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► To cite this version:

Adèle Bressy, Claudia Paijens, Damien Tedoldi, Bertrand Frère, Romain Mailler, et al.. How to estimate biocide mass loads in urban water discharges and their impact on the river contamination?. 17th International Conference on Environmental Science and Technology, Sep 2021, Athens, Greece. hal-03429502

HAL Id: hal-03429502

<https://hal.science/hal-03429502v1>

Submitted on 15 Nov 2021

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How to estimate biocide mass loads in urban water discharges and their impact on the river contamination?

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Abstract Biocidal substances are ubiquitous in urban areas; they are used as preservatives in daily products, building materials, and as domestic pesticides. Despite these facts, urban sources of biocides, contrary to agricultural inputs, have been overlooked in terms of environmental risk assessment. The overall objective of this communication is to explore the use of a stochastic approach to assess the impact of biocide urban discharges on the river contamination. Biocide contamination in surface waters up- and downstream the Paris conurbation was investigated. The urban origins of these biocides were explored by targeting wastewater treatment plant and combined sewer overflow discharges from comparable watersheds, and by assessing biocide mass loads (discharged and transiting in the river) using a stochastic approach based on Monte-Carlo simulations. The 18-targeted biocides were all quantified, and several were found at concentrations that can present high risk for the aquatic ecosystem. An increase in biocide loads between up- and downstream the Paris conurbation for several molecules and the contribution of urban discharges to biocide loads towards the receiving waters were ascertained. The results illustrate the interest of a stochastic approach to quantify the uncertainty on the determined values from a realistic description of the variability of biocide concentrations.

Keywords: Mass loads; Stochastic approach; Stormwater; Surface water; Wastewater

1. Introduction

Biocides are intensively used in household products and in building materials in urban areas. Despite the suspicion of their emission in domestic wastewater, the well-established knowledge of their leaching during wet weather at the roof or building scales, and the ascertained impacts to aquatic receiving environments, few studies have focused on their presence in urban waters (Paijens et al. 2020a). Biocides are of emerging concern and consequently not yet well integrated into aquatic

monitoring programs. As a result, few data exist in the receiving environment and they mostly concern biocidal substances also used as pesticides. Even for molecules whose use as pesticides has been prohibited for several years now, their persistence in the environment suggests the existence of hitherto neglected urban sources (Wieck et al. 2016; Kresmann et al. 2018; Merel et al. 2018). This work focused on 18 biocides and aimed at (i) collecting data on their occurrence and (ii) assessing mass loads in urban water discharges (*i.e.*, wastewater treatment plant discharges - WWTPs, and combined sewer overflows - CSOs) and in surface waters. The final objective was to prioritize biocide pathways into the aquatic environment during both dry and wet weather conditions at the Paris conurbation scale. To this end, a statistical modelling approach has been proposed to characterize the variability of biocide concentrations as well as other sources of uncertainty, and thus to allow a stochastic extrapolation of the measurements to the non-analyzed events and non-sampled urban sources within the study area.

2. Methodology

2.1. Presentation of the study area

This study focused on urban discharges from the Paris conurbation into the Seine River, between Alfortville (upstream the Paris conurbation) and Conflans-Sainte-Honorine (downstream). This area includes both the inner city of Paris and a part of its suburbs. Both are characterized by a high population density (>20,000 inhabitants/ km²), a high impervious surface area and few industrial activities. The 80-km stretch of river under study includes the confluence with the Marne River, and the discharges of two WWTPs, as well as several CSOs (*Clichy*, *La Briche* and *Parisian CSOs*) of various sizes during heavy rains. Stormwater discharges were not accounted for, as the sewer system is essentially combined in the Paris conurbation. The sampling campaigns targeted: (i) the Marne and the Seine Rivers upstream the

Paris conurbation, before their confluence, and the Seine River downstream (10 sampling campaigns covering all hydrological characteristics of the year), (ii) effluents from the *Seine centre* WWTP (6 sampling campaigns), and (iii) the biggest Parisian CSO, *i.e.*, *Clichy* CSO (8 sampling campaigns). These two latter sites have comparable urban catchments, that may be considered as representative of the entire study area, since they drain wastewater and stormwater from different neighborhoods located both in the city of Paris and in its suburbs.

2.2 Biocide analysis

Eighteen biocides were selected on the basis of their intensive use in urban areas, known exposure of aquatic populations, ecotoxicity and technical feasibility (Paijens et al. 2020b): diuron, isoproturon, methylisothiazolinone (MIT), chloromethylisothiazolinone (CMIT), benzisothiazolinone (BIT), octylisothiazolinone (OIT), dichloro-octylisothiazolinone (DCOIT), benzalkonium chlorides (BZK C12, C14 and C16), terbutryn, cybutryn, terbuthylazine, carbendazim, iodopropynyl butylcarbamate (IPBC), thiabendazole, tebuconazole and mecoprop. They were analyzed by ultra-performance liquid chromatography coupled with tandem mass spectrometry in the dissolved and particulate fractions (Paijens et al. 2020c). The data produced were published on the Pangaea data warehouse (Paijens et al. 2020d).

2.3 Data treatment

The representativeness of surface water, WWTP and CSO samples, was verified by comparing the main water quality parameters routinely monitored at the sampling points throughout the year and measured in the panel of samples. The method used for the assessment of biocide loads at the annual scale relies on Monte-Carlo simulations to propagate the inherent variability and uncertainties of the measured variables to the quantities of interest (Paijens et al. 2021). Only biocides with a sufficient frequency of quantification (>75%) were considered for these simulations. For each type of water (*i.e.*, surface waters, WWTP effluents, and CSOs), theoretical distributions

(log-normal or uniform) were first fitted to the experimental data, to characterize the temporal variability of concentrations; the goodness of fit was evaluated *via* the Kolmogorov-Smirnov test, which systematically led to *p*-values >0.05. These distributions were then used to randomly reconstruct a 1-year series of daily biocide concentrations, to which a Gaussian error term was added to represent the analytical uncertainties. These concentrations, multiplied by the daily flow rates continuously measured during the study period (likewise with an error term), provided a point estimate of the annual load of each biocide. This procedure was repeated 100,000 times in order to achieve a statistical distribution of the biocide loads, thus enabling the associated uncertainty to be characterized. In order to get an estimation at the Paris conurbation scale, the statistical distributions of biocide concentrations were additionally assumed to be representative of the non-sampled urban sources of biocides (other WWTP and CSOs). While there were more uncertainties in extrapolating the results up to the whole city scale, the data did allow us to obtain a first assessment of the impacts of a megacity such as 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 river pollution.

3. Results

3.1 Biocide occurrence in the urban discharges and in the rivers

In WWTP effluent samples, the frequency of quantification reached 100% for most of the biocides, except BZK C14, OIT, BZK C16, cybutryn and CMIT. Three levels of concentrations could be observed (Fig. 1): (i) concentrations of MIT and BZK C12 were consistently higher than 100 ng/L, (ii) median concentrations of BIT, diuron, BZK C14, terbutryn, carbendazim, and thiabendazole ranged between 10 and 100 ng/L, and (iii) concentrations of BZK C16, isoproturon, CMIT, OIT, DCOIT, cybutryn, terbuthylazine, IPBC, and mecoprop were lower than 10 ng/L.

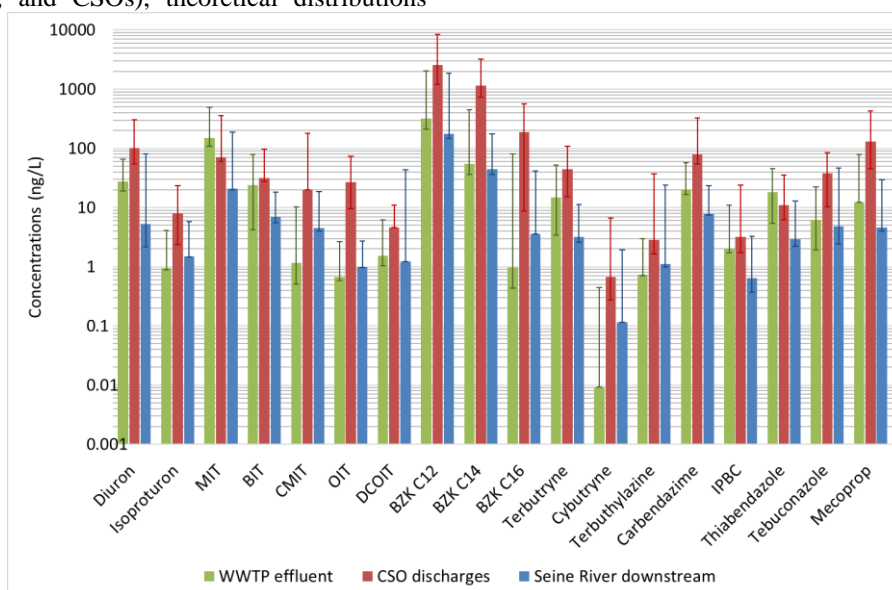


Figure 1. Median concentrations (min-max) measured in WWTP effluent, CSO and in the Seine River downstream Paris

In CSOs, most biocides were quantified in all samples. Only cybutryn and IPBC displayed a frequency of quantification below 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 displayed concentrations of the order of 100 ng/L; (iii) MIT, BIT, CMIT, OIT, terbutryn, carbendazim, IPBC, thiabendazole, and tebuconazole were measured between 10 and 100 ng/L; (iv) concentrations of isoproturon, DCOIT, cybutryn, and terbuthylazine were often lower than 10 ng/L.

For the three River sites, most biocides were quantified in more than 8 samples out of 10. Median total concentrations were generally below 10 ng/L for the three sites, except for diuron downstream Paris (14 ng/L), tebuconazole in the Marne River (20 ng/L), MIT (13-21 ng/L), BZK C14 (30 - 54 ng/L) and BZK C12 (> 100 ng/L) upstream or downstream the Paris conurbation. The Environmental Quality Standards (EQS, Directive 2013/39/EU), when they exist, were never reached. We observed that diuron, DCOIT, BZK C12, BZK C14 and carbendazim were measured at concentrations that can reach or exceed the Predicted No Effect Concentrations (PNECs) and so present high risk to the aquatic ecosystem.

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

Annual biocide loads in WWTP effluents (Table 1) were found to range in the following order: isoproturon, terbuthylazine (< 1 kg/yr) < DCOIT, thiabendazole, tebuconazole (1-10 kg/yr) < diuron, BIT, terbutryn, carbendazim, mecoprop (10-100 kg/yr) < MIT, BZK C12 and C14 (> 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 and C14 (> 10 kg/yr). Therefore, at the annual 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 greater discharged volumes. 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.

3.3 Comparison of loads up- and downstream the Paris conurbation at the annual scale

Annual loads up- and downstream the Paris conurbation were compared. Biocide mass loads presented three orders of magnitude: (i) from 10 to ~100 kg/yr for isoproturon, terbutryn, terbuthylazine, IPBC, thiabendazole; (ii) around 100-200 kg/yr for diuron, BIT, carbendazim, tebuconazole and mecoprop; (iii) from 500 to 7000 kg/yr for MIT, BZK C12 and C14. A significant increase in biocide loads could

be observed between up- and downstream the study area for diuron, isoproturon, terbutryn, and thiabendazole (Fig. 2). The evolution of this four biocide loads before and after the Paris conurbation was put into perspective with the annual mass loads discharged by the sewer system during both dry (WWTP effluents) and wet (CSOs) weathers. Fig. 2 illustrates to which extent these urban sources of biocides contribute to the load increase in the surface waters. For these four substances, the mass balance was not closed as the difference between up- and downstream the Paris conurbation was significantly higher than the estimated contributions from WWTPs and CSOs.

First, it is likely that several urban sources of biocides have been overlooked so far (direct runoff or stormwater discharges, neglected “small” CSOs, leaching of boat hulls, or untreated wastewater discharges from boats). Moreover, biocide concentrations in WWTP effluents have been extrapolated from dry weather campaigns, while the treatment performance may be lessened during wet weather. Concerning the methodology itself, our approach might have led to an underestimation of these values due to the limited size of the dataset in terms of campaign number and sampling sites.

Table 1. Annual loads discharged by the sewer system during both dry (WWTP effluents) and wet (CSOs) weathers using Monte-Carlo simulations (mean with 95% confidence intervals)

Annual mass loads (kg/year)	Σ WWTP effluents (Seine aval + Seine centre)	Σ CSO discharges (Clichy + La Briche + Parisian CSOs)
Diuron	12 (11 – 12)	1.2 (0.95 – 1.6)
Isoproturon	0.99 (0.93 – 1.1)	0.10 (0.08 – 0.12)
MIT	107 (100 – 110)	1.1 (0.72 – 1.9)
BIT	17 (16 – 18)	0.36 (0.26 – 0.51)
OIT	Not Calculated	0.31 (0.25 – 0.39)
DCOIT	1.4 (1.3 – 1.5)	0.042 (0.031 – 0.058)
BZK C12	530 (480 – 580)	29 (21 – 40)
BZK C14	120 (110 – 130)	12 (8.6 – 17)
Terbutryn	11 (10 – 12)	0.45 (0.39 – 0.53)
Terbuthylazine	0.68 (0.63 – 0.73)	0.08 (0.04 – 0.14)
Carbendazim	11 (0 – 12)	1.0 (0.74 – 1.5)
Thiabendazole	8.5 (8.0 – 9.1)	0.13 (0.10 – 0.17)
Tebuconazole	5.1 (4.7 – 5.4)	0.40 (0.34 – 0.46)
Mecoprop	20 (19 – 22)	1.7 (1.3 – 2.3)

4. Conclusion

The main lessons learned from this study are as follows: (i) the 18 selected biocides were quantified at least three times over ten campaigns in the Seine and Marne rivers; several were measured at concentrations that could reach the PNEC values and therefore present a risk for the aquatic environment, even if EQS were never reached; (ii) an increase in biocide mass loads between upstream and downstream of the Paris conurbation has been observed for several molecules; (iii) urban discharges (*i.e.*, effluents from WWTPs and CSOs) significantly contribute to

biocide mass loads transiting in rivers, with a higher contribution of WWTPs at the annual scale due to higher discharged volumes.

The results illustrate the interest of the proposed stochastic approach based on Monte-Carlo simulations to quantify the uncertainty on the determined values from a realistic description of the variability of biocide concentrations. The results of this work also open different perspectives such as the in-depth study of the emission sources, the possible mitigation actions at different scales or the transformation products investigation.

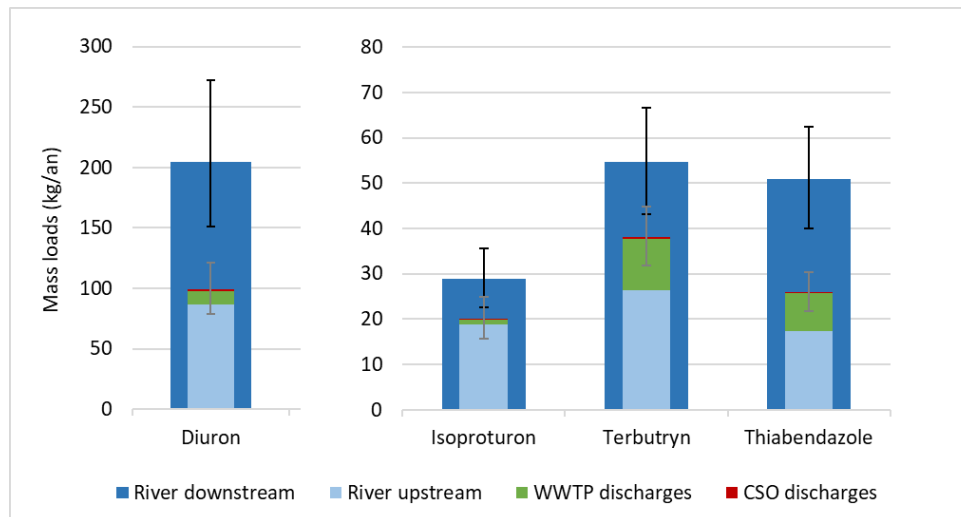


Figure 2. Comparison of the annual biocide loads upstream (River upstream + WWTP discharges + CSO discharges) and downstream (River downstream) the Paris conurbation

Fundings

This work was supported by the Central Laboratory of the Police Prefecture (LCPP) and the OPUR research program funded by the Seine-Normandie Water Agency, the City of Paris, the greater Paris sanitation authority (SIAAP), the Hauts-de-Seine Departmental Council, the Seine Saint-Denis Departmental Council and the Val-de-Marne Departmental Council.

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