An original approach combining biogeochemical signatures and a mixing model to discriminate spatial runoff-generating sources in a peri-urban catchment

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Abstract.

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 ~~Such approach is not yet widely used for the spatial decomposition of flow. However, it has great potential for estimating~~ contributions linked to ~~specific~~ geological, pedological, and ~~or~~ ~~land-use~~land use characteristics, as well as ~~or to particular~~ anthropogenic contaminant sources~~, in addition to a vertical decomposition~~. In this study, ~~A~~a Bayesian mixing model ~~approach~~ was applied to the Ratier peri-urban sub-catchment of the OTHU Yzeron observatory. Eight runoff-generating sources were identified and sampled, ~~corresponding~~ including ~~to~~ different land uses (e.g. forest, grassland, ~~breeding)~~agricultural areas), a colluvium aquifer~~hydrological compartments (e.g. aquifer),~~ and urban point discharges (e.g. sewer system, urban and road surface runoff). A wide range of biogeochemical parameters were analysed including classical (i.e., major chemical compounds, dissolved metals) and innovative tracers (i.e., characteristics of dissolved organic matter~~ characteristics~~, microbial indicators). Streamwater samples collected under contrasting hydro-meteorological conditions revealed distinct source signatures and highly variable contributions, with wastewater dominating under dry weather and rapid surface runoff during summer storms. Using these results, we improved a previously designed perceptual hydrological model of the Ratier and Mercier catchments, at the hillslope scale, which highlighted the potential of spatial tracer-based decomposition in addition to classical vertical hydrological separation. More broadly, this study demonstrates the potential of such mixing model, using classical but also more innovative tracers, to provide insights for validating distributed hydrological models and to anticipate the influence of land use, urbanisation, and climate changes on runoff generation.~~A Bayesian mixing model method was used to decompose streamwater compositions sampled at the outlets of two sub-catchments, under contrasted hydro-meteorological conditions. Results showed distinct biogeochemical signatures mostly linked to the land-use and the geological compartments. The estimated contributions were contrasted and strongly influenced~~

~~by the hydro-meteorological conditions. The inferred contributions were used to improve an existing perceptual hydrological model of the Ratier and Mercier catchments, at the hillslope scale. This confirmed the potential of biogeochemical data to discriminate spatial runoff-generating sources according to land use, in addition to a more traditional vertical decomposition.~~

Keywords: runoff-generating sources, fingerprints, spatial decomposition, ~~OTHU, OZCAR~~geochemical tracers, Yzeron

1. Introduction

Peri-urban catchments are characterised by contrasting landscapes that can include natural areas (e.g. forests, moorlands), agricultural areas (e.g. crops, grassland) and urban areas (e.g. residential, commercial or industrial areas). These catchments are under considerable pressure from increasing urbanisation, particularly around large cities (Mejía & Moglen, 2010). Peri-urban landscapes are evolving quickly as natural and agricultural areas are decreasing in favour of urban areas (Jacqueminet et al., 2013). ~~The growing~~This increasing urbanisation ~~presence of anthropogenic contaminants~~ can alter water pathways and increase transfer of anthropogenic contaminants, leading to serious deterioration of surface water and groundwater quality. Sewer overflows are major vectors for a large number of contaminants such as organic matter, organic micropollutants, trace metal elements (e.g. Cu, Ni, Pb, Zn), nutrients or pathogens (Chocat et al., 2001; Lafont et al., 2006; Pozzi et al., 2024; Walsh et al., 2005). Impervious surfaces act as vectors for many contaminants, via rainwater runoff on urban surfaces, such as certain metals (e.g. Cu, Pb, Zn; Charters et al., 2016) or polycyclic aromatic hydrocarbons (Bomboï & Hernandez, 1991), and microbes (Bouchali et al., 2024). Agricultural activities can also bring significant contributions of contaminants in water such as pesticides (Giri & Qiu, 2016), veterinary products (Martins et al., 2019), animal ~~fecal~~faecal contamination (Marti et al., 2017) or nutrients via fertilization (Penuelas et al., 2023). Small catchments (~10 km²) are particularly sensitive to the degradation of the surface water quality, as they generally consist of streams close to contaminant sources associated with low dilution capacity (Giri & Qiu, 2016). Effective management of water resources and water quality requires precise knowledge of the water pathways and sources in peri-urban catchments (Gonzales et al., 2009). However, identifying runoff-generating sources and estimating their contribution is difficult, as direct measurement of each contribution is almost impossible (Tardy et al., 2004).

Runoff-generating sources are numerous in peri-urban catchments and can be of different kinds due to the diversity of land uses and the presence of artificial elements that divert water such as sewer systems, sewer overflow devices and impervious areas (Birkinshaw et al., 2021; Jankowfsky, 2011). These sources can be defined as hydrological components (e.g. surface runoff, soil water or groundwater flow; Cooper et al., 2000), as specific land uses (e.g. forest, agriculture, urbanized area; Ramon, 2021), or as point contribution (e.g. sewer overflow or wastewater treatment plant outlet; Pozzi et al., 2024). Runoff-generating sources can also be considered as sub-catchments representing a combination of specific geological, pedological and ~~land-use~~land use factors (Barthold et al., 2010).

It is now recognised that the biogeochemical composition of water can provide information on the contributions of runoff-generating sources, which cannot be deduced from rainfall-runoff dynamics alone (Birkel & Soulsby, 2015). The use of geochemical signatures through a mixing model is now commonly applied to estimate contributions of runoff-generating sources to streamflow (e.g. Burns et al., 2001; Christophersen et al., 1990; Ladouche et al., 2001; Lamprea & Ruban, 2011; McElmurry et al., 2014). To this day, 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; F. 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 both vertical and spatial runoff-generating sources, although it shows~~To this day, this approach is often limited to a vertical decomposition of streamflow according to groundwater flow, subsurface flow and surface runoff (Gonzales et al., 2009; Ladouche et al., 2001). However, this method has also a~~ strong potential for spatial decomposition according to~~o runoff-generating~~ sources linked to the geological, pedological and land use characteristics of the catchment (Nascimento et al., 2023; Liu et al., 2023; Uber et al., 2019). In addition, the use of tracers is often limited to classical geochemical tracers such as stable isotopes, major ions (Singh & Stenger, 2018) or metals (Barthold et al., 2010). Yet, many other biogeochemical parameters show potential for discriminating additional sources, such as the characteristics of dissolved organic matter (Begum et al., 2023; McElmurry et al., 2014; Sun et al., 2024) or microbial parameters (Colin et al., 2020; Marti et al., 2017).

The objective of the present study is to identify runoff-generating sources linked to both vertical and spatial characteristics of a small peri-urban catchment (e.g. geology, land use), and estimate their contributions to streamwater in contrasted hydro-meteorological conditions. This approach is based on the creation of a large biogeochemical dataset through the sampling and analysis of runoff water in a catchment. ~~including c~~Classical and innovative tracers we~~a~~re used as input data ~~for~~in ~~within the application of~~ a mixing model. ~~This method is applied~~We applied this approach to the Ratier peri-urban catchment, and its nested Mercier sub-catchment, in France, ~~so as to~~to better understand their hydrological behaviour and to identify potential sources of contamination. First, we present the sampling campaigns for runoff-generating sources and streamwater, as well as sample pre-treatment and analysis~~ and the construction of the biogeochemical dataset~~. ~~Second~~Then, we describe the characterization of biogeochemical signatures of the sources and their contributions to streamwater obtained ~~through the~~via hydrograph separation. Finally, we discuss ~~assess an~~the ~~evaluation~~ estimated~~of the constructed~~ signatures and contributions for each source, ~~an evaluation of the estimated contributions, as well as~~then propose a revision of the initial perceptual hydrological model ~~proposed~~ presented by Grandjouan et al. (2023), to provide a better understanding of the Ratier and Mercier catchments hydrological behaviour.

2. Materials and methods

2.1 Study area: the Ratier catchment

The Ratier catchment is located west of Lyon, in France. It is part of the Yzeron basin and a site of the Field Observatory in Urban Hydrology (OTHU; https://www.graie.org/othu/) and the Critical Zone Observatories: Research and Application OZCAR (https://www.ozcar-ri.org/). It covers an area of 19.8 km² and has an altitude ranging between 250 and 780 m. The catchment climate is temperate with ~~mediterranean~~Mediterranean and continental influences (Gnouma, 2006). The bedrock is predominantly crystalline with gneiss underlying 96% of the total surface (Figure 1~~Figure 1~~.A). The shallower part of the gneiss is fractured and provides low perennial groundwater storage (Delfour et al., 1989) The fractured gneiss gradually changes to a weathered clayous-sandy saprolite layer, which varies from less than 1 m thick in the upper part of the catchment to 10 to 20 m in the valley bottom (Goutaland, 2009). The delimitation between this layer and the thin sandy to loamy soils is not clear (Braud et al., 2011). The soils are associated with low to medium field capacities, with the exception of valley bottoms characterised by high field capacities (Figure 1~~Figure 1~~.B). Downstream of the catchment, the eastern part is covered by colluvium deposits holding a local aquifer (Figure 1~~Figure 1~~.A). This catchment is typically peri-urban with ~~44~~48% of agricultural areas, ~~42~~30% of forest and ~~15~~21% of urban areas (Jacqueminet et al., 2013). Field surveys performed by Bétemps (2021) provided information about agricultural activities, which include cereal crop cultures (10% of the catchment area), bovine (10%) and equine breeding (2%) (Figure 1~~Figure 1~~.C). In the urbanized areas, wastewater and rainwater are managed by a combined sewer network and transferred outside the limits of the catchment; however, they can be released in streams during rainstorms via a sewer overflow device located directly upstream of the Ratier outlet (Figure 1~~Figure 1~~.D). The Mercier stream is a tributary of the Ratier stream with a catchment area of 7.8 km². Its geology consists entirely of gneiss bedrock. Land use is predominantly agriculture (49~~52~~%) and forest (38~~42~~%), with a small proportion of urban areas (~~5~~13%), including therefore less rainwater drainage facilities than the Ratier catchment.

The Pollionnay pluviometric station (Fig. 1.D) records rain and air temperature since 1997. The mean annual precipitation is 750 mm and the mean annual minimum and maximum temperatures are 6.6 and 18.4°C from 2010 to 2022 (Grandjouan, 2024). Two gauging stations located at the outlets of the Mercier and Ratier catchments allow a continuous hydrological monitoring since 2010 and 1997, respectively (Figure 1~~Figure 1~~.D). Hydrological data show a contrasted hydrological regime, with marked low-flow periods between June and September, particularly upstream where runoff is low throughout the year. The Mercier stream is frequently observed to be dry, unlike the Ratier stream, which is continuously supplied by the colluvium aquifer (Grandjouan et al., 2023). According to the rain and discharge data, the response time (i.e., the time elapsed between the peak of rainfall and the corresponding peak in discharge) for the Ratier catchment is around 30 minutes.

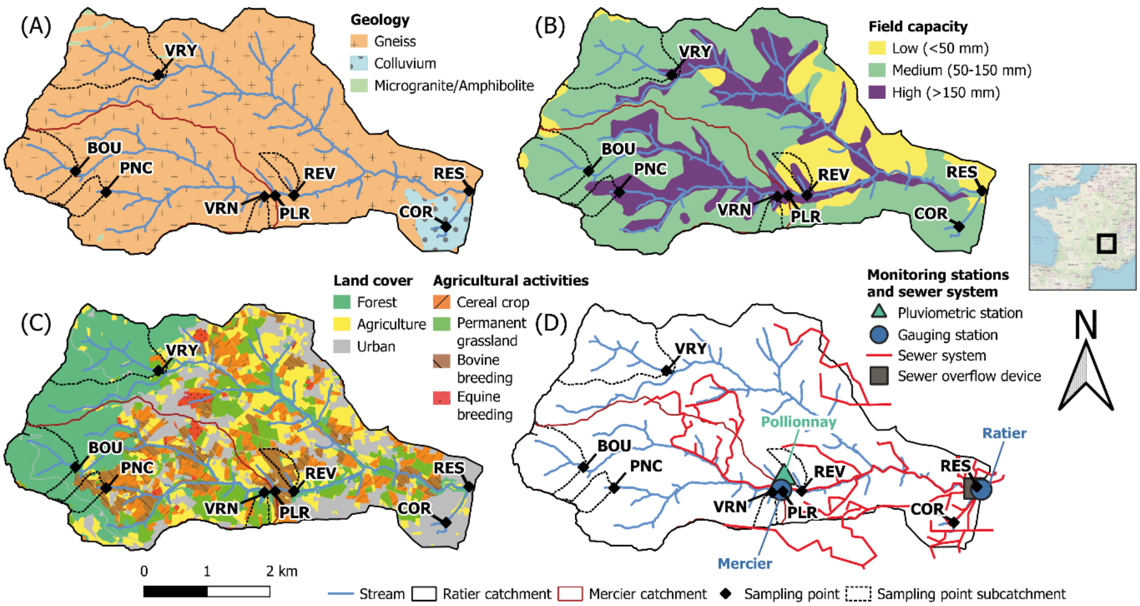


Figure 1 – Maps of the Ratier and Mercier catchments showing the sampling points (see Table 1~~Table 1~~ for details) and (A) geology (David et al., 1979; Delfour et al., 1989; Gnouma, 2006), (B) field capacity (Labbas, 2014), (C) land use (Jacqueminet et al., 2013) and agricultural activities (Bétemps, 2021) and (D) monitoring stations and sewer system (from Grand Lyon and SIAHVY).

2.2 Field data acquisition

2.2.1 Source identification and sampling

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~~, and the sewer~~. We based our work on ~~the~~ two hypothese~~i~~s~~-~~: (1) ~~that~~ the biogeochemical composition of streamwater at the outlet of ~~these~~ each sub-catchment~~s~~ is representative of ~~these~~its associated factors (Barthold et al., 2010); and (2) the runoff contributions from a specific source is proportional to its spatial extent within the catchment.

The first step in identifying these sources involv~~es~~ed the superposition of geological, field capacity, land use and agricultural activities maps (Figure 1~~Figure 1~~). ~~This allowed us to obtain~~~~determine which combinations of factors are~~ In this way, we identified the most spatially representative combinations of factors ~~most spatially represented~~ in the catchment, as detailed in~~.~~ Table A1~~ shows the relative areas corresponding to each combination obtained~~. Based on these results, we identified the main sources and named them according to their associated land use: forest (FOR), grassland (GRA), agriculture (AGR), colluvium aquifer (AQU), and urban and road surface runoff from impervious areas (URB) (see Table 1). We considered quick surface runoff from other areas (SUR) as an additional source, resulting from infiltration excess or saturation excess overland flow (Beven, 2012). ~~A last source~~ W~~w~~e identified ~~is~~ wastewater (SEW) as a last source that~~, which~~ can be ~~transferred~~discharged from the combined sewer system into the stream via through an overflow device located downstream of the Ratier catchment (Figure 1.D), or other overflow pipes. Table 1 provides a description of the factors corresponding to these sources. the main combinations of factors existing in the catchment. Then, Wwe then selected sampling points where representative of samples could be taken from each source. These points are located . We selected Ssampling points are selected at the outlet of several selected sub-catchments (Table 1Table 1 and Figure 1 Figure 1), according to the predominantly represented combinations of factors as well asand a field reconnaissance surveys, which allowed to check the consistency of the dataland use, particularly for agricultural activities, which that may evolve from year to year. The presence of even a permanent small flow, even a weak one, at the sub-catchments outlets wasis also a requirement for the sampling points selection. The localisation of each sampling point is illustrated in Figure 1Figure 1. We selected the colluvium groundwater sampling point (COR) in the upstream section of a stream draining this aquifer. In the case of forest FOR and grasslandGRA sources, we selected two sampling points are selected for each source to compare the biogeochemical signatures obtained from two sub-catchments of the same type (i.e., BOU and VRY,; VRN and REV, respectively). As no homogeneous sub-catchment could be identified for single agricultural activities, anThe agricultural sub-catchment (PNC) includinges bovine breeding and cereal crops is preferred. The colluvium groundwater sampling point (COR) is chosen in the upstream section of a stream draining this aquifer. Two distinct runoff-generating sources associated to surface runoff are considered: (1) urban and road surface runoff from impervious areas, and (2) quick surface runoff from other areas resulting from infiltration excess or saturation excess overland flow (Beven, 2012). For the first type ofthe URB runoff, we selected a storm water discharge point (PLR) fed by runoff from a road and an upstream urban area iss selected. For the second typeSUR runoff, we choseplanned to collectsample sampling of didirect surface runoff during rainfall events, directly from the surface of forest and agricultural sub-catchments (BOU, VRY, REV and PNC) is selected. In order to approach sewer system overflow condition, wWe sampledcollected An additional source is wastewater, which can be transferred from the combined sewer system to the stream through an overflow device located downstream the Ratier catchment (Fig. 1.D), or other overflow pipes. Sampling of wastewater is chosen directly in the sewer system (RES) during rainy periodperiods of rainfall, to approach a sewer system overflow situation.

Table 1 – Identified -runoff-generating source sources and, corresponding Sselected sampling points withfor runoff generating sources andand their relative sub-catchments areas, geology, field capacity, land use and main features, based on information provided in Figure 1Figure 1 and field observations. n.a. : non available

Source: Code	Source: Description	Sampling point	Sub-catchment area (ha)	Geology	Field capacity[1]	Land use (%) and main features: Forest		Agriculture		Urban	
AQU	Colluvium aquifer	COR	-	-	-	-		-		-	
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	15
URB	Urban and road surface runoff	PLR	-	-	-	-	-	-	-	-	-
SUR	Quick surface runoff	n.a.	-	-	-	_	-	_	-	_	-
SEW	Sewer system	RES	-	-	-	-	-	-	-	-	-

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

Sampling point: Site/Source	Code	Sub-basin area (ha)	Geology	Field capacity [1]	Land use (%) and main features: Forest		Agriculture		Urban		
Bouillon stream	BOU	88	Gneiss	Medium	Deciduous, coniferous	100	-	0	-	0	
Verdy stream	VRY	151	Gneiss	Medium	Deciduous, coniferous	100	-	0	-	0	
Varennes	VRN	13	Gneiss	Medium	Decidous	30	Grassland	70	-	0	
Le Revay	REV	18	Gneiss	Low	Decidous	30	Grassland	70	-	0	
Ponce	PNC	28	Gneiss	Medium	-	40	Grassland, bovine breeding, cereal crop	25	Landfill [2]	15	
Corlevet spring	COR	-	-	-	-	-	-	-	-	-	
Wastewater	RES	-	-	-	-	-	-	-	-	-	
Urban and road runoff	PLR	-	-	-	-	-	-	-	-	-	
Quick surface runoff		-	-	-		-		-		-	-

[1] Among low, medium and high field capacities identified by Labbas (2014).
[2] Soils displaced from urban building sites

In order to assess the seasonal variability of the biogeochemical water composition, ~~sources are sampled~~we sampled sources in contrasted hydro-meteorological conditions. We considered l~~L~~ow flow conditions ~~are considered~~ from June to September, and high flow conditions from October to May. We considered ~~W~~wet weather conditions ~~are considered~~ when the cumulative rain over 5 days exceed~~s~~ed 3 mm, and dry weather when it ~~is~~was below 3 mm, this value being the median of daily rainfall recorded between 2011 and 2023 at the Pollionnay station.~~.~~ We performed ~~E~~eight source sampling campaigns ~~were carried out~~ between February 2022 and March 2023. We collected ~~Four~~4 to 5 water samples ~~were collected~~ manually ~~in sampling bottles~~ for each sampling point, for a total of 38 source samples.

Some field observations differed from the initial information provided in Figure 1~~Figure 1~~:~~.~~ n~~N~~o bovine breeding was observed at REV during the campaigns, whereas cereal crops were observed at PNC; ~~. N~~no direct surface runoff was observed during the campaigns at BOU, VRY, VRN and REV,~~; as a consequence,~~ so we could not sample the ~~quick surface runoff~~SUR source ~~could not be sampled~~.

2.2.2 Streamwater sampling during hydrological events

We also sampled streamwater at the outlet~~s~~ of the Mercier and Ratier catchments, targeting contrasted hydrological events. To do so, we extracted past hydrological events f~~were extracted f~~rom the data available for years 2011-2021, and analysed them following the approach presented by ~~(~~Braud et al.~~,~~ (2018)~~Braud et al. (2018)~~. We calculated ~~S~~seven hydro-meteorological indicators ~~were calculated~~ to characterise the 315 extracted events, namely,~~:~~ duration of rain, cumulative rainfall, total runoff, 5-day cumulative reference evapotranspiration, dry period duration, antecedent precipitation index, and 5-day cumulative rainfall (Figure 2~~Figure 2~~). Based on a Hierarchical Clustering Analysis (HCA), the events were classified according to these indicators. We identified an optimal number of three classes using the “elbow” method (Thorndike, 1953); then,~~and associated~~assigned a class to the ~~them to~~ ~~Three classes of hydrological events were identified~~ different types of events: small winter events, summer storm events and major events. Figure 2~~Figure 2~~ shows a Principal Component Analysis (PCA) visualisation of this classification. Major events are defined by high precipitation rate, long duration and high total runoff volume. Summer storm events are characterised by a long dry period before the beginning of the event and high evapotranspiration rate. Small winter events represent the majority of the extracted events ~~(63%)~~ and are characterised by low values for all the indicators. Antecedent precipitation index (API), which corresponds to the sum of daily precipitation weighted according to a multiplying factor (k = 0.8;~~,~~ ~~(~~Sarrazin~~,~~, ~~(~~2012~~)~~), and the cumulative rainfall 5 days (R5) before the event, did not mark any specific event class. Based on this classification, we defined a sampling objective of two hydrological events by class to study intra-class variability and taking in account the difficulty ~~to~~of targeting major and summer storm events.~~events.~~

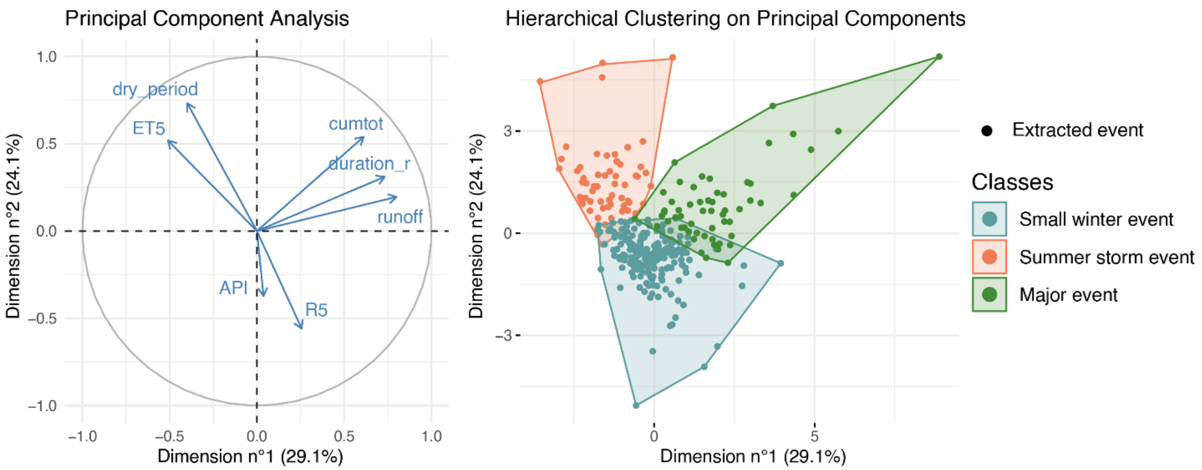


Figure 2 – Principal Component Analysis visualisation of the hydrological event classification based on a Hierarchical Clustering Analysis. duration_r~~-~~: duration of raining event; cumtot~~-~~: cumulative rain during the event; runoff~~-~~: total runoff during the event; ET5~~-~~: cumulative reference evapotranspiration 5 days before the event; dry_period~~-~~: duration of dry period before the event; API~~-~~: antecedent precipitation index at the beginning of the event; R5~~-~~: cumulative rain 5 days before the event.

We used au~~Au~~tomatic samplers (Endress+Hauser Liquiport CSP44) ~~were used~~ to sample streamwater at the Mercier and Ratier gauging stations (Figure 1~~Figure 1~~). We carried out ~~A~~a weather alert ~~monitoring was carried out~~ to launch the sampling campaigns according to the targeted hydrological events. We adapted ~~S~~sampling time steps ~~were fixed and adapted~~ to each event, from 10 to 45 minutes, according to the expected duration of the rain. Six hydrological events were sampled between March 2019 and March 2023, ensuring two events per class. The March 2019 and June 2022 events were not sampled at the Ratier and Mercier station, respectively, due to technical issues on the automatic samplers. We obtained ~~Twenty~~20 to 24 samples ~~were obtained~~ for each event, and mixed them two by two in order to ensure sufficient volume for analysis. After pairing, 10 to 12 samples were finally obtained for each event and at each gauging station. Table 2~~Table 2~~ shows the hydro-meteorological indicators calculated for these events.

Table 2 – Hydro-meteorological indicators calculated for the hydrological events sampled at the Mercier and Ratier gauging stations. The Sampled station column indicates at which gauging station the event was sampled. duration_r: duration of raining event; cumtot: ~~cummulative~~cumulative rain during the event; runoff: total runoff during the event; ET5: cumulative reference evapotranspiration 5 ~~-~~days before the event; dry_period: duration of dry period before the event; API: antecedent precipitation index at the beginning of the event; R5: cumulative rain 5 days before the event.

Event sampling campaign	duration_r (h)	cumtot (mm)	runoff (mm)	ET5 (mm)	dry_period (h)	API (mm)	R5 (mm)	Event class	Sampled station
06/03/2019	20	7	0.3	8	55	0	3	Small winter event	Mercier
10/05/2021	44	92	11.6	13	70	0	10	Major event	Mercier/Ratier
03/10/2021	80	89	5.8	13	147	0	0	Major event	Mercier/Ratier
22/06/2022	116	57	0.3	38	291	0	0	Summer storm event	Ratier
14/09/2022	44	9	0.1	15	94	0	2	Summer storm event	Mercier/Ratier
13/03/2023	19	18	0.7	7	13	1	27	Small winter event	Mercier/Ratier

2.2.3 Streamwater sampling during dry weather

We also considered ~~S~~streamwater composition ~~was also considered~~ at dry weather. Data used come from an available dataset described in Grandjouan et al. (2023). In this ~~latter~~ study, monthly monitoring campaigns were conducted from March 2017 to December 2019 at the outlets of the Mercier and Ratier catchments; ~~, and~~ a total of 24 samples were collected manually. These samples were classified into low flow (June to September) and high flow (October to May) conditions.

2.2.4 Sample pre-treatment and analysis of biogeochemical parameters

All source and streamwater samples were filtered at 0.45 µm and analysed for a set of 35 ~~44~~ biogeochemical parameters in order to obtain a more accurate characterisation and discrimination of the identified sources. This list includes geochemical parameters, characteristics of the dissolved organic matter (DOM), and two microbial parameters (Table 3). 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+}, SiO_2 and Sr for crystalline formations like gneiss (Fröhlich, Breuer, Frede, 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 trace urban origin of water, as for Cd, Cr, Cu, Ni, Pb, Rb or Zn (Becouze-Lareure, 2010; Coquery et al., 2011; Froger et al., 2020; Lamprea & Ruban, 2011). Finally, major ions such 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 of DOM. The spectral slope 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). The HPSEC indicators A0, A1, A2 and A3 represent very large, large, small and very small molecules, respectively (Boukra et al., 2023). We selected the *HF183* and *rum-2-bac* host-specific microbial DNA targets to detect and trace faecal contamination from human and ruminant, respectively.

~~including geochemical parameters, characteristics of the dissolved organic matter (DOM), and 8~~two ~~microbial parameters (Table 3).~~ Additional parameters were analysed for these samples but not used in th~~ise~~ present study. The full set of 55 biogeochemical parameters is available at : https://entrepot.recherche.data.gouv.fr/dataverse/chypster/ (Masson et al., 2025a, 2025b).

Geochemical parameters included 6~~10~~ major ions, silica and 15~~17~~ trace metal elements. Major ions were analysed by ion chromatography, silica by colorimetry and trace elements by inductively coupled mass spectrometry (ICP-TQ-MS). The absence of contamination was systematically verified by the analysis of blanks. L~~im~~imits of quantification (LQ) and analytical uncertainties are detailed in Table A2 ~~Table A1~~. The accuracy and uncertainties of the methods were routinely checked using certified standard solutions and reference materials, as well as regular participation in interlaboratory testing.

Characteristics of the DOM included Dissolved Organic Carbon (DOC) ~~and total dissolved nitrogen (DTN)~~ concentrations, ~~82~~two Ultra Violet-Visible (UV-Vis) indicators and ~~5~~five~~7~~ High Pressure Size Exclusion Chromatography (HPSEC) indicators. The DOC ~~and DTN~~ analyses were performed by high temperature catalytic combustion. The UV-Vis indicators were calculated from absorbance spectra obtained between 200 and 800 nm from UV-Visible spectrophotometry analyses, as described by Li & Hur (2017) and Boukra et al. (2023). The HPSEC analyses were performed as described by Boukra et al. (2023) and HPSEC indicators were calculated from chromatogram obtained with UV detection at a wavelength of 254 nm according to Peuravuori & Pihlaja (1997).

Microbial parameters included ~~7~~ ~~2~~two host-specific microbial DNA targets, markers of human faecal bacterial contamination (*HF183* DNA target) and ruminant contamination (*rum-2-bac* DNA target). Targets were tracked ~~tracked~~ using a quantitative Polymerase Chain Reaction method (qPCR). The DNA extractions~~s~~ were performed as indicated in Pozzi et al. (2024) and~~. T~~ the qPCR assays ~~for human (*HF183* DNA target) and ruminant (*rum-2-bac* DNA target) fecal bacterial tracers, and for tracking classes 1 and 2 integrons PCR assays were~~ performed according to Bouchali et al. (2024).

~~Integrons are genetic shuttles that can encode antibiotic resistances, biocide degradation genes, and other functional genes involved in quick adaptive processes (e. g. Colinon et al., 2010).~~

Table 3 – Measured biogeochemical parameters and ~~respective~~ analytical methods. The tracers in bold correspond to ~~reductionist~~ the final selection of tracers used in the mixing model (see Section 3.2).~~Measured biogeochemical parameters and respective analytical methods~~

Parameter family~~**Parameter family**~~	**Biogeochemical parameter**~~**Biogeochemical parameter**~~	**Analytical method**~~**Analytical method**~~
Major anions~~Major anions~~	**Cl^-, SO_4^{2-}**~~Cl^-, NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}~~	Ionic chromatography NF EN ISO 14911 (1999)
Major cations~~Major cations~~	**Ca^{2+}, K^+, Mg^{2+}, Na^+**~~Ca^{2+}, K^+, Mg^{2+}, Na^+, NH_4^+~~	Ionic chromatography NF EN ISO 10304-1 (2009)

Silica~~Silica~~	**SiO_2~~SiO_2~~**	Colorimetry NF T 90-007 (2001)
Dissolved metals ~~Dissolved organic carbon and dissolved nitrogen~~	Al, **As**, B, **Ba**, Cd, Co, **Cr**, Cu, **Li**, Mo, Ni, Pb, **Rb**, **Sr**, Ti, U, V, Zn ~~Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Rb, Sr, Ti, U, V, Zn~~ ~~DOC, DTN~~	ICP-MS NF T 90-007 (2001) ~~Catalytic combustion~~ ~~NF EN 1484~~
Dissolved organic carbon	**DOC**	Dosage NF EN 1484
UV-Visible indicators	~~E2:E3, E2:E4, E3:E4, E4:E6,~~ S1, **S2**~~, SR, SUVA~~	UV–visible spectroscopy~~UV–visible spectroscopy~~
HPSEC indicators	Mn-254, A0-254, A1-254, A2-254, A3-254	High Pressure Size Exclusion Chromatography
~~HPSEC indicators~~	~~Mn-254, Mw-254, disp-254, A0-254, A1-254, A2-254, A3-254~~	~~High Pressure Size Exclusion Chromatography~~
Microbial qPCR assays	*~~Total bacteria (G16S), total Bacteroidales (BTT),~~ ~~h~~Human marker Bacteroides (HF183), ruminant marker Bacteroides (rum-2-bac)~~, sewer system marker (BTS), classes 1 and 2 integrons~~*	qPCR

2.2.5 Quick surface runoff from non-urban areas

As no surface runoff could be sampled for the SUR source, we considered that the biogeochemical composition of quick surface runoff away from impervious areas was~~is~~ close to the composition of rainwater, assuming that it does not have enough time to acquire significant biogeochemical elements from the soil it flows over. Such hypothesis is supported by the concentrations of several parameters in streamwater during rainy weather (e.g. Cl^-, SO_4^{2-}, SiO_2, Mg^{2+}, Na^+), which are lower than all concentrations measured in the source samples. This observation suggests dilution by low-mineralised inputs. However, this assumption does not take into account the enrichment of water by soil leaching. Therefore, we examined final results ~~will be examined~~ considering that this assumption may lead to an underestimation of the quick surface runoff contribution when applying the mixing model for hydrological events (see Sections 4.1 and 4.2). ~~Therefore, t~~The~~his~~ SUR source ~~(SUR)~~ ~~is~~ was ~~then~~ associated to rainwater ~~biogeochemical~~ composition obtained ~~from~~ at the Pollionnay pluviometric station (Figure 1~~Figure 1~~; Lagouy et al., 2022), sampled between 2017 and 2023, for major ions, DOC and UV-Vis indicators (n = 9). We used ~~D~~data from the Ecully pluviometric station (10 km from Pollionnay) ~~is used~~ for trace metal element concentrations, produced by (Becouze-Lareure, 2010) between 2008 and 2009 (n = 32). No data ~~is~~ was ~~considered~~ available for HPSEC and microbial indicators for the quick surface runoff source.

2.3 Characterization and biogeochemical signatures of runoff-generating sources

2.3.1 Biogeochemical composition and typology of runoff-generating sources

All data obtained from the 3~~8~~8 source water samples and the ~~52~~ 35 analysed parameters we~~a~~re used to provide a ~~detailed~~ global characterization of the biogeochemical composition for each source. This description ~~is~~ was used to compare the biogeochemical composition of the identified sources, as well as to study their variability according to the hydro-meteorological conditions, in order to confirm similarities, and thus the grouping of samples collected from the same type of source (BOU and VRY for forest; VRN and REV for ~~agriculture~~grasslands) or, on the contrary, the distinction between groups of samples. We used a~~A~~ Hierarchical Cl~~assification~~ustering Analysis (HCA) ~~is used~~ to classify the samples according to the biogeochemical dataset and to create a typology of sources. We applied HCA based on an optimal number of class determined with the “elbow” method (Thorndike, 1953), using absolute concentrations that we centred and scaled. The purpose of this typology is to describe the nature of the sources that will be considered in the mixing model.

2.3.2 Building-up the biogeochemical signatures

A biogeochemical signature can be defined as a limited selection of discriminating and representative tracers.~~(Fröhlich, Breuer, Frede, et al., 2008; White et al., 1999)(Fröhlich, Breuer, Frede, et al., 2008; F. Liu et al., 2008),(Cooper et al., 2000)(El Azzi et al., 2016)(Vian, 2019)(Yokel & Delistraty, 2003)trace(Coquery et al., 2011; Froger et al., 2020; Lamprea & Ruban, 2011; Froger et al., 2020)such (Fröhlich, Breuer, Frede, et al., 2008)(Helms et al., 2008)The , respectively(Boukra et al., 2023)(Reischer et al., 2006)(Seurinck et al., 2005)~~ Using selected tracers, we built biogeochemical signatures that fed a mixing model to estimate the contribution of sources at the catchment outlet.~~ with the selected tracers from which it is possible to apply a mixing model approach to estimate the contribution of sources at the catchment outlet.~~ The tracers ~~used in a mixing model~~ must be additive~~, conservative and,~~ discriminating, ~~(Christophersen & Hooper, 1992; Tiecher et al., 2015)~~and must be considered as conserv~~ed~~ative through the mixing process (Christophersen & Hooper, 1992; Stock et al., 2018; Tiecher et al., 2015) (see~~.~~ s~~S~~ection 2.4 ~~provides~~for more details on the assumptions required when applying a mixing model). ~~To build these biogeochemical signatures,~~ W~~w~~e appl~~y~~ied a reductionist tracers selection approach based on the biogeochemical dataset for ~~52~~ 35 parameters. This approach aimed at selecting the smallest combination of tracers showing the highest inter-source variability and the lowest intra-source variability. All major parameters and metals ~~are~~ were considered additives regarding their chemical characteristics (Benjamin, 2014). The bacterial DNA targets ~~*Non-additive UV-Vis (E2:E3, E2:E4, E3:E4, E4:E6, SUVA, SR) and HPSEC indicators (Mw 254, disp254) are eliminated according to laboratory tests performed by Baduel (2022). Conservative (HF183*~~*HF183* and *rum-2-bac* ~~and ruminant *Bacteroides* DNA markers) and non-conservative (integrons, 16S rRNA *rrs* gene, *Bacteroidales* DNA marker)~~ bacterial DNA targets show undefined relations with abiotic parameters, which prevent their use in a mixing model. Although we discarded them from the reductionist tracer approach, we used them afterwards to evaluate the biogeochemical signatures and the estimations obtained.

We eliminated ~~are used in this investigation, but their undefined relations with abiotic parameters led to their removal from the parameter list for this particular task. Phosphates (PO_4^{3-}), nitrogen compounds (DTN, NO_3^-, NO_2^-, NH_4^+), Fe and Mn are considered too reactive and therefore non-conservative. Other n~~non-conservative parameters ~~are eliminated~~ by applying a range-test method (Sanisaca et al., 2017; Wilkinson et al., 2013), that check that the concentrations measured in a mixture (here the streamwater sampled at the Mercier and Ratier outlets during the hydrological events) are comprised within the limits represented by the concentrations observed in the source samples. Failure of this test suggest~~s~~ed a non-conservative parameter or a missing source (Collins et al., 2017). We then eliminated ~~N~~non-discriminating parameters ~~are eliminated~~ using a Kruskal-Wallis test (Kruskal & Wallis, 1952) followed by a Dunn post hoc test (Dunn, 1964), with a p-value threshold of 0.05. The null hypothesis is that the distributions of each parameter are identical across all groups; parameter for which this hypothesis could not be rejected are considered non-discriminating. Lastly, we selected the most discriminating tracers ~~are selected~~ using a Linear Discriminant Analysis (LDA) coupled to a Wilks lambda approach (Collins et al., 1997). We used ~~This method is used to select the smallest combination of tracers showing the highest inter-source variability and the lowest intra-source variability. T~~the remaining tracers ~~are used~~ to build the biogeochemical signatures of the runoff-generating sources, in the form of radar plots, using min-max standardized concentrations to obtain values between 0 and 1.~~.~~

2.4 Estimation of the source contributions at the outlet of the catchments

We applied a~~A~~ mixing model ~~is applied~~ to decompose streamwater for samples collected at the Ratier and Mercier sub-catchment outlet stations. We respected the basic assumptions when applying a mixing model provided by ~~(~~Stock et al.~~,~~ (2018), suggesting that a user must verify that : (1) all sources which contributes to streamwater are identified, (2) the signature from source to the mixture is not altered (see Section 2.3.2), (3) the source signatures are fixed, (4) the contributions sum to 100% and the signature of sources differ. We estimated the source contributions during dry weather~~,~~ and during the ~~6~~ six targeted hydrological events. In the absence of rain, we did not~~n't~~ consider urban/~~n and~~ road surface runoff and ~~, as well as~~ quick surface runoff ~~are not considered~~ as sources contributing to the streamwater samples. ~~(Stock et al., 2018)(Stock et al., 2018)~~We chose a Bayesian approach to resolve the mixing model equations, using the package *MixSIAR* in R (Stock et al., 2018), this approach allowing for the incorporation of uncertainty in both source and mixture data. The prior information chosen for source contributions, representing the initial assumption about the relative contributions of each source, correspond to $1/n$, where n is the number of sources considered. The prior information on the biogeochemical parameter concentration for the sources, representing the initial assumption about these concentrations, ~~is~~ was modelled as a normal distribution, defined by the mean and covariance matrix of the measured concentration.

As indicated above, ~~As a prior hypothesis, we~~we expected the contributions from each source to be proportional to their spatial extent, with the exception of wastewater. Results that would invalidate this ~~assumption~~hypothesis 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~~or inputs associated to ~~the presence of~~ the sewage network.

3. Results

3.1 Biogeochemical composition and typology of runoff-generating sources

The median and range of concentrations of the biogeochemical parameters measured ~~for the runoff-generating sources~~at the sampling points are reported in Table A3 ~~Table A2~~ for major parameters, Table A4 ~~Table A3~~ for metals, ~~,~~Table A5 ~~Table A4~~ for the characteristics of DOM and Table A6 for the microbial parameters~~, and Table A5 for microbial parameters~~. ~~These concentrations~~Concentrations are illustrated in the form of a heatmap in Figure 3~~Figure 3~~, coupled with a Hierarchical Cluster Analysis on the parameters and the sampling points.

The ~~biogeochemical compositions of~~ samples collected from the first forest sub-catchment (BOU) are all clustered together, ~~indicating similar concentrations~~marked by higher concentrations for Al and Cd, and higher values for S1 compared to the other samples.~~.~~ Samples collected from the second forest sub-catchment (VRY) ~~do not show clear clustering~~are also clustered together but show a different pattern, marked by higher concentrations of SiO$_2$.~~, showing a variable biogeochemical composition, different from the BOU samples.~~ Samples collected at both grassland sub-catchments (VRN and REV) are well grouped~~, showing similar compositions,~~ despite their expected differences in terms of field capacity (Figure 1~~Figure 1~~.B). They show high values for A1-254 and A2-254, indicating the presence of large organic matter molecules. ~~Three~~ Three of the five samples collected from the agricultural sub-catchment (PNC) are clustered, ~~showing a similar composition,~~ mostly characterised by higher concentrations of As and~~,~~ Co.~~, Mn, Fe. The other two PNC samples are not grouped with the other three, indicating different compositions.~~ Only one PNC sample is marked by high concentrations for the *rum-2-bac* DNA marker. Results show a ~~general~~ good clustering for ~~the five~~ four COR samples representing the colluvium aquifer, marked by significantly higher concentrations for a group of parameters including SiO$_2$, Li and Ba, in comparison to all other source samples. Among the five samples representing the colluvium aquifer (COR), two showed concentrations of human marker *Bacteroides* (HF183) higher than 6 log$_{10}$ number of copies/100 mL~~ of human marker *Bacteroides* (HF183;~~ (see concentration range in ~~-~~Table A6~~Table A4~~), close to the SEW samples concentration, taken directly from wastewater (median 7 log$_{10}$ number of copies/100 mL). We considered that these samples were contaminated by wastewater, and removed them from the dataset. Three of the five ~~W~~wastewater samples (~~SEW~~RES) are also well clustered and ~~, showing similar compositions,~~ linked to a large group of parameters comprised of major ions (e.g. Na~~Ca^{2+}~~, K^+~~PO_4^{3-}~~), dissolved metals (e.g. Pb, Cu, Zn), DOC and~~,~~ ~~DTN,~~ DOM indicators (A3-254~~4 and SR~~)~~ and microbial parameters (e.g. *int1*, *HF183*)~~. The urban and road runoff samples (PLR) show more variability as only ~~two~~ three of the four samples are grouped and marked by high concentrations of ~~NO_3^- and~~ V.

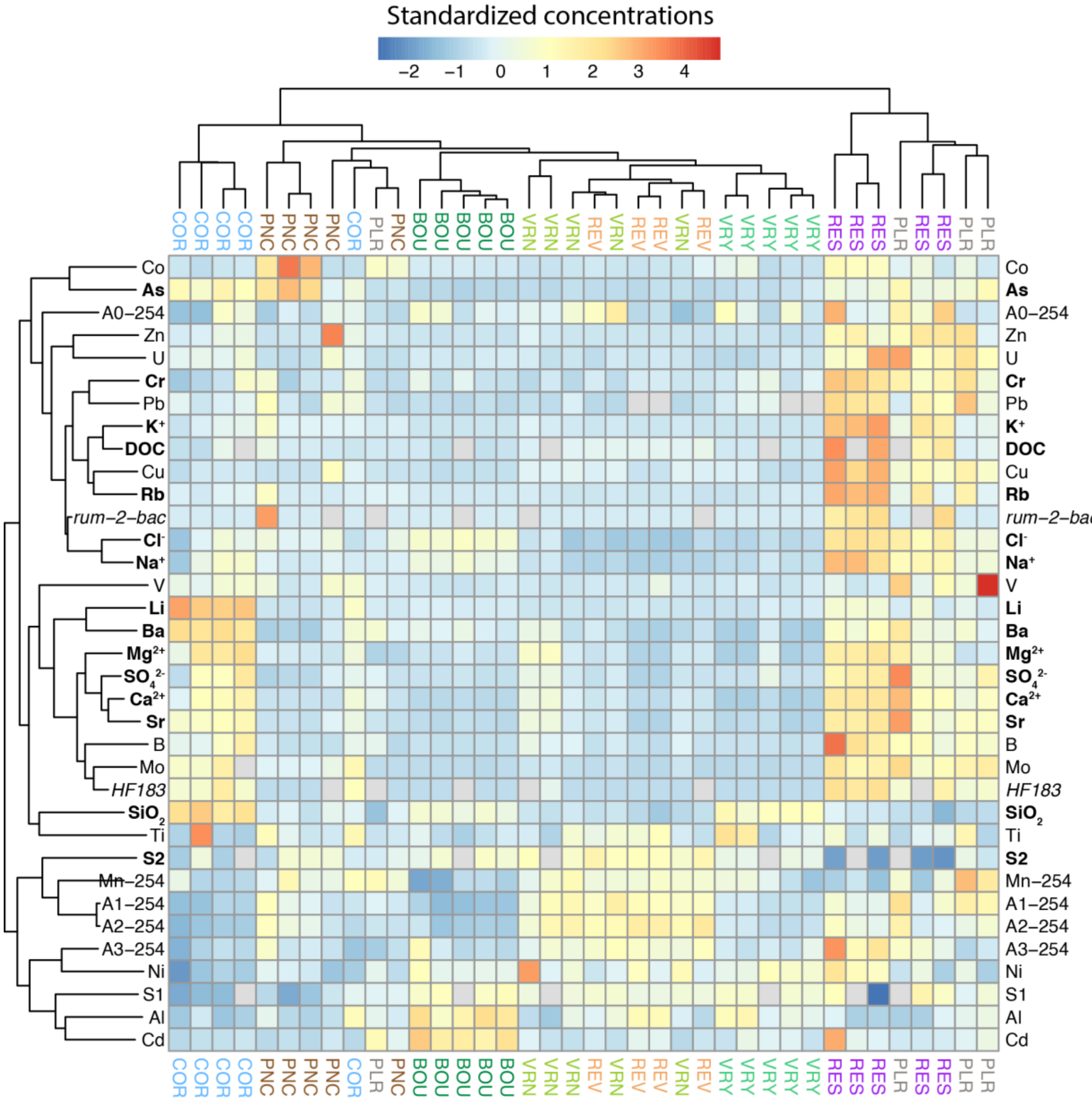


Figure 3 – Heatmap representation of the median concentrations of the biogeochemical parameters in source samplessamples from all selected sampling points of the Ratier and Mercier catchments. Standardised concentrations are shown in a range of colours from blue for negative values to red for positive values. Positive values represent high concentrations for a specific parameter and source sample, compared with the other samples. Negative values represent low concentrations for a specific parameter and source sample, compared with the other samples. Biogeochemical parameters and source samples are classified into groups based on Hierarchical Classification Analysis. Quick surface runoff (SUR) was not considered as all biogeochemical parameters were not available for this source. Bold parameters represent the final selection of tracer used in the Bayesian mixing model.

The differences between the BOU and VRY biogeochemical compositions do not suggest a unique biogeochemical signature associated to forest land use. Thus, wWe thus preferred to consider two different sources related to forest (FOR-1 and FOR-

2)). In contrast, we considered a single source associated to the presence of grassland, based on the clustering of the VRN and REV samples. Each of the remaining sampling points was considered as a distinct source. Table 1 ~~Table 4~~ shows the final typology proposed to describe the runoff-generating sources; it ~~and~~was used for the next step of ~~our~~ the present study, including the new codes used to describe the nature of each source (AQU, FOR-1, FOR-2, GRA, AGR, ~~AQU,~~ SEW, URB and SUR).

~~**Table 4 – Typology of the runoff-generating sources describing the nature of the sources that will be used for the creation of the biogeochemical signatures and in the mixing model (source and colours codes are used thereafter in this study).**~~

~~**Sampling point**~~	~~**Source**~~	~~**Source code**~~
~~BOU~~	~~Gneiss – Medium field capacity – Forest n°1~~	~~FOR-1~~
~~VRY~~	~~Gneiss – Medium field capacity – Forest n°2~~	~~FOR-2~~
~~VRN / REV~~	~~Gneiss – Low/Medium field capacity – Grassland~~	~~GRA~~
~~PNC~~	~~Gneiss – Medium field capacity – Agriculture~~	~~AGR~~
~~COR~~	~~Colluvium aquifer~~	~~AQU~~
~~RES~~	~~Sewer system~~	~~SEW~~
~~PLR~~	~~Urban and road surface runoff~~	~~URB~~
~~SUR~~	~~Quick surface runoff~~	~~SUR~~

3.2 Building-up the biogeochemical signatures

After discarding the parameters considered to be non-additive and non-conservative according to their nature, 33 parameters remained. Application of the range-test pointed out 13 other non-conservative parameters, with concentrations or values outside the range observed for the source samples, mostly concerning the HPSEC indicators and the dissolved metals Al and Co. The Kruskal-Wallis and Dunn tests showed two non-discriminant parameters: Ni and Ti with respective *p-values* of 0.06 and 0.93. Finally, the application of the LDA-Wilks lambda approach (Figure 4~~Figure 4~~) showed that an optimal selection of 15 tracers was sufficient to discriminate the ~~8~~ eight sources. These tracers correspond to ~~7~~ seven major parameters (Cl^-, SO_4^{2-}, Ca^{2+}, Na^{2+}, K^+, Mg^{2+} and SiO_2), six~~6~~ dissolved metals (As, Ba, Cr, Li, Rb, Sr), and two DOM characteristics (DOC, spectral slope S2). These parameters were used to build the biogeochemical signatures of each source. We~~,~~ represented these signatures~~in the form of radarplots~~ in Figure 5~~Figure 5~~.~~.~~

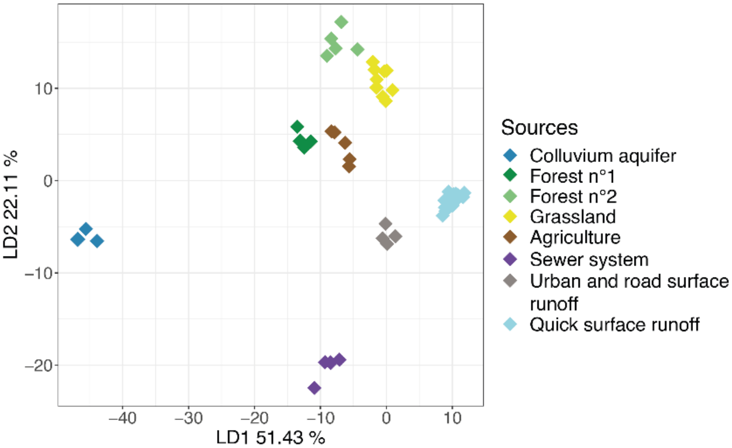


Figure 4 – Source samples coloured according to the sources identified and projected along the axes created by the Linear Discriminant Analysis. The concentrations used correspond to the optimal selection of tracers resulting from the selection by minimisation of Wilks' lambda.

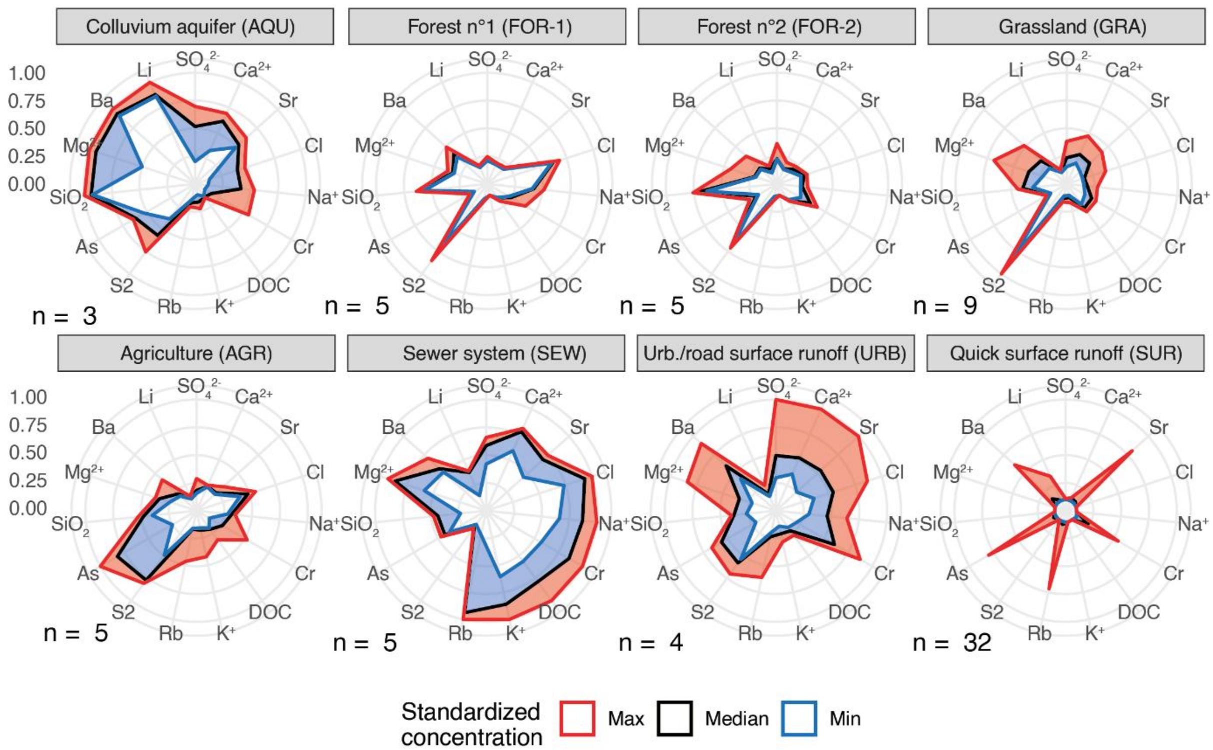


Figure 5 – Biogeochemical signatures of the identified sources, in the form of a radar plot. The 15 tracers correspond to the optimal selection resulting from the reductionist approach. Maximum, median and minimum concentrations are presented after standardization across all 15 tracers. n: the number of samples per source; Urb: urban.

The FOR-1 and FOR-2 signatures show low and stable concentrations, with high values of the parameter S2, which is a spectral slope calculated from absorption coefficients (350-400 nm), negatively correlated with the amount of aromatic carbon (Helms et al., 2008). The GRA signature is even more marked by high values of S2. Headwater from forests and grasslands is thus characterised by poorly aromatic DOM, which could be linked with high soil weathering (~~Y. H.~~ Wang et al., 2023). Boukra et al. (2023) showed similar results for surface waters from forest sub-catchments within the Ratier catchment, with a significant difference between water from forest watershed, less aromatic and water from agricultural areas (vineyards), more aromatic. Samples from the agricultural sub-catchment (AGR) also show higher values of the parameter S2, indicating low aromaticity, but are also characterised by even higher concentrations of the trace element As. According to Liu et al. (2020), significant concentrations of As can be observed in bovine manure, ranging from 2 to 17 mg/kg, which can explain the concentrations obtained for the AGR samples (median of 4.25 µg/L). The AQU signature is particularly characterised by high values of SiO_2, Mg^{2+}, Ba and Li. Grandjouan et al. (2023) pointed out that this runoff generating source is mainly fed by a colluvium aquifer, which significantly contributes to the Ratier stream volume outside of rainfall events, and attributed the high Li, Ba and Mg^{2+} concentrations to a geological origin. High SiO_2 concentrations are often observed in groundwater (Iorgulescu et al., 2005). The URB signature shows variable concentrations, with wide ranges, for SO_4^{2-}, Ca^{2+}, Sr, Cr, Mg^{2+} and Ba. This composition can be explained by the leaching of urban soils during rainy events, leading to the release of the elements that could have been emitted by urban and road pollutions sources and deposited at the surface of these soils. This phenomenon can be amplified by a first-flush effect, which favours the transport of elements for the first rains after long periods of dry weather (Deletic & Orr, 2005). The SEW signature is marked by high concentrations for Cl^-, Na^{2+}, Cr, DOC, K^+, Rb and Mg^{2+}, which is in line with the classical composition of wastewater seen in the literature (e.g. Eme & Boutin, 2015; Fröhlich et al., 2008). The variability observed for this source can be explained by the choice to collect the SEW samples during periods of rain (see Section~~.~~ 2.2.1). Therefore, water samples from the SEW source consist of a mix of wastewater, rainwater and road surface runoff, since this is a combined sewer network. Finally, the signature obtained for SUR shows very low concentrations for most of the 15 tracers, with the exception of high maximum concentrations for Sr, Cr, Rb, As, Ba. According to Becouze-Lareure (2010), these high concentrations are associated with atmospheric inputs to rainwater from the industrial Rhône valley, in the south-east of the Ratier catchment.

3.3 Hydrograph separation

3.3.1 Dry weather

Figure 6~~Figure 6~~ shows the ~~results of the mixing model decomposition~~relative contributions estimated for the 24 streamwater samples collected at the Mercier and Ratier outlets outside from rainfall events. Figure A1 represents the equivalent contributions in daily volumes (in m^3) that we calculated considering that the discharge measured at the time of sampling was representative of the daily discharge. Results for the Mercier catchment showed little seasonality with similar results between low and high flow. The AGR source contributed the most at low flow (up to 40% of total runoff) and the GRA source at high flow (up to 50%). The SEW contribution was significant at both low and high flow conditions (between 10 and 50%),), despite the absence of sewer overflow devices within the Mercier catchment. The higher contributions at low flow suggest a continuous input of wastewater that may originate from the sewer system itself to the Mercier streamwater. Wastewater from domestic inputs or non-collective sanitation, not connected to the sewer system, could also contribute continuously to the Mercier streamwater. We estimated median volume contributions of wastewater close to 30 m^3/day at low flow and 800 m^3/day at high flow. As a comparison, Dubois et al. (2022) estimated the average daily wastewater flow from a French household around 0.311 m^3/day, and Aussel et al. (2004) the wastewater discharge per inhabitants in France around 0.2 m^3/day. Wastewater contribution to the Mercier stream therefore represents the equivalent of a contribution of 100 households or 150 inhabitants. (Dubois et al., 2022)(Aussel et al., 2004)Wastewater from domestic inputs or non-collective sanitation, not connected to the sewer system, could also contribute continuously to the Mercier streamwater.

Results for the Ratier catchment show a significant influence of the AQU source with a high seasonality. Contribution of AQU was predominant at low flow, up to 85% of total runoff (more than 500 m^3/day). At high flow, although the estimated daily volume for groundwater was higher than low flow (around 2 000 m^3/day), the relative contribution was lower (around 20%).; iIt was, from the colluvium aquifer was diluted by the other sources, such as and GRA, which showed a major relative contribution (between 30 and 50%). The relative contributions estimated for SEW were lower than for the Mercier station (below 10%), but the volume contribution remained stable (around 30 m^3/day at low flow and 1 000 m^3/day at high flow)., supporting the hypothesis of a constant wastewater transfer to streamwater, as seen for the Mercier catchment, which may be diluted in the Ratier stream by the larger water flow.

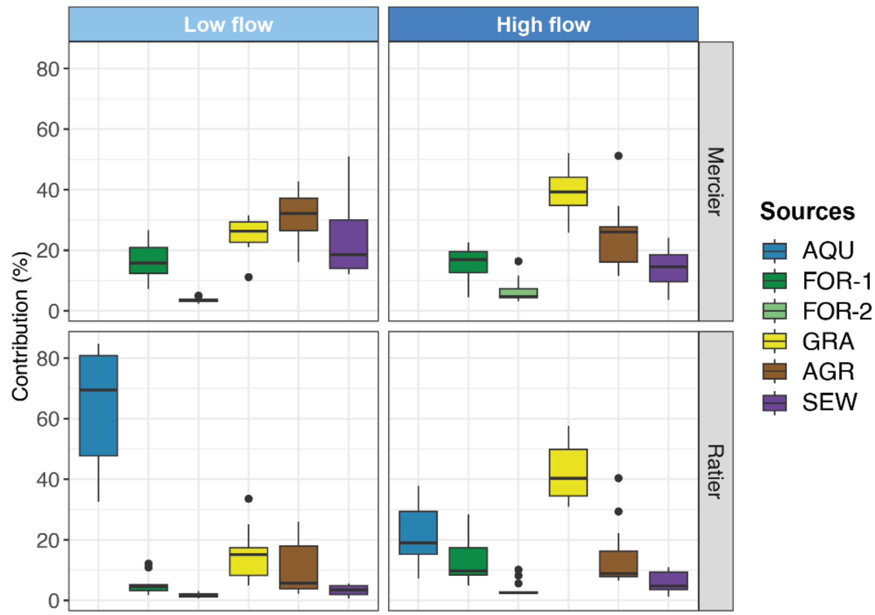


Figure 6 – Sources contribution to runoff estimated for dry weather samples by the application of a biogeochemical decomposition using a Bayesian mixing model ~~approach~~ for the Mercier and Ratier catchments. Boxplots represent the median contribution, interquartile range (1st and 3rd quartiles), minimum and maximum values. Low flow samples correspond to a mean daily discharge lower than 20 L/s and high flow samples to a mean daily discharge higher than 20 L/s.

3.3.2 Hydrological events: mean contributions

Figure 7~~Figure 7~~ shows the mean of the source contributions estimated for each sampled hydrological event. ~~These means were~~We calculated these means ~~calculated~~ from the individual results obtained by the application of the Bayesian mixing model ~~approach~~ on each streamwater sample (10 to 12 by event, see Section~~.~~ 2.2.2). Figure 7~~Figure 7~~ also illustrates the uncertainty obtained for each event, in the form of the mean of the standard deviations obtained by applying each Bayesian mixing model decomposition, calculated from the sum of the squares of each deviation. Further results ~~will be~~are ~~presented~~detailed below as the mean ~~together~~ with ~~their~~associated uncertainty (noted as *s.d.* for standard deviation). Figure A2 represents the contributions of each event in total volume, ~~which we~~ calculated based on the relative contributions for each source and the total flow in m^3.

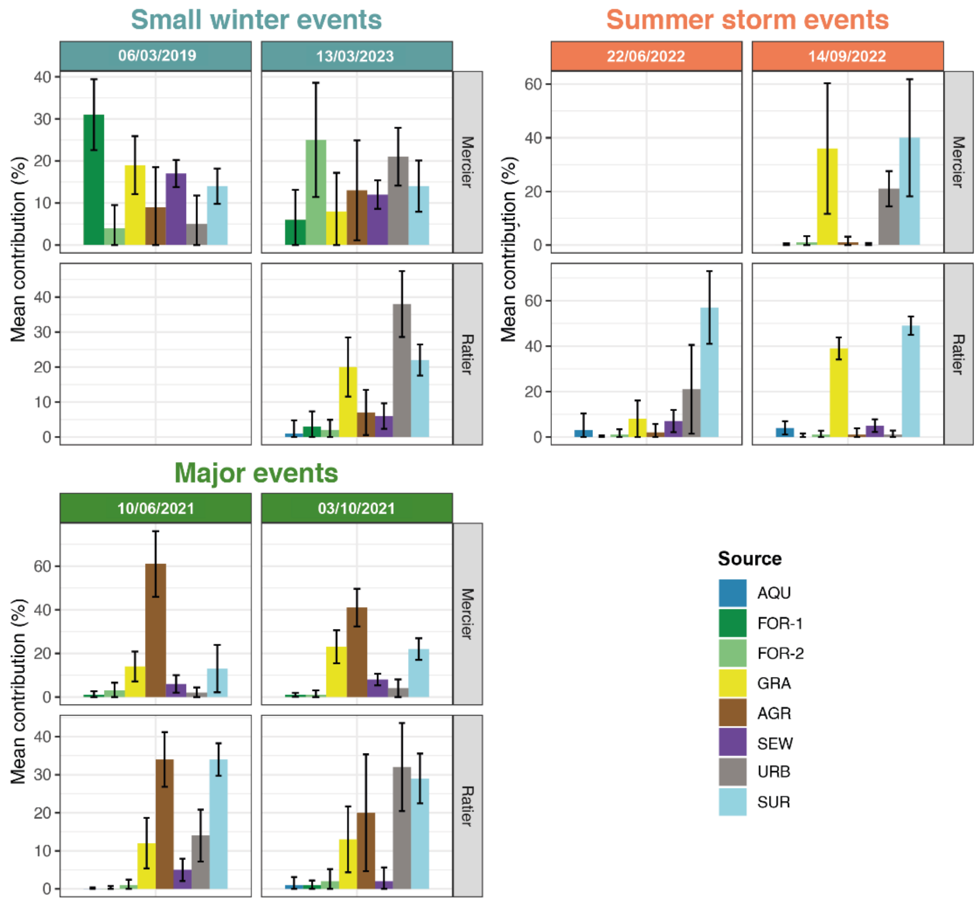


Figure 7 – Mean source contributions to the hydrological events sampled between March 2019 and March 2023 at the outlets of the Mercier and Ratier catchments. The contributions correspond to the mean of the results obtained for each sample~~s~~ decomposition by the Bayesian mixing model ~~approach~~. The error bars correspond to the mean of the standard deviation calculated from the sum of the squares of the deviation. The events of 6 March 2019 at the Ratier station and 22 June 2022 at the Mercier station were not collected.

Results for small winter events show contrasted contributions. At the Mercier station, the major contribution was FOR-1 in March 2019 (31%, *s.d.* 8%). ~~We calculated t~~The ~~and~~ FOR-2 source was the major contribution in March 2023 (25%) but with relatively high uncertainty (*s.d.* 14%). ~~In comparison~~These contributions remained higher than those~~, the contributions~~ estimated at the Ratier station ~~were much lower~~ for both forest sources (5% in total~~, ;~~ ~~X~~3 and ~~Y~~2 %, *s.d.* 4 and 3%, respectively), which is consistent with the results obtained ~~in~~ for dry weather. The c~~C~~ontributions of URB were significantly higher for the March 2023 event than for the March 2019 one, with 21% (*s.d.* 7%) at the Mercier station and 38% (*s.d.* 9%) at the Ratier station. This contrast can be explained by three times more rain in March 2023 (18 mm) than in March 2019 (7 mm). The source SEW showed~~ed~~ high contributions at the Mercier station, similar to those estimated for~~in~~ dry weather (17 and 12% respectively for March 2023 and March 2019~~;)~~ ~~and~~with ~~calculated with~~ low uncertainty, ~~(~~*s.d.* 3% for both events).

Results for the summer storm events showedd predominant contributions of GRA, URB and SUR (>40%), but with relatively higher uncertainties for the September 2022 event at the Mercier station (*s.d.* 24%, 7% and 22%, respectively) compared to the Ratier station (*s.d.* 5%, 2% and 4%, respectively). The URB contribution for the September 2022 event was lower at the Ratier (1%, *s.d.* 1%) than at the Mercier station (21%, *s.d.* 7%), despite a higher urban spatial extent at the Mercier catchment. which can be explained by the greater presence stormwater management structures for the Ratier than for the Mercier catchment. However, the contributionWe calculated high contribution of URB was high for the June 2022 event at the Ratier station (21%), which we but associated withto high uncertainty (*s.d.*, 20%). . This result can be explained by the contribution from SEW (7%), 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.

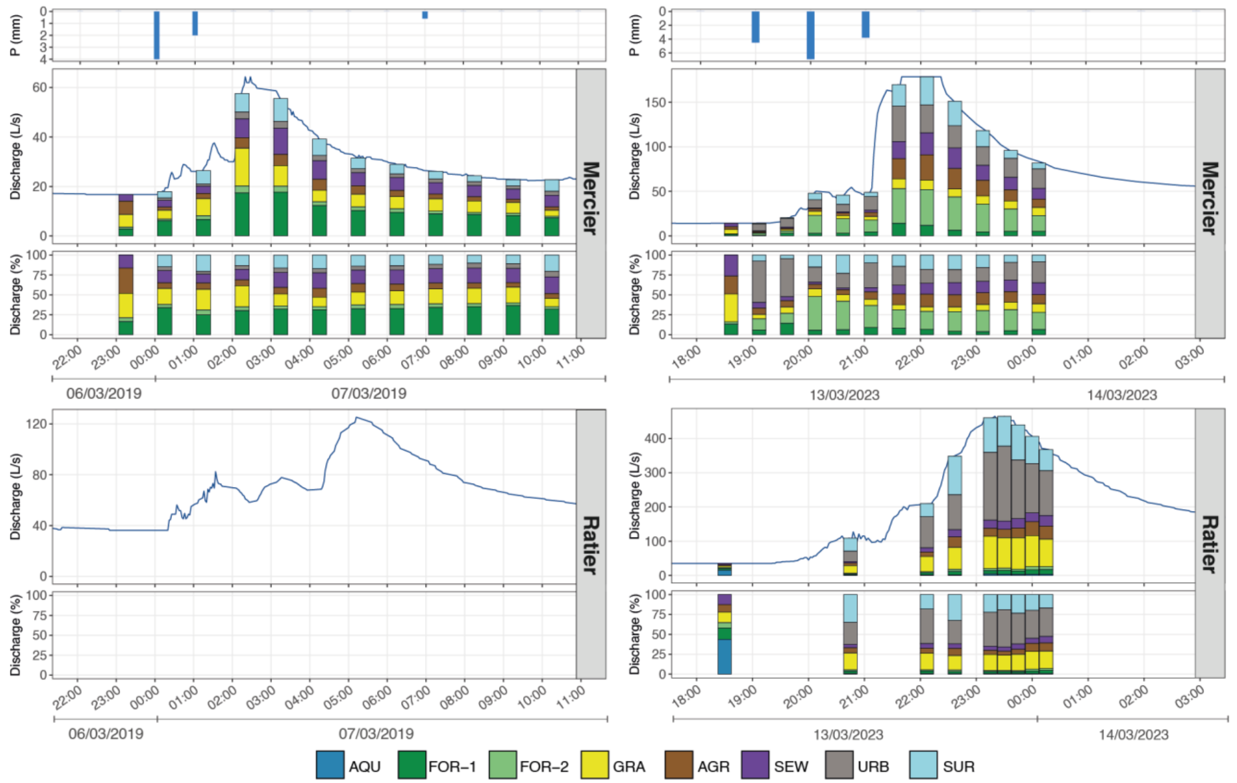
Results for both major events showed predominant contributions for AGR: 61% (*s.d.* 15%) and 41% (*s.d.* 9%) at the Mercier station, 34% (*s.d.* 7%) and 20% (*s.d.* 15%) -at the Ratier station. Uncertainty of the results were relatively low -(<10%), with the exception of the October 2021 event at the Ratier station- (up to 20%). TheWe calculated significant SUR and URB contributions were significant at the Ratier station station, but with higher uncertainties for the urban source: (14% (*s.d.* 7%)3 and 322% (*s.d.* 12%) for URB, 34% (*s.d.* 4%) -and 29% *s.d.* 7%) for SUR.R). Those estimatedThe SUR and URB contributions estimated at the Mercier station were lower (<4% for URB and <22% for SUR), despite the high rainfall recorded for these events (92 and 89 mm). High SUR and URB contributions at the Ratier station can once again be explained by the sewer system overflows, spilling wastewater, rainwater and urban and road runoff water, which are less important in the Mercier catchment due to the absence of sewer overflow devices. The relative contributions estimated for SEW are were low, but showeded high wastewater volumes when related to the total flow volume observed for each event. By applying relative contributions to the observed discharge, wWe estimated SEW contributions in terms of volumevolume flows aroundt 900 and 2 000 m^3 at the Mercier and Ratier stations, respectively, during for the May 2021 event, and around -960 and 1 000 m^3 for both stations during the October 2021 event (Figure A2). Such volumes of wastewater transferred to the stream are equivalent to the mean daily wastewater discharge for 3 000 to 6 500 French households, or for 5 000 to 10 000 inhabitants (Aussel et al., 2004; Dubois et al., 2022).

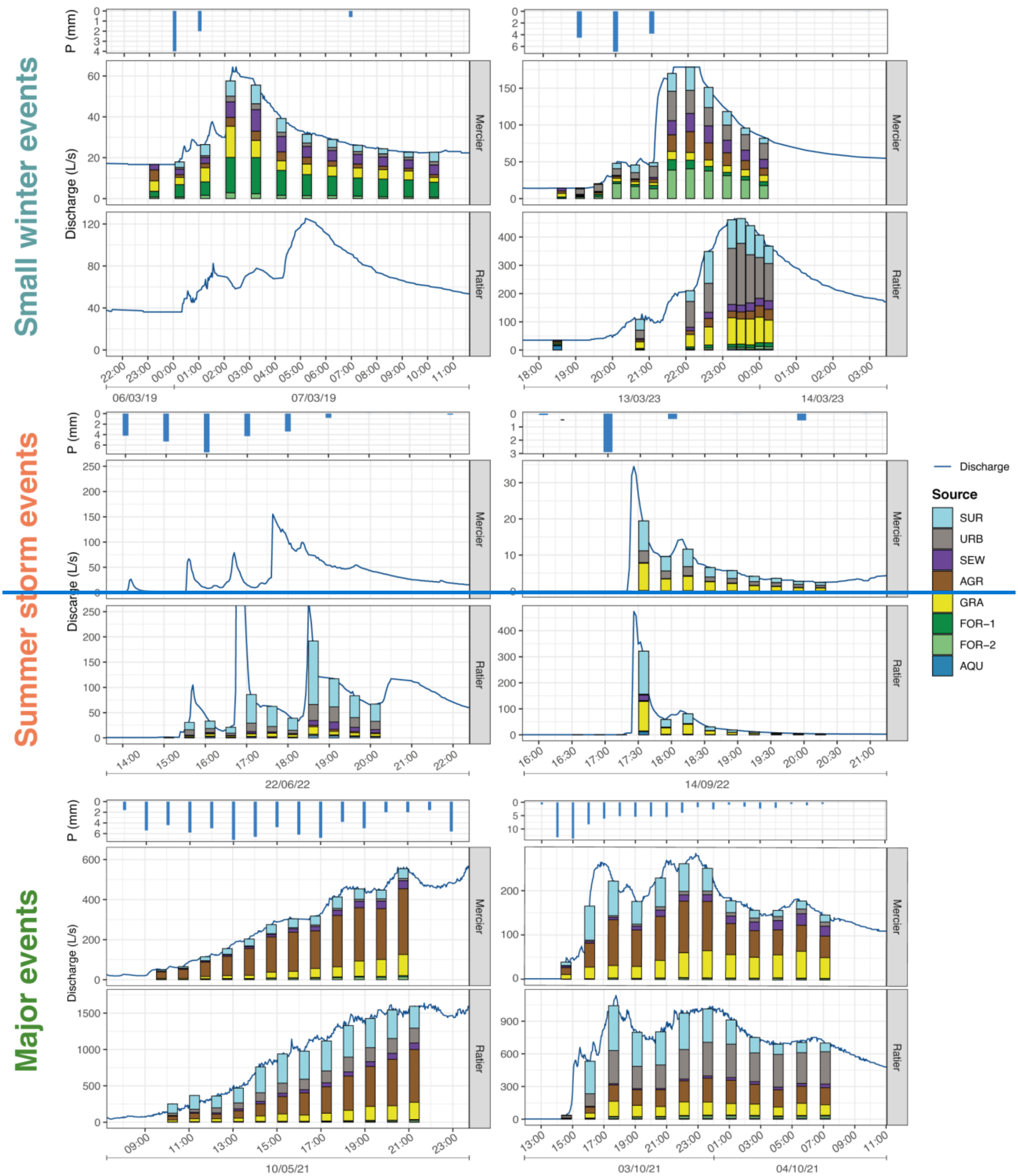
The hydro-meteorological conditions of the events appear to have a strong influence on the activated sources and their contributions. For the two small winter events, the contributions from grassland, agricultural areas, the sewer network and surface runoff are broadly consistent. However, there are significant differences in the contributions from urban and road runoff, which was higher in March 2023, and for those of the two forests between the March 2019 (FOR-1 as the main contribution) and the March 2023 events (FOR-2 as the main contribution). For summer storm events, the mean contributions estimated for both events are very consistent, with the exception of grassland and urban and road runoff. The major events showed the best consistency between the results for the Mercier and Ratier stations, despite some differences for sources linked to agriculture and urban road runoff. The spatial distribution of rainfall within the Ratier and Mercier catchments may also help explain the differences observed between the two stations. Local rainfall variability may have influenced the activation of specific sources, particularly those related to urban runoff and road surfaces.

The estimated results showed that similar sources have impacted the Mercier and Ratier catchments, with contributions showing similar trends. However, mean contributions showed significant differences, which will require a more precise study of the temporal variations over rain events.

3.3.3 Hydrological events: temporal variability of contributions

Figure 8Figure 8, Figure 9 and **Erreur ! Source du renvoi introuvable.** presents the results obtained by applying the biogeochemical mixing model to the Mercier and Ratier streamwater samplesdecomposition results for the small winter events, the summer storm events and the major events, respectively.; Theyand. It illustrates the temporal variability of the estimated contributions for each source. The results are presented in the form of the figures of bars whose sizes correspond to the instantaneous discharges associated to the decomposed samples;. detailed tThese results and the associated uncertainties are detailed for each sampling time in Table A7, Table A8 and Table A9.


P (mm)
Discharge (L/s)
Discharge (%)
Mercier
Ratier
06/03/2019
07/03/2019
13/03/2023
14/03/2023
AQU
FOR–1
FOR–2
GRA
AGR
SEW
URB
SUR



559

560 **Figure 8 – Precipitation and hydrograph separation results for the sampled events at the Mercier and Ratier stations** for the small
561 winter events of March 2021 and March 2023. The upper parts show bars whose sizes correspond to the instantaneous discharges
562 (in L/s) associated to the decomposed samples. The lower parts show stacked the relative contributions in a range from 0 to 100%.

~~**The results are shown according to the total outlet discharge(upper part) (below). The size of the bars corresponds to the instantaneous discharge associated to each sample.**~~

~~In the case of~~ For the two small winter events of March 2019 and March 2023 (Figure 8), the first sample was taken before the arrival of the rain. The contributions obtained for these samples prior to rainfall ~~are~~are consistent with the contributions estimated for samples collected under dry weather conditions: the contribution of FOR-1 was around 15%, that of GRA around 30%, and that of AQU around 44% (*s.d.* 11%). However, r~~R~~esults for FOR-1 and GRA are ~~, however,~~ associated with relatively high uncertainties (*s.d.* 10 to 11% for FOR-1 and 1 to 23% for GRA). As for dry weather results, the contribution of SEW was higher on the Mercier (up to 26%, *s.d.* 4 to 5%) than on the Ratier (13%, *s.d.* 7%). These results confirm the estimations obtained for dry weather. These contributions changed once the rain started, but remained stable until the end for each small winter event, despite the evolution of discharge. All these contributions estimated during rainfall ~~are~~were very close to the mean contributions shown in Figure 7~~Figure 7~~. The contribution of urban and road surface runoff in March 2023 for the Ratier was the largest, right from the start of rainfall (52%, *s.d.* 7%), which might suggest particularly localized rainfall in urban areas. The contribution of the sewer system remained stable over the March 2019 event for the Mercier, showing a rising input of wastewater into the stream proportional to the total discharge. For the March 2023 event, the contribution of the sewer system decreased during rainfall, suggesting a dilution of wastewater by rainwater in the sewer system.

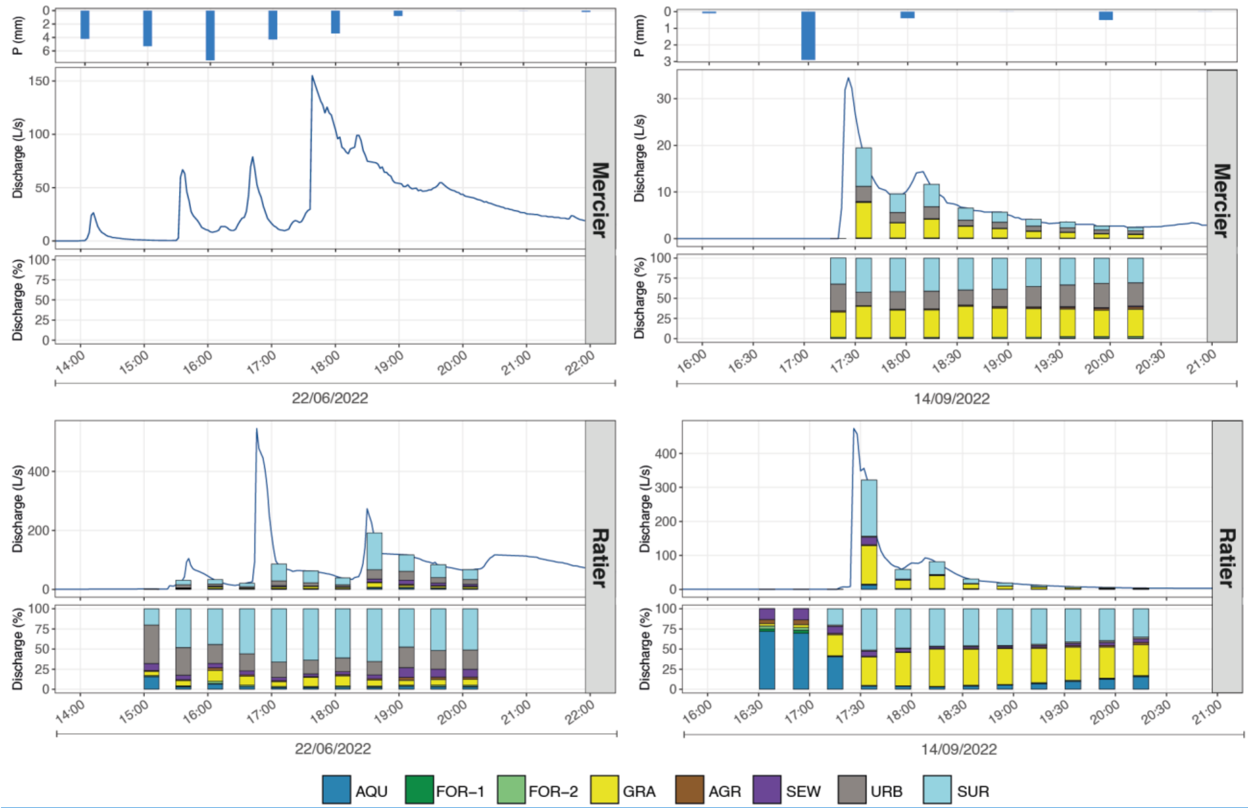


Figure 9 – Precipitation and hydrograph separation results for the sampled events at the Mercier and Ratier stations for the summer storm events of June 2022 and September 2022. The upper parts show bars whose sizes correspond to the instantaneous discharges (in L/s) associated to the decomposed samples. The lower parts show stacked the relative contributions in a range from 0 to 100%.

For the two summer storm events, most of the contributions remained relatively stable (Figure 9). The quick surface runoff (SUR) contributions remained the largest and the most variable ones. The estimated contributions for this source varied widely for the Ratier (from 20 to 65%), but were more stable for the Mercier (from 30 to 40%). However, uncertainties weare ~~relatively~~ lower for the Ratier (*s.d.* between 9 and 23%), than for the Mercier (*s.d.* between 17 and 28%). The largest contributions for the Ratier were estimated during peak flows with relatively low uncertainty (max 65% ~~for the Ratier~~ for the June 2022 event, *s.d.* 15%;~~,~~ and 50% for the September 2022 event, *s.d.* 4%). The estimated contributions from the sewer system (SEW) also varied along the events for the Ratier: from 3 to 12% (*s.d.* from 3 to 7%) in June 2022 and from 2 to 14% (*s.d.* from 1 to 6%) in September 2022. ~~As with quick surface runoff, the largest contribution of wastewater was estimated for the peak flow for the Ratier (7% of total discharge). Such high contribution might be linked to the overflow of the sewer system, via the sewer overflow device or any other points of the sewer system.~~

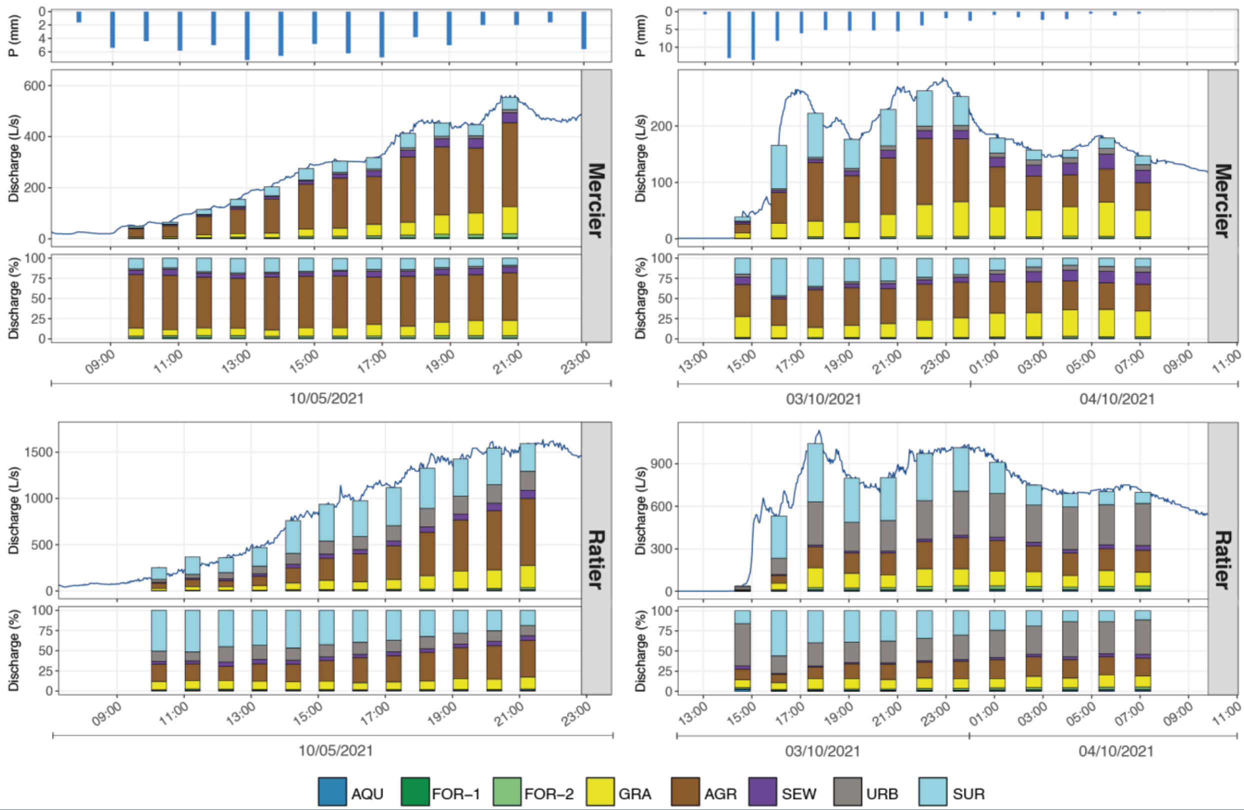


Figure 10 – Precipitation and hydrograph separation results for the sampled events at the Mercier and Ratier stations for the major events of May 2021 and October 2021. The upper parts show bars whose sizes correspond to the instantaneous discharges (in L/s) associated to the decomposed samples. The lower parts show stacked the relative contributions in a range from 0 to 100%.

Finally, the contributions estimated for the two major events also showed relatively low temporal variability (Figure 10). The predominant contribution was from agricultural areas (AGR), which varied from 33~~40~~ to ~~60~~66% for the Mercier (*s.d.* from 8 to 17%), and from ~~20~~10 to ~~30~~45% for the Ratier. The AGR contributions at the Ratier showed higher uncertainties for the October 2021 event (*s.d.* from 9 to 20%) than for May 2021 event (*s.d.* 4 to 11%). The contribution of quick surface runoff showed higher variability, particularly for the event of October 2021, with a predominant part during the peak flow (47~~5~~% for the Mercier, *s.d.* 6%, and 5~~5~~% for the Ratier, *s.d.* 6%). For the May 2021 event, the quick surface runoff contribution never represented the majority. ~~, which can be explained by a less intense rainfall, favouring infiltration into the soil and the progressive rise of discharge.~~ The contribution of wastewater was stable for the Ratier (around 5%, *s.d.* from 2 to 7%), but increased significantly for the Mercier (up to 15%, *s.d.* from 1 to 4%). ~~These proportions represented contributions in volume up to 90 L/s at the Ratier for the May 2021 event, compared with the total discharge up to 1 500 L/s. In the case of this event,~~

~~the cumulative contribution could therefore represent volumes of wastewater transferred to the stream between 1 000 and 2 000 m^3, equivalent to the mean daily wastewater discharge of 4 000 inhabitants (Aussel et al., 2004).~~

4 Discussion

4.1 Questioning the representativeness and nature of the sources

The application of a mixing model for decomposition of streamflow implies that the sources are well represented by their biogeochemical signatures. In ~~our~~the present study, ~~T~~these signatures ~~seem to have been~~were particularly well defined for forests and grasslands. The signature of the colluvium aquifer (AQU) was more variable, but remained significantly marked by high concentrations of Li, Ba and SiO_2 in all the samples. However, t~~T~~he concentrations of human-specific faecal markers measured in several AQU samples confirm ~~however,~~ a contamination of the colluvium groundwater by wastewater. ~~. However, t~~The signatures for other sources showed much more variability (Figure 5~~Figure 5~~). Our ~~The~~ results question the representativeness of these signatures and the initial assumptions on which the identification and sampling of these sources were based.

Defining the biogeochemical signatures of agricultural sources based on a single sub-catchment turned out to be challenging and highlighted three main difficulties. First, the catchment's characteristics made it difficult to delineate homogeneous sub-catchments associated with specific agricultural activities (e.g. crop culture, bovine breeding). Second, observing even a small flow at the outlets of agricultural sub-catchments was challenging due to the small size of these catchments and the predominance of crops and grasslands, which are linked with lower field capacity. As a result, only one agricultural sub-catchment could be identified and sampled. Third, 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 the biogeochemical signatures. An example is the absence of ruminant-specific bacterial faecal marker (*rum-2-bac*) 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). The use of more specific and persistent tracers, such as organic micropollutants, could improve the identification and characterization of agricultural sources, in a more precise manner than the general tracers used in this study, which were selected for their simplicity (Grandjouan et al., 2023). Previous studies have explored alternative approaches.~~:~~ El Azzi et al. (2016) compared commonly used pesticides concentrations with results from a chemical mixing model in an agricultural catchment. In doing so, they established a link between specific pesticides and vertical contributions (surface runoff, subsurface runoff and groundwater). Banned p~~P~~esticides that have not been used for several years could also be used, as long-term storage often occurs in agricultural soils (Sandin et al., 2018). Our study could benefit from th~~ese~~is approach, specifying the contribution from the agricultural areas while taking into account and evaluating the vertical contributions estimated by ~~(~~Grandjouan et al.~~, (~~(2023) (i.e., saprolite flow, fractured gneiss flow and colluvium groundwater;~~,~~ see Section 4.3). ~~(Sandin et al., 2018)~~

We chose to sample water from the sewer system during rainfall events, in order to characterize the biogeochemical signature of the water transferred to streamwater during overflows. However, our results show that the heterogeneous nature of these ~~water~~samples, being a mixture of wastewater and urban and road surface runoff, has a strong influence on the contributions estimated for the SEW and URB sources. The mixing model faces a first limitation as it is unable to distinguish wastewater alone from urban and road surface runoff. Indeed, the SEW signature may have been diluted and influenced by the URB signature, which already showed a variable biogeochemical composition. As a consequence, we may have overestimated the SEW contributions during the events. Moreover, ~~while Tran et al. (2019) investigated the presence of emerging contaminants, including veterinary products, to characterise different sources such as agricultural stormwater runoff, but also encountered high variability in concentrations.~~

~~For wastewater, our objective was to characterise the biogeochemical signature of the water discharged from the sewer system by overflow. To achieve this, we sampled water from the sewer system during rainfall events. Given that the water sampled is a mixture of wastewater and urban and road surface runoff, the obtained signature allowed us to estimate the contribution from the sewer system during these events. However,~~ the results for dry weather conditions ~~may be~~are less reliable, as only wastewater is released through leaks ~~in~~ from the sewer system to the stream. ~~-~~Ideally, we should have built the wastewater signature ~~should have been built~~ using samples collected from the sewer system under ~~both~~ dry weather ~~and rainfall~~ conditions, ~~.~~to better distinguish the URB contributions from wastewater. ~~The mixing model therefore faces a first limitation as it is unable to distinguish wastewater alone from urban and road surface runoff.~~

~~Kuhlemann et al. (2021) estimated the contribution of wastewater in the Erpe peri-urban catchment (Germany) using an end member mixing analysis, but also faced high uncertainties due to the similarities in concentrations between the composition of wastewater and other runoff sources. The use of isotopic tracers (e.g. δ²H, δ¹⁸O) appears as a better way to estimate the contribution of wastewater in a Bayesian mixing model (Marx et al., 2021).~~

In the case of urban and road runoff (URB), the first flush effect, implying the leaching of urban soils which favours high concentrations of contaminants (e.g. Cu, Pb, Zn) after longer dry periods (Deletic & Orr, 2005), makes it difficult to characterise a proper and unique signature. Indeed, ~~(~~Simpson et al.~~, (~~(2023) characterised the runoff water quality from 13 urban watersheds using classical tracers (i.e. nutrients, total suspended solids and ~~heavy~~ metals), but showed that the pollutant concentration depend~~s~~ed on the rainfall intensity, and that a first flush effect ~~is~~was not systematically observed. Innovative tracers could help characterising this source, as ~~for~~showed by Lin et al. (2024) who used ~~characteristics of DOM~~DOM characteristics (with a fluorescence excitation-emission matrices spectroscopy technique) to estimate the contribution of road runoff in an urban catchment. They found that the water generated by road runoff exhibited high aromaticity of DOM. In ~~our~~the present study, ~~T~~the values of the DOM parameter S2, which is negatively correlated with aromaticity, were indeed lower for the URB signature than for the other sources. Hence, we~~Our results~~ ~~thus encourage~~confirmed the usefulness of using such DOM characteristics as tracers in a mixing model. ~~In their study, Fröhlich et al. (2008) deduced the urban surface runoff~~

composition from the composition of streamwater during a peak flow, and from a Principal Component Analysis (PCA) as described in Christophersen & Hooper (1992). They used a PCA prior to the application of a mixing model, which allowed to confirm the correct number of sources and their biogeochemical composition.

Finally, as the quick surface runoff (SUR) composition was inferred from rainwater composition, it may be more or less distant from reality. The hypothesis of a quick surface runoff keeping the biogeochemical signature of rainwater is questionable as these waters can quickly accumulate elements (Langlois & Mehuys, 2003). Proper sampling of quick surface runoff should be done in order to better estimate their contributions to streamwater, although such sampling can be difficult. Yet, Fröhlich et al. (2008) conducted a similar study in the Dill Catchment (Germany), aimed at identifying runoff sources, including wastewater, groundwater and stormwater flow, in which they regrouped surface and subsurface runoff. To do this, they sampled streamwater from the outputs of sub-catchments characterized by specific geological formations, during baseflow and hydrological events. They thus showed that the geochemical composition of stormflow was similar to the composition of precipitation, showed in their study that the composition of stormflow headwaters was similar to precipitation, and 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 s-ampling of quick surface runoff in order to better estimate their contributions to streamwater. Several studies analysed direct surface runoff water collected on soil surface during hydrological events. (Le et al. , (2022) and Omogbehin & Oluwatimilehin (2022) both showed high concentrations of DOC transferred from soils to the stream by overland flow. (Omogbehin & Oluwatimilehin, (2022) also showed low-mineralised composition of the direct surface runoff water sampled. However, these two studies were conducted in a tropical area, where direct surface runoff often occurs outside of urban areas. Such sampling appears to be difficult in temperate areas, with less intensive rainfalls.(Omogbehin & Oluwatimilehin, 2022)

Another method to characterise sources is the use of stable isotopes (Le et al., 2022)(Wan et al., 2023)(Omogbehin & Oluwatimilehin, 2022)(e.g. δ^2H, $\delta^{18}O$). While many studies have used isotopic tracers in mixing models to estimate the contributions from different runoff-generating sources, few of them were applied to peri-urban catchments with complex land use distributions. Kuhlemann et al. (2021) estimated the contribution of wastewater in the Erpe peri-urban catchment (Germany) using isotopic tracers together with physico-chemical parameters of water (i.e. conductivity and temperature of water), in an Bayesian mixing model (using MixSIAR). However, they also faced high uncertainties due to the similarities in concentrations between the composition of wastewater and other runoff sources. They concluded by recommending the use of both isotopic and geochemical tracers to overcome these limitations.

4.2 Evaluating the estimated source contributions

The estimated contributions clearly invalidate the null hypothesis that source contributions are proportional to their spatial extent (see Section 2.4). Spatial extent alone cannot explain the observed variability, and several additional factors appear to influence source activation and the hydrological response of the catchments.

Contributions of the colluvium aquifer was constant, regardless of the hydro-meteorological conditions, as already shown by Grandjouan et al. (2023).

The major contribution of forests to the Mercier stream during small winter events, and the fact that we sampled the two forest sources at every campaign, independently from the hydro-meteorological conditions could be explained by the geological characteristics of the upper part of the catchment. The saprolite horizon being thin in this area, it ~~is unable~~cannot ~~to~~ store a large volume of water. Alternatively, t~~T~~he constant flow generated by these springs may ~~thus~~ originate from the fractured gneiss, fed by infiltrating rainwater. Recharge water can have a piston effect, pushing the groundwater retained within the fractures towards the stream. Lachassagne et al. (2021) described a similar behaviour on another catchment characterised by fractured crystalline formations and thin saprolite layer with (1) a vertical piston effect in the saprolite layer and (2) a preferential deep horizontal flow in the fractures of the basement. During summer period, the minor forest's contribution can be linked to the favoured retention of rainwater by the vegetation over runoff (Bruijnzeel, 2004).

The variable contributions from grasslands and agricultural areas can be explained by the highly variable thickness of the saprolite horizon downwards from forest - 1 to 20 m according to Goutaland (2009). The absence of runoff for the GRA and AGR sources under low flow conditions in dry weather suggests the existence of throughs at the saprolite-gneiss interface in which water can be stored and released discontinuously. This process was described as "fill-and-spill" by McDonnell et al. (2021), and observed in the Panola catchment by Tromp-van Meerveld & McDonnell (2006), and in the Pocket lake catchment by Spence & Woo (2003), both being characterised by a similar crystalline bedrock. They showed that the generation of subsurface and surface flow in this context can be delayed, as it requires to meet sufficient rainfall amount to increase water storage at the soil-bedrock boundary. When these conditions were not observed, Spence & Woo (2003) and Tromp-van Meerveld & McDonnell (2006) noticed intermittent flow, which is similar to what we observed at the Mercier and Ratier catchments. Indeed, contribution from agricultural lands are low or absent during summer storm events, and major during major events, when rainfall amounts are sufficient. However, grasslands showed quicker and more frequent responses under storm conditions. This difference may be linked to lower interception by vegetation, shallower root systems, and reduced water demand in grasslands compared to forests or crops (Madani et al., 2017; Robinson & Dupeyrat, 2005).

Our results also show that summer storm events are often associated with generation of quick surface runoff. Indeed, ~~(~~Shi et al., (2021) showed ~~indeed~~ that low antecedent soil moisture during summer periods can enhance the generation of quick surface runoff. The lower general water demand from grassland may also favour the quick surface runoff for this particular land use. As seen in Section 4.1, DOC can easily be transferred from soils to runoff water. As a consequence, the quick surface runoff contribution generated on the surface of grasslands could have been considered as grassland contribution by the mixing model.

These results suggest that both vegetation type and antecedent soil moisture jointly influence the likelihood of quick surface runoff generation.

(Grandjouan et al., 2023)(Grandjouan et al., 2023)(Grandjouan et al., 2023)The high contributions of SEW to the Mercier streamwater suggest continuous wastewater inputs, either from sewer leakage or from non-collective sanitation. At the Ratier, similar wastewater volumes awere observed but diluted by larger baseflow. Grandjouan et al. (2023) already showed that the sewer system has a strong influence on streamwater at dry weather, as they measured high concentrations for the *HF183* human-specific faecal markers in both Mercier and Ratier streams (mean values of 2.4 and 2.5 $\log_{10}$ copy nb/100mL, respectively). Tran et al. (2019) observed a similar trend in agricultural areas with low residential and urban extent, with runoff water composition similar to the composition of raw wastewater. They also suggest that these contributions come from leaks from the sewer system. In ourthe present study, during hydrological events, the increase in wastewater contributions can be explained by sewer overflows, occurring both at the combined sewer overflow device and at other points of the network. According to local sewer network managers, such overflows are frequent even during small winter events (<10 mm), due to underside sewer infrastructure. Such wastewater transfer remains difficult to characterise in terms of both dynamics and volume. Numerical modelling of the sewer leakage and overflow appears to be a promising way of quantifying these impacts on groundwater (Nguyen et al., 2021).

Estimated contributions for urban and road runoff carry high uncertainty, partly because of the difficulty for the mixing model dto distinguish wastewater from urban runoff (see Section 4.1), which may have influenced our calculations. Another factor that could have influenced the URB contributions is the spatial rainfall variability, for example for the September 2022 event where the Mercier showed higher URB contribution compared to the Ratier, despite being less urbanised. This phenomena is particularly relevant during convective 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).

(Grandjouan et al., 2023)Overall, these findings emphasize the role of the sewer system, rainfall spatial variability, water pathways and transfer time in influencing source contributions, in addition to land use diversity.

4.3 Improvement of the hydrological perceptual model of the Ratier and Mercier catchments

(Grandjouan et al., (2023) built aAn initial perceptual hydrological model of the Ratier catchment, describingt was built by Grandjouan et al. (2023). This model describes the general hydrological behaviour of the catchment and the main contributions to streamflow. That model was based primarily on dry-weather observations; it allowed to and identifyied three main sources including The represented hydrological processes were deduced from catchment characteristics, field observations and a mixing model applied on the basis of the biogeochemical quality of streamwater at the Mercier and Ratier outlets at dry weather

~~only.~~ colluvium groundwater, fractured gneiss groundwater and the saprolite layer. The authors~~y~~ reported positive correlations between discharge and saprolite contribution, and negative correlations between discharge and gneiss groundwater contribution. However, they also showed unclear boundaries between both contributions, and suggested land use could play a stronger role than geology in runoff generation. The extensive dataset obtained in the present study, ~~including samples of runoff generating sources, and the contributions estimated in our study,~~ ~~and~~together with the insights gained from results presented in Sections 4.1 and 4.2, allow~~s~~ us to ~~for the improvement of~~ improve the~~is~~ initial representation of the catchment hydrological behaviour by ~~(~~Grandjouan et al.~~,~~ (2023) ~~model, particularly in terms of hydrological behaviour at the hillslope scale~~. ~~(Grandjouan et al., 2023)~~

Figure 11~~Figure 9~~ illustrates the new hydrological perceptual model proposed for the Ratier and Mercier catchments. It represents the hydrological dynamics of each identified source ~~inferred from the contributions estimated during dry weather and for different types of hydrological events~~that we~~a~~re consistently supported both by the results of the present study and literature. ~~. We considered small winter events to occur at high flow, summer storm event at low flow, and major events either at low or high flow.~~

In order to simplify the model, we chose to merge the two forest sources FOR-1 and FOR-2 as they represent similar areas of the catchment. These sources are characterised by a shallow or absent saprolite depth, with the fractured gneiss formation sometimes outcropping. The dominant process is groundwater contribution from fractured gneiss, recharged by rainfall and mobilised through a piston effect. Contributions of forest is therefore considered stable in baseflow conditions, and higher during small winter events. During summer storms, forest contributions remain minor due to strong canopy interception and high evapotranspiration. For grasslands, generation of runoff is generally driven by a fill-and-spill mechanism within the saprolite layer, producing intermittent sub-surface contributions. Hence, t~~T~~he contribution from grasslands ~~therefore~~ strongly depends on the topography of the saprolite-gneiss boundary. Under storm conditions, grasslands also generate rapid surface runoff due to low canopy interception and lower water demand. For agricultural lands, the same geological context suggests fill-and-spill dynamics, but contributions diverge from grasslands because of higher crop water demand. Their role appears minor in summer storms but can increase during major events. The sewer system contributes wastewater continuously through leakage and sanitation losses. These contributions are especially marked in the Mercier catchment. Episodically during hydrological events, ~~it transfers~~ a mixture of wastewater, urban and road surface runoff and rainwater is transferred to the stream~~,~~ through sewer overflows. ~~-~~The urban and road surface runoff contributions vary considerably as ~~it~~they strongly depend~~s~~ on the urban area extent, on the presence of urban infrastructures that collect~~s~~ runoff water, and mostly on rainfall spatial variability. Finally, the colluvium aquifer provides a nearly constant contribution regardless of hydrological conditions. Evidence of wastewater contamination indicates that this source is characterised by both natural groundwater and anthropogenic inputs.

This revised perceptual model show that runoff-generating sources are driven by both natural controls (geology, subsurface storage, vegetation) and anthropogenic drivers (sewer leakage, urban runoff). The model confirms that land use and urban elements (sewage system, impervious areas) exert a first-order control on hydrological responses. This new representation provides a robust perceptual basis for future modelling and management of peri-urban catchments.

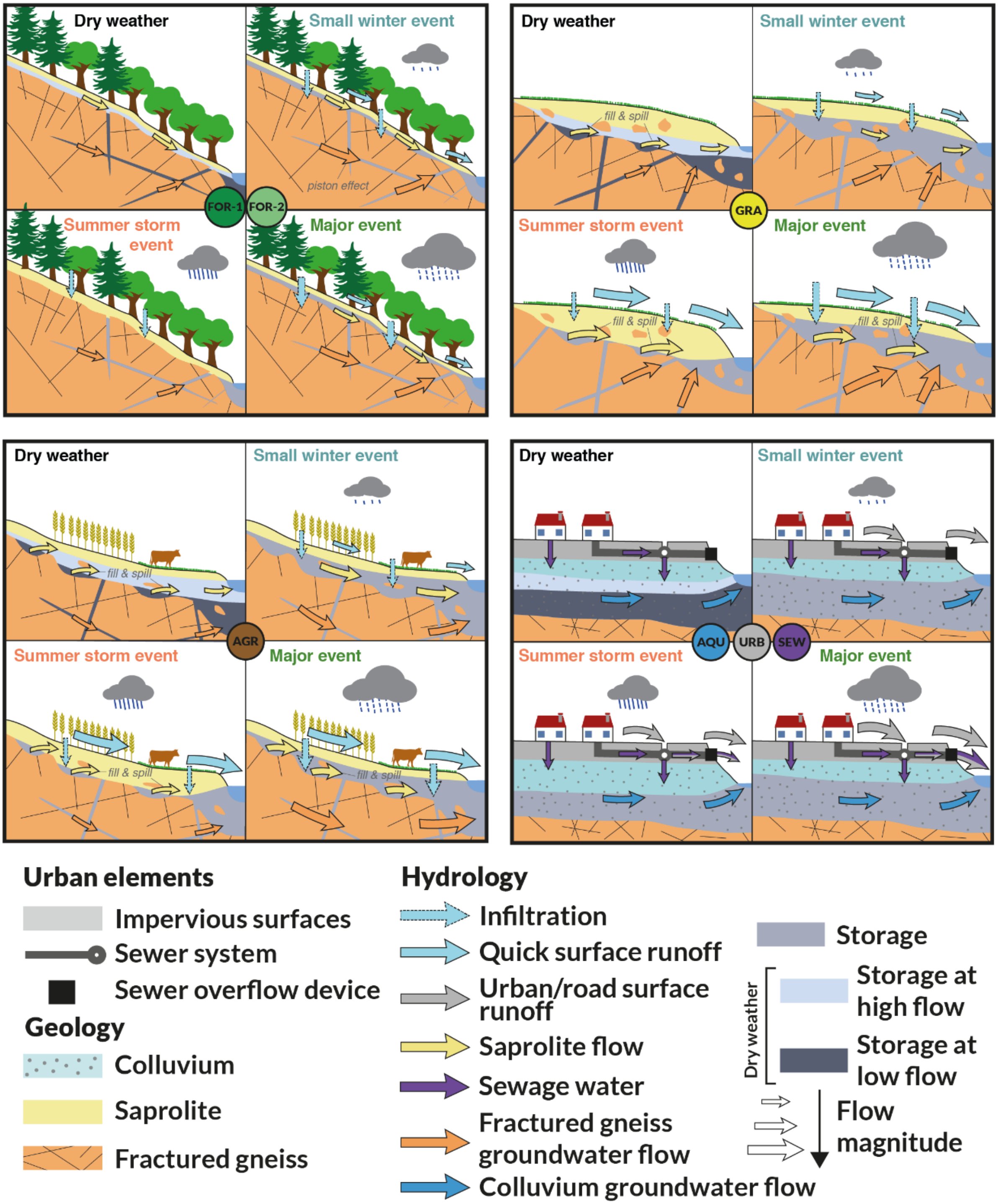


Figure 119 – Improved perceptual model of the Ratier catchment, initially build by Grandjouan et al. (2023). Main contributions, estimated by the mixing model, are illustrated according to the nature of the sources and the four hydro-meteorological conditions studied, including dry weather, small winter event, summer storm event, major event. FOR-: forest; GRA-: grassland; AGR-: agricultural; AQU-: aquifer; URB-: urban and road surface runoff; SEW-: wastewater.

The two forest sources FOR-1 and FOR-2 were merged as they represent similar areas of the catchment. As their estimated contributions were close, we assumed they have a similar hydrological behaviour. These sources are characterised by a shallow or absent saprolite depth, with the fractured gneiss formation sometimes outcropping. The two forest sources were sampled for every campaign, independently from the hydro-meteorological conditions. As the saprolite horizon below the forest is unable to store a large volume of water, the constant flow generated by these springs is expected to originate mainly from fractures in the gneiss. These fractures are fed by infiltrating rainwater. Recharge water can have a piston effect, pushing the groundwater retained within the fractures towards the stream. Lachassagne et al. (2021) described a similar behaviour on another catchment characterised by fractured crystalline formations and thin saprolite layer (e.g. Alazard et al., 2016) with (1) a vertical piston effect in the saprolite layer and (2) a preferential deep horizontal flow in the fractures of the basement. This phenomenon could explain the major contribution of forests to the Mercier stream during small winter events. For summer storm event, the forest's contribution is minor, as the retention of rainwater by the vegetation is favoured over runoff (Bruijnzeel, 2004).

The runoff generated by grasslands could not be sampled under low flow conditions in dry weather. The highly variable thickness of the saprolite horizon in this part of the catchment – 1 to 20 m according to Goutaland (2009) – suggests the existence of throughs at the saprolite-gneiss interface in which water can be stored and released discontinuously. This process was described as "fill-and-spill" by(McDonnell et al., 2021) Tromp-van Meerveld & McDonnell (2006), (Spence & Woo, 2003)for the Panola catchment, characterised by a similar crystalline geological formation. (Spence & Woo, 2003)(Tromp-van Meerveld & McDonnell, 2006)During summer storm events, the quick surface runoff is favoured in grasslands(Madani et al., 2017; Robinson & Dupeyrat, 2005). The water demand is lower than in forested or cultivated areas (Madani et al., 2017). Shi et al. (2021) showed that quick surface runoff is favoured with dry soils during summer periods.

Agricultural lands in the Ratier catchment are characterised by the same geological features as for grassland, and thus share similar hydrological behaviour. The main difference was observed for the summer storm event, where the contributions of agricultural lands were low compared to grasslands, which can be explained by the water demand of the crops culture. The high contributions during major events are difficult to interpret, and could be due to local discontinuities, or the leaching of agricultural soils containing agricultural-specific tracers. But it is difficult to assess on the genericity of the results for agricultural lands on the basis of a single sub-catchment.

The contribution of the urban impacted colluvium aquifer was constant, regardless of the hydro-meteorological conditions, as already shown by Grandjouan et al. (2023). The concentrations of human-specific fecal markers measured in several AQU samples suggest a contamination of the colluvium groundwater by wastewater. Grandjouan et al. (2023) showed the significant and constant input of wastewater into the soil and groundwater, through leaks in the sewer system or the use of septic tanks in residential areas disconnected from the public network. This input is particularly significant in the Mercier catchment, where wastewater represents a higher relative contribution than in the Ratier catchment when associated with their respective total flow. (Tran et al., 2019)This wastewater contamination remains difficult to characterise in terms of both dynamics and volume.

~~Numerical modelling of the sewer leakage appears to be a promising way of quantifying these impacts on groundwater (Nguyen et al., 2021).~~

~~(Kermadi et al., 2012)(Cristiano et al., 2017)(Emmanuel et al., 2012)~~

5 Conclusions

The objective of this study was to identify runoff-generating sources in a small peri-urban catchment, and estimate their contributions to streamwater with a mixing model based on a biogeochemical dataset comprised of classical and original tracers. ~~This approach highlighted eight main sources linked to the spatial characteristics of the catchment: two types of forest (FOR-1 and FOR-2), grassland (two sampled and merged as GRA), agricultural lands (AGR), a colluvium aquifer (AQU), wastewater from the sewer system (SEW), urban and road surface runoff (URB) and quick surface runoff (SUR). A comprehensive biogeochemical dataset was built to determine the signatures of these sources using a reductionist tracer selection approach. Each signature included 15 tracers: seven major parameters (Cl^-, SO_4^{2-}, Ca^{2+}, Na^{2+}, K^+, Mg^{2+}), six dissolved metals (As, Ba, Cr, Li, Rb, Sr) and two characteristics of DOM (DOC, spectral slope S2). Results showed that the use of indicators that are simple and cheap to analyse was sufficient to differentiate each source according to geological, pedological and land-use characteristics, or according to anthropogenic inputs.~~

~~The estimated source contributions were particularly stable in dry conditions, and significantly influenced by wastewater at the Mercier catchment, and by the colluvium groundwater at the Ratier catchment. At the hydrological event scale, the source contributions followed trends according to the hydro-meteorological state of the catchment: major contributions for forest, grassland and agricultural sources during small winter events, predominant quick surface runoff contributions for summer storm events, and major grassland and agricultural contributions for major events.~~

This approach showed the potential of the use of biogeochemical tracers to perform a spatial decomposition of water, based on the physical characteristics of a catchment, in addition to a more traditional vertical decomposition. Results showed that the use of indicators that are simple and cheap to analyse (major parameters, metals) together with more original tracers (characteristics of DOM) was sufficient to differentiate each source according to geological, pedological and ~~land-use~~land use characteristics, or according to anthropogenic inputs. This study also showed the need for ~~precise~~ accurate methods to identify the runoff-generating sources and their biogeochemical signatures. An improvement of the approach would be a better characterisation of the most variable sources, such as agricultural lands, urban and road surface runoff and sewer system wastewater. Moreover, quick surface runoff needs to be collected and characterised to better estimate its contribution to streamwater. The initial campaign plan aimed to sample this runoff at various locations representing forest, grassland and agricultural areas. However, such sampling is challenging, as it requires being present at the right location and time due to the ephemeral nature of surface runoff. The deployment of automatic samplers could help overcome these limitations and improve data collection. Such sampling has already been implemented using a gutter-based collection system, as part of the ANR CHYPSTER project, in the Claduègne catchment (Ardèche, France).

This study demonstrated the effectiveness of the proposed method in estimating the water pathways and the main contributions within the studied catchments. The mixing model provided reliable estimates for several source contributions. Confidence in the results was reinforced by the use of additional tracers beyond those used in the mixing model, such as DOM characteristics, microbial parameters and other dissolved metals. The results obtained with the mixing model were consistent with the initial perceptual hydrological model built for the Ratier catchment, and allowed us to build an improved version at the hillslope scale. This new perceptual model provides a better understanding of the behaviour of these two nested catchments and their hydrological dynamics depending on each hydro-meteorological condition.

More broadly, the application of mixing models in relation to land use remains relatively unexplored in the literature. This study highlights the potential of such an approach when incorporating biogeochemical parameters and highlights the need for further research in this direction.

This work illustrates the broader potential of mixing models to identified the spatial origin of streamflow and improve our understanding of catchment hydrological behaviour. Such approaches could provide valuable insights for validating spatially distributed hydrological models, which often face difficulties in adequately representing source contributions. More generally, combining mixing models with land use and hydro-meteorological data may help to better anticipate the impacts of land management or climate change on runoff-generation processes. Future research should therefore focus on integrating tracer-based source characterisation with modelling frameworks, to improve both process representation and predictive capacity in peri-urban catchments.

Appendixces

Table A1 – Combinations obtained from the superimposition of factors describing sub-catchments (geology, field capacity, land use). The relative surface areas associated with each combination is provided for the Mercier and Ratier sub-catchments. Combinations with a relative area of less than 1% of the Ratier catchment are not detailed.

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

Table A2 – Limits of quantification (LQ) and uncertainties (expanded U, k=2) for chemical parameters; they were calculated according to standard method NF-T90-210 (AFNOR, 2018) and NF ISO 11352 (AFNOR, 2013), respectively. For dissolved organic carbon (DOC), total dissolved nitrogen (NTD) and major ions, uncertainties were derived from results of interlaboratory tests. For trace elements, uncertainties were derived from regular analyses of Certified Reference Material TM-27-4 (lake water, Environment and Climate Change Canada).

	Parameter	Unit	LQ	Uncertainty
Organic matter	DOC	mgC/L	0.2	20%
	NTD	mgN/L	0.2	20%
Major ions	Ca^{2+}	mg/L	4.0	10%
	K^{+}	mg/L	1.0	15%
	Mg^{2+}	mg/L	1.0	13%
	Na^{+}	mg/L	1.0	12%
	NH_4^{+}	mg/L	0.02	14%
	Cl^{-}	mg/L	1.0	7%
	NO_2^{-}	mg/L	0.05	14%
	NO_3^{-}	mg/L	1.0	13%
	PO_4^{3-}	mg/L	0.1	14%
	SO_4^{2-}	mg/L	1.00	9%
	SiO_2	mgSi/L	0.5	12%
Trace elements	Al	µg/L	2.0	20%
	As	µg/L	0.010	20%
	B	µg/L	2.00	25%
	Ba	µg/L	0.01	10%
	Cd	µg/L	0.005	15%
	Co	µg/L	0.005	15%
	Cr	µg/L	0.02	20%
	Cu	µg/L	0.05	15%
	Fe	µg/L	0.10	15%
	Li	µg/L	0.010	20%
	Mn	µg/L	0.05	15%
	Mo	µg/L	0.010	20%
	Ni	µg/L	0.02	20%
	Pb	µg/L	0.01	20%
	Rb	µg/L	0.010	15%*
	Sr	µg/L	0.05	10%
	Ti	µg/L	0.05	25%
	U	µg/L	0.005	20%
	V	µg/L	0.005	20%
	Zn	µg/L	0.50	25%

* uncertainty calculated using coefficient of variation of measured values only (no certified value for this element)

Table A3 – Summary of analytical results for major parameters in source samples. Values are concentrations in mg/L. All analytical results~~, quantification results~~ and quality controls are available at: https://entrepot.recherche.data.gouv.fr/dataverse/chypster/)

	BOU (n=5)		VRY (n=5)		VRN (n=5)		REV (n=4)		PNC (n=5)	
Parameter	**Median**	**Range**	**Median**	**Range**	**Median**	**Range**	**Median**	**Range**	**Median**	**Range**
Ca^{2+}	11.1	10.5 - 12.3	6.2	5.5 – 13.0	22.7	21.1 - 40.4	14.6	12.1 - 18.6	15.7	15.3 - 16.9
Cl^-	51.0	49.5 - 56.9	16.0	13.2 - 18.6	6.6~~3~~	5.8 - 26.7	9.7	7.0 - 16.7	38.0	30.7 - 44.8
K^+	1.0	1.0 – 1.0	1.0	1.0 – 1.0	1.6	1.5 - 2.6	1.0	1.0 – 1.0	2.7	2.2 - 8.3
Mg^{2+}	2.8	2.7 - 3.2	1.9	1.8 - 3.7	3.2	3.0 - 5.7	2.4	2.0 - 3.1	3.0	2.2 - 3.3
Na^+	26.8	25.7 - 34.2	11.3	10.2 - 15.3	8.6	8.1~~0~~ - 15.4	6.3	5.6 - 7.8	18.6	15.6 - 21.1
SiO_2	20.4	18.4 - 21.1	24.1	20.8 - 25.6	12.7	10.7 - 13.5	11.1	8.3 - 11.9	14.9	11.9 - 16.8
SO_4^{2-}	13.8	12.2 - 15.9	14.1	13.6 – 28.0	18.7	14.9 – 30.0	9.3	6.6 - 13.4	9.5	6.8 - 20.4

	COR (n=5)		PLR (n=4)		RES (n=5)	
Parameter	**Median**	**Range**	**Median**	**Range**	**Median**	**Range**
Ca^{2+}	55.8	25.3 - 64	45.4	28.6 - 96.3	72.8	52.9 - 76.2
Cl^-	29.9	4.6 - 45.7	43.4	25.9 - 74.4	80.8	61.9 - 87.4
K^+	2.9	0.9 - 3.8	3.5	1.9 - 5.2	18.3	12.5 - 21.5
Mg^{2+}	7.5	4.2 - 8.2	3.0	2.0 - 6.9	7.1	4.9 - 7.6
Na^+	26.5	2.3 – 37.0	30.3	17.0 - 44.7	63.2	46.4 - 73.6
SiO_2	32.0	15.5 - 34.8	11.1	6.8 – 12.0	13.3	5.5 - 14.8
SO_4^{2-}	43.7	11.4 - 62.2	41.6	21.1 - 93.2	50.8	33.8 - 58.3

Table A4 – Summary of analytical results for dissolved metals in source samples. Values are concentrations in µg/L. All analytical results~~, quantification results~~ and quality controls are available at: https://entrepot.recherche.data.gouv.fr/dataverse/chypster/)

	BOU (n=5)		VRY (n=5)		VRN (n=5)		REV (n=4)		PNC (n=5)	
Parameter	**Median**	**Range**	**Median**	**Range**	**Median**	**Range**	**Median**	**Range**	**Median**	**Range**
Al	126	82.8 - 142	62.5	45.3 - 105	43.2	8.40 - 70.5	75.1	24.3 - 102	29.2	18.9 - 55.9
As	0.49	0.25 - 0.52	0.73	0.58 - 1.11	0.63	0.43 - 0.68	0.53	0.45 - 0.66	4.25	0.93 - 5.28
B	3.00	2.80 - 4.70	3.90	3.70 - 5.00	11.4	8.30 - 18.6	2.80	2.20 - 4.20	2.60	0.20 - 7.30
Ba	20.0	17.9 - 24.4	10.4	9.70 - 18.4	15.4	13.3 - 25.4	13.4	10.4 - 18.7	11.2	9.73 - 20.5
Cd	0.073	0.064 - 0.096	0.023	0.010 - 0.030	0.008	0.005 - 0.021	0.020	0.012 - 0.027	0.009	0.005 - 0.024
Co	0.160	0.144 - 0.173	0.109	0.063 - 0.320	0.125	0.112 - 0.135	0.139	0.115 - 0.213	0.779	0.079 - 1.28
Cr	0.23	0.20 - 0.43	0.37	0.23 - 0.46	0.19	0.15 - 0.29	0.30	0.24 - 0.31	0.26	0.08 - 0.61
Cu	0.42	0.10 - 0.67	0.66	0.10 - 2.75	3.70	3.23 - 4.23	1.77	0.77 - 2.89	0.94	0.74 - 11.3
~~Fe~~	~~24.4~~	~~9.10 - 34.1~~	~~46.6~~	~~13.1 - 106~~	~~30.3~~	~~5.79 - 59.6~~	~~35.3~~	~~16.9 - 48.8~~	~~285~~	~~13.4 - 897~~
Li	1.84	1.75 - 2.27	1.42	0.29 - 2.15	0.692	0.622 - 0.753	0.756	0.391 - 1.08	0.759	0.483 - 1.23
~~Mn~~	~~11.7~~	~~9.15 - 12.2~~	~~12.6~~	~~4.84 - 34.6~~	~~1.17~~	~~0.66 - 4.03~~	~~3.86~~	~~1.16 - 8.52~~	~~556~~	~~1.17 - 1209~~
Mo	0.045	0.029 - 0.058	0.048	0.029 - 0.057	0.158	0.108 - 0.185	0.0305	0.010 - 0.037	0.304	0.067 - 0.488
Ni	1.13	1.09 - 1.66	1.42	1.14 - 1.67	1.35	0.99 - 2.80	0.99	0.85 - 1.61	0.88	0.44 - 1.08
Pb	0.019	0.005 - 0.032	0.130	0.082 - 0.146	0.013	0.005 - 0.094	0.014	0.005 - 0.024	0.060	0.005 - 0.312
Rb	0.850	0.719 - 1.21	0.724	0.327 - 1.06	0.716	0.598 - 1.19	0.396	0.209 - 0.471	1.30	1.13 - 6.53
Sr	44.1	41.4 - 51.3	40.5	26.5 – 56.0	81.4	75.5 - 138	46.8	27.0 - 68.2	58.9	51.7 - 94.4
Ti	0.52	0.05 - 1.29	1.26	0.27 - 3.94	0.90	0.18 - 2.14	1.80	0.58 - 2.68	0.86	0.75 - 2.73
U	0.298	0.211 - 0.349	0.157	0.005 - 0.303	0.244	0.117 - 0.316	0.148	0.033 - 0.257	0.120	0.079 – 1.00
V	0.289	0.213 - 0.357	0.331	0.229 - 0.403	0.308	0.276 - 0.344	0.297	0.276 - 0.683	0.381	0.258 - 1.02
Zn	1.74	1.33 - 2.16	1.57	0.10 - 1.85	2.63	1.79 - 6.81	2.18	0.93 - 2.76	1.95	1.30 - 73.4

	COR (n=5)		PLR (n4)		RES (n=5)	
Parameter	**Median**	**Range**	**Median**	**Range**	**Median**	**Range**
Al	13.8	7.99 - 97.9	54.3	15.5 - 62.7	17.1	13.9 - 47.5
As	3.05	1.99 - 3.47	2.75	0.68 - 3.34	1.97	1.68 - 2.20
B	17.7	14.9 - 46.5	31.4	15.6 - 36.4	47.9	21.3 - 89.6
Ba	46.4	28.8 - 49.2	29.7	21.0 - 44.5	27.8	25.6 - 34.7
Cd	0.008	0.005 - 0.013	0.027	0.014 - 0.058	0.021	0.014 - 0.107
Co	0.116	0.066 - 0.137	0.276	0.145 - 0.482	0.503	0.122 - 0.579
Cr	0.226	0.033 - 0.65	0.72	0.19 - 1.08	1.06	0.67 - 1.25
Cu	2.00	0.10 - 3.66	8.57	1.07 - 14.3	19.6	9.98 - 24.8
~~Fe~~	~~64.1~~	~~37.1 - 99.5~~	~~22.8~~	~~8.00 - 62.3~~	~~50.4~~	~~27.9 - 104~~
Li	21.1	9.93 - 24.9	1.79	1.15 - 4.22	7.68	1.40 - 8.08
~~Mn~~	~~33.2~~	~~17.8 - 81.6~~	~~13.8~~	~~0.69 - 59.7~~	~~28.9~~	~~3.91 - 54.4~~
Mo	0.901	0.747 - 1.19	1.20	0.05 - 1.57	1.06	0.749 - 1.39
Ni	0.509	0.020 - 0.594	0.960	0.580 - 1.19	1.56	0.560 - 2.15
Pb	0.124	0.049 - 0.202	0.142	0.039 - 0.588	0.460	0.322 - 0.528
Rb	1.55	0.831 – 2.00	2.53	1.81 - 9.15	14.9	2.22 – 16.0
Sr	181	126 - 219	186	64.1 - 379	247	148 - 272
Ti	0.236	0.126 - 5.67	0.48	0.320 - 3.07	1.45	0.520 - 2.13
U	0.558	0.544 - 0.906	1.69	0.100 - 2.80	1.29	1.12 - 2.73
V	0.919	0.561 - 0.985	1.51	0.408 - 3.53	0.598	0.272 - 1.30
Zn	13.6	4.3 - 13.7	18.6	4.56 - 48.6	36.6	20.4 - 44.2

Table A5 – Summary of analytical results for characteristics of dissolved organic matter in source samples. All analytical results~~,~~ ~~quantification results~~ and quality controls are available at: https://entrepot.recherche.data.gouv.fr/dataverse/chypster/)

		BOU (n=5)		**VRY** (n=5)		**VRN** (n=5)		**REV** (n=4)		**PNC** (n=5)	
Parameter	**Unit**	**Median**	**Range**	**Median**	**Range**	**Median**	**Range**	**Median**	**Range**	**Median**	**Range**
DOC	mg/L	2.9	2.7 - 4.6	4.2	3.8 - 4.7	7.5	6.2 - 8.2	8.4	8.4 - 10.1	5.3	4.6 - 10.8
~~E2:E3~~	~~-~~	~~7.4~~	~~6.8 - 7.7~~	~~6.4~~	~~6.1 - 6.6~~	~~6.7~~	~~6.3 - 6.9~~	~~6.9~~	~~6.4 - 7.3~~	~~4.7~~	~~4.5 - 6.3~~
~~E2:E 4~~	~~-~~	~~24.9~~	~~21.2 - 28.9~~	~~20.6~~	~~19.2 - 21.8~~	~~25.2~~	~~22.8 - 26.5~~	~~27.7~~	~~24.0 - 29.6~~	~~17.7~~	~~13.5 - 21.5~~
~~E3:E4~~	~~-~~	~~6.9~~	~~6.2 - 7.1~~	~~5.9~~	~~5.7 - 6.1~~	~~6.7~~	~~6.3 - 7.0~~	~~7.1~~	~~6.5 - 7.6~~	~~5.3~~	~~4.5 - 6.4~~
~~E4:E6~~	~~-~~	~~8.8~~	~~3.5 - 12.8~~	~~10.2~~	~~7.2 - 17.4~~	~~11.2~~	~~6.4 - 30.3~~	~~9.1~~	~~6.0 - 12.4~~	~~11.6~~	~~5.9 - 21.1~~
~~SUVA~~	~~L/mgC/m~~	~~2.2~~	~~2.1 - 2.4~~	~~2.7~~	~~2.5 - 3.0~~	~~2.9~~	~~2.6 - 3.0~~	~~2.8~~	~~2.6 - 3.0~~	~~3.1~~	~~2.9 - 4.3~~
S1	nm^{-1}	0.0160	0.0158 - 0.0163	0.0156	0.0153 - 0.0158	0.0153	0.0151 - 0.0155	0.0151	0.0150 - 0.0155	0.0134	0.0119 - 0.0144
S2	nm^{-1}~~nm-1~~	0.0196	0.0184 - 0.0203	0.0185	0.0183 - 0.0187	0.0205	0.0199 - 0.0209	0.0213	0.0207 - 0.0220	0.0194	0.0162 - 0.0198
~~SR~~	~~-~~	~~0.83~~	~~0.79 - 0.86~~	~~0.84~~	~~0.83 - 0.86~~	~~0.76~~	~~0.72 - 0.77~~	~~0.71~~	~~0.70 - 0.73~~	~~0.71~~	~~0.60 - 0.83~~
Mn-254	Da	417	323 - 460	542	394 - 593	616	548 - 695	607	596 - 636	569	526 - 703
~~Mw-254~~	~~Da~~	~~1718~~	~~1352 - 2365~~	~~1644~~	~~1049 - 2364~~	~~1543~~	~~1146 - 1766~~	~~1266~~	~~1188 - 1649~~	~~1423~~	~~1198 - 1858~~
~~disp-254~~	~~-~~	~~4.19~~	~~3.02 - 7.04~~	~~2.77~~	~~2.52 - 5.13~~	~~2.42~~	~~1.86 - 2.96~~	~~2.05~~	~~1.93 - 2.77~~	~~2.31~~	~~2.02 - 3.28~~
A0-254	-	4552	2486 - 7349	4772	2165 - 8337	4627	407 - 10478	2404	1501 - 7710	2265	1209 - 4962
A1-254	-	21850	15215 - 34702	47737	46348 - 59736	117263	86123 - 138631	110027	104294 - 117502	67331	50782 - 114518
A2-254	-	48675	38354 - 83965	78227	70245 - 93519	188721	146038 - 204308	216676.5	185118 - 228952	121649	80952 - 176082
A3-254	-	54560	47984 - 128755	65957	54730 - 85950	96041	77790 - 123959	112563	102393 - 121161	62096	53834 - 112852

		COR (n=5)		**PLR** (n=4)		**RES** (n=5)	
Parameter	**Unit**	Median	Range	Median	Range	Median	Range
DOC	mg/L	3.5	2.0 - 10.1	6.1	4.4 - 8.4	32.7	22.1 - 42.6
~~E2:E3~~	~~-~~	~~5.2~~	~~4.8 - 6.9~~	~~5.9~~	~~5.8 - 6.1~~	~~5.4~~	~~4.9 - 7.6~~
~~E2:E4~~	~~-~~	~~14.9~~	~~11.9 - 23.3~~	~~18.9~~	~~17.2 - 20.6~~	~~11.3~~	~~10.5 - 14.9~~
~~E3:E4~~	~~-~~	~~5.0~~	~~4.6 - 7.1~~	~~5.5~~	~~5.3 - 5.9~~	~~4.3~~	~~3.9 - 5.7~~
~~E4:E6~~	~~-~~	~~5.6~~	~~3.0 - 15.1~~	~~9.1~~	~~7.8 - 10.5~~	~~6.8~~	~~5.9 - 8.7~~
~~SUVA~~	~~L/mgC/m~~	~~2.0~~	~~0.8 - 2.6~~	~~2.8~~	~~2.4 - 3.0~~	~~1.3~~	~~0.9 - 1.4~~
S1	nm^{-1}~~nm-1~~	0.0123	0.0118 - 0.0145	0.0144	0.0144 - 0.0153	0.0161	0.0104 - 0.0168
S2	nm^{-1}~~nm-1~~	0.0163	0.0150 - 0.0192	0.0172	0.0167 - 0.0186	0.0127	0.0123 - 0.0128
~~SR~~	~~-~~	~~0.80~~	~~0.64 - 0.85~~	~~0.84~~	~~0.77 - 0.92~~	~~1.28~~	~~0.82 - 1.33~~
Mn-254	Da	451	434 - 670	727	621 - 885	424	383 - 579
~~Mw-254~~	~~Da~~	~~2031~~	~~941 - 2432~~	~~1765~~	~~1571 - 1974~~	~~1390~~	~~1204 - 2201~~
~~disp-254~~	~~-~~	~~3.03~~	~~2.17 - 5.39~~	~~2.21~~	~~2.00 - 3.18~~	~~3.14~~	~~2.88 - 4.00~~
A0-254	-	4797	144 - 7402	3085	2560 - 9811	6713	4296 - 14343
A1-254	-	33782	18214 - 53643	128469	65410 - 156480	73927	61653 - 100544
A2-254	-	45994	20069 - 65362	137524	86234 - 207418	116338	93322 - 171777
A3-254	-	43102	16900 - 55750	54241	35715 - 114897	129258	85384 - 218065

Table A6 – Summary of analytical results for microbial parameters in source samples. Values are concentrations in log10 number of copies/100 mL.

	BOU (n=5)		VRY (n=5)		VRN (n=5)		REV (n=4)		PNC (n=5)	
Parameter	**Median**	**Range**	**Median**	**Range**	**Median**	**Range**	**Median**	**Range**	**Median**	**Range**
~~G16S~~	~~7.3~~	~~7.0 - 7.5~~	~~7.8~~	~~7.4 - 9.1~~	~~7.8~~	~~7.8 - 8.6~~	~~8.8~~	~~8.8 - 8.9~~	~~8.4~~	~~7.2 - 9.4~~
~~BTT~~	~~3.7~~	~~2.6 - 4.2~~	~~4.0~~	~~0.0 - 5.1~~	~~5.0~~	~~0.0 - 5.5~~	~~6.3~~	~~0.0 - 6.7~~	~~6.2~~	~~5.1 - 6.7~~
HF183	0.0	0.0 – 0.0	0.0	0.0 – 0.0	0.0	0.0 - 1.9	0.0	0.0 – 0.0	0.0	0.0 – 0.0
rum-2-bac	0.0	0.0 – 0.0	0.0	0.0 – 0.0	0.0	0.0 – 0.0	0.0	0.0 – 0.0	0.0	0.0 – 6.0
~~BTS~~	~~0.0~~	~~0.0 - 3.5~~	~~0.0~~	~~0.0 - 0.0~~	~~0.0~~	~~0.0 - 2.2~~	~~0.0~~	~~0.0 - 0.0~~	~~0.0~~	~~0.0 - 3.0~~
~~*int1*~~	~~0.0~~	~~0.0 - 4.1~~	~~0.0~~	~~0.0 - 3.9~~	~~0.0~~	~~0.0 - 4.8~~	~~3.3~~	~~0.0 - 3.4~~	~~0.0~~	~~0.0 - 0.0~~
~~*.int2*~~	~~0.0~~	~~0.0 - 3.8~~	~~0.0~~	~~0.0 - 0.0~~	~~0.0~~	~~0.0 - 0.0~~	~~0.0~~	~~0.0 - 0.0~~	~~1.4~~	~~0.0 - 3.4~~

	COR (n=5)		PLR (n=4)		RES (n=5)	
Parameter	**Median**	**Range**	**Median**	**Range**	**Median**	**Range**
~~G16S~~	~~9.4~~	~~8.6 - 9.6~~	~~9.4~~	~~9.2 - 9.5~~	~~10.4~~	~~9.5 - 11.4~~
~~BTT~~	~~6.3~~	~~6.2 - 7.3~~	~~6.5~~	~~6.5 - 6.6~~	~~8.80~~	~~7.9 - 9.6~~
HF183	3.7	3.5 - 6.3	3.5	3.1 - 3.6	7.05	5.7 - 7.5
rum-2-bac	0.0	0.0 – 0.0	0.0	0.0 – 0.0	4.15	3.4 - 4.6
~~BTS~~	~~3.6~~	~~3.3 - 4.6~~	~~5.1~~	~~5.0 - 6.2~~	~~7.05~~	~~6.6 - 7.9~~
~~*int1*~~	~~0.0~~	~~0.0 -3.0~~	~~4.0~~	~~0.0 - 4.5~~	~~5.25~~	~~4.3 - 6.0~~
~~*int2*~~	~~4.4~~	~~0.0 - 6.0~~	~~2.8~~	~~0.0 - 3.4~~	~~6.30~~	~~5.0 -6.5~~

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Table A7 – Mean contributions and standard deviations of estimations obtained for the decomposition of streamwater 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*

		13/03/23 18:37		13/03/23 19:07		13/03/23 19:37		13/03/23 20:07		13/03/23 20:37		13/03/23 21:07		13/03/23 21:37		13/03/23 22:07		13/03/23 22:37		13/03/23 23:07		13/03/23 23:37		14/03/23 00:07	
		Mean	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*
13/03/2023 - Mercier	**FOR_1**	13	*11*	6	*5*	14	*12*	5	*5*	6	*6*	9	*8*	8	*7*	7	*6*	4	*4*	4	*3*	5	*5*	6	*6*
	FOR_2	3	*3*	14	*6*	12	*9*	43	*19*	36	*18*	27	*15*	23	*13*	23	*13*	25	*14*	26	*15*	26	*15*	22	*13*
	GRA	35	*23*	6	*6*	8	*8*	9	*6*	8	*6*	8	*9*	7	*12*	6	*13*	6	*13*	8	*13*	9	*11*	11	*10*
	AGR	23	*22*	8	*4*	8	*8*	6	*9*	6	*8*	9	*7*	13	*6*	16	*5*	15	*5*	15	*7*	13	*8*	12	*9*
	URB	0	*0*	52	*7*	48	*11*	19	*5*	19	*5*	31	*7*	23	*8*	18	*7*	17	*7*	18	*7*	22	*7*	27	*8*
	SEW	26	*5*	7	*3*	5	*3*	2	*1*	2	*1*	5	*2*	11	*4*	14	*4*	15	*4*	14	*4*	15	*4*	15	*4*
	SUR	0	*0*	7	*2*	5	*3*	15	*8*	23	*8*	10	*6*	14	*7*	18	*7*	18	*7*	16	*7*	9	*6*	8	*5*

		13/03/23 18:30		13/03/23 20:45		13/03/23 22:07		13/03/23 22:37		13/03/23 23:15		13/03/23 23:30		13/03/23 23:45		14/03/23 00:00		14/03/23 00:15	
		Mean	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*
13/03/2023 - Ratier	**FOR_1**	14	*10*	3	*3*	3	*4*	3	*3*	2	*2*	2	*2*	2	*2*	3	*3*	4	*4*
	FOR_2	7	*6*	2	*2*	2	*2*	2	*2*	1	*2*	1	*2*	1	*2*	2	*3*	2	*3*
	GRA	13	*11*	21	*6*	21	*9*	18	*7*	20	*8*	19	*8*	21	*8*	22	*8*	22	*8*
	AGR	9	*8*	7	*4*	6	*6*	9	*7*	5	*5*	5	*5*	6	*6*	10	*8*	10	*8*
	AQU	44	*11*	1	*1*	1	*1*	1	*1*	1	*1*	1	*1*	1	*1*	1	*1*	1	*1*
	URB	0	*0*	28	*6*	44	*12*	29	*9*	43	*10*	47	*11*	39	*10*	35	*10*	36	*10*
	SEW	13	*7*	4	*2*	6	*4*	6	*3*	5	*3*	5	*3*	6	*3*	6	*3*	8	*3*
	SUR	0	*0*	35	*4*	18	*5*	32	*4*	22	*5*	19	*5*	23	*5*	20	*5*	17	*5*

Table A8 – Mean contributions and standard deviations of estimations obtained for the decomposition of streamwater samples collected during summer storm events in June 2022 and September 2022. The values correspond to the relative parts of flow for each time step as a percentage.

		22/06/22 15:07		22/06/22 15:37		22/06/22 16:07		22/06/22 16:37		22/06/22 17:07		22/06/22 17:37		22/06/22 18:07		22/06/22 18:37		22/06/22 19:07		22/06/22 19:37		22/06/22 20:07	
-	-	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*
22/06/2022 - Ratier	**FOR_1**	0	*0*	0	*1*	1	*1*	0	*1*	0	*1*	0	*1*	0	*1*	0	*1*	0	*1*	0	*1*	0	*1*
	FOR_2	1	*1*	1	*2*	3	*5*	2	*3*	1	*2*	1	*2*	1	*2*	1	*2*	1	*2*	2	*2*	2	*2*
	GRA	5	*4*	6	*7*	14	*10*	11	*10*	6	*6*	11	*10*	12	*11*	8	*7*	6	*6*	7	*7*	7	*7*
	AGR	1	*2*	1	*2*	3	*4*	2	*3*	1	*2*	1	*2*	2	*3*	2	*3*	3	*7*	3	*5*	3	*5*
	AQU	16	*21*	3	*4*	6	*7*	3	*4*	2	*2*	2	*3*	2	*3*	2	*3*	3	*4*	3	*3*	3	*3*
	URB	48	*34*	34	*26*	23	*17*	21	*17*	19	*15*	17	*14*	17	*14*	17	*13*	26	*19*	23	*18*	24	*18*
	SEW	8	*8*	6	*5*	6	*4*	5	*4*	4	*3*	3	*3*	4	*3*	5	*3*	12	*7*	10	*6*	10	*6*
	SUR	20	*9*	48	*23*	44	*15*	56	*17*	66	*15*	64	*17*	61	*16*	65	*13*	48	*15*	52	*15*	51	*17*

		14/09/22 17:20		14/09/22 17:35		14/09/22 17:55		14/09/22 18:15		14/09/22 18:35		14/09/22 18:55		14/09/22 19:15		14/09/22 19:35		14/09/22 19:55		14/09/22 20:15	
-	-	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*
09/09/2022 - Mercier	**FOR_1**	0	*0*	0	*0*	0	*0*	0	*0*	0	*1*	0	*1*	0	*1*	0	*1*	1	*1*	1	*1*
	FOR_2	1	*1*	1	*1*	1	*2*	1	*2*	1	*2*	1	*3*	2	*3*	2	*3*	2	*3*	2	*3*
	GRA	31	*22*	39	*28*	34	*24*	34	*24*	38	*27*	36	*25*	35	*24*	34	*23*	33	*22*	34	*23*
	AGR	1	*5*	1	*4*	1	*5*	1	*5*	1	*6*	1	*7*	2	*7*	2	*8*	2	*8*	3	*8*
	URB	33	*1*	17	*1*	22	*1*	22	*1*	19	*2*	22	*2*	25	*2*	27	*3*	30	*3*	29	*4*
	SEW	1	*0*	0	*0*	0	*0*	0	*1*	0	*1*	1	*1*	1	*1*	1	*1*	1	*1*	1	*1*
	SUR	32	*22*	42	*28*	42	*24*	41	*23*	40	*24*	38	*21*	35	*20*	34	*19*	32	*17*	31	*18*

		14/09/22 16:35		14/09/22 16:55		14/09/22 17:15		14/09/22 17:35		14/09/22 17:55		14/09/22 18:15		14/09/22 18:35		14/09/22 18:55		14/09/22 19:15		14/09/22 19:35		14/09/22 19:55		14/09/22 20:15	
-	-	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*
09/09/2022 - Ratier	**FOR_1**	3	*3*	3	*4*	0	*0*	0	*0*	0	*0*	0	*0*	0	*0*	0	*1*	0	*1*	0	*1*	1	*1*	1	*1*
	FOR_2	4	*3*	4	*4*	1	*1*	0	*1*	0	*1*	0	*1*	1	*1*	1	*1*	1	*1*	1	*2*	1	*2*	1	*2*
	GRA	3	*3*	4	*4*	26	*4*	35	*5*	41	*5*	46	*5*	45	*5*	44	*5*	43	*5*	41	*6*	38	*6*	38	*7*
	AGR	5	*4*	6	*6*	2	*2*	1	*1*	1	*1*	1	*1*	1	*1*	1	*2*	1	*2*	2	*2*	2	*3*	3	*4*
	AQU	72	*5*	70	*5*	40	*3*	4	*2*	4	*2*	3	*1*	4	*2*	5	*2*	7	*2*	10	*2*	12	*2*	15	*3*
	URB	0	*0*	0	*0*	2	*2*	1	*2*	1	*1*	1	*1*	1	*1*	1	*1*	1	*2*	2	*2*	2	*3*	3	*4*
	SEW	13	*6*	14	*6*	9	*2*	7	*1*	4	*1*	2	*1*	2	*1*	2	*1*	2	*1*	3	*1*	3	*1*	4	*2*
	SUR	0	*0*	0	*0*	20	*3*	51	*4*	49	*4*	47	*4*	46	*4*	46	*4*	44	*4*	41	*5*	40	*5*	35	*5.66*

Table A9 – Mean contributions and standard deviations of estimations obtained for the decomposition of streamwater samples collected during major events in May 2021 and October 2021. The values correspond to the relative parts of flow for each time step as a percentage.

Event	Source	10/05/21 09:45		10/05/21 10:45		10/05/21 11:45		10/05/21 12:45		10/05/21 13:45		10/05/21 14:45		10/05/21 15:45		10/05/21 16:45		10/05/21 17:45		10/05/21 18:45		10/05/21 19:45		10/05/21 20:45	
		Mean	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*
10/05/2021 - Mercier	FOR_1	1	*1*	2	*3*	1	*2*	1	*2*	1	*1*	1	*1*	1	*1*	1	*1*	1	*1*	1	*2*	1	*1*	1	*1*
	FOR_2	2	*3*	2	*3*	3	*4*	3	*4*	2	*3*	2	*3*	2	*3*	2	*3*	2	*3*	3	*4*	3	*4*	3	*4*
	GRA	10	*4*	7	*5*	9	*6*	9	*6*	8	*6*	10	*7*	11	*7*	14	*7*	12	*7*	17	*8*	19	*9*	19	*9*
	AGR	66	*11*	67	*15*	63	*16*	62	*17*	66	*17*	64	*16*	64	*16*	59	*15*	62	*15*	59	*14*	57	*14*	59	*14*
	URB	2	*2*	2	*2*	2	*2*	2	*2*	2	*2*	2	*2*	2	*2*	2	*3*	2	*3*	2	*3*	2	*3*	2	*2*
	SEW	6	*3*	7	*4*	5	*4*	5	*4*	4	*4*	4	*4*	5	*4*	7	*4*	6	*4*	7	*4*	8	*4*	7	*4*
	SUR	13	*9*	12	*11*	17	*12*	18	*13*	17	*13*	16	*12*	15	*12*	14	*11*	14	*11*	11	*9*	10	*8*	9	*7*
		10/05/21 10:15		10/05/21 11:15		10/05/21 12:15		10/05/21 13:15		10/05/21 14:15		10/05/21 15:15		10/05/21 16:15		10/05/21 17:15		10/05/21 18:15		10/05/21 19:15		10/05/21 20:15		10/05/21 21:15	
		Mean	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*
10/05/2021 - Ratier	FOR_1	0	*0*	1	*1*	1	*1*	1	*1*	0	*1*	0	*1*	0	*1*	0	*1*	0	*1*	0	*1*	0	*1*	1	*1*
	FOR_2	1	*1*	1	*2*	1	*2*	1	*1*	1	*1*	1	*1*	1	*1*	1	*1*	1	*1*	1	*1*	1	*2*	1	*2*
	GRA	10	*4*	11	*6*	11	*6*	10	*6*	10	*6*	11	*7*	9	*6*	10	*6*	11	*7*	13	*8*	13	*8*	15	*9*
	AGR	21	*4*	21	*6*	17	*6*	22	*6*	22	*6*	26	*7*	31	*7*	33	*7*	35	*7*	39	*8*	41	*9*	45	*11*
	AQU	0	*0*	0	*0*	0	*1*	0	*1*	0	*0*	0	*0*	0	*0*	0	*0*	0	*0*	0	*0*	0	*0*	0	*0*
	URB	12	*5*	11	*5*	19	*7*	18	*7*	15	*7*	15	*7*	15	*7*	15	*7*	15	*7*	14	*7*	13	*7*	13	*7*
	SEW	4	*2*	4	*2*	5	*3*	5	*3*	5	*3*	5	*3*	4	*3*	5	*3*	4	*3*	5	*3*	5	*3*	6	*4*
	SUR	51	*3*	52	*3*	45	*4*	43	*4*	47	*4*	43	*4*	40	*5*	37	*5*	33	*5*	28	*5*	25	*5*	19	*5*
		03/10/21 14:37		03/10/21 16:07		03/10/21 17:37		03/10/21 19:07		03/10/21 20:37		03/10/21 22:07		03/10/21 23:37		04/10/21 01:07		04/10/21 02:37		04/10/21 04:07		04/10/21 05:37		04/10/21 07:07	
		Mean	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*
03/10/2021 - Mercier	FOR_1	1	*1*	0	*0*	0	*1*	0	*1*	0	*1*	1	*1*	0	*1*	1	*1*	1	*1*	1	*1*	1	*1*	1	*1*
	FOR_2	1	*1*	1	*1*	1	*2*	1	*2*	1	*2*	1	*2*	1	*2*	2	*2*	2	*3*	2	*3*	2	*2*	2	*2*
	GRA	26	*6*	16	*9*	13	*6*	15	*7*	17	*7*	21	*8*	24	*8*	30	*8*	30	*8*	33	*8*	34	*8*	32	*8*
	AGR	40	*6*	33	*8*	47	*8*	47	*9*	43	*9*	45	*9*	44	*9*	39	*9*	38	*9*	36	*9*	33	*9*	33	*9*
	URB	4	*3*	2	*2*	2	*2*	3	*3*	3	*3*	3	*3*	3	*3*	4	*4*	6	*5*	6	*5*	6	*6*	7	*6*
	SEW	9	*2*	2	*2*	2	*1*	5	*2*	6	*2*	5	*2*	6	*3*	10	*3*	13	*3*	13	*3*	14	*3*	15	*3*
	SUR	20	*4*	47	*6*	35	*5*	29	*6*	28	*6*	24	*6*	20	*6*	15	*5*	11	*4*	9	*4*	10	*4*	11	*4*
		03/10/21 14:37		03/10/21 16:07		03/10/21 17:37		03/10/21 19:07		03/10/21 20:37		03/10/21 22:07		03/10/21 23:37		04/10/21 01:07		04/10/21 02:37		04/10/21 04:07		04/10/21 05:37		04/10/21 07:07	
		Mean	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*	**Mean**	*sd*
03/10/2021 - Ratier	FOR_1	1	*1*	0	*1*	1	*1*	1	*1*	1	*1*	1	*1*	1	*1*	1	*1*	1	*1*	1	*1*	1	*2*	1	*2*
	FOR_2	2	*2*	1	*2*	1	*2*	2	*3*	2	*3*	2	*3*	2	*3*	3	*4*	3	*4*	2	*4*	3	*4*	3	*4*
	GRA	10	*5*	9	*7*	13	*10*	13	*9*	11	*8*	13	*9*	12	*8*	12	*8*	14	*9*	12	*9*	16	*10*	14	*10*
	AGR	13	*9*	10	*9*	14	*12*	18	*14*	19	*15*	20	*15*	22	*16*	24	*17*	24	*18*	23	*20*	22	*17*	22	*17*
	AQU	2	*6*	0	*1*	1	*1*	1	*1*	1	*1*	1	*1*	1	*1*	1	*1*	1	*2*	1	*2*	1	*2*	1	*2*
	URB	52	*11*	22	*8*	29	*11*	26	*11*	27	*11*	28	*12*	31	*12*	34	*12*	35	*12*	44	*14*	40	*12*	43	*11*
	SEW	5	*7*	1	*1*	1	*1*	1	*2*	2	*2*	2	*2*	2	*2*	3	*3*	3	*4*	3	*5*	4	*4*	5	*5*
	SUR	16	*4*	56	*6*	40	*8*	39	*7*	38	*7*	34	*7*	30	*7*	24	*7*	19	*7*	14	*7*	13	*6*	11	*6*

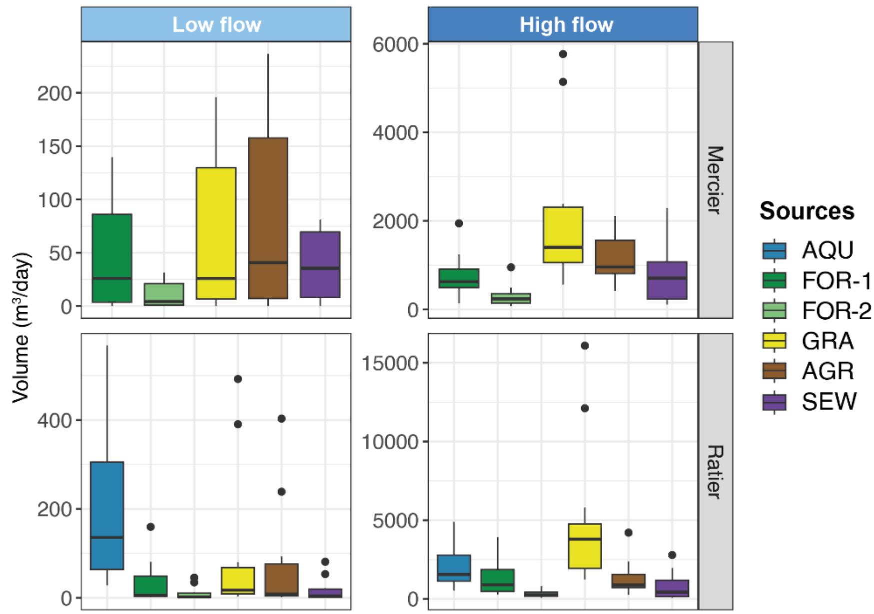

Figure A1 – Daily volume contributions in m^3 estimated for dry weather streamwater samples by the application of a biogeochemical decomposition using a Bayesian mixing model for the Mercier and Ratier catchments. Contributions in terms of volume were calculated based on the relative contributions for each source and the total flow for each sampled day in m^3. Boxplots represent the median contribution, interquartile range (1st and 3rd quartiles), minimum and maximum values. Low flow samples correspond to a mean daily discharge lower than 20 L/s and high flow samples to a mean daily discharge higher than 20 L/s.

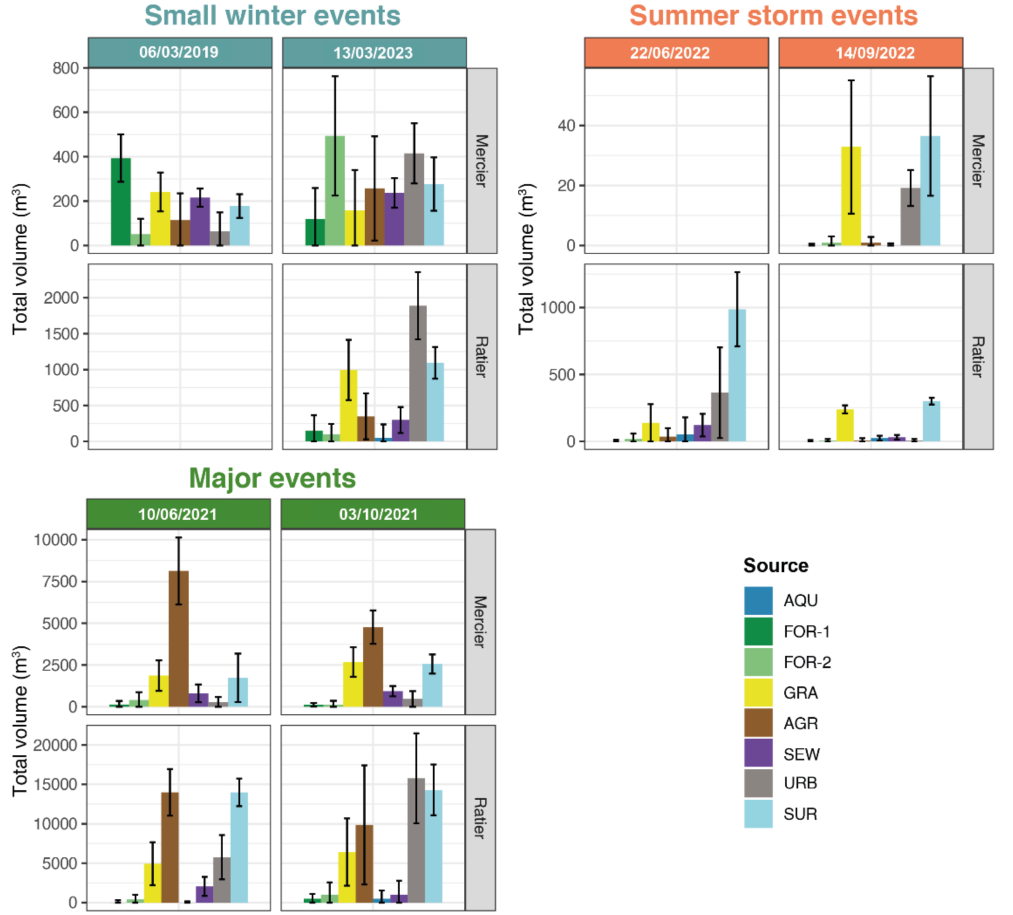

Figure A2 – Total volume contributions to the hydrological events sampled between March 2019 and March 2023 at the outlets of the Mercier and Ratier catchments. Contributions in terms of volume were calculated based on the relative contributions from each source and the total flow in m^3. The contributions correspond to the mean of the results obtained for each samples decomposition by the Bayesian mixing model ~~approach~~. The error bars correspond to the mean of the standard deviation calculated from the sum of the squares of the deviation. The events of 6 March 2019 at the Ratier station and 22 June 2022 at the Mercier station were not collected.

Data availability

Hydro-meteorological data and biogeochemical data at the catchment outlets during dry weather is available online at https://bdoh.irstea.fr/YZERON/station/V3015810 and https://bdoh.irstea.fr/YZERON/station/V301502401, respectively for the Mercier and the Ratier station (https://doi.org/10.57745/VVQ2X9; https://doi.org/10.17180/obs.yzeron). Metadata relative to the sampling of sources and of the catchment outlets are detailed at: https://doi.org/10.57745/K3S9YV. Biogeochemical data of the sources and at the catchment outlets during hydrological events is available at https://doi.org/10.57745/HQPIFQ for major parameters and dissolved metals, and at https://doi.org/10.57745/IYJ2VE for characteristics of DOM.

Author contributions

OG: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **FB**: Writing – review & editing, Investigation, Methodology, Conceptualization. **MM**: Writing – review & editing, Investigation, Methodology, Conceptualization. **BC**: Writing – review & editing, Investigation, Methodology. **NR**: Writing – review & editing, Investigation, Methodology. **PD**: Writing – review & editing, Investigation, Methodology. **ADL**: Writing – review & editing, Investigation, Methodology. **MC**: Writing – review & editing, Investigation, Methodology, Conceptualization, Funding acquisition, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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