1 **Insights on the water mean transit time in a high-elevation**

2 **tropical ecosystem**

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19 **Abstract**

20 This study focuses on the investigation of the mean transit time (MTT) of water and its spatial

21 variability in a tropical high-elevation ecosystem (wet Andean páramo). The study site is the

22 Zhurucay River Ecohydrological Observatory (7.53 km^2) located in south Ecuador. A lumped

23 parameter model considering five transit time distribution (TTD) functions was used to

24 estimate MTTs under steady-state conditions (i.e., baseflow MTT). We used a unique data set

25 of the $\delta^{18}O$ isotopic composition of rainfall and streamflow water samples collected for three

26 years (May 2011-May 2014) in a nested monitoring system of streams. Linear regression

between MTT and landscape (soil and vegetation cover, geology, and topography) and hydrometric (runoff coefficient and specific discharge rates) variables was used to explore controls on MTT variability, as well as mean electrical conductivity (MEC) as a possible proxy for MTT. Results revealed that the exponential TTD function best describes the hydrology of the site, indicating a relatively simple transition from rainfall water to the streams through the organic horizon of the wet páramo soils. MTT of the streams is relatively short (0.15-0.73 yr, 53-264 days). Regression analysis revealed a negative correlation between the catchment's average slope and MTT ($R^2 = 0.78$, $p < 0.05$). MTT showed no significant correlation with hydrometric variables whereas MEC increases with MTT ($R^2 = 0.89$ $p < 0.001$). Overall, we conclude that: 1) baseflow MTT confirms that the hydrology of the ecosystem is dominated by shallow subsurface flow; 2) the interplay between the high storage capacity of the wet páramo soils and the slope of the catchments provides the ecosystem with high regulation capacity; and 3) MEC is an efficient predictor of MTT variability in this system of catchments with relatively homogeneous geology.

Keywords: Ecohydrology, MTT, runoff generation, wet Andean páramo, tropical wetlands, Histosols, Ecuador

1   Introduction

Investigating ecohydrological processes through the identification of fundamental catchment descriptors, such as the MTT, specific discharge, evapotranspiration to precipitation ratios, and others, is fundamental in order to: 1) advance global hydrological, ecological, and geochemical processes understanding and 2) improve the management of water resources. This is particularly critical in high-elevation tropical environments, such as the wet Andean páramo (further referred as "páramo"), in which, hydrological knowledge remains limited, despite its importance as the major water provider for millions of people in the region (De Bièvre and Calle, 2011; IUCN, 2002). Water originated from the páramo sustains the socio-economic development in this region by fulfilling urban, agricultural, industrial, and hydropower generation water needs (Célleri and Feyen, 2009). Here we focus on the MTT of water, which we define as the average time elapsed since a water molecule enters a catchment

1   as recharge to when it exits it at some discharge point (Bethke and Johnson, 2002; Etcheverry

2   and Perrochet, 2000; Rodhe et al., 1996).

3   Despite the importance of tropical biomes as natural sources and regulators of streamflow,

4   there are very few studies of MTT in tropical environments (e.g., Farrick and Branfireun,

5   2015; Muñoz-Villers et al., 2016; Roa-García and Weiler, 2010; Timbe et al., 2014). The

6   majority of MTT studies have been conducted in catchments with strong climate seasonality,

7   i.e., located in the northern and southern hemispheres (e.g., Lyon et al., 2010; McGlynn and

8   McDonnell, 2003; McGuire et al., 2005), and considerably less attention has been devoted to

9   tropical environments. Most tracer-based studies conducted in tropical latitudes focused on

10 isotope hydrograph separation at storm event scale (e.g., Goller et al., 2005; Muñoz-Villers

11 and McDonnell, 2012), the isotopic characterization of precipitation patterns (e.g., Vimeux et

12 al., 2011; Windhorst et al., 2013), and the identification of ecohydrological processes (e.g.,

13 (Crespo et al., 2012; Goldsmith et al., 2012; Mosquera et al., 2016). However, studies

14 focusing on MTTs in order to improve the understanding of rainfall-runoff processes and their

15 dependence on landscape biophysical features in tropical regions are still lacking and urgently

16 needed in order to improve water resources management.

17 The páramo is widely recognized by its high runoff regulation capacity (i.e., páramo water

18 yield is sustained year-round regardless of precipitation inputs) (Buytaert et al., 2006; Célleri

19 and Feyen, 2009). However, efforts to investigate the processes that control such hydrological

20 behavior are scarce. Recent investigations in our study site suggest that runoff originates from

21 the shallow organic horizon of the páramo soils located near the streams (Histosol soils or

22 Andean wetlands), thus favoring shallow subsurface flow. On the contrary, deep groundwater

23 contributions to discharge are minimal and saturation excess overland flow (even in the nearly

24 saturated Histosol soils) rarely occur (Buytaert and Beven, 2011; Crespo et al., 2011). The

25 hydrological importance of shallow subsurface flow to runoff generation has also been

26 demonstrated in a variety of ecosystems around the globe (e.g., Freeze, 1972; Hewlett, 1961;

27 Penna et al., 2011), but yet, MTTs have not been explored in these systems. Our study site

28 provides a unique opportunity to gain understanding of the MTT of a shallow subsurface flow

29 dominated system in a tropical setting. In addition, the study of the MTT in natural wetland

1 systems has been limited to sites located in northern boreal catchments in Sweden (Lyon et

2 al., 2010), and peatlands in Scottish mountainous regions (e.g., Hrachowitz et al., 2009a;

3 Tetzlaff et al., 2014). While streams draining these catchments have significant contributions

4 from spring snowmelt and groundwater, respectively, neither of these allows for the isolation

5 of the effect of wetlands in the shallow subsurface and/or near surface (i.e., overland flow)

6 transport of the water within the catchments.

7 Another critical issue is the identification of controls on MTT variability among catchments.

8 As detailed observations of combined hydrometric and isotopic information are not feasible in

9 many regions due to limited funding and site accessibility, identifying controls of MTT

10 variability in nested and paired monitoring systems of streams is fundamental towards

11 regionalization of ecohydrological processes (Hrachowitz et al., 2009a) and prediction in

12 ungauged basins (Tetzlaff et al., 2010). Yet, investigation of controls on MTT variability is

13 still fairly scarce (Tetzlaff et al., 2013). Most studies have found that MTT scales with

14 topographic and/or hydropedological controls. For instance, topographical controls on MTT

15 variability were found in New Mexico, USA catchments (slope direction and exposure)

16 (Broxton et al., 2009) and a system of streams in Oregon, USA (ratio between flow path

17 length and flow path gradient) (McGuire et al., 2005); whereas the proportion of wetlands and

18 responsive soils were reported as major MTT controls in Swedish catchments (Lyon et al.,

19 2010) and Scottish streams (Soulsby et al., 2006), respectively.

20 In the last few decades, MTT modeling has been conducted applying an approach that

21 assumes steady-state conditions in the hydrologic systems, i.e., the lumped convolution

22 approach (LCA) (Amin and Campana, 1996; Maloszewski and Zuber, 1996). However, this

23 assumption is often violated as a result of precipitation variability, strong climate seasonality,

24 and heterogeneities in the landscape configuration and hydropedological distribution of

25 catchments (Kirchner, 2016a, 2016b). This has led to a growing recognition of the time-

26 variant nature of transit times (e.g., Birkel et al., 2015; Harman, 2015; Hrachowitz et al.,

27 2013), which a number of studies have begun to explore. Most of this initial work has yielded

28 results with high degree of uncertainty (Harman, 2015; Klaus et al., 2015; McMillan et al.,

29 2012), or uncertainty has not been estimated (Davies et al., 2013; Heidbüchel et al., 2012; van

1 der Velde et al., 2015) as a result of expensive computation costs or high uncertainties related

2 to the spatial variability of the input hydrometric and tracer field measurements. It is clear

3 however, that given the mathematical limitations to represent systems' non-stationarities

4 (Duvert et al., 2016; Seeger and Weiler, 2014), the high-temporal resolution of tracer data

5 (Harman, 2015; Heidbüchel et al., 2012), and the general unavailability of long-term tracer

6 records (Hrachowitz et al., 2010; Klaus et al., 2015) required for hydrological modeling under

7 non-stationary conditions, the LCA remains to be a useful methodology for MTT estimation.

8 This holds true not only in understudied regions such as the tropics (e.g., Farrick and

9 Branfireun, 2015; Muñoz-Villers et al., 2016; Timbe et al., 2014), but also elsewhere (e.g.,

10 Duvert et al., 2016; Hale and McDonnell, 2016; Hale et al., 2016; Hu et al., 2015; Seeger and

11 Weiler, 2014).

12 Given the relatively homogenous landscape features and very low seasonality in the

13 hydrometeorological conditions in our páramo site, applying the LCA to our unique water

14 stable isotopic dataset represents a robust first step to build-up improved catchment

15 functioning understanding using hydrometric-tracer based hydrologic modeling. To our

16 knowledge, this is the first contribution regarding the modeling of MTT in páramo

17 ecosystems, and more generally, in regions with low climate seasonality and catchments with

18 low degree of heterogeneity. Future efforts building on the monitoring infrastructure and

19 continuously collected datasets will allow for continual improvement in hydrologic

20 interpretation, eventually incorporating alternative modeling techniques that explicitly

21 recognize non-stationarity and storage dynamics in the hydrological behavior of this tropical

22 ecosystem (e.g., Birkel et al., 2015; Harman, 2015; Hrachowitz et al., 2013).

23 In this study, we seek to add to the current geographical scope of MTT studies by addressing

24 two questions which remain open in hydrological science, and have received little attention in

25 high-elevation tropical ecosystems: "How old is stream water?" (McDonnell et al., 2010) and

26 "How does landscape structure influence catchment transit time across different geomorphic

27 provinces?" (Tetzlaff et al., 2009). Detailed hydrometric observations highlighting subsurface

28 dominated rainfall-runoff response (Crespo et al., 2011; Mosquera et al., 2016) together with

29 information of the landscape biophysical characteristics in our páramo study site will allow

1   for process-based understanding regarding: i) the spatial variability of baseflow MTTs and ii)

2   the factors controlling such variability. Based on our current knowledge of the hydrology of

3   the ecosystem, in particular, the apparent dominance of shallow subsurface flow to runoff

4   generation, we hypothesize relatively short baseflow MTTs compared to systems dominated

5   by groundwater contributions to discharge. Also, based on the hydropedological and climatic

6   similarities between our páramo site and the peatland-podzols dominated ecosystems in the

7   Scottish highlands (e.g., Soulsby et al., 2006; Tetzlaff et al., 2014), we hypothesize the

8   proportion of wetlands to be a dominant control on the variability of the MTT in this high-

9   elevation tropical ecosystem.

10   **2   Materials and methods**

11   **2.1   Study site**

12   The Zhurucay River Ecohydrological Observatory is a basin located within a tropical alpine

13   biome, locally known as wet Andean páramo. It is situated in south Ecuador (3º04'S,

14   79º14'W) on the west slope of the Atlantic-Pacific continental divide and discharges into the

15   Jubones River (Pacific Ocean tributary). The basin has a drainage area of 7.53 km^2 and

16   extends within an elevation range of 3400 to 3900 m a.s.l. Climate is mainly influenced by the

17   Pacific Ocean regime and to a lesser degree to the continental air masses from the Amazon

18   basin. Mean annual precipitation at the observatory is 1345 mm at 3780 m a.s.l. Precipitation

19   shows low seasonality with two relatively drier months (August and September) and primarily

20   falls as drizzle (Padrón et al., 2015). Mean annual temperature is 6.0 °C at 3780 m a.s.l. and

21   9.2 °C at 3320 m a.s.l. (Córdova et al., 2015).

22   The geology of the region is characterized by volcanic rock deposits compacted by glacial

23   activity during the last ice age (Coltorti and Ollier, 2000). The Quimsacocha formation,

24   composed by basaltic flows with plagioclases, feldspars, and andesitic pyroclastics, covers the

25   northern part of the basin. The Turi formation covers the southern part of the catchment and

26   its lithology mainly corresponds to tuffaceous andesitic breccias, conglomerates, and

27   horizontally stratified sands. Both formations date from the late Miocene period (Pratt et al.,

28   1997). The geomorphology of the landscape bears the imprint of glaciated U-shaped valleys.

1 The average slope of the basin is 17%. The majority of the basin (72%) has mean gradients

2 between 0-20 %, although slopes up to 40% are also found (24%). There is an interesting

3 geomorphic feature in the northeastern side of the basin corresponding to a ponded wetland at

4 a flat hilltop. As indicated by geologists from INV metals mining company, this structure

5 most likely resulted from the eutrophication of a lagoon due to high accumulation of volcanic

6 material. This area is locally known as "Laguna Ciega" ("Blind Lagoon" in Spanish) and

7 drains towards the outlet of catchment M7 (see Figure 1). The analysis of the water stable

8 isotopic composition of soil water and streamflow in this area indicated that the hydrologic

9 processes of this site occur in the shallow ponded water that is directly connected to the

10 drainage network; while deeper water stored in the soil profile has little influence for

11 discharge generation most likely as a results of the eutrophic condition of the wetland

12 (Mosquera et al., 2016).

13 Andosols are the dominant soil type in the study site. They cover approximately 80% of the

14 total basin area and are mainly found in the hillslopes. Histosols (Andean wetlands) cover the

15 remaining portion of the basin and are mainly found in flat areas where rock geomorphology

16 allows water accumulation (Mosquera et al., 2015). These soils, formed from the

17 accumulation of volcanic ash in flat valley bottoms and low gradient slopes, are black, humic,

18 and acid soils rich in organic matter with low bulk density and high water storage capacity

19 (Quichimbo et al., 2012). The organic fraction of the Histosol soils corresponds to an H

20 horizon (median depth 76.5 cm); while in the Andosol soils it corresponds to an Ah horizon

21 (median depth 40cm). The mineral fraction of both soils corresponds to a C horizon (median

22 depth of 31 cm in the Histosols and 40 cm in the Andosols). A complete description of soil

23 properties can be found in Mosquera et al. (2015) and Quichimbo et al. (2012). Vegetation

24 coverage is highly correlated with the soil type. Cushion plants (such as *Plantago rigida,*

25 *Xenophyllum humile, Azorella spp.*) grow primarily in Histosols, while tussock grass (mainly

26 *Calamagrostis* sp.) (Ramsay and Oxley, 1997; Sklenar and Jorgensen, 1999) grow in

27 Andosols. The main landscape characteristics are summarized in Table 1.

2.2 Hydrometric information

Discharge and precipitation were continuously monitored since October 2010. A nested monitoring network was used to measure discharge. The network consisted of seven tributary catchments (M1 to M7) draining to the outlet of the basin (M8). Catchments M1 to M6 comprise the main stream network draining towards the outlet of the Zhurucay basin (M8), whereas catchment M7 is a small catchment originating in a ponded wetland at a flat hilltop (Figure 1). V-notch weirs were constructed to measure discharge at the outlet of the tributaries M1-M7 and a rectangular weir at the outlet of the basin M8. Each catchment was instrumented with pressure transducers (Schlumberger DI500) with a precision of ±5 mm. Water levels were recorded at a 5-minute resolution, and transformed into discharge using the Kindsvater-Shen relationship (U.S. Bureau of Reclamation, 2001). The discharge equations were calibrated by applying the constant rate salt dissolution technique (Moore, 2004). Precipitation was recorded using tipping buckets with a resolution of 0.2 mm at two stations located at 3780 and 3700 m a.s.l. (Figure 1).

2.3 Collection and analysis of water stable isotopic and electrical conductivity data

We used a three-year record (May 2011 – May 2014) of ^{18}O and ^{2}H isotopic compositions of water samples collected in precipitation and streamflow. Data were collected at different resolutions, from event-based to biweekly, given logistic constraints and opportunities. Higher resolution data were aggregated to biweekly using precipitation weighted means for record consistency. The same nested monitoring network used for measuring discharge was implemented for stable isotopes in streamflow at the seven tributary catchments M1 to M7, and including M8 at the outlet of the basin. Water samples in precipitation were collected using two rain collectors located at 3780 and 3700 m a.s.l. Each collector consisted of a circular funnel and a polypropylene bottled covered with aluminum foil. Evaporation was prevented by placing a plastic sphere (4 cm diameter) in the funnel and a layer of 0.5 cm mineral oil within the polypropylene bottle. Due to the sampling procedure and the local climate, kinetic fractionation by evaporation can be neglected and hence both stable isotopes

1   yield the same results (Mosquera et al., 2016). Therefore only the results using the isotopic

2   composition of ^{18}O are reported. Rainwater samples are cumulative representations of the

3   isotopic signature between sampling dates while stream grab water samples represent discrete

4   points in time. The collected water samples were stored in 2 ml amber glass bottles, covered

5   with parafilm, and kept away from the sunlight to prevent fractionation by evaporation as

6   recommended by the International Atomic Energy Agency (Mook, 2000). The isotopic

7   composition of the water samples was measured using a cavity ring-down spectrometer

8   L1102-i (Picarro, USA) with a 0.5‰ precision for deuterium (^{2}H) and 0.1‰ precision for

9   oxygen-18 (^{18}O). Isotopic concentrations are presented in the δ notation and expressed in per

10   mill (‰) according to the Vienna Standard Mean Ocean Water (V-SMOW) (Craig, 1961).

11   Electrical conductivity (EC) was measured directly in-stream simultaneously with the water

12   isotopic data starting in 2012, the second year of the monitoring period. EC was measured

13   using the digital conductivity sensor Tetracon 925 (WTW, Germany) with a precision of ±

14   0.5%.

15   **2.4   Mean transit time modeling and transit time distributions**

16   Given the homogeneous landscape and hydrometeorological conditions in the Zhurucay

17   basin, we estimated mean transit times (MTTs) using an inverse solution of the LCA (Amin

18   and Campana, 1996; Małoszewski and Zuber, 1982), which assumes steady-state conditions

19   (i.e., baseflow MTTs). The LCA seeks for the parameter set of the model that best describes

20   the hydrologic system represented by a predefined transit time distribution (TTD) function

21   (Maloszewski and Zuber, 1996). The TTD describes the transition of an input signal (e.g.,

22   precipitation, snow) of tracer (e.g., δ^{18}O, δ^{2}H) to the signal at an outlet point (e.g.,

23   groundwater, streamflow) resulting from the subsurface transport of water molecules within a

24   catchment. Mathematically the TTD is described by a convolution integral that transforms the

25   input signal (δ_{in}) into an output signal (δ_{out}), considering a time lag between them ($t - \tau$)

26   through a transfer function (TTDs or $g(\tau)$) describing the subsurface transport of tracer as

27   follows:

$$\delta_{out}(t) = \int_0^\infty g(\tau)\, \delta_{in}(t - \tau)\, d\tau \quad (1)$$

2   where τ is the integration variable representing the MTT of the tracer. A more robust

3   approximation weights the isotopic concentration of the input by considering recharge mass

4   variation ($w(\tau)$) so that the outflow composition reflects the mass flux leaving the catchment:

$$\delta_{out}(t) = \frac{\int_0^\infty g(\tau)\, w(t - \tau)\, \delta_{in}(t - \tau)\, d\tau}{\int_0^\infty g(\tau)\, w(t - \tau)\, d\tau} \quad (2)$$

6   where $w(t - \tau)$ can be described in terms of rainfall magnitude, intensity, or effective

7   precipitation (McGuire and McDonnell, 2006). Precipitation intensity was used to volume

8   weight the isotopic composition of precipitation in our study. Recharge was represented by

9   the rainfall isotopic composition weighted by precipitation rate and accounted for relatively

10   small recharge (i.e., lower precipitation inputs) during the less wet months (August and

11   September).

12   MTT was estimated by adjusting the response function or TTD to fit the measured and

13   simulated stream water isotopic composition. Five TTDs were considered to describe the

14   subsurface transport of water molecules in the Zhurucay basin. We used the exponential

15   model (EM), exponential-piston flow model (EPM), the dispersion model (DM)

16   (Małoszewski and Zuber, 1982), the gamma model (GM) (Kirchner et al., 2000), and the two

17   parallel linear reservoir model (TPLR) (Weiler et al., 2003). Each model is briefly described

18   below and Table 2 summarizes their equations, fitting parameters, and the range of initial

19   parameters used in this study.

20   The EM represents a well-mixed system and assumes contributions from all flow paths. It

21   assumes a relatively simple transition of the tracer towards the stream network. The EPM is

22   an extension of the EM in which a delay in the shortest flow paths is assumed by the piston

23   flow portion of the system. In addition to the MTT, it has an additional fitting parameter (η),

24   which represents the ratio of the total volume to the volume represented by the exponential

25   distribution. The DM arises from the solution of the one-dimensional advection-dispersion

26   equation (Kreft and Zuber, 1978) and assumes that there is influence of hydrodynamic

dispersion in the system's flow paths. It also has two fitting parameters, the MTT and the dispersion parameter (Dp), which relates to the tracer transport process. The GM is a more flexible and general version of the exponential model in which the product of two parameters provides an estimation of the MTT of the system. These parameters are the shape parameter (α) and the scale parameter (β) (Kirchner et al., 2000). The TPLR represents two parallel reservoirs each one represented by a single exponential distribution. It has three fitting parameters, the MTT of the slow (MTT_s) and fast (MTT_f) reservoirs and a parameter representing the fraction of each of them with respect to total flow (φ) (Weiler et al., 2003).

The MTT approach is based on the following assumptions: 1) the tracer concentration is conservative (i.e., the tracer does not react with other elements present in the system); 2) the input tracer concentration is input in flux mode (i.e., volumetrically weighted); 3) the tracer enters the system only once and uniformly; 4) a representative tracer input can be identified; 5) transport of solute is one-dimensional and represented by a single TTD; and 6) there is a uniform storage of water within the catchment (i.e., steady-state flow in the system) (Małoszewski and Zuber, 1982). The steady-state assumption is assumed to be accomplished in humid environments during baseflow conditions (McGuire et al., 2002). In order to comply with the latter assumption, streamflow water samples collected during extreme rainfall events were excluded for the MTT simulations (McGuire and McDonnell, 2006; Muñoz-Villers et al., 2016). As a result, estimates correspond to baseflow MTTs, hereafter simply referred to as MTT. To obtain more stable results, we looped the available three years of isotopic data ten times during calibration in order to extend the data series for 30 years as a warm-up period following Hrachowitz et al. (2011) and Timbe et al. (2014).

2.5   Model performance and uncertainty analysis

The model performance was evaluated using the Kling–Gupta efficiency coefficient (KGE) (Gupta et al., 2009). KGE ranges from -∞ to 1, where unity indicates an ideal optimization. KGE can be viewed from a multi-objective perspective because it accounts for correlation (i.e., balancing dynamics, r), variability error (γ), and bias error (β) within a single objective function. The efficiency is mathematically represented by the Euclidean distance (ED) in each of the three dimensions (r, γ, and β) to an ideal point where all of them are maximized (i.e.,

1   where ideally the three factors are set to one). Efficiencies lower than 0.45 were considered

2   poor predictions (Timbe et al., 2014).

3   Depending on the TTD function used, 1 to 3 parameters were fitted during the simulations.

4   Models were built using parameter sets generated through a uniform Monte Carlo sampling

5   procedure (Beven and Freer, 2001). Each model was first run 10,000 times within a wide

6   range of parameter values (Table 2). Once a parameter value that yielded the best KGE was

7   clearly identified, the model was run again within a narrowed range of parameters until

8   obtaining at least 1,000 behavioral solutions (i.e., solutions corresponding to at least 95% of

9   the highest KGE) (Timbe et al., 2014) and their 5 and 95% limit bounds (i.e., 90% confidence

10   interval) were estimated using the Generalized Likelihood Uncertainty Estimation

11   methodology (GLUE) (Beven and Binley, 1992). The Akaike Information Criterion (AIC,

12   Akaike, 1974) was used as a parsimoniousness metric for model selection that penalizes

13   model performance based on the number of fitted parameters used to calibrate each model.

14   The model with the lowest AIC is the most efficient at fitting the observed values. A visual

15   inspections of the parameter space (Figure 4) was also conducted to qualitatively analyze the

16   models' parameter identification. The best model describing the hydrologic conditions of the

17   system was selected using the following criteria: 1) best goodness of fit using the KGE

18   criterion, 2) lowest AIC, 3) results that yielded the lower uncertainty estimations, and 4)

19   strong parameter identification.

20   **2.6   Correlation analysis of MTT and catchment characteristics**

21   We used linear regression to investigate relations between landscape characteristics and

22   hydrological behavior with the MTT of the catchments. For this analysis, we included the

23   catchments which comprise the main drainage network (i.e., catchments M1 to M6) and the

24   catchment outlet (M8) given that they possess comparable hydropedological and

25   geomorphological characteristics. That is, catchments situated at the valley bottom have well-

26   defined interconnections between wetlands in the riparian areas and the surrounding Andosol

27   soils at the slopes. Catchment M7 on the other hand, is located at a flat hilltop at the outlet of

28   a wetland area which remains ponded throughout the year. The geomorphology of this

29   concave (lagoon shaped) structure and its ponded eutrophic condition has allowed for the

1 hydrologic processes to mainly occur in the shallowest ponded portion of the water directly

2 connected to the stream network (with little influence of the most likely immobile water

3 which remains stored in the deeper soil fraction) (Mosquera et al., 2016). Therefore, its

4 hydrological response is not comparable to the other catchments where hydrologic processes

5 mainly occur in the soils and consequently was excluded from the regression analysis.

6 Statistical significance of the correlations was tested using the F-test at a 95% confidence

7 level (i.e., $p < 0.05$).

8 The landscape and hydrometric variables tested for correlation were obtained from previous

9 studies at the site (Mosquera et al., 2015) and from detailed soil, vegetation, and topographic

10 information provided by INV Metals. The landscape features considered were: soil type,

11 vegetation, geology, catchment size, slope, flow path length and gradient, and topographic

12 wetness index (TWI) (Beven and Kirkby, 1979b) (Table 1). The hydrometric variables

13 considered were: annual runoff, annual precipitation, runoff coefficient, and streamflow rates

14 (Table 3). Weekly collected EC for three years (June 2012-June 2015) was averaged and also

15 tested for correlation with MTT.

3   Results

3.1   Hydrologic and isotopic characterization in rainfall and streamflow

18 Precipitation in the Zhurucay basin is evenly distributed throughout the year (Figure 2a),

19 except for two months with relatively lower precipitation inputs (i.e., August and September),

20 both accounting for less than 8% of total annual precipitation. Spatially, annual precipitation

21 (P) is evenly distributed across the basin with an average of $1,275 \pm 9$ mm. Total annual

22 runoff (Q) and runoff coefficients (Q/P) are spatially more heterogeneous, varying between

23 684 and 864 mm per year and 0.55 and 0.68, respectively (Table 3). The hydrograph at the

24 outlet of the basin (M8) also depicts a flashy response to precipitation inputs, even during

25 these less humid months (see zoom in Figure 2a). Similar behavior is observed at all

26 catchments.

27 The $\delta^{18}O$ isotopic composition in rainfall is highly variable throughout the year (e.g., average

28 -10.2 ± 0.32‰ at the upper station) (Figure 2b) and follows a seasonal pattern with

1   isotopically enriched values during highest precipitation rates (April-May), and isotopically

2   depleted values in the less humid period (August-September). The δ^{18}O isotopic composition

3   in streamflow collected during low flows on the other hand, is much more damped (average -

4   10.0 ± 0.06‰, at M8) than the isotopic composition in precipitation (Table 4).

5   **3.2   TTD evaluation and selection**

6   In order to identify the TTD that best describes the hydrologic system in the Zhurucay basin,

7   we tested and evaluated the performance of all TTDs at all catchments. Considering that

8   similar results were obtained for all catchments and for brevity, only results for M8, the basin

9   outlet, are shown.

10   All TTDs reproduce the δ^{18}O isotopic composition at the outlet of the basin (M8) with

11   efficiencies varying between 0.50 and 0.76, i.e., above the threshold of model acceptance (KGE

12   > 0.45) (Table 5). The more flexible models, GM and TPLR yield the highest performances

13   with KGEs of 0.75 and 0.76, respectively. The EM and the EPM yield similar efficiencies (KGE

14   = 0.63), while the DM yields the lowest efficiency among all (KGE = 0.50). The models

15   associated with the highest KGEs yield the highest uncertainty bounds according to their

16   threshold of behavioral solutions; whereas the EM shows the lowest uncertainty (Figure 3). The

17   lowest AIC value was determined for the EM (AIC = 2.92), indicating that this model is the

18   most parsimonious for the system under investigation. Higher AIC values were determined for

19   the other models which fit more than one parameter (GM, 4.58; EPM, 4.92; DM, 5.39; TPLR,

20   6.55). The models' visual parameter identification inspection indicates that even though the

21   TPLR model yields the highest KGE, the identification of its parameters is poor, particularly

22   the one representing the MTT of the slow reservoir (MTT$_s$, Figure 4).For the DM and GM

23   models one parameter is well identified (MTT and α, respectively); while the others are not

24   well identified by the models. For the EPM, both parameters are not well identified. The single

25   parameter that defines the EM is very well identified. This coupled analysis of model efficiency

26   and parsimoniousness in combination with parameter identifiability indicates that although

27   models with a higher number of fitting parameters provide higher efficiencies, their parameters

28   are more uncertain.

1   Taking into account the goodness of fit, parsimoniousness, uncertainty bounds, and the

2   identifiability of the models' parameters, the EM is the model that best describes the temporal

3   variability of the baseflow $\delta^{18}O$ isotopic composition across the Zhurucay basin. These results

4   are supported by previous findings of Mosquera et al. (2015, 2016) at the study site, hinting

5   towards a fast response system with minimal impact of old water sources, and the further

6   discussion in the final part of this paper. Although the contribution of old water component/s

7   cannot be definitely neglected, it seems unfeasible that given the biophysical features of the

8   landscape and its pedological and geomorphological structure, baseflow MTTs on the range

9   of those yielded by the GM and TPLR TTDs are reliable. The EM represents a well-mixed

10 reservoir with relatively simple transition of the water (i.e., tracer) in the subsurface towards

11 the stream network. In the Zhurucay basin, the organic and porous páramo soils allow for the

12 efficient mixing of water within the whole profile of these poorly developed soils. This effect

13 particularly occurs in the Histosols (Andean wetlands) which are directly connected,

14 hydrologically, to the drainage network (Mosquera et al., 2016). These factors result in a

15 relatively simple transition of infiltrated precipitation from a well-mixed reservoir towards the

16 catchment outlet. This process-based analysis of physical characteristics of the system further

17 support the EM as the model that best describes the transport of water across the Zhurucay

18 basin. The EM was also found to describe the subsurface transport of water in another system

19 of catchments in eastern Mexico, where soil have predominantly formed by volcanic ash

20 accumulation (Muñoz-Villers et al., 2016).

21 **3.3 Baseflow MTT**

22 Results of the EM for selected catchments with the longest (M3), intermediate (M6), and

23 lowest (M7) MTTs are shown in Figure 5 and statistics of the EM simulations at all

24 catchments are summarized in Table 6. The EM overcomes the modeling acceptance criterion

25 of KGE > 0.45 at all catchments with KGE values ranging between 0.48 and 0.84. The

26 longest MTTs is found in catchment M3 (0.73 years, 264 days) whereas the shortest at M7

27 (0.15 years, 53 days). The MTT for the other catchments vary within this range. On average,

28 within the 90% confidence level for the catchments forming the main drainage network (M1-

29 M6 and M8), MTT estimations show small variations (25 days at the lower confidence bound

1   and 35 days at the upper confidence bound) with small standard deviation (4 days for the

2   upper bound and 6 days for the lower bound). For catchment M7, variations are even smaller

3   (9 days at the lower confidence bound and 11 days at the upper confidence bound). In

4   addition, the model performs best for catchments with high variability in their isotopic

5   composition during the monitoring period. For instance, catchment M3 (Figure 5a) shows the

6   smallest amplitude in isotopic variation for the observed and simulated data (Table 6),

7   coupled with the lowest KGE (0.48) and the highest MTT. On the other hand, catchment M7

8   (Figure 5c) shows the highest amplitude in isotopic variation for the observed and simulated

9   data, coupled with the highest KGE (0.84) and the shortest MTT. Similarly, catchment M6

10   (Figure 5b), which has a MTT shorter than the one in M3 and longer than the one in M7, has

11   an amplitude and KGE varying between the ones in M3 and M7. The Monte Carlo

12   simulations for the fitted parameter MTT (Figure 5) clearly depict how the MTT which yield

13   the highest KGE in each catchment decreases as the variation in their isotopic composition

14   increases as described above. Results from all the catchments are also described by this trend.

15   The MTT probability density functions (PDFs), which indicate the distribution of MTTs in

16   the hydrologic system, and cumulative density functions (CDFs), which express the tracer

17   ''mass recovery from an instantaneous, uniform tracer mass addition'' (McGuire et al., 2005)

18   based on the fitted parameter distributions, not shown for brevity, exhibit a dominance of

19   relatively short MTTs in the hydrology of the Zhurucay basin. The CDFs also indicate that the

20   tracer is completely recovered (~ 100%) in all catchments at around 160 weeks, except for

21   M7, where the tracers is even more rapidly recovered (~ 38 weeks). As we used a stable

22   isotopic record of 156 weeks (3 years), these results indicate that a three years record of tracer

23   data is sufficient to estimate the MTT of waters using the LCA in this páramo basin.

24   **3.4   Correlations of baseflow MTT with landscape and hydrometric variables**

25   Correlation analysis showed no statistically significant correlations (p-values > 0.05) between

26   MTT and landscape features and hydrometric variables of the nested monitoring system when

27   all catchments were included. This lack of correlation is likely related to the previously

28   reported distinct responsiveness of catchment M7 to precipitation inputs due to its different

29   geomorphologic configuration (i.e., ponded eutrophic wetland disconnected from the slopes)

1 and catchments M3 and M4 (Figure 1) driven by a spring water contribution during low flow

2 generation. In general, deep subsurface flow and groundwater contributions to discharge seem

3 to be minimal and geology has not been found to directly control the hydrology in this páramo

4 ecosystem (Mosquera et al., 2015). However, the existence of this shallow spring sourced at

5 the interface between the soil mineral horizon and the shallow bedrock upstream the outlet of

6 M3 and M4, favors the generation of higher low flows (Mosquera et al., 2016) and increases

7 MTTs in these catchments. The latter indicates that geology (fractures in the shallow bedrock)

8 influence the hydrology of these small headwater catchments; thus, masking relationships

9 between landscape features and MTT of the whole system. Therefore, we tested the MTT

10 correlations without including these small catchments (M3 and M4) and M7.

11 The reanalysis with the modified data set revealed significant relations of MTT with

12 topographical indexes (Figure 6). The relations between MTT and average slope (Figure 6a,

13 $R^2 = 0.78$ and p = 0.047) and percent area having slopes in the range 20%-40% are negative

14 (Figure 6b, $R^2 = 0.90$, p = 0.015). Conversely the relation between the percent area having

15 slopes 0%-20% and MTT is positive ($R^2 = 0.85$, p = 0.026). No significant correlations (p-

16 values > 0.05) between MTT and vegetation, soil types, geology, flow path length,

17 topographic wetness index, and hydrometric variables were found (Table 7). However, a

18 relatively strong relation between MTTs and low flows with smaller significance was also

19 found. That is, catchments with higher MTTs yielded lower low flows ($R^2 = 0.62$, p = 0.11 for

20 Q_5 and $R^2 = 0.61$, p = 0.12 for Q_{10}). The regression analysis including all catchments also

21 showed that mean electrical conductivity (MEC) of the waters explains 89% (p = < 0.001) of

22 the catchments' MTT variability (Figure 7). Streams with higher MEC have longer MTTs.

23 **4   Discussion**

24 **4.1   General hydrometric and isotopic characterization**

25 The rainfall-runoff process evidences a rapid response of discharge to precipitation inputs in

26 the Zhurucay basin. This rapid response occurs even during the less humid periods (August-

27 September) in which relatively small rainfall events result in peak flow generation (Figure

28 2a). This high responsiveness results from the combined effect of the relatively uniform

29 distribution of precipitation year-round – common in tropical regions – and the unique

1   properties of the Histosol soils or Andean wetlands located near the streams. The high storage

2   capacity of wetlands was also highlighted by Roa-García and Weiler (2010) after the

3   comparison of three paired catchments in the growing coffee region of Colombia at lower

4   elevations (2000-2200 m a.s.l.). Similarly, Histosol soils in our study site are rich in organic

5   matter content (mean 86% by volume), allowing for high water storage capacity. In addition,

6   due to their relatively low saturated hydraulic conductivity (0.72-1.55 cm h^{-1}), these soils

7   remain near saturation throughout the year. These factors, in combination with the local

8   climate, allow páramo soils to regulate and maintain a sustained discharge throughout the

9   year. Moreover, as these processes occur in the shallow organic horizon of the soils, the

10 hydrology of the Zhurucay basin páramo ecosystem is dominated by shallow subsurface water

11 flow. This is supported by the similar isotopic composition between streams and soil waters in

12 the organic layer of the Histosols in the Zhurucay basin (Mosquera et al., 2016).

13 Although the δ^{18}O isotopic composition of stream waters is damped and lagged with respect

14 to that of precipitation, streamflow samples in the Zhurucay basin still reflect the variability

15 of the δ^{18}O composition of rainfall (Figure 2b), as expected in a system dominated by shallow

16 subsurface flow. However, catchments are differently influenced by precipitation. M7, located

17 at the outlet of a wetland that remains constantly ponded, shows a faster response to rainfall

18 (Figure 5c), most likely as a result of the rapid mixing of rainfall water with the shallow water

19 moving in the shallow organic horizon of the soils and the ponded water above it. All of the

20 other catchments show considerably less influence of rainfall (Figures 5a and 5b) due to the

21 mixing of rainfall water with the water stored within the whole profile of the Histosol soils.

22 **4.2   What is the baseflow MTT?**

23 The high performance (KGE > 0.48, Table 6), low uncertainty (Figure 3), high AIC (Table 5),

24 and strong parameter identification (Figure 4) of the exponential model (EM) indicate that

25 this model best mimics the subsurface transport of water in all catchments within the

26 Zhurucay basin (Figure 5). In addition, the model captures some particularities in the

27 functioning of each catchment. For instance, results indicate relatively long MTTs in two of

28 the headwater catchments, M3 and M4 (0.73 and 0.67 years, respectively). This likely results

29 from a shallow spring water contribution to these catchments during low flow generation

1   (Mosquera et al., 2015). The model seems to capture the effect of the shallow spring

2   contribution by yielding the longest MTTs estimations in these catchments, and an intrinsic

3   influence of geology on MTT variability. In addition, the performance of the model in these

4   two catchments is the lowest within the basin. The latter most likely because of less efficient

5   mixing of water due to the influence of the spring water source; suggesting that this effect is

6   also captured by the model which assumes a well-mixed reservoir. This observation led us to

7   consider that another model representing an additional slow flow reservoir (e.g., TPLR or

8   GM) might better represent the subsurface movement of water in these catchments. Results,

9   however, (Figures 3 and 4, Table 5) indicate that the contribution from this additional water

10 source is small and an additional reservoir is not well distinguished by these TTDs as their

11 parameters are not well identified. Recently, Muñoz-Villers et al. (2016) also identified the

12 EM as the model that best mimics subsurface flow in 7 of 12 nested catchments underlain by

13 volcanic soils (Andosols) in a tropical montane cloud forest (TMCF) located in Veracruz,

14 Mexico. These authors estimated even longer MTTs (1.2-2.2 years) due to deeper

15 groundwater contributions to discharge.

16 On the other end, M7, dominated by the contribution from the shallowest part of the organic

17 horizon of the soils and the ponded fraction of water accumulated in a ponded wetland –

18 which is directly connected to the stream channel – presents the shortest MTT of all

19 catchments (0.15 years, 53 days), linked to the highest model performance. Our results

20 support the hypothesis that this catchment presents a shorter MTT, indicating that the ponded

21 condition of the wetland allows for a rapid and efficient mixture of precipitated water with

22 ponded water and water stored in and released from the shallow organic horizon of the soil.

23 The latter resulting in a rapid delivery of event (new) water to the stream; whereas water

24 stored deeper in the soil seems to remain mostly immobile with minimal influence in the

25 hydrology of the catchment. The well-mixing and simpler delivery of water to the stream is

26 also captured by the high model performance. The MTTs estimated for the rest of the

27 catchments lie in between these two extremes and their values and efficiencies vary

28 depending on the amplitude of the isotopic tracer variation, with longer MTTs in catchments

29 where the amplitude of the signal is more damped – evidencing lower influence of

30 precipitation and less efficient mixing with the soil storage – and vice versa. The MTT in

these catchments vary between 0.43 and 0.53 years (156 to 191 days). Overall, the MTTs are relatively short, further supporting previous evidence that shallow subsurface flow dominates the hydrology of the ecosystem.

In other tropical latitudes, MTTs higher than 300 days were found in three paired Colombian catchments applying the TPLR model (Roa-García and Weiler, 2010). These basins show higher MTTs than the catchments in the Zhurucay basin most likely as a result of the higher development of the volcanic ash soils (> 10 m), which allow the water to be stored for longer periods in the subsurface. MTTs longer than two years were also found in a TMCF in southern Ecuador (Timbe et al., 2014), evidencing that differently from our findings, this lower elevation ecosystem is dominated by deep groundwater contributions. Preliminary MTT estimations in another TMCF biome located in central Mexico (Muñoz-Villers and McDonnell, 2012) yielded a MTT of three years. Although the ecosystem is dominated by soils formed by volcanic ash accumulation, as the páramo soils are, a combination of deeper hillslope soils (1.5-3 m depth) with highly fractured and permeable geology allows for the formation of longer flow paths of water and longer MTTs. Therefore, the relatively young and little weathered geology in the Zhurucay basin allows for a dominance of shallow subsurface flows. The results of these studies suggest that the particular shallow development of the rich organic soils with low saturated hydraulic conductivities, in combination with an homogeneous and low permeable geology provide the páramo basin of the Zhurucay River with a high water retention capacity, and relatively long transit times and flow paths considering the little development of the organic horizon of the soils. Hrachowitz et al. (2009b) reported MTTs (135-202 days) around the ones found in the Zhurucay basin catchments in a montane catchment in Scotland dominated by peatland soils and relatively little weathering geology. Nevertheless, the models which provided the best fit were the GM and the TPLR, as opposed to the EM in our study site. As in the Zhurucay basin, these authors attributed this short transit time to the dominance of ecohydrological processes occurring in the upper horizon of the peat soils. Therefore, we can conclude that in these two ecosystems, located at different latitudes but with similar hydropedological conditions, the hydrology is dominated by shallow subsurface flows. Nevertheless, the soils development of the shallow peaty soils in Scotland is lower (40 cm) in comparison to the soil development of the

1   Histosols (80 cm) in the Zhurucay basin. These factors, in combination with differences

2   underlying geologies suggest that their overall hydrologic functioning might differ as

3   evidenced by different TTDs describing the subsurface transport of solutes.

4   Although we used a methodology that assumes stationary conditions in the hydrologic system

5   (LCA), it is relevant to note here the results of a recent application of conceptual modeling for

6   the investigation of non-stationary conditions in a hydrologically similar region (Birkel et al.,

7   2015). These authors detected non-stationary effects in water age distributions only during

8   extreme weather conditions (extensive dry or wet periods) and attributed this behavior to the

9   large mixing capacity of the Histosol soils. Although future investigations of the non-

10   stationary nature of MTTs are needed at the páramo, based on the dominance of flow

11   generation in the Histosols at the Zhurucay basin, in combination with low annual changes in

12   the environmental conditions, we consider our results from the LCA provide robust MTTs

13   estimates in our study site.

14   ## 4.3   Controls on baseflow MTT variability

15   We found significant correlations ($R^2 \geq 0.78$, $p < 0.05$) between catchment slope dependent

16   indexes and MTT using a subset of the main stream catchments (Table 7 and Figure 6).

17   Results of the correlation analysis indicate that: 1) the higher the average slope of the

18   catchments, the shorter their MTTs; 2) the higher the percent of area corresponding to slopes

19   between 0% and 20%, the longer the MTT; and 3) the higher the percent of area

20   corresponding to slopes between 20% and 40%, the shorter the MTT. These results indicate a

21   clear control of the catchments' slopes in the Zhurucay basin´s MTTs. Locally, the same

22   topographical features were found to control low flow generation. Mosquera et al. (2015)

23   attributed the latter to expected contributions from the water originated in the slopes (Andosol

24   soils) during low flow generation as a result of the gravitational potential of the water that

25   drains downslope from these soils. These authors also found that wetlands (Histosols soils

26   located near the streams) control the generation of moderate and high flows. Although we did

27   not find significant correlations with other landscape features, vegetation showed expected

28   trends in relation to MTT. That is, catchments with higher proportion of cushion plants

29   (wetlands) ($R^2 = 0.29$, $p = 0.35$) have longer MTTs and an inverse relation with tussock grass

1   vegetation ($R^2 = 0.31$, p = 0.33). In another tropical system of catchments in Colombia, a

2   catchment with higher areal proportion of wetlands was found to prolong the water MTTs, but

3   appeared to reduce water yield (Roa-García et al., 2011). Although these authors did not

4   report the slope of the catchments, we can infer that the catchment with the highest proportion

5   of wetlands – as they form in flat areas – is also the catchment with the lowest gradients.

6   Therefore, their observations might result from the combination of the deeper soil

7   development (> 10 m) with high water retention capacity and low saturated hydraulic

8   conductivity, perhaps in combination with low slope gradients. This would support the result

9   of our study, where the catchments with the lower slopes and higher proportion of wetlands

10   present the longer MTTs.

11   In other latitudes, in 20 Scottish catchments with different geomorphologies and climate,

12   MTT variability was controlled by the areal proportion of peat soils and no influence of

13   catchments' slopes was found (Hrachowitz et al., 2009a). As such, and given the similarities

14   between these soils and our Histosol soils (Andean wetlands), we hypothesized MTT

15   variability to be controlled by the areal extent of wetlands. Even though we found that MTT

16   variability is rather mainly controlled by topography in our tropical alpine site, a small trend

17   of wetlands' cover to increase MTT was also identified. Although the later relation is not

18   statistically significant, the latter most likely results from the influence of topography on

19   Histosol soils (wetlands) formation, where the formation of this soil mainly occurs in

20   catchments with lower slopes where water accumulation is favored. This finding indirectly

21   suggests that wetlands influence MTT spatial variability to a lesser extent. Therefore, it

22   appears that although relatively similar processes control the ecohydrology of both

23   ecosystems, controls on MTT variability cannot be extended from one ecosystem to the other.

24   MTT variability was also found to be controlled by the proportion of wetlands in cold snow

25   dominated boreal catchments in Sweden for the MTT of spring snowmelt water (Lyon et al.,

26   2010). These authors attributed this effect to the formation of shallow ice acting as

27   impermeable barriers above the wetlands, and thus changing the flow paths of water.

28   Nevertheless, because of the different climate and geological features between their

29   catchments and ours, we did not find wetlands as major controls on MTT variability.

1   Other slope topographic indexes – e.g., flow path length (L), flow path gradient (G), and the

2   ratio between both (L/G) (e.g., McGuire et al., 2005; Tetzlaff et al., 2009) – have been

3   identified as controls of MTT variability in catchments in other latitudes. Although these

4   landscape features did not significantly explain MTT variability in the Zhurucay basin, the

5   L/G ratio was reported as the major control of MTT variability ($R^2 = 0.91$) in steep temperate

6   catchments in the central western Cascades of Oregon (McGuire et al., 2005), suggesting that

7   this relation "reflects the hydraulic driving force of catchment-scale transport (i.e., Darcy's

8   law)". Similarly to our study site, they also found average slope of these catchments to be one

9   of the most important individual controls on MTT, explaining 78% of the MTT variability.

10 Recently, topography was also identified as a major control on the MTT of 12 TMCF

11 catchments in eastern Mexico (Muñoz-Villers et al., 2016). Results from these studies reflect

12 that the integrated effect of catchment slope on MTT variation can be identified in distinct

13 geological and hydropedological provinces. The latter also suggests that rather than using a

14 predictor which indicates more local effects of hydraulic force driving in the stream channel

15 (e.g., L/G), catchment slope might be a better measure to compare catchment functioning as it

16 integrates the hydrologic connectivity of hillslope, riparian, and stream areas.

17 The topographic controls on MTT in the Zhurucay basin indicate that water resides for a

18 longer time in catchments having lower slope gradients. These results also indicate that in

19 catchments having higher areal proportions of low gradients and lower areal proportions of

20 steeper gradients coupled with higher wetlands coverage, water resides longer in the shallow

21 reservoir of the soils. The control of the proportion of steeper gradients in MTT variability

22 suggests that the gravitational potential of water draining downslope in the Andosol soils also

23 indirectly influences MTTs. Therefore, it is our interpretation that the hydrology of this

24 ecosystem is mainly dominated by the interplay of two factors: 1) the high storage capacity in

25 the shallow organic horizon of the porous páramo soils and 2) the catchment slope. Factor 1

26 driving the high water retention capacity and factor 2 controlling the high regulation capacity

27 of the ecosystem, and thus, maintaining a sustained delivery of water to the streams along the

28 year. Without the interplay storage-slope, water would remain stored in the soils, and perhaps

29 the delivery of water towards the streams would be dominated by saturated overland flow

1   (SOF), affecting the regulation capacity of the ecosystem. Nevertheless, SOF rarely occurs in

2   the Zhurucay basin (Mosquera et al., 2015).

3   Mean electrical conductivity (MEC) was also found to be significantly correlated with MTT

4   using all catchments of the nested system in the basin (Figure 7). The regression analysis,

5   showed strong correlation, with MEC increasing as MTT increases. As EC is an intrinsic

6   property of water, due to the time it spends in contact with the surrounding pore space, rather

7   than a control on MTT variability, this result indicates that this property might be used as a

8   proxy to estimate MTT spatial variability. The well-defined connection between MTT and

9   MEC most likely resulting from the relatively homogenous geology of the Zhurucay basin. To

10   our knowledge, there are no studies that have identified similar (or different) relations

11   between MEC and MTT in other biomes.

12   Given that estimating MTT using isotope tracer methodologies is financially expensive due to

13   the logistical set up of a monitoring network and the processes of data collection and analysis,

14   finding proxies (i.e., predictors) which allow inferring MTTs at lower operational costs is

15   critical to improve water resources management. In this sense, the strong relation between

16   MEC and MTT indicates that MEC could be used as a relatively inexpensive and directly

17   measurable proxy for MTT in this wet Andean páramo catchment. Therefore, although this

18   result cannot be expanded beyond páramo areas, perhaps not even beyond the study site, it

19   seems that it is worth evaluating whether or not MTTs can be inferred from MEC in other

20   hydrologic systems. Nevertheless, one should be careful that EC measurements can be

21   relatively variable over time. As a result, a single measurement of EC is most likely not

22   enough to provide robust MTT estimates. Therefore, longer EC measurement records are

23   recommended to reduce MEC variability and provide more robust MTT estimates.

24   **5   Conclusions**

25   The baseflow MTT evaluation using a LCA indicated that the EM best describes the

26   subsurface transport of water in the basin. This result indicates efficient mixing in the high

27   organic and porous wet Andean páramo soils and a simple subsurface transition of rainfall

28   water towards the streams. MTT estimations showed relatively short MTTs linked to

29   relatively short subsurface flow paths. Therefore, we confirm that the hydrologic system of

1   the tropical alpine biome of the Zhurucay basin is dominated by shallow subsurface flow.

2   MTT estimations showed that catchment M7, located at a flat hilltop at the outlet of a wetland

3   which remains ponded year-round and disconnected from the slopes – most likely as a result

4   of the eutrophication of a lagoon – showed a particularly low MTT (0.15 yr – 53 days) in

5   relation to the MTT in all of the other catchments (0.40-73 yr, 156-250 days) in which the

6   morphology corresponds to U-shaped valleys, with the wetlands located at the valley bottoms

7   near the streams and connected to the slopes. Two headwater catchments, M3 and M4,

8   showed the longest MTTs, related to a small contribution from a spring shallowly sourced.

9   These results indicate that in this páramo ecosystem, the geomorphology of the wetlands and

10 geology to a lesser extent, influence the responsiveness of the streams to precipitation inputs.

11 Correlation analysis between landscape variables and MTT indicates that MTT variability is

12 mainly explained by the slope of the catchments, and a related influence of vegetation to a

13 lesser extent. Catchments with the steepest average slopes and lower proportion of wetlands

14 have the shortest MTTs. The lack of significant correlations between the MTTs and

15 hydrological response variables (runoff coefficient and specific discharge rates) indicate that

16 neither water yield, nor streamflow rates control the time water resides in the subsurface of

17 the páramo soils. These results indicate that the interplay between the high storage capacity of

18 the páramo soils and the slope of the catchments define the ecosystem's high regulation

19 capacity. Mean electrical conductivity (MEC) of stream waters – with the oldest waters

20 presenting the highest MECs – seems to be a promising proxy of MTT in system of

21 catchments under homogeneous geological conditions. Finally, we want to highlight the

22 usefulness of a nested monitoring system for acquiring better process-based hydrologic

23 functioning understanding. For instance, if M3, M4, and/or M7 catchments would not have

24 been monitored, the influence of geology and/or geomorphology on catchment hydrological

25 response could not have been identified and important information about the whole ecosystem

26 functioning would remain unknown.

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Table 1. Main landscape characteristics of the monitored catchments.

Catchment	Area (km²)	Altitude (m a.s.l)	Distribution of soil types[a] (%)			Vegetation cover[b] (%)				Topography[c] (%)				Geology[e] (%)			EC[f] (μS/cm)
			AN	HS	LP	TG	CP	QF	PF	AS	L[d]	G	TWI	Qm	Tu	Qd	
M1	0.20	3777 – 3900	85	13	2	85	15	0	0	14	0.9	1.9	9.6	100	0	0	35.7
M2	0.38	3770 – 3900	83	15	2	87	13	0	0	24	0.8	1.9	12.8	66	1	33	32.0
M3	0.38	3723 – 3850	80	16	3	78	18	4	0	19	1.0	2.0	9.4	59	41	0	62.4
M4	0.65	3715 – 3850	76	20	4	79	18	3	0	18	1.3	2.0	12.5	50	48	1	47.9
M5	1.40	3680 – 3900	78	20	2	78	17	0	4	20	2.5	1.9	11.8	70	1	30	37.0
M6	3.28	3676 – 3900	74	22	4	73	24	1	2	18	3.3	1.8	8.2	50	30	20	35.6
M7	1.22	3771 – 3830	37	59	4	35	65	0	0	12	0.4	1.7	10	87	0	13	15.3
M8	7.53	3505 – 3900	72	24	5	71	24	2	2	17	4.6	1.9	16.7	56	31	13	33.5

[a] AN = Andosol; HS = Histosol; LP = Leptosol

[b] TG = tussock grasses; CP = cushion plants; QF = *Polylepys forest*; PF = pine forest.

[c] AS = average slope, L = flow path length ; G = flow path gradient; TWI = topographic wetness index (Beven and Kirkby, 1979a).

[d] L units in km.

[e] Qm = Quimsacocha formation; Tu = Turi formation; Qd = Quaternary deposits.

[f] EC = mean electrical conductivity. Data collected weekly for a three years period (June 2012-June2015)

1 Table 1. Models considered to describe water mean transit time (MTT) in the study area and

2 their transit time distribution (TTD) functions, parameters, and range of initial parameters.

Model	Transit time distribution ($g(\tau)$)	Parameter(s) range
Exponential model (EM)	$\dfrac{1}{\tau}\exp\left(\dfrac{-t}{\tau}\right)$	$\tau\ [0-65]$
Exponential-piston model (EPM)	$\dfrac{\eta}{\tau}\exp\left(-\dfrac{t\cdot\eta}{\tau}+\eta-1\right)$ for $t\geq\tau\left(1-\eta^{-1}\right.$	$\tau\ [0-65]$ $\eta\ [0.5-4]$
Dispersion model (DM)	$\left(\dfrac{4\pi D_p t}{\tau}\right)^{-1/2}t^{-1}\exp\left[-\left(1-\dfrac{t}{\tau}\right)^2\left(\dfrac{\tau}{4D_p t}\right)\right]$	$\tau\ [0-65]$ $D_p\ [0.5-4]$
Gamma model (GM)	$\dfrac{\tau^{\alpha-1}}{\beta^{\alpha}\Gamma(\alpha)}\exp^{-\tau/\beta}$	$\alpha\ [0.01-4]$ $\beta\ [0-500]$ $\tau=\alpha\cdot\beta$
Two parallel linear reservoir (TPLR)	$\dfrac{\varphi}{\tau_f}\exp\left(\dfrac{-t}{\tau_f}\right)+\dfrac{1-\varphi}{\tau_f}\exp\left(\dfrac{-t}{\tau_s}\right)$	$\tau_s\ [0-65]$ $\tau_f\ [0-8]$ $\varphi\ [0-1]$

3 τ = tracer's mean transit time (MTT) [months]; η = parameter that indicates the percentage of

4 contribution of each flow type [-]; Dp = dispersion parameter [-]; α = shape parameter [-]; β =

5 scale parameter [-]; τ_f and τ_s = transit time of fast and slow flows in months; φ = flow partition

6 parameter between fast and slow flow reservoirs [%]. [-] Indicates parameters are unitless.

Table 3. Main hydrometric variables of the catchments.

Catchment	Precipitation (mm yr⁻¹)	Total runoff (mm yr⁻¹)	Runoff Coefficient[b]	Average specific discharge (1 s⁻¹ km⁻²)	Flow rates as frequency of non-exceedance (1 s⁻¹ km⁻²)						
					Q_{min}	Q_{10}	Q_{30}	Q_{50}	Q_{70}	Q_{90}	Q_{max}
M1	1300	729	0.56	23.1	0.7	2.7	6.6	14.3	26.4	50.1	1039.0
M2	1300	720	0.55	22.8	1.2	4.8	7.9	14.9	26.7	49.0	762.9
M3	1293	841	0.65	26.7	2.3	7.3	10.8	17.7	28.1	52.4	894.2
M4	1294	809	0.62	25.6	4.2	6.2	9.8	16.6	27.3	52.1	741.2
M5	1267	766	0.6	24.3	1.5	4.1	8.3	15.3	26.9	50.8	905.7
M6	1254	786	0.63	24.9	1.2	3.7	8.2	15.9	27.5	53.2	930.4
M7	1231	684	0.56	21.7	0.3	1.8	5.2	11.0	23.3	53.9	732.0
M8	1277	864	0.68	27.4	1.9	4.0	8.7	15.2	29.2	60.8	777.9

[a] Total runoff as a proportion of precipitation.

1   Table 4. Statistics of the $\delta^{18}O$ isotopic composition in precipitation and streamflow used as

2   input data for the MTT modeling.

Sampling Station	Altitude (m a.s.l.)	$\delta^{18}O$ (‰)				
		n[a]	Average	SE[b]	Max	Min
M1	3840	123	−10.6	0.06	−9.0	−12.6
M2	3840	124	−10.4	0.07	−8.8	−12.6
M3	3800	121	−10.7	0.05	−8.8	−12.1
M4	3800	122	−10.6	0.05	−8.7	−11.9
M5	3800	118	−10.5	0.06	−9.1	−12.8
M6	3780	121	−10.3	0.06	−8.9	−12.2
M7	3820	121	−8.9	0.15	−6.2	−13.9
M8	3700	118	−10.0	0.06	−8.3	−11.6
Upper Precip.	3779	137	−10.2	0.32	−1.2	−25.0
Middle Precip.	3700	134	−10.1	0.32	−2.7	−20.0

3   [a] n: number of samples collected.

4   [b] SE: Standard error.

Table 5. Statistical parameters of observed and modeled $\delta^{18}O$ for the stream at the outlet of the basin (M8).

Model	Observed $\delta^{18}O$		Simulated $\delta^{18}O$						Model Parameters[b]	
	Mean (‰)	σ[a] (‰)	Mean (‰)	σ[a] (‰)	KGE[a] (-)	RMSE[a] (‰)	Bias (‰)	AIC[a] (-)		
EM	-10.05	0.45	-10.02	0.52	0.63	0.59	0.03	2.92	τ (days)	191 (166-224)
EPM			-10.02	0.52	0.63	0.59	0.03	4.92	τ (days)	120 (90-205)
									η (-)	0.63 (0.53-0.92)
DM			-9.95	0.64	0.50	0.72	0.10	5.39	τ (days)	666 (480-755)
									Dp (-)	3.99 (2.74-3.93)
GM			-10.02	0.45	0.75	0.47	0.03	4.58	τ (days)	392 (296-1478)
									α (-)	0.70 (0.51-0.76)
									β (-)	40 (26-108)
TPLR			-10.02	0.45	0.76	0.47	0.03	6.55	τ_f (days)	1664 (356-1738)
									τ_s (days)	45 (12-90)
									φ (-)	0.31 (0.10-0.48)

[a] σ = Standard deviation; KGE = Kling-Gupta Efficiency (Gupta et al., 2009), AIC = Akaike Information Criterion (Akaike, 1974). Statistical parameters of the simulated results correspond to the best-matching value of the objective function KGE.

[b] τ = tracer's mean transit time; η = parameter that indicates the ratio between the contribution of piston and exponential flow; Dp = dispersion parameter; α = shape parameter; β = scale parameter; τ_f and τ_s = transit time of fast and slow flows; φ = flow partition parameter between fast and slow flow reservoirs. (-) = Dimensionless parameter. Uncertainty bounds shown in parenthesis were estimated using the generalized likelihood uncertainty estimation (GLUE, Beven and Binley, 1992).

Table 6. Statistical parameters of observed and simulated $\delta^{18}O$ for all catchments using the exponential model (EM).

Catchment	Observed $\delta^{18}O$		Simulated $\delta^{18}O$			Simulated MTT[b]	
	Mean (‰)	σ[a] (‰)	Mean (‰)	σ[a] (‰)	KGE[a] (-)	(years)	(days)
M1	−10.63	0.37	−10.51	0.44	0.48	0.54 (0.48 − 0.63)	194 (171 − 227)
M2	−10.46	0.53	−10.51	0.63	0.61	0.43 (0.38 − 0.51)	156 (137 − 183)
M3	−10.64	0.23	−10.51	0.26	0.48	0.73 (0.64 − 0.86)	264 (232 − 310)
M4	−10.63	0.27	−10.51	0.3	0.48	0.67 (0.59 − 0.78)	240 (212 − 280)
M5	−10.51	0.39	−10.51	0.46	0.53	0.52 (0.46 − 0.61)	188 (165 − 219)
M6	−10.37	0.42	−10.43	0.5	0.59	0.52 (0.46 − 0.61)	188 (164 − 220)
M7	−8.93	2.92	−10.02	2.93	0.84	0.15 (0.12 − 0.18)	53 (45 − 64)
M8	−10.05	0.45	−10.02	0.52	0.63	0.53 (0.46 − 0.62)	191 (167 − 224)

[a] σ = Standard deviation; KGE = Kling-Gupta Efficiency. Statistical parameters of the simulated results correspond to the best-matching value of the objective function KGE.

[b] Uncertainty bounds (5-95 percentiles) of the simulated mean transit time (MTT) shown in parenthesis were estimated using the generalized likelihood uncertainty estimation (GLUE).

1 Table 7. Coefficient of determination (R^2) between the mean transit time (MTT) and i)

2 landscape features and ii) hydrological variables for each of the catchments. Catchments M3

3 and M4 (additional spring water source, see Figure 1) and M7 (at a flat hilltop disconnected

4 from the hillslopes) are not included in the regressions; except for electrical conductivity, i.e.,

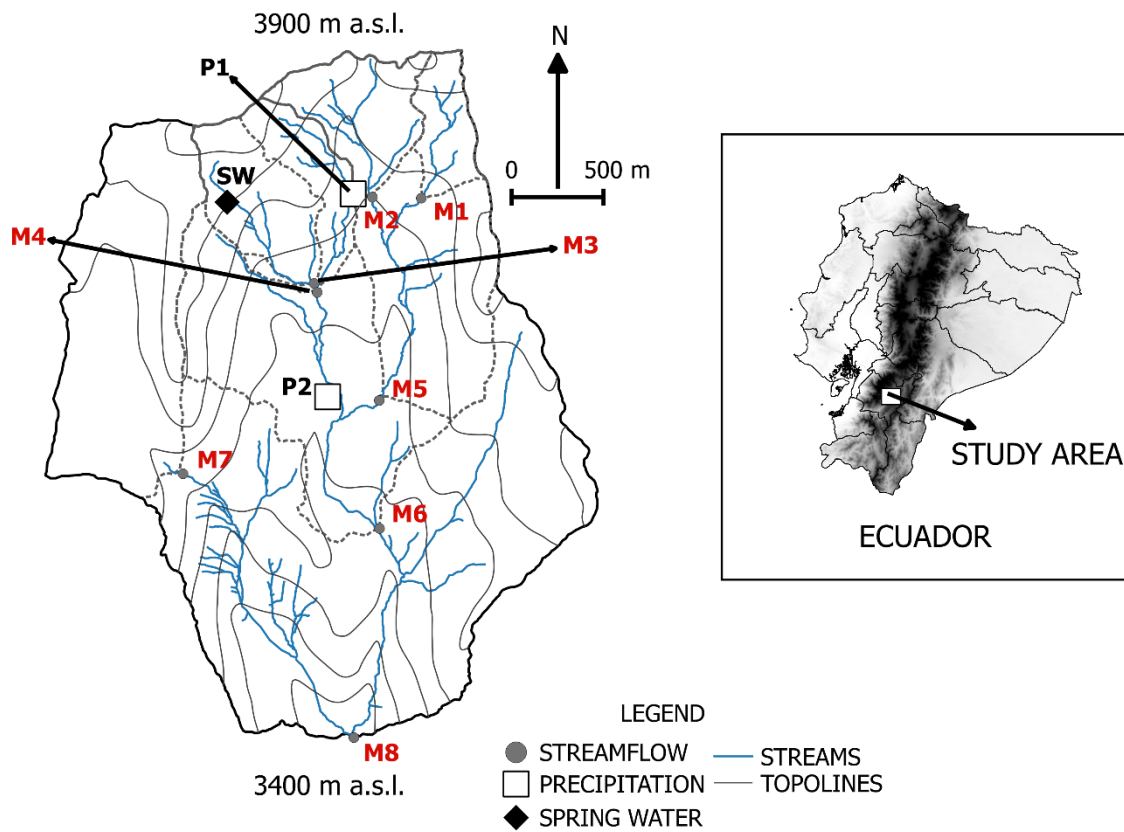
5 all catchments are considered (Figure 7).

Landscape features			Hydrologic variables		
Vegetation			*General features*		
Cushion plant	0.29	(0.35)	Runoff coefficient	0.25	(0.39)
Tussock grass	− 0.31	(0.33)	Total runoff	0.21	(0.44)
			Precipitation	− 0.17	(0.48)
Soil Type			Average specific discharge	0.21	(0.44)
Histosol	0.13	(0.56)			
Andosol	− 0.13	(0.55)	*Streamflow rates*		
			Q_{99}	0.42	(0.24)
Geologic formation			Q_{90}	0.18	(0.48)
Quimsacocha	0.04	(0.75)	Q_{80}	0.06	(0.68)
Turi	0.12	(0.57)	Q_{70}	0.09	(0.63)
Quaternary deposits	− 0.51	(0.18)	Q_{60}	0.06	(0.68)
			Q_{50}	0.01	(0.86)
Topographic features			Q_{40}	0.10	(0.61)
Average slope	**− 0.78**	**(0.05)**	Q_{30}	− 0.02	(0.82)
Slope 0%−20%	**0.85**	**(0.03)**	Q_{20}	− 0.14	(0.53)
Slope 20%−40%	**− 0.90**	**(0.01)**	Q_{10}	− 0.61	(0.12)
Area	0.13	(0.56)	Q_5	− 0.62	(0.11)
TWI	− 0.03	(0.79)			
Flow path length (L)	0.23	(0.42)	*Water intrinsic properties*		
Flow path gradient (G)	− 0.20	(0.45)	Electrical conductivity	**0.89**	**(< 0.001)**
L/G	0.23	(0.45)			

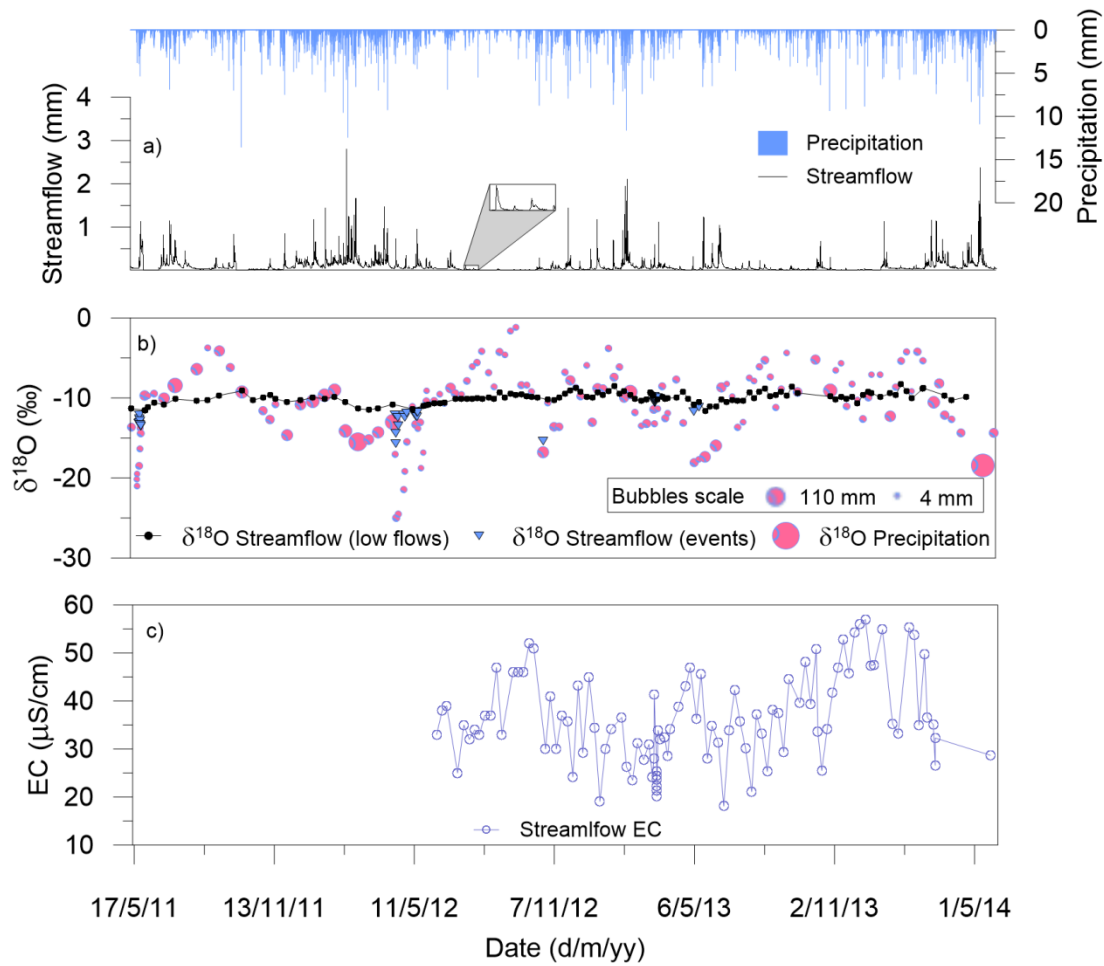
6 Signs indicate positive (no sign) or negative (−) correlation between parameters.

7 Values in bold are statistically significant to a 95% level of confidence ($p < 0.05$). Values in

8 parenthesis are the p-values of the correlations.

9 [a] TWI = Topographic wetness index (Beven and Kirby, 1979).

2   Figure 1. Location of the study area, and the isotopic monitoring stations in the Zhurucay

3   observatory for: Streamflow (M), and Precipitation (P). SW is a spring water source upstream

4   the outlet of catchments M3 and M4.

2 Figure 2. a) Hourly precipitation and unit area streamflow; b) $\delta^{18}O$ isotopic composition in

3 precipitation and streamflow for 3 years (May 2011-May 2014); and c) electrical conductivity

4 for 2 years (May 2012-May 2014) at the catchment outlet (M8, see location in Figure 2). The

5 size of the bubbles in plot b) indicates the relative cumulative rainfall in millimeters for each

6 collected sample.

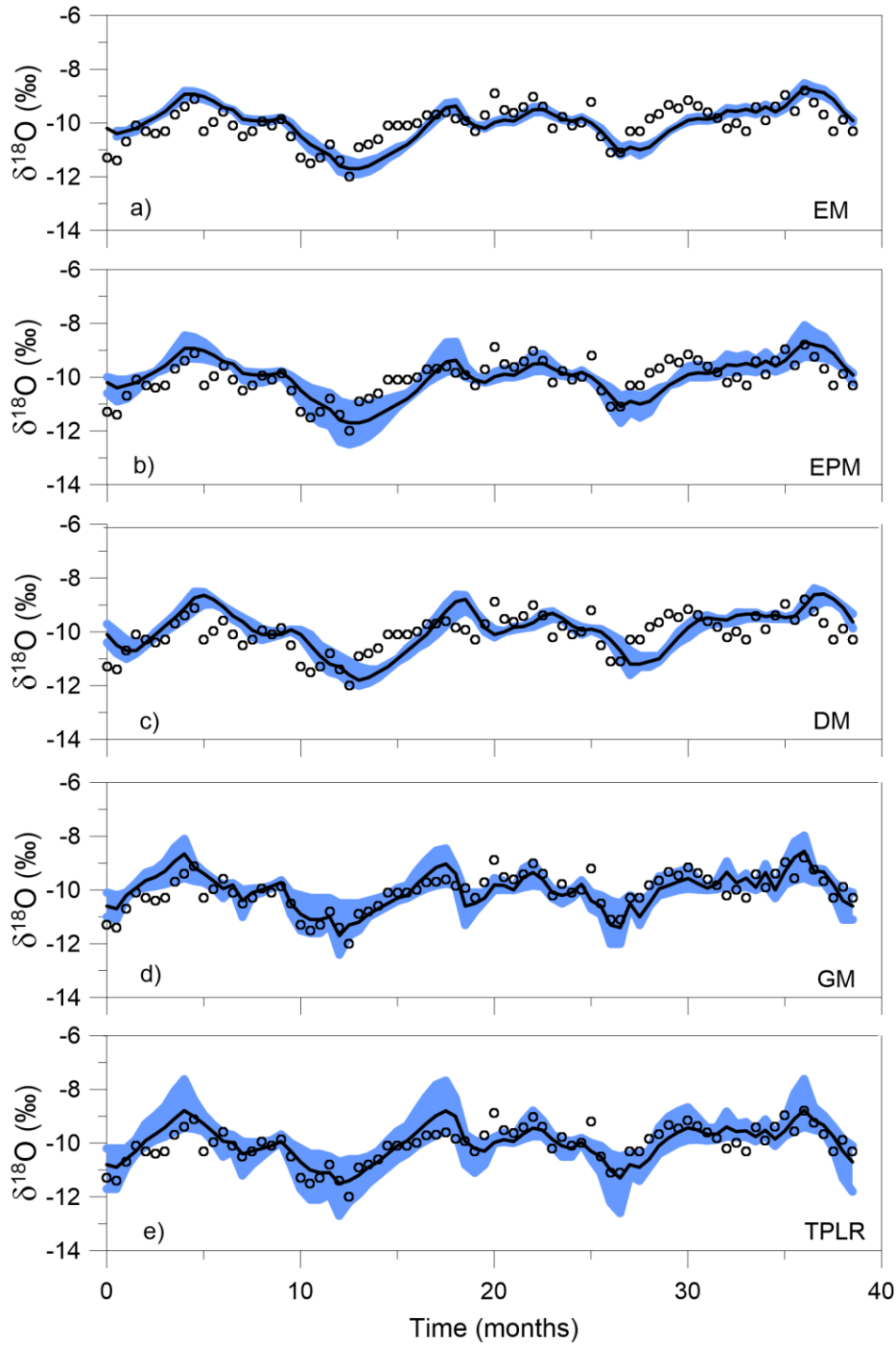



Figure 3. Fitted results of the five lumped parameter models used to simulate the temporal

variability in the δ¹⁸O streamflow composition at the outlet of the basin (M8). (a) Exponential

1   model (EM); (b) exponential-piston model (EPM); (c) dispersion model (DM); (d) gamma

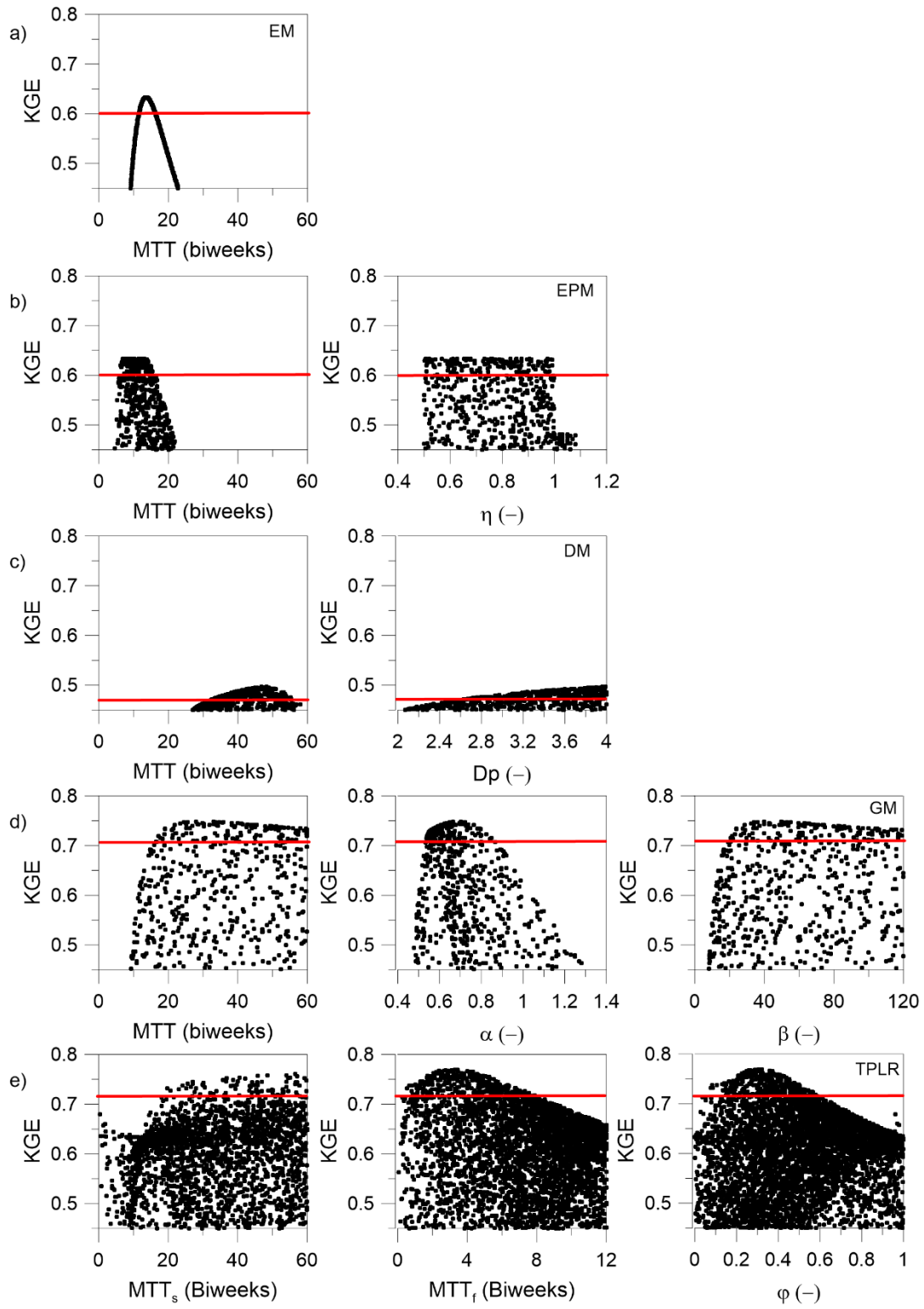
2   model (GM); and (e) two parallel linear reservoir model (TPLR). The open circles represent

3   the observed isotopic composition in streamflow; the black line represents the best simulated

4   isotopic composition in streamflow according to the KGE (Gupta et al., 2009) objective

5   function; and the blue shaded area corresponds to the 5-95% confidence limits of the possible

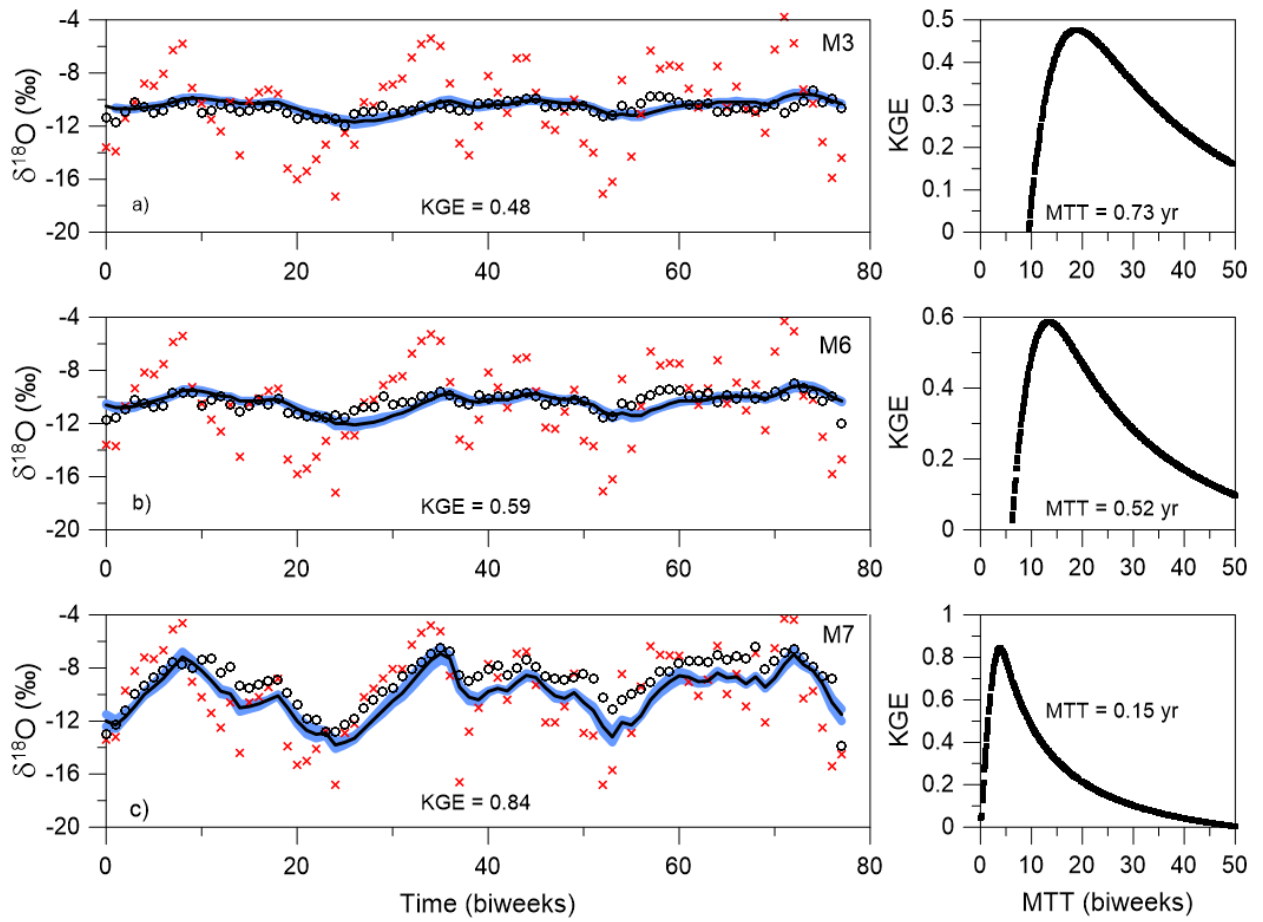
6   solutions from the parameter sets within the range of behavioral solutions, i.e., solutions

7   which yield at least 95% KGE.

2 Figure 4. Monte Carlo simulations of the fitted parameters of the five lumped parameter

3 models used to simulate the δ¹⁸O streamflow composition at the outlet of the basin (M8). a)

1 EM; b) EPM; c) DM; d) GM; and e) TPLR. The (-) symbol in the x-axes denotes that fitting

2 parameter is dimensionless. Horizontal red lines indicate threshold of behavioral solutions (at

3 least 0.95 of maximum KGE).

2   Figure 5. Fitted results and Monte Carlo simulations of the fitted parameters of the

3   exponential model (EM) used to simulate the $\delta^{18}O$ streamflow composition in the catchments:

4   a) M3; b) M6; and c) M7. The open circles represent the observed isotopic composition in

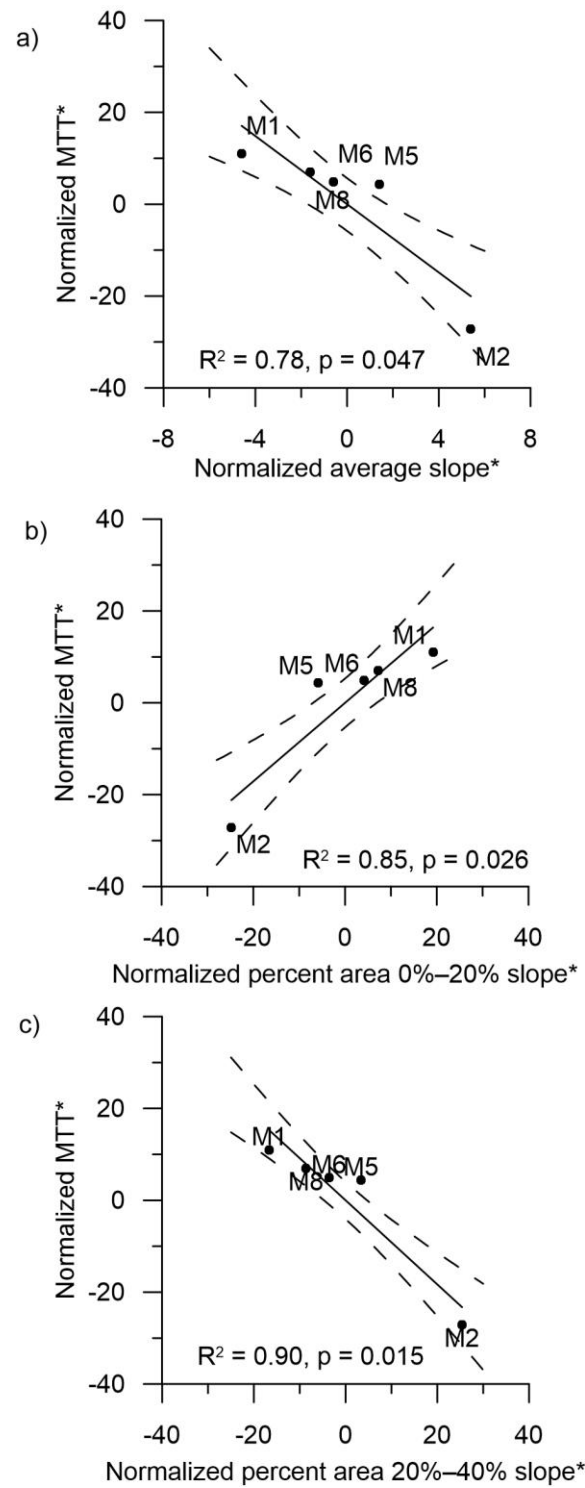
5   streamflow; the red crosses represent the isotopic composition in precipitation; the black line

6   represents the best simulated isotopic composition in streamflow according to the KGE

7   objective function; and the blue shaded area corresponds to the 5-95% confidence limits of

8   the possible solutions from the MTT fitting parameters within the range of behavioral

9   solutions, i.e., solutions which yield at least 95% KGE. Panels on the right represent the

10   explored parameter range for the MTT parameter and the KGEs associated to each of them.

2   Figure 6. Correlations between mean transit time (MTT) and topographic indexes of the

3   catchments: a) average catchment slope; b) catchment area with slopes between 0% and 20%;

4   and c) catchment area with slopes between 20% and 40%. Catchments M3 and M4 (additional

1   spring water source, see Figure 1) and M7 (at a flat hilltop disconnected from the hillslopes)

2   are not included in the regressions. Solid lines are linear regressions and dashed lines are the

3   90% confidence intervals of the regressions. * Indicates variables are normalized by their

4   means.

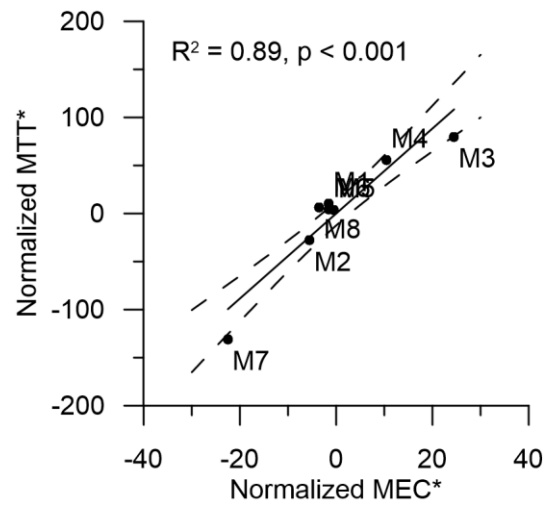



Figure 7. Correlation between mean transit time (MTT) and mean electrical conductivity
(MEC) for weekly measurements of stream water samples collected during three years (June
2012-June 2015). Solid line is the linear regression and the dashed lines are the 90%
confidence intervals of the regression. * Indicates variables are normalized by their means.