

Dear Editor, dear Referees,

We would like to thank you for the valuable feedback provided for our manuscript “Land use alters dominant water sources and flow paths in tropical montane catchments in East Africa” and for the opportunity to resubmit a revised version.

5 The comments from the referees were very helpful to improve the manuscript. We restructured the manuscript, included the Young Water Fraction approach (Kirchner, 2016) and re-evaluated our results, as suggested by the referees and the editor. Please find our point-by-point responses (in blue) to the comments of all referees (in black) below. Page and line number in the responses refer to the revised version of the manuscript (no tracked changes). We believe that the modifications based on the referees’ comments have resulted in an improved manuscript and hope that it is now suitable for consideration for
10 publication as research paper in Hydrology and Earth System Sciences.

We look forward to hearing from you.

Kind regards,

15 Suzanne Jacobs

Referee #1

General comments:

The subject of the manuscript may be of interest for HESS readers, it represents a relevant work volume and is well presented,
20 but there are several formal and methodological issues that deserve a major revision of the manuscript before being acceptable for publication. The first issue is in the title of the paper itself. It is very assertive while the results of the work, taking into account the associated uncertainties, are much less convincing. So, I suggest to change the title or just to put it into an interrogative form.

25 *Reply:* We understand the concern of the referee and changed the title to: “Assessment of hydrological pathways in East African montane catchments under different land use”.

The second but main issue is respect to how Mean Transit Times (MTTs) have been obtained for stream waters. The several aspects of this issue are the following ones:

1) The MTT methodological explanation is adequate (if some citation of GLUE development papers is included) but it fails to
30 describe how a (400?) year-long ^{18}O input function has been obtained to feed the lumped models when the rainfall sampling period was just 75 weeks long.

Reply: The values between brackets shown in the third column of Table 2, i.e., $\tau = [1-400]$, correspond to the range of values that the MTT parameter could take for solving the convolution integral. The units of this parameter (weeks) were unfortunately omitted from the original manuscript, but this has been corrected in the revised version. The 400 weeks (= 7.7 y) is a period

long enough to cover the maximum possible values that the MTT could take for solving the convolution function. According to the literature, it is appropriate to use stable water isotopes for MTT estimations of up to 4 or 5 years, but we mention the potential limitation of this method in P. 14, L. 28–30. We acknowledge that it is advisable the length of the sampling period to be at least comparable to (or longer than) the length of the estimated MTT. However, for remote tropical montane catchments, data are generally scarce because of limited funding and challenging accessibility. We added an explanation and a justification on how the data obtained during the sampling period were used to feed the lumped models (P. 7, L. 8–12).

2) It has been shown that MTT determinations using seasonal variations of tracer signals (such as the ^{18}O one) cannot provide acceptable results longer than a few months in stream (mixed) waters due to the strong non-linearity of the driving function (Kirchner, 2016).

Reply: We acknowledge that the approach presented by Kirchner (2016) is a valuable contribution to the study of the rainfall-runoff behaviour of natural systems and that natural systems are implicitly heterogeneous. We added P. 6, L. 20–31 to the methods to explain how we used the YWF as indicator of the degree of heterogeneity. The amplitude of precipitation and stream water signals and YWF in the three sub-catchments (presented in Section 3.4) suggest that the study area is fairly homogeneous, which would justify for the use of the convolution method for MTT estimates, as applied in our study.

3) For such damped tracer signals in the stream waters and low model efficiencies, much larger MTT uncertainties should be obtained, showing results coherent with point 2. My opinion is that the small uncertainties obtained are an artefact due to the way the behavioural models have been selected in the GLUE exercise. Accepting only parameter sets with efficiency just 5% lower than the optimal one might be appropriate for high efficiency values, but not in the case of such low efficiency values because the range of behavioural parameters becomes too narrow. Some GLUE published works dealing with large uncertainties sensibly used all parameter sets with positive efficiencies. Alternatively, all the parameter sets with such low efficiencies might be rejected as a way to resolve that the method is inappropriate.

Reply: We agree with the comment of the referee, and explained the choice and limitations of the applied subjective limits: “Due to the low fitting efficiencies and selected threshold of 5 % below the highest obtained NSE, the uncertainty bands for all sites were relatively narrow (Fig. S5–18). The uncertainties should therefore be considered as means of comparison of model parameters between sites and cannot be compared to uncertainties obtained in other studies with higher NSE values.” (P. 10, L. 16–19). Additionally, we provided the results of the GLUE analysis as supplement to the manuscript (Fig. S5–18).

In the case of stream waters, I suggest to remove the proposed MTT determinations, unless the above points are adequately answered. The authors may reasonably continue using the clear damping of the tracer signal in the stream waters as an indicator of several-year old waters, and even the differences in the temporal variability of the tracer signals might be used to indirectly rank the waters MTTs. In the case of soil mobile waters, I suggest the application of some analysis of the significance of MTT differences found, using the MTTs likelihood distributions provided by the GLUE exercise.

Reply: After clarifying all aspects requested by the referee (detailed in responses to previous comments and incorporated in the revised manuscript), we believe that it is worth keeping the MTT determinations, since these results will provide a knowledge base in this remote study area for which no previous data are available. We included the cumulative density functions (CDF) for all analysed stream water and mobile soil water sites and for both models (EPM and GM), considering the range of associated uncertainty, as supplemental information to the manuscript (Fig. S19–20), and compared the transit time distributions of results from both models for each site.

The third but also relevant issue refers to the End Member Mixing Analysis (EMMA) for the Small Holder Agriculture (SHA) stream waters. The use of the well SHA-WE.b as end member representative of groundwater chemistry is not reasonable. One well in the headwaters with solute concentrations very different from those in other nine wells may represent either a different water source or some pollution effect, but it is not sensible to hypothesize that it can be a relevant source for stream water when its chemistry is very local as it is not transmitted to the other well waters. The analysis done can be shown as a test, but it cannot be taken as representative because groundwater contribution becomes underestimated and the other components overestimated. If well understood, the use this end member with very low contributions as representative of groundwater is depicted in Figure 7 (b), although this is inconsistent with some text in the conclusions: “A second, different groundwater source was identified in the smallholder agriculture catchment, which was an important end member during baseflow”.

Reply: We understand the concern of the referee about the use of a single ‘outlier’ to explain stream water chemistry and mixing of different end members in a catchment and, ideally, we would have identified another end member which would fit the end member model better than SHA-WE.b. Nevertheless, of the sampled end members, SHA-WE.b is the only end member that explains the stream water chemistry of samples taken during the dry season (Fig. 4). As mentioned in the discussion (P. 13, L. 8–10), it is likely that end members are missing. Considering that this is the first effort to characterize hydrological flow paths and water provenance in Kenya, we think that the use of SHA-WE.b is reasonable to present preliminary findings, given the available data.

We argue that SHA-WE.b is a groundwater source based on its chemical composition: “Shallow well SHA-WE.b had trace element concentrations that were much higher than those of the other nine sampled shallow wells SHA-WE.a, but similar in magnitude to solute concentrations in a spring in the Andean Páramo (Correa et al., 2017) and deep groundwater in Tanzania (Koutsouris and Lyon, 2018). Since the trace elements with high concentrations in SHA-WE.b correspond with elements related to geology (e.g. Li, K, Na and Rb), it is likely that this source is groundwater-related.” (P. 10–11, L. 31–4). Additionally, we consider both the wetland SHA-WL and SHA-WE.a/SHA-WE.b as groundwater sources. Since SHA-WL is an important groundwater end member, especially during the wet seasons, referring to SHA-WE.b as a second groundwater source seems a reasonable conclusion. We did, however, remove the questionable sentence from the manuscript.

Another more formal issue is the use of the ‘soil water’ expression to identify the samples of mobile waters sampled at different soil depths. In the current water isotope literature, ‘soil water’ refers to the total (bulk) water contained in the soil, including

mobile and immobile waters. In the methods section it is clearly justified that just mobile water was sampled, but in the abstract, figures and conclusions, some adjective such as ‘mobile’ or ‘free’ should be added to ‘soil water’ in order to avoid any misunderstanding.

5 Reply: We agree with the referee that this could cause misunderstanding and have therefore added ‘mobile’ to all references to the soil water samples throughout the manuscript.

Specific comments:

P. 3, L. 21: some hypothesis on how rain water reaches the stream should be added

10 Reply: We revised our hypotheses to: “Based on these results, we hypothesised that (a) the natural forest sub-catchment has a longer MTT than the tea plantation and the smallholder agriculture sub-catchments, because precipitation contributes less to streamflow in the forest catchment, and (b) the precipitation that contributes directly to streamflow will reach the stream through surface runoff in the tea plantation and smallholder agriculture sub-catchments and through shallow sub-surface flow in the forest sub-catchment.” (P. 3, L. 20–24).

15 P. 7, L. 8: Nash & Sutcliffe (1970)

Reply: We included the reference in the sentence (P. 7, L. 19).

P. 8, L. 11: GLUE was first described in Beven & Binley (1992)

Reply: We included the reference in the sentence (P. 7, L. 22).

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P. 3, L. 21: “Ten shallow wells (nine named SHA-WE.a and one SHA-WE.b)...”

Reply: We revised the sentence: “Ten shallow wells (nine named SHA-WE.a and one SHA-WE.b) in SHA were sampled twice.” (P. 5, L. 24–25).

25 P. 8, L. 10 and 15: the units for the slopes are not correct.

Reply: Thank you, that is correct, we removed the incorrect units from the text (P. 8, L. 21; P. 8, L. 25).

P. 8, L. 15; P. 10, L. 9: this slope value seems too small looking to the graphs.

30 Reply: We repeated the analysis and had a closer look at the data. Although it does indeed look incorrect based on Fig. 2, the value for the slope is correct.

P. 8, L. 31: the contribution of precipitation to SHA stream waters is overestimated due to the role of SHA-WE.b commented above.

Reply: We agree with the reasoning of the referee, but decided to keep SHA-WE.b in the analysis for the reasons explained above. However, we emphasized that overestimation of the contribution of precipitation is likely due to the absence of a more appropriate end member: “However, the contribution of precipitation (57.4, 45.3–78.6 %) in SHA is probably overestimated due to the inclusion of shallow well SHA-WE.b as end member.” (P. 12, L. 7–8).

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Referee #2

General comments:

(1) Data presentation and analysis

There is some concern with taking these isotopic data into the convolution modeling. Specifically, the length of observation record is not overly long which limits the ability to map out some realistic travel times here. The uncertainty gets very high in this regard. So, at best one could argue that the MTT estimations are just first-order assessments for comparing between the catchments. Further, taking on a classic time invariant MTT estimation is a bit troublesome with regard to the potential for comparisons. Namely, the travel times for each catchment likely shift with wetness (storage) condition and this dynamic shifting (mixing) likely represents itself differently throughout the one and a half year been considered here. As such, it is difficult to separate the impact of the land use on MTT from the variability of the flow on the MTT – more likely these aspects compound (and confound) the issue (see van der Velde et al., 2015, Consequences of mixing assumptions for time-variable travel time distributions, Hydrological Processes). Some consideration of these aspect must be taken up within the analysis – or at a minimum in the discussion with regards to impacts on the results and interpretations. As these estimates are currently presented they tend to over-sell the ability of such analysis and what we can truly learn from them. These MTT estimation techniques are far from perfect and difficult to connect with mechanisms. It would be unfortunately for the uncertainty inherent in them to conflate with our understanding of these sites. Actually upon deeper reading, I am not sure the MTT analysis is truly justified or even needed in this study. The high uncertainty and extrapolation needed to make the convolution effort make sense and to interpret the results are not justified. This study would be more powerful to be a data presentation with an EMMA analysis constrained by the uncertainty inherent in these data which were hard to collect. The current MTT analysis is just too thinly supported by the minimal data and has no real consideration of variability versus uncertainty to allow for a rigorous interpretation. I would strongly recommend removing these parts of the study and focusing in on the other aspects to make for a sound and clear analysis. If the MTT estimates are to be kept, I think they need to be made much more robust through uncertainty analysis and/or mechanistic model explorations (the GLUE presented just gets at modeling fitting). Further, the role of variability versus errors given limited sampling in time and space must be extensively considered. Given the audience of HESS I feel this loose application of MTT convolution efforts weakens the case for this research and is not needed given there are several strong aspects already.

Reply: We thank the referee for the insights provided. We certainly acknowledge that the application of the convolution method to estimate MTTs, generally applied for time-invariant conditions, does not allow a precise estimation of the effect of land use on MTT. However, due to the limited information on transit times for tropical montane catchments of Africa, compared to the amount of information available for montane catchments of high latitudes, we consider valuable to include our stable isotope data and the MTT estimations in the manuscript. In the revised manuscript, we emphasized that our isotope data and the MTT estimates derived from them, serve as a first characterization of the water MTTs in these tropical catchments (P. 13, L. 21–23). Based on the magnitude of the estimated MTTs of stream water (of the order of years), we also recognise that with the available data it is not possible to discern whether these small differences (among catchments MTTs) are actually caused by

differences in land use (P. 12, L. 22–24). We explained the criteria used to assume stationary conditions (Section 2.4 and 3.5), and emphasised the limitation of the MTT estimates due to these assumptions and the sampling period. We included the plots of the best fitting efficiencies and the associated GLUE uncertainties as supplementary material to address uncertainty in the MTT of stream water (Fig. S5–18).

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(2) Manuscript structuring

The introduction lacks any logical structure and must be improved. As currently presented, several topics are touch in an apparently random order. First montane landscapes then isotopes then MTT then tracers then EMMA and finally Kenya. The must be a general building of argument to highlight a knowledge gap that this study is trying to fill. The review of literature is rather surficial and must be improved to highlight better the current landscape surround this study to help the reader see where this study fits in with previous work.

Reply: We revised the introduction section following the suggestions of the referee.

In addition, there is some concern with regards to mixing results in with methods. The section 2.5.2 is a good example of this. To alleviate this, I would recommend adding a results section whereby you present the raw data collected (isotopic and chemistry) and characterize these data fully. That type of an overview and statistic presentation will then lay a groundwork for the more advance results. In practice, this means to expand sections 3.1 and 3.2 and allow the data to take center stage for this study – which is valid as these data are a significant contribution to the literature. As such, the data collected should be thoroughly reviewed and presented for the reader.

Reply: We expanded Section 3.1 and 3.2 to put more emphasis on the field data collected for this study. We also moved part of the methods section to the results section.

Last, the discussion section left a bit to be desired. I felt there was much text in this section that could find a better home in results as it just highlights the findings of this current study. There could be expansion on the limitations and implications of this study for the region or these types of regions. That shift in emphasis would likely resonate better with readers helping this study move from a place-based investigation to a more general research investigation.

Reply: We followed the suggestions of the referee to put more emphasis on the limitations and implications of this study (Section 4.4). We also moved certain parts to the results section, when we felt that it would be more appropriate.

Referee #3

General comments:

The mean transit time (MTT) estimates based on a data set covering ca. 1.5 years are likely to be highly uncertain.

5 Reply: With respect to this concern, we emphasized in the revised manuscript that the presented MTT estimates for stream water, are meant for a first characterization and comparison of the travel times of water between the sub-catchments, assuming stationary conditions. We also emphasized that this information will serve as baseline for future research in which methods like time-variant techniques, could be used: “Due to the low fitting efficiencies of the MTT models, specifically for stream water, we consider the presented MTT estimations as valuable preliminary findings. These can serve as a baseline for future studies, in which more sophisticated methods like time-variant approaches can be used.” (P. 13, L. 21–23).

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This is evident, for instance, in the similar numbers of NSE, RMSE and Bias for the streamwater and soil water samples at the sites SHA and TF (Table 3): While streamwater was sampled weekly at these sites ($n > 100$), MTT estimates were similarly uncertain for streamwater as for soil water - from which only a small number of samples was collected ($n < 17$)! Thus, based on the model performance criteria presented in the manuscript, I would not strictly believe the values obtained for streamwater either.

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Reply: We would like to clarify that the goodness of fit (NSE), RMSE and Bias, are not the same for soil water and stream water. Since the observed isotope signals of soil water have a larger amplitude than of stream water, estimations of MTT of soil waters have, in general, higher NSE, but also higher values of RMSE and Bias. Further, neither the associated uncertainties of estimations of MTT for soil water are comparable to those of stream water: uncertainty ranges for stream water (Table 5) are expressed in years while for soil waters these are in the order of weeks (Table 6). Regarding the number of samples taken for the convolution approach in order to estimate MTTs, for stream water we took $n = 75$ samples for each of the four catchments (not $n > 100$ as suggested by the referee), while for MTT estimations of soil water sites, the number of samples was $n = 46$ (OUT-S50) and $n = 47$ (NF-S15, OUT-S15) (not $n < 17$ as it is stated by the referee).

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25 Although the authors elaborate on the shortcomings of their data set with regard to estimate MTTs (Sect. 4.3), they do not consider using an alternative approach such as the young-water fraction framework (Kirchner, 2016a, b). This framework uses the seasonal cycle amplitudes of streamwater and precipitation amplitudes to estimate the fraction of water younger than ca. 3 months. Thus, with the data set presented by Jacobs et al., such an analysis might result in estimates of the young-water fractions of streamwater that are more robust than the MTTs. (Using the soil water samples from the sites NF and OUT might also reveal some interesting results, however, the data from the sites SHA and TTP are clearly too incomplete for such an analysis.)

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Reply: We thank the referee for this suggestion and have included estimates of the Young Water Fractions of stream water (YWF) in our revised manuscript (Section 3.4).

In the catchment SHA, the samples from a wetland (WL, n=4) and the shallow well (WE.b, n=2) comprised two important end-members in the 3-component mixing analysis, whereas no wetlands or shallow wells were sampled in the other two catchments. Thus, I question the comparison made between the three sub-catchments: the relative contribution of precipitation at a site is inevitably linked to the contributions of the other two end members (all components must add up to 1), and therefore the precipitation contributions of NF and TTP cannot simply be compared with the precipitation contributions of SHA.

5 Reply: The main reason that no shallow wells or wetlands were sampled in the two other sub-catchments, was that there were no similar accessible wetlands in these two sub-catchments. Specifically, the natural forest sub-catchment is highly inaccessible due to the dense vegetation and absence of footpaths. We assume, however, that springs and wetlands represent similar groundwater sources, as supported by their similar chemical composition (P. 11, L. 6–8) and are therefore comparable between the three sub-catchments. This hopefully also clarifies the referee’s comment: “[...] wetlands were only analysed for one catchment (SHA), and in the Abstract it appears as if wetlands and springs were considered equivalent end members”. With regards to shallow wells, as mentioned in the discussion (P. 13, L. 15–16) there are no shallow wells in the forest, because of absence of habitation, and within the tea plantations shallow wells are not present as all settlements have access to piped water. Therefore, although we tried to include similar end members for each sub-catchment in the design of the study, we were limited in the availability and accessibility of end member sampling sites. We acknowledge in the discussion that the models have considerable uncertainty and that this has led to over- and underestimation of end member contributions, specifically in SHA and TTP (P. 21, L. 7–16).

In general, I find the presentation of the solute concentrations of the different end members and streamwater insufficient - although this data set builds the foundation for the whole study. In the box plot (Figure 2) it is very difficult to distinguish between the different sites (vertical gridlines would help here) and end-members (distinction between the different end members would be impossible in a BW print). I suggest that the authors elaborate more on the data set, incl. uncertainties and times of sampling. Are the times of sampling representative for the flow regime at the sites or were the samples only collected during low-flow conditions? A presentation of the data similar to Figure 4 might be useful for this.

25 Reply: We changed the presentation of the data from box plots to a table (Table 3), to improve the interpretation of the solute data used in the EMMA. We also added Fig. S1–4, where the time series and sampling times for stream water samples and all end members are indicated, which is similar to Fig. 3 for the isotope data.

Abstract:

30 - The numbers presented in P. 1, L. 27–29 for the average relative contributions of springs and wetlands to streamwater are confusing: wetlands were only analyzed for one catchment (SHA), and in the Abstract it appears as if wetlands and springs were considered equivalent end members. In addition, I don’t understand how the numbers presented in P. 1, L. 29–31 confirm that “. . . catchment hydrology is strongly influenced by land use, which could have serious consequences for water-related ecosystem services, such as provision of clean water.”. Do the authors compare agricultural (i.e., de-forested) catchments to

an un-altered forested catchment (i.e., baseline scenario)? If this is the case, then the results should be presented within such a framework.

Reply: We indeed tried to identify the effect of land use (i.e. forest vs. agriculture) on hydrological flow paths, and in our understanding this is also clear from the aims and hypotheses posed in the introduction: “In this study, we used a combination of mean transit time (MTT) analysis and end member mixing analysis (EMMA) to assess the effect of land use on spatial and temporal dynamics of water sources and flow paths in catchments with contrasting land use (i.e. natural forest, smallholder agriculture and commercial tea and tree plantations) in the Mau Forest Complex.” (P. 3, L. 2–5). As explained in a response to an earlier comment of Referee #3, the similarity in solute concentrations in springs and wetlands, we consider that these end members, although named differently, represent the same groundwater source (P. 11, L. 6–8).

10

Introduction:

The different sub-sections of the introduction should be linked better. For instance, paragraphs 1 and 2 present two very different topics (tropical montane catchments and stable water isotopes, respectively), which have to be put into a common context, otherwise the reader is lost.

15 Reply: We revised the introduction to address these comments and those of referee 1 and 2.

The authors hypothesize that (a) streamwater in the natural forest sites is (on average) older than streamwater in agricultural catchments (smallholder agriculture, tea and tree plantations); (b) precipitation comprises a larger fraction of streamflow in the agricultural catchments than in the naturally forested catchment; and (c) that seasonality in rainfall causes temporal variability of these streamwater sources throughout the year. The formulations of the working hypotheses (a) and (b) are somewhat redundant: when streamflow at site A contains more precipitation (i.e., “new” water) relative to another site B, we should expect the mean transit time of Site A to be shorter. Thus, hypothesis (a) results from hypothesis (b). Regarding hypothesis (c), I don’t understand how accepting/rejecting this statement adds to the conclusions of this study. The authors discuss hypothesis (c) only briefly later in the manuscript (P. 11, L. 21–23), which makes me wonder why it is stated so prominently in the Introduction?

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Reply: We agree with the observations of the referee. We revised the hypotheses, merging (a) and (b) and removing (c) due to its lack of relevance for the presented results presented. We formulated a second hypothesis based on recommendations by Referee #1. “Based on these results, we hypothesised that (a) the natural forest sub-catchment has a longer MTT than the tea plantation and the smallholder agriculture sub-catchments, because precipitation contributes less to streamflow in the forest catchment, and (b) the precipitation that contributes directly to streamflow will reach the stream through surface runoff in the tea plantation and smallholder agriculture sub-catchments and through shallow sub-surface flow in the forest sub-catchment.” (P. 3, L. 20–24).

30

Methods:

P. 3, L. 30: What are the areal fractions of different land-use types in the main catchment (OUT)? This information would also be required to elaborate on the authors' statement on P. 13, L. 18–20: “One could also expect that, since OUT is a mixture of the three land use types dominating the sub-catchments, the MTT should be similar to or an average of the estimated MTTs of the sub-catchments.”. This statement would only be true if the three sub-catchments are representative for the areal fractions of land use in the main catchment.

We included the areal fractions in the methods: “These were nested in a 1 021 km² large catchment, referred to as the main catchment (OUT), which is characterized by a mixture of these three land use types (NF = 37.6 %, SHA = 51.0 % and TTP = 11.4 %).” (P. 3, L. 29–31).

10

2.3 Sampling and laboratory analysis: What are the instruments' measurement precision and accuracy? Especially in the case of Li, the measured concentrations ($\ll 1\mu\text{g/L}$) might be highly uncertain for precipitation and throughfall.

Reply: We did not have accuracy and precision information for all instruments used, but presented the limits of quantitation in Table S1.

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Results:

3.2 Isotopic composition: “There was no significant effect of elevation on $\delta^{18}\text{O}$ values of the precipitation samples, but precipitation samples collected at higher altitude (SHA-PC) were generally more depleted than those collected at lower altitudes (NF-PC, TTP-PC and OUT-PC).“. This sentence is confusing, please reformulate.

20 Reply: We reformulated to: “Precipitation samples collected at higher altitude (SHA-PC) were generally more depleted than those collected at lower altitudes (NF-PC, TTP-PC and OUT-PC), with a change of -0.099‰ $\delta^{18}\text{O}$ per 100 m. However, linear regression analysis revealed there was no effect of elevation on $\delta^{18}\text{O}$ values of the precipitation samples ($p = 0.08$).” (P. 8, L. 25–28).

25 Figure 6 and analysis of Figure 6: Some of the relative contributions are highly uncertain, however, I miss a proper uncertainty analysis here. Although the authors discuss various sources of uncertainty in Sect. 4.2., a quantitative uncertainty analysis is still missing. At least, showing the error bars in Figure 6 would be helpful to interpret the results with more caution (i.e., Could the variability of the end members be an artefact of uncertainty in the EMMA?, P. 11 L. 21–23)). In addition, the Abstract, the authors present the average contributions without any uncertainty measures, which might be misleading.

30 Reply: We ran an uncertainty analysis with bootstrapping and included the uncertainty measures in Fig. 5. We also emphasized the uncertainty in our results in the discussion, to make clear that the results presented in this study are preliminary findings, forming a knowledge base for more in-depth research into the hydrological functioning of these and other African tropical montane catchments.

Discussion:

4.2 Dominant water sources: Based on another study in the NF catchment (Jacobs et al., in review) the authors conclude that in the NF catchment precipitation reaches the stream network via shallow sub-surface flow. Short residence times in the shallow subsurface thus result in dilution effects in streamwater. However, for the TTP catchment, the authors claim that “. . . surface runoff could have a different chemical signature than precipitation. . .” (P. 11, L. 13), which somewhat contradicts their previous statement in L. 3: “Therefore, if event water, i.e. precipitation or throughfall, is only in contact with the soil for a short time (e.g. several hours), the chemical composition of the water that enters the stream might be comparable to the composition of precipitation or throughfall.” Please clarify this.

Reply: Revision of the discussion to address comments by all referees removed this confusing point from the manuscript.

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Specific comments:

P. 8, L. 13: Were these evaporated samples used in the analysis? Please clarify.

Reply: We added: “Although these samples were not used for the development of the LMWL, they were included in the mean transit time (MTT) analysis.” (P. 8, L. 23–24) to clarify.

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P. 9, L. 28: “. . . has been observed elsewhere as well.” – Where exactly? Are these sites comparable to the sites of this study?

Reply: We changed this sentence to: “This has also been observed in Canada (Ali et al., 2010) and the Brazilian Amazon (Chaves et al., 2008; Germer et al., 2007), and can be attributed to seasonal variations in plant growth and dry and wet atmospheric deposition of K and Mg originating from biomass burning in our study area.” (P. 10, L. 28–31).

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P. 12, L. 15: An alternative method to sample soil water would be suction lysimeters.

Reply: We agree with the observation of the referee that lysimeters could be used for soil water sampling. We therefore added: “Alternatives for wick samplers, such as suction lysimeters, should be used to avoid contamination of soil water samples.” (P. 13, L. 19–20).

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P. 14, L. 23: “Due to the similar soils. . .”

Reply: This sentence was removed during revision of the manuscript.

Referee #4

General comments:

Given that, the available isotopic data is only 1.5 years long the authors should provide an assessment of the uncertainty in the computed MTT? The performance of the fits by the Gamma and EPM are actually similar yet the MTT for OUT_S15 was different between these two models. How do you explain that? It is not clear how the authors chose the Gamma and EPM functions. Did they consider what model had better constrained parameters? In addition to the modelling shortcomings, how can MTT estimates calculated from 1.5 years of data provide information about the hydrologic impacts of different land covers?

Reply: We added a supplement with detailed plots of the best solutions and associated uncertainty ranges for every stream and mobile soil water site (Fig. S5–18). Indeed, the performance of the fits to the objective function (NSE) for Gamma and EPM are quite similar for soil water, but the estimated MTTs are not different. We discuss the performance of both models for soil water in the discussion: “However, a simpler exponential distribution model (EM) might have been equally appropriate, since the parameter range of behaviour solutions of the gamma model (GM) and the exponential piston flow model (EPM) suggest that both models could be simplified to an exponential distribution model (EM). In order to avoid over-parametrization, models with fewer parameters (in this case EM) are preferred when they provide comparable results.” (P. 14, L. 2–5). Furthermore, the justification of model selection is described in Section 2.5 (P. 7, L. 13–16): “Two-parameter models such as the gamma model (GM) or the exponential piston flow model (EPM) are commonly used for MTT estimations (Hrachowitz et al., 2010; McGuire and McDonnell, 2006). These models were identified by Timbe et al. (2014) as most suited to infer MTT estimations of spring, stream and mobile soil water in an Andean tropical montane forest catchment, and were therefore applied in our study (Table 2).” We agree that a 1.5-year dataset is not long and that ideally it should cover a period as long as or longer than the MTT, but one has to consider that no data were available for the African montane forest. Furthermore, due to limited funding and accessibility in such remote areas, it is challenging to collect a long-term dataset for stable isotopes. Considering the conditions in the study area and the requirements for MTT analysis, we think it is reasonable to present the estimated MTTs for the three sub-catchments and main catchments as first and preliminary findings, as long as its uncertainty is shown.

I wonder if a first step should be a hydrometric analysis that compares land covers and that can informed the findings form the MTT in light of physical processes. In addition, there might be interesting patterns in the isotopic data alone in terms of means per location, per season, comparisons across soil, stream, groundwater, and precipitation that would allow contrasting the different land covers. I am looking a figure 3 thinking: there is many data that have not been appropriately described in the paper. My point is that the isotopic data can we used on other ways different from in convolution equation for MTT.

Reply: As suggested by other referees, we expanded the presentation of the raw isotope data in Section 3.2 to give it a more prominent position in the manuscript. This hopefully also addresses the concern of Referee #4 that not all data has been described appropriately in the paper. Additionally, we included the calculation and analysis of the young water fraction (YWF) (Kirchner, 2016) of the analysed catchments (Section 3.4).

The organization of the paper and its content is insufficient. a. The introduction is no short and does not set up the problem well. It is not clear what would the contribution of this study be nor how it fits with previous literature.

Reply: The introduction section is completely revised based on suggestions by several referees.

- 5 b. Methods: It to short and refers the reader to a paper in review. A more comprehensive description is in order. The methods indicated that precipitation was estimated using Thiessen polygons based on the information (I assumed, from the nine tipping buckets) however the results from this analysis is never presented in the results section. How variable is precipitation in space and time in this system?

10 Reply: The current version of the manuscript is already quite long. The study area and collection of discharge and precipitation has been described extensively in other publications (e.g. Jacobs et al. 2017 and the manuscript under review, which is now published as Jacobs et al. 2018). We therefore decided not to repeat this in the current manuscript. The precipitation results have indeed not been presented separately in the results, as this has been done elsewhere and is not the objective of this manuscript, but rainfall data is displayed in Fig. 4 as weekly precipitation. This also clearly shows the temporal variation and differences in precipitation between the four catchments.

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c. The result section is vague. For instance on 3.1. (Solute concentrations) the authors do not describe any one solute but instead talk all simultaneously as high or low. The result sections should include some actual numbers so that the reader knows what low or high mean. Likewise, there is no information in the results about how the values for the isotopic concertation vary in space and time per precipitation, stream, soil water, etc.

20 Reply: The challenge with the presentation of a large dataset, as used for this analysis, is that the text can become very long when all solutes for all sites and end members are described in detail. We modified Section 3.1 to include more detailed information, but decided against explaining all variations in solute concentrations in detail in the text, as this would make the results section unnecessarily long. We nevertheless hope that the modifications provide a satisfactory level of detail to address the concern of Referee #4. With regards to the variations in isotopic values, we added a table with mean, standard deviation,
25 minimum and maximum values for $\delta^{18}\text{O}$ to the manuscript (Table 4).

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Land use alters dominant water sources and flow paths in tropical montane catchments in East Africa Assessment of hydrological pathways in East African montane catchments under different land use

5 Suzanne R. Jacobs^{1,2,3,4*}, Edison Timbe⁵, Björn Weeser^{3,6}, Mariana C. Rufino^{2,7}, Klaus Butterbach-Bahl^{1,4}, Lutz Breuer^{3,6}

¹Karlsruhe Institute of Technology – Institute of Meteorology and Climate Research, Atmospheric Environmental Research (KIT/IMK-IFU), Kreuzeckbahnstr. 19, 82467 Garmisch-Partenkirchen, Germany

10 ²Centre for International Forestry Research (CIFOR), c/o World Agroforestry Centre, United Nations Avenue, Gigiri, P.O. Box 30677 – 00100 Nairobi, Kenya

³Institute for Landscape Ecology and Resources Management (ILR), Justus Liebig University, Heinrich-Buff-Ring 26, 35392 Giessen, Germany

⁴Mazingira Centre, International Livestock Research Institute (ILRI), P.O. Box 30709 – 00100 Nairobi, Kenya

⁵Faculty of Agricultural Sciences, University of Cuenca, Av. Doce de Octubre, Cuenca, Ecuador

15 ⁶Centre for International Development and Environmental Research (ZEU), Justus Liebig University, Senckenbergstr. 3, 35390 Giessen, Germany

⁷Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, United Kingdom

*Current address: Centre for International Development and Environmental Research (ZEU), Justus Liebig University, Senckenbergstr. 3, 35390 Giessen, Germany

20 *Correspondence to:* Suzanne R. Jacobs (suzanne.r.jacobs@zeu.uni-giessen.de)

Abstract. Conversion of natural forest to other land uses could lead to significant changes in catchment hydrology, but the nature of these changes has been insufficiently investigated in tropical montane catchments, especially in Africa. To address this knowledge gap, we ~~identified~~ aimed to identify stream water sources and flow paths in three tropical montane sub-catchments (27–36 km²) with different land use (natural forest, smallholder agriculture and commercial tea plantations) within a 1 021 km² catchment in the Mau Forest Complex, Kenya. Weekly samples were collected from stream water, precipitation and mobile soil water for 75 weeks and analysed for stable water isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) for mean transit time estimation with two lumped parameter models (gamma model and exponential piston flow model), whereas ~~trace element~~ samples from stream water and potential end members were collected over a period of 55 weeks and analysed for Li, Na, Mg, K, Rb, Sr and Ba for end member mixing analysis. Solute concentrations in precipitation were lower than in stream water in all catchments ($p < 0.05$), whereas concentrations in springs, shallow wells and wetlands were generally more similar to stream water. The stream water isotope signal was considerably damped compared to the isotope signal in precipitation. ~~Stream water m~~Mean transit time analysis suggested long transit times for stream water was similar (~up to 4 years) in the three sub-catchments, but model efficiencies were very low. and Mean transit times of mobile soil water ranged from 3.2–3.3 weeks in forest soils and 4.5–7.9 weeks in pasture soils at 15 cm depth to 10.4–10.8 weeks in pasture soils at 50 cm depth. The dominant stream water source in the tea plantation sub-catchment was spring water (56 %), while precipitation was dominant in the smallholder agriculture

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~~(59 %) and natural forest (45 %) sub-catchments. The contribution of springs and wetlands to stream discharge increased from median 48.16.5 (95% confidence interval: 11.3–22.9), 2.1 (–3.0–24.2) and 48–50.2 (30.5–65.5) % during low flow to 22.7 (15.2–34.7), 51–53.0 (23.0–91.3) and 69.4 (43.0–123.9) % during high flow in the natural forest, smallholder agriculture and tea plantation sub-catchments, respectively. The dominant stream water source in the tea plantation sub-catchment was spring water (56 %), while precipitation was dominant in the smallholder agriculture (59 %) and natural forest (45 %) sub-catchments. These Our results confirm indicate that groundwater is an important component of stream catchment hydrology is strongly influenced by land use, which could have serious consequences for water related ecosystem services, such as provision of clean waterwater, irrespective of land use. The results further suggest that the selected transit time models might not be appropriate in tropical catchments with highly damped stream water isotope signatures. Further research, using, for example, time-variant approaches could therefore shed more light on potential land use effects on the hydrological behaviour of tropical montane catchments.~~

1 Introduction

Tropical montane forests are under high anthropogenic pressure through deforestation. Evidence from tropical montane regions in Central and South America shows that conversion of montane forests to pastures increases the contribution of surface runoff to streamflow, caused by changes in flow paths and stream water sources (Ataroff and Rada, 2000; Germer et al., 2010; Muñoz-Villers and McDonnell, 2013). This could affect the timing and quantity of water supply through reduced infiltration of precipitation and increased occurrence of flood events, and could ~~decrease-reduce~~ water quality as a result of soil erosion. In Africa, where much of the population relies on surface water as main water source, understanding the effect of land use change on water supply and quality is crucial to manage resources sustainably. However, the hydrological functioning of tropical catchments is generally less well understood than that of temperate catchments. This is specifically true for tropical montane forest catchments, as those have received less attention in hydrological research compared to the tropical lowlands. ~~Nevertheless, tropical montane forests are known for their high biodiversity (Burgess et al., 2007; Martínez et al., 2009) and provision several other important ecosystem services, including carbon storage (Spracklen and Righelato, 2014) and water supply (Céleri and Feyen, 2009; Martínez et al., 2009).~~

~~Most case~~ Several studies investigated the hydrological functioning in of tropical montane areas catchments are from in Latin America (e.g. Correa et al., 2017; Crespo et al., 2012; Mosquera et al., 2016b; Roa-García and Weiler, 2010; Timbe et al., 2014; Windhorst et al., 2014). These studies highlight the importance of soil and groundwater as source of stream water, as both Andean Páramo catchments and tropical montane cloud forest catchments showed a high contribution of pre-event water to streamflow (Correa et al., 2017; Crespo et al., 2012; Mosquera et al., 2016a). Land use change could, however, affect the relative contribution of different water sources and flow paths. Pasture catchments showed, for example, a higher contribution of event water to streamflow compared to forest catchments in the Amazon (Chaves et al., 2008; Neill et al., 2011) and shorter transit times than montane forest catchments in Mexico and the Ecuadorian Andes (Muñoz-Villers et al., 2016; Timbe et al.,

2014). Furthermore, montane catchments in the Colombian Andes showed a faster response to events in catchments with a higher grassland cover than in catchments with a higher forest cover (Roa-García and Weiler, 2010). In contrast, Crespo et al. (2012) found that montane catchments in the Ecuadorian Andes were dominated by deep ground water, irrespective of topography or land cover. Differences in climate, land use types, topography and geology, limit the potential to extrapolate the results obtained from studies in Latin America to other tropical montane catchments. This highlights the need for research on hydrological processes in relation to land use in less-studied regions, such as East Africa, where population growth puts significant pressure on forests and water resources, but where little is known about the consequences of deforestation for water supply and quality.

The Mau Forest Complex in western Kenya is the largest tropical montane rainforest in the country and considered a major 'water tower', supplying fresh water to approximately 5 million people living downstream (Kenya Water Towers Agency, 2015). However, conversion of forest to agricultural land resulted in a 25 % forest loss in the past decades (Kinyanjui, 2011). This has supposedly led to changes in flow regime (Baldyga et al., 2004; Mango et al., 2011; Mwangi et al., 2016) and increased surface runoff (Baker and Miller, 2013). This suggests that changes in dominant flow paths occurred as a consequence of land use change, but no scientific evidence is available to confirm this. In this study, we used a combination of mean transit time (MTT) analysis and end member mixing analysis (EMMA) to assess the effect of land use on spatial and temporal dynamics of water sources and flow paths in catchments with contrasting land use (i.e. natural forest, smallholder agriculture and commercial tea and tree plantations) in the Mau Forest Complex. Stable water isotopes (^2H , ^{18}O) provide a useful tool to study the movement of water through a catchment (McGuire and McDonnell, 2007). Stable isotopes, usually expressed as the ratio of heavy to light isotopes (e.g. ^2H to ^1H) relative to a known standard (e.g. VSMOW, the Vienna Standard Mean Ocean Water), are useful tracers in hydrology, since these enter the environment naturally through precipitation. The isotopic composition of water only changes due to mixing with other water sources and fractionation by evaporation and condensation. Due to decreasing costs of analysis, stable isotope based methods are used more frequently worldwide to trace water through catchments and to identify the origin and flow paths of water inputs to streams. Most case studies in tropical montane areas are from Latin America (e.g. Correa et al., 2017; Crespo et al., 2012; Mosquera et al., 2016b; Roa-García and Weiler, 2010; Timbe et al., 2014; Windhorst et al., 2014), whereas no data is available from African tropical montane catchments.

Mean transit time (MTT) (Mean transit time), i.e. the time required for rainfall to reach the stream, is a good indicator to assess flow paths, water storage capacity and mixing at the catchment scale (Asano and Uchida, 2012). Transit time also has implications for water quality, since the contact time between water and the soil will affect the chemical composition of the water that finally enters the stream through biogeochemical processes (McGuire and McDonnell, 2006). Since MTT can be influenced by catchment characteristics that are often affected by land use, such as soil cover (Capell et al., 2012; Rodgers et al., 2005; Soulsby et al., 2006) and soil depth, hydraulic conductivity properties and topographic parameters, such as slope (Heidbüchel et al., 2013; Mosquera et al., 2016b; Muñoz-Villers et al., 2016), MTT is a useful indicator to assess the effect of land use on hydrological processes, or a combination of these factors (Hrachowitz et al., 2009). Changes in vegetation cover and especially soil hydraulic properties as consequence of changes in land management can also modify MTT.

Other naturally occurring tracers, such as the elements Ca, Mg, K, Na and Fe, can also be used to study water flow through a catchment, for example through end member mixing analysis (EMMA). In EMMA, stream water is assumed to be a mixture of different 'end members' or water sources, such as precipitation, throughfall, groundwater and soil water (Christophersen et al., 1990). A quantification of the contribution of different 'end members' or water sources in a catchment, through the application of EMMA, provides relevant insight into dominant flow paths and stream water sources (Barthold et al., 2010; Burns et al., 2001; Correa et al., 2017; Crespo et al., 2012; Soulsby et al., 2003) or water provenance (Fröhlich et al., 2008a, 2008b). Previous studies have shown the advantage of combining the two approaches to improve the understanding of hydrological systems (Crespo et al., 2012; Katsuyama et al., 2009). Application of EMMA in the south-western Amazon revealed, for example, a higher contribution of surface runoff in catchments converted from forest to pasture (Chaves et al., 2008; Neill et al., 2011). Increased surface runoff could result in higher soil erosion and changes in flow paths that generally affect transport of solutes and contaminants to streams, potentially resulting in decreased water quality.

The Mau Forest Complex in western Kenya is the largest tropical montane rainforest in the country and considered a major 'water tower', supplying fresh water to approximately 5 million people living downstream (Kenya Water Towers Agency, 2015). However, conversion of forest to agricultural land resulted in a 25 % forest loss in the past decades (Kinyanjui, 2011). This has supposedly led to changes in flow regime (Baldyga et al., 2004; Mango et al., 2011; Mwangi et al., 2016) and increased surface runoff (Baker and Miller, 2013). These observations strongly suggest changes in dominant flow paths as a consequence of land use change, but no scientific evidence is available to confirm this. In this study, we combined MTT analysis and EMMA (Crespo et al., 2012; Katsuyama et al., 2009) to assess the effect of land use on spatial and temporal dynamics of water sources and flow paths in catchments with contrasting land use (i.e. natural forest, smallholder agriculture and commercial tea and tree plantations) in the Mau Forest Complex. This

We used stable water isotopes (^2H and ^{18}O) and trace element data collected over a 55 to 75 week period in the South-West Mau block of the Mau Forest Complex to assess water provenance and flow paths in three sub-catchments, dominated by either natural forest, smallholder agriculture or tea and tree plantations. knowledge is essential in the tropics, where population growth puts significant pressure on forests and water resources, but where little is known about the consequences of deforestation.

Earlier studies in the South-West Mau block of the Mau Forest Complex observed reduced infiltration rates in agricultural compared to forested land use types (Owuor et al., 2018). Furthermore, analysis of nitrate concentration–discharge relationships of rainfall events suggested more surface runoff in catchments dominated by smallholder agriculture or commercial tea and tree plantations than in a montane forest catchment (Jacobs et al., 2018)(Jacobs et al., in review). Based on these results, we hypothesised that (a) the natural forest sub-catchment has a longer MTT than the tea and tree-plantation catchment and the smallholder agriculture sub-catchments, because precipitation contributes less to streamflow in the forest catchment, and (b) the precipitation that contributes directly to streamflow will reach the stream through surface runoff in the tea plantation and smallholder agriculture sub-catchments and through shallow sub-surface flow in the forest sub-catchment. precipitation contributes more to streamflow in the smallholder catchment, followed by the tea and tree-plantation

catchment and forest catchment. Furthermore, we expected that (c) the contribution of different end members varies throughout the year due to seasonality in rainfall.

2 Methods

2.1 Study area

5 This study was conducted in the South-West Mau block of the Mau Forest Complex, western Kenya (Fig. 1, Table 1). Three sub-catchments (27–36 km²) were characterised by different land use types: natural forest (NF), smallholder agriculture (SHA) and commercial tea and tree plantations (TTP). These were nested in a 1 021 km² large catchment, referred to as the main catchment (OUT), which ~~was~~ characterized by a mixture of these three land use types (NF = 37.6 %, SHA = 51.0 % and TTP = 11.4 %). The natural forest is classified as Afromontane mixed forest, with species including *Podocarpus milanjianus*,
10 *Juniperus procera* and *Olea hochstetteri* (Kinyanjui, 2011; Krhoda, 1988). The vegetation ~~changes-transitions~~ into bamboo forest, characterised by ~~(*Arundinaria alpina*)~~, above 2 300 m elevation. The north-western side of the forest, bordering smallholder agriculture, is degraded through encroachment of farms, livestock grazing, charcoal burning and logging (Bewernick, 2016). The smallholder agriculture area is characterised by small farms of less than 2 ha, where beans, maize, cabbage and potatoes are grown interspersed with grazing fields for livestock and small woodlots of *Eucalyptus*, *Pinus* and
15 ~~*Cypressus*~~*Cupressus* spp. The riparian zones are severely degraded by vegetation clearance for grazing or cultivation and access to the river by humans and livestock. Commercial tea plantations, covering approximately 20 000 ha, are found at lower elevation (1 700–2 200 m) closer to Kericho town (0°_22'_08" S, 35°_17'_10" E) and consist of a mosaic of tea fields and *Eucalyptus* plantations, the latter mainly being used for tea processing. Riparian forests of up to 30 m width are well-maintained and contain native tree species, such as *Macaranga kilimandscharica*, *Polyscias kikuyuensis*, *Olea hochstetteri* and *Casearia*
20 *battiscombei* (Ekirapa and Shitakha, 1996). A more detailed description of land use in the study area can be found in Jacobs et al. (2017).

The geology in OUT originates from the early Miocene, with the lower part, encompassing NF and TTP, dominated by phonolites and the upper part, covering SHA, by phonolitic nephelinites with a variety of Tertiary tuffs (Binge, 1962; Jennings, 1971). The soils are deep and well-drained, classified as humic Nitisols (ISRIC, 2007; Krhoda, 1988). The area has a bi-modal
25 rainfall pattern with highest rainfall between April and July (long rains) and October and December (short rains). January to March are the driest months. Long-term annual precipitation at 2 100 m elevation is 1 988±328 mm yr⁻¹ (Jacobs et al., 2017).

2.2 Hydroclimatic instrumentation

Hydroclimatic data has been measured in the study area since October 2014 at a 10 minute interval (Jacobs et al., 2018)~~(Jacobs et al., in review)~~. Water level data was recorded at the outlet of each catchment with a radar based sensor (VEGAPULS WL61,
30 VEGA Grieshaber KG, Schiltach, Germany). Discharge was estimated from this data using a site-specific second order polynomial rating curve (Jacobs et al., 2018)~~(Jacobs et al., in review)~~. Nine tipping bucket rain gauges (Theodor Friedrichs,

Schenefeld, Germany and ECRN-100 high resolution rain gauge, Decagon Devices, Pullman WA, USA) were installed in the study area across an elevation gradient of 1 717 to 2 602 m (Fig. 1). Each tipping bucket recorded cumulative precipitation (resolution of 0.2 mm per tip) per 10 minutes. Precipitation in each catchment was calculated using Thiessen polygons.

2.3 Sampling and laboratory analysis

5 Each catchment had one site with a precipitation and throughfall sampler, constructed of a 1 litre glass bottle covered with aluminium foil and a funnel of 12.5 cm diameter with a table tennis ball to reduce sample fractionation due to evaporation (Windhorst et al., 2013). The throughfall sampler was placed inside the forest, underneath maize or sugar cane (depending on growing season) and underneath tea bushes in NF, SHA and TTP, respectively. The main catchment only had a precipitation sampler. Additionally, a passive capillary wick sampler was installed in each catchment to collect mobile soil water (Brown et al., 1989). Three polythene PE-plates of 30 by 30 cm were inserted horizontally at 15, 30 and 50 cm depth in the soil with as little disturbance of the soil above and around the plate as possible. A glass fibre wick was unravelled and draped on top of each plate to maximize surface area. The remaining wick length was led through a hosepipe to a 1 litre glass bottle, which was placed at 1 to 1.5 m depth in the soil. The installation of all samplers was carried out in September 2015 and stable isotope samples were collected from 15 October 2015 to 17 March 2017. Stream water samples were taken at the outlet of all catchments on a weekly basis. The samples were filtered with 0.45 μm polypropylene filters (Whatman Puradisc 25 syringe filter, GE Healthcare, Little Chalfont, UK or KX syringe filter, Kinesis Ltd., St. Neods, UK) and stored in 2 ml glass vials with screw cap. Weekly integrated stable isotope samples were collected from the wick, precipitation and throughfall samplers. Water-The samples were analysed for isotopic composition in the laboratory of Justus Liebig University Giessen, Germany, with cavity ring-down spectroscopy (Picarro, Santa Clara CA, USA). Precipitation water samples from all four sites were used to calculate the local meteoric water line (LMWL) with a linear regression model and the 95 % confidence interval was estimated for the slope and intercept. Only samples with a sampling volume of more than 100 ml were included to avoid the effect of evaporative enrichment of small sample volumes stored in the collector over the period between sample collections (Prechsl et al., 2014). A linear regression model was also used to assess the effect of elevation on isotope signatures. For end member mixing analysis (EMMA), samples were filtered with 0.45 μm polypropylene filters and collected in 25 to 30 ml-HDPE bottles (25–30 ml) with screw cap. Samples were immediately acidified with nitric acid to $\text{pH} < 2$ with nitric acid and stored frozen until analysis for trace elements Li, Na, Mg, Al, Si, K, Ca, Cr, Fe, Cu, Zn, Rb, Sr, Y, Ba, Ce, La and Nd with inductively coupled plasma mass spectrometry (ICP-MS) in the laboratory of Justus Liebig University Giessen, Germany ($n = 122$) or the University of Hohenheim, Germany ($n = 231$). At the University of Hohenheim, samples were analysed for Al, Ca, K, Mg, Na and Si with inductively coupled plasma optical emission spectrometry (ICP-OES) instead of ICP-MS. Samples with values below the limit of quantitation (Table S1) were excluded. Differences in solute concentration between end members within each catchment and between catchments were assessed using the non-parametric Kruskal-Wallis test and Conover-Iman posthoc test. Samples for EMMA were collected between 15 October 2015 and 21 October 2016. Weekly samples were taken for stream water, while precipitation and throughfall were sampled approximately every 4–6 weeks ($n =$

9–11). Due to difficult access to sampling sites, other potential water sources were sampled less frequently: wetland SHA-WL ($n = 4$) and spring NF-SP.b ($n = 3$). Springs NF-SP.a and TTP-SP.a were a combination of samples taken at different locations rather than different points in time with $n = 2$ and $n = 5$, respectively. Ten shallow wells (nine named SHA-WE.a and one SHA-WE.b) in SHA were sampled twice. Initially all samples for this end member were combined, but SHA-WE.b showed a strongly different chemical composition ~~that strongly differed from than~~ the remaining other samples and was therefore treated as a separate end member. No separate end member sampling was carried out for OUT, except for one spring sample and regular precipitation samples. Since all end members from the sub-catchments were sampled within OUT, these end members were used to identify potential streamflow stream water sources for OUT. It was not possible to use samples collected from the wick samplers for EMMA, because the glass fibre wick could have contaminated the samples and the sample volume was generally too low (< 25 ml).

2.4 End member mixing analysis

In EMMA, stream water is assumed to be a mixture of different ‘end members’ or water sources, such as precipitation, throughfall, groundwater and soil water (Christophersen et al., 1990). The EMMA was carried out following the procedures described in Christophersen and Hooper (1992) and Hooper (2003). The final set of solutes to be included in the EMMA was selected based on conservative behaviour of the solutes, which was assessed with bivariate scatter plots of all possible solute combinations, including stable water isotopes. A solute was considered conservative when it showed at least one significant ($p < 0.01$) linear relationship with another solute with $R^2 > 0.5$ (Hooper, 2003; James and Roulet, 2006). ~~In our case these were Li, Na, Mg, K, Rb, Sr and Ba, i.e. elements which are commonly used in EMMA (Barthold et al., 2011).~~

The relative root mean square error (RRMSE) was calculated based on the measured and projected stream water concentrations for the selected solutes for up to four dimensions (i.e. principal components in EMMA). This was used in combination with residual analysis (Hooper, 2003) and the ‘Rule of One’ (last included dimension needs to explain at least $1/n^{\text{th}}$ of the variation, where n is the number of solutes included in the analysis) to assess how many dimensions (d) should be included in the analysis. ~~Although higher dimensional end member mixing models had lower RRMSE scores, the residual analysis (Hooper, 2003) and ‘Rule of One’ (last included dimension needs to explain at least $1/n^{\text{th}}$ of the variation, where n is the number of solutes included in the analysis) both indicated that a 2 dimensional end member mixing model with three end members was sufficient for all catchments.~~ Median end member concentrations were projected in the 2d-dimensional mixing space of the stream water samples of the respective catchments and the three- $d + 1$ end members enclosing most of the stream water samples in this mixing space were selected for EMMA. Then, contributions of each end member to streamflow were calculated. Although it is common practice to project stream water samples that fall outside the triangle enclosed by the three selected end members back into the mixing space to constrain end member contributions to a range of 0 to 100 %, we decided to omit this step as it is indicative of uncertainty in the analysis caused by uncertainty in field and laboratory analyses, non-conservative solute behaviour, unidentified end members, and temporal variability of end members (Barthold et al., 2010). To quantify the uncertainty in end member contributions, we used a Monte Carlo approach, whereby the EMMA was performed 10^4 times for

every stream water sample in each catchment. For each simulation, the input values for the three selected end members were sampled randomly using bootstrapping. The 5th and 95th percentile were then calculated from the simulations and presented as uncertainty range.

5 2.5 Mean transit time analysis

The degree of heterogeneity in a catchment determines the methods that can be used to estimate mean transit time (MTT). According to Kirchner (2016), the estimation of MTT through tracer cycles and methods like the lumped convolution approach should be limited to homogeneous catchments for which steady state conditions apply. We used the young water fraction (YWF) (Kirchner, 2016) as indicator for the degree of heterogeneity in the study area and thus to test the appropriateness of the selected method for MTT estimation. The YWF in stream water is defined as the fraction of discharge with transit times of less than approximately 0.2 years, and can be calculated as the ratio of the amplitude of the stable isotope signal in stream water to the amplitude in precipitation. This is based on the assumption that the amplitude ratio will be proportional to the fraction of precipitation that bypasses storage (i.e. a near-zero transit time) (Kirchner, 2016). In a nested catchment set-up, as in our study, the homogeneity assumption can be tested by comparing the amplitude in the isotope signals and the YWF of the sub-catchments, since similarity in the amplitude of isotope signals and YWF of different sub-catchments is a preliminary indication of homogeneity (Kirchner, 2016), in which case traditional steady state approaches can be applied. We used the standard deviation as a proxy of the amplitude of the isotopic signal following Garvelmann et al. (2017).

2.5.1 Model selection

Because the YWF for our sub-catchments (Section 3.4) suggested homogeneity, MTT estimations of stream and mobile soil water were obtained through lumped parameter models. In this approach, the transport of a tracer through a catchment is expressed mathematically by a convolution integral (Maloszewski and Zuber, 1982) in which the composition of the outflow (e.g. stream or mobile soil water) C_{out} at a time t (time of exit) consists of a tracer C_{in} that falls uniformly on the catchment in a previous time step t' (time of entry). C_{in} becomes lagged according to its transit time distribution $g(t - t')$. Having in mind that the time span $t - t'$ is in fact the tracer's transit time τ , the convolution integral could be expressed as Eq. (1), in which $g(\tau)$ is the weighting function (i.e. the tracer's transit time distribution TTD) that describes the normalized distribution of the tracer added instantaneously over an entire area (McGuire and McDonnell, 2006).

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

The isotopic composition of precipitation was used as input, while stream water and mobile soil water were used as output. Because of the limited length of the collected time series and assuming that the seasonality of the isotopic precipitation signal was similar every year, we artificially extended the input time series of precipitation by repeating the available sampled

precipitation time series 20 times in a loop. This is common practice in studies where input data is limited (e.g. Hrachowitz et al., 2010, 2011; Muñoz-Villers and McDonnell, 2012; Timbe et al., 2014).

When using the convolution approach, any type of weighting function is referred as a lumped parameter model. In case preliminary insights of a system are to be obtained with scarce data, it is common practice to apply a set of models to analyse whether they yield similar results. Among the diverse model types, two-parameter models such as the gamma model (GM) or the exponential piston flow model (EPM) are commonly used for MTT estimations (Hrachowitz et al., 2010; McGuire and McDonnell, 2006). These models were identified by Timbe et al. (2014) as most suited to infer MTT estimations of spring, stream and mobile soil water in an Andean tropical montane forest catchment, and were chosen to apply these models applied in our study (Table 2). For EPM, the parameter η is the ratio of the total volume to the volume of water with exponential distribution of transit times. If $\eta = 1$, the function corresponds to a fully exponential one parameter model (EM), but there is no physical meaning for cases where $\eta < 1$. GM is a more general and flexible exponential type of model. If $\alpha = 1$, the GM becomes an exponential model, but when $\alpha < 1$, a significant part of the flow is quickly transported to the river. Conversely, the signal of the concentration peak is delayed for $\alpha > 1$.

The selection of acceptable model parameters was based on the statistical comparison of 5010⁴ random simulations (Monte Carlo approach), which assumes a uniform random distribution of the variables of each model. For each site and model, the performance was evaluated based on the best matches to a predefined objective function: the Nash-Sutcliffe efficiency (NSE) (Nash and Sutcliffe, 1970). Quantification of errors and deviations from the observed data were calculated using the root mean square error (RMSE) and the bias, respectively. MatLab R2017a was used for data handling and solving the convolution equation, while R was used for weighting the range of behavioural solutions (generalised likelihood uncertainty estimation, GLUE) (Beven and Binley, 1992). When using GLUE, the range of behavioural solutions is discrete. In our case, the lower limit was set to 5 % below the best fitting efficiency. In order to refine the limits of behavioural solutions, the 90 % of the prediction limits were calculated for every variable through weighted quantiles between 0.05 and 0.95.

2.5.2 — Selection of isotope data for the MTT analyses

Only $\delta^{18}\text{O}$ was used for MTT analysis, because the two measured conservative isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) showed a strong linear relationship, meaning that similar estimations could be obtained by using just one isotope (Mosquera et al., 2016a). The isotopic signals of precipitation (weekly scheme, $n = 75$) were considered as input function of the lumped parameter models. The isotopic composition of throughfall samples, which were also collected (data not presented here) were not significantly different from that of precipitation, hence the same MTT could be obtained using data from throughfall samples. All the available weekly isotope data for stream water ($n = 75$) were included in the analysis, because the seasonal isotopic signatures of stream water (i.e., TTP RV, SHA RV, NF RV and OUT RV) were considerably damped compared to the seasonal isotopic signatures of rainfall (Fig. 4). This means that, although some of the stream water samples could have been taken during interflow or high flow conditions, the isotopic signatures of those samples still showed a major component of 'old' or baseflow water.

The number of soil water samples ($n = 4-47$) was smaller than for stream water ($n = 75$). This was because wick samplers—the devices used to collect soil water—only collect the portion of the water moving through the soil, i.e. they start to collect water for soil conditions near to saturation. Only three sites had enough data to perform model calibration and were therefore considered: NF-S15 ($n = 47$), OUT-S15 ($n = 47$) and OUT-S50 ($n = 46$).

5 3 Results

3.1 Solute concentrations

Most end-members and stream water showed differences in median solute concentrations (Fig. 2). Solute concentrations were significantly lower in precipitation (PC) than in stream water (RV) in all catchments ($p < 0.05$; Table 3). Concentrations of Rb, Sr, Mg and K in throughfall (TF) were 3–40 times higher than in precipitation in the natural forest (NF), smallholder agriculture (SHA) and tea and tree plantation (TTP) sub-catchments ($p < 0.05$) and had a larger range. For throughfall, only Rb showed a significantly lower concentration in (median: $2.6 \mu\text{g L}^{-1}$) SHA than in NF ($23.8 \mu\text{g L}^{-1}$) and TTP ($15.6 \mu\text{g L}^{-1}$). All other solute concentrations in throughfall did not differ significantly between catchments. Solute concentrations in springs SP.b in NF and the main catchment (OUT), wetland WL in SHA and springs SP.a in TTP were generally not significantly different from stream water samples of the respective catchments ($p > 0.05$). Solute concentrations in spring samples SP.a in NF were up to 4 times higher than in stream water. Especially samples from shallow well WE.b in the smallholder agriculture catchment SHA (SHA) had up to 8 times higher solute concentrations for most solutes than other end-members stream water. Concentrations of Li and Na were higher in groundwater-related end members than in precipitation and throughfall. Concentrations were lowest in precipitation (PC) in all catchments, while throughfall (TF) in some catchments showed higher concentrations and more variation. These patterns were reflected in the total solute concentrations of the different end-members, although the difference between shallow well WE.b and the other end members was not as pronounced, with median concentrations ranging from 1.3 to $5.0 \mu\text{g L}^{-1}$ for Li and 1.1 to 3.5mg L^{-1} for Na in springs, wetland and shallow wells (SP.a, SP.b, WE.a, WE.b and WL) versus 0.19 to $0.62 \mu\text{g L}^{-1}$ for Li and 0.20 to 0.71mg L^{-1} for Na in precipitation and throughfall. Rb and K were correspondingly high in groundwater-related end members (median concentrations ranging from 3.2 to $34.7 \mu\text{g L}^{-1}$ for Rb and 0.6 to 10.0mg L^{-1} for K), but concentrations in throughfall in NF and TTP were similar with median concentration of 23.8 and $15.6 \mu\text{g L}^{-1}$ for Rb, and 6.1 and 4.2mg L^{-1} for K in NF and TTP, respectively. These elements (Li, Na, Rb and K), which are indicative of mineral origin, contributed on average $90.1 \pm 10.7\%$ of the total dissolved solute concentration in all samples. In NF, solute concentrations in stream water were fairly constant throughout the year, with a small increase at the start of rainy season in March 2016 (Fig. S1). A similar increase was observed for most solutes in stream water in SHA and OUT, but not in TTP (Fig. S2–4). Concentrations of K in stream water did not differ between the catchments ($p = 0.22$). The solute composition of stream water was most similar for TTP and OUT, with most solutes showing no significant difference, while NF had generally lowest concentrations for all solutes. Sr and Ba concentrations in stream water were significantly higher in SHA (median: 33.3 and $19.8 \mu\text{g L}^{-1}$, respectively) than in all other catchments ($p < 0.05$).

3.2 Isotopic composition

Isotopic values for precipitation plotted slightly above the global meteoric water line (GMWL), resulting in a local meteoric water line (LMWL) with a slope of $8.05 \pm 0.21 \delta^{18}\text{O}$ and an intercept of $15.31 \pm 0.61 \delta^2\text{H}$ ($p < 0.001$, $R^2 = 0.962$; Fig. 32). The slopes of the LMWL and GMWL were not significantly different ($p = 0.619$), but the intercepts were ($p < 0.001$). Samples with low volume (< 100 ml) fell far below the LMWL, which suggests ~~represented samples with a low sample volume (< 100 ml) affected by~~ evaporative enrichment. ~~Although these samples were not used for the development of the LMWL, they were included in the mean transit time (MTT) analysis. The slope of the linear regression for stream water samples was 5.00 ± 0.54 , which was significantly smaller than the slope of the LMWL ($p < 0.001$). There was no significant effect of elevation on $\delta^{18}\text{O}$ values of the precipitation samples, but~~ Precipitation samples collected at higher altitude (SHA-PC) were generally more depleted than those collected at lower altitudes (NF-PC, TTP-PC and OUT-PC), with a change of -0.099‰ $\delta^{18}\text{O}$ per 100 m. However, linear regression analysis revealed there was no effect of elevation on $\delta^{18}\text{O}$ values of the precipitation samples ($p = 0.08$).

~~The linear regression slope for stream water samples was $5.00 \pm 0.54 \delta^{18}\text{O}$, which was significantly lower than the slope of the LMWL ($p < 0.001$). There was very little variation in $\delta^{18}\text{O}$ isotopic values in streamflow stream water throughout the study period, as indicated by the low standard deviation ($0.26\text{--}0.47 \text{‰}$; Table 4). ~~while~~ Conversely, values for precipitation showed pronounced minima in November 2015, May 2016 and November 2016 in all catchments, coinciding with periods of high rainfall (Fig. 43). The isotopic composition of throughfall was similar to precipitation, with a Spearman correlation coefficient (r) for $\delta^{18}\text{O}$ values of 0.962, 0.978 and 0.962 for NF, SHA and TTP, respectively. The isotopic composition of mobile soil water showed more variation than stream water (standard deviation of 1.64, 1.20 and 1.35 ‰ for NF-S15, OUT-S15 and OUT-S50, respectively), but the signal was more damped than that of precipitation (Fig. 3). It was not possible to collect mobile soil water samples ($n = 4\text{--}47$) every week, because the wick samplers – the devices used to collect the samples – only collect the portion of the water moving through the soil, i.e. they start to collect water for soil conditions near to saturation.~~

3.3 End member ~~contributions~~ mixing analysis

~~The trace elements Li, Na, Mg, K, Rb, Sr and Ba in our case these displayed conservative behaviour in all catchments were Li, Na, Mg, K, Rb, Sr and Ba, i.e. elements which are commonly used in EMMA (Barthold et al., 2011) and were therefore retained for EMMA. The relative root mean square error (RRMSE; Table S2), based on measured and projected trace element concentrations in stream water, indicated that ~~Although higher-dimensional end member mixing models had lower RRMSE scores were more appropriate. However, the residual analysis (Hooper, 2003) and 'Rule of One' (last included dimension needs to explain at least $1/n^{\text{th}}$ of the variation, where n is the number of solutes included in the analysis) both indicated that a 2-~~ dimensional end member mixing model with three end members was sufficient for all catchments. The first two eigenvectors (dimensions) explained 92.4, 90.7, 89.5 and 92.4 % of the variance in stream water solute concentrations in NF, SHA, TTP and OUT, respectively.~~

Based on the projection of all end members in the stream water mixing space for each catchment, ~~it was possible to identify three end members that would enclose most of the stream water samples for NF and SHA~~ three end members were selected that enclosed most of the stream water samples (Fig. 54). However, this involved selection of two very specific sources with a low number of samples ($n = 2$), i.e. a combination of two springs NF SP.a located close to each other, sampled on the same day for NF, and two samples taken from shallow well SHA WE.b in the smallholder area. Although most stream water samples fell within the triangle of the three selected end members in NF, 42, 49 and 33 % of the samples fell outside the triangle in SHA, TTP and OUT, respectively. The sampled end members were not sufficient to capture the variability in stream water samples in TTP and OUT, with more than a third of the stream water samples falling outside the area enclosed by the three selected end members. Precipitation in all catchments plotted similarly in the mixing space of OUT. Also springs OUT SP.b and NF SP.b and the combination of nine shallow wells SHA WE.a, as well as springs TTP SP.a and NF SP.a and wetland SHA WL were similar, whereas there was considerable variation in chemical composition of throughfall (TF) samples, both within and between sub-catchments. Shallow well SHA WE.b plotted far outside the mixing space of NF, TTP and OUT.

Predicted stream water solute concentrations, based on median solute concentrations of the selected end members, matched well with observed stream water solute concentrations ($R^2 > 0.85$ for most solutes). The poorest predictions were for Li in TTP ($R^2 = 0.683$) and Ba in SHA ($R^2 = 0.755$). The EMMA resulted in a dominant contribution of precipitation (PC) in NF (median: 45–46.4%, 95 % confidence interval: 30.5–54.4 %) and SHA (59–57.4%, 45.3–78.6 %), while spring water (TTP-SP.a) dominated in TTP (55.6–%, 45.3–70.7 %) (Fig. 65). The three selected end members for OUT generally had similar contributions ranging from (30– to 40 %). In NF and OUT the contribution of precipitation dropped towards the end of the dry season from more than 50 % to less than 10 % (March–April) and increased again to around 25 % during the long rains. In this period, the contribution of throughfall was higher in NF (62 %) and OUT (65 %). Conversely, in SHA a strong drop in contribution of precipitation (from 86 to 30 %) was observed at the start of the long rains in May 2016. Contributions of end members during the second half of the study period in SHA differed from the first half, with an increase in contributions of wetland SHA WL from 1 to 58 %. Generally, the contribution of the wetland WL in SHA was increased from 2.1 (–3.0–24.2) % during low flow to 53.0 (23.0–91.3) % higher during periods of high flow, in SHA (51 %) — similar to contributions of springs SP.a in NF (16.5, 11.3–22.9 % to 20.7, 15.2–34.7 %) and TTP (50.2, 30.5–62.5 % to 69.4, 43.0–123.9 %). Conversely, shallow well SHA-WE.b in SHA showed highest contributions during the dry season (up to 54 %). The EMMA resulted in large over- and underestimations and uncertainty in TTP (e.g. Precipitation did not contribute to streamflow in TTP during the dry season, whereas the contribution of spring water TTP-SP.a contribution of was highly overestimated (up to 853 %). Contributions of end members during the second half of the study period in SHA differed from the first half, with an increase in contributions of wetland SHA WL from 1 to 58 %. Generally, the contribution of the wetland was higher during periods of high flow in SHA (51 %) — similar to contributions of springs SP.a in NF and TTP. Conversely, shallow well SHA WE.b in SHA showed highest contributions during the dry season (up to 54 %).

3.4 Young water fraction

Based on the standard deviations of the observed rainfall and streamflow isotopic signatures (Table 4), we estimated a young water fraction (YWF) of 12.4, 11.4 and 10.2 % for NF, SHA and TTP, respectively. The similarity between the amplitudes and YWF of the three sub-catchments indicated homogeneous characteristics, meaning that they could be characterized by a single transit-time distribution. The small fraction of young water also suggested that stream water in the three sub-catchments corresponded to baseflow dominated catchments in which steady state conditions would apply.

3.5 MTT estimates for stream and mobile soil water

Only $\delta^{18}\text{O}$ was used for MTT analysis, because the two measured conservative isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) showed a strong linear relationship (Fig. 2), meaning that similar estimations could be obtained by using just one isotope (Mosquera et al., 2016a). The isotopic signals of precipitation (weekly scheme, $n = 75$) were considered as input function of the lumped parameter models. All the available weekly isotope data for stream water ($n = 75$) were included in the analysis. Although some of the stream water samples could have been taken during interflow or high flow conditions, the highly damped isotopic signature of stream water suggested that those samples still showed a major component of 'old' or baseflow water. For mobile soil water, only three sites had enough data to perform model calibration and were therefore considered: NF-S15 ($n = 47$), OUT-S15 ($n = 47$) and OUT-S50 ($n = 46$).

Based on the Nash-Sutcliffe efficiency (NSE), ~~it was clear that~~ the gamma model (GM) provided a better mean transit time (MTT) estimate for stream water than the exponential piston flow model (EPM; Table 35). ~~The best performance was observed for OUT RV (NSE = 0.33), while~~ The results of TTP-RV ~~were discarded because of had a a~~ very low performance ~~of both models~~ (NSE = 0.05) ~~and was therefore discarded~~. The generally low fitting efficiencies were caused by the low amplitude of seasonal isotopic signatures of $\delta^{18}\text{O}$ in stream water samples from all four catchments ~~(see standard deviation of observed values in Table 3; Fig. 3–4)~~. There was a moderate positive relationship between the standard deviation of the observed values and corresponding NSE of modelled results ($R^2 = 0.84$). NF-RV and SHA-RV had a similar estimated MTT of approximately 4 years (Table 35). ~~However, similar to TTP RV, the poor fit to the objective functions (NSE = 0.15 and NSE = 0.22, respectively) could be related to the highly damped isotopic signature and should be interpreted with care.~~ The shortest estimated MTT of 2.5 years was for OUT-RV. ~~Due to the low fitting efficiencies and selected threshold of 5 % below the highest obtained NSE, the uncertainty bands for all sites were relatively narrow (Fig. S5–18). The uncertainties should therefore be considered as means of comparison of model parameters between sites and cannot be compared to uncertainties obtained in other studies with higher NSE values.~~

For mobile soil water, both models (GM and EPM) yielded similar results in terms of fitting efficiencies (NSE), MTT estimations and uncertainty ranges (Table 64), ~~although comparison of transit time distributions using quantile plots suggests that the models resulted in slightly different distributions (Fig. S19–20).~~ NF-S15 showed the shortest estimated transit time

(3.2–3.3 weeks). ~~The , while~~ estimated transit time for OUT-S15 ~~was (4.5–7.5–9 weeks) was longer than for NF-S15, but shorter than for and for~~ OUT-S50 (10.4–10.8 weeks).

4 Discussion

4.1 Hydrochemistry

5 ~~Low solute concentrations in precipitation (PC) compared to other end members are commonly observed in the tropics (Chaves et al., 2008; Correa et al., 2017; Crespo et al., 2012). Similar to observations in the Amazon (Chaves et al., 2008), concentrations of K and Mg were higher in throughfall (TF) than in precipitation, while Na concentrations were similar. While precipitation (PC) had low solute concentrations at all sites, Furthermore, throughfall solute (TF) concentrations in throughfall were much more variable in space and time than in precipitation, although solute concentrations were generally not significantly different between sites.~~ This has also been observed ~~elsewhere in Canada (Ali et al., 2010) and the Brazilian Amazon (Chaves et al., 2008; Germer et al., 2007) as well, (e.g. Ali et al., 2010; Germer et al., 2007)~~ and can ~~be~~ attributed to seasonal variations in plant growth and dry and wet atmospheric deposition of ~~elements such as Na, K and Mg~~ originating from ~~sea salts or biomass burning in our study area.~~ Shallow well SHA-WE.b had trace element concentrations that were much higher than those of the other nine sampled shallow wells SHA-WE.a, but similar in magnitude to solute concentrations in a spring in the Andean Páramo (Correa et al., 2017) and deep groundwater in Tanzania (Koutsouris and Lyon, 2018). Since the trace elements with high concentrations in SHA-WE.b correspond with elements related to geology (e.g. Li, K, Na and Rb), it is likely that this source is groundwater-related. Wetland SHA-WL, located near shallow well SHA-WE.b, did not show these high concentrations, which could indicate that the shallow well received water from a different ~~groundwater~~ source than the wetland and other shallow wells. Conversely, ~~S~~similarity in solute concentrations in springs NF-SP.b and OUT-SP.b and shallow wells SHA-WE.a indicate that these end members represent the same water source, despite their different geographical location. The same was observed for wetland SHA-WL and springs NF-SP.a and TTP-SP.a.

The higher intercept of the local meteoric water line (LMWL) than of the global meteoric water line (GMWL) indicates deuterium-excess (d -excess) as consequence of more arid vapour sources (McGuire and McDonnell, 2007) or re-evaporated rainfall (Goldsmith et al., 2012). ~~Similar~~ The d -excess value (5.31 ‰) corresponds to values have been observed in ~~many other~~ tropical montane environments (e.g. Goldsmith et al., 2012; Mosquera et al., 2016a; Muñoz-Villers et al., 2016; Otte et al., 2017; Windhorst et al., 2013). The value for the slope of the linear relationship between stream water isotopic values (5.00 ± 0.54) was similar to ~~that the slope of ~5~~ found by Craig (1961) for East African rivers and lakes and suggests evaporative enrichment of stream water. The observed change in $\delta^{18}\text{O}$ with altitude effect ($-0.099 \text{ ‰ } \delta^{18}\text{O}$ per 100 m) is smaller than the $-0.22 \text{ ‰ } \delta^{18}\text{O}$ per 100 m found in an Andean tropical montane forest (Windhorst et al., 2013), $-0.31 \text{ ‰ } \delta^{18}\text{O}$ per 100 m in an Ecuadorian Páramo ecosystem (Mosquera et al., 2016a), but similar to values of -0.10 and $-0.11 \text{ ‰ } \delta^{18}\text{O}$ per 100 m observed on Mt. Kilimanjaro in Tanzania (Mckenzie et al., 2010; Otte et al., 2017). The occurrence of the lowest precipitation $\delta^{18}\text{O}$ values during the rainy seasons also agrees with seasonal observations by Otte et al. (2017) on Mt.

Kilimanjaro and is most likely related to the different isotopic composition of precipitation from storms caused by the movement of the intertropical convergence zone (ITCZ) over the study area during the rainy seasons (Otte et al., 2017). Furthermore, most storm trajectories originate from south-easterly direction during the long and short rainy season, while coming from an easterly direction during the dry season, suggesting different origin and thus isotopic composition of precipitation (Soderberg et al., 2013). Stream water isotope signals that were equally damped compared to precipitation (−8.0 to −6.2 ‰ versus −15.2 to −0.4 ‰ for $\delta^{18}\text{O}$ in stream water and precipitation, respectively) were observed in a Mexican tropical montane forest catchment with similar deep volcanic soil (Muñoz-Villers and McDonnell, 2012).

4.2 Dominant water sources

The end member mixing analysis (EMMA) showed that precipitation (PC) was ~~always~~ one of the three selected end members in all catchments, as depicted in our conceptual model of the rainfall–runoff generation processes in the three sub-catchments with different land use (Fig. 76). The high contribution of precipitation (median: 46.4, 95 % confidence interval: 30.5–54.4 %) to streamflow in the natural forest (NF) sub-catchment is unexpected, as a major contribution of surface runoff is unlikely due to high infiltration rates and hydraulic conductivity of forest soils (Owuor et al., 2018). Although surface runoff can occur in tropical forests (e.g. Chaves et al., 2008; Johnson et al., 2006; de Moraes et al., 2006), we suggest that the observed signatures were caused by shallow sub-surface flow during rainfall events, which agrees with findings in NF by Jacobs et al. (2018), and is commonly observed in tropical montane forested catchments (e.g. Boy et al., 2008; Muñoz-Villers and McDonnell, 2012; Saunders et al., 2006). Although the use of a single throughfall sampler might not be sufficient to capture the spatial variation in throughfall chemistry (Zimmermann et al., 2007), throughfall (TF) was selected as an additional end member for all catchments, except in the smallholder agriculture sub-catchment (SHA). The high contribution of precipitation (21–59 %) in all catchments and throughfall (31–40 %) in the natural forest (NF) sub-catchment and the main catchment (OUT) suggest high contributions of channel precipitation, surface runoff or rapid sub-surface flow. However, given the size of streams, it is unlikely that channel precipitation alters the stream’s composition to such an extent. Although surface runoff can occur in tropical forests (e.g. Chaves et al., 2008; Johnson et al., 2006; de Moraes et al., 2006) and was observed on paths in NF, a major contribution of surface runoff is unlikely due to high infiltration rates and hydraulic conductivity of forest soils (Owuor et al., 2018). We therefore conclude that the observed signatures were caused by shallow sub-surface flow during rainfall events, which agrees with findings in NF by Jacobs et al. (in review) and is commonly observed in tropical montane forested catchments (e.g. Boy et al., 2008; Muñoz-Villers and McDonnell, 2012; Saunders et al., 2006). The extent to which the chemical composition of water changes through contact with the soil depends on the contact time (McGuire and McDonnell, 2006; Mulholland et al., 1990). Therefore, if event water, i.e. precipitation or throughfall, is only in contact with the soil for a short time (e.g. several hours), the chemical composition of the water that enters the stream might be comparable to the composition of precipitation or throughfall. Furthermore, if the riparian zone is near saturation, which occurs in the relatively flat valley bottoms in NF, only a small fraction of the precipitation can infiltrate and storage capacity is limited, resulting in Additionally, shallow flow from the riparian zone during rainfall events could occur during rainfall events, when the riparian

~~zone is near saturation~~ (von Freyberg et al., 2014; Mosquera et al., 2015). ~~Similar to our study, Chaves et al. (2008) found that the precipitation/throughfall end member contributed most to streamflow in a forested Amazonian catchment.~~

~~Results from the EMMA support our hypothesis that surface runoff occurs in the smallholder agriculture (SHA) sub-catchment, which agrees with observations from, for example, Mexico (Muñoz-Villers and McDonnell, 2013) and the Amazon (Neill et al., 2011). However, the contribution of precipitation (57.4, 45.3–78.6 %) in SHA is probably overestimated due to the inclusion of shallow well SHA-WE.b as end member. The latter end member was required to explain stream water chemistry during the dry season, but would ideally not have been used due to its small sample size. However, Correa et al. (2017) found that inclusion of a spring with similarly high solute concentrations was required in their end member model. Similar to SHA-WE.b, this spring contributed more to streamflow during the dry season (Correa et al., 2017). In contrast to SHA,~~

~~The relatively low contribution of precipitation to streamflow in the tea and tree plantation sub-catchment (TTP) compared to the other sub-catchments suggests a minor input of surface runoff to streamflow during both wet and dry conditions (Fig. 76). This seemingly contradicts previous findings in the same sub-catchment, where rainfall events led to significant dilution of nitrate concentrations in stream water due to surface runoff (Jacobs et al., 2018)(Jacobs et al., in review). The role of precipitation as stream water source in TTP might, however, have been underestimated due to the poor performance of the end member model and high uncertainty in results. However, surface runoff could have a different chemical signature than precipitation (Chaves et al., 2008). Most of the surface runoff in TTP seems to be generated on footpaths and roads. Emissions from traffic and wear of tyres could also change the surface runoff composition (Gan et al., 2008). However, the chemical composition of stream water samples did not correspond to trace elements related to traffic (Mn, Pb, Cu, Zn and Cr; Gunawardena et al., 2015), but rather indicated mineral origin (high concentrations of Si, Li, K, Na and Rb; data not presented here). Specific sampling of surface runoff and subsequent inclusion as separate end member could improve the end member mixing model performance.~~

~~Similar to findings by Muñoz-Villers and McDonnell (2012) in Mexico and Chaves et al. (2008) in the Brazilian Amazon, the contribution of precipitation and throughfall decreased in all sub-catchments during high flows (Fig. 76, right hillslopes in each graph). This suggests increased inputs from groundwater through wetlands (SHA-WL) or springs (TTP-SP.a and NF-SP.a) during the rainy season. These findings support our hypothesis that there are temporal changes in the contribution of the different end members in this African tropical montane ecosystem, similar to South American tropical montane catchment (Chaves et al., 2008; Correa et al., 2017). Groundwater end member SHA-WE.b in SHA showed contrasting behaviour, with highest contributions during low flow periods, suggesting that this is a different groundwater source and an important component of baseflow in SHA.~~

4.3 Mean transit times

~~The low fitting efficiencies, high uncertainty and the long estimated MTT (i.e. in the order of years), did not allow us to accept, nor to reject our hypothesis that agricultural catchments have a shorter MTT than forested catchments due to increased importance of faster flow paths such as surface runoff. However, the long estimated MTTs and the low fraction of young water~~

(YWF) suggest that the majority stream water in all catchments originates from 'old' water or groundwater. This could be explained by the deep and well-drained soil in our study area (Cooper, 1979; Edwards and Blackie, 1981), compared to the shallower soils and steep slopes in, for example, Andean tropical montane forest catchments with shorter mean transit times (e.g. Crespo et al., 2012; Timbe et al., 2014). Such deep soils promote slow flow paths through deeper soil layers and thus result in longer transit times (Asano and Uchida, 2012). This finding agrees with the selection of groundwater-related end members springs TTP-SP.a and NF-SP.a and wetland SHA-WL in the EMMA (Fig. 6). The importance of groundwater does, however, contradict the generally high contribution of precipitation and throughfall to streamflow in most catchments. The longer MTT for mobile soil water for OUT-S15, located in a pasture, than for NF-S15 contradicts findings in an Andean tropical montane catchment: Timbe et al. (2014) compared pasture and forest soil water MTTs and found longer MTTs for forested sites. In our case, the difference could be caused by differences in hydraulic conductivity, since soil hydraulic properties can influence MTT (Geris et al., 2015; Mueller et al., 2013; Muñoz-Villers et al., 2016). Pasture soils in our study area had a generally lower hydraulic conductivity (2–53 cm h⁻¹) than natural forest soils (10–207 cm h⁻¹) due to soil compaction by livestock trampling (Owuor et al., 2018). The estimated MTTs fell within the range observed for soil water from 30 to 60 cm depth (20–62 days) in a tropical montane catchment in Mexico (Muñoz-Villers and McDonnell, 2012).

4.4 Methodological limitations and implications for further research

There was a large uncertainty in end member contributions, which is related the large number of samples falling outside the triangle bounded by the three selected end members in SHA, TTP and OUT (Fig. 4–5). The triangle bounded by the three selected end members in the stream water mixing space of NF (precipitation, throughfall and springs SP.a; Fig. 5) encompassed most of the stream water samples, with only 9 % of the samples falling outside the triangle. However, in SHA, TTP and OUT 42, 49 and 33 % of the samples fell outside the triangle of the three selected end members, respectively. Although this could be attributed to the variability in end member composition, uncertainty in laboratory analysis or non-conservative solute behaviour (Barthold et al., 2010), it is very likely that one or more important end members are missing, ~~which could be better suited to explain the observed chemical composition of stream water at the catchment outlet. Alternatively~~ Furthermore, inclusion of additional end members to increase dimensionality of the end member model may be required ~~to satisfactorily represent the behaviour and stream water sources in these catchments, as observed was necessary for in~~ an Andean Páramo ecosystem (Correa et al., 2017) and a tropical forested catchment in Panama (Barthold et al., 2017). The selection of tracers and number of end members is highly subjective and can therefore significantly affect the outcomes of the EMMA (Barthold et al., 2011). Furthermore, although the chemical signature of end members should be invariable in space and time according to the EMMA assumptions, a more consistent sampling approach whereby all end members are sampled on a regular basis could also improve the performance of the models, because the full range of chemical variation in time would be captured (Neill et al., 2011). In our case this was not possible, because most sampling sites were difficult to access.

Another shortcoming of our sampling approach is that springs, shallow wells and wetlands might not accurately represent groundwater. Since our results suggest that our catchments are largely groundwater dominated, deep groundwater is most

~~likely although this could be~~ an important ~~missing~~ end member ~~in our analysis~~, as observed in many studies (e.g. Barthold et al., 2011; Chaves et al., 2008; Crespo et al., 2012; Katsuyama et al., 2009). ~~However, A~~access to groundwater in the study area is complicated by the absence of wells or boreholes in NF and TTP, ~~and~~ ~~Furthermore~~, the existing wells in SHA are often not properly sealed, which means that ~~deep~~ groundwater can mix with water from shallower soil layers and precipitation, obscuring the groundwater signal. ~~In addition to groundwater, inclusion of soil water might improve the mixing models, as Jacobs et al. (in review) suggested that discharge contributing zones change with the seasons, other studies in tropical montane regions showed the importance of soil water as source of streamflow (Chaves et al., 2008; Correa et al., 2017). Alternatives for which could be tested by inclusion of soil water as end member. This was not possible with the current experimental set-up, because the glass fibre wick in the wick samplers could contaminate the trace element samples.~~ ~~wick samplers, such as suction lysimeters, should be used to avoid contamination of soil water samples. Especially soil water from different topographical locations within the catchment (e.g. riparian zone and hillslope) or different soil types could yield further insight in the dynamics of discharge contributing zones and important flow paths during different seasons.~~

~~Due to the low fitting efficiencies of the MTT models, specifically for stream water, we consider the presented MTT estimations as valuable preliminary findings. These can serve as a baseline for future studies, in which more sophisticated methods like time-variant approaches can be used. Through the application of such methods in combination with high frequency sampling, more subtle differences in the movement of water through the soil could be distinguished and related to catchment characteristics, such as land use, where appropriate. Furthermore, time-variant approaches could deal with shifts in storage conditions, which can confound the potential impact of land use on MTT (Van der Velde et al., 2014). The latter was not considered in our study, since the sub-catchments are subjected to similar rainfall patterns (Fig. 3).~~

~~The long estimated transit time of up to 4 years might be beyond the reliability of the present used method with $\delta^{18}\text{O}$ or $\delta^2\text{H}$ tracers, which adds to the uncertainty of our results. Better predictions might be obtained by using more appropriate tracers for estimating transit times of several years to decades, such as tritium (^3H) (Cartwright et al., 2017). Although a longer sampling period of at least 4 years might also improve the fitting efficiencies that were obtained (McGuire and McDonnell, 2006), we believe that the low fitting efficiencies were mainly a result of the highly damped isotope signal of stream water, suggesting that the applied method and models for MTT estimation are less suitable for groundwater-dominated tropical catchments with a similarly damped stream water isotope signal. Conversely, both selected MTT models provided reasonable results for mobile soil water. However, a simpler exponential distribution model (EM) might have been equally appropriate, since the parameter range of behaviour solutions of the gamma model (GM) and the exponential piston flow model (EPM) suggest that both models could be simplified to an exponential distribution model (EM). In order to avoid over-parametrization, models with fewer parameters (in this case EM) are preferred when they provide comparable results.~~

4.3 — Mean transit times

~~The low variation in isotopic signatures (-3.6 to -0.3 ‰ for $\delta^{18}\text{O}$) observed for stream water compared to precipitation (-9.9 to 4.4 ‰) at all sites suggests long travel times. Equally damped signals (-8.0 to -6.2 ‰ versus -15.2 to -0.4 ‰ for $\delta^{18}\text{O}$ in~~

stream water and precipitation, respectively) were observed in a Mexican tropical montane forest catchment (Muñoz-Villers and McDonnell, 2012). The long transit time could be explained by the deep and well-drained soils in our study area (Cooper, 1979; Edwards and Blackie, 1981), which promote slow flow paths through deeper soil layers and longer transit times (Asano and Uchida, 2012). The most damped isotopic signature was observed at TTP (SD = 0.26 ‰ for $\delta^{18}\text{O}$; Table 3), which suggests that stream water in this sub-catchments is older than at all other sites. Most likely, the MTT is longer than 4 years and is therefore beyond the reliability of the present used method with $\delta^{18}\text{O}$ or $\delta^2\text{H}$ tracers, which also explains the very low Nash-Sutcliffe efficiency (NSE). Better predictions could be obtained by using more appropriate tracers for estimating transit times of several years to decades, such as tritium (^3H) (Cartwright et al., 2017). A longer sampling period of at least 4 years would also improve the reliability of the mean transit time estimates (McGuire and McDonnell, 2006). Although the gamma model (GM) used in this study was found to be most suitable for the estimation of stream water MTT in other tropical montane catchments (Muñoz-Villers and McDonnell, 2012; Timbe et al., 2014), it is also possible that the applied method for MTT estimation is less suitable for tropical catchments with highly damped isotope signals and low seasonal variation, as indicated by the low NSE for all stream water sites.

Because of the similar estimated MTTs for NF and SHA and the most likely longer MTT for TTP, we rejected our hypothesis that agricultural catchments have a shorter MTT than forested catchments due to increased importance of faster flow paths such as surface runoff. Evidence from other studies suggests that the role of vegetation cover in water storage and MTT could be suppressed by geomorphology (Timbe et al., 2017) or soil hydraulic properties (Geris et al., 2015; Mueller et al., 2013; Muñoz-Villers et al., 2016). The latter, however, can also be influenced by land use. The MTT of ~4 years in the three sub-catchments suggests that most of the stream water originates from 'old' water or groundwater, which corresponds with the importance of groundwater-related end-members springs TTP-SP.a and NF-SP.a and wetland SHA-WL in the sub-catchments. The runoff ratios in all catchments (0.323–0.387) confirm that a small part of the precipitation leaves the catchment as discharge. Similar runoff ratios (0.30) and MTT (~3 years) were obtained in a Mexican montane forest catchment with deep volcanic soils, but higher annual precipitation (Muñoz-Villers and McDonnell, 2012). However, Andean tropical montane catchments had higher runoff ratios (0.76–0.81) and correspondingly shorter MTTs (<1 year) (Crespo et al., 2012), which could be caused by steeper slopes and shallower soils compared to our study area. The importance of groundwater does, however, contradict the generally high contribution of precipitation and throughfall to streamflow in most catchments. direct effect of storm events on stream water isotope composition are removed from the analysis (McGuire and McDonnell, 2006). Although samples obtained during high flow in the rainy season were not removed from our analysis, the use of bulked samples could have underestimated the importance of faster flow paths during rainfall events and therefore partly explain the discrepancy between the long transit times and high contribution of precipitation and throughfall to streamflow in most catchments. ~~The use of bulked precipitation and weekly stream water samples as input could cause a bias towards older groundwater, because the direct effect of storm events on stream water isotope composition are removed from the analysis (McGuire and McDonnell, 2006). Although samples obtained during high flow in the rainy season were not removed from our analysis, the use of bulked samples could have underestimated the importance of faster flow paths during rainfall events and~~

~~therefore partly explain the discrepancy between the long transit times and high contribution of precipitation and throughfall to streamflow in most catchments.~~

The shorter estimated MTT for OUT compared to the sub-catchments is counterintuitive, since it is the largest catchment. One could also expect that, since OUT is a mixture of the three land use types dominating the sub-catchments, the MTT should be similar to or an average of the estimated MTTs of the sub-catchments. MTT is, however, not always correlated to catchment area (McGuire et al., 2005; Rodgers et al., 2005), but seems more related to other hydrological and topographical metrics such as drainage density and slope (Capell et al., 2012). Also geology and presence of hydrologically responsive soils seem to be important determinants for MTT (Capell et al., 2012; Tetzlaff et al., 2007). The occurrence of other soil types (mollic Andosols) and underlying geology (pyroclastic unconsolidated rock) in the upper part of OUT (ISRIC, 2007) compared to the humic Nitisols and igneous rock dominating the three sub-catchments could lead to differences in soil hydraulic properties and sub-surface water storage and eventually MTT, but not enough data are available for the study area to test this.

The longer MTT for soil water for OUT-S15, located in a pasture, than for NF-S15 contradicts findings by Timbe et al. (2014), who compared pasture and forest soil water MTT and found longer MTTs for forested sites. In our case, the difference could be caused by differences in hydraulic conductivity. Pasture soils in our study area had a generally lower hydraulic conductivity ($2\text{--}53\text{ cm h}^{-1}$) than natural forest soils ($10\text{--}207\text{ cm h}^{-1}$) due to soil compaction by animal trampling (Owuor et al., 2018). Differences in soil hydraulic properties between land use types are, however, mainly restricted to the topsoil, while deeper soil layers are usually less affected by land management (Zimmermann et al., 2006). The estimated MTTs fell within the range observed for soil water from 30 to 60 cm depth (20–62 days) in a tropical montane catchment in Mexico (Muñoz-Villers and McDonnell, 2012). For soil water MTT estimation, the second parameter (α) for GM was around 1.5 for the best modelled efficiencies for NF-S15 and OUT-S50. However, according to the range of behavioural solutions, all soil sites could be well represented by gamma functions with α values of 1 (Table 4), which means a simple exponential distribution function (EM). Similarly, the exponential piston flow model (EPM) can yield similar results with $\eta = 1$ for all analysed cases, meaning that EPM could also be simplified as EM, i.e. without any portion of piston flow participating in the transport. Therefore, results from both models point out that the same predictions could be obtained with a simpler, single parameter exponential model, as was used for estimation of MTT of soil water at 30 cm by Muñoz-Villers and McDonnell (2012). In order to avoid over-parametrization, models with less parameters are preferred when they provide comparable results.

5 Conclusion

In this study we aimed to identify the dominant water sources and flow paths in three sub-catchments with contrasting land use (i.e. natural forest, smallholder agriculture and commercial tea and tree plantations) using mean transit time (MTT) analysis and end member mixing analysis (EMMA) to assess the effect of land use on catchment hydrology. The low fitting efficiencies of the MTT analysis did not allow us to relate differences in estimated MTT between the catchments to land use and we were thus unable to confirm or reject our hypothesis that the natural forest sub-catchment would have a longer MTT than the

catchments dominated by smallholder agriculture or commercial tea plantations. The long estimated MTT (up to 4 years) and high contributions of groundwater-related end members did, however, suggest that the catchments in our study area are generally groundwater-dominated. The analyses revealed a similar MTT of approximately 4 years in all catchments, which is longer than observed in other tropical montane headwater catchments. In the three sub-catchments, springs and wetlands fed by groundwater were selected as important end member, with increased contribution to streamflow during high flows. A second, different groundwater source was identified in the smallholder agriculture catchment, which was an important end member during baseflow. These results emphasize the importance of sufficient groundwater recharge and sustainable management of groundwater resources to maintain streamflow throughout the year.

The differences in contribution of end members to streamflow, based on EMMA, suggest that land use could affect hydrological flow paths. Despite the observed similarities, the three sub-catchments showed clear differences in the contribution of precipitation and throughfall to stream water, with highest contributions in the natural forest and smallholder agriculture and lowest contribution in the tea and tree plantations. However, we expect that the observed high contribution of precipitation and throughfall in the natural forest sub-catchment occurs as shallow sub-surface flow, while precipitation in the smallholder agriculture sub-catchments could contribute to streamflow as surface runoff could still play a significant role in the smallholder agriculture sub-catchment. Further evidence to support this statement is necessary, because surface runoff generally has negative impact on soil fertility, erosion and sedimentation. Due to the similar soils and geology in the three sub-catchments, the differences in end member selection and behaviour can mainly be attributed to land use. However, over- and under-prediction of end member contributions, especially during the dry season and at the peak of the rainy season, indicate that important end members were missing in the mixing models, indicate that the mixing models could be improved by identification of additional end members and regular sampling of all end members to capture the variation in chemical composition of the end members throughout the year, might therefore improve the end member mixing models and thus the use of more appropriate methods to estimate transit times could further improve our knowledge of the hydrological behaviour of tropical catchments under different dominant water sources and flow paths in the three land use types under different hydrological regimes. Nevertheless, due to the lack of data on the hydrological behaviour of African tropical montane catchments, our study provides a good baseline for future research. Due to the close linkage of forests, land use and water, such research is required to support decision making on forest protection and land management. To ensure the supply of clean and sufficient water to communities living in and downstream of tropical montane areas because changes in flow paths will affect the transport and fate of nutrients and pollutants, which could have an adverse effect on montane ecosystems and downstream areas, the results of this study can be used to assess the potential impact of future land use changes on surface water supply and quality.

Data availability

Hydroclimatic data (discharge and precipitation) and the full isotope and trace element dataset for all study sites is available from the online database <http://fb09-pasig.umwelt.uni-giessen.de:8050/wiki/publications> hosted by Justus Liebig University, Giessen, Germany.

5 Author contributions

The study was designed by SJ, BW and LB. SJ and BW installed all instruments. SJ was in charge of field campaigns, instrument maintenance and sample collection, and performed end member mixing analysis. BW managed the laboratory analysis. ET performed the analysis for mean transit time estimation. SJ, MR, KBB and LB prepared the manuscript.

Competing interests

10 The authors declare that they have no conflict of interest.

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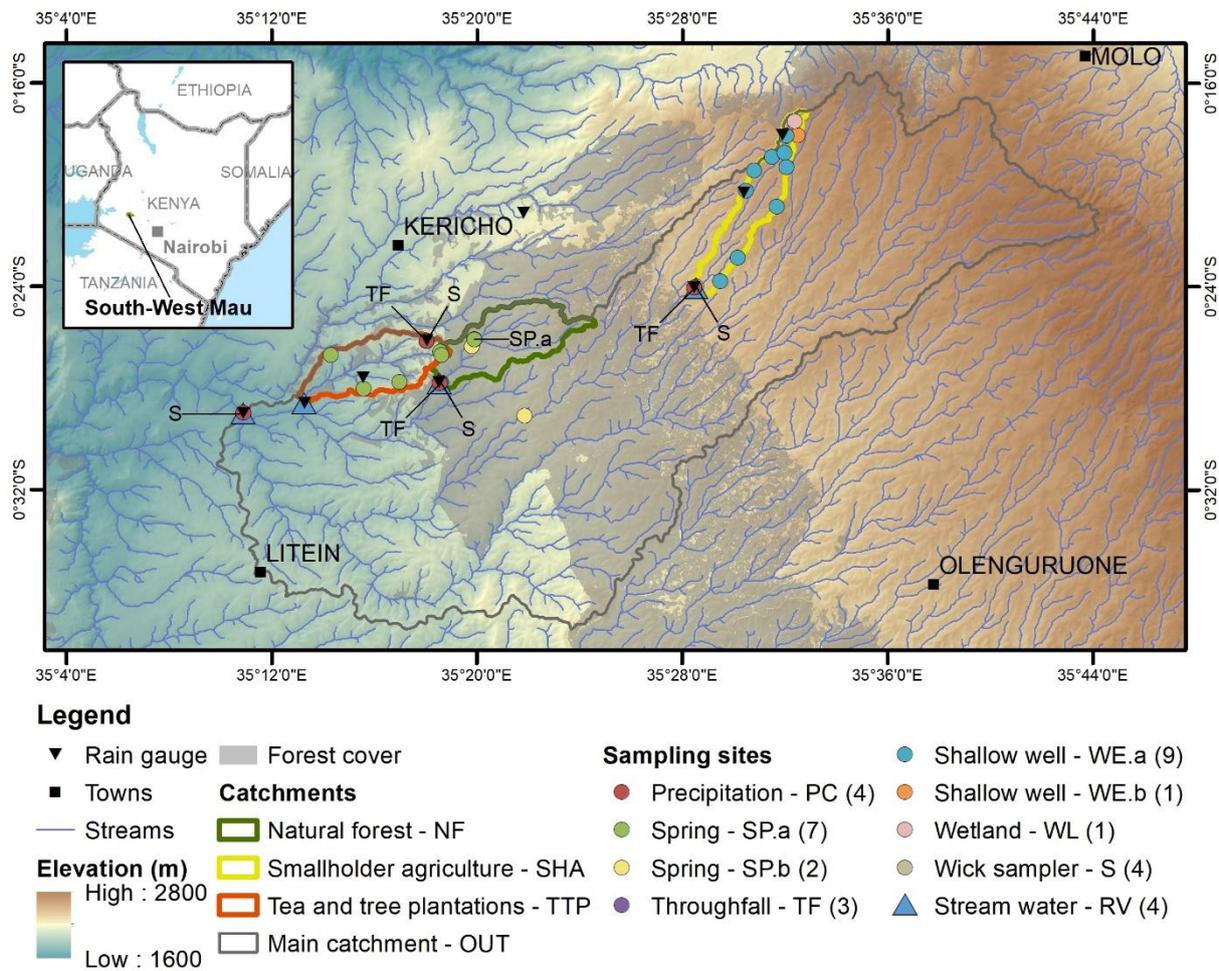


Figure 1. Map of the study area in the South-West Mau, Kenya, showing the three sub-catchments with different land use types within the main catchment, location of rain gauges, and sampling sites for stream water and selected end members. Sampling sites with overlapping symbols are indicated with labels instead of symbols. Numbers in brackets in the legend indicate the number of sampling sites per end member.

5

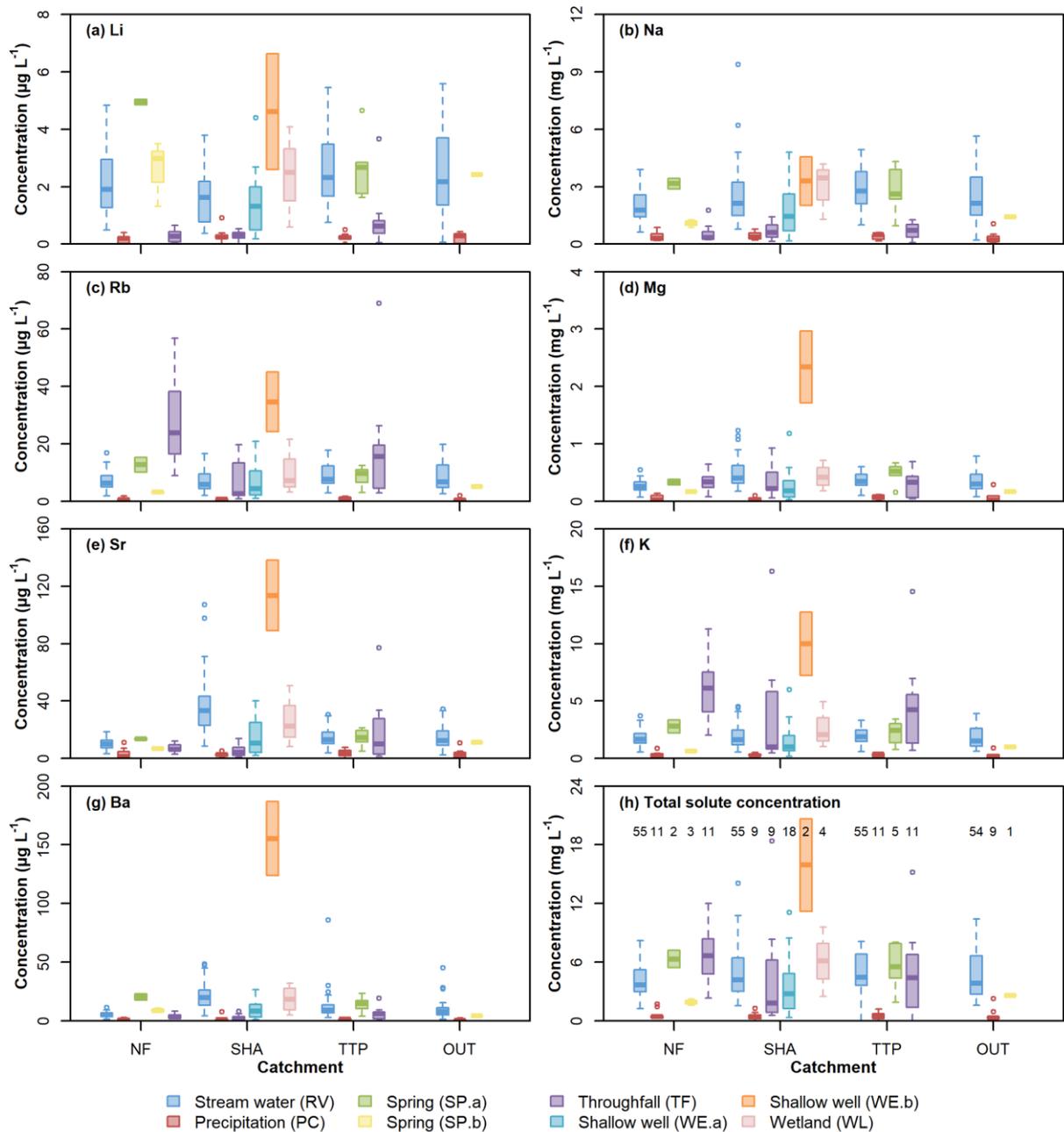


Figure 2. Box plots with concentrations of (a) Li, (b) Na, (c) Rb, (d) Mg, (e) Sr, (f) K and (g) Ba, and (h) total concentration of the selected solutes in stream water and sampled end members in the three sub-catchments with different land use (NF = natural forest, SHA = smallholder agriculture, TPP = tea and tree plantations) and the main catchment (OUT) between 15 October 2015 and 21 October 2016 in the South-West Mau, Kenya. The thick line represents the median, the box shows the interquartile range and the whiskers the minimum and maximum values within 1.5 times the interquartile range. Outliers are indicated with open circles. Numbers in plot (h) indicate the number of samples per end member.

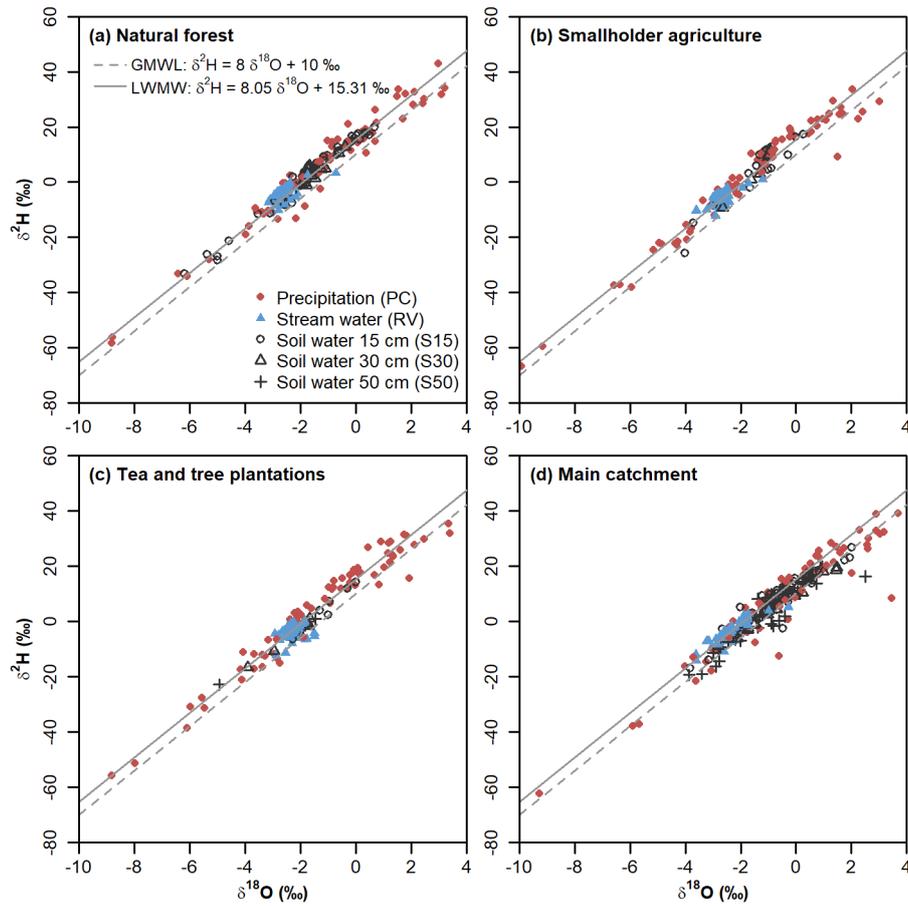


Figure 32. Relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in precipitation (PC), stream water (RV) and mobile soil water at 15, 30 and 50 cm depth (S15, S30 and S50, respectively) for the (a) natural forest (NF), (b) smallholder agriculture (SHA), and (c) tea and tree plantations (TTP) sub-catchments, and (d) the main catchment (OUT) between 15 October 2015 and 17 March 2017 in the South-West Mau, Kenya.

5 The global meteoric water line (GMWL) and local meteoric water line (LMWL) are indicated as dashed and solid lines, respectively.

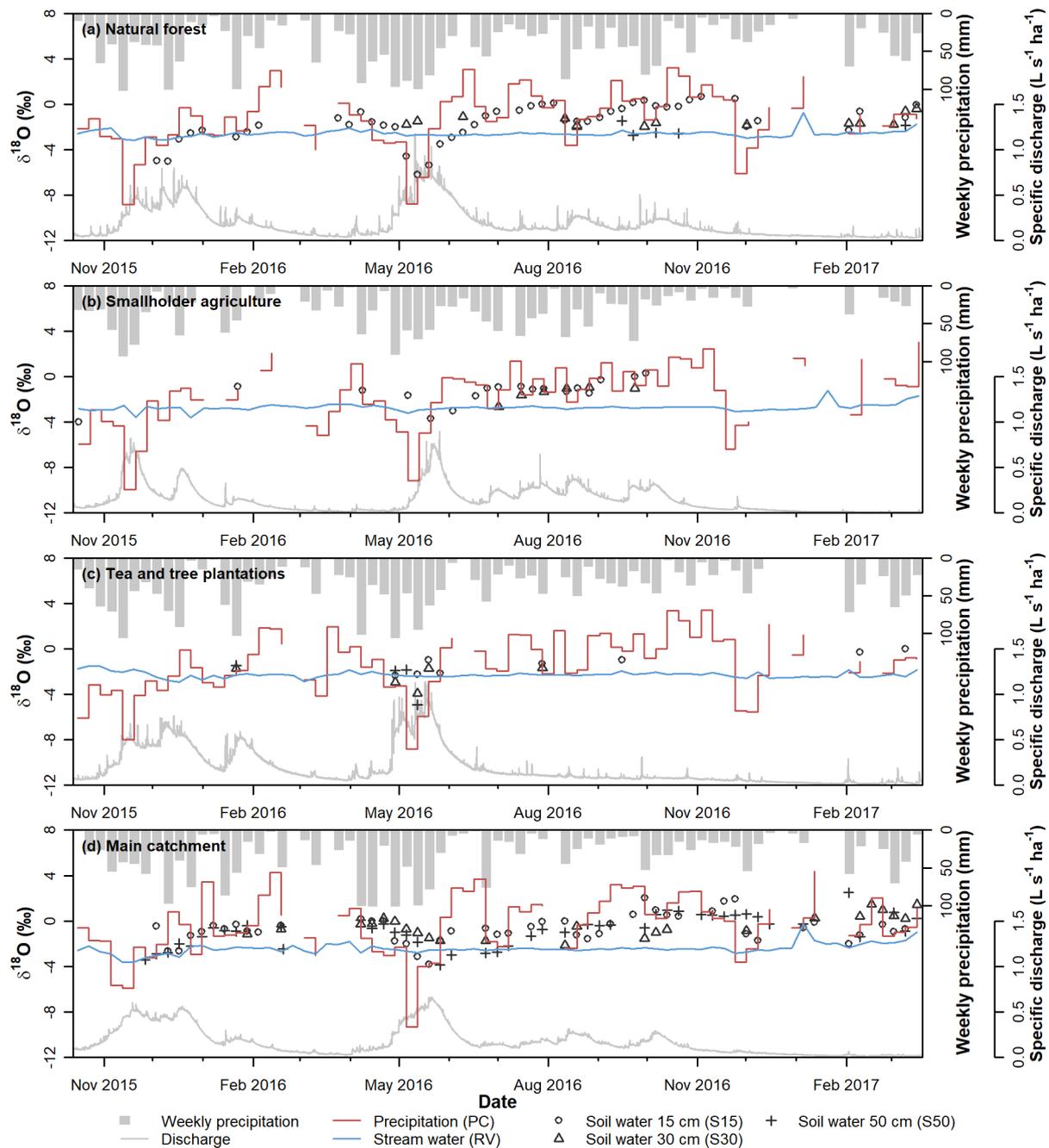


Figure 43. Time series of $\delta^{18}\text{O}$ values in precipitation (PC), stream water (RV) and mobile soil water at 15, 30 and 50 cm depth (S15, S30 and S50, respectively), specific discharge and weekly precipitation in the (a) natural forest (NF), (b) smallholder agriculture (SHA), and (c) tea and tree plantations (TTP) sub-catchments, and (d) the main catchment (OUT) between 15 October 2015 and 17 March 2017 in the South-West Mau, Kenya.

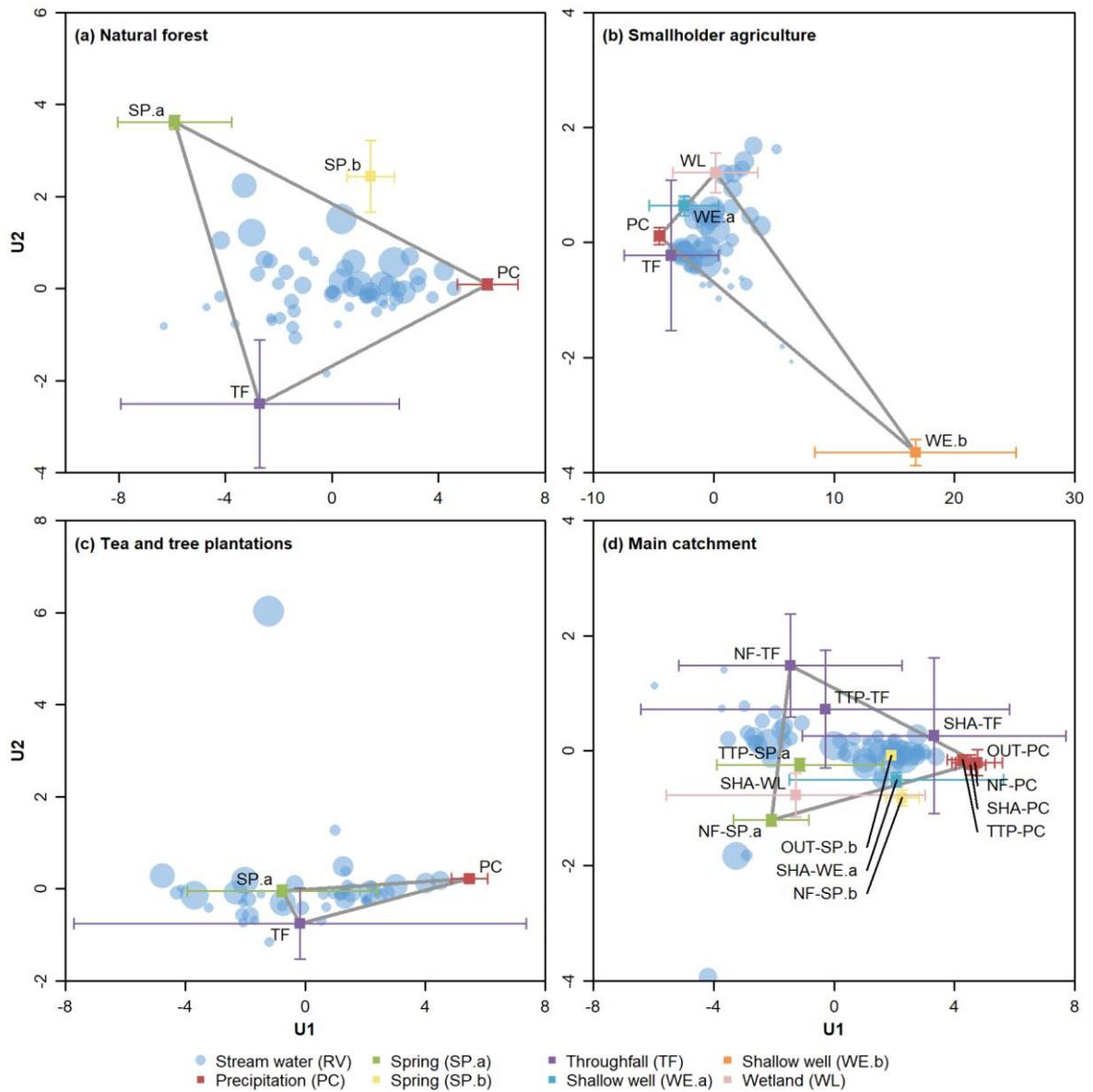
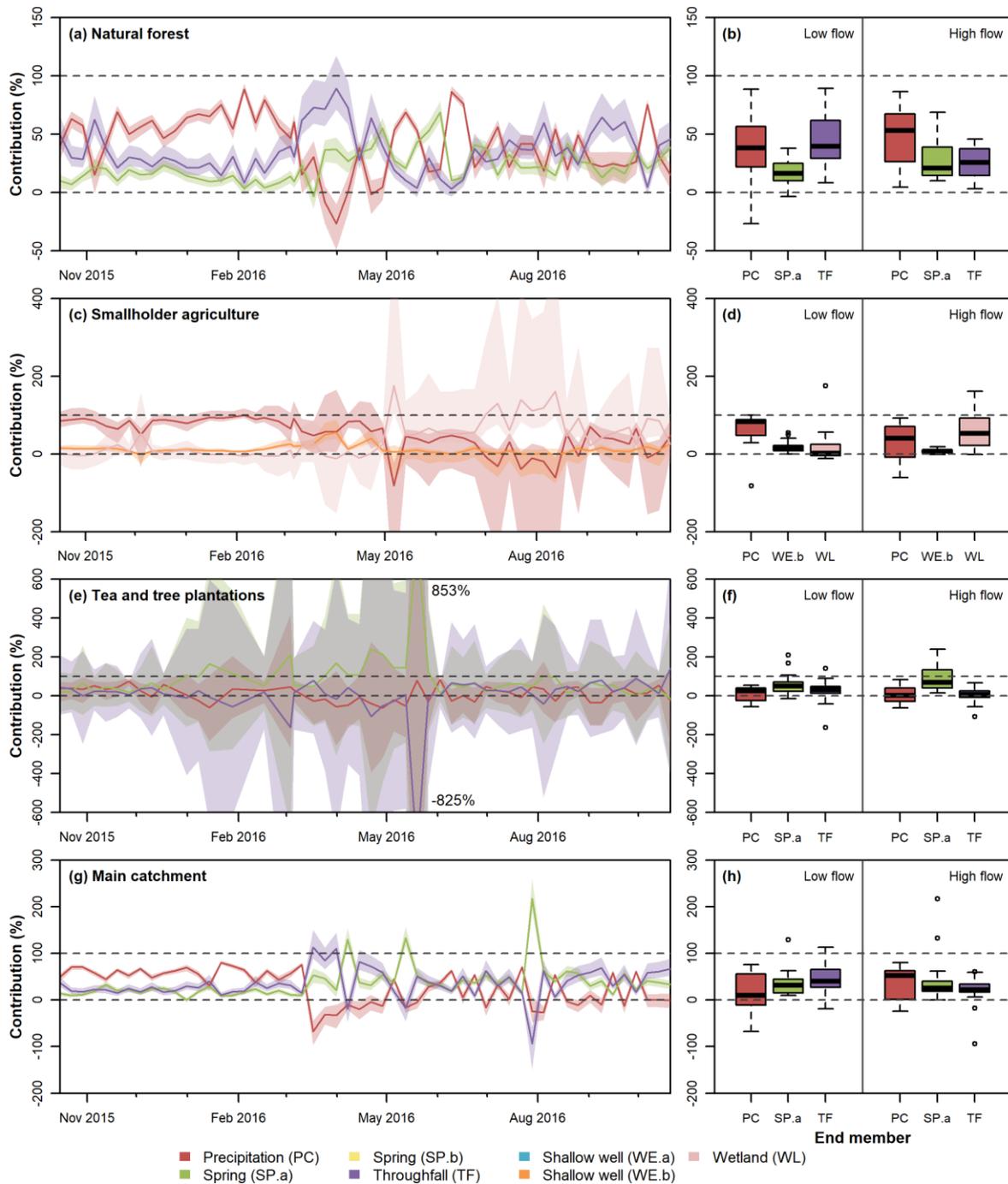
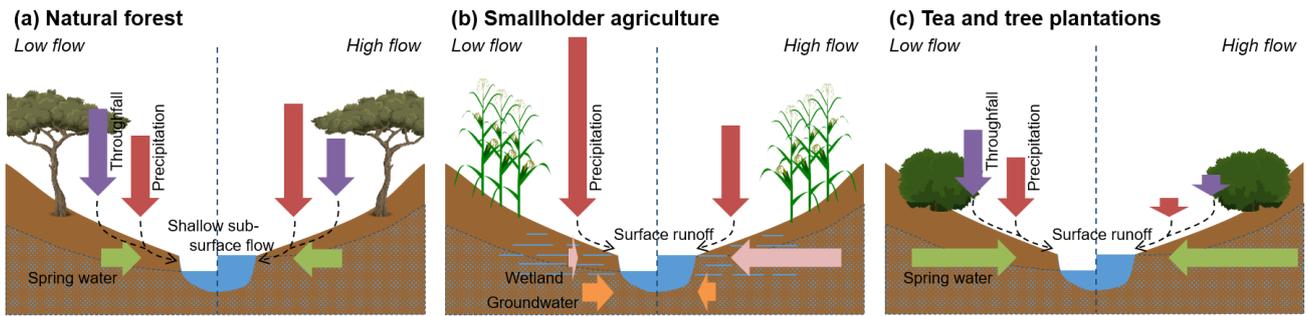


Figure 54. Projection of end members in the 2-dimensional (U1 and U2) mixing space of stream water samples of the (a) natural forest (NF), (b) smallholder agriculture (SHA), and (c) tea and tree plantation (TTP) sub-catchments and (d) the main catchment (OUT) between 15 October 2015 and 21 October 2016 in the South-West Mau, Kenya. The size of the symbol for stream water represents the relative discharge at the time of sampling (larger symbol means higher discharge).



5 **Figure 65.** Specific discharge (shaded) and eContribution of selected end members to streamflow for the (a–b) natural forest (NF), (c–d) smallholder agriculture (SHA) and (e–f) tea and tea plantation (TTP) sub-catchments and (g–h) the main catchment (OUT) between 15 October 2015 and 21 October 2016 in the South-West Mau, Kenya. The grey dashed lines indicate the realistic range of end member contributions and arrows show sampling dates for end members. Shaded areas represent the 5th to 95th percentile of 10 000 Monte Carlo simulations of the EMMA, while the line represents the median end member contribution. The thick line in the box plots represents the

median end member contribution, separated by flow condition, ~~the~~ The box shows the interquartile range and the whiskers the minimum and maximum values within 1.5 times the interquartile range. Outliers are indicated with open circles.



5 **Figure 76.** Conceptual model of dominant water sources and flow paths in different land use types during low (\leq mean discharge) and high flows ($>$ mean discharge) in a tropical montane area: (a) natural forest (NF), (b) smallholder agriculture (SHA) and (c) commercial tea and tree plantations (TTP), based on results of end member mixing and mean transit time analysis in the South-West Mau, Kenya. Arrow length represents the median contribution (%) of each end member. Black dashed arrows show the most likely pathway for precipitation and throughfall to reach the stream.

Table 1. Physical and hydroclimatic characteristics of the study catchments in the South-West Mau, Kenya. Precipitation, specific discharge and runoff ratio are presented for the study period of 15 October 2015 to 14 October 2016.

Catchment	Area	Elevation	Slope ^a	Precipitation	Specific discharge	RR ^b
	<i>km²</i>	<i>m</i>	<i>%</i>	<i>mm yr⁻¹</i>	<i>mm yr⁻¹</i>	-
Natural forest (NF)	35.9	1 954–2 385	15.5±8.0	2 299	744	0.323
Smallholder agriculture (SHA)	27.2	2 380–2 691	11.5±6.5	1 738	607	0.349
Tea and tree plantations (TTP)	33.3	1 786–2 141	12.2±7.3	2 045	791	0.387
Main catchment (OUT)	1021.3	1 715–2 932	12.8±7.7	2 019	701	0.347

^a Mean±SD; ^b Runoff ratio, i.e. ratio of specific discharge to precipitation

Table 2. The lumped parameter models used for the estimation of mean transit times in the South-West Mau, Kenya.

Model	Transit time distribution $g(\tau)$	Parameter range for Monte Carlo simulations ^a
Gamma model (GM)	$\frac{\tau^{\alpha-1}}{\beta^\alpha \Gamma(\alpha)} \exp\left(-\frac{\tau}{\beta}\right)$	α [0.0001–10] τ [1–400] $\beta = \alpha/\tau$
Exponential piston flow model (EPM)	$\frac{\eta}{\tau} \exp\left(-\frac{\eta t}{\tau} + \eta - 1\right)$ for $t \geq \tau(1 - \eta^{-1})$ 0 for $t < \tau(1 - \eta^{-1})$	τ [1–400] η [0.1–4]

^a τ = tracer's mean transit time; α and β = shape parameters; η ratio of the total volume to the volume of water with exponential distribution of transit times. Units for parameters and their respective ranges are a-dimensional except for τ , which has units of ~~time~~weeks.

Table 3. Number of samples (*n*), median and range (in parentheses) solute concentrations for all sampled end members and stream water collected between 15 October 2015 and 21 October 2016 in the South-West Mau, Kenya. Different letters after median values indicated significant differences in solute concentrations between sources.

Source ^a	<i>n</i>	Li <i>μg L⁻¹</i>	Rb <i>μg L⁻¹</i>	Sr <i>μg L⁻¹</i>	Ba <i>μg L⁻¹</i>	Na <i>mg L⁻¹</i>	Mg <i>mg L⁻¹</i>	K <i>mg L⁻¹</i>
<i>Natural forest (NF)</i>								
RV	55	1.91 ^a (0.49–4.83)	6.34 ^a (1.91–16.84)	10.15 ^a (3.17–18.70)	5.35 ^a (1.70–11.68)	1.78 ^{ac} (0.63–3.91)	0.25 ^a (0.07–0.55)	1.66 ^a (0.56–3.71)
PC	11	0.19 ^b (0.01–0.41)	0.52 ^b (0.13–1.94)	1.20 ^b (0.39–11.12)	0.63 ^b (0.21–2.99)	0.30 ^b (0.18–0.87)	0.02 ^b (0.01–0.14)	0.24 ^b (0.05–0.87)
SP.a	2	4.95 ^a (4.85–5.05)	12.75 ^{ac} (10.16–15.34)	13.58 ^a (12.96–14.20)	20.45 ^a (17.82–23.07)	3.16 ^a (2.88–3.44)	0.33 ^a (0.28–0.38)	2.79 ^{ac} (2.22–3.36)
SP.b	3	2.98 ^a (1.32–3.49)	3.16 ^b (2.73–3.60)	6.80 ^{ab} (6.29–7.26)	8.73 ^a (8.32–10.82)	1.11 ^{bc} (0.86–1.28)	0.17 ^{ab} (0.17–0.18)	0.63 ^b (0.53–0.78)
TF	11	0.27 ^b (0.03–0.65)	23.80 ^c (8.88–56.78)	6.37 ^{ab} (2.94–12.10)	3.26 ^c (1.99–8.43)	0.33 ^b (0.22–1.78)	0.34 ^a (0.08–0.65)	6.14 ^c (2.02–11.27)
<i>Smallholder agriculture (SHA)</i>								
RV	55	1.63 ^a (0.37–3.79)	5.85 ^a (2.01–16.54)	33.33 ^a (8.68–107.27)	19.84 ^a (4.38–48.63)	2.13 ^a (0.79–9.40)	0.40 ^a (0.17–1.24)	1.62 ^{ac} (0.57–4.54)
PC	9	0.24 ^b (0.01–0.92)	0.70 ^b (0.38–1.18)	2.61 ^b (0.34–5.37)	1.17 ^b (0.34–8.11)	0.37 ^b (0.22–0.78)	0.02 ^b (0.01–0.10)	0.23 ^b (0.20–0.52)
TF	9	0.31 ^b (0.01–0.53)	2.63 ^a (0.85–19.75)	4.14 ^{bc} (0.95–13.89)	1.51 ^{bc} (0.56–8.35)	0.59 ^{bc} (0.14–1.42)	0.22 ^{ab} (0.05–0.92)	1.01 ^{ac} (0.47–16.32)
WE.a	18	1.32 ^a (0.18–4.41)	4.33 ^a (1.00–20.87)	10.69 ^{cd} (2.06–40.05)	8.47 ^{cd} (1.36–26.92)	1.45 ^{ab} (0.16–4.80)	0.18 ^b (0.03–1.18)	1.01 ^c (0.18–6.01)
WE.b	2	4.62 ^a (2.6–6.63)	34.65 ^a (24.26–45.04)	113.54 ^a (88.93–138.15)	155.32 ^a (123.88–186.76)	3.29 ^{ac} (2.02–4.57)	2.34 ^a (1.72–2.97)	9.99 ^a (7.23–12.74)
WL	4	2.49 ^a (0.6–4.08)	7.26 ^a (3.23–21.60)	22.30 ^{ad} (8.20–50.71)	18.53 ^{ad} (5.13–32.32)	3.45 ^a (1.29–4.18)	0.42 ^a (0.19–0.71)	2.06 ^{ac} (1.03–4.96)
<i>Tea and tree plantations (TTP)</i>								
RV	55	2.32 ^a (0.75–5.45)	7.69 ^a (2.86–17.81)	13.11 ^a (3.81–30.55)	9.18 ^a (3.01–86.18)	2.77 ^a (1.01–4.95)	0.34 ^a (0.10–0.60)	1.88 ^a (0.58–3.34)
PC	11	0.22 ^b (0.00–0.51)	0.91 ^b (0.16–1.66)	3.44 ^b (0.13–7.60)	1.42 ^b (0.12–2.82)	0.49 ^b (0.17–0.61)	0.06 ^b (0.01–0.12)	0.37 ^b (0.06–0.50)
SP.a	5	2.67 ^a (1.63–4.66)	9.72 ^a (3.00–12.55)	14.56 ^a (5.17–21.26)	14.82 ^a (4.22–23.57)	2.61 ^a (0.95–4.31)	0.52 ^a (0.16–0.67)	2.43 ^a (0.79–3.43)
TF	11	0.62 ^b (0.05–3.68)	15.59 ^a (2.93–69.08)	10.06 ^a (1.4–77.26)	6.08 ^b (0.42–19.42)	0.71 ^b (0.07–1.26)	0.33 ^a (0.04–0.69)	4.23 ^a (0.70–14.56)
<i>Main catchment (OUT)</i>								
RV	54	2.17 ^a (0.06–5.59)	6.81 ^a (2.59–19.84)	12.46 ^a (2.39–34.63)	8.11 ^a (1.59–45.30)	2.13 ^a (0.21–5.64)	0.30 ^a (0.08–0.79)	1.53 ^a (0.62–3.93)
PC	9	0.28 ^b (0.01–0.43)	0.34 ^b (0.09–2.10)	1.67 ^b (0.27–10.93)	0.32 ^b (0.22–2.48)	0.20 ^b (0.08–1.08)	0.02 ^b (0.01–0.29)	0.14 ^a (0.03–0.92)
SP.b	1	2.42	5.06	11.36	4.59	1.42	0.16	0.99

^a RV = stream water, PC = precipitation, SP.a = SP.b = spring, TF = throughfall, WE.a = WE.b = shallow well, WL = wetland

Table 4. Number of samples (*n*), coordinates, elevation, and summary statistics of $\delta^{18}\text{O}$ values of samples collected at all sampling sites between 15 October 2015 and 21 October 2016 in the South-West Mau, Kenya.

Source ^a	<i>n</i>	Coordinates	Elevation	Mean	Standard deviation	Minimum	Maximum
			<i>m</i>	‰	‰	‰	‰
<i>Natural forest (NF)</i>							
<u>RV</u>	<u>75</u>	<u>35° 18' 32.616" E, 0° 27' 48.570" S</u>	<u>1 969</u>	<u>-2.58</u>	<u>0.32</u>	<u>-3.15</u>	<u>-0.73</u>
<u>PC</u>	<u>68</u>	<u>35° 18' 32.232" E, 0° 27' 47.862" S</u>	<u>1 964</u>	<u>-1.20</u>	<u>2.49</u>	<u>-8.80</u>	<u>3.20</u>
<u>S15</u>	<u>47</u>	<u>35° 18' 35.508" E, 0° 27' 46.938" S</u>	<u>1 971</u>	<u>-1.62</u>	<u>1.64</u>	<u>-6.18</u>	<u>0.68</u>
<u>S30</u>	<u>13</u>	<u>35° 18' 35.508" E, 0° 27' 46.938" S</u>	<u>1 971</u>	<u>-1.46</u>	<u>0.49</u>	<u>-1.94</u>	<u>-0.38</u>
<u>S50</u>	<u>6</u>	<u>35° 18' 35.508" E, 0° 27' 46.938" S</u>	<u>1 971</u>	<u>-2.20</u>	<u>0.49</u>	<u>-2.72</u>	<u>-1.44</u>
<u>SP.a</u>	<u>2</u>	<u>35° 19' 53" E, 0° 26' 5" S</u>	<u>2 081</u>	<u>-2.31</u>	<u>0.02</u>	<u>-2.32</u>	<u>-2.29</u>
<u>SP.b</u>	<u>3</u>	<u>35° 19' 47.292" E, 0° 26' 21.246" S</u>	<u>2 070</u>	<u>-2.67</u>	<u>0.04</u>	<u>-2.71</u>	<u>-2.63</u>
<u>TF</u>	<u>66</u>	<u>35° 18' 35.268" E, 0° 27' 46.842" S</u>	<u>1 965</u>	<u>-0.83</u>	<u>2.32</u>	<u>-8.37</u>	<u>3.22</u>
<i>Smallholder agriculture (SHA)</i>							
<u>RV</u>	<u>75</u>	<u>35° 28' 31.452" E, 0° 24' 3.930" S</u>	<u>2 386</u>	<u>-2.72</u>	<u>0.31</u>	<u>-3.62</u>	<u>-1.21</u>
<u>PC</u>	<u>65</u>	<u>35° 28' 27.324" E, 0° 24' 2.322" S</u>	<u>2 401</u>	<u>-1.62</u>	<u>2.68</u>	<u>-9.93</u>	<u>3.02</u>
<u>S15</u>	<u>18</u>	<u>35° 28' 31.812" E, 0° 24' 0.504" S</u>	<u>2 395</u>	<u>-1.39</u>	<u>1.14</u>	<u>-4.02</u>	<u>0.27</u>
<u>S30</u>	<u>6</u>	<u>35° 28' 31.812" E, 0° 24' 0.504" S</u>	<u>2 395</u>	<u>-1.43</u>	<u>0.65</u>	<u>-2.65</u>	<u>-0.94</u>
<u>TF</u>	<u>64</u>	<u>35° 28' 28.002" E, 0° 24' 2.550" S</u>	<u>2 393</u>	<u>-1.52</u>	<u>2.63</u>	<u>-9.27</u>	<u>2.86</u>
<u>WE.a</u>	<u>18</u>	<u>35° 29' 28.590"-35° 32' 3.468" E, 0° 18' 3.918"-0° 23' 47.700" S</u>	<u>2 492-2 612</u>	<u>-2.64</u>	<u>0.17</u>	<u>-2.89</u>	<u>-2.29</u>
<u>WE.b</u>	<u>2</u>	<u>35° 32' 29.316" E, 0° 18' 3.450" S</u>	<u>2 655</u>	<u>-2.52</u>	<u>0.16</u>	<u>-2.64</u>	<u>-2.40</u>
<u>WL</u>	<u>4</u>	<u>35° 32' 22.554" E, 0° 17' 30.186" S</u>	<u>2 614</u>	<u>-3.06</u>	<u>0.27</u>	<u>-3.40</u>	<u>-2.77</u>
<i>Tea and tree plantations (TTP)</i>							
<u>RV</u>	<u>75</u>	<u>35° 13' 16.086" E, 0° 28' 35.826" S</u>	<u>1 788</u>	<u>-2.29</u>	<u>0.26</u>	<u>-2.92</u>	<u>-1.49</u>
<u>PC</u>	<u>68</u>	<u>35° 18' 1.266" E, 0° 26' 9.348" S</u>	<u>2 106</u>	<u>-1.29</u>	<u>2.54</u>	<u>-8.80</u>	<u>3.40</u>
<u>S15</u>	<u>8</u>	<u>35° 18' 1.206" E, 0° 26' 9.144" S</u>	<u>2 106</u>	<u>-1.29</u>	<u>0.90</u>	<u>-2.34</u>	<u>0.00</u>
<u>S30</u>	<u>5</u>	<u>35° 18' 1.206" E, 0° 26' 9.144" S</u>	<u>2 106</u>	<u>-2.40</u>	<u>1.00</u>	<u>-3.90</u>	<u>-1.67</u>
<u>S50</u>	<u>4</u>	<u>35° 18' 1.206" E, 0° 26' 9.144" S</u>	<u>2 106</u>	<u>-2.54</u>	<u>1.61</u>	<u>-4.93</u>	<u>-1.46</u>
<u>SP.a</u>	<u>5</u>	<u>35° 14' 17.592"-35° 18' 36.252" E, 0° 26' 34.044"-0° 28' 1.698" S</u>	<u>1 862-2 079</u>	<u>-2.51</u>	<u>0.15</u>	<u>-2.63</u>	<u>-2.26</u>
<u>TF</u>	<u>65</u>	<u>35° 18' 1.110" E, 0° 26' 9.288" S</u>	<u>2 106</u>	<u>-1.29</u>	<u>2.49</u>	<u>-8.50</u>	<u>3.23</u>
<i>Main catchment (OUT)</i>							
<u>RV</u>	<u>75</u>	<u>35° 10' 53.046" E, 0° 28' 59.232" S</u>	<u>1 717</u>	<u>-2.42</u>	<u>0.47</u>	<u>-3.62</u>	<u>-0.28</u>
<u>PC</u>	<u>69</u>	<u>35° 10' 53.904" E, 0° 28' 58.824" S</u>	<u>1 718</u>	<u>-0.34</u>	<u>2.53</u>	<u>-9.29</u>	<u>4.37</u>
<u>S15</u>	<u>47</u>	<u>35° 10' 53.712" E, 0° 29' 0.720" S</u>	<u>1 721</u>	<u>-0.68</u>	<u>1.20</u>	<u>-3.83</u>	<u>2.03</u>
<u>S30</u>	<u>24</u>	<u>35° 10' 53.712" E, 0° 29' 0.720" S</u>	<u>1 721</u>	<u>-0.43</u>	<u>0.99</u>	<u>-2.12</u>	<u>1.47</u>
<u>S50</u>	<u>46</u>	<u>35° 10' 53.712" E, 0° 29' 0.720" S</u>	<u>1 721</u>	<u>-0.84</u>	<u>1.35</u>	<u>-3.87</u>	<u>2.50</u>
<u>SP.b</u>	<u>1</u>	<u>35° 21' 50.682" E, 0° 29' 5.208" S</u>	<u>2 159</u>	<u>-2.61</u>	<u>n.a.</u>	<u>-2.61</u>	<u>-2.61</u>

^a RV = stream water, PC = precipitation, SP.a = SP.b = spring, TF = throughfall, WE.a = WE.b = shallow well, WL = wetland, S15 = S30 = S50 = mobile soil water at 15, 30 and 50 cm depth, respectively.

Table 35. Main statistical parameters of observed and modelled $\delta^{18}\text{O}$ for stream water in the three sub-catchments and the main catchments for the gamma model (GM) and exponential piston flow model (EPM). Uncertainty bounds of the modelled parameters (τ and α or η), in parentheses, were calculated through generalized likelihood uncertainty estimation (GLUE).

Site ^a	Area	Elevation	Observed $\delta^{18}\text{O}$		Modelled $\delta^{18}\text{O}$						
			Mean	SD ^b	Mean	SD ^b	NSE ^c	RMSE ^d	Bias	MTT ^e	α/η^f
	<i>km</i> ²	<i>m</i>	‰	‰	‰	‰	-	‰	‰	years	-
<i>Gamma model (GM)</i>											
NF-RV	35.9	1 969	-2.58	0.32	-2.56	0.13	0.15	0.30	0.021	4.0 (3.3–4.6)	0.65 (0.63–0.71)
SHA-RV	27.2	2 386	-2.72	0.31	-2.69	0.16	0.22	0.27	0.029	3.8 (3.1–4.5)	0.61 (0.57–0.66)
TTP-RV	33.3	1 788	-2.29	0.26	-2.29	0.06	0.05	0.25	0.000	3.3 (2.8–4.3)	1.09 (0.99–1.17)
OUT-RV	1021.3	1 717	-2.42	0.47	-2.36	0.26	0.33	0.38	0.061	2.5 (1.8–3.4)	0.48 (0.43–0.54)
<i>Exponential piston flow model (EPM)</i>											
NF-RV	35.9	1 969	-2.58	0.32	-2.58	0.10	0.09	0.31	0.000	2.4 (2.1–2.9)	1.000 (0.994–1.003)
SHA-RV	27.2	2 386	-2.72	0.31	-2.72	0.11	0.12	0.29	0.000	2.2 (1.9–2.6)	1.001 (0.994–1.004)
TTP-RV	33.3	1 788	-2.29	0.26	-2.29	0.07	0.07	0.25	0.000	3.5 (3.1–4.1)	1.011 (1.009–1.018)
OUT-RV	1 021.3	1 717	-2.42	0.47	-2.42	0.20	0.14	0.43	0.001	1.2 (1.0–1.4)	1.001 (0.998–1.007)

^a NF = natural forest, SHA = smallholder agriculture, TTP = tea and tree plantations, OUT = main catchment, RV = stream water; ^b standard deviation; ^c Nash-Sutcliffe efficiency of objective function; ^d root mean square error; ^e estimated mean transit time (in years); ^f model parameters for GM (α) and EPM (η).

Table 46. Main statistical parameters of observed and modelled $\delta^{18}\text{O}$ for mobile soil water at 15 cm depth in the natural forest sub-catchment and at 15 and 50 cm depth in the main catchment for the gamma model (GM) and exponential piston flow model (EPM). Uncertainty bounds of the modelled parameters (τ and α or η), in parentheses, were calculated through generalized likelihood uncertainty estimation (GLUE).

Site ^a	n^b	Elevation	Observed $\delta^{18}\text{O}$		Modelled $\delta^{18}\text{O}$						
			Mean	SD ^c	Mean	SD ^c	NSE ^d	RMSE ^e	Bias	MTT ^f	α/η^g
-	m		‰	‰	‰	‰	-	‰	‰	weeks	-
<i>Gamma model (GM)</i>											
NF-S15	47	1 971	-1.62	1.64	-1.74	1.48	0.79	0.75	-0.12	3.2 (2.8–4.1)	1.5 (0.9–2.2)
OUT-S15	47	1 721	-0.68	1.20	-0.71	0.99	0.50	0.84	-0.03	7.9 (6.1–11.3)	0.9 (0.6–1.2)
OUT-S50	46	1 721	-0.84	1.35	-0.92	0.93	0.47	0.97	-0.08	10.4 (8.8–12.6)	1.4 (1.1–2.0)
<i>Exponential piston flow model (EPM)</i>											
NF-S15	47	1 971	-1.62	1.64	-1.67	1.38	0.78	0.77	-0.05	3.3 (2.6–4.4)	1.0 (0.9–1.1)
OUT-S15	47	1 721	-0.68	1.20	-0.58	0.94	0.52	0.82	0.11	4.5 (3.2–6.7)	0.8 (0.7–1.1)
OUT-S50	46	1 721	-0.84	1.35	-0.90	0.85	0.46	0.99	-0.06	10.8 (8.0–13.9)	1.0 (0.9–1.3)

^a NF = natural forest, OUT = main catchment, S15 = mobile soil water 15 cm depth, S50 = mobile soil water 50 cm depth; ^f number of samples; ^c standard deviation; ^d Nash-Sutcliffe efficiency of objective function; ^e root mean square error; ^f predicted mean transit time (in weeks); ^g model parameters for GM (α) and EPM (η).