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1 **Identification and assessment of ecotoxicological hazards attributable to pollutants in**  
2 **urban wet weather discharges**

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11

12 Abstract

13 The phenomenon of urbanization leads to considerable pressure on urban/suburban aquatic ecosystems.  
14 Urban Wet Weather Discharges (UWWDs) during rainfall events are a major source of pollutants  
15 leached onto and into urban surfaces and sewers, which in turn affect aquatic ecosystems. The aim of  
16 this study is to assess the ecotoxicity of the different compounds identified in UWWDs and identify the  
17 hazard represented by each of them. To this end, hazard quotients (HQ) were calculated for each  
18 compound detected in UWWDs, based on their Predicted No Effect Concentration (PNEC) values and  
19 their maximum concentration (MEC<sub>max</sub>) found in the dissolved part of UWWDs. For the 207 compounds  
20 identified in UWWDs, sufficient data existed for 165 of them to calculate their PNEC. The ecotoxicity  
21 of these compounds is greatly variable. Pesticides represent a high proportion of the wide variety of  
22 hazardous compounds whose HQ were calculated (a total of 94 HQ), and they are among the most  
23 hazardous pollutants (HQ >1000) transported by stormwater. On the contrary, the hazard of Combined  
24 Sewer Overflows (CSO) is mainly linked to heavy metals and pharmaceutical compounds.  
25 Consequently, the monitoring of these pollutants is a priority in the future. Lastly, it is to bear in mind  
26 that the hazard level of certain pollutants could be underestimated, due to their adsorption on particles,  
27 leading their low presence in the dissolved phase of UWWDs. So, an in-depth study of these pollutants  
28 will be required to clarify their effects on aquatic organisms.

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32 Introduction

33 Urban Wet Weather Discharges (UWWDs) are complex and variable polluted matrices, notably  
34 due to the different types of catchments leached by the rain, and the variable flows for different events.<sup>1</sup>  
35 Many micropollutants have been detected in these effluents as a function of population density and  
36 anthropogenic activities. Among them, we can cite here: (i) European priority substances such as  
37 Polycyclic Aromatic Hydrocarbons (PAHs),<sup>2-5</sup> diethylexylphthalate,<sup>4,6</sup> 4-nonylphenol,<sup>4,6</sup> bisphenol A and  
38 alkylphenolethoxylate<sup>7</sup>, (ii) other micropollutants like heavy metals (copper, lead, zinc, etc.),  
39 polychlorobiphenyls (PCBs), pesticides, phthalates<sup>3,5,8,9,10</sup>, and (iii) pharmaceutical residues (PC) in the  
40 particular case of the Combined Sewer Overflows (CSO)<sup>11,12</sup>. These micropollutants have also already  
41 been detected in receiving river water having received these discharges.<sup>13,14</sup> Many of them are potentially  
42 hazardous for aquatic organisms. That is why UWWDs have toxic effects on aquatic species,<sup>15,16,17</sup> and  
43 can thus modify biological communities.<sup>15,18,19,20,21</sup> Treatment to diminish UWWD pollutants through  
44 abatement are nonexistent or very limited depending on municipal sewer systems, and raw UWWD are  
45 often release into (sub)urban aquatic ecosystems. It is therefore necessary to optimize their management.  
46 This optimization can concern: (i) a better monitoring of toxic pollutants and their effects, including  
47 continuous monitoring with biosensors;<sup>22,23</sup> (ii) a specific treatment of pollutants;<sup>24</sup> and (iii) the  
48 suppression or the substitution at source of the toxic products at the origin of these pollutants (in  
49 particular, certain detergents, disinfectants and pharmaceuticals) by less toxic but equally efficient  
50 products. For that, it is necessary to identify and prioritize the hazardous pollutants present in UWWDs.

51 To establish the list of the compounds most concerned by the ecotoxicological hazard  
52 represented by a specific urban effluent, many authors have proposed to formulate and apply a hazard  
53 quotient based on the ratio “Concentration of the selected pollutant in filtered polluted  
54 matrices”/“Predicted No Effect Concentration (PNEC) of the molecules selected”.<sup>25,26</sup> This quotient is  
55 used to distinguish the hazardousness of the different compounds and families of compounds found in  
56 UWWDs. Orias and Perrodin<sup>25</sup> proposed comparing the maximum Measured Effluent Concentrations  
57 (MECmax) measured in hospital effluents to their PNEC value, which is the method used in the current  
58 study. This method was also applied by many other authors for contaminated matrices such as rivers  
59 polluted by raw or treated municipal wastewaters polluted by various pharmaceuticals,<sup>26</sup> pesticides,<sup>27</sup> or

60 lakes by antibiotics.<sup>28</sup> The choice of using the maximum value of MEC (MEC<sub>max</sub>) is to be place us in  
61 the worst (extreme conditions) case scenario<sup>25,27</sup> and in the context of the precautionary principle. This  
62 method was applied here for the first time to the UWWDs, translating its originality.

63 Consequently, the main objectives of our study were to: (i) conduct a review of the ecotoxicity  
64 data available for the different compounds commonly detected in UWWDs; (ii) assess the  
65 concentrations of these pollutants in UWWDs performing a literature review of UWWDs pollutant  
66 compositions; and (iii) calculate the potential hazard of these pollutants for aquatic ecosystems. Several  
67 studies have already proposed to identify and prioritize hazardous pollutants in UWWDs.<sup>29-32</sup>  
68 Nevertheless, they generally considered only the stormwater (no studies were reported for the CSO).  
69 Moreover, these pollutant hazard assessments were based only on the intrinsic properties of the  
70 pollutants (bioaccumulation, biodegradability, physicochemistry, ecotoxicity) and did not take into  
71 account the concentrations found *in situ*.

72 In this article, we present the PNEC values inventoried for all the pollutants identified in  
73 UWWDs, and the MEC<sub>max</sub> found in these discharges. Lastly, we calculated the HQ for each pollutant  
74 found in UWWDs. We also chose to focus on combined and separate stormwater systems (named here  
75 “CSO” and “stormwater” systems) due to the very different sources and types of pollutants they contain.

## 76 2. Methodology

77 All the pollutants used and analyzed (on dissolved and particles phases of UWWDs) in this  
78 study were classified into families of chemical compounds, as detailed in Table 1. Scientific research  
79 papers for UWWD pollutants identification were obtained using databases such as the Web of  
80 Knowledge, Science Direct and Google Scholar, using key search terms (e.g. “stormwater”, “CSO”,  
81 “UWWD”, “pollutants”, “chemicals”). An identified paper’s bibliography and citations were also  
82 checked to find other suitable studies. Finally, papers used in this study were restricted to peer-reviewed  
83 research articles published between 1995 and 2016. Other scientific productions (e.g. conference papers,  
84 non-peer reviewed procedures) were not retained for this study.

### 85 2.1 Obtaining and determining the PNEC values of micropollutants in UWWDs

86 To define the hazard of the different pollutants identified in UWWD physico-chemical studies,  
87 the first step of our method was to determine their ecotoxicity by seeking or calculating their PNEC.  
88 PNEC values were found/calculated for all pollutants sought in physico-chemical studies (on particle  
89 and dissolved phases). In this study, the PNEC values were obtained for all the pollutants using the  
90 following approach: (i) When they were available, PNEC values were obtained from free European  
91 databases<sup>33,34</sup> (INERIS and AGRITOX) containing ecotoxicological data from international scientific  
92 literature, (ii) When values were not available in these databases, PNEC values were calculated using  
93 experimental ecotoxicological data found in the EPA ECOTOX database<sup>35</sup>, following the method  
94 proposed by Orias et Perrodin,<sup>36</sup> and in agreement with the guidelines proposed by the EU (European  
95 Union) in the Technical Guidance Document (TGD)<sup>37</sup> (see Table 2). This method is the following: for  
96 each compound, bibliographical research using the EPA ECOTOX database allowed identifying all the  
97 bioassays performed, the trophic level concerned (decomposers, primary producers, primary consumers  
98 and secondary consumers) and the chronicity (or not) of the bioassay (e.g. reproduction). Using all the  
99 ecotoxicity data, an Extrapolation Factor (EF), calculated following the criteria presented in Table S1,  
100 was applied to the lowest toxicity values to establish the PNEC of the compound concerned. No  
101 differentiation was done between the ecotoxicity data used (e.g. EC<sub>50</sub>, EC<sub>10</sub>) for the EF and PNEC  
102 calculation. However, several minor modifications in comparison to TGD were made: ecotoxicity data  
103 on fungi were considered as data on decomposers while data on periphyton were considered to originate  
104 from chronic bioassays on decomposers. In the case where only acute ecotoxicity data were available,  
105 but not for all trophic levels, PNEC values were calculated with the ECOSAR model, by applying an  
106 EF to the lowest ecotoxicological value. In all cases, no PNEC values were calculated if at least one  
107 acute ecotoxicity value was available for each trophic level. The chronic algae and macrophyte bioassays  
108 did not permit lowering the EF when they were the only ecotoxicological data available. Finally, the EF  
109 was not reduced when rotifer (*Brachionus calyciflorus*, noted “Bc”) bioassays were the only tests  
110 performed on the trophic level of secondary consumers.<sup>37</sup> Finally, when no PNEC and ecotoxicity data  
111 were available in databases and literature, PNEC values were estimated with modelled ecotoxicological  
112 data obtained using the ECOSAR method.<sup>38</sup>

113 It is important to point out that the authors of several studies did not indicate the speciation or  
114 the isomer of the compounds measured. This is the case of chromium, for which we chose to keep the  
115 two speciation forms (chromium III and chromium VI), as it has been reported that the annual  
116 concentrations of these two chromium species in rainwater samples are similar.<sup>39</sup> In the case of  
117 dichloroethane, we chose to keep the two isomers (1-1 and 1-2-dichloroethane), while the hazard  
118 quotient was calculated twice for this pollutant, using two PNECs.

## 119 2.2 Obtaining micropollutant MEC<sub>max</sub>

120 The second step for UWWD pollutant hazard assessment was the MEC<sub>max</sub> determination for  
121 each of them. As described in Orias and Perrodin<sup>25</sup>, two different approaches can be used to obtain the  
122 concentration of micropollutants in UWWDs: (i) a theoretical method based on the calculation of PEC  
123 (Predicted Effluent Concentration) with the design of a scenario, and (ii) an experimental approach  
124 based on analyses of the pollutants in the dissolved phase of the UWWDs. The second method  
125 (MEC<sub>max</sub> determination) is more realistic, because it is based on real measured concentrations in  
126 UWWDs, contrary to the calculation of PEC values presenting a high level of uncertainty due to the  
127 parameters used (e.g. product consumption). Therefore, this option was selected although not all the  
128 compounds were analyzed in the discharges.

129 In this study, we will discuss the different choices made to select concentration data (see section  
130 3.5). Firstly, we considered studies providing compound concentration values only in the soluble phase  
131 (<1.2 µm). Indeed, ecotoxicity assays performed to calculate PNEC values for the different pollutants  
132 have relied only on pure liquid solutions. Moreover, it is impossible to evaluate the bioavailability of  
133 the contaminants in the particulate phase for aquatic organisms. Additionally, taking into account the  
134 concentrations on particles could lead to overestimating the hazard (see section 3.5). Regarding the  
135 formulation of the Hazard Quotient (HQ), we also chose to separate concentration values for separate  
136 and combined sewer systems, thus we calculated the hazard for both cases. The hazards of these two  
137 systems differ, as the source and type of pollutants (i.e. the presence of pharmaceuticals in discharges  
138 from combined sewer overflows) are also different.

139 For each compound sought in the dissolved part of the stormwater/CSO samples, the MEC of  
140 the events observed was reported for each study. Finally, the highest effluent concentration ever  
141 measured in UWWDs ( $MEC_{max}$ ) was determined by seeking the highest MEC reported previously, with  
142 the aim to be situated in the worst-case scenario, as explained in the introduction. In further research, it  
143 would be interesting to make the same work with the median and the lowest values, but that will be  
144 limited by the fact that for some compounds, only one concentration value was available in scientific  
145 literature.

### 146 2.3 Calculation of the hazard quotients

147 Finally, for each compound detected in discharges (section 2.2) with an available PNEC value  
148 (section 2.1), we calculated an hazard quotient using the equation (1):

$$149 \quad (1) \text{ HQ} = \text{MEC}_{max} / \text{PNEC}$$

150 With:

151  $MEC_{max}$ : the highest effluent concentration ever measured in UWWDs in  $\mu\text{g}\cdot\text{L}^{-1}$ ;

152 PNEC: Predicted No Effect Concentration in  $\mu\text{g}\cdot\text{L}^{-1}$ .

153 It was considered that compounds with an HQ up to 1 are potentially hazardous for the  
154 environment, and that compounds with the highest HQ are the most hazardous for aquatic ecosystems.  
155 On the contrary, compounds with an HQ lower than 1 were considered slightly hazardous.

156 In this study, 207 compounds were identified in UWWDs. We found or calculated/modelled a  
157 PNEC value representing the ecotoxicity of 165 of them. By seeking the dissolved proportion analyzed  
158 in UWWDs, we were finally able to determine a  $MEC_{max}$  for only 61 compounds in “stormwater” and  
159 49 in “CSO”. Consequently, we calculated 94 hazard quotients using equation (1) to prioritize their  
160 hazardousness for freshwater ecosystems.

## 161 3. Results and discussion














### 162 3.1 Pollutant classification and available data.

163 Pollutants analyzed in UWWDs were classified as shown in Table 1. All the PNECs,  
 164 concentrations and hazard data were analyzed as per the pollutant ranking presented in Table 1.

165 Table 1: Families of compounds considered in this study and colour codes associated in the  
 166 various figures.

167

168

Abbreviation	Family of pollutants	Figure colour code
ALK	Alkylphenols	
FR	Flame Retardants	
M	Metals	
O	Others	
ORG	Organotins	
P	Pesticides	
PAH	Polycyclic Aromatic Hydrocarbons and derivatives	
PBDE	Polybrominated Diphenyl Ethers	
PC	Pharmaceutical Compounds	
PCB	Polychlorobiphenyls	
PFAA	Perfluoroalkyl Acids	
PHT	Phtalates	
VOC	Volatile Organic Compounds	

169

### 170 3.2 Ecotoxicity of the pollutants sought in UWWDs

171 Of the 207 compounds sought in the UWWD samples (total, dissolved and/or particle phases),  
 172 161 were obtained by calculation using data from the European database and the international literature.  
 173 In addition, we formulated ourselves 52 new PNEC values based on experimental data and 4 were  
 174 modelled using ECOSAR model, as detailed in Table 2. Finally, we listed a total of 165 PNEC values.  
 175 Figure 1 presents the distribution of available PNEC values for each pollutant family. This figure shows  
 176 that 5 families present a large number of molecules for which PNEC data are not available: PAH, PC,  
 177 ALK, O and PCB. This lack of data poses a problem for estimating UWWD compound hazards.

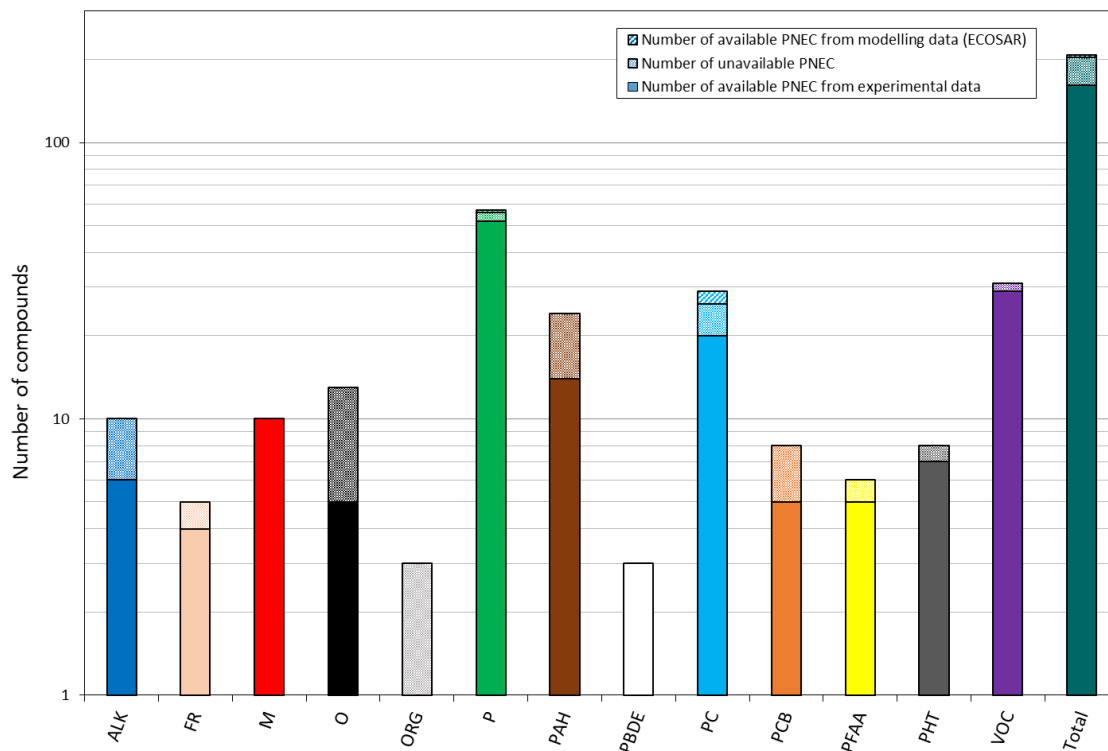
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182 Figure 1: Distribution of the number of molecules and their PNEC available for the different families of  
 183 pollutants identified in UWWDs.

184 The 165 PNEC values obtained have been separated into three categories according to the  
 185 ranking of Orias and Perrodin (2014): a PNEC less than  $0.1 \mu\text{g L}^{-1}$  (the most hazardous, the most  
 186 ecotoxic) (Figure 2), a PNEC between 1 and  $0.1 \mu\text{g L}^{-1}$  (intermediate ecotoxicity) (Figure 3) and a PNEC  
 187  $> 1 \mu\text{g L}^{-1}$  (less ecotoxic) (Figure 4). Finally, due to the results obtained, 59 of the compounds were  
 188 ranked as very ecotoxic, 30 as ecotoxic and 76 as slightly ecotoxic.

189 Among the 59 very ecotoxic compounds, pesticides feature predominantly in the most  
 190 hazardous category of pollutants sought in UWWDs. Indeed, 33 of the compounds with a PNEC less  
 191 than  $0.1 \mu\text{g L}^{-1}$  are pesticides. Moreover, regarding the PNEC values of a very large number of pesticides  
 192 sought in UWWDs (54 compounds), they represent a potentially considerable source of hazard for this  
 193 kind of matrix: 43 compounds have a PNEC value under  $1.0 \mu\text{g L}^{-1}$  and 33 have a PNEC value under  
 194  $0.1 \mu\text{g L}^{-1}$ . Two other families represent a significant share of the most ecotoxic pollutants: PCs (7  
 195 compounds) and PAHs (also 7). The share of the other families is lower. The most ecotoxic compound  
 196 is Endrin, a pesticide with a PNEC of  $1.22 \cdot 10^{-8} \mu\text{g.L}^{-1}$ . However, when examining slightly ecotoxic  
 197 compounds ( $\text{PNEC} > 1 \mu\text{g.L}^{-1}$ ), VOCs are largely represented, with 24 of the compounds listed in this

198 category. The gap between the share of the other families is narrower: FR (3 compounds), PHT (6),  
199 PFAA (3), PAH (5), P (11), O (5), M (6), PC (10), ALK (1). The least toxic compound sought in  
200 UWWDs is Iohexol, a PC with a PNEC value of 45705  $\mu\text{g.L}^{-1}$ .

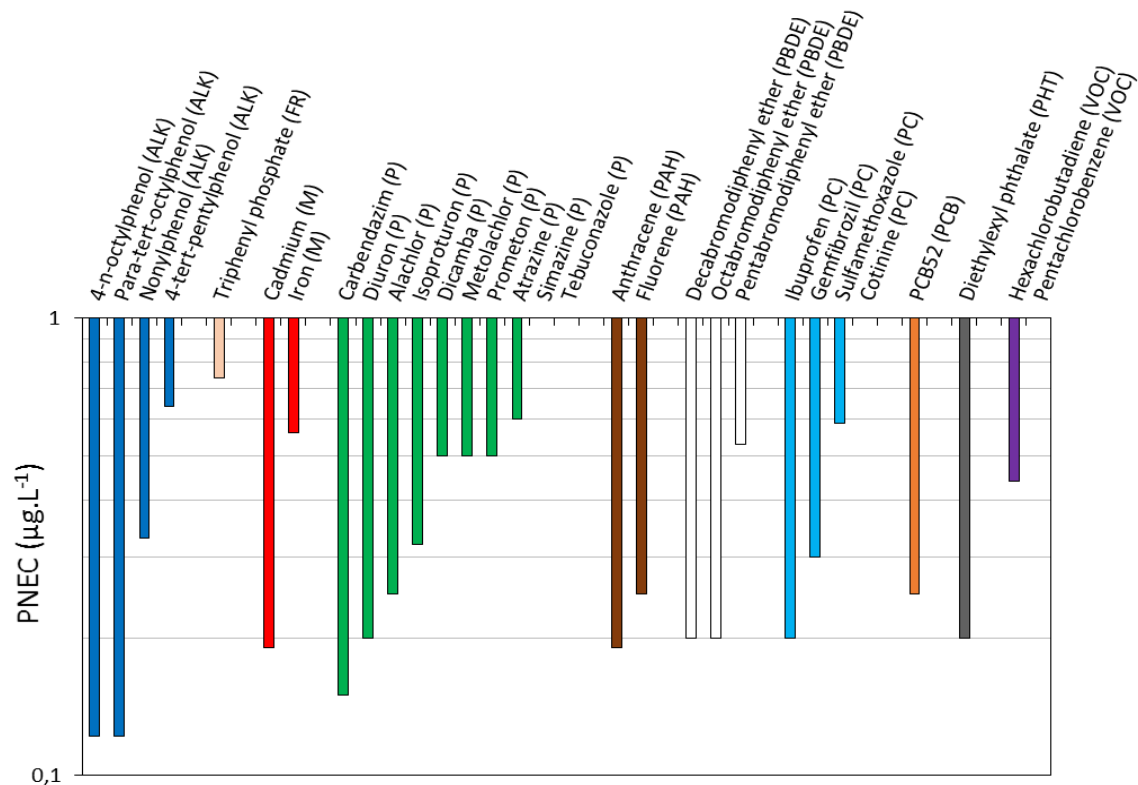
201         The large number of very ecotoxic pollutants sought in UWWDs can be explained by the fact  
202 that many substances found in UWWDs were developed to eliminate certain families of organisms, thus  
203 they have a considerable impact on many aquatic species belonging to the same family (the most relevant  
204 example is pesticides). Nevertheless, a large number of pollutants of this family present low toxicity  
205 regarding PNEC values. This observation may be explained by three possibilities: the pollutant  
206 specifically affects the organism targeted without having any effect on the others (the case of similar  
207 pesticides), it is only slightly toxic for aquatic organisms, or there are not enough data to lower the  
208 PNEC value.

209         We also note that no or insufficient ecotoxicity data are available for 13 of the compounds (3  
210 PC, 6 PAH, 2 ALK, 1 ORG, 1 PFAA) detected in UWWDs. These compounds include a high number  
211 of PCs and PAHs. More ecotoxicity data are necessary for these families of compounds to avoid an  
212 underestimation of the hazard represented by UWWDs. Moreover, as it can be seen in Table 2, the  
213 PNECs of certain pollutants, such as PCBs, propylparaben and cotinine, were calculated using a small  
214 number of ecotoxicological data, and consequently their toxicity could be underestimated. However, we  
215 should bear in mind that these PNEC values were created with high safety factors (1000).

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0,1  $\mu\text{g.L}^{-1}$  < UWWD pollutant PNECs  $\leq$  1  $\mu\text{g.L}^{-1}$

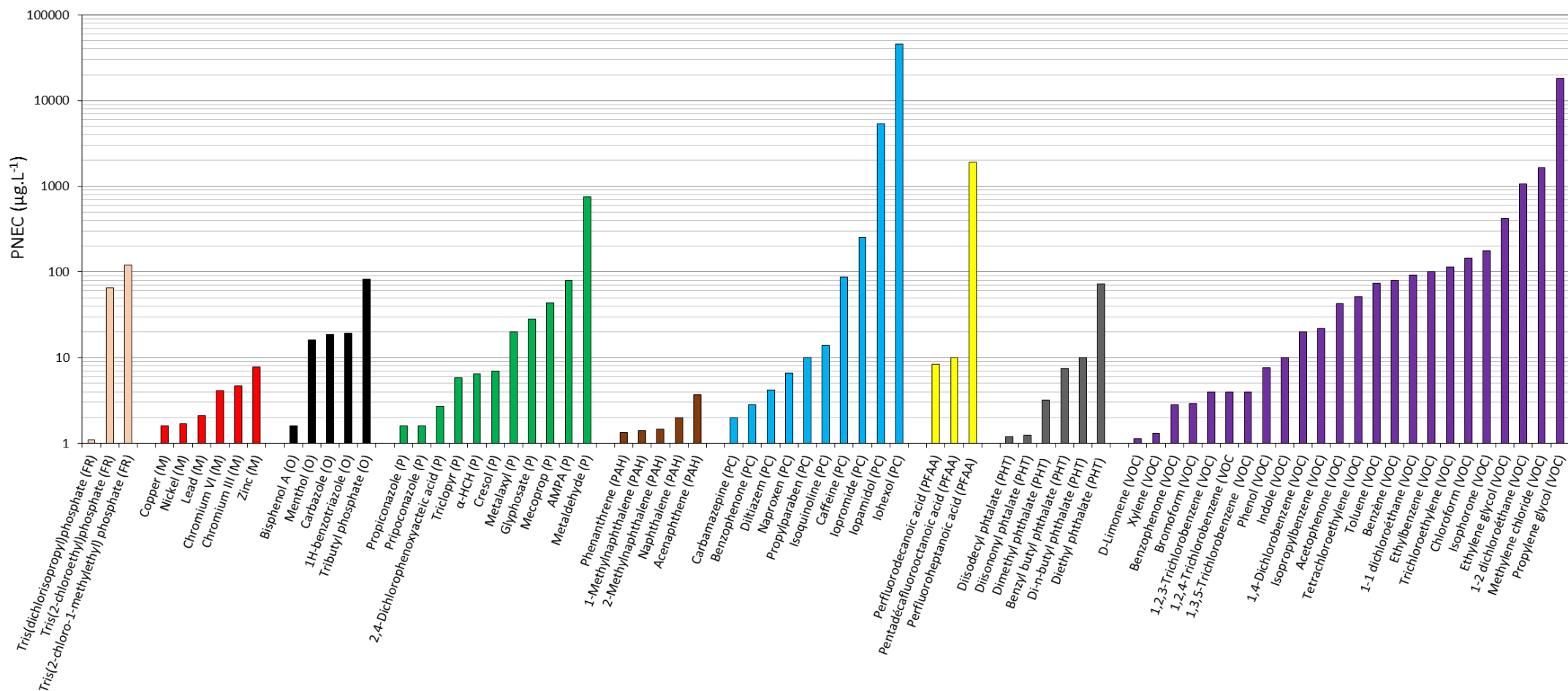


225 Figure 3: PNEC values between 0.1  $\mu\text{g L}^{-1}$  and 1  $\mu\text{g L}^{-1}$  for the different compounds sought in UWWDs. Letters in brackets correspond to the classification in  
 226 Table 1. PNEC values are ranked in ascending order into each separated pollutant family.

227

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UWWD pollutant PNECs > 1 µg.L<sup>-1</sup>



229 Figure 4: PNEC > 1 µg L<sup>-1</sup> for the different compounds sought in UWWDs. Letters in brackets correspond to the classification in Table 1. PNEC values are  
 230 ranked in ascending order into each separated pollutant family.

231

232 Table 2: Summary of ecotoxicity data and PNEC formulated by calculation or modelling for 60 pollutants sought in UWWDs. (Legend: D: Decomposers; P:  
 233 Primary producers; 1C: Primary consumers; 2C: Secondary consumers; C: ecotoxicity data available for organism community bioassays; Bc: *Brachionus*  
 234 *calyciflorus*; EF: Extrapolation factor).

N°CAS	Compound	Family	Experimental ecotoxicity								Data used for PNEC calculation				EF	PNEC (ug/L)	Ref.	
			Test species	Trophic level				Chronic test				Specie	Parameter	Endpoint				Value (ug/L)
				D	P	1C	2C	D	P	1C	2C							
104-40-5	4-(para)-nonylphenol	ALK	77+C	0	5	19	36+17 (Bc)	0	5	6	11+17 (Bc)	<i>Pimephales promelas</i>	Reproduction	LOEC	3.31E-02	10	3.31E-03	35
80-46-6	4-tert-pentylphenol	ALK	4	0	0	1	3	0	0	1	2	<i>Danio rerio</i>	Development	LOEC	3.20E+01	50	6.40E-01	35
78-51-3	Tris(2-butoxyethyl)phosphate	FR	3	0	0	0	3	0	0	0	0	<i>Danio rerio</i>	Mortality	NOEC	4.00E+03			35
7439-89-6	Iron	M	6	0	1	2	3	0	1	0	0	<i>Cyprinus carpio</i>	Mortality	LC50	5.60E+02	1000	5.60E-01	35
86-74-8	Carbazole	O	4	0	1	2	1	0	1	1	0	<i>Pimephales promelas</i>	Mortality	LC50	9.30E+02	50	1.86E+01	35
789-02-6	2,4'-DDT	P	4	0	0	0	4	0	0	0	2	<i>Oryzias latipes</i>	Reproduction (fertility)	LOEC	2.30E-01	100	2.30E-03	35
50-29-3	4,4'-DDT	P	40	0	11	21	8	0	11	5	0	<i>Hyallela azteca</i>	Mortality	LC50	7.00E-02	50	1.40E-03	35
309-00-2	Aldrin	P	55	0	0	18	37	0	0	0	0	<i>Paratelphusa jacquemontii</i>	Mortality	LC50	9.70E-02			35
218-01-9	Chrysene	P	3	0	0	2	1	0	0	0	0	<i>Aedes aegypti</i>	Mortality	LC50	1.70E+03			35
1319-77-3	Cresol	P	6	0	1	2	3	0	1	0	0	<i>Gammarus fasciatus</i>	Immobilization	EC50	7.00E+03	1000	7.00E+00	35
52315-07-8	Cypermethrin	P	68	0	6	28	33+1 (Bc)	0	6	7	2+1 (Bc)	<i>Palaemonetes argentinus</i>	Mortality	LOEC	1.00E-04	10	1.00E-05	35
6190-65-4	Desethylatrazine	P	11	0	8	3	0	0	7	1	0	<i>Stagnicola elodes</i>	Mortality	NOEC	3.30E-01	50	6.60E-03	35
1007-28-9	Desethylsimazine	P	10	0	7	2	1	0	7	0	0	<i>Pseudokirchneriella subcapitata</i>	Growth	NOEC	6.00E-01	1000	6.00E-04	35
333-41-5	Diazinon	P	131	0	9	53	69	0	9	8	18	<i>Daphnia magna</i>	Reproduction	EC50	2.00E-04	10	2.00E-05	35
60-57-1	Dieldrin	P	98+C	0	7	43	45+1 (Bc)	0	7	2	1+1 (Bc)	<i>Brachionus calyciflorus</i>	Population growth	LOEC	1.00E-03	10	1.00E-04	35
72-20-8	Endrin	P	89	0	1	22	66	0	1	0	1	<i>Asellus aquaticus</i>	Mortality	LC50	6.10E-07	50	1.22E-08	35

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2682-20-4	Methylisothiazolinone	P	3	0	0	1	2	0	0	0	0	<i>Oncorhynchus mykiss</i>	Mortality	LC50	7.00E+01			35
51218-45-2	Metolachlor	P	63	0	37	12	14	0	35	6	5	<i>Stuckenia pectinata</i>	Photosynthesis disturbance	LOEC	5.00E+00	10	5.00E-01	35
134-62-3	N,N-diethyl-3-méthylbenzamide	P	6	0	0	3	3	0	0	1	0	<i>Pimephales promelas</i>	Growth	NOEC	6.00E-01	100	6.00E-03	35
134-62-3	N,N-diethyl-meta-toluamide	P	6	0	0	3	3	0	0	0	0	<i>Pimephales promelas</i>	Growth (condition index)	NOEC	6.00E-01	1000	6.00E-04	35
26530-20-1	N-Octylisothiazolinone	P	6	0	0	1	5	0	0	0	1	<i>Pimephales promelas</i>	Growth	NOEC	8.50E+00	100	8.50E-02	35
52645-53-1	Permethrine	P	4	0	1	2	1	0	0	0	0	Daphnid	Mortality	LC50	3.00E-02	1000	3.00E-05	38
1610-18-0	Prometon	P	15	0	5	1	9	0	5	1	1	<i>Chlorella fusca var. vacuolata</i>	Population growth (growth rate)	EC01	5.00E+00	10	5.00E-01	35
886-50-0	Terbutryn	P	21	0	9	2	10	0	6	0	0	<i>Craticula accomoda</i>	Growth	EC10	1.90E-02	1000	1.90E-05	35
101-20-2	Triclocarban	P	11	0	1	5	5	0	1	2	1	<i>Daphnia magna</i>	Reproduction	NOEC	2.50E-01	10	2.50E-02	35
319-84-6	$\alpha$ -HCH	P	21	0	1	8	12	0	1	2	4	<i>Lymnaea stagnalis</i>	Reproduction	EC50	6.50E+01	10	6.50E+00	35
33213-65-9	$\beta$ -endosulfan	P	15	1	0	6	8	0	0	0	0	<i>Oncorhynchus mykiss</i>	Mortality	LC50	3.30E+00	1000	3.30E-03	35
319-85-7	$\beta$ -HCH	P	4	0	0	0	4	0	0	0	0	<i>Oryzias latipes</i>	Behavioural changes (general)	NOEC	3.20E+01			35
90-12-0	1-Methylnaphthalene	PAH	6	0	3	1	2	0	1	0	0	<i>Daphnia magna</i>	Immobilization	EC50	1.42E+03	1000	1.42E+00	35
91-57-6	2-Methylnaphthalene	PAH	5	0	2	1	2	0	0	0	0	<i>Oncorhynchus mykiss</i>	Mortality	EC50	1.46E+03	1000	1.46E+00	35
84-65-1	Anthraquinone	PAH	6	0	2	2	2	0	2	0	0	<i>Lemna gibba</i>	Photosynthesis	IC50	1.00E-02	1000	1.00E-05	35
132-65-0	Dibenzothiophene	PAH	3	0	0	1	2	0	0	0	0	<i>Daphnia magna</i>	Mortality	LC50	4.20E+02			35
119-61-9	Benzophenone	PC	5	0	0	4	1	0	0	0	1	<i>Daphnia magna</i>	Immobilization	EC50	2.80E+02	100	2.80E+00	35
486-56-6	Cotinine	PC	1	0	1	0	0	0	1	0	0	<i>Lemna gibba</i>	Biomass	NOEC	1.00E+03	1000	1.00E+00	35
42399-41-7	Diltiazem	PC	3	0	1	1	1	0	0	0	0	<i>Paspalum vaginatum</i>	Calcium uptake	LOEC	4.16E+03	1000	4.16E+00	35
58-73-1	Diphenhydramine	PC	2	0	0	1	1	0	0	1	0	<i>Ceriodaphnia dubia</i>	Reproduction	LC50	3.94E+03	100	3.94E+01	35
119-65-3	Isoquinoline	PC	5	0	1	2	2	0	1	0	0	<i>Poecilia reticulata</i>	Mortality	LC50	1.40E+04	1000	1.40E+01	35
94-13-3	Propylparaben	PC	2	0	0	2	0	0	0	1	0	<i>Daphnia magna</i>	Immobilization	NOEC	1.00E+03	100	1.00E+01	35

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37680-73-2	PCB101	PCB	4	0	0	3	1	0	0	0	1	<i>Pimephales promelas</i>	Growth	LOEC	2.50E+00	100	2.50E-02	35
35065-28-2	PCB138	PCB	2	0	0	0	2	0	0	0	1	<i>Pimephales promelas</i>	Growth	LOEC	2.50E+00	100	2.50E-02	35
35065-27-1	PCB153	PCB	4	0	0	1	3	0	0	1	1	<i>Pimephales promelas</i>	Growth	LOEC	2.50E+00	50	5.00E-02	35
35065-29-3	PCB180	PCB	1	0	0	0	1	0	0	0	1	<i>Pimephales promelas</i>	Growth	LOEC	2.50E+00	100	2.50E-02	35
35693-99-3	PCB52	PCB	2	0	0	1	1	0	0	0	1	<i>Pimephales promelas</i>	Reproduction	NOEC	2.50E+01	100	2.50E-01	35
335-67-1	Pentadécafluorooctanoic acid	PFAA	12	0	2	3	6 + 1 (Be)	0	2	2	2	<i>Oryzias latipes</i>	Mortality	LOEC	1.00E+02	10	1.00E+01	35
335-76-2	Perfluorodecanoic acid	PFAA	3	0	1	1	1	0	1	0	0	<i>Danio rerio</i>	Mortality	LC50	8.40E+03	1000	8.40E+00	35
375-85-9	Perfluoroheptanoic acid	PFAA	1	0	1	0	0	0	1	0	0	<i>Chlorella vulgaris</i>	Growth	EC50	1.90E+06	1000	1.90E+03	35
375-95-1	Perfluorononanoic acid	PFAA	4	0	2	1	1	0	2	0	0	<i>Danio rerio</i>	Growth	LOEC	1.00E+01	1000	1.00E-02	35
1763-23-1	Perfluorooctanesulfonic acid	PFAA	4	0	0	2	2	0	0	1	0	<i>Oryzias latipes</i>	Mortality	LOEC	1.00E+01	100	1.00E-01	35
2058-94-8	Perfluoroundecanoic acid	PFAA	2	0	0	1	1	0	0	0	0	<i>Daphnia magna</i>	Immobilization	NOEC	5.64E+04			35
117-81-7	Diethylexyl phthalate	PHT	29	0	3	5	21	0	3	2	3	<i>Danio rerio</i>	Reproduction	NOEC	2.00E+00	10	2.00E-01	35
26761-40-0	Diisodecyl phthalate	PHT	7	0	1	1	5	0	1	1	0	<i>Daphnia magna</i>	Mortality	LOEC	6.00E+01	50	1.20E+00	35
27554-26-3	Diisononyl phthalate	PHT	7	0	1	2	4	0	1	1	0	<i>Daphnia magna</i>	Reproduction	NOEC	6.20E+01	50	1.24E+00	35
131-11-3	Dimethyl phthalate	PHT	9	0	1	2	6	0	1	0	0	<i>Cyprinodon variegatus</i>	Mortality	NOEC	3.20E+03	1000	3.20E+00	35
98-86-2	Acetophenone	VOC	4	0	1	2	1	0	0	0	0	<i>Tetrahymena pyriformis</i>	Population Growth	EC50	4.28E+04	1000	4.28E+01	35
119-61-9	Benzophenone	VOC	5	0	0	4	1	0	0	1	0	<i>Daphnia magna</i>	Immobilization	EC50	2.80E+02	100	2.80E+00	35
75-25-2	Bromoform	VOC	5	0	1	2	2	0	1	0	0	<i>Cyprinodon variegatus</i>	Mortality	NOEC	2.90E+03	1000	2.90E+00	35
138-86-3	D-Limonene	VOC	11	0	1	7	3	0	1	0	0	<i>Lymnaea acuminata</i>	Mortality	LC50	1.13E+03	1000	1.13E+00	35
107-21-1	Ethylene glycol	VOC	20	1	1	7	11	0	1	1	1	<i>Ceriodaphnia dubia</i>	Reproduction	NOEC	4.20E+03	10	4.20E+02	35
120-72-9	Indole	VOC	3	0	1	2	0	0	1	1	0	<i>Oryzias latipes</i>	Mortality	LC50	1.00E+03	100	1.00E+01	35
124-76-5	Isoborneol	VOC	1	0	0	0	1	0	0	0	0	Fish	Mortality	LC50	5.90E+04			38



236 3.3 Concentration of pollutants in separate and combined systems

237 Maximum pollutant concentrations found in UWWDs were assessed using available literature  
238 and are presented in Tables 3 and 4. MEC<sub>max</sub> were very variable, with some pollutants (e.g.  
239 hexachlorobenzene) found at several ng.L<sup>-1</sup>, while others (e.g. copper) were found at a few mg.L<sup>-1</sup>.  
240 However, the compound concentrations generally ranged between ng.L<sup>-1</sup> and several hundred µg.L<sup>-1</sup>.

241 On one hand, as observed in Table 3, 61 compounds were detected in stormwater samples, and  
242 50 were sought but not detected. We found the highest concentrations for zinc (2.12 mg.L<sup>-1</sup>). High  
243 concentrations of pollutants such as other heavy metals (copper, nickel) and pesticides (such as  
244 glyphosate and AMPA) and PAH (e.g. pyrene) were also detected. The main families of pollutants  
245 detected at high concentrations were PAH, VOC, ALK, PHT, P and M.

246 On the other hand, out of the 81 chemicals of interest sought in the dissolved part of the CSO  
247 samples, 49 were reported (see Table 4). The highest concentration was obtained for zinc (236 µg.L<sup>-1</sup>).  
248 The main families found at high concentrations were M, P and PC. The occurrence of high  
249 concentrations of heavy metals in separate systems and CSO is not surprising due to the source of  
250 wastewater and rainfall runoff. More precisely, tyre wear, vehicle brake deposition, conveyance system  
251 infrastructure (e.g. downspouts and culverts), and atmospheric deposition can lead to the presence of heavy  
252 metals.<sup>4</sup> Moreover, the remobilization of wastewater and in-sewer deposits (due to pollutant  
253 water/particle partition) can represent a large share of the pollutant load in CSO, such as Cu and PAH.<sup>58</sup>  
254 Launay et al.<sup>64</sup> observed the same phenomenon for pharmaceutical compounds and industrial chemicals.  
255 Contrary to stormwater, we note the presence of PC compounds sought and detected in the dissolved  
256 phase (18 compounds), probably due to the contribution of urban wastewater to the pollution of CSO.

257 If we compare the Maximum concentrations of UWWD pollutants with other urban effluents  
258 (e.g. urban wastewater and hospital wastewater), such as phthalates, heavy metals, pharmaceutical  
259 compounds and pesticides, MEC<sub>max</sub> were close to those detected in these other matrices.<sup>60,61,62,63</sup> Some  
260 of them, such as Bisphenol A, concentrations in UWWDs (max. 130 µg L<sup>-1</sup>) can be even higher than in  
261 wastewater (max. 2.14 µg L<sup>-1</sup>). This fact was also observed with heavy metals such as copper and zinc.

262 Consequently, since they undergo hardly any or no treatment, and that most of few current treatment

263 methods employed do not reduce concentration of many identified pollutants, considerable amounts of  
264 these substances may enter surface waters.

265           Nevertheless, it is important to point out that the data collected and discussed above have some  
266 limitations. Firstly, few studies have analyzed the dissolved phase of discharges and thus many  
267 compounds identified and sought in UWWDs are not taken into account here because they are found in  
268 only the particle or total phase (due to their low solubility and high affinity for the particle phase).  
269 Consequently, the number of compounds detected here is limited (see Table 3 and Table 4). Secondly,  
270 concentrations found in UWWDs need to be considered with caution because, as stated in the study of  
271 Huber et al.,<sup>52</sup> concentrations measured in stormwater samples can be influenced by different parameters  
272 such as sample collection, preparation and analysis, which can also affect the concentrations observed  
273 in discharges.

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286 Table 3: Maximum Measured Effluent Concentrations (MECmax) of micropollutants in the dissolved part sought in stormwater samples (ND: Not detected, \*:  
287 Unspecified).

Pollutant family	Pollutant	MECmax (µg/L)	Country	Ref.	Pollutant family	Pollutant	MECmax (µg/L)	Country	Ref.
ALK	4-n-octylphenol (ALK)	ND	France	4	PAH	Dibenzothiophene (PAH)	0.0417	USA (Washington D.C.)	2
ALK	4-nonylphenol di-ethoxylate (ALK)	ND	France	4	PAH	Acenaphthylene (PAH)	0.070	Australia; France; Sweden; USA (Alabama); USA (Washington D.C.)	2 ; 4 ; 5 ; 47 ; 48
ALK	4-tert-pentylphenol (ALK)	0.7	Sweden	5	PAH	Perylene (PAH)	0.12	USA (Washington D.C.)	2
ALK	Para-tert-octylphenol (ALK)	0.99	France, Sweden	4 ; 5	PAH	Dibenzo[a,h]anthracene (PAH)	0.13	France; Sweden; USA (Alabama); USA (Washington D.C.)	2 ; 4 ; 5 ; 47
ALK	4-Octylphenol monoethoxylate (ALK)	4.39	Sweden	5	PAH	Benzo[a]anthracene (PAH)	0.34	Australia; France; Sweden; USA (Alabama); USA (South Carolina); USA (Washington D.C.)	2 ; 4 ; 5 ; 47 ; 48 ; 49
ALK	4-(para)-nonylphenol (ALK)	7.7	France, Sweden	4 ; 5	PAH	Benzo[k]fluoranthene (PAH)	0.40	France; Sweden; USA (Alabama); USA (Washington D.C.)	2 ; 4 ; 5 ; 47
ALK	4-tert-butylphenol (ALK)	7.82	France, Sweden	4 ; 5	PAH	Benzo[e]pyrene (PAH)	0.42	USA (South Carolina); USA (Washington D.C.)	2 ; 48
ALK	4-nonylphenol mono-ethoxylate (ALK)	8.36	Sweden	5	PAH	Indeno[1,2,3-cd]pyrene (PAH)	505	Australia; France; Sweden; USA (Alabama); USA (South Carolina); USA (Washington D.C.)	2 ; 4 ; 5 ; 47 ; 48 ; 49
M	Platinum (M)	ND	France	4	PAH	Benzo[a]pyrene (PAH)	0.54	Australia; France; Sweden; USA (Alabama); USA (South Carolina); USA (Washington D.C.)	2 ; 4 ; 5 ; 47 ; 48 ; 49
M	Mercury (M)	0.01	Canada; France	4 ; 41	PAH	Benzo[g,h,i]perylene (PAH)	0.55	Australia; Sweden; USA (Alabama); USA (South Carolina); USA (Washington D.C.)	2 ; 5 ; 47 ; 48 ; 49
M	Lead (M)	15.9	Australia; China; France; USA (Alabama); USA (California); *	4 ; 5 ; 47 ; 50 ; 51 ; 52	PAH	Anthracene (PAH)	0.56	Australia; France; Sweden; USA (Alabama); USA (South Carolina); USA (Washington D.C.)	2 ; 4 ; 5 ; 47 ; 48 ; 49
M	Cadmium (M)	31.1	Australia; France; USA (Alabama); USA (California); *	4 ; 47 ; 50 ; 52 ; 55	PAH	Chrysene (PAH)	0.62	Australia; France; Sweden; USA (Alabama); USA (South Carolina); USA (Washington D.C.)	2 ; 4 ; 5 ; 47 ; 48 ; 49
M	Chromium (M)	32	Australia; France; USA (Alabama); USA (California); *	4 ; 47 ; 50 ; 52 ; 55	PAH	Acenaphthene (PAH)	0.72	Australia; France; Sweden; USA (Alabama); USA (Washington D.C.)	4 ; 5 ; 47 ; 49
M	Nickel (M)	49	France; USA (Alabama); USA (California); *	4 ; 5 ; 47 ; 52	PAH	Benzo[b]fluoranthene (PAH)	0.98	Australia; France; USA (Alabama); USA (South Carolina); USA (Washington D.C.)	2 ; 4 ; 47 ; 48 ; 49

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M	Copper (M)	1520	Australia; China; France; USA (Alabama); USA (California); *	4 ; 5 ; 47 ; 50 ; 51 ; 52	PAH	Phenanthrene (PAH)	1.32	Australia; France; Sweden; USA (Alabama); USA (South Carolina); USA (Washington D.C.)	2 ; 4 ; 5 ; 47 ; 48 ; 49
M	Zinc (M)	2118	Australia; China; France; USA (Alabama); USA (California); *	4 ; 5 ; 47 ; 50 ; 51 ; 52	PAH	Fluorene (PAH)	1.37	Australia; France; Sweden; USA (Alabama); USA (South Carolina); USA (Washington D.C.)	2 ; 4 ; 5 ; 47 ; 48 ; 49
O	Bisphenol A (O)	130	Sweden	5	PAH	Fluoranthene (PAH)	14	Australia; France; Sweden; USA (Alabama); USA (South Carolina); USA (Washington D.C.)	2 ; 4 ; 5 ; 47 ; 48 ; 49
ORG	Dibutyltin (ORG)	ND	France	4	PAH	Naphthalene (PAH)	17	Australia; France; Sweden; USA (Alabama); USA (Washington D.C.)	2 ; 4 ; 5 ; 47 ; 49
ORG	Tributyltin (ORG)	ND	France	4	PAH	Pyrene (PAH)	20	Australia; France; Sweden; USA (Alabama); USA (South Carolina); USA (Washington D.C.)	2 ; 4 ; 5 ; 47 ; 48 ; 49
ORG	Monobutyltin (ORG)	0.025	France	4	PBDE	Decabromodiphenyl ether (PBDE)	ND	France	4
P	2,4'-DDT (P)	ND	France	4	PBDE	Octabromodiphenyl ether (PBDE)	ND	France	4
P	4,4'-DDT (P)	ND	France	4	PBDE	Pentabromodiphenyl ether (PBDE)	ND	France	4
P	Alachlor (P)	ND	France	4	PCB	PCB101 (PCB)	ND	France	4
P	Aldrin (P)	ND	France; USA (Alabama)	4 ; 47	PCB	PCB118 (PCB)	ND	France	4
P	Atrazine (P)	ND	France	4	PCB	PCB138 (PCB)	ND	France	4
P	Chlordane (P)	ND	France; USA (Alabama)	4 ; 47	PCB	PCB153 (PCB)	ND	France	4
P	Chlorfenvinphos (P)	ND	France	4	PCB	PCB180 (PCB)	ND	France	4
P	Chlorpyrifos (P)	ND	France	4	PCB	PCB194 (PCB)	ND	France	4
P	Desethylsimazine (P)	ND	France	4	PCB	PCB28 (PCB)	ND	France	4
P	Dieldrin (P)	ND	France	4	PCB	PCB52 (PCB)	ND	France	4
P	Endrin (P)	ND	France; USA (Alabama)	4 ; 47	PFAA	Perfluoroheptanoic acid (PFAA)	0.011	Japan; Singapour; Switzerland; USA (Minnesota)	42 ; 43 ; 44 ; 45
P	Esfenvalerate (P)	ND	France; USA (Alabama)	4 ; 47	PFAA	Perfluoroundecanoic acid (PFAA)	0.045	Japan; Singapour; Switzerland; USA (Minnesota)	42 ; 43 ; 44 ; 45 ; 46
P	Lindane (P)	ND	France	4	PFAA	Perfluorodecanoic acid (PFAA)	0.077	Japan; Singapour; Switzerland; USA (Minnesota)	42 ; 43 ; 44 ; 45 ; 46
P	Simazine (P)	ND	France	4	PFAA	Perfluorononanoic acid (PFAA)	0.093	Japan; Singapour; Switzerland; USA (Minnesota)	42 ; 43 ; 44 ; 45 ; 46

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P	Trifluralin (P)	ND	France	4	PFAA	Perfluorooctanesulfonic acid (PFAA)	0.16	Japan; Singapour; Switzerland; USA (Minnesota)	42 ; 43 ; 44 ; 45 ; 46
P	$\alpha$ -endosulfan (P)	ND	France	4	PFAA	Pentadecafluorooctanoic acid (PFAA)	0.17	Japan; Singapour; Switzerland; USA (Minnesota)	42 ; 43 ; 44 ; 45 ; 46
P	$\beta$ -endosulfan (P)	ND	France	4	PHT	Dimethyl phthalate (PHT)	ND	USA (Alabama)	47
P	Lambda-cyhalothrin (P)	0.007	USA (California)	40	PHT	Di-n-octyl phtalate (PHT)	ND	France	4
P	Cyfluthrin (P)	0.023	USA (California)	40	PHT	Di-n-butyl phthalate (PHT)	1	Sweden; USA (Alabama)	5 ; 47
P	Cypermethrin (P)	0.026	USA (California)	40	PHT	Diisodecyl phtalate (PHT)	1.2	Sweden	5
P	Bifenthrin (P)	0.034	USA (California)	40	PHT	Diisononyl phtalate (PHT)	2	Sweden	5
P	Metaldehyde (P)	0.05	France	4	PHT	Diethyl phthalate (PHT)	15.9	Sweden; USA (Alabama)	5 ; 47
P	Permethrin (P)	0.13	USA (California)	40	PHT	Benzyl butyl phthalate (PHT)	16	Sweden; USA (Alabama)	5 ; 47
P	Deltamethrin (P)	0.25	USA (California)	40	PHT	Diethylhexyl phthalate (PHT)	45	France; Sweden; USA (Alabama)	4 ; 5 ; 47
P	Aminotriazole (P)	0.5	France	4 ; 47 ; 48	VOC	1,2,3-Trichlorobenzene (VOC)	ND	France	4
P	Isoproturon (P)	0.6	France	4	VOC	1,2,4-Trichlorobenzene (VOC)	ND	France	4
P	Diuron (P)	0.64	France	4	VOC	1,3,5-Trichlorobenzene (VOC)	ND	France	4
P	AMPA (P)	19	France; Switzerland	4 ; 53 ; 54	VOC	1-2 dichloroéthane (VOC)	ND	France	4
P	Glyphosate (P)	150	France; Switzerland	4 ; 53 ; 54	VOC	Benzène (VOC)	ND	France	4
					VOC	Chloroform (VOC)	ND	France	4
					VOC	Ethylbenzene (VOC)	ND	France	4
					VOC	Hexachlorobenzene (VOC)	ND	France	4
					VOC	Hexachlorobutadiene (VOC)	ND	France	4
					VOC	Isopropylbenzene (VOC)	ND	France	4
					VOC	Pentachlorobenzene (VOC)	ND	France	4
					VOC	Tetrachloroethylene (VOC)	ND	France	4
					VOC	Toluene (VOC)	ND	France	4
					VOC	Trichloroethylene (VOC)	ND	France	4
					VOC	Xylene (VOC)	ND	France	4
					VOC	Pentachlorophenol (VOC)	0.2	France	4
					VOC	Dichloromethane (VOC)	13	France	4
					VOC	1,4-Dichlorobenzene (VOC)	47	USA (Alabama)	48

290 Table 4: Maximum Measured Effluent Concentrations (MECmax) of the micropollutants sought in the dissolved part of CSO samples (ND: Not detected, \*:  
291 Unspecified).

Pollutant family	Pollutant	MECmax (µg/L)	Country	Ref.	Pollutant family	Pollutant	MECmax (µg/L)	Country	Ref.
ALK	4-n-octylphenol (ALK)	ND	France	57	PC	Estrone (PC)	ND	South Korea	12
ALK	Para-tert-octylphenol (ALK)	ND	France	57	PC	Diltiazem (PC)	ND	South Korea	12
ALK	4-tert-butylphenol (ALK)	0.080	France	57	PC	Trimethoprim (PC)	ND	South Korea	12
ALK	Nonylphenol (ALK)	0.390	France	57	PC	Meprobamate (PC)	ND	South Korea	12
FR	Tris(2-chloro-1-methylethyl) phosphate (FR)	1.140	South Korea	12	PC	Diclofenac (PC)	ND	South Korea	12
M	Nickel (M)	1.1	France	15 ; 57 ; 58	PC	Gemfibrozil (PC)	0.006	South Korea	12
M	Chromium (M)	1.8	France	15 ; 57 ; 58	PC	Diphenhydramine (PC)	0.023	South Korea	12
M	Cadmium (M)	9.9	France, United Kingdom	15 ; 57 ; 58 ; 59	PC	Primidone (PC)	0.040	South Korea	12
M	Copper (M)	65.4	France, United Kingdom	15 ; 57 ; 58 ; 59	PC	Triclosan (PC)	0.055	South Korea	12
M	Lead (M)	143.4	France, United Kingdom	15 ; 57 ; 58 ; 59	PC	Carbamazepine (PC)	0.060	South Korea	12
M	Zinc (M)	236.1	France, United Kingdom	15 ; 57 ; 58 ; 59	PC	Propylparaben (PC)	0.069	South Korea	12
O	1H-benzotriazole (O)	0.078	South Korea	12	PC	Sulfamethoxazole (PC)	0.070	South Korea	12
ORG	Dibutyltin (ORG)	ND	France	57	PC	Trimethoprim (PC)	0.073	South Korea	12
ORG	Tributyltin (ORG)	ND	France	57	PC	Benzophenone (PC)	0.136	South Korea	12
ORG	Monobutyltin (ORG)	0.013	France	57	PC	Atenolol (PC)	0.363	South Korea	12
P	Aldrin (P)	ND	France	57	PC	Acesulfame (PC)	0.727	South Korea	12
P	Dieldrin (P)	ND	France	57	PC	Naproxen (PC)	0.750	South Korea	12
P	Desethylatrazine (P)	0.017	France	57	PC	Ibuprofen (PC)	0.773	South Korea	12
P	Atrazine (P)	0.030	France	57	PC	Sucralose (PC)	0.818	South Korea	12
P	N,N-diéthyl-3-méthylbenzamide (P)	0.035	South Korea	12	PC	Iopamidol (PC)	1.550	South Korea	12
P	Isoproturon (P)	0.040	France	57	PC	Iohecol (PC)	1.770	South Korea	12
P	Triclocarban (P)	0.061	South Korea	12	PC	Caffeine (PC)	2,54	South Korea	12

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P	Aminotriazole (P)	0.460	France	57	PC	Iopromide (PC)	2,66	South Korea	12
P	Diuron (P)	0.470	France	57	PCB	PCB101 (PCB)	ND	France	57
P	AMPA (P)	1.600	France; Switzerland	53 ; 57	PCB	PCB118 (PCB)	ND	France	57
P	Glyphosate (P)	3.4	France; Switzerland	53 ; 57	PCB	PCB138 (PCB)	ND	France	57
PAH	Acenaphthene (PAH)	ND	France	15 ; 57	PCB	PCB153 (PCB)	ND	France	57
PAH	Benzo[a]anthracene (PAH)	ND	France	15 ; 57	PCB	PCB180 (PCB)	ND	France	57
PAH	Benzo[b]fluoranthene (PAH)	ND	France	15 ; 57	PCB	PCB194 (PCB)	ND	France	57
PAH	Benzo[g,h,i]perylene (PAH)	ND	France	15 ; 57	PCB	PCB28 (PCB)	ND	France	57
PAH	Benzo[k]fluoranthene (PAH)	ND	France	15 ; 57	PCB	PCB52 (PCB)	ND	France	57
PAH	Chrysene (PAH)	ND	France	15 ; 57	PHT	Diethylhexyl phthalate (PHT)	ND	France	57
PAH	Dibenzo[a,h]anthracene (PAH)	ND	France	15 ; 57	VOC	Ethylbenzene (VOC)	ND	France	57
PAH	Benzo[a]pyrene (PAH)	0.005	France	15 ; 57	VOC	Tetrachloroethylene (VOC)	ND	France	57
PAH	Benzo[e]pyrene (PAH)	0.006	France	15 ; 57	VOC	Toluene (VOC)	ND	France	57
PAH	Indeno[1,2,3-cd]pyrene (PAH)	0.008	France	15 ; 57	VOC	Trichloroethylene (VOC)	ND	France	57
PAH	Anthracene (PAH)	0.009	France	15 ; 57	VOC	Xylene (VOC)	ND	France	57
PAH	Acenaphthylene (PAH)	0.020	France	15 ; 57	VOC	Hexachlorobenzene (VOC)	0.002	USA (New York)	56
PAH	Pyrene (PAH)	0.021	France	15 ; 57					
PAH	Fluoranthene (PAH)	0.025	France	15 ; 57					
PAH	Fluorene (PAH)	0.027	France	15 ; 57					
PAH	Phenanthrene (PAH)	0.085	France	15 ; 57					
PAH	Naphthalene (PAH)	0.180	France	15 ; 57					

292

293

294 3.4 Hazard of pollutants in separate and combined systems

295 Using ecotoxicological (PNEC) and chemical ( $MEC_{max}$ ) results previously enunciated we were  
296 able to calculate a very wide range of HQs in discharges (see Figures 5 and 6). The high dispersion of  
297 HQ values calculated could be explained by the heterogeneity of PNEC values observed in Figures 2 to  
298 4 and the heterogeneity of pollutant concentrations due to the high variability of anthropic activities, and  
299 thus that of the catchment leached by rain, and the variability of rainfall events (length, height, flow rate,  
300 etc.). Due to the relatively different nature and composition of stormwater and CSO, pollutant hazards  
301 associated to these two matrices are discussed separately in the following sections.

302 3.4.1 Hazard quotients in separate systems

303 Concerning stormwater samples, only 51 hazard quotients were calculated due to the low  
304 number of compounds found in the dissolved part (Figure 5). We found 14 compounds with an HQ  
305 lower than 1. The lowest hazard quotient was calculated for Metaldehyde (P) with an HQ of  $6.7 \cdot 10^{-5}$ .  
306 On the contrary, the majority of the micropollutants detected in stormwater samples had an HQ as high  
307 as 1 and are therefore potentially hazardous for aquatic ecosystems. Among these 37 compounds, 10  
308 (27.1%) were pesticides, and 9 PAHs (24.32%). It is also noteworthy that 4 of the 6 most hazardous  
309 compounds ( $HQ > 1000$ ) were pesticides. Among these very hazardous compounds, we also observed  
310 the presence of one ALK (4-p-nonylphenol) and one PAH (fluoranthene). The most hazardous  
311 compound found was permethrin, with a hazard quotient of 4166.6. The important hazard from  
312 pesticides (pyrethroids) linked to high HQ could be explained by the high ecotoxicity of these pesticides  
313 rather than by the concentrations found in discharges (around  $100 \text{ ng.L}^{-1}$ ). As pointed out before, most  
314 of these pesticides (such as bifenthrin, cypermethrin) have a very low PNEC value, lower than  $0.1 \text{ ng.L}^{-1}$ .  
315 <sup>1</sup>.

316 3.4.2 Hazard quotients in combined systems

317 Regarding CSO, only 43 HQs were calculated, also due to the low number of molecules  
318 measured in dissolved phase in CSO (Figure 6). The HQs obtained were lower than for separate systems.



319 Indeed, the highest HQ was found for lead, with a value of 68.29. Contrary to separate systems, the  
320 highest hazards were due to heavy metals, pesticides and pharmaceutical compounds. Only five families  
321 were found in this ranking (HQ >1): PC (3 compounds), M (4), PAH (1), P (5) and ALK (1), and were  
322 potentially hazardous for aquatic ecosystems. Results highlighted for heavy metals can be explained by  
323 the fact that certain heavy metals in these effluents were in high concentrations (e.g. 2.1  $\mu\text{g.L}^{-1}$  for lead  
324 and 1.6  $\mu\text{g.L}^{-1}$  for copper), and not because of their low ecotoxicity, as shown by their relatively high  
325 PNEC values. The presence of hazardous PC in CSO can be easily explained by the discharge of large  
326 amounts of these often very ecotoxic molecules coming from urban wastewater in stormwater, without  
327 any treatment. Comparing hazard quotients from CSO samples to those of separate systems, we can  
328 observe that calculated HQs are often lower (e.g. 65.4 in CSO against 950 in stormwater for copper).  
329 We can simply explain these results by a dilution of stormwater pollutants by wastewater in CSO.

#### 330 3.4.3 The case of pharmaceutical compounds in CSO studies

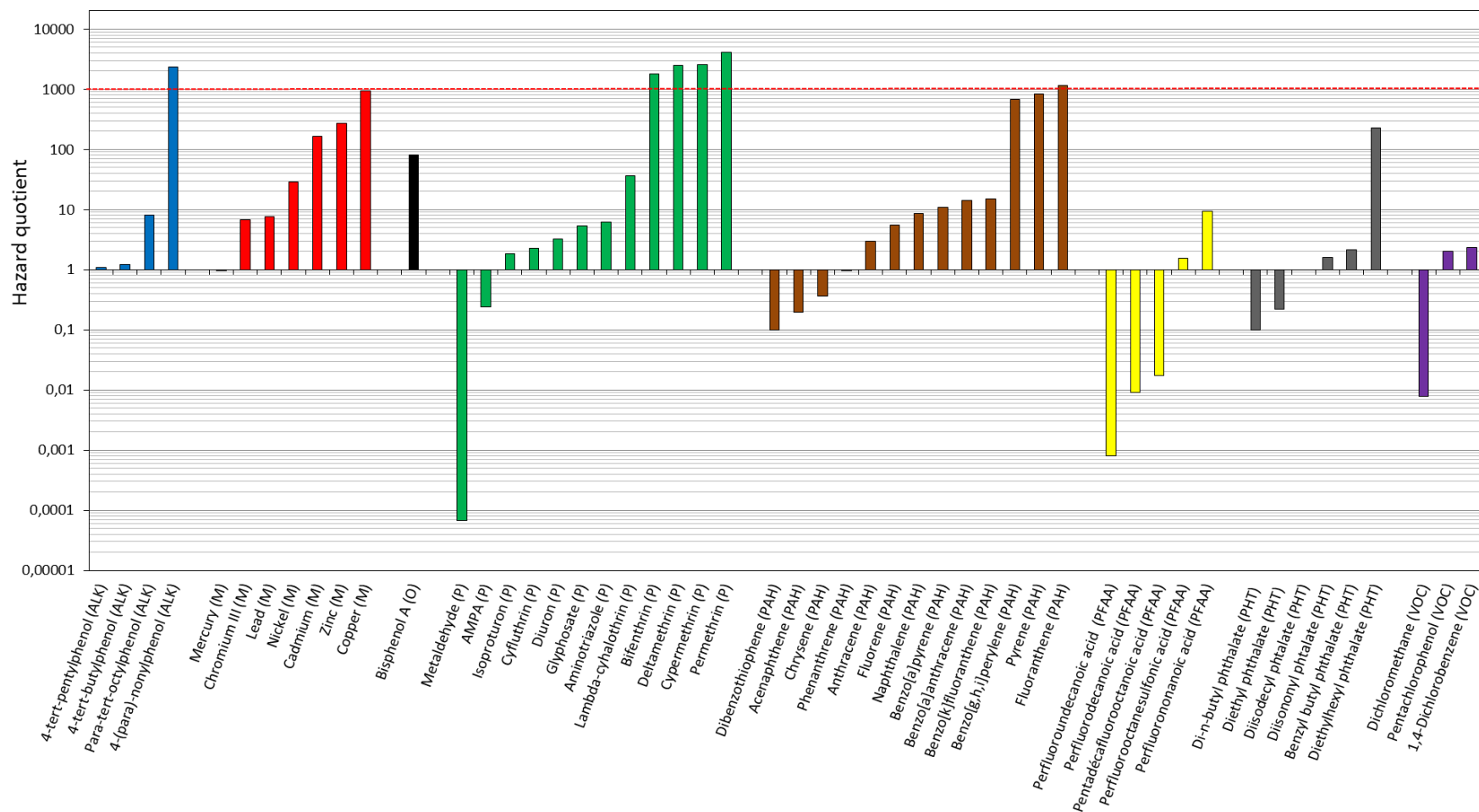
331 With the hazardous pharmaceutical compounds that have been highlighted above, 15 HQs have  
332 been calculated only and presented in Figure 6. As urban wastewater is mixed with stormwater in  
333 combined sewers, all the pharmaceutical compounds classically consumed in cities could be found in  
334 this type of discharge. However, few of them (28) have been taken into account to date in scientific  
335 literature. Consequently, our study and all the other ecotoxicological studies dealing with CSO contain  
336 a bias attributable to the fact that the potentially considerable hazard represented by these types of  
337 molecules is not taken into account. Indeed, as shown by Orias et al.<sup>36</sup>, many of them can have very low  
338 PNEC values (e.g. 17 $\beta$ -estradiol: 8  $\text{pg.L}^{-1}$ , clotrimazole: 0.5  $\text{pg.L}^{-1}$ ), and/or are widely consumed (e.g.  
339 ibuprofen and salicylic acid).

#### 340 3.4.4 The case of molecules (e.g., pesticides) forbidden by European legislation

341 Some of the pesticides involved in the hazard of UWWDs (found in both stormwater and CSO,  
342 such as diuron) were forbidden in 2008 by European legislation. However, several European  
343 studies<sup>65,66,67</sup> have detected the presence of these pesticides (with concentrations reaching 0.64  $\mu\text{g L}^{-1}$  in  
344 discharges). This observation can be notably explained by the fact that farmers have stored pesticides

345 purchased in the past and that they continue to use. Moreover, some of them linger on in the environment  
346 for long periods (due to their high half-life times) and their release can continue due to rainfall events.  
347 Consequently, it is true to say that the hazard represented by these pesticides continues to exist even if  
348 they are no longer on the market.

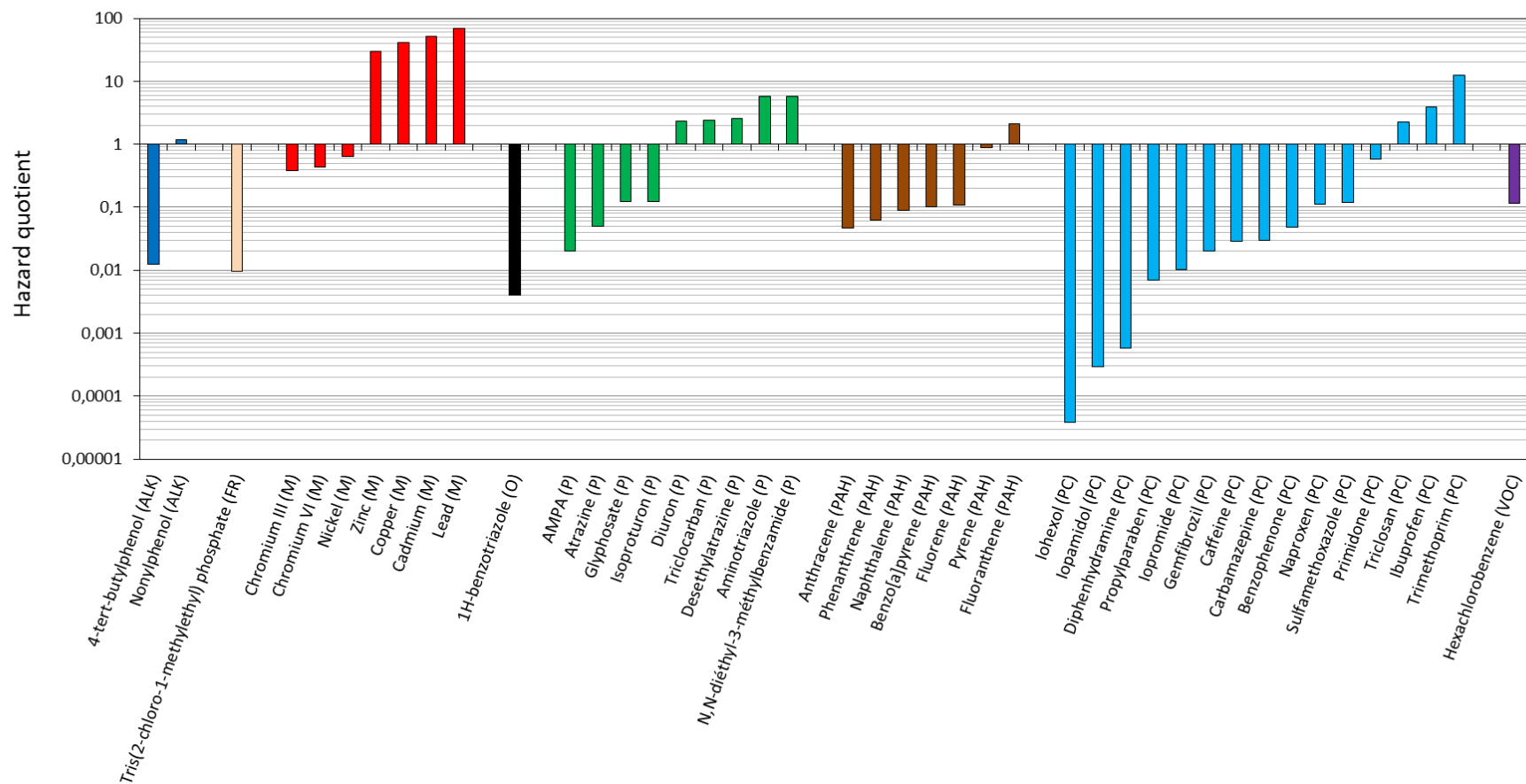
### Stormwater pollutant hazard quotients



349 Figure 5: Hazard quotients calculated for micropollutants detected in stormwater samples (the red line delimits the compounds with an HQ up to 1000,  
 350 considered very hazardous). Hazard quotients are ranked in ascending order into each separated pollutant family.

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### CSO pollutant hazard quotients



351 Figure 6: Hazard quotients calculated for micropollutants detected in CSO samples. Hazard quotients are ranked in ascending order into each separated  
 352 pollutant family.

353

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354 3.5 Discussion of the method and data used

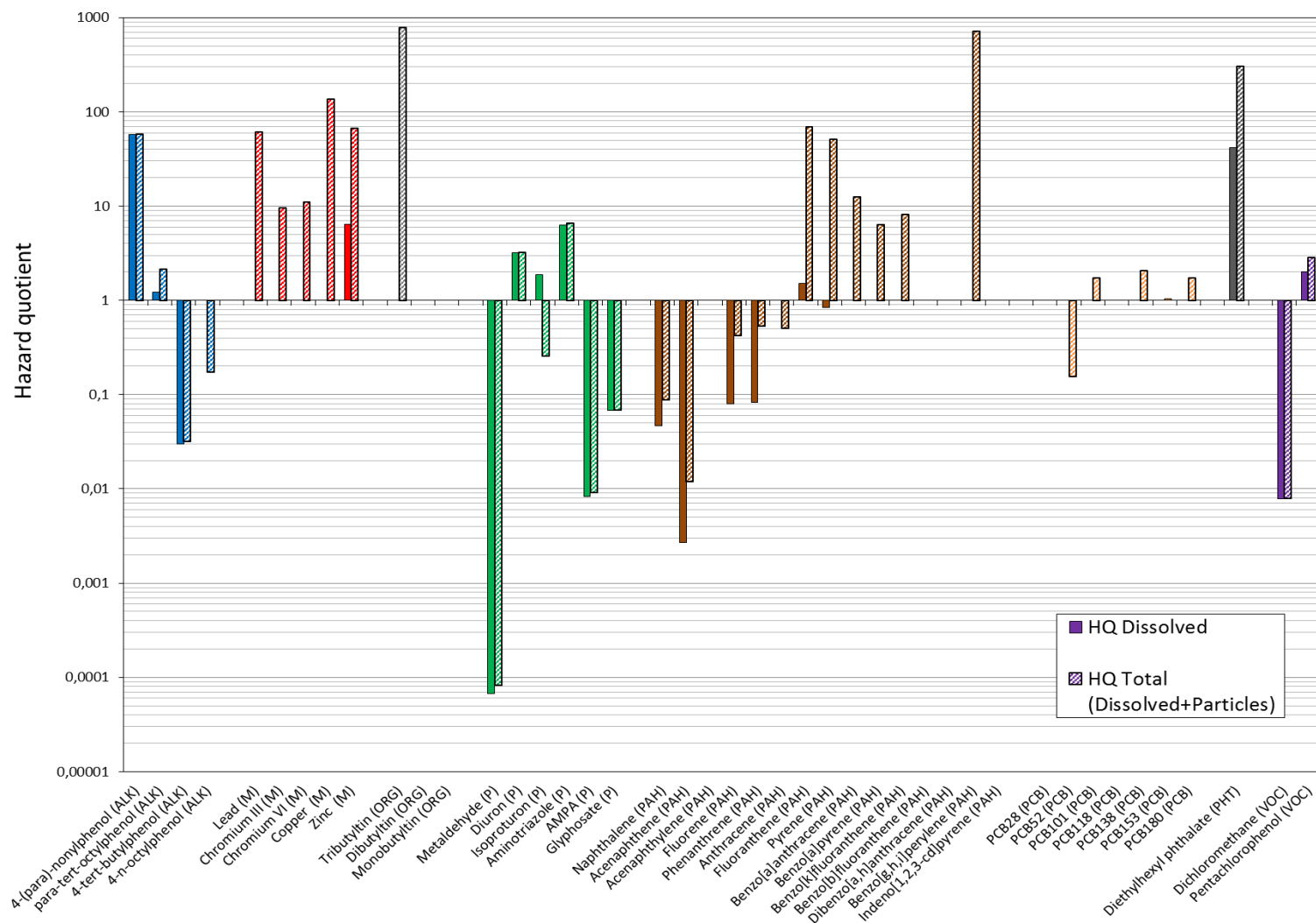
355           The method presented in this study proved to be relevant to detect UWWD pollutant hazards. It  
356 could be applied for many other matrices, and included in many risk assessment scenarios or chemical  
357 prioritization programs. Nevertheless, our method and results are subject to limitations that need to be  
358 developed. The first one is the non-consideration of certain parameters, such as the bioconcentration,  
359 bioaccumulation<sup>30</sup> and biomagnification of pollutants in the aquatic food web, which could amplify  
360 considerably the hazard of UWWDs pollutants. Indeed, these phenomena have already been  
361 demonstrated for many families of pollutants, such as the most hazardous found in UWWDs: heavy  
362 metals<sup>68</sup>, pesticides<sup>69,70</sup> and pharmaceutical compounds.<sup>71,72,73,74</sup> Other parameters such as pH,  
363 temperature, water chemistry (pH, hardness) can also modify pollutant toxicity. The “mixture” effect,  
364 linked to antagonisms of synergisms effects between sought, but also non-potentially thousand  
365 molecules not yet identified in UWWDs, are not considered into this study and can modify their  
366 hazardousness. Secondly, the use of NOECs for PNEC values construction can be discussed. The  
367 authors are aware that ECx values are more accurate than NOEC. ECx values are calculated from the  
368 modeling of the dose-response curve, which is itself based on the results of the whole range of  
369 concentration, whereas NOEC corresponds only to the identification of the last concentration of the  
370 range without effect. However, in the context of this work, it has been chosen to use to the largest set of  
371 values available in the literature and in international databases for the two reasons: (1) In the specific  
372 context of the PNEC calculation (i.e., a no-effect value for all aquatic organisms), considering the  
373 scarcity of existing data in the literature, it seems more useful to consider values for one or several  
374 additional species than using accurate values for a limited number of species. In other words, inter-  
375 species variability is more important to take into account than intra-species variability, (2) This is the  
376 most common approach adopted by international Agencies in charge of the establishment of PNECs for  
377 substances, such as INERIS in France, or the European Chemical Bureau in Europe, through the TGD  
378 guidelines. Thirdly, our method considers only the maximum concentrations of the different pollutants  
379 in UWWDs. Consequently, these values represent only the maximum hazard for each compound. This  
380 work could also have been done with median values if sufficient data had been available. This problem

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381 of limited data collection is at the origin of another limit: most of the chemical studies focusing on  
382 dissolved compound concentrations found in stormwater and CSO have dealt with relatively small areas  
383 of the world and many of them were published in Europe. Thus data are lacking for some continents, a  
384 factor which limits our studies due to differences in, for example, PC consumption, pesticide use (e.g.  
385 glyphosate is widely used in South America), sewer systems, etc. Consequently, we can confidently  
386 assert that the HQs calculated here are underestimated and would probably increase if more data were  
387 available. Fourthly, dissolved part of UWWDs were only considered in this study because the PNEC  
388 values were established for dissolved substances and it was impossible to extend them to pollutants  
389 whose bioavailability is unknown but present on particles in UWWDs. Indeed, pollutant bioavailability  
390 is linked to particle desorption which depends on multiple parameters like pH, molar mass,  
391 solubility/lipophily, and the number of carboxyl groups (for organic pollutants).<sup>75</sup> It is therefore possible  
392 that our method underestimated the hazard of these UWWD pollutants for aquatic environments. For  
393 example, as in the study of Zgheib et al.<sup>4</sup> if we had considered the concentration of fluoranthene in the  
394 dissolved phase ( $0.018 \mu\text{g L}^{-1}$ ) and the total effluent ( $0.832 \mu\text{g L}^{-1}$ ), assuming that all the pollutants are  
395 available, the hazard index of the pollutants would have increased from 1.5 to 69.33, making it one of  
396 the most hazardous compounds for aquatic organisms. This point is illustrated in Figure 7. Similar  
397 findings were recorded by Baun et al.<sup>30</sup> who prioritized 56 organic pollutants in the water phase of  
398 stormwater, against 121 in the solid phase. Fifthly, many chemical studies have considered only mineral  
399 and organic priority pollutants from the EU Water Framework Directive and other international  
400 legislations. However, many emerging compounds currently used present proven ecotoxic effects but  
401 have not yet been analyzed. For example, pesticides used massively in Europe like metam-sodium and  
402 epoxiconazole present relatively low PNEC values (respectively  $0.79$  and  $0.18 \mu\text{g L}^{-1}$ ). We can therefore  
403 expect high hazard quotients linked to these kinds of molecule. Finally, the presence of high  
404 concentrations of bacteria in CSO has already been detected, for example by Passerat et al. (with  
405 concentrations up to  $10^7$  cell/L for *E.coli*).<sup>76</sup> It is now known that bacteria can transform pollutants and  
406 create by-products that are more or less toxic than their parent compounds detected in CSO. These  
407 bacteria can therefore influence the composition of CSO and their toxicity with time.

408           Despite these limits, our method enabled us to highlight new outlooks in terms of prioritization  
409 and management of UWWD pollutants. Comparing our results to previous works done with the same  
410 purpose, we can observe that considering only intrinsic characteristics (e.g. particle solubility, sorption  
411 potential, ecotoxicity) of the pollutants selected, Baun et al.<sup>30</sup> classified 56 organic compounds as  
412 priority pollutants dissolved in water using their RICH (Ranking and Identification of Chemical  
413 Hazards) method against 37 in our case (of which 31 are organic). The difference between the two  
414 studies is particularly notable for pesticides (10 against 33 pesticides for the method of Baun et al.<sup>30</sup>).  
415 This difference can be explained by non-detected or low environmental concentrations of many  
416 pesticides dissolved in water of our studied discharges. On the contrary, we revealed here 9 hazardous  
417 PAH and 3 hazardous PHT instead of respectively 5 and 2 in Baun et al.<sup>30</sup> An explanation of this  
418 discrepancy could be the multiplication of decision filters (sorption/volatilization, technical problems,  
419 persistence, bioaccumulation, toxicity) applied by Baun et al. when selecting their compounds, and the  
420 lack of data for some pollutants that can lead to the rejection or selection of the priority list, as suggested  
421 by these authors. In the case of CSO linked hazard, no studies have investigated a similar prioritization  
422 method. Consequently, no comparison can be done.

423           Looking for the scientific literature, our study enabled us to find new hazardous and priority  
424 pollutants. The same observation could be made for the European (Urban Wastewater Directive (UWD  
425 91/271/EEC)) and American (USA EPA) priority pollutant lists. In fact, as stated in Table S2, some  
426 pollutant identified here as hazardous such as diuron or fluoranthene are already under the regulation of  
427 international instances. On the contrary, some pollutants are absent from these lists. For example, some  
428 heavy metals (e.g. copper and zinc in UWD list), pesticides as glyphosate or pyrethrinoids in stormwater,  
429 phthalates (e.g. diisononyl phthalate) and pharmaceuticals such as ibuprofen or trimethoprim in CSO  
430 absent in UWD and EPA priority lists, are revealed to be at the origin of an important hazard for aquatic  
431 receiving ecosystems, and thus should be so the object of reinforced controls and could be proposed to  
432 be added to these lists.



433 Figure 7: Example of hazard quotients (HQ) calculated with dissolved and total concentrations of pollutants in stormwater samples from Zgheib et al.<sup>4</sup>

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435 Conclusion and perspectives

436           The aim of our study was to develop and apply a methodology to determine and calculate hazard  
437 quotients associated with the different pollutants sought and found in UWWDs. A wide range of  
438 pollutants was sought in the latter, with highly variable ecotoxicity and concentrations. Although many  
439 families of pollutants (PC, PAH, VOC, ALK, M, P, O, PFAA and PHT) play a role in the UWWD  
440 hazards identified, we emphasize that they are comprised of a large number of pesticides and heavy metals  
441 (e.g. pyrethroids, copper and cadmium). The hazards of the pollutants identified in this study have  
442 different origins: (i) the presence of high concentrations of certain highly ecotoxic compounds (e.g.  
443 Pyrene in stormwater), (ii) the presence of high concentrations of slightly ecotoxic compounds (e.g.  
444 heavy metals in CSO), (iii) the presence of weak concentrations of certain highly ecotoxic compounds  
445 (e.g. pesticides like Bifenthrin and Permethrin in stormwater samples), (iv) the presence of intermediate  
446 concentrations of compounds with intermediate ecotoxicity (e.g. alkylphenols in UWWDs). We showed  
447 that the hazard linked to CSO was lower than that linked to stormwater from separate systems. However,  
448 these results should be considered with caution because only a few pharmaceutical compounds (just 28  
449 compounds) were sought in CSO, compared to the huge range of drugs consumed by human beings.  
450 Moreover, no ecotoxicity data were available for 13 of the compounds (3 PC, 6 PAH, 2 ALK, 1 ORG,  
451 1 PFAA) detected in UWWDs, and therefore no PNEC or HQ values could be calculated. Consequently,  
452 it will be necessary in further studies to obtain more ecotoxicity data on these compounds. Moreover,  
453 current hazard and risk assessment methods must be improved to take into account pollutant  
454 bioconcentration/accumulation, which can represent a serious risk for higher trophic levels.

455           To conclude, this work enabled us to identify the potential hazard of UWWDs and the pollutants  
456 involved. We now know which pollutants require an in-depth monitoring. We have also identified  
457 different points which require in-depth studies. In particular, it is now necessary to better assess the  
458 hazard of certain pollutants bound to the particulate phase. Lastly, this work should help managers to identify  
459 the largest and most hazardous pollution sources in order to treat them in priority.

460

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593 Table S1: Extrapolation Factor assessment criteria derivate from Orias and Perrodin<sup>36</sup> and TDG<sup>37</sup>.

Available data	EF (Extrapolation Factor)
At least one short-term L(E)C50 from each of three trophic levels of the base-set (e.g. algae, daphnids and fishes)	1000
One long term chronic data (e.g. invertebrate or fish)	100
Two long term chronic data from species representing two trophic levels (e.g. algae and/or daphnids and/or fishes)	50
Two long term chronic data from species representing three trophic levels (e.g. algae, daphnids and fishes)	10
Statistics method (e.g. species sensitivity distribution (SSD)), field data or model ecosystem	5-1 (Reviewed case by case)

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Pollutant	Identified as hazardous		Identification as a priority substance	
	In stormwater	In combined sewer overflows	In European Water Framework Directive (WFD, 2000/60/EC) pollutant priority list	In Environmental Protection Agency pollutant priority list
4-(para)-nonylphenol (ALK)	Yes	No	Yes	No
4-tert-pentylphenol (ALK)	Yes	No	Yes	No
4-tert-butylphenol (ALK)	Yes	No	Yes	No
Nonylphenol (ALK)	No	Yes	Yes	No
Para-tert-octylphenol (ALK)	Yes	No	Yes	No
Cadmium (M)	Yes	Yes	Yes	Yes
Chromium III (M)	Yes	No	No	Yes
Copper (M)	Yes	Yes	No	Yes
Lead (M)	Yes	Yes	Yes	Yes
Nickel (M)	Yes	No	Yes	Yes
Zinc (M)	Yes	Yes	No	Yes
Bisphenol A (O)	Yes	No	No	No
Aminotriazole (P)	Yes	Yes	No	No
Bifenthrin (P)	Yes	No	No	No
Cyfluthrin (P)	Yes	No	No	No
Cypermethrin (P)	Yes	No	Yes	No
Deltamethrin (P)	Yes	No	No	No
Desethylatrazine (P)	Yes	Yes	No	No
Diuron (P)	Yes	Yes	Yes	No
Glyphosate (P)	Yes	No	No	No
Isoproturon (P)	Yes	No	Yes	No
Lambda-cyhalothrin (P)	Yes	No	No	No
N,N-diethyl-3-méthylbenzamide (P)	No	Yes	No	No
Permethrin (P)	Yes	No	No	No
Triclocarban (P)	No	Yes	No	No
Anthracene (PAH)	Yes	No	Yes	Yes
Benzo[a]anthracene (PAH)	Yes	No	Yes	Yes
Benzo[k]fluoranthene (PAH)	Yes	No	Yes	Yes
Benzo[g,h,i]perylene (PAH)	Yes	No	Yes	Yes
Benzo[a]pyrene (PAH)	Yes	No	Yes	Yes
Fluoranthene (PAH)	Yes	Yes	Yes	Yes
Fluorene (PAH)	Yes	No	Yes	Yes
Naphthalene (PAH)	Yes	No	Yes	Yes
Pyrene (PAH)	Yes	No	Yes	Yes
Ibuprofen (PC)	No	Yes	No	No
Triclosan (PC)	No	Yes	No	No
Trimethoprim (PC)	No	Yes	No	No
Perfluorooctanesulfonic acid (PFAA)	Yes	No	Yes	No
Perfluorononanoic acid (PFAA)	Yes	No	Yes	No
Benzyl butyl phthalate (PHT)	Yes	No	No	Yes
Diethylhexyl phthalate (PHT)	Yes	No	Yes	Yes
Diisononyl phthalate (PHT)	Yes	No	No	No
1,4-Dichlorobenzene (VOC)	Yes	No	No	Yes

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	Pentachlorophenol (VOC)	Yes	No	Yes	Yes
617	Table S2: Comparison of hazardous compounds list identified in UWWDs in this study with the				
618	classification of these compounds as priority pollutants or not by European Water Framework				
619	Directive and In Environmental Protection Agency.				