



Influence of surface water – groundwater interactions on the spatial distribution of pesticide metabolites in groundwater



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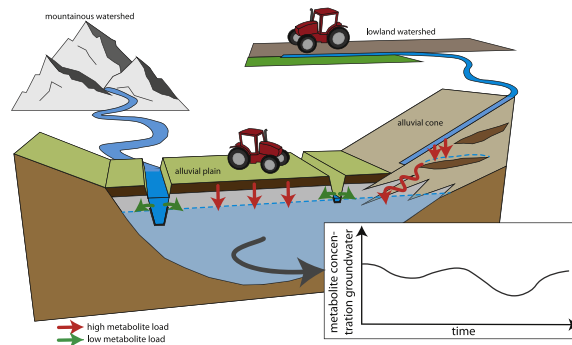
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HIGHLIGHTS

- Pesticide metabolites propagate via surface water – groundwater interactions.
- Lowland catchments with intense land use are an important source.
- Propagation influences concentration levels and long-term dynamics in pumping wells.

GRAPHICAL ABSTRACT



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ABSTRACT

In groundwater, pesticide metabolites tend to occur more frequently and at higher concentrations than their parent pesticides, due to their higher mobility and persistence. These properties might also favor their transfer across surface water – groundwater interfaces. However, the effect of surface water – groundwater interactions on the metabolite occurrence in groundwater and pumping wells has so far received little attention. We investigated the spatial distribution of metabolites in an unconsolidated aquifer, which interacts with two surface water bodies originating from catchments with contrasting land use. We focused on metabolites of the herbicide chloridazon, namely desphenyl-chloridazon (DPC) and methyl-desphenyl-chloridazon (MDPC) and characterized surface water – groundwater interactions with various environmental tracers (e.g. electrical conductivity, stable water isotopes, wastewater tracers). In zones influenced by a river from a mountainous area, metabolite concentrations were low (median values $\leq 0.50 \mu\text{g L}^{-1}$ for DPC, $\leq 0.19 \mu\text{g L}^{-1}$ for MDPC). In contrast, high concentrations occurred in areas dominated by recharge from agricultural fields and/or influenced by a stream from an adjacent intensely farmed catchment (median values up to $1.9 \mu\text{g L}^{-1}$ for DPC and up to $0.75 \mu\text{g L}^{-1}$ for MDPC). An endmember analysis using hydro-chemical data suggested that about 20% of the DPC mass in a pumping well originated from the neighboring catchment and on its own would cause a concentration above $0.1 \mu\text{g L}^{-1}$ for DPC. Our findings highlight that the mobile metabolites can be imported from zones with intense agriculture outside of the exploited aquifer via surface-water groundwater interactions influencing the metabolite concentration level and long-term dynamics in the aquifer.

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1. Introduction

The contamination of groundwater by pesticides is a common problem and therefore, the fate of pesticides in the environment has been widely investigated (Buttiglieri et al., 2009; Cuevas et al., 2008; Loos et al., 2010). In the last years, degradation products of pesticides (metabolites) have gained increasing attention and have become a growing concern for waterworks, especially in countries with low regulatory limits for metabolites. Their detection frequency in groundwater is often high, with concentrations often exceeding those of their parent compounds (Baran and Gourcy, 2013; Fuhrmann et al., 2014; Stuart and Lapworth, 2014). On the one hand, this is due to the improvement of analytical methods enabling the detection of numerous metabolites at very low concentrations in water (Hernández et al., 2008; Kuster et al., 2009; Schuhmann et al., 2016). On the other hand, the metabolites of pesticides are usually more polar, less volatile and less biodegradable than their parent compounds, which results in a higher mobility (Buttiglieri et al., 2009; Holtze et al., 2008; Schuhmann et al., 2016; Stuart and Lapworth, 2014) and widespread groundwater contamination. For groundwater quality management, it is important to understand what controls the concentrations levels and spatial patterns of pesticide metabolites in aquifers.

The spatial distribution of pesticide metabolites in groundwater is influenced by land use patterns via leaching through agricultural soils. Whereas pesticide leaching is often dominated by preferential flow (Flury, 1996), the more mobile metabolites are also transported through the soil matrix resulting in an input into groundwater over longer periods. For example, Schuhmann et al. (2016) observed high concentrations of two polar metabolites of the herbicide chloridazon (CLZ), namely desphenyl-chloridazon (DPC) and methyl-desphenyl-chloridazon (MDPC), in lysimeter leachates over >2 years after a single application of the herbicide. Hence, the repeated application of a pesticide can potentially lead to a continuous input of metabolites into groundwater. However, the resulting spatial distribution of metabolite concentration in groundwater may be modified by surface water – groundwater interactions. The infiltration of surface water bodies may either decrease or increase the metabolite concentration in groundwater, depending on their metabolite load. This effect has been already observed for the nitrate concentration in groundwater (Baillieux et al., 2014). The load of metabolites in surface water bodies can be variable. Surface water bodies from lowland watersheds with intense agriculture are expected to have a higher load than surface water bodies from mountainous watersheds. The load of metabolites in surface water bodies can be influenced by infiltrating groundwater or by agricultural drains (Brown and van Beinum, 2009; Puckett and Hughes, 2005). The role of drains has for example been shown for two of the atrazine metabolites (Jayachandran et al., 1994). Compared to pesticides, the seasonal variability of metabolite concentrations in surface water bodies tends to be smaller, as it has been shown for the metabolite desphenyl-chloridazon (Buttiglieri et al., 2009).

Transport of pesticides between surface water bodies and groundwater and their fate during riverbank filtration has been investigated in several studies (Blum et al., 1993; Bruchet et al., 2011; Dragon et al., 2018; Nagy-Kovács et al., 2018; Squillace et al., 1996; Squillace et al., 1997; Verstraeten et al., 2002; Verstraeten et al., 2003). Only few include also metabolites (Nagy-Kovács et al., 2018; Verstraeten et al., 2002; Verstraeten et al., 2003). These studies suggest that the metabolites can persist during river infiltration (Nagy-Kovács et al., 2018; Verstraeten et al., 2002; Verstraeten et al., 2003). However, such studies are usually restricted to the zone between rivers and pumping wells, and there is little information on processes controlling aquifer-scale patterns of pesticide metabolites.

The aim of the study is to investigate the influence of surface water – groundwater interactions on the spatial pattern of pesticide metabolites in groundwater and its implication for concentration levels in pumping wells. We focused on an unconsolidated aquifer, which is in contact

with two surface water bodies, one from an intensely farmed lowland area, and the other from a mountainous region, to evaluate their respective influence on groundwater quality. We used a series of environmental tracers (electrical conductivity, major ions, stable water isotopes, tracers in wastewater) to characterize surface water – groundwater interactions. We focused on chloridazon (CLZ) and its two predominant metabolites, desphenyl-chloridazon (DPC) and methyl-desphenyl-chloridazon (MDPC) as the chloridazon metabolites are among the most frequently detected pesticide-related compounds in Swiss and European groundwater (Loos et al., 2010; Postigo and Barceló, 2015; Reemtsma et al., 2013; Reinhardt et al., 2017). We investigated the spatial patterns of the pesticide metabolites and their relation to the surface water bodies by sampling piezometers, including some multi-level systems, the surface water bodies and a groundwater pumping well, which is used for drinking water supply, over one hydrological year.

2. Material and methods

2.1. Study site

The study site is located in the western part of Switzerland on the Swiss Plateau in the canton of Vaud about 15 km northwest of the city of Lausanne (Fig. 1A). About half of the area of the study site is used for intensive agriculture and around 30% of the area is covered by forest (Canton de Vaud, 2019b) (Fig. 1A). The herbicide CLZ is applied pre-emergence or early post-emergence in sugar beet crops for weed control (Schuhmann et al., 2016). Sugar beet crops typically account for around 12% and 14% of the agricultural area of the study site. The maximum permitted application amount of CLZ in Switzerland is 2.6 kg ha⁻¹ within 3 years (BLW, 2019). Due to crop rotation, CLZ is very likely applied only once within 3 years. The average annual precipitation sum for the region was 940 mm (1990–2018) (MeteoSwiss station Cossonay; MeteoSwiss, 2019). The annual precipitation sum in the year 2018, when the main part of the study was conducted, was with 820 mm lower than the average (MeteoSwiss station Cossonay; MeteoSwiss, 2019).

The aquifer is comprised of glaciofluvial deposits and recent alluvial sediments deposited by the Venoge River, which is now channelized (CSD INGENIEURS SA, 2014). The aquifer is delimited at depth and laterally by a basal moraine from the last glacial period overlying the lower fresh water molasse (IMPACT-CONCEPT SA, 2006). The top layer of the aquifer consists of fine-grained alluvial or eluvial sediments (CSD INGENIEURS SA, 2014). The hydraulic conductivity of the aquifer was between 9×10^{-4} and 1.5×10^{-2} m s⁻¹, with a mean value of 4×10^{-3} m s⁻¹ (Colombi Schmutz Dorthé, 1987). The thickness of the aquifer varies between 1 and 16 m. The depth to the water table varied between 1 and 6 m (median: 2 m) during the study period, depending on the location on the alluvial plain and on the hydrological conditions. The main flow direction of the groundwater is from northeast to southwest. A groundwater contour map based on the median groundwater levels is provided in Fig. 1B. In the monitoring wells B1, B2, B3 and B4, the groundwater level showed higher fluctuations during the wetter months (December – June) (maximum: 1–1.5 m), whereas, during the drier months (July – November), only minor variations occurred (maximum: 0.25–0.5 m). In the monitoring wells B5 and B6, the groundwater level was less dynamic. It increased during December and January by up to 2 m and remained at this level until June. During the drier months (July–November), the groundwater level decreased again.

The Venoge is the largest surface water body that crosses the alluvial plain (Fig. 1B) and has its source at the foot of the Jura Mountains. Its regime is characterized as Jurassic nivo-pluvial with a strong contrast between low and high flow, a rapid response to precipitations and high flow during snow melt (CSD INGENIEURS SA, 2014). The second surface water body is the stream Combe, which has its source on the eastern molasse plateau and is strongly influenced by runoff from a highway and an agricultural drainage system

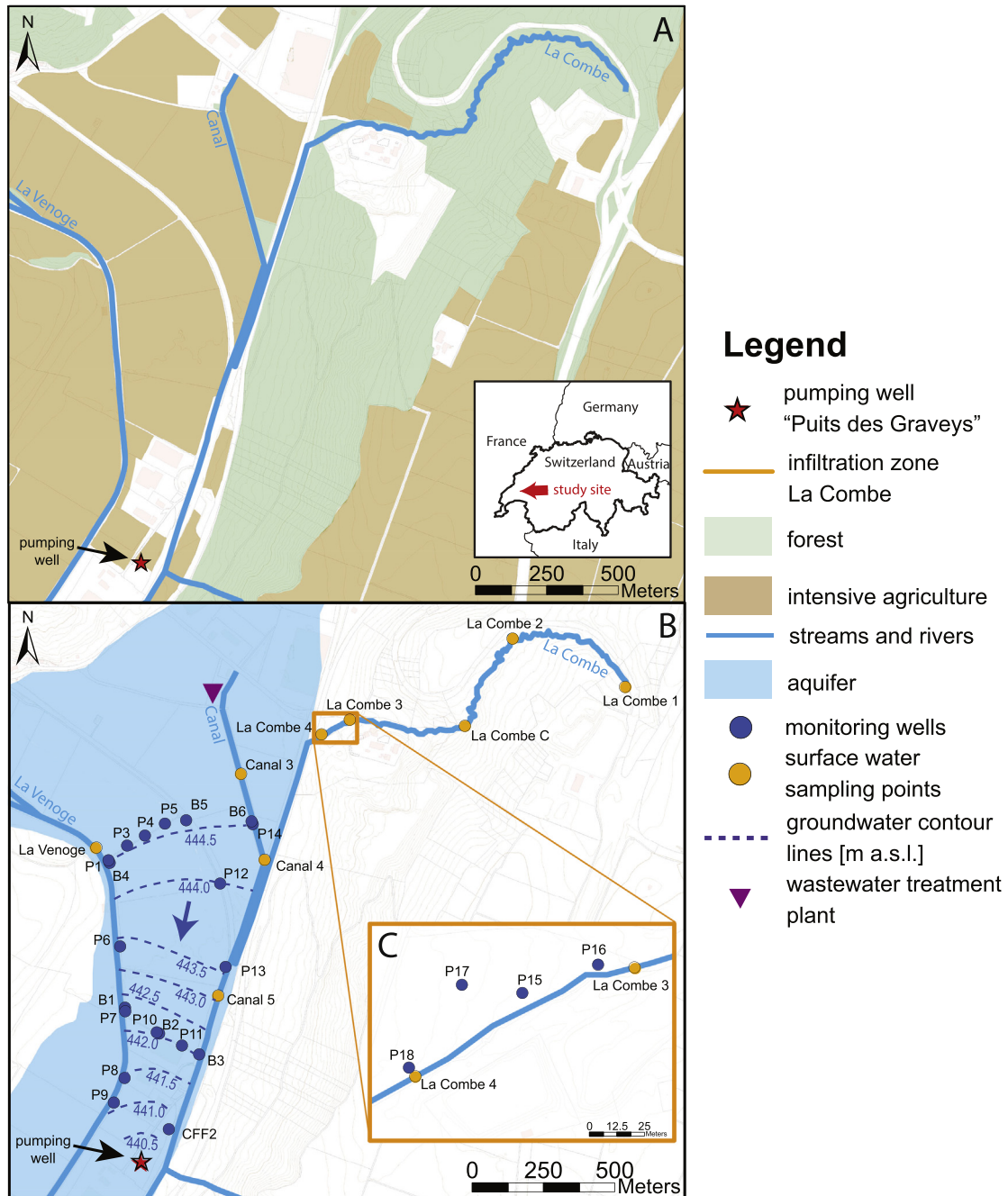


Fig. 1. A) Land use of the study site, B) aquifer with groundwater contour lines (median values), the location of the pumping well for drinking water supply, the monitoring wells (P1, P3–P14, B1–B6) and surface water sampling points and C) the infiltration zone of the stream Combe and the location of the monitoring wells in this zone (P15–P18). The background of the map is based on Canton de Vaud (2019b), Canton de Vaud (2019a) and Swisstopo (2019).

(Fig. 1B). It descends to the alluvial plain via a forested ravine and alluvial cone (Fig. 1A). During dry periods, the stream completely infiltrates into the alluvial cone supplying a purged aquifer. In the lower part, a small canal is connected to the Combe (Fig. 1B). This canal receives its water from a rainwater retention basin and a wastewater treatment plant (WWTP).

In the lower part of the study site, the aquifer is used by a pumping well for drinking water supply (Fig. 1B). The pumping well (Puits des Graveys) consists of a horizontally filtered well with a depth of 16 m (Colombi Schmutz Dorthe, 1987). Four radial filter tubes are arranged at two levels (Colombi Schmutz Dorthe, 1987). The length of each filter tube is 22 m for the first level (8 m depth)

and 15 m for the second level (12 m depth) (Colombi Schmutz Dorthe, 1987).

The alluvial plain was equipped with 20 monitoring wells to characterize the spatial distribution of CLZ and its two main metabolites (DPC, MDPC) in the aquifer (Fig. 1B, Table 1). Three of the monitoring wells (B1, B2 and B5) have screened intervals at different depths. In addition, we installed four shallow piezometers (P15–P18) in the infiltration zone of the stream Combe to investigate the transfer of CLZ and its two metabolites to groundwater via stream water infiltration (Fig. 1C, Table 1). We sampled the surface water bodies Venoge, Combe and the canal at different points (Fig. 1B, Table 1).

Table 1

Details of the monitoring wells including the multi-level systems, the shallow piezometers in the infiltration zone of the stream Combe and the pumping well Puits des Graveys.

Piezometer name	Tube diameter	Screened intervals			
	cm (inch)	m b. ground			
P1, P3–P10	5.08 (2)	2.0–6.0			
P11	5.08 (2)	2.0–7.0			
P12–P14	2.54 (1)	2.0–5.0			
P15	2.54 (1)	0.8–5.8			
P16–P18	2.54 (1)	0.7–5.7			
CFF2	15.24 (6)	4.7–19.7			
B1	5.08 (2)	3.2–5.2	6.2–10.2		
B2	5.08 (2)	2.1–4.1	5.1–7.1		
B3	5.08 (2)	2.9–4.9			
B4	5.08 (2)	3.1–6.1			
B5	5.08 (2)	3.0–5.0	6.0–8.0	9.0–11.0	12.0–14.0
B6	5.08 (2)	2.1–5.1			
Pumping well (Puits des Graveys)	200 (–)	2 levels of horizontal filter tubes at 7.9 and 12.5 m			

2.2. Water sampling and analysis

In order to cover different hydrological conditions and seasons of the year, we carried out regular sampling campaigns between November 2017 and April 2019 with a total of 204 samples. We took samples every second month, namely in November/December 2017, February 2018, April 2018, June 2018, August/September 2018, December 2018, February 2019 and April 2019. Each sampling campaign comprised one to six sampling points of surface waters (Venoge, canal, Combe), 11 to 23 groundwater sampling points (piezometers and different depth intervals of the multi-level systems), two to three shallow piezometers of the infiltration zone of the stream Combe and the pumping well Puits des Graveys (Table 1, Fig. 1B, C).

We filled bottles for stream and river samples directly in the corresponding surface water body around 5 to 10 cm below the water surface. We sampled the multi-level monitoring wells (B1, B2, B5) with a double packer system (Comdrill Bohrausrüstungen GmbH) for the MP1 pump (Grundfos). We collected groundwater from the remaining monitoring wells with a submersible pump and from the shallow piezometers in the infiltration zone (P15–P18) with a peristaltic pump. We sampled the pumping well from a tap. We stored all samples in the dark at 4 °C until analysis.

Samples were analyzed for CLZ and its two metabolites (DPC, MDPC). The properties of these three compounds, the regulatory limits and the degradation chain of CLZ are available in the supporting information (Section S1.3.1). In addition, we chose different environmental tracers to identify the surface water – groundwater interactions. The electrical conductivity and the stable water isotopes were selected to track the influence of the Venoge River. The latter has a lower electrical conductivity and a more depleted stable water isotope signature compared to the aquifer, as it has its source at the foot of the Jura Mountains. To distinguish between the influence of the stream Combe and the canal, we chose the wastewater tracers, as the canal receives effluents from a wastewater treatment plant. The major ions were selected to further differentiate between the influence on the groundwater quality of the stream Combe or of the recharge from agricultural fields. The following sections provide details about the analysis of CLZ, DPC and MDPC as well as about the analysis of the different environmental tracers.

We measured field parameters (electrical conductivity, pH, dissolved oxygen and temperature) with a HACH multi-parameter device (HACH HQ40d multi) directly in the stream/river or using a flow-through cell in the case of groundwater. We analyzed the concentration of bicarbonate in duplicates by titration (Metrohm 848 Titrino plus connected to a Metrohm 869 Compact Sample Changer). The details about

the standard deviations of the HACH multi-meter device and the sample treatment are available in the supporting information (Sections S1.1 and S1.2).

Prior to the analysis of CLZ, DPC and MDPC, isotopically labeled standards for CLZ (CLZ-d5, 100 µg mL⁻¹ in acetonitrile, Dr. Ehrensdorfer, LGC Standards), DPC (DPC-¹⁵N₂, 100 µg mL⁻¹ in acetonitrile, HPC Standards) and MDPC (MDPC-d3, 10 µg mL⁻¹ in acetonitrile, HPC Standards) were added to each water sample for a final concentration of 2.5 µg L⁻¹. Standards for the calibration curve were prepared by diluting different stock solutions of CLZ (powder (Chemos GmbH & Co. KG)), DPC (10 µg mL⁻¹ in acetonitrile, Dr. Ehrensdorfer, LGC Standards) and MDPC (100 ng mL⁻¹ in acetonitrile, Dr. Ehrensdorfer, LGC Standards) in methanol (Fisher chemicals) or ultrapure water (MilliQ-Direct-Q 3UV-R, Merck).

We analyzed CLZ, DPC and MDPC by direct injection in ultra-high performance liquid chromatography hyphenated to tandem mass spectrometry (UHPLC-MS/MS). For the first six sampling campaigns, we used an Ultimate 3000 RSLC chromatographic system (Dionex-Thermo Fisher Scientific) coupled to a 4000 QTRAP mass spectrometer (AB Sciex) (method 1). The analytes were separated on an Acquity UPLC BEH Shield RP-18 column (2.1 × 100 mm, 1.7 µm particle size, Waters) in gradient mode using formic acid 0.05% in H₂O (phase A) and formic acid 0.05% in acetonitrile (phase B) as mobile phases. More details about the analytical method as well as about the limits of detection (LOD) and quantification (LOQ) can be found in the supporting information (Section S1.3.2).

Due to instrument availability, we analyzed the samples from the last two campaigns with a different instrument using an Acquity UPLC system coupled to a TQ-S mass spectrometer (Waters) (method 2). The column and mobile phases remained the same, except mobile phase A (formic acid 0.05% in water), which was supplemented with 5 mM ammonium formate. More details about the analytical method as well as about LOD and LOQ are available in the supporting information (Section S1.3.2).

We analyzed the major ions by ion chromatography using a Dionex ICS-1600 (ThermoScientific) for anions (chloride, nitrate, sulfate) and a Dionex DX-120 (ThermoScientific) for cations (sodium, potassium, magnesium, calcium). We determined the stable hydrogen ($\delta^2\text{H}_{\text{H}_2\text{O}}$) and oxygen ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$) isotopes of water using a Picarro Cavity Ringdown Spectrometer L2130-I. The reported values are an average of the last six of nine injections and were normalized to the VSMOW/SLAP scale. The standard deviations of the major ions and stable water isotopes are listed in the supporting information (Section S1.1).

We also determined common wastewater tracers in the campaign of April 2019. The analyzed wastewater tracers comprised drug residues, X-ray contrast agents, triazoles and an artificial sweetener. A detailed list about all analyzed wastewater tracers is available in the supporting information (Section S1.4). The analysis was conducted in the laboratory for quality monitoring of the water supply of Zurich (Switzerland) by a liquid chromatography tandem mass spectrometry system (LC-MS/MS) (Stadt Zürich - Wasserversorgung, 2020). The limit of quantification (LOQ) was 10 ng L⁻¹ for all analyzed wastewater tracers (Stadt Zürich - Wasserversorgung, 2020). Only benzotriazole and acesulfame will be considered further as they were among the substances with the highest concentrations and were found in the highest number of measuring stations with values above the LOQ. Benzotriazole has many potential sources (Breedveld et al., 2003; Careghini et al., 2015; Durjava et al., 2013; Hem et al., 2003; Jia et al., 2007; Shi et al., 2019; Vetter and Lorenz, 2013), whereas acesulfame is only used as an artificial sweetener (Buerge et al., 2009; Castronovo et al., 2017; Storck et al., 2016). Benzotriazole is considered as conservative as its degradation is slow and it is only sorptive in soils with high organic carbon content (e.g. peat) (Breedveld et al., 2003; Careghini et al., 2015). Acesulfame cannot be generally considered as a conservative tracer, its persistence has to be confirmed for each study environment by the use of other tracers (Castronovo et al., 2017).

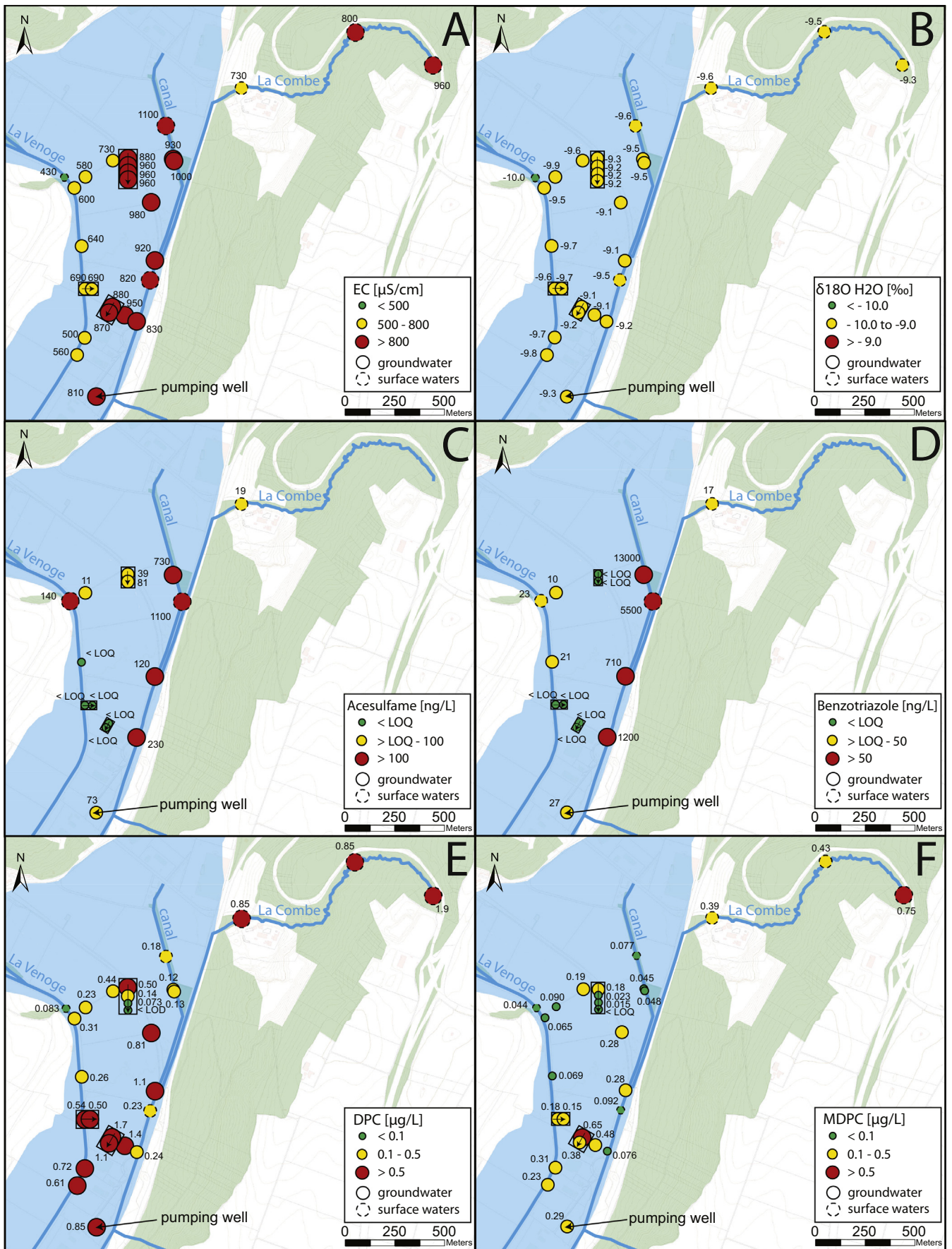


Fig. 2. Median spatial distribution of A) the electrical conductivity, B) the stable water isotopes ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$), C) the concentration of acesulfame, D) the concentration of benzotriazole, E) the concentration of DPC and F) the concentration of MDPC in groundwater and surface water (background based on Canton de Vaud (2019b), Canton de Vaud (2019a) and Swisstopo (2019)).

2.3. Continuous record of the water level and conductivity in the piezometers and river and precipitation data

We equipped six monitoring wells (B1–B6) with a combined pressure and electrical conductivity probe (Keller DCX-22 CTD). In addition, we monitored the water level of the Venoge River with a pressure probe (Solinst 3001 LT F6/ 2M). We corrected the pressure readings for changes in atmospheric pressure to obtain water levels. We used daily precipitation data from the MeteoSwiss measuring station Cossonay (MeteoSwiss, 2019).

3. Results & discussion

3.1. Spatial distribution and temporal dynamics of groundwater composition

In a first step, the results for different environmental tracers (e.g. stable water isotopes, wastewater tracers) will be presented to highlight the interactions of the different surface water bodies (Venoge River, stream Combe, canal) with the aquifer. In a second step, we evaluate

the influence of the surface water – groundwater interactions on the CLZ metabolite concentrations in the aquifer and in the pumping well. The spatial patterns will be discussed based on median values for each sampling point. Due to the large data set, the temporal trends will only be illustrated for selected locations and parameters. Detailed spatial plots for a dry and wet period are available in the supporting information (Figs. S1, S2, S3A, C).

3.1.1. Electrical conductivity and stable water isotopes

The median electrical conductivity was much lower in the Venoge, than in the Combe and the canal (Fig. 2A). In groundwater, the median electrical conductivity was higher in the eastern part of the aquifer (P11, P12, P13, P14, B2, B3, B5, B6) than in the western part (P3, P5, P6, P8, P9, B1, B4; Fig. 2A). The electrical conductivity of the pumping well was within the range of the eastern part of the aquifer with a median value of $810 \mu\text{S cm}^{-1}$ (Fig. 2A). The median $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of the surface waters and monitoring wells were in the range of -9.1 to -10.0% (Fig. 2B). Similar to electrical conductivity, the median $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values were partitioned into two zones with slightly more negative values in the western part of the aquifer and in the Venoge River compared to

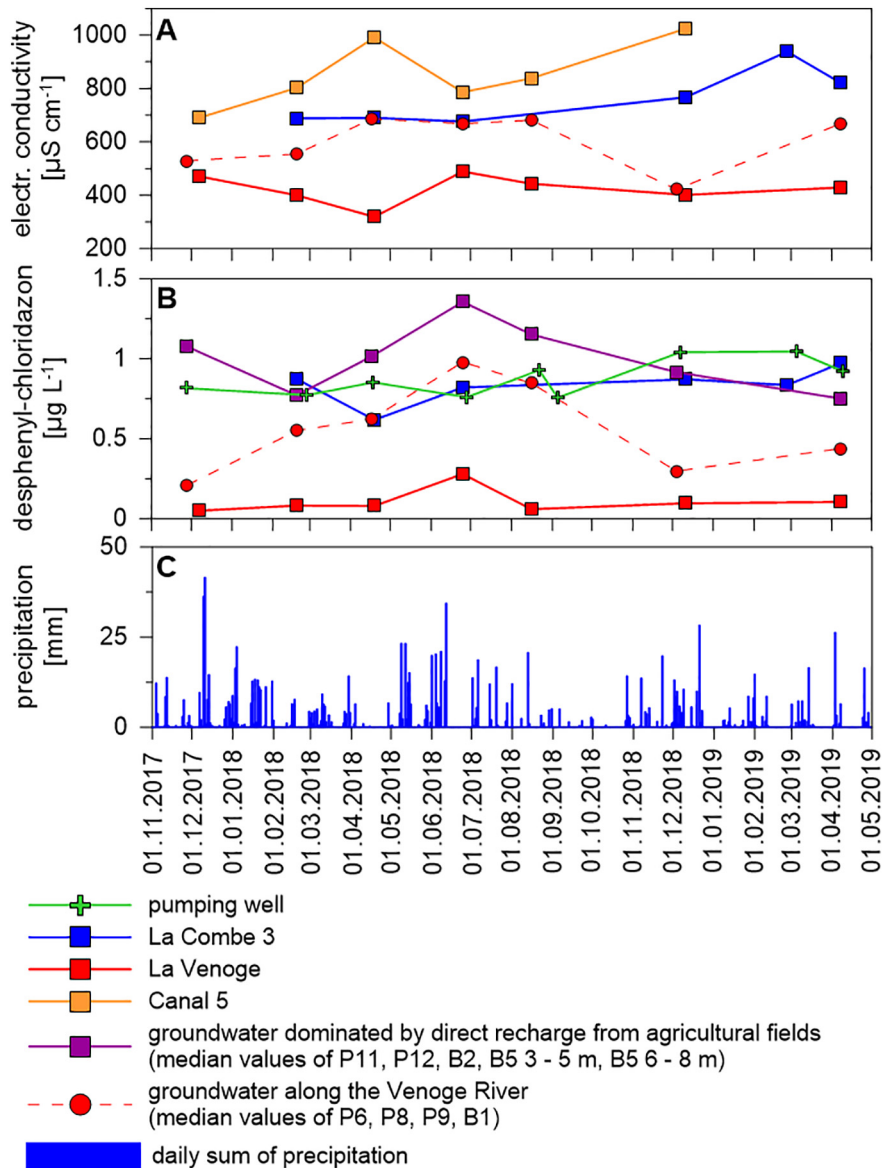


Fig. 3. Temporal variation of A) the electrical conductivity and B) the DPC concentration in the pumping well, in the surface water bodies, in groundwater dominated by direct recharge from agricultural fields and in groundwater along the Venoge River. C) Temporal variation of the precipitation (MeteoSwiss station Cossonay (MeteoSwiss, 2019)).

the eastern part of the aquifer (Fig. 2B). The $\delta^2\text{H}_{\text{H}_2\text{O}}$ values were strongly correlated with the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and are provided in the supporting information (Fig. S3). The more depleted isotopic signature of the Venoge can be explained by the altitude effect leading to a more depleted isotopic signature in precipitation with increasing altitude (Clark and Fritz, 1997), which is transferred to surface water bodies originating from these mountainous watersheds. The lower electrical conductivity and the more negative signature of the stable water isotopes in the western part of the aquifer suggest an influence of the Venoge River.

In the following, we focus on the electrical conductivity as the spatial variations relative to the uncertainty of the parameters were more pronounced than for the stable water isotopes. In the Venoge River, the electrical conductivity varied little over time (Fig. 3A). Only the snowmelt in spring 2018 caused a lower electrical conductivity (Fig. 3A). In the stream Combe, the temporal variability of the electrical conductivity was also small, except for a higher value in February 2019 (Fig. 3A). In the canal, the temporal variability of the electrical conductivity was higher (Fig. 3A). Its high electrical conductivity resulting from the effluents of the WWTP was diluted each time when the rainwater retention basin had been opened, leading to the higher temporal variability. In the groundwater along the Venoge River (median values of P6, P8, P9, B1), the electrical conductivity is only in the wetter periods (e.g. December

2018 and 2019) close to that of the Venoge (Fig. 3A, Fig. S1B supporting information). During the remaining time, the electrical conductivity in the groundwater along the Venoge deviated significantly from that of the Venoge (Fig. 3A, Fig. S1A supporting information). This suggests a temporal variable influence of the Venoge on the groundwater quality in the western part.

The continuous data of water levels of the Venoge and an adjacent piezometer (B4) in combination with the electrical conductivity of groundwater (B1, due to a lack of data in B4) provide further insight into surface water - groundwater interactions. Between July 2018 and April 2019, the water level was always higher in the Venoge than in the aquifer (B4) suggesting losing stream conditions (Fig. 4B). However, a decrease in the electrical conductivity of groundwater only occurred when the water level of the Venoge exceeded a threshold of 0.45 m (e.g. December 2018; Fig. 4C, D). This threshold value corresponds to the height of walls of the low flow channel. Thus, river water infiltration likely occurred across the banks above the low flow channel. The continuous water level and electrical conductivity data confirm that the groundwater quality of the western part of the aquifer was affected by infiltration of the Venoge with a greater influence during the wet periods (e.g. December 2018). However, the electrical conductivity and stable water isotopes were not suitable to identify interactions between

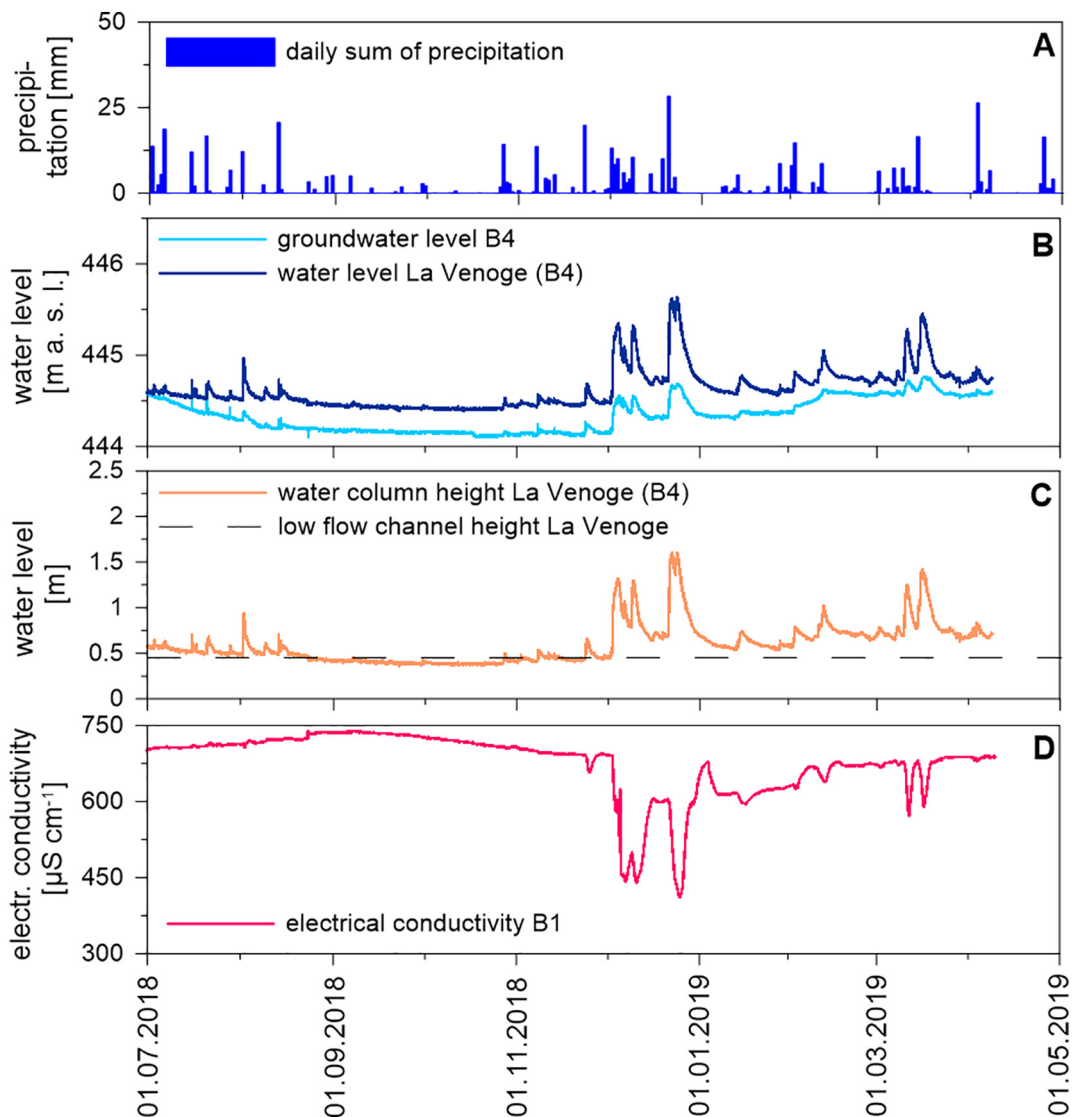


Fig. 4. Temporal variation of A) the precipitation (MeteoSwiss station Cossonay (MeteoSwiss, 2019)), B) the absolute water level of the groundwater (B4) and the Venoge River, C) the height of the water column of the Venoge River and D) the electrical conductivity of the piezometer B1 between July 2018 and April 2019.

the Combe and the canal, which both had elevated electrical conductivities, and the aquifer.

3.1.2. Tracers in wastewater

We used wastewater tracers to further evaluate surface water – groundwater interactions (e.g. canal, Combe). The concentrations of benzotriazole and acesulfame were much higher in the canal than in the Venoge and Combe (Fig. 2C, D). These values are consistent with the origin of water in these surface water bodies. The canal receives a large fraction of its discharge from a WWTP, while for the Venoge, the WWTP input is strongly diluted by water from the Jura mountains. The Combe is not linked to a WWTP. Elevated benzotriazole and acesulfame concentrations occurred in the piezometers along the canal (B6, P13, B3) (Fig. 2C, D). In contrast, all other piezometers showed low or not quantifiable benzotriazole and acesulfame concentrations (Fig. 2C, D). The pumping well, which is located further away from the canal, also exhibited low benzotriazole and acesulfame concentrations (Fig. 2C, D).

The high benzotriazole and acesulfame concentrations in the piezometers close to the canal confirmed a connection between the

groundwater and the canal. The effect was only local and did not have a significant influence on the groundwater quality of the eastern part of the aquifer, as the piezometers in greater distance to the canal already showed lower concentrations. The limited infiltration of the canal can be justified by its streambed characteristics, as a high load of organic matter resulting from the WWTP effluents might clog the streambed. Therefore, an infiltration might be only possible during high flow events. However, as the canal has no natural source and receives its water only from the WWTP and the rainwater retention basin, the high flow events were limited to some hours per day when the rainwater retention basin had been opened. Thereby, the infiltration of the canal occurred more like a short “spillover” during the short high flow periods resulting only in a local influence on the groundwater quality. Hence, the influence of the canal on the groundwater quality in the eastern part is small.

3.1.3. Major ions

The major ion content of the surface water bodies and groundwater (Fig. S4 (supporting information), Fig. 5A, B, C) was dominated by calcium (median values up to 170.0 mg L^{-1}) and bicarbonate (median

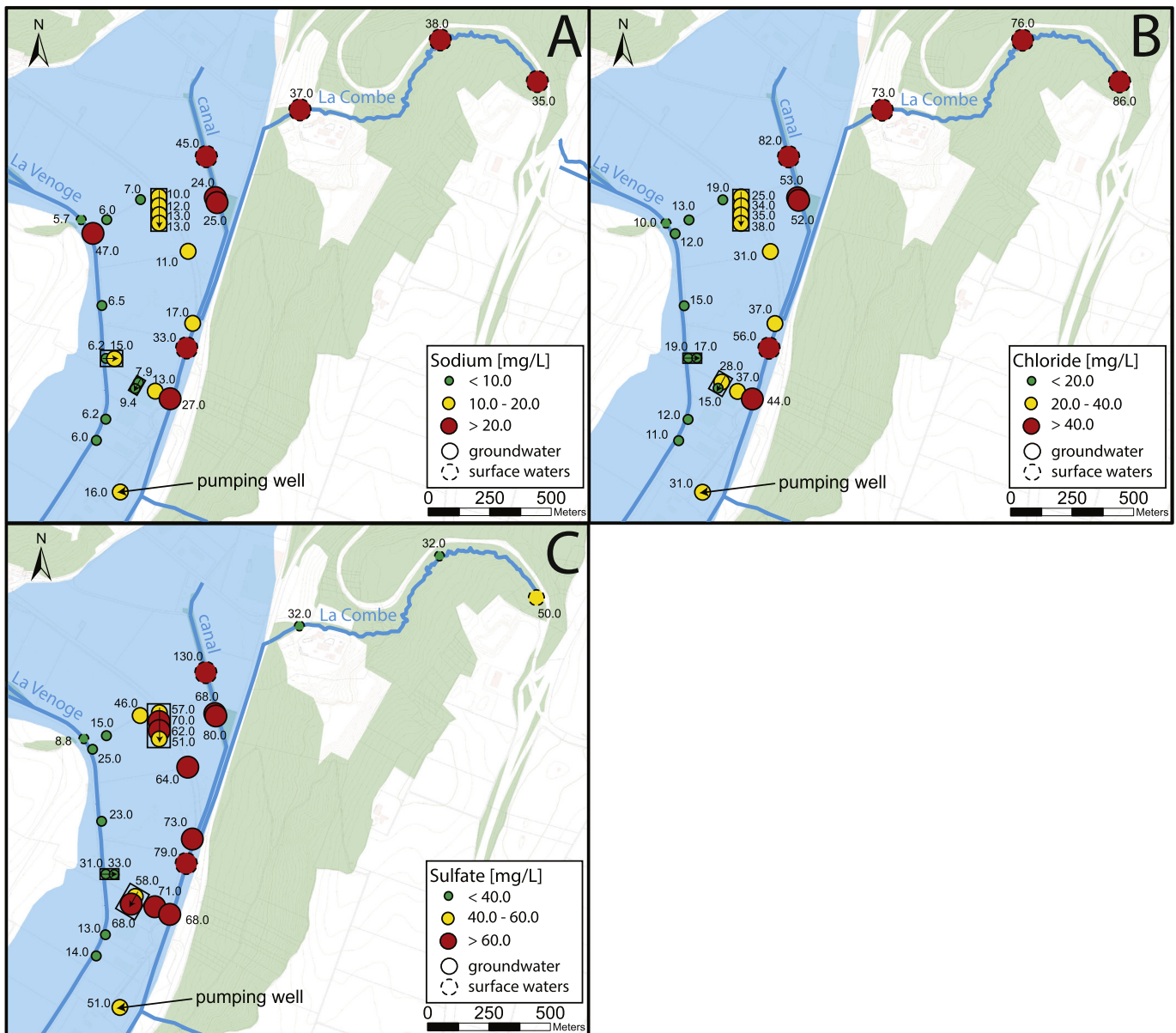


Fig. 5. Median spatial distribution of A) the sodium concentration, B) the chloride concentration and C) the sulfate concentration in groundwater and surface water (background based on Canton de Vaud (2019b), Canton de Vaud (2019a) and Swisstopo (2019)).

values up to 510.0 mg L^{-1}). The highest spatial variations occurred for sodium ($5.7\text{--}47.0 \text{ mg L}^{-1}$), chloride ($10.0\text{--}86.0 \text{ mg L}^{-1}$) and sulfate ($8.8\text{--}130.0 \text{ mg L}^{-1}$) (Fig. S4 (supporting information), Fig. 5A, B, C). Therefore, we investigated the spatial distribution of these major ions to explore whether these strongly varying parameters provide additional insight into the origin of water in the aquifer. In Fig. 5, the spatial variations of the median concentrations of these parameters is illustrated. In the western part of the aquifer and in the Venoge River, the concentrations of sodium, chloride and sulfate were low (Fig. 5A, B, C). In contrast, in the eastern part of the aquifer, the sodium, chloride and sulfate concentrations were higher with a spatial division (Fig. 5A, B, C). The stream Combe had high sodium and chloride concentrations and low to intermediate sulfate concentrations (Fig. 5A, B, C). The pumping well exhibited intermediate sodium, chloride and sulfate concentrations (Fig. 5A, B, C). The spatial division of the sodium, chloride and sulfate concentrations in the eastern part of the aquifer (Fig. 5A, B, C) suggests that there is an additional endmember to the stream Combe and the Venoge River influencing the groundwater quality of the aquifer and pumping well. This endmember has intermediate sodium, chloride and sulfate concentrations.

A cross-plot of the sum of sodium and chloride versus sulfate provide further insight into the water composition of the aquifer and the pumping well. For the Combe, we only used the sampling point Combe 3, as it is located at the upgradient end of the alluvial fan and thus is representative for the infiltrating stream water. The canal and piezometers along the canal (P13, P14, B3, B6, CFF2) were excluded as it has been shown above that the influence of the canal was only locally. The cross-plot of the sum of sodium and chloride versus sulfate (Fig. 6) suggests that the hydro-chemical composition is influenced by three endmembers. One endmember is the stream Combe with a high and seasonally varying sum of sodium and chloride consistent with the influence of the highway drainage system (road salt; Fig. 6). The typical signature of the stream Combe for the sampling period was around 80 mg L^{-1} for the sum of sodium and chloride and 30 mg L^{-1} for sulfate (Fig. 6). A second endmember includes monitoring well B5 (3–5 & 6–8 m) at the greatest distance from surface water bodies in the center of the alluvial plain and monitoring wells downgradient of it (B2, P10, P11, P12), which are likely dominated by direct recharge

from agricultural fields. These piezometers had high sulfate concentrations (Fig. 6). The high sulfate concentrations might mainly derive from fertilizers, which are a common source of sulfate. Especially rapeseed requires S-fertilizers as it has a high sulfur demand (Grant et al., 2012). The third endmember was the Venoge, as it has already been demonstrated in Section 3.1.1, with low sodium, chloride and sulfate concentrations (Fig. 6).

Almost all piezometers of the alluvial plain were located along a mixing line between the endmembers Venoge and the groundwater dominated by direct recharge from the agricultural fields (Fig. 6). The water chemistry of the piezometers at a greater distance to surface water bodies (e.g. B2, B5, P10, P11, P12) was mainly dominated by the direct recharge from the agricultural fields during the complete sampling period (Fig. 6). In contrast, the signature of the other piezometers and especially of those along the Venoge varied along this mixing line, depending on the influence of the Venoge as described above (Fig. 6). However, the pumping well was not located on this mixing line (Fig. 6). Its water composition was shifted towards higher sodium and chloride concentrations, which can be explained by the influence of the infiltrating water of the Combe (Fig. 6). The infiltration of the Combe water into the alluvial fan is demonstrated by the sodium, chloride and sulfate concentration. The concentrations in the monitoring wells adjacent to the Combe (P15, P16, P18) were during the entire sampling period very similar to those in the stream Combe (data not shown). Under the assumption of a ternary mixing system, the percentages of water of the pumping well, which derives from the different endmembers, have been estimated as follow: 71% from groundwater dominated by direct recharge from the agricultural fields, 20% from the Combe and 9% from the Venoge River (Fig. 6).

3.1.4. Pesticides and metabolites

The concentration of CLZ was below the detection limit (LOD) in 76% of the surface water and groundwater samples, taken between November 2017 and April 2019. If detected in surface water bodies, the concentration ranged between 0.0074 and $0.073 \mu\text{g L}^{-1}$, with one exception in the canal with a CLZ concentration of $0.91 \mu\text{g L}^{-1}$. This exceptional high CLZ concentration might be caused by washing of spray equipment, which ended up in the WWTP and entered the canal. If detected in

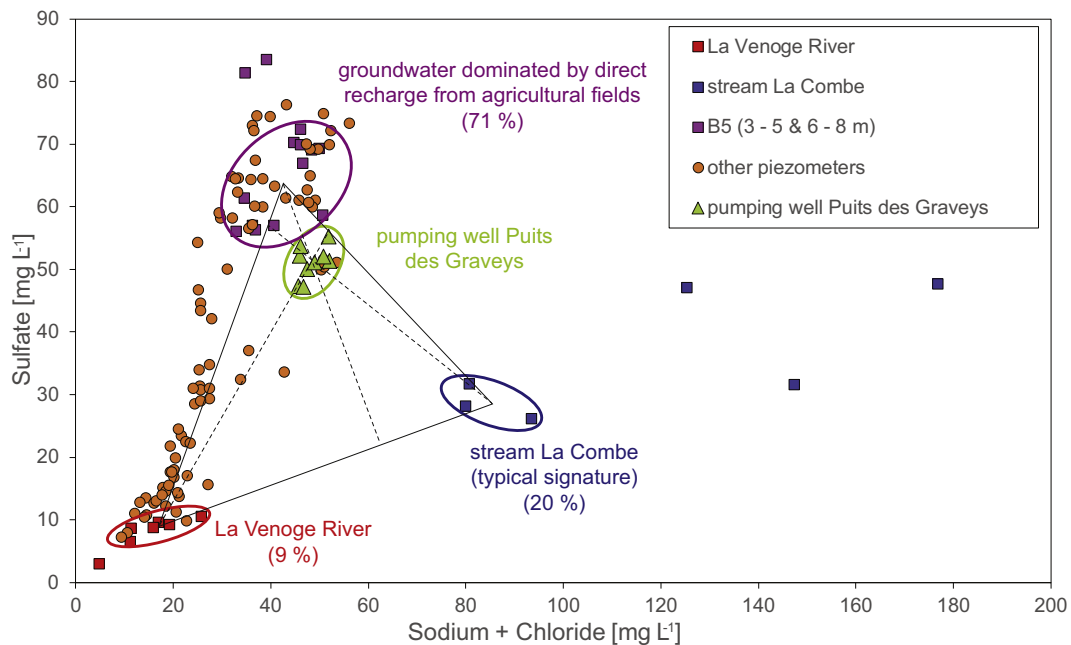


Fig. 6. Cross-plot of the sum of sodium and chloride vs. sulfate for the Venoge River, the stream Combe (Combe 3), the piezometers and the pumping well Puits des Graveys during the sampling period between November 2017 and April 2019 including the ternary mixing system and the percentage of the water of the pumping well, which derives from the different endmembers. The piezometers along the canal (B6, B3, P13, P14) and the piezometer B4 were excluded.

groundwater, the concentration ranged between 0.0060 and 0.053 $\mu\text{g L}^{-1}$ with one exception (0.12 $\mu\text{g L}^{-1}$). CLZ concentration above the LOQ occurred mainly in the canal and in the monitoring wells along the canal. It is most likely that CLZ enters the canal via the WWTP effluents, as the other surface water bodies (Venoge, Combe) rarely showed CLZ concentration above the LOD. In contrast, the detection frequency and concentrations of DPC and MDPC were much higher. DPC and MDPC were detected in 82% and 100% of the surface water samples and in 90% and 95% of the groundwater samples. DPC concentrations reached up to 2.7 $\mu\text{g L}^{-1}$ in surface waters and up to 2.3 $\mu\text{g L}^{-1}$ in groundwater. MDPC concentrations were lower with maximum values of 1.3 $\mu\text{g L}^{-1}$ in surface waters and 0.85 $\mu\text{g L}^{-1}$ in groundwater.

In the Venoge River, the median metabolite concentrations were very low (0.083 $\mu\text{g L}^{-1}$ for DPC and 0.044 $\mu\text{g L}^{-1}$ for MDPC; Fig. 2E, F). In contrast, the Combe stream showed elevated concentrations with median values ranging from 0.85 to 1.9 $\mu\text{g L}^{-1}$ for DPC and 0.39 to 0.75 $\mu\text{g L}^{-1}$ for MDPC (Fig. 2E, F). The median concentrations decreased along the Combe by a factor of about two (Fig. 2E, F). As the stream flows from the intensely used agricultural plateau through the forested ravine, it receives additional inflow as indicated by the increase in discharge, leading to a dilution of the metabolite concentration in the stream (Fig. 2E, F). The piezometers in the alluvial cone (P15–P18) adjacent to the Combe showed similar metabolite concentrations (0.60–0.89 $\mu\text{g L}^{-1}$ for DPC and 0.26–0.35 $\mu\text{g L}^{-1}$ for MDPC) as the most downstream sampling point of the Combe (Combe 3), suggesting that groundwater in this zone is dominated by infiltrating stream water. The metabolite levels in the canal (canal 3 and canal 5) were between those of the Venoge and the Combe, with median concentrations of 0.18 and 0.23 $\mu\text{g L}^{-1}$ for DPC and 0.077 and 0.092 $\mu\text{g L}^{-1}$ for MDPC (Fig. 2E, F). In groundwater, median DPC (Fig. 2E) and MDPC (Fig. 2F) concentrations were lower (DPC \leq 0.50 $\mu\text{g L}^{-1}$; MDPC \leq 0.19 $\mu\text{g L}^{-1}$) in the northwestern part of the aquifer (B4, B5, P3, P5, P6) and along the canal (P14, B3, B6). In contrast, higher median concentrations (DPC: 0.50–1.7 $\mu\text{g L}^{-1}$; MDPC: 0.15–0.65 $\mu\text{g L}^{-1}$) were observed in the eastern piezometers at a greater distance to the canal (P11, P12, B2), including piezometer P13, and in the southwestern piezometers (P8, P9, B1) (Fig. 2E, F). Elevated metabolite concentrations also occurred at the pumping well with a median value of 0.85 $\mu\text{g L}^{-1}$ for DPC and 0.29 $\mu\text{g L}^{-1}$ for MDPC (Fig. 2E, F). The temporal variability of the DPC concentration in the Venoge and the Combe was small (Fig. 3B). The DPC concentrations in groundwater dominated by direct recharge from agricultural fields showed a peak in early summer (Fig. 3B). In the pumping well, the DPC concentrations showed a small temporal variability (Fig. 3B). In the western part of the aquifer, the DPC concentration showed a stronger temporal variability (Fig. 3B). The temporal variability of MDPC was similar and will be not discussed here.

The lower median DPC and MDPC concentration in the northwestern part of the aquifer and in groundwater along the canal was caused by the infiltration of the Venoge and the local influence of the canal (Sections 3.1.1, 3.1.2), which both had lower DPC and MDPC concentration. The strong temporal variability of the DPC concentration in the groundwater along the Venoge was caused by the temporal variable influence of the Venoge, as discussed in Section 3.1.1. The eastern piezometers at greater distance to the canal were mostly influenced by groundwater dominated by direct recharge from agricultural fields (Section 3.1.3) leading to high DPC and MDPC concentrations. The peak of the DPC concentration in early summer in the groundwater dominated by direct recharge from agricultural fields might be caused by a higher mobilization during the preceding wetter winter/ spring period.

The hydro-chemical endmember analysis (Fig. 6) can be used to understand the origin of the elevated concentration of metabolites in the pumping well as illustrated for DPC. Although the endmembers showed some temporal variability, which is not uncommon for endmember analysis, their concentrations are consistently different. Furthermore, the concentrations vary little in the pumping well, which can be

explained by mixing processes in the aquifer, which smooth out the variations. Therefore, for quantifying the mixing ratios in the pumping well, we used the median DPC concentration of the endmembers, which are the following: 1.0 $\mu\text{g L}^{-1}$ for groundwater dominated by direct recharge from agricultural fields (P11, P12, B2, B5 3–5 m, B5 6–8 m), 0.85 $\mu\text{g L}^{-1}$ for the Combe at the alluvial cone (Combe 3) and 0.083 $\mu\text{g L}^{-1}$ for the Venoge (Fig. 2E). By multiplying these endmember concentrations with their respective fractions, we obtain a concentration of 0.89 $\mu\text{g L}^{-1}$, which agrees well with the measured median concentration (0.85 $\mu\text{g L}^{-1}$, Fig. 2E). According to these calculations, 80% of the DPC mass originates from groundwater dominated by direct recharge from agricultural fields of the alluvial plain, 19% stems from the molasse plateau via the Combe stream and only 1% originates from the Venoge. Thereby, the influence of the infiltrating water of the Combe on the water chemistry in the pumping well is demonstrated.

3.2. Influences of the different water sources on the metabolite distribution in groundwater

Our case study based on CLZ and its metabolites demonstrates that the spatial distribution of metabolites in an aquifer deriving from the recharge from agricultural fields can be modified by surface water – groundwater interactions (Fig. 7). Depending on the surface water origin, the effect of these interactions on the groundwater quality can either decrease or increase the metabolite concentration (Fig. 7). Especially small streams from lowland watersheds with intense agriculture should be the focus of attention as they can have high metabolite loads. In our case, the relevance of the imported mass can be highlighted by calculating the expected concentration if DPC did not originate from the alluvial plain itself. A DPC concentration of 0.18 $\mu\text{g L}^{-1}$ would be expected, which would be above the reference value of 0.1 $\mu\text{g L}^{-1}$ which is also applied to pesticide metabolites in some countries.

The behavior of compounds during surface water infiltration depends on their physico-chemical properties, as suggested by studies on riverbank filtration (e.g. Verstraeten et al., 2002; Verstraeten et al., 2003; Dragon et al., 2018). In our study, CLZ was detected in low concentrations in the canal and in some of the monitoring wells along the canal, which suggests that CLZ can reach groundwater via surface water infiltration. However, the CLZ in the canal might enter via the WWTP effluents, as the other surface water bodies, especially the Combe, which was connected to an agricultural drainage system, never showed CLZ concentration above the LOQ. Thus, the CLZ concentration in our surface water bodies tends to be low. This has been also shown by Buttiglieri et al. (2009). In addition, Buttiglieri et al. (2009) have illustrated that the occurrence of CLZ in surface water bodies is often restricted to the spring period after the CLZ application. Therefore, even though CLZ can reach groundwater via surface water infiltration, surface water – groundwater interactions might have a negligible influence on the spatial distribution of CLZ in aquifers. In contrast, elevated CLZ metabolite concentration in surface water bodies can occur over the entire year and not only during a limited time (Buttiglieri et al., 2009), which is consistent with our findings. In addition, metabolites are usually more polar and less sorptive compared to their parent compounds. Therefore, surface water – groundwater interactions might be especially important for the metabolites. Previous studies, which included also metabolites, have shown that they can be also found in groundwater after riverbank filtration (Nagy-Kovács et al., 2018; Verstraeten et al., 2002; Verstraeten et al., 2003). This has been shown for metazachlor-ESA, metolachlor-ESA, metolachlor-OXA, alachlor-ESA, acetochlor-ESA, acetochlor-OXA and different metabolites of atrazine (e.g. deethylatrazine, deisopropylatrazine, hydroxyatrazine) (Nagy-Kovács et al., 2018; Verstraeten et al., 2002; Verstraeten et al., 2003). The physico-chemical properties of DPC and MDPC are similar to those of the above-mentioned metabolites (Table 2). Therefore, we can expect a similar persistence for DPC and MDPC during surface water infiltration, which is in accordance with our findings.

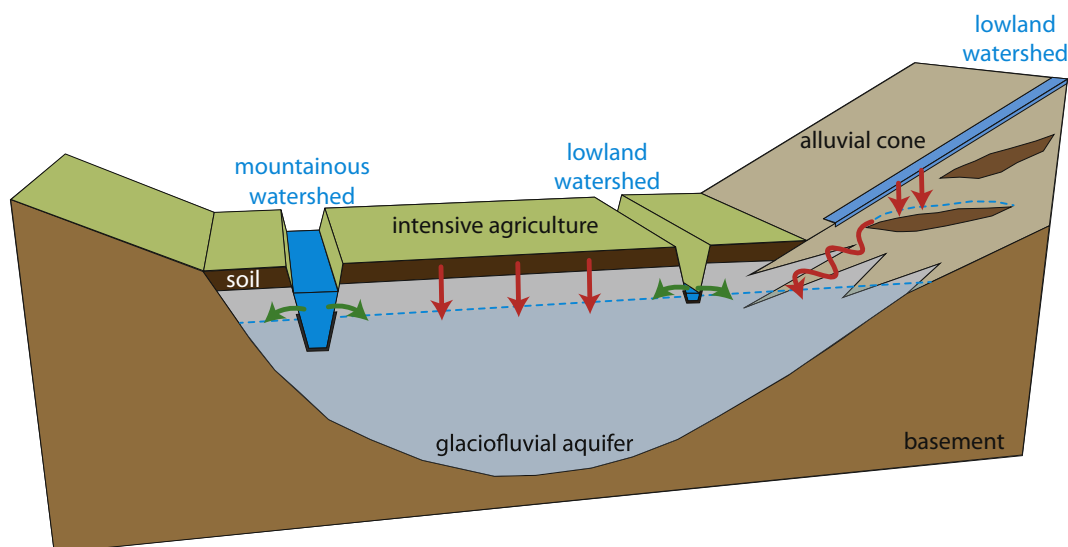


Fig. 7. Conceptual model with the different metabolite input from surface water bodies, soil and unsaturated zone. Arrows indicate the metabolite load (red: high load; green: low load).

The input of metabolites via surface water – groundwater interactions cannot only modify the spatial distribution of metabolites in groundwater, it can also influence the long-term dynamics of metabolites in groundwater and pumping wells after the application stop of the parent pesticide. The input of metabolites from outside of the exploited aquifer can result in a prolongation of travel times until the metabolites reach the pumping well. Due to the propagation, metabolites from outside of the exploited aquifer might still reach the aquifer even if the input from the soil and unsaturated zone above the exploited aquifer has stopped. This can result in a delayed response of metabolite concentrations in groundwater to such measures (e.g. application stop). This delay cannot be estimated by common groundwater age dating methods and it is not included in the groundwater age of the pumping well. Therefore, it is important to consider potential metabolite inputs through surface water – groundwater interactions for the evaluation of the metabolite concentrations and long-term dynamics of pumping wells.

4. Conclusions

Our case study on the herbicide CLZ and its metabolites has illustrated that surface water – groundwater interactions have an impact on the metabolite distribution in groundwater. The physico-chemical properties (higher mobility and polarity) of the metabolites might

favor an easy migration between surface water and groundwater. Especially the interactions between streams from agriculturally used lowland catchments and groundwater should be considered here, as these streams can have high metabolite loads. These streams can impact groundwater quality. Nevertheless, surface water – groundwater interactions (e.g. with rivers from mountainous watersheds) also have the potential to decrease the metabolite concentrations in groundwater.

Depending on the metabolite load of the river or stream, surface water – groundwater interactions can lead to an import of metabolites from zones outside of the exploited aquifer, which can have implications for the long-term dynamics of metabolites in groundwater pumping wells after stopping the application of the parent pesticide. Due to the propagation, resulting in a prolongation of travel times, metabolites from further away can still reach groundwater, even if the input from the soil and unsaturated zone) has stopped. This can cause a delayed response of metabolite concentrations in groundwater to such measures and should be considered for the evaluation of metabolite long-term dynamics in pumping well.

CRedit authorship contribution statement

Simone Hintze: Conceptualization, Investigation, Writing - original draft, Visualization, Writing - review & editing, Methodology, Formal analysis, Resources, Data curation. **Gaëtan Glauser:** Methodology, Writing - review & editing, Validation. **Daniel Hunkeler:** Conceptualization, Writing - review & editing, Supervision, Project administration, Methodology, Funding acquisition.

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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Table 2
Octanol-water partition coefficients, adsorption coefficients and half-life for selected metabolites (Lewis et al., 2016).

Name	Octanol-water partition coefficient (pH 7, 20 °C)	K_{oc} [mL g^{-1}]	K_{foc} [mL g^{-1}]	DT_{50} (typical) [days]
Metazachlor-ESA	–	8.8	5	123
Metolachlor-ESA	1.29×10^{-2}	9	–	400
Metolachlor-OXA	–	17	18.3	325
Alachlor-ESA	–	–	–	–
Acetochlor-ESA	–	28.8	104	90
Acetochlor-OXA	–	24.3	49.8	59
Deethylatrazine	3.24×10^1	110	–	45
Deisopropylatrazine	1.41×10^1	130	–	–
Hydroxyatrazine	1.23×10^2	–	–	164
Desphenyl-chloridazon	–	–	50	108
Methyl-desphenyl-chloridazon	4.17×10^{-2}	–	92	145

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2020.139109>.

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