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

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Abstract

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

Keywords

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

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1. Introduction

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

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

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

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

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

2. Materials and methods

2.1 Site description and rain event characteristics

Paris proper (*intra-muros*) is drained by a combined sewer system covering a land area of 105 km². This area is densely populated (2.15 million inhabitants, i.e., approximately 20,500 inhabitants/km²) and features many small shops, offices and very little industrial activity. In this study, the largest CSO outfall, located in Paris' north-western district, has been considered ("Clichy" outfall, Figure 1). Over the 2009-2010 period, some 52 discharges occurred annually, responsible for discharging between 25,000 and 1,000,000 m^3 into the Seine River. This outfall is supervised by the Paris public sanitation service (SIAAP).

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

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

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

2.2 Experimental procedure

Routine wastewater parameters

For each sample, routine wastewater parameters, such as total solids (TS), chemical and biochemical oxygen demands (COD and BOD_5), ammonium (NH_4^+), total Kjeldahl nitrogen (TKN), total phosphorous (Ptot) and orthophosphates (PO_4^{3-}), were analysed. As reported in Supporting Table 1, these parameters were measured in accordance with French standards.

Priority substances

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

3. Results and discussion

3.1 Wastewater quality parameters in combined sewer overflows

Routine wastewater quality parameters for the collected discharges as well as for a large number of rain events (SIAAP CSO database, n=52) are given in Table 3. Data for wastewater (on the same site) and runoff (Kafi *et al.*, 2008) are also reported. In spite of a high runoff proportion, the CSO reveals an organic strength (COD concentrations greater than 140 $mg.l^{-1}$, BOD_5 above 40 $mg.l^{-1}$), albeit with less household wastewater than is typical (Tchobanoglous *et al.*, 2003). While C1 and C4 discharges were quite similar in their

concentrations of carbonaceous pollution, differences were still observed between C2 (the lowest concentration) and C4 (the highest). These differences may be partially tied to: i) the relative proportion of wastewater that gets mixed with runoff, and ii) the previous dry period prior to these rain events. A rougher comparison of CSO and wastewater concentrations allows differentiating two groups of parameters. The first group, which includes BOD_5, TKN and NH_4^+, exhibits higher wastewater concentrations than the group observed during the storm period, thus underscoring the fact that wastewater constitutes the major source for these pollutants. In the literature, it is well documented that most of these elements originate mainly from human sources (especially via urine and faeces) and from various activities such as washing and cooking (Wilkie *et al.*, 1996; Tchobanoglous *et al.*, 2003). More recently, Gasperi *et al.* (2010) confirmed that wastewater is the major source of organic and nitrogenous pollution in CSOs. The second group comprised COD, TS and Ptot, with these parameters presenting comparable wastewater and CSO concentrations. While urban runoff contains rather low COD, TS and Ptot concentrations, wastewater dilution by runoff should induce even lower CSO concentrations. This trend however was not observed, owing to the erosion of in-sewer deposits accumulated during dry weather flow periods in sewer trunks (Gromaire *et al.*, 2001). At the scale of Paris' combined sewer, Gasperi *et al.* (2010) indicated that from 47% to 69% for TS and from 34% to 61% for COD are tied to the erosion of in-sewer deposits; on the other hand, runoff only plays a minor role.

3.2 Priority pollutants in combined sewer overflows

Priority pollutants and detection frequency

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

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

Priority pollutant concentrations and comparison with levels found in wastewater and stormwater

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

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

Metals

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

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

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

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

Polycyclic Aromatic Hydrocarbons (PAHs)

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

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

Polychlorinated biphenyls (PCBs)

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

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

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

Tributyltin compounds

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

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

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

Volatile organic compounds (VOCs)

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

Pesticides

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

Polyethoxylate alkylphenols (APEOs)

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

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

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

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

Diethylhexyl phthalate (DEHP)*

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

*Chloroalkanes**

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

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

3.3 CSO concentrations vs. Environmental Quality Standards

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

4. Conclusion

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

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

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

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

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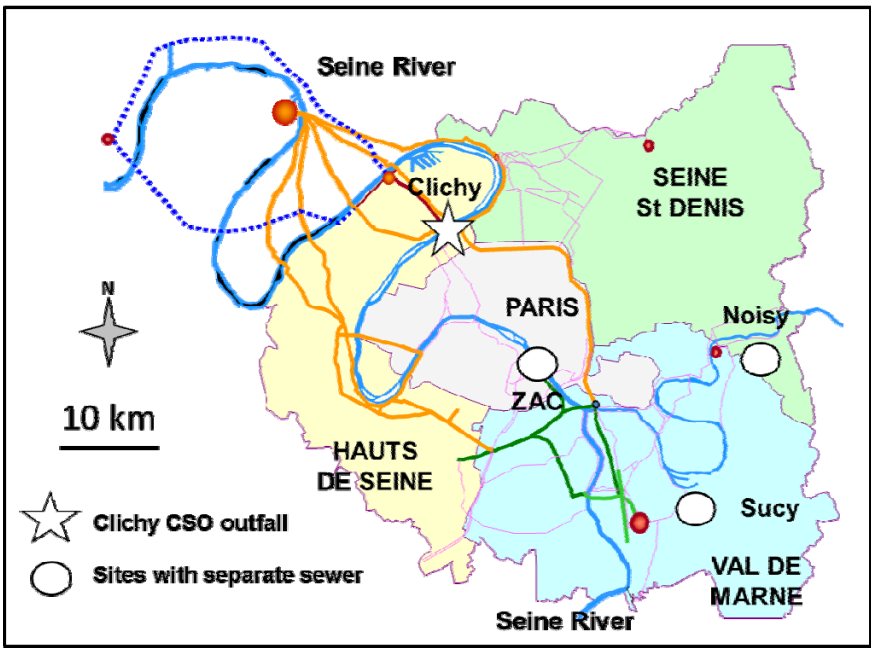
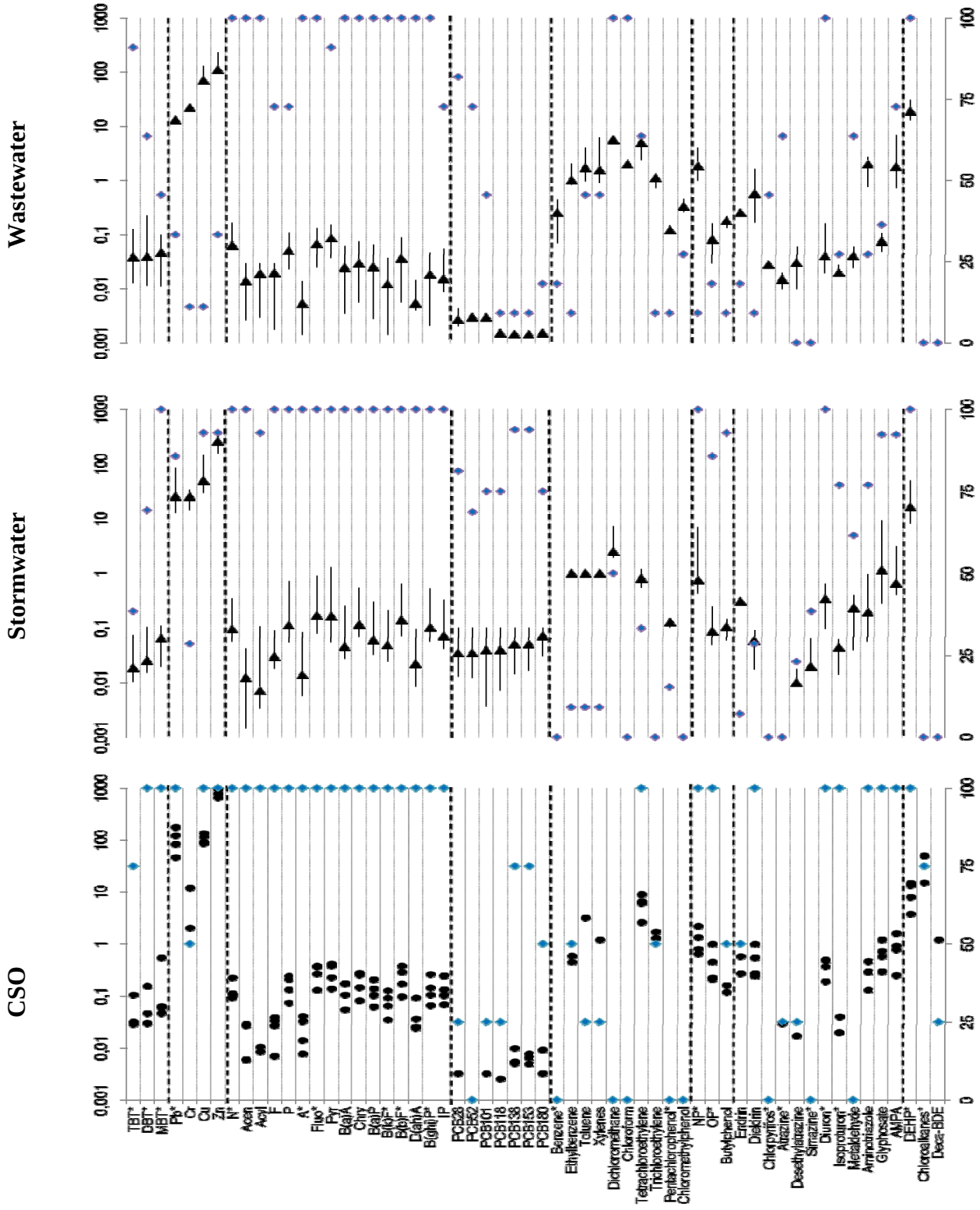


Figure 1: Sites considered within OPUR research program. The Clichy outfall was considered for CSO, while Noisy, Sucy and ZAC sites were dedicated to study the stormwater quality in connection with the urbanisation gradient (Zgheib et al., 2011a)



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

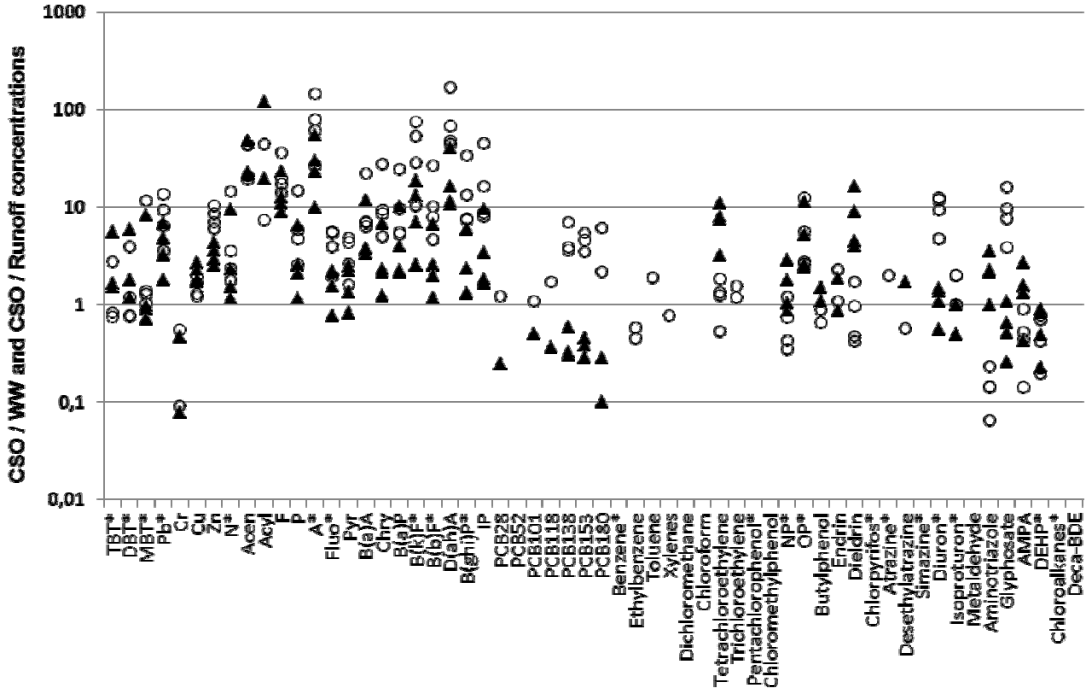


Figure 3: Ratios between CSO and median wastewater concentrations (white circles) and between CSO and median stormwater concentrations (black triangles)

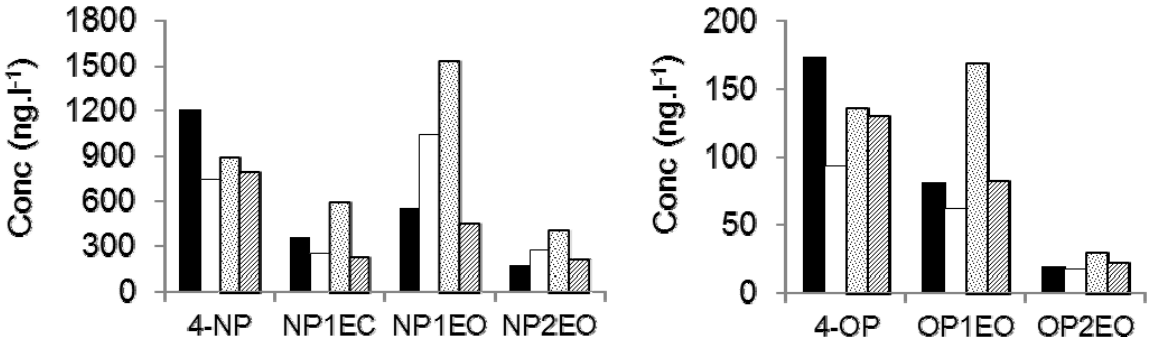


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Table 1: Main characteristics of the rain events studied and runoff proportions

Date		H[1] (mm)	Volume (m^3)	ADP[2] (d)	Cond[3] ($\mu S.cm^{-1}$)	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

(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 $\mu S.cm^{-1}$, (4) runoff proportion, estimation based on conductivity measurement.

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.*

Table 3: Wastewater quality parameters for the studied CSO discharges

	C1	C2	C3	C4	CSO database[1]	WW database[2]	Runoff[3]
TS $mg.l^{-1}$	193	135	353	153	121-394 237	190 – 314 252	30-75 36
COD $mg\ O_2.l^{-1}$	254	136	446	260	157-491 336	322-520 436	43-113 56
BOD_5 $mg\ O_2.l^{-1}$	78	36	180	95	54-200 135	130-230 180	8-25 11
TKN $mg\ N.l^{-1}$	17	7.2	27	18	15-37 22	31-49 41	< 4
NH_4^+ $mg\ N.l^{-1}$	6.4	3.3	9.3	8.1	5.8-22.2 9.9	20-32 28	-
PO_4^{3-} $mg\ P.l^{-1}$	0.8	0.5	1.4	1.1	0.8-2.2 1.2	2.0-3.0 2.6	-
Ptot $mg\ P.l^{-1}$	2.7	1.2	5.4	3	2.3-5.4 3.5	4.1-6.4 5.4	-

(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.)***

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*

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

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*	-