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1 **PRIORITY POLLUTANTS IN URBAN STORMWATER:**
2 **PART 2 - CASE OF COMBINED SEWERS**

3 Johnny Gasperi^{1*}, Sally Zgheib^{2,3}, Mathieu Cladière¹, Vincent Rocher⁴,
4 Régis Moilleron¹, Ghassan Chebbo²

- 5 1. Université Paris-Est, LEESU, UMR MA 102 - AgroParisTech, 61 avenue du Général de
6 Gaulle, 94010 Créteil Cedex, France.
7 2. Université Paris-Est, LEESU, UMR MA 102 - AgroParisTech, 77455 Marne-la-Vallée 2,
8 France.
9 3. Lebanese Center for Water Management and Conservation / United Nations Development
10 Programme (UNDP), Ministry of Energy and Water, Corniche du fleuve, Beirut (Lebanon).
11 4. SIAAP, Direction du Développement et de la Prospective, 82 avenue Kléber, 92700
12 Colombes, France.
13

14 **Abstract**

15 This study has evaluated the quality of combined sewer overflows (CSO) in an urban
16 watershed, such as Paris, by providing accurate data on the occurrence of priority pollutants
17 (PPs) and additional substances, as well as on the significance of their concentrations in
18 comparison with wastewater and stormwater. Of the 88 substances monitored, 49 PPs were
19 detected, with most of these also being frequently encountered in wastewater and stormwater,
20 thus confirming their ubiquity in urban settings. For the majority of organic substances,
21 concentrations range between 0.01 and 1 µg.l⁻¹, while metals tend to display concentrations
22 above 10 µg.l⁻¹. Despite this ubiquity, CSO, wastewater and stormwater feature a number of
23 differences in both their concentration ranges and pollutant patterns. For most hydrophobic
24 organic pollutants and some particulate-bound metals, CSOs exhibit higher concentrations
25 than those found in stormwater and wastewater, due to the contribution of in-sewer deposit
26 erosion. For pesticides and Zn, CSOs have shown concentrations close to those of
27 stormwater, suggesting runoff as the major contributor, while wastewater appears to be the
28 main source of volatile organic compounds. Surprisingly, similar concentration ranges have
29 been found for DEHP and tributyltin compounds in CSOs, wastewater and stormwater. The
30 last section of this article identifies substances for which CSO discharges might constitute a
31 major risk of exceeding Environmental Quality Standards in receiving waters and moreover
32 indicates a significant risk for PAHs, tributyltin compounds and chloroalkanes. The data
33 generated during this survey can subsequently be used to identify PPs of potential
34 significance that merit further investigation.

35 **Keywords**

36 Combined sewer overflows, priority pollutants, urban area, stormwater, Water Framework
37 Directive.
38

* Corresponding author: Fax: +33 (0)1 45 17 16 27, e-mail: gasperi@u-pec.fr

1 **1. Introduction**

2 The European Community's strategy for combating surface water pollution by means
3 of a control policy was set forth in the European Water Framework Directive 2000/60/EC
4 (WFD). Decision no. 2455/2001/EC, adopted by the European Parliament and Council on
5 November 20, 2001, established the list of priority substances in the field of water policy and
6 amended Directive 2000/60/EC. This decision provided the first list of 33 substances or
7 groups of substances to be identified as action priorities at the Community level. Among these
8 priority pollutants (PPs), some have been identified as "priority hazardous substances", whose
9 emissions, discharges and losses are scheduled to be phased out or completely removed. More
10 recently, on July 17, 2006, the Commission adopted a Directive intended to set mandatory
11 environmental quality standards on priority substances, requiring Member States to come into
12 compliance by 2015 in order to ensure a "satisfactory chemical status for surface water".

13 In pursuit of these WFD objectives through identifying possible pollutant reduction
14 measures, an inventory of sources in the urban environment has definitely proven necessary.
15 Since priority pollutants can enter aquatic ecosystems via effluents from wastewater treatment
16 plants and industries, as well as via combined sewer overflows (CSOs) and stormwater,
17 accurate knowledge of the PPs discharged by such sources is required. Even though a number
18 of studies or National Action Plans have been undertaken to identify the occurrence and
19 significance of specific PPs in wastewater (Rule *et al.*, 2006a, b; Rowsell *et al.*, 2010;
20 Eriksson *et al.*, 2010), in wastewater treatment plant effluent (Ruel *et al.*, 2010) and in the
21 aquatic system (Gasperi *et al.*, 2009), no comprehensive broad overview of the PP
22 contamination of stormwater in both separate and combined sewers is available. The
23 continued existence of uncontrolled or poorly-controlled discharges from stormwater and
24 CSOs could however constitute a major reason for the long-term persistence of low-quality
25 water (Clark *et al.*, 2006). Moreover, the magnitude of stormwater pollutant loads, their

1 subsequent acute impact on receiving waters and their reliable and sensitive modelling have
2 all remained key issues since 1990 (Chebbo and Saget, 1995; Deletic, 1998; Suarez and
3 Puertas, 2005; Lau *et al.*, 2009; Dotto *et al.*, 2010). Although Eriksson *et al.* (2007) proposed
4 a list of substances based on a theoretical assessment of stormwater substances (CHIAT:
5 Chemical Hazard Identification and Assessment Tool), this list has not yet been
6 experimentally screened on stormwater samples. To date, only limited information is
7 available on a number of historical substances such as metals, polycyclic aromatic compounds
8 (PAHs) and polychlorinated biphenyls (PCBs) (Iannuzzi *et al.*, 1997; Gromaire *et al.*, 2001;
9 Davis *et al.*, 2001; Rossi *et al.*, 2004).

10 Due to this lack of information available on PP levels in urban stormwater in both
11 separate and combined sewers, the OPUR research programme (Observatory of Urban
12 Pollutants, 2006-2012) has sought to investigate stormwater quality in urban watersheds. The
13 general objective herein has been to provide data on both the occurrence and concentration of
14 PPs along with a few additional substances in stormwater and CSOs. A methodology based
15 on the EU's list of priority substances and the CHIAT approach was therefore developed by
16 Zgheib *et al.* (2008) in conjunction with a list of 88 pollutants (containing 80 organic
17 substances and 8 metals) and ultimately adopted in order to monitor stormwater quality. In
18 considering that the analyses carried out on unfiltered samples yield poor-quality data with
19 respect to the representativeness of sample contamination in addition to offering only partial
20 information on the chemical fate, the applicable methodology requires analysing both the
21 dissolved and particulate fractions. The first step of the OPUR programme was dedicated to
22 stormwater quality in connection with the urbanisation gradient (from residential to more
23 densely urbanised areas, **Figure 1**). This work is partially described in Zgheib *et al.* (2011a)
24 and then more extensively discussed in Zgheib *et al.* (2011b, same issue). In accordance with
25 the same methodology and approach, the present study, as the second part in a two-article

1 series, focuses on CSO quality. The largest CSO outfall in the Paris metropolitan area was
2 equipped and a total of 4 CSO discharges were considered. Since CSOs make up a mixture of
3 untreated wastewater and stormwater, the wastewater quality was also investigated according
4 to the same methodology (i.e. through monitoring of the 88 pollutants identified). This study
5 therefore is the first relevant assessment to provide new and accurate knowledge on the
6 occurrence and concentrations of a wide array of pollutants in CSOs and on their significance
7 in comparison with concentrations found in wastewater and stormwater. The final objective of
8 this paper is to determine the potential impact of CSO discharges in receiving waters, as
9 regards Environmental Quality Standards (EQS).

10 **2. Materials and methods**

11 *2.1 Site description and rain event characteristics*

12 Paris proper (*intra-muros*) is drained by a combined sewer system covering a land area
13 of 105 km². This area is densely populated (2.15 million inhabitants, i.e., approximately
14 20,500 inhabitants/km²) and features many small shops, offices and very little industrial
15 activity. In this study, the largest CSO outfall, located in Paris' north-western district, has
16 been considered ("Clichy" outfall, [Figure 1](#)). Over the 2009-2010 period, some 52 discharges
17 occurred annually, responsible for discharging between 25,000 and 1,000,000 m³ into the
18 Seine River. This outfall is supervised by the Paris public sanitation service (SIAAP).

19 In order to collect CSO samples, flow was continuously monitored using an automatic
20 flowmeter that combined water level and velocity sensors; moreover, water samples were
21 collected by two automatic vacuometric samplers equipped with glass and plastic bottles for
22 organic and inorganic sampling, respectively. Teflon pipes were also used. Samples were
23 removed at a fixed time interval (about 5 min), and 6 sub-samples per bottle were collected.
24 The bottles were then picked up in order to produce a flow-weighted composite sample

1 representative of the entire rain event as determined by flow rate measurements. A total of 4
2 CSO discharges were thus collected. Table 1 summarises the main characteristics of the rain
3 events and discharges (precipitation height, volume discharged, conductivity, etc.). Two
4 exceptional discharges, corresponding to summer storms, were collected on July 12th and
5 14th, 2010 (**C1 and C2 event designation**), with volumes of roughly 600,000 and 1,000,000
6 m³, respectively. Moderate discharges (September 8th and 24th, 2010) were also collected (**C3
7 and C4 event designation**). This type of discharge has been the most frequently observed at
8 the Clichy outfall over the last 2 years, during which time a discharge range from 40,000 to
9 300,000 m³ has encompassed about 80% of all discharges. At the same site, wastewater was
10 also collected and analysed. **According to the conductivity of raw sewage (between 1,050-
11 1,170 $\mu\text{S}\cdot\text{cm}^{-1}$ measured on the site during dry periods) and values provided by Kafi *et*
12 *al.* (2008) for runoff (80 - 150 $\mu\text{S}\cdot\text{cm}^{-1}$), the runoff and wastewater proportions can be
13 calculated with a simple linear regression using the conductivity of the flow-weighted
14 composite sample since conductivity is conservative. To consider uncertainties in the
15 method calculation, the minimal and maximal runoff proportions were calculated
16 (hypothesis min: 1,050 and 150 $\mu\text{S}\cdot\text{cm}^{-1}$ for runoff and wastewater, hypothesis max:
17 1,170 and 80 $\mu\text{S}\cdot\text{cm}^{-1}$, respectively).**

18 For the studied discharges, the proportion of runoff remains especially high (at least
19 69%-75% of runoff). The discharges on July 14th (C2) exhibited the highest runoff
20 proportion, while the September 8th (C3) value was noteworthy for its slightly lower runoff
21 proportion (Table 1). Other discharges (**C1 and C4**) revealed runoff proportions of between
22 75% and 89%. Similar estimations based on nitrogen concentration provided comparable
23 results.

1 **2.2 Experimental procedure**

2 *Routine wastewater parameters*

3 For each sample, routine wastewater parameters, such as total solids (TS), chemical
4 and biochemical oxygen demands (COD and BOD₅), ammonium (NH₄⁺), total Kjeldahl
5 nitrogen (TKN), total phosphorous (P_{tot}) and orthophosphates (PO₄³⁻), were analysed. As
6 reported in Supporting Table 1, these parameters were measured in accordance with French
7 standards.

8 *Priority substances*

9 As described by Zgheib et al. (2011b, same issue), a total of 88 substances were
10 monitored for each sample (Table 2). Except for metals and volatile organic compounds
11 (VOCs) including halogenated volatile organic compounds and BTEX (benzene* (in this
12 article, priority hazardous substances are marked with *), toluene, ethylbenzene and
13 xylenes) which were analysed on the total fraction, both dissolved and particulate fractions
14 were assessed for each individual compound. Analysis was performed by the IPL-Brittany
15 Laboratory, certified by the French Ministry of Ecology, Sustainable Development, Transport
16 and Housing (via the COFRAC accreditation committee).

17 **3. Results and discussion**

18 *3.1 Wastewater quality parameters in combined sewer overflows*

19 Routine wastewater quality parameters for the collected discharges as well as for a
20 large number of rain events (SIAAP CSO database, n=52) are given in Table 3. Data for
21 wastewater (on the same site) and runoff (Kafi *et al.*, 2008) are also reported. In spite of a
22 high runoff proportion, the CSO reveals an organic strength (COD concentrations greater than
23 140 mg.l⁻¹, BOD₅ above 40 mg.l⁻¹), albeit with less household wastewater than is typical
24 (Tchobanoglous *et al.*, 2003). While C1 and C4 discharges were quite similar in their

1 concentrations of carbonaceous pollution, differences were still observed between C2 (the
2 lowest concentration) and C4 (the highest). These differences may be partially tied to: i) the
3 relative proportion of wastewater that gets mixed with runoff, and ii) the previous dry period
4 prior to these rain events. A rougher comparison of CSO and wastewater concentrations
5 allows differentiating two groups of parameters. The first group, which includes BOD₅, TKN
6 and NH₄⁺, exhibits higher wastewater concentrations than the group observed during the
7 storm period, thus underscoring the fact that wastewater constitutes the major source for these
8 pollutants. In the literature, it is well documented that most of these elements originate mainly
9 from human sources (especially via urine and faeces) and from various activities such as
10 washing and cooking (Wilkie *et al.*, 1996; Tchobanoglous *et al.*, 2003). More recently,
11 Gasperi *et al.* (2010) confirmed that wastewater is the major source of organic and
12 nitrogenous pollution in CSOs. The second group comprised COD, TS and P_{tot}, with these
13 parameters presenting comparable wastewater and CSO concentrations. While urban runoff
14 contains rather low COD, TS and P_{tot} concentrations, wastewater dilution by runoff should
15 induce even lower CSO concentrations. This trend however was not observed, owing to the
16 erosion of in-sewer deposits accumulated during dry weather flow periods in sewer trunks
17 (Gromaire *et al.*, 2001). At the scale of Paris' combined sewer, Gasperi *et al.* (2010) indicated
18 that from 47% to 69% for TS and from 34% to 61% for COD are tied to the erosion of in-
19 sewer deposits; on the other hand, runoff only plays a minor role.

20 **3.2 Priority pollutants in combined sewer overflows**

21 *Priority pollutants and detection frequency*

22 Depending on the rain event under consideration (C1, C2, C3 and C4), between 34 and
23 44 PPs were detected. While the number of detected PPs ranges between 34 and 38 for C1,
24 C2 and C3, C4 with the highest wastewater proportion exhibited the greatest number of
25 detected PPs (n=44). On the whole, 39 PPs were never detected in CSOs. In comparison, 33

1 and 25 PPs were never quantified in stormwater (Zgheib *et al.*, 2011, same issue) and
2 wastewater (Zgheib *et al.*, 2010), respectively. Out of these 39 never detected PPs and by
3 comparing all matrices (CSO, wastewater and runoff), 30 substances were either never
4 detected or only detected with a frequency of less than 15% (Table 4). The full list of
5 undetected molecules, as well as their detection and quantification limits, is provided in
6 Supporting Table 2. The non-quantification of most molecules may be explained by the levels
7 of these chemicals lying below the available analytical limits of detection (as is typically the
8 case for low-level metals such as Cd* or Pt, PCB 194, or octa-BDE). For other substances,
9 their non-quantification is indicative of being phased out in France and removed from the
10 market (which is the case for several banned pesticides, hexachlorobenzene* or carbon
11 tetrachloride). Of the 88 priority substances monitored in both the particulate and dissolved
12 phases, 49 different PPs including 19 priority hazardous substances* (PHS*) were detected
13 (Table 4).

14 *Priority pollutant concentrations and comparison with levels found in wastewater and*
15 *stormwater*

16 To better visualise the PP contamination of CSOs, the total even mean concentrations
17 (expressed in $\mu\text{g.l}^{-1}$) for the discharges considered have been reported in Figure 4. The
18 concentrations of 58 PPs (i.e. 88 PPs monitored minus 30 PPs never detected) are illustrated.
19 Additional information on dissolved and particulate concentrations is provided in Supporting
20 Table 3. In comparing the quality of CSO with that of other matrices, the concentrations
21 found for stormwater (n=15, Zgheib *et al.*, 2011 - same issue) and for wastewater have also
22 been given in Figure 4. For both matrices, the median concentrations (d50) as well as the first
23 and last deciles (d10 and d90) are listed. For wastewater, since no significant differences in
24 wastewater contamination were observed between Clichy (n=7) and other experimental sites
25 (n=4), all data on wastewater quality were compiled (n=11). For each matrix and compound,

1 the frequency of detection (%) is also indicated. Moreover, Figure 4 illustrates the ratios
2 between CSO concentrations and the median wastewater or runoff concentrations.

3 *Metals*

4 High concentrations of Zn (658-1,137 $\mu\text{g.l}^{-1}$), Cu (86-134 $\mu\text{g.l}^{-1}$) and Pb* (46-175 $\mu\text{g.l}^{-1}$)
5 were observed in CSOs. Cr was also noticeable yet at lower concentrations (12-20 $\mu\text{g.l}^{-1}$),
6 in accordance with the low levels reported in domestic wastewater (Comber and Gunn, 1996).
7 From an overall perspective, the metal concentrations found were close to those reported by
8 Gromaire *et al.* (2002) in wet weather flows at the scale of the Marais catchment (centre of
9 Paris, 4th arrondissement): 1,024-3,343 $\mu\text{g.l}^{-1}$ for Zn, 132-377 $\mu\text{g.l}^{-1}$ for Pb*, and 58-208 $\mu\text{g.l}^{-1}$
10 for Cu. These results resembled those found by Kafi *et al.* (2008) at the largest Paris city scale
11 (760-1,832 $\mu\text{g.l}^{-1}$ for Zn, 55-289 $\mu\text{g.l}^{-1}$ for Pb* and 66-231 $\mu\text{g.l}^{-1}$ for Cu).

12 As illustrated in Figures 1 and 2, CSO exhibits higher Cu and Pb* concentrations and
13 a much higher Zn concentration than those of wastewater. As initially reported by Gromaire
14 *et al.* (2001), and depending on the metal under consideration, these differences may be
15 explained by: i) the high metal concentrations found in runoff, or ii) in-sewer deposit erosion.
16 As regards Cu and according to the authors, runoff and wastewater are only minor
17 contributors (less than 30%), while exchanges with in-sewer stocks remain a considerable
18 source (30%-70%). For Zn and Pb*, runoff serves as the main source of CSO pollution at the
19 scale of the Paris sewer network. This strong contribution from runoff is highly correlated
20 with the heavy metal contamination of roof runoff. Gromaire *et al.* (2002) demonstrated that
21 such heavy metal contamination is mainly correlated with Paris' roofs since most of them
22 feature metal roof coverings and fittings.

23 As for Zn and Pb*, CSOs also exhibit higher concentrations than those measured in
24 stormwater by Zgheib *et al.* (2011b, same issue). The difference observed is mainly explained
25 by the change in land use between suburban catchments and the Paris metropolitan area.

1 While the suburban catchments considered by Zgheib et al. (2011b, same issue) to
2 characterise stormwater are residential (most buildings equipped with tile roofs), the majority
3 of roofs within the Paris city limits have been fitted with metal materials, such as lead fittings
4 and zinc sheets, thus leading to high metal concentrations.

5 *Polycyclic Aromatic Hydrocarbons (PAHs)*

6 In this study, all 16 US-EPA PAHs were monitored: naphthalene* (N), acenaphthalene
7 (Acen), acenaphthylene (Acyl), fluorene (F), phenanthrene (P), anthracene* (A*),
8 fluoranthene* (Fluo*), pyrene (Pyr), benzo[*a*]anthracene (B(a)A), chrysene (Chry),
9 benzo[*a*]pyrene* (B(a)P*), benzo[*b*]fluoranthene* (B(b)F*), benzo[*k*]fluoranthene* (B(k)F*),
10 dibenz[*ah*]anthracene (D(ah)A), benzo[*ghi*]perylene* (B(ghi)P*), and indeno[*cd*]pyrene *
11 (IP*). The CSO concentrations of Σ 16 PAHs ranged from 0.98 to 2.58 $\mu\text{g.l}^{-1}$. Concentrations
12 found in CSOs were typically within the same range as those reported by Kafi *et al.* (2008)
13 (1.04-4.81 $\mu\text{g.l}^{-1}$ for Σ 16 PAHs, with the median equalling 2.12 $\mu\text{g.l}^{-1}$). No special
14 relationship between PAH concentrations and the proportion of runoff was observed. PAHs
15 were correlated with TS since they are preferentially associated with particulate matter (>
16 85% for Σ 16 PAHs). PAHs with light molecular weights (LMW, 2 or 3 benzene rings) were
17 predominant in dissolved phase, while PAHs with high molecular weights (HMW, 4 to 6
18 benzene rings) were predominant in particulate phase. For Σ 16 PAHs, HMW contributes to
19 more than 75% of total PAHs. As suggested by this predominance and the high contributions
20 of fluoranthene* and pyrene (approx. 15% each), the PAH distribution confirms the pyrolytic
21 origins of this contamination (Soclo *et al.*, 2000). This contamination can certainly be
22 correlated with the high density of combustion sources inside Paris city limits. The Paris
23 metropolitan area indeed generates heavy road traffic; consequently, both diesel- and
24 gasoline-powered vehicles are responsible for emitting great quantities of PAH into the
25 environment.

1 In sum, CSO concentrations appear to be higher than those measured in wastewater
2 and stormwater at suburban catchment outlets (spanning the range from residential to
3 densely-populated urbanised areas). Stormwater concentrations actually varied between 0.77
4 and 6.14 $\mu\text{g.l}^{-1}$ (with the median at 1.36 $\mu\text{g.l}^{-1}$), while the concentrations found in wastewater
5 occupied the 0.20-1.22 $\mu\text{g.l}^{-1}$ range (median: 0.47 $\mu\text{g.l}^{-1}$). As previously explained for Cu and
6 organic matter, the erosion of in-sewer deposits can explain the differences observed.
7 According to Gasperi *et al.* (2010), who established the mass balance of PAH loads during
8 wet weather flows, the wastewater and runoff contributions do not exceed 30%, while in-
9 sewer processes constitute a major source of PAHs (between 40% and 70%).

10 *Polychlorinated biphenyls (PCBs)*

11 Despite being banned in France since 1987, six congeners (PCB 28, 101, 118, 138,
12 153 and 180) were commonly detected in CSOs with total concentrations ranging from 12 to
13 26 ng.l^{-1} (Fig. 1). These concentrations found in CSOs were lower than those reported by
14 Rossi *et al.* (2004) in stormwater (0.11-403 ng.l^{-1}). The authors however have reported similar
15 PCB distributions dominated by heavy congeners (PCB 138, 153 and 180), thus reflecting
16 typically diffuse inputs (Chevreuil *et al.*, 1996).

17 As for PAHs, rainy periods enhance PCB wastewater concentrations (Figs. 1 and 2).
18 During dry periods, low PCB levels have been measured in wastewater (2.0-12.0 ng.l^{-1} , with
19 the median at 4.2 ng.l^{-1}), which shows good agreement with the values reported by Vogelsang
20 *et al.* (2006) (3.4-4.1 ng.l^{-1}). Since CSO concentrations are higher than concentrations found
21 in bulk deposition for Paris (0.6 and 8.1 ng.l^{-1} for Σ 7 PCBs, according to Blanchard *et al.*,
22 2007), the difference in PCB concentrations during dry and wet periods can most certainly be
23 explained by the remobilisation of PCB stock either on the urban surfaces or within the
24 combined sewer. The difference in PCB distributions between bulk deposition and CSO, as
25 characterised by a more pronounced contribution of heavy congeners (PCB 138, 153 and

1 180), has confirmed these local inputs. Surprisingly, CSO concentrations are far less than the
2 values reported for stormwater by Zgheib et al. (2011b, same issue), i.e. 74, 272 and 711 ng.l⁻¹
3 for d10, d50 and d90, respectively, based on Σ 7 PCBs. These differences may be due to
4 either a higher probability of finding PCB stock in suburban catchments or the higher
5 remobilisation of PCB stock on these catchments. Further investigation is now required to
6 better understand these differences.

7 *Tributyltin compounds*

8 The concentrations of tributyltin* (TBT*), dibutyltin* (DBT*) and monobutyl*
9 (MBT*) compounds are all illustrated in Figure 4. Whereas C1, C2 and C4 discharges exhibit
10 similar concentration ranges (29-32 ng.l⁻¹ for TBT*, 30-47 ng.l⁻¹ for DBT* and 47-64 ng.l⁻¹
11 for MBT*), discharge C3, which features a higher wastewater proportion, revealed 2-10 times
12 higher concentrations (105, 220 and 750 ng.l⁻¹ for TBT*, DBT* and MBT*, respectively).
13 These concentrations were explained by a higher TS concentration, along with an increase of
14 the organotin contents in these particles. As an example, for MBT*, a distinct content
15 difference was observed (0.75 $\mu\text{g.g}^{-1}.\text{dw}$ vs. 0.18-0.35 $\mu\text{g.g}^{-1}.\text{dw}$). In CSOs, the distributions
16 were clearly marked by the predominance of MBT* (38%-68%), followed by DBT* (19%-
17 38%). Up until this point however, the occurrences of MBT* and DBT* have primarily been
18 correlated with the microbial and/or photochemical degradation of TBT*, as the presence of
19 both compounds and their lack of dependence on TBT* provide support to the notion that
20 DBT* and MBT* occur not only as degradation products of TBT*.

21 Except for discharge C3, which clearly exhibits higher concentrations than those
22 reported in either stormwater (Zgheib *et al.*, 2011, same issue) or wastewater, no notable
23 difference in concentration ranges appears for TBT*, DBT* and MBT* in CSO, wastewater
24 and stormwater (Figs. 1 and 2). These similar concentration ranges observed across all
25 matrices are certainly derived from the frequency of organotin occurrence and its wide

1 industrial applications (pesticides used in agriculture, wood preservatives, industrial water
2 cooling towers, and many types of PVC applications). Recent evidence has been found of the
3 direct input of MBT* and DBT*, most likely caused by leaching from PVC materials and
4 house paint (Hoch, 2001). Even if the concentration ranges were quite similar for all matrices,
5 the wastewater was characterised by a higher TBT* proportion, whereas stormwater and CSO
6 distributions were more readily dominated by MBT* and DBT*. This finding could confirm
7 that the leaching of building materials (PCV, house paint, etc.) releases both compounds.

8 *Volatile organic compounds (VOCs)*

9 Out of the 12 VOCs monitored, only tetrachloroethylene was detectable in all samples
10 ($2.6-9.0 \mu\text{g.l}^{-1}$), while ethylbenzene, toluene, xylene and trichloroethylene were occasionally
11 detected (occurrence frequency varied from 25% to 50%). For the discharge C3 (i.e. with the
12 highest wastewater proportion), 5 VOCs were detected vs. 1 or 2 compounds for the other
13 discharges, thus suggesting that wastewater constitutes the major source of VOCs. The results
14 published by Zgheib et al. (2011b, same issue), which indicate that VOCs are never
15 quantified in stormwater except for methylene chloride ($1.5-13 \mu\text{g.l}^{-1}$) and tetrachloroethylene
16 ($0.5-1.3 \mu\text{g.l}^{-1}$), along with the levels reported in the literature for wastewater (Wilkie *et al.*,
17 1996; Rule *et al.*, 2006a) have confirmed this hypothesis. A higher number of VOCs were
18 indeed detected in wastewater (at least 10 compounds, Fig. 1). In wastewater, methylene
19 chloride ($4.8-6.4 \mu\text{g.l}^{-1}$) and tetrachloroethylene ($1.6-6.7 \mu\text{g.l}^{-1}$) were predominant, while
20 other compounds lie in the $0.1-2.3 \mu\text{g.l}^{-1}$ range. According to US-EPA, methylene chloride is
21 used in various industrial processes, spanning many different industries including paint
22 stripping, pharmaceutical manufacturing, paint remover manufacturing and metal cleaning
23 and degreasing. Similarly, owing to its excellent degreasing properties, tetrachloroethylene is
24 a widely preferred degreasing agent and solvent, therefore explaining its presence in
25 numerous household products (automobile cleaners, paint removers and strippers, etc.).

1 *Pesticides*

2 Out of the 25 pesticides monitored, 9 corresponding for the most part to herbicides
3 were detected in CSOs (Fig. 1). Aldrin, atrazine* and desethylatrazine were also occasionally
4 detected (occurrence rates of between 25% and 50%), while dieldrin (0.20-0.98 $\mu\text{g.l}^{-1}$),
5 diuron* (0.19-0.50 $\mu\text{g.l}^{-1}$), isoproturon* (0.02-0.04 $\mu\text{g.l}^{-1}$), aminotriazole (0.13-0.46 $\mu\text{g.l}^{-1}$),
6 glyphosate (0.29-1.2 $\mu\text{g.l}^{-1}$) and amino methyl phosphonic acid - AMPA (0.25-1.6 $\mu\text{g.l}^{-1}$)
7 were detected in all samples. On the whole, these pesticides were ubiquitous and found in
8 CSOs, wastewater and stormwater. As demonstrated in Figures 1 and 2 however, pesticide
9 patterns and levels differed depending on the matrix under consideration. The CSO discharges
10 featured concentrations of diuron*, isoproturon* and glyphosate 5 to 20 times higher than
11 those observed in wastewater, yet remaining in a range similar to what was reported by
12 Zgheib et al. (2011b, same issue) for stormwater. It can therefore be assumed that these
13 pollutants mainly originate from stormwater and are due to the leaching of these herbicides on
14 impervious urban surfaces. As underscored by Blanchoud *et al.* (2004) for diuron*, these
15 herbicides are indeed capable of being remobilised during a rainfall event. For AMPA, the
16 CSO concentrations were found in the lower range of what was observed for wastewater, far
17 less than those reported for stormwater. This finding indicates that wastewater can be a major
18 contributor of AMPA in CSOs. According to Skark *et al.* (1998), the presence of AMPA in
19 wastewater is more likely to be correlated with the degradation of phosphonic acids in
20 detergents than with the primary degradation of glyphosate (Skark *et al.*, 1998).

21 *Polyethoxylate alkylphenols (APEOs)*

22 For polyethoxylate alkylphenols (APnEOs), nonylphenols* (NP*, 0.6-2.2 $\mu\text{g.l}^{-1}$) and
23 4-tert-octylphenol* (OP*, 0.1-0.2 $\mu\text{g.l}^{-1}$) were initially monitored in CSOs. NP* was
24 predominant, as compared to OP ($10 < \text{NP}^*/\text{OP}^* < 35$, which is in good agreement with their
25 use and production specifications (Ying *et al.*, 2002), and mainly associated with particles

1 (from 58% to 86%). Given that APnEOs containing between 6 and 12 ethoxylate units
2 (NPnEO and OPnEO) are the most significant from a commercial standpoint, a monitoring
3 campaign devoted solely to both the endocrine-disrupting chemicals NP* and OP* is not
4 sufficiently accurate and provides just very limited information. Complementary analyses
5 were therefore also carried out in order to analyse NP1EO, NP2EO, OP1EO and OP2EO, as
6 well as nonylphenol ethoxyacetic acid (NP1EC), a known degradation product of long-chain
7 NPnEOs (Fig. 3). The concentrations found in CSOs ranged from 448 to 1,526 ng.l⁻¹ for
8 NP1EO, from 171 to 401 ng.l⁻¹ for NP2EO, and from 221 to 591 ng.l⁻¹ for NP1EC.

9 As for PAHs or some of the pesticides, NP* and OP* were quantified in CSO,
10 wastewater and stormwater, thus confirming their dissemination into the urban environment.
11 From an overall perspective, CSOs presented similar or higher NP* and OP* concentrations
12 than those found in wastewater, though exceeding by far the values reported for stormwater
13 (Zgheib *et al.*, 2011, same issue), suggesting the contribution of in-sewer deposit erosion.
14 This trend was confirmed by Gilbert *et al.* (2010) for long-chain APnEOs within the Paris
15 sewer network. Although the presence of APEOs in wastewater is now well documented and
16 related to their widespread use as surfactants in numerous industrial and commercial
17 applications or in plastics (Ying *et al.*, 2002), the presence of APEOs in stormwater must be
18 pointed out and these concentrations must be taken into consideration. Current knowledge on
19 APnEO emissions in runoff is however rather limited. Based on the values reported by Zgheib
20 *et al.* (2011b, same issue), Bressy *et al.* (2011) and Björklund *et al.* (2009) confirmed that
21 high levels of APEOs could be found in runoff. For instance, Björklund *et al.* (2009) reported
22 NP* concentrations ranging from 100 (suburban residential catchment) to 1,200 ng.l⁻¹ (a high-
23 density traffic catchment). According to both studies, the high levels of APEOs in runoff can
24 be explained by local contributions from building and road runoff, since APEOs are used in
25 civil engineering materials, paints and the production of sealants. The initial investigations on

1 stormwater identified levels close to 70-100 ng.l⁻¹ for NP1EO and roughly 100-140 ng.l⁻¹ for
2 NP2EO, yet confirmation will require further experimentation. It is surprising that NP1EC,
3 generally considered as **an aerobic** degradation product of NPnEO, were also quantified in
4 stormwater at levels of around 300 ng.l⁻¹; its origins need to be studied in greater detail.

5 *Diethylhexyl phthalate (DEHP*)*

6 Concentrations of diethylhexyl phthalate* (DEHP*) in CSOs ranged between 3.8 and
7 14.8 µg.l⁻¹; these values tended towards the lower range of what was reported by Gasperi *et*
8 *al.* (2008) for CSOs in the Paris sewer network (16-57 µg.l⁻¹, with a median of 22 µg.l⁻¹). No
9 clear relationship appeared between DEHP* concentrations and the proportion of either
10 runoff or wastewater. On the whole and given the high variability of DEHP* concentrations,
11 the levels found in CSOs were comparable to those measured in both wastewater (n=11, 13.1-
12 57.3 µg.l⁻¹ with a median of 19.1 µg.l⁻¹) and stormwater (n=14, 3.4-55.9 µg.l⁻¹, median: 16.4
13 µg.l⁻¹), thus confirming the large spread of DEHP* in the urban environment. Many studies
14 have actually identified DEHP* as the most frequently detected phthalate found at the highest
15 concentrations in urban environments. As for the other chemicals, phthalates and more
16 specifically DEHP* are widely used throughout industry and in households, particularly as
17 additives in plastics and PVC products pipes. According to Björklund *et al.* (2009), phthalates
18 in runoff are likely to originate from vehicle components and reclaimed asphalt conveyed
19 during traffic flow.

20 *Chloroalkanes**

21 Chloroalkanes*, which are also called short-chain chlorinated paraffins (SCCP*), have
22 been observed in CSOs (at an occurrence rate of 75%), with concentrations ranging from 15
23 to 50 µg.l⁻¹. Using the same analytical methodology (with a quantification limit set at 10 µg.l⁻¹
24 ¹), chloroalkanes* were not observed in wastewater or stormwater (Zgheib *et al.*, 2011, same
25 issue). Even if SCCP* are expected to be present in wastewater and CSOs since these

1 compounds are used as lubricants and additives, as well as flame retardants in a wide range of
2 applications, no definitive conclusion can be clearly drawn for SCCP* and moreover results
3 must be considered carefully. As highlighted by Eljarrat and Barcelo (2006), it should be
4 recalled that SSCP* represent a difficult analytical problem caused by their instrumental
5 determination and quantification, which is related to the complexity of these mixtures.

6 **3.3 CSO concentrations vs. Environmental Quality Standards**

7 In order to identify substances capable of representing a major risk to the environment,
8 CSO concentrations were compared to the Environmental Quality Standards (EQS)
9 established by the European Commission (Table 5). The relevant Directive defines two types
10 of standards: i) the annual average concentration (EQS-AAC) of the substance over a 1-year
11 period, and ii) the maximum allowable concentration (EQS-MAC) of the substance measured
12 at specific points in time. As previously described by Zgheib *et al.* (2011), this approach was
13 simple and easy, yielding an indicative rate of dilution required in the receiving environment
14 for compliance with the WFD. Of the substances quantified in CSOs for which an EQS has
15 been proposed, a limited number may pose environmental risks as regards compliance with
16 standards established at the European level. No risk of exceeding EQS-AAC and EQS-MAC
17 was observed for tri- and tetra-chloroethylenes, atrazine*, isoproturon*, octylphenol*,
18 anthracene* and naphthalene* ($F < 1$), while only a limited risk was observed for diuron*,
19 DEHP*, nonylphenols*, benzo(a)pyrene* and fluoranthene* ($1 < F < 10$). On the other hand,
20 major dilution factors were required for PAHs (sum of B(b)F* + B(k)F* and sum of IP* +
21 B(ghi)P*, only for EQS-AAC) and, to a greater extent, for tributyltin compounds* (TBT*,
22 DBT* and MBT*) and chloroalkanes* in terms of both EQS-AAC and EQS-MAC. As for
23 EQS-MAC, tributyltin* should be carefully considered, since a significant dilution factor was
24 required (from 19 to 300). For chloroalkanes*, dilution factors were lower yet remained
25 between 10 and 35.

1 **4. Conclusion**

2 This study, as part of the OPUR research programme, has been aimed at investigating
3 the quality of combined sewer overflow in urban watersheds. By monitoring priority
4 pollutants as well as additional substances, this study constitutes the first relevant approach to
5 providing accurate knowledge on the occurrence and concentrations of a broad spectrum of
6 pollutants in CSOs and their significance compared to wastewater and stormwater.

7 This work has served, first and foremost, to confirm that a wide range of PPs are
8 indeed present in CSOs. Of the 88 stormwater priority substances monitored in both the
9 particulate and dissolved phases, 49 different PPs, including 19 priority hazardous
10 substances*, could be detected. Most of these were also frequently observed in wastewater
11 and stormwater, thus confirming that PPs are now ubiquitous in our urban environment.
12 Nevertheless, some differences relative to concentration ranges and/or pollutant patterns from
13 one matrix to the next can still be drawn. For most hydrophobic organic pollutants, such as
14 PAHs and APnEOs, and some preferentially particulate-bound metals (Pb* and Cu), CSOs
15 exhibit higher concentrations than those found in stormwater and wastewater. As previously
16 demonstrated, this result is highly correlated with the significant in-sewer deposit erosion. For
17 less hydrophobic pollutants, such as pesticides or preferentially dissolved metals like Zn,
18 CSOs yield concentrations close to stormwater, thus suggesting that runoff is the major
19 contributor while wastewater and in-sewer processes remain minor sources. For VOCs,
20 wastewater seems to be the major contributor in CSOs since these compounds were not
21 detected in stormwater. Similar concentration ranges were found for DEHP and tributyltin
22 compounds* in CSOs, wastewater and stormwater as a result of their high inter-event
23 variability. Lastly, a comparison of CSO concentrations with European standards underscores
24 that CSO discharges may pose a significant environmental risk as regards PAHs, tributyltin

1 compounds* and chloroalkanes*, since high dilution factors were required to comply with
2 EQS-AAC or EQS-MAC. Further investigation is now required to better evaluate this risk.

3 By providing significant knowledge on the quality of CSO, wastewater and
4 stormwater, this study and, more generally, the data provided by the OPUR research
5 programme might be used in the future to identify PPs of potential significance. In the near
6 future, such data could also serve to establish accurate mass balances in order to apportion the
7 contributions of wastewater, runoff and in-sewer deposit erosion to CSO loads in combined
8 sewers. This information will soon be of prime importance in reducing priority pollutant
9 discharges within the urban environment and as part of the effort to prioritise "control at the
10 source" interventions. Among the various issues on the horizon, one OPUR research
11 programme priority will consist of investigating the occurrence and significance of priority
12 pollutants in atmospheric inputs, so as to better understand the role of atmospheric fallout in
13 urban environmental contamination.

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19 OPUR research programme.

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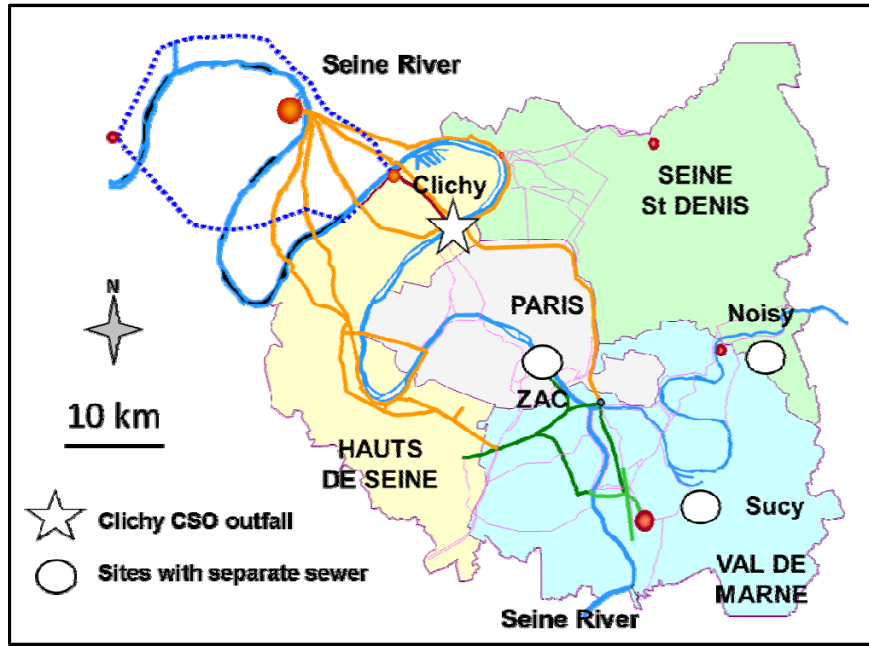
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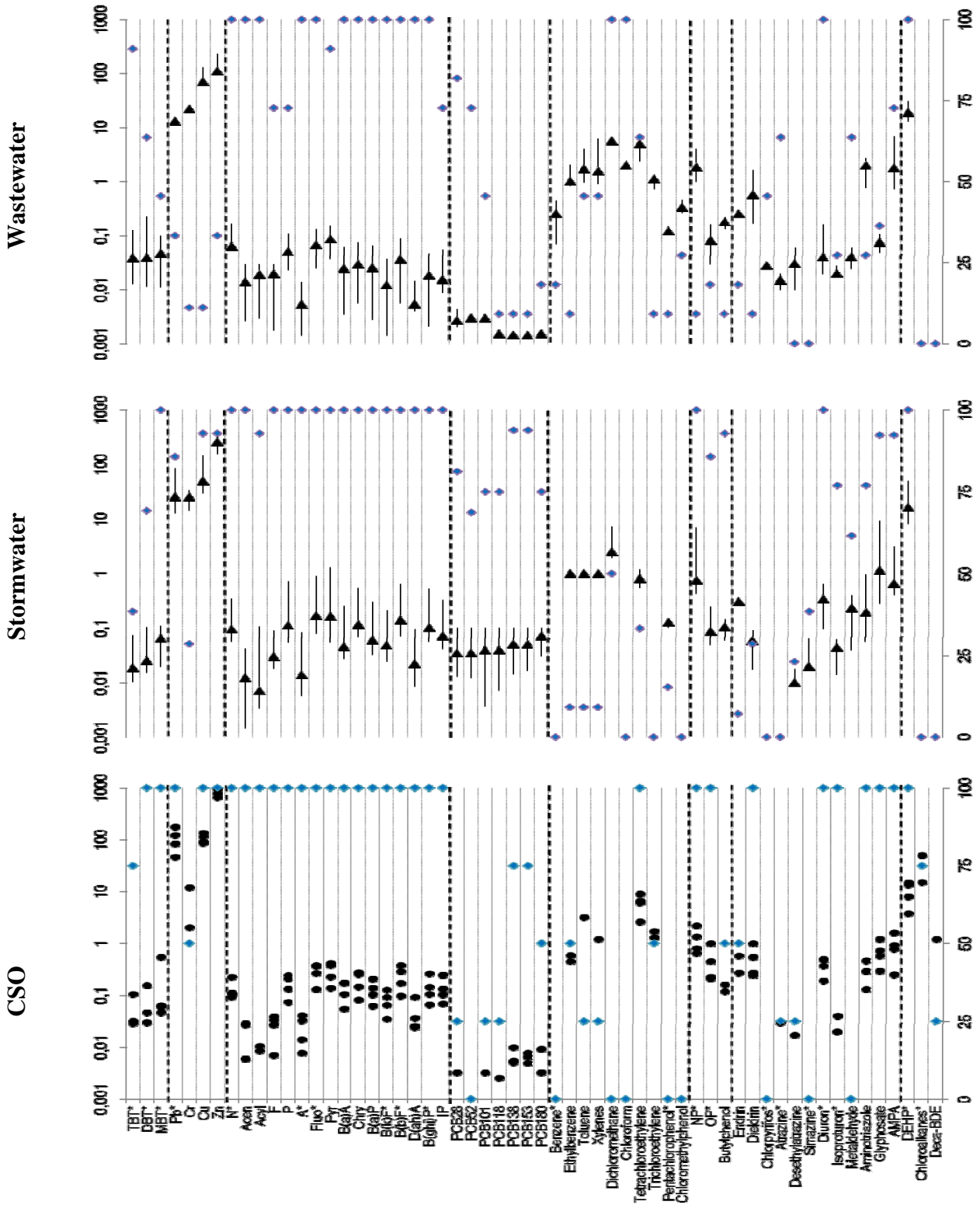
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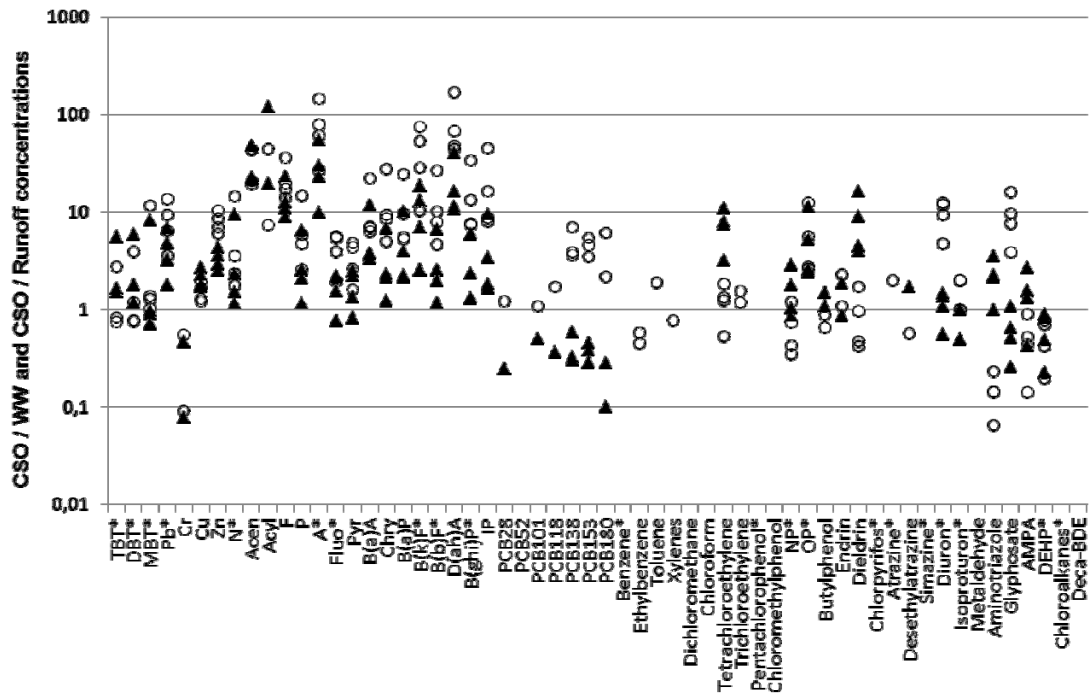
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Figure 1: Sites considered within OPUR research program. The Clichy outfall was considered for CSO, while Noisy, Sucy and ZAC sites were dedicated to study the stormwater quality in connection with the urbanisation gradient (Zgheib et al., 2011a)



2
 3 Figure 2: Total concentration ($\mu\text{g.L}^{-1}$, left axis) for CSOs (n=4), wastewater (n=11) and stormwater in
 4 a separated sewer (n=17), as well as occurrence rates (blue lozenges, in %, right axis). CSO samples
 5 were collected in 2010, wastewater in 2009-2010, and stormwater over the 2008-2010 period. For
 6 stormwater and wastewater, lines illustrate the first and last decile concentrations (d10 and d90),
 7 and black triangles refer to median (d50).
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Figure 3: Ratios between CSO and median wastewater concentrations (white circles) and between CSO and median stormwater concentrations (black triangles)

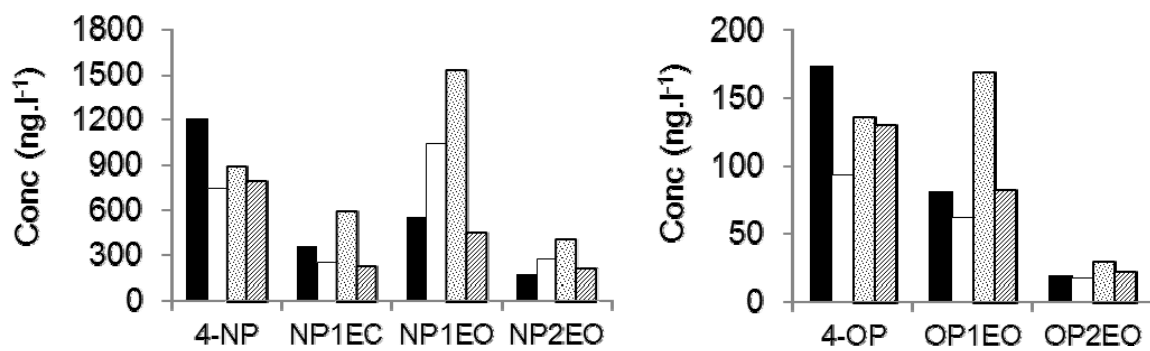


Figure 4: APnEOs concentrations (ng.l⁻¹) in CSOs (C1, C2, C3 and C4)

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2 **Table captions**

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Table 1: Main characteristics of the rain events studied and runoff proportions

Date		H ¹ (mm)	Volume (m ³)	ADP ² (d)	Cond ³ ($\mu\text{S}\cdot\text{cm}^{-1}$)	Runoff (%) ⁴ Min-Max
2010/07/12	C1	32.9	559,390	9	284	78-87
2010/07/14	C2	43.1	1,005,150	2	201	87-95
2010/09/08	C3	13.2	39,200	16	380	69-77
2010/09/24	C4	16.5	325,175	16	260	75-89

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(1) H = precipitation height for each rain event (mm), (2) ADP = antecedent dry period, time period since the previous rain event (day), (3) Cond = conductivity, in $\mu\text{S}\cdot\text{cm}^{-1}$, (4) runoff proportion, estimation based on conductivity measurement.

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Table 2: List of monitored priority pollutants and analytical methods

Groups ¹	Total ²	Standards	Methods ³	Phase ⁴
Alkylphenols	5 (2)	ISO 18857-1	GC-MSMS	P + D
BTEX	5 (1)	NF EN ISO 11423-1	GC-MS	T
Chloroalkanes	1 (1)	Internal method	GC-ECD	P + D
Chlorobenzenes	5 (3)	EN ISO 6468	GC-MS	P + D
Chlorophenols	1 (1)	NF EN 12673 + ISO 6468	GC-MSMS	P + D
HVOCs	7 (4)	NF EN ISO 10301 + 6468	GC-MS	T
PAHs	16 (8)	ISO 17993	HPLC-Fluo	P + D
Metals	8 (4)	NF EN ISO 11885 + 1483	ICP and AAS	T + D
Organotins	3 (3)	NF EN ISO 17353	GC-MS	P + D
PBDEs	3 (1)	ISO 22032	GC-ECD	P + D
PCBs	8	NF EN ISO 6468	GC-MS-MS	P + D
Pesticides	25 (12)	NF EN ISO 11369 + Internal method	GC-MS UPLC-MSMS	P + D
Phthalates	1 (1)	Internal method	GC-MS	P + D

(1) Compound groups: BTEX = benzene*, toluene, ethylbenzene and xylenes, HVOC = halogenated volatile organic compounds, PAHs = polycyclic aromatic hydrocarbons, PBDE = polybromodiphenylethers, PCB = polychlorinated biphenyls, (2) The substance in brackets is listed in the WFD, (3) Analytical methods: ICP = inductively coupled plasma, AAS = atomic absorption spectrometry, GC = gas chromatography, GC-ECD = GC with electron capture detector, GC-MS = GC with mass spectrometer, GC-MSMS = GC gas chromatography with tandem mass spectrometer, HPLC-fluo = High pressure liquid chromatography with fluorescent detector, UPLC-MSMS = ultra performance liquid chromatography with tandem mass spectrometer, (4) Phase considered with: D = dissolved, P = particulate, T = Total.

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Table 3: Wastewater quality parameters for the studied CSO discharges

	C1	C2	C3	C4	CSO database ¹	WW database ²	Runoff ³
TS					121-394	190 – 314	30-75
mg.l ⁻¹	193	135	353	153	237	252	36
COD					157-491	322-520	43-113
mg O ₂ .l ⁻¹	254	136	446	260	336	436	56
BOD ₅					54-200	130-230	8-25
mg O ₂ .l ⁻¹	78	36	180	95	135	180	11
TKN					15-37	31-49	< 4
mg N.l ⁻¹	17	7.2	27	18	22	41	
NH ₄ ⁺					5.8-22.2	20-32	-
mg N.l ⁻¹	6.4	3.3	9.3	8.1	9.9	28	
PO ₄ ³⁻					0.8-2.2	2.0-3.0	-
mg P.l ⁻¹	0.8	0.5	1.4	1.1	1.2	2.6	
P _{tot}					2.3-5.4	4.1-6.4	-
mg P.l ⁻¹	2.7	1.2	5.4	3	3.5	5.4	

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(1) CSO database from SIAAP (n=52) for the 2009-2010 period, (2) Wastewater database from SIAAP on the Clichy site (n=460), (3) runoff, data from Kafi et al. (2008). *For CSO database, wastewater database, and runoff rows, first line refers to d10 and d90 concentrations; second line is median concentration (d50.)*

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4

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Table 4: Pollutants detected and undetected in CSOs

Never detected in CSOs, wastewater and runoff or when detected with an occurrence < 15% (30 PPs, incl. 14 PHS*)	Cd*, Hg*, Ni*, Pt dichloroethane*, trichlorobenzenes* (3), pentachlorobenzene*, hexachlorobenzene*, carbon tetrachloride, isopropylbenzene hexachlorobutadiene*, hexachlorocyclohexane* endosulfan* (2), alachlor*, isodrin, lindane*, chlorfenvinphos*, desethylsimazine, endrin, trifluralin*, DDT (2) PCB 194, octa-BDE, penta-BDE, 4-n-octylphenol*, 4-para-nonylphenol
Undetected in CSOs, but detected in wastewater and runoff (9 PPs, incl. 5 PHS*)	chloromethylphenol, benzene*, chloroform*, dichloromethane*, chlorpyrifos*, simazine*, metaldehyde, PCB 52, pentachlorophenol*
Detected in CSOs (49 PPs, incl. 19 PHS)	4 metals (Pb*, Cr, Cu, Zn) 5 COVs (ethylbenzene, toluene, xylenes, tetrachloroethylene, trichloroethylene) 9 pesticides (aldrin, dieldrin, atrazine*, desethylatrazine, diuron*, isoproturon*, aminotriazole, glyphosate, AMPA) 3 organotins (TBT*, DBT*, MBT*) 3 alkylphenols (nonylphenol*, octylphenol*, butylphenol) 16 US-PAHs (N*, Acen, Acyl, F, P, A*, Fluo*, Pyr, B(a)A, Chry, B(a)P*, B(b)F*, B(k)F*, D(ah)A, B(ghi)P*, IP*) 7 PCBs (28, 101, 118, 138, 153 and 180) Deca-BDE, chloroalkanes*, DEHP*

2

*In parentheses: Number of congeners considered, * for priority hazardous substances*

3

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Table 5: Ratios of CSO concentrations and EQS-AAC or EQS-MAC

	CSO concentration / EQS-AAC	CSO concentration / EQS-MAC
Undetected	24 PPs	15 PPs
< 1	7 PPs: tri- and tetra-chloroethylenes atrazine*, isoproturon* octylphenol* anthracene*, naphthalene*	8 PPs: tri- and tetra-chloroethylenes atrazine*, isoproturon*, diuron* nonylphenols* anthracene*, fluoranthene*
1 - 10	5 PPs: diuron*, DEHP*, nonylphenols*, benzo(a)pyrene* fluoranthene*	1 PP: benzo(a)pyrene*
10 - 100	4 PPs: aldrin, dieldrin, chloroalkanes* Sum of B(b)F* + B(k)F*	4 PPs: TBT*, DBT*, MBT* chloroalkanes*
> 100	4 PPs: TBT*, DBT*, MBT* Sum of IP* + B(ghi)P*	-

2