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LINKING DISSOLVED ORGANIC CARBON SPATIAL HETEROGENEITY TO GROUNDWATER DYNAMICS AND SOIL ORGANIC CARBON CONTENT IN A SUBTROPICAL HEADWATER CATCHMENT

RELAÇÃO ENTRE A HETEROGENEIDADE ESPACIAL DO CARBONO ORGÂNICO DISSOLVIDO E A DINÂMICA DO AQUÍFERO RASO E CARBONO ORGÂNICO DO SOLO EM UMA BACIA HIDROGRÁFICA DE CABECEIRA SUBTROPICAL

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Abstract:

Storage and fluxes of dissolved organic carbon (DOC) are triggered by interactions between hydrological and biogeochemical processes in the landscape. However, the relationship between DOC sources and catchment water storage is poorly understood due to uncertainties about the interactions between shallow groundwater (GW) dynamics and soil organic carbon (SOC). To investigate the relationships between catchment functioning and the spatiotemporal variability of DOC concentrations in shallow GW, we monitored a network of 12 shallow GW wells in a 0.24 km² catchment in Southern Brazil using DOC analysis and SOC measurements together with GW and stream gauging and statistical analyses. The greatest DOC concentration was observed in wells in the zero-order basin with highly dynamic saturation of the soil profile (50% with water table level below 0.5 m, mean DOC = 4.83 ± 2.53 mg L^{-1}), where GW was characterized by a fast rise and slow decay during storm events. In these areas, the relationship between DOC concentration and GW level followed a decay with soil depth and higher DOC concentrations were found when GW level was within 0.1 m of the soil surface (ranging from 2.00 to 14.8 mg L^{-1}). Wells in mid-slope locations were characterized by the lowest SOC content and DOC concentration in GW (1.96 ± 0.91 mg L^{-1}). During the driest period, lower slopes showed higher DOC concentrations than riparian zones due to the persistent near saturation of GW and the occurrence of DOC-enriched water due to the high SOC content in superficial layers. When the riparian zone and hillslopes showed a low water storage deficit and a quasi-permanent hydrological connectivity, DOC produced between rainfall events was transported continuously from saturated areas in hillslopes to riparian zones, with a higher DOC concentration in wells near streams. This study demonstrates that spatial sources of DOC in a subtropical headwater system are linked to streamflow generation processes and GW dynamics.

Resumo:

O armazenamento e os processos de transferência de carbono orgânico dissolvido (DOC) são governados pelas interações entre os processos hidrológicos e biogeoquímicos na paisagem. Entretanto, a relação entre as fontes de DOC e o armazenamento de água nas bacias hidrográficas são parcialmente compreendidas em função de incertezas sobre a interação entre a dinâmica do aquífero raso e o carbono orgânico no solo (SOC). Para investigar a relações entre o comportamento hidrológico da bacia e a variabilidade espaço-temporal da concentração de DOC no aquífero raso, uma rede de 12 piezômetros foi implementada para monitoramento do aquífero raso em uma bacia de 0,24 km², na região sul do Brasil, em conjunto com análises de concentração de DOC e SOC, monitoramento fluviométrico e análises estatísticas. As maiores concentrações de DOC foram observadas nos poços localizados na bacia de zero-ordem em uma área de saturação dinâmica do solo (50% do tempo com nível do aquífero inferior a 0,5m, DOC médio = DOC = 4.83 ± 2.53 mg L^{-1}), onde o aquífero raso é caracterizado por uma rápida ascensão e lento decaimento durante eventos pluviométricos. Nestas áreas, a relação entre a concentração de DOC e o nível do aquífero segue padrão de decaimento com relação a profundidade do solo e as maiores concentrações de DOC foram observadas quando o nível do aquífero raso estava até 0,1m abaixo da superfície (variando entre 2,00 e 14,8 mg L^{-1}). Poços na porção intermediária da encosta apresentam as menores concentrações de SOC e DOC no aquífero (1,96 ± 0,91 mg L^{-1}). Durante o período de estiagem, as porções inferiores das encostas apresentaram as maiores concentrações de DOC em comparação a zona ripária devido a um estágio persistente próximo a saturação do solo e a ocorrência de escoamento subsuperficial enriquecido com DOC próximo da superfície e em horizontes do solo com alto teor de SOC. Quando a zona ripária e as encostas apresentam um baixo déficit de armazenamento e conectividade hidrológica *quasi*-permanente, o DOC produzido entre os eventos pluviométricos é transportado de forma contínua das áreas saturadas nas encostas para as zonas ripárias, com as maiores concentrações de DOC sendo observadas em poços próximo ao canal. Este estudo demonstrou que as fontes de DOC em uma bacia de cabeceira subtropical estão relacionadas com os mecanismos de geração de escoamento e a dinâmica do aquífero raso.

1. INTRODUCTION

Dissolved Organic Carbon (DOC) is a key component of not only the global carbon cycle but also surface water quality as it connects sources of organic matter in the soil to carbon cycling and sequestration in aquatic ecosystems (Cole *et al.*, 2007; Tranvik *et al.*, 2009; Chaplot & Ribolzi, 2013). Thus, describing how hydrological and biogeochemical processes interact across landscapes is critical to understanding shifts in DOC concentration in shallow groundwater (GW) and streams (Siefert & Santos, 2018). Previous studies have shown that catchment functioning, in terms of the spatial and temporal variation of GW contributions to runoff generation, and DOC fluxes can exhibit evidence of threshold-mediated and connectivity-controlled processes (McGlynn & McDonnell, 2003; Dick *et al.*, 2015; Solomon *et al.*, 2015), creating uncertainties about DOC spatiotemporal dynamics and their movement across landscapes to streams.

The mobilization and flux of DOC is governed by complex interactions, including biogeochemical and hydrological processes that connect landscapes and riverscapes (Billet *et al.*, 2006; Ågren *et al.*, 2014). These connections facilitate the production and transport of DOC due to runoff generation processes and hydrological connectivity between riparian zones and hillslopes, thus controlling DOC concentrations in stream water (McGlynn & McDonnell, 2003; Morel *et al.*, 2009; Sanderman *et al.*, 2009; Winterdahl *et al.*, 2011; Birkel *et al.*, 2014; Dick *et al.*, 2015; Peralta-Tapia *et al.*, 2015; Tunaley *et al.*, 2017). Landscape units (i.e., hillslopes and riparian zones) show distinct storage–discharge relationships and shallow groundwater connectivity due to water table continuity. As such, they represent the links between the dominant catchment landscape elements and streams (Jencso *et al.*, 2009; Camporese *et al.*, 2014; Blumstock *et al.*, 2016). However, the implications of DOC production and connection to catchment-scale hydrological functioning are poorly understood in terms of the hydrological responsiveness of landscape units, specifically in subtropical environments. These issues are particularly important for headwater catchments due to the relationship among runoff processes, spatial patterns of soil organic carbon (SOC), and the heterogeneity of DOC production and its flow into streams (Lyon *et al.*, 2011; Lambert *et al.*, 2011; Laudon *et al.*, 2011; Chaplot & Ribolzi, 2013; Lambert *et al.*, 2013; Wallin *et al.*, 2015). Moreover, previous studies have shown that SOC pools and soil solution DOC concentration could be used as predictors of streamwater DOC concentration (Aitkenhead *et al.*, 1999; Billet *et al.*, 2006; Mei *et al.*, 2012; Mineau *et al.*, 2016).

Temperature, runoff processes, and physical characteristics of catchments have been identified as the main drivers of varying DOC concentrations in streams (Davidson *et al.*, 2006; Dawson *et al.*, 2008; Winterdahl *et al.*, 2011; Wu *et al.*, 2014; Oswald & Branfireun, 2014; Mengitsu *et al.*, 2014). Land use also influences DOC quality and quantity (Oni *et al.*, 2013). DOC is produced across the landscape with higher concentrations related to SOC pools particularly due the adsorption that regulates the flux of carbon from soil organic horizons and transferring DOC with runoff across the landscape to streams (Aitkenhead *et al.*, 1999; Dawson *et al.* 2011). Given the importance of runoff generation processes to catchment functioning, it is crucial to document the GW dynamics linked to DOC source behavior for a hydrological and biogeochemical process-based understanding of DOC production and movement across the landscape.

Generally, shallow GW flow paths are the primary source of runoff in headwater catchments (O'Driscoll & DeWalle, 2010; Shaw *et al.*, 2014; Gannon *et al.*, 2014). Topographically driven lateral redistribution of water from upland hillslopes across riparian zones leads to spatially and temporally relative contributions of water and DOC sources to streams (Sanderman *et al.*, 2009; Strohmeier *et al.*, 2013; Gannon *et al.*, 2015). Topographic features (i.e., slopes, hillslope curvatures, and catchment areas) are some of the main drivers behind the spatial patterning of SOC pools across the landscape (Schwanghart *et al.*, 2011; Fissore *et al.*, 2017). DOC is mobilized from the most superficial organic-rich soil horizons with higher hydraulic conductivity, thus increasing DOC in the runoff generation process due to spatial variability of GW level dynamics (Lyon *et al.*, 2011; Wallin *et al.*, 2015).

Conceptual models based on GW dynamics and nutrient fluxes suggest that saturation of the soil profile by rising water levels mobilizes DOC stored in soil organic layers, which then increases DOC concentrations in shallow GW (Lyon *et al.*, 2011; Winterdahl *et al.*, 2011a). While DOC fluxes from saturated areas in headwater catchments contribute up to 84% of the total DOC transported to streams and shallow GW provides a stable source of DOC to streams dominant in driest periods, the most dynamic contribution of DOC comes from hillslopes (Dick *et al.*, 2015), underscoring the importance of the landscape's spatial heterogeneity in runoff generation processes for DOC sources in catchments.

Furthermore, information about DOC spatial and temporal sources across the landscape are required to estimate changes in streams during and between rainfall events. Attention must be given to areas where the water table levels occur near to surface soil organic horizons in low lying areas and riparian zones where organic-rich soils can develop immediately adjacent to stream channels (Billet *et al.*, 2006; Singh *et al.*, 2015). Previous field studies in temperate and cold, humid catchments have shown the major role quasi-permanently saturated riparian zones play as a zone for mixing water sources and controlling DOC dynamics in streams (Grabs *et al.*, 2012; Tetzlaff *et al.*, 2014; Dick *et al.*, 2015; Tunaley *et al.*, 2016; Lessels *et al.*, 2016). Some studies have also highlighted that hillslopes may act like DOC sources when enriched DOC water from organic soil horizons are delivered to streams due to hydrological connections across hillslopes, valley bottom saturated areas, and streams (McGlynn & McDonnell, 2003; Terajuma & Moriizumi, 2013; Mei *et al.*, 2014).

In this study, we monitored a headwater catchment located in Southern Brazil through a network of 12 GW wells to determine the links between GW DOC spatial patterns during low flows and SOC content in the soil profile. Multivariate statistical (Hierarchical Cluster Analysis) and correlation analyses were used to describe spatiotemporal DOC source behavior, as well as identify landscape units based on the catchment's physical characteristics and GW dynamics. Through a combination of these analyses, we describe the interactions between runoff generation processes, SOC content, and the spatial heterogeneity of DOC concentration in shallow GW as a function of water table fluctuations and the catchment's wetness conditions. Furthermore, we address the following questions to better understand the role of runoff processes in the sources and fluxes of DOC: 1) How are DOC production and mobilization in riparian zones and hillslopes linked to shallow GW spatiotemporal dynamics?; 2) How does SOC spatial distribution and runoff generation processes interact to determine spatial heterogeneity of shallow GW DOC concentrations in a headwater catchment?

2. METHODS

2.1 Study Site

The Sagui stream is a headwater catchment (Longitude - 49°31'55.23"; Latitude - 26°29'38.31") of the Iguaçu Basin (70,800 km²) with an area of 0.24 km², located along the border between Paraná and Santa Catarina States, Southern Brazil (Figure 1). Elevations range from 926 to 982 meters above sea level, with the highest point located at the southern edge of the catchment (Figure 1b). The mean slope gradient is 6.3°, with values that range from 0.35° in the bottomland to 35° on steep slopes nearest the outlet. The climate is classified as Cfa (humid subtropical) (Köppen, 1948) in a tropical/humid subtropical transition zone, usually with cool summers, mild winters, and no dry season. The mean annual air temperature ranges from 15.5 °C to 17 °C, with daily means between 12 °C and 21 °C in winter and summer, respectively. Frosts are common in winter (June and July). Mean annual rainfall (30-year) is 1685 mm/year with 138 to 164 rainy days per year and limited seasonality. Of the annual precipitation, 20% falls during events of less than 10 mm d^{-1}; 40% falls during low-intensity and high-frequency events of less than 20 mm d^{-1}; and 25% occurs during rainfall events > 40 mm d^{-1}. Mean daily evapotranspiration is ~4 mm (Uda *et al.*, 2014). Mean discharge at the outlet of the Sagui River was 3.83 L s^{-1} ± 5.68 L s^{-1} between March and December 2015.

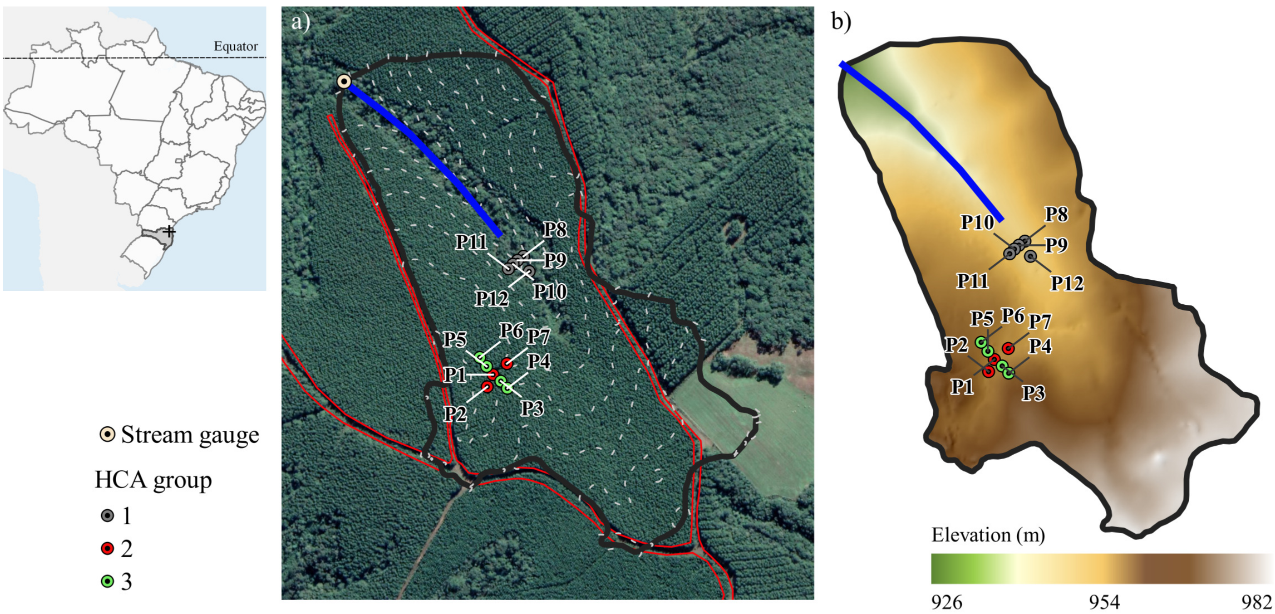

Figure 1 - Location and topography of Sagui catchment and of DOC sampling points at GW wells by HCA group and stream (a) and elevation (b).

The geology of the region consists of horizontal layers of sandstone and shale of the Itarare Supergroup, a glacial and periglacial sedimentary group. Land cover in the Sagui catchment shows a predominance of forests with *Pinus taeda spp*. (< 5 years) on hillslopes and Mixed Ombrophilous Forest in riparian zones.

The Sagui catchment is characterized by three hydropedological units that affect shallow GW dynamics. Soils on Sagui's hillslopes are characterized as Cambisols (WRB/FAO) derived from sedimentary rocks, with low fertility, medium/high organic matter content in a humic A horizon (< 50cm) that overlays a free-draining mineral subsurface horizon, and medium to high silt/clay ratio (Bognola, 2013). Steeper hillslopes are characterized by a deep soil-bedrock interface (> 300 cm), well-drained soils whose vertical drainage facilitates GW recharge, and a water table level that is rarely passes 0.5 m below the surface on mid- and upper slopes. The soil profile on lower slopes includes an organic horizon in the upper 15 cm with areas of quasi-permanent saturation; GW is higher than 0.5 m below the surface for most of the year, thus generating excess overland flow in organic horizons in the upper soil profile. Riparian zones are characterized by organic soils with poorly developed horizons and a shallow soil-bedrock interface (< 100 cm) (Histosols, WRB/ FAO). Soils have a well-structured porous media (on average >60% of soil particles greater than 0.002 mm from 0-70 cm in depth; measured at 0-10, 10-30, 30-50, and 50-70 cm for each GW well) resulting in greater permeability and quick GW response during rainfall events, with a fast-rising and falling limb, and an associated reduced water storage deficit.

2.2 Discharge, precipitation, and shallow groundwater monitoring

Beginning in 2007, stream stage height (10 min) was measured at the catchment outlet using a conventional Parshall flume coupled to a pressure transducer (GE - Druck PTX 1030) and recorded with a data logger (model Waterlog H500XL). Stream discharge was calculated based on a stage-discharge equation.

Precipitation was measured ~3 km away from the Sagui catchment using a Waterlog H-340 Tipping Bucket Rain Gauge (considering a 0.254 mm increment) coupled to a Waterlog H500XL data logger. The tipping bucket was previously calibrated in the laboratory to correct for underestimated measurements associated with extreme rainfall events.

We installed a network of 12 wells (Figure 1) across the hillslopes and riparian zones in the first-order Sagui catchment. Wells were placed in landscape units that present a range of topographic positions relative to stream, elevation, topographic wetness index (TWI), LS factor (slope length and steepness), and slope gradient (Table 1). The monitoring thus encompassed a catena sequence in the zero-order basin from mid-slope to valley bottom (P1 - P7) and the riparian zone (P8 – P12).

GW wells were installed to measure water table level and collect water samples for DOC analysis. Wells were dug with a 7.5 cm hand auger to varying depths (90 cm up to 440 cm) until reaching soil-bedrock interface and were monitored with water level sensors. GW levels were measured with pressure transducers and recorded with a Global Water GL-500 7-2 capacitance logger at 10-minute intervals and each well was analyzed in terms of GW water level dynamics, mean, median, range (i.e., the difference between maximum and minimum water level), and standard deviation from March to December 2015.

2.3 DOC water sampling, SOC soil sampling, and laboratory analyses

Field measurements were carried out from August 2014 to June 2015. Water samples from shallow GW were simultaneously collected from each well (Aug 23, 2014; Jan 20, Feb 11, Mar 31, and Jun 26, 2015) with a synthetic Bailer sampler and from the stream at the catchment outlet using grab sampling. Samples were stored in 300 ml high-density polyethylene bottles (previously washed with acid and rinsed with deionized water) and held in cold storage (Buffam *et al.*, 2007; Tiwari *et al.*, 2014) for less than three days until laboratory analysis. The 12 wells distributed along the study area were sampled for DOC analysis, resulting in 3 to 11 samples from each well (73 samples) and 18 stream samples at the catchment outlet.

Samples were filtered through 0.45 µm cellulose ester membranes and acidified with a solution of H_2SO_4 P.A. (2%) to remove free inorganic carbon. In the laboratory, DOC concentrations (three repetitions per sample) were analyzed using a Shimadzu TOC-V_{CPH} (SHIMADZU Corporation®). DOC concentrations in water samples were determined using the combustion catalytic oxidation method (680 °C), while the resulting CO_2 was detected using a non-dispersive infrared sensor (Matilainen *et al.*, 2011).

In February 2015, disturbed soil samples (~200 g) were collected using a soil auger at five depths across the soil profile to estimate vertical distribution of SOC (i.e., 0-10 cm, 10-30 cm, 30-50 cm, 50-70 cm, 70-100 cm). We collected 59 samples at 12 points near to each monitored GW well. In the laboratory, moisture was removed from the soil using a drying oven (40 °C for 48 hours). After sieving the soil samples (2 mm sieve), the samples were acidified with 10 ml HCl 1 mol L^{-1}

and heated (150 °C, until completely dry) to eliminate inorganic compounds. SOC contents (three repetitions per sample) were analyzed using a Shimadzu TOC-V_{CPH} and the combustion catalytic oxidation method (1000 °C), as described above for water samples.

2.4 Data processing and statistical analysis

We based our statistical analysis on hydrological data from August 2014 to June 2015, DOC samples (*n*= 91), and SOC contents (*n*= 59). Descriptive statistics (i.e., minimum, mean, median, coefficient of variation (CV), and standard deviation (SD)) were calculated for GW, DOC, and SOC data. Furthermore, GW dynamics, DOC and SOC data were grouped and analyzed according to the landscape position.

An individual run of Hierarchical Cluster Analysis (HCA) was conducted together with correlation analyses based on GW data (mean/median GW level, standard deviation, and range), well characteristics (depth and saturated hydraulic conductivity), and landscape properties (elevation, topographic wetness index, and LS factor) to identify groups with similar spatiotemporal GW dynamics and evaluate the DOC storage relationship in each HCA group.

HCA was applied to identify similarities in GW dynamics with distinct landscape characteristics using the k-means method "k.means function" and the Euclidean distance as a method to calculate the similarity (R Development Core Team, 2009). Correlation analyses were performed to assess DOC storage and fluxes in order to understand and describe the main landscape characteristics of each HCA group in relation to GW dynamics, SOC content, and DOC behavior.

3 RESULTS AND DISCUSSION

3.1 Groundwater dynamics in the Sagui catchment

During the study period, total precipitation was 1752.6 mm, with a wet spring season due to intense and frequent rainfall events (45% of total rainfall after September). The Sagui catchment presented elevated discharge rates (up to 155.6 L s^{-1}) and GW levels close to the surface in the spring. Time series for discharge rate, precipitation, and GW levels for sites P1 and P10 are shown in Figure 2.

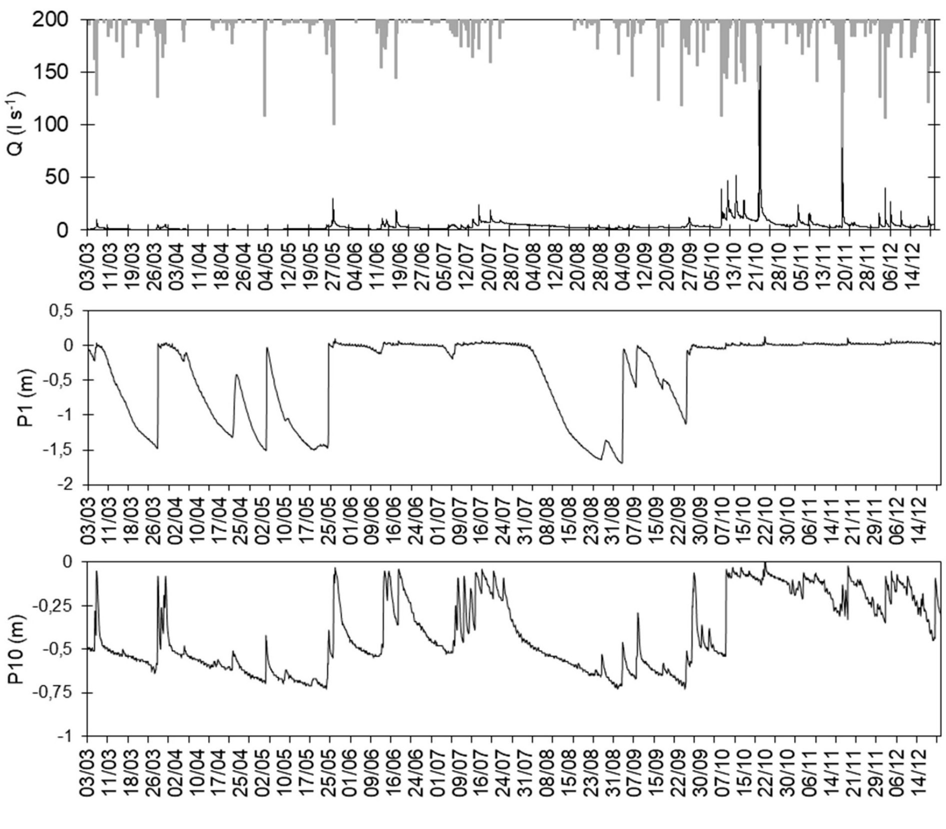

Figure 2 - a) Discharge (Q) and precipitation (P); GW levels at b) groundwater well P1 and c) groundwater well P10.

The hierarchical cluster analysis (HCA) of the 12 wells was based on GW data (mean, median, range, and SD of water table level) and landscape properties (elevation, TWI, *Ks*, LS, and soil depth to bedrock interface) (Figure 3). This approach was used by Blumstock *et al.* (2016) to organize the spatiotemporal response of GW in a montane catchment but with some differences in the data used. This method enabled us to differentiate three major groups based on the spatial distribution of wells and main landscape characteristics in the catchment (Figure 1): HCA1 – wells located close to the stream (P8, P9, P10, P11, and P12); HCA2 – wells in the dynamic saturation area on low slopes of the zero-order basin (P1, P2, and P7); and HCA3 – wells located on mid-slopes (P3, P4, P5, and P6).

GW levels differed according to landscape position and distance to stream (Figure 4). Dynamic saturation areas in the zero-order basin (P1, P2, and P7) with the highest TWI values showed water table levels close to the surface (mean of -36, -51, and -80 cm, median of -3, -24, and -62 cm below the surface, respectively) (Table 1). These wells (P1, P2, and P7) also showed *Ks* values greater than 15 m/d and soil depth to bedrock up to 3.5 m, with shallow GW often close to the soil surface. As for wetness conditions, P1, P2, and P7 regularly presented GW levels close to the surface (water level was in the upper 20 cm of the soil profile 64%, 26%, and 40% of the time), with P1 and P7 showing indications of saturation--excess overland flow (water table level > 0 cm 46% and 34% of the time; Figure 5). This was also evident in the field through the observation of overland flow when GW occurred permanently in the upper soil layers at P1, P2 and P7, resulting in higher discharge rates from May to July and after September 2015. Dynamic soil saturation was identified in the zero-order basin along with the riparian zone wells through shallow lateral flow triggered by precipitation. In these situations, hillslopes and the riparian zone were intermittently hydrologically connected to the stream (as indicated by GW level on hillslopes and riparian zone wells, and also observed in the field).

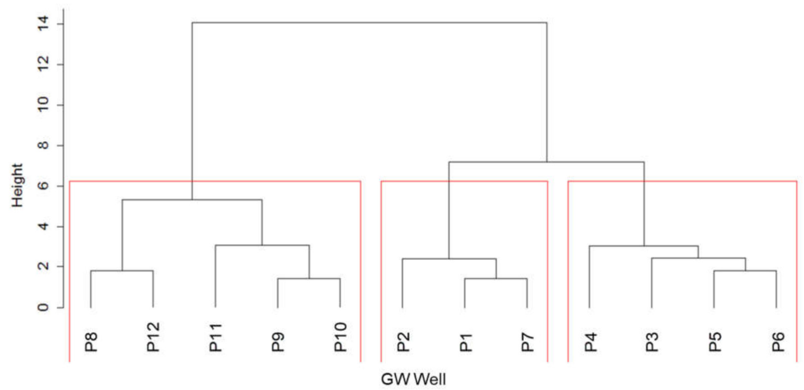

Figure 3 - Dendrogram of HCA based on groundwater data and landscape properties.

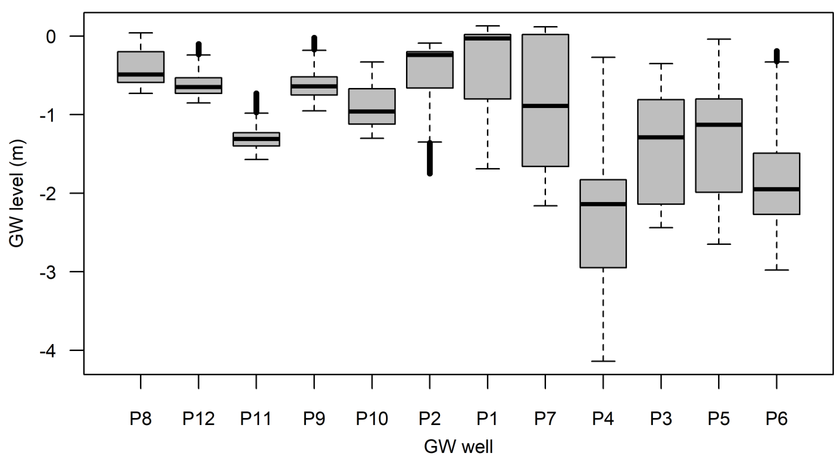

Figure 4 - Ranges in groundwater levels between March to December/2015.

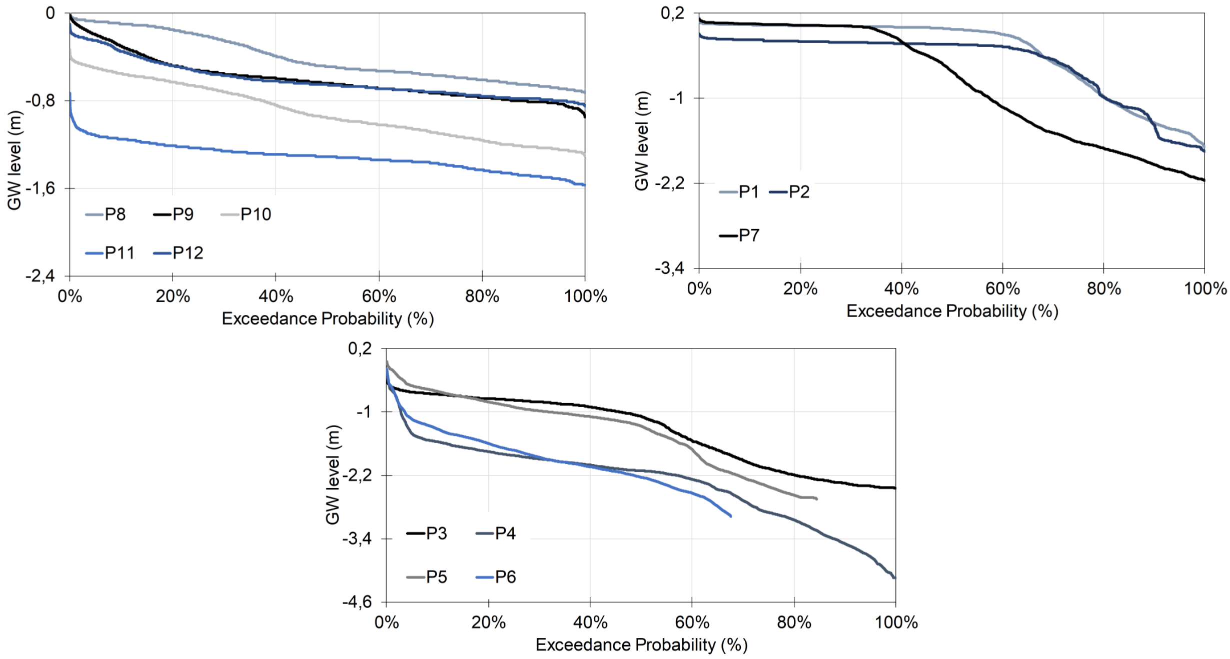

Figure 5 - Exceedance probability of groundwater levels between March to December/2015 for a) HCA1 wells, b) HCA2 wells and c) HCA3 wells.

In contrast, the zero-order basin wells showed discontinuous periods of soil profile saturation in drier conditions. Shallow GW level presented rapid rising limb and gradual falling limb at soil depths below 2 m, with an increase in catchment water storage during precipitation events above 15 mm. This resulted in a water table level close to the surface (> -10 cm) between rainfall events and during re-wetting conditions (i.e., the transition from autumn to winter; an example of P1 levels in Figure 2b). These results are similar to those found by Detty & McGuire (2010) who found that the C horizon in lower sites remained at or near saturation and only small inputs of water were required to saturate the soil profile even during events with low antecedent moisture.

Wells closer to the stream (P8, P9, P10, and P12) had a broadly similar response showing *Ks* > 9 m/d and soil depths < 1.2 m (Table 1). At these sites, GW levels showed a prompt response to precipitation inputs with rising and falling limbs that were steeper than the zero-order basin GW levels. These wells showed low standard deviation for GW levels (Table 1) and were not fully saturated, while the water table was in the upper 40 cm of the soil profile for 41%, 15%, 1%, and 1% of the time and in the upper 60 cm for 79%, 42%, 17%, and 35% of the time for P8, P9, P10, and P12, respectively (Figure 5). When GW levels rise to near saturation (> -20 cm) during precipitation events, lateral near-surface flow is triggered at valley bottoms, even with a low topographic gradient (i.e., riparian zones composed of highly permeable, shallow organic soils, with macropores). The studies by Tetzlaff *et al.* (2014) and Blumstock *et al.* (2016) support the assumption that soils with dominant lateral flow paths and little recharge to depth are strictly correlated with low water storage capacity and location in the landscape. For riparian zone wells in the Sagui catchment, the increase in flow accumulation and drainage area also led to an increase in lateral flow paths in the organic layer and were inversely correlated with soil depth. Although P11 is located near a low hillslope–riparian zone transition (low TWI value and high slope), water table behavior at this point rarely reached levels in the upper 1 m of the soil profile even in wetness conditions.

For P3, P4, P5 and P6, a very similar GW behavior was observed even though these wells are located on different mid-slopes with greater slope and lower drainage area than HCA1 and HCA2 wells. P4 exhibited anomalous GW behavior with the water table at levels below 3 m even in drier conditions. Mid-slope wells showed a deeper water table level in the Sagui catchment (mean of -137.0, -232.7, 134.3, and -188.5 cm below surface) and high variability of GW levels (Table 1). In comparison with low slopes in the zero--order basin, P3 and P6 showed slower rising and falling limb on the hydrographs during rainfall events when the water table rarely rose above -60 cm from the soil surface (i.e., 4%, 1%, 10%, and 1%, respectively), and a confined drawdown by the soil-bedrock interface until the re-wetting season in May to July 2015.

3.2 Spatial heterogeneity and vertical distribution of soil organic carbon

For the three identified clusters based on GW and landscape data, SOC concentration showed clear differences in the soil profile and spatial distribution across the landscape (Table 2). Figure 6 shows the relationship between SOC content by depth (0-100 cm) and flow duration curves for water table level data per GW well. The highest SOC content was found in riparian zone wells (HCA1), mostly in the more permeable near-surface soil (0-10 cm) with a mean SOC value of 127.74 ± 71.24 g kg^{-1} (average value ± standard deviation), and showing a limited relationship between depth and decay after a soil depth of 0 - 30 cm (P8, P9, and P11, shown in Figure 6h, Figure 6i, and Figure 6k, respectively). In general, organic soils in riparian zones (i.e. Histosols) show low of SOC content in depth due to the effects of successive high wetness conditions that prevent the incorporation of organic matter into the deeper soil causing a depletion of SOC content in depth (Drouin *et al.*, 2011; Saint-Laurent *et al.*, 2013; Saint-Laurent *et al.*, 2017).

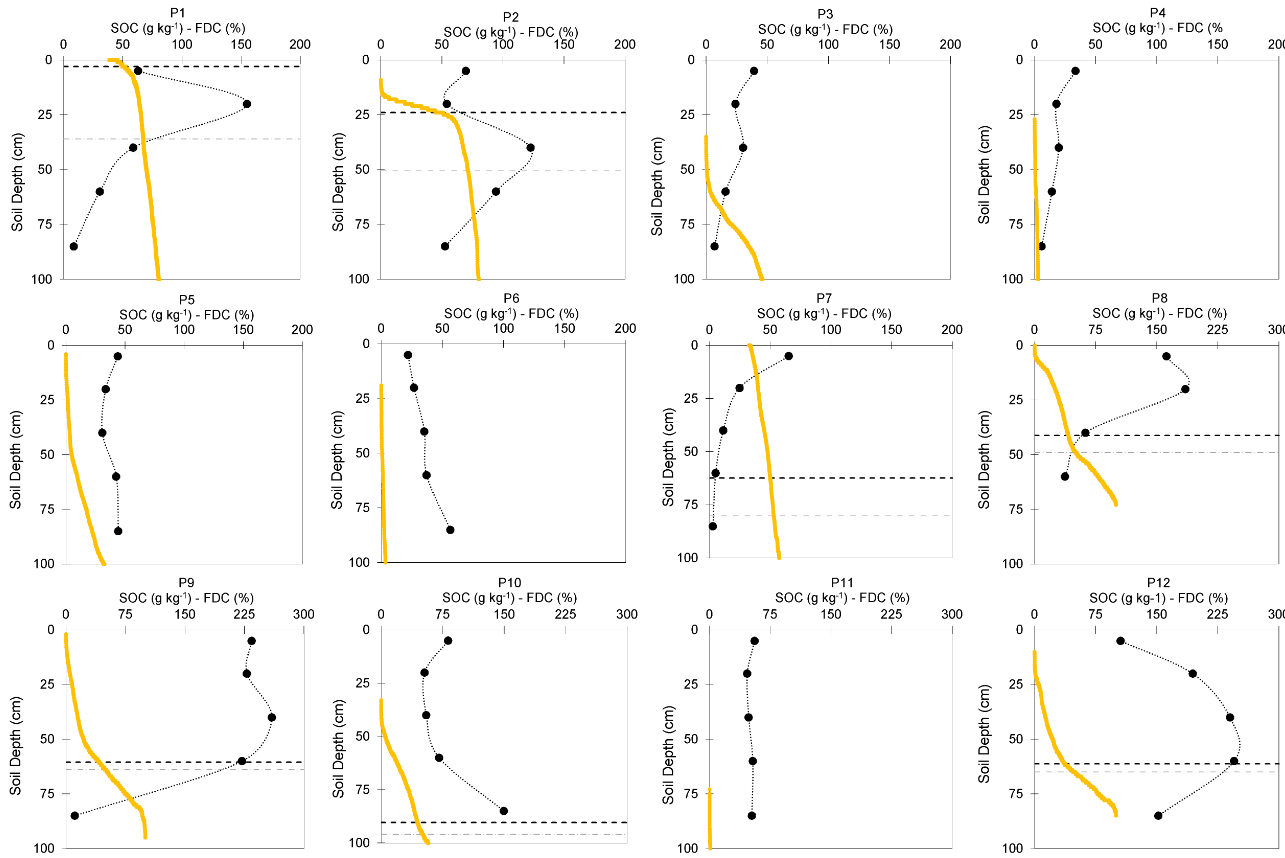

Figure 6 - Vertical distribution of soil organic carbon (g kg-1) in the soil profile per groundwater well (P1 to P12). Dashed lines in black and grey represents, respectively, mean and median of shallow groundwater water table level. Yellow line represents the flow duration curve (%) for each groundwater well for 0 - 100 cm depth range.

A broad pattern was observed in HCA2 wells (P1 and P2, Figure 6a and Figure 6b; mean SOC at 0 – 10 cm, 65.91 ± 3.33 g kg^{-1}) showing lower variability of SOC content than in the riparian zone soils (Table 2). The lowest SOC content by soil horizons were recorded in HCA3 wells. In five out of seven sites in the zero--order basin we found a clear relationship between soil depth and SOC decay: P1 and P2 with a decrease in SOC content below 0 – 30cm; and P3 (Figure 6c), P4 (Figure 6d), and P7 (Figure 6g) with a continuous decrease with depth (0-100 cm). In hillslope soils, SOC accumulates in surface horizons with the mineral material remaining as a well-defined layer (Billet *et al.*, 2006). Litter (i.e. dead leaves, twigs, stems) and decomposition of organic matter are the main sources of SOC, ensuring a constant input in superficial layers of riparian soils (i.e., Figure 6c, Figure 6d and Figure 6e) (Rieger *et al.*, 2004; Saint-Laurent *et al.*, 2017). SOC content in reforestation areas is also affected by the transfer rate of organic carbon from litter to soil (i.e., litter quality and humidification rate), with an increase in SOC accumulation as a consequence of increased wetness conditions (Paul *et al.*, 2002).

We found a major influence of topography on SOC content (0-100 cm) for wells on two transects consisting of P4 - P3 - P1 and P6 - P5 - P1 (concave slope), where upland areas have less SOC than soils in lowland areas (Table 2). These results are similar to those found by Ritchie *et al.* (2007), Hancock *et al.* (2010), and Li *et al.* (2013), suggesting that soil redistribution patterns and topographic gradient contribute to spatial patterns of SOC across the landscape.

Vertical redistribution of SOC in the soil profile can be triggered by water infiltration and nutrient leaching during rainfall events (Dosskey & Bertsch, 1997; Jobbagy & Jackson, 2000) whilst lateral redistributions can be related to the flushing of organic carbon by shallow groundwater in the upslope soils (Gannon *et al.*, 2015). Consequently, we found an increase in SOC content in subsurface soil horizons as observed in the hillslope (i.e., P6, Figure 6f) and in the riparian zone soils (i.e., P8, P9, P10, and P12, Figure 6h, 6i, 6j, and 6l, respectively). Here, there was a clear relation between shallow soils in the riparian zone and organic carbon content (SOC > 80 g kg^{-1}) with higher TWI values, low soil moisture deficits, and quick water drainage due to macropores ($Ks > 6$ m d^{-1}). Furthermore, landscape SOC patterns can be derived from the soil water regime where higher TWI values show larger biomass production and lower rates of mineralization (Terra *et al.*, 2004).

Simple relationships between SOC content (0-30 cm), groundwater data (mean and median), and landscape properties (TWI and LS factor) were tested (Figure 7). We found a strong linear correlation for mean GW (r= 0.82; r= 0.93; r= 0.81 for HCA 1, HCA2, and HCA3) and median GW (r= 0.84; r= 0.95; r= 0.88 for HCA 1, HCA2, and HCA3) for the three groups: GW closer to the surface led to greater SOC contents. Thus, the persistence of high GW levels in organic-rich soil horizons may cause shifts from an anaerobic to an aerobic condition. GW at or very near saturation results in a lack of available CO_2 in the soil profile allowing an increase and maintenance of SOC in soil surface horizons (Meersmans *et al.*, 2008). This is due to limited levels of microbial activity because water obstructs organic matter decomposition in the soil (Reichstein *et al.*, 2005). As a consequence, we can assume that with higher moisture content in the soil profile, more SOC is preserved and DOC produced (Birkel *et al.*, 2014). The influence of topography on SOC was evident through a significant and negative relationship with LS factor. In contrast, the lowest correlation was found with TWI values (r= 0.45; r= 0.5; r= 0.35 for HCA 1, HCA2, and HCA3). GW behavior and topographic characteristics of hillslopes and riparian zones show distinct SOC patterns through the transient saturation of the soil profile (i.e., time and frequency) as shown for the HCA groups (Figure 7).

3.3 Spatial and temporal dynamics of DOC production in different landscape units (hillslopes, riparian zones, and stream) related to GW dynamics and SOC vertical content

The average DOC concentration for the Sagui River was 2.46 ± 1.34 mg L^{-1} (n= 18) with low variability (0.80 mg L^{-1} – 6.2 mg L^{-1}). Other studies in headwater systems have shown slightly higher DOC concentrations in streams, ranging from 2.7 to 4.7 mg L^{-1} (Liu & Sheu, 2003; Chaplot & Ribolzi, 2014). However, the mean DOC for the Sagui River could be underestimated as it was collected mainly during low flows (1.77 L s^{-1} to 46.47 L s^{-1}). We found a non-linear relationship between DOC and discharge, which is similar to the results presented by Dawson *et al.* (2008), Oswald & Beanfireun (2014), and Kasurinen *et al.* (2016). In general, this non-linear behavior could be related to runoff source areas which gradually extend from the riparian zone to the hillslope area and considering that storm flow chemistry dynamics are associated with GW dynamics (Katsuyama *et al.*, 2001).

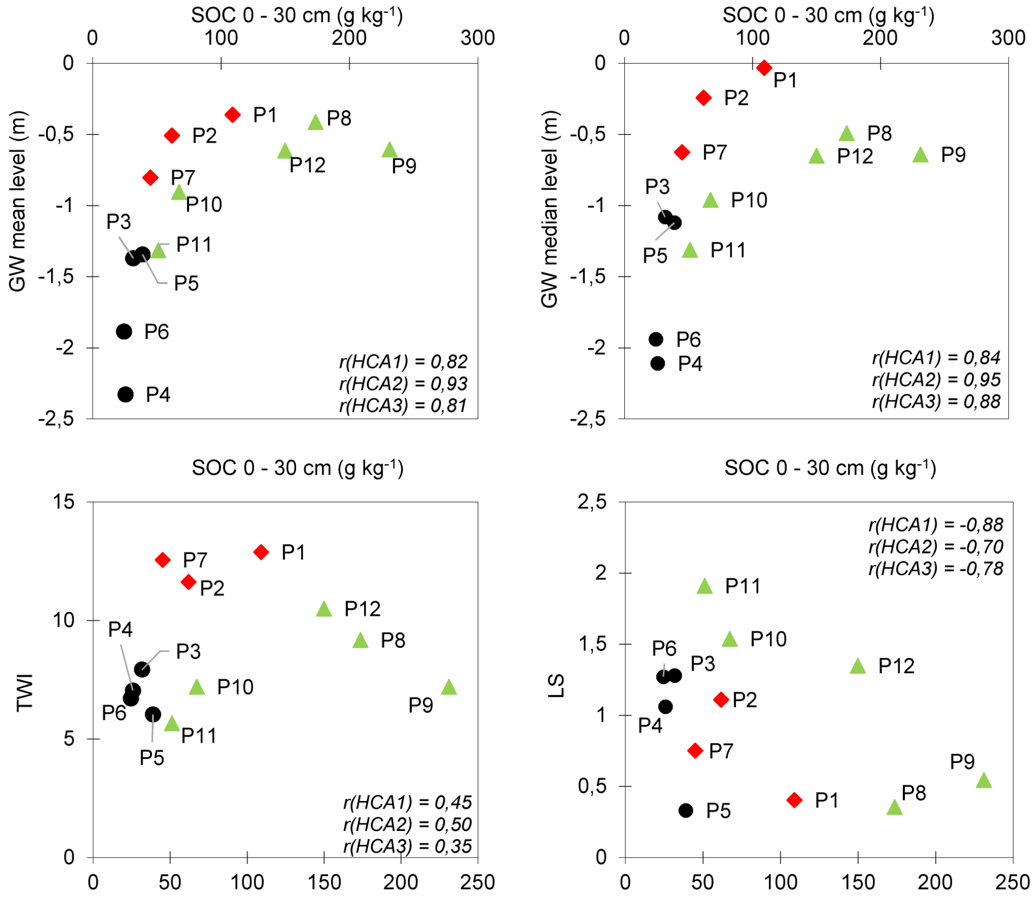

Figure 7 - a) Groundwater mean levels; b) Groundwater median levels; c) Topographic Wetness Index (TWI) and d) LS factor versus soil organic carbon (0-30 cm) for each groundwater well.

GW DOC data also differed widely in terms of time, landscape position (Figure 8), and HCA group (Figure 11). The highest mean concentration of DOC in GW was observed in the dynamic saturation area on low slopes in the zero-order basin, P1, P2, and P7 (4.83 ± 2.53 mg L^{-1}, *n*= 25). Higher variability was observed in HCA1 wells in the riparian zone (3.86 ± 2.93 mg L^{-1}, n= 25), which is consistent with the spatial heterogeneity of SOC in the landscape. Our data (Table 3) suggest that due to the spatial heterogeneity of DOC in GW, subsurface DOC enrichment processes could be related to: I) SOC redistribution processes across the landscape following topographic patterns (i.e., upland areas to valley bottom areas) (Ritchie *et al.*, 2007; Schwanghart & Jarmer, 2011); and II) the interception between GW level with organic rich horizons on the soil surface (Winterdahl *et al.*, 2011a; Winterdahl *et al.*, 2011b; Lambert *et al.*, 2013); thereafter, the breakdown of SOC for DOC production and pathways for its transformation. Other studies have shown changes in GW DOC could be explained by soil/air temperature, CO_2 concentration in the atmosphere, microbial activity, water storage in the soil profile, and runoff generation processes (Kalbitz, *et al.*, 2000; Erlandsson *et al.*, 2008; Laudon *et al.*, 2011; Grabs *et al.*, 2012; Birkel *et al.*, 2014).

Wells clustered by hydrological behavior and landscape characteristics also presented similar DOC patterns (i.e., HCA2 and HCA3; Figure 8). HCA1 and HCA2 showed a high temporal variability of GW DOC. Enrichment of DOC in a dynamic saturation area or riparian zone can originate from: I) leached organic matter in the soil profile during rainfall events; II) DOC transfer from upland soils and runoff generation processes; and III) hyporheic fluxes between the riparian zone and streams (Grabs *et al.*, 2012). In Sagui's catchment, zero--order basin soils which remained fully or almost fully saturated (P1, P2, and P7) showed higher DOC contents providing a stable source of DOC downslope by lateral flow. The relationship between dynamic saturated areas, organic matter decomposition, and DOC production and fluxes was modeled by Birkel *et al.* (2014) and Dick *et al.* (2015) for peat-dominated catchments. Their analysis is consistent with the results found herein for groups HCA1 and HCA2 in the Sagui catchment demonstrating that hydrological hotspots can control DOC production and mobilization from landscapes to riverscapes.

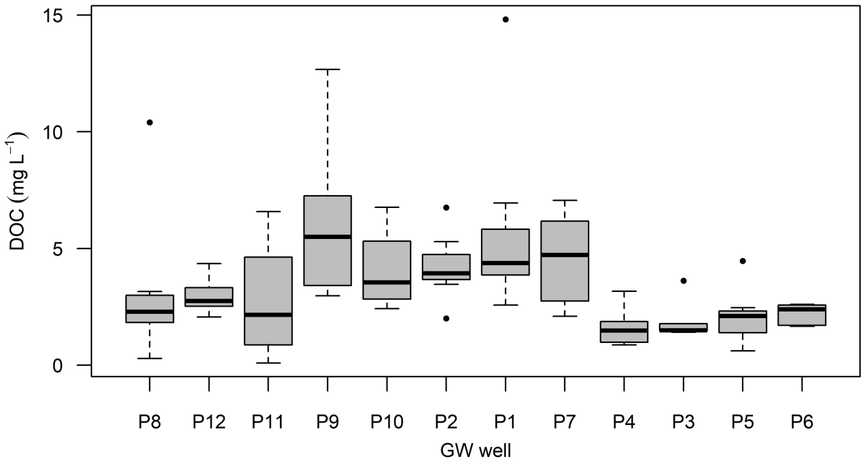

Figure 8 - Ranges in groundwater DOC concentrations for groundwater wells (P1 – P12).

DOC concentrations in GW wells changed according to the water table level on low slopes and in the riparian zone (Figure 9). This is consistent with Lyon *et al.* (2011) who emphasized a decrease in total organic carbon concentration with depth of the soil profile for riparian zones. As for HCA2 and HCA3, GW DOC concentration tended to show higher values when the water table level was nearer to the surface (> -10cm). There was also a strong, exponential decrease in DOC concentration with depth in the soil profile (Figure 9). However, there was less of a pattern for HCA1 wells, as shown for SOC content in the soil profile, where DOC concentrations ranged from 0.28 mg L^{-1} to 12.68 mg L^{-1} and a water table level between 0-50 cm in the soil profiles. These findings support the evidence that DOC concentration in headwater streams is highly correlated with the nutrient flushing mechanism in which DOC peak occurs before discharge peak (Boyer *et al.*, 1996; Inamdar *et al.*, 2004; McGlynn & McDonnell, 2003; Mei *et al.*, 2014). The main hypothesis underlying this mechanism is based on catchment residence time and the spatial heterogeneity of saturated areas in the landscape. Water table rising at or close to the surface increases GW DOC concentration in areas with higher SOC labile fractions (i.e., riparian zones and dynamic saturated areas), which is then transported laterally into streams through runoff processes (Mei *et al.*, 2014) that are driven by the degree of hydrological connectivity between DOC sources on hillslopes and riparian zones (Tunaley *et al.*, 2017).

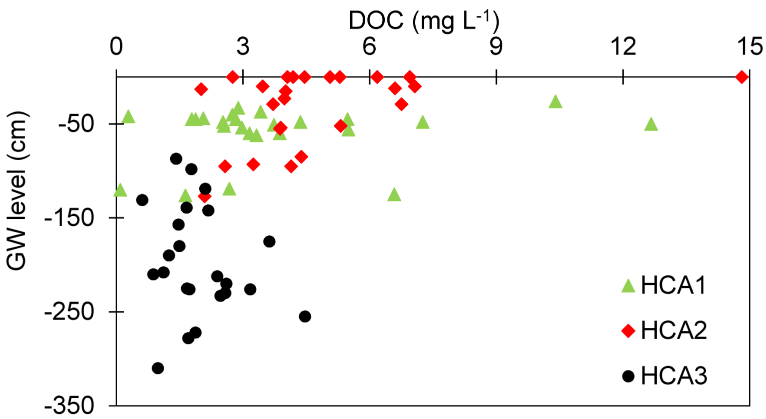

Figure 9 - DOC concentration versus groundwater water table position for HCA groups.

As for HCA2 wells, DOC production was increased when the catchment presented wetter conditions due to the significant active water storage in the catchment and persistent GW level in the upper (0-30 cm) soil layers (i.e., highest SOC content). This is highlighted by mean DOC concentrations for P1 (5.44 mg L^{-1}), P2 (4.18 mg L^{-1}), and P7 (4.59 mg L^{-1}) that showed greater DOC concentration limits when the water table level was above -30 cm from the soil surface. Moreover, for HCA1 wells we found evidence of a continuous DOC mobilization in GW due to permanent wet conditions (i.e., low water deficit) and SOC content in riparian soils. Thus, DOC enrichment of GW was observed even in the driest conditions for the riparian zone wells due to intermittent leaching of organic carbon from the soil profile mixed with DOC--enriched water from upslope dynamic saturation areas. The role of wet conditions in DOC-enriched water storage has been presented elsewhere; Oswald & Beanfireun (2014) showed an accumulation of potentially mobile DOC in the organic soil layer during the warm and dry summer period. As the catchment became wetter in the autumn, the authors found an increase in soil water DOC concentrations which were subsequently flushed during rainfall events. The nature of this relationship (DOC concentration and GW) is associated with highly dynamic GW behavior triggered by rainfall inputs on low slopes and in riparian zones. The soil profile in these locations could be eventually leached during wet conditions due to upland (HCA1) or local (HCA2) saturation-excess overland flow.

Several studies, including those by McGlynn & McDonnell (2003), Billet *et al.* (2006), Grabs *et al.* (2012), and Dick *et al.* (2015), have shown the influence of landscape characteristics on DOC dynamics. We also tested simple regression models for correlation analysis to describe the major factors affecting DOC heterogeneity in the Sagui catchment through mean DOC concentration for each well versus mean and median GW level and TWI (Figure 10). We found a clear relationship between DOC concentration and mean (r= 0.8) and median (r= 0.81) GW level (Figure 10a and Figure 10b). A moderate statistical correlation between DOC concentration and TWI (r= 0.66) (Figure 10c) was also found. Thus, the wetter the well (high TWI and mean/median GW level close to the soil surface), the higher the mean DOC production at the hillslope scale. Even though hillslopes and riparian zones showed distinct hydrological behavior and landscape characteristics, DOC concentration dynamics in the catchment were linked to spatiotemporal GW dynamics. This is consistent with Grabs *et al.* (2012), who used a combination of TWI values and GW levels to improve a modeling framework used to describe DOC dynamics in temperate riparian zones.

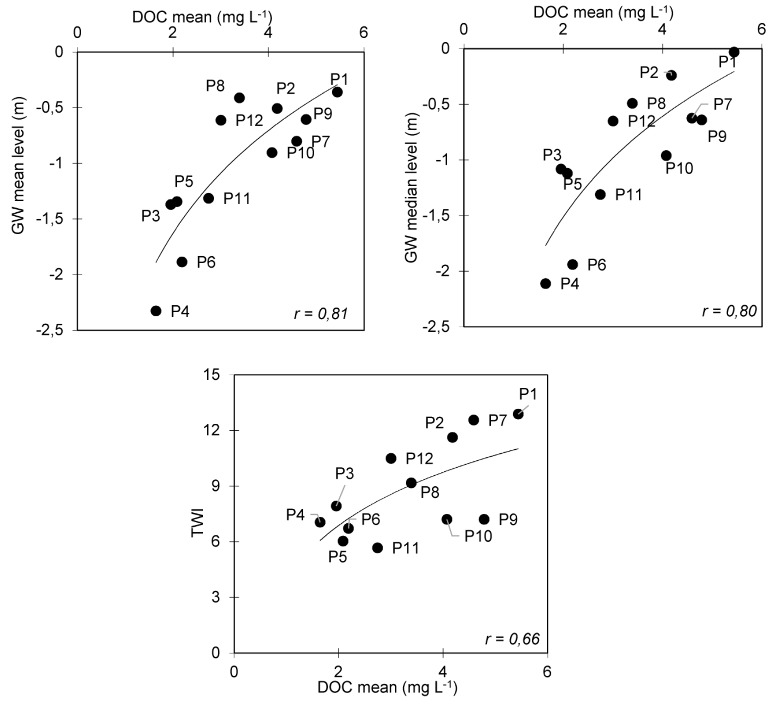

Figure 10 - DOC concentration for each well versus a) Groundwater level (mean), b) Groundwater level (median), c) Topographic Wetness Index (TWI).

Mean DOC values for GW on hillslopes and riparian zones in the Sagui catchment were slightly lower than other studied catchments in temperate climates (McGlynn & McDonnell, 2003) or peat-dominated headwaters (Dawson *et al.*, 2008; Lyon *et al.*, 2011; Grabs *et al.*, 2012; Dick *et al.*, 2015). Landscape characteristics (Thomas *et al.*, 2004; Buffam *et al.*, 2007) and catchment hydrological and biochemical behavior (Aitekenhead *et al.*, 1999; Laudon *et al.*, 2011) have been identified as the major drivers of allochthonous DOC inputs to streams. Thus, we found that in dynamic saturation areas (HCA1 and HCA2), mean DOC concentration in GW is 60% and 95% higher, respectively, than the stream during low flows (Figure 11). The mobilization of DOC-enriched GW to streams is triggered by precipitation events and transfer of DOC between source areas and streams. However, GW is constantly transferred to streams during low flows and has a more stable and lower DOC concentration (Tiwari *et al.*, 2014; Dick *et al.*, 2015) than other compartments of streamflow generation processes (i.e. overland flow, streamflow, and soil water) (Chaplot & Ribolzi, 2014).

We observed a shift in spatial patterns of GW DOC concentration (Figure 12) as a function of GW levels and precipitation events, as described by Dawson *et al.* (2008) and Van den Berg *et al.* (2012). During the August 2014 and June 2015 sampling surveys, a higher mean GW DOC concentration was observed in the near-stream riparian zone (HCA1: 6.54 mg L^{-1} and 4.23 mg L^{-1}) in comparison with HCA2 (4.18 mg L^{-1} and 3.27 mg L^{-1}, for GW level above -90 cm for P1, -50 for P2, and -130 cm for P7), and HCA3 wells (1.54 mg L^{-1} and 1.55 mg L^{-1}).

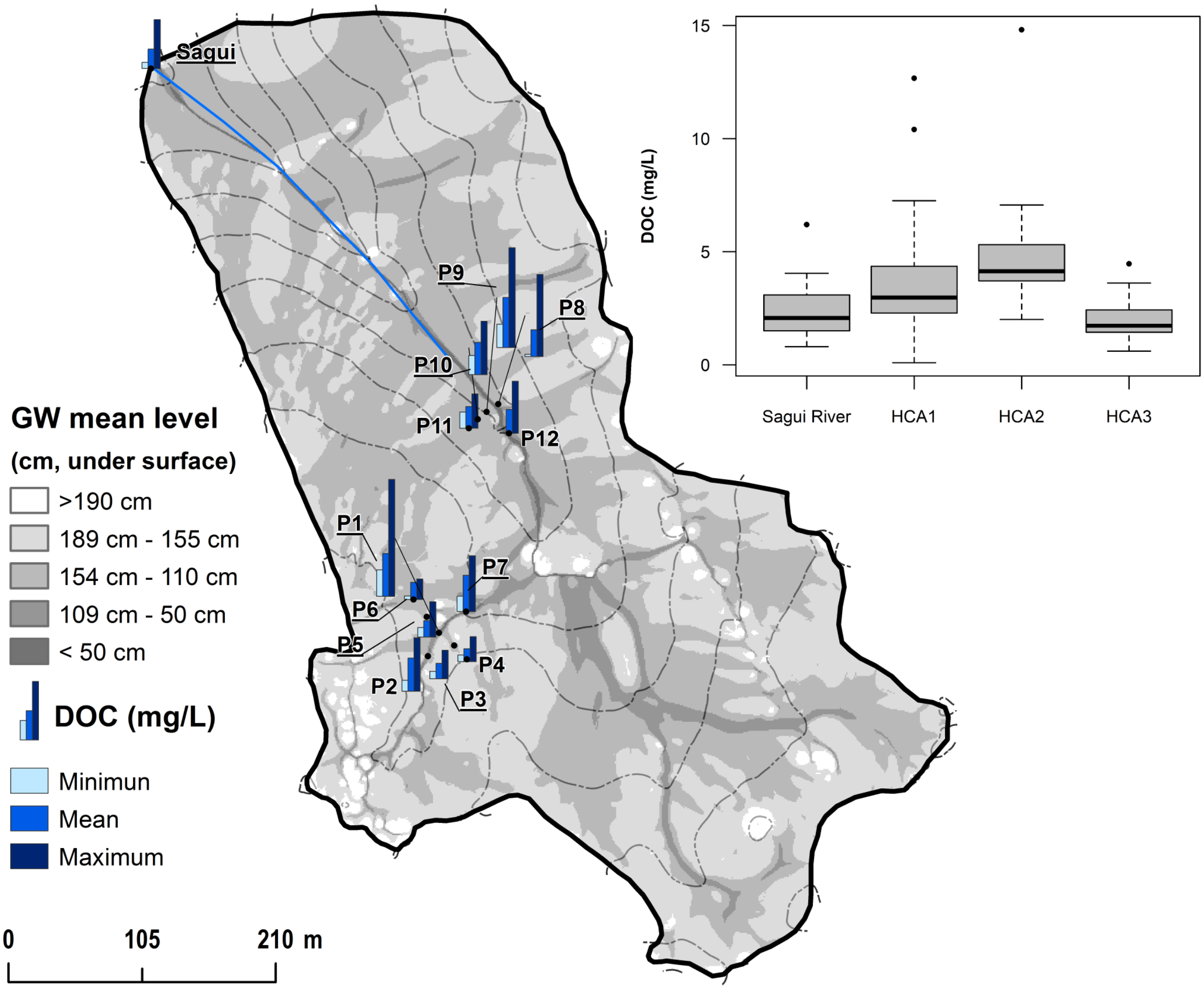

Figure 11 - Groundwater mean level for Sagui's catchment, DOC minimum, mean and maximum production for each Groundwater well and ranges in DOC concentration for each HCA group

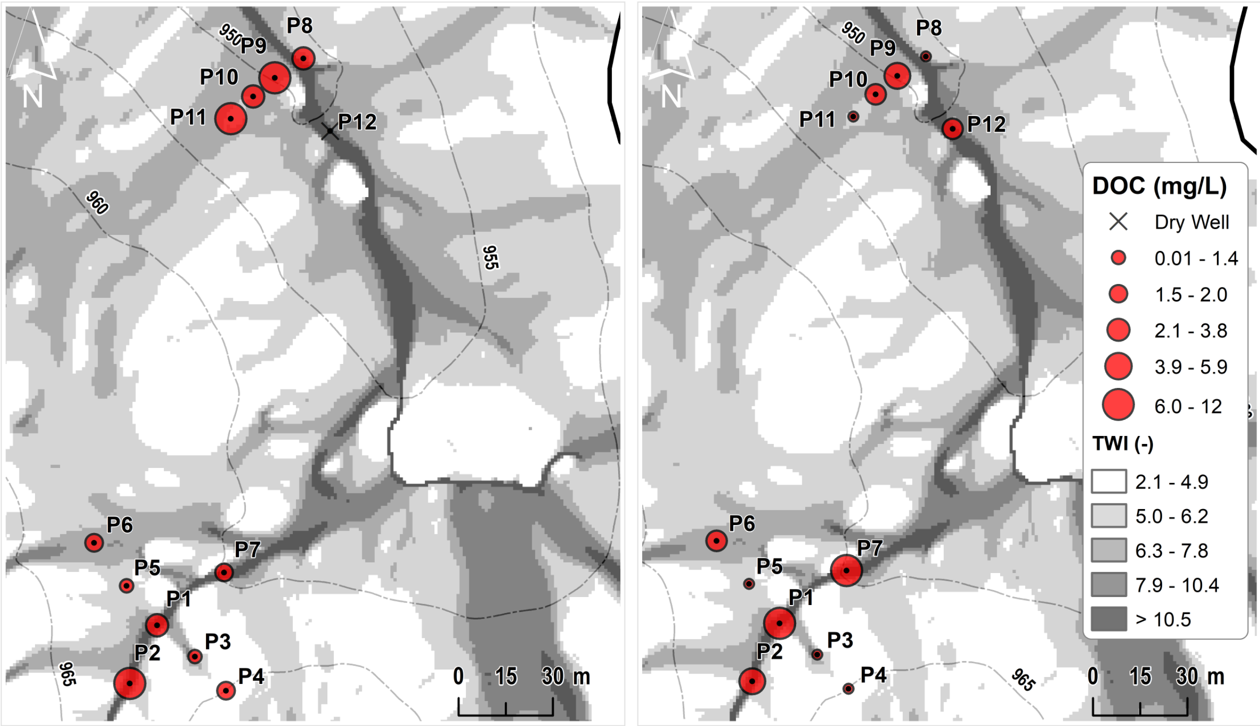

Figure 12 - DOC concentration for each well for simultaneous sampling in August/2014 (left) and March/2015 (right).

In these situations, riparian zone wells (i.e., P8, P9, and P12) showed a low soil moisture deficit and rapid water table fluctuations during rainfall events reflecting the ability of landscape and connectivity to control near-surface runoff generation processes (Tetzlaff *et al.*, 2007), where hydrological behavior is associated with interactions with dynamic saturation zones on hillslopes (Tetzlaff *et al.*, 2008). These findings may complement results found by Boyer *et al.* (1996) and Mei *et al.* (2014) who described DOC dynamics as a function of the flushing hypothesis, where DOC delivered to streams originates primarily from DOC stored during low flows in near-stream riparian soils. In short, pre-rainfall event water stored in riparian soils that have been enriched with DOC can be quickly transferred during rainfall events due to the rising and lateral flow of GW (Bishop *et al.*, 2011), connecting soils from dynamic saturated areas to streams (Grabs *et al.*, 2012).

In contrast, for sampling surveys in January, February, and March 2015, the mean DOC concentration in HCA2 wells (4.04 mg L^{-1}, 5.12 mg L^{-1}, and 6.43 mg L^{-1}, for a GW level above -20cm for P1 and P2) were up to 100% greater than HCA1 riparian wells (3.01 mg L^{-1}, 3.39 mg L^{-1}, and 3.16 mg L^{-1}) and up to 320% greater than mid- and upslope HCA3 wells (1.92 mg L^{-1}, 1.92 mg L^{-1}, and 1.53 mg L^{-1} for GW level below -90 cm for P3, P4, P5, and P6). This result could indicate a quasi-permanent hydrological connection across DOC sources in hillslopes, riparian zones, and streams that is triggered in precipitation events due to the near or full saturation of the soil profile in a dynamic saturation area of the zero-order basin (P1, P2, and P7). Fractions of the produced DOC could be mobilized downslope during rainfall events due to lateral GW flow, generating the movement of DOC enriched water from hillslopes, across the riparian zone, to the adjacent stream.

Chaplot & Ribolzi (2014) argued that the main reason for lower DOC concentrations in riparian zones could be related to the slow downslope movement of water from hillslopes and loss of DOC due to microbiological interactions with soils (i.e., organic matter decomposition and DOC absorption of inorganic fractions). Although a dynamic saturated area in a zero-order basin shows higher relative DOC concentrations due to a large production of DOC and storage characteristics of the landscape (Dick *et al.*, 2015), water and DOC transfer from hillslope soils is related to the occurrence of precipitation events when hydrological connectivity enables DOC transfer across the landscape to streams (Gannon *et al.*, 2015).

4. CONCLUSIONS

Our results suggest the critical importance of dynamic saturation areas for DOC production and storage that are linked to GW level dynamics. In addition, the results showed that mobilization of DOC fractions in the landscape is strictly related to hydrological connectivity between runoff and DOC source areas with streams, as dynamic saturation areas demonstrated higher DOC production that may be transferred downslope due to lateral GW flow during precipitation events. Higher SOC contents (0 – 1 m) exhibit a strong, positive correlation with mean and median GW level near the surface due to shifts from anaerobic to aerobic conditions, allowing an increase in SOC storage in the soil profile and, as a consequence, DOC production and mobilization. Although there was slightly less SOC in the soil profile, DOC concentration in GW in the zero-order basin wells was greater than in the near-stream riparian zone wells, particularly when GW level was within 0.1 m of the soil surface. For mid- and bottom slopes, the relationship between GW level variations and DOC concentration, which showed an exponential decrease with depth, is highly affected by soils with lower SOC contents within 0.5 m of the surface. Moreover, we also observed changes in DOC production patterns on hillslopes and riparian zones as a function of GW levels and precipitation patterns.

This study highlights the role of GW dynamics linked to SOC content and DOC sources in a subtropical headwater catchment with a highly dynamic saturated area, thus improving our understanding of how DOC is produced and mobilized across the landscape. The approach presented herein can be applied to other geographical settings and supports conceptual or quantitative analyses of hydrological functioning within catchment areas, particularly in terms of runoff generation, shallow GW fluctuations, and vertical distribution of SOC content in the soil profile, and how they are linked to DOC sources and exportation from headwater systems into the broader landscape.

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