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Mathon B. [1, *], Ferreol M. [1], Togola A. [2], Lardy-Fontan S. [3], Dabrin A. [1], Allan I.J. [4, 5], Staub P.-F. [7], Mazzella N. [6], Miège C. [1]

[1] INRAE, 5 rue de la Doua, 69616 Villeurbanne, France
[2] BRGM, 3 avenue Claude Guillemin, 45060 Orléans, France
[3] LNE, 1 rue Gaston Boissier, 75724 Paris, France
[4] Ifremer, rue de l'Ile d'Yeu, 44980 Nantes, France
[5] Norwegian Institute for Water Research (NIVA), Gaustadalleen 21, 0349 Oslo, Norway
[6] INRAE, 50 avenue de Verdun, 33612 Cestas, France
[7] OFB, 5 allée Félix Nadar, 94300 Vincennes, France

* Corresponding author : B. Mathon, email address : baptiste.mathon@inrae.fr

Abstract :

In an effort to support European Union Water Framework Directive goals, we have set up a national demonstrator project to identify the advantages and limitations of passive samplers for regulatory monitoring of polar contaminants in surface waters. Here we carried out successive 14 day-deployments of polar organic chemical integrative samplers (POCIS) for one year at three sites. In parallel, we used the passive sampler deployment/retrieval operations to collect spot water samples for comparative analysis. We observed that frequency of quantification was significantly higher in POCIS than spot samples for 29 contaminants, similar for 15, and lower for one, because POCIS lowered the limits of quantification for most contaminants (median value factor of 11). We built a database of sampling rates (Rs) according to quality indices to convert concentrations in POCIS to concentrations in water (23 contaminants with a high-quality median Rs value, 20 with an approximate Rs and two with no usable Rs). Several phenomena were observed over one-year monitoring period. For example, after a flood episode, dilution phenomenon in rivers is correctly observed by using POCIS sampling whereas significant concentration increased due to soil leaching is observed with both passive and spot sampling. Cases of episodic contamination that were missed by spot sampling were observed with POCIS as it was able to capture contamination of short duration but sufficient intensity. Contamination by pharmaceuticals was found to come from wastewater treatment plant discharges and showed relatively little variation over the course of the year in both POCIS and spot samples. POCIS enables more reliable annual monitoring of pesticide and pharmaceutical contamination than spot sampling. Furthermore, POCIS also improves the environmental quality standards based assessment of chemical status and on annual average concentrations compared to spot sampling. This study demonstrates the value and practicability of POCIS-based chemical monitoring for use in regulatory control networks.

Graphical abstract

Highlights

► POCIS allowed to monitor 45 pesticides and pharmaceuticals (DCE substances). ► POCIS improved the frequency of substances quantification in waters. ► POCIS improved the detection of contaminations over a year of monitoring. ► POCIS improved their comparison with Environmental Quality Standards for WFD compliance checking. ► This study demonstrated the maturity of POCIS to be used in WFD monitoring.

Keywords : POCIS, Spot sampling, Organic contaminants, Aquatic environment, Regulatory monitoring

1 Introduction

More than a third of renewable fresh water is used for agricultural, industrial and domestic activities, all of which involve organic contaminants that can affect the quality of surface water (Schwarzenbach et al., 2006). A study on the contamination of 4000 European surface water sites by 223 contaminants showed that nearly half of these sites were exposed to proven ecotoxicological risks linked to agricultural or urban activity in the upstream catchment (Malaj et al., 2014).

The European Union Water Framework Directive (WFD) 2000/60/EC implemented in 2000 established a common framework for monitoring water quality and committed member states to achieve good ecological and chemical status for all water bodies by 2015 (EC, 2000), with extended deadlines set for 2021 and 2027. In this context, some chemical contaminants are listed as European priority substances (PS) or national specific pollutants (SP) for which levels in water are to be compared against environmental quality standards (EQS) (EC, 2015) in order to assess water quality status at the river catchment scale (compliance checking). In France, we also consider Environmental Guideline Values (EGV) as thresholds for substances without EQS. Moreover, the 'surveillance' order passed on 25 January 2015 (French order, 2015) introduced the concept of "relevant substances to monitor" (RS) with provisions for extended monitoring. The primary objective is to acquire information on levels of occurrence in order to specify the damage these RS can cause on aquatic resources.

Compliance control checks require analyses of at least four representative water samples per year (taken every three months). These analyses are currently performed by spot water sampling followed by extraction of analytes and chromatographic analysis, as the method is simple to implement and widely

used for regulatory WFD monitoring programmes (Poulier et al., 2014). However, spot sampling has drawbacks, including a lack of temporal representativeness (Allan et al., 2006). Moreover, 75% of the data from chemical monitoring of rivers carried out by EU members is below limits of quantification (LoQ) (Heiss & Küster, 2015).

Using passive sampling for chemical monitoring of water appears to be a good solution to overcome these problems (Miège al., 2015). Polar organic chemical integrative samplers (POCIS) are already widely used for hydrophilic molecules with a $\log K_{ow}$ between 0 and 4 (Alvarez et al., 2004; Mazzella et al., 2007, Morin et al., 2012, Ibrahim et al., 2013). POCIS can lower the LoQ values (Lissalde et al., 2011; Poulier et al., 2015) and integrate peaks of contamination (Mazzella et al., 2008; Novic et al., 2017). A number of studies have already focused on the comparison between spot sampling and POCIS, and they highlight the benefits of using POCIS for environmental contamination assessment (Hayden et al., 2022; Bernard et al., 2019; Guibal et al., 2018; Criquet et al., 2017; Van Metre et al., 2016; Poulier et al.; 2015, Zhang et al., 2008). However, passive samplers such as POCIS are not yet applied as part of WFD regulatory controls, and their utility for this purpose still needs to be demonstrated.

In this context, a large-scale French monitoring study assigned to the AQUAREF consortium, a national reference laboratory for monitoring aquatic environments (www.aquaref.fr), included the continuous monitoring of 45 hydrophilic organic contaminants at three river stations from April 2017 to June 2018. These stations, which are monitored as part of the WFD surveillance network, are characterized by a diversity of land uses involving various contamination profiles. In parallel to continuous POCIS sampling, we collected spot water samples every 14 days at each POCIS deployment/collection operation, to serve for comparative analysis. The 14 days of exposure correspond to the optimal exposure duration allowing to be in the linear accumulation for a maximum of contaminants (Morin et al., 2012). A total of 162 spot samples and 156 duplicates of POCIS served to evaluate the use of the two methods in monitoring programmes. Here we present and discuss i) the limits of quantification (LoQ) and frequencies of quantification (FoQ) achieved with the two methods, ii) the reliability of the conversion of concentrations in POCIS to concentrations in the dissolved water compartment, and iii) the capacity of POCIS to improve monitoring of the temporal dynamics of contamination. Finally, we compare and discuss confidence levels

on calculated annual average (AA) concentrations obtained by the two sampling methods, in order to compare them to the environmental quality standards annual averages (EQS-AA) and EGV.

2 Material and methods

2.1 The three study sites

Our study was carried out at three monitoring stations located on three rivers in France: the Clain, the Gier and the Jalle.. The sites were selected to minimize losses due to theft or damage (only 2% loss). The first station was at the Clain River in Naintré (coordinates = Lambert 93, kilometres = X 509079; Y 6631019). The Clain River flows 144 km in a rural area and drains a catchment of 3,217 km^2. The Clain watershed is composed of 81% "agricultural land", 14% "forests and semi-natural environments" and 5% "urban areas" (CORINE Land Cover 2018). Its population density is 85 inhabitants/km². There is a wastewater treatment plant with an extended-aeration secondary activated sludge treatment sized at 3,500 p.e. (population equivalent) located 5 km upstream of the sampling point. The second station was at the Gier River in Givors (coordinates = Lambert 93, X 835601.98; Y 6499186.43). The Gier River flows 40 km in a rural area and drains a catchment of 425 km^2. The Gier watershed is composed of 54% "agricultural land", 35% "forests and semi-natural environments" and 11% of "urban areas" (CORINE Land Cover 2018). Its population density is 232 inhabitants/km². There is a wastewater treatment plant with a medium-load secondary activated sludge treatment of 45,580 p.e. located 5 km upstream of the sampling point. The third station is at the Jalle River in Blanquefort (coordinates = X 419053.00; Y 6430159.99). The Jalle River flows 32 km in a forest area and drains a catchment of 371 km^2. The Jalle watershed is composed of 8% "agricultural land", 82% "forests and semi-natural environments" and 10% "urban areas" (CORINE Land Cover 2018). Its population density is 306 inhabitants/km². There is a wastewater treatment plant with a (very low load) extended-aeration secondary activated sludge treatment sized at 67,000 p.e. located 2.5 km upstream of the sampling point. Information on flow rates during the sampling campaigns together with the physical-chemical characteristics of the water (pH, temperature, conductivity, dissolved oxygen concentration, flow rate (continuous), total suspended solids (TSS) concentration, total organic carbon (TOC) concentration, and major ions (Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}, HCO_3-, N_{tot}.) are available in supplementary material S2.

2.2 Sampling strategy

Two sampling methods for measuring levels of contaminants were compared: the commonly-used spot sampling method (162 samples), and passive sampling by POCIS (156 duplicates). Results published by Lissalde et al. (2011) show very similar repeatability between replicates of POCIS and replicates of spot sampling. The study was conducted continuously for a full year with 26 successive series of campaigns, during which duplicate POCIS devices were exposed for 14 days. To process the results, we averaged the results obtained by the POCIS duplicates for the same campaign.

The POCIS devices were purchased from Exposmeter (Exposmeter Water Hydrophilic Pharmaceuticals). They are composed of 200 mg of Oasis® HLB phase between two polyether sulfone membranes (diameter 900 mm, pore size 0.1 µm) sandwiched by metal washers with an open surface of 45 cm². Each POCIS was covered with aluminium foil before and after in-situ deployment. The POCIS exposure system consists of a stainless steel canister from Exposmeter.

Spot water samples (1 L) were taken every 14 days in the first 50 cm of sub-surface water, at the time of installation and/or collection of the POCIS. The spot water samples and POCIS devices were transported to the laboratory in a coolbox (temperature 5°C ± 3°C, within 24 hours according to standard ISO 5667).

2.3 Analysis by chromatography coupled with mass spectrometry

The panel of 45 contaminants studied counted pesticides and pharmaceuticals from different families/therapeutic classes, including 3 metabolites, i.e. 15 herbicides, 7 fungicides, 6 insecticides, 5 antibiotics, 2 anti-depressants, 2 non-steroidal anti-inflammatories, 1 anti-cancer drug, 1 anti-convulsant, 1 analgesic, 1 anti-diabetic, and 1 lipid lowering agent (*Table 1*). Analyses were performed by three laboratories: INRAE Lyon, INRAE Bordeaux, and the BRGM. POCIS and water from the same site were analyzed by the same laboratory. Each laboratory implemented its own method and QA/QC strategy. The methods are detailed in S5. We did not measure pharmaceuticals at the Clain station.

Table 1: Limits of quantification (LoQ), frequencies of quantification (FoQ), and minimum and maximum concentrations for POCIS (ng/L and ng/POCIS) and spot sampling (ng/L), and EQS-AA or EGV (ng/L) for the 45 contaminants.

Contaminants	WFD assessment	Family	POCIS					Spot				EQS-AA or EGV for surface water (ng/L)
			POCIS-LoQ (ng/L)	POCIS-LoQ (ng/ POCIS)	MIN (ng/L)	MAX ng/L	FoQ (%)	LoQ Spot ng/L	MIN (ng/L)	MAX ng/L	FoQ (%)	
Acetochlor	RS	Herbicide	0.4	1.5	<LoQ	1,24	2	20	<LoQ	<LoQ	0	13
Fenofibric acid	RS	Lipid-lowering agent	0.05	0.1	1.4	18	100	0.04	<LoQ	290	98	N.A.
Alachlor	PS	Herbicide	0.5	1.5	<LoQ	7.3	24	10	<LoQ	22	2	300
Atrazine	PS	Herbicide	0.4	1.5	<LoQ	7.2	46	10	<LoQ	24	17	600
Atrazine deisopropyl	RS	Metabolite	0.4	1.3	<LoQ	2.7	21	10	<LoQ	24	14	N.A.
Atrazine desethyl	RS	Metabolite	0.5	1.3	<LoQ	7.2	95	0.1	<LoQ	2.2	40	N.A.
Azoxystrobin	SP	Antibiotic	8.9	18.6	<LoQ	<LoQ	0	1	<LoQ	<LoQ	0	950
Azithromycin	RS	Fungicide	0.9	2.4	<LoQ	148	71	2.82	<LoQ	33	36	N.A.
Boscalid	SP	Fungicide	0.2	0.4	<LoQ	7.1	66	10	<LoQ	36	1	11600
Carbamazepine	RS	Anti-depressant	0.01	0.01	2.25	415	100	0.06	0.5	476	100	2500
Carbamazepine epoxide	RS	Metabolite	0.01	0.01	0.2	42	100	0.03	<LoQ	51	98	N.A.
Carbendazim	RS	Fungicide	0.3	1.2	<LoQ	44	29	20	<LoQ	108	4	100
Chlorfenvinphos	PS	Insecticide	0.1	0.4	<LoQ	0.6	47	10	<LoQ	<LoQ	0	100
Chlorpyriphos	PS	Insecticide	1.0	0.4	<LoQ	1.38	5	10	<LoQ	<LoQ	0	30
Chlortoluron	SP	Herbicide	1.3	4.1	<LoQ	76	38	20	<LoQ	51	14	100
Clarithromycin	RS	Antibiotic	0.3	1.6	<LoQ	58	73	3	<LoQ	24	28	N.A.
Cyclophosphamide	RS	Anticancer	0.01	0.01	<LoQ	109	89	0.2	<LoQ	29	75	N.A.
Cyprodinil	SP and RS	Fungicide	1.1	2.3	<LoQ	3.9	3	1.80	<LoQ	174	7	26
Diazepam	RS	Anti-depressant	0.01	0.01		6.5	10	0.03	<LoQ	6.2	85	N.A.
Dichlorvos	PS	Insecticide	2.9	0.4	<LoQ	4	1	10	<LoQ	<LoQ	0	1
Diclofenac	RS	Anti-inflammatory	0.01	0.01	2.9	1,11	100	0.15	0.3	924	100	150
Dimethenamid	RS	Herbicide	0.3	2.0	<LoQ	9.3	42	5.80	<LoQ	24	6	200
Dimethoate	RS	Insecticide	0.7	2.0	<LoQ	16	6	5.80	<LoQ	<LoQ	0	100
Diuron	PS	Herbicide	0.8	2.2	<LoQ	51	66	20	<LoQ	126	21	200
Epoxiconazole	RS	Fungicide	0.6	2.2	<LoQ	3.2	7	5	<LoQ	<LoQ	0	200
Erythromycin	RS	Antibiotic	0.4	1.2	<LoQ	4.3	75	2	<LoQ	24	13	N.A.
Imidacloprid	SP	Insecticide	1.0	3.2	<LoQ	15	96	20	<LoQ	61	31	200
Isoproturon	PS	Herbicide	1.1	3.4	<LoQ	1.8	7	20	<LoQ	<LoQ	0	300
Ketoprofen	RS	Anti-inflammatory	0.01	0.01	0.2	82	100	0.04	<LoQ	63	96	N.A.
Linuron	SP and RS	Herbicide	3.4	9.1	<LoQ	76	60	40	<LoQ	331	20	1000
Metazachlor	SP and RS	Herbicide	0.3	1.2	<LoQ	20	25	10	<LoQ	28	9	19
Metformin	RS	Anti-diabetic	N.A.	0.01	<LoQ	N.A.	98	0.03	<LoQ	438	80	N.A.
Metolachlor	RS	Herbicide	0.3	1.3	<LoQ	50	69	10	<LoQ	266	52	N.A.
Ofloxacin	RS	Antibiotics	0.8	2.0	<LoQ	165	61	10	<LoQ	46	27	N.A.
Oxadiazon	SP	Herbicide	0.7	0.4	<LoQ	46	93	10	<LoQ	38	4	90
Oxazepam	RS	Anti-depressant	0.01	0.01	<LoQ	786	99	0.05	0.8	792	100	N.A.
Paracetamol	RS	Anti-inflammatory	N.A.	0.02	<LoQ	N.A.	96	0.03	0.12	563	100	N.A.
Pirimicarb	RS	Insecticide	0.4	1.5	<LoQ	1.0	2	2	<LoQ	<LoQ	0	N.A.
Prochloraz	RS	Fungicide	0.7	2.0	<LoQ	<LoQ	0	5	<LoQ	<LoQ	0	N.A.
Propyzamide	RS	Herbicide	0.7	2.0	<LoQ	28	44	5	<LoQ	30	33	N.A.
Simazine	PS	Herbicide	0.4	1.3	<LoQ	7.6	56	20	<LoQ	<LoQ	0	1000
Sulfamethoxazole	RS	Antibiotic	0.01	0.01	0.6	203	100	0.11	<LoQ	83	98	N.A.
Tebuconazole	SP	Fungicide	1.3	2.0	<LoQ	43	77	10	<LoQ	81	12	1000
Terbuthylazine	RS	Herbicide	0.5	2.2	<LoQ	1.4	1	5	<LoQ	25	2	60
Terbutryne	RS	Herbicide	0.7	2.0	<LoQ	3.2	52	5	<LoQ	<LoQ	0	65

N.A.: not available; SP: Specific pollutant; PS: Priority substance; RS: Relevant substances to monitor

2.4 Calculation of C_W with POCIS

For chemicals whose uptake is in the kinetic (or integrative) regime of accumulation in POCIS, the concentration in water (ng/L, C_W) can be estimated by the following equation (Alvarez et al., 2004; Alvarez et al., 2007; Mazzella et al., 2007; Morin et al., 2012):

$$C_W = \frac{C_{POCIS}}{k_u \times t} \quad (1)$$

where C_{POCIS} is analyte concentration in the receiving phase (ng/g), t is exposure period (days) and k_u is uptake rate value, which is compound-specific (L/g/d). This constant k_u can be calculated with the sampling rate value (R_s in L/d) and the mass of receiving phase recovered inside the POCIS ($m_{sorbent}$

in g), using equation 2:

$$k_u = \frac{R_s}{m_{sorbent}} \quad (2)$$

The R_s values used to obtain k_u constants can be determined for each analyte by laboratory calibration. We reviewed the R_s data available in the literature for the 45 contaminants under study and used that data in this paper to calculate time-weighted average concentrations (TWAC; part 3.1,*Table 2*).

2.5 Selection and compilation of Rs from the literature

Calibration experiments to measure sampling rate (Rs) in passive samplers require logistics that are difficult to achieve for routine measurements. However, there is various Rs already available in the literature for different molecules and exposure conditions.

We compiled Rs constants from 29 scientific papers or theses published between 1999 and 2017 (list presented in S1). We used the international Scopus and Web of Science abstract citation databases. The queries entered were "sampling rate" or "Rs", associated with "POCIS" and the name of each contaminant.

We thus built a Rs database (309 values) for the 45 studied contaminants. We also compiled information on the experimental conditions used to produce these Rs, i.e. temperature, agitation, type of water, calibration system, calibration time, period of kinetic (or integrative) regime of accumulation, phase type, membrane.

A majority of the 309 Rs (253 out of the 309 values) were for temperatures between 15°C and 25°C. Only two Rs values were obtained at temperatures < 15°C, and 23 Rs were obtained at temperatures > 25°C. Temperature information was not available for 31 Rs.

Rs values were obtained using 3 types of water: drinking water for 155 Rs, ultrapure water for 40 Rs, and environmental water for 76 Rs (surface water, wastewater, etc.). There was no information given on type of water for 38 reported Rs values.

There were 11 Rs obtained under non-stirred conditions and 259 Rs obtained under stirred conditions. Water stirring conditions were not given for 39 Rs.

The Rs calibration system used no water renewal for 37 Rs, lab-controlled water renewal for 258 Rs, and water renewal with *in situ* calibration for 13 Rs (in river, lake or wastewater). There was no information given on water renewal for one Rs.

3 Results and discussion

3.1 Selection of a sampling rate value (Rs) for calculating TWAC (ng/L)

First, to select relevant Rs values, we ran a statistical treatment to remove outlier Rs corresponding to data below the 1st quartile or above the 3rd quartile. Second, we chose Rs obtained with calibration conditions representative of those encountered during our sampling campaigns. On that point, we rejected:

- Rs values obtained by POCIS with an exposure area of 11.5 cm^2 or 18 cm^2 (smaller than that of our POCIS, i.e. 45.8 cm^2).
- Rs values obtained under static conditions (with a non-stirred calibration system).
- Rs values obtained with a calibration system without any water renewal.
- In situ Rs values obtained on waters not representative of our study (wastewaters, etc.) and corresponding to very heterogeneous values.
- Rs values when time–course accumulation in POCIS did not prove linear over 14 days of exposure.

Finally, out of the original 309 Rs values, we retained 248 Rs. These 248 Rs ranged from 0.01 $L.d^{-1}$ for dichlorvos to 0.44 $L.d^{-1}$ for dimethenamid. The median Rs was calculated for all contaminants in order to be representative of the dispersion of the literature data.

We then defined a quality index of the median Rs value. A high-quality index needs to reach the three criteria below:

- a relative standard deviation (RSD) < 100%;
- number of Rs values > 4;
- linear time–course of accumulation in the POCIS for > 14 days.

In *Table 2*, we used a colour code:

- green indicates a high-quality index of the median Rs value: all three of the above criteria achieved;
- orange indicates a poor-quality index of the median Rs value (approximate value): only one or two of the above criteria achieved;
- red indicates the absence of a usable Rs median value: none of the of the three criteria achieved, which in these cases was due to very low accumulation of the contaminant inside the POCIS.

Of the 45 contaminants, 23 had a high-quality median Rs value, 20 had an poor quality median Rs value, and two had no workably usable median Rs value. With all contaminants pooled together, the mean of all median Rs values is $\overline{Rs} = 0.23 \pm 0.07\ L.d^{-1}$, and the median is $\mathrm{Med}_{\overline{Rs}}(\mathrm{total}) = 0.21 \pm 0.06\ L.d^{-1}$. RSD ranged from 11% for dimethoate to 170% for erythromycin, with a mean RSD of 28%.

This information shows that the range of Rs values compiled from the literature varies only slightly. It is therefore conceivable to use the median value $\mathrm{Med}_{\overline{Rs}}(total)$ as a default value ($0.21 \pm 0.06\ L.d^{-1}$) for contaminants with no Rs value in the literature. Prior to using this value, it is necessary to check that the contaminant can accumulate on the POCIS. However, this default approximate Rs value remains unsatisfactory and cannot be definitive as its leads to higher TWAC uncertainties than a measured Rs.

Table 2: Median POCIS Rs values and associated relative standard deviation with information on 14-day time–course linearity for the 45 contaminants

Contaminants	Family	*Rs median* (L/j)	Standard deviation on median Rs (L/j)	RSD (%)	Number of data	Linearity over 14 days
Acetochlor	Herbicide	0.24	0.06	26	6	YES
Fenofibric acid	Lipid-lowering agent	0.17	N.A.	N.A.	1	YES
Alachlor	Herbicide	0.23	0.20	87	8	YES
Atrazine	Herbicide	0.24	.05	23	13	YES
Atrazine deisopropyl	Metabolite	0.18	0.0	53	9	YES
Atrazine desethyl	Metabolite	0.21	0.07	34	11	YES
Azithromycin	Antibiotic	0.20	N.A.	N.A.	1	YES
Azoxystrobin	Fungicide	0.15	0.10	66	5	YES
Boscalid	Fungicide	0.18	N.A.	N.A.	1	YES
Carbamazepine	Anti-convulsant	0.29	0.21	73	18	YES
Carbamazepine epoxide	Metabolite	0.25	N.A.	N.A.	1	YES
Carbendazim	Fungicide	0.30	0.12	38	3	YES
Chlorfenvinphos	Insecticide	0.24	N.A.	N.A.	2	YES
Chlorpyriphos	Insecticide	0.03	N.A.	N.A.	1	YES
Chlortoluron	Herbicide	0.22	0.09	41	7	YES
Clarithromycin	Antibiotic	0.42	N.A.	N.A.	2	YES
Cyclophosphamide	Anti-cancer drug	0.10	N.A.	N.A.	1	YES
Cyprodinil	Fungicide	0.15	N.A.	N.A.	1	YES
Diazepam	Anti-depressant	0.25	0.23	94	20	YES
Dichlorvos	Insecticide	0.01	0.07	22	4	Not confirmed
Diclofenac	NSAID	0.17	0.07	39	13	YES
Dimethenamid	Herbicide	0.44	0.10	22	3	YES
Dimethoate	Insecticide	0.20	0.02	11	4	YES
Diuron	Herbicide	0.20	0.06	30	10	YES
Epoxiconazole	Fungicide	0.28	0.09	31	4	YES
Erythromycin	Antibiotic	0.21	0.35	170	4	YES
Imidacloprid	Insecticide	0.23	0.11	48	3	YES
Isoproturon	Herbicide	0.22	0.07	30	5	YES
Ketoprofen	NSAID	0.23	0.17	75	15	YES
Linuron	Herbicide	0.19	0.07	36	6	YES
Metazachlor	Herbicide	0.27	0.03	12	6	YES
Metformin	Antidiabetic	N.A.	N.A.	-	0	NO
Metolachlor	Herbicide	0.27	0.10	37	7	YES
Ofloxacin	Antibiotic	0.17	0.05	27	5	Not confirmed
Oxadiazon	Herbicide	0.04	N.A.	N.A.	1	Not confirmed

Oxazepam	Anti-depressant	0.21	0.05	23	8	YES
Paracetamol	Analgesic	N.A.	N.A.	-	-	NO
Pirimicarb	Insecticide	0.26	0.05	18	4	YES
Prochloraz	Fungicide	0.11	0.04	31	4	YES
Propyzamide	Herbicide	0.24	0.03	14	4	YES
Simazine	Herbicide	0.22	0.22	101	11	YES
Sulfamethoxazole	Antibiotic	0.11	0.12	105	8	Not confirmed
Tebuconazole	Fungicide	0.11	0.12	105	8	YES
Terbuthylazine	Herbicide	0.30	0.11	37	8	YES
Terbutryn	Herbicide	0.25	N.A.	N.A.	2	YES

Contaminants marked in green (high-quality index) have a linearity range > 14 days, a RSD < 100%, and a number of data > 4 (3 criteria reached). Contaminants marked in orange (poor-quality index) achieve only one or two criteria. Contaminants marked in red fail to reach any of the three criteria reached (no usable median Rs). All Rs reference papers are available in S1.

N.A.: not applicable

*Available at http://www.chemspider.com/

3.2 The limits of quantification and the higher frequencies of quantification obtained by POCIS can enhance the comparison against threshold values

LoQ values found for the 45 contaminants after POCIS (POCIS-LoQ) or spot (Spot-LoQ) sampling are presented in *Table 1*. Only metformin and paracetamol do not have POCIS-LoQ in ng/L (noted N.A. in *Table 1*) since no Rs values were available in the literature (very low accumulation in POCIS; see Table 2). Using POCIS instead of spot sampling lowers the LoQ for all contaminants except azoxystrobin and atrazine desethyl for which matrix effects are greater with POCIS than in water. This gain in LoQ varies from a factor of 3 for diazepam and carbamazepine epoxide to 84 for chlorfenvinphos, with a median value of 11. These observations highlight that LoQ is very significantly improved by using POCIS after a deployment period of 14 days.

These LoQ were then compared with WFD EQS and EGV values in order to meet the criteria established for chemical monitoring (LoQ < (EQS or EGV)/3). EU regulations have established an annual-average environmental quality standard (EQS-AA) for 18 out of the 45 contaminants for surface waters, and 8 contaminants have an EGV (Table 1). Ultimately, for the 18 contaminants with an EQS-AA, there were 17 POCIS-LoQ and 16 Spot-LoQ that met the criteria. For the 8 contaminants with an EGV, there were 8 POCIS-LoQ and 7 Spot-LoQ that met the criteria. The performances of both sampling methods were satisfactory, except for dichlorvos with POCIS and dichlorvos, metazachlor and acetochlor with spot sampling.

We compared frequencies of quantification (FoQ) found with the POCIS (FoQ-POCIS, n=5043)

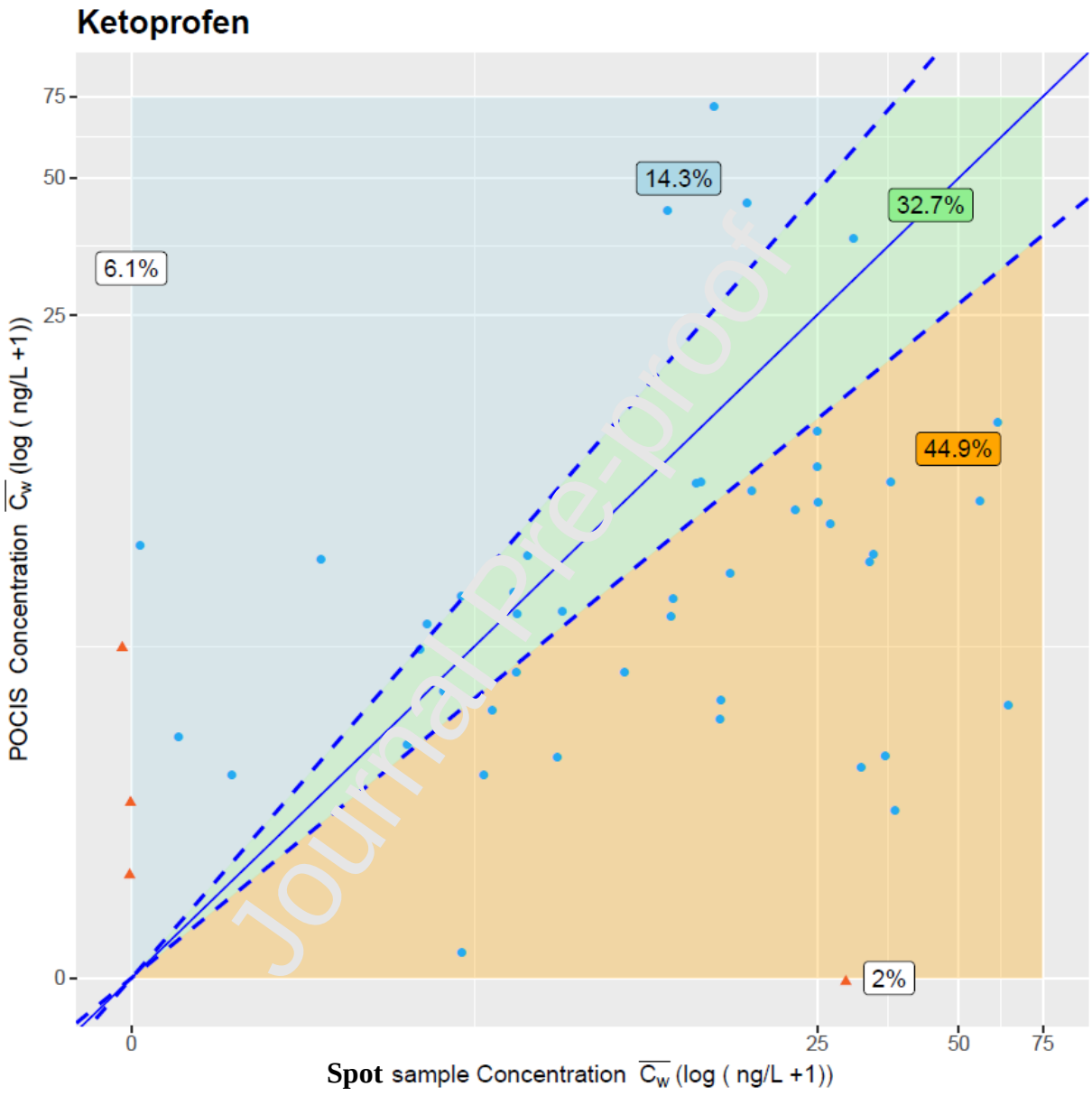
against the FoQ found with spot sampling (FoQ-Spot, n= 2756). FoQ-POCIS ranged from 0% (Prochloraz) to 100% (carbamazepine, carbamazepine-epoxide, diazepam, diclofenac, ketoprofen, sulfamethoxazole) with a median of 60±33%. FoQ-Spot ranged from 0% (acetochlor, azoxystrobin, chlorfenvinphos, chlorpyriphos, dichlorvos propyzamide and prochloraz) to 100% (carbamazepine, diclofenac, oxazepam, paracetamol) with a median of 13±32%. POCIS allows to increase by a factor 4.7 the median FoQ. Among the 45 contaminants studied, 33 contaminants were quantified at least once, in both POCIS and spot water samples. Only two contaminants were never quantified in POCIS nor in spot samples: azoxystrobin and prochloraz. On the other hand, there are 10 contaminants that were quantified only using POCIS: acetochlor, chlorfenvinphos, chlorpyriphos, dichlorvos, dimethoate, epoxiconazole, isoproturon, pirimicarb, simazine and terbutryn. We observed that FoQ-POCIS is significantly higher than FoQ-Spot for 29 contaminants, equal for 15 contaminants and lower for one contaminant (Mc Nemar test (Dagnelie, 2011), p-value>0.05). This observation has been verified in other studies with a systematic higher frequency of quantification with POCIS for pesticides (Bernard et al., 2019) and pharmaceuticals (Hayden et al., 2022, Criquet et al., 2017). This highlighted the advantage of using POCIS to quantify very low concentrations remaining below the LoQ of spot samples.

We also compared our FoQ-POCIS to the FoQ obtained through the French Monitoring Control Network (MCN) based on spot sampling (data registered in the French portal to access public data on surface water quality "Naïades"; http://www.naiades.eaufrance.fr/) over the same one-year exposure period and at the same sites (dates of spot sampling are illustrated in Figures 4, 5, 7 and 8 and in S3). The FoQs-MCM range from 0% (e.g. acetochlor, alachlor, carbendazim) to 100% (e.g. carbamazepine, diclofenac) with a median at 17±25%. POCIS leads to a 3.5-fold increase in median FoQ compared to MCN, thus confirming the utility value of POCIS to better assess levels of water contamination.

3.3 Contaminant concentrations in water: POCIS and spot sampling approaches

In this part of the study, we compared contaminant concentrations in water (in ng/L) estimated with POCIS and with spot samples. The methodology, described in Dalton et al. (2014), consisted in projecting concentrations on two x and y axes (*Figure 1*, one x/y coordinate for two associated spot/POCIS concentrations). Two regressions (y=2x and y=0.5x) define a confidence interval for

these measured values as already used and described by (Bernard et al., 2019). The spot-sample concentrations are a mean of the concentrations measured in two spot samples collected at the beginning and at the end of POCIS exposure. Concentrations below the LoQ have been replaced by the LoQ value. All graphed output is available in S4.



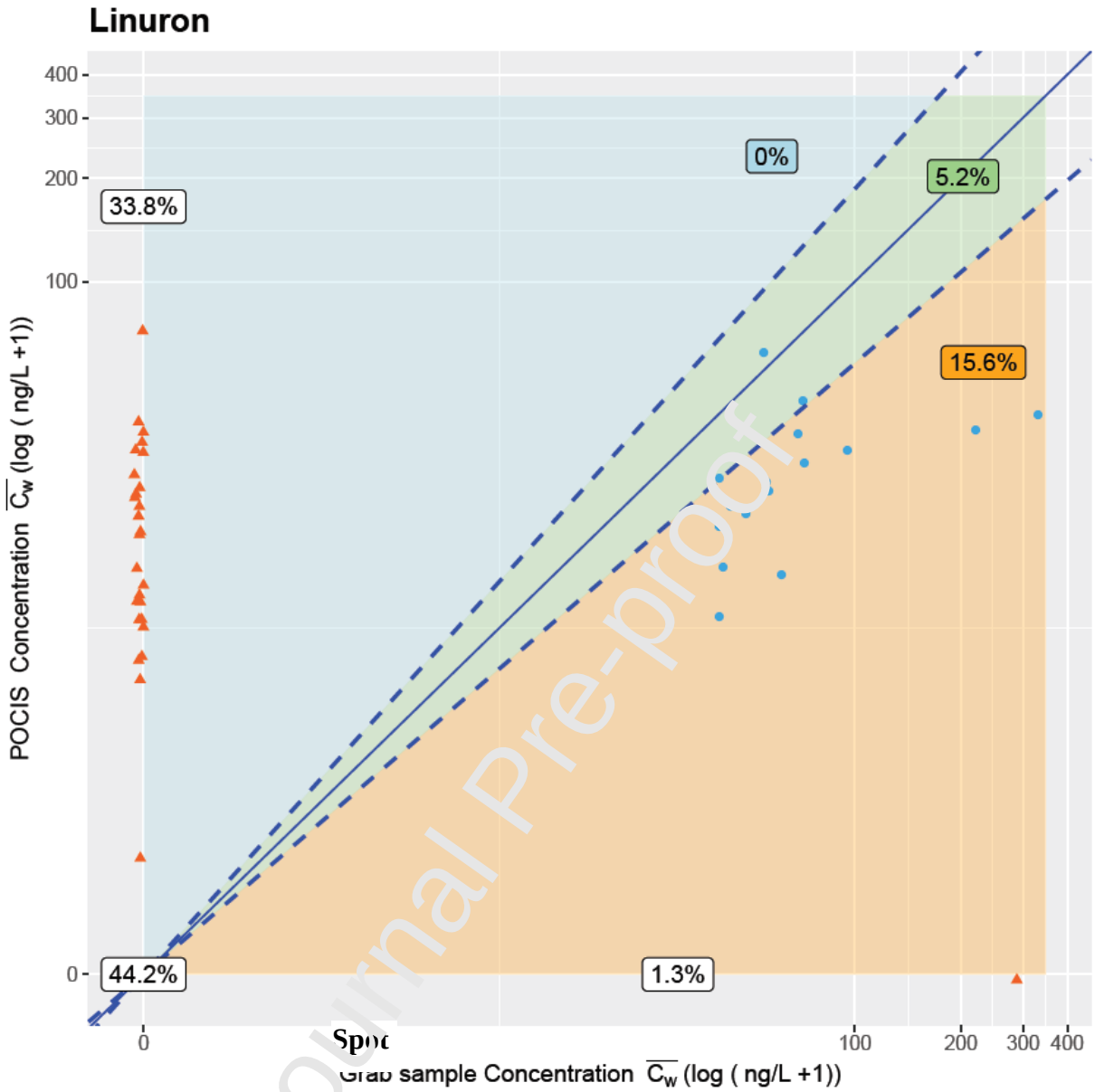


Figure 1: Illustration of co-plotted ketoprofen and linuron concentrations (blue circles) measured with POCIS (in ng/L, y-axis) and spot samples (in ng/L, x-axis) at the time period

The solid blue line corresponds to the 1:1 regression, and dashed blues lines correspond to the 2:1 and 1:2 regressions. The green area maps POCIS Concentrations = Spot Concentration, the orange area maps POCIS Concentration < Spot Concentration, and the blue area maps POCIS Concentration > Spot Concentration. The percentages on the x and y-axes correspond to the number of data only quantified in POCIS or in spot samples at the same period of time (orange triangles). The percentage at the origin indicates the number of data not quantified by both POCIS and spot sampling.

Figure 1 shows projections for ketoprofen and linuron. When considering only concentrations that were above the LoQ with both sampling methods, 44.9% of ketoprofen concentrations and 15.6% of linuron concentrations were lower with POCIS than with spot sampling, and 32.7% of ketoprofen concentrations for 5.2 % of linuron concentrations were similar between POCIS and spot sampling. In addition, 14.3% of ketoprofen concentrations and no linuron concentrations were higher with POCIS.

For ketoprofen, a non-steroidal anti-inflammatory drug released in surface waters mainly via domestic wastewater treatment plant (WWTP) effluents, the sampling schedule for spot samples (during the morning) explains why nearly 50% of POCIS concentrations were lower than spot concentrations. Indeed, it has been shown that there is hourly variability in contaminant concentrations (especially pharmaceutical compounds) in WWTP discharges, with peak contaminant loads at between 5:00 and 8:00 am (Nelson et al., 2011). The 3 sites are located in proximity to a WWTP, and the timing of spot sampling roughly corresponds to the likely peak of in-stream contaminant load. With their ability to integrate contamination over time, POCIS devices tend to smooth (average) the contamination observed in the environment, and thus to have lower concentrations than that in spot samples.

For the herbicide linuron, the FoQ in spot samples is very low (33.8% of concentrations are <LoQ in spot samples *vs* only 1.3% in POCIS). When considering only concentrations above LoQ with both sampling methods, we again found that POCIS concentrations were mostly lower than spot concentrations.

Considering all contaminants and the whole dataset, POCIS concentrations were similar within a factor of two, to spot concentrations in 6% of cases for pesticides and 23% of cases for pharmaceuticals, lower in 12% of cases (pesticides) and 23% (pharmaceuticals), and higher in 0% of cases (pesticides) and 15% (pharmaceuticals). Note that concentrations cannot be compared in 82% of cases for pesticides and 39% for pharmaceuticals as they had not been quantified by both POCIS and spot sampling.

3.4 Relevance of POCIS for studying temporal dynamics of contamination

S2 reports the hydrological conditions and variations in physical-chemical parameters measured during temporal monitoring on the Clain, Gier and Jalle rivers. S3 gives graph plots of contaminant concentrations measured at the Clain, Gier and Jalle rivers with POCIS, our spot samples, and by the French Monitoring Control Network over one year. In order to describe the distribution of the data, we ran classifications using from dissimilarity matrices based on Euclidean distance and then using an

ascending hierarchical classification procedure according to Ward's aggregation criterion, which is a minimum variance method that aims to find compact, spherical clusters (Legendre & Legendre, 2012). The results are expressed graphically using heatmaps (Figure 2 and S6). In the following sections, we focus on results from the Gier rivers (results for the Jalle and Clain can be found in S6).

Temporal dynamics of the Gier river

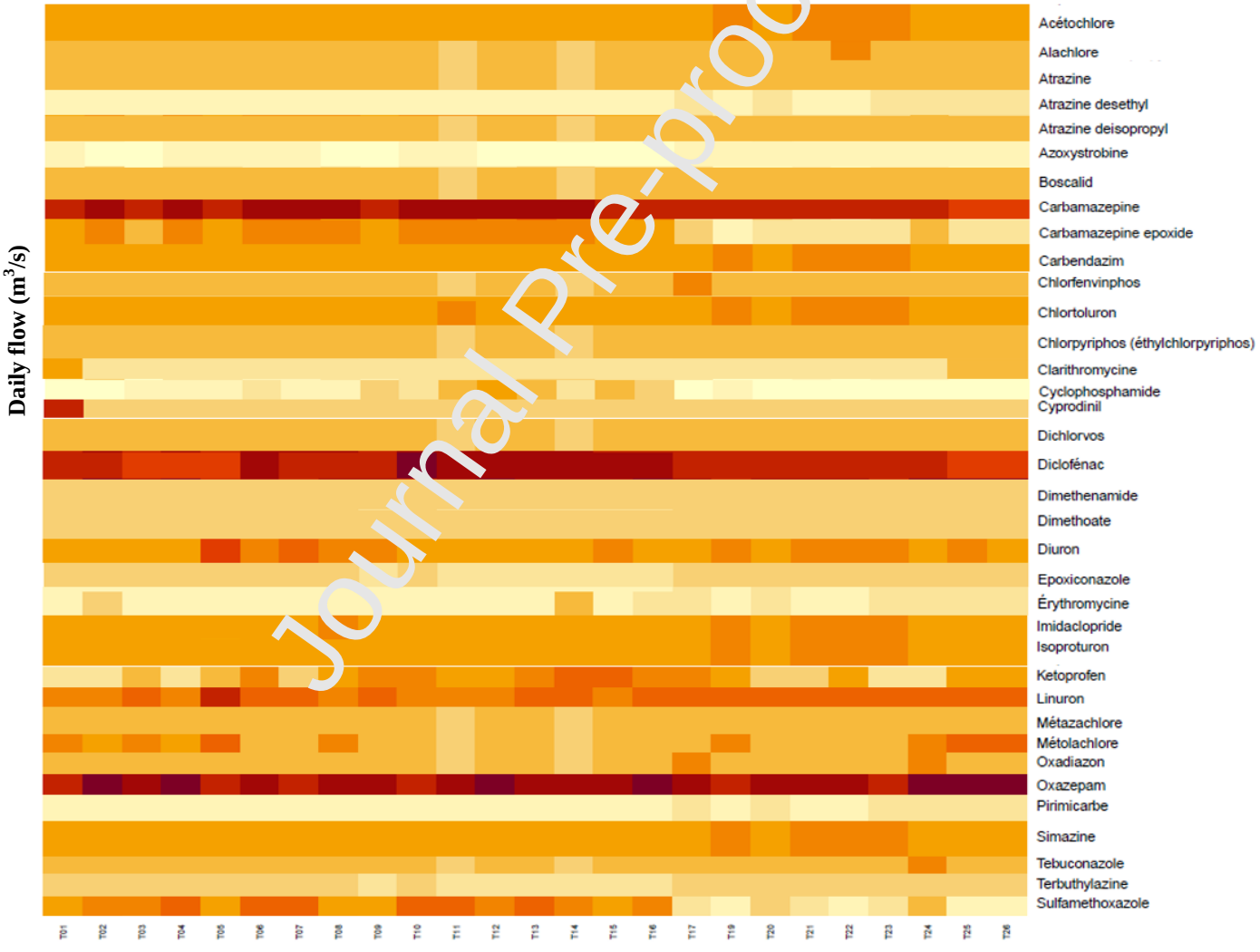
In this watershed characterized by agricultural and urban activities, we considered 37 pesticides and pharmaceuticals for which contamination dynamics were studied from May 2017 to May 2018 (Figure 2). The hydrological conditions at the Gier River show three heavy rainfall episodes: end of January (T17-18), mid-March (T22-23), and mid-May (T25-26) (S 2). Linuron contamination increased slightly during winter then decreased after the rainy episode at the end of January (Figure 2). The second rainy episode in mid-March led to an increase in atrazine, diuron and dimethoate contamination in the river, and the third rainy episode in May led to an increase in tebuconazole, metolachlor and dimethenamid contamination. Pesticides that are persistent and stored in soils after application are transported to surface waters by soil leaching due to heavy rainfall. Other studies have also reported that rainfall events following pesticide application drive pesticide transport to downstream rivers (e.g. Tediosi et al., 2012; Bloodworth et al., 2019). Spot monitoring only managed to capture the contamination with metolachlor, whereas POCIS quantified all these pesticides.

Cases of episodic contamination were observed for dichlorvos and metazachlor in September and chlortoluron in September/October with POCIS but not with spot samples. On the other hand, some contamination events were only observed with the spot samples, i.e. cyprodinil (T01), alachlor (T22), oxadiazon (T24 and T17) and chlorfenvinphos (T17). This can be explained by a very short peak contamination that likely occurred at the time of spot sampling, whereas the 14-day mean concentration from passive sampling was very low. Tebuconazole (Figure 3) was an instructive case, as both types of sampling captured tebuconazole contamination during 2018 whereas only POCIS captured contamination related to a period of use of this fungicide in cereal crops at this period (T3; BRGBernard et al., 2019), thus confirming the relevance of using POCIS to monitor periodic contamination.

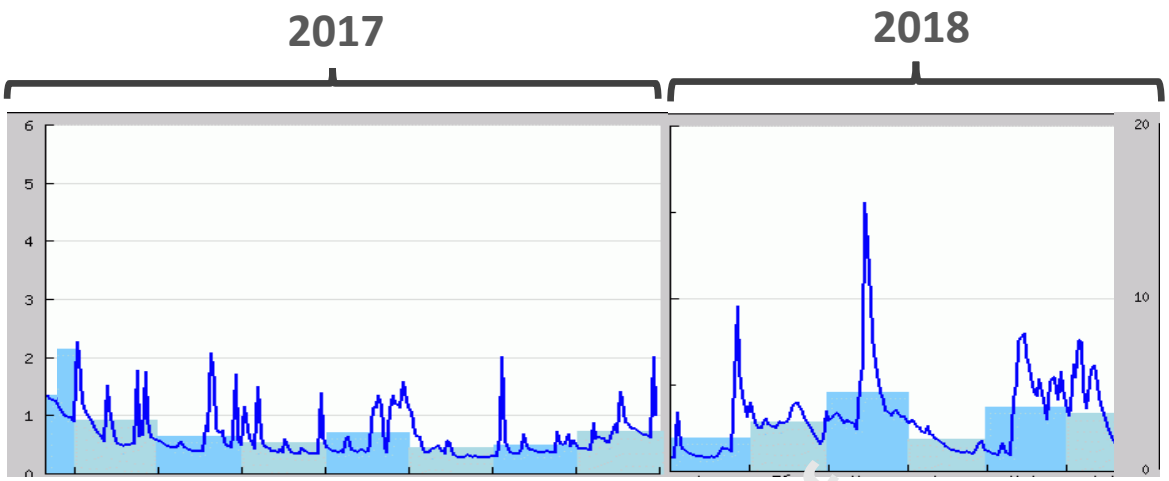
Contamination by pharmaceuticals mostly comes from WWTP discharges. Monitoring with POCIS showed that pharmaceutical contamination showed relatively little variation over the course of the year (see Figure 4), with a slight tendency to increase to a peak in December, which is a period

marked by greater use of pharmaceuticals and/or less efficient degradation mechanisms (biodegradation, photodegradation, etc.) in WWTPs and rivers (Patel et al., 2019). Then, following the first rainy episode, the contamination in pharmaceutical contamination decreased and stabilized (Figure 2). Monitoring carried out with spot samples led to larger amplitudes of variations and higher levels of concentrations, as explained in section 3.3.

Ultimately, the Gier River seems to be exposed to a net-constant contamination by pharmaceuticals released by the WWTP located upstream of the sampling location. It is also exposed to slight diffuse agricultural pressure, with accentuated impact during rainy episodes.



(A)



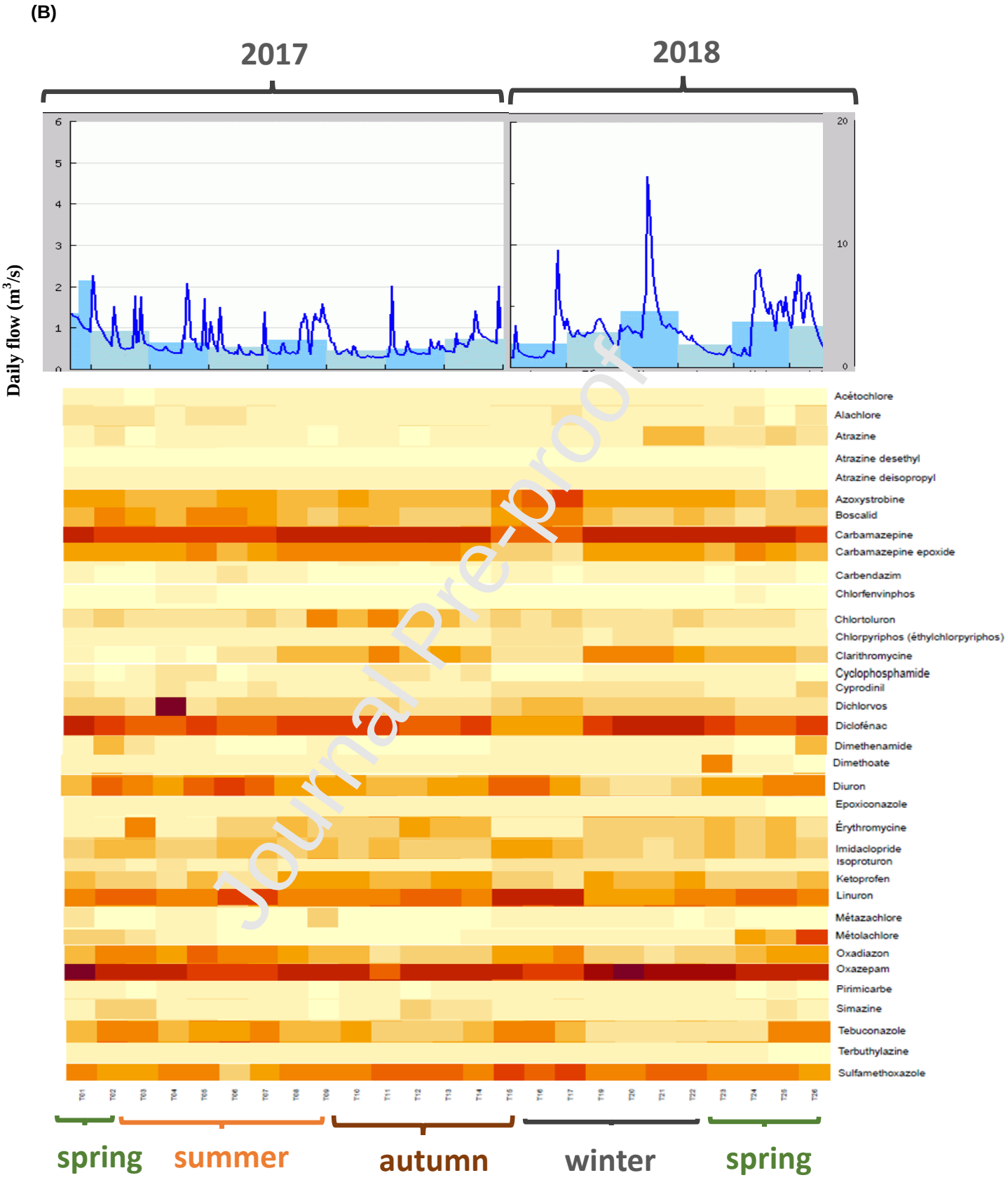


Figure 2: Heatmap graphs of 37 contaminant concentrations in the Gier River from May 2017 (T01) to May 2018 (T26) with spot sampling (A) and POCIS sampling (B) and associated daily flows (m^3/s)

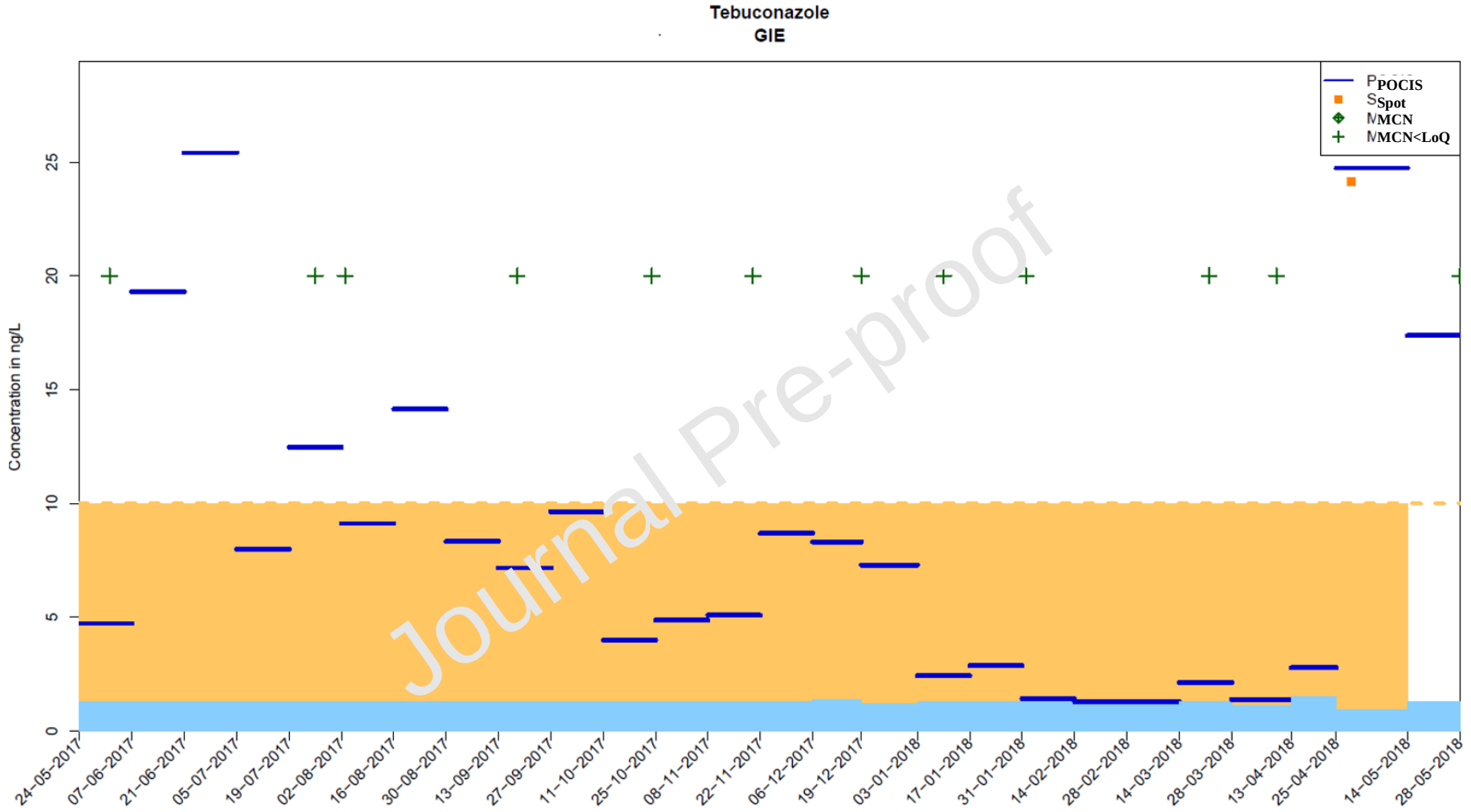


Figure 3: Graphical plot of tebuconazole concentrations (in ng/L) measured at the Gier River with POCIS (blue lines), our spot samples (orange squares), and by the French Monitoring Control Network (MCN, green diamonds) over one year
The orange zone represents the LoQ of the spot samples and the blue zone represents the LoQ of the POCIS

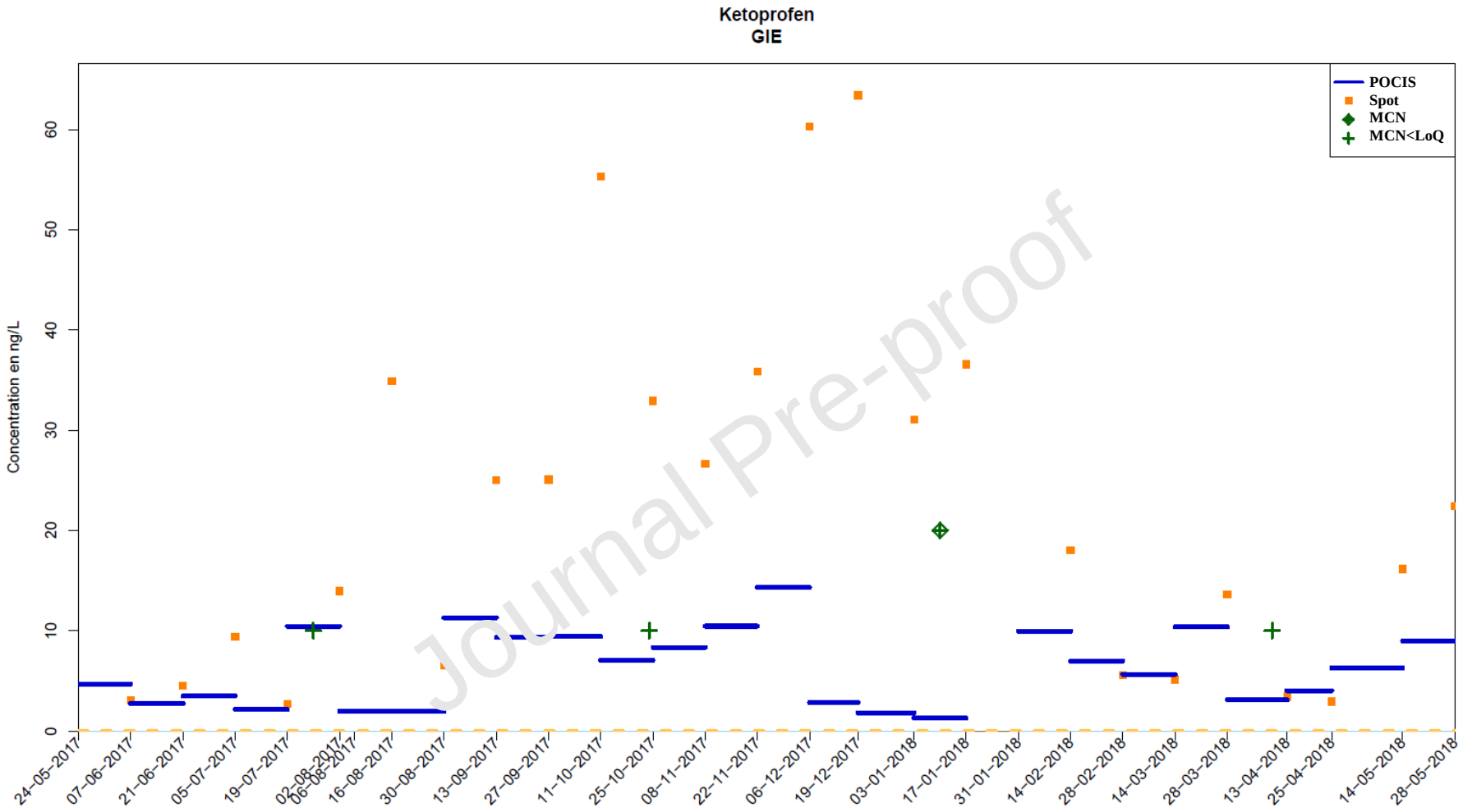


Figure 4: Graphical plot of ketoprofen concentrations (in ng/L) measured at the Gier River with POCIS (blue lines), our spot samples (orange squares), and by the French Monitoring Control Network (MCN, green diamonds) over one year
The orange zone represents the LoQ of the spot samples and the blue zone represents the LoQ of the POCIS

3.7. Comparison of annual-average concentrations in water determined by POCIS and spot sampling (POCIS-AA vs. Spot-AA)

We calculated the annual-average water concentrations (AA) of the contaminants for all three sites (Clain, Gier and Jalle) during the 26 campaigns. The annual averages were calculated by replacing the concentrations < LoQ by the LoQ value. Uncertainty on these AA was estimated by a bias-corrected and accelerated bootstrap interval (the BCa interval). This non-parametric method aims to correct for bias and skewness based on the distribution of bootstrap estimates (which means a given confidence interval is not necessarily symmetrical; Efron & Tibshirani, 1993). *Figure 5* illustrates the correspondence between the AA obtained by spot sampling and by POCIS using the median Rs values in Table 2. In order to limit the impact of the values < LoQ while keeping enough data, we only compared contaminants with FoQ > 25% with both sampling methods (arbitrary threshold). There was a positive correlation between POCIS-AA and Spot-AA, with nearly 60% of the POCIS-AAs between half and twice the Spot-AA value, thus confirming the relevance of the Rs values given in Table 2. On the other hand, two pesticides (metolachlor (all 3 sites) and imidacloprid (Jalle)) and 5 pharmaceutical compounds (fenofibric acid (Jalle and Gier), carbamazepine (Gier), cyclophosphamide (Gier), diclofenac (Gier) and ketoprofen (Gier)) were above the Spot-AA, probably due to several high peaks of contamination that were captured by the spot samples at their high levels but integrated (and thus averaged to a lower level) by POCIS. Only sulfamethoxazole (Jalle) showed the opposite pattern, with contamination that was not detected in the spot samples (<LoQ) but temporally integrated and concentrated by POCIS. This might be explained by diffuse contamination from veterinary and breeding uses (not captured with spot sampling).

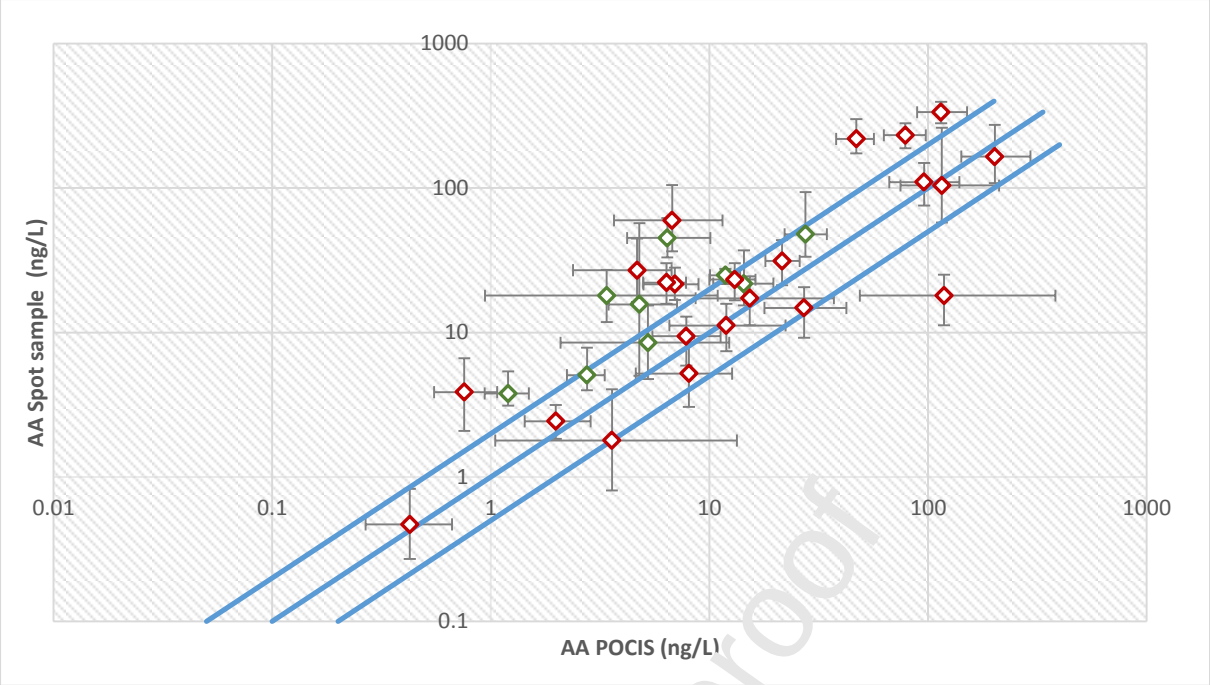


Figure 5: Graphical projection of POCIS-AAs versus Spot-AAs for pesticides (green dots) and pharmaceutical compounds (red dots) with FoQ > 25% and their associated uncertainties (bars), with data values < LoQ replaced by the LoQ value

The continuous blue lines correspond to the 1:1, 1:2 and 2:1 regressions

3.8. Chemical status assessment - Comparison of annual-average water concentrations with threshold values (EQS-AA and EGV)

Based on the method from Poulier et al. 2014, we calculated AA-MIN and AA-MAX concentrations by integrating the uncertainties for POCIS and spot samples by replacing the concentration values < LoQ by 0 for AA MIN and taking the lower-bound value of the confidence interval, or by the LoQ value for AA MAX and taking the higher-bound value of the confidence interval (reported in *Table 3*). If AA MIN > EQS-AA, then good chemical status is not achieved; if AA MAX < EQS-AA, then good chemical status is achieved; if AA MIN < EQS-AA < AA MAX, then it is not possible to conclude on chemical status.

In the Clain River, POCIS and spot sampling reached the same conclusions on chemical status (*Table 3*). Nine of the 26 contaminants with EQS-AA and EGV were not monitored at the Clain site. For the remaining 17 contaminants, the POCIS-AA or Spot-AA MAX concentrations did not exceed the EQS-AA or EGV over the whole monitoring year. The Clain river can be classified as having good

chemical status in terms of the contaminants studied here.

In the Gier River, POCIS and spot sampling reached the same conclusions, except for diclofenac and acetochlor. One of the 26 contaminants with EQS-AA and EGV was not monitored at the Gier site. (*Table 3*). For 22 of the remaining contaminants, both POCIS-AA and Spot- AA MAX concentrations did not exceed the EQS-AA or EGV over the whole monitoring year. However, the AA MAX concentrations exceeded the EQS-AA or EGV for dichlorvos with both POCIS and spot sampling (i.e. not possible to conclude on chemical status). In contrast, Spot-AA MAX concentrations exceeded the EQS-AA or EGV (i.e. not possible to conclude on chemical status) for diclofenac and acetochlor, but POCIS-AA MAX did not exceed the EQS-AA and EGV (i.e. good chemical status). It is impossible to conclude on the chemical status for the Gier River based on spot sampling due to 3 contaminants: dichlorvos, diclofenac, and acetochlor. POCIS has provided more information on assessment of chemical status because it allowed to conclude that the EQS-AA or EGV of diclofenac and acetochlor are not exceeded but still could not firmly conclude due to one contaminant, dichlorvos.

In the Jalle River, POCIS and spot sampling reached the same conclusions, except for cyprodinil and acetochlor. One of the 26 contaminants with EQS-AA and EGV contaminant was not monitored at the Jalle site. (*Table 3*). For 21 of the remaining contaminants, the POCIS-AA or Spot- AA MAX concentrations did not exceed the EQS-AA or EGV over the whole monitoring year (i.e. good chemical status). On the other hand, the AA MAX concentrations exceeded the EQS-AA and EGV for dichlorvos and diclofenac with both POCIS and spot sampling (i.e. not possible to conclude on chemical status). In contrast, Spot-AA MAX concentrations exceeded the EQS-AA or EGV (i.e. not possible to conclude on chemical status) for cyprodinil and acetochlor, but POCIS-AA MAX did not exceed the EQS-AA and EGV (i.e. good chemical status). It is impossible to conclude on the chemical status for the Jalle river based on spot sampling due to 4 contaminants: dichlorvos, diclofenac, cyprodinil and acetochlor. POCIS has provided more information on assessment of chemical status because it allowed to conclude that the EQS-AA or EGV of cyprodinil and acetochlor are not exceeded but still could not firmly conclude due to 2 contaminants: dichlorvos and diclofenac.

The use of POCIS sampling improves the comparison of AA water concentrations against threshold values (EQS-AA and EGV), especially for contaminants with low threshold values (cyprodinil, acetochlor) or contaminants with large daily variability (diclofenac).

Table 3: Chemical status assessment of Clain, Gier and Jalle rivers over a one-year monitoring period (mid 2017-mid 2018) - AA MIN and MAX concentrations based on POCIS and spot sampling, and comparison with EQS-AA and EGV.

Contaminants	AA-EQS/EGV (ng/L)	Clain						Gier						Jalle					
		MIN POCIS (ng/L)	MAX POCIS (ng/L)	Chemical status report (POCIS)	MIN spot (ng/L)	MAX spot (ng/L)	Chemical status report (SPOT)	MIN POCIS (ng/L)	MAX POCIS (ng/L)	Chemical status report (POCIS)	MIN spot (ng/L)	MAX spot (ng/L)	Chemical status report (SPOT)	MIN POCIS (ng/L)	MAX POCIS (ng/L)	Chemical status report (POCIS)	MIN spot (ng/L)	MAX spot (ng/L)	Chemical status report (SPOT)
Acetochlor	13	0.00	0.70	*	0.00	5.00	*	0.00	0.45	*	0.00	20.00	*	0.00	0.45	*	0.00	20.00	*
Fenofibric acid	N.A.	n.m.	n.m.		n.m.	n.m.		3.64	11.46		36.87	106.78		2.38	6.71		16.41	44.41	
Alachlor	300	0.00	0.64	*	0.00	6.15	*	0.10	0.80	*	0.00	11.38	*	0.00	1.80	*	0.00	11.20	*
Atrazine	600	2.13	3.35		2.12	9.27		0.40	2.07		0.00	10.00	*	0.03	0.90	*	0.00	10.00	*
Atrazine deisopropyl	N.A.	0.72	1.59		1.15	6.65		0.00	0.52	*	0.00	10.00	*	0.00	0.52	*	0.00	11.68	*
Atrazine desethyl	N.A.	10.06	13.79		21.65	27.58		0.03	0.05		0.00	2.00	*	0.02	0.02		1.04	9.04	*
Azithromycin	N.A.	n.m.	n.m.		n.m.	n.m.		18.04	43.21		8.41	21.[illegible]		5.95	19.01		0.00	10.35	*
Azoxystrobin	950	0.00	0.98	*	0.00	6.92	*	0.00	8.97	*	0.00	[illegible]00	*	0.00	9.01	*	0.00	1.00	*
Boscalid	11600	0.00	1.63	*	0.00	8.23	*	5.71	11.71		[illegible].00	[illegible].00	*	2.72	4.89		0.00	10.00	*
Carbamazepine	2500	n.m.	n.m.		n.m.	n.m.		62.58	98.93		187.88	279.[illegible]		66.17	137.23		74.88	148.69	
Carbamazepine epoxide	N.A.	n.m.	n.m.		n.m.	n.m.		10.07	16.21		16.41	30.12		5.48	11.18		6.01	13.05	
Carbendazim	100	n.m.	n.m.		n.m.	n.m.		0.14	0.7[illegible]		0.00	20.00	*	0.00	8.99	*	0.00	31.48	*
Chlorfenvinphos	100	n.m.	n.m.		n.m.	n.m.		[illegible]05	0.23		0.00	17.69	*	0.04	0.25		0.00	10.00	*
Chlorpyriphos	30	n.m.	n.m.		n.m.	n.m.		[illegible]	0.99	*	0.00	10.00	*	0.00	0.97	*	0.00	10.00	*
Chlortoluron	100	1.91	11.96		2.69	17.08		2.02	6.10		0.81	23.38	*	0.00	1.35	*	0.00	20.00	*
Clarithromycin	N.A.	n.m.	n.m.		n.m.	n.m.		4.20	8.28		0.31	6.64	*	4.53	12.78		2.02	9.99	
Cyclophosphamide	N.A.	n.m.	n.m.		n.m.	n.m.		0.55	1.06		2.12	6.57		1.05	13.36		0.77	4.05	
Cyprodinil	26	0.00	0.98		0.00	6.15		0.00	1.63	*	0.00	25.21	*	0.00	1.11	*	2.52	30.34	*
Diazepam	N.A.	n.m.	n.m.		n.m.	n.m.		1.41	2.83		1.83	3.18		0.27	0.67		0.26	0.82	
Dichlorvos	1	n.m.	n.m.		n.m.	n.m.		0.00	139.45	*	0.00	10.00	*	0.00	2.91	*	0.00	10.00	*
Diclofenac	150	n.m.	n.m.		n.m.	n.m.		38.23	56.49		174.14	302.33		74.33	212.75		58.51	260.47	
Dimethenamid	200	0.64	1.32		0.54	9.50	*	0.13	2.22	*	0.00	5.80	*	0.10	0.58		0.00	5.80	*
Dimethoate	100	n.m.	n.m.		n.m.	n.m.		0.00	2.82	*	0.00	5.80	*	0.00	0.94	*	0.00	5.80	*

Contaminants	AA-EQS/EGV (ng/L)	Clain						Gier						Jalle					
		MIN POCIS (ng/L)	MAX POCIS (ng/L)	Chemical status report (POCIS)	MIN spot (ng/L)	MAX spot (ng/L)	Chemical status report (SPOT)	MIN POCIS (ng/L)	MAX POCIS (ng/L)	Chemical status report (POCIS)	MIN spot (ng/L)	MAX spot (ng/L)	Chemical status report (SPOT)	MIN POCIS (ng/L)	MAX POCIS (ng/L)	Chemical status report (POCIS)	MIN spot (ng/L)	MAX spot (ng/L)	Chemical status report (SPOT)
Diuron	200	0.00	0.83	*	0.00	10.58	*	10.36	19.59		7.42	43.69		3.83	8.35		2.80	25.44	*
Epoxiconazole	200	0.03	0.62	*	0.00	6.85	*	0.00	0.57	*	0.00	5.00	*	0.00	1.13	*	0.00	5.00	*
Erythromycin	N.A.	n.m.	n.m.		n.m.	n.m.		3.02	6.94		0.27	5.12	*	0.84	4.28		0.00	2.36	*
Imidacloprid	200	n.m.	n.m.		n.m.	n.m.		3.67	5.18		1.12	24.42	*	5.01	9.01		9.64	31.96	

Isoproturon	300	0.00	0.67	*	0.00	6.15	*	0.04	1.14	*	0.00	20.00	*	0.00	1.14	*	0.00	20.00	*
Ketoprofen	N.A.	n.m.	n.m.		n.m.	n.m.		5.01	7.86		15.99	29.92		6.44	22.19		7.55	15.93	
Linuron	1000	0.00	0.83	*	0.00	6.15	*	21.99	34.71		19.77	104.00		7.65	17.05		7.88	98.24	*
Metazachlor	19	0.96	2.21		0.77	9.81	*	0.00	1.13	*	0.00	10.00	*	0.00	3.99	*	0.00	10.00	*
Metolachlor	N.A.	3.43	7.11		3.19	58.00		0.83	10.83	*	7.92	29.69		4.16	10.15		31.32	62.96	
Ofloxacin	N.A.	n.m.	n.m.		n.m.	n.m.		8.46	36.04		7.82	26.04		3.64	19.59		0.00	10.00	*
Oxadiazon	90	n.m.	n.m.		n.m.	n.m.		6.95	14.12		0.00	19.85	*	1.56	2.95		0.00	10.00	*
Oxazepam	N.A.	n.m.	n.m.		n.m.	n.m.		89.50	151.45		280.29	395.86		142.57	294.15		106.96	271.78	
Pirimicarb	N.A.	n.m.	n.m.		n.m.	n.m.		0.00	0.54	*	0.00	2.00	*	0.00	0.42	*	0.00	2.00	*
Prochloraz	N.A.	0.00	0.68	*	0.00	6.15	*	n.m.	n.m.		n.m.	n.m.		n.m.	n.m.		n.m.	n.m.	
Propyzamide	N.A.	0.00	3.84		2.81	13.19		n.m.	n.m.		n.m.	n.m.		n.m.	n.m.		n.m.	n.m.	
Simazine	1000	1.12	2.41	*	0.00	6.77		0.54	1.68		0.00	20.00	*	0.05	0.69	*	0.00	20.00	*
Sulfamethoxazole	N.A.	n.m.	n.m.		n.m.	n.m.		18.09	25.62		21.36	43.21		48.60	379.46		11.41	25.24	
Tebuconazole	1000	1.01	2.99		0.19	8.00	*	5.41	11.41		0.00	12.08		7.73	16.64		3.00	26.76	*
Terbuthylazine	60	0.00	0.56	*	0.00	8.46	*	0.00	0.53	*	0.00	5.00	*	0.00	0.53	*	0.00	5.00	*
Terbutryne	65	0.00	2.82		0.00	6.15	*	n.m.	n.m.		n.m.	n.m.		n.m.	n.m.		n.m.	n.m.	

n.m. *not monitored*

N.A. *not available*

* *Proportion of data >LoQ <25%*

Good status achieved

Impossible to conclude on the chemical status as MIN < AA-EQS/EGV < MAX

No diagnosis possible because no threshold value was available or the contaminant was not part of a monitoring program

4 Conclusion

This study highlighted the value of using POCIS to improve the quality of chemical contaminant data obtained via monitoring programmes. Compared with spot sampling, POCIS led to a decrease in LoQ for almost all contaminants (by a factor 3 to 84, with a median value of 11). Due the lower LoQs, we observed that FoQ-POCIS was significantly higher than FoQ-Spot for 29 contaminants, similar for 15 contaminants, and lower for just one contaminant. POCIS increased FoQ by a median factor of 4.7 compared to our spot sampling data and 3.5 compared with French Monitoring Control Network spot sampling. Cases of episodic pesticide and/or pharmaceutical contamination were detected either only with POCIS (e.g. metazachlor or chlortoluron) or only with spot samples (e.g. cyprodinil). Post-flood-episode contaminant dilution phenomena were better observed by using POCIS sampling (e.g. atrazine).

We have built a database of Rs values selected according to quality indices to convert post-exposure contaminant concentrations in POCIS into concentrations in water. Among the 45 contaminants studied here, 23 have a high-quality median Rs value, 20 have a poor-quality median Rs value, and

two do not have any usable median Rs value.

The use of POCIS sampling improved the comparison of annual-average water concentrations against threshold values (EQS-AA and EGV), especially for contaminants with low threshold values (cyprodinil, acetochlor) or contaminants with large daily variability (diclofenac, maximized concentration with spot sampling vs mean concentration with POCIS).

Thus, chemical monitoring using POCIS not only enables better temporal integration of contamination but can also gain in relevance if sampling periods are planned to coincide with the periods of contaminant use. The improvement of DCE water monitoring also depends on river hydrology factors (high waters can favour the detection of diffuse pollutions whereas low waters can favour the detection of channelled pollutions such as wastewater treatment plant discharges). There are still development needs for a use under the WFD rules, especially for contaminants without Rs data, but also on the improvement of uncertainties on measured Rs (bias between laboratory vs in situ). Two methods have been proposed to account for the effects of in situ exposition on Rs. The first method adapted the performance reference compounds (PRC) approach for the POCIS. The second method uses passive flow monitors (PFMs). Nevertheless, these tools can be used for water monitoring (even if future developments will improve their performances). In fact, in France the regulation is being modified to integrate them in 2022.

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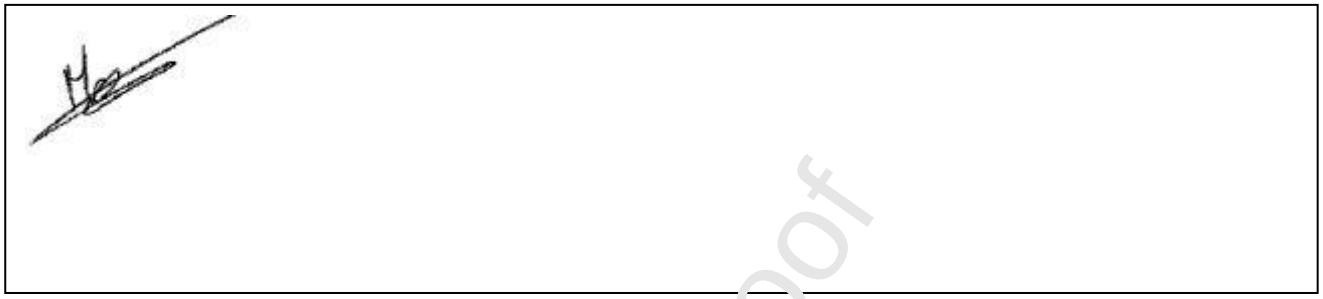
Declaration of interests

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

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



CRediT author statement:

B. Mathon: Conceptualization, Writing - Original Draft, Writing - Review & Editing, Project administration, Investigation

M. Ferreol: Software, Formal analysis

A. Togola: Conceptualization, Resources, Project administration, Investigation, Validation

S. Lardy-Fontan: Conceptualization, Investigation, Validation

A. Dabrin: Conceptualization, Validation

I.J. Allan: Conceptualization, Validation

P-F. Staub: Resources, Funding acquisition

N. Mazzella: Resources, Project administration

C. Miège: Conceptualization, Resources, Supervision, Validation

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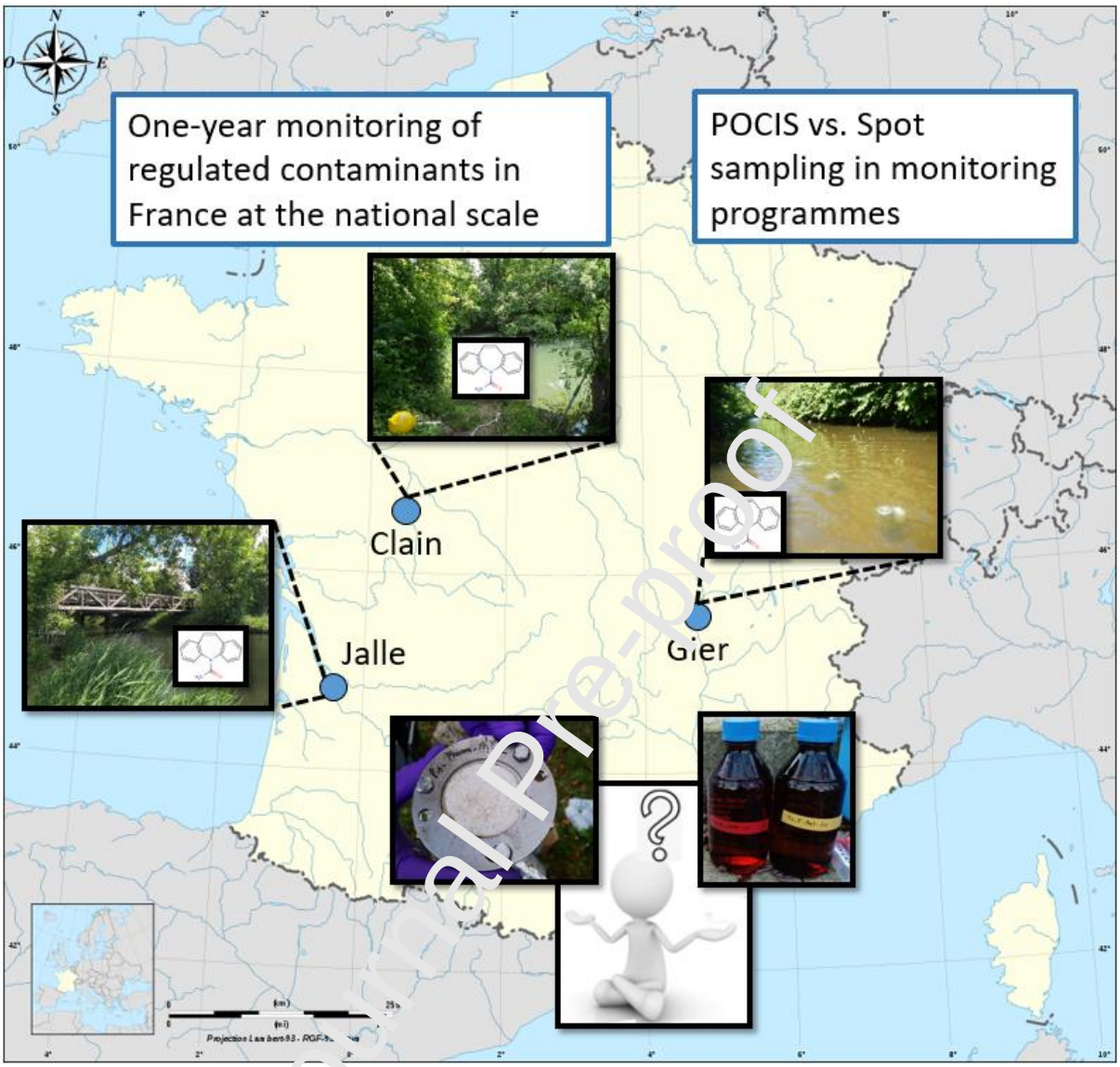

Highlights:

- POCIS allowed to monitor 45 pesticides and pharmaceuticals (DCE substances)
- POCIS improved the frequency of substances quantification in waters
- POCIS improved the detection of contaminations over a year of monitoring
- POCIS improved their comparison with Environmental Quality Standards for WFD compliance checking
- This study demonstrated the maturity of POCIS to be used in WFD monitoring