Point-by-point response to the Referee 1's review

GENERAL COMMENTS

I appreciate the authors' kind and detailed replies and I think the paper is now improved. Still, there are in my opinion some misunderstandings on the concept of Mean Transit Time (MTT) that I will try to explain with more detail. I think the authors had a good point in limiting the analysis to baseflow conditions, but some more efforts could be put to clarify the meaning of their analyses.

Reply: We are glad to hear that the reviewer finds the paper is improved and appreciate his/her constructive suggestions to further improve our manuscript's scientific quality.

-The MTT is the mean of a distribution and as such it has some very useful mathematical properties. When the distributions are skewed, the mean is strongly affected by the "heaviness" of the tail, which is typically quite pronounced in catchments [see Kirchner, 2000]. The tail of the distribution is very difficult to estimate, especially in systems where the output signal is not very informative. This can be because the output is very damped with respect to the input, or because the input is characterized by regular fluctuations around a constant trend. Both of these are typical situations with water stable isotopes. In these cases, one may well be able to describe the measured solute response with a number of different functions which have the same 'young' component but very different 'old' components (or tails). Unfortunately, this has a huge impact on the mean of the distribution, which then remains very uncertain. Some authors have started to describe other properties of the transit time distributions (TTDs) other than the mean, like the median transit time [e.g. Soulsby et al., 2015], or the "young water fraction" [e.g. Kirchner et al., 2016ab].

Reply: As has been stated in the manuscript (P. 9, L. 17-21; P. 11, L. 9-20), we are aware of the mathematical properties of the transit time distributions (TTDs) used for modeling MTTs through the lumped convolution approach, as well as the advantages and limitations of this methodology. Because of those, the selection of the TTD distribution that best describes our system was conducted through a detailed statistical analysis to evaluate model's performance for each TTD in combination with available information about catchment functioning and runoff generation at the study site.

As the referee mentions, other authors have attempted to describe alternative properties of TTDs. However, Soulsby et al. (2015) do not provide theoretical basis for justifying the use and analysis of the median of TTDs instead of the MTT. The "young water fraction" metric proposed by Kirchner (2016a, 2016b) is on the other hand introduced with a detailed theoretical basis which should definitely be explored by catchment hydrologists. However, it is out of the scope of our current work to incorporate such analysis. We have clearly specified and justified the use of the LCA for estimating MTTs in our páramo catchment (P. 11, L. 9-20).

-Given the point above, it is clear that estimating catchment TTDs is not a trivial task, and uncertainty is often inevitable. For this reason, I am a bit skeptical about the fact that the exponential distribution is the most appropriate to describe the paramo catchments. In my opinion, such a distribution is better identified because it has not enough degrees of freedom and the same distribution is used to fit short-term and long-term output features. As the

short-term features are the only one providing information, they dominate the identification of the function. However, I would argue this is an "apparent" identification because it explains stream chemistry fairly well and parsimoniously, but is not able to reliably estimate the older water components, which have a large impact on the MTT. Other functions tested by the authors are less determined, in my opinion, because they allow a de-coupling between short-term and long-term information. Indeed, both the GM and TPLR predict MTT which are less constrained (296-1478 days and 356-1738) but also much larger than the EP (166-224 days). Doesn't this suggest that there may be a larger old water contribution than the one predicted by the EP? To further explore this problem it may be interesting to compare the results in terms of other metrics (e.g. are the median or the young water fraction similar in the EP and GM models?).

Reply: We agree that selecting catchment TTDs is not a trivial task. Given that, we did not only rely on the results of the detailed statistical analysis conducted for selecting the TTD that best describes the system under study, but also on the process-based knowledge of catchment functioning at the study site (Mosquera et al., 2015, 2016). These authors have determined that the Zhurucay catchment is a fast response system, where runoff generation is mainly controlled by water flowing in the shallowest 30-40 cm of the low developed páramo soils (~ 1 m depth) underlain by a young and compact geology. Additionally, these authors concluded that deep-groundwater contribution (old water) to discharge is minimal at the Zhurucay catchment. Our MTT estimates corroborate their findings. Although the contribution of old water component/s cannot be definitely neglected, it seems unfeasible that given the biophysical features of the landscape and its pedological and geomorphological structure. baseflow MTTs on the range of those yielded by the GM and TPLR TTDs are reliable. A note about this issue has been added in P. 15, L. 3-9. Therefore, we are confident that the results yielded by the EM provide robust baseflow MTT estimates in this páramo catchment. Regarding your last point, as we have already mentioned above, although comparing our results with those yielded by other metrics (e.g., the young water fraction) would definitely be interesting, that is out of the scope of this study.

-Finally, the idea that one single TTD exists is misleading. Any natural hydrologic domain responds differently before, during and after being forced by a storm event. This is not just about seasonality, it's also about each storm that crosses the catchment after the considered precipitation event and makes transit time distributions intrinsically non-smooth curves. Moreover, stream concentration is affected by the specific hydrologic conditions that take place at the time of sampling, and not by the average catchment conditions. This of course does not mean that stationary analyses are meaningless, but it should be clear that they try to depict an average catchment condition, which is often very different from any actual situation.

Reply: We agree that hydrologic systems are temporally dynamic and that such behavior needs to be accounted in models to better understand system's response. Although the LCA lacks to characterize such dynamics, assumptions of this methodology are quite clear and as such, we have carefully evaluated them in light of the conditions in our study site (). Here, we again want to clarify that our study aims to set a baseline for the application of modeling techniques using stable water isotopes in tropical ecosystems above the tree line, and that one of our future goals using this dataset includes the application of modeling techniques that explicitly recognize non-stationarity and storage dynamics in the hydrological behavior

(e.g.,Birkel et al., 2015; Harman, 2015; Hrachowitz et al., 2013). However, those are out of the scope of our manuscript.

Overall, I don't want to look too critical about this work, but I think the paper would benefit from acknowledging a more realistic view on transit time distributions.

Reply: We agree and appreciate the referee's point of view. As so, based on the suggestions of both reviewers in the prior revision of our manuscript, we have already acknowledged the more realistic view on TTDs in light of the time-variant nature of MTTs (P. 4., L. 11-P. 5, L. 11). As such, we considered this point has been already addressed in our manuscript.

Other general comments are:

-as the AIC criterion was introduced, which takes into account the number of parameters, I think the Measure of Identification (MI) could be removed from the analysis, as it is redundant and applied rather arbitrarily given the lack of prior knowledge on the parameters.

Reply: We agree. The MI has been removed from the manuscript.

-I think it may be worth reducing the discussion section, which is currently very long and include the repetition of concepts which were already mentioned in the results.

Reply: We believe, that the readers will strongly benefit from the comprehensive discussion in its current form. Based on the suggestion from the reviewer, the section was again thoroughly reviewed and few small changes have been included to clarify the main ideas in the discussion though.

DETAILED COMMENTS

Abstract: it may be worth to specify from the beginning that the MTT refers to baseflow conditions

Reply: This was already specified in the abstract in P. 1, L. 24.

Page 4, line 7: please specify that you mean MTT variability among catchments

Reply: Thanks for the suggestion. Updated accordingly in P. 4, L. 7.

P. 4, I. 23: the first source of non-stationarity which should be mentioned is precipitation variability

Reply: We agree. Precipitation variability is now mentioned in L.4, P. 23.

P. 4, I. 27: what do you mean by stating that the cited works "have yielded results with high degree of uncertainty"? I personally think those works just show the complexity of the problem in more realistic terms.

Reply: We agree that those studies show the complexity of the problem. As such, results yielded from them provide high uncertainties as the methods used yet provide low capability to represent reality. This, to our view, is an important limitation of the used methodologies. Such uncertainty is highly dependent on the usually poorly recorded temporal variability of

the input hydrometric and tracer field measurements, as we have already acknowledged in P. 5, L. 2-7. Therefore, we consider that the statement above is justified and appropriate in the context used in the manuscript.

P.5, I.3: what is a mathematical limitation?

Reply: We mean mathematical limitations to represent systems' non-stationarities. This has been updated in P. 5, L. 3.

P.9, I.19: I think this is a good point to mention that, as you do a steady-state analysis, you limit your study to the transit times of baseflow.

Reply: We agree. Updated accordingly in L. 9, P. 16.

P.11, I.15: I think this is a too strong sentence, which needs more context.

Reply: We agree. The sentence has been updated in P. 11, L. 15-16.

P.12, I.14: as mentioned in the general comments, I don't think the MI is necessary anymore.

Reply: We agree. The MI has been removed from the manuscript.

P. 12, I.25-27: first you say that total runoff is "spatially more heterogeneous", but then you say that Runoff coefficients show "relatively low spatial variability". This sounds inconsistent.

Reply: We think you mean P.13, L. 25-27. You are correct. Thanks for catching this inconsistency. We have updated the text accordingly in P. 13, L. 22-23.

P.14, I.16: I think the threshold on the KGE is critical for the parameter uncertainty. Could the author observe important differences with a different values? I am also wondering whether the models with a higher number of parameters would require a higher threshold.

Reply: We see your point about the critical threshold selection of the KGE value for parameter uncertainty. As such, we used a threshold already published in hydrologic science literature. We considered the threshold of 0.45 used by Timbe et al. (2014), who assed uncertainties in MTT estimations using the lumped convolution approach. Using different threshold values would be somehow arbitrary. Regarding your last point about models with higher number of parameters, we have already accounted for that in our model selection evaluation by using the AIC metric (P. 14, L. 16-20).

P.14, I.21 (Figure 3): I thinks there is no need to show the isotopic content of precipitation in this figure, as it was already presented in figure 2b. Moreover, such broad Y-axis makes it difficult to assess modeled and measured 18O in streamflow. I think the authors could reduce the Y-axis to e.g. [-8, -14]. Please also avoid the use of biweeks at the x-axis.

Reply: We agree. The figure has been replaced to show the observed and modeled isotopic composition in streamflow only. Biweeks has also been replaced by months in the x-axis.

P.15, I.9-10: "rather than from a more realistic representation of the hydrologic functioning of the catchments". This is a very strong and not justified statement.

Reply: We agree that this statement is not clearly justified. As so, we have decided to delete this sentence (see P. 15, L. 3).

P. 16, I. 20-24: I had already commented on this, but I see that we probably did not understand each others. First, the unit "biweeks" is rather unusual and I recommend using days (or months, or years) instead. As the exponential function integrates to 1 only in the limit to infinity, the notion of "completely recovered" is linked to a threshold (e.g. 99%) and I suggest to mention it. Finally, I don't fully agree with the last sentence. Even in a 3 years dataset, the first months are strongly affected by hydrologic events that had happened before the beginning of the measurements.

Reply: Thanks for the recommendation. We have changed the unit biweeks to weeks in the text. You are correct that the notion of completely recover might be ambiguous, and that mentioning a threshold is more appropriate. This has been updated in P. 16, L. 19-22. Lastly, we were careful to minimize the effect of prior hydrologic events before the beginning of the measurements. To minimize this effect, and has been done by other authors (e,g., Hrachowitz et al., 2011; Timbe et al., 2014), 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 as stated in P. 11, L., 20-22.

ADDITIONAL LITERATURE

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Point-by-point response to Christian Birkel (Referee 2)'s review

I had the opportunity to read the revised version of the manuscript "Insights on the water mean transit time in a high-elevation tropical ecosystem" by Mosquera et al. and found the paper much improved. The authors have extensively discussed and addressed all my comments, clarified my initial doubts about some aspects of the model approach, process interpretations and how parsimony was assessed, included new and significant analysis (re-run models, AIC calculated), and now they refer to the more up-to-date discussion around time-variable transit times (their incredibly fast responding system makes for an interesting contrast to most studies). The paper now makes for an excellent contribution to the literature about a geographical region with relatively sparse data and research. Therefore, I fully support publication of this paper.

All the best,

Christian Birkel

Reply: We are glad to hear that the reviewer finds that all his comments have been satisfactory addressed. We thank him for his constructive suggestions to improve the scientific quality of the manuscript and look forward to publishing this work in HESS hoping to improve the understanding of hydrologic processes in tropical ecosystems.

The only suggestion left is that the sentence on page 14, line 21 sounds rather odd and could be reformulated.

Reply: We agree with the suggestion. This sentence has been rewritten in P. 14, L. 16-17.

Insights on the water mean transit time in a high-elevation tropical ecosystem

- 3
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- 18

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 km²) located in south Ecuador. A lumped
- 23 parameter model considering five transit time distribution (TTD) functions was used to
- estimate MTTs under steady-state conditions (i.e., baseflow MTT). We used a unique data set
- 25 of the δ^{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

1 between MTT and landscape (soil and vegetation cover, geology, and topography) and 2 hydrometric (runoff coefficient and specific discharge rates) variables was used to explore 3 controls on MTT variability, as well as mean electrical conductivity (MEC) as a possible 4 proxy for MTT. Results revealed that the exponential TTD function best describes the 5 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 6 7 short (0.15-0.73 yr, 53-264 days). Regression analysis revealed a negative correlation 8 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 ($R^2 =$ 9 0.89 p < 0.001). Overall, we conclude that: 1) baseflow MTT confirms that the hydrology of 10 the ecosystem is dominated by shallow subsurface flow; 2) the interplay between the high 11 12 storage capacity of the wet páramo soils and the slope of the catchments provides the 13 ecosystem with high regulation capacity; and 3) MEC is an efficient predictor of MTT 14 variability in this system of catchments with relatively homogeneous geology. Keywords: Ecohydrology, MTT, runoff generation, wet Andean páramo, tropical wetlands, 15

- 16 Histosols, Ecuador
- 17

18 **1** Introduction

19 Investigating ecohydrological processes through the identification of fundamental catchment descriptors, such as the MTT, specific discharge, evapotranspiration to precipitation ratios, 20 21 and others, is fundamental in order to: 1) advance global hydrological, ecological, and 22 geochemical processes understanding and 2) improve the management of water resources. 23 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, 24 25 despite its importance as the major water provider for millions of people in the region (De 26 Bièvre and Calle, 2011; IUCN, 2002). Water originated from the páramo sustains the socio-27 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 28 29 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 isotope hydrograph separation at storm event scale (e.g., Goller et al., 2005; Muñoz-Villers 10 11 and McDonnell, 2012), the isotopic characterization of precipitation patterns (e.g., Vimeux et al., 2011; Windhorst et al., 2013), and the identification of ecohydrological processes (e.g., 12 13 (Crespo et al., 2012; Goldsmith et al., 2012; Mosquera et al., 2016). However, studies focusing on MTTs in order to improve the understanding of rainfall-runoff processes and their 14 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 vield is sustained vear-round regardless of precipitation inputs) (Buvtaert et al., 2006; Célleri 19 and Feyen, 2009). However, efforts to investigate the processes that control such hydrological behavior are scarce. Recent investigations in our study site suggest that runoff originates from 20 21 the shallow organic horizon of the páramo soils located near the streams (Histosol soils or Andean wetlands), thus favoring shallow subsurface flow. On the contrary, deep groundwater 22 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; Penna et al., 2011), but yet, MTTs have not been explored in these systems. Our study site 27 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 many regions due to limited funding and site accessibility, identifying controls of MTT 9 variability in nested and paired monitoring systems of streams is fundamental towards 10 11 regionalization of ecohydrological processes (Hrachowitz et al., 2009a) and prediction in ungauged basins (Tetzlaff et al., 2010). Yet, investigation of controls on MTT variability is 12 13 still fairly scarce (Tetzlaff et al., 2013). Most studies have found that MTT scales with topographic and/or hydropedological controls. For instance, topographical controls on MTT 14 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

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-

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

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

In this study, we seek to add to the current geographical scope of MTT studies by addressing two questions which remain open in hydrological science, and have received little attention in high-elevation tropical ecosystems: "How old is stream water?" (McDonnell et al., 2010) and "How does landscape structure influence catchment transit time across different geomorphic provinces?" (Tetzlaff et al., 2009). Detailed hydrometric observations highlighting subsurface dominated rainfall-runoff response (Crespo et al., 2011; Mosquera et al., 2016) together with information of the landscape biophysical characteristics in our páramo study site will allow

for process-based understanding regarding: i) the spatial variability of baseflow MTTs and ii) 1 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 by groundwater contributions to discharge. Also, based on the hydropedological and climatic 5 similarities between our páramo site and the peatland-podzols dominated ecosystems in the 6 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 (3°04'S, 79°14'W) on the west slope of the Atlantic-Pacific continental divide and discharges into the 14 15 Jubones River (Pacific Ocean tributary). The basin has a drainage area of 7.53 km² and 16 extends within an elevation range of 3400 to 3900 m a.s.l. Climate is mainly influenced by the Pacific Ocean regime and to a lesser degree to the continental air masses from the Amazon 17 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 material. This area is locally known as "Laguna Ciega" ("Blind Lagoon" in Spanish) and 6 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 total basin area and are mainly found in the hillslopes. Histosols (Andean wetlands) cover the 14 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 depth of 31 cm in the Histosols and 40 cm in the Andosols). A complete description of soil 22 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 Calamagrostis sp.) (Ramsay and Oxley, 1997; Sklenar and Jorgensen, 1999) grow in 26 Andosols. The main landscape characteristics are summarized in Table 1. 27

1 2.2 Hydrometric information

2 Discharge and precipitation were continuously monitored since October 2010. A nested 3 monitoring network was used to measure discharge. The network consisted of seven tributary 4 catchments (M1 to M7) draining to the outlet of the basin (M8). Catchments M1 to M6 5 comprise the main stream network draining towards the outlet of the Zhurucay basin (M8), 6 whereas catchment M7 is a small catchment originating in a ponded wetland at a flat hilltop 7 (Figure 1). V-notch weirs were constructed to measure discharge at the outlet of the 8 tributaries M1-M7 and a rectangular weir at the outlet of the basin M8. Each catchment was 9 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 10 11 Kindsvater-Shen relationship (U.S. Bureau of Reclamation, 2001). The discharge equations were calibrated by applying the constant rate salt dissolution technique (Moore, 2004). 12 13 Precipitation was recorded using tipping buckets with a resolution of 0.2 mm at two stations 14 located at 3780 and 3700 m a.s.l. (Figure 1).

15 2.3 Collection and analysis of water stable isotopic and electrical conductivity 16 data

17 We used a three-year record (May 2011 – May 2014) of ¹⁸O and ²H isotopic compositions of 18 water samples collected in precipitation and streamflow. Data were collected at different resolutions, from event-based to biweekly, given logistic constraints and opportunities. 19 20 Higher resolution data were aggregated to biweekly using precipitation weighted means for 21 record consistency. The same nested monitoring network used for measuring discharge was 22 implemented for stable isotopes in streamflow at the seven tributary catchments M1 to M7, 23 and including M8 at the outlet of the basin. Water samples in precipitation were collected 24 using two rain collectors located at 3780 and 3700 m a.s.l. Each collector consisted of a 25 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 26 mineral oil within the polypropylene bottle. Due to the sampling procedure and the local 27 28 climate, kinetic fractionation by evaporation can be neglected and hence both stable isotopes

yield the same results (Mosquera et al., 2016). Therefore only the results using the isotopic 1 2 composition of ¹⁸O are reported. Rainwater samples are cumulative representations of the isotopic signature between sampling dates while stream grab water samples represent discrete 3 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 recommended by the International Atomic Energy Agency (Mook, 2000). The isotopic 6 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 (²H) and 0.1% precision for 9 oxygen-18 (¹⁸O). Isotopic concentrations are presented in the δ notation and expressed in per mill (‰) according to the Vienna Standard Mean Ocean Water (V-SMOW) (Craig, 1961). 10

Electrical conductivity (EC) was measured directly in-stream simultaneously with the water isotopic data starting in 2012, the second year of the monitoring period. EC was measured using the digital conductivity sensor Tetracon 925 (WTW, Germany) with a precision of \pm 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 (i.e., baseflow MTTs). The LCA seeks for the parameter set of the model that best describes 19 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., precipitation, snow) of tracer (e.g., δ^{18} O, δ^{2} H) to the signal at an outlet point (e.g., 22 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 – τ) through a transfer function (TTDs or $g(\tau)$) describing the subsurface transport of tracer as 26

27 follows:

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

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:

5
$$\delta_{\text{out}}(t) = \frac{\int_0^\infty g(\tau) w(t-\tau) \,\delta_{\text{in}}(t-\tau) \,d\tau}{\int_0^\infty g(\tau) w(t-\tau) d\tau}$$
(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

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 1 2 dispersion parameter (Dp), which relates to the tracer transport process. The GM is a more 3 flexible and general version of the exponential model in which the product of two parameters 4 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 5 reservoirs each one represented by a single exponential distribution. It has three fitting 6 7 parameters, the MTT of the slow (MTT_s) and fast (MTT_f) reservoirs and a parameter 8 representing the fraction of each of them with respect to total flow (φ) (Weiler et al., 2003).

9 The MTT approach is based on the following assumptions: 1) the tracer concentration is 10 conservative (i.e., the tracer does not react with other elements present in the system); 2) the 11 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; 12 13 5) transport of solute is one-dimensional and represented by a single TTD; and 6) there is a 14 uniform storage of water within the catchment (i.e., steady-state flow in the system) 15 (Małoszewski and Zuber, 1982). The steady-state assumption is assumed to be accomplished 16 in humid environments during baseflow conditions (McGuire et al., 2002). In order to 17 comply with the latter assumption, streamflow water samples collected during extreme 18 rainfall events were excluded for the MTT simulations (McGuire and McDonnell, 2006; 19 Muñoz-Villers et al., 2016). As a result, estimates correspond to baseflow MTTs, hereafter 20 simply referred to as MTT. To obtain more stable results, we looped the available three years 21 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). 22

23 **2.5** Model performance and uncertainty analysis

24 The model performance was evaluated using the Kling–Gupta efficiency coefficient (KGE)

25 (Gupta et al., 2009). KGE ranges from $-\infty$ to 1, where unity indicates an ideal optimization.

26 KGE can be viewed from a multi-objective perspective because it accounts for correlation

27 (i.e., balancing dynamics, *r*), variability error (γ), and bias error (β) within a single objective

28 function. The efficiency is mathematically represented by the Euclidean distance (*ED*) in each

29 of the three dimensions $(r, \gamma, \text{ and } \beta)$ to an ideal point where all of them are maximized (i.e.,

where ideally the three factors are set to one). Efficiencies lower than 0.45 were considered
poor predictions (Timbe et al., 2014).

Depending on the TTD function used, 1 to 3 parameters were fitted during the simulations. 3 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 interval) were estimated using the Generalized Likelihood Uncertainty Estimation 10 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 inspections of the parameter space (Figure 4) was also conducted to qualitatively analyze the 15 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 geomorphological characteristics. That is, catchments situated at the valley bottom have well-25 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.

16 3 Results

17 **3.1** Hydrologic and isotopic characterization in rainfall and streamflow

Precipitation in the Zhurucay basin is evenly distributed throughout the year (Figure 2a), 18 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 these less humid months (see zoom in Figure 2a). Similar behavior is observed at all 25 26 catchments.

27 The δ^{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 $\delta^{18}O$ isotopic composition
- 3 in streamflow collected during low flows on the other hand, is much more damped (average -
- 4 $10.0 \pm 0.06\%$, at M8) than the isotopic composition in precipitation (Table 4).

5 3.2 TTD evaluation and selection

In order to identify the TTD that best describes the hydrologic system in the Zhurucay basin,
we tested and evaluated the performance of all TTDs at all catchments. Considering that
similar results were obtained for all catchments and for brevity, only results for M8, the basin
outlet, are shown.

All TTDs reproduce the δ^{18} O isotopic composition at the outlet of the basin (M8) with 10 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 = 0.63), while the DM yields the lowest efficiency among all (KGE = 0.50). The models 14 15 associated with the highest KGEs yield the highest uncertainty bounds according to their threshold of behavioral solutions; whereas the EM shows the lowest uncertainty (Figure 3). The 16 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 the one representing the MTT of the slow reservoir (MTT_s, Figure 4). For the DM and GM 22 models one parameter is well identified (MTT and α , respectively); while the others are not 23 well identified by the models. For the EPM, both parameters are not well identified. The single 24 25 parameter that defines the EM is very well identified. This coupled analysis of model efficiency and parsimoniousness in combination with parameter identifiability indicates that although 26 27 models with a higher number of fitting parameters provide higher efficiencies, their parameters 28 are more uncertain.

Taking into account the goodness of fit, parsimoniousness, uncertainty bounds, and the 1 2 identifiability of the models' parameters, the EM is the model that best describes the temporal 3 variability of the baseflow δ^{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 towards a fast response system with minimal impact of old water sources, and the further 5 discussion in the final part of this paper. Although the contribution of old water component/s 6 cannot be definitely neglected, it seems unfeasible that given the biophysical features of the 7 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 reservoir with relatively simple transition of the water (i.e., tracer) in the subsurface towards 10 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, hydrologically, to the drainage network (Mosquera et al., 2016). These factors result in a 14 relatively simple transition of infiltrated precipitation from a well-mixed reservoir towards the 15 16 catchment outlet. This process-based analysis of physical characteristics of the system further support the EM as the model that best describes the transport of water across the Zhurucay 17 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
- 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 composition during the monitoring period. For instance, catchment M3 (Figure 5a) shows the 5 smallest amplitude in isotopic variation for the observed and simulated data (Table 6), 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 increases as described above. Results from all the catchments are also described by this trend. 14 The MTT probability density functions (PDFs), which indicate the distribution of MTTs in 15 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 relatively short MTTs in the hydrology of the Zhurucay basin. The CDFs also indicate that the 19 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.

3.4 Correlations of baseflow MTT with landscape and hydrometric variables

Correlation analysis showed no statistically significant correlations (p-values > 0.05) between MTT and landscape features and hydrometric variables of the nested monitoring system when all catchments were included. This lack of correlation is likely related to the previously reported distinct responsiveness of catchment M7 to precipitation inputs due to its different 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 M3 and M4, favors the generation of higher low flows (Mosquera et al., 2016) and increases 6 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, $R^2 = 0.78$ and p = 0.047) and percent area having slopes in the range 20%-40% are negative 13 14 (Figure 6b, $R^2 = 0.90$, p = 0.015). Conversely the relation between the percent area having slopes 0%-20% and MTT is positive ($R^2 = 0.85$, p = 0.026). No significant correlations (p-15 16 values > 0.05) between MTT and vegetation, soil types, geology, flow path length, topographic wetness index, and hydrometric variables were found (Table 7). However, a 17 18 relatively strong relation between MTTs and low flows with smaller significance was also found. That is, catchments with higher MTTs yielded lower low flows ($R^2 = 0.62$, p = 0.11 for 19

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

The rainfall-runoff process evidences a rapid response of discharge to precipitation inputs in the Zhurucay basin. This rapid response occurs even during the less humid periods (August-September) in which relatively small rainfall events result in peak flow generation (Figure 2a). This high responsiveness results from the combined effect of the relatively uniform 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 matter content (mean 86% by volume), allowing for high water storage capacity. In addition, 5 due to their relatively low saturated hydraulic conductivity (0.72-1.55 cm h⁻¹), these soils 6 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 hydrology of the Zhurucay basin páramo ecosystem is dominated by shallow subsurface water 10 flow. This is supported by the similar isotopic composition between streams and soil waters in 11 the organic layer of the Histosols in the Zhurucay basin (Mosquera et al., 2016). 12 Although the δ^{18} O isotopic composition of stream waters is damped and lagged with respect 13 14 to that of precipitation, streamflow samples in the Zhurucay basin still reflect the variability of the δ^{18} O composition of rainfall (Figure 2b), as expected in a system dominated by shallow 15 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 (Figure 5c), most likely as a result of the rapid mixing of rainfall water with the shallow water 18 moving in the shallow organic horizon of the soils and the ponded water above it. All of the 19

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?

The high performance (KGE > 0.48, Table 6), low uncertainty (Figure 3), high AIC (Table 5), and strong parameter identification (Figure 4) of the exponential model (EM) indicate that this model best mimics the subsurface transport of water in all catchments within the Zhurucay basin (Figure 5). In addition, the model captures some particularities in the functioning of each catchment. For instance, results indicate relatively long MTTs in two of the headwater catchments, M3 and M4 (0.73 and 0.67 years, respectively). This likely results from a shallow spring water contribution to these catchments during low flow generation

(Mosquera et al., 2015). The model seems to capture the effect of the shallow spring 1 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 also captured by the model which assumes a well-mixed reservoir. This observation led us to 6 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, Mexico. These authors estimated even longer MTTs (1.2-2.2 years) due to deeper 14 groundwater contributions to discharge. 15

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 support the hypothesis that this catchment presents a shorter MTT, indicating that the ponded 20 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 stored deeper in the soil seems to remain mostly immobile with minimal influence in the 24 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.

4 In other tropical latitudes, MTTs higher than 300 days were found in three paired Colombian 5 catchments applying the TPLR model (Roa-García and Weiler, 2010). These basins show 6 higher MTTs than the catchments in the Zhurucay basin most likely as a result of the higher 7 development of the volcanic ash soils (> 10 m), which allow the water to be stored for longer 8 periods in the subsurface. MTTs longer than two years were also found in a TMCF in 9 southern Ecuador (Timbe et al., 2014), evidencing that differently from our findings, this lower elevation ecosystem is dominated by deep groundwater contributions. Preliminary 10 11 MTT estimations in another TMCF biome located in central Mexico (Muñoz-Villers and 12 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 13 14 hillslope soils (1.5-3 m depth) with highly fractured and permeable geology allows for the 15 formation of longer flow paths of water and longer MTTs. Therefore, the relatively young and 16 little weathered geology in the Zhurucay basin allows for a dominance of shallow subsurface 17 flows. The results of these studies suggest that the particular shallow development of the rich 18 organic soils with low saturated hydraulic conductivities, in combination with an homogeneous and low permeable geology provide the páramo basin of the Zhurucay River 19 20 with a high water retention capacity, and relatively long transit times and flow paths 21 considering the little development of the organic horizon of the soils. Hrachowitz et al. 22 (2009b) reported MTTs (135-202 days) around the ones found in the Zhurucay basin 23 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 24 25 and the TPLR, as opposed to the EM in our study site. As in the Zhurucay basin, these authors 26 attributed this short transit time to the dominance of ecohydrological processes occurring in 27 the upper horizon of the peat soils. Therefore, we can conclude that in these two ecosystems, 28 located at different latitudes but with similar hydropedological conditions, the hydrology is 29 dominated by shallow subsurface flows. Nevertheless, the soils development of the shallow 30 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 nonstationary nature of MTTs are needed at the páramo, based on the dominance of flow 10 generation in the Histosols at the Zhurucay basin, in combination with low annual changes in 11 the environmental conditions, we consider our results from the LCA provide robust MTTs 12 13 estimates in our study site.

14 **4.3** Controls on baseflow MTT variability

15 We found significant correlations ($R^2 \ge 0.78$, p < 0.05) between catchment slope dependent indexes and MTT using a subset of the main stream catchments (Table 7 and Figure 6). 16 17 Results of the correlation analysis indicate that: 1) the higher the average slope of the 18 catchments, the shorter their MTT_s; 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 topographical features were found to control low flow generation. Mosquera et al. (2015) 22 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 (wetlands) ($R^2 = 0.29$, p = 0.35) have longer MTTs and an inverse relation with tussock grass 29

vegetation ($R^2 = 0.31$, p = 0.33). In another tropical system of catchments in Colombia, a 1 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. Therefore, their observations might result from the combination of the deeper soil 6 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 catchments' slopes was found (Hrachowitz et al., 2009a). As such, and given the similarities 13 14 between these soils and our Histosol soils (Andean wetlands), we hypothesized MTT variability to be controlled by the areal extent of wetlands. Even though we found that MTT 15 16 variability is rather mainly controlled by topography in our tropical alpine site, a small trend of wetlands' cover to increase MTT was also identified. Although the later relation is not 17 18 statistically significant, the latter most likely results from the influence of topography on Histosol soils (wetlands) formation, where the formation of this soil mainly occurs in 19 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.

Other slope topographic indexes -e.g., flow path length (L), flow path gradient (G), and the 1 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 L/G ratio was reported as the major control of MTT variability ($R^2 = 0.91$) in steep temperate 5 6 catchments in the central western Cascades of Oregon (McGuire et al., 2005), suggesting that this relation "reflects the hydraulic driving force of catchment-scale transport (i.e., Darcy's 7 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. Recently, topography was also identified as a major control on the MTT of 12 TMCF 10 catchments in eastern Mexico (Muñoz-Villers et al., 2016). Results from these studies reflect 11 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 predictor which indicates more local effects of hydraulic force driving in the stream channel 14 (e.g., L/G), catchment slope might be a better measure to compare catchment functioning as it 15 integrates the hydrologic connectivity of hillslope, riparian, and stream areas. 16

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 catchments having higher areal proportions of low gradients and lower areal proportions of 19 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 of the ecosystem, and thus, maintaining a sustained delivery of water to the streams along the 27 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

(SOF), affecting the regulation capacity of the ecosystem. Nevertheless, SOF rarely occurs in
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 our knowledge, there are no studies that have identified similar (or different) relations 10

11 between MEC and MTT in other biomes.

12 Given that estimating MTT using isotope tracer methodologies is financially expensive due to the logistical set up of a monitoring network and the processes of data collection and analysis, 13 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 measurable proxy for MTT in this wet Andean páramo catchment. Therefore, although this 17 18 result cannot be expanded beyond páramo areas, perhaps not even beyond the study site, it seems that it is worth evaluating whether or not MTTs can be inferred from MEC in other 19 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**

The baseflow MTT evaluation using a LCA indicated that the EM best describes the subsurface transport of water in the basin. This result indicates efficient mixing in the high organic and porous wet Andean páramo soils and a simple subsurface transition of rainfall water towards the streams. MTT estimations showed relatively short MTTs linked to relatively short subsurface flow paths. Therefore, we confirm that the hydrologic system of

the tropical alpine biome of the Zhurucay basin is dominated by shallow subsurface flow. 1 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 morphology corresponds to U-shaped valleys, with the wetlands located at the valley bottoms 6 7 near the streams and connected to the slopes. Two headwater catchments, M3 and M4, 8 showed the longest MTT_s, 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 geology to a lesser extent, influence the responsiveness of the streams to precipitation inputs. 10 11 Correlation analysis between landscape variables and MTT indicates that MTT variability is mainly explained by the slope of the catchments, and a related influence of vegetation to a 12 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 hydrological response variables (runoff coefficient and specific discharge rates) indicate that 15 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 presenting the highest MECs – seems to be a promising proxy of MTT in system of 20 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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Catchment	Area (km ²)	Altitude (m a.s.l)	Distribu of soil (%)	ribution vil types	ution types ^a	Vege (%)	tatio	Vegetation cover ^b (%)	er ^b	Topc (%)	Topography ^c (%)	hy ^c		Geol (%)	Geology ^e (%)		EC ^f (μS/cm)
			AN	AN HS	LP	TG	CP	QF	ΡF	AS L ^d	L^{d}	IJ	IWI	Qm	Tu	Qd	
M1	0.20	3777 – 3900	85	13	7	85	15	0	0	14	0.9	0.9 1.9	9.6	100	0	0	35.7
M2	0.38	3770 - 3900	83	15	7	87	13	0	0	24	0.8	1.9	12.8	66	1	33	32.0
M3	0.38	3723 - 3850	80	16	ю	78	18	4	0	19	1.0	2.0	9.4	59	41	0	62.4
M4	0.65	3715 - 3850	76	20	4	<i>4</i>	18	\mathfrak{c}	0	18	1.3	2.0	12.5	50	48	1	47.9
M5	1.40	3680 - 3900	78	20	7	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	7	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	7	2	17	4.6	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)

36

1

Table 1. Main landscape characteristics of the monitored catchments.

- 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)	$\frac{1}{\tau}\exp\left(\frac{-t}{\tau}\right)$	τ [0 – <mark>65</mark>]
Exponential-piston model (EPM)	$\frac{\eta}{\tau} \exp\left(-\frac{t \cdot \eta}{\tau} + \eta - 1\right) \text{ for } t \ge \tau (1 - \eta^{-1})$	$ au \ [0 - {65}] \eta \ [0.5 - 4]$
Dispersion model (DM)	$\left(\frac{4\pi D_p t}{\tau}\right)^{-1/2} t^{-1} \exp\left[-\left(1-\frac{t}{\tau}\right)^2 \left(\frac{\tau}{4D_p t}\right)\right]$	$ au [0 - \frac{65}{65}]$ $D_p [0.5 - 4]$
Gamma model (GM)	$\frac{\tau^{\alpha-1}}{\beta^{\alpha}\Gamma(\alpha)}\exp^{-\tau/\beta}$	$ \begin{array}{c} \alpha \; [0.01 - 4] \\ \beta \; [0 - 500] \\ \tau = \alpha \cdot \beta \end{array} $
Two parallel linear reservoir (TPLR)	$\frac{\varphi}{\tau_f} \exp\left(\frac{-t}{\tau_f}\right) + \frac{1-\varphi}{\tau_f} \exp\left(\frac{-t}{\tau_s}\right)$	$ au_{s} [0 - 65] \ au_{f} [0 - 8] \ arphi [0 - 1] \ $

3 $\overline{\tau}$ = 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.

Catchment	Catchment Precipitation (mm vr ⁻¹)	Total runoff	Runoff Coefficient ^b	Average specific discharge	Flow rates (1 s ⁻¹ km ⁻²)	rates a km ⁻²)	Flow rates as frequency of non-exceedance (1 $\rm s^{-1}~km^{-2})$	ency of	non-e	xceeda	nce
	,	(mm yr ¹)		(1 s ⁻¹ km ⁻²)	Q_{min}	Q_{min} Q_{10} Q_{30}		Q50	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	9.777

Table 3. Main hydrometric variables of the catchments.

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

Sampling	Altitude		δ ¹⁸ O (‰)			
Station	(m a.s.l.)	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

2 input data for the MTT modeling.

3 ^a n: number of samples collected.

4 ^b SE: Standard error.

	Observed $\delta^{18}O$	d 8 ¹⁸ O		•••	Simulat	Simulated $\delta^{18}O$			
Model	Mean	σ ^a	Mean	σ^{a}	KGE ^a	$\sigma^a KGE^a RMSE^a Bias AIC^a$	Bias	AIC ^a	Model Parameters ^b
	(%)	(%)	(%)	(%)	-)	(%) (%) (%) (-) (%) (%) (%)	(00)	(-)	
EM			-10.02 0.52 0.63	0.52	0.63	0.59	0.59 0.03 2.92	2.92	τ (days) 191 (166-224)
EDM					0 62	0 20			$\frac{\tau}{\tau}$ (days) $120(90-205)$
			- 10.02	70.0	c0.0	ec.u	cu.u	4.72	η (-) 0.63 (0.53-0.92)
			0.05	0 64	0 2 0		010	20	τ (days) 666 (480-755)
MICI			.6.6-	0.0	00.0	0.12	01.0	60.0	Dp (-) 3.99 (2.74-3.93)
	-10.05 0.45	0.45							τ (days) 392 (296-1478)
GM			-10.02	0.45	0.75	-10.02 0.45 0.75 0.47 0.03 4.58	0.03	4.58	α (-) 0.70 (0.51-0.76)
									β (-) 40 (26-108)
									$\tau_{\rm f}$ (days) 1664 (356-1738)
TPLR			-10.02	0.45	0.76	-10.02 0.45 0.76 0.47 0.03 6.55	0.03	6.55	τ _s (days) 45 (12-90)
									φ (-) 0.31 (0.10-0.48)
$a \sigma = Stand$	ard devia	tion; KG	E = Kling	-Gupt	ι Effici	ency (Gu	ıpta et ;	al., 2009	$^{a} \sigma =$ Standard deviation; KGE = Kling-Gupta Efficiency (Gupta et al., 2009), AIC = Akaike Information Criterion (Akaike,
1974). Stat	istical par	ameters -	of the sim	nulated	results	correspc	ond to t	he best-	1974). Statistical parameters of the simulated results correspond to the best-matching value of the objective function KGE.

Table 5 Statistical narameters of observed and modeled δ^{18} O for the stream at the outlet of the basin (M8).

1

^b τ = tracer's mean transit time; η = parameter that indicates the ratio between the contribution of piston and exponential flow; Dp = dispersion parameter; $\alpha = shape$ parameter; $\beta = scale$ parameter; τ_f and $\tau_s = transit time of fast and slow flows; <math>\varphi = flow$ GE. percentiles) of simulated parameters shown in parenthesis were estimated using the generalized likelihood uncertainty partition parameter between fast and slow flow reservoirs. (-) = Dimensionless parameter. Uncertainty bounds (5-95 estimation (GLUE, Beven and Binley, 1992).

	Observed $\delta^{18}O$	d 8 ¹⁸ O	Simulated δ^{18} O	ed δ ¹⁸ (0	C:milotof MTTh	
Catchment	Mean	G ^a	Mean o ^a	Qa	KGE ^a	SIMULATED INT L	
	(%)	(%)	(%)	(-) (0%)	(-)	(years)	(days)
<u></u>	-10.63	0.37	-10.51 0.44	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)
A 3	-10.64	0.23	-10.51	0.26	0.48	0.73 (0.64 - 0.86)	264 (232 – 310)
Л4	-10.63	0.27	-10.51	0.3	0.48	$0.67 \ (0.59 - 0.78)$	240 (212 – 280)
A5	-10.51	0.39	-10.51	0.46 (0.53	$0.52\ (0.46 - 0.61)$	188 (165 – 219)
46	-10.37	0.42	-10.43	0.5	0.59	$0.52\ (0.46 - 0.61)$	188 (164 – 220)
LV	-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)

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

1

 $^{a} \sigma =$ Standard deviation; KGE = Kling-Gupta Efficiency. Statistical parameters of the simulated results correspond to the best-matching value of the objective function KGE.

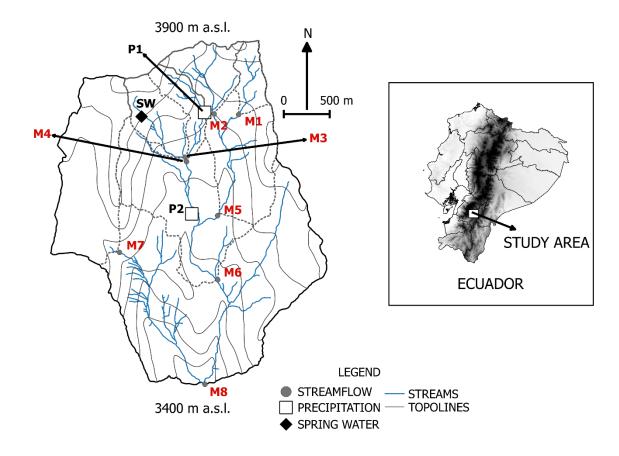
^b Uncertainty bounds (5-95 percentiles) of the simulated mean transit time (MTT) shown in parenthesis were estimated using the generalized likelihood uncertainty estimation (GLUE).

- 1 Table 7. Coefficient of determination (R²) 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).

	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		
				- •	Q99	0.42	(0.24)
ſes	Geologic formation			oles	Q90	0.18	(0.48)
atu	Quimsacocha	0.04	(0.75)	urial	Q80	0.06	(0.68)
e fe	Turi	0.12	(0.57)	c va	Q70	0.09	(0.63)
Landscape features	Quaternary deposits	- 0.51	(0.18)	Hydrologic variables	Q60	0.06	(0.68)
JdSC				Irol	Q50	0.01	(0.86)
Laı	Topographic features			Hyd	Q40	0.10	(0.61)
Ι	Average slope	-0.78	(0.05)	Н	Q30	-0.02	(0.82)
	Slope 0%–20%	0.85	(0.03)		Q20	-0.14	(0.53)
	Slope 20%-40%	- 0.90	(0.01)		Q10	- 0.61	(0.12)
	Area	0.13	(0.56)		Q5	- 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).
- 10



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.

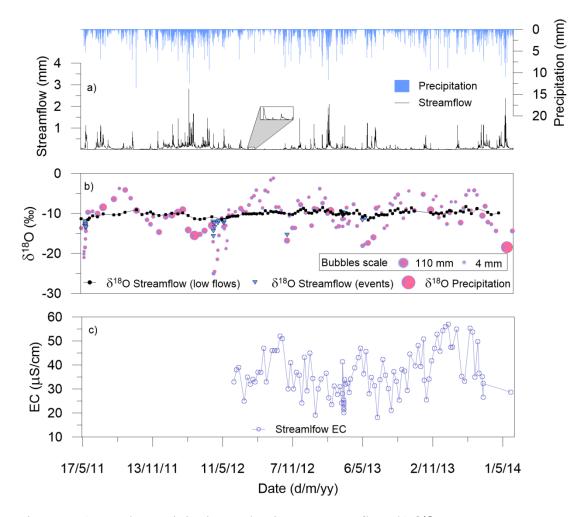
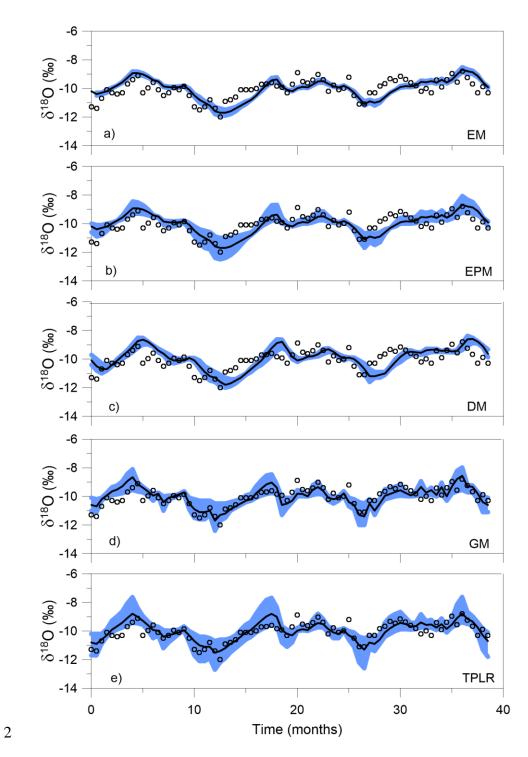
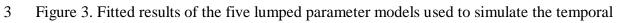


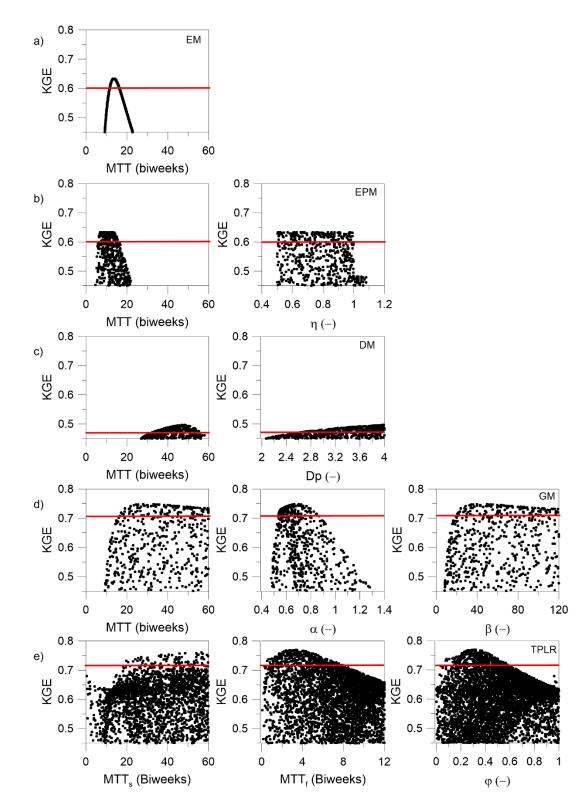
Figure 2. a) Hourly precipitation and unit area streamflow; b) δ^{18} O isotopic composition in precipitation and streamflow for 3 years (May 2011-May 2014); and c) electrical conductivity for 2 years (May 2012-May 2014) at the catchment outlet (M8, see location in Figure 2). The size of the bubbles in plot b) indicates the relative cumulative rainfall in millimeters for each collected sample.





4 variability in the δ^{18} O streamflow composition at the outlet of the basin (M8). (a) Exponential

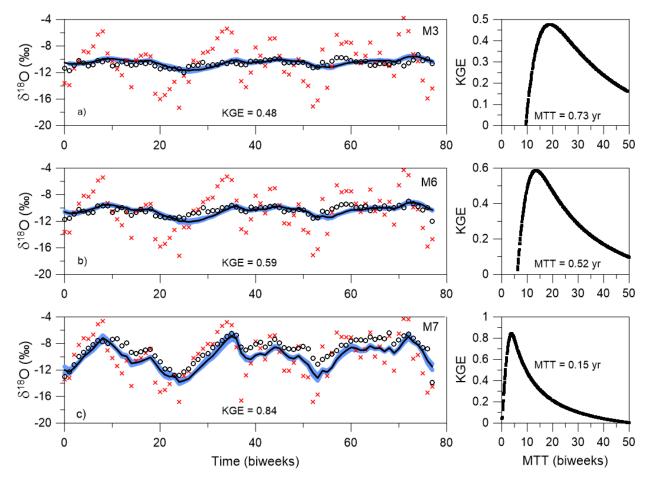
- 1 model (EM); (b) exponential-piston model (EPM); (c) dispersion model (DM); (d) gamma
- 2 model (GM); and (e) two parallel linear reservoir model (TPLR). The open circles represent
- 3 the observed isotopic composition in streamflow; the black line represents the best simulated
- 4 isotopic composition 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.



1

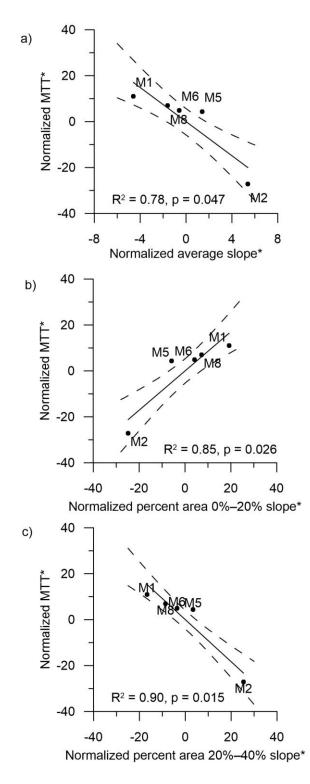
2 Figure 4. Monte Carlo simulations of the fitted parameters of the five lumped parameter 3 models used to simulate the δ^{18} O streamflow composition at the outlet of the basin (M8). a)

- 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).



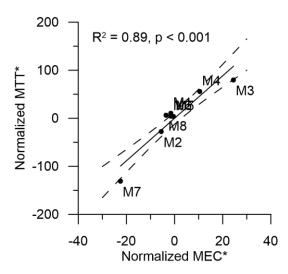
1

2 Figure 5. Fitted results and Monte Carlo simulations of the fitted parameters of the 3 exponential model (EM) used to simulate the δ^{18} O streamflow composition in the catchments: a) M3; b) M6; and c) M7. The open circles represent the observed isotopic composition in 4 5 streamflow; the red crosses represent the isotopic composition in precipitation; the black line represents the best simulated isotopic composition in streamflow according to the KGE 6 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.
- 5



- 1
- 2 Figure 7. Correlation between mean transit time (MTT) and mean electrical conductivity
- 3 (MEC) for weekly measurements of stream water samples collected during three years (June
- 4 2012-June 2015). Solid line is the linear regression and the dashed lines are the 90%
- 5 confidence intervals of the regression. * Indicates variables are normalized by their means.