

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

Reply: We really appreciate the review provided by referee 1 (R1) and are glad that our work gives rise to an interesting discussion of catchment heterogeneity and non-stationarity in the context of robust MTT estimations. R1 comments focus on four main aspects: 1) site conditions, 2) aggregation bias, 3) model evaluation and performance, and 4) selected methodology. Hence, we provide responses to each of them separately below.

R1: The paper attempts to explore transit time distributions (TTD) in a high-elevation tropical ecosystem by using a detailed hydrologic and isotopic record from eight nested catchments located in southern Ecuador.

Reply: First, we want to emphasize that our system is characterized by unique hydrometeorological and landscape characteristics in comparison to other systems: i) mean annual precipitation, runoff, and evapotranspiration are similar across the entire catchment ( $1284 \pm 18 \text{ mm yr}^{-1}$ ,  $788 \pm 54 \text{ mm yr}^{-1}$ ,  $496 \pm 61 \text{ mm yr}^{-1}$ , respectively) (Mosquera et al., 2015), ii) precipitation is evenly distributed year-round with very low degree of seasonality (Padrón et al., 2015), iii) isotopic fractionation by evaporative effects is virtually negligible (Mosquera et al., 2016) as a result of the year-round high relative humidity (~90%) (Córdova et al., 2015), iv) the soils are shallow and poorly developed across the entire catchment (~1m deep), and v) the geology is relatively young and homogeneous (Coltorti and Ollier, 2000). We believe our system presents a high degree of homogeneity across the entire basin as a result of the mentioned landscape configuration and local hydrometeorological conditions as is noted in Page.9, Lines. 16-19 (P. 9, L. 16-19).

R1: Although the data are extremely interesting and unique in quality and location, the transit time analysis is performed through a method (the lumped convolution approach) which is likely to include an aggregation bias, especially for systems with a high degree of heterogeneity and non-stationarity (see the recent papers by Kirchner, [2016a,b]).

Reply: We appreciate the comment and have significantly expanded the text to more fully recognize recent advances in MTT estimation, and more clearly place the paper within them. Regarding our approach, we will first focus on the issue of heterogeneity. It is certainly true that heterogeneity is “a fundamental problem” in the investigation of catchment behavior, because the scale of investigation influences the type of hydrological processes that can be identified. This issue is very well captured in Figure 4 of Kirchner (2016a) which exemplifies how MTT estimations can be affected as a result of aggregation across scales in heterogeneous catchments. We recognized this issue in our study design by considering a nested monitoring configuration. This configuration allowed us to investigate the variability of hydrological processes across scales and to characterize the system's degree of heterogeneity. As mentioned above, the characteristics of the Zhurucay basin, provide quasi-homogeneous conditions or low degree of heterogeneity, which most likely significantly reduces the issue of aggregation bias in MTT estimations. The landscape homogeneity in our system is evident considering that the same TTD represent the subsurface hydrologic system's behavior at all catchments, with a relatively small range of variation of the estimated MTTs ( $0.51 \pm 0.17 \text{ yr}$ ). Thus, we consider that given the homogeneous catchment characteristics and small seasonality of local environmental conditions in our system, applying the LCA to our water stable isotopic dataset is a first step with which to build-up improved catchment functioning understanding.

Regarding the nonstationarity issue (Kirchner, 2016b), we first want to clarify that using a certain methodology does not imply that other ones are ignored. The LCA is an approach that assumes steady-state conditions in the system, which we explicitly acknowledge in our paper (P. 9, L. 18-19 and P. 11, L. 13-15). However, as highlighted in the manuscript title (i.e., “Insights”), our study aims to set a baseline for the application of modeling techniques using stable water isotopes in tropical ecosystems above the tree line. We make the case that this is an important feature of the earth system, in which there is generally only very scarce hydrologic information. In fact, to our knowledge, this is the first contribution regarding the modeling of MTT in páramo ecosystems.

Although recent advances in hydrologic research, such as the ones listed by R1, have provided theoretical evidence of the importance of recognizing the unsteady nature of hydrologic processes highlighting the possible shortcomings of the LCA, our paper is not designed as a methodological contribution regarding MTT modeling theory. Instead, this paper is about understanding catchment functioning in a high-elevation tropical region. Indeed, one of our future goals is to apply modeling techniques that explicitly recognize non-stationarity and storage dynamics in the hydrological behavior of this tropical ecosystem (e.g., Birkel et al., 2015; Harman, 2015; Hrachowitz et al., 2013). These analyses, however, are beyond the scope of this paper. That said, we also believe our data set is valuable because it provides a concrete example to test the applicability, limitations, and constraints of different MTT modeling methodologies. In fact, based on the homogeneous and uniform hydrometeorological characteristics of our site, in contrast to many of the temperate regions in which time-variant MTT modeling has been developed, we anticipate our dataset and the results from this study to allow for benchmark testing of MTT methodologies in regions with low climate seasonality. At the same time, we acknowledge the growing recognition of the time-variant nature of transit times and highlight the value of such modeling methodologies and recent findings related to them in P. 4, L.20 to P5. L7.

It is relevant to note a recent application of conceptual modeling for the investigation of non-stationary conditions in a wet Scottish upland catchment where runoff generation processes mainly occur in the riparian Histosol soils with high storage capacity (Birkel et al., 2015), as in our study site. These authors detected non-stationary characteristics in water age distributions only during extreme weather conditions (extensive dry or wet periods) and attributed this behavior to the large mixing capacity of the Histosol soils, “which acts as an isostat moderating isotope variability and limiting the time variance of water age”. The latter has been clearly observed in the Zhurucay basin, where the isotopic composition of the organic horizon of the Histosol soils remains virtually constant and matches the isotopic composition in the streams year-round (Mosquera et al., 2016). This, in combination with the nearly uniform climate characteristics in our site, supports the utility of steady-state approaches in our system. We have included a discussion of these findings in relation to the ones at our site in P. 21, L. 4-13.

R1: In simple terms, even if the transfer function approach allows a fair simulation of the measured isotopic signal, the system mean transit time is not necessarily realistic, due to the structural uncertainties in the quantification of the older water components. This emerges in Figures 4 and 6, where different TTD (with different MTT) result in similar model performances.

Reply: With regards to the uncertainties related to the quantification of old water components, we consider this is not a significant issue in our system. Evidence of very low (insignificant) “old” water contributions (i.e., deep groundwater contributions to discharge) in the Zhuruca basin has been found by Crespo et al. (2011) and Mosquera et al. (2016) and by Buytaert and Beven (2011) in a nearby páramo catchment in South Ecuador. It appears that this results from the combination of: 1) the relatively young and homogeneous geology, 2) the high storage capacity of the porous organic horizon of the páramo soils, and 3) their low level of development (soils are generally less than 1 m deep). Results from our study support this interpretation. This is evidenced by the fact that the two TTDs functions (Gamma and two parallel linear reservoir) that incorporate an “old” water component yield parameter values that are not well constrained (see P. 19, L. 6-11). Instead the exponential model provided a robust representation with a clearly defined parameter. In this sense, it must be highlighted that our procedure to identify the TTD that best describes our system hydrologic behavior did not only take into account the goodness-of-fit of the objective function but also the level of identification of the function parameters and a process-based interpretation of the results (see below).

Regarding the similar performance of the model using different TTDs, Timbe et al. (2014) conducted a detailed analysis of the uncertainties related to the use of different TTDs in MTT modeling using the LCA. They also found that several TTDs provide high goodness-of-fit between predictions and observations, but poor parameter identifiability for some TTDs calibrated parameters, as has also been observed by other researchers (e.g., Hrachowitz et al., 2009). As such they recommend that for achieving meaningful MTT estimates from the LCA, it is at least needed to: 1) used several TTDs, 2) evaluate predictions uncertainty, and 3) assess parameter identifiability for each TTD function. Following these recommendations, we conducted an assessment of the performance of different TTDs, considering not only the best fit but also the uncertainty of the predictions, the parameter identifiability, and a process-based interpretation in light of the detailed hydrometric, isotopic, and biophysical landscape information which has been collected at our study site over the last five years (Córdova et al., 2015; Mosquera et al., 2015, 2016; Padrón et al., 2015; Quichimbo et al., 2012) to select the model that best describes the hydrologic functioning of the system. In addition, we have included an analysis using a metric for model selection (Akaike information criterion, AIC). This analysis has confirmed the EM as the one that best describes the hydrologic functioning in our system (see P. 14, L. 21-24).

R1: Moreover, the paper ignores the recent advances in hydrologic transport and TTD (see the list of suggested literature), which are now widespread within the hydrologic community and have clarified the concept of TTD in the light of non-stationarity. The manuscript is clear, well written and easy to follow, but the methods pose some serious concern on the paper's conclusions.

Reply: We appreciate this comment and have included a clear discussion about the recent time variant advances in hydrologic modeling in P. 4, L.20 to P. 5, L. 21. However, given the high degree of homogeneity of our system we believe that assuming steady-state conditions is justified. This conditions allows us to use LCA to develop an improved understanding of catchment function using hydrometric-tracer based hydrologic modeling. There is information in the LCA approach, information which we explore and highlight in this paper. Limiting transit time modeling efforts only to recent methodologies suggests that these baseline MTT

estimates, developed with a well-established approach (with well-established limitations) are of no value. We disagree wholeheartedly. MTT modeling under non-stationary conditions is an idea that is currently under development, and as result, there is yet no unified methodology that can be globally applied. Indeed there are very few applications of such methodology, most of which have yield results with high degree of uncertainty (Harman, 2015; Klaus et al., 2015; McMillan et al., 2012) or it is not even estimated (Davies et al., 2013; Heidebüchel et al., 2012; van der Velde et al., 2015), mainly as a result of expensive computation costs or high uncertainties related to the spatial variability of the input hydrometric and tracer field measurements. It is clear however, that given the mathematical limitations (Duvert et al., 2016; Seeger and Weiler, 2014), high-temporal resolution of tracer data required (Harman, 2015; Heidebüchel et al., 2012), and general unavailability of long-term tracer records (Hrachowitz et al., 2010; Klaus et al., 2015) also required for hydrological modeling under non-stationary conditions, the LCA is still a useful metric of storage and catchment functioning not only in understudied regions such as the tropics (e.g., Farrick and Branfireun, 2015; Muñoz-Villers et al., 2015; Timbe et al., 2014) but also elsewhere (e.g., Duvert et al., 2016; Hale and McDonnell, 2016; Hale et al., 2016; Hu et al., 2015; Seeger and Weiler, 2014). In this sense, we agree with Christian Birkel (referee 2, R2) comment: “there are merits in using the MTT to characterize catchment systems particularly considering the constraints and limitations working in tropical environments” and are convinced that this “experimentally derived dataset for this tropical ecosystem is unique and interesting to the HESS readership and beyond”, particularly taking into account the system’s particular characteristics. We believe this contribution will become a benchmark study over which to build-up further hydrological processes understanding not only in this remote understudied region, but also more generally, in regions with low climate seasonality and catchments with low degree of heterogeneity. Future efforts will built upon the monitoring infrastructure and datasets that continue to be collected in the Zhurucay River Ecohydrological Observatory, which will allow for continual improvement in hydrologic interpretation by eventually incorporating some alternative modeling techniques (e.g., Birkel et al., 2015; Harman, 2015; Hrachowitz et al., 2013).

## DETAILED COMMENTS

Page 7, line 18: the authors say that kinetic fractionation by evaporation can be neglected, however looking at Figure 3 it seems that the majority of stream water samples plot below the LMWL. How can this behavior be explained?

Reply: You are correct. Fractionation by evaporation is not negligible. A detailed analysis of the deuterium-oxygen-18 relation in rainfall and stream waters in the Zhurucay basin has shown that kinetic fractionation by evaporation is yet very low (Mosquera et al., 2016). However, Figure 3 has been removed as the information it conveyed is not relevant for the discussion of the paper and a thorough discussion of such information can be found in the manuscript of Mosquera et al. (2016), currently under review and accepted with minor revisions in Hydrological Processes.

P. 9, l. 3: the variable tau in Eq. (1) and (2) is not the mean transit time. It is just the dummy variable in the integral, which spans the transit time domain  $[0, +\infty]$ .

Reply: Thank you catching this typo. We have make a correction by removing this from the manuscript.

P. 10, l. 22-26: I did not get why the model is run twice to get the behavioral set of parameters.

Reply: We first run the model 10,000 times considering a wide range of parameter values. This provided an idea about the range of acceptable values. Based on the latter, we narrowed the parameter space and run the model again until 1,000 solutions or more, corresponding to at least 95% of the KGE objective function (i.e., at least 1,000 behavioral solutions), were obtained. These 1000 solutions allowed strong identification of the 90% confidence interval using the GLUE methodology. This procedure is been clarified in P. 12, L. 4-9.

P. 10, l. 28: the MI index seems to be very arbitrary depending on the choice of the prior parameter distribution. Segura et al., [2012] provide a partial explanation for their choice of the prior, which is here missing.

Reply: We appreciate this observation. Our initial choice of parameters ranges was selected based on the work of Timbe et al. (2014) in their analysis of uncertainties related to the use of the LCA for MTT estimations. This is been clarified this in P. 12, L. 16-18.

P. 13, l. 27: the terminology “MTT probability density function” seems to refer to the pdf of MTT obtained from the posterior parameter distribution.

Reply: You are correct. The pdf and cdf we referred to in the text correspond to the distributions described based on the fitted parameter distributions. This is been clarified in the text in P. 16, L. 19.

P. 14, l. 1-13: this is to me a clear example of the indetermination of the MTT. Different parameterizations of the TTD are able to provide good, similar simulations of the isotopic signal, but result in rather different MTT. While it is reasonable to choose a model because its parameters are more constrained in the simulation of a specific target, this does not allow to extrapolate that its MTT is the “right” one.

Reply: This issue is been already discussed above in the general comment and we just want to emphasize that we carefully considered the uncertainty of the predictions and the parameter identifiability, in addition to the results of the simulation of the isotopic signal against the objective function and have further included the results from the AIC model selection metric that support that the EM is the one that best describes our system in P. 14, L. 21-24 and Table 5, as suggested by R2. Additionally, we conducted a process-based interpretation of these results in light of the detailed hydrometric, isotopic, and biophysical landscape information which has been collected at the Zhurucay basin over the last five years (Córdova et al., 2015; Mosquera et al., 2015, 2016; Padrón et al., 2015; Quichimbo et al., 2012) for selecting the TTD that best suites the hydrologic conditions of the system.

P. 15, l. 21: what is meant by “completely” recovered? Is there a threshold (e.g. 99%) on the recovered mass?

Reply: This means that if the tracer would have been injected as a single pulse, how much it would take to completely leave the system. In effect, certain proportion of the total injection will be recovered at a certain time after the injection, For example, Figure 6 depicts that for the EM 80% of the tracer is recovered at around 20 biweeks. Analogous analysis have been reported by Hrachowitz et al. (2009) and McGuire et al. (2005).

## SUGGESTED LITERATURE

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## **Point-by-point response to Christian Birkel (Referee 12)'s review**

The manuscript "Insights on the water mean transit time in a high-elevation tropical ecosystem" by Mosquera et al. under review in Hydrol. Earth Syst. Sci. Discuss., doi:10.5194/hess-2015-546, 2016 presents an attempt to investigate MTTs of a nested paramo catchment system in Ecuador with the purpose to tease out dominant controls on water transit time. The authors were able to identify relatively short transit times ( $< 1$  yr) compared to other environments in different climatic regions. The MTTs in their study site are mainly controlled by the catchment slope in relation to the dominant wetland soils. The experimentally derived dataset for this tropical ecosystem is unique and interesting to the HESS readership and beyond. The analysis is mostly sound and the paper generally well-written and structured.

Having said that, the paper struggles in parts to clearly convey the main points in line with the objectives of the study and could be shortened. I am missing a discussion around arguments that the MTT is not a meaningful catchment descriptor and the recent tendency towards the recognition of the time-variant nature of transit times. I do think that there are merits in using the MTT to characterize catchment systems particularly considering the constraints and limitations working in tropical environments; it should, however, be more clearly argued. Furthermore, there are some model decisions that should be more clearly explained, which also likely leads to additional analysis strengthening the paper and its line of arguments. Nevertheless, I think this is nothing that cannot be fixed with a careful revision to improve clarity and focus of the paper and I therefore support publication of this paper with some revisions.

Reply: We appreciate Christian Birkel's (R2) revision and 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. We agree that the paper could be shorter to focus its content in the objectives. We also acknowledge that some details of the modeling procedure deserve clarification along with a discussion about recent theoretical frameworks that explicitly incorporate time-variant transit times (please see response to R1). Our responses to R2 comments are outlined below.

We also want to highlight here, the major changes incorporated into the manuscript in relation to R2 suggestions. First, in the revised version of the manuscript we acknowledge the time-variant nature of MTTs (in P. 4, L 22-27) and justify why the LCA methodology (assuming steady-state conditions) is applicable for our study site in P. 5, L. 11-14 and P. 9, L. 16-19. Secondly, to shorten the paper and focus on its main objectives we removed two figures (Figures 3 and 6). Figure 3, the deuterium-oxygen18 relations for precipitation and stream waters, was removed as the information it conveyed was not relevant for the discussion of the paper and a thorough discussion of such information can be found in the manuscript of Mosquera et al. (2016), currently under review and accepted with minor revisions in Hydrological Processes. As recommended by R2 below, we also shortened the results and discussion regarding the probability and cumulative density functions in P. 16, L. 16-24 and removed Figure 6 as this do not add relevant information to the paper's discussion. Finally, we split section 3.2 (Model selection and mean transit time evaluation) into two shorter ones focused in different points. Section 3.2 (TTD evaluation and selection) regarding the selection of the best TTD and section 3.3 (Baseflow MTT) regards to the estimation of MTTs across the basin.

Specific comments:

Abstract:

Line 21: I'm not sure if the paper is about streamwater MTT as you excluded high-flow events from the analysis.

Reply: We agree, based on the discussion below, it is clear that MTT estimations correspond to baseflow MTTs. This is been specified in the abstract in P. 1, L. 24 and P. 2, L. 10 and throughout the rest of manuscript.

Key words:

Line 15: I suggest to simplify and reduce the key words to attract more online search results, e.g.: Ecohydrology, MTT, runoff generation, Andean páramo, Histosols, Ecuador.

Reply: We agree with the suggestion and have simplified and reduce the key words to the following: Ecohydrology, MTT, runoff generation, wet Andean páramo, tropical wetlands, Histosol, Ecuador

Introduction:

Page 3, Line 2: This is true for Latin America, but there are a few more studies in the tropics. You could even refer to Muñoz-Villers and McDonnell (2012) in this context.

Reply: We agree and have included additional references (Farrick and Branfireun, 2015; Muñoz-Villers et al., 2015) of studies recently conducted in the tropics in P. 3, L. 4-5.

Page 3, Line 17: I will come back to this point, but I think it's very likely that there's also a considerable near-surface runoff component as seen in other environments (you refer to Scotland and Sweden below) with organic rich wetland soils that remain saturated for much of the year. I, however, don't know the paper in review you cite here.

Reply: We see that this point can cause confusion. However, by "shallow subsurface flow" we refer to water moving in the first 30-40 cm within the soil matrix (i.e., "shallow organic horizon of the páramo soils located near the streams"). This is supported by water isotopic concentrations observed in the shallow organic horizon of the Histosol soils and stream waters in the study area. These observations and further discussion are presented in a manuscript which has been recently accepted with minor revision in Hydrological Processes receiving minor comments. We have provided the editor of this paper with a copy of the referred manuscript to pass it along to the reviewers.

Page 3, Line 29: This isn't entirely true, I'm afraid, because the dominating runoff generation process based on various tracer studies is a rapid near-surface flow. The subsurface component is a deeper and slower groundwater flux. Therefore, the wetland contribution can be quantified very well in form of near-surface saturation overland flow.

Reply: We partially agree with this comment. Although it is true that "rapid near-surface flow" has been observed in other environments, it mostly refers to "near-surface saturation

overland flow". However, the hydrologic functioning of this particular system takes place in the first 30-40 cm of the soils, here referred to as "shallow subsurface flow", and saturation excess overland flow rarely occurs in the Zhurucay basin (i.e., high flows occur less than 3% of the time at the study site, see figure 3 in Mosquera et al., 2015). Thus, the term "rapid near-surface flow" does not apply to our system. We therefore have replaced the term "subsurface" by "shallow subsurface and/or near surface (i.e., overland flow)" to clarify this in P. 4, L. 5.

Page 4, Line 9: I think Broxton et al. (2009) worked in Arizona, USA. You could also specify the control you are referring to as in this case it was "aspect".

Reply: We appreciate the suggestion. We have corrected the site where this study was conducted and specified the controls on MTT in P. 4, L. 15-17.

Study site:

Page 5, Line 8: This is an awkward sentence, please revise.

Reply: We agree and have restructured the sentence in P. 6, L. 15-17.

Line 10: seasonality, primarily.

Reply: These suggestions have been incorporated in P. 6, L. 8.

Line 23: please, spell out INV.

Reply: INV is the name of the mining company (<http://www.invmetals.com/about/history/>).

Page 6, Line 4-5: Please, revise this sentence.

Reply: The sentences referring to soil distribution in the catchment have been restructured in P. 7, L. 12-15.

Line 27: Please, indicate model and make of the equipment.

Reply: Model and make of the instrument (Schlumberger DI500) are indicated in P. 8, L. 9.

Methods:

Page 9, Line 26: ...is based...

Reply: We agree with this suggestion and have corrected it accordingly in P. 11, L. 9.

Line 27: I'm not sure I follow the second point.

Reply: This refers to input (recharge) function of the precipitation tracer composition to take into account recharge (i.e., volumetrically weighted isotopic composition) (McGuire and McDonnell, 2006). This has been clarified in P. 11, L. 10-11.

Page 10, Line 6: In this case, I suggest to consistently refer to a baseflow MTT and not streamwater MTT.

Reply: We agree. The following has been added in P. 11, L. 19-20: "As a result, estimations correspond to baseflow MTTs, hereafter simply referred to as MTT."

Page 11, Line 2-5: I fully agree that you seek to identify the best-performing and most parsimonious model. However, you don't really compare the models using a criterion for model selection (e.g., AIC, BIC or adjusted R<sup>2</sup>) that penalizes the number of parameters in combination with a goodness-of-fit measure. The MI criterion looks at how identifiable one parameter is, but not at the combined effect of more than one parameter used to calibrate the model.

Reply: We appreciate this comment. We applied the AIC metric for model selection as stated in P. 12, L. 11-14. Results from this analysis are reported in table 5 and P. 14, L. 21-24.

Page 11: How were models generated? Using a uniformly sampled Monte Carlo procedure?

Reply: This is correct. The fitting procedure included two steps for each model. 1) Initially 10,000 sets of parameter values were evaluated considering a wide range of parameter values sampled according to a uniform Monte Carlo procedure (Beven and Freer, 2001). The parameter ranges were wide. For instance the parameter range of the MTT of the EM model varied between 0 and 130 biweeks (5 yrs). 2) After the initial 10,000 runs, the range of the set of parameters that displayed relatively well identified were narrowed and the model was run again until 1,000 behavioral parameter sets were obtained (i.e., sets of parameters that yielded solutions corresponding to at least 95% of the highest KGE). This has been clarified in P. 12, L. 4-5.

Line 16: mainly?

Reply: We appreciate the suggestion "Majorly" is been changed by "mainly" in P. 13, L. 5.

Results:

Page 12, Line 12: Runoff coefficients show...

Reply: This sentence has been updated accordingly in P. 13, L. 27.

Page 13, Line 4-26: I'm not convinced by some of the statements present in this paragraph. For example, the best-fit gamma model compared to the best-fit exponential model does show a quite significant increase in performance (from 0.63 to 0.75) that can justify the use of one additional fitting parameter. On the other hand, a third fitting parameter resulted in an increased performance of only 0.01. The poorest model seems to be the DM with a best-fit of KGE=0.5. Based on this, one could qualitatively reject the DM and TPLR models as suitable models compared to the EM and GM. However, the decision between the EM and GM models should be informed by a model selection criterion such as the AIC (see comment above) that evaluates the combined effect of the parameters on model performance.

Reply: We completely agree and appreciate the suggestion. As indicated above we have now conducted an AIC evaluation and reports its results in Table 5 and P. 14, L. 21-24.

Page 14, Line 12: Please, revise this sentence.

Reply: Thank for the suggestion, sentence has been revised and corrected in P. 15, L. 11-12.

Page 14: I think that large parts here could be moved into the discussion or simply be deleted as later sections pick up on these issues. This would allow to shorten the m/s focusing on presenting the key results and later discussion in the light of the wider literature.



Reply: We agree with this suggestion. We have trim down irrelevant text in this section. See P. 15, L. 13-21.

Page 15, Line 26: just use MTT

Reply: This has been corrected accordingly in P. 16, L. 25.

Page 16, Line 5-12: Please, separate this very long sentence into smaller parts.

Reply: We appreciate the suggestion. This sentence has been split into three in P. 17, L. 3-10.

Discussion:

Page 17, Line 26: more depleted?

Reply: This was removed from the manuscript.

Page 18, Line 1: I think it would be better to indicate that baseflow MTT was analysed.

Reply: We agree. Changed in P. 18, L. 23.

Line 3: identifiability?

Reply: Correct. Changed in P. 18, L. 25.

Line 20: Was TMCF previously defined?

Reply: Thank you catching this. TMCF defined in P. 19, L. 13 and abbreviation consistently used thereafter.

Line 30: remain.

Reply: We agree. Corrected in P. 19, L. 24.

Page 19, Line 10: You somehow have to convince me that this actually is subsurface stormflow. I haven't seen the in review paper you mention in this context and all the evidence you show tells me that the dominating runoff generation mechanism is near-surface saturation overland flow due to little mixing with deeper soil horizons, short MTTs, etc.

Reply: Based on the characterization of the weekly isotopic composition of stream and soil waters conducted over a two-years period, it is evident that the isotopic composition of the shallow organic horizon of the Histosol soils consistently matches that of the streams, and that precipitation has essentially no direct influence in the streamflow isotopic composition (Mosquera et al., 2016). As such, even "subsurface stormflow" appears to inappropriately describe the system's functioning, as water is preferentially delivered from the shallow 30-40 cm of the organic horizon of the Histosols to the streams regardless of the precipitation dynamics. Moreover, saturation excess overland flow rarely occurs at the study site (Mosquera et al., 2015) as stated in P. 3, L. 23-24. Therefore, we consider that "shallow subsurface flow" is indeed the appropriate term to define the delivery of water from the Histosols situated at the bottom of the slopes to the streams. As mentioned above, we have provided the editor with a copy of the cited paper currently in revision after minor changes have been addressed.

Line 20: You previously said up to 2.2 years in this context.

Reply: We referred to two different studies conducted in central Mexico. Muñoz-Villers and McDonnell (2012) reported MTTs of three years and recently Muñoz-Villers et al. (2015) reported MTTs ranging between 1.2-2.2 years. Therefore, this statement in the manuscript is correct.

Page 20, Line 6: I think Hrachowitz et al. (2009) argued with saturation overland flow.

Reply: Hrachowitz et al. (2009) actually reported that at the Lord Arch catchment runoff generation shows a flashy catchment response “dominated by runoff processes in the upper soil horizons.” That is, in the 40 cm depth peaty soils, overlaying the mineral horizons,

Line 11: solutes.

Reply: Agree. Corrected in P. 21, L. 3.

Page 22, Line 1: explain.

Reply: Agree. Corrected in P. 23, L. 4.

Line 8: Please, revise this sentence.

Reply: We agree. Sentence is been corrected in line P. 23, L. 11-13.

Line 14: Isn't this simply the slope?

Reply: Yes, you are correct. Changed in lines P. 23, L. 17.

Line 24: I find the “regulation capacity” is coming a bit out of nowhere. What exactly do you mean by this? Is it in the sense of resilience or simply that the turn-over is quick and what goes in comes out with little delay?

Reply: We acknowledged how this can lead to confusion. Basically the páramo is an ecosystem recognized for its high discharge regulation capacity (i.e., páramo generates runoff year-round regardless of variability in precipitation inputs to the system). This characteristic is essential to the sustainability of human activities of downstream populations. However, little is known about the factors driving this regulation capacity. The results from this study provide information that improves our understanding of catchment functioning by identifying some of these drivers (see P. 1, L. 11-13 and P. 23, L. 23-28). That is, the interplay between soil storage and topography. We have explained the regulation capacity notion of the ecosystem in the introduction section of the manuscript in P. 3, L. 17-20.

Page 23, Line 2: It's the first time that you mention that SOF wasn't previously observed in the study catchment. This information needs to come earlier. I also think this whole paragraph can be shortened towards the key messages presented at the very end.

Reply: We agree. We have added information regarding SOF earlier in the manuscript in P. 3, L. 23-24. We have trimmed this paragraph to reduce its length in P. 23, L. 17 to P. 24, L. 2.

Line 29: Please, revise this sentence.

Reply: We agree, we have reworded the sentence in P. 24, L. 22-23.

Tables:

Shouldn't the current Table 2 come before you present the models (Table 1)?

Reply: We appreciate this suggestion and completely agree. Order of tables has been changed.

Current Table 1: I'm a bit confused about some decisions concerning the choice of initial parameter intervals. Why was the upper limit of tau set at 200 biweeks? This makes 2800days and over 7 yrs of TT, something stable isotopes aren't able to detect anyways (Stewart et al., 2010). Further, why was the lower limit of beta (GM) set to 0.5? In the case of low TT this could be well below 0.5 and on a global scale the average resulted to be at around 0.5 (Godsey et al., 2009). With the current lower limit in place you potentially miss suitable parameters that would also result in lower MTTs compared to current best-fit results; an argument you used to reject the GM. Also, it seems odd to me that you don't report the parameter interval for beta as this is the parameter you calibrate. The MTT (tau) is only the result of  $\beta \cdot \alpha$ .

Reply: We really appreciate this comment. We used the MTT parameter ranges suggested by Timbe et al., (2014). However, we recognize that these authors had a different objective in their study and that it is reasonable that we constrain our parameter values range for MTT up to 5 years (130 weeks) (McGuire and McDonnell, 2006). As such, we have run all models again for all catchments, and statistics and figures have been updated accordingly. Regarding the parameter in the GM, we believe R2 refers to the alpha parameter. The alpha parameter lower limit was originally set up at 0.01, and the 0.5 value was just mistakenly reported in the table. We have corrected the lower limit value in the table and also reported the parameter range considered for beta.

Table 5: Similar issue here with the GM. I suggest to report the parameters alpha and beta.

Reply: Same as above. Beta parameter is now reported in the table.

Table 7: R2-values of 0.62 did not result significant? However, there's a relationship with flow characteristics particularly for the extremes and the runoff coefficient does seem to explain some of the spatial variability among catchments.

Reply: We appreciate this comment. The mentioned relations are not statistically significant at a 95% confidence level. Results are as follows:

Runoff coefficient:	$R^2$ 0.62	p-value: 0.39
Q99:	$R^2$ -0.42	p-value 0.24
Q10:	$R^2$ -0.61	p-value 0.12
Q5:	$R^2$ -0.62	p-value 0.11

P-values are now shown in table 7 and the relation between low flows and MTT is reported in P. 17, L. 18-21.

Figures:

Figure 2: What's the purpose of the streamflow inlet box? Could you not just show a log-scale to emphasize the low flow periods? Those event samples do show quite a bit of

response to rainfall. What's the effect of pooling these out? Quite a bit shorter MTTs? Please, consider adjusting the different EC sampling period for comparison purposes.

Reply: 1) Streamflow inlet box: The purpose of the streamflow inlet box is to emphasize the response of low flows to rainfall inputs during the less humid periods. The box indicates flashy response even during these periods. We therefore still believe that the non-log-scale representation of the hydrograph in combination with the inlet box provides the best impression of the observed dynamics. 2) Event samples: The model runs reported were originally conducted once these referred event samples were pooled out from the streamflow isotopic composition time series. 3) EC sampling period: Sampling period for EC has been adjusted to hydrometric and isotopic data sampling period.

Figure 5: Please, clarify if sampling was started below  $\alpha = 0.5$  (GM) contrary to the information from Table 1. Again, I suggest to present the parameters alpha and beta.

Reply: We apologize for the confusion. The lower limit of the alpha parameter was originally set up at a value of 0.01. This was updated in Table 2. We now present both alpha and beta parameters as suggested, together with the MTT.

Figure 6: Is EPM missing in the right panel?

Reply: No, it is not. It just plots behind the EM curves in both panels. A note is been added to the caption of the figure.

Figure 8: If the MTT is normalized shouldn't it be unitless?

Reply: You are correct. We changed the text accordingly in figures 8 and 9.

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

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## Abstract

This study focuses on the investigation of the mean transit time (MTT) of water and its spatial variability in tropical high-elevation ecosystems (wet Andean páramo). The study site is the Zhurucay River Ecohydrological Observatory (7.53 km<sup>2</sup>) located in south Ecuador. A lumped 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 of the  $\delta^{18}\text{O}$  isotopic composition of rainfall and streamflow water samples collected for three years (May 2011-May 2014) in a nested monitoring system of streams. Linear regression



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

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

## **1 Introduction**

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

as recharge to when it exits it at some discharge point (Bethke and Johnson, 2002; Etcheverry and Perrochet, 2000; Rodhe et al., 1996).

Despite the importance of tropical biomes as natural sources and regulators of streamflow, there are very few studies of MTT in tropical environments (e.g., Farrick and Branfireun, 2015; Muñoz-Villers et al., 2015; Roa-García and Weiler, 2010; Timbe et al., 2014). The majority of MTT studies have been conducted in catchments with strong climate seasonality, i.e., located in the northern and southern hemispheres (e.g., Lyon et al., 2010; McGlynn and McDonnell, 2003; McGuire et al., 2005), and considerably less attention has been devoted to 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 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., 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 dependence on landscape biophysical features in tropical regions are still lacking and urgently needed in order to improve water resources management.

The páramo is widely recognized by its high runoff regulation capacity (i.e., páramo water yield is sustained year-round regardless of precipitation inputs) (Buytaert et al., 2006; Céleri 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 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 contributions to discharge are minimal and saturation excess overland flow (even in the nearly saturated Histosol soils) rarely occur (Buytaert and Beven, 2011; Crespo et al., 2011). The hydrological importance of shallow subsurface flow to runoff generation has also been 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 provides a unique opportunity to gain understanding of the MTT of a shallow subsurface flow 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. As detailed  
8 observations of combined hydrometric and isotopic information are not feasible in many  
9 regions due to limited funding and site accessibility, identifying controls of MTT variability  
10 in nested and paired monitoring systems of streams is fundamental towards regionalization of  
11 ecohydrological processes (Hrachowitz et al., 2009a) and prediction in ungauged basins  
12 (Tetzlaff et al., 2010). Yet, investigation of controls on MTT variability is still fairly scarce  
13 (Tetzlaff et al., 2013). Most studies have found that MTT scales with topographic and/or  
14 hydrogeological controls. For instance, topographical controls on MTT variability were  
15 found in New Mexico, USA catchments (slope direction and exposure) (Broxton et al., 2009)  
16 and a system of streams in Oregon, USA (ratio between flow path length and flow path  
17 gradient) (McGuire et al., 2005); whereas the proportion of wetlands and responsive soils  
18 were reported as major MTT controls in Swedish catchments (Lyon et al., 2010) and Scottish  
19 streams (Soulsby et al., 2006), respectively.

20 In the last few decades, MTT modeling has been conducted applying an approach that  
21 assumes steady-state conditions in the hydrologic systems, i.e., the lumped convolution  
22 approach (LCA) (Amin and Campana, 1996; Maloszewski and Zuber, 1996). However, this  
23 assumption is often violated as a result of strong climate seasonality and heterogeneities in the  
24 landscape configuration and hydrogeological distribution of catchments (Kirchner, 2016a,  
25 2016b). This has led to a growing recognition of the time-variant nature of transit times (e.g.,  
26 Birkel et al., 2015; Harman, 2015; Hrachowitz et al., 2013), which a number of studies have  
27 begun to explore. Most of this initial work has yielded results with high degree of uncertainty  
28 (Harman, 2015; Klaus et al., 2015; McMillan et al., 2012), or uncertainty has not been  
29 estimated (Davies et al., 2013; Heidbüchel et al., 2012; van der Velde et al., 2015) as a result

of expensive computation costs or high uncertainties related to the spatial variability of the input hydrometric and tracer field measurements. It is clear however, that given the mathematical limitations (Duvert et al., 2016; Seeger and Weiler, 2014), the high-temporal resolution of tracer data (Harman, 2015; Heidbüchel et al., 2012), and the general unavailability of long-term tracer records (Hrachowitz et al., 2010; Klaus et al., 2015) required for hydrological modeling under non-stationary conditions, the LCA remains to be a useful methodology for MTT estimation. This holds true not only in understudied regions such as the tropics (e.g., Farrick and Branfireun, 2015; Muñoz-Villers et al., 2015; Timbe et al., 2014), but also elsewhere (e.g., Duvert et al., 2016; Hale and McDonnell, 2016; Hale et al., 2016; Hu et al., 2015; Seeger and Weiler, 2014).

Given the relatively homogenous landscape features and very low seasonality in the 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 functioning understanding using hydrometric-tracer based hydrologic modeling. To our knowledge, this is the first contribution regarding the modeling of MTT in páramo ecosystems specifically, and more generally in regions with low climate seasonality and catchments with low degree of heterogeneity. Future efforts building on the monitoring infrastructure and continuously collected datasets will allow for continual improvement in hydrologic interpretation, eventually incorporating alternative modeling techniques that explicitly recognize non-stationarity and storage dynamics in the hydrological behavior of this tropical 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)

the factors controlling such variability. Based on our current knowledge of the hydrology of the ecosystem, in particular, the apparent dominance of shallow subsurface flow to runoff generation, we hypothesize relatively short baseflow MTTs compared to systems dominated by groundwater contributions to discharge. Also, based on the hydrogeological and climatic similarities between our páramo site and the peatland-podzols dominated ecosystems in the Scottish highlands (e.g., Soulsby et al., 2006; Tetzlaff et al., 2014), we hypothesize the proportion of wetlands to be a dominant control on the variability of the MTT in this high-elevation tropical ecosystem.

## 2 Materials and methods

### 2.1 Study site

The Zhurucay River Ecohydrological Observatory is a basin located within a tropical alpine 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 Jubones River (Pacific Ocean tributary). The basin has a drainage area of 7.53 km<sup>2</sup> and 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 basin. Mean annual precipitation at the observatory is 1345 mm at 3780 m a.s.l. Precipitation shows low seasonality with two relatively drier months (August and September) and primarily falls as drizzle (Padrón et al., 2015). Mean annual temperature is 6.0 °C at 3780 m a.s.l. and 9.2 °C at 3320 m a.s.l. (Córdova et al., 2015).

The geology of the region is characterized by volcanic rock deposits compacted by glacial activity during the last ice age (Coltorti and Ollier, 2000). The Quimsacocha formation, composed by basaltic flows with plagioclases, feldspars, and andesitic pyroclastics, covers the northern part of the basin. The Turi formation covers the southern part of the catchment and its lithology mainly corresponds to tuffaceous andesitic breccias, conglomerates, and horizontally stratified sands. Both formations date from the late Miocene period (Pratt et al., 1997). The geomorphology of the landscape bears the imprint of glaciated U-shaped valleys. The average slope of the basin is 17%. The majority of the basin (72%) has mean gradients

1 between 0-20 %, although slopes up to 40% are also found (24%). There is an interesting  
2 geomorphic feature in the northeastern side of the basin corresponding to a ponded wetland at  
3 a flat hilltop. As indicated by geologists from INV metals mining company, this structure  
4 most likely resulted from the eutrophication of a lagoon due to high accumulation of volcanic  
5 material. This area is locally known as “Laguna Ciega” (“Blind Lagoon” in Spanish) and  
6 drains towards the outlet of catchment M7 (see Figure 1). The analysis of the water stable  
7 isotopic composition of soil water and streamflow in this area indicated that the hydrologic  
8 processes of this site occur in the shallow ponded water that is directly connected to the  
9 drainage network; while deeper water stored in the soil profile has little influence for  
10 discharge generation most likely as a results of the eutrophic condition of the wetland  
11 (Mosquera et al., 2016).

12 Andosols are the dominant soil type in the study site. They cover approximately 80% of the  
13 total basin area and are mainly found in the hillslopes. Histosols (Andean wetlands) cover the  
14 remaining portion of the basin and are mainly found in flat areas where rock geomorphology  
15 allows water accumulation (Mosquera et al., 2015). These soils, formed from the  
16 accumulation of volcanic ash in flat valley bottoms and low gradient slopes, are black, humic,  
17 and acid soils rich in organic matter with low bulk density and high water storage capacity  
18 (Quichimbo et al., 2012). The organic fraction of the Histosol soils corresponds to an H  
19 horizon (median depth 76.5 cm); while in the Andosol soils it corresponds to an Ah horizon  
20 (median depth 40cm). The mineral fraction of both soils corresponds to a C horizon (median  
21 depth of 31 cm in the Histosols and 40 cm in the Andosols). A complete description of soil  
22 properties can be found in Mosquera et al. (2015) and Quichimbo et al. (2012). Vegetation  
23 coverage is highly correlated with the soil type. Cushion plants (such as *Plantago rigida*,  
24 *Xenophyllum humile*, *Azorella spp.*) grow primarily in Histosols, while tussock grass (mainly  
25 *Calamagrostis* sp.) (Ramsay and Oxley, 1997; Sklenar and Jorgensen, 1999) grow in  
26 Andosols. The main landscape characteristics are summarized in Table 1.



## 2.2 Hydrometric information

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

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

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

yield the same results (Mosquera et al., 2016). Therefore only the results using the isotopic composition of  $^{18}\text{O}$  are reported. Rainwater samples are cumulative representations of the isotopic signature between sampling dates while stream grab water samples represent discrete points in time. The collected water samples were stored in 2 ml amber glass bottles, covered 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 composition of the water samples was measured using a cavity ring-down spectrometer L1102-i (Picarro, USA) with a 0.5‰ precision for deuterium ( $^2\text{H}$ ) and 0.1‰ precision for oxygen-18 ( $^{18}\text{O}$ ). Isotopic concentrations are presented in the  $\delta$  notation and expressed in per mill (‰) according to the Vienna Standard Mean Ocean Water (V-SMOW) (Craig, 1961).

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  $\pm 0.5\%$ .

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

As a result of the homogeneous landscape and hydrometeorological conditions in the Zhurucay basin, we estimated mean transit times (MTTs) using an inverse solution of the LCA (Amin and Campana, 1996; Małoszewski and Zuber, 1982), which assumes steady-state conditions. The LCA seeks for the parameter set of the model that best describes the hydrologic system represented by a predefined transit time distribution (TTD) function (Małoszewski and Zuber, 1996). The TTD describes the transition of an input signal (e.g., precipitation, snow) of tracer (e.g.,  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ) to the signal at an outlet point (e.g., groundwater, streamflow) resulting from the subsurface transport of water molecules within a catchment. Mathematically the TTD is described by a convolution integral that transforms the input signal ( $\delta_{\text{in}}$ ) into an output signal ( $\delta_{\text{out}}$ ), considering a time lag between them ( $t - \tau$ ) through a transfer function (TTDs or  $g(\tau)$ ) describing the subsurface transport of tracer as follows:

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

where  $\tau$  is the integration variable representing the MTT of the tracer. A more robust approximation weights the isotopic concentration of the input by considering recharge mass variation ( $w(\tau)$ ) so that the outflow composition reflects the mass flux leaving the catchment:

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

where  $w(t - \tau)$  can be described in terms of rainfall magnitude, intensity, or effective precipitation (McGuire and McDonnell, 2006). Precipitation intensity was used to volume weight the isotopic composition of precipitation in our study. Recharge was represented by the rainfall isotopic composition weighted by precipitation rate and accounted for relatively small recharge (i.e., lower precipitation inputs) during the less wet months (August and September).

MTT was estimated by adjusting the response function or TTD to fit the measured and simulated stream water isotopic composition. Five TTDs were considered to describe the subsurface transport of water molecules in the Zhurucay basin. We used the exponential model (EM), exponential-piston flow model (EPM), the dispersion model (DM) (Małoszewski and Zuber, 1982), the gamma model (GM) (Kirchner et al., 2000), and the two parallel linear reservoir model (TPLR) (Weiler et al., 2003). Each model is briefly described below and **Table 2** summarizes their equations, fitting parameters, and the range of initial parameters used in this study.

The EM represents a well-mixed system and assumes contributions from all flow paths. It 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 flow portion of the system. In addition to the MTT, it has an additional fitting parameter ( $\eta$ ), which represents the ratio of the total volume to the volume represented by the exponential distribution. The DM arises from the solution of the one-dimensional advection-dispersion equation (Kreft and Zuber, 1978) and assumes that there is influence of hydrodynamic

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

The MTT approach is based on the following assumptions: 1) the tracer concentration is conservative (i.e., the tracer does not react with other elements present in the system); 2) the input tracer concentration is input in flux mode (i.e., volumetrically weighted); 3) the tracer enters the system only once and uniformly; 4) a representative tracer input can be identified; 5) transport of solute is one-dimensional and represented by a single TTD; and 6) there is a uniform storage of water within the catchment (i.e., steady-state of the flow in the system) (Małoszewski and Zuber, 1982). The steady-state assumption is valid for humid environments during specific flow characteristics (i.e., baseflow) (McGuire et al., 2002). In order to comply with the latter assumption, streamflow water samples collected during extreme rainfall events were excluded for the MTT simulations (McGuire and McDonnell, 2006; Muñoz-Villers et al., 2015). As a result, estimates correspond to baseflow MTTs, hereafter simply referred to as MTT. To obtain more stable results, we looped the available three years of isotopic data ten times during calibration in order to extend the data series for 30 years as a warm-up period following Hrachowitz et al. (2011) and Timbe et al. (2014).

## 2.5 Model performance and uncertainty analysis

The model performance was evaluated using the Kling–Gupta efficiency coefficient (KGE) (Gupta et al., 2009). KGE ranges from  $-\infty$  to 1, where unity indicates an ideal optimization. KGE can be viewed from a multi-objective perspective because it accounts for correlation (i.e., balancing dynamics,  $r$ ), variability error ( $\gamma$ ), and bias error ( $\beta$ ) within a single objective function. The efficiency is mathematically represented by the Euclidean distance ( $ED$ ) in each of the three dimensions ( $r$ ,  $\gamma$ , 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. Models were built using parameter sets generated through a uniform Monte Carlo sampling procedure (Beven and Freer, 2001). Each model was first run 10,000 times within a wide range of parameter values (Table 2). Once a parameter value that yielded the best KGE was clearly identified, the model was run again within a narrowed range of parameters until obtaining at least 1,000 behavioral solutions (i.e., solutions corresponding to at least 95% of 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 methodology (GLUE) (Beven and Binley, 1992). The Akaike Information Criterion (AIC, Akaike, 1974) was used as a parsimoniousness metric for model selection that penalizes model performance based on the number of fitted parameters used to calibrate each model. The model with the lowest AIC is the most efficient at fitting the observed values. The measure of identification (MI) (Segura et al., 2012) was calculated as a metric of the model parameter identifiability. The MI is defined as the ratio between the behavioral parameters range to the initial range (based on Timbe et al., 2014) and indicates how well a parameter is identified. This metric is expressed as a percentage and by definition, the smaller the value, the better the parameter identifiability. We considered a parameter is well-identified if its MI is lower than 10%. The best model describing the hydrologic conditions of the system was selected using the following criteria: 1) best goodness of fit using the KGE criterion, 2) lowest AIC, 3) results that yielded the lower uncertainty estimations, and 4) higher parameter identifiability using the MI criterion.

## 2.6 Correlation analysis of MTT and catchment characteristics

We used linear regression to investigate relations between landscape characteristics and hydrological behavior with the MTT of the catchments. For this analysis, we included the catchments which comprise the main drainage network (i.e., catchments M1 to M6) and the catchment outlet (M8) given that they possess comparable hydropedological and geomorphological characteristics. That is, catchments situated at the valley bottom have well-

defined interconnections between wetlands in the riparian areas and the surrounding Andosol soils at the slopes. Catchment M7 on the other hand, is located at a flat hilltop at the outlet of a wetland area which remains ponded throughout the year. The geomorphology of this concave (lagoon shaped) structure and its ponded eutrophic condition has allowed for the hydrologic processes to mainly occur in the shallowest ponded portion of the water directly connected to the stream network (with little influence of the most likely immobile water which remains stored in the deeper soil fraction) (Mosquera et al., 2016). Therefore, its hydrological response is not comparable to the other catchments where hydrologic processes mainly occur in the soils and consequently was excluded from the regression analysis. Statistical significance of the correlations was tested using the F-test at a 95% confidence level (i.e.,  $p < 0.05$ ).

The landscape and hydrometric variables tested for correlation were obtained from previous studies at the site (Mosquera et al., 2015) and from detailed soil, vegetation, and topographic information provided by INV Metals. The landscape features considered were: soil type, vegetation, geology, catchment size, slope, flow path length and gradient, and topographic wetness index (TWI) (Beven and Kirkby, 1979b) (Table 1). The hydrometric variables considered were: annual runoff, annual precipitation, runoff coefficient, and streamflow rates (Table 3). Weekly collected EC for three years (June 2012-June 2015) was averaged and also tested for correlation with MTT.

### 3 Results

#### 3.1 Hydrologic and isotopic characterization in rainfall and streamflow

Precipitation in the Zhurucay basin is evenly distributed throughout the year (Figure 2a), except for two months with relatively lower precipitation inputs (i.e., August and September), both accounting for less than 8% of total annual precipitation. Spatially, annual precipitation (P) is evenly distributed across the basin with an average of  $1,275 \pm 9$  mm. Total annual runoff (Q) is spatially more heterogeneous, varying between 684 and 864 mm per year. Runoff coefficients (Q/P) show relatively low spatial variability between 0.55 and 0.68 (Table 3). The hydrograph at the 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 catchments.

The  $\delta^{18}\text{O}$  isotopic composition in rainfall is highly variable throughout the year (e.g., average  $-10.2 \pm 0.32\text{‰}$  at the upper station) (Figure 2b) and follows a seasonal pattern with isotopically enriched values during highest precipitation rates (April-May), and isotopically depleted values in the less humid period (August-September). The  $\delta^{18}\text{O}$  isotopic composition in streamflow collected during low flows on the other hand, is much more damped (average  $-10.0 \pm 0.06\text{‰}$ , at M8) than the isotopic composition in precipitation (Table 4).

### 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  $\delta^{18}\text{O}$  isotopic composition at the outlet of the basin (M8) with efficiencies varying between 0.50 and 0.76, i.e., above the threshold of model acceptance ( $\text{KGE} > 0.45$ ) (Table 5). The more flexible models, GM and TPLR yield the highest performances with KGEs of 0.75 and 0.76, respectively. The EM and the EPM yield similar efficiencies ( $\text{KGE} = 0.63$ ), while the DM yields the lowest efficiency among all ( $\text{KGE} = 0.50$ ). The models 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 model parsimoniousness analysis evaluated using the AIC indicates that the EM ( $\text{AIC} = 2.92$ ) is the best model structure, whereas higher AIC values were determined for all model with more than one fitting parameters (GM, 4.58; EPM, 4.92; DM, 5.39; TPLR, 6.55). The models' parameter identification analysis indicates that even though the TPLR model yields the highest KGE, the level of identification of its parameters is the poorest (Figure 4). The identification metric (IM, i.e., the ratio of the behavioral to the initial parameter ranges, Table 5) yields high values for all parameters for the TPLR model (MIs ranges between 31% and 85%). For the EPM and GM models one parameter is well identified (MIs  $< 10\%$ ), while the others show higher MI values. For the DM, both parameters

are not well identified. The MI for the single parameter that defines the EM is very strong (MI = 4%). This coupled analysis of model efficiency and parsimoniousness in combination with parameter identifiability indicates that although models with a higher number of fitting parameters provide higher efficiencies, their parameters are more uncertain.

Taking into account the goodness of fit, parsimoniousness, uncertainty bounds, and the identifiability of the models' parameters, the EM is the model that best describes the temporal variability of the baseflow  $\delta^{18}\text{O}$  isotopic composition across the Zhurucay basin. It is also clear that the higher efficiencies yielded by the more flexible models, GM and TPLR, result from a higher number of fitting parameters rather than from a more realistic representation of the hydrologic functioning of the catchments. The EM was also found to describe the subsurface transport of water in another system of catchments in eastern Mexico, where soil have predominantly formed by volcanic ash accumulation (Muñoz-Villers et al., 2015).

The EM represents a well-mixed reservoir with relatively simple transition of the water (i.e., tracer) in the subsurface towards the stream network. In the Zhurucay basin, the organic and porous páramo soils allow for the efficient mixing of water within the whole profile of these poorly developed soils. This effect 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 relatively simple transition of infiltrated precipitation from a well-mixed reservoir towards the 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 basin.

### 3.3 Baseflow MTT

Results of the EM for selected catchments with the longest (M3), intermediate (M6), and lowest (M7) MTTs are shown in Figure 5 and statistics of the EM simulations at all catchments are summarized in Table 6. The EM overcomes the modeling acceptance criterion of  $\text{KGE} > 0.45$  at all catchments with KGE values ranging between 0.48 and 0.84. The longest MTTs is found in catchment M3 (0.73 years, 264 days) whereas the shortest at M7 (0.15 years, 53 days). The MTT for the other catchments vary within this range. On average, within the 90% confidence level for the catchments forming the main drainage network (M1-

M6 and M8), MTT estimations show small variations (25 days at the lower confidence bound and 35 days at the upper confidence bound) with small standard deviation (4 days for the upper bound and 6 days for the lower bound). For catchment M7, variations are even smaller (9 days at the lower confidence bound and 11 days at the upper confidence bound). In 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 smallest amplitude in isotopic variation for the observed and simulated data (Table 6), coupled with the lowest KGE (0.48) and the highest MTT. On the other hand, catchment M7 (Figure 5c) shows the highest amplitude in isotopic variation for the observed and simulated data, coupled with the highest KGE (0.84) and the shortest MTT. Similarly, catchment M6 (Figure 5b), which has a MTT shorter than the one in M3 and longer than the one in M7, has an amplitude and KGE varying between the ones in M3 and M7. The Monte Carlo simulations for the fitted parameter MTT (Figure 5) clearly depict how the MTT which yield 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.

The MTT probability density functions (PDFs), which indicate the distribution of MTTs in the hydrologic system, and cumulative density functions (CDFs), which express the tracer “mass recovery from an instantaneous, uniform tracer mass addition” (McGuire et al., 2005) 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 tracer is completely recovered in all catchments at around 80 biweeks, except for M7, where the tracers is even more rapidly recovered (~ 19 biweeks). As we used a stable isotopic record of 78 weeks (3 years), these results indicate that a three years record of tracer 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) and catchments M3 and M4 (Figure 1) driven by a spring water contribution during low flow generation. In general, deep subsurface flow and groundwater contributions to discharge seem to be minimal and geology has not been found to directly control the hydrology in this páramo ecosystem (Mosquera et al., 2015). However, the existence of this shallow spring sourced at 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 MTTs in these catchments. The latter indicates that geology (fractures in the shallow bedrock) influence the hydrology of these small headwater catchments; thus, masking relationships between landscape features and MTT of the whole system. Therefore, we tested the MTT correlations without including these small catchments (M3 and M4) and M7.

The reanalysis with the modified data set revealed significant relations of MTT with 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 (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 ( $p$ -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 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  $Q_5$  and  $R^2 = 0.61$ ,  $p = 0.12$  for  $Q_{10}$ ). The regression analysis including all catchments also showed that mean electrical conductivity (MEC) of the waters explains 89% ( $p = < 0.001$ ) of the catchments' MTT variability (Figure 7). Streams with higher MEC have longer MTTs.

## 4 Discussion

### 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 properties of the Histosol soils or Andean wetlands located near the streams. The high storage capacity of wetlands was also highlighted by (Roa-García and Weiler, 2010) after the comparison of three paired catchments in the growing coffee region of Colombia at lower 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, due to their relatively low saturated hydraulic conductivity ( $0.72\text{--}1.55\text{ cm h}^{-1}$ ), these soils remain near saturation throughout the year. These factors, in combination with the local climate, allow páramo soils to regulate and maintain a sustained discharge throughout the 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 flow. This is supported by the similar isotopic composition between streams and soil waters in the organic layer of the Histosols in the Zhurucay basin (Mosquera et al., 2016).

Although the  $\delta^{18}\text{O}$  isotopic composition of stream waters is damped and lagged with respect to that of precipitation, streamflow samples in the Zhurucay basin still reflect the variability of the  $\delta^{18}\text{O}$  composition of rainfall (Figure 2b), as expected in a system dominated by shallow subsurface flow. However, catchments are differently influenced by precipitation. M7, located 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 moving in the shallow organic horizon of the soils and the ponded water above it. All of the other catchments show considerably less influence of rainfall (Figures 5a and 5b) due to the mixing of rainfall water with the water stored within the whole profile of the Histosol soils.

## 4.2 What is the baseflow MTT?

The high performance ( $\text{KGE} > 0.48$ ) of the exponential model (EM) and its strong parameter identifiability (Table 6) 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 contribution by yielding the longest MTTs estimations in these catchments, and an intrinsic influence of geology on MTT variability. In addition, the performance of the model in these two catchments is the lowest within the basin. The latter most likely because of less efficient 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 consider that another model representing an additional slow reservoir (e.g., TPLR or GM) might better represent the subsurface movement of water in these catchments. Results, however, (Figures 3 and 4, Table 5) indicate that the contribution from this additional water source is small and an additional reservoir is not well distinguished by these TTDs as their parameters are not well identified. Recently, Muñoz-Villers et al. (2015) also identified the EM as the model that best mimics subsurface flow in 7 of 12 nested catchments underlain by 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 groundwater contributions to discharge.

On the other end, M7, dominated by contribution from the shallowest part of the organic horizon of the soils and the ponded fraction of water accumulated in a ponded wetland – which is directly connected to the stream channel – presents the shortest MTT of all 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 condition of the wetland allows for a rapid and efficient mixture of precipitated water with ponded water and water stored in and released from the shallow organic horizon of the soil. 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 hydrology of the catchment. The well-mixing and simpler delivery of water to the stream is also captured by the high model performance. The MTTs estimated for the rest of the catchments lie in between these two extremes and their values and efficiencies vary depending on the amplitude of the isotopic tracer variation, with longer MTTs in catchments where the amplitude of the signal is more damped – evidencing lower influence of precipitation and less efficient mixing with the soil storage – and vice versa. The MTT in these catchments

1 vary relatively little in comparison to the rest of the catchments (0.43 to 0.53 years, 156 to  
2 191 days). Overall, the MTTs are relatively short, further supporting previous evidence that  
3 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  
10 lower elevation ecosystem is dominated by deep groundwater contributions. Preliminary  
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  
13 soils formed by volcanic ash accumulation, as the páramo soils are, a combination of deeper  
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  
19 homogeneous and low permeable geology provide the páramo basin of the Zhurucay River  
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  
24 little weathering geology. Nevertheless, the models which provided the best fit were the GM  
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 hydrogeological 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



Histosols (80 cm) in the Zhurucay basin. These factors, in combination with differences underlying geologies suggest that their overall hydrologic functioning might differ as evidenced by different TTDs describing the subsurface transport of solutes.

Although we used a methodology that assumes stationary conditions in the hydrologic system (LCA), it is relevant to note here the results of a recent application of conceptual modeling for the investigation of non-stationary conditions in a hydrologically similar region (Birkel et al., 2015). These authors detected non-stationary effects in water age distributions only during extreme weather conditions (extensive dry or wet periods) and attributed this behavior to the large mixing capacity of the Histosol soils. Although future investigations of the non-stationary nature of MTTs are needed at the páramo, based on the dominance of flow generation in the Histosols at the Zhurucay basin, in combination with low annual changes in the environmental conditions, we consider our results from the LCA provide robust MTTs estimates in our study site.

#### 4.3 Controls on baseflow MTT variability

We found significant correlations ( $R^2 \geq 0.78$ ,  $p < 0.05$ ) between catchment slope dependent indexes and MTT using a subset of the main stream catchments (subgroup 2) (Table 7, Figure 6). Results of the correlation analysis indicate that 1) the higher the average slope of the catchments, the shorter the MTT; 2) the higher the percent of area corresponding to slopes between 0% and 20%, the longer the MTT; and 3) the higher the percent of area corresponding to slopes between 20% and 40%, the shorter the MTT. These results indicate a 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) attributed the latter to expected contributions from the water originated in the slopes (Andosol soils) during low flow generation as a result of the gravitational potential of the water that drains downslope from these soils. These authors also found that wetlands (Histosols soils located near the streams) control the generation of moderate and high flows. Although we did not find significant correlations with other landscape features, vegetation shown expected 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

1 vegetation ( $R^2 = 0.31$ ,  $p = 0.33$ ). In another tropical system of catchments in Colombia, a  
2 catchment with higher areal proportion of wetlands was found to prolong the water MTTs, but  
3 appeared to reduce water yield (Roa-García et al., 2011). Although these authors did not  
4 report the slope of the catchments, we can infer that the catchment with the highest proportion  
5 of wetlands – as they form in flat areas – is also the catchment with the lowest gradients.  
6 Therefore, their observations might result from the combination of the deeper soil  
7 development ( $> 10$  m) with high water retention capacity and low saturated hydraulic  
8 conductivity, perhaps in combination with low slope gradients. This would support the result  
9 of our study, where the catchments with the lower slopes and higher proportion of wetlands  
10 present the longer MTTs.

11 In other latitudes, in 20 Scottish catchments with different geomorphologies and climate,  
12 MTT variability was controlled by the areal proportion of peat soils and no influence of  
13 catchments' slopes was found (Hrachowitz et al., 2009a). As such, and given the similarities  
14 between these soils and our Histosol soils (Andean wetlands), we hypothesized MTT  
15 variability to be controlled by the areal extent of wetlands. Even though we found that MTT  
16 variability is rather mainly controlled by topography in our tropical alpine site, a small trend  
17 of wetlands' cover to increase MTT was also identified. Although the later relation is not  
18 statistically significant, the latter most likely results from the influence of topography on  
19 Histosol soils (wetlands) formation, where the formation of this soil mainly occurs in  
20 catchments with lower slopes where water accumulation is favored. This finding indirectly  
21 suggests that wetlands influence MTT spatial variability to a lesser extent. Therefore, it  
22 appears that although relatively similar processes control the ecohydrology of both  
23 ecosystems, controls on MTT variability cannot be extended from one ecosystem to the other.  
24 MTT variability was also found to be controlled by the proportion of wetlands in cold snow  
25 dominate boreal catchments in Sweden for the MTT of spring snowmelt water (Lyon et al.,  
26 2010). These authors attributed this effect to the formation of shallow ice acting as  
27 impermeable barriers above the wetlands, and thus changing the flow paths of water.  
28 Nevertheless, because of the different climate and geological features between their  
29 catchments and ours, we did not find wetlands as major controls on MTT variability.

1 Other slope topographic indexes – e.g., flow path length (L), flow path gradient (G), and the  
2 ratio between both (L/G) (e.g., McGuire et al., 2005; Tetzlaff et al., 2009) – have been  
3 identified as controls of MTT variability in catchments in other latitudes. Although these  
4 landscape features did not significantly explain MTT variability in the Zhurucay basin, the  
5 L/G ratio was reported as the major control of MTT variability ( $R^2 = 0.91$ ) in steep temperate  
6 catchments in the central western Cascades of Oregon (McGuire et al., 2005), suggesting that  
7 this relation “reflects the hydraulic driving force of catchment-scale transport (i.e., Darcy’s  
8 law)”. Similarly to our study site, they also found average slope of these catchments to be one  
9 of the most important individual controls on MTT, explaining 78% of the MTT variability.  
10 Recently, topography was also identified as a major control on the MTT of 12 TMCF  
11 catchments in eastern Mexico (Muñoz-Villers et al., 2015). Results from these studies reflect  
12 that the integrated effect of catchment slope on MTT variation can be identified in distinct  
13 geological and hydrogeological provinces. The latter also suggests that rather than using a  
14 predictor which indicates more local effects of hydraulic force driving in the stream channel  
15 (e.g., L/G), catchment slope might be a better measure to compare catchment functioning as it  
16 integrates the hydrologic connectivity of hillslope, riparian, and stream areas.

17 The topographic controls on MTT in the Zhurucay basin indicate that water resides for a  
18 longer time in catchments having lower slope gradients. These results also indicate that in  
19 catchments having higher areal proportions of low gradients and lower areal proportions of  
20 steeper gradients coupled with higher wetlands coverage, water resides longer in the shallow  
21 reservoir of the soils. The control of the proportion of steeper gradients in MTT variability  
22 suggests that the gravitational potential of water draining downslope in the Andosol soils also  
23 indirectly influences MTTs. Therefore, it is our interpretation that the hydrology of this  
24 ecosystem is mainly dominated by the interplay of two factors: 1) the high storage capacity in  
25 the shallow organic horizon of the porous páramo soils and 2) the catchment slope. Factor 1  
26 driving the high water retention capacity and factor 2 controlling the high regulation capacity  
27 of the ecosystem, and thus, maintaining a sustained delivery of water to the streams along the  
28 year. Without the interplay storage-slope, water would remain stored in the soils, and perhaps  
29 the delivery of water towards the streams would be dominated by saturated overland flow

(SOF), affecting the regulation capacity of the ecosystem. Nevertheless, SOF rarely occurs in the Zhurucay basin (Mosquera et al., 2015).

Mean electrical conductivity (MEC) was also found to be significantly correlated with MTT using all catchments of the nested system in the basin (Figure 7). The regression analysis, showed strong correlation, with MEC increasing as MTT increases. As EC is an intrinsic property of water, due to the time it spends in contact with the surrounding pore space, rather than a control on MTT variability, this result indicates that this property might be used as a proxy to estimate MTT spatial variability. The well-defined connection between MTT and 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 between MEC and MTT in other biomes.

Given that estimating MTT using isotope tracers and the LCA is financially expensive due to the logistical set up of a monitoring network and the processes of data collection and analysis, finding proxies (i.e., predictors) which allow inferring MTTs at lower operational costs is critical to improve water resources management. In this sense, the strong relation between 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 result cannot be expanded beyond páramo areas, perhaps not even beyond the study site, it seems that it is worth evaluating whether or not MEC can infer MTT in other hydrologic systems. Nevertheless, one should be careful that EC measurements can be relatively variable over time. As a result, a single measurement of EC is most likely not enough to provide robust MTT estimates. Therefore, longer EC measurement records reduce MEC variability and provide more robust MTT estimates.

## 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. MTT estimations showed that catchment M7, located at a flat hilltop at the outlet of a wetland which remains ponded year-round and disconnected from the slopes – most likely as a result of the eutrophication of a lagoon – showed a particularly low MTT (0.15 yr – 53 days) in 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 near the streams and connected to the slopes. Two headwater catchments, M3 and M4, showed the longest MTT, related to a small contribution from a spring shallowly sourced. 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. 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 lesser extent. Catchments with the steepest average slopes and lower proportion of wetlands have the shortest MTTs. The lack of significant correlations between the MTTs and hydrological response variables (runoff coefficient and specific discharge rates) indicate that neither water yield, nor streamflow rates control the time water resides in subsurface of the páramo soils. These results indicate that the interplay between the high storage capacity of the páramo soils and the slope of the catchments define the ecosystem's high regulation 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 catchments under homogeneous geological conditions. Finally, we want to highlight the usefulness of a nested monitoring system for acquiring better process-based hydrologic functioning understanding. For instance, if M3, M4, and/or M7 catchments would not have been monitored, the influence of geology and/or geomorphology on catchment hydrological response could not have been identified and important information about the whole ecosystem functioning would remain unknown.

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Table 1. Main landscape characteristics of the monitored catchments.

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

<sup>a</sup> AN = Andosol; HS = Histosol; LP = Leptosol<sup>b</sup> TG = tussock grasses; CP = cushion plants; QF = *Polylepys forest*; PF = pine forest.<sup>c</sup> AS = average slope, L = flow path length ; G = flow path gradient; TWI = topographic wetness index (Beven and Kirkby, 1979a).<sup>d</sup> L units in km.<sup>e</sup> Qm = Quimsacocha formation; Tu = Turi formation; Qd = Quaternary deposits.<sup>f</sup> EC = mean electrical conductivity. Data collected weekly for a three years period (June 2012-June2015)

1 Table 1. Models considered to describe water mean transit time (MTT) in the study area and  
2 their transit time distribution (TTD) functions, parameters, and range of initial parameters.

Model	Transit time distribution ( $g(\tau)$ )	Parameter(s) range
Exponential model (EM)	$\frac{1}{\tau} \exp\left(\frac{-t}{\tau}\right)$	$\tau$ [0 – 130]
Exponential-piston model (EPM)	$\frac{\eta}{\tau} \exp\left(-\frac{t \cdot \eta}{\tau} + \eta - 1\right)$ for $t \geq \tau (1 - \eta^{-1})$	$\tau$ [0 – 130] $\eta$ [0.5 – 4]
Dispersion model (DM)	$\left(\frac{4\pi D_p t}{\tau}\right)^{-1/2} t^{-1} \exp\left[-\left(1 - \frac{t}{\tau}\right)^2 \left(\frac{\tau}{4D_p t}\right)\right]$	$\tau$ [0 – 130] $D_p$ [0.5 – 4]
Gamma model (GM)	$\frac{\tau^{\alpha-1}}{\beta^{\alpha} \Gamma(\alpha)} \exp^{-\tau/\beta}$	$\alpha$ [0.01 – 4] $\beta$ [0 – 500] $\tau = \alpha \cdot \beta$
Two parallel linear reservoir (TPLR)	$\frac{\varphi}{\tau_f} \exp\left(\frac{-t}{\tau_f}\right) + \frac{1-\varphi}{\tau_s} \exp\left(\frac{-t}{\tau_s}\right)$	$\tau_s$ [0 – 130] $\tau_f$ [0 – 15] $\varphi$ [0 – 1]

3  $\tau$  = tracer's mean transit time (MTT) [biweeks];  $\eta$  = parameter that indicates the percentage of  
4 contribution of each flow type [-];  $D_p$  = dispersion parameter [-];  $\alpha$  = shape parameter [-];  $\beta$  =  
5 scale parameter [-];  $\tau_f$  and  $\tau_s$  = transit time of fast and slow flows in biweeks;  $\varphi$  = flow  
6 partition parameter between fast and slow flow reservoirs [%]. [-] Indicates parameters are  
7 unitless.

Table 3. Main hydrometric variables of the catchments.

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

<sup>a</sup> Total runoff as a proportion of precipitation.

1 Table 4. Statistics of the  $\delta^{18}\text{O}$  isotopic composition in precipitation and streamflow used as  
 2 input data for the MTT modeling.

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

3 <sup>a</sup> n: number of samples collected.

4 <sup>b</sup> SE: Standard error.

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

Model	Observed $\delta^{18}\text{O}$		Simulated $\delta^{18}\text{O}$					Model Parameters <sup>b</sup>	MI <sup>c</sup> (%)
	Mean (‰)	$\sigma^a$ (‰)	Mean (‰)	$\sigma^a$ (‰)	KG <sup>a</sup> (-)	RMSE <sup>a</sup> (‰)	Bias (‰)		
EM	-10.02	0.52	0.52	0.63	0.63	0.59	0.03	$\tau$ (days) 191 (166-224)	4
EPM	-10.02	0.52	0.63	0.63	0.63	0.59	0.03	$\tau$ (days) 120 (90-205)	7
								$\eta$ (-) 0.63 (0.53-0.92)	11
DM	-9.95	0.64	0.50	0.72	0.10	5.39		$\tau$ (days) 666 (480-755)	17
								Dp (-) 3.99 (2.74-3.93)	38
GM	-10.05	0.45						$\tau$ (days) 392 (296-1478)	59
								$\alpha$ (-) 0.70 (0.51-0.76)	7
								$\beta$ (-) 40 (26-108)	18
TPLR	-10.02	0.45	0.76	0.47	0.03	6.55		$\tau_f$ (days) 1664 (356-1738)	85
								$\tau_s$ (days) 45 (12-90)	31
								$\varphi$ (-) 0.31 (0.10-0.48)	43

<sup>a</sup>  $\sigma$  = Standard deviation; KGE = Kling-Gupta Efficiency (Gupta et al., 2009), AIC = Akaike Information Criterion (Akaike, 1974). Statistical parameters of the simulated results correspond to the best-matching value of the objective function KGE.

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

<sup>c</sup> MI = Measure of identification (Segura et al., 2012), i.e., ratio of behavioral parameter range to initial parameter range.

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

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

<sup>a</sup>  $\sigma$  = Standard deviation; KGE = Kling-Gupta Efficiency. Statistical parameters of the simulated results correspond to the best-matching value of the objective function KGE.

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



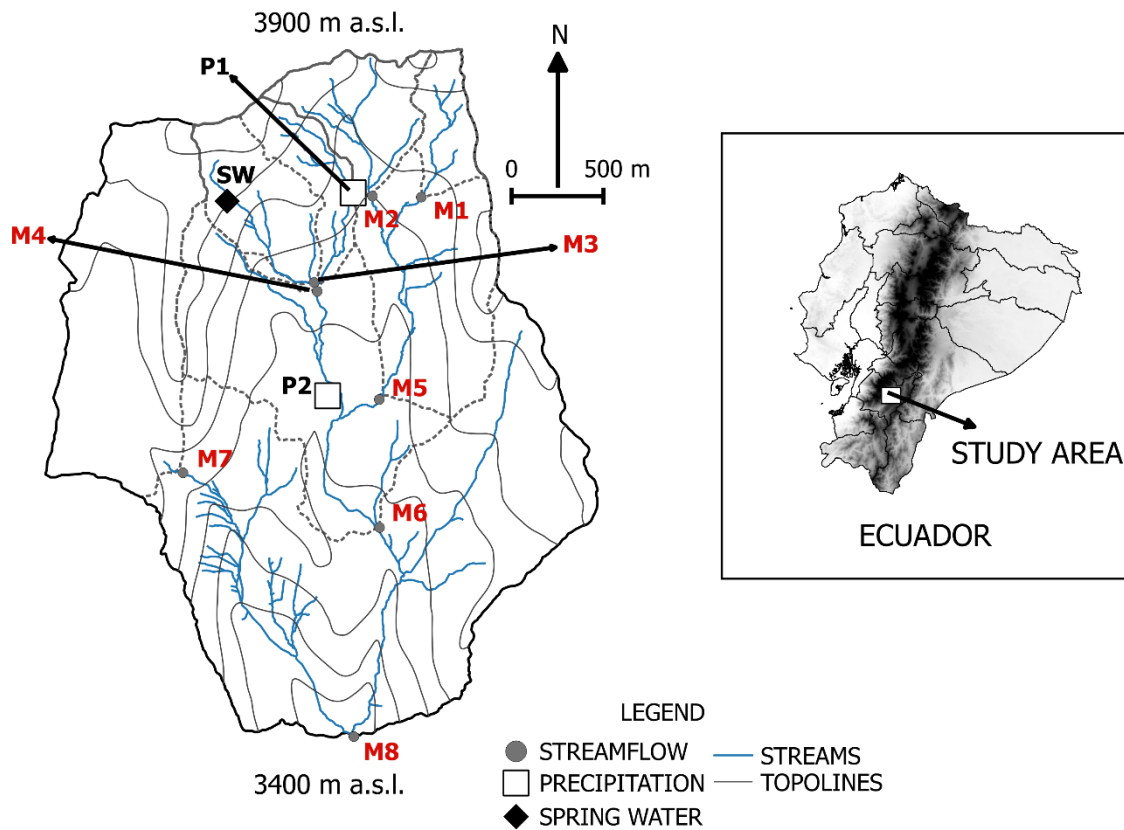
Table 7. Coefficient of determination ( $R^2$ ) between the mean transit time (MTT) and i) landscape features and ii) hydrological variables for each of the catchments. Catchments M3 and M4 (additional spring water source, see Figure 1) and M7 (at a flat hilltop disconnected from the hillslopes) are not included in the regressions; except for electrical conductivity, i.e., all catchments are considered (Figure 7).

Landscape features	<i>Vegetation</i>			Hydrologic variables	<i>General features</i>		
	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)
	<i>Soil Type</i>				Average specific discharge	0.21	(0.44)
	Histosol	0.13	(0.56)				
	Andosol	− 0.13	(0.55)		<i>Streamflow rates</i>		
					Q <sub>99</sub>	0.42	(0.24)
	<i>Geologic formation</i>				Q <sub>90</sub>	0.18	(0.48)
	Quimsacocha	0.04	(0.75)		Q <sub>80</sub>	0.06	(0.68)
	Turi	0.12	(0.57)		Q <sub>70</sub>	0.09	(0.63)
	Quaternary deposits	− 0.51	(0.18)		Q <sub>60</sub>	0.06	(0.68)
					Q <sub>50</sub>	0.01	(0.86)
	<i>Topographic features</i>				Q <sub>40</sub>	0.10	(0.61)
	Average slope	− 0.78	(0.05)		Q <sub>30</sub>	− 0.02	(0.82)
	Slope 0%–20%	0.85	(0.03)		Q <sub>20</sub>	− 0.14	(0.53)
	Slope 20%–40%	− 0.90	(0.01)		Q <sub>10</sub>	− 0.61	(0.12)
	Area	0.13	(0.56)		Q <sub>5</sub>	− 0.62	(0.11)
	TWI	− 0.03	(0.79)				
Flow path length (L)	0.23	(0.42)	<i>Water intrinsic properties</i>				
Flow path gradient (G)	− 0.20	(0.45)	Electrical conductivity	0.95	(< 0.001)		
L/G	0.23	(0.45)					

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

Values in bold are statistically significant to a 95% level of confidence ( $p < 0.05$ ). Values in parenthesis are the p-values of the correlations.

<sup>a</sup> TWI = Topographic wetness index (Beven and Kirby, 1979).



1

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.

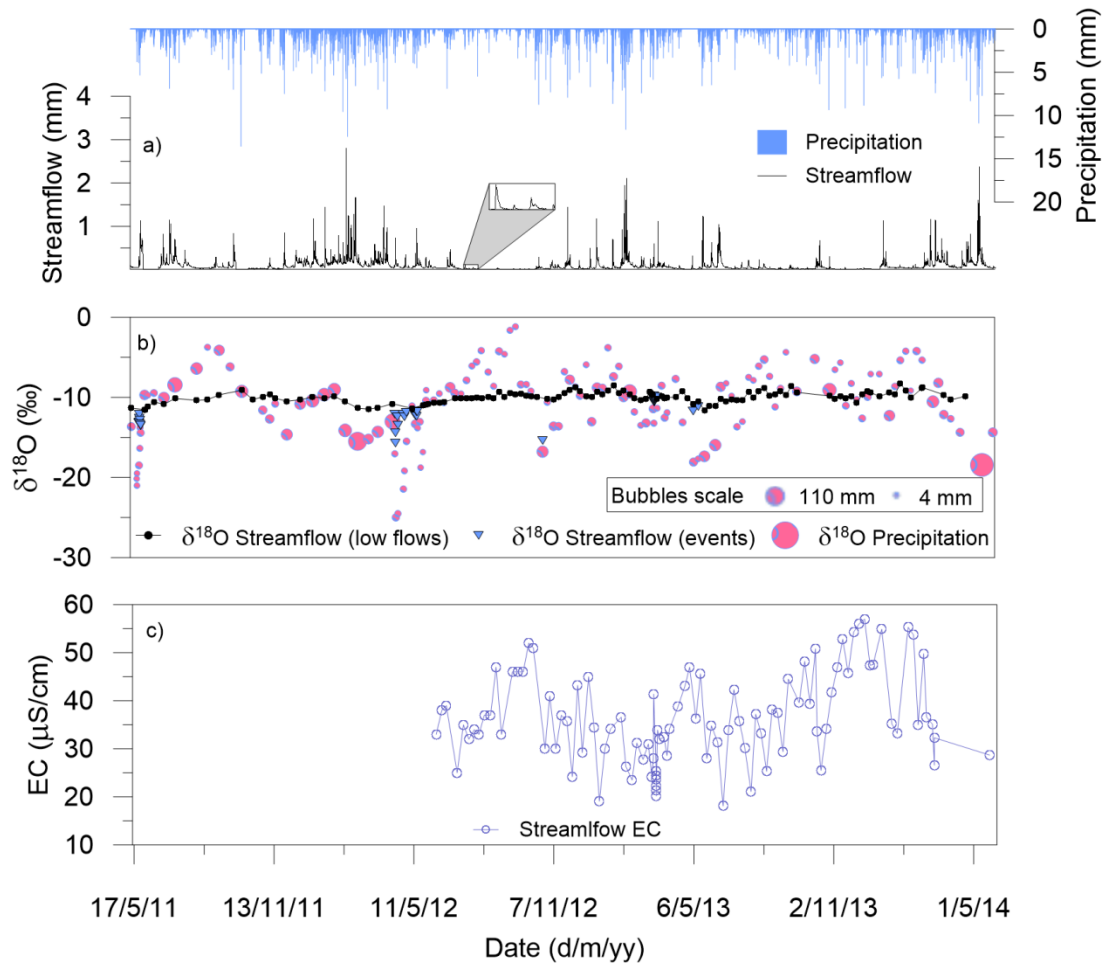


Figure 2. a) Hourly precipitation and unit area streamflow; b)  $\delta^{18}\text{O}$  isotopic composition in precipitation and streamflow for 3 years (May 2011-May 2014); and c) electrical conductivity for 2 years (May 2012-May 2014) at the catchment outlet (M8, see location in Figure 2). The size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

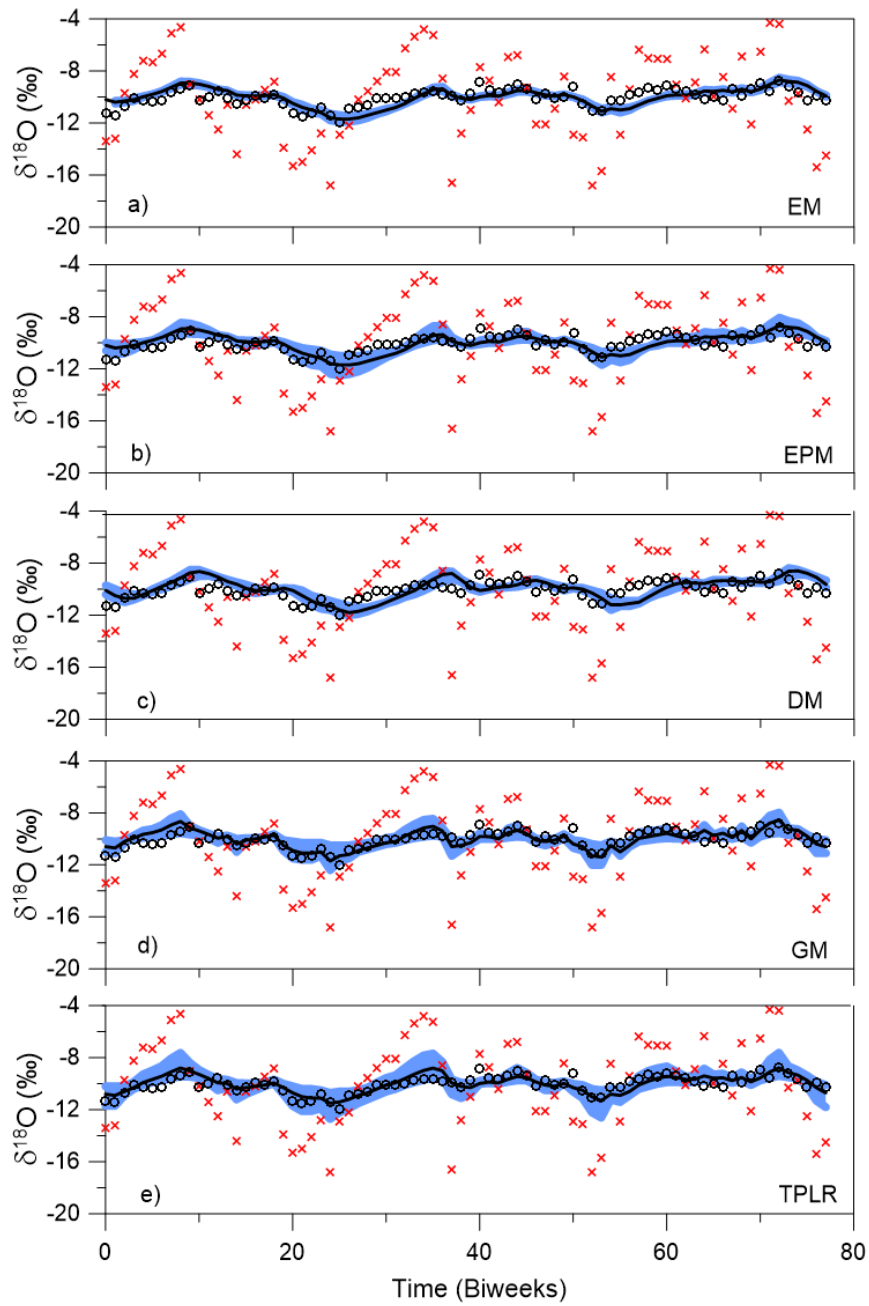


Figure 3. Fitted results of the five lumped parameter models used to simulate the temporal variability in the  $\delta^{18}\text{O}$  streamflow composition at the outlet of the basin (M8). (a) Exponential model (EM); (b) exponential-piston model (EPM); (c) dispersion model (DM); (d) gamma model (GM); and (e) two parallel linear reservoir model (TPLR). The open circles represent the observed isotopic composition in streamflow; the red crosses represent the isotopic composition in precipitation; the black line represents the best simulated isotopic composition

1 in streamflow according to the KGE (Gupta et al., 2009) objective function; and the blue  
2 shaded area corresponds to the 5-95% confidence limits of the possible solutions from the  
3 parameter sets within the range of behavioral solutions, i.e., solutions which yield at least  
4 95% KGE.

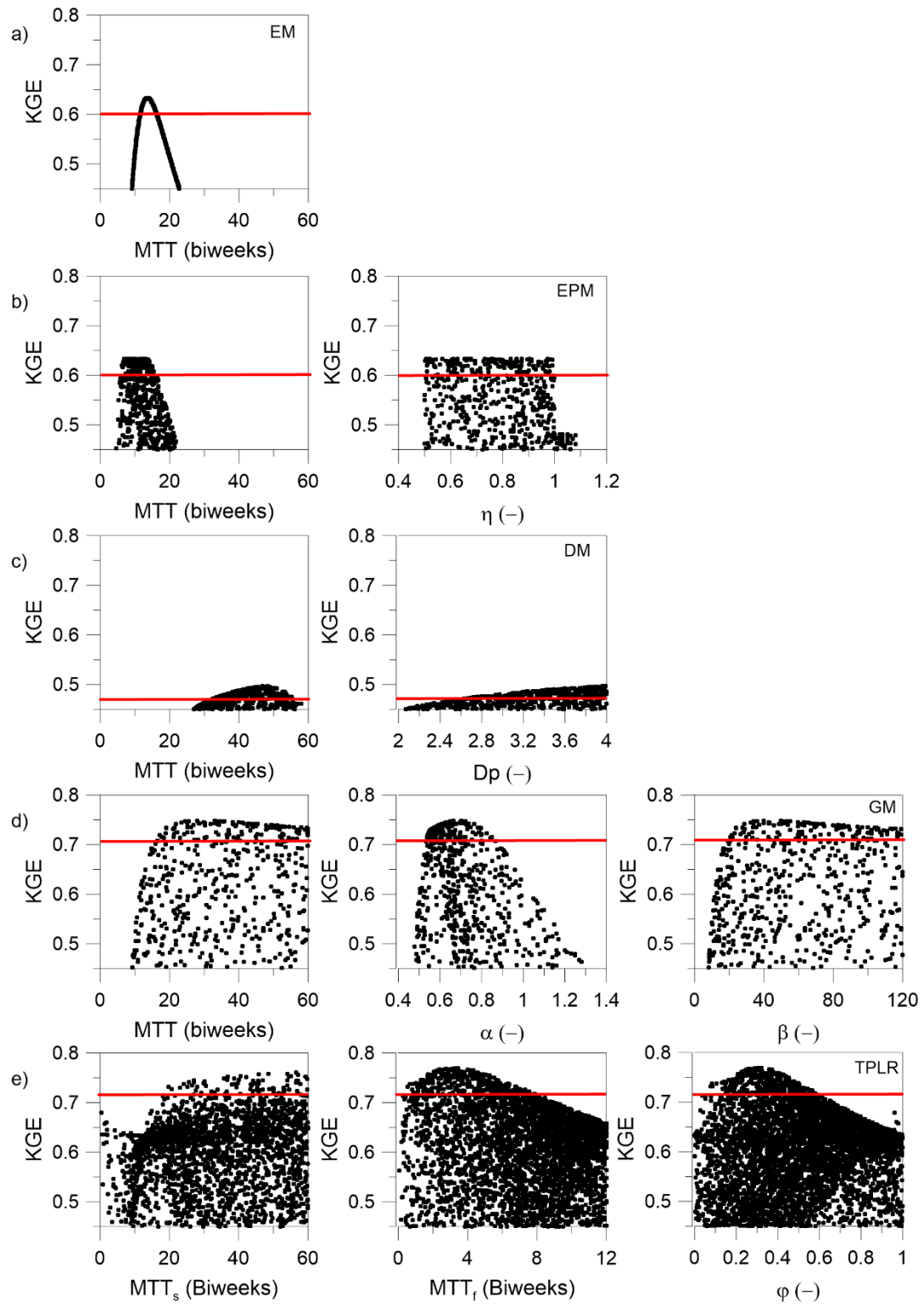


Figure 4. Monte Carlo simulations of the fitted parameters of the five lumped parameter models used to simulate the  $\delta^{18}\text{O}$  streamflow composition at the outlet of the basin (M8). a)

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).

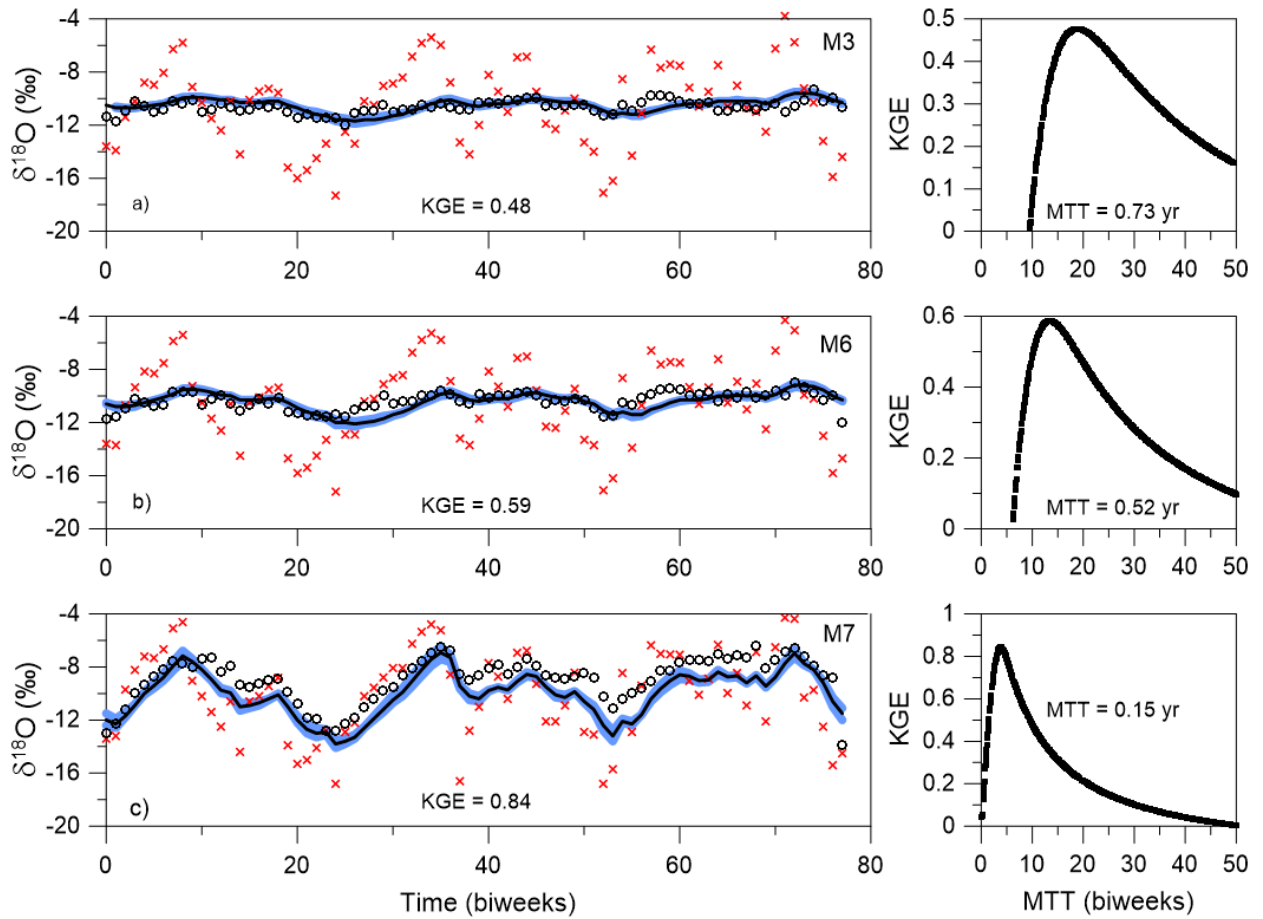
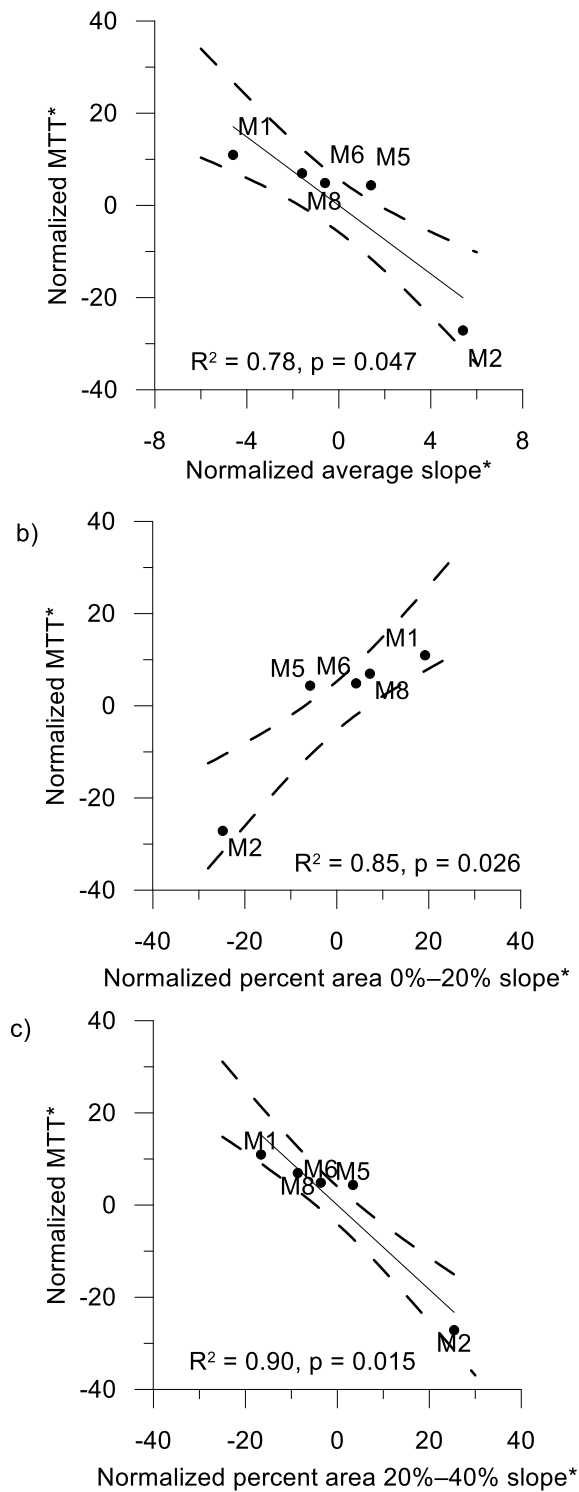


Figure 5. Fitted results and Monte Carlo simulations of the fitted parameters of the exponential model (EM) used to simulate the  $\delta^{18}\text{O}$  streamflow composition in the catchments: a) M3; b) M6; and c) M7. The open circles represent the observed isotopic composition in streamflow; the red crosses represent the isotopic composition in precipitation; the black line represents the best simulated isotopic composition in streamflow according to the KGE objective function; and the blue shaded area corresponds to the 5-95% confidence limits of the possible solutions from the MTT fitting parameters within the range of behavioral solutions, i.e., solutions which yield at least 95% KGE. Panels on the right represent the explored parameter range for the MTT parameter and the KGEs associated to each of them.



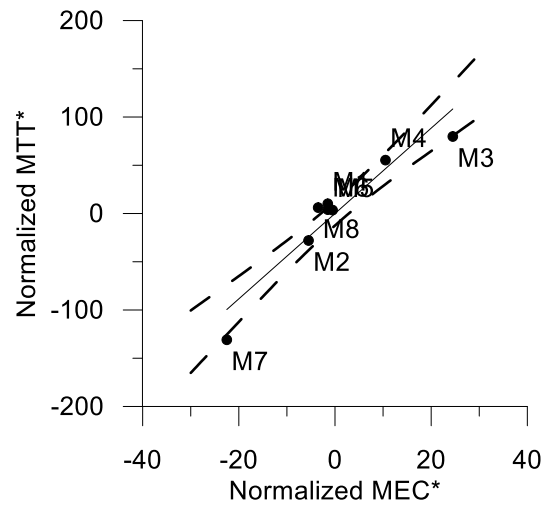


1

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%;

1 and c) catchment area with slopes between 20% and 40%. Catchments M3 and M4 (additional  
2 spring water source, see Figure 1) and M7 (at a flat hilltop disconnected from the hillslopes)  
3 are not included in the regressions. Solid lines are linear regressions and dashed lines are the  
4 90% confidence intervals of the regressions. \* Indicates parameters are normalized by their  
5 mean.

6



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 parameters are normalized by their mean.