Submission of revised version of manuscript titled “HydroMix v1.0: a new Bayesian mixing framework for attributing uncertain hydrological sources ”

We would like to thank Bethanna Jackson, David Ham, along with the three reviewers for their valuable feedback. Their inputs led to significant improvements in the manuscript.

We have incorporated the suggestions made by the reviewers in the revised manuscript. We have now implemented a Markov Chain Monte Carlo (MCMC) sampler to infer the posterior distribution of the model parameters. As recommended by Executive editor David Ham, we have made the model along with the datasets used through zenodo, which is available at http://doi.org/10.5281/zenodo.3475429.

We hope that with these additions and all modifications discussed below, the revised manuscript is now ready for publication in Geoscientific Model Development.

Regards,
Harsh Beria

Response to reviewer 1

We would like to thank this anonymous reviewer for his/her detailed reading of our manuscript and the very useful comments. One main concern raised by the reviewer is about the statistical validity of this approach, specifically the usage of importance sampling instead of an Markov chain Monte Carlo (MCMC) approach to sample the posterior distribution of the mixing ratio. We implemented an MCMC sampler as discussed hereafter. Responses to the specific comments are below. The reviewer comments are in bold, answers in normal style and the quoted text from the revised manuscript in italics.

P2L30: Are there really "n" linear Equations? Since k is the number of tracers, I would assume that we have a system of k linear equations. Then, if k=n we have "n" equations and "n" unknown variables. Why "n-1"?

Assuming we have "*k*" tracers, there will be "*k*+1" linear equations. The first "k" equations are:

$$\boldsymbol{\rho_1 S_1^k + \rho_2 S_2^k + \cdots + \rho_n S_n^k = Y^k}. \quad 1$$

The last equation corresponds to the aggregation of different sources in the mixture, i.e. $\sum_{i=1}^{n} \rho_i = 1$. In order to solve this system of linear equations, "n-1" different tracers are required.

In order to provide more clarity as also proposed by Reviewer 2, we moved Eq. 1 to the beginning of Section 2 (Model description and implementation) (P3L43-P4L4) in the revised manuscript. We also clarified the text which now reads as:

"A system with n sources mixing linearly in a target water body can be written as:

$$\boldsymbol{\rho_1 S_1^k + \rho_2 S_2^k + \cdots + \rho_n S_n^k = Y^k}, \quad 2$$

where Y^k is the concentration of the k^{th} tracer in the target mixture, S_i^k is the concentration of the k^{th} tracer in source i. ρ_i (i=1, .., n) are the fractions of all sources in the mixture, with $\sum_{i=1}^{n} \rho_i = 1$, corresponding to the aggregation of different sources in the mixture. In order to solve this system of linear equations, "n-1" different tracers are required."

P3L14: The authors state that it is a major shortcoming of traditional mixing models that the source concentrations are assumed to come from standard statistical distributions, which are described by some parameters. The authors should acknowledge that this can be a useful approach to account for the fact that the measurements of tracer concentrations in the same source are related to each other in some way, which is a very reasonable assumption. It is a priori not entirely clear that omitting such an assumption is beneficial to solving the mixing problem, since we might neglect reasonable prior knowledge in that case.

We thank the reviewer for this very important comment. The reviewer correctly points out that the traditional approach of fitting a statistical distribution to the source concentrations reflects *a priori* knowledge, which may be useful in a lot of cases. We now mention this in the 'Limitations and Opportunities' Section of the revised manuscript (P21L10-12), where we think this discussion is best located. The text reads as:

"Also HydroMix might not be an appropriate method in instances where fitting statistical distributions to source and target compositions reflect a priori knowledge of the system."

Furthermore, the authors do not directly compare the performance of their approach to the approaches they criticize (e.g. in a synthetic case study). The added value remains therefore rather vague.

We first would like to point out that we did not mean to criticize existing approaches in our manuscript. We indeed do not compare our approach to existing approaches in detail here, since our objective is to present a new method for data sparse situations in which existing methods are not appropriate. To accomplish that, we simulated synthetic case studies to evaluate the results of HydroMix (Section 4.1 of the revised manuscript). As these are statistical tests, the correct answer is known *a priori*, and HydroMix converges to the correct results as is shown in Figures 2 and 3. Given that the paper is already rather long, as also pointed out by reviewer 2, we decided not to increase the complexity and length of the paper by adding a new case study to compare the results of HydroMix with existing methods.

P3L20-25: Arguments 1) and 2) seem to be very similar, if not the same. The authors should either provide two more distinct wordings, or combine the two arguments into one. Argument 3) is not entirely clear. Of course, the true mean and variance of the entire population can only be estimated with high uncertainty from a small sample. But this can be formally considered and should not pose a fundamental problem.

The reviewer refers here to the following statements in the original manuscript:

"1) The mean and variance may not accurately reflect the statistical properties of the source composition. 2) If there is a large amount of information on the source composition, the mean and variance may be an unnecessary simplification of its variability. 3) If the source compositions have a low number of samples, then the mean and variance estimates may be poorly constrained."

We agree that the stated arguments look very similar. This is because we argue mostly based on the very commonly assumed normality condition for the pdf of the different source concentrations, obtained empirically with small sample sizes. We now combine the three points into one sentence (P3L4-L9) in the revised manuscript which reads as:

"This limits both the potential applicability and the insights that can be gained from tracer information in hydrology because the sample mean and variance may not accurately reflect the statistical properties of the actual source composition and the Gaussian approach represents an unnecessary simplification in cases where a large amount of information on source composition is available."

P3L37: Please specify what is exactly meant by the "above limitations". The list 1)-3)? Or additional things in the text above?

We were referring to the previous two paragraphs, we have clarified this in the revised manuscript (P3L20) which reads as:

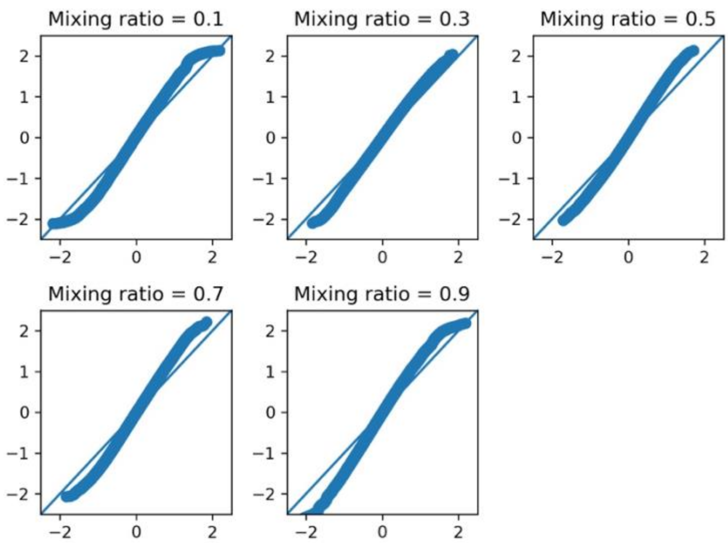
"To overcome the limitations of source heterogeneity and the previously discussed restriction to Gaussian distributions, we present a new mixing approach for hydrological applications, called HydroMix."

P3L37-46: The authors claim that the most important advantage of HydroMix is that there is no assumption about the distribution of the source tracer concentrations, if I understand correctly. While technically true, I think that this argument is misleading. Also HydroMix makes an assumption about the probabilistic nature of the model, namely that the residuals are normally distributed with mean zero and constant variance. It is not clear to me why this should be a milder / better assumption than the one about the observations of the source concentrations being realizations of e.g. a normal distribution. All the uncertainty is just treated in a lumped way, by epsilon, which implicitly contains the deviations of the observed and the true source concentrations. Therefore, the assumptions on the source concentration distribution are not really avoided, they are just all "hidden away" in epsilon.

This is an important comment, which we have carefully addressed in the revised manuscript and also discussed the same in the "Limitations and opportunities" section of the revised manuscript (P21L14-21), which reads as:

"A key difference between HydroMix and other Bayesian mixing approaches is that HydroMix parameterizes the error function whereas other Bayesian approaches parameterize the statistical distribution of source and mixture compositions. Parameterizing source compositions require large sample sizes, which is seldom the case in tracer hydrology. Error parameterization offers a useful alternative and can be also verified against the posterior error distribution. In the case studies demonstrated in this paper, a normal error model was found to be appropriate. However, error models other than Gaussian can be used by formulating the respective likelihood function."

Parameterizing source concentrations requires large sample sizes, which is seldom the case in tracer hydrology. Error parameterization offers a useful alternative and is interesting since our methodological set-up allows increasing the error sample size compared to the input observation sample size. Furthermore, since the model error results from the aggregation of a large number of simplifications and observational errors, i.e. it aggregates a large number of random variables, the error can reasonably be assumed (central limit theorem) to follow a normal distribution. Despite this point, and as in any comparable inference approach (based on model residuals), assessing a posteriori the validity of the underlying distributional assumptions is a key step and we have included an error plot showing the evolution of mean and variance of the error in the revised version (Figure 3 in the revised manuscript, also reproduced below). Also, we have shown Q-Q plots below verifying that posterior distribution of model error closely resemble a normal distribution for different mixing ratios. Given that the paper is already rather long, as also pointed out by reviewer 2, we have not included this figure in the revised manuscript.



Supplementary Figure. Q-Q plots showing the posterior distribution of model errors for five distinct mixing ratios for the low variance dataset.

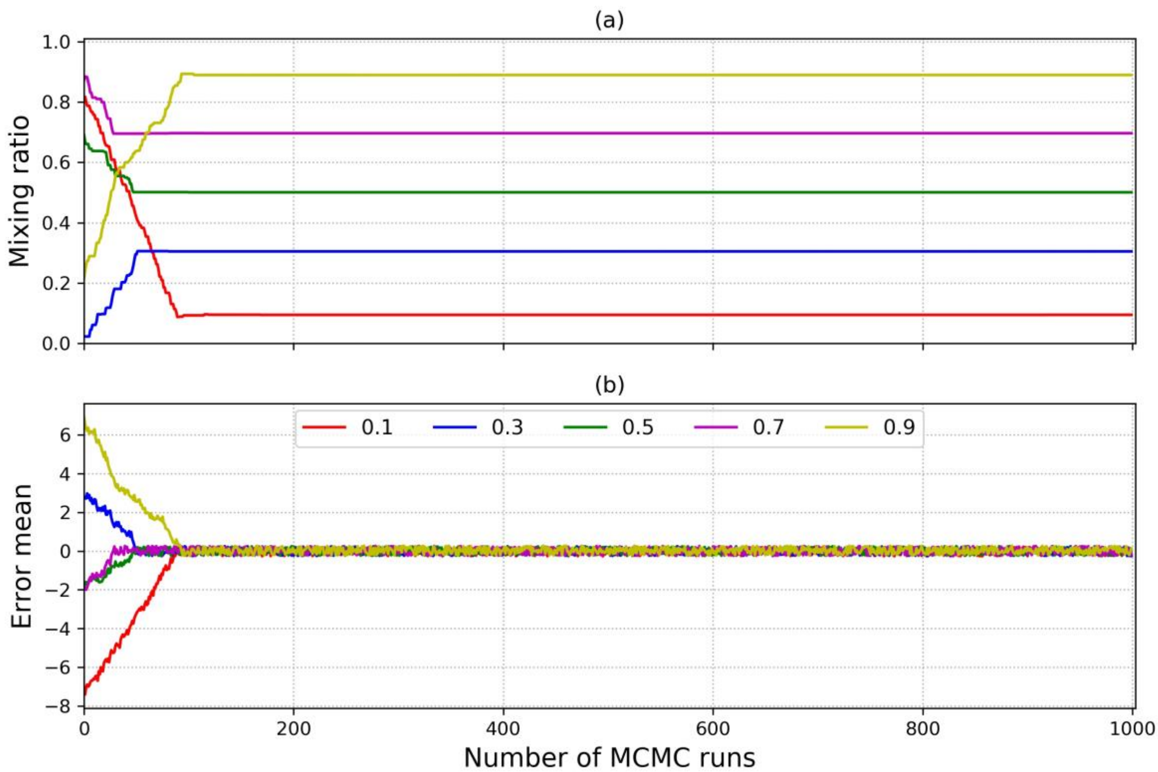


***Figure 1.** Diagnostic plots showing the convergence characteristics of MCMC chains for five different mixing ratios for the low variance dataset (shown in **Error! Reference source not found.**). Subplots (a) and (b) show variations in the inferred mixing ratio and the error mean with increasing MCMC runs.*

In addition, as the reviewer correctly states above, the proposed approach lumps all error sources into a single error term (i.e. input observational uncertainties, model uncertainties, output observational uncertainties, parameter uncertainties). This is standard in hydrological model inference (e.g. Schaefli et al., (2007)) but there is indeed a large body of literature that discusses how this could be relaxed (e.g. via explicit accounting for observational uncertainties (Kavetski et al., 2006)), with the inherent limit that we do not know how to account for model structural uncertainties (e.g. a missing source in our case).

P3L44-46: unclear what the authors mean here

The reviewer refers to the following sentence:
"*An advantage of this approach is that additional model parameters can be incorporated in the framework to describe how the source tracer concentrations might be modified according to specific hydrologic processes that can be decided and explored by the user*."

In HydroMix, the model parameter (mixing ratio) is inferred in an inverse modeling setup. Theoretically, multiple parameters can be inferred in this framework. We demonstrate this in case study 3.5, where isotopic lapse rate is inferred along with the mixing ratio. We have clarified this in the revised manuscript (P3L27-29) which reads as:

"Multiple model parameters can be inferred in such a setup allowing parameterization of additional hydrologic processes that can modify source tracer concentrations (shown in Section ***Error! Reference source not found.****)."*

P5Eq4: I don't understand why Eq. 4 is a solution to limitation ii)

This was a typo, correct would have been "to limitation iv)" (P5L1). We have rectified it in the revised manuscript. Besides, we also removed the statement "*Section 3.5 introduces such an example and proposes a solution in these cases*" since it cuts the flow of text.

P5L11: Timestep of what? Explain what you mean by "assuming a timestep". Isn't the timestep given by the times at which the samples were taken (observed)? I don't see why "tau" can be neglected for short and long timesteps.

The formulation was not clear in the paper. t is indeed the sampling time. We assume however, that all observed samples are samples from the long term (>> 1 year) source and target compositions, i.e. the modelling time step is much larger than the lag, which can thus be removed from the equation. We clarified this in the revised manuscript (P5L7-L10). We also removed the sentence that *tau* could also be short as it was misleading. The new text read as:

"Limitation iii) can be relaxed by assuming a long enough timestep (eg: long term groundwater recharge dynamics), where the observed samples are samples from the long term (>> 1 year) source and target compositions. This allows to replace the timestep 't' and 't+ τ' with Δt and write Eq. (2) as:"

P5Eq5: What do you mean exactly by time-integrated processes? S is a state, not a process, I believe. Please clarify. You might need to provide an equation to clarify which quantity is integrated and what the lower and upper limits of integration are.

We use here the term process in a generic sense to designate a stochastic process. To clarify the explanation, we dropped the word "process" (P5L14-L19).The new text reads as:.

"where the ′ signifies the new time-integrated variables. Now, any observed point-scale tracer concentration p_i in a given source i or in the output (e.g., the isotopic ratio of snowmelt) can be assumed to represent a sample from a stationary process (from S'_1 or S'_2 or Y'),. This assumption is in fact implicitly underlying most of the existing hydrological mixing models where point samples are used to characterize a spatial process and where the time reference of the samples is discarded."

P5Eq6: how do "i" and "j" relate to "t"? "t" seems to disappear in the following equations.

We did indeed not explicitly mention that we omit the time stamp of each sample and simply number them (thus the shift from *t* to *i*). This happens because we do not consider our samples as being a time series but simply as being a set of samples from a random variable, the source composition. As also stated in the reply to the previous comment, this has now been clarified in the revised manuscript (P5L14-L19).

"where the ′ signifies the new time-integrated variables. Now, any observed point-scale tracer concentration p_i in a given source i or in the output (e.g., the isotopic ratio of snowmelt) can be assumed to represent a sample from a stationary process (from S'_1 or S'_2 or Y'),. This assumption is in fact implicitly underlying most of the existing hydrological mixing models where point samples are used to characterize a spatial process and where the time reference of the samples is discarded."

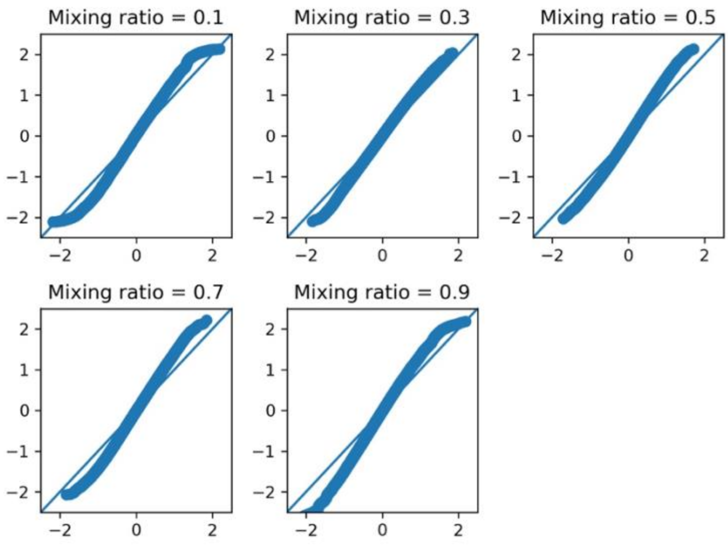
Is it reasonable to compare all the samples of the sources to all the samples of the target mixture? The authors should expand on this. When does it make sense and when not?

HydroMix does not take into account the time at which a source was sampled exactly because we assume that each sample provides a sample of a random variable, which is the source composition. To build the model residuals, we need to compare the model output (modeled target compositions) with observed samples. Assuming that all available source samples are independent, building all possible model simulations from the available source samples is the most natural solution. It is noteworthy that even if the source and target samples are taken at the same time, this does not mean *a priori* that they are dependent since the target samples result from water that has travelled a certain time in the catchment, i.e. target sample from a time step *t* do not result from the source composition at the same time *t*. If in a system we have instantaneous mixing, then the source and target samples taken at the same moment in time will necessarily be strongly correlated. In this case the assumption of independent samples and thus the combination of all samples would not make sense. We have specified this in the "Limitations and opportunities" section of the revised version (P21L23-L31).

"HydroMix builds the model residuals by comparing all the observed source samples with all the observed samples of the target mixture, assuming that all available source and target samples are independent. Interestingly, the assumption of independence holds even if the source and target samples are taken at the same time, since the target samples result from water that has travelled for a certain amount of time in the catchment, and hence is not related to the water entering the catchment. However, if a system has instantaneous mixing, then the source and target samples taken at the same moment of time will necessarily be strongly correlated. In such cases, the assumption of independent samples would not make sense and the method might give spurious results."

P6L1: I believe that the citation provided here is not justified. The cited paper has nothing to do with mixing problems, it is about spectral domain likelihoods for modeling streamflow. However, it would be important to have a reference here that justifies the assumption of the Gaussian distribution for the errors in the specific case of how it is applied in this study (comparing all the measurements of source to all measurements of the mixture concentrations with normal errors). An alternative would be to check the statistical characteristics of the resulting "epsilon" and see if the normal assumption was justified.

The cited paper is indeed about spectral calibration, which is insensitive to the distribution of errors in the time-domain. Therefore it compares spectral-domain to time-domain calibration and an important result is that time-domain calibration is very robust under wrong distributional assumptions, and in particular much more robust than commonly assumed in hydrological modelling. We also show the Q-Q plots below verifying that posterior distribution of model error closely resemble a normal distribution for different mixing ratios.



Supplementary Figure. Q-Q plots showing the posterior distribution of model errors for five distinct mixing ratios for the low variance dataset.

P6L29-30: Please provide the original reference for importance sampling and Metropolis algorithm.

We have include the original references in the revised manuscript (P6L26-L27).

P6L31-33: This sentence is not entirely correct and can be omitted

We have removed this sentence in the revised manuscript.

My most important comment refers to P6L42 – P7L4. The approach that the authors chose to sample from the posterior distribution is not a valid approach. Random sampling of the parameter space with retaining the best X % of the likelihood function does not yield the correct posterior distribution. Instead, the authors obtain some arbitrary measure of spread of the parameters and neither the parameter range nor the predictions done with them have any probabilistic interpretation. This is also one of the potential reasons why they do not manage to reproduce the known "rho" in Figure 2. The true value of "rho" should be inside the confidence limits also for the overlapping (high-variance) case. Also, the higher uncertainty of the mixing ratio "rho" should be visible in the high variance case, but the estimated "rhos" seem to have the same or even less uncertainty associated to them in the high variance case than in the low variance case. This seems odd to me. I would recommend that the authors implement a proper MCMC sampler (e.g. Metropolis) to obtain an actual sample from the posterior distribution. Also, the convergence of the chains needs to be checked, either by visual assessment or by convergence tests. Only converged results should be reported, otherwise meaningful conclusions are not possible.

We agree with the comments of the reviewer and have implemented a MCMC sampler to sample the posterior function in the revised manuscript.

P8Eq15: Does this consider rain on snow events? This might not be so important but could be mentioned

In the hydrologic model used, heat exchange within the snowpack from rain-on-snow events are not considered as that lies beyond the scope of this paper. We have mention this in the revised manuscript (P8L31-L32):

"Rain-on-snow events are not explicitly considered as this lies beyond the scope of this paper."

P9L26: When are samples taken in the model? How many of them are taken?

In this case study, isotopic ratios are simulated and all the rain and snowmelt isotopic ratios are used with HydroMix. The number of rainfall, snowfall and snowmelt samples are 39, 24 and 107, as mentioned in the labels of Figures 6 and 7.

Section 4.1: From the design of the case study, it is not clear if HydroMix is a statistically coherent framework. The authors should provide a proof of concept instead of or in addition to Section 4.1. The basic design of the experiment could be similar to 4.1, but it should be done with a large number of samples, to demonstrate that HydroMix converges to the correct solution in that case. This should also be possible for the high variance case, I think. As I mentioned before, this should be done via proper MCMC sampling, and convergence needs to be checked. For a large number of samples, the uncertainty intervals should contain the true value of "rho", also in the high variance case.

Thank you for this very valuable comment. We have now implemented a MCMC sampler and included a model diagnostic plot showing convergence of the model parameters along with the variation in error mean (Figure 3 in the revised manuscript). We have reproduced figure 2, which reinstates that error decreases with increasing sample size. We added a case with a sample size of 100, where there was a sharp drop recorded in the error statistic when compared to the original simulation size of 40. We did not perform simulations for sample sizes larger than 100 as the computational requirement increases exponentially with increasing sample sizes. Additionally, figure 2b clearly shows decreasing error with increasing sample size and figure 3 shows that the MCMC chains converge rather quickly. This we believe tests the statistical validity of the approach. The figures have been reproduced below:

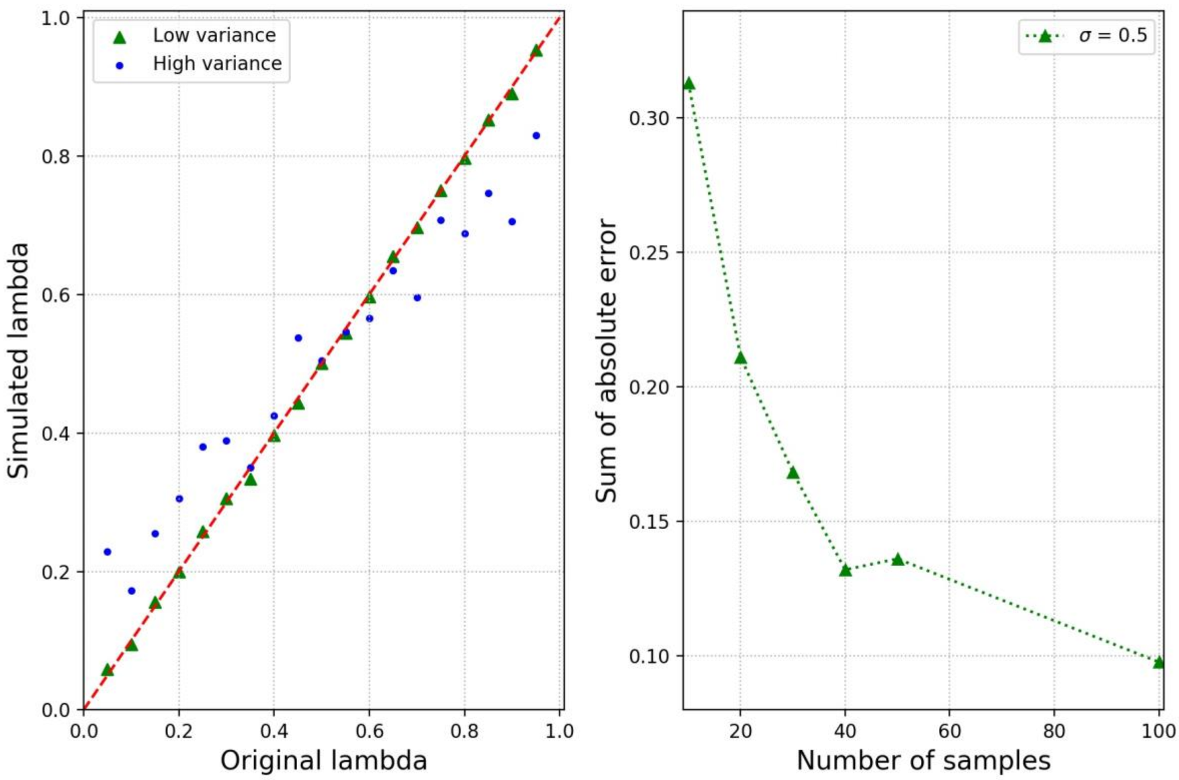


Figure 2. *(a) Scatterplot showing the mixing ratio (ρ) values inferred using HydroMix for the low and high variance synthetic case of* ***Error! Reference source not found.****. The number of source and target samples are 100. (b) Performance of HydroMix in terms of the absolute error between the posterior mixing ratio mean and the true mean for the low variance dataset, summed over all tested ratios plotted as a function of the number of samples drawn for the two sources.*

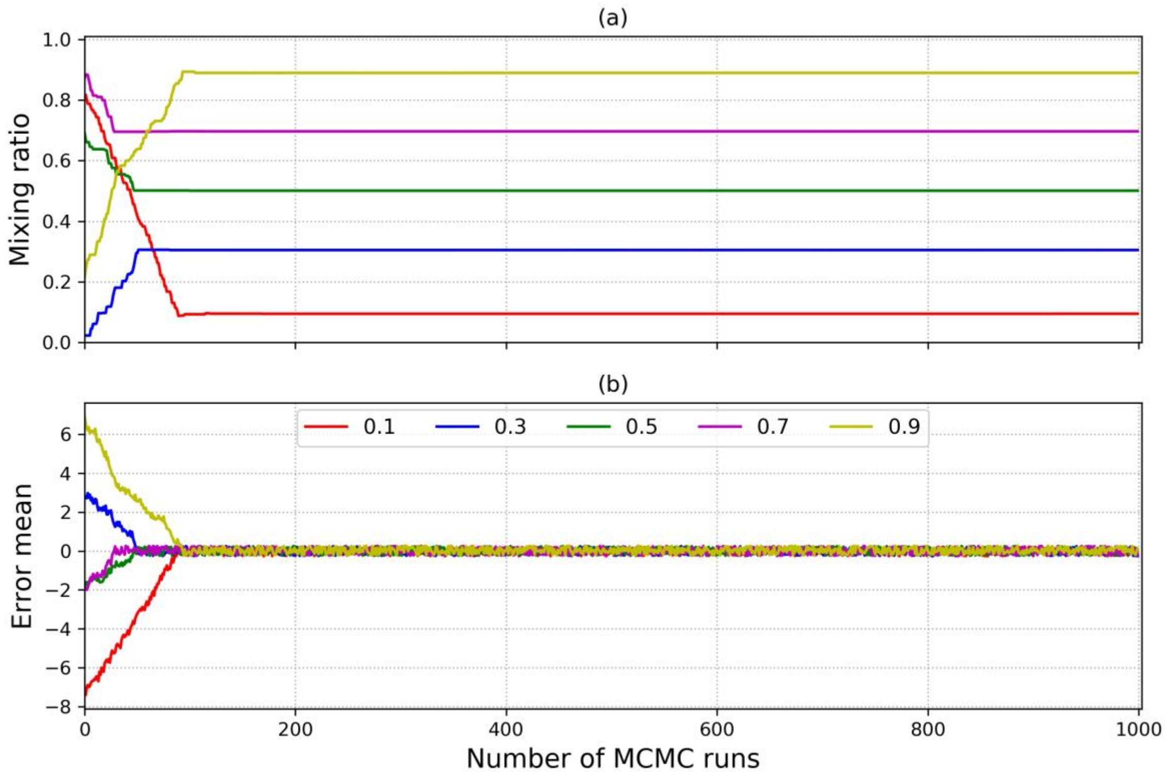


Figure 3. *Diagnostic plots showing the convergence characteristics of MCMC chains for five different mixing ratios for the low variance dataset (shown in* ***Error! Reference source not found.****). Subplots (a) and (b) show variations in the inferred mixing ratio and the error mean with increasing MCMC runs.*

As it stands, conclusion 1 is favorable and it would indicate that HydroMix is a statistically valid method, but it is not supported by the results. If one replaces the word "uncertainty" by "bias", then the conclusion is supported by the results, but it is not a favorable conclusion anymore and indicates major deficiencies of the used approach. The authors should aim to obtain results that support conclusion 1.

We do not fully understand the point that the reviewer is trying to make here. Conclusion 1 now reads as:

"*HydroMix gives reliable results for mixing applications with small sample sizes (< 20-30 samples). As expected, the variance in source tracer composition and the ensuing composition overlap determines the uncertainty in the mixing ratio estimates. The uncertainty in mixing ratio estimates increases with increasing variance in source tracer compositions. Mixing ratio estimates improve (in terms of lower error) with increasing number of source samples.*"

We believe that the MCMC test along with the model convergence plots prove the reliability and validity of HydroMix.

Reference:

Kavetski, D., Kuczera, G., & Franks, S. W. (2006). Bayesian analysis of input uncertainty in hydrological modeling: 1. Theory. *Water Resources Research*, *42*(3), n/a-n/a.

https://doi.org/10.1029/2005WR004368
Schaefli, B., Talamba, D. B., & Musy, A. (2007). Quantifying hydrological modeling errors through a mixture of normal distributions. *Journal of Hydrology*, *332*(3), 303–315. https://doi.org/10.1016/j.jhydrol.2006.07.005

Response to reviewer 2

We would like to thank the anonymous reviewer for his/her valuable comments and important insights into the manuscript. The reviewer raised three broad concerns:

There is heavy referencing especially at the introduction, which sometimes appears to be inadequate (see comments in attached manuscript). Also, some literature on uncertainty in hydrograph separation is missing.
P2L8-13, L15-17, L35-36: please remove some of the references. A good statement doesn't need more than 3 references for support...

We have optimized the number of references in the introduction section, limiting the reference count to 3 for each point being made. Also, we have added references relevant to hydrograph separation in the revised manuscript (P2L25-L30) which reads as:

"Classically, attribution analysis is done by assigning an average tracer concentration to each source, estimated typically from time or space-averages of observed field data (Maule et al., 1994; Winograd et al., 1998), and then solving a serious of linear equations. In order to express uncertainty in the attribution analysis, a tracer-based hydrograph separation approach was first proposed in the work of Genereux, (1998) and has subsequently been used in many studies (Genereux et al., 2002; Koutsouris and Lyon, 2018; Zhu et al., 2019)."

Some work is necessary at section 2 (Model description and implementation) to add more clarify and structure to this section. It is hard to understand what the authors are doing here.
P4L10 (Section 2): Some serious work is necessary to add more clarify and structure to this section. It is hard to understand what the authors are doing here...

We moved some of the discussion in the introduction section about linear mixing problems to this section to provide a context behind the theoretical underpinnings of HydroMix (P3L43-P4L4). As also recommended by reviewer 1, we have simplified the explanation in Section 2.1 of the revised manuscript.

Do you really need so many case studies? They make the paper long and heavy. If you don't need them to make your point, please reduce to 1 or two of them.
P7L13-15: Do you really need 5 case studies? They make the paper long and heavy. If you don't need them to make your point, please reduce to 1 or two of them...

The first case study evaluates whether HydroMix converges to the correct results in standard statistical tests. As also suggested by reviewer 1, we have implemented a MCMC sampler in the benchmark test to prove the validity of the new mixing approach. The second case study evaluates HydroMix using a conceptual hydrologic model and highlights a key deficiency in commonly used mixing approaches. The third case study shows how to account for the deficiency identified earlier. The fourth case study uses HydroMix in a real case study, with the fifth one showing the flexibility offered by this HydroMix to infer additional model parameters. We feel that it is important to demonstrate both the reliability and flexibility of HydroMix and hence have retained the case studies in the revised manuscript.

Responses to the specific comments are mentioned below:

P2L23-L31, P3L4-12: too methodological for an introduction

We moved Eq. 1 to the beginning of "Model description and implementation" section in the revised manuscript (P3L43-P4L4). For P3L4-12, we condensed the discussion with key insights from the studies, instead of providing a detailed explanation in the introduction.

P3L37-38: Some improvement is necessary to provide a proper state-of-the-art with more information on what was exactly done in the many references provided above. Also, here seems to be some missing literature on methods that quantify uncertainty of mixing models. There should be many of them as first studies have been published in the 90s already:
Genereux, D., 1998. Quantifying uncertainty in tracer-based hydrograph separations. Water Resour. Res. 34, 915–919. doi:10.1029/98wr00010

We agree with the reviewer that we had not done an exhaustive review of tracer-based hydrograph separation studies because hydrograph separation is only one of the common applications of mixing models used in hydrology. HydroMix is meant for applications beyond the classic hydrograph separation. However, we do understand that it might be useful to include studies spanning various hydrograph separation techniques and have included a short overview of the same in the revised manuscript (P2L27-L30).

"In order to express uncertainty in the attribution analysis, a tracer-based hydrograph separation approach was first proposed in the work of Genereux, (1998) and has subsequently been used in many studies (Genereux et al., 2002; Koutsouris and Lyon, 2018; Zhu et al., 2019)."

P4L30: The time lag only accounts for advection right? what about dispersion or retardation?

The time lag accounts for any transport effect, including advection and flow path dispersion. Exchange with tightly bound water (bound to the soil matrix) could lead to retardation effects at much longer time scales than the one considered here. We updated the revised manuscript (P4L23-L25), without, however, adding details of what might potentially cause retardation of stable water isotopes since this would go too far for the context of this paper in our view.

"In other words, the time lag (τ) stands for any delay caused by tracer transport from the source to the output; we assume that the source components are conservative in nature."

P4L42: these studies use the storage selection functions approach, which is somewhat different from the approach introduced here. How do they link to this list?

The time scale for subsurface flow strongly depends on the catchment moisture conditions. The studies cited (Benettin et al., 2017; Harman, 2015) show that the fraction of young water in streamflow depend on catchment moisture conditions, often referred to as the "inverse storage effect", i.e. there is more event water in the stream when catchment soil moisture is high. That is what we want to say. We have clarified this in the revised manuscript (P4L40-L42):

"ρ and τ strongly vary in time depending on catchment conditions such as soil moisture (as previously discussed in the context of the 'inverse storage effect' (Benettin et al., 2017; Harman, 2015))."

P6L29-40: This is a small state-o-the-art which rather belongs to the introduction. Please keep the methods section as clear as possible.

This section discusses the different approaches for inferring model parameters, which is why we have retained this in the "*Parameter inference in a Bayesian framework*" section.

Reference:

Benettin, P., Bailey, S. W., Rinaldo, A., Likens, G. E., McGuire, K. J., & Botter, G. (2017). Young runoff fractions control streamwater age and solute concentration dynamics. *Hydrological Processes*, *31*(16), 2982–2986. https://doi.org/10.1002/hyp.11243

Genereux, D. (1998). Quantifying uncertainty in tracer-based hydrograph separations. *Water Resources Research*, *34*(4), 915–919. https://doi.org/10.1029/98WR00010

Genereux, D. P., Wood, S. J., & Pringle, C. M. (2002). Chemical tracing of interbasin groundwater transfer in the lowland rainforest of Costa Rica. *Journal of Hydrology*, *258*(1–4), 163–178. https://doi.org/10.1016/S0022-1694(01)00568-6

Harman, C. J. (2015). Time-variable transit time distributions and transport: Theory and application to storage-dependent transport of chloride in a watershed. *Water Resources Research*, *51*(1), 1–30. https://doi.org/10.1002/2014WR015707

Koutsouris, A. J., & Lyon, S. W. (2018). Advancing understanding in data-limited conditions: estimating contributions to streamflow across Tanzania's rapidly developing Kilombero Valley. *Hydrological Sciences Journal*, *63*(2), 197–209. https://doi.org/10.1080/02626667.2018.1426857

Maule, C. P., Chanasyk, D. S., & Muehlenbachs, K. (1994). Isotopic determination of snow-water contribution to soil water and groundwater. *Journal of Hydrology*, *155*(1), 73–91. https://doi.org/10.1016/0022-1694(94)90159-7

Winograd, I. J., Riggs, A. C., & Coplen, T. B. (1998). The relative contributions of summer and cool-season precipitation to groundwater recharge, Spring Mountains, Nevada, USA. *Hydrogeology Journal*, *6*(1), 77–93. https://doi.org/10.1007/s100400050135

Zhu, X., Wu, T., Zhao, L., Yang, C., Zhang, H., Xie, C., et al. (2019). Exploring the contribution of precipitation to water within the active layer during the thawing period in the permafrost regions of central Qinghai-Tibet Plateau by stable isotopic tracing. *Science of The Total Environment*, *661*, 630–644. https://doi.org/10.1016/J.SCITOTENV.2019.01.064

Response to reviewer 3

We would like to thank this anonymous reviewer for his/her valuable comments and detailed insights into the manuscript. The reviewer raises two major points stated below:

It remains unclear how the model is initiated and which data coming from field data or other studies were used. In this context, I recommend to report more experimental data, on which you rely in a second step to drive your modelling approach.
Figure 3: What do you mean by "different random seeds"? Please see also the general comment regarding the modelling initiation.

HydroMix is initiated by setting a prior distribution for the model parameters. HydroMix requires concentration data for the different components that mix linearly. In the revised version we have clarified this in P6L43:

"Apart from the prior distribution of the model parameters, HydroMix requires tracer concentration of the different sources and of the mixture."

In order to sample the prior distribution of the model parameters, a random number generator is required. To make the results reproducible, it is a recommended practice to specify what is sometimes called the random seed, i.e. a number used to set the random number generator to a specified state, which results in a reproducible set of random numbers (the same seed will give the same random numbers). We have removed this from the text in the revised manuscript to avoid confusion.

As also suggested by the Executive editor, we have provided the experimental data along with the model code through zenodo and included a link of the same in the "*Code and data availability"* section of the revised manuscript.

The study partly relies on the mixing model of precipitation and snow, not snowmelt. While snow and snowmelt have different isotopic signatures, it is conceptually more correct to use snowmelt for mixing models to estimate its contribution to groundwater. I strongly recommend to better justify why snow instead of snowmelt was used to infer the meltwater supply of groundwater if you cannot extend your calculations to snowmelt.
P11L20: It is well known that the isotopic signature of snow is isotopically much more negative and thus much different from the one of snowmelt, which actually forms the 'true liquid' runoff component. Beside, which logistical constraints did prevent from sampling? Snowmelt sampling can easily be carried out by installing PCS collectors or grab sampling the dripping snowmelt

We agree with the reviewer's point on the usage of snowmelt isotopic ratio instead of snowfall or snowpack isotopic ratio as it is the water from snowmelt that infiltrates and recharges groundwater. However, a recent review of previous investigations that explored the differences in isotopic ratio between snowfall and snowmelt by Beria et al., (2018) revealed that snowfall and snowmelt isotopic ratios have similar mean values but different variances, with lower variance in snowmelt than snowfall isotopic ratios. Snowfall isotopic ratio was found to be the most variable followed by snowpack and then snowmelt isotopic ratio. The lower variance in snowmelt isotopic ratios is because of snowpack homogenization caused by mixing of liquid meltwater between different snowpack layers due to diffusion and dispersion.

We have moved this discussion to Section 4.2 (P15L14-L21):

"The mixing ratio is estimated with HydroMix using: (1) samples of the isotopic ratio in snowfall, and (2) samples of the isotopic ratio in snowmelt. The two sample distributions differ, as shown in ***Error! Reference source not found.****, where the variability of the isotopic ratio is lower in snowmelt when compared to snowfall. In the model at hand, this reduction is obtained because of mixing occurring within the snowpack, leading to homogenization, thus reducing the variability in the isotopic ratio of snowmelt. In field data, such a reduction in variability is also generally observed (Beria et al., 2018), as a result of the homogenization as modelled here and from more complex snow physical processes, which lie beyond the scope of this study."*

There also exists a strong temporal variability in the meltwater isotopic ratios, with more negative isotopic ratios in the early part of the melt season (also referred to as the 'melt-out effect'), and less negative isotopic ratios in the later part of the melt season. However, on an aggregate basis, the mean values of the snowfall and snowmelt isotopic ratios are similar, except in regions with substantial sublimation, which is not the case in the Swiss Alps. This makes snowfall isotopic ratios a reasonable proxy for snowmelt isotopic ratios, which is also supported by results of the synthetic case study (Figure 5). We use snowpack isotopic ratio in the mixing case study because Vallon de Nant is a remotely located catchment with very limited winter access. The catchment experiences frequent winter avalanches and mudslides ("https://www.20min.ch/schweiz/news/story/Schlammlawine-begraebt-Strasse-unter-sich-30186734," 2019), making it hard to monitor during the winter season. This is why we were unable to install snowmelt lysimeters or PCS collectors to regularly sample meltwater. Also, as shown in the review paper of Beria et al., (2018), it is reasonable to replace snowmelt with snowpack isotopic ratios. We have clarified this in P11L25-P12L1:

"Vallon de Nant is remotely located with very limited winter access, frequently experiencing winter avalanches. Due to these logistical constraints, snowmelt lysimeters or passive capillary samplers could not be setup to sample snowmelt water; accordingly, grab snowpack samples are used here as a proxy for snowmelt."

P3L37: Please consider to address also the assumptions of mixing models and the corresponding violation. This aspect may also help to justify Bayesian mixing approaches you describe well.

Some limitations of the different mixing approaches were already discussed in the original Section 5 (Limitations and Opportunities). We have expanded on the additional assumptions in the Section 5 (P21L10-L31), as also suggested by reviewer 1.

P4L3: Please add here that the case studies you report later refer to mountainous (high-elevation) catchments

Thanks for pointing this out. We have mentioned the Vallon de Nant case study here in the revised manuscript (P3L37-L38).

"The real-world case study applies HydroMix in a high-elevation headwater catchment in Switzerland."

P5L17: Please clarify the time-integrated processes you refer to

This refers to a comment also made by reviewer 1 about the model formulation and the time step change. We have clarified this paragraph in the revised manuscript (P5L14-L19) which now reads as:

"where the ' signifies the new time-integrated variables. Now, any observed point-scale tracer concentration p_i in a given source i or in the output (e.g., the isotopic ratio of snowmelt) can be assumed to represent a sample from a stationary process (from S'_1 or S'_2 or Y'),. This assumption is in fact implicitly underlying most of the existing hydrological mixing models where point samples are used to characterize a spatial process and where the time reference of the samples is discarded."

P8L14-15: How is the sine function defined? How do you derive the amplitude and time lag? Table 4: How do you justify the values of precipitation isotopic lapse rate? Can you provide field data or further references on experimental data?

The precipitation isotopic ratio time series was assumed to be sampled from a sinusoidal distribution, which is in-line with previous studies in Switzerland (Allen et al., 2018). The mean value and amplitude of the precipitation isotopic ratio closely corresponds with values obtained with the field data in Vallon de Nant. As already pointed out by the Executive editor, we have provided the used database of precipitation isotopic data through zenodo and include the link in the revised manuscript.

We used an offset value of ($-\pi/2$) in the sine function of the precipitation isotopic ratio (mentioned in Table 4). This corresponds to the commonly obtained seasonal variation of the precipitation isotopic ratio in Switzerland, where the ratio is lower (or more negative) during the winters and higher (or less negative) during the summers. Such a seasonal trend has also been reported previously (Allen et al., 2018; Beria et al., 2018).

P8L22: Please add some references to justify the temperature boundaries you have chosen? Other common boundaries are -1 to 3_C or-1.5 to -1.5, for example.

We have included the relevant references in the revised manuscript (P8L19).

P10L39: Please clarify, to which small glaciers do these area proportions of 4.4 % and 10.1 % belong to?

The line mentioned by the reviewer reads: "*Despite the relatively low elevation, there is a small glacier with an extended moraine that covers 4.4% and 10.1% of the catchment area*"

Vallon de Nant has a small glacier on its South-western tip which covers around 4.4% of the catchment area, below which an extended moraine occupies 10.1% of the catchment area. We have reformulated the text (P10L42-L44) to add clarity:

"Despite the relatively low elevation, there is a small glacier on its South-western tip, which covers around 4.4% of the catchment area, below which an extended moraine occupies 10.1% of the catchment area."

Table 1: What do you mean by top snowpack layer?

Top snowpack layer refers to the top most layer of the snowpack, which we use as a proxy for recent snowfall as we do not sample snowfall.

P12L34- 35: Please rephrase and clarify here. The catchment average isotopic ratio does not simply depend on the elevation gradient, which may hold better for precipitation variabilities. But on the presence of the snowpack and where the snowpack is isothermal so that melting could start.

We agree with the reviewer that the spatial variability in precipitation isotopes is not only a function of elevation, but also depends on the source of moisture origin, cloud condensation temperature and snow metamorphism effects. The case study of lapse rate effect is a mere demonstration that HydroMix allows inference of additional parameters that can account for various physical processes that may modify precipitation isotopic ratio.

With regards to the spatial variability in snowpacks, we use a spatially lumped hydrological model and do not explicitly simulate the spatial variability in snowpack isotopic ratios. We acknowledge that snowpacks at lower elevations melt first and they have isotopic ratios which are different from higher elevation snowpacks. We do not account for this spatial heterogeneity as this lies beyond the scope of this paper. We have expanded upon this in Section 3.5 of the revised manuscript (P13L5-L11):

"It is important to note that precipitation isotopic ratio is not only a function of elevation, but also depends on other factors such as the source of moisture origin, cloud condensation temperature, secondary evaporation, etc. Similarly, a strong spatial variability exists in the isotopic ratio of snowmelt water, depending on catchment aspect, snow metamorphism, wind distribution, etc. This case study is a mere demonstration that HydroMix allows inference of additional parameters that can account for various physical processes that may modify isotopic ratios."

P15L4-8: Please consider moving this paragraph to section 3.2

The reviewer refers to the following text:

"The parameters used to generate daily precipitation, air temperature and precipitation isotopic ratios for a run time of 100 years are shown in Table 4. The static volume of groundwater that does not interact directly with the stream, GC is set to 1000 mm. Figure 4 shows the resulting variation in the isotopic ratio of groundwater over the entire 100 year period, showing the system achieves a steady state condition after ~15 years of simulation"

Thank you for the suggestion. We have moved this to section 3.2 in the revised manuscript.

Figure 6: How did you define the number of days on which rainfall, snowfall and snowmelt occurred?

In order to simulate precipitation, time between two successive precipitation events is modelled as a Poisson process, with the number of yearly precipitation events specified as 30. The snow accumulation and the degree-day snowmelt model are then used to compute the number of snowfall days and of snowmelt events. This has been clarified in Section 3.2 (P9L20-L25) in the revised version.

P17L17, P20L3-59: Please rephrase

P17L17 reads:
"In this study, we have used a relatively simple normalization based weighting function (Eq. (24)). Testing other weighting functions which have been proposed in the past (Vasdekis et al., 2014) is certainly possible, and is left for future research."

The last sentence part is indeed not well formulated. We have rephrase it in the revised manuscript (P17L29-P18L2) as:

"In this study, we have used a relatively simple normalization based weighting function (Eq. (24)). Testing other weighting functions which have been proposed in the past (Vasdekis et al., 2014) and is left for future research."

Figure 9: Please enlarge axis tick labels. Why did you use different x axis scales?

We have use larger tick labels in the revised manuscript.

The x axis of the top subplot of Figure 9 shows the lapse rate in ^{2}H whereas the bottom subplot shows the lapse rate in ^{18}O. As the isotopic ratios in ^{2}H and ^{18}O are different, the lapse rates are also different, which is why the two subplots have different x-axis scales.

P22L7: What is small sampling number in your opinion?

Small sampling sizes can be anywhere less than 20-30 samples. We have mentioned this in the conclusion #1 in revised version (P22L28-29).

P21L31: I do not see how sediment dynamics fit in here. Sediment dynamics may be coupled with specific runoff components or also decoupled.

Mixing models are frequently used in sediment fingerprinting to quantify the sediment contribution from different parts of a catchment. Blake et al., (2018) is a recent example where a Bayesian mixing model was used to understand the spatial origin of river sediments. This has been clarified in the revised version (P22L6-L7).

Typing errors: P1L29: Please change to "that effectively weight"

P21L17: Rephrase to “tracer data being available”

Thanks, this has been rephrased in the revised manuscript.

Reference:

Allen, S. T., Kirchner, J. W., & Goldsmith, G. R. (2018). Predicting spatial patterns in precipitation isotope (δ2H and δ18O) seasonality using sinusoidal isoscapes. *Geophysical Research Letters*, *45*(10), 4859–4868. https://doi.org/10.1029/2018GL077458

Beria, H., Larsen, J. R., Ceperley, N. C., Michelon, A., Vennemann, T., & Schaefli, B. (2018). Understanding snow hydrological processes through the lens of stable water isotopes. *Wiley Interdisciplinary Reviews: Water*, *5*(6), e1311. https://doi.org/10.1002/wat2.1311

Blake, W. H., Boeckx, P., Stock, B. C., Smith, H. G., Bodé, S., Upadhayay, H. R., et al. (2018). A deconvolutional Bayesian mixing model approach for river basin sediment source apportionment. *Scientific Reports*, *8*(1), 13073. https://doi.org/10.1038/s41598-018-30905-9

https://www.20min.ch/schweiz/news/story/Schlammlawine-begraebt-Strasse-unter-sich-30186734. (2019). Retrieved from https://www.20min.ch/schweiz/news/story/Schlammlawine-begraebt-Strasse-unter-sich-30186734

Vasdekis, V. G. S., Rizopoulos, D., & Moustaki, I. (2014). Weighted pairwise likelihood estimation for a general class of random effects models. *Biostatistics*, *15*(4), 677–689. https://doi.org/10.1093/biostatistics/kxu018

HydroMix v1.0: a new Bayesian mixing framework for attributing uncertain hydrological sources

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Abstract

Tracers have been used for over half a century in hydrology to quantify water sources with the help of mixing models. In this paper, we build on classic Bayesian methods to quantify uncertainty in mixing ratios. Such methods infer the probability density function (pdf) of the mixing ratios by formulating pdfs for the source and target concentrations and inferring the underlying mixing ratios via Monte Carlo sampling. However, collected hydrological samples are rarely abundant enough to robustly fit a pdf to the sources. Our approach, called HydroMix, solves the linear mixing problem in a Bayesian inference framework where the likelihood is formulated for the error between observed and modelled target variables, which corresponds to the parameter inference set-up commonly used in hydrological models. To address small sample sizes, every combination of source samples is mixed with every target tracer concentration. Using a series of synthetic case studies, we evaluate the performance of HydroMix using a Markov Chain Monte Carlo sampler. We then use HydroMix to show that snowmelt accounts for 60-62% of groundwater recharge in a Swiss Alpine catchment (Vallon de Nant), despite snowfall only accounting for 40-45% of the annual precipitation. Using this example, we then demonstrate the flexibility of this approach to account for uncertainties in source characterization due to different hydrological processes. We also address an important bias in mixing models that arises when there is a large divergence between the number of collected source samples and their flux magnitudes. HydroMix can account for this bias by using composite likelihood functions that effectively weight the relative magnitude of source fluxes. The primary application target of this framework is hydrology, but it is by no means limited to this field.

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Keywords: Markov Chain Monte Carlo; stable water isotopes; hydrograph separation; isotopic lapse rate; rain; snow;

1 Introduction

Most water resources are a mixture of different water sources that have travelled via distinct flow paths in the landscape (e.g. streams, lakes, groundwater). A key challenge in hydrology is to infer source contributions to understand the flow paths to a given water body using a source attribution technique. A classic example is the two-component hydrograph separation model to quantify the proportion of groundwater and rainfall in streamflow, often referred to as “pre-event” water vs “event” water (Burns et al., 2001; Klaus and McDonnell, 2013; Schmieder et al., 2016). Other examples include estimating the proportional contribution of rainfall and snowmelt to groundwater recharge (Beria et al., 2018; Jasechko et al., 2017; Jeelani et al., 2010), fog to the amount of throughfall (Scholl et al., 2011, 2002; Uehara and Kume, 2012), and soil moisture (at varying depths) and groundwater to vegetation water use (Ehleringer and Dawson, 1992; Evaristo et al., 2017; Rothfuss and Javaux, 2017).

The primary goal of such attribution in hydrology is to infer the contribution of different sources to a target water body, where the tracer can be an observable compound like a dye, or a conservative solute, or even a proxy for chemical composition such as electrical conductivity. The key requirement is that the concentration of the tracer is distinguishable between different sources. The stable isotope composition of hydrogen and oxygen in water (subsequently referred to as ‘stable isotopes of water’) are used as tracers in hydrology. Other commonly used tracers include electrical conductivity (Hoeg et al., 2000; Laudon and Slaymaker, 1997; Lopes et al., 2018; Pellerin et al., 2007; Weijs et al., 2013) and conservative geochemical solutes such as chloride and silica (Rice and Hornberger, 1998; Wels et al., 1991).

Classically, attribution analysis is done by assigning an average tracer concentration to each source, estimated typically from time or space-averages of observed field data (Maule et al., 1994; Winograd et al., 1998), and then solving a serious of linear equations. In order to express uncertainty in the attribution analysis, a tracer-based hydrograph separation approach was first proposed in the work of Genereux, (1998) and has subsequently been used in many studies (Genereux et al., 2002; Koutsouris and Lyon, 2018; Zhu et al., 2019). Bayesian mixing approaches offer a useful alternative to classic hydrograph separation, as Bayesian approaches explicitly acknowledge the variability of source tracer concentrations estimated from observed samples (Barbeta and Peñuelas, 2017; Blake et al., 2018). Rather than a single estimate of source contributions, Bayesian approaches yield full probability density functions (pdfs) of the fraction of different sources in the target mixture (Parnell et al., 2010; Stock et al., 2018), hereafter referred to as ‘mixing ratios’.

Bayesian mixing was first developed in ecology to estimate the proportion of different food sources to animal diets (Parnell et al., 2010; Stock et al., 2018). Hydrological applications of such models are still rare (Blake et al., 2018; Evaristo et al., 2016, 2017; Oerter et al., 2019). In a Bayesian mixing model, a statistical distribution is fitted to both the measured source tracer concentrations, and to the measured tracer concentrations from the target (e.g. river, groundwater, vegetation). The distribution of the mixing ratios is then inferred via Bayesian inference. With recent advances in probabilistic programming languages like Stan (Carpenter et al., 2017), Bayesian inference has become a relatively simple task.

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where Y^k is the concentration of the k^{th} tracer in the target mixture, S_i^k is the concentration of the k^{th} tracer in source *i*. ρ_i (*i=1, .., n*) are the fractions of all sources in the mixture, with $\sum_{i=1}^{n} \rho_i = 1$. The system of the *n* linear equations can be solved if the number of tracers is *n*-1, leading to a system of *n* equations and *n* unknown variables

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Deleted: as follows: Random samples are drawn from the source distributions and from a given prior distribution of the mixing ratios. Based on these samples, the target tracer concentrations are calculated according to Eq. (1). The likelihood of a given (drawn) set of mixing ratios is calculated by comparing the modelled target tracer concentrations with their observed values

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However, the key limitation with the above approach is that the source compositions are assumed to come from standard statistical distributions. Typically, the sources are assumed to be drawn from Gaussian distributions, which can be fully characterized by the mean and variance of the data available for each source (Stock et al., 2018). This limits both the potential applicability and the insights that can be gained from tracer information in hydrology because the sample mean and variance may not accurately reflect the statistical properties of the actual source composition and the Gaussian approach represents an unnecessary simplification in cases where a large amount of information on source composition is available.

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The mean and variance may not accurately reflect the statistical properties of the source composition.¶
If there is a large amount of information on the source composition, the mean and variance may be an unnecessary simplification of its variability.¶
If the source compositions have a low number of samples, then the mean and variance estimates may be poorly constrained.¶

An additional complication in hydrology comes from the fact that observed point-scale samples do not necessarily capture the tracer concentrations in the actual sources, which are spatially distributed and whose contribution can be temporally variable depending on the state of the catchment (Harman, 2015). For instance, if we were to characterize the contribution of snowmelt to groundwater, we need to capture (1) the temporal evolution of the isotopic ratio of snowmelt, which strongly varies in space (Beria et al., 2018; Earman et al., 2006), and (2) the temporal evolution of the area actually covered by snow. This spatially and temporally distributed nature of the sources can be hard to account for in both the analytical and the Bayesian mixing approaches.

To overcome the limitations of source heterogeneity and the previously discussed restriction to Gaussian distributions, we present a new mixing approach for hydrological applications, called HydroMix. This approach does not require a parametric description of observed source or target tracer concentrations. Instead, HydroMix formulates the linear mixing problem in a Bayesian inference framework similar to hydrological rainfall-runoff models (Kavetski et al., 2006a), where the mixing ratios of the different sources are treated as model parameters. Multiple model parameters can be inferred in such a setup allowing parameterization of additional hydrologic processes that can modify source tracer concentrations (shown in Section 3.5). A more detailed account of the advantages and limitations of this new approach is given in Section 5.

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In this paper, we first describe the theoretical details of HydroMix for a simple case study with two sources, one mixture and one tracer (Section 2). Section 3 presents synthetic and real-world case studies that demonstrate the accuracy, robustness and flexibility of HydroMix. In the synthetic case study, we use a conceptual hydrologic model to simulate tracer concentrations. We also introduce a composite likelihood function that accounts for the magnitude of the different sources. The real-world case study applies HydroMix in a high-elevation headwater catchment in Switzerland. The results of these applications are presented in Section 4 before summarizing the main outcomes, applicability, and limitations of HydroMix in Section 5.

2 Model description and implementation

A system with n sources mixing linearly in a target water body can be written as:

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$$\rho_1 S_1^k + \rho_2 S_2^k + \cdots + \rho_n S_n^k = Y^k, \qquad (1)$$

where Y^k is the concentration of the k^{th} tracer in the target mixture, S_i^k is the concentration of the k^{th} tracer in source *i*. ρ_i (*i=1, .., n*) are the fractions of all sources in the mixture, with $\sum_{i=1}^{n} \rho_i = 1$, corresponding to the aggregation of different sources in the mixture. In order to solve this system of linear equations, "*n-1*" different tracers are required.

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Section 2.1 details the general modeling approach for a simplified system with two sources and one tracer. This is followed by a detailed discussion on the choice of the parameter inference approach used.

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2.1 Linear mixing model with non-concomitant observed data

For a system with two sources that combine linearly to form a mixture, the mixing model can be formulated as:

$$\rho S_1(t) + (1-\rho) S_2(t) = Y(t+\tau), \qquad 2$$

where $S_1(t)$ is the concentration of tracer in source 1 at timestep t, $S_2(t)$ is the concentration of tracer in source 2 at timestep t, $Y(t+\tau)$ is the concentration of the mixture (i.e. the tracer concentration in the target) at timestep $t+\tau$, ρ is the mixing ratio and τ is the time delay between the time when source enters the system and the time when it is observed in the mixture. As an example, for a case where the two sources are snowmelt and rainfall and the mixture is groundwater, ρ represents the proportional groundwater recharged from snowmelt and τ represents the average time lag for rain and snowmelt to reach the groundwater once they enter into the soil. In other words, the time lag (τ) stands for any delay caused by tracer transport from the source to the output; we assume that the source components are conservative in nature.

The two parameters in this system, the mixing ratio (ρ) and the time delay (τ), can be inferred via classical Bayesian parameter inference which is widely used in hydrology (Kavetski et al., 2006a, 2006b; Schaefli and Kavetski, 2017). This implies taking an observed timeseries of the target (e.g. the tracer concentration in groundwater) and building a vector of model residuals:

$$\varepsilon_t = \tilde{Y}_t - \hat{Y}_t, \qquad 3$$

where $\tilde{Y}_t$ represents the observed mixture concentration and $\hat{Y}_t$ represents the simulated mixture concentration. However, in real environmental systems like that of groundwater recharge from rainfall and snowmelt, there are four major difficulties which can prevent the inference of ρ and τ from the observed data.

i. ρ and τ strongly vary in time depending on catchment conditions such as soil moisture (as previously discussed in the context of the 'inverse storage effect' (Benettin et al., 2017; Harman, 2015)).
ii. Long time series of the tracer concentration in both the sources and mixture are rare.
iii. The effect of seasonality in precipitation can make the inference of τ very difficult in case the goal is to understand the intra-annual recharge dynamics.
iv. The tracer concentration in the different sources are generally measured at point scales whereas the tracer concentration in the target integrates inputs over the entire source area.

Deleted: Section 3.5 introduces such an example and proposes a solution in these cases.

Our practical solution to limitation iv) is to assume that tracer concentrations in the two sources are functions of observable point processes:

$$S_i(t) = f_i\big(P_i(t)\big), \tag{4}$$

where the function f_i represents the transformation from the point to the catchment scale for source i. Limitation iii) can be relaxed by assuming a long enough timestep (eg: long term groundwater recharge dynamics), where the observed samples are samples from the long term (>> 1 year) source and target compositions. This allows to replace the timestep 't' and '$t+\tau$' with Δt and write Eq. (2) as:

$$\rho S_1'(\Delta t) + (1-\rho) S_2'(\Delta t) = Y'(\Delta t), \tag{5}$$

where the $'$ signifies the new time-integrated variables. Now, any observed point-scale tracer concentration p_i in a given source i or in the output (e.g., the isotopic ratio of snowmelt) can be assumed to represent a sample from a stationary process (from S'_1 or S'_2 or Y'). This assumption is in fact implicitly underlying most of the existing hydrological mixing models where point samples are used to characterize a spatial process and where the time reference of the samples is discarded.

By utilizing all the available measurements $\{p_1'\}_{i=1..n}$ and $\{p_2'\}_{j=1..m}$ of the two sources in the above model, with n samples of source 1 and m samples of source 2, we can build $n \times m$ predictions and compare them with the q observed samples of the target as:

$$\varepsilon_{ij}^k = \tilde{Y}_{obs}^k - \hat{Y}_{ij}, \tag{6}$$

where $\tilde{Y}_{obs}^k$ is the k-th observed target concentration out of a total number of q target concentrations.

Assuming that the residuals can be described with a Gaussian error model with a mean of zero and constant variance σ,

$$\varepsilon \sim N(0, \sigma), \tag{7}$$

we can compute the likelihood function of the residuals as the joint probability of all the residuals:

$$L_j(\tilde{Y}_{obs} | S_1, S_2, \boldsymbol{\theta}) = \prod_{k=1}^{q} \prod_{j=1}^{m} \prod_{i=1}^{n} (2\pi\sigma^2)^{-0.5} \exp\left(-\frac{1}{2}\frac{(\tilde{Y}_{obs}^k - \hat{Y}_{ij})^2}{\sigma^2}\right), \tag{8}$$

where $\boldsymbol{\theta}$ represents all the model parameters. The above Gaussian error model could in principle be replaced with any other stochastic process. However, the Gaussian error model has been shown to be relatively robust in this kind of an application (Lyon, 2013; Schaefli and Kavetski, 2017).

In the case of linear mixing between two sources, the two model parameters considered at this stage are the mixing ratio ρ and the error variance σ. The error variance can either be

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computed from the observed residuals or be treated as a model parameter (Kuczera and Parent, 1998; Schaefli et al., 2007). For the examples shown in this paper, the error variance is computed from the residuals.

In order to avoid numerical problems, we use the log-likelihood form of Eq. (8):

$$\log L_j(\tilde{Y}_{obs}|S_1, S_2, \theta) \; = \; \sum_{k=1}^{q} \sum_{j=1}^{m} \sum_{i=1}^{n} -0.5 \left[2\pi\sigma^2 + \frac{\left(\tilde{Y}_{obs}^{k} - \hat{Y}_{ij}\right)^2}{\sigma^2}) \right]. \qquad 9$$

2.2 Parameter inference in a Bayesian framework

Following the general Bayes' equation, the posterior distribution of the model parameters can be written as:

$$p(\boldsymbol{\theta}|S_1, S_2, \tilde{Y}) = \frac{p(\tilde{Y}|\theta, S_1, S_2)p(\theta)}{p(\tilde{Y}|S_1, S_2)}, \qquad 10$$

where $p(\boldsymbol{\theta})$ is the prior distribution of the model parameters and $p(\tilde{Y}|\boldsymbol{\theta}, S_1, S_2)$ is the likelihood function. The denominator of Eq. (10) can generally not be computed as that would require integration over the whole parameter space which is computationally expensive, which is why Eq. (10) is reduced to:

$$p(\boldsymbol{\theta}|S_1, S_2, \tilde{Y}) \propto p(\tilde{Y}|\boldsymbol{\theta}, S_1, S_2)p(\boldsymbol{\theta}). \qquad 11$$

Two methods are traditionally used in hydrology to infer the posterior distribution from Eq. (11), Markov Chain Monte Carlo (MCMC) sampling (Hastings, 1970; Metropolis and Ulam, 1949) and importance sampling (Glynn and Iglehart, 1989; Neal, 2001). In the case of MCMC sampling, a common approach is the Metropolis algorithm (Kuczera and Parent, 1998; Schaefli et al., 2007; Vrugt et al., 2003). In importance sampling, the posterior distribution is obtained from weighted samples drawn from the so-called importance distribution. For typical multivariate hydrological problems, the only possible choices for the importance distribution are either uniform sampling over a hypercube or sampling from an over-dispersed multi-normal distribution (Kuczera and Parent, 1998). A stochastic process is defined as over-dispersed when the variance of the underlying distribution is greater than its mean (Inouye et al., 2017). The sampling distributions in such cases have large variance, allowing sufficient sampling over the entire parameter range.

We implement a MCMC sampling algorithm using a Metropolis-Hastings (Hastings, 1970) criterion to infer the posterior distribution of the mixing ratio. For the synthetic case study (Section 3.1), we setup 10 parallel MCMC chains to monitor convergence according to the classical Gelman-Rubin convergence criterion (Gelman and Rubin, 1992). Each chain is initiated by assigning a uniform prior distribution for the mixing ratio, where the mixing ratio varies between 0 and 1. For the subsequent case studies, we use importance sampling for the sake of simplicity. The prior distribution of additional model parameters (if applicable) are discussed in the corresponding case study section. Apart from the prior distribution of the model parameters, HydroMix requires tracer concentration of the different sources and of the

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mixture. The error model variance is not jointly inferred with other model parameters but calculated for each sample parameter set from the residuals according to Eq. (6).

3 Case studies

We provide a comprehensive overview of the performance of HydroMix based on a set of synthetic case studies (case studies 3.1 and 3.2) and a real-world application to demonstrate the practical relevance for hydrologic applications (case studies 3.4 and 3.5). The first case study demonstrates the ability of HydroMix to converge on the correct posterior distribution for synthetically generated data. The second case study uses a synthetic dataset of rain, snow and groundwater isotopic ratios using a conceptual hydrologic model, and compares the results of HydroMix to the actual mixing ratios assumed to generate the data set. It then weights the sources samples and evaluates the effect of weighting on the mixing ratio. In the third and fourth case studies, HydroMix is applied to observed tracer data from an Alpine catchment in the Swiss Alps to infer source mixing ratios and an additional parameter (isotopic lapse rate).

3.1 Mixing using Gaussian distributions

In this example, sources S_1 and S_2 are drawn from two Gaussian distributions with different means (μ_1, μ_2) and standard deviations (σ_1, σ_2) and combined to form the mixture *Y* with a constant mixing ratio ρ:

$$\rho S_1 + (1-\rho)S_2 = Y. \qquad 12$$

Assuming the two distributions are independent, the resultant mixture is normally distributed with mean and variance defined as:

$$Y \sim N(\rho\mu_1 + (1-\rho)\mu_2,\ \rho^2\sigma_1^2 + (1-\rho)^2\sigma_2^2). \qquad 13$$

A given number of samples are drawn from the distributions of S_1 and S_2 and of the mixture Y. The posterior distribution of the mixing ratio, $p(\boldsymbol{\rho}|\widetilde{S_1}, \widetilde{S_2}, \widetilde{Y})$, is then inferred using HydroMix for i) a case where the two source distributions are well identifiable, and ii) a case where the distributions have a large overlap. Different values of mixing ratios are tested, with ratios varying from 0.05 to 0.95 in steps of 0.05.

The sensitivity of HydroMix to the number of samples drawn from S_1, S_2 and Y, along with the time to convergence is assessed based on the sum of the absolute error between the estimated mixing ratio $\hat{\rho}$ and its true value ρ.

3.2 Mixing with a time series generated using a hydrologic model

In this case study, we build a conceptual hydrologic model where groundwater is assumed to be recharged directly from rainfall and snowmelt. Stable isotopes of water in deuterium (δ^2H) is used to see how the isotopic ratio in groundwater evolves under different assumptions of rain and snow recharge efficiencies.

Synthetic time series are generated for precipitation, isotopic ratio in precipitation and air temperature at a daily timestep. For generating the precipitation time series, the time between two successive precipitation events is assumed to be a Poisson process with the precipitation intensity following an exponential distribution (Botter et al., 2007; Rodriguez-Iturbe et al., 1999). Time series of air temperature and of isotopic ratios in precipitation are obtained by generating an uncorrelated Gaussian process with the mean following a sine function (to emulate a seasonal signal) and with constant variance (Allen et al., 2018; Parton and Logan, 1981). The separation of precipitation into rainfall (P_r) and snowfall (P_s) is done based on a temperature threshold approach (Harpold et al., 2017a), where the fraction of rainfall $f_r(t)$ at time step t is computed as a function of air temperature $T(t)$:

$$f_r(t) = \begin{cases} 0 & \text{if } T(t) < T_L \\ \frac{T(t)-T_L}{T_H-T_L} & \text{if } T_L \leq T(t) \leq T_H \\ 1 & T(t) > T_H, \end{cases} \tag{14}$$

where T_L and T_H are the lower and upper threshold bounds. A double air temperature threshold approach has been shown to be more accurate than a single temperature threshold (Harder and Pomeroy, 2014; Harpold et al., 2017a, 2017b). In this case study, T_L and T_H are set to -1 °C and +1 °C. The evolution of the snow water equivalent (SWE) in the snowpack (h_s) is computed as:

$$\frac{dh_s(t)}{dt} = P_s(t) - M_s(t), \tag{15}$$

where M_s is the magnitude of snowmelt, computed using a degree-day approach as proposed by Schaefli et al., (2014):

$$M_s = \begin{cases} a_s(T(t) - T_m), & \text{if } T(t) > T_m \\ 0 & \text{otherwise} \end{cases}, \tag{16}$$

where a_s is the degree-day factor (set here to 2.5 mm/°C/day) and T_m is the threshold temperature at which snow starts to melt (set to 0 °C). Rain-on-snow events are not explicitly considered as this lies beyond the scope of this paper. The snowpack is assumed to be fully mixed, and the isotopic ratio of snowpack is computed as:

$$\frac{d(h_s(t)C_s(t))}{dt} = C_p(t)P_s(t) - C_s(t)M_s(t), \tag{17}$$

where C_s is the isotopic ratio of snowpack and C_p is the isotopic ratio of precipitation. The amount of groundwater recharge (R) is the sum of groundwater recharged from rainfall and snowmelt:

$$R(t) = R_r P_r(t) + R_s M_s(t), \tag{18}$$

where R_r and R_s are the rainfall and snowmelt recharge efficiencies. Recharge efficiency is defined as the fraction of rainfall or snowmelt that reaches groundwater and is assumed to be a constant value. The groundwater storage is assumed to be fully mixed, and the isotopic ratio of groundwater is computed as:

$$\frac{d(G(t)C_g(t))}{dt} = R_r C_p(t) P_r(t) + R_s C_s(t) M_s(t) - C_g(t) Q(t), \tag{19}$$

where C_g is the isotopic ratio in groundwater, G is the volume of groundwater and Q is the amount of groundwater outflow to the stream defined as:

$$Q(t) = k(G(t) - G_C), \tag{20}$$

where k is the recession coefficient and G_C is a constant groundwater storage that does not interact with the stream (added here to avoid zero flow). This formulation follows the linear groundwater reservoir assumption used in numerous hydrological modeling frameworks (Beven, 2011). The volume of the groundwater storage is computed as:

$$\frac{dG(t)}{dt} = R(t) - Q(t). \tag{21}$$

The model is run for a period of 100 years, allowing the system to reach a long term steady state. The parameters used to generate daily precipitation, air temperature and precipitation isotopic ratios are shown in Table 4. The number of yearly precipitation events is set to 30. The snow accumulation and the degree-day snowmelt models are then used to compute the number of snowfall days and of snowmelt events The static volume of groundwater that does not interact directly with the stream, G_C, is set to 1000 mm.

Only the last 2 years of the model runs are used to obtain the time series of isotopic ratios in rainfall, snowmelt and groundwater. These years are then used to estimate the mixing ratio of snowmelt in groundwater, which is the fraction of groundwater recharged from snowmelt. Rainfall and snowmelt samples are the two sources and groundwater samples represent the mixture. For the HydroMix application, all the rainfall and snowmelt samples are used, whereas for groundwater, only one isotopic ratio per month is used (randomly sampled). The mixing ratios inferred using HydroMix are compared to the actual recharge ratio obtained from the hydrologic model as:

$$R_s^a = \frac{\sum_t R_s M_s(t)}{\sum_t R(t)}, \tag{22}$$

where R_s^a represents the proportion of groundwater recharge derived from snowmelt, summed over all the time steps. The numerical implementation of the evolution of isotopic ratio in snowpack and groundwater are given in the Appendix.

3.3 Weighting mixing ratios in the hydrologic model

In Section 3.2, rainfall and snowmelt samples are not weighted by the magnitude of their fluxes while computing the mixing ratios with HydroMix. As all rainfall and snowmelt samples are used, the weights are implicitly determined by the number of rainfall and snowmelt events, instead of their magnitudes. This is a general problem in all mixing approaches and has not been adequately acknowledged in the literature. Ignoring the weights may lead to biased mixing estimates if the proportional contribution of one of the components (e.g.: rainfall or snowmelt) is low, but the number of samples obtained to represent that component is proportionally much higher (Varin et al., 2011). For example, in a given catchment, the amount of total snowfall maybe a small proportion of the annual precipitation, but the number of days when snowmelt occurs maybe comparable to the total number of rainfall days in a year. If this is not specified *a priori*, HydroMix may overestimate the proportion of groundwater being recharged from snowmelt. To account for this, we introduce a weighting factor in the likelihood function originally formulated in Eq. (8), to make a new composite likelihood (Varin et al., 2011):

$$L_j(\tilde{Y}_{obs}|S_1, S_2, \boldsymbol{\theta}) = \prod_{k=1}^{q} \prod_{j=1}^{m} \prod_{i=1}^{n} \left[(2\pi\sigma^2)^{-0.5} \exp\left(-\frac{1}{2}\frac{(\tilde{Y}_{obs}^{k} - \hat{Y}_{ij})^2}{\sigma^2}\right)\right]^{w_i w_j}, \tag{23}$$

where i and j correspond to snowmelt and rainfall samples, and the weights w_i and w_j reflect the proportion of snowmelt and rainfall contributing to groundwater recharge (Vasdekis et al., 2014), where w_i is expressed as:

$$w_i = \frac{R_i S_i}{\sum_{i=1}^{n} R_i S_i}, \tag{24}$$

where R_i is the magnitude and S_i is the isotopic ratio of the i^{th} snowmelt event. Rain weights (w_j) are also expressed similarly to Eq. (24). The obtained mixing ratio estimates are then compared with the unweighted estimates (in Section 3.2) to see if weighting by magnitude makes a significant difference.

3.4 Real case study: Snow ratio in groundwater in Vallon de Nant

The objective of this case study is to infer the proportional contributions of snow versus rainfall to the groundwater of an Alpine headwater catchment, Vallon de Nant (Switzerland), using stable water isotopes.

3.4.1 Catchment description

Vallon de Nant is a 13.4km^2 catchment located in the Vaud Alps in South-West of Switzerland (Figure 1), with elevation ranging from 1253 m to 3051 m asl. Steep slopes form a major part of the catchment with a mean catchment slope of around 36° (Thornton et al., 2018). At lower elevations, a dense forest dominated by *Picea abies* covers 14% of the catchment area. At around 1500 m asl., there is an active pasture area with scattered trees and an open forest dominated by *Larix decidua*. Additional species scattered throughout the catchment include *Pinus sp., Alnus sp.* and *Acer pseudoplatanus*. Alpine meadows cover most of the higher elevation land surfaces. Despite the relatively low elevation, there is a small glacier on its South-western tip, which covers around 4.4% of the catchment area, below which an extended moraine occupies 10.1% of the catchment area. A large part (28% of catchment

Deleted: with an extended moraine that cover 4.4% and area) of the hillslopes are composed of steep rock walls. At lower to mid-elevations, talus slopes account for about 6% of the catchment area.

Vallon de Nant has a typical Alpine climate, with around 1900 mm of annual precipitation and a mean air temperature of 1.8 °C (Michelon, 2017). For this paper, long term climate statistics are computed using MeteoSwiss gridded precipitation and air temperature dataset from 1961-2015 (Isotta et al., 2013; MeteoSwiss, 2016, 2017). Applying a simple temperature threshold (0 and 1 °C) to observed precipitation indicates that on average, 40-45% of the total precipitation falls as snow in the catchment. There is a small degree of seasonality in precipitation, with higher precipitation between June to August, and lower precipitation in the months of September and October.

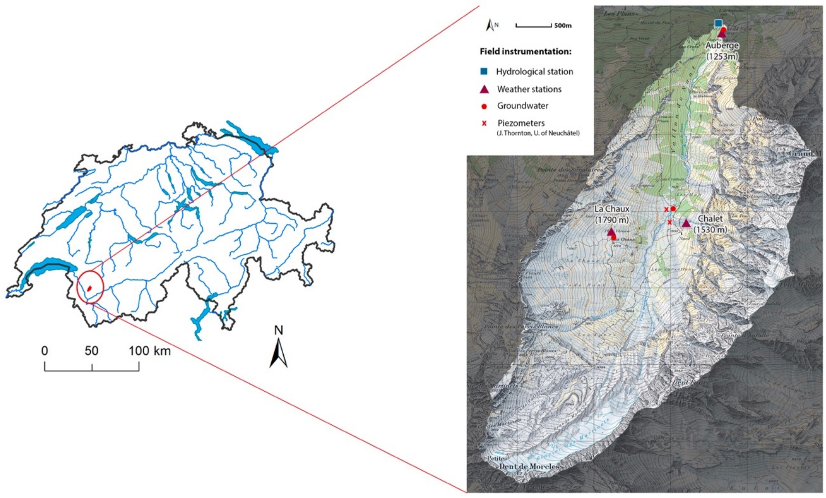

Figure 1. Map showing Vallon de Nant along with the locations of meteorologic and hydrologic observations and the frequent sampling sites. Composite samples of precipitation were collected at the weather stations. Groundwater samples were collected at the groundwater monitoring points and the installed piezometers. The groundwater piezometers were installed by James Thornton from University of Neuchâtel (Thornton et al., 2018).

3.4.2 Data collection

Vallon de Nant has been extensively monitored since February 2016. Water samples are collected from streamflow, rain, snowpacks and groundwater at different elevations, which are then analyzed for the isotopic ratios in deuterium (δ^2H) and oxygen-18 ($\delta^{18}O$). Vallon de Nant is remotely located with very limited winter access, frequently experiencing winter avalanches. Due to these logistical constraints, snowmelt lysimeters or passive capillary samplers could not be setup to sample snowmelt water; accordingly, grab snowpack samples are used here as a proxy for snowmelt. A summary of the isotopic data is shown in Table 1.

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Table 1. Summary of the isotopic data (δ^2H and $\delta^{18}O$) collected in Vallon de Nant between February 2016 to July 2017

Sample name	Number of samples	Lowest elevation	Highest elevation
Rainfall	32	1253	1773
Top snowpack layer	80	1241	2455
Groundwater	22	1253	1779

3.4.3 Model implementation

HydroMix is used to estimate the proportion of snow recharging groundwater (subsequently referred to as 'snow recharge coefficient'). In order to obtain a pdf of the snow recharge coefficient, isotopic ratios in all the water samples from rain, snowpack and groundwater are used. A uniform prior distribution is assigned to the snow recharge coefficient, which varies between 0 and 1, representing the entire range of possible values. Groundwater isotopic ratio is estimated using Eq. (12).

3.5 Introduction of an additional model parameter

In any mixing analysis, it may be useful or desirable for users to specify an additional model parameter that is able to modify the tracer concentrations based on their process understanding of the system. In the case of Alpine catchments with large elevation gradients, stable isotopes in precipitation often exhibit a systematic trend with elevation, becoming more depleted in heavier isotopes with increasing elevation. This is also known as the 'isotopic lapse rate' (Beria et al., 2018). In typical field campaigns, because of logistical challenges, precipitation samples are collected only at a few points in a catchment, with often fewer precipitation samples at high elevations. This leads to oversampling at lower elevations, and under sampling at higher elevations, which can bias mixing estimates. This has been found specially relevant for hydrograph separation in forested catchments (Cayuela et al., 2019). To allow a process compensation for this, an additional lapse rate factor is introduced in which each observed point scale sample (observed at a given elevation) is corrected to a reference elevation as follows:

$$\bar{r} = \frac{\sum_{j=1}^{k}[\alpha(e_j - e) + r]a_j}{\sum_{j=1}^{k} a_j}, \quad 25$$

where r is the isotopic ratio in precipitation collected at elevation e, $\bar{r}$ is the catchment averaged isotopic ratio in precipitation, α is the isotopic lapse rate factor, and e_j is the elevation of the *j*-th elevation band where the catchment is divided into *k* elevation bands. These bands are obtained by constructing a hypsometric curve of the catchment (Strahler, 1952).

The lapse rate factor is allowed to modify both rainfall and snowpack isotopic ratios to obtain a catchment averaged isotopic ratio, which is then used in the mixing model. Using this formulation of an isotopic lapse rate makes the following implicit assumptions: (1) precipitation storms on aggregate move from the lower part of the catchment to the upper part of the catchment thus creating a lapse rate effect, and (2) precipitation falls uniformly over the catchment. It is important to note that the isotopic lapse rate is different from the precipitation lapse rate, i.e., the rate of change of precipitation with elevation is different from the rate of change of precipitation isotopic ratio with elevation.

It is important to note that precipitation isotopic ratio is not only a function of elevation, but also depends on other factors such as the source of moisture origin, cloud condensation temperature, secondary evaporation, etc. Similarly, a strong spatial variability exists in the isotopic ratio of snowmelt water, depending on catchment aspect, snow metamorphism, wind distribution, etc. This case study is a mere demonstration that HydroMix allows inference of additional parameters that can account for various physical processes that may modify isotopic ratios.

The prior distribution of the isotopic lapse rate is specified based on isotopic data collected across Switzerland under the Global Network of Isotopes in Precipitation (GNIP) program (IAEA/WMO, 2018). Using the monthly isotopic values collected in between 1966 and 2014, average lapse rate values are obtained for both δ^2H and $\delta^{18}O$. These were (-)1.94 ‰/100m for δ^2H, and (-)0.27 ‰/100m for $\delta^{18}O$ (Beria et al., 2018).

A uniform prior distribution is assigned to the isotopic lapse rate parameter, with the lower bound specified as three times the Swiss lapse rate for both δ^2H and $\delta^{18}O$. The observed isotopic lapse rate data from Switzerland suggests average lapse rates are weakly negative; however, positive lapse rates can *a priori* not be excluded for the case study catchment. Accordingly, we do not specify an upper lapse rate bound of zero but set it as three times the Swiss lapse rate (Table 2). In the case of Vallon de Nant, the elevation ranges from 1253 m to 3051 m asl. For computing the Swiss lapse rate, the elevation range over which the monthly precipitation samples were collected was 300 m to 2000 m asl.

Table 2. Prior distribution of the different model parameters as specified to HydroMix

Variable	Prior distribution	Lower bound	Upper bound
Snow recharge coefficient	Uniform	0	1
Isotopic lapse rate in δ^2H	Uniform	(-)5.82 ‰/100m	(+)5.82 ‰/100m
Isotopic lapse rate in $\delta^{18}O$	Uniform	(-)0.81 ‰/100m	(+)0.81 ‰/100m

4 Results

The results for the different case studies are discussed in the sections below.

4.1 Mixing with normal distributions

The mean and standard deviations used to generate the low and high variance source distributions for the synthetic case studies are summarized in Table 3. We randomly generated 100 samples from each of the two source distributions and from the target distribution, and varied the mixing ratios between 0.05 and 0.95 in 0.05 increments. However, it should be noted that HydroMix permits using different number of samples for the sources and the mixture.

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For the low variance case, the mixing ratio inferred with HydroMix with 1000 Monte Carlo (MC) simulations reproduce closely the theoretical mean of the mixing ratios used to generate the synthetic data (Figure 2a). However, for the high variance case, the inferred mixing ratios do not match the true underlying mixing ratios, especially for low and high mixing ratios. This is partly due to the poor identifiability of the sources (given that their distributions are highly overlapping), and partly due to the relatively small sample size of 100. The inferred mean should reproduce the theoretical mean with increasing sample size and we clearly see this in Figure 2b, where the model performance markedly improves with increasing number of samples. The performance is measured here in terms of the absolute error between the posterior mixing ratio mean and the true mean, summed over all tested ratios from 0.05 to 0.95. We did not perform inferences for sample sizes larger than 100 as the computational requirement increases exponentially with increasing sample sizes.

The model converges fairly quickly for the low variance case after ~100 runs as shown in Figure 3(a). The obtained model residuals have zero mean and are approximatively normally distributed as revealed by quantile-quantile plots (not shown), in line with the assumption of an unbiased normally distributed error model, as stated in Eq. 7.

Table 3. Mean and variance of the two sources S_1 and S_2 drawn from Normal distribution

Dataset	S_1 mean (standard deviation)	S_2 mean (standard deviation)
Low variance	10 (0.5)	20 (0.5)
High variance	10 (5.0)	20 (5.0)

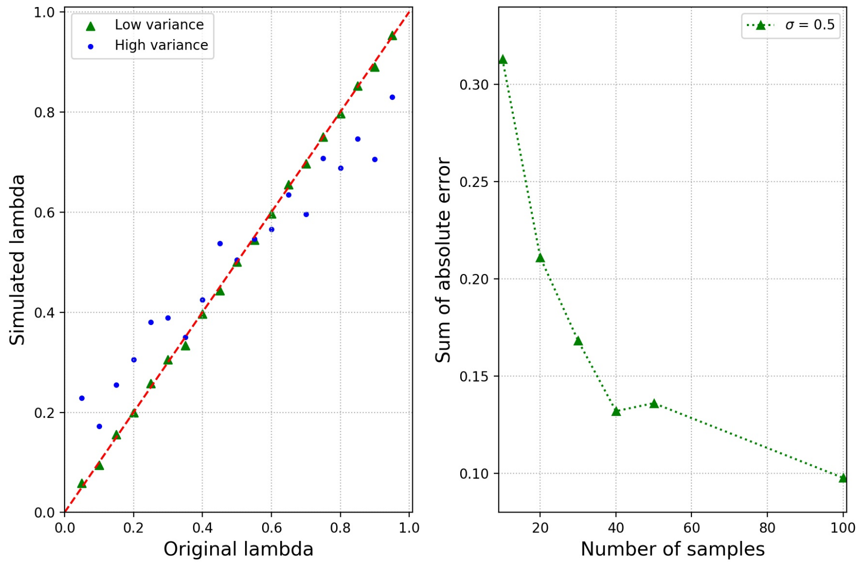

Figure 2. (a) Scatterplot showing the mixing ratio (ρ) values inferred using HydroMix for the low and high variance synthetic case of Table 3. The number of source and target samples are 100. (b) Performance of HydroMix in terms of the absolute error between the posterior mixing

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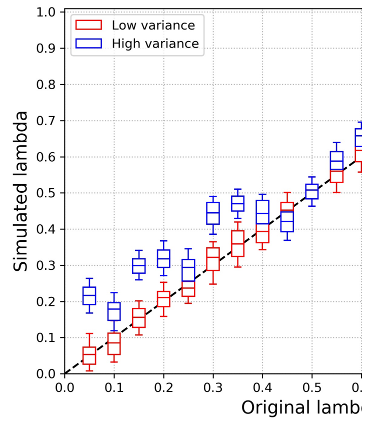

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ratio mean and the true mean for the low variance dataset, summed over all tested ratios plotted as a function of the number of samples drawn for the two sources.

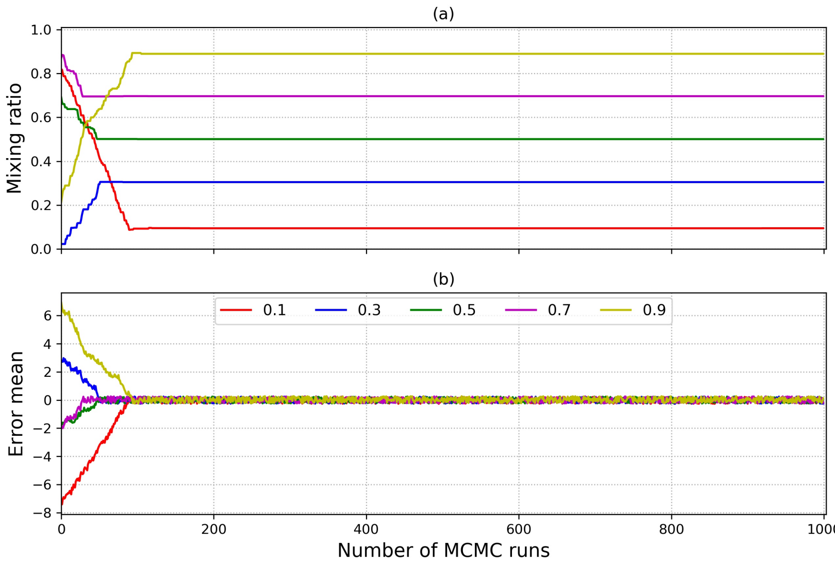


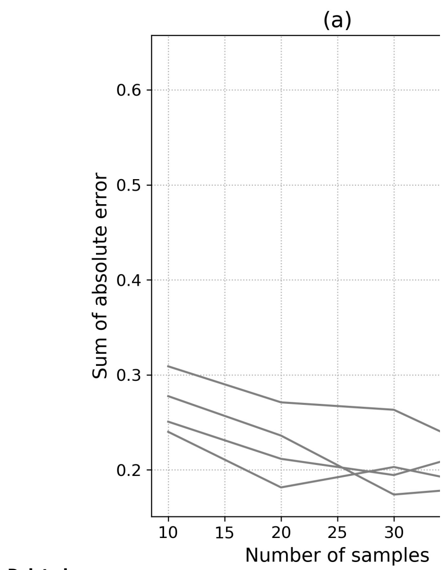
Figure 3. Diagnostic plots showing the convergence characteristics of MCMC chains for five different mixing ratios for the low variance dataset (shown in Table 3). Subplots (a) and (b) show variations in the inferred mixing ratio and the error mean with increasing MCMC runs.

4.2 Contribution of rain and snow to groundwater recharge using a hydrologic model

Figure 4 shows the variation in the isotopic ratio of groundwater over the entire 100 year period, showing the system achieves a steady state condition after ~15 years of simulation. The mixing ratio is estimated with HydroMix using: (1) samples of the isotopic ratio in snowfall, and (2) samples of the isotopic ratio in snowmelt. The two sample distributions differ, as shown in Figure 5, where the variability of the isotopic ratio is lower in snowmelt when compared to snowfall. In the model at hand, this reduction is obtained because of mixing occurring within the snowpack, leading to homogenization, thus reducing the variability in the isotopic ratio of snowmelt. In field data, such a reduction in variability is also generally observed (Beria et al., 2018), as a result of the homogenization as modelled here and from more complex snow physical processes, which lie beyond the scope of this study.

Table 4. Parameters used to generate time series of precipitation, air temperature and isotopic ratios in precipitation. μ represents the mean, A is the amplitude and ϕ the time lag of the underlying sine function. For the precipitation process, μ is the mean intensity on days with precipitation. The resulting mean winter length (air temp. below 0°C) is 119.5 days.

Variable	Parameter values
Precipitation	# events/year = 30, μ = 33.45 mm/day
Air temperature	μ = 4 °C, A = 8 °C, ϕ = -π/2



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Deleted: Performance of HydroMix in terms of the absolute error between the posterior mixing ratio mean and the true mean, summed over all tested ratios plotted as a function of (a) number of samples drawn for the two sources (100 Monte Carlo simulations) and (b) number of MC simulations for sample size 10. The four lines in the plot correspond to four different random seeds that were used to initialize HydroMix. The underlying dataset used is the low variance dataset shown in Table 3.

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Precipitation isotopic ratio	μ = (-80) ‰, A = 40 ‰, ϕ = -π/2

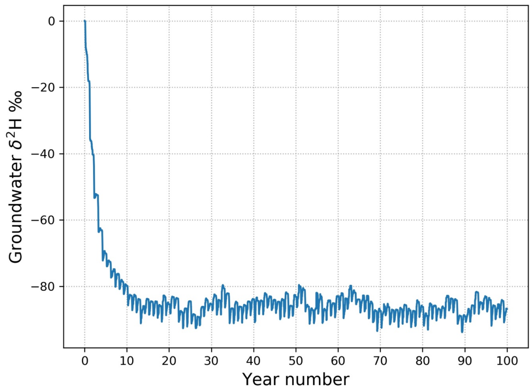

Figure 4. Evolution of the modeled isotopic ratio in groundwater over a 100-year period with $\boldsymbol{R_r}$= 0.3 and $\boldsymbol{R_s}$=0.6.

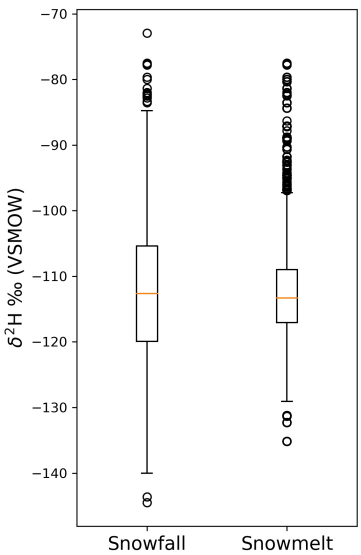

Figure 5. Boxplot showing the variability in the isotopic ratio of snowfall and snowmelt as simulated by the hydrologic model. The boxplot extends from 25th to 75th percentile value, with the median value depicted by the orange line. The whiskers extend up to 1.5 times of the interquartile range. The black circles are the outliers.

Moved up [2]: The mixing ratio is estimated with HydroMix using: (1) samples of the isotopic ratio in snowfall, and (2) samples of the isotopic ratio in snowmelt. The two sample distributions differ, as shown in Figure 5, where the variability of the isotopic ratio is lower in snowmelt when compared to snowfall. In the model at hand, this reduction is obtained because of mixing occurring within the snowpack, leading to homogenization, thus reducing the variability in the isotopic ratio of snowmelt. In field data, such a reduction in variability is also generally observed (Beria et al., 2018), as a result of the homogenization as modelled here and from more complex snow physical processes, which lie beyond the scope of this study.

The mixing ratios inferred with HydroMix are very similar regardless of whether snowfall or snowmelt is used across the entire range of recharge efficiencies (Figure 6). This provides confidence in the use of snowfall samples as a proxy for snowmelt when estimating mixing ratios. However, it is clear from Figure 6 that an important bias emerges between the estimated mixing ratio from HydroMix and the actual mixing ratio known from the hydrologic model, especially for high and low mixing ratios.

This bias can be expected to emerge where the source contributions are not weighted according to their fluxes, which to our knowledge has not been explicitly addressed in the hydrological literature. As already discussed in Section 3.3, the absence of sample weighting typically induces a bias when there is a large divergence between the amount of samples taken over a certain period (e.g. one year) to characterize a source, and the magnitude of source flux over that period (e.g. 40 snow and 10 rain samples taken to characterize the two sources, where snow only accounts for a very small portion (e.g. 10%) of the annual precipitation).

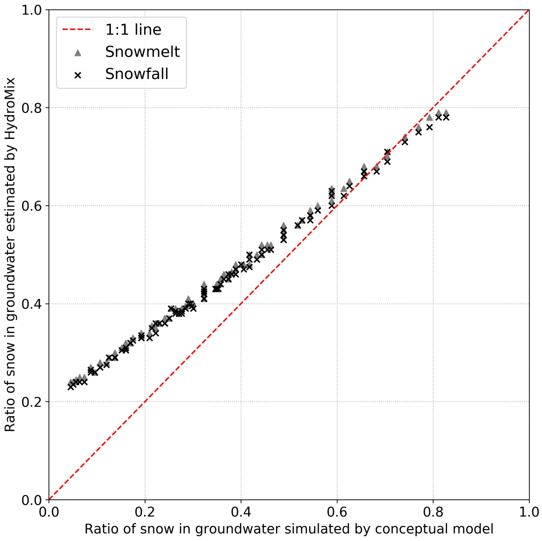

Figure 6. Ratios of snow in groundwater estimated with HydroMix plotted against ratios obtained from the hydrologic model for the last two years of simulation. Also shown are the separate results obtained by using samples of either snowmelt or snowfall. The full range of ratios is obtained by varying rainfall and snowmelt recharge efficiencies from 0.05 to 0.95. The number of rainfall, snowfall and snowmelt days are 39, 24 and 107 in the last two years of simulation.

4.3 Effect of weights on estimates of mixing ratios using a hydrologic model

After taking into account the magnitude of rainfall and snowmelt events in the composite likelihood function of Eq. (23), it is clear that much of the un-weighted biases can be removed (Figure 7). The most significant improvement is seen at very low mixing ratios where the divergence between the conceptual model and the mixing model estimates error reduces by almost 50%. In this study, we have used a relatively simple normalization based weighting function (Eq. (24)). Testing other weighting functions which have been proposed in the past (Vasdekis et al., 2014) and is left for future research.

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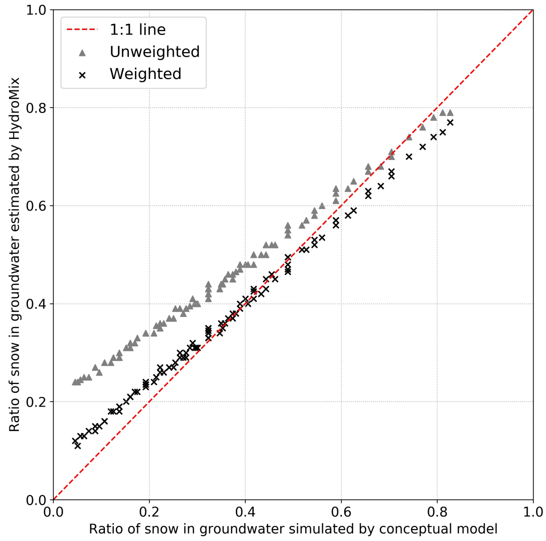


Figure 7. Ratios of snow in groundwater estimated using HydroMix plotted against ratios obtained from the hydrologic model, for both weighted and unweighted mixing scenarios. The full range of ratios is obtained by varying rainfall and snowmelt recharge efficiencies from 0.05 to 0.95. The number of rainfall, snowfall and snowmelt days are 39, 24 and 107 in the last two years of simulation.

4.4 Inferring fraction of snow recharging groundwater in a small Alpine catchment along with an additional model parameter

Using the dataset from an Alpine catchment (Vallon de Nant, Switzerland), HydroMix estimates that 60-62% of the groundwater is recharged from snowmelt (using unweighted approach), with the full posterior distributions shown in Figure 8a. This estimate is consistent for both the isotopic tracers (δ^2H and $\delta^{18}O$), which are often used interchangeably in the hydrologic literature (Gat, 1996). Comparing this recharge estimate to the proportion of total precipitation that falls as snow (around 40-45%, see Section 3.4.1), suggests that snowmelt is more effective at reaching the aquifer than an equivalent amount of rainfall falling at a different period of the year. Similar results have been obtained in a number of previous studies across the temperate and mountainous regions of the world (see Table 1 in the work of Beria et al., (2018) for a summary).

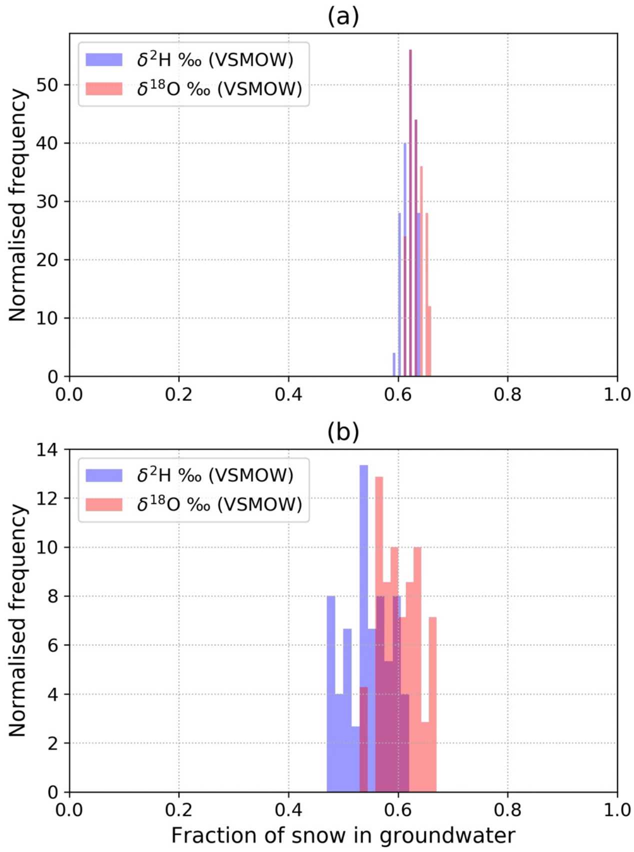
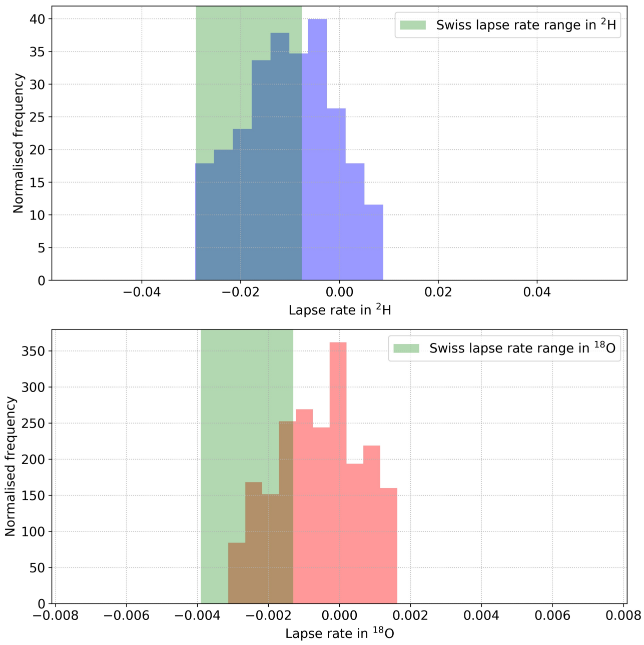


Figure 8. Histogram showing the fraction of snow recharging groundwater in Vallon de Nant using the isotopic ratios in δ^2H and $\delta^{18}O$ (a) without correcting for lapse rate and (b) after correcting for lapse rate.

As can be seen from Figure 8a, the estimated distribution of snow ratio in groundwater is very narrow. This can be explained by the fact that we assume that the collected precipitation samples represent the variability actually occurring in the catchment. To overcome this limitation, we infer an additional parameter called the isotopic lapse rate that accounts for the spatial heterogeneity in terms of catchment elevation. As shown in Figure 9, the posterior distributions of the isotopic lapse rate (for both δ^2H and $\delta^{18}O$) largely overlap with the spatially averaged isotopic lapse rate as estimated from precipitation isotopes across Switzerland. The overlap with the average Swiss isotope lapse rate suggests our inferred lapse rates are reasonable, with the spread in the estimates likely reflecting the temporal variation in the catchment specific isotope lapse rate that can develop from a wide range of moderating factors (e.g. air masses contributing precipitation without traversing the full elevation range of the catchment due to varying trajectories). The Swiss lapse rate is constructed as a long term spatial average, whereas the inferred isotopic lapse rate in Vallon de Nant is constructed from the temporal variations in the isotopic ratios. This makes the comparison more informative than definitive. In any case, these results demonstrate that it is relatively straightforward to jointly infer multiple parameters within the HydroMix modeling framework provided users have a mechanistic basis for their interpretation.

However, an important consequence of additional parameter inference without providing additional data or constraints is an increase in the degree of freedom, which can then increase the uncertainty on source contributions. This effect is seen in Figure 8b, especially in contrast with the previous result in Figure 8a, where the median mixing ratios of the posterior distributions remain similar (~0.6), but the spread increase drastically, from 0.005 to 0.2.



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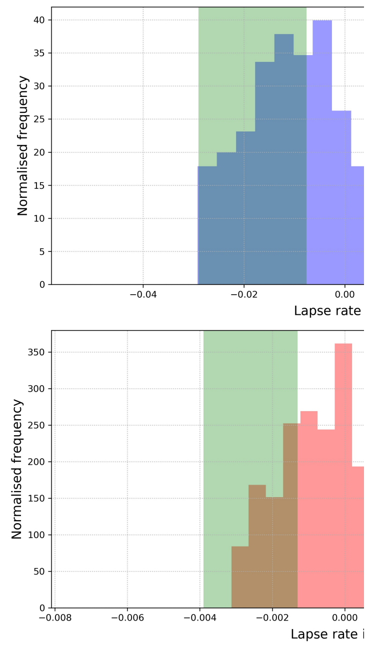

Figure 9. Histogram showing the posterior distribution of the isotope lapse rate parameter in δ^2H and δ^{18}O. The green region shows the confidence bounds (significant at α =0.01) of lapse rate computed over Switzerland by using inverse variance weighted regression. Limits of the prior distribution of the isotopic lapse rates correspond to limits of the x-axis. The slope of the isotopic ratio when plotted against elevation for the Swiss-wide data is shown in Figure 3 of Beria et al. (2018).

5 Limitations and opportunities

As with all linear mixing models, the quality of the underlying data determines the accuracy and utility of the results. If the tracer compositions of the different sources are not sufficiently distinct, the uncertainty in the estimated mixing ratios will become very large. This means that if either the underlying data quality is poor, or the source contribution dynamics are not well conceptualized, then the uncertainty in the mixing ratios will be too high to be useful.

In cases where a large number of source samples are available, the computational requirements of HydroMix outweigh the benefit from using it. These are likely cases where the statistical distribution of the source tracer composition is well understood, therefore fitting a probability density curve to the source and target samples, and then inferring the distribution of the mixing ratio using a probabilistic programming approach is more appropriate (Carpenter et al., 2017; Parnell et al., 2010; Stock et al., 2018). Also HydroMix might not be an appropriate method in instances where fitting statistical distributions to source and target compositions reflect *a priori* knowledge of the system.

A key difference between HydroMix and other Bayesian mixing approaches is that HydroMix parameterizes the error function whereas other Bayesian approaches parameterize the statistical distribution of source and mixture compositions. Parameterizing source compositions require large sample sizes, which is seldom the case in tracer hydrology. Error parameterization offers a useful alternative and can be also verified against the posterior error distribution. In the case studies demonstrated in this paper, a normal error model was found to be appropriate. However, error models other than Gaussian can be used by formulating the respective likelihood function.

HydroMix builds the model residuals by comparing all the observed source samples with all the observed samples of the target mixture, assuming that all available source and target samples are independent. Interestingly, the assumption of independence holds even if the source and target samples are taken at the same time, since the target samples result from water that has travelled for a certain amount of time in the catchment, and hence is not related to the water entering the catchment. However, if a system has instantaneous mixing, then the source and target samples taken at the same moment of time will necessarily be strongly correlated. In such cases, the assumption of independent samples would not make sense and the method might give spurious results.

Finally, it is noteworthy that adding additional parameters to characterize the source tracer composition increases the degree of freedom of the model, which implies that adding such parameters leads to an increase in the uncertainty of the source contribution estimates unless new information, i.e. new observed data, is added to the model. This means that users who are interested in incorporating additional modification processes by adding parameters should ideally provide additional tracer data able to constrain this process, subject to tracer data being available.

For consistency and simplicity, the case studies and synthetic hydrological examples provided here focused on the contribution of rain and snow in recharging groundwater. However, it is important to emphasize that the opportunities to implement HydroMix extend to all cases where mixing contributions are of interest, and where it is difficult to build extensive databases of source tracer compositions. Such examples include quantifying the amount of "pre-event" vs. "event water" in streamflow, where "pre-event water" refers to groundwater and "event water" refers to rainfall or snowmelt. Another interesting use case might be to quantify the proportion of streamflow coming from the different source areas in a catchment, to capture the spatial dynamics of streamflow. Other uses include quantifying the amount of fog contributing to throughfall, the proportion of glacial melt vs. snowmelt flowing into a stream, the amount of vegetation water use from soil moisture at different depths vs groundwater, the interaction between surface water and groundwater at the hyporheic zone(Leslie et al., 2017), sediment fingerprinting to quantify the spatial origin of river sediments, etc. In all of these cases, understanding source water contributions, both spatially and temporally, will improve the physical understanding of the system.

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6 Conclusions

We develop a new Bayesian modeling framework for the application of tracers in mixing models. The primary application target of this framework is hydrology, but it is by no means limited to this field. HydroMix formulates the linear mixing problem in a Bayesian inference framework that infers the model parameters using a Metropolis-Hastings based MCMC sampling algorithm, based on differences between observed and modelled tracer concentrations in the target mixture, using all possible combinations between all source and target concentration samples. For data scarce environments, this represents an advance over existing probabilistic mixing models that compute mixing ratios based on the formulation of probability distribution functions for the source and target tracer concentrations. HydroMix also makes the inclusion of additional model parameters to account for source modification processes straightforward. Examples include known spatial or temporal tracer variations (e.g. isotopic lapse rates or evaporative enrichment).

An evaluation of HydroMix with data from different synthetic and field case studies leads to the following conclusions:

1. HydroMix gives reliable results for mixing applications with small sample sizes (< 20-30 samples). As expected, the variance in source tracer composition and the ensuing composition overlap determines the uncertainty in the mixing ratio estimates. The uncertainty in mixing ratio estimates increases with increasing variance in source tracer compositions. Mixing ratio estimates improve (in terms of lower error) with increasing number of source samples.
2. As revealed by our synthetic case study with a conceptual hydrological model, at low source contributions (i.e. < 20%), a strong divergence between the actual and estimated mixing ratios emerges. This arises if HydroMix assigns equal weights to all source samples proportionally oversampling the less abundant source, which then leads to significant biases in mixing estimates. This problem is inherent to all mixing approaches, and to our knowledge has not been adequately addressed in the literature.
3. The use of composite likelihoods to weight samples by their amounts can significantly reduce the bias in the mixing estimates. At low source proportions, the estimated mixing ratio improves by more than 50% after accounting for the amount of all the sources. We show this using a simple normalization based weighting function. Future studies should explore the usage of different weighting functions that have been proposed in the past (Vasdekis et al., 2014).

4. A synthetic application of HydroMix to understand the amount of snowmelt induced groundwater recharge, revealed that using snowfall isotopic ratio instead of snowmelt isotopic ratio leads to similar mixing ratio estimates. This is particularly useful in high mountainous catchments, where sampling snowmelt is logistically difficult.
5. A real case application of HydroMix in a Swiss Alpine catchment (Vallon de Nant) showed a clear winter bias in groundwater recharge. About 60-62% of the groundwater is recharged from snowmelt (unweighted mixing approach), when snowfall only accounts for 40-45% of the total annual precipitation. This has also been previously suggested elsewhere in the European Alps (Cervi et al., 2015; Penna et al., 2014, 2017; Zappa et al., 2015).

To conclude, HydroMix provides a Bayesian approach to mixing model problems in hydrology that takes full advantage of small sample sizes. Future work will show the full potential of this approach in hydrology as well as other environmental modelling applications.

7 Appendix

The equations below show the numerical implementation of the evolution of isotopic ratios in snowpack and groundwater at a daily timestep.

$$C_s(t) = \frac{C_s(t-1)h_s(t-1)+C_p(t)P_s(t)-C_s(t-1)M_s(t)}{h_s(t-1)+P_s(t)-M_s(t)} \quad 26$$

$$C_g(t) = \frac{C_g(t-1)G(t-1)+C_p(t)R_rP_r(t)+C_s(t)R_sM_s(t)-C_g(t-1)Q(t)}{G(t-1)+R_rP_r(t)+R_sM_s(t)-Q(t)} \quad 27$$

Author contributions

The paper was written by HB with contributions from all co-authors. HB and BS formulated the conceptual underpinnings of HydroMix. JRL helped in framing the statistical and hydrological tests to evaluate HydroMix. AM and NCC helped in compiling data used for model evaluation and provided critical feedback during model validation.

Code and data availability

The model code is implemented in python 2.7 and can be downloaded along with the dataset from Zenodo at http://doi.org/10.5281/zenodo.3475429. The most recent version of the model code is available on GitHub at https://github.com/harshberia93/HydroMix/tree/20191007_GMD.

Competing interests

The authors declare that they have no conflict of interest.

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Deleted: the following link https://github.com/harshberia93/HydroMix. The synthetically generated time series used in Sections 4.1, 4.2 and 4.3, along with the hypsometric curve for Vallon de Nant used in Section 4.4 are available with the model code on GitHub. The isotope data used in Section 4.4 will be made available on request.

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