Asmala, E., Massicotte, P., Tonetta, D., et al. (2018). Distinctive effects of allochthonous and autochthonous organic matter on CDOM spectra in a tropical lake. *Biogeosciences*, *15*(9), 2931–2943. https://doi.org/10.5194/bg-15-2931-2018

Brooks, P. D., McKnight, D. M., & Bencala, K. E. (1999). The relationship between soil heterotrophic activity, soil dissolved organic carbon (DOC) leachate, and catchment-scale DOC export in headwater catchments. *Water Resources Research*, *35*(6), 1895–1902. https://doi.org/10.1029/1998WR900125

Brunet, F., Dubois, K., Veizer, J., Nkoue Ndondo, G. R., Ndam Ngoupayou, J. R., Boeglin, J. L., & Probst, J. L. (2009). Terrestrial and fluvial carbon fluxes in a tropical watershed: Nyong basin, Cameroon. *Chemical Geology*, *265*(3-4), 563–572. https://doi.org/10.1016/j.chemgeo.2009.05.020

Butman, D. E., Wilson, H. F., Barnes, R. T., Xenopoulos, M. A., & Raymond, P. A. (2015). Increased mobilization of aged carbon to rivers by human disturbance. *Nature Geoscience*, *8*(2), 112–116. https://doi.org/10.1038/ngeo2322

Chen, W., Westerhoff, P., Leenheer, J. A., & Booksh, K. (2003). Fluorescence excitation— emission matrix regional integration to quantify spectra for dissolved organic matter. *Environmental Science & Technology*, *37*(24), 5701–5710. https://doi.org/10.1021/es034354c

Chowdhury, S. (2013). Trihalomethanes in drinking water: Effect of natural organic matter distribution. *Water SA*, *39*(1), 1–7. https://doi.org/10.4314/wsa.v39i1.1

Cook, S., Peacock, M., Evans, C. D., Page, S. E., Whelan, M. J., Gauci, V., & Kho, L. K. (2017). Quantifying tropical peatland dissolved organic carbon (DOC) using UV-visible spectroscopy. *Water Research*, *115*, 229–235. https://doi.org/10.1016/j.watres.2017.02.059

Cory, N., Buffam, I., Laudon, H., Köhler, S., & Bishop, K. (2006). Landscape control of stream water aluminum in a boreal catchment during spring flood. *Environmental Science & Technology*, *40*(11), 3494–3500. https://doi.org/10.1021/es0523183

da Costa, E. N. D., de Souza, J. C., Pereira, M. A., de Souza, M. F. L., de Souza, W. F. L., & da Silva, D. M. L. (2017). Influence of hydrological pathways on dissolved organic carbon fluxes in tropical streams. *Ecology and Evolution*, *7*(1), 228–239. https://doi.org/10.1002/ece3.2543

Dehaspe, J., Birkel, C., Tetzlaff, D., Sánchez-Murillo, R., Durá-Quesada, A. M., & Soulsby, C. (2018). Spatially distributed tracer-aided modelling to explore water and isotope transport, storage and mixing in a pristine, humid tropical catchment. *Hydrological Processes*, *32*, 3206–3224. https://doi.org/10.1002/hyp.13258

Dhillon, G. S., & Inamdar, S. (2013). Extreme storms and changes in particulate and dissolved organic carbon in runoff: Entering unchartedwaters? *Geophysical Research Letters*, *40*, 1322–1327. https://doi.org/10.1002/grl.50306

Dittmar, T., Hertkorn, N., Kattner, G., & Lara, R. J. (2006). Mangroves, a major source of dissolved organic carbon to the oceans. *Global Biogeochemical Cycles*, *20*, GB1012. https://doi.org/10.1029/2005GB002570

Dubinsky, E., Silver, W. L., & Firestone, M. K. (2010). Tropical forest soil microbial communities couple iron and carbon biogeochemistry. *Ecology*, *91*(9), 2604–2612. https://doi.org/10.1890/09-1365.1

Fasching, C., Ulseth, A. J., Schelker, J., Steniczka, G., & Battin, T. J. (2015). Hydrology controls dissolved organic matter export and composition in an Alpine stream and its hyporheic zone. *Limnology and Oceanography*, *61*(2), 558–571. https://doi.org/10.1002/lno.10232

Grieve, I. C., Proctor, J., & Cousins, S. A. (1990). Soil variation with altitude on volcano Barva, Costa Rica. *Catena*, *17*(6), 525–534. https://doi.org/10.1016/0341-8162(90)90027-B

Gröning, M., Lutz, H. O., Roller-Lutz, Z., Kralik, M., Gourcy, L., & Pöltenstein, L. (2012). A simple rain collector preventing water re-evaporation dedicated for $\delta^{18}O$ and δ^2H analysis of cumulative precipitation samples. *Journal of Hydrology*, *448-449*, 195–200. https://doi.org/10.1016/j.jhydrol.2012.04.041

Hansen, A. M., Kraus, T. E. C., Pellerin, B. A., Fleck, J. A., Downing, B. D., & Bergamaschi, B. A. (2016). Optical properties of dissolved organic matter (DOM): Effects of biological and photolytic degradation. *Limnology and Oceanography*, *61*(3), 1015–1032. https://doi.org/10.1002/lno.10270

Johnson, M. S., Lehmann, J., Couto, E. G., Filho, J. P. N., & Riha, S. J. (2006). DOC and DIC in flowpaths of Amazonian headwater catchments with hydrologically contrasting soils. *Biogeochemistry*, *81*(1), 45–57. https://doi.org/10.1007/s10533-006-9029-3

Khadka, M. B., Martin, J. B., & Jin, J. (2014). Transport of dissolved carbon and CO_2 degassing from a river system in a mixed silicate and carbonate catchment. *Journal of Hydrology*, *513*, 391–402. https://doi.org/10.1016/j.jhydrol.2014.03.070

Klaus, J., & McDonnell, J. J. (2013). Hydrograph separation using stable isotopes: Review and evaluation. *Journal of Hydrology*, *505*, 47–64. https://doi.org/10.1016/j.jhydrol.2013.09.006

Knorr, K. H. (2013). DOC-dynamics in a small headwater catchment as driven by redox fluctuations and hydrological flow paths—Are DOC exports mediated by iron reduction/oxidation cycles? *Biogeosciences*, *10*(2), 891–904. https://doi.org/10.5194/bg-10-891-2013

Köchy, M., Hiederer, R., & Freibauer, A. (2015). Global distribution of soil organic carbon—Part 1: Masses and frequency distributions of SOC stocks for the tropics, permafrost regions, wetlands, and the world. *The Soil*, *1*(1), 351–365. https://doi.org/10.5194/soil-1-351-2015

Lee, L. C., Hsu, T. C., Lee, T. Y., Shih, Y. T., Lin, C. Y., Jien, S. H., et al. (2019). Unusual roles of discharge, slope and SOC in DOC transport in small mountainous rivers, Taiwan. *Scientific Reports*, *9*(1), 1574. https://doi.org/10.1038/s41598-018-38276-x

Li, M., Peng, C., Zhou, X., Yang, Y., Guo, Y., Shi, G., & Zhu, Q. (2019). Modeling global riverine DOC flux dynamics from 1951 to 2015. *Journal of Advances in Modeling Earth Systems*, *11*(2), 514–530. https://doi.org/10.1002/2018MS001363

Lloret, E., Dessert, C., Pastor, L., Lajeunesse, E., Crispi, O., Gaillardet, J., & Benedetti, M. F. (2011). Dynamic of particulate and dissolved organic carbon in small volcanic mountainous tropical watersheds. *Chemical Geology*, *351*, 229–244. https://doi.org/10.1016/j.chemgeo.2013.05.023

Masese, F. O., Salcedo-Borda, J. S., Gettel, G. M., Irvine, K., & McClain, M. E. (2017). Influence of catchment land use and seasonality on dissolved organic matter composition and ecosystem metabolism in headwater streams of a Kenyan river. *Biogeochemistry*, *132*(1-2), 1–22. https://doi.org/10.1007/s10533-016-0269-6

McDonnell, J. J., & Beven, K. (2014). Debates—The future of hydrological sciences: A (common) path forward? A call to action aimed at understanding velocities, celerities, and residence time distributions of the headwater hydrograph. *Water Resources Research*, *50*, 5342–5350. https://doi.org/10.1002/2013WR015141

McDowell, W. H., & Asbury, C. E. (1994). Export of carbon, nitrogen, and major ions from three tropical montane watersheds. *Limnology and Oceanography*, *39*(1), 111–125. https://doi.org/10.4319/lo.1994.39.1.0111

Mei, Y., Hornberger, G. M., Kaplan, L. A., Newbold, J. D., & Aufdenkampe, A. K. (2014). The delivery of dissolved organic carbon from a forested hillslope to a headwater stream in southeastern Pennsylvania, USA. *Water Resources Research*, *50*, 5774–5796. https://doi.org/10.1002/2014WR015635

Moore, R. D. (2005). Slug injection using salt in solution. *Streamline Watershed Management Bulletin*, *8*(2), 1–6.

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

Mulholland, P. J. (1997). Dissolved organic matter concentration andflux in streams. *Journal of the North American Benthological Society*, *16*(1), 131–141. https://doi.org/10.2307/1468246

Muñoz-Villers, L. E., & McDonnell, J. J. (2012). Runoff generation in a steep, tropical montane cloud forest catchment on permeable volcanic substrate. *Water Resources Research*, *48*, W09528. https://doi.org/10.1029/2011WR011316

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

Newbold, J. D., Sweeney, B. W., Jackson, J. K., & Kaplan, L. A. (1995). Concentrations and export of solutes from six mountain streams in Northwestern Costa Rica. *Journal of the North American Benthological Society*, *14*(1), 21–37. https://doi.org/10.2307/1467722

Osburn, C. L., Oviedo-Vargas, D., Barnett, E., Dierick, D., Oberbauer, S. F., & Genereux, D. P. (2018). Regional groundwater and storms are hydrologic controls on the quality and export of dissolved organic matter in two tropical rainforest streams, Costa Rica. *Journal of Geophysical Research: Biogeosciences*, *123*(3), 850–866. https://doi.org/10.1002/2017JG003960

Pagiola, S. (2008). Payments for environmental services in Costa Rica. *Ecological Economics*, *65*(4), 712–724. https://doi.org/10.1016/j.ecolecon.2007.07.033

Pesántez, J., Mosquera, G. M., Crespo, P., Breuer, L., & Windhorst, D. (2018). Effect of land cover and hydro-meteorological controls on soil water DOC concentrations in a high-elevation tropical environment. *Hydrological Processes*, *32*(17), 2624–2635. https://doi.org/10.1002/hyp.13224

Ramírez-Leiva, A., Sánchez-Murillo, R., Martínez-Cruz, M., Calderón, H., Esquivel-Hernández, G., Delgado, V., et al. (2017). Stable isotopes evidence of recycled subduction fluids in the hydrothermal/volcanic activity across Nicaragua and Costa Rica. *Journal of Volcanology and Geothermal Research*, *345*, 172–183. https://doi.org/10.1016/j.jvolgeores.2017.08.013

Raymond, P. A., McClelland, J. W., Holmes, R. M., Zhulidov, A. V., Mull, K., Peterson, B. J., et al. (2007). Flux and age of dissolved organic carbon exported to the Arctic Ocean: A carbon isotopic study of the five largest arctic rivers. *Global Biogeochemical Cycles*, *21*, GB4011. https://doi.org/10.1029/2007GB002934

Raymond, P. A., & Saiers, J. E. (2010). Event controlled DOC export from forested watersheds. *Biogeochemistry*, *100*(1-3), 197–209. https://doi.org/10.1007/s10533-010-9416-7

Raymond, P. A., & Spencer, R. G. M. (2015). Riverine DOM. In *Biogeochemistry of marine dissolved organic matter*, (pp. 509–533). Amsterdam: Elsevier.

Regnier, P., Friedlingstein, P., Ciais, P., Mackenzie, F. T., Gruber, N., Janssens, I. A., et al. (2013). Anthropogenic perturbation of the carbon fluxes from land to ocean. *Nature Geoscience*, *6*(8), 597–607. https://doi.org/10.1038/ngeo1830

Richardson, M., Moore, R. D., & Zimmermann, A. (2017). Variability of tracer breakthrough curves in mountain streams: Implications for streamflow measurement by slug injection. *Canadian Water Resources Journal/Revue Canadienne des Rssources Hydriques*, *42*(1), 21–37. https://doi.org/10.1080/07011784.2016.1212676

Riveros-Iregui, D. A., Covino, T. P., & González-Pinzón, R. (2018). The importance of and need for rapid hydrologic assessments in Latin America. *Hydrological Processes*, *32*(15), 2441–2451. https://doi.org/10.1002/hyp.13163

Rochelle-Newall, E., Hulot, F. D., Janeau, J. L., & Merroune, A. (2014). CDOM fluorescence as a proxy of DOC concentration in natural waters: a comparison of four contrasting tropical systems. *Environmental Monitoring and Assessment*, *186*(1), 589–596. https://doi.org/10.1007/s10661-013-3401-2

Salas-Navarro, J., Sánchez-Murillo, R., Esquivel-Hernández, G., & Corrales-Salazar, J. L. (2018). Hydrogeological responses in tropical mountainous springs. *Isotopes in Environmental and Health Studies*, *55*(1), 25–40. https://doi.org/10.1080/10256016.2018.1546701

Sánchez-Murillo, R., & Birkel, C. (2016). Groundwater recharge mechanisms inferred from isoscapes in a complex tropical mountainous region. *Geophysical Research Letters*, *43*, 5060–5069. https://doi.org/10.1002/2016GL068888

Sánchez-Murillo, R., Brooks, E. S., Elliot, W. J., & Boll, J. (2015). Isotope hydrology and baseflow geochemistry in natural and human-altered watersheds in the Inland Pacific Northwest, USA. *Isotopes in Environmental and Health Studies*, *51*(2), 231–254. https://doi.org/10.1080/10256016.2015.1008468

Sánchez-Murillo, R., Esquivel-Hernández, G., Sáenz-Rosales, O., Piedra-Marín, G., Fonseca-Sánchez, A., Madrigal-Solís, H., et al. (2016). Isotopic composition in precipitation and groundwater in the northern mountainous region of the Central Valley of Costa Rica. *Isotopes in Environmental and Health Studies*, *53*(1), 1–17. https://doi.org/10.1080/10256016.2016.1193503

Schmidt, M. W., Torn, M. S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I. A., et al. (2011). Persistence of soil organic matter as an ecosystem property. *Nature*, *478*(7367), 49–56. https://doi.org/10.1038/nature10386

Schwendenmann, L., & Veldkamp, E. (2005). The role of dissolved organic carbon, dissolved organic nitrogen, and dissolved inorganic nitrogen in a tropical wet forest ecosystem. *Ecosystems*, *8*(4), 339–351. https://doi.org/10.1007/s10021-003-0088-1

Shih, Y. T., Chen, P. H., Lee, L. C., Liao, C. S., Jien, S. H., Shiah, F. K., et al. (2018). Dynamic responses of DOC and DIC transport to different flow regimes in a subtropical small mountainous river. *Hydrology and Earth System Sciences*, *22*(12), 6579–6590. https://doi.org/10.5194/hess-22-6579-2018

Spencer, R. G. M., Butler, K. D., & Aiken, G. R. (2012). Dissolved organic carbon and chromophoric dissolved organic matter properties of rivers in the USA. *Journal of Geophysical Research*, *117*(G3), G03001. https://doi.org/10.1029/2011JG001928

Suhett, A. L., Amado, A. M., Enrich-Prast, A., Esteves, F. . A., & Farjalla, V. F. (2007). Seasonal changes of dissolved organic carbon photo-oxidation rates in a tropical humic lagoon: the role of rainfall as a major regulator. *Canadian Journal of Fisheries and Aquatic Sciences*, *64*(9), 1266–1272. https://doi.org/10.1139/f07-103

Team, R.C. 2014. R: A language and environment for statistical computing. Vienna, Austria: R Foundation for Statistical Computing; 2014. https://www.r-project.org/

Tetzlaff, D., Carey, S. K., McNamara, J. P., Laudon, H., & Soulsby, C. (2017). The essential value of long-term experimental data for hydrology and water management. *Water Resources Research*, *53*, 2598–2604. https://doi.org/10.1002/2017WR020838

Topping, J. (1972). *Errors of observation and their treatment*, (Vol. 62). Dordrecht: Springer Science & Business Media. https://doi.org/10.1007/978-94-011-6928-8

Tranvik, L. J., Cole, J. J., & Prairie, Y. T. (2018). The study of carbon in inland waters-from isolated ecosystems to players in the global carbon cycle. *Limnology and Oceanography Letters*, *3*(3), 41–48. https://doi.org/10.1002/lol2.10068

United States Department of Agriculture (USDA). Soil Survey Staff. 2014. Soil survey field and laboratory manual. Soil survey investigations report No 51. Version 2.0. R. Burt and soil survey staff (ed.) U.S. Department of Agriculture and Natural Resources Conservation Service.

Van Stan, J. T., & Stubbins, A. (2018). Tree-DOM: Dissolved organic matter in throughfall and stemflow. *Limnology and Oceanography*, *3*(3), 199–214. https://doi.org/10.1002/lol2.10059

Vignola, R., Kuzdas, C., Bolaños, I., & Poveda, K. (2018). Hybrid governance for drought risk management: The case of the 2014/2015 El Niño in Costa Rica. *International Journal of Disaster Risk Reduction*, *28*, 363–374. https://doi.org/10.1016/j.ijdrr.2018.03.01

Wallbott, L., Siciliano, G., & Lederer, M. (2019). Beyond PES and REDD+: Costa Rica on the way to climate-smart landscape management? *Ecology and Society*, *24*(1), 24. https://doi.org/10.5751/ES-10476-240124

Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., & Mopper, K. (2003). Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environmental Science & Technology*, *37*(20), 4702–4708. https://doi.org/10.1021/es030360x

Wiegner, T. N., Tubal, R. L., & MacKenzie, R. A. (2009). Bioavailability and export of dissolved organic matter from a tropical river during baseflow and stormflow conditions. *Limnology and Oceanography*, *54*(4), 1233–1242. https://doi.org/10.4319/lo.2009.54.4.1233

Wymore, A. S., Brereton, R. L., Ibarra, D. E., Maher, K., & McDowell, W. H. (2017). Critical zone structure controls concentration-discharge relationships and solute generation in forested tropical montane watersheds. *Water Resources Research*, *53*, 6279–6295. https://doi.org/10.1002/2016WR020016

Zhang, M., Chen, X., Kumar, M., Marani, M., & Goralczyk, M. (2017). Hurricanes and tropical storms: A necessary evil to ensure water supply? *Hydrological Processes*, *31*(24), 4414–4428. https://doi.org/10.1002/hyp.11371