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Urban pathways of biocides towards surface waters during dry and wet weathers: assessment at the Paris conurbation scale

Claudia Paijens^{1,2}, Adèle Bressy^{1}, Bertrand Frère², Damien Tedoldi¹, Romain Mailler³, Vincent Rocher³, Pascale Neveu⁴ and Régis Moilleron¹*

¹ Leesu, Ecole des Ponts, Univ Paris Est Creteil, Marne-la-Vallée, France

² Laboratoire Central de la Préfecture de Police, Paris, France

³ SIAAP, Direction de l'Innovation, Colombes, France

⁴ Mairie de Paris, Direction de la Propreté et de l'Eau, Service Technique de l'Eau et de l'Assainissement, Paris, France

* Corresponding author: adele.bressy@enpc.fr

HIGHLIGHTS

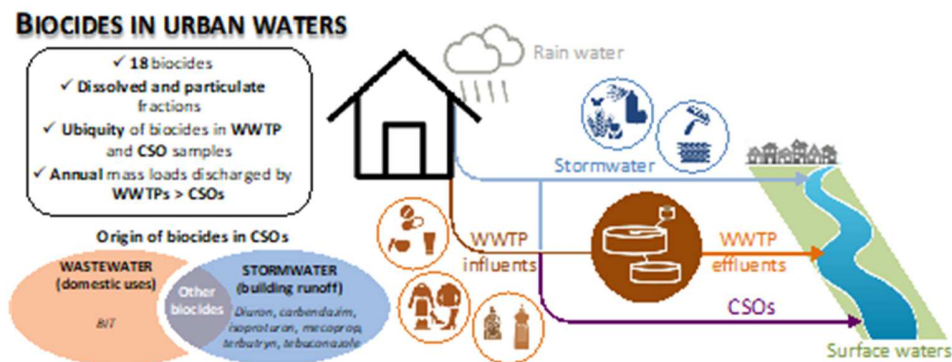
- 18 biocides used in buildings and domestic activities were monitored in urban waters
- Quantification in both dissolved and particulate fractions of WWTP and CSO samples
- Poor WWTP removals were observed for most of the biocides except isothiazolinones
- In CSOs, most of the biocides came from both wastewater and stormwater
- Annual mass loads discharged in the Seine River were higher for WWTPs than CSOs

ABSTRACT

Eighteen biocides used in building materials and domestic products were monitored in wastewater treatment plants (WWTPs) during dry weather and in combined sewer overflows (CSOs) during wet weather in the Paris conurbation. The aims of this study were to (i) acquire data on biocides in urban waters, which are very scarce up to now, (ii) identify their origins in CSOs with the perspective of reducing these contaminants at source, and (iii) compare and rank biocide pathways to the river (dry vs. wet weather) at the annual and conurbation scales. The results

showed the ubiquity of the 18-targeted biocides in WWTP waters and CSOs. High concentrations of methylisothiazolinone, benzisothiazolinone (0.2-0.9 µg/L) and benzalkonium C12 (0.5-6 µg/L) were measured in wastewater. Poor WWTP removals (< 50%) were observed for most of the biocides. Both wastewater (mainly domestic uses) and stormwater (leaching from building materials) contributed to the CSO contamination. However, benzisothiazolinone mainly came from wastewater whereas diuron, isoproturon, terbutryn, carbendazim, tebuconazole, and mecoprop mainly came from stormwater. Annual mass loads discharged by WWTPs and CSOs into the Seine River were estimated using a stochastic approach (Monte Carlo simulations) at the conurbation scale and showed that WWTP discharges are the major entry pathway.

GRAPHICAL ABSTRACT



KEYWORDS

Combined sewer overflows; Mass loads; Stochastic approach; Stormwater; Wastewater treatment plant removal

Introduction

According to the European Biocidal Product Regulation, a biocidal product is a chemical substance or mixture that is used “with the intention of destroying, deterring, rendering harmless, preventing the action of, or otherwise exerting a controlling effect on, any harmful organism by any means other than mere physical or mechanical action” [1]. In recent years, these substances have received increasing attention. Biocides are used in domestic products (pharmaceuticals, cosmetics, disinfectants, detergents, sweeteners, etc.) and are therefore emitted in wastewater. However, despite recent progress in conventional treatments, wastewater treatment plants (WWTPs) seem to be still unsuitable for these substances [2–5]. Biocides are also widely used in building materials (paints, renders, tiles, wood, bitumen membranes) to prevent the growth of microorganisms, such as mosses, fungi, bacteria, algae and lichens, on their surfaces [6]. In order to have the intended effect on microorganisms, they are meant to move within the material during wet weather and to migrate from the deeper layer to the surface of the coating [7]. A few studies have thus highlighted the contamination of building runoff by biocides [8–13]. After entering the sewer network [14–20], biocides are released into the aquatic environment, leading to concentrations that could have a harmful impact on aquatic organisms [21–24]. However, these substances are still poorly regulated and monitored in surface waters [25,26] despite their adverse effects on aquatic life [27,28]. Much attention has been paid to pesticides in rural area, but the NORMAN network (independent organization at the interface between science and policy, gathering more than 80 reference laboratories and research centres from 20 countries in the field of emerging substances [29]) and the German Federal Environment Agency pointed out the lack of data regarding biocides in the aquatic environment, preventing a full risk assessment. They also indicated the need of stormwater and wastewater monitoring programs, which may enable the estimation of biocide loads from urban discharges and thus fill the current knowledge gap for source assignment [30]. So far, few studies have addressed the link between the biocide emissions from different urban sources, including buildings, and their impact on receiving waters [15,31] or focused on their origins in combined sewer overflows (CSOs), i.e. domestic uses (wastewater) vs. outdoor urban surfaces (stormwater) [14,16]. Additionally, these studies were restricted to a small number of compounds and a limited urban area, as a result of which little is known about the impacts of a megacity like Paris.

This work focuses on 18 biocides, which were previously prioritized [32] according to their use, among others, in building materials (paints, renders, wood, bitumen membranes and tiles), their emission into runoff and receiving waters, and the associated risk for aquatic organisms. The present study aims to collect data on the 18 targeted biocides in urban waters (untreated and treated wastewaters, combined sewer overflows - CSOs), thus gaining insight into the origins of biocides in CSOs (wastewater vs. stormwater) but also into WWTP efficiency on these substances, and finally to prioritize biocide pathways into the aquatic environment during both dry and wet weather conditions at the scale of the Paris conurbation. A statistical modelling approach has been proposed to do so, which allows a stochastic extrapolation of the measurements to the non-analysed events and non-sampled urban sources within the study area, and allows additional uncertainties to be taken into account.

1. Materials and methods

1.1. Study area and sample collection

1.1.1. Presentation of the study area

This study focused on urban discharges from the Paris conurbation into the Seine River, between Alfortville and Conflans-Ste-Honorine (figure 1). This area includes both the intramural city of Paris and a part of the suburbs. Both are characterized by a high population density, a high impervious surface area and few industrial activities. In order to set some additional context, all municipalities of the Paris region are deeply involved in the “*zero phyto*” program, which aims at a total ban of all pesticides used in both public (parks, cemeteries, sidewalks, roads, etc.) and private areas.

Between Alfortville and Conflans-Ste-Honorine, effluents from two WWTPs and nine CSOs are discharged into the river. The *Seine aval* (5 000 000 inhabitant equivalent) and *Seine centre* (900 000 inhabitant equivalent) WWTPs, which are operated by the greater Paris sanitation authority (SIAAP), treated 540 M m³ and 80 M m³ in 2018 respectively before discharge in the Seine River. During heavy rain, a part of the wastewater mixed with stormwater cannot be treated by WWTPs, and is hence discharged after coarse pre-treatment into the Seine River via CSOs. Two CSOs operated by the SIAAP, located in Clichy and La Briche, and seven CSOs operated by

the city of Paris, discharged 5.7 M m³ (54% of the total CSOs volume), 3.2 M m³ (30%) and 1.7 M m³ (16%) in 2018. Stormwater discharges were not accounted for, as the sewer system is essentially combined in the Paris area.

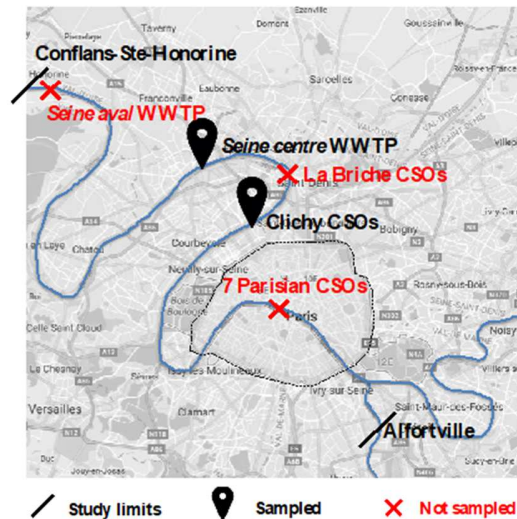


Figure 1. Location of sampling sites in the Paris conurbation, France

1.1.2. Presentation of the sampled sites

The sampling campaigns targeted *Seine centre* WWTP and the biggest CSO, i.e. Clichy CSO. These two sites have comparable catchments, as the greatest part of the *Seine centre* influents have first transited in the Clichy pre-treatment plant. This catchment may be considered representative of the entire study area, since it drains wastewater and stormwater from different neighbourhoods located both in the city of Paris and in the suburbs.

Seine centre WWTP treats wastewater up to 240,000 m³ per day. Wastewater is treated following three steps: (i) pre-treatment (screening, grit and oil removal units), (ii) primary treatment (removal of particles and colloids by a physico-chemical lamellar unit in which ferric chloride and anionic polymer are added), and (iii) biological treatment (carbon removal, total nitrification and post denitrification by a three-stage biofiltration system). The flow rate of the discharged effluents is continuously monitored with a good accuracy using 5 Venturi flowmeters; the resulting uncertainty has been estimated at $\leq 5\%$ by the SIAAP. During wet weather, the WWTP is able to

switch to a degraded configuration (partial nitrification and no denitrification) in order to treat up to 405,000 m³ per day of wastewater. During heavy rain, the part of the wastewater that cannot be treated is discharged into the Seine River via CSOs at the Clichy pre-treatment plant. Flow rate measurement at CSOs is achieved by means of pre-established rating curves combined with continuous monitoring of the water level (uncertainty ~ 15%).

1.1.3. Sampling campaigns

Detailed information on each campaign is provided in supplementary material (tables S1 and S2). WWTP influents and effluents were collected during dry weather from the *Seine centre* WWTP, and CSO samples were collected in the pre-treatment plant of Clichy, allowing a comparison between dry and wet weather conditions. Six sampling campaigns were carried out between April 2018 and April 2019 in the WWTP (table S1). For each campaign, 20 L composite samples (24 h) were collected in cleaned plastic bottles refrigerated at 4°C by automatic samplers equipped with Teflon® pipes. Influent and effluent were sampled during the same days. For Clichy CSOs, eight rain events were sampled (flow-dependent samples) between March 2018 and May 2019 using similar automatic samplers so as to get event mean concentrations (table S2).

The representativeness of WWTP and CSO samples was verified using a comparison of the main water quality parameters measured in the sampled panel and throughout the year (total suspended solids (TSS), chemical and biochemical oxygen demand (resp. COD and BOD), total Kjeldahl nitrogen (TKN), and total phosphorus (TP) – all of which are monitored by SIAAP for each day/event). Results are provided in supplementary material (figures S1, S2 and S3). Values were not statistically different from the parameters of the entire set of discharged waters over the complete study period (Mann-Whitney test, p-value > 0.05). Furthermore, the eight CSO events generated a wide range of discharged volumes, from 34,000 to 1,420,000 m³, thus showing the diversity of rainfall characteristics. Hence, it is reasonable to consider that the acquired data are representative of the sewer system's behavior.

1.2. Biocide analysis

As presented in the introduction, 18 biocides were targeted: diuron, isoproturon, methylisothiazolinone (MIT), benzisothiazolinone (BIT), chloro-methylisothiazolinone (CMIT), octylisothiazolinone (OIT), dichloro-octylisothiazolinone (DCOIT), benzalkonium chlorides (BZK C12-C16), terbutryn, cybutryn (irgarol 1051), terbuthylazine, carbendazim, iodopropynyl butylcarbamate (IPBC), thiabendazole, tebuconazole and mecoprop. Information on the 18-targeted biocides is provided in supplementary files (table S3). All standards of high purity (> 90%) were commercially available and purchased from A2S (France), Dr. Ehrenstorfer (Germany), Sigma Aldrich (France) and CDN Isotopes (Canada). The procedure applied for the analysis of these compounds was previously described by Pajjens et al. (2020) [33]. Briefly, samples were filtered within 24 h after sampling through 0.7 µm glass fibre filters (GF/F, Whatman, UK) previously heated at 500 °C for 2 h. Both the dissolved and particulate fractions of water samples were analysed. After filtration, the dissolved fraction (100 mL for WWTP influents and CSO samples, and 200 mL for WWTP effluents) was extracted on an SPE cartridge, Chromabond HR-X (200 mg, 6 mL) from Macherey-Nagel, and eluted by methanol (6 mL), ethyl acetate (3 mL) and dichloromethane (2 mL). A microwave-assisted extraction procedure (Multiwave 3000, Anton Paar, France) was applied to the particulate fraction (5-10 mg for WWTP effluents, 50-80 mg for WWTP influents, and 30-130 mg for CSO samples): extraction at 100 °C in methanol/dichloromethane, 60/40. Recoveries were published in Pajjens et al. (2020) [33]. Biocides were separated on an Acquity UPLC® HSS T3 column (100 mm x 2.1 mm, 1.7 µm) from Waters and quantified by internal calibration using high performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS, UPLC® Aquity TQD, Waters). To determine biocide concentrations in real samples, each measured concentration was corrected by the recovery in the corresponding matrix. The detection and quantification limits (LOD and LOQ, respectively) are provided in supplementary files (table S4 and table S5). All the data of this project were published online on Pangaea Data Center [34].

1.3. Data processing

1.3.1. Pre-treatment of the dataset

For each sample, biocides were quantified in both the dissolved (ng/L) and particulate ($\mu\text{g/g}$) fractions. Total concentrations were calculated as the sum of the concentrations in the two phases, after converting the particulate concentration into ng/L according to equation 1.

$$C_p(\text{ng/L}) = C_p^*(\mu\text{g/g}) \times C_{TSS}(\text{mg/L})$$

Equation 1. Calculation of the concentration in the particulate fraction C_p (ng/L) from the biocide content in the particles C_p^* ($\mu\text{g/g}$) and the concentration of total suspended solids C_{TSS} (mg/L).

The values below the limit of detection (LOD) or limit of quantification (LOQ) were handled differently depending on the situation.

Case 1: one fraction (dissolved or particulate) was \geq LOQ and the other one was \geq LOD and $<$ LOQ, *i.e.*, the total concentration fell between $C_{\text{quantified}} + \text{LOD}$ and $C_{\text{quantified}} + \text{LOQ}$. By approximating the undetermined term by $\max(\text{LOD}, \text{LOQ}/2)$, as recommended by the US-EPA and French guidance [35,36], the maximum relative error amounts to $\text{LOQ}/(2 \times C_{\text{quantified}})$. As discussed in the subsequent developments, this upper limit was generally $< 20\%$, so the approximation may be considered acceptable.

Case 2: one fraction (dissolved or particulate) was \geq LOQ and the other one was $<$ LOD, *i.e.*, the total concentration fell between $C_{\text{quantified}}$ and $C_{\text{quantified}} + \text{LOD}$. The undetermined value was taken equal to zero, inducing a maximum relative error of $\text{LOD}/C_{\text{quantified}}$.

Case 3: both fractions were $<$ LOQ in one or several sample(s). Such situation has been addressed by Antweiler and Taylor (2008) and Antweiler (2015) [36,37], who compared a wide variety of treatments for left-censored environmental data, with two distinct objectives: (i) deriving summary statistics [37] and (ii) performing group comparisons [38]. It appeared that below 20-30% of censoring, four to five methods were almost equally effective: for the objective (i), replacing the undetermined term by $\text{LOQ}/2$ or by a random number between 0 and LOD, regression on order statistics, or the Kaplan-Meier technique; for the objective (ii), replacing the undetermined term by $\text{LOQ}/2$, $\text{LOQ}/\sqrt{2}$, or LOQ , maximum likelihood estimation techniques, or approaches based on the generalized Wilcoxon test. Conversely, for higher degrees of censoring, all treatments

performed poorly whatever the objective. Interestingly, the only method that satisfactorily met both objectives was the replacement of non-quantified values by LOQ/2. Antweiler and Taylor (2008) [37] cautioned that this substitution approach “requires a thorough understanding of how the laboratory censored the data”, which is evidently the case for the present study, as the analytical method was specifically developed for this study. Considering the aforementioned elements, this third case had itself to be declined in two situations.

Case 3.1: the frequency of quantification was $\geq 75\%$. The same treatment as mentioned in Cases 1 and 2 was applied to the concentrations $< \text{LOQ}$, then the theoretical distribution of the dataset was estimated according to the method presented in the subsequent paragraph 1.3.3.

Case 3.2: the frequency of quantification was $< 75\%$. No particular treatment was applied to the data (*i.e.*, $< \text{LOQ}$ values were retained as such), and no attempt was made to perform inferential statistics the dataset, which was only described by its range and median values.

1.3.2. Evaluation of biocide removal in WWTP

The joint measurement of biocide concentrations in WWTP influents and effluents enabled the evaluation of the treatment efficiency E for each compound and each sampling campaign. The latter was calculated according to equation 2a when both influent and effluent concentrations were quantified in at least one phase (dissolved or particulate). In case both dissolved and particulate concentrations were $< \text{LOQ}$ in the effluent sample (*resp.* influent sample), but quantified in the paired sample, a lower bound (*resp.* upper bound) of the removal E could be estimated according to equation 2b (*resp.* 2c). Conversely, when the concentrations in all fractions were $< \text{LOQ}$ in both influent and effluent samples, the treatment efficiency was indeterminate.

Standard descriptive statistics (*i.e.* min-max and median value) were then applied to the set of 6 values resulting from the 6 sampling campaigns in WWTP.

$$E(\%) = \left(1 - \frac{C_{\text{effluent}}}{C_{\text{influent}}}\right) \times 100 \quad (\text{a})$$

$$E(\%) > \left(1 - \frac{\text{LOQ}_{\text{effluent}}}{C_{\text{influent}}}\right) \times 100 \quad (\text{b})$$

$$E(\%) < \left(1 - \frac{C_{\text{effluent}}}{\text{LOQ}_{\text{influent}}}\right) \times 100 \quad (\text{c})$$

Equation 2. Calculation of the WWTP removal E : (a) when both the influent concentration C_{influent} and the effluent concentration C_{effluent} were quantified; (b) when the effluent concentration was $< \text{LOQ}_{\text{effluent}}$; (c) when the influent concentration was $< \text{LOQ}_{\text{influent}}$.

1.3.3. Statistical modelling of the concentration data

The acquired data are by nature punctual in time and space: they correspond to specific days/storm events and sources in the study area (i.e., *Seine centre* WWTP and Clichy CSO). The objective of this statistical modelling approach is (i) to allow a stochastic extrapolation of the measurements to the non-analysed events and non-sampled urban sources, and (ii) to explicitly account for additional uncertainties, such as analytical errors for biocide concentrations and measurement errors for flow rates. In the subsequent developments, for each biocide with a sufficient number of quantified values ($\geq 75\%$), concentrations from each type of source will be considered as random variables, the statistical distributions of which are fitted to the concentration datasets.

In doing so, it is assumed that the collected data are representative of the inter-day/inter-event variability of biocide concentrations over the whole study period (i.e., March 2018 – May 2019); as a reminder, diurnal variations were already integrated through the sampling protocol which consisted of collecting flow-dependent composite samples, over 24h for WWTP influents and effluents, and over the event duration for CSO discharges. As presented above, *a posteriori* verifications were carried out to guarantee that the distribution of various water quality parameters over the sampled days/events was not statistically different from the whole study period, so it may be considered acceptable to extend this assumption to the quantified biocides.

On one hand, in order to avoid over-parametrization considering the small number of measurements in WWTP influents and effluents ($n = 6$), the retained statistical model was a continuous uniform distribution on $[C_{\text{min}}, C_{\text{max}}]$, where C_{min} and C_{max} are respectively the minimum and maximum measured concentrations for the considered biocide, or $[0, C_{\text{max}}]$ when one value was $< \text{LOQ}$. For the effluents, the choice of this model was also consistent with the fact that treatment processes in WWTPs tend to smooth the variability of influent concentrations. On the other hand, the log-normal distribution has been reported to be well suited to describe event mean concentrations of various micropollutants in stormwater [39]. It was considered that this model could be retained for CSO data, in view of the size of the datasets ($n = 8$) as well as the

typical shape of empirical cumulative distribution functions (the example of diuron is provided on figure 2; the other ones are presented as supplementary material, figures S4 and S5). The parameters of the distribution were estimated via the method of moments (equation 3). The adequacy of all fitted model was verified by the Kolmogorov-Smirnov test, which systematically led to p-values > 0.05 whether for WWTP influents and effluents or for CSOs, indicating that the retained models can be considered appropriate to describe the data (see supplementary material, figures S4 and S5).

$$\begin{cases} \exp\left(\mu + \frac{\sigma^2}{2}\right) = m_n \\ (\exp(\sigma^2) - 1) \cdot \exp(2\mu + \sigma^2) = s_n^2 \end{cases} \Leftrightarrow \begin{cases} \sigma^2 = \ln\left(1 + \left(\frac{s_n}{m_n}\right)^2\right) \\ \mu = \ln(m_n) - \frac{\sigma^2}{2} \end{cases}$$

Equation 3. Estimation of the parameters (μ , σ) of the log-normal distribution via the method of moments, where m_n and s_n are the empirical mean and standard deviation of the concentrations, respectively.

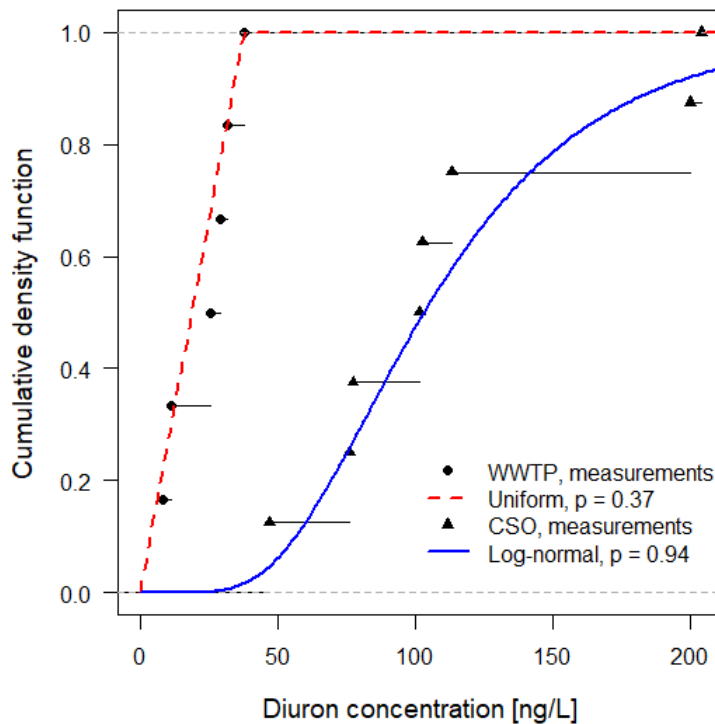


Figure 2. Empirical cumulative density functions of diuron concentrations in WWTP effluents and CSO discharges (step functions); fitted uniform and log-normal distributions.

As regards the analytical uncertainties, the dissolved and particulate fractions have to be considered separately. Uncertainty on dissolved concentrations was estimated via the coefficient of variation (c_V) of the replicates obtained during the validation of the method [33]. Concerning the particulate fraction, uncertainty related to TSS concentration was previously determined as 10% [40,41] and that related to the particulate extraction is unknown but supposed to be lower than uncertainty on the dissolved fraction, as previously reported by Wieck et al. (2018) [42] for most of the analysed biocides. Hence, uncertainty on the total concentration was conservatively estimated as the highest one (i.e. that on the dissolved fraction), and modelled as a Gaussian term with a null mean and a coefficient of variation of c_V .

Reasoning with statistical distributions enables Monte Carlo simulations to be carried out, in order to propagate the inherent uncertainties of the measured variables to different quantities of interest such as the annual loads of biocides. The latter are then appraised as distributions instead of punctual values, from which confidence intervals can be estimated [39]. The ranges presented in the following sections to compute the modelling uncertainties are all based on a 95% confidence level. The data processing and subsequent stochastic approach were performed with R software, version 3.6.

1.3.4. Estimation of stormwater proportion in CSOs

Stormwater proportions in CSOs can be estimated, in accordance with a method developed and validated by the SIAAP, using sample conductivity as a conservative tracer and assuming that CSO waters were only made of stormwater and wastewater [39] leading to equation 4.

$$\begin{cases} x_{SW} + x_{WW} = 1 \\ \lambda_{CSO} = x_{SW} \times \lambda_{SW} + x_{WW} \times \lambda_{WW} \end{cases} \Rightarrow x_{SW} = \frac{\lambda_{WW} - \lambda_{CSO}}{\lambda_{WW} - \lambda_{SW}}$$

Equation 4. Estimation of the stormwater proportion in CSO sample (x_{SW}), from the relationships with the wastewater proportion (x_{WW}) and the electrical conductivities in CSO, stormwater, and wastewater (λ_{CSO} , λ_{SW} , and λ_{WW} respectively).

The conductivity in raw stormwater, λ_{SW} (resp. wastewater, λ_{WW}) has been demonstrated to fall within the range 80-150 $\mu\text{S}/\text{cm}$ (resp. 1050-1170 $\mu\text{S}/\text{cm}$). So as to account for this uncertainty, Monte Carlo simulations were used to estimate x_{SW} in CSOs. Pairs of values ($\lambda_{SW}, \lambda_{WW}$) were randomly sampled from uniform distributions on these intervals, then x_{SW} calculated for each

sampled event using equation 4. The procedure was repeated 100,000 times in order to derive statistical distributions and confidence intervals on these 8 values.

1.3.5. Estimation of concentrations in stormwater

A similar approach was carried out to estimate the concentrations of biocides in raw stormwater – not sampled in the present study – from the acquired data in CSOs (wet weather) and WWTP influents (dry weather), both coming from comparable watersheds. Dilution between stormwater and wastewater is assumed to be the prevailing process during biocide transport in sewers, which may be acceptable since the transfer time in the sewer system (several hours) is lower than the typical values of biocide half-lives (several days), so degradation may be neglected [6]. Thus, an analogous relationship to equation 4 may be proposed for biocide concentrations, leading to equation 5.

$$C_{SW} = \frac{1}{x_{SW}} [C_{CSO} - (1 - x_{SW}) \times C_{WW}]$$

Equation 5. Estimation of biocide concentration in stormwater C_{SW} (ng/L), where x_{SW} is the proportion of stormwater in the CSOs sample, C_{WW} and C_{CSO} are the concentrations (ng/L) in wastewater and CSOs, respectively.

Again, a stochastic approach was carried out to estimate C_{SW} , applying additional random terms since C_{CSO} and C_{WW} values were not matched (because sampling of CSOs and WWTP influents was not undertaken on the same day). Hence, for each sampled CSO event and retained biocide:

- i. x_{SW} was computed as mentioned above (*cf.* paragraph 1.3.4);
- ii. C_{CSO} was estimated as $C_{CSO}^{meas} \times (1 + \delta_C)$, where C_{CSO}^{meas} is the measured value, and δ_C represents the (relative) analytical error, randomly computed from a normal distribution $\mathcal{N}(0, c_V)$ (c_V being the coefficient of variation of the replicates obtained during the validation of the method – *cf.* paragraph 1.3.3);
- iii. C_{WW} was modelled as $C_{WW}^{rand} \times (1 + \delta_C)$, where C_{WW}^{rand} is a random value sampled from the fitted distribution for wastewater;
- iv. C_{SW} was calculated from equation 5.

The procedure was repeated 100,000 times as well, leading to statistical distributions of biocide concentrations in stormwater for the 8 CSO events.

1.3.6. Annual mass loads estimation at the scale of the Paris conurbation

The objective of this section is to compare the order of magnitude of the annual mass loads of biocides discharged into the Seine River from WWTPs and CSOs at the Paris conurbation scale. Contaminant loads are typically calculated from equation 6, however, although the flow rate is continuously monitored by SIAAP with a controlled accuracy – so that the discharged volumes $V_{\text{discharge}}^i$ are available on a daily (resp. event) basis for the WWTPs (resp. CSOs) – only a few samples were collected and analysed for biocide concentrations C_{source}^i .

$$\phi_{\text{source}} = \sum_{i=1}^N C_{\text{source}}^i \cdot V_{\text{discharge}}^i$$

Equation 6. Calculation of the annual mass load of one biocide (ϕ_{source}) discharged into the Seine river from one urban source, where $N = 365$ for WWTPs and $N =$ number of discharged events for CSOs, C_{source}^i is the daily/event mean concentration of biocide in the WWTP effluents/CSO discharges, and $V_{\text{discharge}}^i$ is the discharged volume for day/event i .

In order to get an estimation at the scale of the Paris conurbation, the statistical distributions of biocide concentrations were assumed to be representative of (i) the annual variability of biocide concentrations in urban discharges, and (ii) the non-sampled urban sources of biocides (*Seine aval* WWTP, *La Briche* and the seven Parisian CSOs). While there are more uncertainties in extrapolating the results up to the whole city scale, the data do allow us to gain a first assessment of the impacts of a megacity like Paris on biocide contamination in the receiving water bodies, which in turn contributes to fill a knowledge gap regarding the contribution of urban areas to riverine pollution.

As regards the temporal variability, it should be kept in mind that the sampling campaigns were carried out on different days, so that the data can be considered representative of a typical work week. The assumption that Clichy CSO is representative of the other CSOs in the study area (hypothesis ii) is supported by two elements: on one hand, the relative uniformity of land use and population density; on the other hand, the aforementioned regulation on pesticide use in the entire metropolitan area of Paris. This ban is likely to limit the importance of outdoor practice-related sources of biocides, whereas the buildings whose materials incorporate biocidal substances may be assumed to be uniformly distributed over the study area. For WWTPs, this hypothesis will be

further discussed in view of the acquired results because the two WWTPs have not the same treatment processes (see supplementary files, part III).

The stochastic approach was conducted as follows for each source (WWTPs and CSOs):

- i. The daily or event volumes $V_{\text{discharge}}^i$ were estimated as $V_{\text{discharge}}^{\text{meas},i} \times (1 + \delta_V)$, where $V_{\text{discharge}}^{\text{meas},i}$ is the measured value for day/event i , and δ_V represents the measurement error, randomly computed from a normal distribution $\mathcal{N}(0, c_V)$, with $c_V = 5\%$ for WWTPs and 15% for CSOs, as mentioned above;
- ii. For each compound, N (= 365 for WWTPs and number of discharged events for CSOs) concentrations C_{source}^i were modelled as $C_{\text{source}}^{\text{rand},i} \times (1 + \delta_C)$, where $C_{\text{source}}^{\text{rand},i}$ were randomly sampled from the adequate statistical distribution, and the term δ_C has the same meaning as above (*cf.* paragraph 1.3.5);
- iii. The annual load was calculated from equation 6.

The procedure was repeated 100,000 times so as to obtain statistical distributions of the annual loads. In doing so, biocide pathways into receiving waters during dry and wet weathers could be prioritized.

2. Results

2.1. Biocides in WWTP influents and effluents

2.1.1. Occurrences of biocides in WWTP influents

The frequencies of quantification, the median, minimum and maximum concentrations, and the proportion of biocide in the particulate fraction are reported in table 1. In WWTP influents, most of the biocides were quantified in almost all samples, except mecoprop (3/6), cybutryn (1/6) and CMIT (0/6). Three levels of concentrations could be distinguished: (i) concentrations of MIT, BIT, BZK C12, and BZK C14 were consistently higher than 100 ng/L, (ii) median concentrations of diuron, BZK C16, terbutryn, carbendazim, and thiabendazole ranged between 10 and 100 ng/L, and (iii) concentrations of isoproturon, CMIT, OIT, DCOIT, cybutryn, terbuthylazine, IPBC, and mecoprop were lower than 10 ng/L.

A temporal variability was observed within the six sampling campaigns. Concentrations could vary within more than one order of magnitude for the same compound, such as diuron (from 3.2 to 35 ng/L) or BZK C12 (from 460 to 5800 ng/L). BZK C12 seems to be the most abundant benzalkonium compound, with a median total concentration of 1.2 µg/L. It is followed by BZK C14 (260 ng/L) and then BZK C16 (73 ng/L). These observations are consistent with the composition of most domestic products containing benzalkonium compounds, which contain proportionally higher concentrations of BZK C12 [43].

In France, Guillossou et al. (2019) [44] reported similar results for diuron in the dissolved fractions of *Seine centre* WWTP influents and similar variability, i.e. 31 ng/L ± 42%. Compared to the present study, higher concentrations of isoproturon were measured by Mailler et al. (2015) [45], from 11 to 62 ng/L. This decrease might be due to change in practice between their study (2013) and the present study (2018-2019), such as the ban of isoproturon as a pesticide in 2017 or the implementation of national programs towards the reduction of pesticide use. In other countries, study sites and conditions are very variable (WWTP size between 23,000 and 530,000 inhabitant equivalent, different sampling techniques, number of campaigns, sewer systems, weather conditions, etc.) and so are the measured concentrations [4,14,21,22,46–48]. For instance, the reported ranges for carbendazim concentrations are 5 ng/L [14] to 920 ng/L [4], and for mecoprop concentrations 1 ng/L [14] to 870 ng/L [21]. Compared to this study, BIT was quantified at higher concentrations (1.7-3.2 µg/L) by Rafoth et al. (2007) [49] in the dissolved fraction of WWTP influents and by Wieck et al. (2018) [42] in the total fraction of domestic wastewater at the outlet of a small catchment. OIT was measured in the same range (total fraction) in untreated wastewater by Wieck et al. (2018) [42] and Östamn et al. (2017) [50], between 1 and 7 ng/L, while they measured higher concentrations of benzalkonium compounds (5 µg/L for BZK C12, 2.7 µg/L for BZK C14 and 0.3 µg/L for BZK C16).

1 **Table 1.** Acquired data in *Seine centre* WWTP and Clichy CSOs (quantification frequencies, median total concentrations (min-max),
 2 particulate proportions and WWTP removal)

	Clichy CSOs			WWTP influents			WWTP effluents			Median WWTP removal (min / max)
	Frequency of quantification	Median concentrations in ng/L (min / max)	Median particulate proportions (min / max)	Frequency of quantification	Median concentrations in ng/L (min / max)	Median particulate proportions (min / max)	Frequency of quantification	Median concentrations in ng/L (min / max)	Median particulate proportions (min / max)	
Diuron	8/8	100 (47 / 200)	4% (1% / 8%)	6/6	20 (3.2 / 35)	<22% *	6/6	27 (8.2 / 38)	<5% *	-60% (-183% / -9%)
Isoproturon	8/8	7.9 (5.6 / 15)	15% (5% / 43%)	5/6	1.5 (<0.6 / 3.1)	14% (8% / 59%)	5/6	1.0 (<0.5 / 3.2)	6% (2% / 10%)	30% (-4% / 44%)
MIT	8/8	70 (9.8 / 290)	33% (10% / >71%)	6/6	620 (350 / 860)	1% (0.3% / 5%)	6/6	150 (39 / 350)	<1% *	78% (55% / 89 %)
BIT	8/8	32 (4.6 / 64)	60% (46% / >90%)	6/6	320 (210 / 660)	7% (2% / 11%)	6/6	24 (20 / 55)	<7% *	92% (88% / 94%)
CMIT	4/8	14 (<9.5 / 160)	40% (<8% / >84%)	0/6	<13	-	0/6	<3.7	-	-
OIT	8/8	27 (18 / 46)	26% (5% / 53%)	6/6	5.9 (1.1 / 9.0)	24% (<11% / 45%)	2/6	<1.8 (<0.7 / 2.0)	<26% *	>78% (65% / >80%)
DCOIT	6/8	4.6 (<0.5 / 6.3)	<7% *	5/6	4.5 (<0.6 / 10)	<20% *	6/6	1.5 (0.5 / 4.6)	<8% *	67% (<-200% / 82%)
BZK C12	8/8	2600 (1300 / 5800)	7% (1% / 33%)	6/6	1200 (460 / 5800)	21% (3% / 84%)	6/6	320 (110 / 1700)	2% (0.4% / 28%)	77% (-53% / 94%)
BZK C14	8/8	960 (420 / 2100)	6% (1% / 33%)	6/6	260 (22 / 4600)	15% (5% / 94%)	4/6	55 (<41 / 400)	6% (1% / 12%)	74% (-130% / >99%)
BZK C16	6/8	190 (<110 / 380)	4% (2% / >6%)	5/6	73 (<29 / 340)	>19% (1% / >82%)	2/6	<41 (<9.8 / 79)	(<3% / >12%)	64% (<-200% / >97%)
Terbutryn	8/8	44 (29 / 64)	6% (1% / 11%)	5/6	11 (<0.7 / 20)	3% (<1% / 5%)	6/6	15 (11 / 37)	<1% *	-77% (<-200% / -13%)

Cybutryn	3/8	<1.1 (<0.7 / 5.9)	<20% *	1/6	<0.7 (<0.7 / 0.7)	<20%	0/6	<2.2	-	-
Terbutylazine	8/8	2.5 (<1.6 / 34)	54% (4% / >79%)	5/6	0.9 (<0.7 / 3.6)	16% (<7% / >28%)	5/6	0.7 (<0.3 / 2.2)	6% (<2% / 10%)	51% (-1% / 69%)
Carbendazim	8/8	79 (24 / 250)	4% (1% / 13%)	5/6	21 (<0.8 / 74)	<2% (<0.2% / 4%)	6/6	20 (3.5 / 37)	<1% *	12% (<-200% / 63%)
IPBC	2/8	<15 (<6.4 / 21)	<54% / >65%	5/6	8.7 (<8.2 / 27)	>42% (19% / >53%)	5/6	3.9 (<3.7 / 8.9)	>41% (11% / >52%)	53% (-60% / >82%)
Thiabendazole	8/8	11 (4.8 / 24)	19% (13% / 71%)	6/6	15 (3.2 / 27)	4% (2% / 15%)	6/6	18 (13 / 28)	< 1% *	-17% (-325% / 10%)
Tebuconazole	8/8	38 (28 / 47)	6% (3% / 17%)	6/6	8.3 (1.3 / 10)	9% (<2% / 58%)	6/6	6.2 (4.3 / 16)	2% (1% / 3%)	-39% (-229% / 49%)
Mecoprop	8/8	130 (86 / 290)	<9%*	3/6	<7.7 (<7.2 / 110)	<14% *	5/6	12 (<3.6 / 66)	<18% *	4% (<-144% / 90%)

3 * All particulate proportions are lower than this value

4

2.1.2. Occurrence in effluents and biocide removal in the WWTP

Similar to influents, most of the biocides were quantified in almost all effluent samples. However, BZK C14 was quantified in four samples, OIT, BZK C16, and cybutryn were quantified in less than two samples, and CMIT was never quantified. Also, similar orders of magnitude were observed regarding concentrations (table 1). For most of the biocides, the three levels of concentrations that were observed for influents were also found for effluents, except for (i) BIT, the median concentration of which decreased by a factor of 10, (ii) DCOIT, the median concentration of which decreased by a factor of 8, and (iii) MIT, and benzalkonium compounds, the median concentrations of which decreased by a factor of 4 to 5.

Almost equivalent quantification frequencies and biocide concentrations in effluents compared to influents suggest a limited efficiency of treatment processes for the 18-targeted biocides. Concentrations were compared using paired Wilcoxon test. The only compounds showing significantly lower concentrations in effluents were MIT and BIT (p-value < 0.05). On the contrary, terbutryn concentrations were significantly higher in effluents.

WWTP removals were then calculated and are presented in table 1. Only isothiazolinone removals were systematically higher than 50%, with medians between 67% for DCOIT and 92% for BIT. A much more irregular treatment efficiency was observed for the other biocides, generally leading to poor removals and even occasionally to negative performances of the WWTP. Median removals ranged from 64% to 77% for benzalkonium compounds (but negative outliers could be observed as well), from 51% to 53% for IPBC and terbuthylazine, and from 4% to 30% for isoproturon, carbendazim, and mecoprop. Four biocides (diuron, terbutryn, thiabendazole and tebuconazole) were not removed at all and median removals were negative (from -77% to -17%). Such increases in concentration were previously observed [22,44,51]. Therefore, two assumptions were made. First, the parent compound might be transformed back through the WWTP from metabolites or other compounds [52]. Indeed, conjugated metabolites were identified for terbutryn (glutathione conjugated [53]), thiabendazole (glucuronide and sulfate ester of 5-hydroxythiabendazole [54]), and tebuconazole (TEB-OH and TEB-COOH, both as free molecules and as glucuronide conjugates [55]), which hence supports the first hypothesis for these three substances. For diuron, more investigations are needed to explain the negative removal. The second assumption concerns analytical uncertainties, generally between 30% and 40% in influents and around 20% in

effluent, which might explain some of the negative removals. Except for terbutryn, the lowest values of removal are associated with the lowest influent concentrations. No correlation was observed between removals and biocide hydrophobicity ($\log K_{ow}$) or hydrophobicity corrected with pH ($\log D$ at pH=7.4) or sorption coefficients ($\log K_{oc}$).

In the literature, biocide removals vary from one study to another but are usually lower than 50% [2,21,22,44,46,48,52,56–58]. Similar to this study, a good removal of DCOIT (75%), OIT (80%) and BIT (> 80%) was observed by Chen et al. (2012) [46], Liu et al. (2017) [58] and Juksu et al. (2019) [48], respectively. In the same way, Östman et al. (2017) [50] found benzalkonium compounds to be very well removed (around 100%) from wastewater in which they were measured between 1.7 and 30 $\mu\text{g/L}$.

The present results allow reconsideration of the assumption made in Section 1.3.4, where it was hypothesized that the data collected at the *Seine centre* WWTP may be considered representative of both treatment plants in the study area. In former studies, treatment processes have been demonstrated to be similar or more efficient in *Seine centre* WWTP compared to *Seine aval* WWTP regarding this type of micropollutants [59,60]. Since it appears that the removal efficiency achieved in *Seine centre* WWTP is either very limited or highly variable for a certain number of biocides, similar values may be expected in the effluents of the other WWTP, so the extrapolation made may be justified for these compounds. As to the biocides which are partially removed by the *Seine centre* WWTP, the extrapolation to *Seine aval* WWTP will likely lead to a lower limit of the annual load.

2.1.3. Distribution between dissolved and particulate fractions in WWTP

Beyond the total concentrations presented above, the collected data enabled the assessment of the distribution of biocides between the dissolved and particulate fractions. The particulate proportions are reported in table 1. Biocides were frequently quantified in both fractions, even though they were mainly present in the dissolved fraction. In both influents and effluents, the median particulate proportions of the studied biocides were generally lower than 20%, but some biocides have occasionally been detected in higher proportions in the particulate fraction of influents (isoproturon, benzalkonium compounds and tebuconazole). The highest particulate proportions were observed for IPBC (> 40% in both matrices). No correlation between particulate proportion and biocide $\log K_{ow}$ or $\log D$ at pH=7.4 or particulate organic matter fraction or $\log K_{oc}$ values was

observed. The 18-targeted biocides have been poorly investigated in the particulate fraction of water samples up to now. Indeed, only two studies have considered both fractions [42,50]. Contrary to this study, Wieck et al. (2018) [42] did not detect diuron, OIT, terbutryn, carbendazim and tebuconazole in particles, and higher particulate proportion of BIT (23% against 7% here) were observed. Higher proportions of benzalkonium compounds were also obtained in these two studies (up to 90% against 21% here for BZK C12).

2.2. Biocides in CSOs

2.2.1. Occurrences of biocides in CSOs

In Clichy CSOs, most of the biocides were quantified in all samples (table 1). DCOIT and BZK C16 were quantified in six of the eight samples and CMIT in five samples. Only cybutryn and IPBC displayed a frequency of quantification < 50%. Four levels of median concentration were observed: (i) concentrations of benzalkonium compounds were significantly higher than 100 ng/L, up to 2600 ng/L for BZK C12; (ii) diuron and mecoprop were quantified in the range of 100 ng/L; (iii) MIT, BIT, CMIT, OIT, terbutryn, carbendazim, IPBC, thiabendazole, and tebuconazole were measured between 10 and 100 ng/L; (iv) median concentrations of isoproturon, DCOIT, cybutryn, and terbuthylazine were lower than 10 ng/L. As well as in WWTP influents, concentrations can vary within more than one order of magnitude, which is the case of MIT (from 10 to 290 ng/L) or carbendazim (from 24 to 250 ng/L) for instance. This variability might be due to rain intensity or duration, leading to variable proportion of stormwater in CSOs (from 50% to 90% in the present study) as discussed below, or temperature, which can favour or limit biocide diffusion in building materials and transfer to runoff [31,61].

Among the few studies that have investigated the presence of biocides in CSOs [16–18,62], only Launay et al. (2016) [16] measured total concentrations, as the analysis was performed on original homogenised and membrane-filtered samples. Carbendazim was quantified between 15 and 42 ng/L [16]. Concentrations were found to exceed 100 ng/L for isoproturon, terbuthylazine, terbutryn (up to 200 ng/L [16,17]), mecoprop (up to 380 ng/L [16]) and diuron (up to 1600 ng/L [18]). These concentrations are consistent with the results of the present study, except for isoproturon. To the best of the authors' knowledge, concentrations of the other biocides are not available in the literature.

2.2.2. Distribution between dissolved and particulate fractions in CSOs

The particulate proportions of biocides in CSOs are reported in table 1. Even if biocides were mainly present in the dissolved fraction, they were frequently quantified in both fractions. Particulate proportions of most of the biocides remain lower than 20%. Proportions of MIT, CMIT, OIT and thiabendazole ranged between 20% and 50% and BIT, terbuthylazine and IPBC were mostly present in particles. Similar to WWTP influents and effluents, these proportions were not correlated neither to $\log K_{ow}$, nor to $\log D$ at pH 7.4, nor to the particulate organic matter fraction, nor the $\log K_{oc}$ values. In the literature, such data are only available for benzalkonium compounds in stormwater [20], in which they were mostly detected in the particulate fraction (> 99%). These proportions are far higher than the present values. The differences might be due to the features of the watersheds (larger watershed and higher impervious surface area in this study, different land use), leading to (i) a different organic matter quality, which influences interactions between substances and TSS [63,64], (ii) a different amount of TSS, from 34 to 105 mg/L for Van de Voorde et al. (2012) [20] and from 113 to 401 mg/L in this study.

3. Discussion on biocide origins and pathways into the aquatic environment

3.1. Origins of biocides in CSOs

3.1.1. Differences between dry and wet weathers influent concentrations

CSO (wet weather) and WWTP (dry weather) influent samples were collected from comparable watersheds as explained in section 1.1.2. Therefore, the fraction of wastewater in CSOs is assumed to have the same composition as what was sampled in *Seine centre* WWTP influents during dry weather. As a first approach to discriminate the origins of biocides in CSOs (wastewater vs. stormwater), the concentrations measured in CSOs and dry weather influents were compared both graphically (figure 3) and via the statistical test of Mann-Whitney. Total concentrations of MIT and BIT were found to be significantly higher (p -value < 0.05) in WWTP influents than in CSO samples, which suggest a dilution of wastewater by stormwater. These compounds are, indeed, widely used in domestic products [65]. On the contrary, total concentrations of diuron, isoproturon,

OIT, terbutryn, cybutryn, terbuthylazine, carbendazim, tebuconazole and mecoprop were significantly lower in WWTP influents than in CSOs. They mostly originated from stormwater due to the lixiviation of building materials during wet weather. Finally, no significant difference was observed for CMIT, DCOIT, benzalkonium compounds, IPBC and thiabendazole. These compounds are hence supposed to be brought almost equally by wastewater and stormwater, which is consistent with their use in domestic products (cosmetics, disinfectants, pharmaceuticals, sweeteners, etc.) and as preservatives in building materials (paints, renders, woods, etc.).

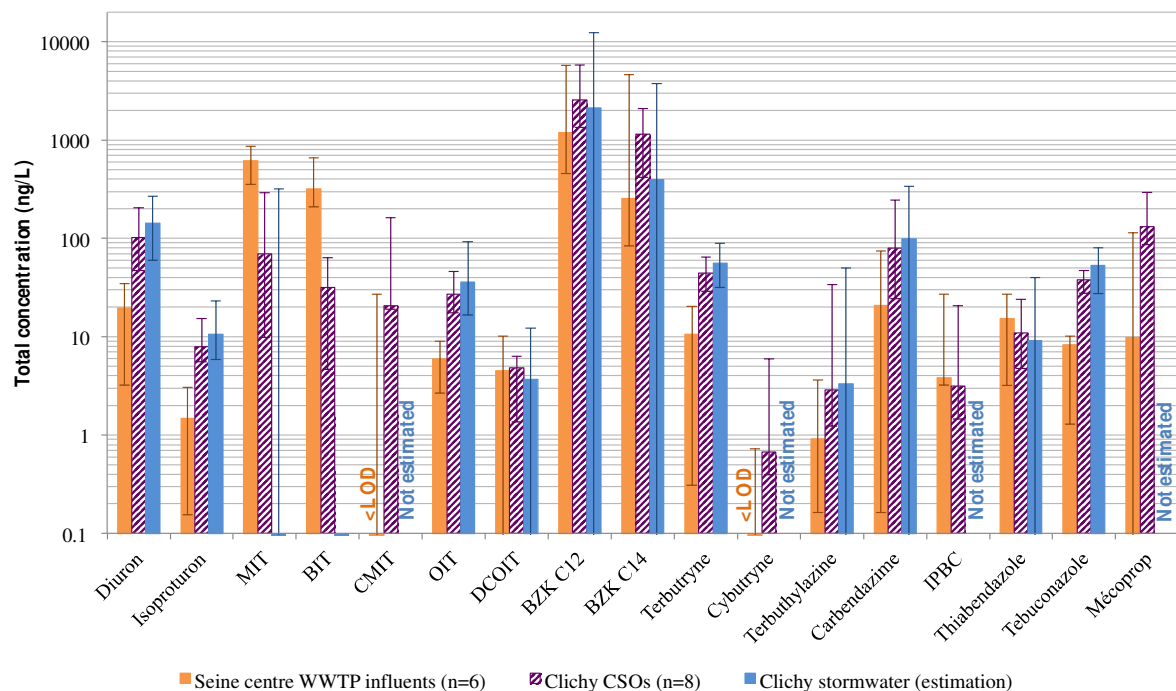


Figure 3. Measured median total concentrations of the 18-targeted biocides in *Seine centre* WWTP influents in dry weather (n=6), Clichy CSOs in wet weather (n=8), and estimated median total concentrations in Clichy stormwater (*cf.* paragraph 1.3.5). The bars represent minimum and maximum values for WWTP influents and CSOs, and the computed 95% confidence interval on these values for stormwater.

3.1.2. Contribution of stormwater in CSOs

The second approach consisted in studying the evolution of concentrations in CSOs with respect to stormwater proportions, which varied from 50 to 90% depending on the rain event. The examples of diuron (mainly brought by stormwater) and BIT (mainly brought by wastewater) are shown in figure 4. For the other biocides, figures are provided in supplementary material

(figures S6, S7 and S8). In the same way as above, three trends could be observed. Concentrations of BIT, BZK C12 and C14, thiabendazole and IPBC appeared to decrease with increasing stormwater proportion. These results suggest a dilution of wastewater by stormwater. However, except for BIT, trends are not clearly marked. On the contrary, concentrations of diuron, isoproturon, terbuthryn, carbendazim, tebuconazole and mecoprop tended to increase with increasing stormwater proportion, which pointed out a major contribution of stormwater to the contamination of CSOs by these biocides. These results are consistent with the study of Launay et al. (2016) [16] for diuron, isoproturon, and mecoprop, which showed the highest contribution of stormwater to discharged loads, and the study of Bollmann et al. (2014) [14] for isoproturon and mecoprop, which were solely related to stormwater inputs, and for terbuthryn, carbendazim and diuron, which were mainly emitted during wet weather. However, contrary to the present study, they showed that wastewater and rainwater contributed in comparable ways for tebuconazole. Finally, no trend was observed for MIT, CMIT, OIT, DCOIT, BZK C16, cybutryn and terbuthylazine, which may originate from both types of water. The statistical significance of these trends was assessed via a correlation test (Pearson or Spearman in accordance with the normality of the distribution), and confirmed for diuron and BIT (p -value < 0.05).

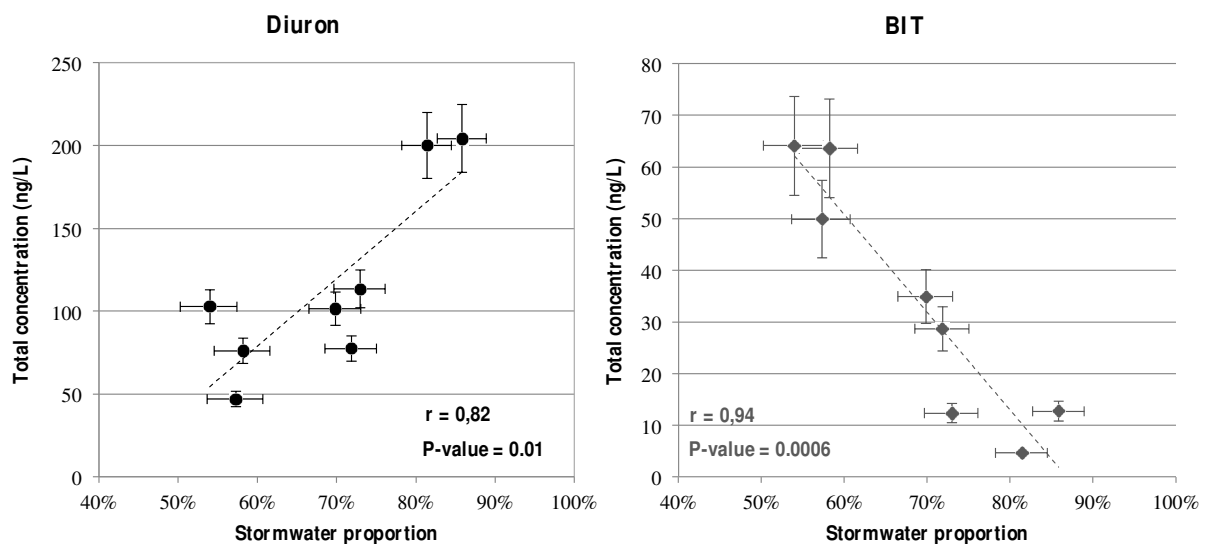


Figure 4. Total concentrations of diuron and BIT in Clichy CSOs versus stormwater proportion.

Previous studies, which were conducted as part of the French OPUR research program, showed that hydrophobic compounds mostly present in the particulate fraction might originate from sewer

deposit erosion [66,67]. In the case of this study, this phenomenon was considered negligible as (i) compounds were mostly measured in the dissolved phase and (ii) a decrease in concentration or no trend was observed with an increase of stormwater proportion for compounds mostly measured in the particulate phase.

3.1.3. Reconstitution of stormwater concentrations

The preceding results have shown that for several compounds stormwater can play a major role in the contamination of water discharged by CSOs. On the basis of the acquired data, concentrations in stormwater were estimated using Monte Carlo simulations (*cf.* paragraph 1.3.5). The results are presented in figure 3, except for the compounds whose frequency of quantification was lower than 75% in CSOs and/or WWTP influents. Benzalkonium compounds were estimated at the highest median concentrations (2 µg/L for BZK C12 and 0.4 µg/L for BZK C14 in average). Median concentrations of diuron and carbendazim were in the range of 100 ng/L; those of isoproturon, OIT, terbutryn, thiabendazole and tebuconazole between 10 and 100 ng/L; those of DCOIT, and terbuthylazine lower than 10 ng/L; and the concentration of MIT and BIT was estimated equal to zero. For most of the biocides, estimated values are in the same order of magnitude than those measured in influents and CSOs (DCOIT, BZK C12, thiabendazole) or higher (diuron, isoproturon, OIT, terbutryn, terbuthylazine, carbendazim, tebuconazole, mecoprop), which highlight an important contribution of stormwater to the contamination of CSOs by biocides. However, the estimated median concentrations of MIT and BIT were equal to zero whereas it largely exceeds 100 ng/L in influents. This corroborates the previously hypothesized dilution of wastewater by stormwater for these compounds.

In a previous assessment carried out in France, BIT, OIT, cybutryn and terbutryn were not detected in stormwater (concentrations were lower than LOD, i.e., lower than 4 ng/L) [19]. These results are consistent with the present study for BIT and cybutryn. However, OIT and terbutryn was estimated with concentrations much higher than 4 ng/L, i.e. 36 and 56 ng/L. Compared to the present study, isoproturon, diuron and carbendazim were measured with higher concentrations (up to 12 µg/L) [19]. These compounds are also used as pesticides but their uses were banned or limited in France (since 2008 for diuron, 2009 for carbendazim and 2017 for isoproturon), which could explain the recent decrease of their concentrations. On the contrary, concentrations of mecoprop in stormwater were presently estimated between 63 and 497 ng/L, whereas Gasperi et al. (2013) [19] measured it from less than 1 ng/L to 10 ng/L. Benzalkonium compounds (sum of BZK C12

and BZK C14) were quantified by Van de Voorde et al. (2012) [20] in the same order of magnitude (7-28 µg/L). In other countries, measured concentrations in stormwater are highly variable: from < 20 to 1500 ng/L for carbendazim, from < 30 to 67 ng/L for OIT, from < 10 to 600 ng/L for phenylureas, from 1 to 260 ng/L for triazines, and from < 20 to 90 ng/L for tebuconazole [14–17]. In general, lower concentrations were estimated in this study.

3.2. Annual contributions of CSOs and WWTPs at the Paris conurbation scale

In order to compare both contributions of CSOs during wet weather and WWTPs during dry weather, discharged mass loads into the Seine River were estimated and compared at the year and conurbation scales (*cf.* paragraph 1.3.6). Results are presented in figure 5, except for compounds for which the frequency of quantification was lower than 75%. Biocide loads in WWTP effluents were found to range in the following order: isoproturon, terbuthylazine (< 1 kg/yr) < DCOIT, IPBC, thiabendazole, tebuconazole (1-10 kg/yr) < diuron, BIT, terbutryn, carbendazim, mecoprop (10-100 kg/yr) < MIT, BZK C12 (> 100 kg/yr). The order appeared to be approximately the same for CSOs, but the mass loads differed by one or two order(s) of magnitude: isoproturon, DCOIT, terbuthylazine (< 0.1 kg/yr) < BIT, terbutryn, thiabendazole, tebuconazole (0.1-1 kg/yr) < diuron, MIT, carbendazim, mecoprop (1-10 kg/yr) < BZK C12 (> 10 kg/yr).

Therefore, at the year and city scales, WWTPs seem to constitute the major pathway of biocides into receiving waters, although the concentrations in effluents are lower than in CSOs, because of much higher discharged volumes (as a reminder, 620 M m³ versus 10.6 M m³ in 2018). However, contrary to WWTP effluents, which are continuously discharged into the river over the year, CSOs are punctual releases and are generally discharged at higher flow rates than WWTP effluents. They can hence have a higher local and one-off impact on aquatic organisms. Environmental risk assessment is thus needed. Comparing local discharges of WWTPs or CSOs with mass loads that are transiting within the Seine River could be a first approach.

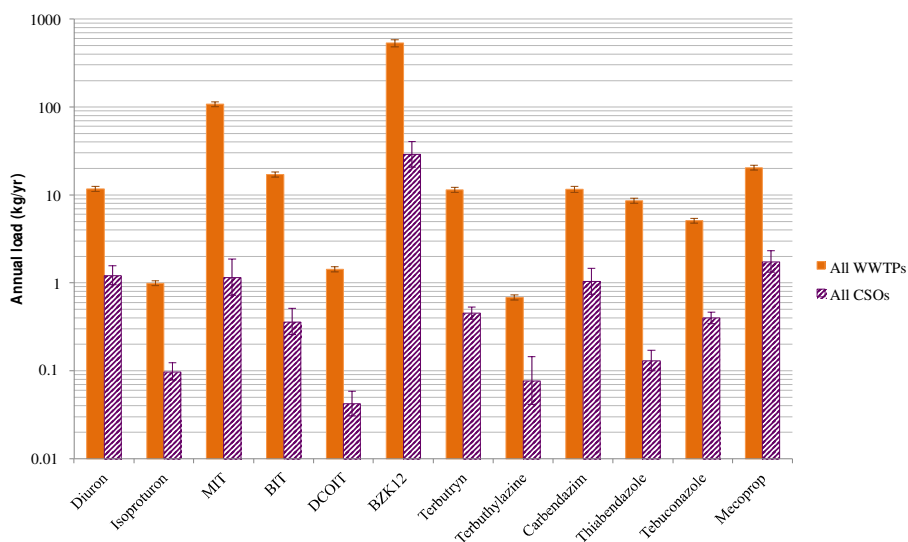


Figure 5. Annual loads discharged in the Seine River by WWTPs (*Seine centre* and *Seine aval*) and by CSOs (Clichy, La Briche and Parisian ones) during wet weather, estimated via Monte Carlo simulations. The error bars represent the computed 95% confidence interval on these values.

The annual loads obtained were normalized by the number of inhabitants within the study area (5.9 M) in order to get a rough estimation of the biocide loads per capita discharged into the river by WWTPs. These values, which overall fell within 0.5-250 $\mu\text{g/d/capita}$ (see supplementary material, table S6), can be compared with previous assessments and offer a perspective to transpose the present results to other case studies. In the available literature, two studies [48,58] addressed the question of biocide loads discharged by WWTPs. The values estimated by Liu et al. (2017) [58] in the Guangdong province (South China) were consistent with the present findings for DCOIT and carbendazim but one order of magnitude lower for BIT and thiabendazole. Loads estimated by Juksu et al. (2019) [48] in several regions of Thailand were in the same order of magnitude for BIT and thiabendazole but seven times higher for carbendazim. These differences may partly originate from the methodology itself (use of average concentrations and daily flow in these studies vs. statistical distributions in the present approach, sampling campaigns, etc.) but might also be explained by the contrasting cultures and thus the different consumption patterns. This approach showed some limits already mentioned in the methodology section. Other factors than population density might play a key role in the results and their interpretation. These factors are related to (i) the study site (type of sewer system, land-use), (ii) the sampling campaigns (number of samples, distribution of the sampling campaigns throughout the week, the year), and

(iii) the methodology itself (uncertainties, pre-treatment of the dataset, extrapolation steps). In particular, it should be noticed that the fitting of the distribution model depends on experimental data, notably on the extreme measured concentrations, so that the restricted number of data might slightly distort the distribution model and thus the results. The latter shall not be taken as definitive values, but rather as a first approximation of the biocide loads at a large scale. However, they are already of primary interest in order to fill a knowledge gap regarding the contribution of urban areas to riverine pollution (acquisition of data, identification and prioritization of sources), and thus may support regulatory developments and emphasize technical solutions for the reduction of biocides, and more generally micropollutants, at source.

CONCLUSIONS

The results from this study showed the ubiquity of the 18-targeted biocides in both WWTP waters and CSOs. In these matrices, biocides were frequently quantified in the dissolved and particulate fractions, even though they were mainly present in the dissolved phase. High concentrations of MIT, BIT (0.2-0.9 $\mu\text{g/L}$ for both) and BZK C12 (0.5-6 $\mu\text{g/L}$) were measured in wastewater. The ubiquity of biocides in wastewater from a heavily urbanized and scarcely industrialized city like Paris, and the measured concentrations raise the issue of human exposure to these substances in everyday life. In CSOs, the dominant biocides were benzalkonium compounds (up to 5.8 $\mu\text{g/L}$ for BZK C12), MIT (up to 0.3 $\mu\text{g/L}$), carbendazim (up to 0.3 $\mu\text{g/L}$), mecoprop (up to 0.3 $\mu\text{g/L}$) and diuron (up to 0.2 $\mu\text{g/L}$). These concentrations measured in urban discharges suggest possible contamination of the receiving aquatic environment and highlight the need for implementing of source control measures. The conventional treatments in WWTP showed a limited efficacy regarding these compounds: poor WWTP median removals (< 60%) were measured for most of the biocides, except for isothiazolinones for which median removals ranged from 67% to 92% and were relatively stable from one campaign to another, and for benzalkonium compounds for which median removals ranged from 64% to 77% but were more variable from one campaign to another. Negative removals were observed for diuron, terbutryn, thiabendazole, and tebuconazole, which is worth investigating in further studies. Advanced treatment in WWTP could be an effective solution to mitigate the release of these contaminants into the aquatic environment from WWTP effluents [44]. However, it is expensive and has no effect on stormwater discharges from separate sewer systems or CSOs. In cities like Paris, where the sewer system is mostly

combined, discriminating the origins of biocides in CSOs (wastewater vs. stormwater) can help identify their sources (domestic uses vs. outdoor uses) and hence can help provide efficient measures to reduce contaminants at source. The present study showed that most of the biocides came in similar proportions from wastewater, i.e. domestic uses such as cleaning products, cosmetics, pharmaceuticals, sweeteners, etc., and stormwater, i.e. leaching of building materials, as pesticide use has been drastically reduced for years in the Paris Conurbation. Conversely, BIT mainly came from wastewater contrary to diuron, isoproturon, terbutryn, carbendazim, tebuconazole, and mecoprop for which stormwater mostly contributed to the CSO contamination. The present study has provided an original statistical modelling approach in order to interpret the obtained data, to go beyond the study period/monitored catchment, and to estimate biocide loads at the annual/global scale. This extrapolation enables to characterize the impacts of a megacity like Paris on the receiving water bodies, with a controlled uncertainty. Annual mass loads discharged by WWTPs and CSOs in the Seine River were estimated at the conurbation scale and showed that WWTP discharges are the major pathway of biocides into the river on a wide scale. However, environmental risk assessment is needed, as CSOs may have a higher local and punctual impact on aquatic organisms (one-time releases at higher flow rates than WWTP effluents).

AUTHOR INFORMATION

Corresponding Author

*Phone: +33 1 64 15 36 26; e-mail: adele.bressy@enpc.fr

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

BIT, 1,2-benzisothiazol-3(2H)-one; BZK, benzalkonium; CMIT, 5-chloro-2-methyl-4-isothiazolin-3-one; CSOs, combined sewer overflows; DCOIT, 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one; DOC, dissolved organic carbon; IPBC, Iodopropynyl butylcarbamate; LOD, limit of detection; LOQ, limit of quantification; MIT, 2-methyl-4-isothiazolin-3-one; OIT, octylisothiazolinone; SIAAP, Paris public sanitation service; TSS, total suspended solids; WWTP, wastewater treatment plant.

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Supplementary material

Urban pathways of biocides towards surface waters during dry and wet weathers: assessment at the Paris conurbation scale

Claudia Paijens^{1,2}, Adèle Bressy^{1}, Bertrand Frère², Damien Tedoldi¹, Romain Mailler³,
Vincent Rocher³, Pascale Neveu⁴ and Régis Moilleron¹*

¹ Leesu, Ecole des Ponts, Univ Paris Est Creteil, Marne-la-Vallée, France

² Laboratoire Central de la Préfecture de Police, Paris, France

³ SIAAP, Direction de l'Innovation, Colombes, France

⁴ Mairie de Paris, Direction de la Propreté et de l'Eau, Service Technique de l'Eau et de
l'Assainissement, Paris, France

* Corresponding author: adele.bressy@enpc.fr

PART I. TABLES

Table S1. Information on sampling campaigns at *Seine centre* WWTP (GPS coordinates: 48.934302, 2.248139)

Sampling date	Day of the week	Treated volumes (10^3 m ³ /day)	Conductivity (μ S/cm)		TSS (mg/L)		DOC (mgC/L)		POC (mgC/L)	
			Influent s	Effluent s	Influent s	Effluent s	Influent s	Effluent s	Influent s	Effluent s
16/04/18	Tuesday	236 \pm 12	965	785	271	2.8	26	6.0	120	1.4
26/06/18	Tuesday	213 \pm 11	1087	926	260	8.3	24	5.1	100	3.0
20/09/18	Thursday	243 \pm 12	998	824	172	2.9	19	5.7	68	1.2
04/02/19	Monday	215 \pm 11	1027	848	155	3.3	31	7.6	51	1.1
12/03/19	Tuesday	241 \pm 12	869	700	236	4.8	28	6.0	106	2.0
02/04/19	Tuesday	238 \pm 12	935	694	228	5.9	42	7.3	98	2.3

TSS: Total Suspended Solid

DOC: Dissolved Organic Carbon

POC: Particulate Organic Carbon

Table S2. Information on sampling campaigns at Clichy CSO (GPS coordinates: 48.906191, 2.296798)

Sampling date	Discharge duration (min)	Discharged volume (10^3 m ³)	xsw (%)	Conductivity (μ S/cm)	TSS (mg/L)	DOC (mgC/L)	POC (mgC/L)
28/03/18	455	178 \pm 27	50-57	573	244	-	-
23/05/18	250	479 \pm 70	78-84	300	139	11	35
05/06/18	141	79 \pm 12	70-76	384	271	12	95
10/06/18	1005	1420 \pm 210	83-89	256	133	5.5	37
11/11/18	255	34 \pm 5	55-62	644	401	19	152
12/11/18	645	244 \pm 37	66-73	497	194	12	79
07/03/19	385	184 \pm 27	69-75	395	396	12	149
08/05/19	1340	1080 \pm 160	54-61	540	481	20	196

TSS: Total Suspended Solid

DOC: Dissolved Organic Carbon

POC: Particulate Organic Carbon

Table S3. Information on the 18-targeted biocides

Biocide	Abbreviation	CAS number	Formula	MW (g/mol)	Log Kow	Log Koc*	pKa	logD*	PNEC (µg/L)
Diuron		330-54-1	C ₉ H ₁₀ Cl ₂ N ₂ O	233.1	2.85	2.134		0.13	0.02
Isoproturon		34123-59-6	C ₁₂ H ₁₈ N ₂ O	206.3	2.5	2.399		2.45	0.021
Methylisothiazolinone	MIT	2682-20-4	C ₄ H ₅ NOS	115.2	-0.49	1.445		-0.23	3.9
Benzisothiazolinone	BIT	2634-33-5	C ₇ H ₅ NOS	151.2	0.64	2.017		1.41	
Chloromethylisothiazolinone	CMIT	26172-55-4	C ₄ H ₄ ClNOS	149.6	0.4	1.655		1.12	0.049
Octylisothiazolinone	OIT	26530-20-1	C ₁₁ H ₁₉ NOS	213.3	2.45	3.326		2.99	0.013
Dichlorooctylisothiazolinone	DCOIT	64359-81-5	C ₁₁ H ₁₇ Cl ₂ NOS	282.2	3.59	3.456		4.43	0.008
Benzyl dimethyldodecyl ammonium chloride	BZK C12	139-07-1	C ₂₁ H ₃₈ ClN	304.5	1.7				0.04
Benzyl dimethyltetradecyl ammonium chloride	BZK C14	139-08-2	C ₂₃ H ₄₂ ClN	346.6	2.5				
Benzyl dimethylhexadecyl ammonium chloride	BZK C16	122-18-9	C ₂₅ H ₄₇ ClN	388.7	3.2				
Terbutryn		886-50-0	C ₁₀ H ₁₉ N ₅ S	241.4	3.7	2.803	4.3	1.38	0.034
Cybutryn (Irgarol 1051)		28159-98-0	C ₁₁ H ₁₉ N ₅ S	253.4	3.7	2.380	4.1	3.21	0.001
Terbutylazine		5915-41-3	C ₉ H ₁₆ ClN ₅	229.7	3.0	2.517	2	2.99	0.06
Carbendazim		10605-21-7	C ₉ H ₉ N ₃ O ₂	191.2	1.5	2.245	4.2	1.61	0.034
Iodopropynyl butylcarbamate	IPBC	55406-53-6	C ₈ H ₁₂ INO ₂	281.1	2.8	2.563		3.2	0.026
Thiabendazole		148-79-8	C ₁₀ H ₇ N ₃ S	201.2	2.4	3.345	4.7 & 12	2.39	1.2
Tebuconazole		107534-96-3	C ₁₆ H ₂₂ ClN ₃ O	307.8	3.7	4.315	5	3.74	1
Mecoprop		93-65-2	C ₁₀ H ₁₁ ClO ₃	214.6	0.1	1.687	3.7	-0.65	44

MW: molecular weight

PNEC: predicted no effect concentration

*: Chemspider

Table S4. Limits of detection (LOD) and quantification (LOQ) in the dissolved fraction of urban waters in ng/L

Biocides	WWTP effluents		WWTP influents		CSOs	
	LOD (ng/L)	LOQ (ng/L)	LOD (ng/L)	LOQ (ng/L)	LOD (ng/L)	LOQ (ng/L)
Diuron	0.5	1.3	1.2	3.1	1.3	3.2
Isoproturon	0.21	2.1	0.44	0.44	0.56	0.56
MIT	9.2	18	13	26	9.7	19
BIT	0.58	4.3	0.98	7.3	1.4	10
CMIT	3.1	16	11	54	7.6	38
OIT	0.49	1.2	1.3	3.2	1.3	3.3
DCOIT	0.11	1.1	0.36	3.6	0.27	2.7
BZK C12	8.1	27	22	73	22	73
BZK C14	11	37	37	120	25	84
BZK C16	7.5	25	20	68	110	360
Terbutryn	0.23	0.23	0.51	0.51	0.63	0.63
Cybutryn	0.27	0.27	0.62	0.62	0.67	0.67
Terbuthylazine	0.23	0.23	0.52	0.52	0.67	0.67
Carbendazim	0.31	0.31	0.61	0.61	0.72	0.72
IPBC	2.2	4.3	5	10	5.1	10
Thiabendazole	0.27	0.27	0.58	0.58	0.69	0.69
Tebuconazole	0.18	0.18	0.38	0.38	0.55	0.55
Mecoprop	3.1	4.1	6.8	9.1	7	9.3

Table S5. Limits of detection (LOD) and quantification (LOQ) (min-max) in the particulate fraction of urban waters in ng/g (dry weight)

	WWTP effluents		WWTP influents		CSOs	
	LOD (ng/g)	LOQ (ng/g)	LOD (ng/g)	LOQ (ng/g)	LOD (ng/g)	LOQ (ng/g)
Mass of particles (mg)	4.3-11		54-84		27-130	
Diuron	9.0-23	23-58	1.0-2.0	3.0-5.0	0.8-3.7	1.9-9.2
Isoproturon	5.0-12	5.0-12	1.0	1.0	0.4-1.8	0.4-1.8
MIT	23-58	45-120	3.0-5.0	6.0-9.0	1.9-9.2	3.9-18
BIT	9.0-23	68-180	1.0-2.0	9.0-14	0.8-3.7	5.8-27
CMIT	45-120	230-580	6.0-9.0	30-47	3.9-18	19-92
OIT	9.0-23	23-58	1.0-2.0	3.0-5.0	0.8-3.7	1.9-9.2
DCOIT	5.0-12	45-120	1.0	6.0-9.0	0.4-1.8	3.9-18
BZK C12	68-180	230-580	9.0-14	30-47	5.8-28	19-92
BZK C14	68-180	230-580	9.0-14	30-47	5.8-28	19-92
BZK C16	68-180	230-580	9.0-14	30-47	5.8-28	19-92
Terbutryn	10-24	5.0-12	2.0	1.0	0.8-3.6	0.4-18
Cybutryn	5.0-12	5.0-12	1.0	1.0	0.4-1.8	0.4-18
Terbuthylazine	5.0-12	5.0-12	1.0	1.0	0.4-1.8	0.4-18
Carbendazim	5.0-12	5.0-12	1.0	1.0	0.4-1.8	0.4-18
IPBC	45-120	90-230	6.0-9.0	12-19	3.9-18	7.7-37
Thiabendazole	5.0-12	5.0-12	1.0	1.0	0.4-1.8	0.4-18
Tebuconazole	10-24	5.0-12	2.0	1.0	0.8-3.6	0.4-18
Mecoprop	68-180	90-230	9.0-14	12-19	3.9-18	7.7-37

Table S6. Biocides loads estimated using Monte Carlo simulation and normalized by the number of inhabitants

	WWTP effluents ($\mu\text{g/d/capita}$)			CSOs ($\mu\text{g/M m}^3\text{/capita}$)		
	Mean	Min	Max	Mean	Min	Max
Diuron	5.4	5.1	5.8	20	15	25
Isoproturon	0.46	0.43	0.49	1.5	1.3	2.0
MIT	50	47	53	18	12	30
BIT	8.0	7.4	8.5	5.8	4.2	8.3
DCOIT	0.66	0.62	0.71	0.5	0.7	0.9
BZK12	250	220	270	470	330	650
Terbutryn	5.3	4.9	5.7	7.3	6.2	8.5
Terbuthylazine	0.32	0.29	0.34	1.2	0.7	2.3
Carbendazim	5.4	5.0	5.8	17	12	23
Thiabendazole	4.0	3.7	4.2	2.1	1.6	2.7
Tebuconazole	2.4	2.2	2.5	6.4	5.5	7.4
Mecoprop	9.5	8.9	10	28	21	37

PART II. FIGURES

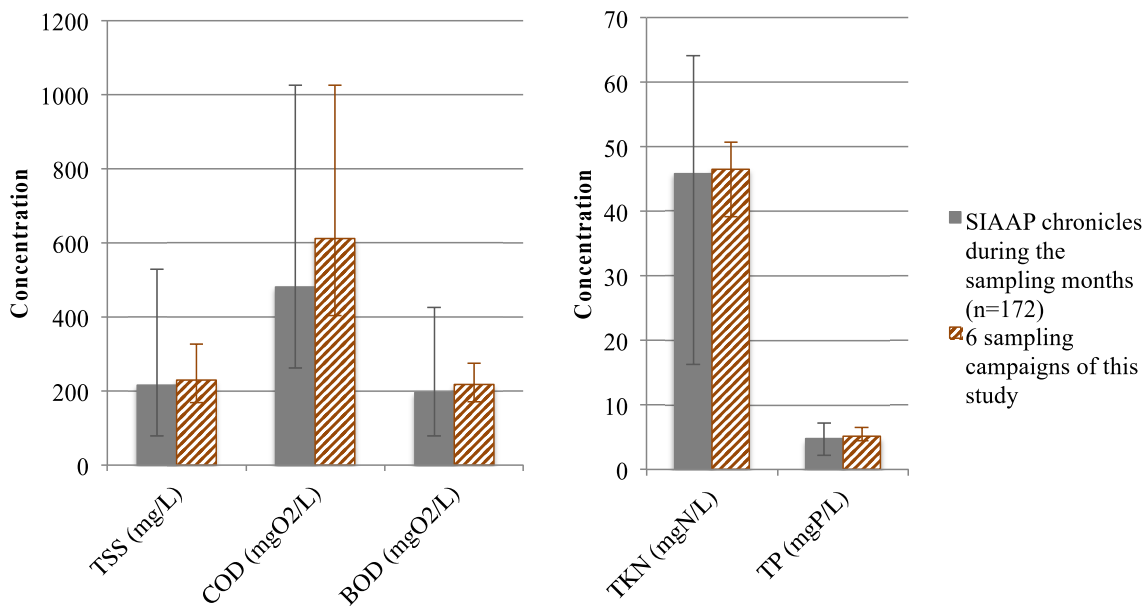


Figure S1. Representativeness of the 6 sampling campaigns in WWTP influents: comparison of the main water quality parameters with SIAAP records (minimum, mean, and maximum values)

TSS: Total Suspended Solid; COD/BOD: Chemical/Biochemical Oxygen Demand; TKN: Total Kjeldahl Nitrogen; TP: Total Phosphorus

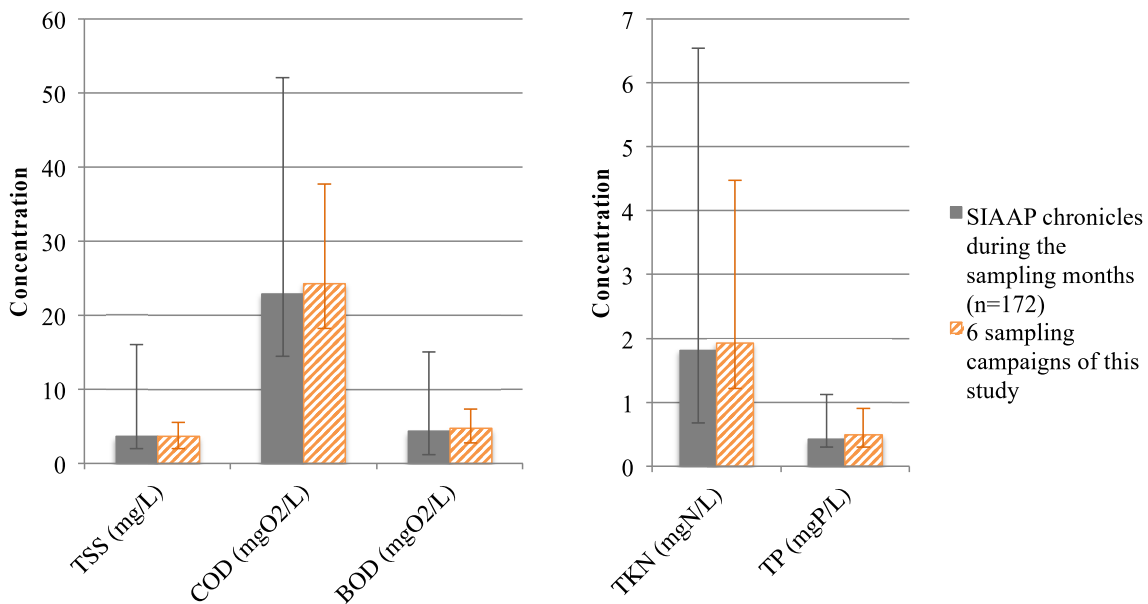


Figure S2. Representativeness of the 6 sampling campaigns in WWTP effluents: comparison of the main water quality parameters with SIAAP records (minimum, mean, and maximum values)

TSS: Total Suspended Solid; COD/BOD: Chemical/Biochemical Oxygen Demand; TKN: Total Kjeldahl Nitrogen; TP: Total Phosphorus

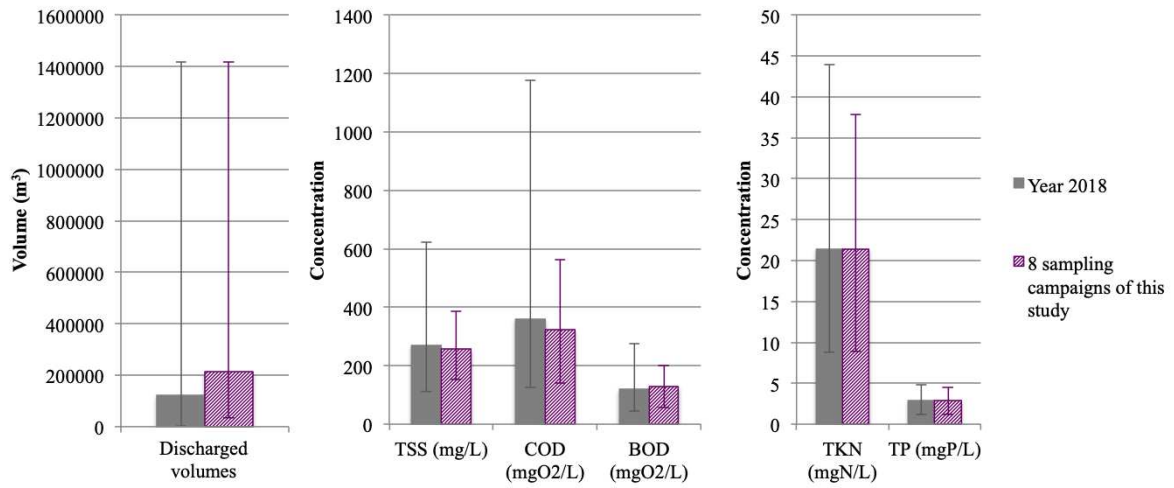


Figure S3. Representativeness of the 8 sampling campaigns in Clichy CSOs: comparison of the main water quality parameters with SIAAP records (minimum, mean, and maximum values)

TSS: Total Suspended Solid; COD/BOD: Chemical/Biochemical Oxygen Demand; TKN: Total Kjeldahl Nitrogen; TP: Total Phosphorus

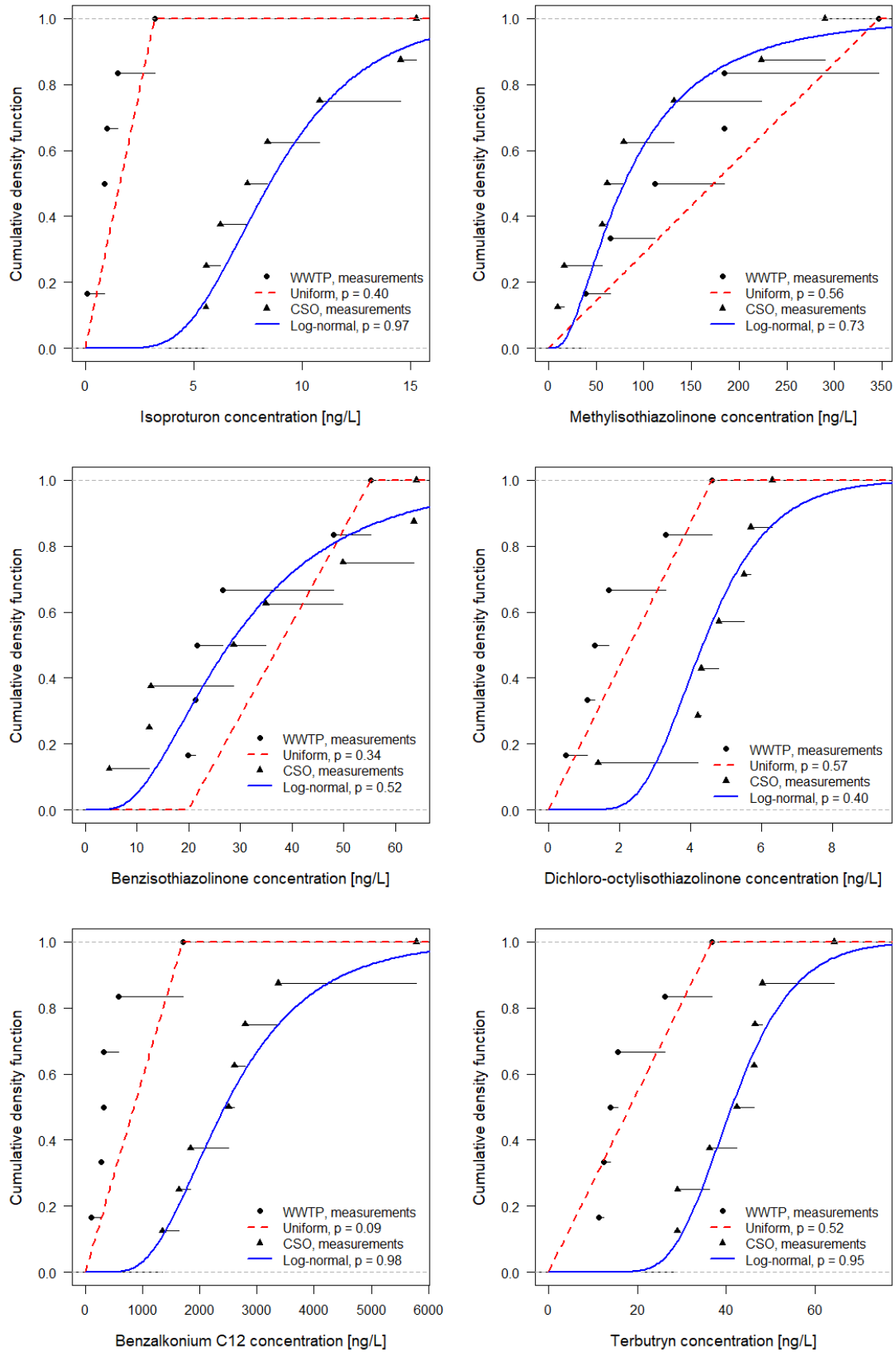


Figure S4. Empirical cumulative density functions of concentrations of isoproturon, MIT, BIT, DCOIT, BZK C12, and terbutryn in WWTP effluents and CSO discharges (step functions); fitted uniform and log-normal distributions.

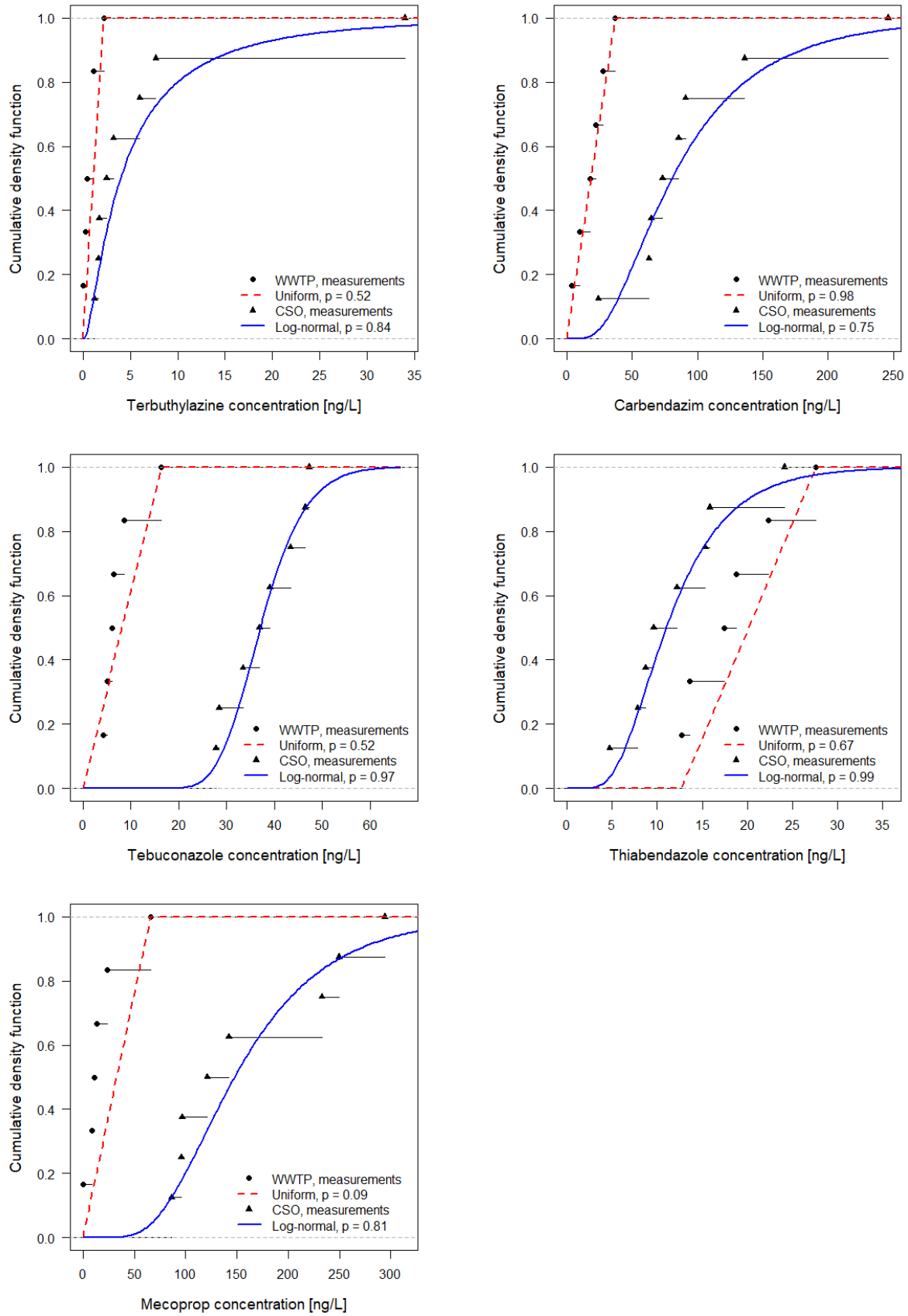


Figure S5. Empirical cumulative density functions of concentrations of terbuthylazine, carbendazim, tebuconazole, thiabendazole, and mecoprop in WWTP effluents and CSO discharges (step functions); fitted uniform and log-normal distributions.

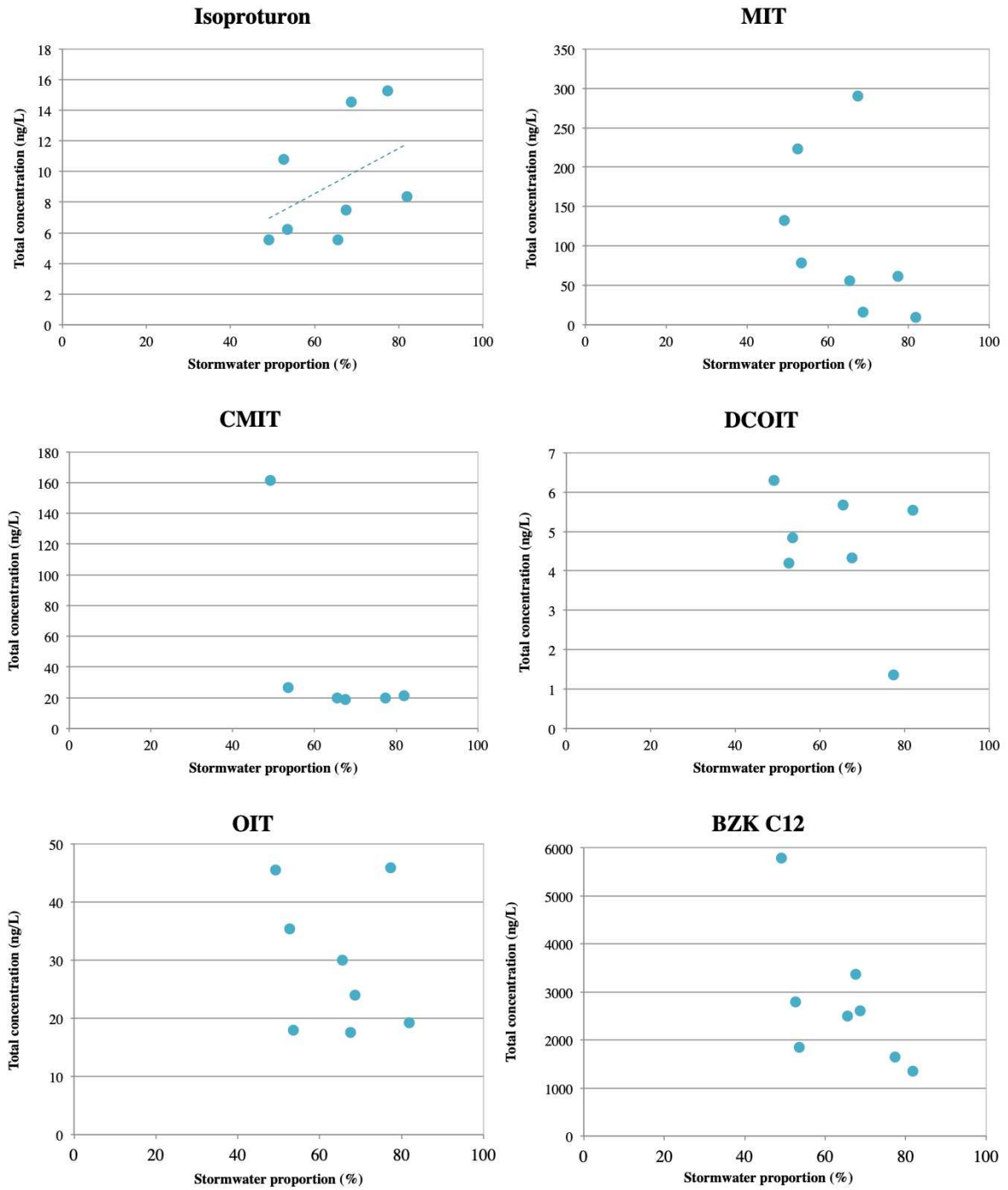


Figure S6. Total concentrations of isoproturon, MIT, CMIT, DCOIT, OIT, and BZK C12 in Clichy CSOs as a function of stormwater proportion

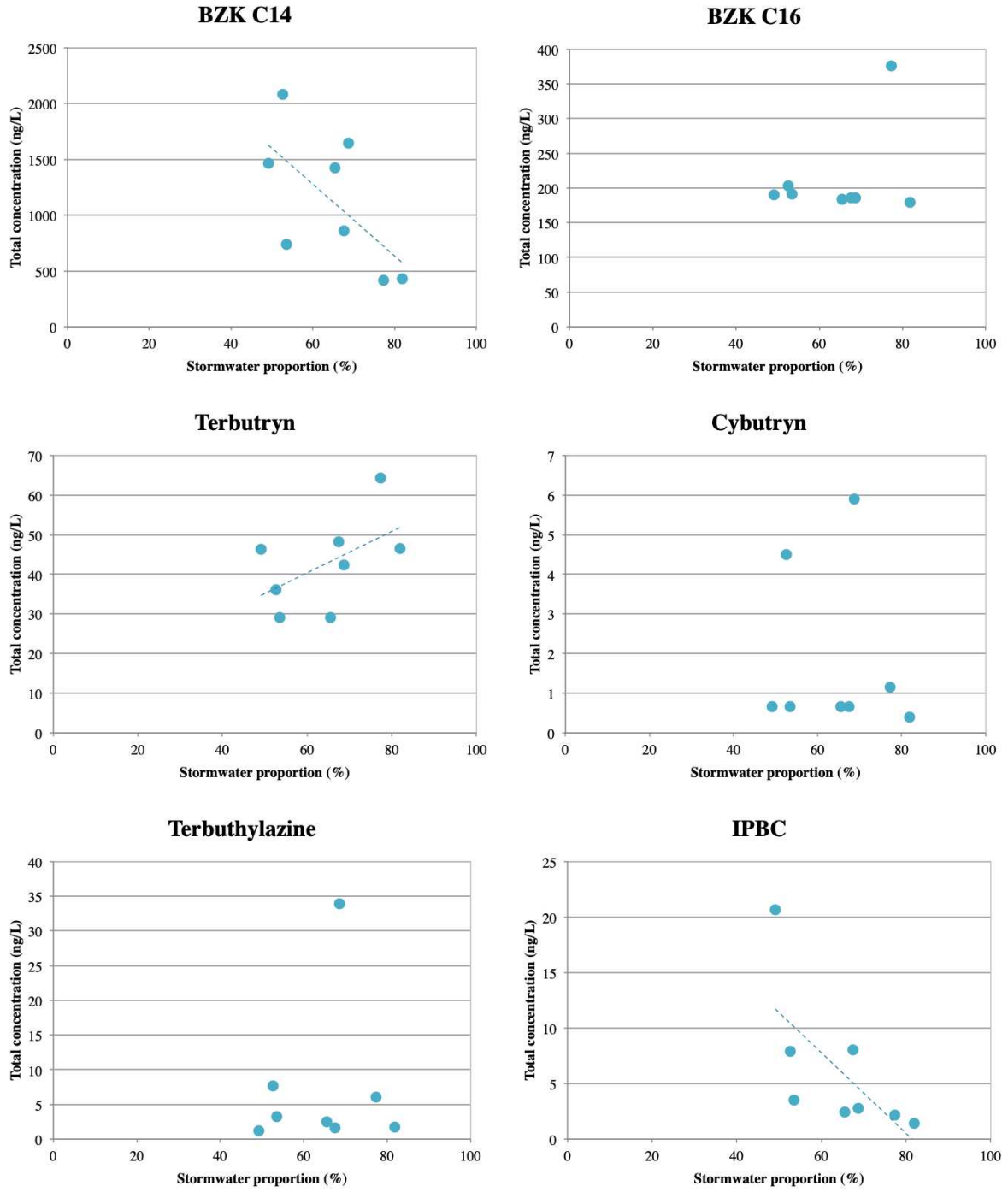


Figure S7. Total concentrations of BZK C14, BZK C16, terbutryn, cybutryn, terbuthylazine, and IPBC in Clichy CSOs as a function of stormwater proportion

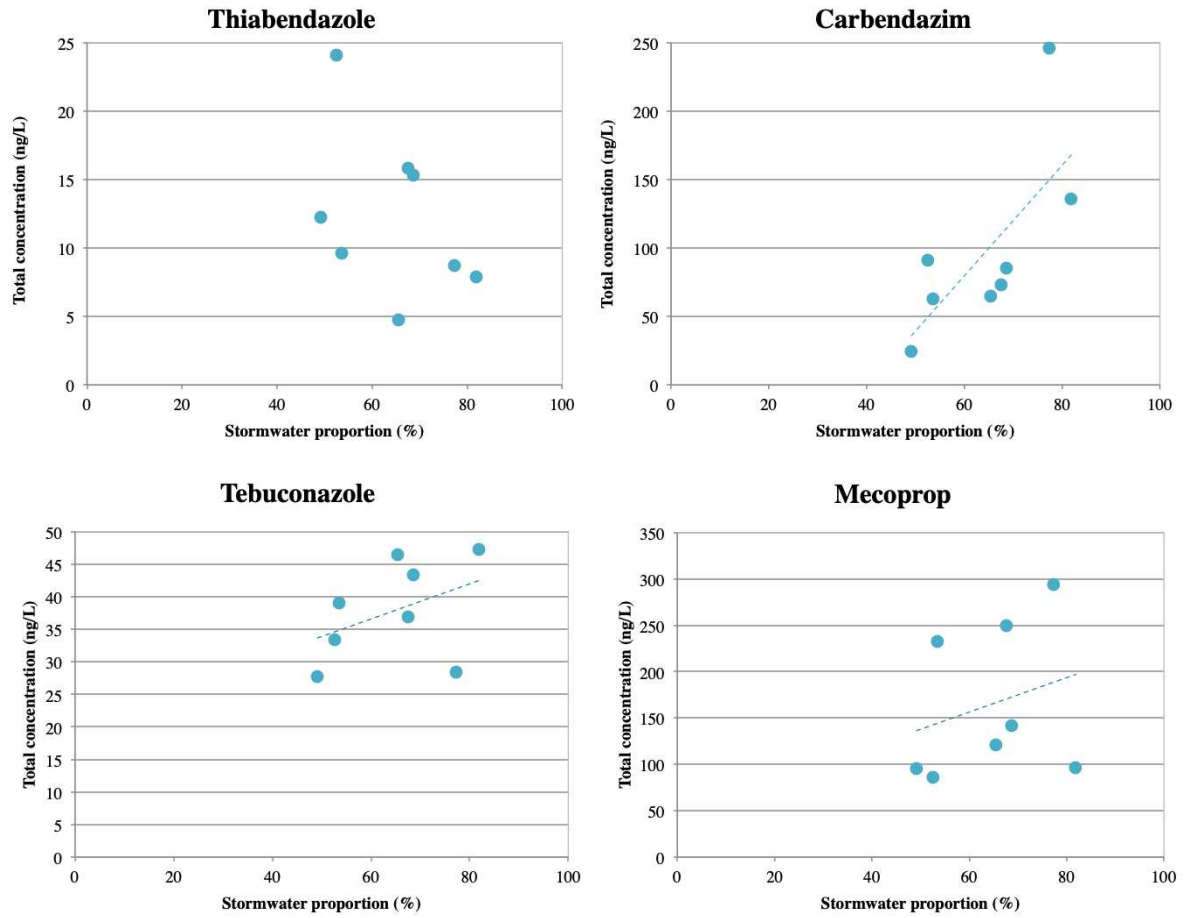
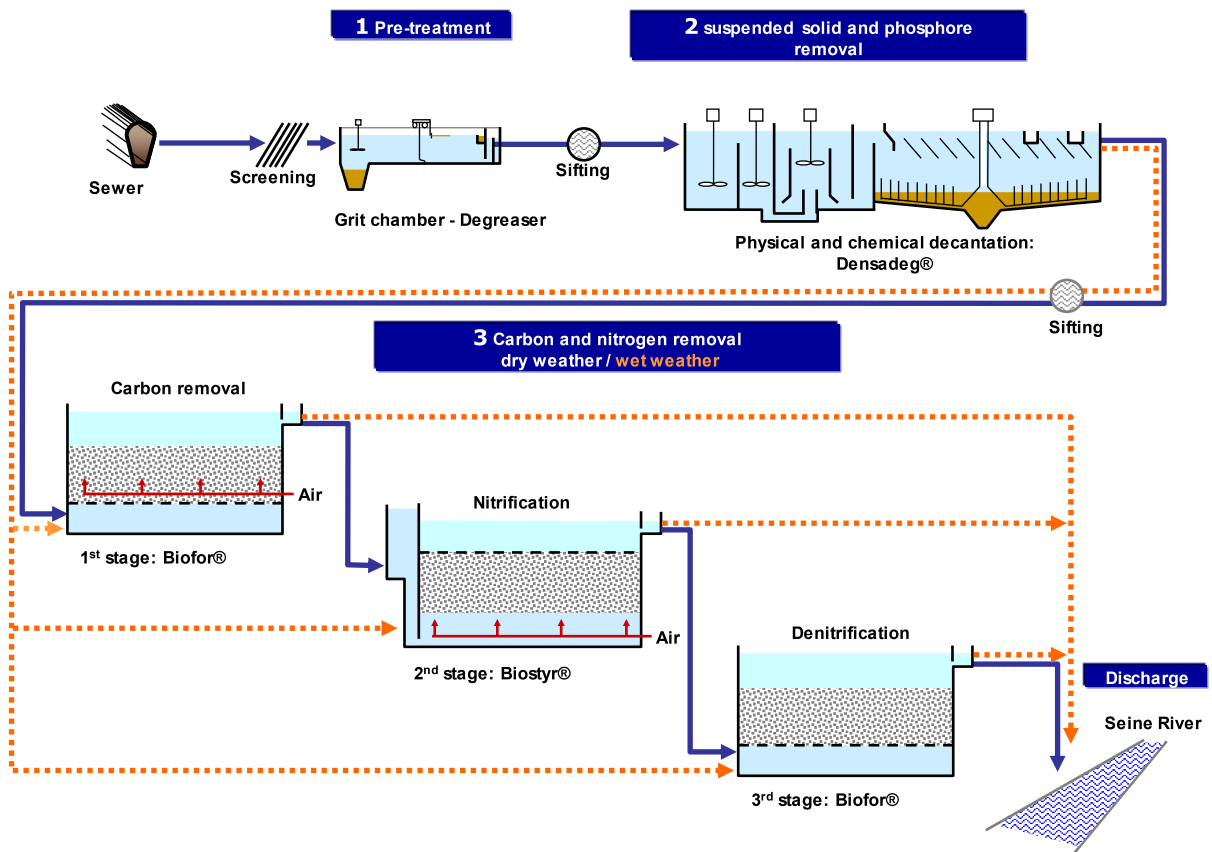


Figure S8. Total concentrations of thiabendazole, carbendazim, tebuconazole, and mecoprop in Clichy CSOs as a function of stormwater proportion

PART III. DESCRIPTION OF WWTP PROCESSES

Seine centre WWTP processes (from SIAAP)



Seine aval WWTP processes (from SIAAP)

Seine aval WWTP has a treatment capacity of 1.5 M m³ per day. After pre-treatment (stripping, screening, grit removal and degreasing), wastewaters are decanted without any reagent. After pre-treatment, wastewaters are decanted. 20% of decanted wastewater undergo biological treatment through membrane bioreactors (cut-off 0.04 μm, Ultrafor®) and 80% of decanted water are decarbonated and denitrified by biofiltration (Biostyr® and Biofor®) in 3 steps (pre-denitrification, nitrification and post-denitrification).

