



HAL
open science

Determination of groundwater origins and vulnerability based on multi-tracer investigations: New contributions from passive sampling and suspect screening approach

Lucie Pinasseau, Florian Mermillod-Blondin, Aurélie Fildier, François Fourel, Félix Vallier, Ludovic Guillard, Laure Wiest, Laurence Volatier

► To cite this version:

Lucie Pinasseau, Florian Mermillod-Blondin, Aurélie Fildier, François Fourel, Félix Vallier, et al.. Determination of groundwater origins and vulnerability based on multi-tracer investigations: New contributions from passive sampling and suspect screening approach. *Science of the Total Environment*, 2023, 876, pp.162750. 10.1016/j.scitotenv.2023.162750 . hal-04350840

HAL Id: hal-04350840

<https://hal.science/hal-04350840v1>

Submitted on 18 Dec 2023

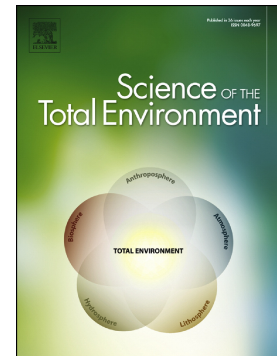
HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Journal Pre-proof

Determination of groundwater origins and vulnerability based on multi-tracer investigations: New contributions from passive sampling and suspect screening approach

Lucie Pinasseau, Florian Mermillod-Blondin, Aurélie Fildier, François Fourel, Félix Vallier, Ludovic Guillard, Laure Wiest, Laurence Volatier



PII: S0048-9697(23)01366-9

DOI: <https://doi.org/10.1016/j.scitotenv.2023.162750>

Reference: STOTEN 162750

To appear in: *Science of the Total Environment*

Received date: 18 January 2023

Revised date: 3 March 2023

Accepted date: 5 March 2023

Please cite this article as: L. Pinasseau, F. Mermillod-Blondin, A. Fildier, et al., Determination of groundwater origins and vulnerability based on multi-tracer investigations: New contributions from passive sampling and suspect screening approach, *Science of the Total Environment* (2023), <https://doi.org/10.1016/j.scitotenv.2023.162750>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Determination of groundwater origins and vulnerability based on multi-tracer investigations: new contributions from passive sampling and suspect screening approach

Lucie Pinasseau^{a*}, Florian Mermillod-Blondin^a, Aurélie Fildier^b, François Fourel^a, Félix Vallier^a, Ludovic Guillard^a, Laure Wiest^b, Laurence Volatier^a

^a Univ Lyon, Université Claude Bernard Lyon 1, CNRS, ENTPE, UMR5023 Laboratoire d'Ecologie des Hydrosystèmes Naturels et Anthropisés (LEHNA), 6 Rue Raphaël Dubois, F-69622, Villeurbanne, France

^b Univ Lyon, CNRS, Université Claude Bernard Lyon 1, Institut des Sciences Analytiques, UMR 5280, 5 Rue de la Doua, F-69100, Villeurbanne, France

***Corresponding author:** lucie.pinasseau@univ-lyon1.fr

Competing interests: the contact author has declared that none of the authors has any competing interests.

Abstract

Knowledge about groundwater origins and their interactions with surface water is fundamental to assess their vulnerability. In this context, hydrochemical and isotopic tracers are useful tools to investigate water origins and mixing. More recent studies examined the relevance of contaminants of emerging concern (CECs) as co-tracers to distinguish sources contributing to groundwater bodies. However, these studies focused on known and targeted CECs a priori selected regarding their origin and/or concentrations. This study aimed to improve these multi-tracer approaches using passive sampling and qualitative suspect screening by exploring a larger variety of historical and emerging concern contaminants in combination with hydrochemistry and water molecular isotopes. With this objective, an *in-situ* study was conducted in a drinking water catchment area located in an alluvial aquifer recharged by several water sources (both surface and groundwater sources). CECs determined by passive sampling and suspect screening allowed to provide in-depth chemical fingerprints of groundwater bodies by enabling the investigation of more than 2500 compounds with an increased analytical sensitivity. Obtained cocktails of CECs were discriminating enough to be used as chemical tracer in combination with hydrochemical and isotopic tracers. In addition, the occurrence and type of CECs contributed to a better understanding of groundwater-surface water interactions and highlighted short-time hydrological processes. Furthermore, the use of passive sampling with suspect screening analysis of CECs lead to a more realistic assessment and mapping of groundwater vulnerability.

Keywords: chemical fingerprint; contaminants of emerging concern; groundwater recharge; passive sampling; hydrochemical tracer; isotopic tracer

1. Introduction

In many countries, shallow alluvial aquifers which are hydraulically connected to large rivers are often exploited by wellfields for drinking water supply (Bourg and Bertin, 1993; Texier et al., 2022). These unconfined alluvial aquifers are highly vulnerable to contaminations by river water as groundwater extraction accelerates the rate of aquifer recharge with river waters (Shamsudduha et al., 2011). Due to these increased recharge rates, the time for self-purification processes occurring in river banks is reduced and then, the vulnerability of the aquifer to contaminations from surface waters increases (Kralik et al., 2014). Under these conditions, knowledge about water origins and movements is fundamental for developing efficient monitoring tools and appropriate groundwater protection strategies (Dillon, 2005).

Various tracers are commonly used to collect information on subsurface processes such as age, travel time, stratification and temporal changes of the flow system. Tracers can be dye, heat, dissolved gases, trace elements and rare earth elements (Benischke, 2021; Díaz-Puga et al., 2016; Kurukulasuriya et al., 2022; Kurylyk et al., 2019; Moeck et al., 2017; Newman et al., 2021; Potot et al., 2012). To estimate the origin of water bodies contributing to groundwater recharge, natural tracers like conservative solutes (i.e. major ions and silica) or stable isotopes of the water molecule (i.e. $\delta^2\text{H}$ and $\delta^{18}\text{O}$) were identified as suitable tools (Blumstock et al., 2015; Díaz-Puga et al., 2016; Innocent et al., 2021; Kurukulasuriya et al., 2022; Moeck et al., 2017; Oyarzún et al., 2016; Poulain et al., 2021). In addition, anthropogenic contaminants such as historical and emerging concern contaminants are increasingly used in groundwater studies to trace water sources. Contaminants of emerging concern (CECs) are anthropogenic contaminants not considered until the recent development of improved analytical method allowing their detection (Richardson and Ternes, 2018). Banzhaf et al. (2012) and Müller et al. (2012) proved that pharmaceuticals (i.e. carbamazepine, sulfamethazine, and sulfamethoxazole) could be used as anthropogenic

tracers of surface water-groundwater interactions. Likewise, Newman et al. (2021) recently demonstrated that a multi-component geochemical dataset, including major ions, stable isotopes, pharmaceutical and wastewater-indicator compounds could be of major interest to characterize groundwater-surface water interactions. Moeck et al. (2017) showed that major ions, stable isotopes of the water molecule and acesulfame highlighted a mixing of infiltrated water and groundwater coming from the regional flow path. Currell et al. (2022) and McCance et al. (2020, 2018) investigated the applicability of CECs as novel groundwater 'co-tracers', *i.e.* in combination with more conventional tracers. These reviews clearly demonstrated the relevance of CECs, combined with hydrochemical and isotopic tracers, as a promising way to more efficiently delimit anthropogenic sources of groundwater in urban, peri-urban or agricultural areas. Furthermore, Lapworth et al. (2015), Sorensen et al. (2015) and Stuart et al. (2014) have highlighted that CECs could be used to assess rapid groundwater recharge pathways in vulnerable hydrogeological settings. In the same way, Erostate et al. (2019) found that CECs with a short half-life time improved the understanding of short-time hydrological processes. They argued that the study of the fate of CECs provided a higher level of resolution than hydrochemical and isotopic tracers alone. Therefore, CECs could complement the information provided by hydrochemical and isotopic tracers, especially in the context of exploited alluvial aquifers where intensive river – groundwater exchanges reduce the physico-chemical contrasts between groundwater and river water. Incorporation of CECs analyses in hydrogeological approaches could thus help to better infer surface water-groundwater exchanges.

CECs analyses could be also useful to identify zones of the aquifers which are the most vulnerable to contaminations. Nevertheless, conventional spot sampling methods and targeted analysis of pre-selected contaminants may suffer from a lack of sensitivity and resolution. Contaminants in groundwater usually occur at low concentrations (ng L^{-1} to pg L^{-1}),

potentially below the detection limits of most analytical methods, and targeted analyses typically cover a few dozen to a few hundred contaminants (Erostate et al., 2019; Newman et al., 2021), sometimes up to 1000 (Lapworth et al., 2015; Stuart et al., 2014). As a result, resolution may not be high enough to establish an in-depth chemical fingerprint of groundwater bodies and to discriminate water bodies with low contrasts. In this context, passive samplers such as solid phase extraction (SPE) disk-based samplers can be useful tools as contaminants accumulate on a receiving phase over several days or weeks (Page et al., 2014; Petrie et al., 2016; Pinasseau et al., 2020a; Shaw and Mueller, 2009; Vermeirssen et al., 2013; Vrana et al., 2005). Therefore, the analyte pre-concentration allows for an increase analytical sensitivity of the procedure and a more accurate assessment of groundwater contaminants (Brack et al., 2017; Jones et al., 2015; Mège et al., 2015; Mills et al., 2014). In addition, among the number of analytical methods developed for the measurement of historical contaminants and CECs in water (Richardson and Ternes, 2018), it has been proven that high resolution mass spectrometry (HRMS) coupled with a suspect screening approach allows the detection of a large number of compounds (i.e. several thousand) without reference standards or pre-selection and facilitates comprehensive screening of contaminants (Leendert et al., 2015; Pinasseau et al., 2019; Taylor et al., 2021). This qualitative approach has several advantages over the quantitative approach: calibration to determine the sampling rate of compounds is not required and an extended list of compounds can be investigated. Therefore, combining passive sampling with suspect screening can be a powerful method to accurately characterize groundwater bodies.

The aim of the present study is to explore the benefits of passive sampling and suspect screening for historical and emerging concern contaminants (both called hereafter CECs for clarity sake) in combination with hydrochemical (NO_3^- , Cl^- , SiO_2) and isotopic ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) tracers to characterize water bodies contributing to alluvial aquifer recharge and the

potential threat for groundwater quality. Nitrate, chloride and silica were monitored as they act as an agricultural practice tracer (Böhlke, 2002; Menció et al., 2011), a conservative tracer (Hem, 1985) and an indicator of groundwater residence time (Marçais et al., 2018), respectively. Concerning CECs, a focus was made on pesticides and pharmaceuticals, which are usually small, polar and mobile molecules that are likely to be found in groundwater (Akay Demir et al., 2019; Dabrowski et al., 2014; Postigo and Barceló, 2015). The study site is an alluvial aquifer used for the drinking water production of the Lyon metropolitan area (more than 1 million inhabitants) which is recharged by mixtures of surface and groundwater sources varying both spatially and temporally (Refloch, 2018). In this context, coupling hydrochemical and isotopic tracers with CECs analyses was expected as an efficient procedure to determine the contributions of several water sources to the alluvial aquifer and to point out potential zones of vulnerability for groundwater quality.

2. Material and Methods

2.1. Study area

The wellfield of Crépieux-Charmy is located immediately upstream of the Lyon metropolitan area (France) in the alluvial plain of the Rhône (Figure 1). The Rhône alluvial aquifer is composed of gravel layers and sand lenses, its depth is comprised between 1 and 10 m below the soil surface and its thickness between 10 and 30 m. The hydraulic conductivity at saturation is about 10^{-3} to $5 \cdot 10^{-2} \text{ m s}^{-1}$ and groundwater globally flows from east to west. The substratum is delimited by a low permeable sandy-clay layer dating from the Miocene age (Loizeau et al., 2017). The natural recharge of the Rhône alluvial aquifer comes mainly from river-groundwater exchanges as well as from underground flows from the fluvio-glacial corridors of Meyzieu and Décines (Est-Lyonnais aquifer) (Figures 1 and S1). At the Crépieux-Charmy site (375 ha), the Rhône alluvial aquifer is strongly influenced by pumping for drinking water production (114 pumping wells for an average pumping rate of $240\,000 \text{ m}^3$

per day). This groundwater extraction accelerates the recharge rate of the alluvial aquifer with several potential sources like surface waters (Miribel channel, Vieux Rhône river, and Jonage channel, Figure 1) and other groundwater sources (Est-Lyonnais aquifer, Dombes aquifer, Figure 1).

2.2. Experimental design and sampling

Two campaigns of fourteen days were performed to match the mean duration of the linear uptake regime of the majority of polar pesticides and pharmaceuticals on passive samplers (Gunold et al., 2008; Moschet et al., 2015; Pinasseau et al., 2020a; Vermeirssen et al., 2009). One campaign took place during summer (from August 1st to August 17th 2021) and the other in autumn (from October 26th to November 9th 2021), to evaluate a potential seasonal effect. Ten sampling locations were selected: three dealing with surface water samples (i.e. rivers surrounding the wellfield: Jonage channel, Miribel channel and Vieux-Rhône river) and seven dealing with groundwater samples from the 7 wells indicated in Figure 1. Sampling locations were selected based on potential vulnerability areas identified by Refloch (2018) using hydro-thermal flow modeling. Minimum distance from the nearest upstream riverbank are given for each groundwater sampling location in Table S1. The wells were built in either polyvinyl chloride or stainless steel (with a minimum internal diameter of 60 mm) perforated along their entire length.

Groundwater was collected in wells with a submerged pump (PP36 inox, SDEC, Reignac sur-Indre, France). The first 50 L pumped were used to rinse the sampling equipment and were discarded. Then, the following 6 L of pumped water were used for physico-chemical analyses. Groundwater and surface water physico-chemical analyses performed were electrical conductivity, temperature (T), pH and dissolved oxygen (DO) using portable electrical conductivity and DO meter probes (HQ20, HACH, Dusseldorf, Germany). Samples

of the 10 sampling locations were collected in 1 L polyethylene bottles previously washed with sampling water and brought back to the laboratory in an isotherm box at 4 °C for hydrochemical and isotopic analyses. Bottles were filled to avoid headspace and water-air equilibration prior to isotopic analyses. In addition, continuous measurements of electrical conductivity (LTC Levellogger® Junior, Solinst, Canada), DO and temperature (HOBO® U26, Onset, USA and Ponsel, Aqualabo, France), and piezometric levels (OTT Orpheus Mini, OTT HydroMet SARL, France) were monitored during the studied periods (depths of probes in piezometers are given in Table S1, mean values for each sampling location and field campaign are reported on Table S2 and evolutions of piezometric level, DO and temperature are displayed on Figure S2).

2.3. Hydrochemical analyses

Water samples dedicated to physico-chemical analyses were filtered (0.7 µm pore size Whatman™ GF/F filters, GE, Healthcare, Boston, MA, USA) to remove particles and stored at 4°C until analyses. Nitrate and nitrite (called N-NO₃⁻ thereafter because N-NO₂⁻ concentrations were negligible compared with N-NO₃⁻ concentrations), chloride (Cl⁻) and silica (SiO₂) concentrations were measured following standard colorimetric methods, using an automatic analyzer (Spectrochem 200, AMS Alliance, Frépillon, France).

2.4. Isotopic analyses

Samples for isotopic analyses were transferred in glass tubes with screw caps to prevent evaporation during storage. The tubes were filled to avoid headspace and water-air equilibration prior to analyses. Oxygen isotope ($\delta^{18}\text{O}$) of the water molecule were measured on samples stored at 4°C using a continuous flow CO₂ equilibration technique (Epstein and Mayeda's 1953; Horita et al., 1989; McCarthy et al., 2005). The analyses were carried out using an isoFLOW automated system (Elementar UK Ltd – Cheadle Hulme UK) configured

in water equilibration mode connected on line in continuous flow mode to a precisiON mass spectrometer (Elementar UK Ltd – Cheadle Hulme UK). Both systems were operated by a visION software developed by Elementar Uk Ltd. 200 μL aliquots of waters were loaded in non-evacuated LABCO Exetainer® 3.7 mL soda glass vials, round bottomed. The sample vial headspace was automatically flushed by helium gas through the isoFLOW double needle setup. The equilibration gas was a mixture of 10% CO_2 in helium. This gas mixture was automatically introduced in contact with the water sample through the isoFLOW valve system. The equilibration reaction took place in a temperature regulated sample tray at 40°C for at least 5 hours (Lécuyer et al., 2009). Once equilibrated, the CO_2 gas was then transferred to the mass spectrometer via the centrION interface. Monitoring gas was a calibrated CO_2 gas. In order to anchor the results to the VSLAP/VSMOW scale, calibrated waters were analysed in the same batches as the water samples. The water working standards were calibrated against the WICO calibrated waters from the WICO intercalibration program (Wassenaar et al., 2018). The working standard used were Apollo ($\delta^{18}\text{O}_{\text{VSMOW}} = -10.05\text{‰}$), EE1 ($\delta^{18}\text{O}_{\text{VSMOW}} = +6.44\text{‰}$), LKD2 ($\delta^{18}\text{O}_{\text{VSMOW}} = -20.95\text{‰}$) and LKD3 ($\delta^{18}\text{O}_{\text{VSMOW}} = -26.03\text{‰}$). Aliquots of Apollo water were placed at the beginning and at the end of each analytical batch to check for potential instrumental drift with time. No significant drift was noticed during the experiments. Delta values are expressed with respect to VSMOW. Although the SI units to report isotopic ratios is the Urey (Ur), the traditional “‰” (permil) notation with $1\text{‰} = 1\text{mUr}$ was used for commodity. Typical external precision for ^{18}O analyses from water samples is 0.05‰ . Samples were systematically run in triplicate.

Deuterium isotope ($\delta^2\text{H}$) method analysis was based on water reduction using a chromium-based reactor following the protocol described by Morrison et al. (2001). Analyses were performed with a EuroEA3028-HTTM elemental analyser from Eurovector SpA (Milan-Italy). This elemental analyser was configured with a EuroAS300 series liquid autosampler

with a heated injector port equipped with a 1 μL 1BR-5 SGE syringe. The elemental analyser was connected online in continuous flow mode to an IsoPrime Isotopic Ratio Mass Spectrometer from Elementar UK Ltd (Cheadle Hulme-UK). The mass spectrometer was equipped with an electrostatic filter to prevent from helium interferences on hydrogen mass 3 beams. The H_3^+ factor was calculated every day and was usually below 5 ppm/nA. The duration for each analytical run is approximately 300 s. Water samples collected were pipetted into 13x32 mm vials with butyl/Teflon sealed caps. Five injections were performed from each water sample. Hydrogen isotope ratios were reported relative to VSMOW in the ‰ unit, after scaling the raw data to the isotopic ratios of calibrated waters from the WICO inter calibration program (Wassenaar et al., 2018). Drift correction was evaluated using the working standard water EE1 ($\delta^2\text{H}_{\text{VSMOW}} = +12.5$ ‰). Typical external precision for $\delta^2\text{H}$ analyses from water samples is 0.5‰.

2.5. Suspect screening of contaminants of emerging concern (CECs)

Passive samplers were deployed during 14 days to sequester CECs like polar pesticides and pharmaceuticals from groundwater and surface water of the 10 sampling locations. Passive samplers were based on polystyrene divinylbenzene (SDB-XC) AttractSPE® disks (47 mm diameter, 12 mm particle size, 0.5 mm thick) purchased from Affinisep (Le Houllme, France). SDB-XC SPE disks are suitable to sequester organic chemical with octanol/water partition coefficient at $\text{pH} = 7.4$ ($\log D_{\text{OW}} \leq 4$) (Charriau et al., 2016). Deployment rigs were designed to fit into piezometer dimensions (see details in Pinasseau et al., 2019). They were placed inside piezometers one meter below the lowest groundwater level recorded since 2016 (Table S1). Each rig held 8 individual SPE disks to obtain duplicated analyses per rig (each SPE disk being extracted independently). Details of SPE disks preparation before deployment in the field and extraction after retrieval are given in Pinasseau et al. (2019). A blank sampler

(procedural blank) was prepared using the same procedure to account for any contamination during each operation. Passive sampler adsorption kinetics are given in Pinasseau et al. (2020a).

Extracts were analysed using an Ultimate 3000 UHPLC system (Thermo Scientific®, MA, USA) equipped with a binary pump and reversed-phase analytical column, coupled to a quadrupole time-of-flight mass spectrometer (Q-ToF) (Maxis Plus, Bruker Daltonics®, Bremen, Germany). Data Analysis® 4.4 and Target Analysis for Screening and Quantitation (TASQ)® 1.4 (Bruker Daltonics®) were used for data processing. TASQ® 1.4 includes two databases (PesticideScreener 2.1 and ToxScreener 2.1) of about 2500 pesticide and pharmaceutical compounds. Separations were carried out using an Acclaim RSLC C18 column (2.1 × 100 mm, 2.2 µm particles, Thermo Fischer Scientific) maintained at 30 °C; the injection volume was 5 µL. The mobile phases consisted of: (A) water/methanol (90/10, v/v); and (B) methanol; with 5 mM ammonium formate and 0.01% formic acid in both phases for positive ionization mode. The analysis were performed in DIA mode (Data Independent Analysis) over the mass range of 80–1000 Da (see Pinasseau et al., 2019 for details on the gradient elution and mass spectrometer parameters).

For quality assurance/quality control (QA/QC), mass accuracy of the detector was monitored at the beginning of each run with a calibrant. A quality control was injected every 14 analyses to check for retention times and sensitivity during data acquisition. This quality control was a mix of standard solution of 53 compounds at 40 µg L⁻¹ in water/methanol (90/10, v/v). These compounds were also used to correct the database retention times. Background signals were identified by analysis of blanks (solvent blank and procedural blank). Solvent blanks were also injected to monitor column carryover.

Data process was performed using suspect screening strategy. Briefly, experimental sample data were compared with theoretical data from databases for each compound. Criteria used for evaluation of precursor and product ions were retention time, mass-to-charge (m/z) ratio and isotopic pattern. Deviations between experimental and theoretical data were scored 1 (high confidence score), 2 (medium confidence score) or 3 (low confidence score) according to tolerance thresholds set for each of the three criteria (see details in Pinasseau et al., 2019). Additionally, the detection of at least one product ion for each precursor ion was mandatory and manual verification of chromatographic peak shapes, $\Delta m/z$ and signal-to-noise (S/N) ratios was carried out in order to reduce false positives. The compounds detected in solvent blank and procedural blank were removed from the final list of detected CECs if they were ubiquitous and/or if the peak area of compounds detected in blanks was higher than 1/3 of the peak area of the same compounds in the field exposed samplers.

2.6. Statistical analysis

To characterize the hydrochemical conditions of sampling points, a Principal Component Analysis (PCA) was performed on hydrochemical and isotopic tracers and electrical conductivity using the R package FactoMineR (Lê et al., 2008), followed by a Hierarchical Clustering on PCA scores (Ward method based on Euclidean distances) to discriminate sample clusters based on hydrochemistry. The mean of each hydrochemical tracer, isotopic tracer and electrical conductivity was then compared among clusters through ANOVA tests. When significant differences were detected, Tukey's HSD post-hoc tests ($p < 0.05$) were performed to determine which clusters differed. The Shapiro-Wilk's test and the Bartlett's test were used to verify the statistical assumptions of normality and homoscedasticity respectively. When these assumptions were not verified, values of hydrochemical tracers, isotopic tracers and electrical conductivity were compared among clusters using Kruskal-

Wallis' tests ($p < 0.05$). When significant differences were detected, Wilcoxon's tests ($p < 0.05$) were performed to determine which clusters differed.

A correspondence analysis (CA) was performed on the presence/absence of the detected CECs to visualize and compare the seven groundwater and the three surface water sampling locations for the two sampling campaigns. A Hierarchical Clustering on CA scores (Ward method based on Euclidean distances) was then performed to discriminate sample clusters. This method allowed to qualitatively regroup the sampling locations characterized by comparable CECs fingerprints.

All statistical analyses were carried out using R version 4.1.2 software (R Development Core Team, 2017).

3. Results and discussion

Hydrochemical and isotopic tracers as well as electrical conductivity were used in combination with CECs to better understand the influence of groundwater bodies (Est-Lyonnais and Dombes aquifers) and surface water bodies (Jonage river, Miribel channel and Vieux-Rhône river) on the Rhône alluvial aquifer used for drinking water production on the Crépieux-Charmy catchment area. CECs were also used for mapping groundwater vulnerability.

3.1 Wellfield groundwater bodies: evidence from hydrochemical and isotopic tracers

PCA was performed using chloride, nitrate and silica concentrations, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values and electrical conductivity of the seven groundwater and the three surface water sampling locations for the two sampling campaigns (Figure 2). Dimensions 1 and 2 of the PCA explained 92% of the variability contained in the data matrix, with 73% on the first axis

(Figure 2a). The correlation circle indicates which tracers had the same distributions among samples. For example, chlorides and silica presented the same distribution among samples with the highest concentrations obtained for samples having a positive score on the dimension 1 and a negative score on the dimension 2 like the samples done in W7 for the two campaigns (Figure 2b).

Hierarchical Clustering on PCA scores allowed to classify the 10 sampling locations into 3 clusters characterized by different concentrations in chloride, nitrate and silica (Kruskal-Wallis' tests, $p < 0.05$ for the three tracers), different water signatures in ^{18}O and ^2H (one-way ANOVAs, $p < 0.05$ for the two isotopic tracers), and different electrical conductivities (Kruskal-Wallis' test, $p < 0.05$).

The cluster 1 is composed of all samples collected in surface water (i.e. Jonage river, Miribel channel and Vieux-Rhône river) and almost all samples collected in groundwater sampling locations (i.e. W1, W2, W3, W4 and W5) (Figure 2b). For these samples, chlorides, nitrate and silica concentrations were comparable (i.e. about 10, 4 and 3 mg L^{-1} respectively; Table 1) as well as $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values (i.e. about -10 and -72 ‰ respectively; Figure 3, Table S3) and electrical conductivity (i.e. about 374 $\mu\text{S cm}^{-1}$; Table S2). The comparable hydrochemical and isotopic values of surface water and groundwater suggest a rapid transfer of water from surface to the alluvial aquifer (Marçais et al., 2018). Consequently, it can be hypothesized that, at the Crépieux-Charmy wellfield, the Rhône alluvial aquifer is mainly recharged by the Rhône surface water, with short hydrological transfers due to an intensive recharge by bank filtration.

The cluster 2 comprises only samples from W7 location (Figure 2b). These samples were characterized by significantly higher chloride and silica concentrations (i.e. about 32 and 18 mg L^{-1} respectively; Table 1) and significantly lower nitrate concentrations (i.e. about 0.5 mg L^{-1} respectively; Table 1).

L^{-1} ; Table 1) than samples from cluster 1 (Wilcoxon's tests, $p < 0.05$ for the 3 parameters). These samples were also enriched in ^{18}O and 2H in comparison with samples from cluster 1 (i.e. about -9 and -63 ‰ respectively; Figure 3, Table S3) and presented significantly higher electrical conductivity (i.e. about $1400 \mu S cm^{-1}$; Table S2) than samples from cluster 1 (Tukey's HSD post-hoc tests, $p < 0.01$ for ^{18}O and 2H ; Wilcoxon, $p < 0.05$ for electrical conductivity). These results highlight that the W7 sampling point is located in a different water body than samples from the cluster 1. Since W7 is located on the right riverbank of the Miribel channel, just outside the wellfield, it can be assumed that the Dombes aquifer was detected at this sampling point (Figure 1). Indeed, the watershed associated with the Dombes aquifer extends to a lower average altitude than the Rhône alluvial aquifer (BURGEAP, 2015), explaining the enrichment of water in $\delta^{18}O_{VSMOW}$ and δ^2H_{VSMOW} compared with samples collected in the alluvial aquifer of the Rhône River (Figure 3, Table S3).

The cluster 3 is only associated with samples collected in W6 (Figure 2b). W6 samples were characterized by significantly higher nitrate, chloride and silica concentrations (i.e. about 13, 18 and $9 mg L^{-1}$ respectively; Table 1) than samples from cluster 1 as well as significantly higher electrical conductivity (i.e. about $591 \mu S cm^{-1}$; Table S2) (Wilcoxon's tests, $p < 0.05$ for the 4 parameters). The higher nitrate concentrations and electrical conductivity measured in W6 samples in comparison with samples from cluster 1 could be due to the presence of a groundwater flow coming to the studied site from the Est-Lyonnais aquifer by the south (Figure 1) via the fluvio-glacial corridors of Meyzieu and Décines (Figure S1). Indeed, nitrate concentrations of the Est-Lyonnais aquifer have been reported to be comprised between 22 and $89 mg L^{-1}$ with an average concentration of $44 mg L^{-1}$ and electrical conductivities were reported between 550 and $750 \mu S cm^{-1}$ (Mermillod-Blondin et al., 2019; Voisin et al., 2018). Therefore, groundwater collected at the W6 sampling location probably corresponded to a mixing of waters from the Rhône alluvial and the Est-Lyonnais aquifers.

Overall, no significant seasonal effects were observed with similar hydrochemical tracer concentrations between the summer and autumn campaigns for the three clusters.

3.2 Insights from contaminants of emerging concerns (CECs)

The application of passive sampling in combination with the suspect screening allowed the detection of 125 contaminants among the 2500 pesticides and pharmaceuticals in the database. One hundred and nine CECs were detected in surface water samples and 51 in groundwater samples. Compound class, formula, theoretical exact masses, theoretical retention times, detection rates for the two sampling campaigns as well as global confidence scores are details in Table S4. From the 51 CECs detected in groundwater, 40 were detected with a global confidence score 1 or 2 (i.e. high or medium), including 22 pesticides and related transformation products (TPs), 15 pharmaceuticals and related TPs and 3 pharmaceutical-like products (Table 2). Octanol/water partition coefficient at pH = 7.4 ($\log D_{OW}$) and soil adsorption coefficient (K_{OC}) are parameters used to predict the behaviour and occurrence of molecules in groundwater. In our case, all detected CECs have $\log D_{OW}$ comprised between -3.1 and 3.2, indicating that they are likely to move easily in water due to their high polarity. Similarly, K_{OC} values ranged between 1 (highly mobile) and 1337 mL g⁻¹ (slightly mobile) with a median value of 34 mL g⁻¹, showing that most detected CECs were mobile. Several CECs corresponded to historical contaminants commonly reported in the literature like atrazine and TPs, caffeine, carbamazepine, carbendazim, simazine and sulfamethoxazole (Bunting et al., 2021; Lapworth et al., 2012; Loos et al., 2010; Lopez et al., 2015). In addition, emerging contaminants, which have never been or rarely reported in the literature were also identified such as amidosulfuron, coumachlor, tritosulfuron, lamotrigine and warfarin (see Table S4 for compound class). Moreover, no differences were detected between the two campaigns as CECs detected during the summer campaign were generally detected during the autumn campaign (Table 2).

A correspondence analysis (CA) was performed on CECs detected from the seven groundwater and the three surface water sampling locations for the two sampling campaigns (Figure 4). Dimensions 1 and 2 of the CA explained 53% of the variability contained in the data matrix, with 27% on the first axis. Hierarchical Clustering on CA scores allowed to classify the 10 sampling locations into 3 clusters (Figure 4a).

The cluster A includes the samples collected in the three Rhône surface water locations (i.e. Jonage river, Miribel channel and Vieux-Rhône river) (Figure 4a). Detected CECs in these samples were historical (e.g. atenolol, diclofenac, terbuthylazine, tramadol) (Mathon, 2022; Tröger et al., 2021; Wilkinson et al., 2022) and emerging concern contaminants (e.g. amfepramone, lacosamide, niflumic acid) (Figure 4b and Table S4).

The cluster B comprises most of the groundwater samples collected in the Rhône alluvial aquifer (i.e. W1, W2, W3, W4, W5, W6). It is characterized by the detection of historic groundwater contaminants such as atrazine and related TPs, carbendazim, carbamazepine and related TPs, simazine and sulfamethoxazole (Figure 4b and Table 2), which have been reported in French and European groundwater for years (Bunting et al., 2021; Lapworth et al., 2012; Loos et al., 2010; Lopez et al., 2015). However, some more unusual contaminants were also associated with cluster B such as lamotrigine, nicosulfuron and thiazafluron (see Table S4 for compound class). It is worth considering that W6 samples belonged to cluster B as samples located on the Rhône alluvial aquifer whereas they were clearly distinct on the PCA analysis based on hydrochemical and isotopic tracers (Figure 2b). The few detected CECs (13) in W6 samples were the same as those detected in the Rhône alluvial aquifer samples (Table 2). Besides, most CECs detected in locations belonging to cluster B were also found in samples of cluster A. However, clusters A and B were discriminated because surface water samples of cluster A were characterized by specific CECs not detected in groundwater locations. This is also due to the fact that more CECs were accumulated in passive samplers

located in surface water than in groundwater sampling point given that CECs uptake is flow dependent (Charriau et al., 2016; Vrana et al., 2006).

The cluster C was associated with samples collected in W7 (Figure 4a) which were contaminated by pharmaceuticals of emerging concern such as methylephedrine, tolbutamide and warfarin (see Table S4 for compound class) (Figure 4b and Table 2), which have never been reported in the groundwater literature. Likewise, the rodenticide coumachlor detected in the W7 sampling point has never been documented in any aquatic environment. These results on CECs were consistent with hydrochemistry analyses demonstrating that W7 sampling point was located in a different groundwater body than the Rhône alluvial aquifer. In addition, the acidic pH and anoxic conditions measured in W7 (Table S2) could also explain why the CECs collected at this location were different from those associated with the Rhône alluvial aquifer. As it has been reported before, pH and redox conditions likely have an influence on CECs biodegradation and adsorption/desorption processes in soils (Greskowiak et al., 2017; Luo et al., 2019; Valhørd et al., 2018).

3.3 Complementarity of hydrochemistry and CECs for characterizing water bodies

Overall, groundwater bodies identified with hydrochemical and isotopic tracers (Figure 2) were also pointed out with the CECs (Figure 4). Rhône river samples (cluster A) were distinguished from Rhône alluvial aquifer samples (cluster B) as more CECs were detected in surface waters than in groundwater (Figure 4). The fact that W7 sampling location (cluster C) was clearly isolated from other clusters on the correspondence analysis on CECs also demonstrates the ability of CECs to distinguish water bodies by providing a chemical fingerprint of groundwater. Such interpretation corroborates the study of Stuart et al. (2014) who argued that a cocktail of micropollutants could be used to characterize groundwater bodies. Nevertheless, to be suitable as groundwater tracers to establish chemical fingerprint,

CECs have to be persistent in the subsurface environment and thus, the attenuation of contaminants have to be taken into consideration (Currell et al., 2022; McCance et al., 2018; Stuart et al., 2014). In the present study, contaminant attenuations likely occurred and were largely expected from data obtained from W6. Indeed, when considering CECs, groundwater collected from W6 had the signature of the Rhône alluvial aquifer (Figure 4). In contrast, when considering hydrochemical and isotopic tracers, its chemistry was distinct from the other sampling points, highlighting a mixing of waters from the Rhône alluvial aquifer and the Est-Lyonnais aquifer (Figure 2). This discrepancy between CECs data and hydrochemical analyses could have been due to the adsorption, the degradation and/or the dilution of the CECs commonly measured in the Est-Lyonnais aquifer during their transfer to the W6 sampling location. Effectively, analyses done in the Est-Lyonnais aquifer with the same methodology detected ubiquitous contaminants such as hexazinone and metolachlor (Pinasseau et al., 2020b, 2019), that were not detected in the present study. Hence, it supports the statement of Gasser et al. (2014) and Massmann et al. (2008) who underlined that the application of several tracers is necessary to avoid missing crucial information on subsurface processes. As specified by Meck et al. (2017), the use of multiple tracers also permits to minimize uncertainties in water body characterization when the chemical characteristics of water sources are not strongly contrasted.

The persistence of CECs also provides useful information on groundwater residence time and self-purification capacities. For instance, the presence of caffeine (Table 2), a marker of recent anthropogenic contamination due to its rapid degradation in the environment, is an evidence of a rapid transfer of water from surface (where contamination occurred) to groundwater (Koroša et al., 2020; Lapworth et al., 2018). In contrast, the occurrence of persistent CECs such as carbamazepine and sulfamethoxazole (Table 2) can reflect the low self-purification capacities of the aquifer (Fram and Belitz, 2011). The application of passive

sampling in combination with suspect screening enabled a more accurate assessment of groundwater chemical fingerprint. It allowed the detection of CECs usually found at very low concentration and/or usually not investigated (Godlewska et al., 2021; Leendert et al., 2015; Taylor et al., 2021). For instance, CECs only detected at the W7 sampling location (i.e. methylephedrine, tolbutamide and warfarin) would not have been detected and/or investigated with conventional spot sampling and target analysis method.

3.4 Groundwater-surface water interactions and assessment of potential vulnerability areas

The mean number of detected CECs during the two campaigns for each groundwater sampling location are shown in Figure 5. The greatest number of detected CECs were found at W3, W2 and W1 sampling locations (from 24 to 31 CECs), with the majority of the detected CECs shared with surface water (8 ± 1 , 81 ± 1 and 91 ± 2 % for W3, W2 and W1 respectively). It is worth noting that these three sampling locations are the closest to the upstream riverbanks (i.e. ≤ 50 m) (Figure S1). Moreover, hourly monitoring of groundwater table levels, DO concentrations and temperatures in W3 and W1 during the experiment followed the fluctuations of the same variables in surface water (Figure S2). These results clearly highlighted that W3 and W1 locations were highly connected to surface water bodies.

In comparison with samples collected from these sampling locations (W1, W2, W3), W7 and W5 contained slightly fewer CECs. All CECs detected in W5 were also present in surface waters and were probably less abundant than in W1 and W3 because this location was less connected to water surface bodies (Figure 5). In comparison, the lowest number of CECs shared with surface water (56 ± 1 %) were detected in W7 because, as underlined by hydrochemical, isotopic tracers and CECs, this sampling point was located in a different water body (i.e. Dombes aquifer; Figures 2 and 4) than the other sampling locations. Indeed,

several pharmaceuticals were only detected in W7 (Table 2 and Figure 4). The lack of water treatment plant or hospital in the vicinity of W7 that could explain the occurrence of these pharmaceuticals suggests a sewage leakage (as observed by Gaston et al., 2019). This observation reveals the usefulness of the methodology based on passive sampling and suspect screening to detect unexpected sources of contamination.

Sampling locations W6 and W4 which were the farthest from upstream riverbanks (i.e. ≥ 200 m) (Table S1) exhibited the lowest numbers of detected CECs (Figure 5). We could expect to detect higher numbers of CECs in W6 given that this sampling location was influenced by the Est-Lyonnais aquifer (Figure 2) that is contaminated with around 70 pesticides and pharmaceuticals (Pinasseau et al., 2019) with median concentrations of about 10 ng L^{-1} (Marmonier et al., 2013; Pinasseau et al., 2020a). However, very few CECs were detected in W6 samples and all of them were also detected in surface waters (Table 2 and Figure 5). We can thus expect that the transfer of groundwater from the East-Lyonnais aquifer to W6 location in the wellfield site was long enough to allow the degradation and/or adsorption of contaminants (Greskowiak et al., 2017; Pitt et al., 1999; Vystavna et al., 2017). Overall, the number of detected CECs at a location appeared to be primarily related to the proximity of this location to rivers (i.e. distance from the nearest upstream riverbanks).

4. Conclusions

This study was the first to combine CECs determined by passive sampling and suspect screening with hydrochemical and isotopic tracer data. This approach allowed improving the determination of groundwater origins and vulnerability. By increasing the sensitivity of the analytical method and the number of CECs that can be investigated, passive sampling and suspect screening provided an in-depth chemical fingerprint of groundwater bodies. This is essential when CECs are used as anthropogenic markers and / or tracers of groundwater

where they occur at very low concentrations, such as wellfield aquifers. Cocktails of CECs combined with hydrochemical and isotopic tracer data were proven to be useful to differentiate water bodies. In addition, occurrence and type of CECs contributed to a better understanding of short-time hydrological processes and groundwater-surface water interactions. Finally, passive sampling and suspect screening improved identification of potential vulnerability areas by allowing the investigation and detection of usually understudied contaminants. In the future, it would be relevant to assess the influence of hydrological and hydrogeological factors (e.g. river water levels, wellfield exploitation) on the findings of this study. Moreover, it would be of great interest to quantify some CECs after their accumulation on passive sampler to improve the understanding of the water flow as undertaken by Erostate et al. (2019) and Moeck et al. (2017), and for groundwater quality assessment purposes.

Acknowledgements

This work was supported by Métropole de Lyon. The authors thank the Greater Lyon Water Agency, the Rhone Mediterranean Corsica Water Agency and the Auvergne Rhône Alpes Region for logistic and financial support. We also acknowledge Yohan Lebon and Simon Navel for assisting with the field work. The $^{18}\text{O}/^{16}\text{O}$ measurements from water samples were done at the “Plateforme d’Ecologie Isotopique” (CNRS-UMR5023-LEHNA) member of the RéGEF network in Lyon (www.regef.fr/spectrometre-stables).

References

- Akay Demir, A.E., Dilek, F.B., Yetis, U., 2019. A new screening index for pesticides leachability to groundwater. *J. Environ. Manage.* 231, 1193–1202. <https://doi.org/10.1016/j.jenvman.2018.11.007>
- Banzhaf, S., Krein, A., Scheytt, T., 2012. Using selected pharmaceutical compounds as indicators for surface water and groundwater interaction in the hyporheic zone of a low permeability riverbank: SELECTED PHARMACEUTICALS AS INDICATORS

- IN A LOW PERMEABILITY RIVERBANK. *Hydrol. Process.* n/a-n/a.
<https://doi.org/10.1002/hyp.9435>
- Benischke, R., 2021. Review: Advances in the methodology and application of tracing in karst aquifers. *Hydrogeol. J.* 29, 67–88. <https://doi.org/10.1007/s10040-020-02278-9>
- Blumstock, M., Tetzlaff, D., Malcolm, I.A., Nuetzmann, G., Soulsby, C., 2015. Baseflow dynamics: Multi-tracer surveys to assess variable groundwater contributions to montane streams under low flows. *J. Hydrol.* 527, 1021–1033. <https://doi.org/10.1016/j.jhydrol.2015.05.019>
- Böhlke, J.-K., 2002. Groundwater recharge and agricultural contamination. *Hydrogeol. J.* 10, 153–179. <https://doi.org/10.1007/s10040-001-0183-3>
- Bourg, A.C.M., Bertin, C., 1993. Biogeochemical processes during the infiltration of river water into an alluvial aquifer. *Environ. Sci. Technol.* 27, 661–666. <https://doi.org/10.1021/es00041a009>
- Brack, W., Dulio, V., Ågerstrand, M., Allan, I., Altenburger, I., Brinkmann, M., Bunke, D., Burgess, R.M., Cousins, I., Escher, B.I., Hernández, F.J., Hewitt, L.M., Hilscherová, K., Hollender, J., Hollert, H., Kase, R., Klauer, B., Lindin, C., Herráez, D.L., Miège, C., Munthe, J., O’Toole, S., Posthuma, L., Rüdol, H., Schäfer, R.B., Sengl, M., Smedes, F., van de Meent, D., van den Brink, P.J., van Gils, J., van Wezel, A.P., Vethaak, A.D., Vermeirssen, E., von der Ohe, F.C., Vrana, B., 2017. Towards the review of the European Union Water Framework Directive: Recommendations for more efficient assessment and management of chemical contamination in European surface water resources. *Sci. Total Environ.* 576, 720–737. <https://doi.org/10.1016/j.scitotenv.2016.10.104>
- Bunting, S.Y., Lapworth, D.J., Crane, E.J., Grima-Olmedo, J., Koroša, A., Kuczyńska, A., Mali, N., Rosenqvist, L., van Viet, M.E., Togola, A., Lopez, B., 2021. Emerging organic compounds in European groundwater. *Environ. Pollut.* 269, 115945. <https://doi.org/10.1016/j.envpol.2020.115945>
- BURGEAP, 2015. Champ captant de Crépieux Charmy (69): Analyse des relations de la nappe alluviale entre rives droite et gauche du Canal de Miribel. In French
- Charriau, A., Lissalde, S., Pouliot, G., Mazzella, N., Buzier, R., Guibaud, G., 2016. Overview of the Chemcatcher® for the passive sampling of various pollutants in aquatic environments Part A: Principles, calibration, preparation and analysis of the sampler. *Talanta* 148, 556–571. <https://doi.org/10.1016/j.talanta.2015.06.064>
- Craig, H., 1961. Isotopic Variations in Meteoric Waters. *Science* 133, 1702–1703. <https://doi.org/10.1126/science.133.3465.1702>
- Currell, M., McCance, W., Jones, O.A.H., 2022. Novel molecular tracers for the assessment of groundwater pollution. *Curr. Opin. Environ. Sci. Health* 26, 100331. <https://doi.org/10.1016/j.coesh.2022.100331>
- Dabrowski, J.M., Shadung, J.M., Wepener, V., 2014. Prioritizing agricultural pesticides used in South Africa based on their environmental mobility and potential human health effects. *Environ. Int.* 62, 31–40. <https://doi.org/10.1016/j.envint.2013.10.001>
- Díaz-Puga, M.A., Vallejos, A., Sola, F., Daniele, L., Molina, L., Pulido-Bosch, A., 2016. Groundwater flow and residence time in a karst aquifer using ion and isotope characterization. *Int. J. Environ. Sci. Technol.* 13, 2579–2596. <https://doi.org/10.1007/s13762-016-1094-0>
- Dillon, P., 2005. Future management of aquifer recharge. *Hydrogeol. J.* 13, 313–316. <https://doi.org/10.1007/s10040-004-0413-6>
- Erostate, M., Huneau, F., Garel, E., Vystavna, Y., Santoni, S., Pasqualini, V., 2019. Coupling isotope hydrology, geochemical tracers and emerging compounds to evaluate mixing

- processes and groundwater dependence of a highly anthropized coastal hydrosystem. *J. Hydrol.* 578, 123979. <https://doi.org/10.1016/j.jhydrol.2019.123979>
- Foulquier, A., Mermillod-Blondin, F., Malard, F., Gibert, J., 2011. Response of sediment biofilm to increased dissolved organic carbon supply in groundwater artificially recharged with stormwater. *J. Soils Sediments* 11, 382–393. <https://doi.org/10.1007/s11368-010-0323-2>
- Fram, M.S., Belitz, K., 2011. Occurrence and concentrations of pharmaceutical compounds in groundwater used for public drinking-water supply in California. *Sci. Total Environ.* 409, 3409–3417. <https://doi.org/10.1016/j.scitotenv.2011.05.053>
- Gasser, G., Pankratov, I., Elhanany, S., Glazman, H., Lev, O., 2014. Calculation of wastewater effluent leakage to pristine water sources by the weighted average of multiple tracer approach. *Water Resour. Res.* 50, 4269–4282. <https://doi.org/10.1002/2013WR014377>
- Gaston, L., Lapworth, D.J., Stuart, M., Arnscheidt, J., 2019. Prioritization Approaches for Substances of Emerging Concern in Groundwater: A Critical Review. *Environ. Sci. Technol.* 53, 6107–6122. <https://doi.org/10.1021/acs.est.8b04490>
- Godlewska, K., Stepnowski, P., Paszkiewicz, M., 2021. Pollutant analysis using passive samplers: principles, sorbents, calibration and applications. A review. *Environ. Chem. Lett.* 19, 465–520. <https://doi.org/10.1007/s10311-020-01079-6>
- Greskowiak, J., Hamann, E., Burke, V., Massmann, G., 2017. The uncertainty of biodegradation rate constants of emerging organic compounds in soil and groundwater – A compilation of literature values for 82 substances. *Water Res.* 126, 122–133. <https://doi.org/10.1016/j.watres.2017.09.017>
- Gunold, R., Schäfer, R.B., Paschke, A., Schürmann, G., Liess, M., 2008. Calibration of the Chemcatcher® passive sampler for monitoring selected polar and semi-polar pesticides in surface water. *Environ. Pollut.* 155, 52–60. <https://doi.org/10.1016/j.envpol.2007.10.037>
- Hem, J.D., 1985. Study and interpretation of the Chemical Characteristics of Natural Water. U.S Geological Survey Water Paper 2254. <https://doi.org/10.3133/wsp2254>
- Innocent, C., Kloppmann, W., Millot, R., Vaute, L., 2021. A multi-isotopic study of the groundwaters from the Lower Triassic Sandstones aquifer of northeastern France: Groundwater origin, mixing and flowing velocity. *Appl. Geochem.* 131, 105012. <https://doi.org/10.1016/j.apgeochem.2021.105012>
- Jones, L., Ronan, J., McHugh, B., McGovern, E., Regan, F., 2015. Emerging priority substances in the aquatic environment: a role for passive sampling in supporting WFD monitoring and compliance. *Anal. Methods* 7, 7976–7984. <https://doi.org/10.1039/C5AY01059D>
- Koroša, A., Brenčič, M., Mali, N., 2020. Estimating the transport parameters of propyphenazone, caffeine and carbamazepine by means of a tracer experiment in a coarse-gravel unsaturated zone. *Water Res.* 175, 115680. <https://doi.org/10.1016/j.watres.2020.115680>
- Kralik, M., Humer, F., Fank, J., Harum, T., Klammler, G., Gooddy, D., Sültenfuß, J., Gerber, C., Purtschert, R., 2014. Using $^{18}\text{O}/^{2}\text{H}$, $^3\text{H}/^3\text{He}$, ^{85}Kr and CFCs to determine mean residence times and water origin in the Grazer and Leibnitzer Feld groundwater bodies (Austria). *Appl. Geochem.* 50, 150–163. <https://doi.org/10.1016/j.apgeochem.2014.04.001>
- Kurukulasuriya, D., Howcroft, W., Moon, E., Meredith, K., Timms, W., 2022. Selecting Environmental Water Tracers to Understand Groundwater around Mines: Opportunities and Limitations. *Mine Water Environ.* 41, 357–369. <https://doi.org/10.1007/s10230-022-00845-y>

- Kurylyk, B.L., Irvine, D.J., Bense, V.F., 2019. Theory, tools, and multidisciplinary applications for tracing groundwater fluxes from temperature profiles. *WIREs Water* 6. <https://doi.org/10.1002/wat2.1329>
- Lapworth, D.J., Baran, N., Stuart, M.E., Manamsa, K., Talbot, J., 2015. Persistent and emerging micro-organic contaminants in Chalk groundwater of England and France. *Environ. Pollut.* 203, 214–225. <https://doi.org/10.1016/j.envpol.2015.02.030>
- Lapworth, D.J., Baran, N., Stuart, M.E., Ward, R.S., 2012. Emerging organic contaminants in groundwater: A review of sources, fate and occurrence. *Environ. Pollut.* 163, 287–303. <https://doi.org/10.1016/j.envpol.2011.12.034>
- Lapworth, D.J., Das, P., Shaw, A., Mukherjee, A., Civil, W., Petersen, J.O., Goody, D.C., Wakefield, O., Finlayson, A., Krishan, G., Sengupta, P., MacDonald, A.M., 2018. Deep urban groundwater vulnerability in India revealed through the use of emerging organic contaminants and residence time tracers. *Environ. Pollut.* 240, 938–949. <https://doi.org/10.1016/j.envpol.2018.04.053>
- Lê, S., Josse, J., Husson, F., 2008. FactoMineR: An R Package for Multivariate Analysis. *J. Stat. Softw.* 25. <https://doi.org/10.18637/jss.v025.i01>
- Lécuyer, C., Gardien, V., Rigaudier, T., Fourel, F., Martineau, F., Cros, A., 2009. Oxygen isotope fractionation and equilibration kinetics between CO₂ and H₂O as a function of salinity of aqueous solutions. *Chem. Geol.* 264, 122–126. <https://doi.org/10.1016/j.chemgeo.2009.02.017>
- Leendert, V., Van Langenhove, H., Demeestere, K., 2015. Trends in liquid chromatography coupled to high-resolution mass spectrometry for multi-residue analysis of organic micropollutants in aquatic environments. *TrAC Trends Anal. Chem.* 67, 192–208. <https://doi.org/10.1016/j.trac.2015.01.010>
- Loizeau, S., Rossier, Y., Gaudet, J.-F., Pefloch, A., Besnard, K., Angulo-Jaramillo, R., Lassabatere, L., 2017. Water infiltration in an aquifer recharge basin affected by temperature and air entrapment. *J. Hydrol. Hydromech.* 65, 222–233. <https://doi.org/10.1515/johh-2017-0010>
- Loos, R., Locoro, G., Comero, S., Confini, S., Schwesig, D., Werres, F., Balsaa, P., Gans, O., Weiss, S., Blaha, L., Bolchi, M., Gawlik, B.M., 2010. Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water. *Water Res.* 44, 4115–4126. <https://doi.org/10.1016/j.watres.2010.05.032>
- Lopez, B., Ollivier, P., Togola, A., Baran, N., Ghestem, J.-P., 2015. Screening of French groundwater for regulated and emerging contaminants. *Sci. Total Environ.* 518–519, 562–573. <https://doi.org/10.1016/j.scitotenv.2015.01.110>
- Luo, Y., Atashgahi, S., Pajnaarts, H.H.M., Comans, R.N.J., Sutton, N.B., 2019. Influence of different redox conditions and dissolved organic matter on pesticide biodegradation in simulated groundwater systems. *Sci. Total Environ.* 677, 692–699. <https://doi.org/10.1016/j.scitotenv.2019.04.128>
- Marçais, J., Gauvain, A., Labasque, T., Abbott, B.W., Pinay, G., Aquilina, L., Chabaux, F., Viville, D., de Dreuzy, J.-R., 2018. Dating groundwater with dissolved silica and CFC concentrations in crystalline aquifers. *Sci. Total Environ.* 636, 260–272. <https://doi.org/10.1016/j.scitotenv.2018.04.196>
- Marmonier, P., Maazouzi, C., Foulquier, A., Navel, S., François, C., Hervant, F., Mermillod-Blondin, F., Vieney, A., Barraud, S., Togola, A., Piscart, C., 2013. The use of crustaceans as sentinel organisms to evaluate groundwater ecological quality. *Ecol. Eng.* 57, 118–132. <https://doi.org/10.1016/j.ecoleng.2013.04.009>
- Massmann, G., Sültenfuß, J., Dünnebier, U., Knappe, A., Taute, T., Pekdeger, A., 2008. Investigation of groundwater residence times during bank filtration in Berlin: a multi-tracer approach. *Hydrol. Process.* 22, 788–801. <https://doi.org/10.1002/hyp.6649>

- Mathon, B., 2022. Polar organic chemical integrative samplers as an effective tool for chemical monitoring of surface waters - Results from one-year monitoring in France. *Sci. Total Environ.* 13.
- McCance, W., Jones, O.A.H., Cendón, D.I., Edwards, M., Surapaneni, A., Chadalavada, S., Wang, S., Currell, M., 2020. Combining environmental isotopes with Contaminants of Emerging Concern (CECs) to characterise wastewater derived impacts on groundwater quality. *Water Res.* 182, 116036. <https://doi.org/10.1016/j.watres.2020.116036>
- McCance, W., Jones, O.A.H., Edwards, M., Surapaneni, A., Chadalavada, S., Currell, M., 2018. Contaminants of Emerging Concern as novel groundwater tracers for delineating wastewater impacts in urban and peri-urban areas. *Water Res.* 146, 118–133. <https://doi.org/10.1016/j.watres.2018.09.013>
- McCarthy, K.T., Pichler, T., Price, R.E., 2005. Geochemistry of Champagne Hot Springs shallow hydrothermal vent field and associated sediments, Dominica, Lesser Antilles. *Chem. Geol.* 224, 55–68. <https://doi.org/10.1016/j.chemgeo.2005.07.014>
- Menció, A., Mas-Pla, J., Otero, N., Soler, A., 2011. Nitrate as a tracer of groundwater flow in a fractured multilayered aquifer. *Hydrol. Sci. J.* 56, 108–122. <https://doi.org/10.1080/02626667.2010.543086>
- Mermillod-Blondin, F., Voisin, J., Marjolet, L., Marmonier, P., Cournoyer, B., 2019. Clay beads as artificial trapping matrices for monitoring bacterial distribution among urban stormwater infiltration systems and their connected aquifers. *Environ. Monit. Assess.* 191, 58. <https://doi.org/10.1007/s10661-019-7190-0>
- Miège, C., Mazzella, N., Allan, I., Dulio, V., Siles, F., Tixier, C., Vermeirssen, E., Brant, J., O'Toole, S., Budzinski, H., Chestem, J.-P., Staub, P.-F., Lardy-Fontan, S., Gonzalez, J.-L., Coquery, M., Vrana, B., 2015. Position paper on passive sampling techniques for the monitoring of contaminants in the aquatic environment – Achievements to date and perspectives. *Trends Environ. Anal. Chem.* 8, 20–26. <https://doi.org/10.1016/j.teac.2015.07.001>
- Mills, G.A., Gravell, A., Vrana, B., Charman, C., Budzinski, H., Mazzella, N., Ocelka, T., 2014. Measurement of environmental pollutants using passive sampling devices – an updated commentary on the current state of the art. *Env. Sci Process. Impacts* 16, 369–373. <https://doi.org/10.1039/C3EM00585B>
- Moeck, C., Radny, D., Poppe, A., Brennwald, M., Stoll, S., Auckenthaler, A., Berg, M., Schirmer, M., 2017. Characterization of a managed aquifer recharge system using multiple tracers. *Sci. Total Environ.* 609, 701–714. <https://doi.org/10.1016/j.scitotenv.2017.07.211>
- Morrison, J., Brockwell, T., Merren, T., Fourel, F., Phillips, A.M., 2001. On-Line High-Precision Stable Hydrogen Isotopic Analyses on Nanoliter Water Samples. *Anal. Chem.* 73, 3570–3575. <https://doi.org/10.1021/ac001447t>
- Moschet, C., Vermeirssen, E.L.M., Singer, H., Stamm, C., Hollender, J., 2015. Evaluation of in-situ calibration of Chemcatcher passive samplers for 322 micropollutants in agricultural and urban affected rivers. *Water Res.* 71, 306–317. <https://doi.org/10.1016/j.watres.2014.12.043>
- Müller, B., Scheytt, T., Asbrand, M., de Casas, A.M., 2012. Pharmaceuticals as indicators of sewage-influenced groundwater. *Hydrogeol. J.* 20, 1117–1129. <https://doi.org/10.1007/s10040-012-0852-4>
- Newman, C.P., Paschke, S.S., Keith, G., 2021. Natural and Anthropogenic Geochemical Tracers to Investigate Residence Times and Groundwater–Surface-Water Interactions in an Urban Alluvial Aquifer. *Water* 13, 871. <https://doi.org/10.3390/w13060871>

- Oyarzún, R., Zambra, S., Maturana, H., Oyarzún, J., Aguirre, E., Kretschmer, N., 2016. Chemical and isotopic assessment of surface water–shallow groundwater interaction in the arid Grande river basin, North-Central Chile. *Hydrol. Sci. J.* 61, 2193–2204. <https://doi.org/10.1080/02626667.2015.1093635>
- Page, D., Miotliński, K., Gonzalez, D., Barry, K., Dillon, P., Gallen, C., 2014. Environmental monitoring of selected pesticides and organic chemicals in urban stormwater recycling systems using passive sampling techniques. *J. Contam. Hydrol.* 158, 65–77. <https://doi.org/10.1016/j.jconhyd.2014.01.004>
- Petrie, B., Gravell, A., Mills, G.A., Youdan, J., Barden, R., Kasprzyk-Hordern, B., 2016. In Situ Calibration of a New Chemcatcher Configuration for the Determination of Polar Organic Micropollutants in Wastewater Effluent. *Environ. Sci. Technol.* 50, 9469–9478. <https://doi.org/10.1021/acs.est.6b02216>
- Pinasseau, L., Wiest, L., Fildier, A., Volatier, L., Fones, G.R., Mills, G.A., Mermillod-Blondin, F., Vulliet, E., 2019. Use of passive sampling and high resolution mass spectrometry using a suspect screening approach to characterise emerging pollutants in contaminated groundwater and runoff. *Sci. Total Environ.* 672, 253–263. <https://doi.org/10.1016/j.scitotenv.2019.03.489>
- Pinasseau, L., Wiest, L., Volatier, L., Fones, G.R., Mills, G.A., Mermillod-Blondin, F., Vulliet, E., 2020a. Calibration and field application of an innovative passive sampler for monitoring groundwater quality. *Talanta* 208, 120307. <https://doi.org/10.1016/j.talanta.2019.120307>
- Pinasseau, L., Wiest, L., Volatier, L., Mermillod-Blondin, F., Vulliet, E., 2020b. Emerging polar pollutants in groundwater: Potential impact of urban stormwater infiltration practices. *Environ. Pollut.* 266, 115387. <https://doi.org/10.1016/j.envpol.2020.115387>
- Pitt, R., Clark, S., Field, R., 1999. Groundwater contamination potential from stormwater infiltration practices. *Urban Water J.*
- Postigo, C., Barceló, D., 2015. Synthetic organic compounds and their transformation products in groundwater: Occurrence, fate and mitigation. *Sci. Total Environ.* 503–504, 32–47. <https://doi.org/10.1016/j.scitotenv.2014.06.019>
- Potot, C., Féraud, G., Schäfer, U., Barats, A., Durrieu, G., Le Poupon, C., Travi, Y., Simler, R., 2012. Groundwater and river baseline quality using major, trace elements, organic carbon and Sr–Pb–O isotopes in a Mediterranean catchment: The case of the Lower Var Valley (southeastern France). *J. Hydrol.* 472–473, 126–147. <https://doi.org/10.1016/j.jhydrol.2012.09.023>
- Poulain, A., Marc, V., Cillon, M., Mayer, A., Cognard-Plancq, A.-L., Simler, R., Babic, M., Leblanc, M., 2021. Enhanced pumping test using physicochemical tracers to determine surface-water/groundwater interactions in an alluvial island aquifer, river Rhône, France. *Hydrogeol. J.* 29, 1569–1585. <https://doi.org/10.1007/s10040-021-02331-1>
- R Core Team, 2017. R: a Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria. <https://www.R-project.org/>.
- Refloch, A., 2018. Compréhension expérimentale et numérique des chemins de l'eau sur l'ensemble du champ captant de la Métropole de Lyon. In French
- Richardson, S.D., Ternes, T.A., 2018. Water Analysis: Emerging Contaminants and Current Issues. *Anal. Chem.* 90, 398–428. <https://doi.org/10.1021/acs.analchem.7b04577>
- Shamsudduha, M., Taylor, R.G., Ahmed, K.M., Zahid, A., 2011. The impact of intensive groundwater abstraction on recharge to a shallow regional aquifer system: evidence from Bangladesh. *Hydrogeol. J.* 19, 901–916. <https://doi.org/10.1007/s10040-011-0723-4>

- Shaw, M., Mueller, J.F., 2009. Time Integrative Passive Sampling: How Well Do Chemcatchers Integrate Fluctuating Pollutant Concentrations? *Environ. Sci. Technol.* 43, 1443–1448. <https://doi.org/10.1021/es8021446>
- Sorensen, J.P.R., Lapworth, D.J., Nkhuwa, D.C.W., Stuart, M.E., Gooddy, D.C., Bell, R.A., Chirwa, M., Kabika, J., Liemisa, M., Chibesa, M., Pedley, S., 2015. Emerging contaminants in urban groundwater sources in Africa. *Water Res.* 72, 51–63. <https://doi.org/10.1016/j.watres.2014.08.002>
- Stuart, M.E., Lapworth, D.J., Thomas, J., Edwards, L., 2014. Fingerprinting groundwater pollution in catchments with contrasting contaminant sources using microorganic compounds. *Sci. Total Environ.* 468–469, 564–577. <https://doi.org/10.1016/j.scitotenv.2013.08.042>
- Taylor, A.C., Mills, G.A., Gravell, A., Kerwick, M., Fones, G.R., 2021. Passive sampling with suspect screening of polar pesticides and multivariate analysis in river catchments: Informing environmental risk assessments and designing future monitoring programmes. *Sci. Total Environ.* 787, 147519. <https://doi.org/10.1016/j.scitotenv.2021.147519>
- Texier, J., Gonçalves, J., Rivière, A., 2022. Numerical Assessment of Groundwater Flowpaths below a Streambed in Alluvial Plains Impacted by a Pumping Field. *Water* 14, 1100. <https://doi.org/10.3390/w14071100>
- Tröger, R., Ren, H., Yin, D., Postigo, C., Nguyen, M.D., Baduel, C., Golovko, O., Been, F., Joerss, H., Boleda, M.R., Polesello, S., Roncoroni, M., Taniyasu, S., Menger, F., Ahrens, L., Yin Lai, F., Wiberg, K., 2021. What's in the water? – Target and suspect screening of contaminants of emerging concern in raw water and drinking water from Europe and Asia. *Water Res.* 198, 117099. <https://doi.org/10.1016/j.watres.2021.117099>
- Valhondo, C., Martinez-Landa, L., Carrera, J., Ayora, C., Nödler, K., Licha, T., 2018. Evaluation of EOC removal processes during artificial recharge through a reactive barrier. *Sci. Total Environ.* 612, 985–994. <https://doi.org/10.1016/j.scitotenv.2017.08.054>
- Vermeirssen, E.L.M., Bramaz, N., Hollender, J., Singer, H., Escher, B.I., 2009. Passive sampling combined with ecotoxicological and chemical analysis of pharmaceuticals and biocides – evaluation of three Chemcatcher™ configurations. *Water Res.* 43, 903–914. <https://doi.org/10.1016/j.watres.2008.11.026>
- Vermeirssen, E.L.M., Detschweiler, C., Escher, B.I., van der Voet, J., Hollender, J., 2013. Uptake and release kinetics of 22 polar organic chemicals in the Chemcatcher passive sampler. *Anal. Bioanal. Chem.* 405, 5225–5236. <https://doi.org/10.1007/s00216-013-6878-1>
- Voisin, J., Cournoyer, B., Vienney, A., Mermillod-Blondin, F., 2018. Aquifer recharge with stormwater runoff in urban areas: Influence of vadose zone thickness on nutrient and bacterial transfers from the surface of infiltration basins to groundwater. *Sci. Total Environ.* 637–638, 1496–1507. <https://doi.org/10.1016/j.scitotenv.2018.05.094>
- Vrana, B., Allan, I.J., Greenwood, R., Mills, G.A., Dominiak, E., Svensson, K., Knutsson, J., Morrison, G., 2005. Passive sampling techniques for monitoring pollutants in water. *TrAC Trends Anal. Chem.* 24, 845–868. <https://doi.org/10.1016/j.trac.2005.06.006>
- Vrana, B., Mills, G.A., Dominiak, E., Greenwood, R., 2006. Calibration of the Chemcatcher passive sampler for the monitoring of priority organic pollutants in water. *Environ. Pollut.* 142, 333–343. <https://doi.org/10.1016/j.envpol.2005.10.033>
- Vystavna, Y., Frkova, Z., Marchand, L., Vergeles, Y., Stolberg, F., 2017. Removal efficiency of pharmaceuticals in a full scale constructed wetland in East Ukraine. *Ecol. Eng.* 108, 50–58. <https://doi.org/10.1016/j.ecoleng.2017.08.009>

- Wassenaar, L.I., Terzer-Wassmuth, S., Douence, C., Araguas-Araguas, L., Aggarwal, P.K., Coplen, T.B., 2018. Seeking excellence: An evaluation of 235 international laboratories conducting water isotope analyses by isotope-ratio and laser-absorption spectrometry. *Rapid Commun. Mass Spectrom.* 32, 393–406. <https://doi.org/10.1002/rcm.8052>
- Wilkinson, J.L., Boxall, A.B.A., Kolpin, D.W., Leung, K.M.Y., Lai, R.W.S., Galbán-Malagón, C., Adell, A.D., Mondon, J., Metian, M., Marchant, R.A., Bouzas-Monroy, A., Cuni-Sanchez, A., Coors, A., Carriquiriborde, P., Rojo, M., Gordon, C., Cara, M., Moermond, M., Luarte, T., Petrosyan, V., Perikhanyan, Y., Mahon, C.S., McGurk, C.J., Hofmann, T., Kormoker, T., Iniguez, V., Guzman-Otazo, J., Tavares, J.L., Gildasio De Figueiredo, F., Razzolini, M.T.P., Dougnon, V., Gbaguidi, G., Traoré, O., Blais, J.M., Kimpe, L.E., Wong, M., Wong, D., Ntchantcho, R., Pizarro, J., Ying, G.-G., Chen, C.-E., Páez, M., Martínez-Lara, J., Otamonga, J.-P., Poté, J., Ifo, S.A., Wilson, P., Echeverría-Sáenz, S., Udikovic-Kolic, N., Milakovic, M., Fatta-Kassinos, D., Ioannou-Ttofa, L., Belušová, V., Vymazal, J., Cárdenas-Bustamante, M., Kassa, B.A., Garric, J., Chaumot, A., Gibba, P., Kunchulia, U., Seidensticker, S., Lyberatos, G., Halldórsson, H.P., Melling, M., Shashidhar, T., Lamba, M., Nastiti, A., Supriatin, A., Pourang, N., Abedini, A., Abdullah, O., Chahida, S.S., Pilla, F., Chefetz, B., Topaz, T., Yao, K.M., Aubakirova, B., Beisenova, R., Olaka, L., Mulu, J.K., Chatanga, P., Ntuli, V., Blama, N.T., Sherif, S., Aris, A.Z., Looi, L.J., Niang, M., Traore, S.T., Oldenkamp, R., Ogunbanwo, O., Ashfaq, M., Iqbal, M., Abdeen, Z., O’Dea, A., Morales-Saldaña, J.M., Custodio, M., de la Cruz, H., Navarrete, I., Carvalho, F., Gogra, A.B., Koroma, B.M., Cerkvenik-Flajs, V., Gombač, M., Thwala, M., Choi, K., Kang, H., Ladu, J.I., Nico, A., Amerasinghe, P., Sobek, A., Horlitz, G., Zenker, A.K., King, A.C., Jiang, J.-J., Kariuki, R., Tumbo, M., Tezel, U., Onay, T.T., Lejju, J.B., Vystavna, Y., Vergeles, Y., Heinzen, H., Pérez-Parada, A., Sims, D.B., Fygy, M., Good, D., Tetra, C., 2022. Pharmaceutical pollution of the world’s rivers. *Proc. Natl. Acad. Sci.* 119, e2113947119. <https://doi.org/10.1073/pnas.2113947119>

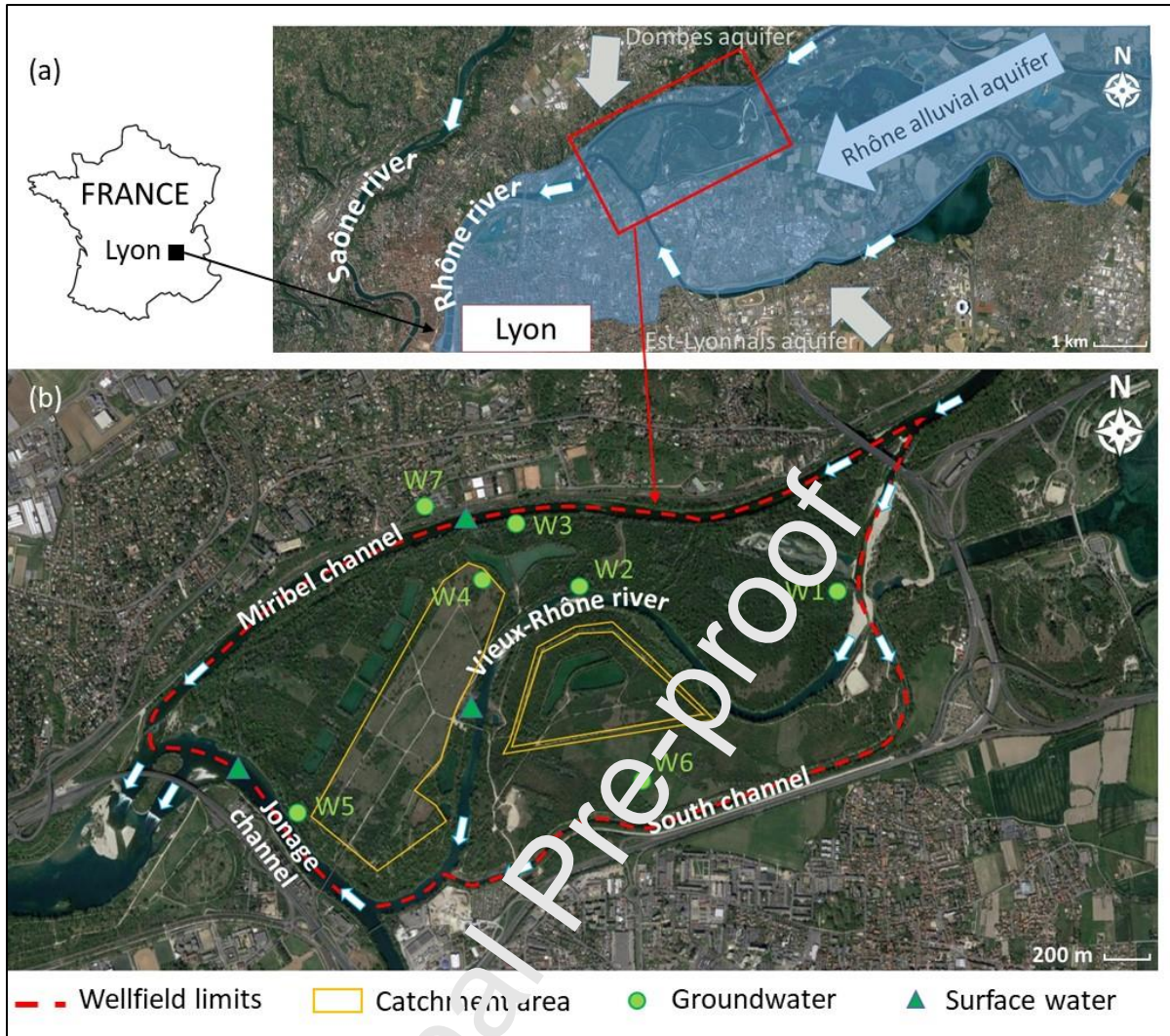


Fig. 1. (a) Location of the study area with a simplified representation of the Rhône alluvial aquifer direction from BURCEAP (2015), and (b) sampling locations.

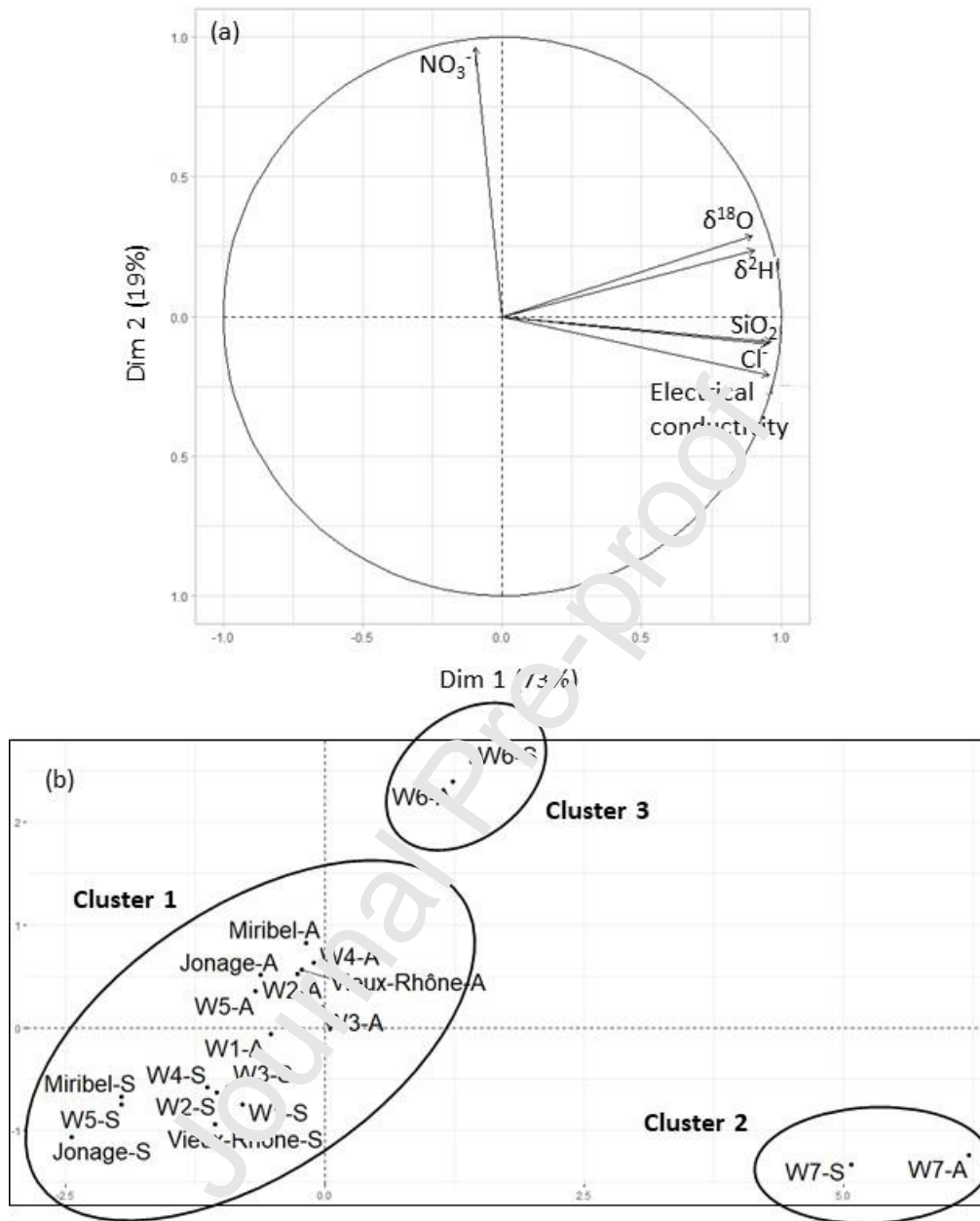


Fig. 2. Principal component analysis (PCA). (a) Correlation circle of chloride (Cl^-), nitrate (NO_3^-) and silica (SiO_2) concentrations, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values and electrical conductivity and (b) factorial scores of samples (values for the seven groundwater and the three surface water sampling locations and the two campaigns). A = autumn campaign, S = summer campaign.

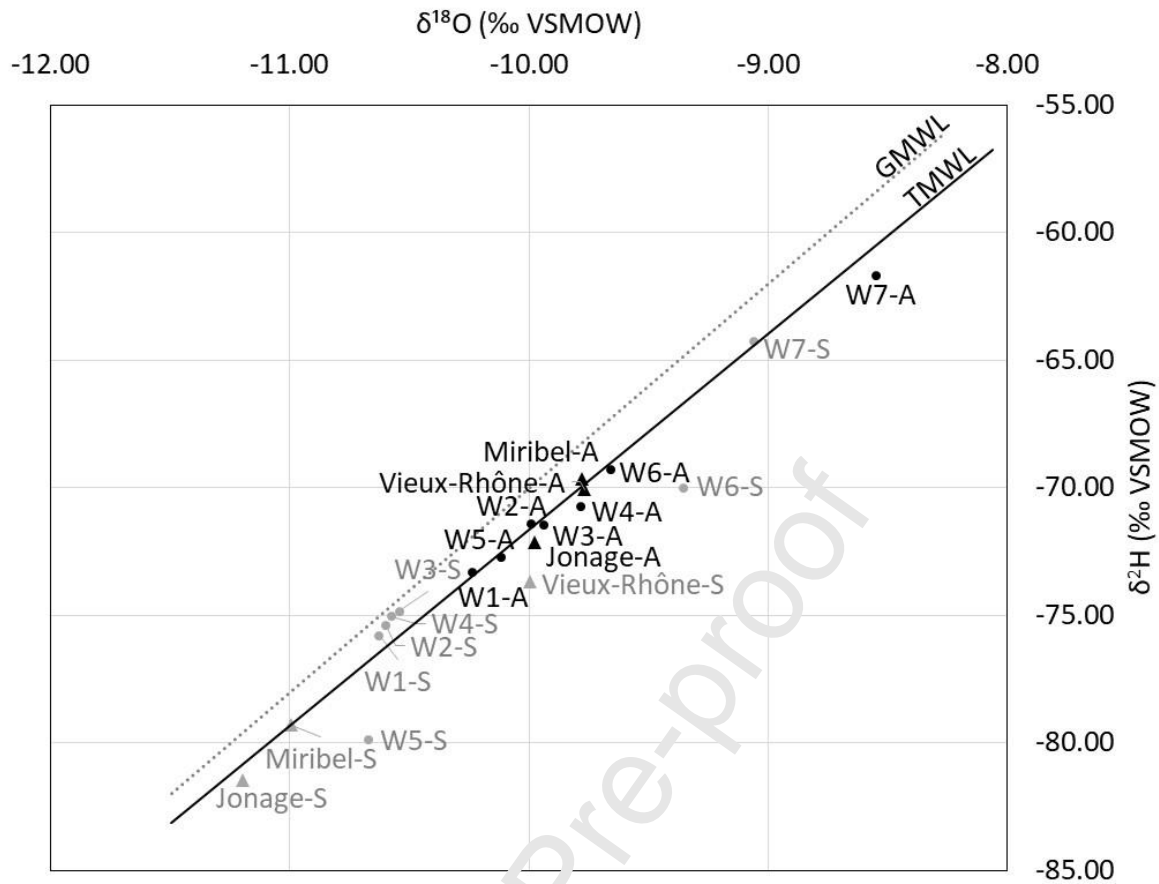


Fig. 3. $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ values measured during the 2 campaigns for the 10 sampling locations.

GMWL: Global Meteoric Water Line from (Craig, 1961) $\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10$, TMWL:

Thonon Meteoric Water Line from (BURGEAP, 2015) $\delta^2\text{H} = 7.68 \times \delta^{18}\text{O} + 5.14$. A = autumn campaign, S = summer campaign.

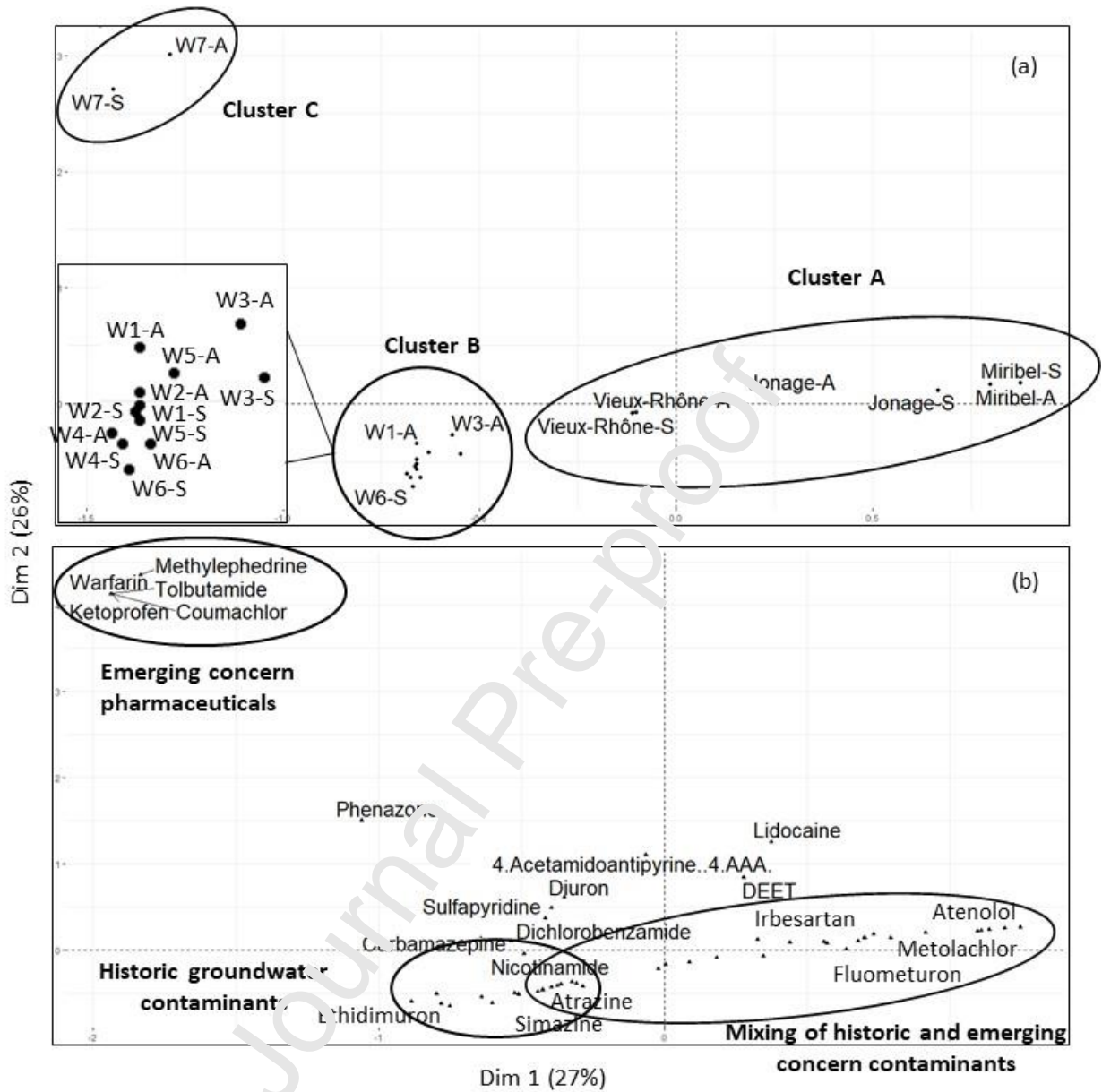


Fig. 4. Correspondence analysis (CA). (a) Factorial scores of samples (values for the seven groundwater and the three surface water sampling locations and the two campaigns) and (b) factorial scores of CECs. A = autumn campaign, S = summer campaign.

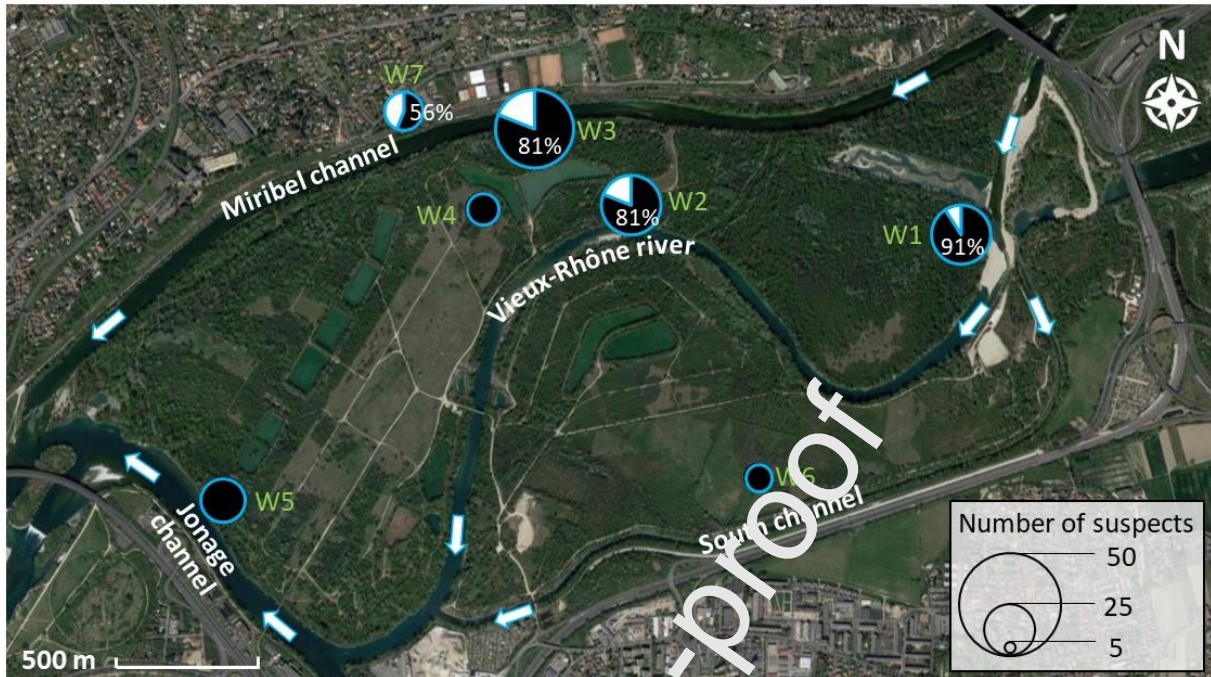


Fig. 5. Representation of the mean number of CECs detected by passive sampling and suspect screening during the 2 campaigns (2021) in the 7 groundwater sampling locations and common between groundwater and surface water (the list of CECs for the 3 surface water sampling locations was combined). Black: proportion of CECs in common with Rhône surface water; white: proportion of CEC only detected in groundwater.

Table 1. Mean hydrochemical tracer values \pm standard deviation measured during the 2 campaigns for the 10 sampling locations.

Sampling location	Cl ⁻ (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)	SiO ₂ (mg L ⁻¹)
Summer campaign			
<i>Groundwater</i>			
W1	14.93 \pm 1.27	3.31 \pm 0.94	4.21 \pm 0.28
W2	8.70 \pm 0.36	3.46 \pm 1.11	4.65 \pm 0.41
W3	9.53 \pm 0.04	3.40 \pm 0.09	4.85 \pm 0.06
W4	9.41 \pm 1.68	3.36 \pm 0.08	3.32 \pm 0.01
W5	7.09 \pm 2.07	3.47 \pm 0.30	2.61 \pm 0.09
W6	18.22 \pm 0.44	12.79 \pm 0.11	8.56 \pm 0.11
W7	29.78 \pm 2.47	0.70 \pm 0.01	17.67 \pm 0.82
<i>Surface water</i>			
Jonage channel	9.55 \pm 0.18	3.44 \pm 0.31	1.42 \pm 0.40
Miribel channel	10.93 \pm 1.58	4.27 \pm 1.03	1.76 \pm 0.82
Vieux-Rhône river	8.11 \pm 0.29	6.58 \pm 0.02	1.20 \pm 0.04
Autumn campaign			
<i>Groundwater</i>			
W1	12.51 \pm 1.54	4.51 \pm 0.36	4.28 \pm 0.22
W2	10.06 \pm 0.51	6.02 \pm 0.21	4.14 \pm 0.28
W3	11.84 \pm 0.15	4.80 \pm 0.09	5.25 \pm 0.04
W4	10.59 \pm 0.64	5.76 \pm 0.65	3.71 \pm 0.01
W5	10.92 \pm 1.93	5.50 \pm 0.23	2.38 \pm 0.10
W6	17.52 \pm 0.26	12.40 \pm 0.47	8.86 \pm 0.12
W7	23.77 \pm 0.47	0.30 \pm 0.05	19.14 \pm 1.01
<i>Surface water</i>			
Jonage channel	9.12 \pm 0.46	5.66 \pm 0.016	2.60 \pm 1.11
Miribel channel	9.79 \pm 1.46	6.10 \pm 0.01	2.87 \pm 1.07
Vieux-Rhône river	10.15 \pm 0.86	5.24 \pm 0.01	2.59 \pm 0.70

Table 2. General data and physico-chemical information properties of compounds of emerging concern (CECs) (in alphabetical order) detected with a global confidence score 1 or 2, during the 2 campaigns for the 7 groundwater sampling locations (W1 to W7).

CEC	CAS No.	Formula	Molecular weight (g mol ⁻¹) ^c	logD _{OW} (pH=7.4) ^c	Koc (mL g ⁻¹) ^c	W 1	W 2	W 3	W 4	W 5	W 6	W 7
Pesticides												
2-hydroxyterbutylazine*	66753-07-9	C ₉ H ₁₇ N ₅ O	211.26	-2.1	1	X ^b	X	X	X	X ^a		
Amidosulfuron	120923-37-7	C ₉ H ₁₅ N ₅ O ₇ S ₂	369.41	-1.4	1			X ^a				
Atrazine	1912-24-9	C ₈ H ₁₄ ClN ₅	215.68	2.7	671	X	X	X	X ^b	X	X ^b	
Atrazine 2-Hydroxy*	2163-68-0	C ₈ H ₁₅ N ₅ O	197.24	-0.7	9.7	X	X	X	X	X ^a	X ^a	
Atrazine-desethyl*	6190-65-4	C ₆ H ₁₀ ClN ₅	187.63	1.5	164	X	X	X	X	X	X	
Atrazine-desisopropyl*	1007-28-9	C ₅ H ₈ ClN ₅	173.60	1.3	16	X	X	X	X	X	X ^b	
Carbendazim + benomyl TP	10605-21-7	C ₉ H ₉ N ₃ O ₂	191.19	1.6	175	X	X	X	X	X	X ^b	
Chlorotoluron	15545-48-9	C ₁₀ H ₁₃ ClN ₂ O	212.68	2.5	530	X ^b	X ^b	X				
Coumachlor	81-82-3	C ₁₉ H ₁₅ ClO ₄	342.71	0.8	4							X
DEET	134-62-3	C ₁₂ H ₁₇ NO	191.27	2.2	392							X ^b
Dichlorobenzamide*	2008-58-4	C ₇ H ₅ Cl ₂ NO	190.02	1.3	118	X		X		X		X
Diuron	330-54-1	C ₉ H ₁₀ Cl ₂ N ₂ O	237.10	0.1	2	X ^b	X ^b	X				X
Ethidimuron	30043-49-3	C ₇ H ₁₂ N ₂ S ₂	264.33	-0.01	23	X ^b	X	X				
Ethoxysulfuron	126801-58-9	C ₁₅ H ₁₆ N ₄ O ₅ S	398.39	-0.7	1			X				
Fluometuron	2164-17-2	C ₁₁ H ₁₇ N ₃ O	232.20	2.4	455			X				
Imidacloprid	138261-41-3	C ₇ H ₁₀ ClN ₅ O	255.66	-0.21	18			X ^b				
Metolachlor	51218-45-2	C ₁₅ H ₂₂ ClNO	283.79	3.2	133			X ^a				
Nicosulfuron	111991-09-4	C ₁₅ H ₁₈ N ₆ O ₆ S	410.41	-2.3	1	X	X	X	X	X ^b		
Simazine	122-34-9	C ₇ H ₁₂ ClN ₅	201.66	2.3	422	X	X	X	X	X	X	
Terbutylazine	5915-41-3	C ₉ H ₁₆ ClN ₅	229.71	3.0	101	X ^b	X ^b	X				
Thiazafluron	25366-23-8	C ₆ H ₇ F ₃ N ₄ OS	240.21	1.6	183	X	X	X	X	X	X	
Tritosulfuron	142469-14-5	C ₁₃ H ₉ F ₆ N ₅ O ₄ S	445.30	1.1	12	X ^b	X	X				
Pharmaceuticals												
4-acetamidoantipyrine*	83-15-8	C ₁₃ H ₁₅ N ₃ O ₂	245.28	0.08	26							X
Carbamazepine	298-46-4	C ₁₅ H ₁₂ N ₂ O	236.27	2.3	415	X	X	X	X	X		X
Carbamazepine-	36507-	C ₁₅ H ₁₂ N ₂ O ₂	252.27	1.3	124	X	X	X	X	X	X ^b	

10.11-epoxid* + oxcarbazepine*	30-9 28721- 07-5			1.9	247							
Irbesartan	138402 -11-6	C ₂₅ H ₂₈ N ₆ O	428.53	1.2	14	X ^b	X ^a					
Ketoprofen	22071- 15-4	C ₁₆ H ₁₄ O ₃	254.28	0.06	1							X
Lamotrigine	84057- 84-1	C ₉ H ₇ Cl ₂ N ₅	256.09	1.7	194	X	X	X	X	X		
Lidocaine	137- 58-6	C ₁₄ H ₂₂ N ₂ O	234.34	1.3	29							X ^b
Methylephedrine	552- 79-4	C ₁₁ H ₁₇ NO	179.26	0.1	5							X ^b
Nikethamide	59-26- 7	C ₁₀ H ₁₄ N ₂ O	178.23	0.5	47			X				
Phenazone	60-80- 0	C ₁₁ H ₁₂ N ₂ O	188.23	0.7	59	X ^b		X				X ^b
Sulfamethoxazole	723- 46-6	C ₁₀ H ₁₁ N ₃ O ₃ S	253.28	-0.6	3	X	X	X	X	X	X	
Sulfapyridine	144- 83-2	C ₁₁ H ₁₁ N ₃ O ₂ S	249.29	0.4	37	X	X			X ^b		X
Theophylline	58-55- 9	C ₇ H ₈ N ₄ O ₂	180.16	-0.03	22		X ^a	X ^a		X ^a	X ^a	
Tolbutamide	64-77- 7	C ₁₂ H ₁₈ N ₂ O ₃ S	270.35	0.3	5							X
Warfarin	81-81- 2	C ₁₉ H ₁₆ O ₄	308.33	2.8	91							X
Others												
Caffeine	58-08- 2	C ₈ H ₁₀ N ₄ O ₂	194.19	0.2	34	X ^a	X ^a	X ^a	X ^a	X	X	
Histidine	4998- 57-6	C ₆ H ₉ N ₃ O ₂	155.15	-2.1	1	X	X	X ^a	X	X	X	
Nicotinamide	98-92- 0	C ₆ H ₆ N ₂ O	122.12	-2.3	1	X	X ^a	X ^b	X ^b	X ^b	X ^b	X ^a

Key: TP, transformation product

*Transformation product

^aDetected only during the summer campaign (August 2021)

^bDetected only during the autumn campaign (October-November 2021)

^cAccording to ChemSpider (<http://www.chemspider.com/>)

CRediT authorship contribution statement

Lucie Pinasseau: Conceptualization, Formal analysis, Writing – original draft, Writing review & editing.

Florian Mermillod-Blondin: Supervision, Conceptualization, Writing – original draft, Writing review & editing, Validation.

Aurélie Fildier: Investigation, Resources.

François Fourel: Investigation, Resources.

Félix Vallier: Investigation, Resources.

Ludovic Guillard: Investigation, Resources.

Laure Wiest: Conceptualization, Validation.

Laurence Volatier: Supervision, Conceptualization, Writing – original draft, Writing review & editing, Validation.

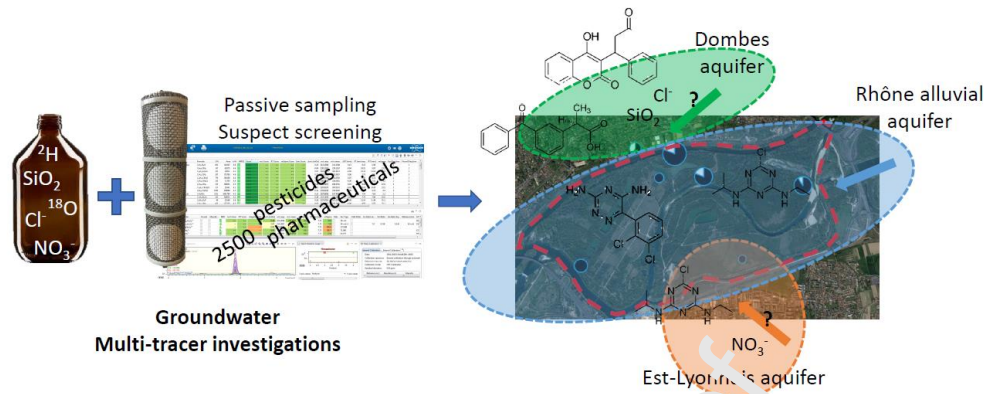
Journal Pre-proof

Declaration of interests

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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Journal Pre-proof



Graphical abstract

Highlights

- Enhanced multi-tracer approach using passive sampling and suspect screening of 2500 CECs
- The 125 detected CECs provided in-depth chemical fingerprint of groundwater bodies
- Water bodies were distinguished using statistical analyses on tracer data
- Cocktails of CECs were sufficiently discriminating to be used as chemical tracer
- The global approach allowed a more realistic assessment of groundwater vulnerability