

1 **Use of passive sampling and high resolution mass spectrometry using a suspect**  
2 **screening approach to characterise emerging pollutants in contaminated groundwater**  
3 **and runoff**

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## 19 **Abstract**

20 Groundwater systems are being increasingly used to provide potable and other water  
21 supplies. Due to human activities, a range of organic pollutants is often detected in  
22 groundwater. One source of groundwater contamination is via stormwater infiltration basins,  
23 however, there is little information on the types of compounds present in these collection  
24 systems and their influence on the underlying groundwater. We developed an analytical  
25 strategy based on the use of passive sampling combined with liquid chromatography/high  
26 resolution quadrupole-time-of-flight mass spectrometry for screening for the presence of  
27 pesticide and pharmaceutical compounds in groundwater and stormwater runoff. Empore™  
28 disk-based passive samplers (SDB-RPS and SDB-XC sorbents) were exposed, using for the  
29 first time a new specially designed deployment rig, for 10 days during a rainfall event in five  
30 different stormwater infiltration systems around Lyon, France. Stormwater runoff and  
31 groundwater (via a well, upstream and downstream of each basin) was sampled. Exposed  
32 Empore™ disks were solvent extracted (acetone and methanol) and the extracts analysed  
33 using a specific suspect compound screening workflow. High resolution mass spectrometry  
34 coupled with a suspect screening approach was found to be a useful tool as it allows a more  
35 comprehensive analysis than with targeted screening whilst being less time consuming than  
36 non-targeted screening. Using this analytical approach, 101 suspect compounds were  
37 tentatively identified, with 40 of this set being subsequently confirmed. The chemicals  
38 detected included fungicides, herbicides, insecticides, indicators of human activity,  
39 antibiotics, antiepileptics, antihypertensive and non-steroidal anti-inflammatory drugs as well  
40 as their metabolites. Polar pesticides were mainly detected in groundwater and  
41 pharmaceuticals were more frequently found in runoff. In terms of detection frequency of the  
42 pollutants, groundwater impacted by infiltration was found not to be significantly more  
43 contaminated than non-impacted groundwater.

44 (281 words)

## 45 Highlights

- 46 • Design of a novel Empore™ disk-based passive sampler to enable the deployment in  
47 well bore holes for groundwater monitoring.
- 48 • Novel passive sampler used to monitor groundwater and stormwater runoff from  
49 infiltration systems.
- 50 • Combination of passive sampling and liquid chromatography/high resolution mass  
51 spectrometry for groundwater and stormwater runoff screening.
- 52 • Development of an analytical procedure based on a suspect screening workflow  
53 providing a rapid and comprehensive analysis.
- 54 • Qualitative screening of polar pesticides and pharmaceuticals in impacted  
55 groundwater sites around Lyon, France.

56

57 **Keywords: stormwater runoff, stormwater infiltration basins, passive sampling, high**  
58 **resolution mass spectrometry, pharmaceuticals, polar pesticides**

59

## 60 1. Introduction

61 Groundwater and associated aquatic systems are used extensively for the supply of potable  
62 water and for agricultural and industrial uses. Urbanisation and a growing global population  
63 have resulted in over-exploitation of this resource, particularly for drinking water supplies  
64 (Danielopol et al., 2004). Although groundwater is a vital and strategic resource, such aquatic  
65 systems are facing a decrease in their quality due to increased anthropogenic activities. Over  
66 the last decade, a wide range of contaminants have been detected in various groundwater

67 sources (Lapworth et al., 2012; Stuart et al., 2012; Vulliet et al., 2014; Postigo and Barceló,  
68 2015; Kurwadkar, 2017; Mali et al., 2017). Some of the pharmaceutical and pesticide  
69 compounds typically found can be present at concentrations of up to hundreds of ng L<sup>-1</sup>.  
70 Some of their transformation products and metabolites were found from sub-ng L<sup>-1</sup> to tens of  
71 µg L<sup>-1</sup>. Atrazine, carbamazepine, desethyl atrazine, DEET (*N,N*-diethyl-meta-toluamide) and  
72 sulfamethoxazole were among the most frequently detected compounds in groundwater  
73 (Vulliet and Cren-Olivé, 2011; Stuart et al., 2014; Lopez et al., 2015).

74 One potential major source of groundwater contamination is associated with stormwater  
75 infiltration systems (SIS) that were initially designed to reduce the risk of flooding in urban  
76 areas (Fletcher et al., 2015). These SISs are often detention and infiltration basins collecting  
77 stormwater runoff from commercial, industrial or residential areas. Stormwater runoff is  
78 infiltrated from the surface to the aquifer through a porous medium (i.e. soil and vadose zone)  
79 acting as a barrier against pollutants (Mason et al., 1999). Nevertheless, the environmental  
80 efficiency of these SISs remains closely dependent on the capacity of infiltration medium to  
81 remove/retain contaminants from infiltrated water (Sébastien et al., 2015). For example,  
82 common urban contaminants such as heavy metals or polycyclic aromatic hydrocarbons  
83 which are often attached to particles are efficiently retained by the soil infiltration basins  
84 (Winiarski et al., 2006). Nevertheless, little is known about the impact of infiltration practices  
85 on groundwater contamination by more polar and emerging organic pollutants. Thus, there is  
86 an urgent need to determine precisely the occurrence of organic contaminants such as certain  
87 polar pesticides and pharmaceuticals in groundwater and runoff in connection with  
88 infiltration basins.

89 A number of analytical methods have been developed for the measurement of polar organic  
90 contaminants in water, in particular high performance liquid chromatography (HPLC)  
91 coupled with a triple quadrupole mass spectrometer (Q-q-Q) (Jansson and Kreuger, 2010;

92 Lissalde et al., 2011; Petrie et al., 2016b). However, this operational mode has some  
93 limitations as, since it is a targeted analysis, only a pre-defined/determined list of compounds  
94 can be analysed and reference standards are needed. To circumvent these limitations, high  
95 resolution mass spectrometry (HRMS) allows the detection of a large number of compounds  
96 without reference standards or pre-selection and enables comprehensive screening of  
97 pollutants to be facilitated (Leendert et al., 2015). Two major approaches for post  
98 measurement processing exist: non-target screening (with no prior information), and suspect  
99 screening (with suspected substances based on prior information) (Schymanski et al., 2014b).  
100 HRMS coupled with a suspect screening approach is a useful tool as it allows a more  
101 comprehensive analysis than with target screening whilst being less time consuming than  
102 non-target screening. When analysing complex samples, suspect screening together with an  
103 adapted workflow is a good balance between target and non-target screening. Workflow is  
104 particularly important as it allows to narrow the positive findings by prioritizing compounds  
105 following specific thresholds while saving time and effort. Several suspect screening  
106 workflows are proposed in the literature. All are filtering strategies based on parameters such  
107 as exact mass, isotope pattern, signal-to-noise (S/N) ratio, retention time, peak shape and  
108 blank removal (Segura et al., 2011; Hug et al., 2014; Sjerps et al., 2016; Causanilles et al.,  
109 2017; Gago-Ferrero et al., 2018). They rely on comparison with commercial (Kaserzon et al.,  
110 2017; Pochodylo and Helbling, 2017) or in-house (Causanilles et al., 2017; Segura et al.,  
111 2011) databases. Replacement or adjustment of parts of HPLC-HRMS system might lead to  
112 changes in chromatography or mass measurement. Even minor, these changes could lead to  
113 non-accurate results when applying the suspect screening workflow. Therefore, it is  
114 absolutely necessary to develop a workflow well adapted to the used analytical instrument, as  
115 well as the environmental matrix analysed.

116 Another challenge concerning the measurement of organic contaminants in groundwater is  
117 that they generally occur at low and variable concentrations. In most studies, spot (bottle or  
118 grab) sampling is the chosen method used for monitoring purposes (Duong et al., 2015;  
119 Lopez et al., 2015; Manamsa et al., 2016; Pitarch et al., 2016; Sorensen et al., 2015).  
120 However, this approach only provides a snapshot of contamination at a given time and,  
121 therefore, may not be truly representative of the appertaining environmental conditions over  
122 time. The use of passive sampling devices such as the polar organic chemical integrative  
123 sampler (POCIS) (Alvarez et al., 2004; Van Metre et al., 2017), Chemcatcher® (Charriau et  
124 al., 2016; Lissalde et al., 2016; Petrie et al., 2016a) or the Empore™ disk (ED)-based sampler  
125 (Stephens et al., 2005; Shaw and Mueller, 2009; Stephens et al., 2009; Vermeirssen et al.,  
126 2013) are potentially able to overcome some of these limitations and to provide a more  
127 representative assessment of groundwater contamination. To the best of our knowledge, only  
128 two studies have been reported on the combination of passive sampling with HRMS for the  
129 assessment of contaminants in groundwater (Soulier et al., 2016) and surface water (Guibal et  
130 al., 2015). Both were based on the use of POCIS. This is the first time that an ED passive  
131 sampler is combined with suspect screening for assessment of groundwater contamination.  
132 This article also describes for the first time a novel type of rig which enabled the deployment  
133 in well bore holes.

134 The aims of the present study were: (i) to develop a novel analytical strategy that combines  
135 ED passive samplers with HRMS analysis for suspect screening of emerging pollutants in  
136 groundwater; (ii) to apply this strategy in the field to study the occurrence of pesticides and  
137 pharmaceuticals and to make assumptions about the potential transfer of compounds from  
138 surface to groundwater. To achieve this, a field study was conducted at five SISs during a  
139 storm weather event. The potential impact of infiltration practices on groundwater

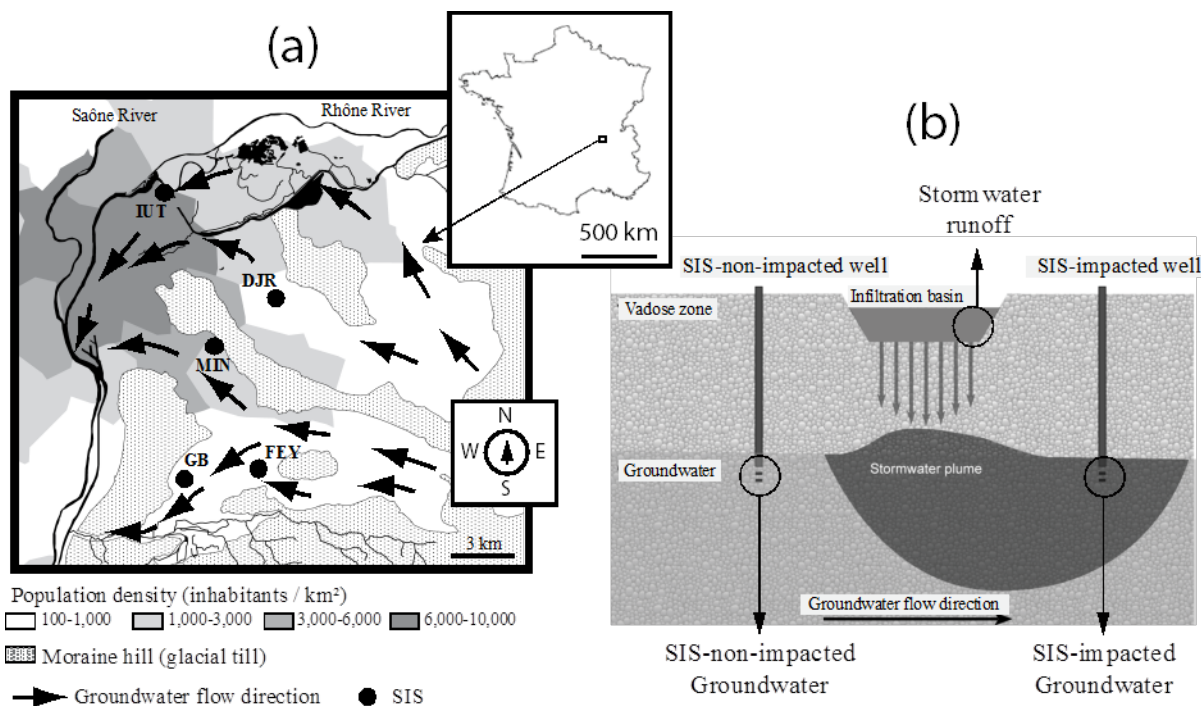
140 contamination was measured by comparing occurrence of pesticides and pharmaceuticals in  
141 stormwater runoff, SIS-non-impacted and SIS-impacted groundwater.

142

## 143 **2. Material and Methods**

### 144 **2.1. Field site description**

145 Field trials were undertaken at five SIS located in the eastern metropolitan area of Lyon,  
146 France (Fig. 1) (further details of the SIS are given in (Marmonier et al., 2013; Voisin et al.,  
147 2018). Unsaturated zone thickness, well depth, infiltration surface, catchment area and  
148 surroundings areas are given in Table S1. The five SIS (Django Reinhardt (DJR), Chemin de  
149 Feyzin (FEY), Grange Blanche (GB), Campus of the University Lyon 1 (IUT) and Minerve  
150 (MIN)) collected stormwater runoff from commercial, residential and/or industrial areas.  
151 Each site had a plastic tank placed at the surface of the SIS for collecting runoff and two  
152 wells (boreholes) to enable groundwater monitoring. One well was located in an upstream  
153 zone not impacted by the stormwater runoff plume (SIS-non-impacted well) and the other  
154 well located in the downstream aquifer zone impacted by stormwater runoff (SIS-impacted  
155 well) (Fig. 1). The wells were lined with either polyvinyl chloride or methacrylate tubes (with  
156 a minimum internal diameter of 5.5 cm) perforated at their lower end (0.5 m) to establish an  
157 efficient hydraulic connection with the aquifer. Previous work has shown that at these five  
158 sites, the bulk water properties (conductivity, dissolved oxygen and temperature) found in the  
159 wells did not differ from that of the groundwater in the aquifer (Foulquier et al., 2010; Voisin  
160 et al., 2018).



162 **Fig. 1.** Stormwater infiltration systems (SIS) in the Lyon conurbation investigated in this  
 163 work; (a) geographical locations of the five SIS, and (b) position of the sampling points in  
 164 each SIS. DJR = Django-Reinhardt, FEY = Feyzin, GB = Grange Blanche, IUT= Campus of  
 165 the University Lyon 1, MIN = Minerve. (Figure modified from Foulquier et al., 2009 and  
 166 Voisin et al., 2018).

167

## 168 2.2. Chemicals and reagents

169 Adenine, adenosine, atenolol, atrazine, atrazine-desethyl, atrazine-desethyl-desisopropyl,  
 170 boscalid, bromacil, caffeine, carbamazepine, carbendazim, cotinine, DEET, 2,6-  
 171 dichlorobenzamide, diclofenac, diuron, fluopyram, hexazinone, imidacloprid, lamotrigine,  
 172 lidocaine, metformin, metolachlor, morphine, nicotinamide, nicotine, paracetamol,  
 173 prochloraz, propiconazole, propyzamide, prosulfocarb, simazine, sulfamethoxazole,  
 174 theobromine, tramadol and venlafaxine were purchased from Sigma-Aldrich (Saint-Quentin  
 175 Fallavier, France). Diflufenican and isoproturon were purchased from Riedel de Haen



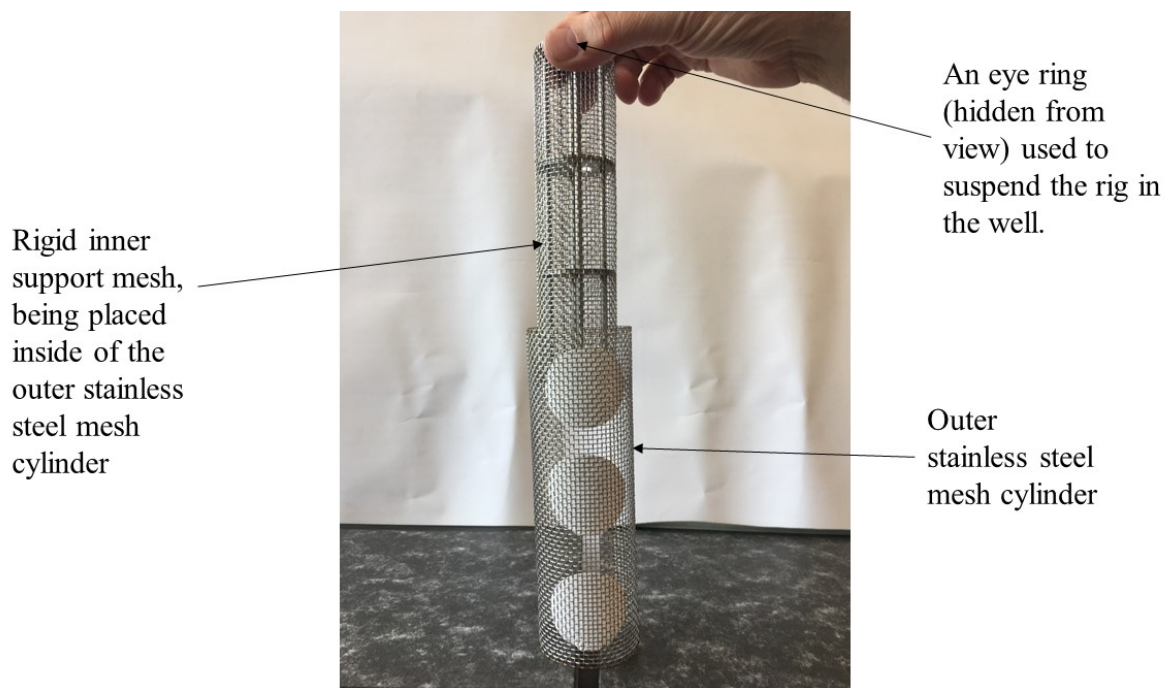
176 (Hanover, Germany). Irbesartan, telmisartan and valsartan were purchased from Tokyo  
177 Chemical Industry (Tokyo, Japan). Ethidimuron was purchased from Dr Ehrenstorfer  
178 (Augsburg, Germany). The purity of all chemicals was > 96%. Methanol (MeOH) (LC-MS  
179 grade) was from BioSolve (Dieuse, France). Acetone, ammonium formate and formic acid  
180 were purchased from Sigma-Aldrich. Milli-Q water (Millipore, Saint-Quentin-en-Yvelines,  
181 France) was used for all procedures. Individual stock solutions (1 mg mL<sup>-1</sup>) were prepared in  
182 methanol (MeOH) or water depending on their specific solubilities. These stock solutions  
183 were then diluted or mixed to obtain the various working solutions.

184

### 185 **2.3. Passive sampler preparation, deployment and extraction**

186 SDB-RPS and SDB-XC Empore™ cross-linked co-polymeric resin EDs (47 mm diameter, 12  
187 µm particle size, 0.5 mm thick (3M, Neuss, Germany)) are poly(styrenedivinylbenzene)  
188 (modified with sulfonic acid groups for SDB-RPS) used as reversed phase sorbent. Both are  
189 100% co-polymeric particles that are spherical and porous. The SDB-RPS exhibits secondary  
190 cationic exchange due to sulfonic acid groups unlike the SDB-XC, which does not have a pH  
191 limitation. These sorbents are known to be able to retain hydrophobic and semi-polar  
192 analytes. These disks were, therefore, well suited to sequester the wide range of emerging  
193 pollutants that were likely to be found in the field trial sites. It should be noted, however, that  
194 the SDB disks will only sequester compounds that have an affinity for the sorbent and are  
195 able to bind to the material. It will not be efficient for the uptake of ionic compounds, such as  
196 acidic drugs; including diclofenac, ibuprofen and naproxen that are widely used as non-  
197 steroidal anti-inflammatory drugs (Lindqvist et al., 2005). Such disks can be pre-cleaned  
198 prior to use and extracted after deployment easily using a simple funnel extraction system.  
199 They were conditioned by soaking in MeOH overnight then in water (5 min) prior to placing

200 them on the deployment rig (Fig 2 and S1a). The deployment rig comprised of two custom  
201 made stainless steel components (AT Engineering, Tadley, UK). An inner mesh ( $0.25 \times 0.25$   
202  $\text{cm}^2$ ) cylindrical cage (19 cm high, 4.5 cm diameter, Fig. 2) with four circular strengthening  
203 rods/supports and 'eye' ring to enable the device to be suspended at the required depth in the  
204 well using a rope line. A similar size outer mesh that was capable of being formed into a  
205 cylinder was used to secure the ED passive samplers (Fig. S1a). Four SDB-RPS and four  
206 SDB-XC EDs were carefully and evenly placed on the outer mesh support (Fig. S1a). The  
207 EDs were held in place by placing the inner mesh inside of the outer mesh and securing it  
208 using four stainless steel cable ties. Using this sized mesh allowed a good exchange of the  
209 surrounding water in the well with each of the ED. The deployment rigs ( $\sim 4.7$  cm overall  
210 external diameter) were designed to fit comfortably down the well bore holes ( $\sim 5.5$  cm  
211 diameter) (Fig. S1b). After assembly, each rig was fully submerged in Milli-Q water (2 L  
212 sealable glass jar) and stored at  $4^\circ\text{C}$  prior to deployment. Jars were transported to the  
213 deployment sites in cool boxes. A total of fifteen deployment rigs were used: five SIS, with  
214 three sampling points per SIS (tanks collecting stormwater runoff entering the basin, and SIS-  
215 non-impacted and SIS-impacted wells). Rigs were deployed for ten days between 8<sup>th</sup> - 18<sup>th</sup> of  
216 December, 2017. The rigs were kept fully submerged in the tanks and at various depths  
217 below the aquifer in the wells (see Table S1). The deployment period coincided with several  
218 successive rainfall events (Fig. S2) so it was hoped that the EDs would sequester different  
219 types of pollutants associated with these stochastic events. Water conductance and  
220 temperature (LTC Levellogger<sup>®</sup> Junior, Solinst, Canada), dissolved oxygen (HOB<sup>®</sup> U26,  
221 Onset, USA) and pH was measured during the trial. pH of the various water samples was  
222 between 7.2 and 8.1 during the deployment period of the rigs.



223

224 **Fig. 2.** Deployment rig showing the inner and outer stainless steel mesh components. In this  
225 example, supporting three Empore™ disks.

226 After the deployment period, the rigs were taken back to the laboratory in cool boxes. The rig  
227 was disassembled and the EDs removed using tweezers. The acetone followed by MeOH  
228 extraction step is known to be a powerful solvent combination and give high extraction  
229 efficiencies of semi-polar and polar analytes sequestered on SDB Empore™ disks  
230 (Vermeirssen et al., 2009, 2013). Consequently, the EDs were stored in acetone (10 mL) at  
231 4°C. For processing, the vials containing the EDs were allowed to reach room temperature  
232 and rolled in a tube rotator (10 min). Subsequently, the acetone was transferred to a new vial.  
233 MeOH (10 mL) was added to the ED and the vial was rolled for another 10 min. The acetone  
234 and MeOH fractions of each of the four SDB-XC or SDB-RPS disks per support were pooled  
235 (80 mL) together in order to subsequently make a more concentrated extract. The combined  
236 extracts were reduced to dryness under a gentle stream of nitrogen and stored at -20°C. Prior  
237 to analysis, extracts were reconstituted (500 µL) in water/MeOH (90/10, v/v).

238

## 239            2.4. Instrumental analysis

240    Extracts were analysed using an Ultimate 3000 UHPLC system (Thermo Scientific<sup>®</sup>, MA,  
241    USA) equipped with a binary pump and reversed-phase analytical column, coupled to a  
242    quadrupole time-of-flight mass spectrometer (Q-ToF) (Maxis Plus, Bruker Daltonics<sup>®</sup>,  
243    Bremen, Germany). The software used to control the instrument and to acquire data was  
244    otofControl 4.1 and Hystar<sup>™</sup> 4.1 (Bruker Daltonics<sup>®</sup>). Data Analysis<sup>®</sup> 4.4 and Target  
245    Analysis for Screening and Quantitation (TASQ)<sup>®</sup> 1.4 (Bruker Daltonics<sup>®</sup>) were used for data  
246    processing. TASQ<sup>®</sup> 1.4 includes two data bases (PesticideScreener 2.1 and ToxScreener 2.1)  
247    of about 2,500 pesticide and pharmaceutical compounds.

248

249    Separations were carried out using an Acclaim RSLC C<sub>18</sub> column (2.1 x 100 mm, 2.2 μm  
250    particles, Thermo Fischer Scientific) maintained at 30 °C; the injection volume was 5 μL.  
251    The mobile phases consisted of: (A) water/MeOH (90/10, v/v); and (B) MeOH; with 5 mM  
252    ammonium formate and 0.01% formic acid in both phases for both positive and negative  
253    ionisation modes. The binary elution gradient started with 1% of (B) at a flow rate of 0.2 mL  
254    min<sup>-1</sup> for 1 min, gradually increasing to 39% (B) for the next 2 min then increasing to 99.9%  
255    (B) at 0.4 mL min<sup>-1</sup> for the following 11 min. The last condition was kept constant for 2 min  
256    (flow rate 0.48 mL min<sup>-1</sup>), then the initial conditions (1% B-99% A) were restored within 0.1  
257    min (flow rate decreased to 0.2 mL min<sup>-1</sup>) to re-equilibrate the column prior to the next  
258    injection.

259

260    The Q-ToF system was equipped with an electrospray ionization interface (ESI) operating in  
261    positive or negative ionization modes with the following settings: capillary voltage of 3,600

262 V, end plate offset of 500 V, nebulizer pressure of 3 bar (N<sub>2</sub>), drying gas of 9 L min<sup>-1</sup> (N<sub>2</sub>),  
263 and drying temperature of 200°C. The analysis was performed in full scan over the mass  
264 range of 80-1000 Da, with a scan rate of 1 Hz. The analysis was carried out in profile mode  
265 with the following transfer parameters: funnel 1 RF of 200 Vpp, multipole RF of 50 Vpp,  
266 quadrupole energy of 5 eV, collision energy of 7 eV, stepping basic and a pre-pulse storage  
267 of 5 ms. The instrument resolution was estimated at 20,738 (FWHM) at  $m/z = 376.0381$ . A  
268 solution of sodium formate and acetate (10 mM) to form clusters was used for external  
269 calibration at the beginning of each run. The ions selected for recalibrating the mass axis  
270 were the protonated reference ions ( $[M+H]^+$ , 34 masses from 90.9766 to 948.8727) with high  
271 precision calibration (HPC) mode at a search range  $\pm 0.05 m/z$ . Accepted standard deviations  
272 were below 0.5 ppm.

273

## 274 **2.5. Liquid chromatography-Q-ToF data acquisition**

275 MS/MS experiments were conducted using three different data acquisition modes: MS,  
276 broadband collision induced dissociation mode (bbCID, data independent analysis) and auto-  
277 MS/MS mode (data dependent analysis) with a cycle time of 3 s and an acquisition frequency  
278 of 1 Hz in order to record 1 spectra s<sup>-1</sup>. Unspiked and spiked extracts (with reference  
279 compounds at 500  $\mu\text{g L}^{-1}$ ) were injected using the auto-MS/MS mode.

280 For quality assurance / quality control (QA/QC), several laboratory control samples were  
281 used. Mass accuracy of the detector was monitored at the beginning of each run and  
282 recalibrated if mass error exceeded 0.5 ppm. A quality control was injected every 12 analyses  
283 to check retention times and sensitivity during data acquisition. This was a mix of 10  $\mu\text{L}$  of  
284 each extract and spiked at 500  $\mu\text{g L}^{-1}$  with a standard solution of eight compounds: atrazine,  
285 atrazine-desethyl-desisopropyl, boscalid, carbendazim, diclofenac, imidacloprid, prochloraz

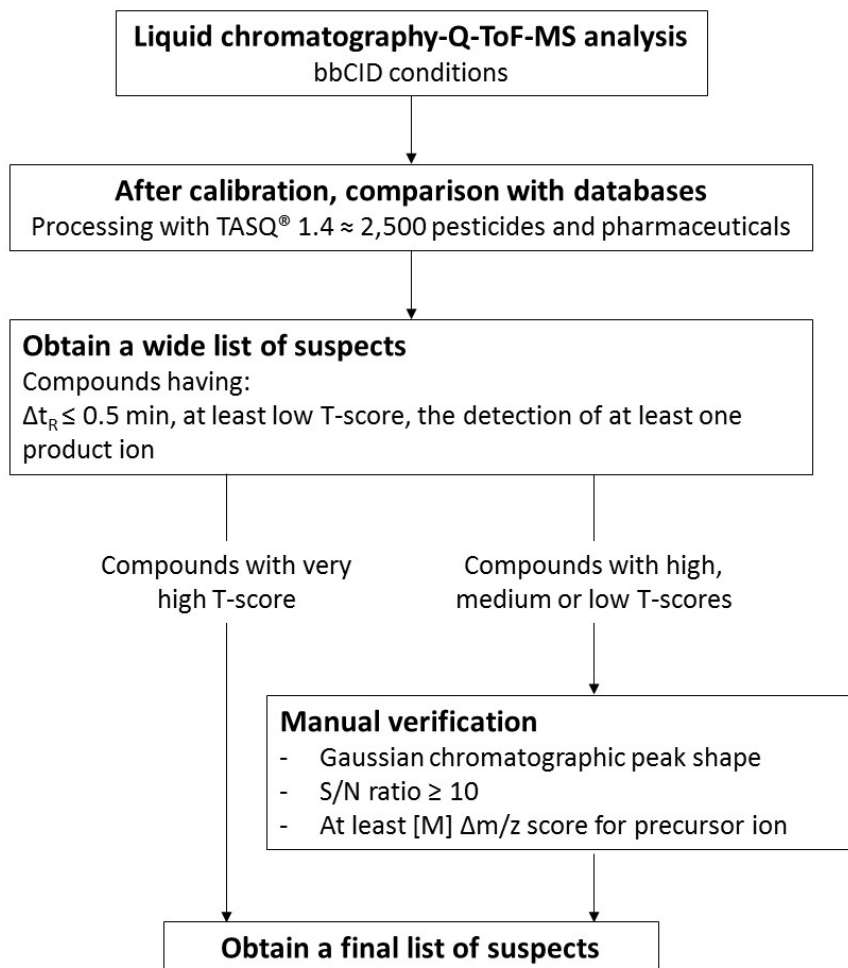
286 and sulfamethoxazole. These compounds were also used to correct the database retention  
287 times. Background signals were identified by analysis of blanks (solvent blank and  
288 procedural blank). Solvent blanks were also injected to monitor column carryover.

289

## 290 **2.6. Filtering strategy**

291 Filtering of information was undertaken by comparing experimental sample data with  
292 theoretical data for each compound. All precursor and product ions were evaluated using  
293 three criteria (i) retention time ( $\Delta t_R$ ), (ii)  $m/z$  ( $\Delta m/z$ ) and (iii) isotope pattern (expressed as  
294 mSigma) (Table S2). Deviations between experimental and theoretical data were scored high  
295 [H], medium [M] or low [L] according to tolerance thresholds set for each of the three  
296 criteria. Additionally, the detection of at least one product ion for each precursor ion was  
297 mandatory. T-scores correspond to the combination of the scores for each of the three criteria  
298 for both precursor and product ions; the detailed calculation of these values is detailed in  
299 Table S2. Compounds had to meet three criteria to appear in the wide list of suspects: a  
300 retention time deviation within the tolerance threshold of  $\pm 0.5$  min, a low T-score and at  
301 least one product ion detected (Fig. 3). Then, the final list of suspects was built as follows:  
302 compounds having a very high T-score were definitively considered as suspects without  
303 further verification; for compounds having high, medium or low T-scores, manual  
304 verification of chromatographic peak shapes,  $\Delta m/z$  and S/N ratios was carried out in order to  
305 reduce false positives. Manual verification of such parameters remains necessary even when  
306 comparing with a database (Hug et al., 2014; Pochodylo and Helbling, 2017; Segura et al.,  
307 2011). Suspects exhibiting a chromatographic peak without Gaussian peak shape or having a  
308 S/N ratio below 10 were excluded. Furthermore, those having a precursor ion with [L]  $\Delta m/z$   
309 score were excluded (Fig. 3). The mSigma parameter was not taken into account at this stage,

310 as a poor peak intensity could lead to a wrong mSigma calculation, even with a true positive  
311 because of possible interferences. Therefore, compounds present at low concentration in the  
312 sample extract or displaying a low sensitivity with the analysis method may be improperly  
313 excluded.



314

315 **Fig. 3.** Schematic of workflow used for the suspect screening of compounds.

316

## 317 2.7. Evaluation of contamination in stormwater runoff and groundwater

318 Based on the list of contaminants detected in the three water types (stormwater runoff, SIS-  
319 non-impacted and SIS-impacted groundwater) at the five SIS, we evaluated the mean number  
320 of pesticide and pharmaceutical compounds found. The 40 confirmed compounds exhibit a  
321 S/N ratio high enough to enable the comparison of the three water types. The range of

322 pesticide and pharmaceutical compounds were compared among the three water types using a  
323 mixed model with SIS as the random factor and water types as the fixed factor to take into  
324 account the statistical dependence of waters collected at the same SIS. When mixed models  
325 gave significant results for water type differences, *post hoc* Tukey's honest significance  
326 difference tests were performed to determine whether significant pairwise differences  
327 occurred among water types. For the two variables (pesticide and pharmaceutical  
328 compounds), the normality and the homoscedasticity of the residues were tested using the  
329 Shapiro-Wilk's test and the Bartlett's test, respectively. As these assumptions were not met  
330 for pharmaceutical compounds, data were log transformed before statistical analyses. Venn  
331 diagrams were also constructed for each site to determine the percentages of pesticide and  
332 pharmaceutical compounds that were obtained from the three water types. This type of  
333 analysis highlighted the percentages of compounds that were found from one, two or the  
334 three water types. The percentages obtained from the five SIS independently were averaged  
335 to obtain Venn diagrams illustrating the mean percentages of pesticides and pharmaceutical  
336 compounds found in each water type and in several water types. In addition, a more precise  
337 description of the compounds found allowed us to evaluate which compounds were only  
338 found in one water type for the five sites. The percentages obtained from the five SIS were  
339 averaged to obtain Venn diagrams for pesticide and pharmaceutical compounds within the  
340 whole dataset. Statistical tests were performed using R software (R Development Core Team  
341 2008) (Bunn and Korpela, n.d.) (<https://www.R-project.org/>) and Venn diagrams were  
342 constructed using Venny 2.1.0 (<http://bioinfogp.cnb.csic.es/tools/venny>).

343

### 344 **3. Results and discussion**

#### 345 **3.1. Design and use of passive samplers**



346 Passive sampling devices have been used for many years to monitor pollutants (mainly low  
347 molecular mass hydrocarbons and other volatile and semi-volatile non-polar chemicals) in  
348 groundwater. There is a wide range of different devices available and these have been  
349 reviewed (Centre d'expertise en analyse environnementale du Québec, 2012). Little work has  
350 been undertaken to monitor polar pollutants e.g. pharmaceuticals and personal care products  
351 in this medium using these devices. To our knowledge there are only three applications of the  
352 use of passive samplers to monitor polar substances in groundwater (Berho et al., 2013;  
353 Soulier et al., 2016; Ahkola et al., 2017).

354

355 We designed a simple sampler based on the Chemcatcher<sup>®</sup> principles, designed to fit  
356 comfortably down the well bore holes, that used only a naked Empore<sup>™</sup> disk as the active  
357 receiving phase (Figure 2, S1a, b). Such an approach has been used previously to sequester a  
358 wide range of polar pollutants (Stephens et al., 2005; Shaw and Mueller, 2009; Stephens et  
359 al., 2009; Vermeirssen et al., 2013) in coastal and surface waters. The attractiveness of this  
360 design over the POCIS is that there is no polyethersulphone (PES) diffusion membrane  
361 overlying the receiving phase. It has been reported that some of the more hydrophobic  
362 compounds (e.g.  $\log K_{ow} > 4.25$ ) can be retained in the PES membrane and, thereby, do not  
363 reach the sorbent layer and be detected in the subsequent analytical screening procedures  
364 (Soulier et al., 2016). Not having a PES membrane also helps to increase the diffusional  
365 uptake of analytes and thereby decrease the resultant analytical detection limits. This simple,  
366 low cost, yet robust, cage design also permitted the deployment of up to nine (similar or  
367 different types of sorbent chemistries) Empore<sup>™</sup> disks on one rig and also maintained an  
368 open structure to allow good lateral flow of water whilst within the bore hole well.

369 No pharmaceuticals or polar pesticides, that were subsequently screened for, were detectable  
370 in the pre-washed Empore™ disks (fabrication blanks) prior to their use in the passive  
371 sampler rigs. After the 10-day deployment all the disks were still retained in place by the  
372 secured outer cage support. There was no visible biofouling of the surface of the Empore™  
373 disks in those rigs deployed in bore hole wells. In addition, the use of a bound sorbent in the  
374 form of an Empore™ disk, ensured that the active sampling area did not alter during the field  
375 deployments. This can be a problem with the use of loose sorbent material, as is used in the  
376 POCIS and can lead to variable results (Mills et al., 2014).

377

### 378 **3.2. Suspect screening and confirmation**

379 All the extracts from the passive sampling devices were analyzed by LC-Q-ToF. Using the  
380 workflow described in the Material and Methods section, 101 suspected compounds were  
381 finally selected. Compounds formula, theoretical exact masses, theoretical retention times,  
382 detection rates in SIS-non-impacted and in SIS-impacted groundwater and in runoff water as  
383 well as average T-scores and levels of confidence are details in Table S3. The workflow  
384 proposed by Schymanski et al. (2014) divides the confidence of identification into 5 levels:  
385 level 5 = exact mass, level 4 = unequivocal molecular formula, level 3 = tentative candidate,  
386 level 2b = probable structure by diagnostic evidence, level 2a = probable structure by library  
387 spectrum match and level 1 = confirmed structure by reference standard. In order to reach the  
388 level 1 confidence, confirmation by injection of a reference standard for the measurement of  
389 retention time, MS and MS/MS spectra was carried out. Among the final list of suspects,  
390 compounds with high and very high T-score and considered to be relevant according to the  
391 literature (Lopez et al., 2015; Marmonier et al., 2013) were selected for confirmation as well  
392 as compounds that were available in our laboratory. In total, 43 compounds were selected in

393 positive ion mode. No compound was selected in negative ion mode as none was suspected  
394 except a few already detected in positive ion mode (bromacil, diuron, propyzamide). Among  
395 the 30 analysed samples, a set of six representative samples of all the compounds to be  
396 confirmed (i.e. with the highest intensities) were selected for re-injection. Unspiked and  
397 spiked samples ( $500 \mu\text{g L}^{-1}$ ) were injected with the auto-MS/MS mode. Thus, 33 compounds  
398 were fragmented and 10 were not fragmented probably due to low concentrations and/or co-  
399 elutions with compounds more concentrated or more sensitive. For these 10 compounds,  
400 specific selected mass by daughter scan mode method was created. Retention time and  
401 MS/MS spectra of unspiked and spiked samples were compared. Furthermore, experimental  
402 product ions were matched with the literature. A schematic workflow of the structure  
403 confirmation of identified compounds is shown [Fig. S3](#) together with an example of  
404 identification of metolachlor ([Fig. S4](#)). The application of the suspect screening workflow is  
405 helpful in the search for contaminants in groundwater. TASQ<sup>®</sup> 1.4 software provides a  
406 turnkey solution for the screening and allows narrowing the search to a list of almost 2,500  
407 pesticides and pharmaceuticals. However, the quasi-systematic verification of some criteria  
408 such as chromatographic peak shape and S/N ratio cannot be neglected. The manual  
409 verification of these criteria for each suspect is time consuming, but the overall suspect  
410 screening workflow remains very helpful to have an overview of the occurrence of  
411 contaminants in groundwater.

412

413 Finally, of the 43 compounds to be confirmed, 40 were effectively confirmed. Only three  
414 were false positives: indomethacin, phenazone and simazine. Although 2-hydroxysimazine  
415 appeared with a high average T-score in the list of suspects of 17 samples, it resulted a false  
416 positive as the retention time differed from that of the reference standard ( $\Delta t_R = 0.2 \text{ min}$ ).

417 Indomethacin and phenazone showed insufficient matching with the reference standard  
418 MS/MS spectra (Table S4).

419

### 420 **3.3. Water quality monitoring using passive samplers**

#### 421 **3.3.1. Comparison of SDB-RPS and SDB-XC disks**

422 A total of 30 samples were analyzed: three samples per site (SIS-non-impacted and SIS-  
423 impacted groundwater and runoff water) with two extraction disks each (SDB-RPS and SDB-  
424 XC). Our results showed that SDB-RPS and SDB-XC extraction disks displayed similar  
425 sampling properties. Indeed, for a given site, the comparison of the positive findings showed  
426 as expected, that the majority of the contaminants sampled were comparable between the  
427 disks (Fig. S5). These results confirmed those of (Vermeirssen et al., 2009) in a study  
428 comparing the performance of the two disks for sampling polar organic compounds in treated  
429 sewage effluent. As a result, in order to take advantage of the complementarity provided by  
430 the two disks, no distinction was made between the two disks and combined results are  
431 presented.

432

#### 433 **3.3.2 Occurrence of contaminants in groundwater and runoff water**

434 The application of passive sampling in combination with the suspect screening allowed the  
435 detection of 101 suspects of pesticides and pharmaceuticals. From the 40 confirmed  
436 compounds, 30 were detected in groundwater (Table 1), including 16 pesticides and 14  
437 pharmaceuticals.

438 **Table 1.** List of contaminants identified (Level 1) in SIS-non-impacted and SIS-impacted  
439 groundwater samples collected from EDs exposed in the five SIS around Lyon, France.

Compound	Formula	Theoretical exact mass	Theoretical $t_R$ (min)	Detection rate in SIS-non- impacted groundwater (%) (n = 10)	Detection rate in SIS- impacted groundwater (%) (n = 10)
<b>Pesticides</b>					
Atrazine	C <sub>8</sub> H <sub>14</sub> ClN <sub>5</sub>	216.1010	8.85	80	80
Atrazine-desethyl	C <sub>6</sub> H <sub>10</sub> ClN <sub>5</sub>	188.0697	6.49	80	80
Bromacil	C <sub>9</sub> H <sub>13</sub> BrN <sub>2</sub> O <sub>2</sub>	261.0233	7.83	50	80
Carbendazim + benomyl	C <sub>9</sub> H <sub>9</sub> N <sub>3</sub> O <sub>2</sub>	192.0768	6.08	0	80
DEET	C <sub>12</sub> H <sub>17</sub> NO	192.1383	8.87	80	100
Dichlorobenzamide	C <sub>7</sub> H <sub>5</sub> Cl <sub>2</sub> NO	189.9821	5.14	80	100
Diuron	C <sub>9</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> O	233.0243	9.24	100	100
Ethidimuron	C <sub>7</sub> H <sub>12</sub> N <sub>4</sub> O <sub>3</sub> S <sub>2</sub>	265.0424	5.63	30	40
Fluopyram	C <sub>16</sub> H <sub>11</sub> ClF <sub>6</sub> N <sub>2</sub> O	397.0537	10.44	20	80
Hexazinone	C <sub>12</sub> H <sub>20</sub> N <sub>4</sub> O <sub>2</sub>	253.1659	7.85	60	50
Imidacloprid	C <sub>9</sub> H <sub>10</sub> ClN <sub>5</sub> O <sub>2</sub>	256.0596	5.53	20	50
Isoproturon	C <sub>12</sub> H <sub>18</sub> N <sub>2</sub> O	207.1492	9.00	20	20
Metolachlor	C <sub>15</sub> H <sub>22</sub> ClNO <sub>2</sub>	284.1412	10.85	100	100
Propiconazole	C <sub>15</sub> H <sub>17</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>2</sub>	342.0771	11.49	10	0
Propyzamide	C <sub>12</sub> H <sub>11</sub> Cl <sub>2</sub> NO	256.0290	10.28	20	40
Simazine	C <sub>7</sub> H <sub>12</sub> ClN <sub>5</sub>	202.0854	7.81	80	80
<b>Pharmaceuticals</b>					
Adenine	C <sub>5</sub> H <sub>5</sub> N <sub>5</sub>	136.0618	2.20	80	60
Adenosine	C <sub>10</sub> H <sub>13</sub> N <sub>5</sub> O <sub>4</sub>	268.1040	3.72	100	80
Caffeine	C <sub>8</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub>	195.0877	5.06	100	100
Carbamazepine	C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O	237.1022	8.21	80	80
Cotinine	C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O	177.1022	4.27	20	0
Diclofenac	C <sub>14</sub> H <sub>11</sub> Cl <sub>2</sub> NO <sub>2</sub>	296.0240	11.00	10	0
Irbesartan	C <sub>25</sub> H <sub>28</sub> N <sub>6</sub> O	429.2397	9.89	0	20
Lamotrigine	C <sub>9</sub> H <sub>7</sub> Cl <sub>2</sub> N <sub>5</sub>	256.0151	5.99	50	100
Lidocaine	C <sub>14</sub> H <sub>22</sub> N <sub>2</sub> O	235.1805	5.21	10	10
Nicotinamide	C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O	123.0553	2.80	20	0

Nicotine	C <sub>10</sub> H <sub>14</sub> N <sub>2</sub>	163.1230	1.98	10	0
Sulfamethoxazole	C <sub>10</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> S	254.0594	5.34	60	80
Theobromine	C <sub>7</sub> H <sub>8</sub> N <sub>4</sub> O <sub>2</sub>	181.0720	3.92	60	30
Tramadol + <i>o</i> -desvenlafaxine	C <sub>16</sub> H <sub>25</sub> NO <sub>2</sub>	264.1958	5.57	0	20

440

441 The majority of the pesticides found in groundwater had already been reported previously in  
442 other European studies. Atrazine, desethyl atrazine, DEET, 2,6-dichlorobenzamide, diuron,  
443 isoproturon, metolachlor, propiconazole, propyzamide and simazine were quantified by  
444 Lopez et al. (2015) during two screening trials of 494 French groundwater sites. Hexazinone  
445 was found by (Berho et al., 2013) during four trials at two French groundwater sites.  
446 Bromacil and imidacloprid were previously detected in Spain (Pitarch et al., 2016) and a  
447 German study reported the presence of carbendazim (Reh et al., 2013). In contrast, to the best  
448 of our knowledge, there is no other study reporting the presence of ethidimuron and  
449 fluopyram in European groundwaters. In the case of pharmaceuticals, caffeine,  
450 carbamazepine, cotinine, diclofenac, sulfamethoxazole and tramadol were detected by Lopez  
451 et al., 2015 in French groundwater. Lidocaine and nicotine have been reported to be present  
452 in European groundwater (Lapworth et al., 2012), irbesartan was found by (Pitarch et al.,  
453 2016) in Spain and lamotrigine and theobromine were detected in Germany (Bollmann et al.,  
454 2016; Reh et al., 2013). To our knowledge, adenine, adenosine and nicotinamide have never  
455 been detected previously in groundwater samples.

456 In runoff, 31 compounds were confirmed (Table S5) that included 11 pesticide and 20  
457 pharmaceutical compounds. Only a few studies have assessed pesticides contamination of  
458 urban runoff in Europe. Bollmann et al. (2014) found diuron and propiconazole in runoff in a  
459 study in Denmark, and metolachlor was reported by (Gasperi et al., 2014) in stormwater  
460 collected in France. Dichlorobenzamide, diflufenican, propyzamide and prosulfocarb were

461 previously detected in Sweden rivers and streams (Jansson and Kreuger, 2010). DEET was  
462 previously reported by (Moschet et al., 2015) during a large field study of urban affected  
463 rivers in Sweden and bromacil was detected in river water in Spain (Pitarch et al., 2016). To  
464 the best of our knowledge, no study has reported the presence of atrazine-desethyl-  
465 desisopropyl (DEDIA) neither in runoff nor in surface water, but it has been found in  
466 groundwater (Lopez et al., 2015). In addition, fluopyram has not been reported to be present  
467 in either groundwater, runoff or surface water. Like pesticides, very few European studies  
468 have dealt with the occurrence of pharmaceuticals in urban runoff. Carbamazepine and  
469 diclofenac were found in stormwater by Launay et al., (2016) in a study undertaken in  
470 Germany. Atenolol, caffeine, irbesartan, lamotrigine, lidocaine, metformin, paracetamol,  
471 telmisartan, tramadol, valsartan and venlafaxine were found by (Moschet et al., 2015) in  
472 urban affected rivers in Sweden. Cotinine, nicotine and morphine have been found in rivers  
473 of the United Kingdom (Petrie et al., 2016a).

474

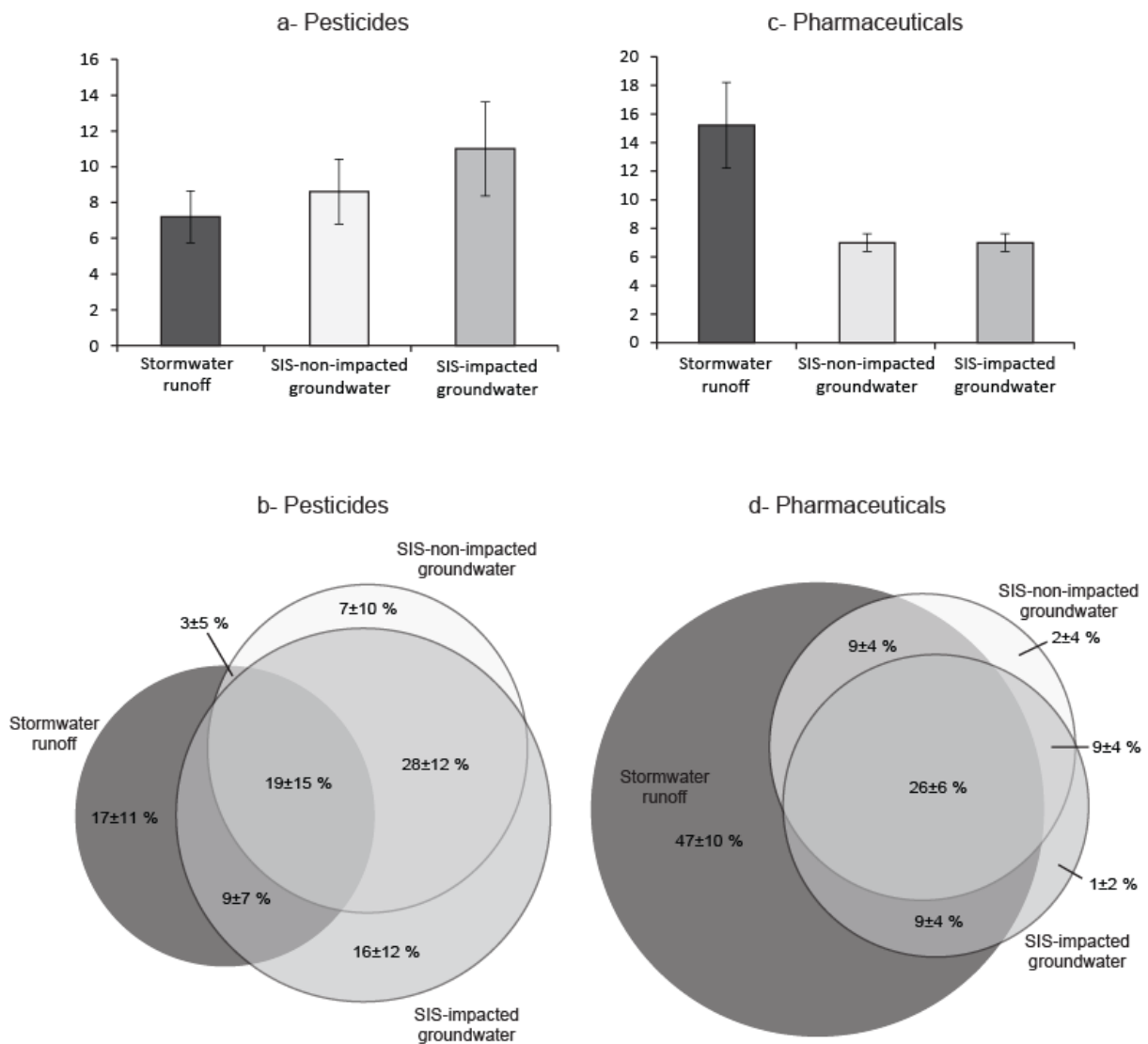
### 475 3.3.3 Potential transfer of pesticides and pharmaceutical compounds from 476 surface to groundwater

477 The number of pesticides detected in the SIS was significantly different among water types  
478 (Fig. 4a, mixed model, water type effect,  $F_{(2,8)} = 14.2$ ,  $p < 0.01$ ) with a higher diversity of  
479 compounds in SIS-impacted groundwater than in stormwater runoff and SIS-non-impacted  
480 groundwater (Tukey's *post hoc* tests,  $p < 0.05$  for comparison between SIS-impacted  
481 groundwater and other water types). This "enrichment" in pesticide compounds of SIS-  
482 impacted groundwater in comparison with SIS-non-impacted groundwater might have been  
483 due to the contamination of groundwater with pesticides occurring in stormwater runoff.  
484 Nevertheless, only  $9 \pm 7$  % of the pesticides were uniquely shared by stormwater runoff and

485 SIS-impacted groundwater (Fig. 4b) and this percentage was not associated with specific  
486 compounds only detected from ED deployed in these two water types (Fig. 5). Thus, our  
487 results did not suggest that some pesticides originating from urban stormwater runoff  
488 significantly contaminated the aquifer. Several pesticides are ubiquitous (detected in the three  
489 water types) and represented 19% of compounds (Fig. 4b) including diuron, DEET,  
490 fluopyram and metolachlor (Fig. 5). Such results are not surprising, as these compounds are  
491 known to be common persistent contaminants in groundwater and are also widely used in  
492 urban areas. For example, diuron is constantly emitted as it is used as film preservatives and  
493 slowly released to the environment (Bollmann et al., 2014) and DEET is a domestic insect  
494 repellent widely used across the world (Loos et al., 2010; Sorensen et al., 2015; Stuart et al.,  
495 2014). We also observed that more than 51% of pesticide compounds were only collected  
496 from EDs deployed in groundwater (SIS-impacted and SIS-non-impacted), highlighting the  
497 impact of agricultural practices on aquifer contamination. Indeed, the listing of pesticides  
498 detected in groundwater showed the occurrence of contaminants such as atrazine, atrazine-  
499 desethyl or simazine associated with agricultural practices (Böhlke, 2002). It is also worth  
500 noting that about 17% of pesticides in stormwater runoff were not detected in groundwater  
501 (Fig. 4b) and could be associated with three molecules: DEDIA, prosulfocarb and  
502 diflufenican (Fig. 5). The lack of detection of these stormwater runoff compounds in  
503 groundwater samples suggests an efficient effect of soil and vadoze zone to prevent the  
504 contamination of groundwater by these pesticides. Such interpretation would be highly  
505 dependent on the chemical properties of the three pesticides that determine their sorption and  
506 their degradability in the environment. Indeed, the Groundwater Ubiquity Score (GUS),  
507 which is a leaching potential indicator based on the physico-chemical properties, is among  
508 the lowest for these pesticides in comparison to all 19 confirmed pesticides (Köck-  
509 Schulmeyer et al., 2014). Our analysis also indicated that 16% of pesticides were only



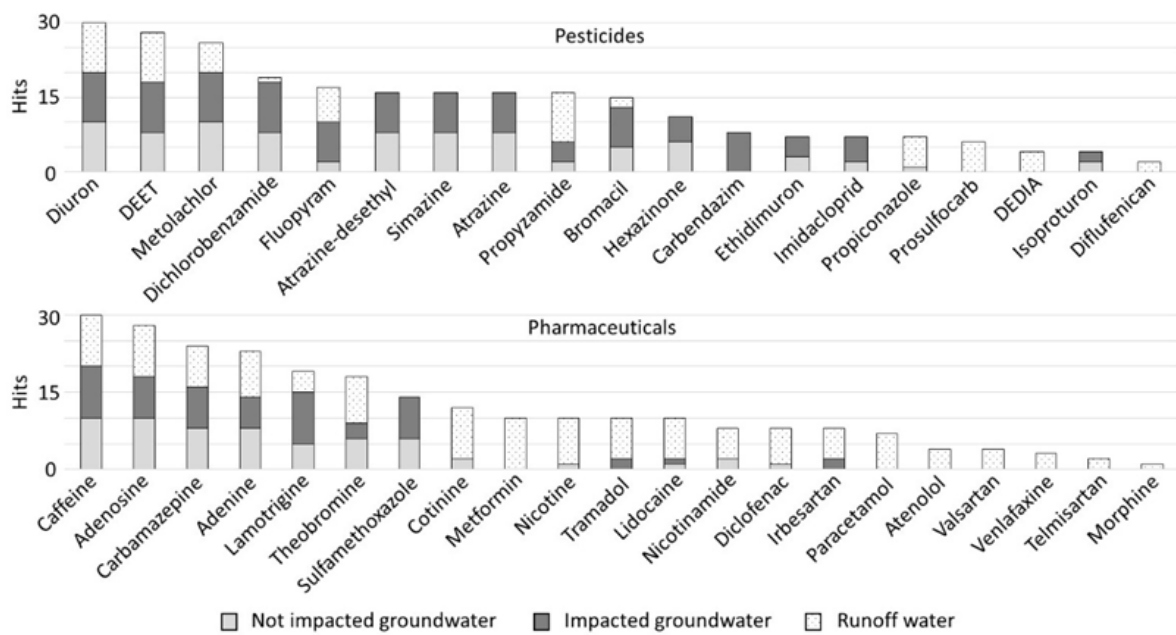
510 detected in SIS-impacted groundwater (Fig. 4b) with one specific compound (carbendazim,  
 511 Fig. 5). This observation suggested that the infiltration of stormwater runoff from surface to  
 512 groundwater might have remobilized and transferred pesticides from the soil and the vadose  
 513 zone, leading to the detection of these compounds in SIS-impacted groundwater whereas they  
 514 were not present in stormwater runoff. These results were also found in a study of the  
 515 effectiveness of a detention basin in removing emerging contaminants (Sébastien et al.,  
 516 2015). It was found that carbendazim might be temporary stored at the bottom of the basin  
 517 and thereafter remobilized and released.



518

519 **Fig. 4.** Mean number of pesticide (a) and pharmaceutical compounds (c) detected in each  
 520 water type (mean  $\pm$  confidence interval %,  $n = 5$  stormwater infiltration systems). Venn  
 521 diagrams showing the percentages of pesticide (b) and pharmaceutical compounds (d) found  
 522 in each water type and common between two or three water types (percentages are means  $\pm$   
 523 confidence interval,  $n = 5$  stormwater infiltration systems)

524



525

526 **Fig. 5.** Detection of confirmed pesticide and pharmaceutical compounds in SIS-non-impacted  
 527 and SIS-impacted groundwater and runoff water. Data for the two extraction disks (SDB-RPS  
 528 and SDB-XC) are combined.

529

530 The number of pharmaceutical compounds detected in SISs was significantly different among  
 531 water types (Fig. 4c, mixed model, water type effect,  $F_{(2,8)} = 30.7$ ,  $p < 0.001$ ) with a higher  
 532 diversity of compounds in stormwater runoff than in groundwater (Tukey's *post hoc* tests,  $p <$   
 533  $0.001$  for comparison between stormwater runoff and other water types). Indeed, only 12% of

534 compounds were detected from EDs deployed in groundwater (Fig. 4d) with  
535 sulfamethoxazole as the unique compound recovered from groundwater and not detected in  
536 stormwater runoff (Fig. 5). It was previously found that sulfamethoxazole is mobile, only  
537 slightly degradable and therefore easily transported to groundwater (Banzhaf et al., 2012).  
538 Thus, the occurrence of this compound in groundwater might be due to an ancient aquifer  
539 contamination without any link with SIS impact. More than 85% of pharmaceutical  
540 compounds were detected in stormwater runoff for the five SISs, including a mean  
541 percentage of 47% that were only detected in stormwater runoff (Fig. 4d). Seven  
542 pharmaceutical compounds were only found in stormwater runoff: atenolol metformin,  
543 morphine paracetamol, telmisartan valsartan and venlafaxine. Our results suggest that these  
544 compounds were not significantly transferred from surface to groundwater in the studied  
545 SISs.

546

547 In addition, the mean percentage of pharmaceutical compounds uniquely shared by  
548 stormwater runoff and SIS-impacted groundwater was quite low  $9 \pm 7\%$  (similar to the mean  
549 percentage uniquely shared by stormwater runoff and SIS-non-impacted groundwater, Fig.  
550 4d) and was due in part to irbesartan and tramadol which were two compounds only detected  
551 in 2 of the 10 analyses performed on EDs deployed in SIS-impacted groundwater (Fig. 5). As  
552 observed for pesticides, our results did not indicate a significant contamination of the aquifer  
553 by pharmaceutical compounds occurring in urban stormwater runoff. It is also worth noting  
554 that around 25% of pharmaceutical compounds were detected in the three water types for the  
555 five SISs (Fig. 4d) including adenosine, adenine, caffeine, carbamazepine, lamotrigine, and  
556 theobromine (Fig. 5). The large distribution of these compounds in both stormwater runoff  
557 and groundwater might have been due to (1) multiple sources of contaminants for aquifers  
558 and urban areas and/or (2) persistence of these compounds in the environment.

559

560 Overall, the results of the present study indicated a low influence of SIS on the contamination  
561 of groundwater by pesticides and pharmaceutical compounds contained in stormwater runoff.  
562 Nevertheless, these conclusions must be taken with caution because the present study was  
563 based on one campaign performed during a classical autumnal rainy period. More  
564 experiments are clearly needed to consider the influence of rainfall characteristics (intensities,  
565 duration) or/and the season on the potential transfer of contaminants through SIS. A  
566 quantification (or semi-quantification) of contaminant concentrations is also of major  
567 importance to evaluate processes occurring in SISs influencing the dynamics of  
568 contaminants.

569

#### 570 **4. Conclusion**

571 This study showed the performance of novel ED passive samplers used in combination with  
572 high resolution mass spectrometry analysis and suspect screening processing workflow to  
573 detect groundwater contamination. Our results highlighted the relevance of our strategy to  
574 characterize the occurrence of pesticides and pharmaceuticals in groundwater in a simple  
575 way. The new design of the passive samplers enables deployment in well bore holes,  
576 allowing a more accurate assessment of groundwater contamination than spot sampling.  
577 Passive samplers allowed the detection of contaminants usually found at very low  
578 concentration in water as compounds were accumulated on the extraction disk. As a result,  
579 our strategy allowed the analysis of a large number of contaminants: a wide list of suspects  
580 was obtained as the suspect screening approach has the ability to prioritize also the less well-  
581 known compounds. 101 suspects were detected in the five SIS, including 40 confirmed  
582 compounds. Overall, pesticides were mainly found in groundwater unlike pharmaceuticals

583 which were more detected in runoff waters. Therefore, the presence of pesticides in  
584 groundwater cannot be explained exclusively by the infiltration of the runoff water. Several  
585 pesticides, like atrazine, have probably reached and contaminated groundwater for many  
586 years. In the case of pharmaceuticals, our results suggest that they were brought by runoff  
587 water. However, pharmaceuticals found in runoff waters were not always found in SIS-  
588 impacted groundwater. In addition, when comparing the frequency of detection, SIS-  
589 impacted groundwater was not significantly more contaminated than non-impacted zones.  
590 This suggests a lower transfer from the infiltration basin to the groundwater. To better  
591 understand the mechanisms involved in the migration of contaminants through the soil, a  
592 supplementary field exposure with a semi-quantitative approach will be undertaken. In  
593 addition, this would allow the approach to be validated and proposed for groundwater  
594 monitoring applications.

595

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603

## 604 **References**

605 Ahkola, H., Tuominen, S., Karlsson, S., Perkola, N., Huttula, T., Saraperä, S., Artimo, A., Korpiharju,  
606 T., Äystö, L., Fjäder, P., Assmuth, T., Rosendahl, K., Nysten, T., 2017. Presence of active

607 pharmaceutical ingredients in the continuum of surface and ground water used in drinking  
608 water production. *Environ. Sci. Pollut. Res.* 24, 26778–26791.

609 Alvarez, D.A., Petty, J.D., Huckins, J.N., Jones-Lepp, T.L., Getting, D.T., Goddard, J.P., Manahan,  
610 S.E., 2004. Development of a passive, in situ, integrative sampler for hydrophilic organic  
611 contaminants in aquatic environments. *Environ. Toxicol. Chem.* 23, 1640.

612 Banzhaf, S., Krein, A., Scheytt, T., 2012. Using selected pharmaceutical compounds as indicators for  
613 surface water and groundwater interaction in the hyporheic zone of a low permeability  
614 riverbank: selected pharmaceuticals as indicators in a low permeability riverbank. *Hydrol.*  
615 *Process.* n/a-n/a.

616 Berho, C., Togola, A., Coureau, C., Ghestem, J.-P., Amalric, L., 2013. Applicability of polar organic  
617 compound integrative samplers for monitoring pesticides in groundwater. *Environ. Sci.*  
618 *Pollut. Res.* 20, 5220–5228.

619 Böhlke, J.-K., 2002. Groundwater recharge and agricultural contamination. *Hydrogeol. J.* 10, 153–  
620 179.

621 Bollmann, A.F., Seitz, W., Prasse, C., Lucke, T., Schulz, W., Ternes, T., 2016. Occurrence and fate of  
622 amisulpride, sulphiride, and lamotrigine in municipal wastewater treatment plants with  
623 biological treatment and ozonation. *J. Hazard. Mater.* 320, 204–215.

624 Bollmann, U.E., Vollertsen, J., Carmeliet, J., Bester, K., 2014. Dynamics of biocide emissions from  
625 buildings in a suburban stormwater catchment – Concentrations, mass loads and emission  
626 processes. *Water Res.* 56, 66–76.

627 Bunn, A., Korpela, M., n.d. An introduction to dplR 16.

628 Centre d'expertise en analyse environnementale du Québec (2012). Sampling Guide for  
629 Environmental Analysis: Booklet 3 – Sampling Groundwater, 54 p., 1 appendix.  
630 [http://www.ceaeq.gouv.qc.ca/documents/publications/echantillonnage/eaux\\_soutC3\\_ang.pdf](http://www.ceaeq.gouv.qc.ca/documents/publications/echantillonnage/eaux_soutC3_ang.pdf)

631 Causanilles, A., Kinyua, J., Ruttkies, C., van Nuijs, A.L.N., Emke, E., Covaci, A., de Voogt, P., 2017.  
632 Qualitative screening for new psychoactive substances in wastewater collected during a city  
633 festival using liquid chromatography coupled to high-resolution mass spectrometry.  
634 *Chemosphere* 184, 1186–1193.

635 Charriau, A., Lissalde, S., Poulier, G., Mazzella, N., Buzier, R., Guibaud, G., 2016. Overview of the  
636 Chemcatcher® for the passive sampling of various pollutants in aquatic environments Part A:  
637 Principles, calibration, preparation and analysis of the sampler. *Talanta* 148, 556–571.

638 Danielopol, D.L., Gibert, J., Griebler, C., Gunatilaka, A., Hahn, H.J., Messana, G., Notenboom, J.,  
639 Sket, B., 2004. Incorporating ecological perspectives in European groundwater management  
640 policy. *Environ. Conserv.* 31, 185–189.

641 Duong, H.T., Kadokami, K., Chau, H.T.C., Nguyen, T.Q., Nguyen, T.T., Kong, L., 2015.  
642 Groundwater screening for 940 organic micro-pollutants in Hanoi and Ho Chi Minh City,  
643 Vietnam. *Environ. Sci. Pollut. Res.* 22, 19835–19847.

644 Fletcher, T.D., Shuster, W., Hunt, W.F., Ashley, R., Butler, D., Arthur, S., Trowsdale, S., Barraud, S.,  
645 Semadeni-Davies, A., Bertrand-Krajewski, J.-L., Mikkelsen, P.S., Rivard, G., Uhl, M.,  
646 Dagenais, D., Viklander, M., 2015. SUDS, LID, BMPs, WSUD and more – The evolution  
647 and application of terminology surrounding urban drainage. *Urban Water J.* 12, 525–542.

648 Foulquier, A., Malard, F., Mermillod-Blondin, F., Datry, T., Simon, L., Montuelle, B., Gibert, J.,  
649 2010. Vertical change in dissolved organic carbon and oxygen at the water table region of an  
650 aquifer recharged with stormwater: biological uptake or mixing? *Biogeochemistry* 99, 31–47.

651 Gago-Ferrero, P., Krettek, A., Fischer, S., Wiberg, K., Ahrens, L., 2018. Suspect Screening and  
652 Regulatory Databases: A Powerful Combination To Identify Emerging Micropollutants.  
653 *Environ. Sci. Technol.* 52, 6881–6894.

654 Gasperi, J., Sebastian, C., Ruban, V., Delamain, M., Percot, S., Wiest, L., Mirande, C., Caupos, E.,  
655 Demare, D., Kessoo, M.D.K., Saad, M., Schwartz, J.J., Dubois, P., Fratta, C., Wolff, H.,  
656 Moilleron, R., Chebbo, G., Cren, C., Millet, M., Barraud, S., Gromaire, M.C., 2014.  
657 Micropollutants in urban stormwater: occurrence, concentrations, and atmospheric  
658 contributions for a wide range of contaminants in three French catchments. *Environ. Sci.*  
659 *Pollut. Res.* 21, 5267–5281.

660 Guibal, R., Lissalde, S., Charriau, A., Poulier, G., Mazzella, N., Guibaud, G., 2015. Coupling passive  
661 sampling and time of flight mass spectrometry for a better estimation of polar pesticide

662 freshwater contamination: Simultaneous target quantification and screening analysis. *J.*  
663 *Chromatogr. A* 1387, 75–85.

664 Hug, C., Ulrich, N., Schulze, T., Brack, W., Krauss, M., 2014. Identification of novel micropollutants  
665 in wastewater by a combination of suspect and nontarget screening. *Environ. Pollut.* 184, 25–  
666 32.

667 Jansson, C., Kreuger, J., 2010. Multiresidue analysis of 95 pesticides at low nanogram/liter levels in  
668 surface waters using online preconcentration and high performance liquid  
669 chromatography/tandem mass spectrometry. *J. AOAC Int.* 93, 1732–1747.

670 Kaserzon, S.L., Heffernan, A.L., Thompson, K., Mueller, J.F., Gomez Ramos, M.J., 2017. Rapid  
671 screening and identification of chemical hazards in surface and drinking water using high  
672 resolution mass spectrometry and a case-control filter. *Chemosphere* 182, 656–664.

673 Köck-Schulmeyer, M., Ginebreda, A., Postigo, C., Garrido, T., Fraile, J., López de Alda, M., Barceló,  
674 D., 2014. Four-year advanced monitoring program of polar pesticides in groundwater of  
675 Catalonia (NE-Spain). *Sci. Total Environ.* 470–471, 1087–1098.

676 Kurwadkar, S., 2017. Groundwater Pollution and Vulnerability Assessment. *Water Environ. Res.* 89,  
677 1561–1577.

678 Lapworth, D.J., Baran, N., Stuart, M.E., Ward, R.S., 2012. Emerging organic contaminants in  
679 groundwater: A review of sources, fate and occurrence. *Environ. Pollut.* 163, 287–303.

680 Launay, M.A., Dittmer, U., Steinmetz, H., 2016. Organic micropollutants discharged by combined  
681 sewer overflows – Characterisation of pollutant sources and stormwater-related processes.  
682 *Water Res.* 104, 82–92.

683 Leendert, V., Van Langenhove, H., Demeestere, K., 2015. Trends in liquid chromatography coupled  
684 to high-resolution mass spectrometry for multi-residue analysis of organic micropollutants in  
685 aquatic environments. *TrAC Trends Anal. Chem.* 67, 192–208.

686 Lindqvist, N., Tuhkanen, T., Kronberg, L., 2005. Occurrence of acidic pharmaceuticals in raw and  
687 treated sewages and in receiving waters. *Water Res.* 39, 2219–2228.

688 Lissalde, S., Charriau, A., Poulier, G., Mazzella, N., Buzier, R., Guibaud, G., 2016. Overview of the  
689 Chemcatcher® for the passive sampling of various pollutants in aquatic environments Part B:  
690 Field handling and environmental applications for the monitoring of pollutants and their  
691 biological effects. *Talanta* 148, 572–582.

692 Lissalde, S., Mazzella, N., Fauvelle, V., Delmas, F., Mazellier, P., Legube, B., 2011. Liquid  
693 chromatography coupled with tandem mass spectrometry method for thirty-three pesticides in  
694 natural water and comparison of performance between classical solid phase extraction and  
695 passive sampling approaches. *J. Chromatogr. A* 1218, 1492–1502.

696 Loos, R., Locoro, G., Comero, S., Contini, S., Schwesig, D., Werres, F., Balsaa, P., Gans, O., Weiss,  
697 S., Blaha, L., Bolchi, M., Gawlik, B.M., 2010. Pan-European survey on the occurrence of  
698 selected polar organic persistent pollutants in ground water. *Water Res.* 44, 4115–4126.

699 Lopez, B., Ollivier, P., Togola, A., Baran, N., Ghestem, J.-P., 2015. Screening of French groundwater  
700 for regulated and emerging contaminants. *Sci. Total Environ.* 518–519, 562–573.

701 Mali, N., Cerar, S., Koroša, A., Auersperger, P., 2017. Passive sampling as a tool for identifying  
702 micro-organic compounds in groundwater. *Sci. Total Environ.* 593–594, 722–734.

703 Manamsa, K., Crane, E., Stuart, M., Talbot, J., Lapworth, D., Hart, A., 2016. A national-scale  
704 assessment of micro-organic contaminants in groundwater of England and Wales. *Sci. Total*  
705 *Environ.* 568, 712–726.

706 Marmonier, P., Maazouzi, C., Foulquier, A., Navel, S., François, C., Hervant, F., Mermillod-Blondin,  
707 F., Vieney, A., Barraud, S., Togola, A., Piscart, C., 2013. The use of crustaceans as sentinel  
708 organisms to evaluate groundwater ecological quality. *Ecol. Eng.* 57, 118–132.

709 Mason, Y., Ammann, A.A., Ulrich, A., Sigg, L., 1999. Behavior of Heavy Metals, Nutrients, and  
710 Major Components during Roof Runoff Infiltration. *Environ. Sci. Technol.* 33, 1588–1597.

711 Mills, G.A., Gravell, A., Vrana, B., Harman, C., Budzinski, H., Mazzella, N., Ocelka, T., 2014.  
712 Measurement of environmental pollutants using passive sampling devices – an updated  
713 commentary on the current state of the art. *Env. Sci Process. Impacts* 16, 369–373.

714 Moschet, C., Vermeirssen, E.L.M., Singer, H., Stamm, C., Hollender, J., 2015. Evaluation of in-situ  
715 calibration of Chemcatcher passive samplers for 322 micropollutants in agricultural and urban  
716 affected rivers. *Water Res.* 71, 306–317.

- 717 Petrie, B., Gravell, A., Mills, G.A., Youdan, J., Barden, R., Kasprzyk-Hordern, B., 2016a. In Situ  
718 Calibration of a New Chemcatcher Configuration for the Determination of Polar Organic  
719 Micropollutants in Wastewater Effluent. *Environ. Sci. Technol.* 50, 9469–9478.
- 720 Petrie, B., Youdan, J., Barden, R., Kasprzyk-Hordern, B., 2016b. Multi-residue analysis of 90  
721 emerging contaminants in liquid and solid environmental matrices by ultra-high-performance  
722 liquid chromatography tandem mass spectrometry. *J. Chromatogr. A* 1431, 64–78.
- 723 Pitarch, E., Cervera, M.I., Portolés, T., Ibáñez, M., Barreda, M., Renau-Pruñonosa, A., Morell, I.,  
724 López, F., Albarrán, F., Hernández, F., 2016. Comprehensive monitoring of organic micro-  
725 pollutants in surface and groundwater in the surrounding of a solid-waste treatment plant of  
726 Castellón, Spain. *Sci. Total Environ.* 548–549, 211–220.
- 727 Pochodylo, A.L., Helbling, D.E., 2017. Emerging investigators series: prioritization of suspect hits in  
728 a sensitive suspect screening workflow for comprehensive micropollutant characterization in  
729 environmental samples. *Environ. Sci. Water Res. Technol.* 3, 54–65.
- 730 Postigo, C., Barceló, D., 2015. Synthetic organic compounds and their transformation products in  
731 groundwater: Occurrence, fate and mitigation. *Sci. Total Environ.* 503–504, 32–47.
- 732 Reh, R., Licha, T., Geyer, T., Nödl, K., Sauter, M., 2013. Occurrence and spatial distribution of  
733 organic micro-pollutants in a complex hydrogeological karst system during low flow and high  
734 flow periods, results of a two-year study. *Sci. Total Environ.* 443, 438–445.
- 735 Schymanski, E.L., Jeon, J., Gulde, R., Fenner, K., Ruff, M., Singer, H.P., Hollender, J., 2014a.  
736 Identifying Small Molecules via High Resolution Mass Spectrometry: Communicating  
737 Confidence. *Environ. Sci. Technol.* 48, 2097–2098.
- 738 Schymanski, E.L., Singer, H.P., Longrée, P., Loos, M., Ruff, M., Stravs, M.A., Ripollés Vidal, C.,  
739 Hollender, J., 2014b. Strategies to Characterize Polar Organic Contamination in Wastewater:  
740 Exploring the Capability of High Resolution Mass Spectrometry. *Environ. Sci. Technol.* 48,  
741 1811–1818.
- 742 Sébastien, C., Becouze-Lareure, C., Lipeme Kouyi, G., Barraud, S., 2015. Event-based quantification  
743 of emerging pollutant removal for an open stormwater retention basin – Loads, efficiency and  
744 importance of uncertainties. *Water Res.* 72, 239–250.
- 745 Segura, P.A., MacLeod, S.L., Lemoine, P., Sauvé, S., Gagnon, C., 2011. Quantification of  
746 carbamazepine and atrazine and screening of suspect organic contaminants in surface and  
747 drinking waters. *Chemosphere* 84, 1085–1094.
- 748 Shaw, M., Mueller, J.F., 2009. Time Integrative Passive Sampling: How Well Do Chemcatchers  
749 Integrate Fluctuating Pollutant Concentrations? *Environ. Sci. Technol.* 43, 1443–1448.
- 750 Sjerps, R.M.A., Vughs, D., van Leerdam, J.A., ter Laak, T.L., van Wezel, A.P., 2016. Data-driven  
751 prioritization of chemicals for various water types using suspect screening LC-HRMS. *Water*  
752 *Res.* 93, 254–264.
- 753 Sorensen, J.P.R., Lapworth, D.J., Nkhuwa, D.C.W., Stuart, M.E., Gooddy, D.C., Bell, R.A., Chirwa,  
754 M., Kabika, J., Liemisa, M., Chibesa, M., Pedley, S., 2015. Emerging contaminants in urban  
755 groundwater sources in Africa. *Water Res.* 72, 51–63.
- 756 Soulier, C., Coureau, C., Togola, A., 2016. Environmental forensics in groundwater coupling passive  
757 sampling and high resolution mass spectrometry for screening. *Sci. Total Environ.* 563–564,  
758 845–854.
- 759 Stephens, B.S., Kapernick, A., Eaglesham, G., Mueller, J., 2005. Aquatic Passive Sampling of  
760 Herbicides on Naked Particle Loaded Membranes: Accelerated Measurement and Empirical  
761 Estimation of Kinetic Parameters. *Environ. Sci. Technol.* 39, 8891–8897.
- 762 Stephens, B.S., Kapernick, A.P., Eaglesham, G., Mueller, J.F., 2009. Event monitoring of herbicides  
763 with naked and membrane-covered Empore disk integrative passive sampling devices. *Mar.*  
764 *Pollut. Bull.* 58, 1116–1122.
- 765 Stuart, M., Lapworth, D., Crane, E., Hart, A., 2012. Review of risk from potential emerging  
766 contaminants in UK groundwater. *Sci. Total Environ.* 416, 1–21.
- 767 Stuart, M.E., Lapworth, D.J., Thomas, J., Edwards, L., 2014. Fingerprinting groundwater pollution in  
768 catchments with contrasting contaminant sources using microorganic compounds. *Sci. Total*  
769 *Environ.* 468–469, 564–577.



770 Van Metre, P.C., Alvarez, D.A., Mahler, B.J., Nowell, L., Sandstrom, M., Moran, P., 2017. Complex  
771 mixtures of Pesticides in Midwest U.S. streams indicated by POCIS time-integrating  
772 samplers. *Environ. Pollut.* 220, 431–440.

773 Vermeirssen, E.L.M., Bramaz, N., Hollender, J., Singer, H., Escher, B.I., 2009. Passive sampling  
774 combined with ecotoxicological and chemical analysis of pharmaceuticals and biocides –  
775 evaluation of three Chemcatcher™ configurations. *Water Res.* 43, 903–914.

776 Vermeirssen, E.L.M., Dietschweiler, C., Escher, B.I., van der Voet, J., Hollender, J., 2013. Uptake  
777 and release kinetics of 22 polar organic chemicals in the Chemcatcher passive sampler. *Anal.*  
778 *Bioanal. Chem.* 405, 5225–5236.

779 Voisin, J., Cournoyer, B., Vienney, A., Mermillod-Blondin, F., 2018. Aquifer recharge with  
780 stormwater runoff in urban areas: Influence of vadose zone thickness on nutrient and bacterial  
781 transfers from the surface of infiltration basins to groundwater. *Sci. Total Environ.* 637–638,  
782 1496–1507.

783 Vulliet, E., Cren-Olivé, C., 2011. Screening of pharmaceuticals and hormones at the regional scale, in  
784 surface and groundwaters intended to human consumption. *Environ. Pollut.* 159, 2929–2934.

785 Vulliet, E., Tournier, M., Vauchez, A., Wiest, L., Baudot, R., Lafay, F., Kiss, A., Cren-Olivé, C.,  
786 2014. Survey regarding the occurrence of selected organic micropollutants in the  
787 groundwaters of overseas departments. *Environ. Sci. Pollut. Res.* 21, 7512–7521.

788 Winiarski, T., Bedell, J.-P., Delolme, C., Perrodin, Y., 2006. The impact of stormwater on a soil  
789 profile in an infiltration basin. *Hydrogeol. J.* 14, 1244–1251.

790