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

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15

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17 **Abstract**

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

41

42 (Highlights)

- 43 • A novel Empore™ disk-based passive sampler for groundwater monitoring
- 44 • Novel passive sampler used to monitor waters from infiltration systems
- 45 • Passive sampler joined with LC-HRMS for groundwater and stormwater runoff
46 screening
- 47 • A rapid and comprehensive analysis based on a suspect screening workflow
- 48 • Qualitative screening of polar pesticides and pharmaceuticals in groundwaters

49

50 **Keywords: stormwater runoff, stormwater infiltration basins, passive sampling, high**
51 **resolution mass spectrometry, polar pharmaceuticals and pesticides, suspect screening**

52

53 1. Introduction

54 Groundwater and associated aquatic systems are used extensively for the supply of potable
55 water and for agricultural and industrial uses. Urbanisation and a growing global population
56 have resulted in over-exploitation of this resource, particularly for drinking water supplies
57 (Danielopol et al., 2004). Although groundwater is a vital and strategic resource, such aquatic
58 systems are facing a decrease in their quality due to increased anthropogenic activities. Over
59 the last decade, a wide range of contaminants have been detected in various groundwater
60 sources (Lapworth et al., 2012; Stuart et al., 2012; Vulliet et al., 2014; Postigo and Barceló,
61 2015; Kurwadkar, 2017; Mali et al., 2017). Some of the pharmaceutical and pesticide
62 compounds typically found can be present at concentrations of up to hundreds of ng L⁻¹. Some
63 of their transformation products and metabolites were found from sub-ng L⁻¹ to tens of µg L⁻¹.
64 Atrazine, carbamazepine, desethyl atrazine, DEET (*N,N*-diethyl-meta-toluamide) and

65 sulfamethoxazole were among the most frequently detected compounds in groundwater
66 (Vulliet and Cren-Olivé, 2011; Stuart et al., 2014; Lopez et al., 2015).

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

82 A number of analytical methods have been developed for the measurement of polar organic
83 contaminants in water, in particular high performance liquid chromatography (HPLC) coupled
84 with a triple quadrupole mass spectrometer (Q-q-Q) (Jansson and Kreuger, 2010; Lissalde et
85 al., 2011; Petrie et al., 2016b). However, this operational mode has some limitations as, since
86 it is a targeted analysis, only a pre-defined/determined list of compounds can be analysed and
87 reference standards are needed. To circumvent these limitations, high resolution mass
88 spectrometry (HRMS) allows the detection of a large number of compounds without reference
89 standards or pre-selection and enables comprehensive screening of pollutants to be facilitated

90 (Leendert et al., 2015). Two major approaches for post measurement processing exist: non-
91 target screening (with no prior information), and suspect screening (with suspected substances
92 based on prior information) (Schymanski et al., 2014b). HRMS coupled with a suspect
93 screening approach is a useful tool as it allows a more comprehensive analysis than with target
94 screening whilst being less time consuming than non-target screening. When analysing
95 complex samples, suspect screening together with an adapted workflow is a good balance
96 between target and non-target screening. Workflow is particularly important as it allows to
97 narrow the positive findings by prioritizing compounds following specific thresholds while
98 saving time and effort. Several suspect screening workflows are proposed in the literature. All
99 are filtering strategies based on parameters such as exact mass, isotope pattern, signal-to-noise
100 (S/N) ratio, retention time, peak shape and blank removal (Segura et al., 2011; Hug et al., 2014;
101 Sjerps et al., 2016; Causanilles et al., 2017; Gago-Ferrero et al., 2018). They rely on
102 comparison with commercial (Kaserzon et al., 2017; Pochodylo and Helbling, 2017) or in-
103 house (Causanilles et al., 2017; Segura et al., 2011) databases. Replacement or adjustment of
104 parts of HPLC-HRMS system might lead to changes in chromatography or mass measurement.
105 Even minor, these changes could lead to non-accurate results when applying the suspect
106 screening workflow. Therefore, it is absolutely necessary to develop a workflow well adapted
107 to the used analytical instrument, as well as the environmental matrix analysed.

108 Another challenge concerning the measurement of organic contaminants in groundwater is that
109 they generally occur at low and variable concentrations. In most studies, spot (bottle or grab)
110 sampling is the chosen method used for monitoring purposes (Duong et al., 2015; Lopez et al.,
111 2015; Manamsa et al., 2016; Pitarch et al., 2016; Sorensen et al., 2015). However, this approach
112 only provides a snapshot of contamination at a given time and, therefore, may not be truly
113 representative of the appertaining environmental conditions over time. The use of passive
114 sampling devices such as the polar organic chemical integrative sampler (POCIS) (Alvarez et

115 al., 2004; Van Metre et al., 2017), Chemcatcher® (Charriau et al., 2016; Lissalde et al., 2016;
116 Petrie et al., 2016a) or the Empore™ disk (ED)-based sampler (Stephens et al., 2005; Shaw and
117 Mueller, 2009; Stephens et al., 2009; Vermeirssen et al., 2013) are potentially able to overcome
118 some of these limitations and to provide a more representative assessment of groundwater
119 contamination. To the best of our knowledge, only two studies have been reported on the
120 combination of passive sampling with HRMS for the assessment of contaminants in
121 groundwater (Soulier et al., 2016) and surface water (Guibal et al., 2015). Both were based on
122 the use of POCIS. This is the first time that an ED passive sampler is combined with suspect
123 screening for assessment of groundwater contamination. This article also describes for the first
124 time a novel type of rig which enabled the deployment in well bore holes.

125 The aims of the present study were: (i) to develop a novel analytical strategy that combines ED
126 passive samplers with HRMS analysis for suspect screening of emerging pollutants in
127 groundwater; (ii) to apply this strategy in the field to study the occurrence of pesticides and
128 pharmaceuticals and to make assumptions about the potential transfer of compounds from
129 surface to groundwater. To achieve this, a field study was conducted at five SISs during a storm
130 weather event. The potential impact of infiltration practices on groundwater contamination was
131 measured by comparing occurrence of pesticides and pharmaceuticals in stormwater runoff,
132 SIS-non-impacted and SIS-impacted groundwater.

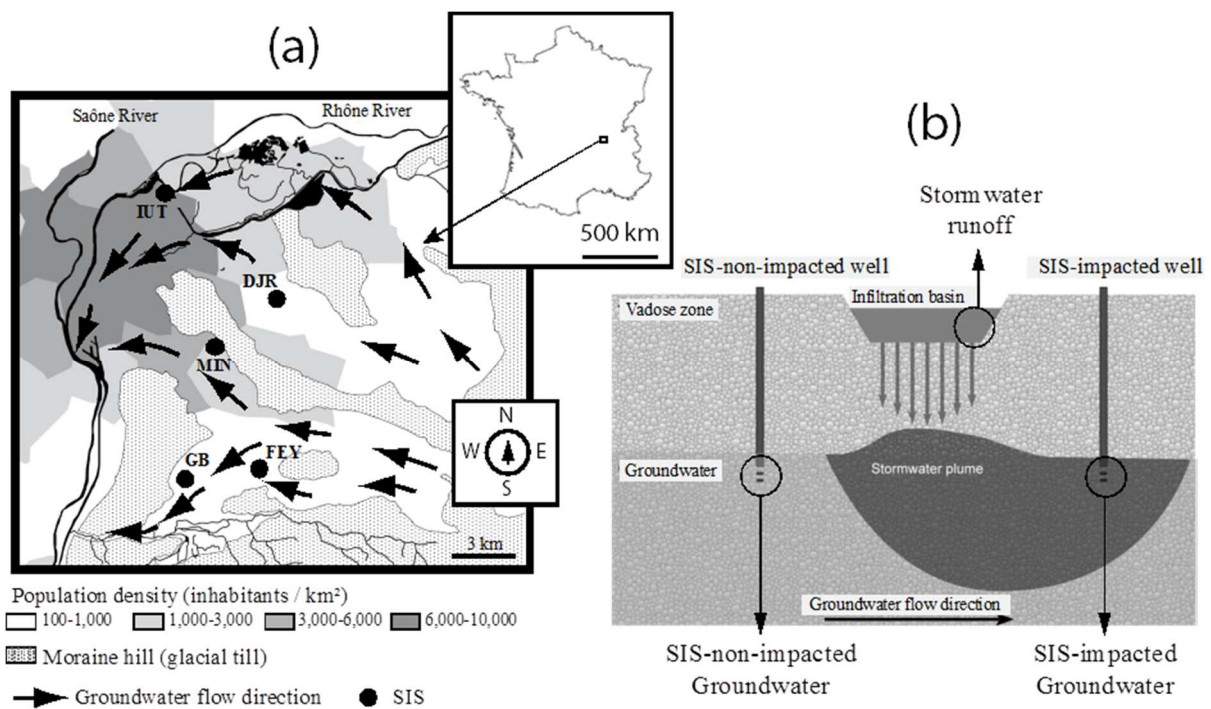
133

134 **2. Material and Methods**

135 **2.1. Field site description**

136 Field trials were undertaken at five SIS located in the eastern metropolitan area of Lyon, France
137 (Fig. 1) (further details of the SIS are given in (Marmonier et al., 2013; Voisin et al., 2018).
138 Unsaturated zone thickness, well depth, infiltration surface, catchment area and surroundings

139 areas are given in Table S1. The five SIS (Django Reinhardt (DJR), Chemin de Feyzin (FEY),
 140 Grange Blanche (GB), Campus of the University Lyon 1 (IUT) and Minerve (MIN)) collected
 141 stormwater runoff from commercial, residential and/or industrial areas. Each site had a plastic
 142 tank placed at the surface of the SIS for collecting runoff and two wells (boreholes) to enable
 143 groundwater monitoring. One well was located in an upstream zone not impacted by the
 144 stormwater runoff plume (SIS-non-impacted well) and the other well located in the
 145 downstream aquifer zone impacted by stormwater runoff (SIS-impacted well) (Fig. 1). The
 146 wells were lined with either polyvinyl chloride or methacrylate tubes (with a minimum internal
 147 diameter of 5.5 cm) perforated at their lower end (0.5 m) to establish an efficient hydraulic
 148 connection with the aquifer. Previous work has shown that at these five sites, the bulk water
 149 properties (conductivity, dissolved oxygen and temperature) found in the wells did not differ
 150 from that of the groundwater in the aquifer (Foulquier et al., 2010; Voisin et al., 2018).



151
 152 **Fig. 1.** Stormwater infiltration systems (SIS) in the Lyon conurbation investigated in this work;
 153 (a) geographical locations of the five SIS, and (b) position of the sampling points in each SIS.
 154 DJR = Django-Reinhardt, FEY = Feyzin, GB = Grange Blanche, IUT= Campus of the

155 University Lyon 1, MIN = Minerve. (Figure modified from Foulquier et al., 2009 and Voisin
156 et al., 2018).

157

158 **2.2. Chemicals and reagents**

159 Adenine, adenosine, atenolol, atrazine, atrazine-desethyl, atrazine-desethyl-desisopropyl,
160 boscalid, bromacil, caffeine, carbamazepine, carbendazim, cotinine, DEET, 2,6-
161 dichlorobenzamide, diclofenac, diuron, fluopyram, hexazinone, imidacloprid, lamotrigine,
162 lidocaine, metformin, metolachlor, morphine, nicotinamide, nicotine, paracetamol, prochloraz,
163 propiconazole, propyzamide, prosulfocarb, simazine, sulfamethoxazole, theobromine,
164 tramadol and venlafaxine were purchased from Sigma-Aldrich (Saint-Quentin Fallavier,
165 France). Diflufenican and isoproturon were purchased from Riedel de Haen (Hanover,
166 Germany). Irbesartan, telmisartan and valsartan were purchased from Tokyo Chemical
167 Industry (Tokyo, Japan). Ethidimuron was purchased from Dr Ehrenstorfer (Augsburg,
168 Germany). The purity of all chemicals was > 96%. Methanol (MeOH) (LC-MS grade) was
169 from BioSolve (Dieuse, France). Acetone, ammonium formate and formic acid were purchased
170 from Sigma-Aldrich. Milli-Q water (Millipore, Saint-Quentin-en-Yvelines, France) was used
171 for all procedures. Individual stock solutions (1 mg mL⁻¹) were prepared in methanol (MeOH)
172 or water depending on their specific solubilities. These stock solutions were then diluted or
173 mixed to obtain the various working solutions.

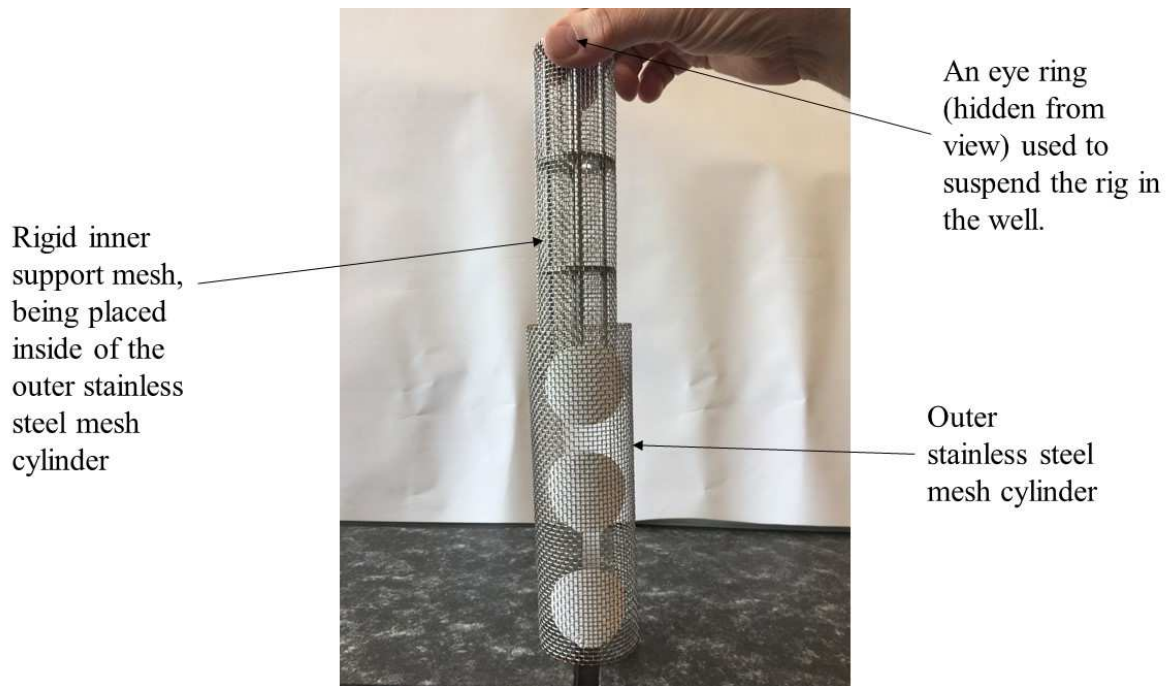
174

175 **2.3. Passive sampler preparation, deployment and extraction**

176 SDB-RPS and SDB-XC Empore™ cross-linked co-polymeric resin EDs (47 mm diameter, 12
177 µm particle size, 0.5 mm thick (3M, Neuss, Germany)) are poly(styrenedivinylbenzene)

178 (modified with sulfonic acid groups for SDB-RPS) used as reversed phase sorbent. Both are
179 100% co-polymeric particles that are spherical and porous. The SDB-RPS exhibits secondary
180 cationic exchange due to sulfonic acid groups unlike the SDB-XC, which does not have a pH
181 limitation. These sorbents are known to be able to retain hydrophobic and semi-polar analytes.
182 These disks were, therefore, well suited to sequester the wide range of emerging pollutants that
183 were likely to be found in the field trial sites. It should be noted, however, that the SDB disks
184 will only sequester compounds that have an affinity for the sorbent and are able to bind to the
185 material. It will not be efficient for the uptake of ionic compounds, such as acidic drugs;
186 including diclofenac, ibuprofen and naproxen that are widely used as non-steroidal anti-
187 inflammatory drugs (Lindqvist et al., 2005). Such disks can be pre-cleaned prior to use and
188 extracted after deployment easily using a simple funnel extraction system. They were
189 conditioned by soaking in MeOH overnight then in water (5 min) prior to placing them on the
190 deployment rig (Fig 2 and S1a). The deployment rig comprised of two custom made stainless
191 steel components (AT Engineering, Tadley, UK). An inner mesh (0.25 × 0.25 cm²) cylindrical
192 cage (19 cm high, 4.5 cm diameter, Fig. 2) with four circular strengthening rods/supports and
193 ‘eye’ ring to enable the device to be suspended at the required depth in the well using a rope
194 line. A similar size outer mesh that was capable of being formed into a cylinder was used to
195 secure the ED passive samplers (Fig. S1a). Four SDB-RPS and four SDB-XC EDs were
196 carefully and evenly placed on the outer mesh support (Fig. S1a). The EDs were held in place
197 by placing the inner mesh inside of the outer mesh and securing it using four stainless steel
198 cable ties. Using this sized mesh allowed a good exchange of the surrounding water in the well
199 with each of the ED. The deployment rigs (~ 4.7 cm overall external diameter) were designed
200 to fit comfortably down the well bore holes (~ 5.5 cm diameter) (Fig. S1b). After assembly,
201 each rig was fully submerged in Milli-Q water (2 L sealable glass jar) and stored at 4°C prior
202 to deployment. Jars were transported to the deployment sites in cool boxes. A total of fifteen

203 deployment rigs were used: five SIS, with three sampling points per SIS (tanks collecting
204 stormwater runoff entering the basin, and SIS-non-impacted and SIS-impacted wells). Rigs
205 were deployed for ten days between 8th - 18th of December, 2017. The rigs were kept fully
206 submerged in the tanks and at various depths below the aquifer in the wells (see Table S1). The
207 deployment period coincided with several successive rainfall events (Fig. S2) so it was hoped
208 that the EDs would sequester different types of pollutants associated with these stochastic
209 events. Water conductance and temperature (LTC Levelogger[®] Junior, Solinst, Canada),
210 dissolved oxygen (HOBO[®] U26, Onset, USA) and pH was measured during the trial. pH of the
211 various water samples was between 7.2 and 8.1 during the deployment period of the rigs.



212
213 **Fig. 2.** Deployment rig showing the inner and outer stainless steel mesh components. In this
214 example, supporting three Empore[™] disks.

215 After the deployment period, the rigs were taken back to the laboratory in cool boxes. The rig
216 was disassembled and the EDs removed using tweezers. The acetone followed by MeOH
217 extraction step is known to be a powerful solvent combination and give high extraction
218 efficiencies of semi-polar and polar analytes sequestered on SDB Empore[™] disks

219 (Vermeirssen et al., 2009, 2013). Consequently, the EDs were stored in acetone (10 mL) at
220 4°C. For processing, the vials containing the EDs were allowed to reach room temperature and
221 rolled in a tube rotator (10 min). Subsequently, the acetone was transferred to a new vial.
222 MeOH (10 mL) was added to the ED and the vial was rolled for another 10 min. The acetone
223 and MeOH fractions of each of the four SDB-XC or SDB-RPS disks per support were pooled
224 (80 mL) together in order to subsequently make a more concentrated extract. The combined
225 extracts were reduced to dryness under a gentle stream of nitrogen and stored at -20°C. Prior
226 to analysis, extracts were reconstituted (500 µL) in water/MeOH (90/10, v/v).

227

228 **2.4. Instrumental analysis**

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

237

238 Separations were carried out using an Acclaim RSLC C₁₈ column (2.1 x 100 mm, 2.2 µm
239 particles, Thermo Fischer Scientific) maintained at 30 °C; the injection volume was 5 µL. The
240 mobile phases consisted of: (A) water/MeOH (90/10, v/v); and (B) MeOH; with 5 mM
241 ammonium formate and 0.01% formic acid in both phases for both positive and negative

242 ionisation modes. The binary elution gradient started with 1% of (B) at a flow rate of 0.2 mL
243 min⁻¹ for 1 min, gradually increasing to 39% (B) for the next 2 min then increasing to 99.9%
244 (B) at 0.4 mL min⁻¹ for the following 11 min. The last condition was kept constant for 2 min
245 (flow rate 0.48 mL min⁻¹), then the initial conditions (1% B-99% A) were restored within 0.1
246 min (flow rate decreased to 0.2 mL min⁻¹) to re-equilibrate the column prior to the next
247 injection.

248

249 The Q-ToF system was equipped with an electrospray ionization interface (ESI) operating in
250 positive or negative ionization modes with the following settings: capillary voltage of 3,600 V,
251 end plate offset of 500 V, nebulizer pressure of 3 bar (N₂), drying gas of 9 L min⁻¹ (N₂), and
252 drying temperature of 200°C. The analysis was performed in full scan over the mass range of
253 80-1000 Da, with a scan rate of 1 Hz. The analysis was carried out in profile mode with the
254 following transfer parameters: funnel 1 RF of 200 Vpp, multipole RF of 50 Vpp, quadrupole
255 energy of 5 eV, collision energy of 7 eV, stepping basic and a pre-pulse storage of 5 ms. The
256 instrument resolution was estimated at 20,738 (FWHM) at $m/z = 376.0381$. A solution of
257 sodium formate and acetate (10 mM) to form clusters was used for external calibration at the
258 beginning of each run. The ions selected for recalibrating the mass axis were the protonated
259 reference ions ($[M+H]^+$, 34 masses from 90.9766 to 948.8727) with high precision calibration
260 (HPC) mode at a search range $\pm 0.05 m/z$. Accepted standard deviations were below 0.5 ppm.

261

262 **2.5. Liquid chromatography-Q-ToF data acquisition**

263 MS/MS experiments were conducted using three different data acquisition modes: MS,
264 broadband collision induced dissociation mode (bbCID, data independent analysis) and auto-

265 MS/MS mode (data dependent analysis) with a cycle time of 3 s and an acquisition frequency
266 of 1 Hz in order to record 1 spectra s^{-1} . Unspiked and spiked extracts (with reference
267 compounds at $500 \mu\text{g L}^{-1}$) were injected using the auto-MS/MS mode.

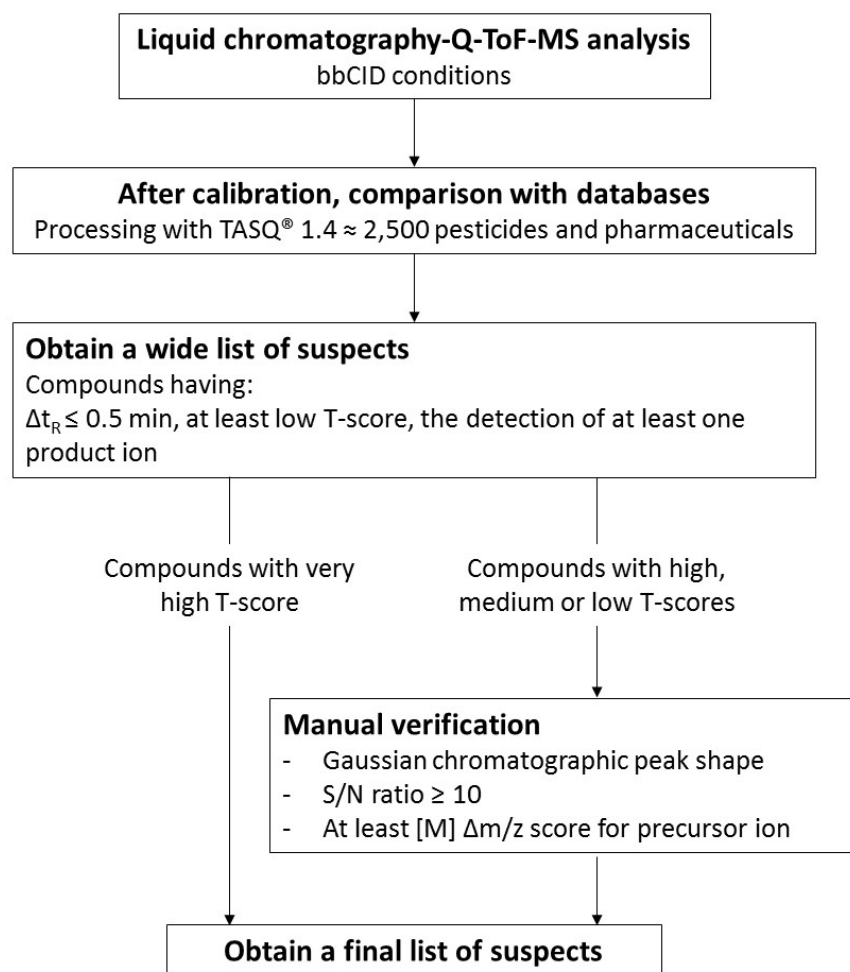
268 For quality assurance / quality control (QA/QC), several laboratory control samples were used.
269 Mass accuracy of the detector was monitored at the beginning of each run and recalibrated if
270 mass error exceeded 0.5 ppm. A quality control was injected every 12 analyses to check
271 retention times and sensitivity during data acquisition. This was a mix of $10 \mu\text{L}$ of each extract
272 and spiked at $500 \mu\text{g L}^{-1}$ with a standard solution of eight compounds: atrazine, atrazine-
273 desethyl-desisopropyl, boscalid, carbendazim, diclofenac, imidacloprid, prochloraz and
274 sulfamethoxazole. These compounds were also used to correct the database retention times.
275 Background signals were identified by analysis of blanks (solvent blank and procedural blank).
276 Solvent blanks were also injected to monitor column carryover.

277

278 **2.6. Filtering strategy**

279 Filtering of information was undertaken by comparing experimental sample data with
280 theoretical data for each compound. All precursor and product ions were evaluated using three
281 criteria (i) retention time (Δt_R), (ii) m/z ($\Delta m/z$) and (iii) isotope pattern (expressed as mSigma)
282 (Table S2). Deviations between experimental and theoretical data were scored high [H],
283 medium [M] or low [L] according to tolerance thresholds set for each of the three criteria.
284 Additionally, the detection of at least one product ion for each precursor ion was mandatory.
285 T-scores correspond to the combination of the scores for each of the three criteria for both
286 precursor and product ions; the detailed calculation of these values is detailed in Table S2.
287 Compounds had to meet three criteria to appear in the wide list of suspects: a retention time
288 deviation within the tolerance threshold of ± 0.5 min, a low T-score and at least one product

289 ion detected (Fig. 3). Then, the final list of suspects was built as follows: compounds having a
290 very high T-score were definitively considered as suspects without further verification; for
291 compounds having high, medium or low T-scores, manual verification of chromatographic
292 peak shapes, $\Delta m/z$ and S/N ratios was carried out in order to reduce false positives. Manual
293 verification of such parameters remains necessary even when comparing with a database (Hug
294 et al., 2014; Pochodylo and Helbling, 2017; Segura et al., 2011). Suspects exhibiting a
295 chromatographic peak without Gaussian peak shape or having a S/N ratio below 10 were
296 excluded. Furthermore, those having a precursor ion with [L] $\Delta m/z$ score were excluded (Fig.
297 3). The mSigma parameter was not taken into account at this stage, as a poor peak intensity
298 could lead to a wrong mSigma calculation, even with a true positive because of possible
299 interferences. Therefore, compounds present at low concentration in the sample extract or
300 displaying a low sensitivity with the analysis method may be improperly excluded.



301

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

303

304 2.7. Evaluation of contamination in stormwater runoff and groundwater

305 Based on the list of contaminants detected in the three water types (stormwater runoff, SIS-

306 non-impacted and SIS-impacted groundwater) at the five SIS, we evaluated the mean number

307 of pesticide and pharmaceutical compounds found. The 40 confirmed compounds exhibit a S/N

308 ratio high enough to enable the comparison of the three water types. The range of pesticide and

309 pharmaceutical compounds were compared among the three water types using a mixed model

310 with SIS as the random factor and water types as the fixed factor to take into account the

311 statistical dependence of waters collected at the same SIS. When mixed models gave significant

312 results for water type differences, *post hoc* Tukey's honest significance difference tests were

313 performed to determine whether significant pairwise differences occurred among water types.
314 For the two variables (pesticide and pharmaceutical compounds), the normality and the
315 homoscedasticity of the residues were tested using the Shapiro-Wilk's test and the Bartlett's
316 test, respectively. As these assumptions were not met for pharmaceutical compounds, data were
317 log transformed before statistical analyses. Venn diagrams were also constructed for each site
318 to determine the percentages of pesticide and pharmaceutical compounds that were obtained
319 from the three water types. This type of analysis highlighted the percentages of compounds
320 that were found from one, two or the three water types. The percentages obtained from the five
321 SIS independently were averaged to obtain Venn diagrams illustrating the mean percentages
322 of pesticides and pharmaceutical compounds found in each water type and in several water
323 types. In addition, a more precise description of the compounds found allowed us to evaluate
324 which compounds were only found in one water type for the five sites. The percentages
325 obtained from the five SIS were averaged to obtain Venn diagrams for pesticide and
326 pharmaceutical compounds within the whole dataset. Statistical tests were performed using R
327 software (R Development Core Team 2008) (Bunn and Korpela, n.d.) ([https://www.R-](https://www.R-project.org/)
328 [project.org/](https://www.R-project.org/)) and Venn diagrams were constructed using Venny 2.1.0
329 (<http://bioinfogp.cnb.csic.es/tools/venny>).

330

331 **3. Results and discussion**

332 **3.1. Design and use of passive samplers**

333 Passive sampling devices have been used for many years to monitor pollutants (mainly low
334 molecular mass hydrocarbons and other volatile and semi-volatile non-polar chemicals) in
335 groundwater. There is a wide range of different devices available and these have been reviewed
336 (Centre d'expertise en analyse environnementale du Québec, 2012). Little work has been

337 undertaken to monitor polar pollutants e.g. pharmaceuticals and personal care products in this
338 medium using these devices. To our knowledge there are only three applications of the use of
339 passive samplers to monitor polar substances in groundwater (Berho et al., 2013; Soulier et al.,
340 2016; Ahkola et al., 2017).

341

342 We designed a simple sampler based on the Chemcatcher[®] principles, designed to fit
343 comfortably down the well bore holes, that used only a naked Empore[™] disk as the active
344 receiving phase (Figure 2, S1a, b). Such an approach has been used previously to sequester a
345 wide range of polar pollutants (Stephens et al., 2005; Shaw and Mueller, 2009; Stephens et al.,
346 2009; Vermeirssen et al., 2013) in coastal and surface waters. The attractiveness of this design
347 over the POCIS is that there is no polyethersulphone (PES) diffusion membrane overlying the
348 receiving phase. It has been reported that some of the more hydrophobic compounds (e.g. log
349 $K_{ow} > 4.25$) can be retained in the PES membrane and, thereby, do not reach the sorbent layer
350 and be detected in the subsequent analytical screening procedures (Soulier et al., 2016). Not
351 having a PES membrane also helps to increase the diffusional uptake of analytes and thereby
352 decrease the resultant analytical detection limits. This simple, low cost, yet robust, cage design
353 also permitted the deployment of up to nine (similar or different types of sorbent chemistries)
354 Empore[™] disks on one rig and also maintained an open structure to allow good lateral flow of
355 water whilst within the bore hole well.

356 No pharmaceuticals or polar pesticides, that were subsequently screened for, were detectable
357 in the pre-washed Empore[™] disks (fabrication blanks) prior to their use in the passive sampler
358 rigs. After the 10-day deployment all the disks were still retained in place by the secured outer
359 cage support. There was no visible biofouling of the surface of the Empore[™] disks in those
360 rigs deployed in bore hole wells. In addition, the use of a bound sorbent in the form of an

361 Empore™ disk, ensured that the active sampling area did not alter during the field deployments.
362 This can be a problem with the use of loose sorbent material, as is used in the POCIS and can
363 lead to variable results (Mills et al., 2014).

364

365 **3.2. Suspect screening and confirmation**

366 All the extracts from the passive sampling devices were analyzed by LC-Q-ToF. Using the
367 workflow described in the Material and Methods section, 101 suspected compounds were
368 finally selected. Compounds formula, theoretical exact masses, theoretical retention times,
369 detection rates in SIS-non-impacted and in SIS-impacted groundwater and in runoff water as
370 well as average T-scores and levels of confidence are details in Table S3. The workflow
371 proposed by Schymanski et al. (2014) divides the confidence of identification into 5 levels:
372 level 5 = exact mass, level 4 = unequivocal molecular formula, level 3 = tentative candidate,
373 level 2b = probable structure by diagnostic evidence, level 2a = probable structure by library
374 spectrum match and level 1 = confirmed structure by reference standard. In order to reach the
375 level 1 confidence, confirmation by injection of a reference standard for the measurement of
376 retention time, MS and MS/MS spectra was carried out. Among the final list of suspects,
377 compounds with high and very high T-score and considered to be relevant according to the
378 literature (Lopez et al., 2015; Marmonier et al., 2013) were selected for confirmation as well
379 as compounds that were available in our laboratory. In total, 43 compounds were selected in
380 positive ion mode. No compound was selected in negative ion mode as none was suspected
381 except a few already detected in positive ion mode (bromacil, diuron, propyzamide). Among
382 the 30 analysed samples, a set of six representative samples of all the compounds to be
383 confirmed (i.e. with the highest intensities) were selected for re-injection. Unspiked and spiked
384 samples (500 µg L⁻¹) were injected with the auto-MS/MS mode. Thus, 33 compounds were

385 fragmented and 10 were not fragmented probably due to low concentrations and/or co-elutions
386 with compounds more concentrated or more sensitive. For these 10 compounds, specific
387 selected mass by daughter scan mode method was created. Retention time and MS/MS spectra
388 of unspiked and spiked samples were compared. Furthermore, experimental product ions were
389 matched with the literature. A schematic workflow of the structure confirmation of identified
390 compounds is shown Fig. S3 together with an example of identification of metolachlor (Fig.
391 S4). The application of the suspect screening workflow is helpful in the search for contaminants
392 in groundwater. TASQ[®] 1.4 software provides a turnkey solution for the screening and allows
393 narrowing the search to a list of almost 2,500 pesticides and pharmaceuticals. However, the
394 quasi-systematic verification of some criteria such as chromatographic peak shape and S/N
395 ratio cannot be neglected. The manual verification of these criteria for each suspect is time
396 consuming, but the overall suspect screening workflow remains very helpful to have an
397 overview of the occurrence of contaminants in groundwater.

398

399 Finally, of the 43 compounds to be confirmed, 40 were effectively confirmed. Only three were
400 false positives: indomethacin, phenazone and simazine. Although 2-hydroxysimazine appeared
401 with a high average T-score in the list of suspects of 17 samples, it resulted a false positive as
402 the retention time differed from that of the reference standard ($\Delta t_R = 0.2$ min). Indomethacin
403 and phenazone showed insufficient matching with the reference standard MS/MS spectra
404 (Table S4).

405

406 **3.3. Water quality monitoring using passive samplers**

407 **3.3.1. Comparison of SDB-RPS and SDB-XC disks**

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

417

418 **3.3.2 Occurrence of contaminants in groundwater and runoff water**

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

423 **Table 1.** List of contaminants identified (Level 1) in SIS-non-impacted and SIS-impacted
424 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)
Pesticides					
Atrazine	C ₈ H ₁₄ ClN ₅	216.1010	8.85	80	80
Atrazine-desethyl	C ₆ H ₁₀ ClN ₅	188.0697	6.49	80	80
Bromacil	C ₉ H ₁₃ BrN ₂ O ₂	261.0233	7.83	50	80
Carbendazim + benomyl	C ₉ H ₉ N ₃ O ₂	192.0768	6.08	0	80
DEET	C ₁₂ H ₁₇ NO	192.1383	8.87	80	100
Dichlorobenzamide	C ₇ H ₅ Cl ₂ NO	189.9821	5.14	80	100
Diuron	C ₉ H ₁₀ Cl ₂ N ₂ O	233.0243	9.24	100	100
Ethidimuron	C ₇ H ₁₂ N ₄ O ₃ S ₂	265.0424	5.63	30	40
Fluopyram	C ₁₆ H ₁₁ ClF ₆ N ₂ O	397.0537	10.44	20	80
Hexazinone	C ₁₂ H ₂₀ N ₄ O ₂	253.1659	7.85	60	50
Imidacloprid	C ₉ H ₁₀ ClN ₅ O ₂	256.0596	5.53	20	50
Isoproturon	C ₁₂ H ₁₈ N ₂ O	207.1492	9.00	20	20
Metolachlor	C ₁₅ H ₂₂ ClNO ₂	284.1412	10.85	100	100
Propiconazole	C ₁₅ H ₁₇ Cl ₂ N ₃ O ₂	342.0771	11.49	10	0
Propyzamide	C ₁₂ H ₁₁ Cl ₂ NO	256.0290	10.28	20	40
Simazine	C ₇ H ₁₂ ClN ₅	202.0854	7.81	80	80
Pharmaceuticals					
Adenine	C ₅ H ₅ N ₅	136.0618	2.20	80	60
Adenosine	C ₁₀ H ₁₃ N ₅ O ₄	268.1040	3.72	100	80
Caffeine	C ₈ H ₁₀ N ₄ O ₂	195.0877	5.06	100	100
Carbamazepine	C ₁₅ H ₁₂ N ₂ O	237.1022	8.21	80	80
Cotinine	C ₁₀ H ₁₂ N ₂ O	177.1022	4.27	20	0
Diclofenac	C ₁₄ H ₁₁ Cl ₂ NO ₂	296.0240	11.00	10	0
Irbesartan	C ₂₅ H ₂₈ N ₆ O	429.2397	9.89	0	20
Lamotrigine	C ₉ H ₇ Cl ₂ N ₅	256.0151	5.99	50	100
Lidocaine	C ₁₄ H ₂₂ N ₂ O	235.1805	5.21	10	10
Nicotinamide	C ₆ H ₆ N ₂ O	123.0553	2.80	20	0

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

425

426 The majority of the pesticides found in groundwater had already been reported previously in
427 other European studies. Atrazine, desethyl atrazine, DEET, 2,6-dichlorobenzamide, diuron,
428 isoproturon, metolachlor, propiconazole, propyzamide and simazine were quantified by Lopez
429 et al. (2015) during two screening trials of 494 French groundwater sites. Hexazinone was
430 found by (Berho et al., 2013) during four trials at two French groundwater sites. Bromacil and
431 imidacloprid were previously detected in Spain (Pitarch et al., 2016) and a German study
432 reported the presence of carbendazim (Reh et al., 2013). In contrast, to the best of our
433 knowledge, there is no other study reporting the presence of ethidimuron and fluopyram in
434 European groundwaters. In the case of pharmaceuticals, caffeine, carbamazepine, cotinine,
435 diclofenac, sulfamethoxazole and tramadol were detected by Lopez et al., 2015 in French
436 groundwater. Lidocaine and nicotine have been reported to be present in European groundwater
437 (Lapworth et al., 2012), irbesartan was found by (Pitarch et al., 2016) in Spain and lamotrigine
438 and theobromine were detected in Germany (Bollmann et al., 2016; Reh et al., 2013). To our
439 knowledge, adenine, adenosine and nicotinamide have never been detected previously in
440 groundwater samples.

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

446 previously detected in Sweden rivers and streams (Jansson and Kreuger, 2010). DEET was
447 previously reported by (Moschet et al., 2015) during a large field study of urban affected rivers
448 in Sweden and bromacil was detected in river water in Spain (Pitarch et al., 2016). To the best
449 of our knowledge, no study has reported the presence of atrazine-desethyl-desisopropyl
450 (DEDIA) neither in runoff nor in surface water, but it has been found in groundwater (Lopez
451 et al., 2015). In addition, fluopyram has not been reported to be present in either groundwater,
452 runoff or surface water. Like pesticides, very few European studies have dealt with the
453 occurrence of pharmaceuticals in urban runoff. Carbamazepine and diclofenac were found in
454 stormwater by Launay et al., (2016) in a study undertaken in Germany. Atenolol, caffeine,
455 irbesartan, lamotrigine, lidocaine, metformin, paracetamol, telmisartan, tramadol, valsartan
456 and venlafaxine were found by (Moschet et al., 2015) in urban affected rivers in Sweden.
457 Cotinine, nicotine and morphine have been found in rivers of the United Kingdom (Petrie et
458 al., 2016a).

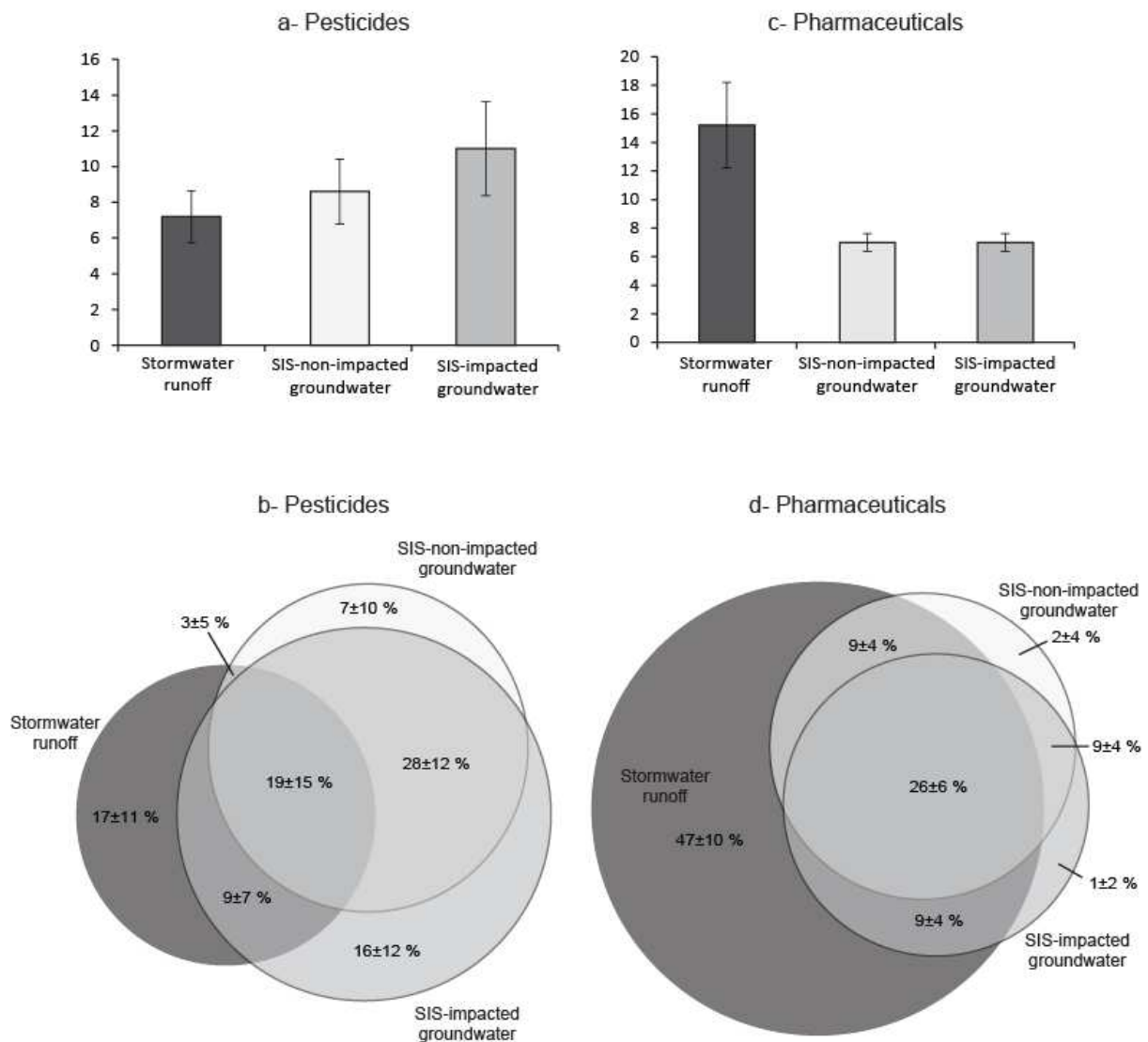
459

460 **3.3.3 Potential transfer of pesticides and pharmaceutical compounds from** 461 **surface to groundwater**

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

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

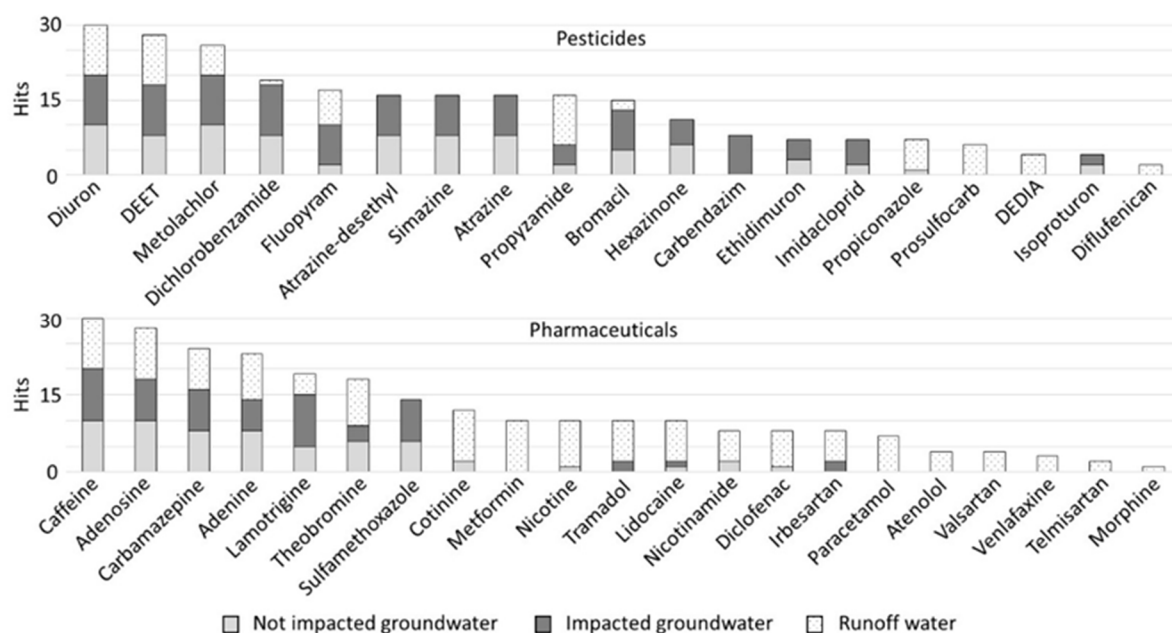
495 compound (carbendazim, Fig. 5). This observation suggested that the infiltration of stormwater
 496 runoff from surface to groundwater might have remobilized and transferred pesticides from the
 497 soil and the vadose zone, leading to the detection of these compounds in SIS-impacted
 498 groundwater whereas they were not present in stormwater runoff. These results were also found
 499 in a study of the effectiveness of a detention basin in removing emerging contaminants
 500 (Sébastien et al., 2015). It was found that carbendazim might be temporary stored at the bottom
 501 of the basin and thereafter remobilized and released.



502
 503 **Fig. 4.** Mean number of pesticide (a) and pharmaceutical compounds (c) detected in each water
 504 type (mean ± confidence interval %, n = 5 stormwater infiltration systems). Venn diagrams

505 showing the percentages of pesticide (b) and pharmaceutical compounds (d) found in each
 506 water type and common between two or three water types (percentages are means \pm confidence
 507 interval, n = 5 stormwater infiltration systems)

508



509

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

513

514 The number of pharmaceutical compounds detected in SISs was significantly different among
 515 water types (Fig. 4c, mixed model, water type effect, $F_{(2,8)} = 30.7$, $p < 0.001$) with a higher
 516 diversity of compounds in stormwater runoff than in groundwater (Tukey's *post hoc* tests, $p <$
 517 0.001 for comparison between stormwater runoff and other water types). Indeed, only 12% of
 518 compounds were detected from EDs deployed in groundwater (Fig. 4d) with sulfamethoxazole
 519 as the unique compound recovered from groundwater and not detected in stormwater runoff

520 (Fig. 5). It was previously found that sulfamethoxazole is mobile, only slightly degradable and
521 therefore easily transported to groundwater (Banzhaf et al., 2012). Thus, the occurrence of this
522 compound in groundwater might be due to an ancient aquifer contamination without any link
523 with SIS impact. More than 85% of pharmaceutical compounds were detected in stormwater
524 runoff for the five SISs, including a mean percentage of 47% that were only detected in
525 stormwater runoff (Fig. 4d). Seven pharmaceutical compounds were only found in stormwater
526 runoff: atenolol metformin, morphine paracetamol, telmisartan valsartan and venlafaxine. Our
527 results suggest that these compounds were not significantly transferred from surface to
528 groundwater in the studied SISs.

529

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

542

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

551

552 **4. Conclusion**

553 This study showed the performance of novel ED passive samplers used in combination with
554 high resolution mass spectrometry analysis and suspect screening processing workflow to
555 detect groundwater contamination. Our results highlighted the relevance of our strategy to
556 characterize the occurrence of pesticides and pharmaceuticals in groundwater in a simple way.
557 The new design of the passive samplers enables deployment in well bore holes, allowing a
558 more accurate assessment of groundwater contamination than spot sampling. Passive samplers
559 allowed the detection of contaminants usually found at very low concentration in water as
560 compounds were accumulated on the extraction disk. As a result, our strategy allowed the
561 analysis of a large number of contaminants: a wide list of suspects was obtained as the suspect
562 screening approach has the ability to prioritize also the less well-known compounds. 101
563 suspects were detected in the five SIS, including 40 confirmed compounds. Overall, pesticides
564 were mainly found in groundwater unlike pharmaceuticals which were more detected in runoff
565 waters. Therefore, the presence of pesticides in groundwater cannot be explained exclusively
566 by the infiltration of the runoff water. Several pesticides, like atrazine, have probably reached

567 and contaminated groundwater for many years. In the case of pharmaceuticals, our results
568 suggest that they were brought by runoff water. However, pharmaceuticals found in runoff
569 waters were not always found in SIS-impacted groundwater. In addition, when comparing the
570 frequency of detection, SIS-impacted groundwater was not significantly more contaminated
571 than non-impacted zones. This suggests a lower transfer from the infiltration basin to the
572 groundwater. To better understand the mechanisms involved in the migration of contaminants
573 through the soil, a supplementary field exposure with a semi-quantitative approach will be
574 undertaken. In addition, this would allow the approach to be validated and proposed for
575 groundwater monitoring applications.

576

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584

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