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“EFFECT OF LAND COVER AND HYDRO-METEOROLOGICAL CONTROLS ON SOIL WATER LEACHATE DOC CONCENTRATIONS IN A HIGH-ELEVATION TROPICAL ENVIRONMENT”

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ABSTRACT

Páramo soils store high amounts of organic carbon. However, climate change and changes in land cover/use may cause a decrease in their carbon storage capacity. As such, a better understanding of the factors influencing the páramo soils carbon storage and export is urgently needed. To fill this knowledge gap we selected the Quinuas Ecohydrological Observatory (91.3 km^2) in south Ecuador, and study the hydro-meteorological conditions controlling the dissolved organic carbon (DOC) content in the soil water for the four main land cover types (tussock grass, natural forest, pine plantations and pasture). Weekly soil water samples for DOC analysis, as well as meteorological variables and soil water content and temperature probes (5-min intervals) from various depth and slope positions were monitored within the soils' organic and mineral horizons between October 2014 and January 2017. These data was used to generate regression trees and random forest statistical models in order to identify controllers of soil water DOC concentrations. Our results evidenced that land cover is the most important predictor in the models, followed by sampling depth and soil moisture. Natural forest have been identified with the higher DOC concentrations in soil water followed by pasture, tussock grass and pine forest. DOC concentrations also increase with decreasing soil moisture (except when soil moisture is >0.56 $m^3 m^{-3}$ in natural forest). The latter shows that land cover change and factors that affect soil moisture conditions over time, are very likely to lead significant changes in DOC concentrations in soil water and therefore in streams.

Key words: páramo, DOC, soil water, soil moisture, soil temperature, meteorological controls, carbon flux, tropical wetlands.

Abbreviations	
CART.	Classification and regression trees method
CNP.	Cajas National Park
DOC.	Dissolved organic carbon
FAO.	Food and Agricultural Organization
IncMSE.	Increase mean square error
IncNodePurity.	Increase node purity
ITCZ	Inter Tropical Convergence Zone
QT	Quinuas catchment transect
RF.	Random forest method
RH.	Relative humidity
SOC.	Soil organic carbon
SOCD.	Soil organic carbon density
TOC.	Total organic carbon
VIF.	Variance Inflation Factor

RESUMEN

Los suelos de páramo almacenan grandes cantidades de carbono orgánico. Sin embargo, el cambio climático y en la cobertura/uso de suelo podría causar un descenso de esta capacidad. Por esto, es urgente generar un mejor entendimiento de los factores que influencian el almacenamiento y exportación de carbono. Para llenar este vacío de conocimiento se seleccionó el observatorio Eco-hidrológico Quinuas (91.3 Km2) en el sur del Ecuador, dentro del observatorio se estudiaron las condiciones hidro-meteorológicas que controlan el contenido de carbono orgánico disuelto (DOC) en el agua de suelos de las cuatro coberturas predominantes de la cuenca (pajonal, bosque natural, bosque de pino y pasto). Se tomaron muestras semanales de agua de suelos para su análisis y se midieron variables meteorológicas, de contenido de agua de suelo (humedad de suelo) y temperatura de suelo (en intervalos de 5 minutos) en las laderas correspondientes a cada cobertura estudiada entre Octubre-2014 y Enero-2017. Estos datos se usaron para generar modelos estadísticos (árboles de regresión y bosques aleatorios) con el objetivo de identificar controladores de las concentraciones de DOC en el agua de suelo. Nuestros resultados evidencian que la cobertura de suelo es el predictor más importante en los modelos, seguido por profundidad de muestreo y humedad de suelo. De esta manera, el cambio de cobertura de suelo y factores que causen un cambio en las condiciones de humedad de suelos a lo largo del tiempo, podrían generar cambios en la concentración en el agua de suelos y por lo tanto en los ríos.

Palabras clave: páramo, DOC, agua de suelos, humedad de suelos, temperatura de suelos, flujos de carbono, humedales tropicales.

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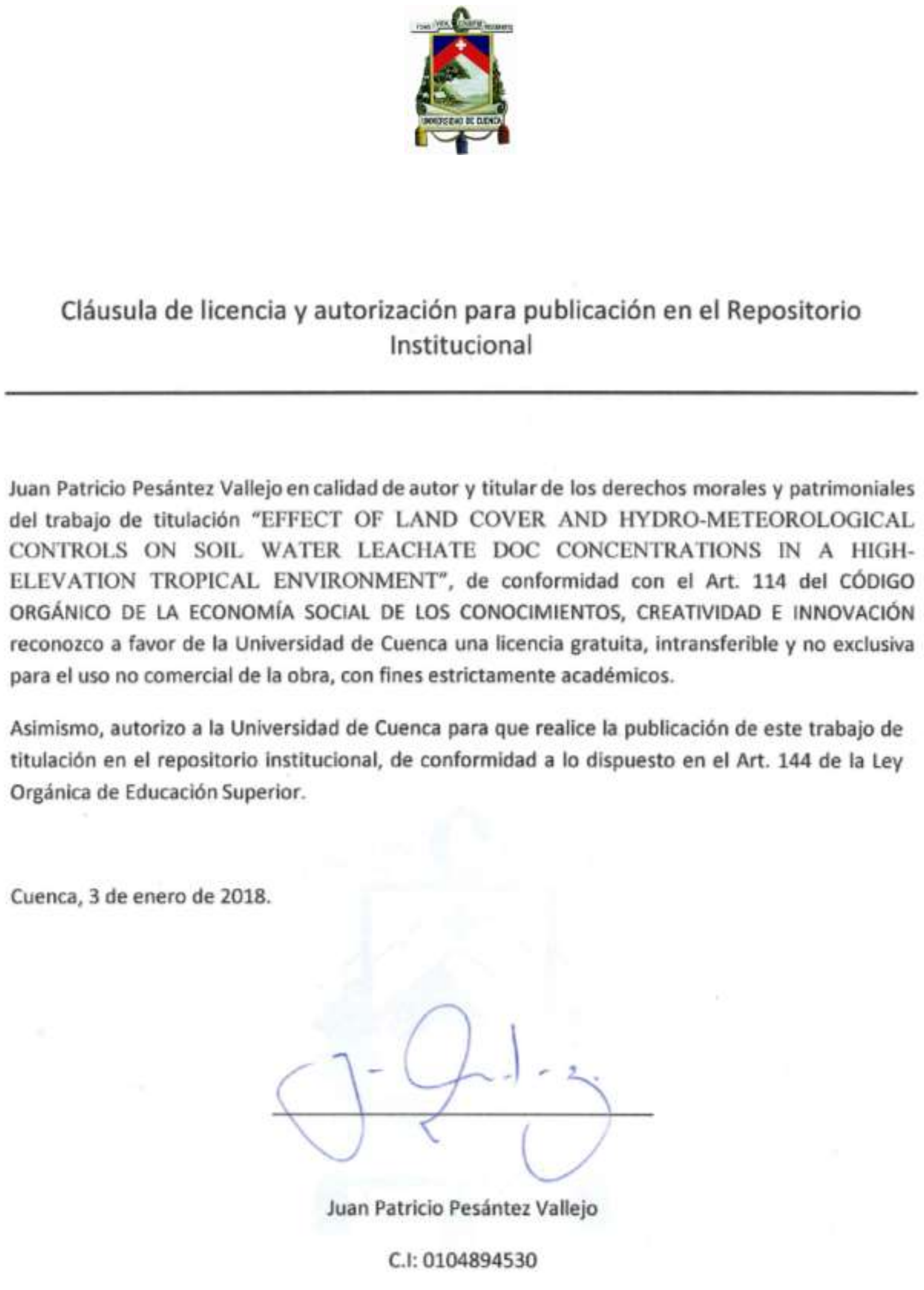

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1. Introduction

The global carbon cycle is one of the most important and complex cycles on earth (Baldock, 2007; Lal, 2004). Within the carbon cycle, the incorporation of carbon into the soil is a decomposition process in which plants and animals break down the organic material into smaller particles. This process continues repeatedly via microbial activity until the organic matter has been converted into the final product: humus (Stockmann et al., 2013). This incorporation of organic matter allows soils to be the largest total carbon reservoirs worldwide (~2500Gt) after the oceans (~38400Gt) and before the atmosphere (~760Gt). Thus, soil carbon storage plays a crucial role in the overall planet´s carbon cycle (IPCC, 1990; Lal, 2004; Stockmann et al., 2013). The amount of soil organic carbon (SOC) (~1550Gt) stored in the Earth´s soil reservoir indicates that any alterations made to it could significantly impact atmospheric CO_2 (Baldock, 2007). These alterations have effects on global greenhouse gases (due to soil respiration) and they could impact several physical and biological processes on the planet (Schlesinger & Andrews, 1999; Stockmann et al., 2013). The increase of greenhouse gases, which enhance the effects of global warming, has sparked interest in the global carbon cycle, especially identifying carbon concentration controllers in the environment (Batjes, 1996; IPCC, 1990; Nieder & Benbi, 2008). Several environmental factors have been identified as controllers of carbon stock and export (Mulholland, 2003). These feedbacks between carbon storage/export and climate/land use change are being investigated around the world and still remains highly uncertain (Cox, Betts, Jones, Spall, & Totterdell, 2000; Schuur et al., 2015; Schwalm & Zeitz, 2015; Stocker, Roth, & Joos, 2013). Nevertheless, it is recognized that it is necessary to understand their importance and how they affect carbon dynamics in different ecosystems (Birkel, Broder, & Biester, 2017; Kalbitz, Solinger, Park, Michalzik, & Matzner, 2000; Stockmann et al., 2013).

In the Andean region, the soils of the páramo ecosystem are known for their high organic matter accumulation (mostly attributed to waterlogging), formation of organometallic complexes (attributed to the fact that they are deposits of volcanic ash) (Buytaert, Deckers, & Wyseure, 2006), and probably physical protection of soil organic matter in their large micropores (Tonneijck et al., 2010). These characteristics that could be supporting water regulation capacity of high Andean ecosystems, are being threatened by land use change and climate change impacts (Celleri & Feyen, 2009). Especially, abrupt temperature increases that are likely to occur in the elevated regions of the mountains of Ecuador, Peru, and Bolivia (Bradley et al. 2006). Global carbon storage analysis suggests that climate and land use change may cause increased transportation of carbon to streams (Poeplau et al., 2013; Sarkkola et al., 2009). However, despite the high ecological, economic, and social importance of the páramo, the mechanisms controlling carbon export in this ecosystem remain poorly understood.

Land use, soil moisture conditions, occurrence of volcanic ashes, and climate, in particular temperature and precipitation, have been identified as the major factors controlling carbon storage in páramo soils (Buytaert et al., 2006; Buytaert, Wyseure, De Bièvre, & Deckers, 2005; Don, Schumacher, & Freibanuer, 2011; Rixen, Baum, Wit, & Samiaji, 2016). Although the previously-mentioned studies identified factors controlling the export of carbon from páramo soils, carbon concentrations in soil water leachate in páramo ecosystems under various land uses types as well as the functional relation between those factors (i.e. land use and climatic) have never been quantified.

The understanding of how and which of the hydro-meteorological factors lead to a quantitative change controlling carbon concentrations in soil water leachate will finally provide accurate information about carbon exportation and concentration dynamics in water in tropical Andean environments. These dynamics are not only of great interest to the hydro-biogeochemical modeling community, modelling the DOC concentration and hydrological conditions in rivers, but also to various stake holders and government agencies, as they also provide information about these ecosystems resilience and therefore practices for their management and/or conservation.

Therefore, the objective of our study is to provide, for the first time, a detailed understanding of soil water carbon concentrations as well as the internal and external factors controlling its variability in the páramo. To this end, we use a dense network of meteorological, hydrometric, in-situ, and manual measurements of soil water chemistry, in addition to soil moisture and temperature measurements at the Ecohydrological Observatory of the Quinuas River basin in south Ecuador.

To study the mechanisms behind the impact of land cover and hydro-meteorological conditions on carbon storage and release at the study site, the following hypotheses have been formulated and will be tested in this study:

(1) Concentration of organic carbon in soil water leachate increases with land cover alteration
(2) Hydro-meteorological and land use factors significantly impact carbon concentrations in soil water leachate

2. Materials and Methods

2.1. Study area

The study was conducted within the Quinuas River Ecohydrological Observatory in the Andean páramo located in south Ecuador, about 25 km northwest of the city of Cuenca (Figure 1a). The study site belongs to the “Cajas Massif UNESCO World Biosphere Reserve” (UNESCO, 2013), and its northern region is part of the Cajas National Park (CNP) protected reserve, situated on the east side of the Andean mountains between an altitude range of 3144-4429 m a.s.l. These ecosystems are considered of high importance as they are the only water suppliers for the Andean cities. The regional climate is mainly influenced by the continental air masses from the Amazon basin and less by fluctuation of the Inter Tropical Convergence Zone (ITCZ) (Carrillo-Rojas et al.2016).

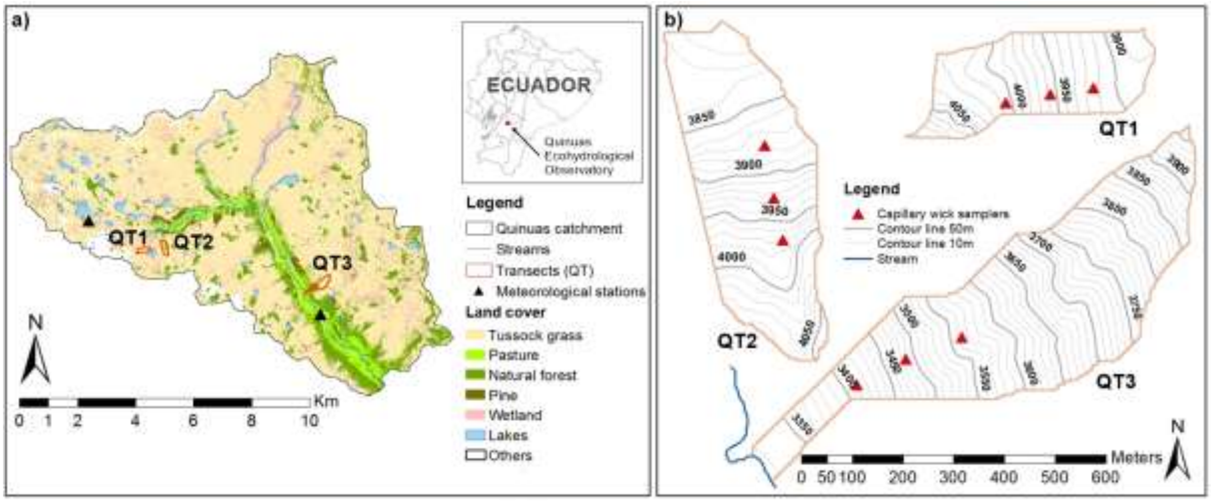

Figure 1. a) Map of the Quinuas River Ecohydrological Observatory (1:90000) showing with its location within Ecuador, the position of the established transects (QT), and meteorological stations (black triangles); and b) Capillary wick samplers and soil moisture/temperature location (red triangles) within the established transects (1:5000).

The landscape in the observatory is of glacier origin, and the geomorphology formed corresponds to U-shaped valleys surrounded by steep slopes with an average slope of 42%. The main vegetation types on the steep slopes are tussock-grass (locally known as “pajonal” and dominated by *Calamagrotis* sp. and *Festustuca* sp.) (67.8%), natural forests (*Polylepis* sp.) (12.7%), and pasture *(Lolium* sp.) and pine plantations (*Pinus patula)* covering a combined total of 5.1% of the total catchment area (Figure 1a).

Within the observatory three hillslopes, covered with those four main vegetation types, were established to study the soil water and carbon fluxes (Figure 1b). The first transect (QT1, Figure 1b) is covered by tussock-grass (*Calamagrotis Intermedia*). It was monitored at the upper, middle, and lower parts of the hillslope at 4006, 3958 and 3913 m a.s.l., respectively. The distance between the upper and lower monitoring stations is 208 m. The second transect (QT2) is covered by natural forest (*Polilepys reticulata*). It was also monitored at the upper, middle, and lower parts of the hillslope at 3969, 3926 and 3881 m a.s.l., respectively. The distance between the upper and lower monitoring stations is 180 m. The third transect (QT3) is covered by a pine plantation (*Pinus patula*) at the upper part of the hillslope and by pasture (*Lolium* sp.) used for cattle grazing at the lower part. In this transect, two points within the pine plantation were monitored at 3562 and 3486 m a.s.l. and one within the pasture area at 3411 m a.s.l.. The distance between the upper and lower monitoring stations is 280 m. QT1 and QT2 are located in the upper and conserved part of the catchment within the CNP about 500 m apart from each other; QT3 is located in the disturbed area outside the CNP about 4 km downstream of QT1 and QT2. The underlying geology is similar for the three transects and belongs to the Tarqui and Celica formations. Tuffs, agglomerates, and andesitic composition are predominant in these formations (Hall & Calle, 1982). The main soil types within the three transects were characterized as Andosols with relatively low development of Ah horizons (mean depth of three positions: QT1 = 0.56 m; QT2 = 0.45 m; QT3 = 0.81 m) above C horizons (mean depth of three positions: QT1 = 0.94 m; QT2 = 0.9 m (with the replacement of a C horizon with the presence of large rocks in the middle and low positions in the slope); QT3 = 1.37 m).

2.2. Measurements and field surveys

Soil water sampling and analysis

Soil water samples for carbon analysis were collected weekly and at the same positions along the transects where soil moisture data were recorded (i.e. three positions per transect). Passive capillary fiberglass wick samplers (Figure 2) were installed along the established transects for the collection of soil water. The wick samplers were installed at 10, 35, and 75 cm depths in QT1 and QT3 and at 10, 25, and 50 cm depths in QT2 because of the existence of thinner soils at this transect. Wick samplers were designed according to Mertens et al. (2007). Fiberglass wicks (Amatex Co., Norristown, PA, US) were unraveled over a length of 1 m, spread out over a 30 × 30 cm polypropylene plate surrounded by 5 cm plastic walls. The samplers were covered with fine-grained soil particles and then put in contact with the undisturbed soil. A vertical suction of 60 cm was applied to the fiberglass wicks (i.e. the wick samplers collected water transported at $\leq$ 60 hPa). Flexible silicon tubing was used to protect the fiberglass wicks, which connected the plastic plates to the 1L glass bottles, where the soil water was stored until it was collected.

Dissolved organic carbon (DOC) concentrations (mg L^{-1}) were measured in the weekly soil water samples using an UV-Vis spectrometer (Spectrolyser, s::can Messtechnik GmbH, Vienna, Austria). Those samples' values were compared with samples (256) analyzed in the lab using a LiquiTOC analyser (Elementar Analytics, Hanau, DE) (Detection limit for TOC was 0.3 mg L^{-1}) obtaining similar results (R-square: 0.96; Regression equation: $y = 1.2885x + 0.3246$). Samples were collected in high density polyethylene bottles and, in general, analyzed up to 24h after their collection. In case they were not analyzed 24h after collection, the samples were stored at -5°C until the day of analysis (no more than a week after the collection date).

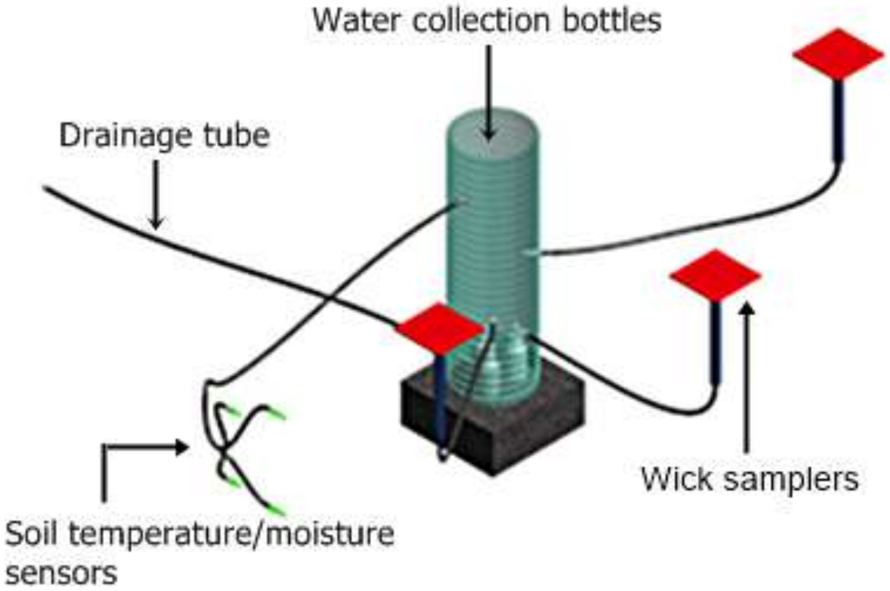

Figure 2. Measurement sites along transects

Physicochemical soil analysis

Soil pits (1.5 m² surface area and depth of 0.5 - 1.5 m) at each sampling point along the transects were excavated to identify and classify the soil profiles according to the FAO guidelines (Jahn, Blume, Asio, Spaargaren, & Schad, 2006). Disturbed soil samples (approximately 1 kg) were collected at the three established research transects (QT1-QT3) for C/N determination. This analysis was conducted via the combustion method using a vario EL cube (Elementar, Germany). Soil texture analyses of the same samples were performed according to ISO 11277:2009, “Soil quality - Determination of particle size distribution in mineral soil material - Method by sieving and sedimentation.” Undisturbed soil samples were also collected and used to determine the bulk density of the organic and mineral soils at each transect. The undisturbed soil samples were collected in 100 cm^3 steel rings.

The soil organic carbon density (SOCD, [kg m^{-2}]) was estimated for each land cover type as the product of carbon content, bulk density, and thickness of each layer. Every estimation was then corrected by removing the percentage of coarse particles as follows:

$$SOCD = C \times 0.01 \times BD \times THK\ (1 - \frac{CPC}{100}) \times 1000 \quad \textbf{(Eq. 1)}$$

where, C is the carbon content (%) from the C/N analysis mentioned before, BD is the bulk density (gr cm^{-3}), THK is the thickness (m) of the sampled horizon, and CPC is the coarse particle content (%) (measured in the field according to the FAO Guidelines for Soil Description (Jahn, Blume, Asio, Spaargaren, & Schad, 2006)).

Hydro meteorological and soil moisture/temperature monitoring

Meteorological data (air temperature, solar radiation, relative humidity, and precipitation) were monitored during the period October 2014-January 2017 at two meteorological stations, QP1 at 3955 m a.s.l. and QP3 at 3298 m a.s.l. QP1 is located at about 2.1 km and 2.8 km from QT1 and QT2, respectively, and QP3 at 0.9 km from QT3. Air temperature and relative humidity (RH) were recorded using Campbell CS-215 sensors with shield protection and with an accuracy of ±0.3°C for temperature and ±2% for RH. Solar radiation was recorded using Campbell CS300 pyranometer sensors with an accuracy of ±5% for the daily total. Precipitation was recorded using Texas TE525MM rain gages with an accuracy of ±1%. All meteorological variables were recorded at 5-min intervals.

Volumetric soil water content and soil temperature were recorded using capacitance sensors (Decagon Devices, model: 10HS and 5TE) for the same period (October 2014-January 2017). The sensors were installed at different depths (5, 20, 45, and 75 cm) within the organic and mineral horizons of the soil profiles, which were monitored at each position within each transect. These data were recorded at 5-min temporal resolution. Given the highly organic nature of the páramo soils, these sensors were calibrated under controlled laboratory conditions. The sensors for each of the monitored soil horizons were calibrated as follows: (i) two undisturbed soil samples (3.8 liters) per location were collected in the field and saturated in the laboratory; (ii) samples were oven dried at 20 °C; (iii) the dielectric permittivity measured by the sensors was recorded at 1-min intervals in the first sample, and the corresponding change in gravimetric soil moisture in the second sample was measured every twelve hours during the drying process; and (iv) the calibration curves were constructed using these measurements. This process was carried out, because the standard calibration method for the sensors (Cobos & Chambers, 2010) is not applicable for organic soils. The improved accuracy achieved using this method was ±1–2% ($r^2 > 0.95$, p-values < 0.05).

2.3. Statistical analysis

Given that our dataset presented non-parametric conditions (Shapiro-Wilks: p-value > 0.05 in the most of groups), descriptive statistics were initially used to detect differences in DOC concentrations in soil water leachate among the different land cover types. Kruskal-Wallis rank sum test in order to identify significant differences between groups followed by pairwise comparisons using Wilcoxon rank sum test in order to identify which of the groups presented high and low values.

Because our dataset included categorically and quantitative variables, and also non-parametric groups, we used the classification and regression method, CART, (Breiman et al., 1984) in order to identify patterns and controllers of carbon concentration using the R package RPART (Therneau et al., 2015). Regression trees can start with highly heterogeneous data inputs and help with the exploration, description, and prediction of patterns and processes that affect the values of a given dataset (De'Ath & Fabricius, 2000). These trees are constructed by repeatedly splitting the data by a condition, thus obtaining two mutually exclusive groups. These groups are as homogeneous as possible, considering the lower mean square error. In the CART, each split minimizes the total sum of square errors of the response variable from the previous split. The partitioning process is repeated for the newly created groups with the objective to better explain the data while keep the trees as small as possible. In order to keep the tree as small as possible, a pruning process could be developed to obtain successively smaller trees from one split to n possibles splits with the available data. Each of the smaller trees (best for each number of splits) was analyzed by cross validation. Cross validation divides the data into subsets, removes one subset and uses the remaining subsets to grow a tree. The removed subset is then used for testing, obtaining a mean R-square and error for each of the trees. The selection process is then limited and required to select the number of splits that most increases the R-square value and minimizes the X-error between the observed and the modeled data.

The objective of the CART is to identify what are the main factors (predictor variables) that influence the response of a target variable in a given system. In our study, the CART analysis aimed to identify the controllers and the dynamics of water DOC concentration associated with different predictor variables such as land cover types and the climatic and soil moisture/temperature conditions. The method of random forests analysis (RF) (Liaw, 2002) was used to hierarchically rank the main predictors of DOC concentration in our study system.

The possible categorical and quantitative predictors used in our analysis were: land use type (páramo, tussock grass, pasture, and pine forest), position on the slope (A = upper, M = medium, and B = bottom), sampling depth, soil moisture, soil temperature, air temperature, RH, pH, and precipitation, respectively. To include possible effects of drying and wetting, or the change from colder to warmer periods on the mobilization of DOC, the cumulative change (Delta) of soil temperature, air temperature, and soil moisture in-between each time step was also considered. Means and accumulated values for the controllers were considered taken in time spans covering the periods from 2 to 15 days prior to sampling collection of water samples.

Two statistical measures in the RF were used to determine the hierarchical importance of the predictor variables explaining the variability in our target variable (DOC concentrations). These were: the increased mean square error (IncMSE) and increased impurity index (IncNodePurity). IncMSE explains the effect of a predictor value on the predicted value result when the former is randomly permuted (using the mean square error). IncNodePurity measures the increase of homogeneity of the resulting groups when the data is split by some variable (Breiman, 2001). Therefore, as the value of IncMSE and IncNodePurity becomes higher, higher is the effect that this variable have on the target variable.

Multicollinearity between the predictors could possibly hinder the interpretation of the resulting regression trees. To identify any multicollinearity, we calculated the Variance Inflation Factor (VIF) (Lin et al., 2011) and correlation between the variables. To see if correlated variables had a considerable influence on the structure of the regression tree, we excluded variables one by one from the CART analysis. Since the structure of the regression trees was very stable, we used all variables in the regression tree analysis, although some variables presented a considerable multicollinearity.

All the statistical analyses were performed using R language program Version 3.3.3 (Team R Core, 2017).

3. Results

3.1. Organic carbon in soil

The results of our preliminary soil survey (Table i) revealed higher bulk density, carbon content, and soil organic carbon density (SOCD) under tussock grass (especially in shallower soil layer (0-30cm depth)) compared to the transects covered with pasture, natural forest, and pine forest. Even where similar soil carbon content values were found under the latter land cover types, shallower SOCD under natural forest resulted higher. Pasture and pine forest both located in the same transect, showed similar SOCD in shallower soil.

Type of sample	Parameter	Natural forest	Pasture	Pine forest	Tussock grass
Soil	Number of samples	2	2	2	3
	Coarse particle content (%)	9	12	7	6.33
	Bulk density (g cm^{-3})	0.28	0.33	0.21	0.39
	Carbon content (%)	15.25	15.71	15.36	21.73
	SOCD (kg m^{-2}) (for the whole organic layer)*	22.35	41.95	36.08	43.37
	SOCD (kg m^{-2}) (0-30cm depth)**	15.86	13.458	13.52	23.17

Table i. Mean values for the physicochemical parameters measured in soil samples collected at all transects in 2016.

3.2. Soil water carbon concentration

The results of our soil water monitoring showed distinct differences in DOC concertation with land use and a high temporal variability (Figure 3). A preliminary characterization of the soil water samples' results indicated that the natural forest transect (10.9 mg L^{-1}) presented the highest median and maximum values for DOC concentrations compared to pasture (6.9 mg L^{-1}), and especially tussock grass (4.7 mg L^{-1}) and pine forest (3.7 mg L^{-1}). After the median DOC concentrations of the water samples collected under natural forest, the median DOC concentrations from the pasture transect were the highest. Even though similar values were obtained at the pine forest and tussock grass transects, slightly higher median values for DOC concentrations were found under tussock grass.

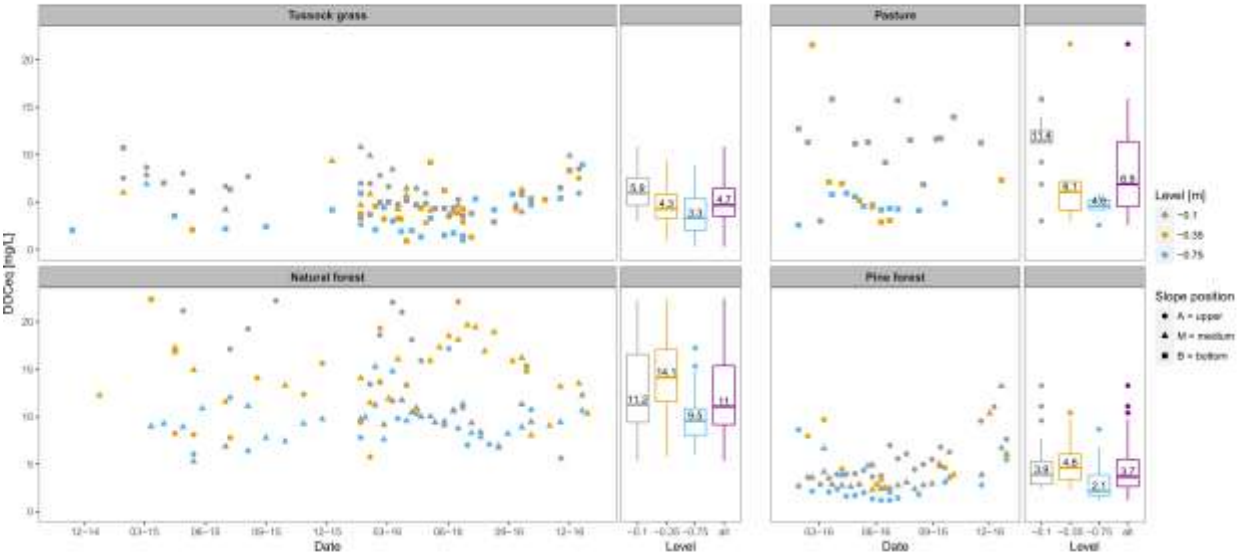

Figure 3. For each land cover type; left:Temporal variability of the data, rigth: boxplots of the DOC concentrations at different levels (depth) and the median of all the samples.

3.3. Change of concentrations of organic carbon in soil water leachate with land cover alteration

The non-parametric Kruskal-Wallis rank sum test depicted a significant effect of land cover in carbon concentrations (p-value < $2.2e^{-6}$). In order to identify differences between pairs of land cover groups, pairwise comparisons using Wilcoxon rank sum tests were performed (Table ii). Significant differences ($p<0.05$) in DOC mean concentrations were found between pairs of land cover types, and ordered from high to low values of DOC as follow: natural forest (median = 10.9 mg L-1), pasture (median = 6.9 mg L-1), tussock grass (median = 4.7 mg L-1), and pine forest (median = 3.7 mg L-1) (Figure 3 and Table ii).

DOC concentrations comparisons	**Natural forest**	**Pasture**	**Pine forest**
Pasture	$7.2e^{-9}$***	-	-
Pine forest	< $2e^{-16}$***	$6.3e^{-12}$***	-
Tussock grass	< $2e^{-16}$***	$7.0e^{-08}$***	0.0011***

Table ii. Pairwise comparisons using Wilcoxon rank sum test among the different land cover types (*highly significant p-values).**

3.4. Impact of hydro-meteorological and land use factors in DOC concentrations in soil water leachate

Classification and regression trees method (CART) (Therneau, Atkinson, & Ripley, 2015) and Random forest (RF) (Breiman, 2001) were completed to understand and for the first time for the Páramo environments quantify, how the selected predictors shape the carbon concentrations (using CART) and to rank the importance of the predictors (using RF).

To test a priori the possible impact of the time span under consideration for the predictors on the model results we tested periods from 2 to 15 days prior to sampling. The model showed similar results and performance (R-square between 0.64-0.74) for all periods, further strengthening the presented results and indicate that the identified processes/relations are relative time invariance. However, the actual time span in between sample collection (7-days) was considered to be the most representative for the collected samples as well as for the hydro-biogeochemical processes shaping the DOC signature of the same sample, and was therefore selected for the presented results.

Prior to the CART and RF analysis we used correlation and VIF analysis to identify possible multicollinearity and relations between our predictors, that could affect our models results (e.g. by overfitting) and interpretation respectively (Breiman, 2001). Through the VIF analysis we found six predictors which presented multicollinearity (VIF > 2) (Table iii). The quantitative predictors were also checked for correlations between them through spearman correlation method for non-parametric data, four pairs of predictors were moderately correlated: air temperature with soil temperature (Spearman correlation = 0.83), soil moisture with soil temperature (0.37), soil sampling depth with soil moisture (Spearman correlation = 0.43) and relative humidity with solar radiation (Spearman correlation = -0.86). Even when multicollinearity and correlated variables were found, the latter mentioned variables were excluded from the CART analysis one by one without significant changes in the tree structure. For this reason all the variables were included in the model and the VIF and correlation results were used in the results interpretation.

Predictor	**VIF**
Air temperature	3.84
Relative humidity	4.17
Precipitation	1.21
Soil moisture	1.23
Soil temperature	4.80
Solar radiation	4.14
Delta soil moisture	6555.72
Delta soil temperature	6560.57
Delta air temperature	1.16

Table iii. Variance Inflance Factor (VIF) for the 7 day means of all the predictors included in the analysis.

CART

Following the multicollinearity and correlation analysis the CART was performed. The optimal CART model showed nine splits within the concentration regression trees with a model performance of R-square of 0.70 (Figure 4b). The CART results showed that the best predictor of DOC concentrations is land cover (Figure 4a). The first split (1) evidenced that pasture, pine forest, and tussock grass land cover yielded lower DOC concentrations (mean = 5.3 mg L^{-1}) in relation to natural forest (mean = 12 mg L^{-1}). Under the same branch (split 2) for DOC, the lower concentrations were under pine forest and tussock grass (mean = 4.7 mg L^{-1}), while higher concentrations were determined under pasture (mean = 8.2 mg L^{-1}). Following the pine forest and tussock grass branch, sampling depth was considered relevant for DOC (split 8), with the higher concentrations found at shallower depths (above 0.55 m depth) (mean = 5.2 mg L^{-1}) compared to the lower part of the soil profiles (mean = 3.4 mg L^{-1}). At the end of these branches, high soil moisture led to low carbon concentrations (splits 8 and 9). In the pasture branch, sampling depth was also found important (split 5), with higher concentrations at shallower depths (above 0.22 m depth) (mean = 12 mg L^{-1}) compared to the rest of concentrations (mean = 5.7 mg L^{-1}). Under the natural forest branch, sampling depth was again found as an important predictor (split 3), with the higher concentrations at shallower depths (above 0.55 m depth) (mean = 13 mg L^{-1}) compared to the rest of concentrations (mean = 9.8 mg L^{-1}). After the sampling depth split in the samples collected above 0.55 m of depth under natural forest, soil moisture was identified controlling DOC (split 7), with significantly high values (mean = 18 mg L^{-1}) for all samples collected under soil moisture conditions lower than 0.54 $m^3\ m^{-3}$ and lower DOC values (mean = 13 mg L^{-1}) in the conditions above this value. Following the same branch, high soil moisture conditions leads to high DOC concentrations.

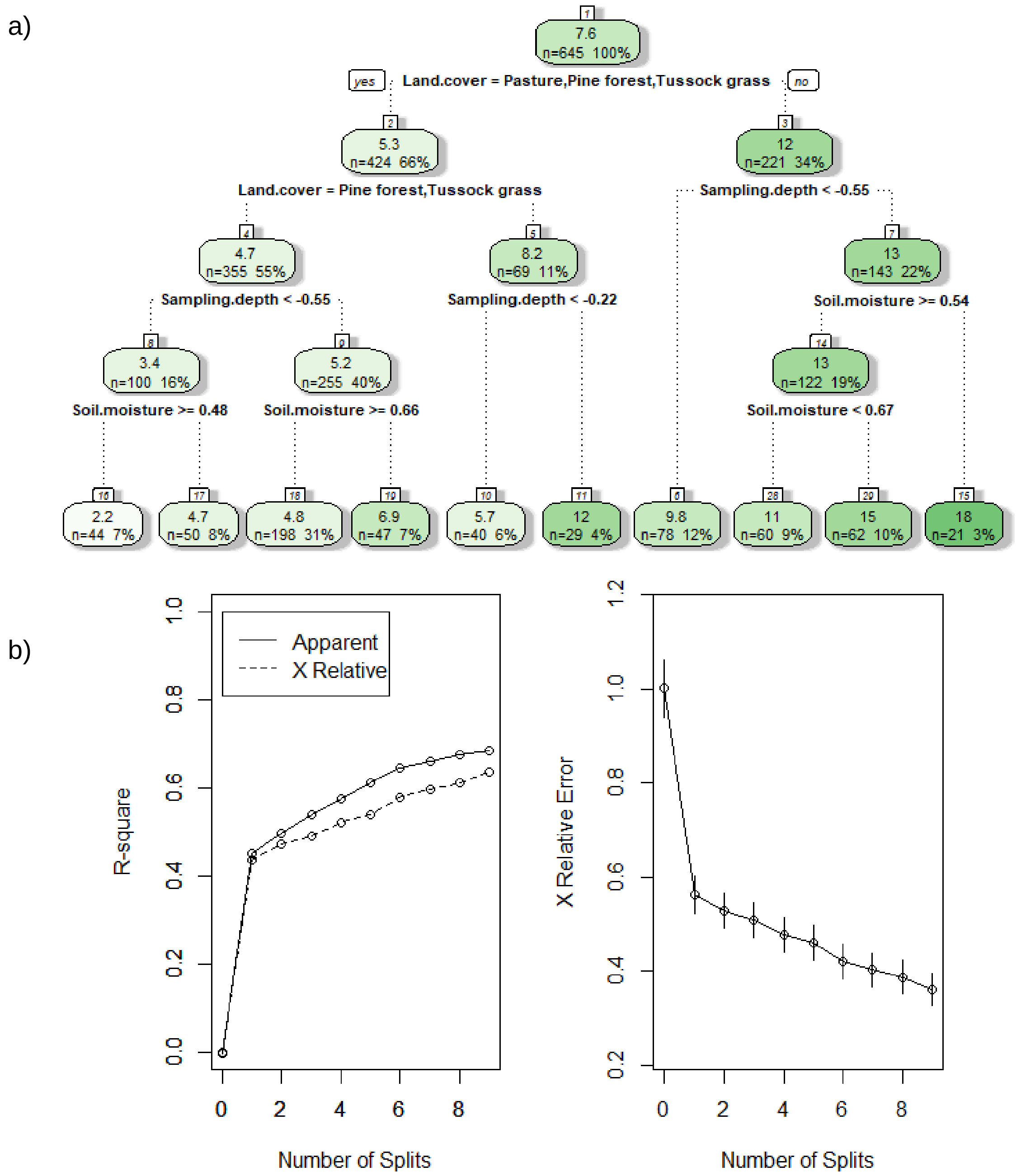

Figure 4. a) DOC concentration regression trees and b) respective cross validation analysis. In the nodes' upper value = mean concentration, n=number of observations and at right %= percentage of observations explained. Differences in the dark to light green show differences in concentrations from high to low respectively. All predictors of the study have been used in the model.

Random forest

After the CART analysis, the random forest method was performed in order to rank the predictor variables based on soil water DOC concentrations. The results of the random forest method showed that all the predictor variables explained 65.20% of the variance for DOC concentrations in the model.

Land cover was the most important predictor variable for IncMSE and IncNodePurity (Figure 5). The second most important predictor was soil moisture, followed by slope position, sampling depth, soil temperature, relative humidity, and air temperature. Finally, with lesser impact on our target are solar radiation, delta soil moisture, precipitation, delta soil temperature, pH, and delta air temperature (Figure 5).

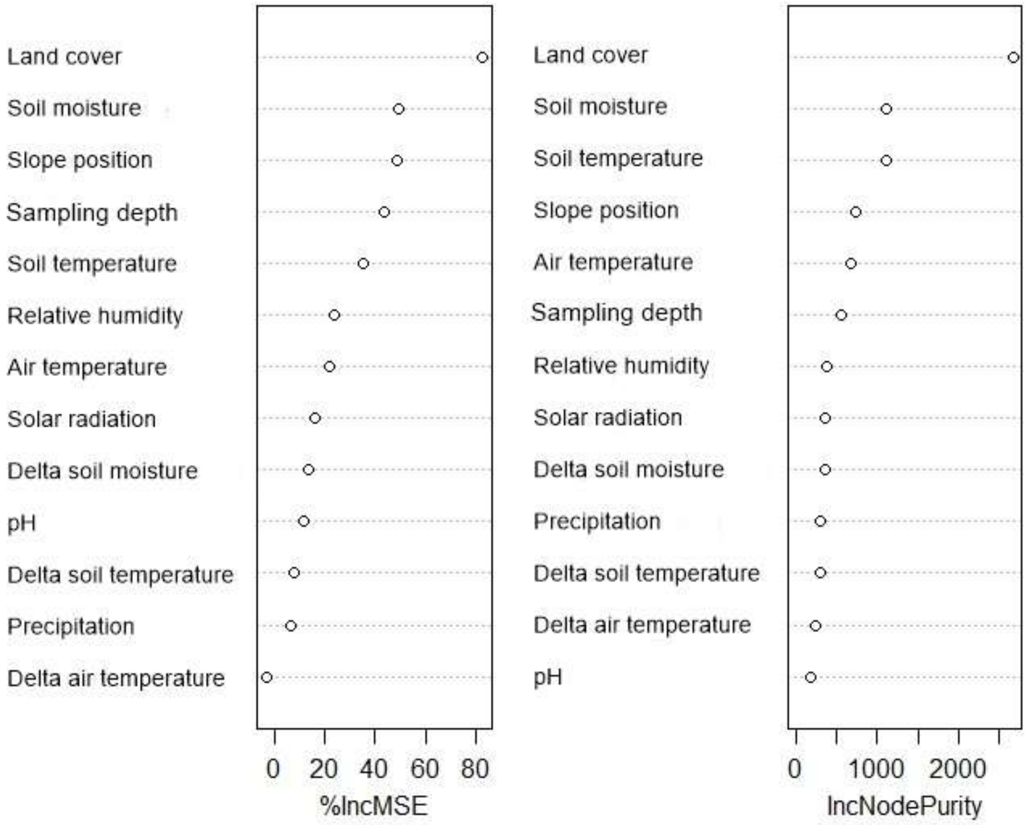

Figure 5. Random forest evaluation. (Mean square error (%IncMSE) and node purity (IncNodePurity)) for all the possible predictor variables. Importance of variables for DOC concentrations.

4. Discussion

4.1. Concentration of organic carbon in soil water leachate increases with land cover alteration

The obtained median DOC soil water concentrations among all transects were 6.45 mg L^{-1} (±4.86). The median values were higher than those reported by other authors for streams at catchments with peat soil cover (3.67 mg L^{-1} (±2.287)) (J. A. Aitkenhead-Peterson, W. H. McDowell, 2003) and similar (in case of natural forest) or lower (for the rest of variables) to those reported for tropical ecosystems (7.9 – 13.9 mg L^{-1}), including tropical forests (Moeller, Kaiser, & Guggenberger, 2005; Rixen, Baum, Wit, & Samiaji, 2016). Significant impacts of land cover were found in soil water DOC concentrations between our four types of land cover studied (Table ii). The higher concentrations were found in natural forest followed by pasture, tussock grass and pine forest (Table ii). These results are in line with several studies that show higher concentrations in forests soil water than grasslands (Chantigny, 2003; Khomutova, Shirshova, Tinz, Rolland, & Richter, 2000). The higher concentrations in forest is continuously being discussed, nevertheless, it has been mainly attributed to the transport of water through the canopy and litter, especially in tropical forests (Meyer, Wallace, & Eggert, 1998; Moeller et al., 2005; Wilcke, Yasin, Valarezo, & Zech, 2001). This is a general pattern observed in tropical forested environments, except for pine forests, in which, low litterfall amounts and low soil organic matter have been reported (J. A. Aitkenhead-Peterson, W. H. McDowell, 2003; Pinos, Studholme, Carabajo, & Gracia, 2017; Quichimbo, Veintimilla, Carrión, & Jiménez, 2016). Lower DOC concentrations in soil water under pine forest could also be attributed to the low quality of pine forests' litter (high lignin content and low soluble carbon content). Effect that could have a direct influence on the microbial biomass carbon (reducing microbial activity) and therefore in the DOC release compared to natural forests (Li et al., 2014; Pinos et al., 2017; Ramírez et al., 2014). High DOC concentrations in soil water under pasture could be attributed to an increase in soil respiration under this land cover, increasing litter decomposition, and therefore DOC mobilization. Increase in soil respiration in pastures is mainly guided by better conditions for microorganisms, due to fertilization, and draining (increasing temperature and oxygen availability) (Fang et al., 2017; Tipping et al., 1999).

4.2. Hydro-meteorological and land use factors significantly impact carbon concentrations and export in soil water leachate

To predict the carbon concentrations the best CART model (R-square of 0.70) included three out of the 12 possible predictor variables: land cover, sampling depth and soil moisture. In the previous section, the reasons for the importance of land cover affecting DOC concentrations were discussed in depth. The importance of land cover on the DOC release was also reflected in the CART analysis, using land cover as the primary and secondary predictor to explain the variability in the observed DOC concentrations in line with the previously presented findings (Fig. 3a). After land cover, a consistent pattern of sampling depth influencing DOC concentrations was observed in the tree. In general, higher DOC concentrations were found in the richer organic top soils transport, which is frequently attributed to a higher content and better degradability of the organic matter in the shallow soil layers (J. A. Aitkenhead-Peterson, W. H. McDowell, 2003; Moeller, Kaiser, & Guggenberger, 2005). Under the lower branches of the regression tree, soil moisture had a clear influence on DOC concentrations. Under all the studied land cover types a high soil moisture contents led to low DOC concentrations. The latter pattern is likely to be controlled by the high microbial activity and thus, DOC mobilization, under low soil moisture conditions, since microbial activity is expected to enhance under an improvement of oxygen conditions and higher temperatures (Bowden, Davidson, Savage, Arabia, & Steudler, 2004; Laine, Strömmer, & Arvola, 2014; Tipping et al., 1999). This pattern was also reflected in the random forest evaluation (Figure 5), which showed soil moisture to be a highly important predictor explaining the DOC concentrations variability by increasing both the IncMSE and IncNodePurity model evaluation indexes. In addition high soil moisture (commonly above field capacity and near saturation) could also lead to shallow subsurface flow, leading to greater exportation of DOC from the litter layer and therefore could be increasing concentrations of DOC in the stream

(Meyer et al., 1998). The latter could support the hypothesis proposed by Weiler & McDonnell (2006), in which they argued for the occurrence of high nutrient mobilization under high soil moisture conditions. In the final branch of the regression tree (split 14) the CART model further separates the impact of the already high soil moisture conditions (>0.54 m^3 m^{-3}) in the shallower soil layers (<0.55m depth) under natural forest on the DOC concentration based on soil moisture above and below 0.67 m^3 m^{-3}. After a thorough analysis of DOC concentrations under these specific conditions (organic and wet soil) a relatively homogeneous soil moisture distribution (between 0.54 - 0.8 m^3 m^{-3}) was found, not enough to corroborate the increase of DOC concentrations with soil moisture.

Regarding the random forest results (Figure 5) and the other variables that did not appeared in the regression tree. We found that the previously-discussed variables (land cover and soil moisture) were also identified as two of the most important predictors in the CART model. Next to those were soil temperature, which could have been influenced by soil moisture (Table iii; Spearman correlation soil moisture/soil temperature = 0.37), slope position, which could be explained by low hillslope positions influenced by water from upslope positions, thus increasing their DOC concentrations, and sampling depth, which is related to high carbon concentrations in the shallower soil layer. In the last positions of the Random Forest model, relative humidity, solar radiation, and air temperature could be influencing soil moisture by evapotranspiration, and precipitation, by soil wetting especially at the temporal scale of sampling collection (seven days of antecedent conditions) (Wetzel & Chang, 1987). Finally, even though pH has been suggested to control DOC concentrations in soil water (Mulholland, 2003) and the carbon stocks in páramos (Buytaert, Deckers, & Wyseure, 2006; Tonneijck et al., 2010), we did not find pH as a highly influential control on DOC concentrations.

5. Conclusions

DOC fluxes in soils represent a large source of carbon to streams and also carbon export from soils that could affect atmospheric carbon concentrations around the world and therefore enhance climate change. The overall DOC concentrations in this study were similar to those found in other tropical ecosystems and peat soils. Given the discrepancy and lack of knowledge regarding the importance of hydro-meteorological factors and land cover on soil water DOC concentrations for páramo environments, our results provide, for the first time, a profound and quantitative understanding of the main factors controlling DOC concentrations and insights into the processes behind these patterns on páramo ecosystems. First, land cover was ranked as the most important predictor variable in our models; thus, evidencing a significant impact on soil water DOC concentrations. Second, sampling depth and slope position were important predictor variables influencing carbon concentrations. This can mainly be attributed to concentration effects in the hillside and carbon concentrations in soil layers. Further, soil moisture could be considered the second most important predictor controlling DOC concentrations under all the investigated land cover types. Finally, the predictors variables related to the meteorological conditions during the study period, did not show significant influences on DOC concentrations as has been found at other ecosystems (Mulholland, 2003). It seems that due to the relatively constant climatic conditions (Córdova et al., 2016) throughout the year parameters like solar radiation, temperature or wind speed do not impact DOC concentrations in soil water as much, and are rather controlled by changes in precipitation regimes.

In conclusion, our findings evidence that in the short term, changes in land cover are likely to have a greater effect on carbon exportation from the soils in the páramo. Temporal changes in the DOC concentration could mostly be attributed by the CART analysis to short term (≤7 days) changes in soil moisture conditions, controlling the conditions for degradation of organic components on the one hand, and the transport of degraded DOC on the other hand. While the weather conditions (i.e. solar radiation, temperature, relative humidity, or wind speed) did not show a pronounced impact on the DOC concentration in the CART analyses, the RF results showed that those climatic variables have important impact on the fine adjustment of the soil water DOC concentrations and therefore is likely due impact the DOC concentration in the long run (e.g. due to climate change).

Future work could be oriented to study if and how soil water DOC concentrations impact streams DOC concentrations. These finding also provide a baseline for the development of prediction models of carbon exportation from the páramo soils to streams. Information that will also support the development of conservation and management policies and decision-making in the páramos of Ecuador and the Andean region.

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