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Removal and persistence of pharmaceuticals in Induced River Bank Filtration system in low-flow regime

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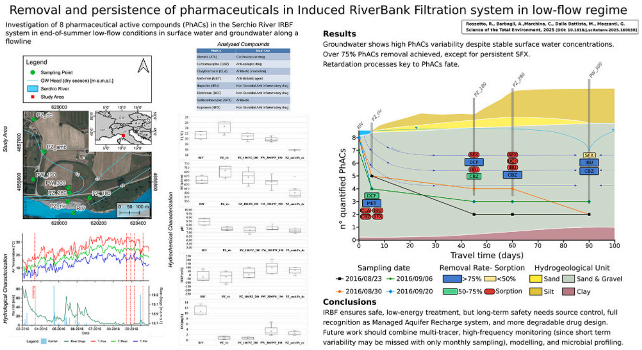
HIGHLIGHTS

- PhACs data from Induced Riverbank Filtration scheme in low-flow conditions
- Groundwater shows high PhACs variability despite stable surface water concentrations.
- Retardation processes key to PhACs fate; monthly sampling may miss it
- Over 75 % PhACs removal achieved, except for persistent Sulfamethoxazole
- IRBF proves a low-energy method for safe drinking water production.

GRAPHICAL ABSTRACT



Removal and persistence of pharmaceuticals in Induced RiverBank Filtration system in low-flow regime

Investigation of 8 pharmaceutical active compounds (PhACs) in the Serchio River IRBF system in end-of-summer low-flow conditions in surface water and groundwater along a flowline

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Analyzed Compounds

PhACs	Main Use
Atenolol (ATL)	Cardiovascular drug
Carbamazepine (CBZ)	Anti-epileptic drug
Clarythromycin (CLA)	Antibiotic (macrolide)
Metformin (MET)	Anti-diabetic agent
Ibuprofen (IBU)	Non-Steroidal Anti Inflammatory drug
Diclofenac (DCF)	Non-Steroidal Anti Inflammatory drug
Sulfamethoxazole (SFX)	Antibiotic
Naproxen (NPX)	Non-Steroidal Anti Inflammatory drug

Results

Groundwater shows high PhACs variability despite stable surface water concentrations.
Over 75% PhACs removal achieved, except for persistent SFX.
Retardation processes key to PhACs fate.

Conclusions

IRBF ensures safe, low-energy treatment, but long-term safety needs source control, full recognition as Managed Aquifer Recharge system, and more degradable drug design. Future work should combine multi-tracer, high-frequency monitoring (since short term variability may be missed with only monthly sampling), modelling, and microbial profiling.

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ABSTRACT

Induced RiverBank Filtration (IRBF) systems may provide reliable and safe drinking water, but at the same time the presence of pharmaceutical active compounds (PhACs) residues in surface- and ground-water raises concerns over their potential health and environmental impacts.

We present here the first field-based dataset on PhACs in an IRBF system during low-flow conditions, highlighting the fate of these compounds in a highly conductive, organic-matter poor aquifer. Data were gathered in four samplings run over a one month time.

Surface water PhACs concentrations remained low and stable (generally lower than 10 ng/L), yet groundwater showed significant variability (from few to one hundred ng/L), with Ibuprofen, Clarithromycin and Diclofenac reaching levels up to 100 times higher, likely due to retardation processes. While Atenolol, Naproxen, and Metformin were rapidly removed, Ibuprofen, Carbamazepine, and Sulfamethoxazole remained detectable at the drinking water well (at about 1 ng/L concentration), likely due to low microbial uptake at low concentrations. All PhACs showed removal rates above 75 %, but Sulfamethoxazole, supporting the effectiveness of IRBF systems, even in advective-dominant aquifers. Increasing travel distances to target wells for improving attenuation may not be a reliable solution, as other sources of contamination may be introduced in the system. Calculated degradation rates were generally higher than in laboratory studies, reinforcing the need for in-situ data,

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capturing the complexity of aquifer conditions, including subsurface heterogeneities, groundwater flow patterns, and geochemical variability. High-resolution monitoring is essential: monthly sampling risks missing critical processes such as sorption/desorption. The Serchio River IRBF system proved effective at reducing PhACs presence in drinking water well below 0.1 μg/L, highlighting its value as an energy-efficient treatment method. To ensure safe use of IRBF, future research must integrate geochemical, and metabolite tracking information, along with a proactive approach to designing degradable PhACs, hence, reducing the need on downstream treatment systems.

1. Introduction

Pharmaceutical active compounds (PhACs) have been detected in aquatic environments worldwide, including surface water (Adeleye et al., 2022) and groundwater (Jurado et al., 2022), with concentrations ranging from a few ng/L to thousands of μg/L. Once released in the environment as treated, poorly treated or even untreated wastewater effluent, they enter the water cycle and may then be found even in drinking water (Petrie et al., 2015). PhACs only slightly transform or degrade during standard wastewater treatment processes (Chefetz et al., 2008). In the aquatic systems, resisting to degradation, they may pose significant ecotoxicological and human health concerns (Bruce et al., 2010). Chronic exposure to trace PhACs in drinking water is linked to endocrine disruption, antimicrobial resistance, genotoxicity, carcinogenicity, and immune-allergic effects (Daughton and Ternes, 1999). Collier (2007) highlighted elevated risks for pregnant women and children. Qin et al. (2020) identified Sulfamethazine as a moderate to high risk, especially for infants. Still, many PhACs lack proper evaluation for developmental toxicity. Despite no legal limits are in place, the risks they pose to the environment and health have led to increased monitoring in aquatic systems (Sui et al., 2015).

In hydraulically connected surface water and groundwater systems, PhACs in surface water may filtrate and then contaminate aquifers (Groeschke et al., 2017; Ma et al., 2022). This is of particular importance in Induced RiverBank Filtration (IRBF) systems. IRBF is a type of Managed Aquifer Recharge (MAR) technique (Dillon et al., 2019) for providing drinking water which combines reliable supply of groundwater and good chemical quality. In IRBF systems, wells set along a nearby surface water body, such as a river, lake, or basin, induce surface water flow in hydraulically connected aquifers. Consequently, the water withdrawn is a blend of natural groundwater and infiltrated surface water. As in similar MAR systems, i.e. Soil Aquifer Treatment (SAT; Amy and Drewes, 2007), processes such as filtration/sorption, dilution, and degradation of a number of pollutants may occur through the riverbed and aquifer sediments (Hiscock and Grischek, 2002; Hoppe-Jones et al., 2010). However, data from real scale IRBF sites, on the removal of PhACs (i.e., Carbamazepine or Sulfamethoxazole), not routinely covered by water utilities monitoring, are still scarce (Muschket et al., 2024). Despite the described abundance of PhACs in natural environments, their transport behavior in surface water/groundwater connected systems remains poorly understood by means of experimental studies (Bradley et al., 2016). Out of a systematic literature review (Rossetto and Dalla Battista, in preparation), to date only data on PhACs from 76 case studies are globally reported in the scientific literature. Experimental field studies are then needed to enhance our knowledge of degradation/persistence factors (Munz et al., 2019).

In particular, few data are available about the removal of PhACs in IRBF during low-flow periods in riverine systems. During such periods, up to 90–98 % of river discharge may consist of treated or poorly treated wastewater (Bradley et al., 2014). Then, conditions become suitable for evaluating the removal of pharmaceutical contaminants under effluent-dominated flow. Bradley et al. (2014) monitored PhACs during drought-related low-flow conditions in October and December 2012 at Fourmile Creek (US). They found that surface water rich in PhACs infiltrated the aquifer and travelled tens of meters from the source, even at concentrations exceeding provisional ecotoxicological thresholds, such as the 10 ng/L action limit set by the European Medicines Agency (2006). Moreover, end-of-summer low-flow conditions in IRBF systems are normally characterized by infiltrating water higher in temperature and poorer in oxygen than during the rest of the year (Munz et al., 2019). This may create conditions for persistence of a number of PhACs.

Commonly, studies compare PhACs loads and concentrations, in flood and low-flow conditions, by performing one single sampling campaign per period (i.e., van Driezum et al., 2019; Oberleitner et al., 2020). Munz et al. (2019) present a study with the highest temporal resolution of about four weeks, between samplings. However, it is not clear if this timing is consistent with PhACs concentration changes in both surface- and ground-water. As such, there is the need for data gathered at high-resolution temporal monitoring, which may allow a deeper understanding of bank filtration processes (Hamann et al., 2016).

We investigated the removal and persistence of eight PhACs under end-of-summer low-flow conditions at the Serchio River IRBF system (Lucca, Italy), through four high-frequency sampling campaigns conducted over the course of one month. Meffe and de Bustamante (2014) reviewed the presence of emerging contaminants in Italy and reported the presence in surface water of Atenolol, Carbamazepine, Naproxen, Ibuprofen, Diclofenac, Clarithromycin, and Sulfamethoxazole. At the same time, they reported little knowledge on the presence of PhACs in groundwater (with no specific information on IRBF systems), while the EU Decision 495/2015defined an initial watchlist for PhACs. Moreover, no data was available for Metformin from field studies, and still to date only four studies are available reporting Metformin data in IRBF at global scale. We then focused our analyses on the above-mentioned compounds. Specifically, we present a comprehensive dataset on PhACs occurrence in surface water, bank filtrate, and ambient groundwater, alongside associated physico-chemical parameters, and their short-term temporal variability. We quantify in-situ removal rates, first-order degradation constants, and half-lives as a function of surface water initial concentrations and groundwater travel distances (in a highly conductive aquifer) to a drinking water well and monitoring piezometers. Our study contributes a unique and robust dataset to the globally scarce data on PhACs in IRBF systems, providing evidences that IRBF can serve as an efficient natural treatment process even under low-flow conditions.

2. Materials and methods

2.1. Study area

The Serchio River IRBF scheme (providing an average annual volume of 16 Mm^3 of drinking water; Rossetto et al., 2020) presents a strong hydraulic connection between the river water and the underlying aquifer. Twelve vertical wells situated between 30 m and 120 m from the river shoreline, extract groundwater from the coarse sand and gravel aquifer. Pumping induces river water into this high-yield aquifer, showing an average transmissivity of 10^{-2} m^2/s (Rossetto et al., 2020). Site and hydrochemical investigations, and numerical simulations demonstrated that, at the well field, the percentage of Serchio River induced bank filtrate ranges from 100 % during the wet season to around 80 % in the dry season (Rossetto et al., 2020). Unconsolidated superficial silty to sandy sediments (5 to 7 m thick) cover the aquifer. Barbagli et al. (2019) present a general characterization of the Sant'Alessio aquifer sediments (collected from a core drilling into the riverbed). The aquifer sediments are characterized by alkaline pH (8.75), and low carbonate content (3.4 %), as well as a generally low mineralization and nutrient availability (Electrical Conductivity is 0.18 mS/cm, P-Olsen is 0.04 mg/kg, and Cation Exchange Capacity 4.9 cmol/kg). Additional information on the Serchio IRBF system can be found in Rossetto et al. (2020) and (2021).

Serchio River surface water quality is impacted by discharge of secondary treated wastewater and poorly treated household wastewater brought by inflowing minor streams, and mountain runoff, peaking during autumn and spring season. In summer time, few m^3/s released from hydro-energy reservoirs partly guarantee discharge for environmental reasons, especially in drought times (Rossetto et al., 2021). The required drinkable water quality standard is naturally obtained at the IRBF by means of several processes along the flowpath from the river to the pumping wells (Rossetto et al., 2021). At the same time, fast and unpredictable pollution events may impact the Serchio River water quality. In example, the herbicide Terbuthylazine contaminated surface water between 2002 and 2005 (Longo and Semplici, 2007), and in turn the abstracted groundwater (Longo et al., 2007), in the order of few tens of μg/L. Thus, requiring derogation respect to the contaminant concentration in drinking water.

2.2. Experimental set-up and environmental conditions

We sampled surface- and ground-water river/aquifer across the Sant'Alessio plain along potential flowpaths at different distances and travel times from the river shoreline to an IRBF pumping well. The experimental set-up includes (Table 1 and Fig. 1): i) the Serchio River surface water (RIV), ii) an instream two-inches piezometer (PZ_riv), iii) two two-inches piezometers (PZ_180 and PZ_280) between the river, and iv) the IRBF well, PW_300 (pumping on average 35 L/s, and about 50 L/s maximum pumping rate), about 70 m away from the river shoreline during the dry season. We also monitored ambient groundwater (not impacted by the IRBF system) at two-inches piezometers (PZ_amb and PZ_dc) out of the IRBF system, upstream the IRBF well PW_300. In March 2016, we also sampled the PW_190 IRBF well and the Freddanella drain (DC). The latter is a small drainage channel collecting poorly treated household wastewater. Although the drainage channel bed is divided by the aquifer by a 6 m thick silty-sandy layer, still diffusion/dispersion processes may allow a potential spreading of PhACs in groundwater. PZ_dc, on the bank of the drainage channel, was then monitored in order to test the Freddanella channel as an alternative source of PhACs to groundwater.

We performed one day exploratory sampling campaign on March 22nd 2016 (Table 2). Then, we performed four sampling campaigns (end-of-summer low-flow conditions) in about one month starting from 23rd August 2016, the 30th, 6th and 20th September (Table 2).

Rainfall and air temperature information are provided in Fig. 2a and b, while Table 2 presents river head during the sampling days. Section 1 (Supplementary material) discusses the hydrologic conditions and presents the calculated river discharge data on the sampling days. Because of the hydrologic conditions at the time of sampling, river head varying between 0.1 and 0.16 m above datum, and air temperature at a rather constant value, we monitored chemical species concentrations in low-flow conditions, avoiding extreme events.

We could not sample the Freddanella ditch (DC) in the end-of-summer sampling campaign since no water flown as result of complete infiltration and evapotranspiration processes. Flow at about 1 km distance upstream of the monitoring point was less than 1 L/s, then completely infiltrating through the channel bed.

Rossetto et al. (2017a and 2020) presented a transient, two year-long (1st December 2014 to 30th November 2016), calibrated MODFLOW-2005 (Harbaugh, 2005) groundwater flow model. Flowlines and estimated travel times from the source river water to the monitored points (Table 1, column *Travel time*[a]) were derived from MODPATH simulations (Pollock, 2016) using simulated groundwater velocities from the MODFLOW model (Rossetto et al., 2017b).

We also calculated for each monitoring point the shortest distance from the river shoreline to account for shortest flowpaths not potentially identified with the available data in the implemented groundwater flow model (Table 1). Using velocities computed in the groundwater flow model, we calculated travel time for these shortest potential flowpaths (Table 1, column *Travel time*[b]).

2.3. Surface water and groundwater sampling

We determined surface water and groundwater chemical-physical parameters temperature (T), electrical conductivity (EC), Dissolved Oxygen (DO), and the Oxidation-Reduction Potential (ORP) at all sampling points using a Hydrolab© QuantaG (Hydrolab Corporation, Austin, Texas 78,754, USA) multiparameter probe.

Surface water samples were collected 30 cm below the water surface, where the flow was sufficiently high to guarantee a representative sample. Groundwater samples in piezometers were collected using a low-flow pump after purging at least three well volumes and reaching stable values of the monitored chemical-physical parameters during sampling (parameters changing less than 10 % in 3 consecutive readings after a 5 min measuring time at the end of purging). Raw groundwater samples at drinking water wells were collected opening a tap at the well. These samples may then show higher DO than the others. Grab sampling was performed both for surface water and groundwater. We collected samples in 1 L polypropylene (PP) bottles and then stored at 4 °C during transportation. They were frozen at −18 °C before the analysis, and analysed within 30 days from sampling.

Table 1
Main characteristics of the monitoring points included in the experimental set-up. SW = surface water; GW = groundwater; NA = not applicable; [a] Travel time computed using groundwater flow model simulations; [b] Travel time range computed using minimum and maximum groundwater flow velocities from the groundwater flow model simulations and shortest distance from river shoreline.

Monitoring points	Type of water	Screened depth from soil surface (m)	Position	Distance from river shoreline along a flowline (m)	Travel time[a] (days)	Shortest distance from river shoreline (m)	Travel time[b] (days)
RIV	SW	NA	River	NA	NA	NA	NA
PZ_riv	GW	13–15	In-stream piezometer	2	<5	2	<5
PZ_180	GW	14–15	IRBF piezometer	180	<45	40	9–12
PZ_280	GW	16–19	IRBF piezometer	280	<60	47	12–24
PW_300	GW	11–24	IRBF well	300	<90	73	16–22
PW_190	GW	6–23	IRBF well	190	<45	102	22–31
PZ_amb	GW	8–9	Upstream IRBF piezometer	NA	NA	245	NA
PZ_dc	GW	8–9	Upstream IRBF piezometer	NA	NA	456	NA
DC	SW	NA	Drainage channel	NA	NA	454	NA

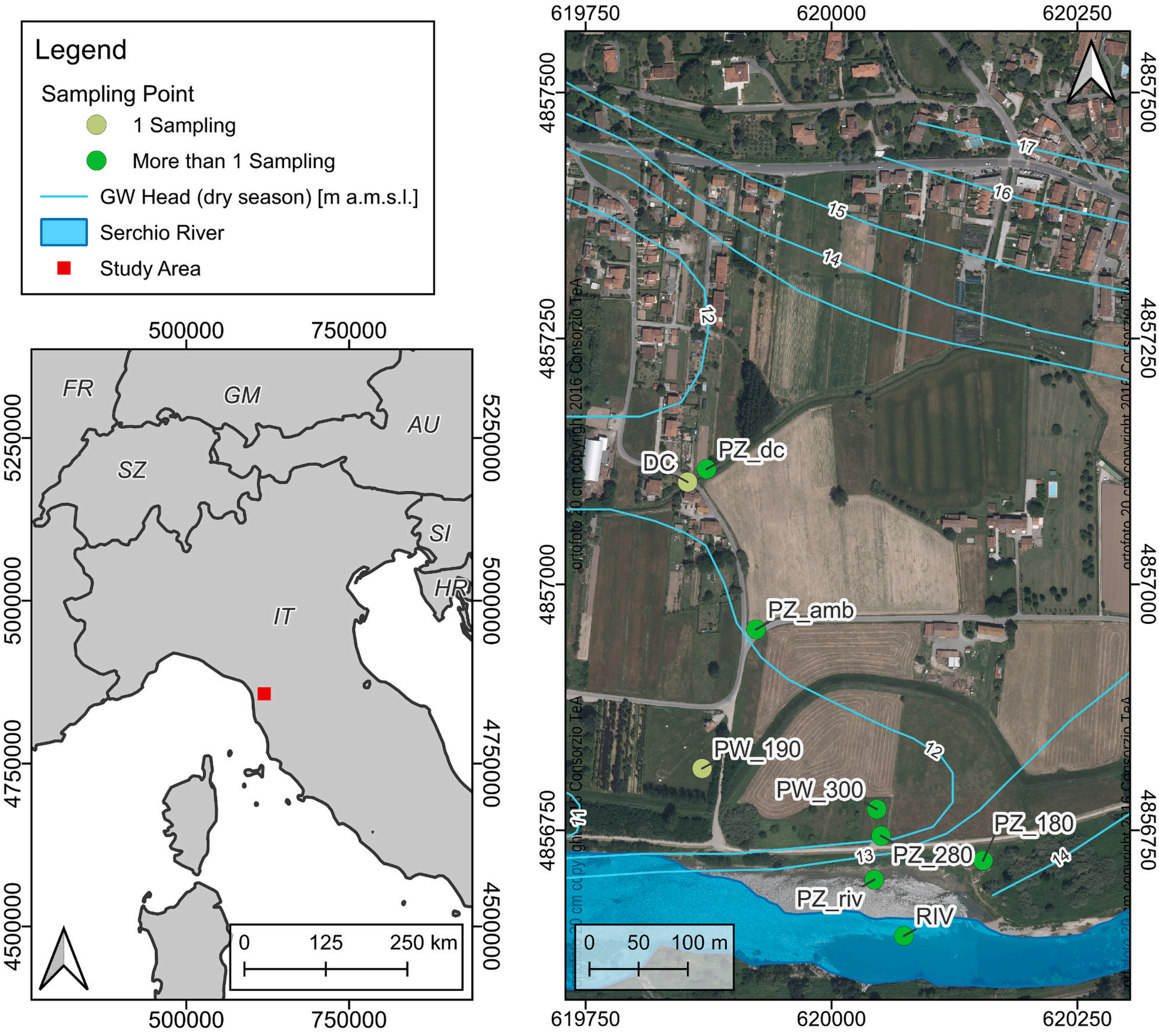

Fig. 1. Geographical setting, sampling points and groundwater head isolines.

Table 2

Date of sampling, river head, river discharge, and n. of collected surface water and groundwater samples. Determination of discharge data is presented in Section 1.1 Supplementary Material. NA = not applicable.

Date	River head (m)	River discharge (m^3/s)	Surface water samples (river)	Surface water samples (drainage channel)	Drinking water wells samples	Piezometers samples	N. of analysed compounds
22/03/2016	0.36	64.06	1	1	2	2	6
23/08/2016	0.10	4.94	1	0	1	5	8
30/08/2016	0.11	5.97	1	0	1	5	8
06/09/2016	0.14	9.68	1	0	1	5	8
20/09/2016	0.16	12.64	1	0	1	5	8
		n. of samples	5	1	6	22	NA

2.4. *Monitored PhACs and instrumental analyses*

We analysed the following PhACs: Atenolol (ATL), Carbamazepine (CBZ), Clarythromycin (CLA), Metformin (MET), Ibuprofen (IBU), Diclofenac (DCF), Sulfamethoxazole (SFX), Naproxen (NPX) (Table S2 Supplementary Material). MET and SFX were included in the PhACs list only after the March 2016 exploratory campaign.

Samples were filtered, and analysed using high-performance liquid chromatography–tandem mass spectrometry (HPLC–MS/MS), after solid phase extraction (SPE), following Riva et al. (2015). Acidified samples were spiked, extracted, and eluted. Eluates were dried, redissolved, and analysed via SRM in both ionization modes. Quantification

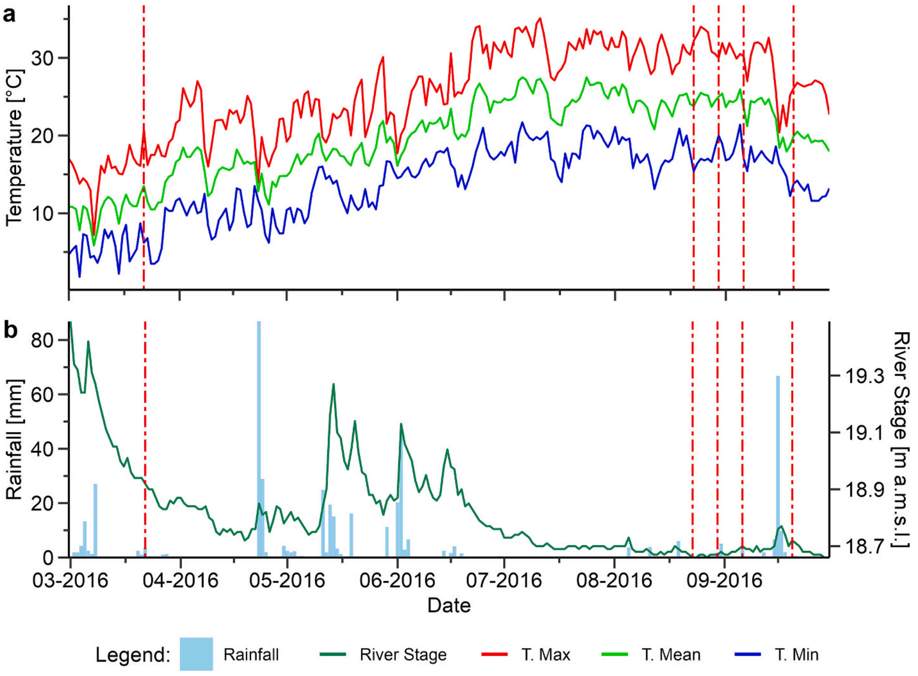

Fig. 2. a) Daily maximum, minimum and average air temperature. b) Rainfall and river head in the investigated area from March 2016 to 30 September 2016. River head data from the Monte S. Quirico monitoring station (TOS02004291; Servizio Idrologico e Geologico, Regione Toscana, www.sir.toscana.it); Daily rainfall and temperature data from Lucca (Orto Botanico) meteo station (TOS02000512; Servizio Idrologico e Geologico, Regione Toscana, www.sir.toscana.it). Vertical red dashed lines represent sampling days.

used isotope dilution, with identification by retention time and Limit of Quantifications (LoQ) based on a signal/noise ratio of 10. Information on instrumental analyses of PhACs are provided in Section 2.1 of Supplementary Material.

2.5. Data analyses

We performed exploratory data analysis and summary statistics to get a general insight on the pattern of the presented data. We calculated the Pearson correlation coefficient between PhACs and groundwater T, DO, ORP, and pH. During data analyses, a concentration of LoQ/2 was attributed to measured PhACs concentrations lower than LoQ (Jasa et al., 2019). For statistical reasons, in some calculations, we averaged data of PZ_180 and PZ_280, representing groundwater between the river and the IRBF well, and PZ_dc and PZ_amb, representing ambient groundwater outside of the IRBF scheme.

We calculated the PhACs removal rate (R_r) in the IRBF system in low-flow conditions using the formula:

$$R_r\ (\%) = \left[(C_{riv} - C_{gw})^{*} 100\right] / C_{riv}$$

where:

C_{riv} is the average surface water concentration of the PhAC [ng/L],

C_{gw} is the groundwater concentration of the PhAC at a specific monitoring point [ng/L].

Removal rate was calculated at all points at all monitored times, and as an average for the whole end-of-summer low-flow period.

Maximum removal rate (R_{rmax}) was calculated considering RIV concentration and PhAC specific LoQ following Muschket et al. (2024):

$$R_{rmax} = 100 - [100/(C_{riv}/LoQ)]$$

When concentration in groundwater was <LoQ, the calculated removal was replaced with the calculated R_{rmax} to take LoQs into account (analytical limits), avoiding reporting complete removal.

Finally, we calculated first order degradation rate constant (k, t^{-1}) and half life ($t_{1/2}$, t) as per:

$$C_t = C_0 \cdot e^{-kt}$$

where C_0 [ng/L] is the average river concentration for the *PhAC*,

C_t [ng/L] is groundwater concentration for the *PhAC* at time t,

and t (day) is travel time as per Table 1 and Section 2.2.

As input concentration, we assumed constant river concentration, given by the average of the four sampling periods for each analytes (average of four values).

As SFX was not quantified once in surface water, average for SFX input concentration was given only for samples with concentrations >LoQ. For that sampling k for SFX was then not calculated.

k was calculated at each groundwater point for two travel times: i) shortest distance travel time; ii) travel time along a flowline (Table 1). Final k values are average of the two values. When the degradation rate was negative, we set it to zero.

3. Results and discussion

3.1. Occurrence and concentrations of monitored PhACs and removal rates

PhACs monitored concentrations on the March 2016 (receding limb condition) and the end-of-summer 2016 (low-flow conditions) samplings are presented in Section 3 (Table S3 and S3.1) of Supplementary Material.

3.1.1. March sampling campaign 2016

All of the PhACs searched in Serchio River surface water were quantified at the lower end of the concentration range (<10 ng/L) compared to surface water data reported in the literature (e.g., Petrie et al., 2015; Adeleye et al., 2022). Similarly, all of the PhACs, were quantified in the Freddanella channel (DC), but showing the highest concentration values, being from one (IBU) to two (ATL) order of magnitude larger that those in the Serchio River. Quantified concentration of ATL, CLA, DCF, IBU and NPX showed values similar to those of a secondary treated effluent at the outlet of a wastewater treatment plant (Petrie et al., 2015). In the IRBF scheme, concentrations of PhACs in groundwater were all lower than in Serchio River. Although located on the bank of the Freddanella ditch, PZ_dc showed no quantification for all of the investigated compounds. The latter may be due to the attenuation processes occurring within the thick unsaturated zone in the sandy/silty surficial layer, combined with dilution processes related to rainfall aquifer recharge.

Assuming infiltrating surface water concentrations were constant in the previous months, removal rates at wells PW_300 and PW_190 are high for ATL, DCF, and NPX (<LoQ), while values lower than 1 ng/L were detected for CBZ and CLA. On the other hand, IBU increasing concentration at PW_190 suggests the occurrence of sorption/desorption processes.

3.1.2. *End-of-summer low-flow condition sampling campaign 2016*

From a qualitative point of view, Fig. 3 shows the number of quantified analytes at each sampling point as a function of travel time along a flowline, and also considering potential travel times for shortest paths not identified in the above-mentioned groundwater flow model. The number of quantified PhACs (two to three out of eight) at the PW_300 well and at the other monitored points does not significantly differ in time.

Table 3 presents statistics for PhACs at each monitoring point. Again, all the searched analytes were always quantified in the Serchio River water. Only at one sampling SFX was below the LoQ. Concentrations in the low-flow period are similar to those in March 2016, in the order of few to ten ng/L, except for MET (reaching up to 150 ng/L, not monitored in March), and no significant variations in time were recorded.

For what concerns groundwater, ATL and NPX were not quantified in all of the samples. CLA and MET were only quantified in PZ_riv (instream piezometer). DCF was only quantified twice in PZ_riv, and once in PZ_180 and PZ_280. CBZ was quantified in the whole IRBF system, but not in the outside piezometers. SFX was not always quantified. IBU was quantified barely in all the samples.

At PW_300 (drinking water well), only CBZ and SFX were always quantified even if at concentrations of about 1 ng/L, and less than 1 ng/L over the LoQ. IBU, still in very low concentrations, was quantified only 2 times out of 4.

Calculated removal rates are shown in Table 4a for each point at each monitoring time, while Table 4b reports average removal rates. Negative removal are here set to zero. Several researchers found that attenuation of PhACs is maximum in the first few meters of the riverbed (Hollender et al., 2018; Zeng et al., 2020), and our results do not substantially differ for ATL, NPX and MET. ATL and NPX were removed within the first few meters, and we did not quantify them either in the instream piezometer (PZ_riv). Similarly, MET, reduced in concentration in the instream piezometer (PZ_riv), was removed up to about 99.6 % (that is R_{rmax}). CLA presented higher concentration values in the instream piezometer PZ_riv than in surface water, and then was removed in all of the other sampled groundwater, up to the R_{rmax} (94.5 %), for travel time between 8 and 45 days. DCF showed varying removal rates, but achieved R_{rmax} at all samples at the PW_300 well. CBZ, despite initial negative R_r, was increasingly removed along the flowpath, but still quantified at the drinking well, without achieving R_{rmax}, and showing different behavior during the four samplings. Similarly, IBU showed varying R_r (from negative to positive) in time, ranging from 44.3 % to R_{rmax}, while SFX showed the smallest R_r varying from 18.7 to 47.5 % at PW_300 well.

Our data shows that in the end-of-summer low-flow period, all of the monitored PhACs are removed at the drinking water well, considering 90 days travel time as longest travel time – but CBZ, IBU and SFX.

3.2. *Main physico-chemical characteristics of surface water and groundwater*

Section 4 - Table S4 Supplementary Material presents data on the

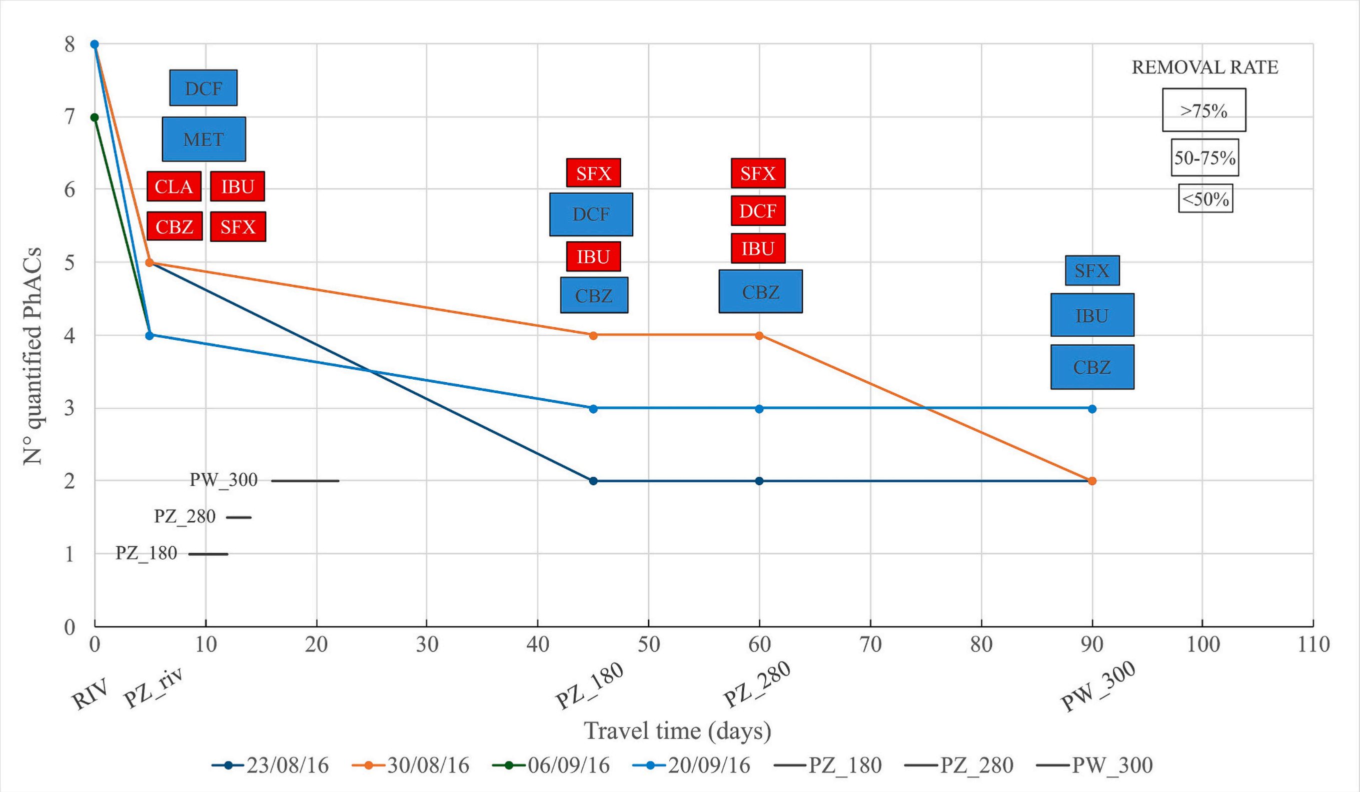

Fig. 3. Number of quantified PhACs as a function of the distance from the river shoreline along a flowline (coloured lines). Black segments show (for three monitored points) the calculated travel time range along potential shortest distance flowpaths from the river shoreline. Red boxes: sorbed PhACs. Blue boxes: removed PhACs.

Table 3

Summary statistics at the different monitoring points for the analysed PhACs. Min: Minimum value; Max: Maximum value; Avg: Average; SD: Standard Deviation.

Sample Id	Atenolol *(LoQ = 0.2 ng/L)*				Carbamazepine *(LoQ = 0.2 ng/L)*				Clarythromycin *(LoQ = 0.5 ng/L)*				Metformin *(LoQ = 0.5 ng/L)*			
	Min	Max	Avg	SD	Min	Max	Avg	SD	Min	Max	Avg	SD	Min	Max	Avg	SD
RIV	1.43	1.87	1.60	0.19	2.80	5.88	4.55	1.50	6.81	12.30	9.11	2.75	111.84	150.63	137.74	18.15
PZ_riv	<LoQ	NA	NA	NA	2.20	5.54	3.73	1.73	5.00	51.00	25.79	19.16	<LoQ	19.16	12.35	8.81
PZ_180/PZ_280	<LoQ	NA	NA	NA	0.40	3.30	1.42	0.99	<LoQ	NA	NA	NA	<LoQ	NA	NA	NA
PW_300	<LoQ	NA	NA	NA	0.60	1.09	0.82	0.26	<LoQ	NA	NA	NA	<LoQ	NA	NA	NA
PZ_amb/PZ_dc	<LoQ	NA	NA	NA	<LoQ	NA	NA	NA	<LoQ	NA	NA	NA	<LoQ	NA	NA	NA

Sample Id	Ibuprofen *(LoQ = 0.1 ng/L)*				Diclofenac *(LoQ = 0.2 ng/L)*				Sulfamethoxazole *(LoQ = 0.4 ng/L)*				Naproxen *(LoQ = 0.5 ng/L)*			
	Min	Max	Avg	SD	Min	Max	Avg	SD	Min	Max	Avg	SD	Min	Max	Avg	SD
RIV	1.42	3.60	2.51	0.90	0.85	4.15	2.98	1.46	<LoQ	2.51	1.35	3.27	0.81	1.60	1.22	0.33
PZ_riv	11.50	153.29	91.95	59.33	<LoQ	2.76	0.99	1.25	<LoQ	2.30	0.73	3.31	<LoQ	NA	NA	NA
PZ_180/PZ_280	<LoQ	35.20	6.51	11.78	<LoQ	72.33	9.24	25.50	<LoQ	2.30	1.29	3.32	<LoQ	NA	NA	NA
PW_300	<LoQ	1.40	0.58	0.65	<LoQ	NA	NA	NA	0.71	1.10	0.91	0.15	<LoQ	NA	NA	NA
PZ_amb/PZ_dc	0.31	23.89	4.14	8.07	<LoQ	NA	NA	NA	<LoQ	NA	NA	NA	<LoQ	NA	NA	NA

Table 4a

Removal rate at the different monitored points and sampling time.

LoQ	Max removal rate (R_{rmax} %)	PhACs	Date	PZ_riv (R_r %)	PZ_180 (R_r %)	PZ_280 (R_r %)	PW_300 (R_r %)
0.2	87.5	Atenolol	23/08/2016	87.5	87.5	87.5	87.5
			30/08/2016	87.5	87.5	87.5	87.5
			09/06/16	87.5	87.5	87.5	87.5
			20/09/2016	87.5	87.5	87.5	87.5
0.2	95.6	Carbamazepine	23/08/2016	0	52.1	83.5	76.0
			30/08/2016	0	27.4	77.8	78.2
			09/06/16	49.4	64.8	91.2	86.8
			20/09/2016	51.6	62.6	91.2	86.8
0.5	94.5	Clarythromycin	23/08/2016	0	94.5	94.5	94.5
			30/08/2016	0	94.5	94.5	94.5
			09/06/16	0	94.5	94.5	94.5
			20/09/2016	0	94.5	94.5	94.5
0.5	99.6	Metformin	23/08/2016	86.1	99.6	99.6	99.6
			30/08/2016	91.7	99.6	99.6	99.6
			09/06/16	86.5	99.6	99.6	99.6
			20/09/2016	99.6	99.6	99.6	99.6
0.1	96.0	Ibuprofen	23/08/2016	0	96.0	0	96.0
			30/08/2016	0	0	0	96.0
			09/06/16	0	52.2	84.1	44.3
			20/09/2016	0	0	4.5	68.2
0.2	93.3	Diclofenac	23/08/2016	7.2	93.3	93.3	93.3
			30/08/2016	67.1	67.4	0	93.3
			09/06/16	93.3	93.3	93.3	93.3
			20/09/2016	93.3	93.3	93.3	93.3
0.4	70.4	Sulfamethoxazhole	23/08/2016	70.4	30.5	70.4	47.5
			30/08/2016	70.4	3.9	26.1	47.5
			09/06/16	70.4	0	33.5	18.7
			20/09/2016	0	0	0	18.7
0.5	58.9	Naproxen	23/08/2016	58.9	58.9	58.9	58.9
			30/08/2016	58.9	58.9	58.9	58.9
			09/06/16	58.9	58.9	58.9	58.9
			20/09/2016	58.9	58.9	58.9	58.9

Table 4b

Average removal rate at the different monitored points for the whole end-of-summer low-flow period. NA: average not calculated when negative rates where present.

PhACs/ R_r %	PZ_riv	PZ_180	PZ_280	PW_300
Atenolol	87.5	87.5	87.5	87.5
Carbamazepine	NA	51.7	85.9	82.0
Clarythromycin	NA	94.5	94.5	94.5
Metformin	91.0	99.6	99.6	99.6
Ibuprofen	NA	NA	NA	76.1
Diclofenac	65.2	86.8	NA	93.3
Sulfamethoxazhole	NA	NA	NA	33.1
Naproxen	58.9	58.9	58.9	58.9

physico-chemical characteristics of monitored surface- and groundwater.

In March 2016, surface water and nearby groundwater (PZ_180) showed winter-like temperatures, while PZ_dc and PW_300 tended to typical ambient groundwater. EC ranged from 344 μS/cm in surface water to about 600 μS/cm at DC and PZ_dc. All sites showed a slightly oxidizing environment (<100 mV), with low DO only at PZ_dc.

Fig. 4 shows box-and-whisker plots for the end-of-summer low-flow condition samplings.

Surface water temperature ranged between 19.7° and 22.6 °C. Its seasonal signal could be detected in the IRBF groundwater, well differentiating the groundwater not impacted by the induced surface water flow (PZ_dc and PZ_amb). pH ranged from 8 to 9 in surface water, and

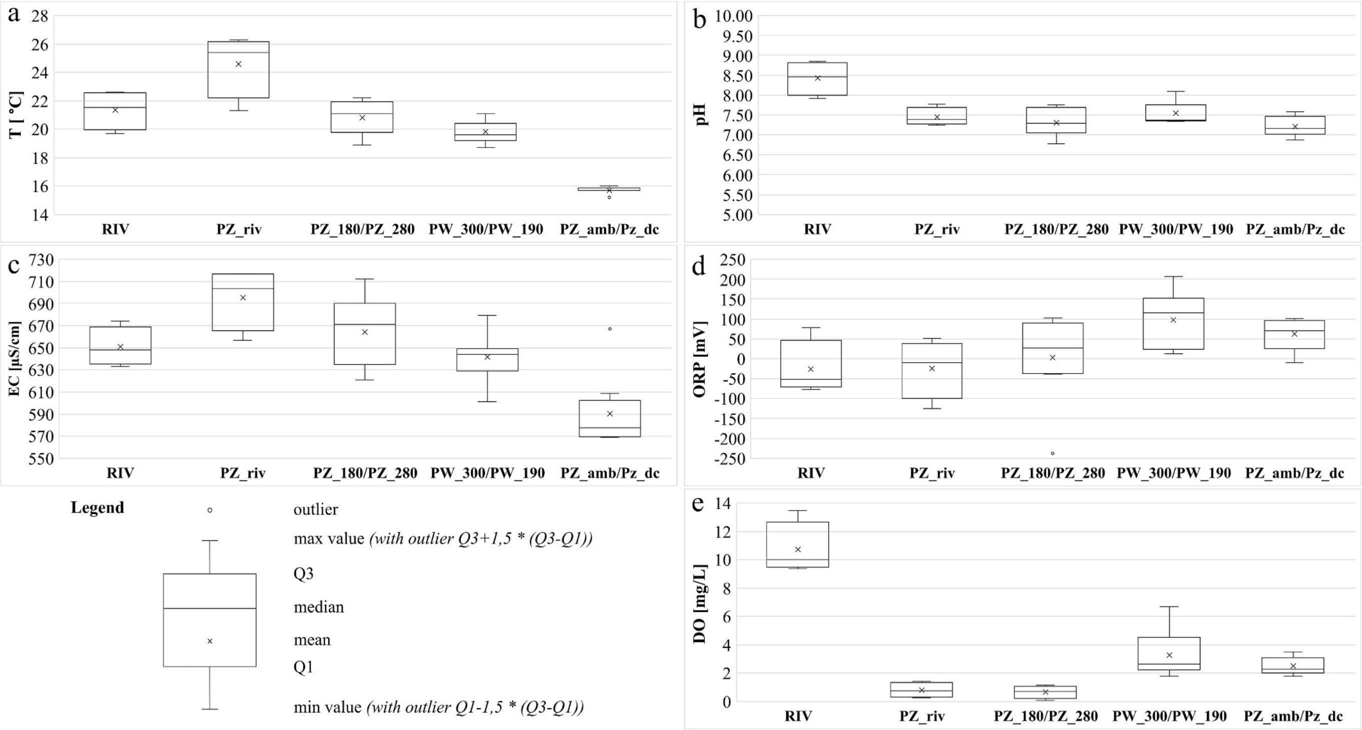

Fig. 4. Box-whiskers plots for T, pH, EC, ORP and DO at the monitoring point during the end-of-summer low-flow regime samplings.

between 7 and 8 in groundwater. EC values in surface water were similar to those of groundwater, even if locally higher values were recorded in groundwater, potentially related to higher mixing of the bank filtrate with local groundwater.

The river showed varying conditions with areas well oxygenated, with high velocity water (where the flow was concentrated), and others, with low velocity water, poor in oxygen and locally in reducing conditions (with small heads). Sampled groundwater was poor in DO (generally lower than 1 mg/L) and moving from oxidizing to reducing environment (103 to −238 mV) in time. Higher DO (1.78 to 6.69 mg/L) and oxidizing conditions were recorded at the PW_300 well, values potentially related to the sampling method. PZ_dc and PZ_amb showed much lower and less varying temperatures (from 15.2 °C to 16 °C), not (or little) impacted by the bank filtrate recharge, and more oxygenated and oxidizing conditions, likely due to their surficial level.

In general, at the investigated depth, parameters clarified that IRBF monitored groundwater shows high temperature, dominant low-oxic and slightly reducing environment, although the latter sometimes fluctuate.

Calculated Pearson correlation between CBZ, IBU and SFX and groundwater T, DO, ORP, and pH only shows significant positive correlation between groundwater temperature and CBZ (0.89) and IBU (0.87).

3.3. Processes governing the PhACs fate

The removal efficiency of organic micropollutants during riverbank filtration is governed by multiple interacting factors. Key ones influencing attenuation include subsurface residence time, temperature (Burke et al., 2014), redox conditions (Wiese et al., 2011), organic carbon content (particulate and dissolved; Hebig et al., 2017; Hoppe-Jones et al., 2012), and the local microbial community (Bertelkamp et al., 2016; Munz et al., 2019). Microbial degradation is generally the dominant removal pathway often described as influenced by redox conditions (Wiese et al., 2011; Burke et al., 2014), though field studies often lack detailed characterization of these dynamics (Jurado et al., 2022). Field scale assessment of degradation processes may be achieved through the quantification of metabolites concentrations. However, this approach is complicated by the high number and often low concentrations of metabolites. Sorption also plays a critical role, with interactions depending on PhACs charge and sediment surface properties. Negatively charged compounds bind to positively charged surfaces, while neutral compounds preferentially associate with organic matter. Sorbed PhACs can be remobilized, contributing to long-term persistence. Due to the site-specific and temporally variable nature of these factors, PhACs removal rates vary by up to three orders of magnitude across MAR systems (Greskowiak et al., 2017), complicating predictive modeling assessment of field-scale behavior.

Table 5
First order degradation rate constant (*this study and literature values*) along with half-life values. Removal processes include degradation, retardation, and dilution. Where sorption was supposed, degradation rate constants and half-lives are within parentheses. [1]field data, [2]laboratory data. [a]Ramil et al. (2010), [b]Munz et al. (2019), [c]Burke et al. (2014), [d]Bradley et al. (2016), [e]Storck et al. (2012), [f]Sanz-Prat et al. (2020), [g]Hamann et al. (2016), [h]Nham et al. (2015), [i]Xu et al. (2009).

PhACs	k (day^{-1})	$k_{literature}$ (day^{-1})	Half life ($t_{1/2}$) (days)	Removal at PW_300 well (travel time > 90 days)
ATL	>0.55	0.30–0.23[1a]	1.3	Fully removed
CBZ	(0.053)	>0.039[1b], 0.011[1c], 0.0087[1d]	(13.1)	Partially removed (*C at about 1 ng/L*)
CLA	(0.136)	0.019[1e], 0.016[2c]	(5.1)	Fully removed
MET	0.435	0.469[1d], <0.0016[1f]	1.6	Fully removed
IBU	(0.047)	>1.11[1g], 0.887[1h] > 0.09[1b]	(14.6)	Partially removed (*C at about 1 ng/L*)
DCF	(0.106)	0.539[1g], 0.0719[1b], 0.022[1c],	(6.5)	Fully removed
SFX	(0.016)	0.0369[1b], 0.032[1c], 0.01[1d]	(44.0)	Partially removed (*C at about 1 ng/L*)
NPX	>0.32	0.041–0.12[2i] 0.092[1g]	2.2	Fully removed

Table 5 presents the first order degradation rate constant (along with data from other studies) and half life values. In our end-of-summer low-flow conditions and low concentrations of PhACs the degradation rate constant values decrease following the order ATL (highest) > MET>NPX > CLA > DCF > CBZ > IBU > SFX (lowest).

ATL, and NPX were not quantified in the bank filtrate, while MET was only quantified in PZ_riv. These substances are highly degradable in high temperature conditions in the aquifer, even in low-oxygen conditions, showing high degradation rates, and then small half life values ($t_{1/2} < 2.2$ days). High biodegradation has already been reported for ATL and MET (Bradley et al., 2014) and NPX (Regnery et al., 2015). Hollender et al. (2018) and Muschket et al. (2024) also report remarkably high removal rates for MET, on the contrary Sanz-Prat et al. (2020) describe it as a persistent PhAC. Field data for this PhAC are still very low in number (only four studies available) and dedicated research is needed.

CLA concentrations increased in PZ_riv in three samplings out of four, demonstrating sorption, and high potential for desorption. However, CLA was not detected in any of the bank filtrate samples at longer distances. This suggests that biodegradation is the primary removal mechanism. On the other hand, in the March sampling it was detected at all IRBF monitored groundwater points. This could be due to lower groundwater temperature, causing lower microbiological activity. Heberer et al. (2008) report high removal of CLA under oxic conditions, and Labad et al. (2023) removal rates >96 %. Jurado et al. (2022), in their review, suggest CLA is degraded rather than sorbed through soil passage. Our data show, even if CLA undergoes degradation, sorption and desorption processes may be relevant, confirming the importance of travel distance. Glorian et al. (2018) relate higher removal efficiency with travel time to the increase of the available surfaces for sorption processes along the flowpaths. Still few field data are available for this PhAC.

Our data on DCF are consistent with Alidina et al. (2015) whose work in columns found DCF better degraded under high temperature. DCF concentrations in groundwater bank filtrate were generally low. Degradation rates are slightly higher, but in agreement with other calculated at field scale. The high concentration at PZ_280 on 30 August demonstrates that changes in aquifer conditions may cause large desorption, but such changes may not be related to changes in ORP (Table S3). Barbagli et al. (2019) also reported that DCF undergoes sorption in soil column test using organic-poor sediments from this IRBF system, in agreement with Chefetz et al. (2008). Nonetheless, DCF was completely removed at well PW_300. Contrarily to our findings, Munz et al. (2019) found DCF to be persistent in summer under high T and low DO, and highly mobile, while van Driezum et al. (2019) consider DCF degradable in oxic groundwater.

CBZ concentrations were generally diminishing with distances from the shorelines, highlighting potential for biodegradation. Yet, CBZ reached removal rate up to 85.9 % at travel time < 60 days. Testing for dilution effects at PW_300, starting from average surface water concentrations and considering a 80/20 ratio surface water/groundwater in bank filtrate (Rossetto et al., 2020), confirms dilution has a marginal impact on CBZ removal. Anyway, concentration increases at PW_300 demonstrates potential for sorption and desorption. Positive correlation between CBZ concentration with increasing groundwater temperature shows desorption is driven by increasing groundwater temperature in our conditions. Yang et al. (2017) found that ORP higher than 200 mV support CBZ and DCF removal. Still, Yang et al. (2017) found CBZ undergone sorption, while contrarily expected to be mainly affected by biodegradation. Also, Barbagli et al. (2019), similarly to DCF, found CBZ to sorb during column tests, and then desorbing. Wiese et al. (2011) and Muschket et al. (2024) report CBZ to be hardly removed under prevailing oxic conditions (<20 %). Munz et al. (2019) observed high removal rates under anoxic conditions. Hamann et al. (2016) consider CBZ to be a persistent organic micropollutant, both under oxic and anoxic conditions.

We found IBU to be persistent and undergoing large sorption processes, increasing about two order of magnitude in concentration from surface water to groundwater, but decreasing along the flowpath to about 1 ng/L. Similarly to CBZ, the positive correlation between IBU concentration and groundwater temperature indicates that desorption is promoted by increasing groundwater temperature. Hiller and Šebesta (2017) conducted sorption–desorption experiments for IBU using agricultural soils. They found that as temperature increased, sorption of IBU decreased, indicating the process is exothermic and, hence, less favourable at higher temperatures. Munz et al. (2019) found IBU, known to be degradable under oxic conditions (van Driezum et al., 2019), removed at short-distance, at low summer river concentrations in low oxygen conditions. Carr et al. (2011) in laboratory experiments support IBU degrades more efficiently under reduced oxygen conditions, with a half-life of 41.2 days, compared to aerobic conditions. Hamann et al. (2016) report IBU to be fully removed. Our k is about 50 % lower than that calculated by Munz et al. (2019). Still, few field studies have been conducted on this compound to generalise its behavior.

SFX is likely the most investigated PhACs in IRBF systems as well as CBZ and DCF. Removal data are often contradictory with removal rates varying from about 10 % to 100 % (Kruć et al., 2019) and SFX is reported only partially attenuated in IRBF field studies (Bradley et al., 2014; Muschket et al., 2024). Also the role of dilution in removing SFX is minor. Hamann et al. (2016) report SFX to be fully removed in IRBF in anoxic conditions, as same as van Driezum et al. (2019). Bradley et al. (2016) presented data on groundwater system in hydraulic connection with a stream impacted by treated wastewater, after the closure of the wastewater treatment plant for one year. SFX and CBZ demonstrated long-term persistence, with sorbed phase to constitute a long-term residual source of contamination for the aquifer. Although Munz et al. (2019) found SFX degradation positively correlated to temperature (likely due to lower microbial activity at lower T), our data show that at low-concentration, SFX is hardly degradable in low-oxygen conditions, even if at high groundwater temperatures. Sorption/desorption processes may be responsible for its presence in bank filtrate, at concentrations of few ng/L.

Calculated degradation rates (Table 5) are higher than previously reported for ATL, CBZ, CLA and NPX, in the same range for MET, IBU and DCF, and in the low range for SFX. Most degradation rate constants, and half-lives are derived from laboratory studies. Such experiments often neglect the heterogeneity and complexity of natural aquifers. Consequently, in-situ assessments are crucial for understanding the fate of micropollutants under realistic IRBF conditions (as also outlined in Jurado et al., 2022). Moving forward with understanding of PhACs fate in IRBF systems will need to better define groundwater flow patterns, to track specific water "*packages*" from surface water through the aquifer, and temporal variability in hydrochemical conditions, to simulate the impact on removal rates of the different processes (Greskowiak et al., 2017). Jurado et al. (2022) suggest characterizing subsurface heterogeneity based on the spatial distribution of porous media types and their hydraulic and geochemical properties to improve understanding of the behavior and fate of organic micropollutants in groundwater.

PhACs concentrations in surface water are generally lower than 10 ng/L and show little variations in time (Table S3 and S3.1 in Supplementary Material). At our case study, ATL, CLA, MET, DCF, and NPX are fully removed for a 90 days travel-time (well PW_300), while CBZ, IBU and SFX are still present even if at very low concentrations. Oberleitner et al. (2020), following Helbling (2015) and Kundu et al. (2019) works in context different from IRBF, relate these low concentrations to negligible uptake by micro-organism and/or down regulation of enzymes – with final reduced biodegradation. On the other hand, Wackett et al. (2002) reports significant biodegradation for high concentrations of micropollutants. Nonetheless, concentration at well PW_300 are two order of magnitudes well below provisional regulatory values, considered at 0.1 μg/L. This proves, at said concentrations, the IRBF technique's reliability in standard operational conditions, making of the

Serchio River IRBF one of the most safe MAR schemes for providing drinking water in Europe (Rodríguez-Escales et al., 2018).

Large variations in concentrations values in groundwater along a flowpath (such as for CLA, IBU, DCF) either testify: a) huge variations in surface water concentrations then reflected in groundwater ones; b) PhACs are not degraded, but retarded. As concentrations do not substantially change in surface water in the investigated period, and assuming they were not even changing in the preceding sixty days given the hydrologic conditions (Fig. 2), we may assume that large fractions of these compounds are sorbed within the medium and then desorbed depending on the local physico-chemical factors.

The high hydraulic conductivity (larger than 10^{-3} m/s), mineral and organic-matter poor, aquifer, with simulated groundwater velocities between 3.3 and 4.7 m/day, shows removal rates as high as those in Oberleitner et al. (2020). Hence, we do not confirm the assumption in Ray et al. (2002) that high conductivities may lead to reduced chemical quality.

Although PhACs concentrations in surface water are relatively constant in the investigated period, the same does not apply for concentrations in groundwater. Hence, description of the fate of emerging organic compounds in an aquifer cannot rely on simple monthly sampling as reported in large part of the published studies. In doing so, there is the high risk of not considering processes such as sorption/desorption (i.e., CLA and DCF in our case). Experimental studies characterizing PhACs dynamics at higher spatial- and temporal- resolution are needed.

3.4. Other sources of pollution

At the points outside the IRBF system, no PhACs were quantified in groundwater but IBU. Despite the Freddanella ditch (DC) is a major source of PhACs, we may infer both the surficial silt layer protects the aquifer, creating a reliable barrier to contamination, and low aquifer recharge rate (due to the low flow in the ditch) reduces contamination risks. Still, specific PhACs (such as IBU) may reach the aquifer from the Freddanella ditch. With no dilution achieved thanks to natural recharge, they may constitute a threat to the drinking water supply. As such, we cannot assume that the concentration of IBU at drinking well PW_300 is only dependent on bank filtration. Our data shows that attenuation of IBU takes place on both sides of the IRBF well.

Several authors discuss the need to consider longer distances in IRBF in order to achieve maximal removal of PhACs. However, this may not be a reliable solution. Increasing distances between the IRBF water body and the target wells may bring into play additional sources of contamination present in the landscape, contributing to worsening groundwater quality.

4. Conclusions

Our research provides the first field-based dataset on the removal and persistence of PhACs in an IRBF system, in a highly conductive and organic-matter poor aquifer, using high temporal resolution sampling, during low-flow conditions, a regime receiving little attention so far. To date, this work also provides data on PhACs in IRBF systems for the first time in Italy.

At our site conditions, PhACs concentrations in surface water are generally lower than 10 ng/L and rather constant in the investigated period. However, the same does not apply to groundwater in the IRBF, showing high PhACs variability along with high temperature, low-oxygen and slightly reducing conditions, although the latter fluctuate. The results underscore the complex interplay between PhAC specific properties, aquifer heterogeneity, and biogeochemical conditions, in controlling PhACs fate.

Despite the robust dataset presented, temporal resolution, although higher than most similar field studies, may still be insufficient to resolve short-term variability in PhACs input or sorption/desorption events. Furthermore, the assumption of temporally invariant surface water PhACs concentrations, while supported by the available data, may not fully reflect pulse contamination events.

To further deepen the understanding of PhAC removal in IRBF systems, future research should incorporate multi-scale and multi-tracer experiments, and high-frequency monitoring of redox-sensitive metabolites (i.e. for persistent parent compounds like CBZ and SFX). Coupling these techniques with reactive transport modeling may enable the resolution of spatially distributed degradation processes and help distinguishing between biodegradation and (reversible) sorption phenomena. Furthermore, integrating microbial community profiling and enzymatic activity assays would facilitate the evaluation of the role of microbial ecology in PhACs attenuation under varying redox regimes, DO and aquifer medium conditions. More field-based experimental data are needed for MET, IBU and CLA in order to improve the understanding of their fate in IRBF systems.

From a water resources management perspective, the Serchio River IRBF system demonstrates excellent performance in maintaining low PhACs concentrations in drinking water, with final levels for all compounds well below 0.1 μg/L. This underscores the viability of IRBF as a passive, low-energy natural treatment method. However, being the hydraulic connection between the surface water body and the aquifer often disregarded, IRBF is not practically recognized as a MAR technique. Then, the persistent detection of selected compounds at ng/L levels in surface water highlights the importance of combining source control strategies with improved process-based monitoring to ensure long-term safety of drinking water and resilience of natural attenuation systems.

Beyond the demonstrated removal potential of IRBF systems, future efforts should focus on the molecular design of PhACs with enhanced degradability under environmental conditions typical of surface- and ground-water. This approach offers a more sustainable alternative to relying solely on energy-intensive and expensive downstream treatment technologies to remove their traces from aquatic ecosystems.

CRediT authorship contribution statement

R. Rossetto: Validation, Supervision, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization, Writing – review & editing, Writing – original draft. **A. Barbagli:** Methodology, Investigation, Formal analysis, Data curation, Conceptualization, Writing – review & editing. **M. Dalla Battista:** Visualization, Data curation. **C. Marchina:** Methodology, Investigation, Data curation, Writing – review & editing. **G. Mazzanti:** Methodology, Investigation, Data curation, Conceptualization, Writing – review & editing.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2025.180639.

Data availability

Data are presented in Supplementary Materials

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