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1 **Emerging polar pollutants in groundwater: potential impact of urban stormwater**
2 **infiltration practices**

3 Lucie Pinasseau^a, Laure Wiest^a, Laurence Volatier^b, Florian Mermillod-Blondin^b,
4 Emmanuelle Vulliet^a

5

6 ^a Univ Lyon, CNRS, Université Claude Bernard Lyon 1, Institut des Sciences Analytiques,
7 UMR 5280, 5 Rue de la Doua, F-69100, Villeurbanne, France

8 ^b Univ Lyon, Université Claude Bernard Lyon 1, CNRS, ENTPE, UMR5023 Laboratoire
9 d'Ecologie des Hydrosystèmes Naturels et Anthropisés (LEHNA), 6 Rue Raphaël Dubois, F-
10 69622, Villeurbanne, France

11

12 ***Corresponding author:** laure.wiest@isa-lyon.fr

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15 **Abstract**

16 The quality of groundwater (GW) resources is decreasing partly due to chemical
17 contaminations from a wide range of activities, such as industrial and agricultural enterprises
18 and changes in land-use. In urban areas, one potential major pathway of GW contamination is
19 associated with urban water management practices based on stormwater runoff infiltration
20 systems (SIS). Data on the performance of the upper layer of soil and the unsaturated zone of
21 infiltration basins to limit the contamination of GW by hydrophilic compounds are lacking.
22 With this aim, the impact of infiltration practices on GW contamination was assessed for 12
23 pesticides and 4 pharmaceuticals selected according to their ecotoxicological relevance and
24 their likelihood of being present in urban stormwater and GW. For this purpose, 3 campaigns
25 were conducted at 4 SIS during storm events. For each campaign, passive samplers based on
26 the use of Empore™ disk were deployed in GW wells upstream and downstream of SIS, as
27 well as in the stormwater runoff entering the infiltration basins. Upstream and downstream
28 GW contaminations were compared to evaluate the potential effect of SIS on GW
29 contamination and possible relationships with stormwater runoff composition were examined.
30 Our results showed two interesting opposite trends: (i) carbendazim, diuron, fluopyram,
31 imidacloprid and lamotrigine had concentrations significantly increasing in GW impacted by
32 infiltration, indicating a contribution of SIS to GW contamination, (ii) atrazine, simazine and
33 2 transformation products exhibited concentrations significantly decreasing with infiltration
34 due to a probable dilution of historic GW contaminants with infiltrated stormwater runoff.
35 The other 7 contaminants showed no general trend. This study demonstrates that passive
36 samplers deployed in GW wells enabled the capture of emerging polar pollutants present at
37 very low concentrations and allowed the assessment of infiltration practices on GW quality.
38 New data on GW and urban stormwater are provided for poorly studied hazardous
39 compounds.

40 **Capsule:** The fate of 16 polar and semi-polar pesticides and pharmaceuticals in groundwater
41 upstream and downstream of stormwater infiltration systems (SIS) was studied.

42 **Keywords:** groundwater; passive sampling; pesticides; pharmaceuticals; stormwater
43 infiltration systems; urban stormwater

44

45 **1. Introduction**

46 Groundwater (GW) is the greatest source of freshwater in the world and provides about 75%
47 of drinking water in the European Union (Danielopol et al., 2004; European Commission,
48 EC, 2006). Aquifers are also vital for industry, agriculture, and groundwater-dependent
49 aquatic ecosystems such as rivers and lakes. However, GW resources are threatened as they
50 are facing a reduction in their quantity and quality due to increased anthropogenic activities.
51 Over the past decade some organic pollutants (e.g. lifestyle and personal care products,
52 industrial chemicals, pesticides, pharmaceuticals and their transformation products (TPs))
53 have been detected in European GW from ng L^{-1} to several $\mu\text{g L}^{-1}$ (Jurado et al., 2012;
54 Lapworth et al., 2012; Loos et al., 2010; Lopez et al., 2015; Postigo and Barceló, 2015; Stuart
55 et al., 2012; Vulliet et al., 2014). From the several sources and pathways of GW
56 contamination (e.g., agricultural practices, industrial contamination of soils, etc), stormwater
57 infiltration practices remain poorly studied whereas they can constitute a potential major
58 pathway for GW contamination. Stormwater infiltration systems (SIS) are etc developed in
59 urban areas to mitigate the risk of flooding and offset reduced GW recharge due to road
60 surfacing. Detention/infiltration basins in urban areas receive stormwater runoff collected
61 from impervious surfaces (roads and car parks), which is then infiltrated through a porous
62 medium (i.e. soil and unsaturated zone) (Marsalek and Chocat, 2002; Mermillod-Blondin et
63 al., 2015; Voisin et al., 2018). However, urban stormwater runoff are often contaminated by

64 heavy metals, polycyclic aromatic hydrocarbons and polar emerging pollutants such as
65 pesticides and more specifically biocides from building materials, pharmaceuticals and
66 personal care products (Bollmann et al., 2014; Fairbairn et al., 2018, Gasperi et al., 2014,
67 2012; Launay et al., 2016, Müller et al., 2020, Pajjens et al., 2020, Spahr et al., 2020; Zgheib
68 et al., 2012). Pesticides come from the maintenance of urban green surfaces such as public
69 parks, gardens, children's play areas, roadside verges or riverside footpaths. Pharmaceuticals
70 are more rarely investigated in stormwater runoff but several studies reported stormwater
71 contamination by sewage pollutants in separate sewer systems (Sidhu et al., 2013; Zgheib et
72 al., 2012). Pharmaceuticals in stormwater can also originate from recreational water
73 discharges or outdoor human dejections. Consequently, SIS designed for rapid infiltration of
74 stormwater runoff increase the risks of aquifer contamination. Previous studies demonstrated
75 that the upper layer of soil and the unsaturated zone could act as efficient filters for
76 hydrophobic contaminants (Datry et al., 2004; Tedoldi et al., 2016; Winiarski et al., 2006),
77 with a minor risk of leaching (Nogaro et al., 2007). However, this retention efficiency of the
78 soil and unsaturated zone has not been proven for more hydrophilic compounds such as
79 pesticides and pharmaceuticals that may be present in stormwater runoff. Several studies
80 have already pointed out that SIS are probably responsible for GW contamination by
81 pesticides. By evaluating the influence of detention basins on GW quality, Fischer et al.
82 (2003) showed a higher frequency of atrazine, carbaryl, metolachlor and prometon in wells
83 impacted by detention basins than in wells located outside the influence of detention basins.
84 Marmonier et al. (2013) observed similar results for almost 12 pesticides by comparing GW
85 located in aquifer zones non impacted and aquifer zones impacted by urban stormwater
86 infiltration basins. Likewise, Hensen et al. (2018) measured the transfer of contaminants
87 through a SIS (basin) and showed that stormwater infiltration contaminated GW with 3
88 biocides applied as preservatives on facades and their TPs. However, it remains several

89 knowledge gaps concerning the assessment of GW contamination by emerging organic
90 contaminants associated with SIS. First, the occurrence and fate of some hazardous pollutants
91 such as certain less-studied polar pesticides, in addition to pharmaceuticals, remain poorly
92 studied. Second, the measurement of organic contaminants in GW is challenging as they
93 occur at low (ng L^{-1} to pg L^{-1}) and variable concentrations. To circumvent this problem,
94 passive sampling approaches have to be deployed to detect contaminants usually found at
95 very low concentrations. Passive sampling also gave a more accurate assessment of
96 groundwater contamination than conventional spot sampling (Brack et al., 2017, Jones et al.,
97 2015, Miège et al., 2015, Mills et al., 2014). Therefore, passive samplers such as Empore™
98 disk-based samplers appear as promising tools for the determination of contaminants in the
99 environment as they are easy to use for a wide range of applications (Page et al., 2014, Petrie
100 et al., 2016; Pinasseau et al., 2020; Shaw and Mueller, 2009; Vermeirssen et al., 2013; Vrana
101 et al., 2005). These disks can accumulate analytes on a receiving phase over several days or
102 weeks and the analyte pre-concentration allows for an overall increase of the analytical
103 sensitivity of the procedure. Moreover, changes in average contaminant concentrations over
104 the sampling period are taken into account. Therefore, these devices are very pertinent to
105 assess the occurrence of emerging polar pollutants in GW impacted by urban stormwater
106 infiltration practices that create pulses of stormwater runoff and solutes in GW during rainfall
107 events (Datry et al., 2003). Nevertheless, to the best of our knowledge, their deployment in
108 GW is still rare and only one study has reported their use for monitoring organic
109 contaminants in such kind of infiltration system (Page et al., 2014).

110 In this context, the present study aimed to assess the effects of urban stormwater runoff
111 infiltration on GW contamination by polar and semi-polar pesticides and pharmaceuticals
112 using Empore™ disk-based sampler. A list of 16 targeted contaminants was selected
113 according to several criteria: their environmental and ecotoxicological interest, their frequent

114 detection at our study sites based on previous studies (Marmonier et al., 2013; Pinasseau et
115 al., 2019, 2020) and their physico-chemical properties. Less-studied hazardous compounds
116 such as bromacil, fluopyram, imidacloprid and lamotrigine were also investigated to
117 supplement these works.

118 Three campaigns of 10 days were conducted at 4 SIS during storm events in winter. For each
119 SIS, the potential impact of infiltration practices on GW contamination was assessed by
120 comparing masses accumulated on passive samplers of the 16 pesticides and pharmaceuticals
121 in GW non impacted by urban stormwater runoff infiltration (aquifer zone located upstream
122 of SIS) and in GW impacted by urban stormwater runoff infiltration (aquifer zone located
123 downstream of SIS in the plume of infiltrated stormwater). Qualitative characterization of the
124 stormwater runoff entering the infiltration basins was also undertaken for the same 16
125 contaminants in order to evaluate the potential relationships between stormwater runoff
126 composition of pollutants and GW contamination by stormwater runoff infiltration.

127

128 **2. Material and Methods**

129 **2.1. Studied sites and experimental design**

130 The experiments were undertaken in 4 SIS located in the eastern metropolitan area of Lyon
131 (France) and monitored in the framework of the field observatory in urban hydrology
132 (OTHU) (further details of the SIS are given in Marmonier et al. (2013), Pinasseau et al.
133 (2019), Voisin et al. (2018). Unsaturated zone thickness, average infiltration time from basin
134 surface to GW, well depth, infiltration surface of the basins, catchment area, and surrounding
135 areas of each SIS are given in Table S1. The 4 SIS (Django Reinhardt (DJR), Chemin de
136 Feyzin (FEY), Grange Blanche (GB) and Campus of the University Lyon 1 (IUT)) collected
137 stormwater runoff from impervious urban areas (mainly roads, car parks and building surface

138 materials) although land use (agricultural, commercial, residential and/or industrial activities)
139 varied among areas surrounding sites. All infiltration basins receive exclusively stormwater
140 runoff. Domestic and industrial wastewaters are conveyed in separate sewer systems and do
141 not reach stormwater infiltration systems. A plastic tank was placed at the bottom of each
142 stormwater infiltration basin (dived in soil) for measurements of contaminants on stormwater
143 runoff entering the basin. Each SIS was equipped with two GW wells: a well located outside
144 the area of influence of the stormwater plume induced by infiltration (SIS-up) which was
145 used as a control well, and a well located in the immediate downstream vicinity of the
146 infiltration basin (SIS-dw) used as a recharge well because it intersected the stormwater
147 plume induced by the infiltration of stormwater runoff (Figs. 1 and S1). As performed for
148 microbial GW assessment using artificial substrates (Mermillod-Blondin et al., 2019; Voisin
149 et al., 2020), these wells were used to incubate passive samplers (see below) during 10 days
150 for contaminant assessment of GW by stormwater infiltration (Pinasseau et al., 2019). The
151 wells consisted in either polyvinyl chloride or methacrylate tubes (with a minimum internal
152 diameter of 5.5 cm) perforated at their lower end (0.5 m) to allow an efficient hydraulic
153 connection with the aquifer. Previous work has shown that at these 4 SIS, the bulk water
154 properties (conductivity, dissolved oxygen, and temperature) measured in the wells was
155 similar to that of the GW in the surrounding aquifer (Foulquier et al., 2010; Voisin et al.,
156 2018).

157

158 Three campaigns were undertaken over a period of ten days in the 4 studied SIS: between 8th
159 – 18th of December, 2017, between 26th of October – 5th of November, 2018 and between
160 14th – 24th of November, 2019. The three campaigns were performed in winter to obtain 3
161 replications of the experiment by limiting a potential seasonal effect on the results. During
162 these three seasons, the amounts of precipitation during the 10 days of passive sampler

163 incubation were 30.3 mm in December 2017, 60.9 mm in November 2018 and 66.1 mm in
164 November 2019. For each campaign, passive samplers were used to analyze target
165 contaminants in runoff drained into the basins (surface plastic tanks) and in GW beneath the
166 basins (SIS-up and SIS-dw wells). Passive samplers were based on polystyrene
167 divinylbenzene (SDB-XC) Empore™ disks (EDs) (47 mm diameter, 12 µm particle size, 0.5
168 mm thick) purchased from 3M (Neuss, Germany). Deployment rigs were designed with the
169 University of Portsmouth (Portsmouth, UK) to fit into GW well dimensions (see details in
170 Pinasseau et al. (2019)). Each rig held 9 individual EDs (only 4 individual EDs for the
171 campaign 2017) to obtain replicated analyses per rig (each ED being analyzed
172 independently). Details of EDs preparation before deployment in the field as well as passive
173 sampler adsorption kinetics are given in Pinasseau et al. (2020). A total of 12 ED rigs were
174 used (one rig per plastic tank and well) and deployed per campaign. As environmental
175 conditions (i.e. water turbidity, water temperature, flow rate) measured in the plastic tanks
176 differ from conditions found in GW, contaminant results from stormwater runoff ED rigs
177 were assessed for qualitative purposes only.

178 In addition, continuous measurements of dissolved oxygen concentration (HOBO® U26,
179 Onset, USA), specific conductance and temperature (LTC Levellogger® Junior, Solinst,
180 Canada) were monitored in GW during the field deployment periods (mean values for each
181 well, SIS and field campaign are reported on Table S2). Physico-chemical measurements
182 were also done on water samples collected in wells with a submerged pump (PP36 inox,
183 SDEC, Reignac sur-Indre, France) at 3 dates during each ED rig deployment period (day 0,
184 day 5 and day 10) to document pH values (portable pH-meter HQ20, HACH, Dusseldorf,
185 Germany), N-NO₃⁻, N-NH₄⁺ and P-PO₄³⁻ concentrations in GW (Table S2).

186

187 **2.2. Studied contaminants**

188 Compounds selected for the study were chosen according to their ecotoxicological relevance
189 and their presence in urban stormwater (biocides from building materials) and GW according
190 to literature (key compounds including key pharmaceuticals and pesticides TPs) (Gasperi et
191 al., 2014, 2012; Jurado et al., 2012; Lapworth et al., 2012; Launay et al., 2016; Loos et al.,
192 2010; Paijens et al., 2020; Postigo and Barceló, 2015; Stuart et al., 2012). Most of them were
193 also frequently detected at our study sites and are presumably indicators of the SIS
194 catchments pollution (Marmonier et al., 2013; Pinasseau et al., 2019, 2020). Their physico-
195 chemical properties (polar and semi-polar with probability of reaching GW) was also a
196 selection criterion. To supplement these works, little studied hazardous compounds such as
197 bromacil, fluopyram, imidacloprid and lamotrigine, for which there are still few or no GW
198 data in the literature, were also investigated (Table 1).

199

200 **2.3. Sampling and analysis**

201 After passive sampler deployment and collection, contaminant extraction from EDs were
202 performed according to Pinasseau et al. (2020). Briefly, EDs were extracted using 10 mL of
203 acetone/methanol (50/50; v/v). With this extraction protocol, more than 81% of the
204 compounds had a recovery between 70% and 120% (Pinasseau et al., 2020). Then, triplicate
205 extracts were pooled and evaporated to dryness. Finally, samples were reconstituted in 500
206 μ L of water/methanol (95/5; v/v) and diluted 30 times.

207 Analysis was performed using an Agilent Series 1200 HPLC system (Agilent Technologies,
208 Massy, France) (binary pump) coupled to a triple quadrupole mass spectrometer (MS) (5500
209 QTrap, AB Sciex, Les Ulis, France) equipped with an electrospray ion (ESI) source working
210 in positive ionization mode. The chromatographic separation was performed with a Poroshell
211 120 EC-C₁₈ column (2.1 \times 50 mm, 2.7 μ m particle size) (Agilent Technologies). The column

212 oven temperature was 30 °C, the injection volume was 20 µL and the flow rate was 500 µL
213 min⁻¹. Mobile phase (A) was water and mobile phase (B) was methanol with 0.1% formic
214 acid in both phases (see Pinasseau et al. (2020) for the gradient elution details). MS detection
215 was performed in the multiple reaction monitoring (MRM) mode (see Pinasseau et al.
216 (2020)). Method detection and quantification limits are reported in Table S3.

217

218 **2.4. Statistical analysis**

219 The influence of SIS on GW contamination was visualized using a principal component
220 analysis (PCA) performed with contents of the 16 contaminants measured after deployment
221 in 8 wells (1 SIS-up well and 1 SIS-dw well per SIS, 4 SIS) for the 3 campaigns (2017, 2018,
222 2019). This analysis allowed to compare samples by transforming pollutant contents to a new
223 set of variables, the principal components (PCs), which were uncorrelated, and which were
224 ordered so that the 2 first PCs retain most of the variation present in all of the original
225 variables. Scores of the samples (24 = 4 SIS * 2 wells * 3 dates) were displayed on a factorial
226 map for comparisons. The variables (pollutants) were represented on a correlation circle
227 indicating the contribution of each variable on PC1 and PC2. Thus, this analysis permitted to
228 determine group of contaminants presenting the same patterns of sample distribution and
229 which contaminants tended to differ between SIS-up and SIS-dw GW extracts. Following this
230 analysis, contents of specific contaminants were compared between SIS-up and SIS-dw wells
231 of each site using repeated-measures ANOVAs (RM-ANOVAs) with site as fixed factor and
232 recharge as repeated factor to take into account the non-independence of SIS-up and SIS-dw
233 wells in each site for each campaign (the 3 campaigns acted as replicates). The Mauchly's
234 sphericity test, the Shapiro-Wilk's test, and the Levene's test, were used to verify the
235 statistical assumptions of sphericity, normality, and homoscedasticity, respectively. When

236 these assumptions were not proved, the variables (contaminant content) were log (x+1)
237 transformed before RM-ANOVA tests. Statistical analyses were carried out using R version
238 3.2.3 software (R Development Core Team, 2015). Significance for statistical tests (RM-
239 ANOVA) was accepted for a first species risk set at $\alpha < 0.05$.

240

241 **3. Results and discussion**

242 **3.1. Stormwater runoff characterization**

243 After each campaign, the deployment rigs placed in the plastic tanks were retrieved and the
244 stormwater runoff extracts were analyzed qualitatively. For each site, results were displayed
245 in a Venn diagram showing the percentage of contaminants that were detected during one,
246 two or three campaigns (Fig. 2). At least, 12 out of the 16 selected contaminants were found
247 in the stormwater runoff extracts of each site by considering all campaigns. Carbendazim,
248 DEET, diclofenac and diuron were detected in all extracts and 50, 54, 62 and 71% of the
249 contaminants were recovered from passive samplers during the 3 campaigns for IUT, FEY,
250 GB and DJR, respectively. In addition, there were only few cases (4.3% in the dataset) where
251 a contaminant was only present in one of the 3 campaigns. This means that the contaminant
252 compositions of stormwater runoff entering each infiltration basin were comparable among
253 the 3 campaigns, suggesting no drastic change in contaminant sources from 2017 to 2019
254 during winter. Moreover, the contaminants detected in urban stormwater runoff of the 4 SIS
255 were classically observed in urban drainage systems (Fairbairn et al., 2018; Spahr et al.,
256 2020).

257

258 **3.2. Consequences of infiltration practices on groundwater contamination by**
259 **pesticides and pharmaceuticals**

260 For each campaign, contaminant masses accumulated on disks (Table S3) were used to
261 evaluate the impact of SIS on GW contamination by comparing results obtained from non-
262 impacted SIS-up well and SIS-dw well for each SIS. This influence of SIS on GW
263 contaminants was visualized using a PCA (Fig. 3). The PC1 and PC2 axes of the PCA
264 explained 57% of the variability contained in the data matrix, with 32% on the first axis (Fig.
265 3a). The correlation circle (Fig. 3b) indicated that groups of contaminants having the same
266 distributions among samples. For example, the three pesticides DEA, simazine and atrazine
267 presented the same distribution among samples with the highest concentrations obtained for
268 samples having a negative score on PC1 and a positive score on PC2 like the sample
269 performed in SIS-up well of Django-Reinhardt in 2017 (left bottom panel in Fig. 3c). To
270 evaluate the impact of stormwater runoff infiltration on GW quality, we observed that
271 extracts obtained from SIS-dw wells tended to have lower scores along axis PC2 than extracts
272 from SIS-up wells for the 4 sites and the 3 campaigns (Fig. 3c). This partitioning was
273 associated with two opposite trends when comparing extracts from SIS-up wells with extracts
274 from SIS-down wells: a decrease in the contents of atrazine, BAM, DEA and simazine and an
275 increase in the contents of carbendazim, diuron, fluopyram, imidacloprid and lamotrigine,
276 and sulfamethoxazole only for FEY site (Fig. 3b). For FEY site, SIS-dw GW extracts also
277 presented lower scores than SIS-up GW extracts along axis PC1, indicating an increase in
278 carbamazepine and hexazinone in SIS-dw GW for the 3 campaigns. For the other 3 sites, we
279 did not observe clear trends along PC1 axis, except for the campaign of 2017 in the SIS-up
280 GW of DJR site characterized by high contents of atrazine, DEA and simazine.

281

282 This PCA analysis allowed to classify the 16 contaminants into 3 main groups depending on
283 their distributions: contaminants with concentrations increasing with infiltration, suggesting a
284 contribution of the SIS on GW contamination (carbendazim, diuron, fluopyram, imidacloprid
285 and lamotrigine), contaminants with concentrations decreasing with infiltration, suggesting a
286 dilution of GW contamination by SIS (atrazine, BAM, DEA and simazine), and contaminants
287 which were apparently not influenced by infiltration in all sites or whose influence differed
288 among sites (bromacil, carbamazepine, DEET, diclofenac, hexazinone, metolachlor and
289 sulfamethoxazole).

290

291 **3.3. Contaminants with concentrations increasing with stormwater infiltration**

292 For imidacloprid, carbendazim, lamotrigine, diuron and fluopyram, concentrations measured
293 in SIS-dw GW were significantly higher than those measured in SIS-up GW (Fig. 4a, RM-
294 ANOVAs, “SIS-up GW *versus* SIS-dw GW” effet, $F_{(1,8)} > 19$, $p < 0.01$ for the 5
295 contaminants), indicating a contribution of SIS to GW pollution by these contaminants. This
296 conclusion was confirmed by the detection of these 5 compounds in runoff collected from the
297 4 SIS (for at least 2 or 3 dates), at the exception of imidacloprid which was not detected in
298 runoff from IUT site (Fig. 2). Diuron was quantified in 96% of GW extracts, with a
299 maximum concentration reaching 34.8 ng disk⁻¹ (Fig. 4a, Table S3). First used in 1951, it is
300 still authorized in some products for the protection of building materials, despite being
301 banned for agricultural uses since 2003 (Table 1). These diuron usages could explain its
302 occurrence in urban runoff (drainage of built areas) and its impact on GW quality because the
303 aquifer was less contaminated by agricultural practices occurring upstream in its catchment
304 area. Our results also confirmed previous observations reporting the presence of diuron in all
305 environmental compartments and in GW due to its wide spreading and persistence in the

306 environment (Cabeza et al., 2012; Hensen et al., 2018; Lapworth et al., 2015; Loos et al.,
307 2010; Reh et al., 2013). In comparison with diuron, imidacloprid, carbendazim, lamotrigine
308 and fluopyram exhibited very low concentrations or, in most cases, no detection at all in SIS-
309 up GW located outside the influence of stormwater infiltration. This observation suggests that
310 stormwater infiltration was almost exclusively responsible for the presence of these
311 contaminants in SIS-dw GW. These 4 contaminants are in use today (Table 1). Carbendazim,
312 found in 96% of GW extracts with a maximum concentration of 4.2 ng disk⁻¹ (Fig. 4a, Table
313 S3), has been banned for agricultural uses since 2009 but is still authorized in some products
314 for the protection of building materials. It has been already detected in European GW by
315 Hernández et al. (2008), Reemtsma et al. (2013) and Vulliet et al. (2014). Lamotrigine and
316 fluopyram, quantified in 79 and 67% of GW extracts with maximum concentrations of 11.3
317 and 1.4 ng disk⁻¹, respectively (Fig. 4a, Table S3), are the most recent contaminants among
318 the 16 investigated. They were used for the first time in the 2000s (Table 1). It could explain
319 the lack of study reporting the presence of fluopyram in GW and the presence in literature of
320 only one study reporting lamotrigine (Bollmann et al., 2016). Despite its introduction in
321 1990s, imidacloprid, an insecticide detected in 71% of GW extracts with a maximum
322 concentration of 5.6 ng disk⁻¹ (Fig. 4a, Table S3), has been poorly investigated in European
323 GW and, consequently, only one study in literature reported the occurrence of this compound
324 in GW (Hernández et al., 2008).

325

326 In the present study, imidacloprid presented singular results: its concentration was higher in
327 SIS-dw GW than in SIS-up GW of IUT site (see campaign 2017 on Fig. 4a) despite its
328 absence in stormwater runoff of IUT site (Fig. 2). This SIS-associated contamination of GW
329 with a compound which was not detected in stormwater runoff might have been due to the
330 leaching of this compound from soil and sediment particles on which it has been previously

331 trapped and accumulated during several years of infiltration basin operation. This adsorption-
332 desorption mechanism has been already observed with carbendazim which can be
333 temporarily trapped on soil and thereafter partly remobilized in water (Sébastien et al., 2015).
334 As described by Hensen et al. (2018), each stormwater infiltration event could have led to the
335 leaching of some contaminants absorbed in the soil and/or the unsaturated zone. However,
336 the role of the infiltration medium to trap hydrophilic compounds is still unclear, even if the
337 soil and the unsaturated zone have the potential to efficiently retain some hydrophobic
338 contaminants like hydrocarbons or heavy metals (Datry et al., 2004; Tedoldi et al., 2016;
339 Winiarski et al., 2006). Thus, more research is needed to confirm the hypothesis that
340 adsorption-desorption mechanisms could explain the GW enrichment in imidacloprid by SIS.

341

342 **3.4. Contaminants with concentrations decreasing with stormwater infiltration**

343 For DEA, simazine, BAM, and atrazine, concentrations observed in SIS-dw GW were
344 significantly lower than those observed in SIS-up GW (Fig. 4b, RM-ANOVAs, “SIS-up GW
345 *versus* SIS-dw GW” effet, $F_{(1,8)} > 8.5$, $p < 0.05$ for the 4 contaminants), indicating that
346 stormwater runoff infiltration reduced the concentrations of these 4 contaminants in GW.
347 Although these compounds were detected in stormwater runoff (Fig. 2), they were probably
348 present at lower concentrations in stormwater runoff than in SIS-up GW because infiltrated
349 stormwater probably reduced their concentrations in SIS-dw GW by dilution. Such
350 interpretation assumes that DEA, simazine, BAM, and atrazine were mainly found in GW
351 and this was probably the case. Indeed, DEA, simazine, BAM and atrazine were detected in
352 100, 96, 88 and 100% of GW extracts with maximum concentrations of 46.9, 29.3, 13.1 and
353 87.9 ng disk⁻¹, respectively (Fig. 4b, Table S3). In comparison, DEA, simazine, BAM and
354 atrazine were detected only in 58, 58, 41 and 66% of runoff extracts, respectively (Fig. 2).

355 This widespread occurrence of atrazine, BAM, DEA and simazine in GW have been largely
356 reported in literature (Lapworth et al., 2015). Atrazine and simazine have been banned since
357 2003 but, like DEA, they have already reached GW for many years (Bono-Blay et al., 2012;
358 Kuster et al., 2010; Lapworth et al., 2015; Loos et al., 2010; Lopez et al., 2015). BAM, a
359 common degradation product of dichlobenil (herbicide banned in 2009) and fluopicolide
360 (fungicide still authorized), has been also frequently detected in European GW (Lapworth et
361 al., 2015; Lopez et al., 2015; Postigo and Barceló, 2015). Although some of these
362 contaminants have been banned, the renewal time of aquifers, which includes the transfer
363 time in the unsaturated zone, may take years to decades and could therefore explain the
364 persistence of these contaminants in GW (Chen et al., 2019a; Gleeson et al., 2012; Gutierrez
365 and Baran, 2009; Swartjes and Van der Aa, 2019; Wang et al., 2016). Moreover, it has been
366 reported that pesticide degradation within GW aquifers was low (Baran et al., 2007). Under
367 these conditions, even if a nil or negligible part of the contamination was provided by soil
368 leaching (explaining the occurrence of atrazine or simazine in stormwater runoff), stormwater
369 runoff infiltration reduced the concentrations of these contaminants in GW by dilution of
370 contaminated GW (SIS-up GW) with less contaminated stormwater runoff.

371

372 **3.5. Contaminants not consistently influenced by stormwater infiltration**

373 No significant influence of stormwater runoff infiltration was observed on concentrations of
374 bromacil, carbamazepine, DEET, diclofenac, hexazinone, metolachlor and sulfamethoxazole
375 over the 4 SIS and 3 campaigns (Fig. 5, RM-ANOVAs, “SIS-up GW *versus* SIS-dw GW”
376 effect, $F_{(1,8)} < 2.1$, $p > 0.15$ for the 7 contaminants). As observed for atrazine or simazine, we
377 could expect a dilution effect in GW for bromacil and hexazinone because (1) these
378 compounds have been banned in 2001 and 2007 respectively (Table 1), (2) they were not

379 detected in stormwater runoff (Fig. 2) and (3) they were present in GW (63 and 83% of GW
380 extracts with maximum concentrations of 8.9 and 9.1 ng disk⁻¹ for bromacil and hexazinone,
381 respectively, Fig. 5, Table S3). However, the opposite results were observed on these
382 compounds in FEY and DJR sites with higher concentrations obtained in SIS-dw GW than in
383 SIS-up GW (Fig. 5). As these results cannot be exclusively explained by the compositions of
384 infiltrated stormwater runoff and SISs-up GW, it can be assumed that two mechanisms
385 (desorption and dilution) are involved in the fate of these contaminants in SIS: each
386 stormwater runoff infiltration event would both leach these compounds from the soil and
387 unsaturated zone, and dilute those already present in the GW in variable proportions
388 depending on SIS. The same mechanisms probably occurred for the 5 other contaminants
389 which did not exhibit consistent changes in concentration with stormwater infiltration.
390 Indeed, stormwater infiltration at FEY site significantly contributed to GW deterioration by
391 sulfamethoxazole and carbamazepine, while these same compounds appear to be diluted at
392 GB site (Fig. 5). In the same way, stormwater infiltration at FEY site tended to increase
393 sulfamethoxazole and carbamazepine concentrations in GW whereas no trend was observed
394 for the same site for diclofenac, DEET and metolachlor concentrations (Fig. 5).

395 The lack of clear stormwater infiltration effect on bromacil, carbamazepine, DEET,
396 diclofenac, hexazinone, metolachlor and sulfamethoxazole concentrations among sites could
397 be also due to the background contamination in the environment and GW that reduced our
398 ability to detect changes associated with SIS. Indeed, carbamazepine, an antiepileptic known
399 to be persistent and frequently detected in GW (Loos et al., 2010; Stuart et al., 2014; Vulliet
400 et al., 2014; Vulliet and Cren-Olivé, 2011), was detected in 100% of GW extracts with a
401 maximum concentration of 47.7 ng disk⁻¹ (Fig. 5, Table S3). Sulfamethoxazole and
402 diclofenac, pharmaceuticals used in human and veterinary medicine and commonly found in
403 European GW (Cabeza et al., 2012; Loos et al., 2010; Reh et al., 2013; Vulliet et al., 2014;

404 Vulliet and Cren-Olivé, 2011), were also quantified in 88 and 58% of GW extracts with
405 maximum concentrations of 4.2 and 0.8 ng disk⁻¹, respectively (Fig. 5, Table S3). DEET, a
406 domestic insect repellent widely used across the world (Lapworth et al., 2015; Loos et al.,
407 2010; Marques dos Santos et al., 2019; Sorensen et al., 2015) was also found in 100% of GW
408 extracts with a maximum concentration of 7.1 ng disk⁻¹ (Fig. 5, Table S3). Metolachlor,
409 detected in 100% of GW extracts with a maximum concentration of 16.6 ng disk⁻¹ (Fig. 5,
410 Table S3) is also ubiquitous in European GW under its both racemic mixture form (forbidden
411 in 2003) and S enantiomer form (Hildebrandt et al., 2008; Kuster et al., 2010; Loos et al.,
412 2010; Lopez et al., 2015).

413

414 To better understand the mechanisms involved in the dynamics of these 7 contaminants, we
415 searched for potential relationships between our contaminant results, the SIS design (Table
416 S1) and the targeted compounds chemical properties (Table 1). Neither the average transit
417 time of stormwater from the basin to GW nor the physico-chemical properties of compounds
418 (i.e. pKa, logD_{ow}, GUS index) can be directly related to the significance of SIS-dw GW
419 contamination, as previously concluded by Baran et al. (2007) and Manamsa et al. (2016).
420 For example, contamination of GW by infiltration practice (SIS-up GW versus SIS-dw GW)
421 was the highest for FEY site (Figs. 3, 4 and 5) whereas the unsaturated zone of this site would
422 be the most efficient to retain contaminants as the average transit time of stormwater from
423 surface to GW was more than 2-fold higher in this site (211.8 ± 90.5 h) than in other sites ($<$
424 86.0 ± 12.4 h, Table S1). The results mean that some additional parameters and mechanisms
425 are involved in the fate of contaminants in SIS during a stormwater runoff infiltration event:
426 soil composition and physico-chemical properties (Regnery et al., 2017), the presence of
427 preferential pathways and/or retention of compounds due to capillary tension (Wang et al.,
428 2016), and the contaminant degradation by microbial communities (Pitt et al., 1999).

429 Concerning soil composition, the high concentrations of organic matter (more than 10% of
430 organic carbon per soil dry mass, (Pigneret et al., 2016)) found in soil of infiltration basins
431 may play a key role on contaminant dynamics. Indeed, organic matter is likely to sorb neutral
432 or non-ionizable compounds, whereas ionizable ones, such as pharmaceuticals, can form
433 electrostatic interactions with clay minerals (Gutierrez and Baran, 2009; Kodešová et al.,
434 2015; Regnery et al., 2017; Valhondo et al., 2018). Moreover, sorption processes can be
435 complicated due to natural heterogeneity, competition for sorption sites and preferential
436 pathways through fractures (Baran et al., 2007; Chen et al., 2019b), and are most certainly
437 reversible (Greskowiak et al., 2017). Consequently, it can be hypothesized that the transport
438 of some contaminants to GW was delayed and/or progressive over several years and that each
439 stormwater runoff infiltration event produced the release of trapped contaminants (Baran et
440 al., 2007; Swartjes and Van der Aa, 2019).

441 It is worth noting that the choices of targeted contaminants together with the sampling
442 campaign periods and the period of GW quality assessment had major influences on our
443 results. Associated with seasons and meteorological conditions, dry periods followed by
444 intense rainfall events are known to have direct impacts on the number of contaminants and
445 their concentrations in stormwater runoff (Bollmann et al., 2014; Burkhardt et al., 2011;
446 Hensen et al., 2018; Pajjens et al., 2020). Indeed, urban pollutants such as herbicides are
447 more likely washed off from building materials and green areas after a long dry period
448 (Burkhardt et al., 2011; Spahr et al., 2020). For pharmaceuticals, it has been reported that
449 they are more transported by stormwater discharge overflow during high volume rainfall
450 events than during low volume rainfall events (Launay et al., 2016; Spahr et al., 2020).
451 Beside seasonal effects that have not been addressed in the present study, another limitation
452 of our work concerns the environmental variability that could have affect passive sampler
453 efficiency. Although the potential value of passive sampling has already been proven for

454 monitoring emerging pollutants in water (Brack et al., 2017, Jones et al., 2015, Miège et al.,
455 2015, Mills et al., 2014), the uptake mechanisms of polar compounds on EDs are still not
456 fully understood (Vrana et al., 2016). Environmental variabilities (flow rate, water
457 temperature, turbidity, etc) can affect uptake mechanisms and contribute to variability of
458 water concentration estimates when calibration data are applied (Lissalde et al., 2016).
459 Therefore, using ng disk⁻¹ values instead of ng L⁻¹ values helps to improve the reliability of
460 the results, as we did in this study. Working on three autumn/winter rainfall events enabled us
461 to obtain experimental replications under comparable climatic conditions but, in future
462 investigations, it would be necessary to undertake additional sampling campaigns during
463 spring/summer in order to evaluate how seasonal effects (climatic conditions, contaminant
464 composition of stormwater runoff) influence the role of SIS on GW quality.

465

466 **5. Conclusions**

467 This study was the first to assess the effects of urban stormwater runoff infiltration on GW
468 contamination by 16 polar and semi-polar pesticides and pharmaceuticals using Empore™
469 disk-based sampler. To our knowledge, it was the first time that such passive samplers were
470 deployed in GW wells to monitor the infiltration of emerging polar pollutants. This work
471 demonstrates that they enable the capture of contaminants at traces level efficiently.
472 Moreover, new data on GW are provided for recent and/or understudied hazardous
473 contaminants like bromacil, fluopyram, imidacloprid and lamotrigine.

474 Obtained results highlighted two interesting opposite trends depending on studied
475 contaminants: 5 contaminants (carbendazim, diuron, fluopyram, imidacloprid and
476 lamotrigine) had concentrations significantly increasing with stormwater runoff infiltration,
477 indicating a contribution of infiltration to groundwater contamination, and 4 contaminants

478 (atrazine, BAM, DEA and simazine) exhibited concentrations significantly decreasing with
479 infiltration due to a probable dilution with stormwater runoff of historic GW contaminants
480 such as atrazine. The fact that the remaining 7 contaminants showed no general trend with
481 site-dependent infiltration effect on their concentrations might be due to: (i) the differences
482 among SIS in historical contaminations of all environmental compartments (urban watershed,
483 soil, unsaturated zone and GW) and (ii) the differences among SIS in soil properties,
484 hydrological transport and microbial processes that would be responsible for the variability
485 observed in contaminant dynamics among SIS.

486 In further studies, it will be therefore necessary to quantify the processes occurring in the soil
487 and unsaturated zone (sorption and desorption processes, microbial degradation of
488 contaminants) of each SIS. Use of proxy for soil/sediment characteristics (organic matter
489 content, clay percentage), hydrogeological functioning (precise measurements of infiltration
490 rates in each infiltration basin) and microbial activity would help to decrypt the main
491 variables influencing contaminant dynamics during their transfer from infiltration basin to
492 GW. As discussed above, monitoring several rainfall events at different seasons would be
493 necessary to take into account the inter-event variability and the seasonal effects on
494 contaminant transfers. Finally, measurements performed during more than 10 years could be
495 also very promising to evaluate the long time-lag between the use of some contaminants,
496 their dynamics in environmental compartments and the resulting changes on GW quality.

497

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507

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