<u>Revision notes on the paper by Grandjouan et al. « An original approach combining biogeochemical signatures and a mixing model to discriminate spatial runoff-generating sources in a 2 peri-urban catchment ».</u>

Reviewer 1

We thank the reviewer for the time dedicated into reviewing our manuscript and for the constructive feedback provided. Our detailed responses and the corresponding changes to the manuscript are presented below. Reviewer comments are shown in black, our response in blue, and proposed modifications to the manuscript in italic blue.

1. The manuscript by Grandjouan et al presents a comprehensive sampling campaign in a mixed land-use catchment in France, aimed at characterizing runoff sources and their contribution to streamflow. A key strength of the study is the use of advanced biogeochemical signatures that combine traditional tracers (major ions, silicon) with less conventional ones (amount of aromatic carbon deduced from the spectral slope parameter), which are rarely applied in hydrologic studies but prove effective here. By employing 15 tracers that are present in variable proportions in the sources, the authors differentiate 8 spatial runoff sources and investigate their mixing ratios in stream water.

I think this is an interesting study that offers a novel way to look at runoff generation processes in heterogeneous catchments and may inspire future research. The authors are also transparent about the study's limitations. What I think is currently missing to reach publication level is some broader implications. As it reads now, the paper may appear like a project's report rather than a scientific paper. I recommend the authors to "fly higher" and strengthen the abstract, introduction and discussion by highlighting broader (though not speculative) scientific implications.

I include various detailed suggestions that the authors should feel free to follow or not. I look forward to a revised version of the manuscript.

We sincerely thank the reviewer for this positive approval of our paper. We also greatly appreciate the constructive comments and suggestions, which helped us to improve the manuscript and to highlight its broader scientific implications. We propose a modification of the abstract as following:

Hydrograph separation using biogeochemical data is a commonly used method for the vertical decomposition of flow into surface, subsurface and groundwater contributions. However, its application to the spatial decomposition of flow remains limited, despite its potential to identify contributions linked to geological, pedological, and land-use characteristics, as well as anthropogenic contaminant sources. In this study, a Bayesian mixing model was applied to the Ratier peri-urban sub-catchment of the OTHU Yzeron observatory. Eight runoff-generating sources were identified and sampled, including different land uses (e.g. forest, grassland, agricultural areas), a colluvium aquifer, and urban point discharges (e.g. sewer system, urban and road surface runoff). A wide range of biogeochemical parameters were analyzed including classical (i.e., major chemical compounds, dissolved metals) and innovative tracers (i.e., dissolved organic matter characteristics, microbial indicators). Streamwater samples collected under contrasting hydro-meteorological conditions revealed distinct source signatures an strongly variable contributions, with wastewater dominating under dry weather and rapid surface runoff during summer storms. These results were used to improve an existing perceptual hydrological model of the Ratier and Mercier catchments, at the hillslope scale, highlighting the potential of spatial tracer-based decomposition in complement to traditional vertical hydrological separation. More broadly, this study demonstrates the potential of mixing model to provide insights for validating distributed hydrological models and to anticipate the influence of land use, urbanisation, and climate variability on runoff generation.

Detailed comments

2. 22: the abstract states that microbial indicators are "analyzed" in the study but I am not sure such indicators are ultimately used in the mixing model.

Indeed, we analyzed several microbial indicators but none were ultimately used in the mixing model. However, we retained two of them to help validating the estimations obtained. These parameters correspond to the qPCR assays for human (HF183 DNA target) and ruminant (rum-2-bac DNA target) fecal bacterial tracers. They were useful to evaluate our results as they can trace the origin of water in case of fecal contamination. Grandjouan et al. (2023) already showed that the *HF183* marker could trace the contribution of the sewer system at dry weather, as they measured high concentrations in both Mercier and Ratier streams (mean values of 2.4 and 2.5 $\log_{10}$ copy nb/100mL, respectively). However, we expected the *rum-2-bac* marker to be consistent in all samples from agricultural areas (PNC sampling point), whereas it was absent in 4 out of 5 PNC samples. This questions the use of qPCR as markers of source contributions, especially since microbial markers are strongly influenced by environmental factors like water temperature (Marti et al., 2017). This also questions the definition of the biogeochemical signature of agricultural sources based on a single sub-catchment as the nature and intensity of agricultural activities can vary from one year to the next, and even within a single year, leading to seasonal variations in biogeochemical signatures. The other 5 microbial parameters (G16S, BTT, integron class1 and class 2, BTS) were not clearly used in the paper and could probably be removed

3. 60-61: "To this day, this approach is often limited to a vertical decomposition of streamflow according to groundwater flow, subsurface flow and surface runoff". The literature on runoff generation sources, especially in forested catchments, is vast and is not limited to the cases mentioned here. I invite the authors to expand the literature.

We aknowledge that the literature on runoff-generating sources is wider than we initially suggested, and that the applications of geochemical signatures, runoff-generating sources and mixing model are numerous and not limited to vertical decompositions. In particular, we found that this approach has been applied to estimate contributions from a wide variety of sources such as groundwater flow, subsurface flow and surface runoff (Gonzales et al., 2009; Ladouche et al., 2001), snow and glacier melt (Kumar et al., 2024; Rai et al., 2019; Wellington & Driscoll, 2004), sources of nutrients (Kaown et al., 2023; Verseveld et al., 2008; Wang et al., 2024), sources of sediments (James et al., 2023; Klages & Hsieh, 1975; Vale et al., 2022), or to study the impact of different forest management methods on water quality (Fines et al., 2023; Motha et al., 2003). However, this approach has rarely been applied to estimate contributions from different land uses, as for a peri-urban catchment characterized by a mix of forest, urban and rural runoff-generating sources. It has been applied even less to estimate contributions from both vertical runoff-generating sources (e.g. groundwater, surface) and spatial ones (e.g. land use). The goal of this paper is to evaluate the potential of this approach in a peri-urban catchment considering both vertical and spatial sources.

4. Section 2.2.1. I found this section generally difficult to follow, partly because the distinction between a source and the sampling point used to represent it is unclear. I suggest following a scheme where first the source is presented and then its sampling strategy is clarified. I also found table 4 much clearer than table 1 to understand the sources but I had to wait until Section 3.1 to see it. Perhaps it could be merged with Table 1 or anyway presented earlier?

We agree that the distinction may not have been sufficiently clear. We chose to keep the distinction between source and sampling points, as a source refers to the whole area of the catchment sharing the same factors, whereas the sampling point is a specific point where water samples are collected and assumed to be representative of that source. We could revise this section to clarify our methodology, by first presenting the sources identified from the combination of geological, land use and agricultural activities factors, and then explain how representative sampling points were selected.

In this study, we mainly considered runoff-generating sources as homogeneous sub-catchments associated with a combination of representative factors including geology, field capacity, land use and agricultural activities. The first step in identifying these sources involved the superposition of geological, field capacity, land use and agricultural activities maps. This allowed us to determine which combinations of factors were the most spatially represented in the catchment. Please see **Erreur ! Source du renvoi introuvable.** which shows the relative areas corresponding to each combination obtained and which we could add in appendix. Based on these results, we identified the main sources and named them according to their associated land use (e.g. forest, grassland). We also considered quick surface runoff from other areas (SUR) and wastewater as additional sources/ We also modified the

Table 1 as suggested to provide a description of the factors corresponding to these sources. We then selected sampling points where representative samples could be taken from each source. Sampling points were selected at specific locations (e.g. directly in the sewer for wastewater) and at the outlet of several sub-catchments according to the predominantly represented combinations of factors and a field reconnaissance to check the consistency of the data.

Table A1 - Combinations obtained from the superimposition of representative factors (geology, field capacity, land use). The relative parts of areas associated with each combination in the Mercier and Ratier catchments is provided. Combinations with a relative area of less than 1% of the Ratier catchment have not been represented. n.a. : non available.

Geology	**Field capacity**	**Land use**	**Agricultural activities**	**Surface (%)**	
				Mercier	**Ratier**
Gneiss	Low	Forest		0	1
		Agriculture		0	3
			Bovine breeding	0	2
		Urban		0	5
	Medium	Forest		30	20
		Agriculture		20	6
			Permanent grassland	5	6
			Bovine breeding	0	3
			Cereal crop	2	5
			Equine breeding	0	1
		Urban		5	11
	High	Forest		0	4
		Agriculture		14	4
			Permanent grassland	1	3
			Bovine breeding	6	4
			Cereal crop	1	2
		Urban		0	2
Colluvium	Medium	Urban		0	3

Table 1 – Identified runoff-generating source sources, selected sampling points and their relative sub-catchments areas, geology, field capacity, land use and main features, based on information provided in *Erreur ! Source du renvoi introuvable.* ***and field observations.***

Source		Sampling point	Sub-basin area (ha)	Geology	Field capacity[1]	Land use (%) and main features					
Code	**Description**					**Forest**		**Agriculture**		**Urban**	
FOR	Gneiss / Medium field capacity / Forest	BOU	88	Gneiss	Medium	Deciduous, coniferous	100	-	0	-	0
		VRY	151	Gneiss	Medium	Deciduous, coniferous	100	-	0	-	0
GRA	Gneiss / Medium to high field capacity / Grassland	VRN	13	Gneiss	Medium	Decidous	30	Grassland	70	-	0
		REV	18	Gneiss	Low to high	Decidous	30	Grassland	70	-	0
AGR	Gneiss / Medium field capacity / Agriculture	PNC	22	Gneiss	Medium to high	-	40	Grassland, bovine breeding, cereal crop	25	Landfill[2]	15
AQU	Colluvium aquifer	COR	-	-	-	-	-	-	-	-	-
SEW	Sewer system	RES	-	-	-	-	-	-	-	-	-
URB	Urban and road surface runoff	PLR	-	-	-	-	-	-	-	-	-
SUR	Quick surface runoff	n.a.	-	-	-		-		-		-

[1] Among low, medium and high field capacities identified by Labbas (2014).

[2] Soils displaced from urban building sites

5. Table 1: the code for the quick surface runoff is missing.

We could not determine any sampling point for this source, so there is no corresponding code. We could set the value to “n.a” in Table 1.

6. 210: It is difficult to justify that field/forest runoff composition is the same as rainfall. This is particularly the case for DOC and elements originating from dry deposition. But perhaps this does not have a great impact on the results. Can the authors just clarify which results may be impacted?

We acknowledge that this represents a strong assumption, which was necessary due to the lack of data on direct surface runoff composition outside urban areas. We made the distinction between the water generated by forest or field areas (through subsurface flow), and the surface runoff occurring by overland flow. In this context, considering surface runoff to have the same composition as rainfall appeared as the most consistent approach in order to apply the mixing model. We assumed that surface runoff does not have enough time to acquire significant biogeochemical elements from the soil it flows over. Such hypothesis does not take into account the enrichment of water by soil leaching, as these waters can quickly accumulate elements (Langlois & Mehuys, 2003). Yet, Fröhlich et al. (2008) conducted a similar study in the Dill Catchment (Germany), where they showed that the geochemical composition of stormflow (regrouping surface and subsurface runoff) was similar to the composition of precipitation, characterised by low-mineralization. Their results suggest the predominant contribution of low-mineralized waters for several events, which support the use of the composition of rain to represent the quick surface runoff source, in cases where runoff water could not be sampled. In any case, our study could benefit from a proper sampling of quick surface runoff in order to better estimate their contributions to streamwater. Several studies analyzed direct surface runoff water collected on soil surface during hydrological events (e.g. Le et al., 2022; Omogbehin & Oluwatimilehin, 2022), but these studies are often conducted in tropical areas, where direct surface runoff often occurs outside of urban areas. Such sampling appears to be difficult in temperate areas, with less intensive rainfalls.

In any case, the assumption of a composition of surface runoff close to the composition of precipitation may lead to an underestimation of the quick surface runoff contribution when applying the mixing model for hydrological events. Therefore, we should analyze the model outputs for hydrological events while explicitly considering the potential influence of this assumption.

7. 2.3.2: The selection of variables is an interesting aspect of the paper. I would recommend clarifying why some elements were considered in the first place (i.e. how they may be helpful even if they have been later discarded). This would be very useful guidance for other people to do a similar analysis. A clear summary of the selected parameters is needed at the end of this section, perhaps moving here some material from section 3.2.

We thank the reviewer for this suggestion and agree that these elements could be useful for further similar studies. We chose to work with a wide range of biogeochemical tracers in order to obtain a more accurate characterisation and discrimination of the identified sources. Classical tracers like major ions, silica and trace elements were selected as they can be closely related to geological characteristics of the catchments, particularly Ca^{2+}, SiO2 and Sr for crystalline formations like gneiss (Fröhlich et al., 2008; White et al., 1999). They can also be helpful to trace the contribution of agricultural activities as K^+ (Cooper et al., 2000), Cd (El Azzi et al., 2016), Cu (Vian, 2019) or As (Yokel & Delistraty, 2003). Trace metals can be markers of an urban origin of water, as for Cd, Cr, Cu, Ni, Pb, Rb or Zn (Coquery et al., 2011; Froger et al., 2020; Lamprea & Ruban, 2011). Finally, such major ions as K^+ and Na^+ can be observed at high concentrations in wastewater (Fröhlich et al., 2008). We selected UV-Visible and HPSEC indicators as they can represent both natural and anthropogenic sources by characterising the molecular weight and aromaticity properties of DOM. The spectral slopes S1 is inversely correlated with this molecular weight and high S2 values are more likely to be associated with terrestrial MOD, compared to fresh algal MOD (Helms et al., 2008). HPSEC indicators A0, A1, A2 and A3 represent respectively very large, large, small and very small molecules (Boukra et al., 2023). We selected the HF183 and rum-2-bac host-specific microbial DNA targets to detected and trace fecal contaminations from humans and ruminants, respectively.

We acknowledge the reviewer's suggestion to further clarify the final selection of parameters used to build the source signatures and apply the mixing model. However, we would like to emphasize that tracer selection and signature building are considered as results in themselves. Indeed, the final selection of tracers necessarily depends on the sources identified. Although the sources were initially described, their detailed characterisation in Section 3.1 led us to reconsider their topology, for example by distinguishing two different forest sources instead of a single one. Consequently, the tracer selection had to be updated at this stage of the results.

8. 227-229: I recommend separating what a biogeochemical signature is and what a mixing model (which require a whole other set of assumptions) is. Also clarify that the tracer does not need to be conservative per se (otherwise no tracer would work), but rather its signature from source to mixture must not be altered. The mixSIAR paper has a clear presentation of the working assumptions behind the mixture model.

We separated the definitions of the biogeochemical signature and the mixing model, and added some information about the biogeochemical signatures and the tracers chosen (see response to comment n°7). We thank the reviewer for this suggestion on clarifying the tracer conservativity assumption, as we acknowledge that the tracers used in a mixing model must be additive, discriminating, and must be conserved through the mixing process. We used the mixSIAR paper from Stock et al. (2018) to detail the assumptions required by the application of a mixing model : (1) all sources which contributes to streamwater are identified, (2) the signature from source to the mixture is not altered, (3) the source signatures are fixed, (4) the contributions sum to 100% and the signature of sources differ.

9. 235-237 “are used in this investigation, but [removed] from the parameter list for this particular task”. Unclear what this means.

By the “particular task”, we refered to the signature building, as the undefined relations between bacterial DNA targets and abiotic factors may not guarantee that these parameters can be used in a mixing model. Indeed, as the bacterial DNA targets HF183 and rum-2-bac bacterial DNA targets show undefined relations with abiotic parameters, we discarded them from the reductionist tracer approach. But we also chose to use them afterwards to evaluate the biogeochemical signatures and the estimations obtained.

10. 2.4: I think the evaluation of the results could be more effective if the authors formulated the “null-hypothesis” that the runoff contributions from the different sources are proportional to their spatial extent. Rejecting the null hypothesis would help a reader see the potential of the approach to discover something new. I also see strong potential for using this method to validate outputs from spatially distributed models, which could provide alternative null hypotheses for comparison.

We thank the reviewer for this pertinent suggestion that could improve the readability of the result and discussion sections. As a prior hypothesis, we could expect the contributions from each source to be proportional to their spatial extent, with the exception of wastewater. Results that would invalidate this assumption would suggest the influence of additional factors beyond the spatial extent of catchment characteristics, such as differences in vertical flow transfer, variations in water transit time or specific losses and inputs associated to the presence of the sewage network. However, the estimated contributions clearly invalidate the null hypothesis that source contributions are proportional to their spatial extent. Spatial extent alone cannot explain the observed variability, and several additional factors appear to influence source activation and the hydrological response of the catchments, such as anthropogenic inputs or water transit time in the different hydrological components.

Concerning the potential to validate outputs from a distributed hydrological model, we have precisely tested this method by evaluating the results of a peri-urban hydrological model applied to the Ratier catchment. A paper is currently under writing for a submission at the end of 2025. We therefore are convinced that a biogeochemical mixing model approach can bring crucial information that could help validating the estimations simulated by a distributed hydrological model. Such models can indeed simulate contributions from spatial extent of a catchment according to their geological, soil or land use characteristics. By estimating the same type of sources with both approaches and by confronting the results, an evaluation can be performed to improve the performance of the hydrological model. We understand that our current paper could benefit from such perspective of application.

11. 3.3: I think the uncertainty in the results for hydrological events should be better acknowledged and I invite the authors to only focus on the stronger results that hold true despite the uncertainty. An example is that FOR-2 is the largest contribution to the second event, since it does not appear a statistically significant result. I strongly advise to always report uncertainty along with the mean contributions. Same comment for figure 8: the plots are nice but do not show the likely very large uncertainty.

We acknowledge that we could systematically reported the uncertainties together with the mean contributions. By doing so, we could emphasise stronger results and suggest the lector to treat weaker results with caution. In some cases of high uncertainties, we could try to explain what could cause such variability in the mixing model estimations. We propose some examples that we could made in Section 3.3.2:

Further results will be presented together with their uncertainty (noted as s.d. for standard deviation).

[…]

At the Mercier station, the major contribution was FOR-1 in March 2019 (31%, s.d. 8%). We calculated the FOR-2 source as the major contribution in March 2023 (25%) but with high uncertainty (s.d. 14%).

[…]

We calculated high contribution of URB for the June 2022 event at the Ratier station (21%), which we associated with high uncertainty (s.d., 20%). This uncertainty could be explained by the contribution from SEW (7%, s.d. 5%), which can be linked to sewer overflows. As these overflows are caused by excessive rainfall inputs in the sewer system, the volume transferred to streamwater during overflows is actually a mixture of wastewater, rainwater and urban surface water, which may have influenced our calculations.

Concerning the temporal variability, we added Tables A7, A8 and A9 in appendix to show the contributions estimated at each time steps of the events, and their respective uncertainties. Here is an extract of the Table A7:

Table A1 – Mean contributions and standard deviations of estimations obtained for the decomposition of samples collected during small winter events in March 2019 and March 2023. The values correspond to the relative parts of flow for each time step as a percentage.

		06/03/19 23:15		07/03/19 00:15		07/03/19 01:15		07/03/19 02:15		07/03/19 03:15		07/03/19 04:15		07/03/19 05:15		07/03/19 06:15		07/03/19 07:15		07/03/19 08:15		07/03/19 09:15		07/03/19 10:15	
		Mean	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*
06/03/2019 - Mercier	**FOR_1**	17	*12*	34	*7*	25	*7*	30	*8*	32	*8*	31	*8*	33	*8*	33	*8*	34	*8*	35	*8*	36	*8*	32	*9*
	FOR_2	5	*5*	4	*4*	6	*8*	5	*6*	4	*5*	4	*5*	5	*6*	5	*7*	4	*6*	4	*5*	4	*5*	3	*3*
	GRA	31	*11*	20	*5*	26	*8*	27	*7*	15	*6*	12	*6*	16	*6*	17	*7*	19	*7*	19	*7*	19	*7*	11	*5*
	AGR	32	*21*	7	*6*	8	*8*	7	*8*	8	*9*	11	*9*	11	*8*	9	*7*	8	*7*	7	*7*	6	*7*	6	*8*
	URB	0	*0*	5	*6*	3	*4*	5	*6*	5	*7*	5	*7*	5	*6*	5	*6*	6	*7*	6	*8*	6	*8*	7	*10*
	SEW	16	*4*	15	*3*	11	*2*	13	*3*	19	*3*	19	*3*	17	*3*	18	*3*	18	*3*	19	*4*	18	*4*	21	*4*
	SUR	0	*0*	15	*3*	21	*5*	13	*4*	16	*5*	17	*5*	14	*4*	13	*4*	12	*4*	10	*4*	11	*4*	20	*5*

In the revised version of the paper, these tables will be used to comment the results in the main text.

12. Finally: I see that the discharge at Mercier vs Ratier changes significantly across storms. Is this attributable to rainfall spatial variability or runoff generation sources?

We expect both differences in runoff-generating sources and rainfall spatial variability to influence the contrasting hydrological responses of the Mercier and Ratier streams. The contrast between both catchment in terms of land use, geological formation and field capacity (e.g. different extent of the urbanised area, presence of the colluvium aquifer, higher field capacity for the Mercier) may have a strong influence on how each catchment responds to a similar rainfall. However, runoff-generating sources alone cannot account for all discharge variations. For example, considering the September 2022 event, we estimated a larger contribution from urban areas (URB) in the Mercier catchment, despite the Ratier catchment being more urbanised. This result could be explained by rainfall spatial variability, with more rainfall occurring over the urbanised area of the Mercier catchment. Rainfall data from three different rain gauges across the catchment illustrate this variability, with higher cumulative rainfall at the Col de la Croix du Ban station (4 km northwest from the Pollionnay station) and no rainfall at all at the Col de la Luère station (4 km west from the Pollionnay station). Data is available at https://bdoh.inrae.fr/YZERON/SPP0602P/PRCP for the Col de la Croix du Ban and https://bdoh.inrae.fr/YZERON/69154002/PRCP for the Col de la Luère. Spatial rainfall variability is particularly marked for summer storm events, where precipitations are localised and lead to quick response of urban areas, as showed by Kermadi et al. (2012) for the Yzeron catchment (which includes the Ratier catchment). The influence of rainfall spatial distribution on hydrological response in urban areas is undergoing increasing study, especially through hydrological modelling (Cristiano et al., 2017). Such studies encourage the use of high spatial resolution radar weather radar images for studying rainfall spatial variability in small peri-urban catchments, although this remains uncommon (Emmanuel et al., 2012).

13. Figure 9 is very nice but I find the difference between the color of storage at high and low flow confusing. Is a different color really needed? I'd also recommend changing the water level in the stream in the different event scenarios.

The yellow storage initially represented the storage amplitude between low water and high water. We acknowledge that this could be confusing as we only precise low and high water at dry weather. Such distinction is thus only relevant under dry weather conditions. We therefore modified the figure to represent a single water storage in the case of events, while distinguishing low from high water in the case of dry weather. We modified the storage colours for clarity, and the water levels of each stream were revised to match the represented hydro-meteorological conditions and the stream responses.

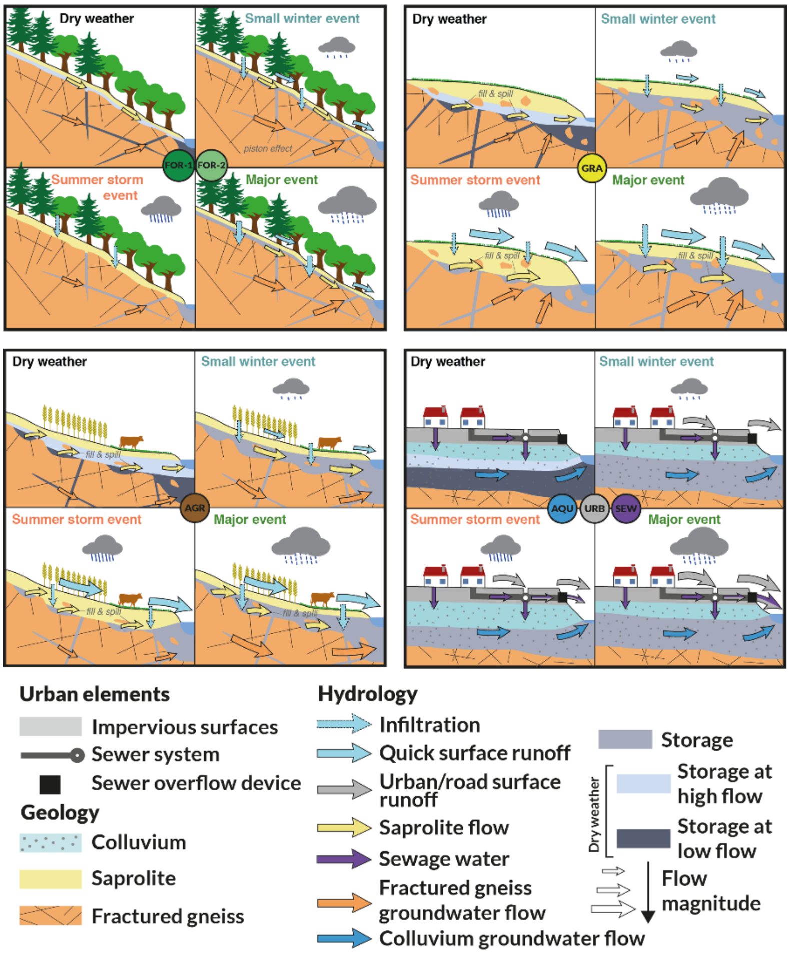

Figure 1 – Improved perceptual model of the Ratier catchment, initially build by Grandjouan et al. (2023). Main contributions, estimated by the mixing model, are illustrated according to the nature of the source and the four hydro-meteorological conditions studied, including dry weather, small winter event, summer storm event, major event. FOR : forest; GRA : grassland; AGR : agricultural; AQU : aquifer; URB : urban and road surface runoff; SEW : wastewater.

Unclear sentences

14. Language is generally fine, but some sentences are overly complex. Feel free to use more often the direct active form, for example "we did this" or "we assume that", rather than the passive form. In English, differently from other languages like French, this is totally fine and not considered informal.

We searched the text for complex sentences and corrected several of them to give them a more direct active form, as suggested.

15. 35: "can alter water pathways": as it is written now, it seems you are saying that pollutants can alter the way in which water flows along a pathway

We acknowledge that there is a confusion in the initial sentence. The idea we wanted to mention is that the increasing urbanisation can alter water pathways and transfer anthropogenic contaminants, leading to serious deterioration of surface water and groundwater quality.

16. 70-72: unclear if the data also comes from the same catchments or only the application

We modified these sentences to make it clearer that the biogeochemical data used in this study do indeed come from the same catchment:

This approach is based on the creation of a large biogeochemical dataset through the sampling and analysis of runoff water in a catchment. Classical and innovative tracers are measured and used as input data for a mixing model. We applied this approach to the Ratier peri-urban catchment, and its nested Mercier sub-catchment, in France, so as to better understand their hydrological behaviour and to identify potential sources of contamination.

17. 117: the "main combination of factors". This sounds rather vague. Can you be more explicit and clarify what this first classification represents?

The "main combination of factors" refers to the most spatially represented combination of factors, including geology, field capacity, land use and agricultural activities. We calculated the relative surfaces of each combination of factors, to help determine which combination is the most represented. We modified the text as follows and added an extra table in appendix. Please see our response to comment n°4 for more details.

References

Alazard, M., Boisson, A., Maréchal, J.-C., Perrin, J., Dewandel, B., Schwarz, T., Pettenati, M., Picot-Colbeaux, G., Kloppmann, W., & Ahmed, S. (2016). Investigation of recharge dynamics and flow paths in a fractured crystalline aquifer in semi-arid India using borehole logs : Implications for managed aquifer recharge. *Hydrogeology Journal*, *24*(1), 35. https://doi.org/10.1007/s10040-015-1323-5

Benjamin, M. M. (2014). *Water Chemistry : Second Edition*. Waveland Press. https://books.google.fr/books?id=dr-VBAAAQBAJ

Beven, K. (2012). *Rainfall-runoff modelling : The primer, second edition* (Vol. 457). John Wiley & Sons, Ltd.

Boukra, A., Masson, M., Brosse, C., Sourzac, M., Parlanti, E., & Miège, C. (2023). Sampling terrigenous diffuse sources in watercourse : Influence of land use and hydrological conditions on dissolved organic matter characteristics. *Science of The Total Environment*, *872*, 162104. https://doi.org/10.1016/j.scitotenv.2023.162104

Bruijnzeel, L. A. (2004). Hydrological functions of tropical forests : Not seeing the soil for the trees? *Agriculture, Ecosystems & Environment*, *104*(1), 185-228. https://doi.org/10.1016/j.agee.2004.01.015

Cooper, D. M., Jenkins, A., Skeffington, R., & Gannon, B. (2000). Catchment-scale simulation of stream water chemistry by spatial mixing : Theory and application. *Journal of Hydrology*, *233*(1-4), 121-137. https://doi.org/10.1016/S0022-1694(00)00230-4

Coquery, M., Pomies, M., Martin Ruel, S., Budzinski, H., Miege, C., Esperanza, M., Soulier, C., & Choubert, J. M. (2011). Mesurer les micropolluants dans les eaux usées brutes et traitées.

Protocoles et résultats pour l'analyse des concentrations et des flux. *Techniques Sciences Méthodes*, *1-2*, 25-43.

Cristiano, E., ten Veldhuis, M.-C., & van de Giesen, N. (2017). Spatial and temporal variability of rainfall and their effects on hydrological response in urban areas – a review. *Hydrology and Earth System Sciences*, *21*(7), 3859-3878. https://doi.org/10.5194/hess-21-3859-2017

El Azzi, D., Probst, J. L., Teisserenc, R., Merlina, G., Baqué, D., Julien, F., Payre-Suc, V., & Guiresse, M. (2016). Trace element and pesticide dynamics during a flood event in the save agricultural watershed : Soil-river transfer pathways and controlling factors. *Water, Air, and Soil Pollution*, *227*(12). https://doi.org/10.1007/s11270-016-3144-0

Emmanuel, I., Andrieu, H., Flahaut, B., & Furusho, C. (2012). *Influence of rainfall spatial variability on rainfall runoff modelling : Case study on a peri-urban catchment*.

Fines, R. W., Stone, M., Webster, K. L., Leach, J. A., Buttle, J. M., Emelko, M. B., & Collins, A. L. (2023). Evaluation of Legacy Forest Harvesting Impacts on Dominant Stream Water Sources and Implications for Water Quality Using End Member Mixing Analysis. *WATER*, *15*(15). https://doi.org/10.3390/w15152825

Froger, C., Quantin, C., Bordier, L., Monvoisin, G., Evrard, O., & Ayrault, S. (2020). Quantification of spatial and temporal variations in trace element fluxes originating from urban areas at the catchment scale. *Journal of Soils and Sediments*, *20*(11), 4055-4069. https://doi.org/10.1007/s11368-020-02766-1

Fröhlich, H. L., Breuer, L., Frede, H.-G., Huisman, J. A., & Vaché, K. B. (2008). Water source characterization through spatiotemporal patterns of major, minor and trace element stream concentrations in a complex, mesoscale German catchment. *Hydrological Processes*, *22*(12), 2028-2043. https://doi.org/10.1002/hyp.6804

Gonzales, A. L., Nonner, J., Heijkers, J., & Uhlenbrook, S. (2009). Comparison of different base flow separation methods in a lowland catchment. *Hydrology and Earth System Sciences*, *13*(11), 2055-2068. https://doi.org/10.5194/hess-13-2055-2009

Goutaland, D. (2009). *Programme ANR AVuPUR - Prospection géophysique par panneau éléctrique de trois parcelles d'un sous-bassin versant de l'Yzeron*. CETE de Lyon.

Grandjouan, O., Branger, F., Masson, M., Cournoyer, B., & Coquery, M. (2023). Identification and estimation of hydrological contributions in a mixed land-use catchment based on a simple biogeochemical and hydro-meteorological dataset. *Hydrological Processes*, *37*(12), e15035. https://doi.org/10.1002/hyp.15035

Helms, J. R., Stubbins, A., Ritchie, J. D., Minor, E. C., Kieber, D. J., & Mopper, K. (2008). Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. *Limnology and Oceanography*, *53*(3), 955-969. https://doi.org/10.4319/lo.2008.53.3.0955

James, R., Amasi, A. I., Wynants, M., Nobert, J., Mtei, K. M., & Njau, K. (2023). Tracing the dominant sources of sediment flowing towards Lake Victoria using geochemical tracers and a Bayesian mixing model. *Journal of Soils and Sediments*, *23*(3), 1568-1580. https://doi.org/10.1007/s11368-023-03440-y

Kaown, D., Koh, D.-C., Mayer, B., Mahlknecht, J., Ju, Y., Rhee, S.-K., Kim, J.-H., Park, D. K., Park, I., Lee, H.-L., Yoon, Y.-Y., & Lee, K.-K. (2023). Estimation of nutrient sources and fate in groundwater near a large weir-regulated river using multiple isotopes and microbial signatures. *Journal of Hazardous Materials*, *446*, 130703. https://doi.org/10.1016/j.jhazmat.2022.130703

Kermadi, S., Braud, I., Jacqueminet, C., Branger, F., Renard, F., & Michel, K. (2012). Quels liens entre climatologie, occupation des sols et inondations dans le bassin versant de l'Yzeron (ouest Lyonnais) ? Apport de l'analyse conjointe de données hydroclimatiques et d'images satellitaires très haute résolution. *Climatologie*, *9*, 83.

Klages, M. G., & Hsieh, Y. P. (1975). Suspended Solids Carried by the Gallatin River of Southwestern Montana : II. Using Mineralogy for Inferring Sources. *Journal of Environmental Quality*, *4*(1), 68-73. https://doi.org/10.2134/jeq1975.00472425000400010016x

Kumar, N., Ganguly, A., Biswal, K., Keesari, T., Pandey, A., & Deshpande, R. D. (2024). Relative contribution from different water sources to supraglacial runoff in western Himalaya. *Journal of Hydrology*, *635*, 131137. https://doi.org/10.1016/j.jhydrol.2024.131137

Lachassagne, P., Dewandel, B., & Wyns, R. (2021). Review : Hydrogeology of weathered crystalline/hard-rock aquifers—guidelines for the operational survey and management of their groundwater resources. *Hydrogeology Journal*, *29*(8), 2561-2594. https://doi.org/10.1007/s10040-021-02339-7

Ladouche, B., Probst, A., Viville, D., Idir, S., Baqué, D., Loubet, M., Probst, J.-L., & Bariac, T. (2001). Hydrograph separation using isotopic, chemical and hydrological approaches (Strengbach catchment, France). *Journal of Hydrology*, *242*(3-4), 255-274. https://doi.org/10.1016/S0022-1694(00)00391-7

Lamprea, K., & Ruban, V. (2011). Pollutant concentrations and fluxes in both stormwater and wastewater at the outlet of two urban watersheds in Nantes (France). *Urban Water Journal*, *8*(4), 219-231. https://doi.org/10.1080/1573062X.2011.596211

Le, H. T., Pommier, T., Ribolzi, O., Soulileuth, B., Huon, S., Silvera, N., & Rochelle-Newall, E. (2022). Overland flow during a storm event strongly affects stream water chemistry and bacterial community structure. *Aquatic Sciences - Research Across Boundaries*, *84*(1), 7. https://doi.org/10.1007/s00027-021-00839-y

Madani, E. M., Jansson, P. E., & Babelon, I. (2017). Differences in water balance between grassland and forest watersheds using long-term data, derived using the CoupModel. *Hydrology Research*, *49*(1), 72-89. https://doi.org/10.2166/nh.2017.154

Marti, R., Ribun, S., Aubin, J.-B., Colinon, C., Petit, S., Marjolet, L., Gourmelon, M., Schmitt, L., Breil, P., Cottet, M., & Cournoyer, B. (2017). Human-driven microbiological contamination of benthic and hyporheic sediments of an intermittent peri-urban river assessed from MST and 16S rRNA genetic structure analyses. *Frontiers in Microbiology*, *8*, 19. https://doi.org/10.3389/fmicb.2017.00019

McDonnell, J. J., Spence, C., Karran, D. J., van Meerveld, H. J. (Ilja), & Harman, C. J. (2021). Fill-and-Spill : A Process Description of Runoff Generation at the Scale of the Beholder. *Water Resources Research*, *57*(5), e2020WR027514. https://doi.org/10.1029/2020WR027514

Motha, J. A., Wallbrink, P. J., Hairsine, P. B., & Grayson, R. B. (2003). Determining the sources of suspended sediment in a forested catchment in southeastern Australia. *Water Resources Research*, *39*(3). https://doi.org/10.1029/2001WR000794

Nguyen, H., Peche, A., & Venohr, M. (2021). Modelling Of Sewer Exfiltration To Groundwater In Urban Wastewater Systems : A Critical Review. *Journal of Hydrology*, 126130. https://doi.org/10.1016/j.jhydrol.2021.126130

Omogbehin, M. H., & Oluwatimilehin, I. A. (2022). Changes of water chemistry from rainfall to stream flow in Obagbile Catchment, Southwest Nigeria. *Regional Sustainability*, *3*(2), 170-181. https://doi.org/10.1016/j.regsus.2022.07.006

Rai, S. P., Singh, D., Jacob, N., Rawat, Y. S., Arora, M., & BhishmKumar. (2019). Identifying contribution of snowmelt and glacier melt to the Bhagirathi River (Upper Ganga) near snout of the Gangotri Glacier using environmental isotopes. *CATENA*, *173*, 339-351. https://doi.org/10.1016/j.catena.2018.10.031

Robinson, M., & Dupeyrat, A. (2005). Effects of commercial timber harvesting on streamflow regimes in the Plynlimon catchments, mid-Wales. *Hydrological Processes*, *19*(6), 1213-1226. https://doi.org/10.1002/hyp.5561

Shi, M.-M., Wang, X.-M., Chen, Q., Han, B.-H., Zhou, B.-R., Xiao, J.-S., & Xiao, H.-B. (2021). Responses of soil moisture to precipitation and infiltration in dry and wet alpine grassland ecosystems. In *Acta Prataculturae Sinica* (Vol. 30, Numéro 12, p. 49-58). https://doi.org/10.11686/cyxb2020436

Spence, C., & Woo, M. (2003). Hydrology of subarctic Canadian shield : Soil-filled valleys. *Journal of Hydrology*, *279*(1), 151-166. https://doi.org/10.1016/S0022-1694(03)00175-6

Stock, B. C., Jackson, A. L., Ward, E. J., Parnell, A. C., Phillips, D. L., & Semmens, B. X. (2018). Analyzing mixing systems using a new generation of Bayesian tracer mixing models. *PeerJ*, *6*(e5096).

Tran, N. H., Reinhard, M., Khan, E., Chen, H., Nguyen, V. T., Li, Y., Goh, S. G., Nguyen, Q. B., Saeidi, N., & Gin, K. Y.-H. (2019). Emerging contaminants in wastewater, stormwater runoff, and surface water : Application as chemical markers for diffuse sources. *Science of The Total Environment*, *676*, 252-267. https://doi.org/10.1016/j.scitotenv.2019.04.160

Tromp-van Meerveld, H. J., & McDonnell, J. (2006). Threshold relations in subsurface stormflow : 2. The fill and spill hypothesis. *Water Resources Research*, *42*(2). https://doi.org/10.1029/2004WR003800

Vale, S., Swales, A., Smith, H. G., Olsen, G., & Woodward, B. (2022). Impacts of tracer type, tracer selection, and source dominance on source apportionment with sediment fingerprinting. *Science of The Total Environment*, *831*, 154832. https://doi.org/10.1016/j.scitotenv.2022.154832

Verseveld, W. J. van, McDonnell, J. J., & Lajtha, K. (2008). A mechanistic assessment of nutrient flushing at the catchment scale. *Journal of Hydrology*, *358*(3), 268-287. https://doi.org/10.1016/j.jhydrol.2008.06.009

Vian, J.-F. (2019). *Agriculture biologique et qualité de l'eau. Etat des lieux des forces et faiblesses des systèmes de production conduits en AB*. ISARA Lyon.

Wang, F., Liu, L., Xu, W., Li, Y., Ruan, Q., & Cao, W. (2024). Multiple stable isotopic approaches for tracing nitrate contamination sources : Implications for nitrogen management in complex watersheds. *Ecotoxicology and Environmental Safety*, *269*, 115822. https://doi.org/10.1016/j.ecoenv.2023.115822

Wellington, B. I., & Driscoll, C. T. (2004). The episodic acidification of a stream with elevated concentrations of dissolved organic carbon. *Hydrological Processes*, *18*(14), 2663-2680. https://doi.org/10.1002/hyp.5574

White, A. F., Bullen, T. D., Vivit, D. V., Schulz, M. S., & Clow, D. W. (1999). The role of disseminated calcite in the chemical weathering of granitoid rocks. *Geochimica et Cosmochimica Acta*, *63*(13), 1939-1953. https://doi.org/10.1016/S0016-7037(99)00082-4

Yokel, J., & Delistraty, D. A. (2003). Arsenic, lead, and other trace elements in soils contaminated with pesticide residues at the Hanford site (USA). *Environmental toxicology*, *18*(2), 104-114. https://doi.org/10.1002/tox.10106