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Claudia Paijens, Damien Tedoldi, Bertrand Frère, Romain Mailler, Vincent Rocher, et al.. Biocidal substances in the Seine River: contribution from urban sources in the Paris megacity. Environmental Science : Water Research and Technology, inPress, 10.1039/d2ew00253a . hal-03772400

HAL Id: hal-03772400

<https://enpc.hal.science/hal-03772400>

Submitted on 8 Sep 2022

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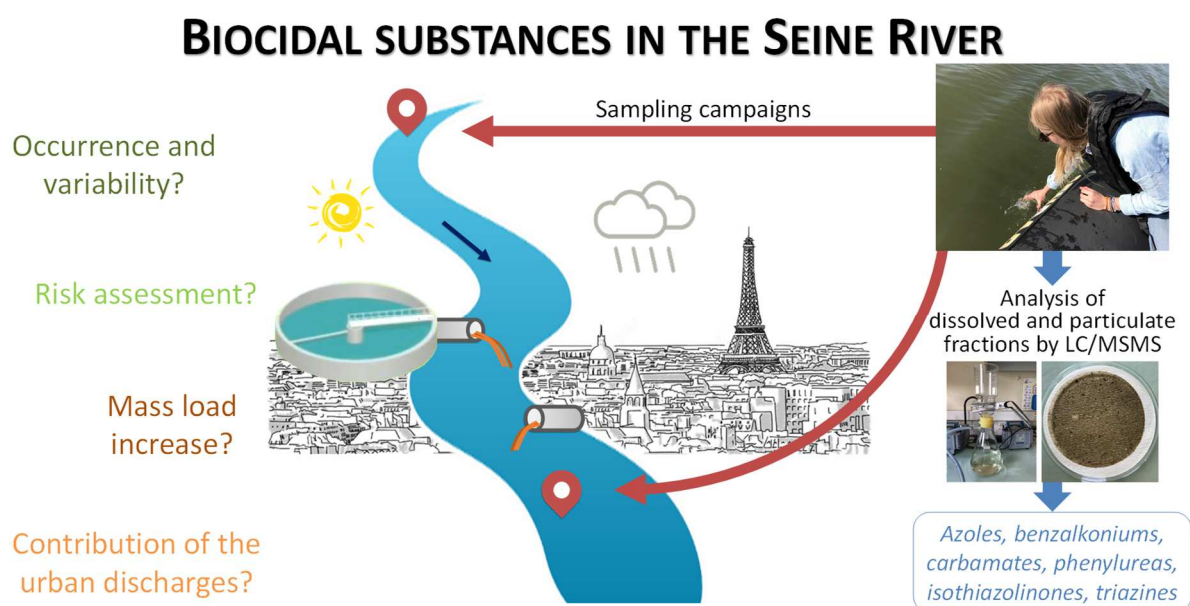
Biocidal substances in the Seine River: Contribution from urban sources in the Paris megacity

Received 10th April 2022,
Accepted 17th August 2022

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DOI: 10.1039/d2ew00253a

This work addresses river contamination by biocidal substances. Several compounds were measured at concentrations that present an environmental risk. The main introduction pathways into the river were elucidated by combining independent approaches leading to consistent conclusions. These novel data could help public authorities to prioritize candidate substances for surface water monitoring and to implement specific and efficient mitigation solutions.



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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

PAPER

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This work addresses river contamination by biocidal substances up- and downstream a megacity, with the aim of investigating the contribution of the urban discharges, and proposing effective and concerted mitigation solutions. To this end, ten campaigns were conducted in the two main rivers of the Paris conurbation. Eighteen previously prioritized biocides were all quantified at three sampling locations, and several were found at concentrations that may present a risk to the aquatic ecosystem (dichloroisothiazolinone, diuron, benzalkonium C12 and C14, with concentrations up to 42, 75, 1700, and 150 ng/L, respectively). The collected data enabled daily mass loads of biocides to be assessed (from <1 g/day to several tens of kg/day, the highest values being observed for benzalkonium C12 and C14) and put into perspective with previously characterized loads from the major urban sources. A shift in the distribution of biocide loads between up- and downstream the Paris conurbation was observed for several molecules (benzisothiazolinone, terbutryn, thiabendazole, the median load of which increased by a factor of 1.5 to 3), thus suggesting the contribution of urban discharges to the contamination of receiving waters by biocides. Analysing the long-term dynamics of biocides in the Seine River showed that even if the ban of several molecules as pesticides did have a noticeable impact on surface water contamination, a background pollution remained ($3 < \text{diuron} < 75$ ng/L, $0.1 < \text{isoproturon} < 5.7$ ng/L), which may be related to urban inputs. Our results offer prospects for specific mitigation solutions at three scales: emissions, transport in the sewer system and treatment before discharge.

1. Introduction

Chemical substances with biocidal properties have become ubiquitous in the environment due to their widespread use as pesticides for plant protection, as insecticides for pest control products or pet treatments, as biocides to protect building materials, but also as preservatives in household products and cosmetics.^{1–4} The latter urban uses generate widespread contamination of urban waters^{5–9} which could contribute to the biocide fluxes towards surface and ground waters, both in dry and wet weathers, and which has been underestimated until now.^{10–17}

Emissions of biocides from urban environments have been evidenced and characterized in a few studies but they were generally restricted to a small scale, a limited number of compounds, and a targeted emission process.^{5,9,11,15,17,18} Numerous studies^{18–23} focused on leaching from biocide-treated building materials during rainfall events, and showed that rain intensity and wind direction were the main influencing factors for this process. After being leached from buildings, biocides can reach surface waters through

runoff/stormwater^{5,11,17,18} or groundwater through infiltration.^{12,22} Up to now, urban inputs of biocides to the receiving environments have generally been modelled by considering emission factors from building materials.^{2,6,19,20} This may have overlooked other sources of biocides such as indoor household uses. The latter have been little studied^{13,24} because these uses are not all covered by the European Biocidal Products Regulation.²⁵ As a result, scientific conclusions concerning the environmental fate of biocidal substances emitted from household sources are less clear-cut, and primarily based on overall trends. Some studies targeting wastewater treatment plants (WWTPs) in different countries highlighted significant biocide concentrations in wastewater that appeared to be independent of rain events, and were therefore attributed to domestic uses.^{5,8,17,26} Finally, some publications have compared dry and wet weather discharges at the scale of the city^{8,11,15,17} Wittmer *et al.*¹⁷ and Tauchnitz *et al.*¹⁵ studied watersheds in Switzerland and Germany and highlighted that the mass loads of urban biocides were in the same range as the most widely used agricultural pesticides. In our previous work⁸, annual mass loads discharged by WWTPs and combined sewer overflow (CSOs) into the Seine River were estimated at the Paris conurbation scale using a stochastic approach and showed that WWTP discharges are the major entry pathway. Also, Gallé *et al.*¹¹ used a passive sampler method to derive source allocation during flood waves and proved that carbendazim originated essentially from wastewater flows, while surface runoff contributed 31% and

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74% respectively to terbutryn and diuron mass flows during flood-waves. It can be noted that the majority of these studies focused on small watersheds and are not at the scale of a megacity.^{11,16,17,26–28}

The environmental and health hazards associated with the use of biocidal substances as plant protection products have been identified for a long time – endocrine disruption, loss of biodiversity, resource degradation for drinking water production.^{29–31} The accumulation of scientific evidence and the growing awareness among public authorities and citizens have led to numerous reduction actions targeting agricultural and urban sources of plant protection products, such as the ban or substitution of certain substances, the reduction of the amounts used, or the implementation of mitigation facilities like ponds or wetlands.^{29,30,32–34} Contrariwise, other urban-derived biocides are still poorly integrated into aquatic monitoring programs despite their potential environmental hazards. Consequently, the available data in the receiving environment are scarce and mostly related to substances also used as pesticides (*e.g.*, diuron, isoproturon, mecoprop, terbutryn, terbuthylazine). To the best of our knowledge, the occurrence of some isothiazolinones, iodopropynyl butylcarbamate (IPBC) and benzalkonium compounds in surface waters suffers from a lack of documentation worldwide.

Filling these knowledge gaps, both in terms of the level of contamination of widely used household biocides and the main sources at the city scale, appears as a first step towards the implementation of effective, comprehensive and concerted mitigation solutions.³⁵ This paper pursues the overall objective to better understand the chemical status of the Seine River regarding biocidal substances and their most contributing sources and pathways at the city scale. The methodology is based on sampling campaigns in the River and on the analysis of 18 previously prioritized biocides³⁶ in the dissolved and particulate fractions. Three main questions were addressed: (i) What is the occurrence and variability of these molecules in an anthropized receiving environment such as the Seine River in Paris? (ii) How do the previously characterized urban-derived loads of biocides from the Paris conurbation compare with the mass loads transiting in the Seine River? (iii) Does this riverine contamination or the local discharges imply an environmental risk?

2. Materials & Methods

2.1. Study area and sample collection

2.1.1. Presentation of the study area. This study focused on the Seine River within the Paris conurbation, between Alfortville (upstream Paris) and Conflans-Sainte-Honorine (downstream), which includes the confluence with the Marne River and

represents a ~80-km stretch of river (Fig. 1). This area comprises the inner city of Paris and a part of the suburbs which are mainly drained by a combined sewer system. Both are characterized by a high degree of urbanization (around 6,000,000 inhabitants on approximately 1,000 km²), a high impervious surface area (around 40%), and a low degree of industrialization (< 2% of the effluents in the sewer system originate from industries in the considered catchment³⁷) or agriculture (< 1% of the study area). Upstream the study area, the Seine and Marne Rivers run for approx. 30 km from the edge of the dense Parisian agglomeration, which already includes several urban discharges (in particular the *Seine Valenton* and *Marne aval* WWTPs). Within the study area, *i.e.* between Alfortville and Conflans-Sainte-Honorine, the effluents from two WWTPs and several combined sewer overflows (CSOs, mix of untreated wastewater and stormwater) of various sizes are discharged into the Seine River (Fig. 1). The two WWTPs are referred to as *Seine centre* (900,000 population equivalent) and *Seine aval* (5,000,000 population equivalent). The total treated volumes in 2018 amounted to 80 Mm³ and 540 Mm³, respectively. Among the major CSOs in the study area, two CSOs located in Clichy and La Briche, and seven CSOs located in Paris, discharged respectively 5.7 Mm³, 3.2 Mm³ and 1.7 Mm³ in 2018, together amounting to > 90% of the total CSO volume.

2.1.2. Presentation of the sampled sites. Surface waters were sampled (i) upstream Paris, in the Marne River at Saint-Maurice (48°48'58.3"N, 2°25'25.3"E) and in the Seine River at Alfortville (48°47'57.2"N, 2°24'57.7"E), and (ii) downstream Paris, in the Seine River at Conflans-Sainte-Honorine (48°59'17.5"N, 2°04'47.9"E) (Fig. 1). The latter sampling point is only 7 km downstream the *Seine aval* WWTP discharge, but it is the furthest location before the confluence with the Oise River. The area of the Marne and Seine watersheds at the sampling points is 12,700 km² and 30,800 km², respectively. Over the period 1970–2010, the inter-annual average flow in the Marne and the Seine Rivers before their confluence was respectively 110 and 218 m³/s. Considering these low flows, the Paris conurbation exerts high pressure on the river: for example, over the study period, the discharges from *Seine centre* and *Seine aval* WWTPs represented up to 30% of the river flow rate in summer.

In addition to surface waters, the major urban discharges from the studied catchment were also investigated, targeting the *Seine centre* WWTP and the *Clichy* CSO. The acquired results have been reported in a previously published article.⁸ Runoff and stormwater discharges were not focused on, due to the above-mentioned predominance of a combined sewer system in the Paris conurbation.

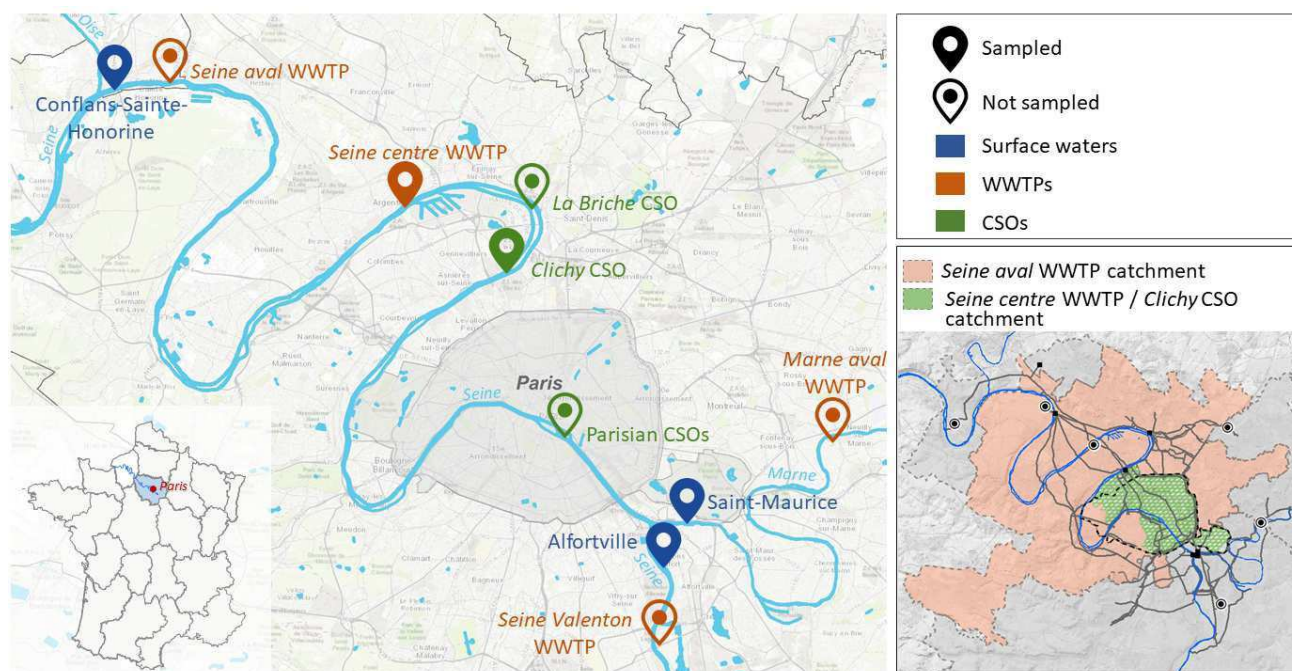


Fig. 1. Location of the study area with the major urban sources of biocides and the three sampling sites for surface waters (other sampling sites refer to Pajens *et al.*⁸)

2.1.3. Sampling campaigns. Ten sampling campaigns were carried out in each river location between March 2018 and May 2019, covering all hydrological characteristics of the year (low-, medium- and high-flow periods), during both dry and wet weather (see ESI Fig. S1). At each sampling location, a boat was used to collect 5-L composite water samples at approx. 1 m depth in the middle of the river, thus avoiding the biases related to the uneven flow conditions and incomplete mixing close to the banks. These samples were stored in cleaned glass bottles at 4°C pending filtration and extraction of the dissolved fraction (maximum 24 h and 48 h respectively). Information on sampling campaigns is provided in the supplementary information (ESI Fig. S1 and Table S1). Upstream sampling campaigns (Marne River at Saint-Maurice and Seine River at Alfortville) were systematically carried out on the same day. However, synchronising the campaigns to account for the transport time between the up- and downstream locations was not always feasible due practical constraints (*e.g.*, the availability of the technical teams who put the boats at our disposal). Consequently, in the subsequent data handling and interpretation, non-paired approaches will be applied to compare up- and downstream values (as detailed below).

The representativeness of surface water samples was verified (i) by comparing the dissolved organic carbon (DOC) and total suspended solids (TSS) concentrations in the river over the period 2017-2019 (available from the French “Naiades” database, www.naiades.eaufrance.fr) and in the collected panel of samples, and (ii) by comparing the river flow over the complete study period (available on the French “Hydro” database, www.hydro.eaufrance.fr) and during the sampling campaigns. Results are provided in the supplementary

information (ESI Fig. S2). Statistical distributions could not be considered as different from the entire set over the complete study period (Mann-Whitney test, p -value > 0.1), so that, it may be reasonable to consider that the acquired data are representative of the overall variability in both the Seine and Marne Rivers.

2.2. Biocide analysis

Based on a state of the art³ and a previous prioritisation work³⁶, a list of 18 substances was chosen according to (i) their use in urban areas, in building materials (paints, coatings, wood, bituminous membranes and tiles) or in household products, (ii) their emission into runoff and receiving waters, and (iii) the associated risk to aquatic organisms. The 18-targeted biocides are: 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 these biocides is provided in the supplementary information (ESI Table S2). The procedure used for biocide analysis has been the core subject of a previous publication³⁸ and therefore will only be briefly described in the present section. The 18-targeted biocides were analysed in both the dissolved and particulate fractions of water samples. After filtration (on GF/F glass fiber filters 0.7µm), the dissolved fraction was extracted by solid phase extraction (Chromabond HR-X cartridge from Macherey-Nagel, 200 mg, 6 mL) while extraction from suspended matter was achieved *via* microwaves (two extraction cycles with 20 mL of methanol/dichloromethane (60/40, v/v) at 100 °C during 10

min). Biocides were quantified using high performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS, UPLC® Acquity TQD, Waters). The separation was then performed on an Acquity UPLC® HSS T3 column (100 mm x 2.1 mm, 1.7 µm) from Waters. The determination of detection and quantification limits (LOD and LOQ) has been explained in the above mentioned article³⁸ and is based on the quantification range. Instrumental limit of detection (LODi) was determined as the lowest concentration for which both quantification and confirmation transitions were achieved. LOQi was defined as the concentration from which the difference between theoretical and measured concentrations was below a targeted value. Dissolved and particulate LOD and LOQ were calculated from LODi, LOQi, and the recovery in the corresponding matrix. Therefore, for some substances, LODi and LOQi happened to be the same. LODs and LOQs are provided in the supplementary information (ESI Tables S3 and S4).

For each sample collected, total concentrations were calculated as the sum of the concentrations in the dissolved and particulate fractions, the latter being calculated from the biocide contents in the particles and the TSS concentration. Methods for handling values below the LOD or LOQ are presented in the supplementary information (ESI Table S5). The justifications for these choices have been given in our previous publication.⁸

2.3. Long-term monitoring of diuron and isoproturon

Several biocides also used as pesticides, in particular those concerned by the Water Framework Directive³⁹, have been monitored up- and downstream the Paris conurbation since 2007 by the Regional and Interdepartmental Direction of Environment and Energy (DRIEE in French), with approximately two measurements per month at each sampling point. These data have been compiled in a publicly available database called “Naiades” (<https://naiades.eaufrance.fr/>), which was used to appraise the long-term evolution of biocidal substances in the Seine River.

Diuron and isoproturon were focused on, as the other compounds were very rarely quantified. It should be noted that several changes in the DRIEE’s chemical analysis service provider (in 2008, 2012, and 2016) resulted in a change in the LOQ: therefore, the dataset was split into time groups with the same LOQ, then concatenated with the present results to appraise the temporal evolution of biocide concentrations over the period 2007-2019.

2.4. Daily mass loads

2.4.1. Load calculation. For each sampling campaign and location, daily mass loads of biocides transiting in the river were estimated by multiplying the determined total concentrations by the daily river flow rate:

$$\phi = a \times C \times Q$$

where ϕ is the daily mass load of biocide [g/day], C is the concentration [ng/L], Q is the daily flow rate [m³/day] and $a = 10^{-6}$ is a conversion factor. Daily records of the river flow upstream Paris are available on the “Hydro” database.

Regarding the Seine River downstream Paris, however, the closest gauging station is located after the confluence with the Oise River. The flow at the downstream sampling point was therefore estimated as the sum of the measurements in the Marne and Seine Rivers upstream Paris, and the effluents from the *Seine centre* and *Seine aval* WWTPs.

Since the campaigns were undertaken on the same day for the two upstream points, it was considered reasonable to compute total upstream daily loads by summing the contributions of the Seine and the Marne Rivers. However, up- and downstream biocide loads could not be compared in pairs, as the sampling dates did not necessarily coincide. Hence, the comparison was made on the statistical distributions of daily loads rather than on paired data. The dataset size led us to prefer non-parametric over parametric statistics, so that comparisons were performed using the Wilcoxon-Mann-Whitney test for each biocide.

2.4.2. Uncertainty calculation. In the presently observed range, the uncertainty of the flow rate has been estimated at around 5% by the department in charge of the “Hydro” database.⁴⁰ Analytical uncertainties that affect the determined concentrations in the dissolved phase (between 10 and 50%) are presented in detail in the above-mentioned methodological article.⁸ Concerning the particulate fraction, uncertainty related to TSS concentration was previously determined as 10%, and that related to the particulate extraction is unknown but supposed to be lower than uncertainty of the dissolved fraction, as previously reported by Wieck *et al.*⁴¹ Hence, uncertainty on the total concentration was conservatively estimated as the highest one (*i.e.*, that of the dissolved fraction).

The combined standard uncertainty u_ϕ of the biocide loads was calculated by applying the law of propagation of uncertainty:

$$\frac{u_\phi}{\phi} = \sqrt{\left(\frac{u_C}{C}\right)^2 + \left(\frac{u_Q}{Q}\right)^2 + 2 r_{CQ} \times \frac{u_C}{C} \times \frac{u_Q}{Q}}$$

where u_C and u_Q are the standard uncertainties of the biocide concentrations and river flow rate, respectively, and r_{CQ} corresponds to the correlation coefficient between these two variables.

2.4.3. Loads associated with urban discharges. As mentioned above, a parallel and previously published work consisted of characterising urban discharges of biocides within the study area, focusing on CSOs and WWTPs.⁸ The loads discharged during the sampled CSO events in *Clichy* were calculated with the same approach as above, *i.e.*, by multiplying the event mean concentrations by the measured overflow volume. Additionally, an assessment was carried out at the annual and city scales, for which a different methodology had been applied, using Monte-Carlo simulations to compute annual loads along with their uncertainties. Estimates of the daily loads from WWTPs were thus obtained by averaging the annual values. These data will be presently used for comparison purposes with daily loads measured in surface waters. A summary of the overall estimation approach is presented in the supplementary information (ESI Fig. S3).

3. Results & discussion

3.1. Biocides in surface waters under strong urban pressure

3.1.1. Occurrence and variability of biocides in the Marne and the Seine Rivers. The frequency of quantification, the median, minimum and maximum concentrations, and the proportion of each biocide in the particulate fraction are reported in Table 1; contents in the particulate fractions are detailed in the supplementary information (ESI Table S6). All data acquired within this project are available on Pangaea Data Center.⁴²

Most of the biocides were quantified in ≥ 8 samples out of 10 at the three sampling sites. Exceptions include BIT, OIT, DCOIT, IPBC, and mecoprop, the frequency of quantification of which increased from 5-7/10 upstream Paris to 7-9/10 downstream, and CMIT, cybutryn, and BZK C16, which were more frequently $< \text{LOQ}$. Median total concentrations were below 10 ng/L for all targeted molecules except MIT, BZK C14 (median concentrations between 10 and 50 ng/L), and BZK C12 which often reached concentrations > 100 ng/L. Biocide dynamics in surface waters were characterized by a significant temporal variability, as illustrated by the ranges between minimum and maximum measured concentrations, which for certain compounds covered almost two orders of magnitude. For instance, concentrations of MIT and BZK C12 downstream the Paris conurbation respectively ranged from < 1 ng/L (unquantified value) to 170 ng/L, and from 28 ng/L to 1.7 $\mu\text{g/L}$. Possible causes for this variability will be investigated in the subsequent developments – examining notably possible links with the weather conditions.

3.1.2. Comparison to reference values. In order to establish a first diagnosis of the severity of biocide contamination in the Seine River, measured dissolved concentrations were compared to regulatory threshold values, *i.e.* Environmental Quality Standards⁴³ (EQS) when available (diuron, isoproturon, terbutryn, and cybutryn), and to Predicted No Effect Concentrations (PNEC), gathered from literature and summarized in supplementary information (ESI Table S2). More precisely, two data sources were used for PNEC estimation: the Norman network⁴⁴ and the European CHemical Agency.⁴⁵ In case the two values differed, the stricter one was conservatively retained. The risk quotient $\text{RQ} = C_{\text{dissolved,river}} / \text{PNEC}$, as defined by the European ecological risk assessment guidelines⁴⁶, was calculated for each biocide and each sample.

This corresponds to a simplified approach of environmental risk, which does not take into account possible synergic effects between compounds or endocrine disruption effects,^{47,48} but helps setting orders of magnitude.

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The comparison was based on the classification proposed by Juksu *et al.*⁴⁹: minimal risk for $\text{RQ} < 0.01$; low risk for $0.01 < \text{RQ} < 0.1$; medium risk for $0.1 < \text{RQ} < 1$; and high risk for $\text{RQ} > 1$.

Annual average EQS were never exceeded during the sampling campaigns of the present study. Fig. 2 shows the RQ values obtained for all the 18-targeted biocides, distinguishing the three sampling sites in the two rivers. The compounds, which appeared to represent the lowest risk (isoproturon, MIT, BIT, thiabendazole, and mecoprop, for which RQ was systematically < 0.1 , if not even < 0.01) actually have high PNEC values compared to the other targeted biocides ($> 0.3 \mu\text{g/L}$). Overall, CMIT, OIT, DCOIT, BZK C16, terbutryn, cybutryn, terbuthylazine, carbendazim, IPBC, and tebuconazole are expected to represent a low to medium risk ($0.01 < \text{RQ} < 1$). Based on the PNEC values we found, the potentially most problematic biocides in the Seine River were diuron, BZK C12, and BZK C14, the concentrations of which frequently placed them in the “medium to high risk” category ($0.1 < \text{RQ} < 100$). Noticeably, for diuron, DCOIT, and cybutryn, the few cases of PNEC exceedance only occurred downstream the Paris conurbation. Conversely, BZK C12 was commonly above the PNEC, both upstream (7-8/10) and downstream (9/10). This result highlights the relevance of addressing benzalkonium compounds because of the environmental risks they represent, especially as they are very poorly documented in surface waters.

3.1.3. Distribution between dissolved and particulate fractions in the Seine and Marne Rivers.

It is common to consider that biocides are only present in the dissolved phase due to their physicochemical properties, and therefore to limit the analysis to filtered water samples.^{26,31,50–54} In the present study, this speciation has been investigated through the joint analysis of the dissolved and particulate fractions in the water samples (Table 1 and ESI Table S6). The dissolved fraction was indeed predominant for most compounds, especially diuron, CMIT, OIT, DCOIT, and mecoprop, which were quantified on the particles for less than 2/10 samples; additionally, diuron, isoproturon, BIT, DCOIT, carbendazim, tebuconazole, and mecoprop systematically displayed particulate fractions $< 20\%$.

However, it appeared that the particulate concentration may represent a non-negligible part of the speciation for certain molecules, especially IPBC (median particulate fraction of 35–40%). Eight biocides (MIT, IPBC, BZK C12 & C14, tebuconazole, thiabendazole, terbutryn, and terbuthylazine) were quantified in the particulate fraction for more than half of the samples, but their speciation was quite variable from one sample to another. No relation could be highlighted between biocide proportions in the particulate fraction, compound hydrophobicity, particulate organic carbon, or the electrical charge of the biocides. No significant spatial variation was observed up- to downstream the Paris conurbation.

When they were quantified, the particle contents (in ng/g) were found to be highly variable depending on the molecules and the campaigns (ESI Table S6), but their orders of magnitude did not vary globally between up- and downstream. The highest contents were measured for benzalkoniums: between 18 ng/g and 11,000 ng/g for BZK C12, and between < 3.5 ng/g and 2,000 ng/g for BZK C14. The only literature data we found do not address contamination levels in the suspended solids of surface waters but in riverine / estuarine sediments.^{49,55,56}

Table 1. Acquired data in the Marne River and in the Seine River up- and downstream the Paris conurbation (quantification frequencies, concentrations and median particulate proportions)

	Upstream the Paris conurbation						Downstream the Paris conurbation		
	Marne River			Seine River			Seine River		
	Number of quantification	Median concentration (min-max) in ng/L	Median particulate proportion	Number of quantification	Median concentration (min-max) in ng/L	Median particulate proportion	Number of quantification	Median concentration (min-max) in ng/L	Median particulate proportion
Diuron	10/10	3.2 (2.1 - 20)	<10%	10/10	2.7 (2.1 - 14)	<8%	10/10	5.3 (3.1 - 75)	<7%
Isoproturon	9/10	0.9 (<0.1 - 5.7)	<19%	9/10	1.0 (<0.1 - 3.4)	<15%	9/10	1.5 (<0.1 - 4.2)	<14%
MIT	9/10	17 (<0.5 - 110)	11%	9/10	13 (<1 - 150)	10%	9/10	21 (<1 - 170)	10%
BIT	7/10	2.5 (<1.6 - 5.5)	<15%	5/10	2.5 (<0.6 - 5.5)	<14%	9/10	7.0 (<2.7 - 11)	<8%
CMIT	3/10	<5 (<2 - 9.4)	-	3/10	<6 (<2 - 9.8)	-	2/10	<9 (<3 - 13)	-
OIT	5/10	0.7 (<0.3 - 1.4)	<24%	5/10	0.6 (<0.3 - 1.3)	<4%	7/10	1.1 (<0.3 - 1.7)	<10%
DCOIT	6/10	1.3 (<0.1 - 1.7)	<2%	7/10	1.1 (<0.1 - 2.9)	<3%	7/10	1.3 (<0.1 - 42)	<2%
BZK C12	10/10	210 (10 - 580)	2%	10/10	230 (30 - 1400)	7%	10/10	170 (28 - 1700)	19%
BZK C14	10/10	26 (0.1 - 71)	3%	10/10	22 (2.2 - 150)	5%	10/10	47 (8.4 - 130)	4%
BZK C16	4/10	<0.9 (<0.6 - 40)	<3%	3/10	<1.0 (<0.3 - 43)	12%	6/10	6.1 (<0.4 - 38)	1%
Terbutryn	10/10	1.1 (0.2 - 4.3)	4%	10/10	1.8 (0.6 - 3.6)	3%	10/10	3.2 (0.6 - 8.0)	<1%
Cybutryn	2/10	<0.1 (<0.1 - 0.2)	-	3/10	<0.1 (<0.1 - 0.2)	-	3/10	<0.1 (<0.1 - 1.8)	-
Terbuthylazine	10/10	1.8 (0.7 - 52)	2%	8/10	0.6 (<0.1 - 29)	4%	9/10	1.1 (<0.1 - 23)	<2%
Carbendazim	10/10	7.9 (0.7 - 16)	1%	10/10	8.5 (0.6 - 17)	<1%	9/10	7.7 (<0.2 - 16)	<1%
IPBC	7/10	0.7 (<0.2 - 18)	35%	5/10	0.8 (<0.2 - 1.4)	39%	9/10	0.6 (<0.3 - 2.6)	35%
Thiabendazole	9/10	1.2 (<0.1 - 4.4)	4%	10/10	1.1 (0.3 - 2.0)	5%	10/10	2.9 (0.7 - 10)	1%
Tebuconazole	10/10	5.7 (2.1 - 160)	4%	10/10	2.9 (1.4 - 54)	3%	10/10	4.8 (2.4 - 42)	1%
Mecoprop	5/10	2.5 (<1.9 - 22)	<6%	7/10	2.6 (<1.9 - 9.5)	<13%	8/10	4.6 (<2.2 - 25)	<5%

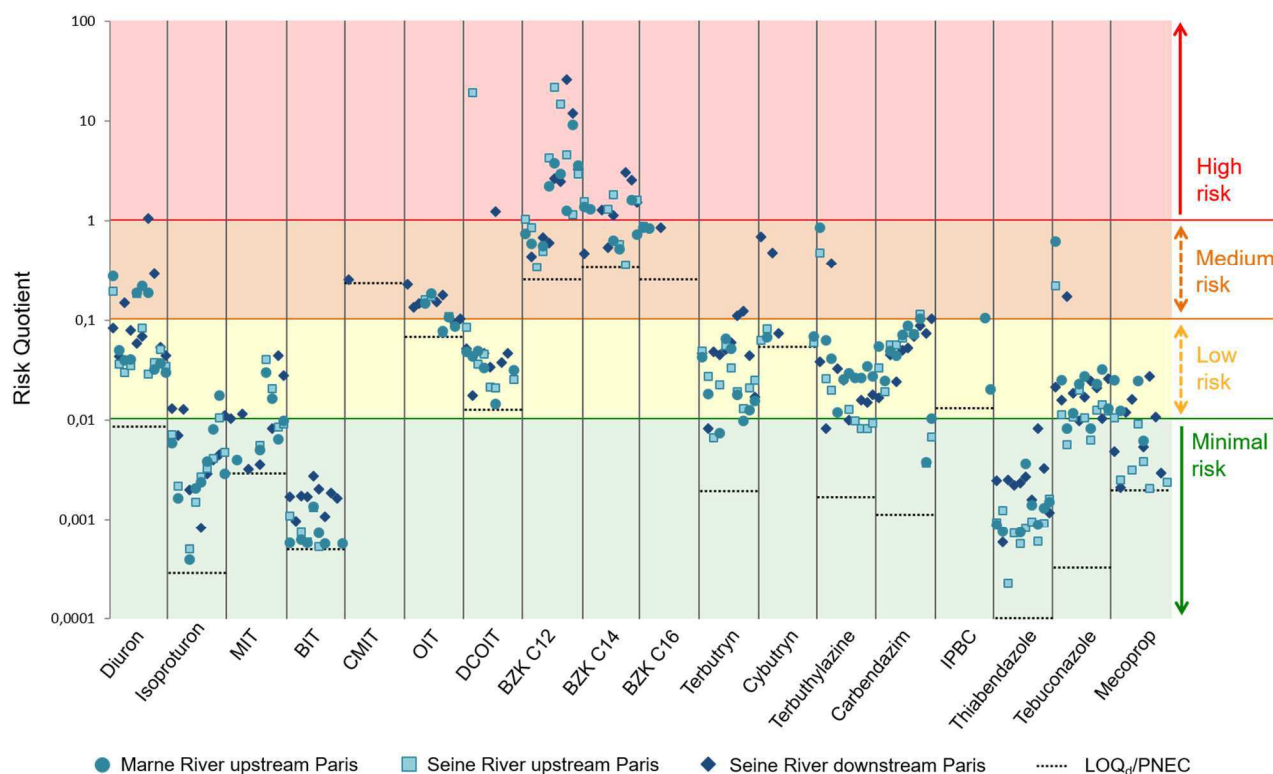


Fig. 2. Risk Quotient for all the 18-targeted biocides in the Marne River and the Seine River (up- and downstream the Paris conurbation).

For benzalkoniums, contents were measured in the same order of magnitude and with the same variability in urban estuarine sediments in China⁵⁷ (between 50 and 1,500 ng/g) in sediments from rivers impacted by WWTPs in Austria⁵⁸ (between 350 and 1,000 ng/g), and in urban estuarine sediments in the United States⁵⁹ (between 100 and 17,700 ng/g).

Isothiazolinones were also quantified at high contents in the particles: between < 6.6 and 3,600 ng/g for MIT. BIT and CMIT were less frequently quantified in the particles than MIT, but when they were, their contents reached up to 110 ng/g and 1,900 ng/g respectively. IPBC contents were between < 11 and 170 ng/g. Isoproturon, terbuthylazine, thiabendazole and tebuconazole contents were in the range of a few ng/g to tens of ng/g. Terbutryn and carbendazim contents were quantified in the order of magnitude of ng/g. These results are consistent with literature data, as thiabendazole and carbendazim were quantified in sediments from the Yangtze River in China by Liu *et al.*⁵⁵ (<LOD - 0.2 ng/g for the former, and 0.1 - 2.9 ng/g for the latter) and in rivers in Thailand by Juksu *et al.*⁴⁹ (0.5 - 10 ng/g, and 1 - 100 ng/g respectively).

3.2. Evidence of urban contribution to river contamination

3.2.1. Long-term evolutions of diuron and isoproturon concentrations: effectiveness of pesticide-related regulations.

The long-term temporal evolution of diuron and isoproturon concentrations is presented in Fig. 3. Concentrations display a clear declining trend following the ban of these substances as pesticides, in 2008 for diuron and 2017 for isoproturon. For the former, the observed decrease by a factor of 10 within a few years, points out the effectiveness of such measures. However,

both compounds are still quantified in surface waters, in particular diuron whose concentrations range between few ng/L and 75 ng/L, even more than 10 years after its ban. These background levels might be related either to the persistence of these molecules in soils or groundwater – even if their half-life times do not exceed 1 year in these media^{60,61} –, or to the contribution of hitherto overlooked urban sources.⁸ The remainder of this work is dedicated to characterizing the latter.

3.2.2 Wet weather-related trends in biocide concentrations.

So as to investigate the impact of weather conditions on the river contamination, surface water concentrations were split into three groups depending on the cumulative rainfall depth over the four days preceding the sampling campaigns (subsequently referred to as H_{rainfall} , ESI Tab S1). The reason for this duration is the following: considering that, after a rain event, the sampling points of Alfortville (Seine River) and Saint-Maurice (Marne River) would be potentially impacted by urban discharges in the area starting from the edge of the dense Parisian agglomeration (~30 km upstream for both rivers), the transport time along these stretches of river had to be accounted for. A previous study on the fate of nonylphenolic compounds in the Seine River⁶² reported that the average velocity during low flow conditions (< 150 m³/s) was ≈ 0.15 m/s. The flow rate in the Marne River being lower than in the Seine River, a conservative value of 0.1 m/s was retained, leading to a maximum transit time of 4 days. Values of H_{rainfall} were categorised as follows: dry weather ($H_{\text{rainfall}} = 0$ mm), small rainfall event(s) ($H_{\text{rainfall}} < 5$ mm), and higher rainfall event(s) ($H_{\text{rainfall}} > 5$ mm).

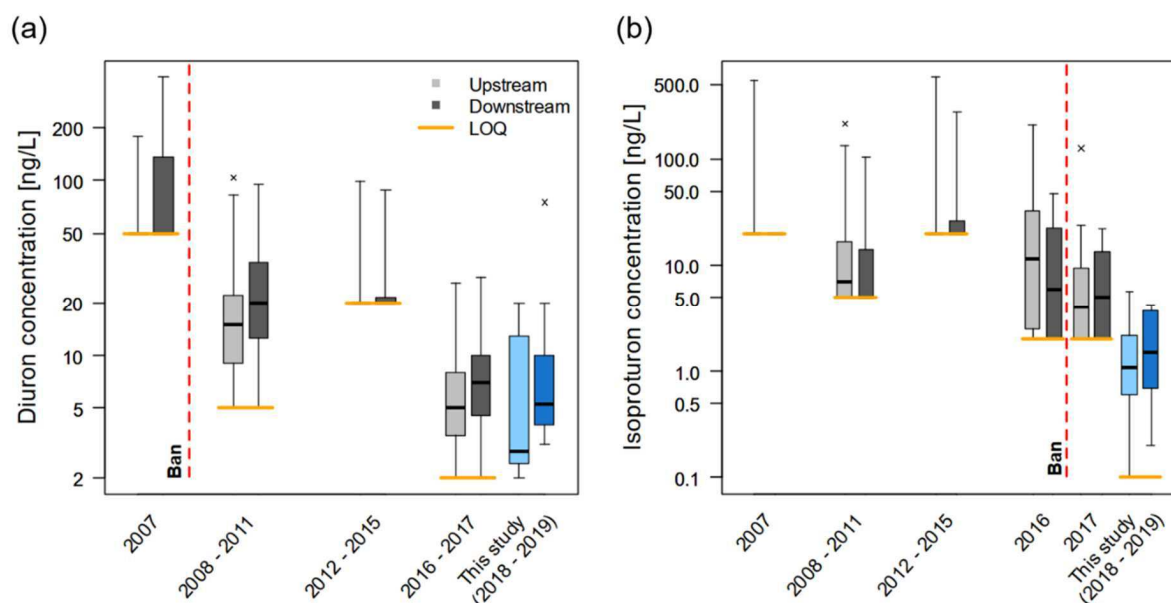


Fig. 3. Evolution of diuron (a) and isoproturon (b) concentrations from 2007 to 2019 in the Seine River (data from the “Naiades” database in grey and from this study in blue).

Fig. 4 shows the concentrations of different biocides in the rivers, as a function of the weather conditions. The classification of certain compounds as primarily stormwater- or wastewater-borne stems from the conclusions of our previous study on biocides in urban discharges.⁸ Briefly, electrical conductivity measurements were used to evaluate stormwater proportion in CSO samples (calculated as a dilution factor, assuming a mixture of raw storm- and wastewater only), which in turn enabled the elucidation of the biocide origins. A positive correlation was evidenced between stormwater proportions and the concentrations of diuron, isoproturon, terbutryn, tebuconazole, and carbendazim, which suggested that stormwater constitutes a dominant pathway (with respect to wastewater) for these compounds. On the contrary, concentrations of most isothiazolinones, as well as IPBC, appeared to decrease with increasing stormwater proportion, which indicated a dilution of wastewater by stormwater. For the remaining biocides, both sources were found to contribute equally.

Interestingly, biocides from the first and third categories generally showed higher concentrations in both rivers after a rainy period. Figs. 4a and 4c present the examples of isoproturon and tebuconazole, on the one hand, and thiabendazole and BZK C12, on the other hand, the concentrations of which were sometimes ten-fold higher after a rain event than in dry weather. Similar patterns were observed for diuron and BZK C14, and to a lesser extent, for terbutryn and mecoprop. Noticeably, even “small” rainfall events appeared to be followed by an increase in river concentrations compared to dry weather. Contrariwise, no significant variation was observed for most wastewater-borne biocides, whatever the weather conditions, as illustrated by the examples of BIT and DCOIT on Fig. 4b. This behaviour was

shared by IPBC; however, for CMIT and OIT, the number of quantified values was insufficient to identify trends.

Hence, the present results tend to confirm that wet weather has no (or at least very little) influence on the concentrations of substances with a mainly domestic use – notably isothiazolinones – even through CSO discharges, while it correlates with an increase in the concentrations of substances with widespread and/or outdoor uses (*e.g.*, as a roof or facade fungicide). This first clue to the causes of the aforementioned variability of concentrations tends to corroborate the role of urban areas in the river contamination by biocides. The lack of a systematic trend between “small” and “high” events (some compounds displayed higher concentrations after $H_{\text{rainfall}} < 5$ mm than after $H_{\text{rainfall}} > 5$ mm) may result from different factors, among which: differences in flow rates, and consequently dilution factors of the urban discharges; different periods of dry weather prior to each rainfall event; or purely stochastic aspects of practice-related biocide emissions in urban areas. Achieving a quantified vision of their respective contributions would undoubtedly require more data; however, a broader conclusion can be drawn by considering that wet-weather related discharges induce a visible impact on the concentrations of stormwater-borne biocides in the river, whatever the rainfall depth. This observation is of particular concern since the sewer system is mainly combined in the study area, and suggests even stronger effects at the outlet of separate sewers. So as to gain further insight into the contribution of urban discharges, the following part is dedicated to assessing mass loads of biocides.

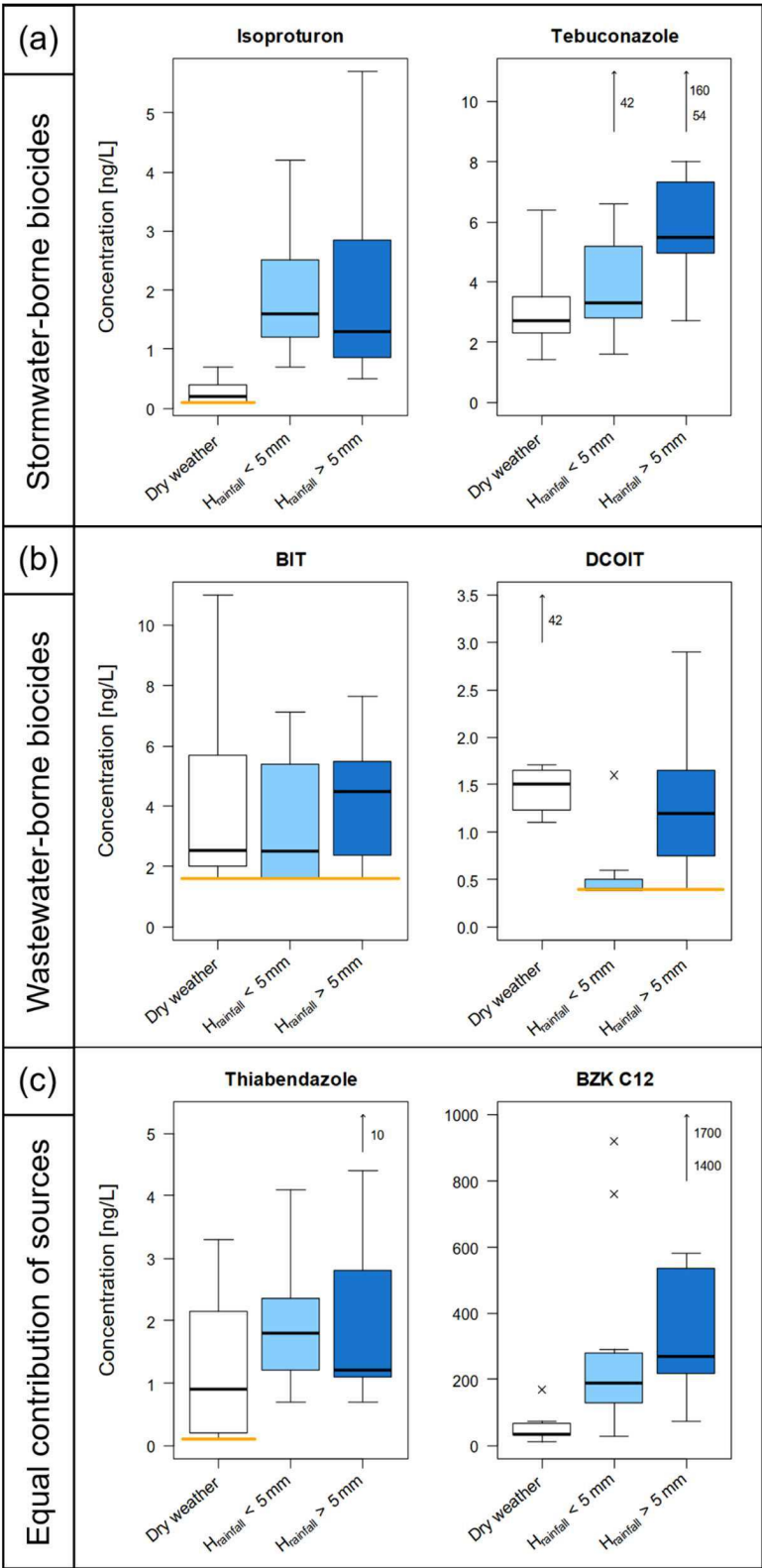


Fig. 4. Distribution of biocide concentrations (all sampling points merged) as a function of the cumulative rainfall depth over the 4 days preceding the sampling campaigns. The orange line indicates the LOQ. [(a) for stormwater-borne biocides, (b) for wastewater-borne biocides, and (c) for biocides with equal contribution of both sources]

3.2.3. Daily loads of biocides in the river and in urban effluents.

Summary statistics about daily mass loads of biocides are presented as supplementary information, ESI Table S7. Different orders of magnitude could be distinguished: from a few tens of g/day (isoproturon, OIT, DCOIT, terbutryn, cybutryn, terbuthylazine, IPBC, thiabendazole) to ~100 g/day (diuron, BIT, CMIT, carbendazim, tebuconazole, mecoprop), to several hundreds of g/day or even > 1 kg/day (MIT and benzalkonium compounds). The results show that both rivers already convey a certain amount of biocides upstream the study area, highlighting the contribution of upstream sources – either urban discharges or agricultural activities in the Marne and Seine watersheds.

The potential impact of the Paris conurbation was investigated by comparing up- and downstream loads, which as mentioned above could not be undertaken with paired data since the sampling dates did not necessarily coincide. Hence, the whole distributions of daily loads were compared. Among the 18 biocides under study, the difference between the computed upstream and downstream values could be considered significant for three of them: BIT (median values: 50±22 g/day upstream, 140±60 g/day downstream, $p = 0.001$), terbutryn (median values: 36±9 g/day upstream, 58±14 g/day downstream, $p = 0.029$), and thiabendazole (median values: 33±7 g/day upstream, 62±14 g/day downstream, $p = 0.035$). Their entire distributions are presented on Fig. 5 (light and dark blue boxplots). For the other compounds, the variability of daily loads among the different sampling campaigns appeared to be higher than a possible shift between the two distributions of values; nevertheless, it is also worth mentioning that none of the investigated biocides showed a significantly decreasing trend between the up- and downstream sites. For further assessments, refining the approach *via* synchronized sampling campaigns may enable additional trends to be detected between these other compounds.

These values were then put into perspective with the mass loads discharged *via* the urban drainage system during both dry and wet weather (which, as a reminder, derived from a previous assessment – *cf.* paragraph 2.4.3). At the annual and city scales, it had been found that the loads discharged from WWTPs typically represent more than 10 times the loads from CSOs (*e.g.*, 11.7±0.8 vs. 1.1±0.3 kg/year for diuron), because of much higher discharged volumes (620 vs. 10.6 M m³). For the present comparison, however, the focus was on the daily/event scale. In order to visualize the potential contribution of the WWTP to the river in Fig. 5, the upstream distributions of river-borne biocide loads were shifted up (light yellow boxplots) by the average daily loads from WWTPs (47±3 g/day for BIT, 31±2 g/day for terbutryn, and 23±2 g/day for thiabendazole). Additionally, the mass loads discharged during the sampled CSO events were represented as orange boxplots. These values have a slightly different interpretation, as they correspond to event loads and not daily loads, but the comparison allows to set some orders of magnitude.

Of interest is the fact that, for the three aforementioned biocides, the upstream loads added to the WWTP loads could

no longer be considered different from the downstream values: when comparing these distributions, the Wilcoxon-Mann-Whitney test resulted in p -values of 0.12 for BIT, 0.91 for terbutryn, and 0.53 for thiabendazole. In other words, the estimated WWTP loads were globally consistent with the observed shift between up- and downstream river-borne loads for these three biocides. This obviously does not correspond to any “mass balance closing” – which was not the purpose of the present assessment, as the dataset is too limited to achieve such a result, and several sources of biocides were not accounted for (*e.g.*, direct discharges of stormwater *via* separate sewers, or the barges moored along the river banks). However, the results enable a first quantification of the contribution of the major urban discharges within the Paris conurbation to the biocide contamination of aquatic systems.

At the event scale, biocide loads discharged through CSOs were generally lower and less variable than those transiting in the Seine River (Fig. 5). The median values of CSO- and river-borne loads differed by a factor of 3 to 25, the most marked differences (among the frequently quantified substances) being observed for MIT, DCOIT, isoproturon, terbuthylazine, and thiabendazole (ESI Table S7). Still, the two distributions partially overlapped for most of the biocides. This indicates that CSO discharges may be punctually responsible for a twofold increase in mass loads in the river, especially during summer periods when the water flow is low.

3.3. Discussion on possible mitigation actions

These results illustrate the impact of large urban areas on biocide contamination in surface waters, and enable specific mitigation solutions to be proposed at three scales: biocide emissions, their transport in the sewer system and their treatment before discharge.

Uncovering the link between biocide uses (domestic vs. outdoor), pathways (wastewater vs. stormwater), and discharges, allows specific actions to be targeted in order to reduce emissions at source. A first solution may consist of replacing current biocides with less persistent and less toxic compounds, which would require to focus on transformation products⁶³; another one would be to reduce the quantities used. In many fields, examples of source reduction of contaminants are mainly based on changes in professional practices (*e.g.*, ban of pesticides in urban areas³², reduction in the consumption of antibiotics⁶⁴, changes in the industrial formulation^{65,66}, encapsulation of biocides in polymer microspheres for building materials⁶⁷). However, it seems that the preservation of surface waters cannot be fully achieved without targeting domestic practices as well. The example of the ubiquitous benzalkonium compounds, which presently display the highest risk quotients, shows the complexity of the problem, and their reduction would require actions towards building professionals – as suggested by Gromaire *et al.*⁶⁸ – but also a decrease in domestic uses. To do so, one way to raise awareness of the impacts of household contaminants may be to link environmental and health issues.⁶⁹

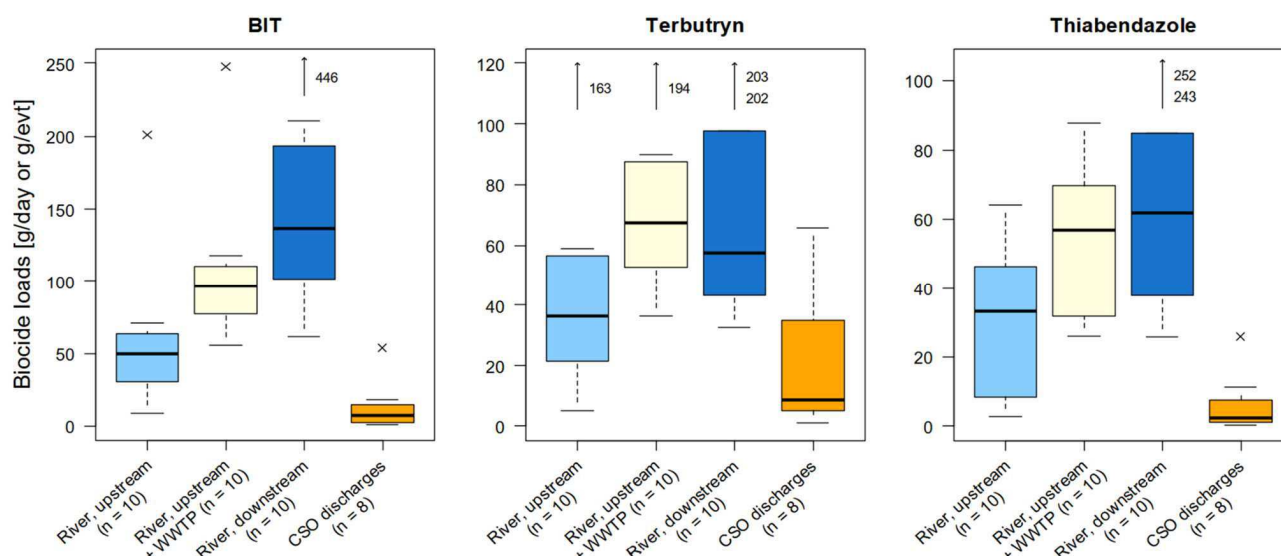


Fig. 5. Statistical distribution of the daily biocide loads in the River upstream and downstream the Paris conurbation and comparison with urban discharges

Another possible improvement lies in stormwater management, the importance of which is highlighted by the observed increase in the concentration of several biocides during wet weather whatever the rainfall depth. The dissemination of Sustainable Drainage Systems is expected to have positive impacts on surface water quality. However, it raises some concerns regarding the fate of biocides in the soil of infiltration-based facilities, as they are not expected to be strongly retained by the soil – contrary to most legacy runoff micropollutants such as metals and polycyclic aromatic hydrocarbons.^{12,70}

At the end-of-pipe level, our previous work proved that the conventional treatments in WWTP showed a limited efficacy regarding biocides (WWTP median removals < 60%), except for isothiazolinones and for benzalkonium compounds.⁸ Advanced treatment in WWTP could be an effective solution to mitigate the release of these contaminants into the aquatic environment through WWTP effluents.^{71,72} However, these solutions are expensive and it would be necessary to verify their effectiveness and relevance, for example *via* a life cycle analysis approach like the one performed at *Seine centre* WWTP for pharmaceuticals.⁷³ An intermediate solution could be to adapt the tertiary treatments according to the mass loads discharged by each plant.

4. Conclusion and perspectives

In the present study, biocide contamination in surface waters up- and downstream the Paris conurbation was investigated *via* sampling campaigns in the Seine and Marne Rivers, in order to complement the insight given by our characterization of urban biocide loads through WWTP and CSO discharges.⁸ The Seine and Marne Rivers appeared to be contaminated with the 18-targeted biocides, most of which were quantified in at least

8/10 samples. Comparison with PNEC values highlighted that diuron, BZK C12 and BZK C14 represent a medium to high risk for the aquatic ecosystem. Contrary to the most common assumptions on biocide speciation, our results demonstrated that the particulate fraction may be non-negligible for certain molecules, especially IPBC.

Some evidence has been gathered regarding the contribution of urban areas to the river contamination. First, long-term series of diuron and isoproturon concentrations showed a clear declining trend following the ban of these substances as pesticides, but appeared to stabilize at non-negligible background values possibly attributable to urban inputs. Second, higher biocide concentrations were measured in the river during or after rain events for various compounds, with the notable exception of isothiazolinones which have mainly domestic uses and are therefore primarily wastewater-borne. Third, between the up- and downstream sampling points, some biocides displayed an increase in their quantification frequencies, and other ones showed an increase in the daily loads conveyed by the river; this increase was in the same order of magnitude as the previously estimated daily loads from WWTP discharges.

In connection with the elucidation of the main pathways for each substance, this work offers various perspectives such as the in-depth study of the upstream sources. In particular, the emissions by and in the house should be focused on, to assess the level of exposure of inhabitants in residential areas, and the contribution of these emissions to environmental contamination. Regarding health risks, biocide measurements in indoor air and greywater are still very limited, but of primary interest, given they are tracers of domestic activities and by extension of the human exposure to domestic biocides. Moreover, biocide degradation can lead to transformation products that are poorly investigated and represent an

unknown exposure risk for inhabitants and receiving environments. The last perspective concerns the most efficient solutions to control biocide emissions. These are precisely the issues that will be addressed in the French project Biocid@Home funded by the French National Agency for research (ANR-20-CE34-0001-01).

Author Contributions

Claudia Paijens: Data curation, Investigation, Formal analysis, Methodology, Validation, Visualization, Writing - original draft, review & editing. Damien Tedoldi: Formal analysis, Methodology, Visualization, Writing - original draft, review & editing. Bertrand Frere: Conceptualization, Methodology, Supervision, Writing - review. Romain Mailler: Methodology, Writing - review. Vincent Rocher: Resources. Régis Moilleron: Conceptualization, Funding acquisition, Methodology, Supervision, Writing - review. Adèle Bressy: Conceptualization, Funding acquisition, Methodology, Project administration, Supervision, Validation, Writing - original draft, review & editing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors want to thank the Brigade Fluviale de la Préfecture de Police and the Brigade Fluviale de la Gendarmerie Nationale des Yvelines; teams of the greater Paris sanitation authority (SIAAP), in particular Celine Briand and the SIAAP central laboratory; and the City of Paris for their assistance for sampling and conventional quality parameters analyses. The authors also gratefully thank Mohamed Saad for his useful help in the sample analysis. We would like to thank the managers of the French “Hydro” and “Naiades” databases for the provision of the data.

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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Electronic Supplementary Information

Biocidal substances in the Seine River: Contribution from urban sources in the Paris megacity

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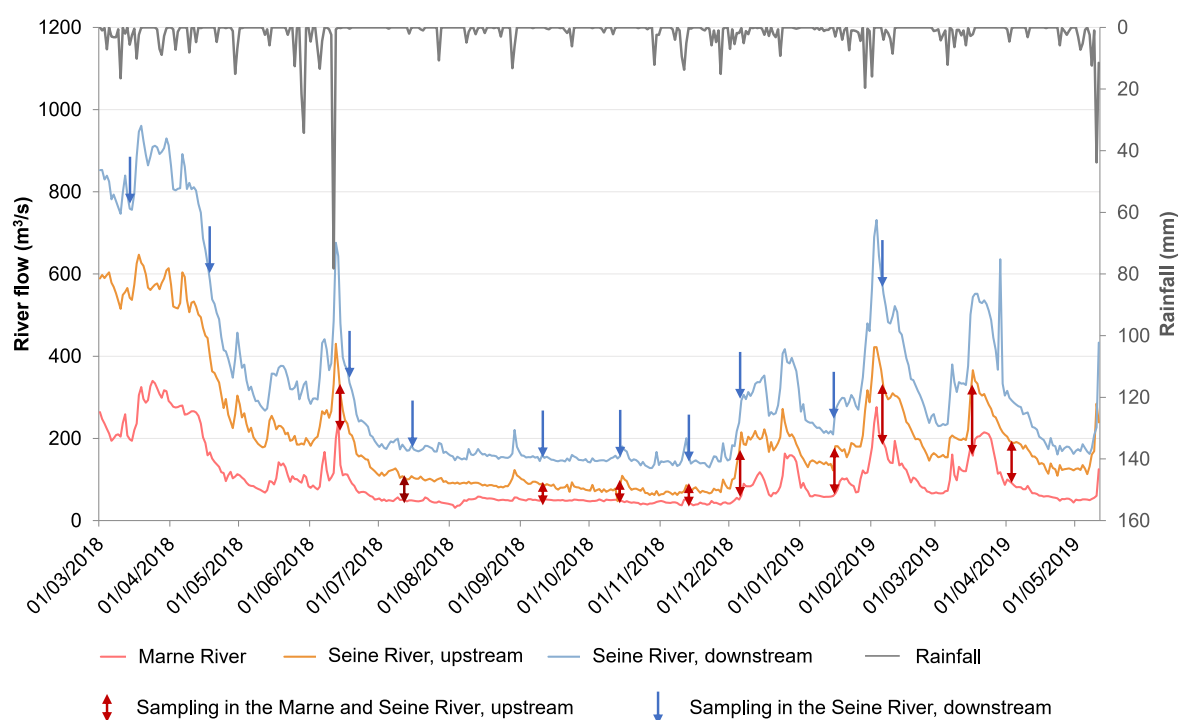


Fig. S1. Flow rate in the Marne and Seine Rivers, rainfall and sampling campaigns

Table S1. Information on sampling campaigns (TSS: total suspended solids; DOC: dissolved organic carbon; POC: particulate organic carbon)

Sampling date dd/mm/yy hh:mm	Flow rate (m ³ /s)	H _{rainfall} over the last 4 days ^c (mm)	TSS (mg/L)	DOC (mgC/L)	POC (mgC/L)
Marne River					
13/06/18 14:35	241 ^a	81.2	200	3.2	6.6
12/07/18 11:00	41 ^a	0	18	1.9	0.92
11/09/18 11:00	52 ^a	0	18	2.6	0.86
16/10/18 10:30	45 ^a	0	10	3.1	5.8
13/11/18 11:00	42 ^a	28.2	5.4	4.2	10
06/12/18 11:00	59 ^a	9.2	7.1	3.7	6.8
14/01/19 11:00	58 ^a	2.8	7.9	3.2	6.1
06/02/19 11:00	189 ^a	4	89	2.6	4.2
18/03/19 11:00	201 ^a	5.2	55	3.2	4.3
05/04/19 11:00	81 ^a	4.8	12	2.0	8.2
Seine River at Alfortville					
13/06/18	372 ^a	81.2	34.1	3.93	2.0
14:5512/07/18 11:30	105 ^a	0	6.77	2.07	0.76
11/09/18 11:30	84 ^a	0	9.68	2.58	0.94
16/10/18 11:00	100 ^a	0	4.89	3.04	12
13/11/18 11:30	84 ^a	28.2	5.63	3.65	20
06/12/18 11:30	215 ^a	9.2	14.88	3.53	9.8
14/01/19 11:30	138 ^a	2.8	5.13	3.41	8.9
06/02/19 11:30	324 ^a	4	47.7	5.52	5.8
18/03/19 11:30	340 ^a	5.2	24.8	2.64	7.1
05/04/19 11:30	191 ^a	4.8	8.87	2.36	6.2
Seine River at Conflans-Sainte-Honorine					
14/03/1810:00	762 ^b	7.7	20.1	-	-
17/04/18 10:00	635 ^b	0.2	10.2	2.64	0.79
19/06/18 10:00	318 ^b	0.4	15.5	3.69	0.98
17/07/18 10:00	171 ^b	2	5.09	2.62	0.71
11/09/18 09:00	150 ^b	0	7.28	3.49	0.82
16/10/18 09:50	174 ^b	0	6.66	3.57	12.7
13/11/18 09:00	160 ^b	28.2	3.92	5.60	25.0
06/12/18 09:00	289 ^b	9.2	5.89	4.30	12.5
15/01/19 09:00	210 ^b	1.6	5.26	4.41	14.3
06/02/19 09:00	552 ^b	4	71.9	3.27	5.03

^a data from "Hydro" database^b calculated flow rate from "Hydro" database and data from SIAAP^c data from Infoclimat, Paris Montsouris station

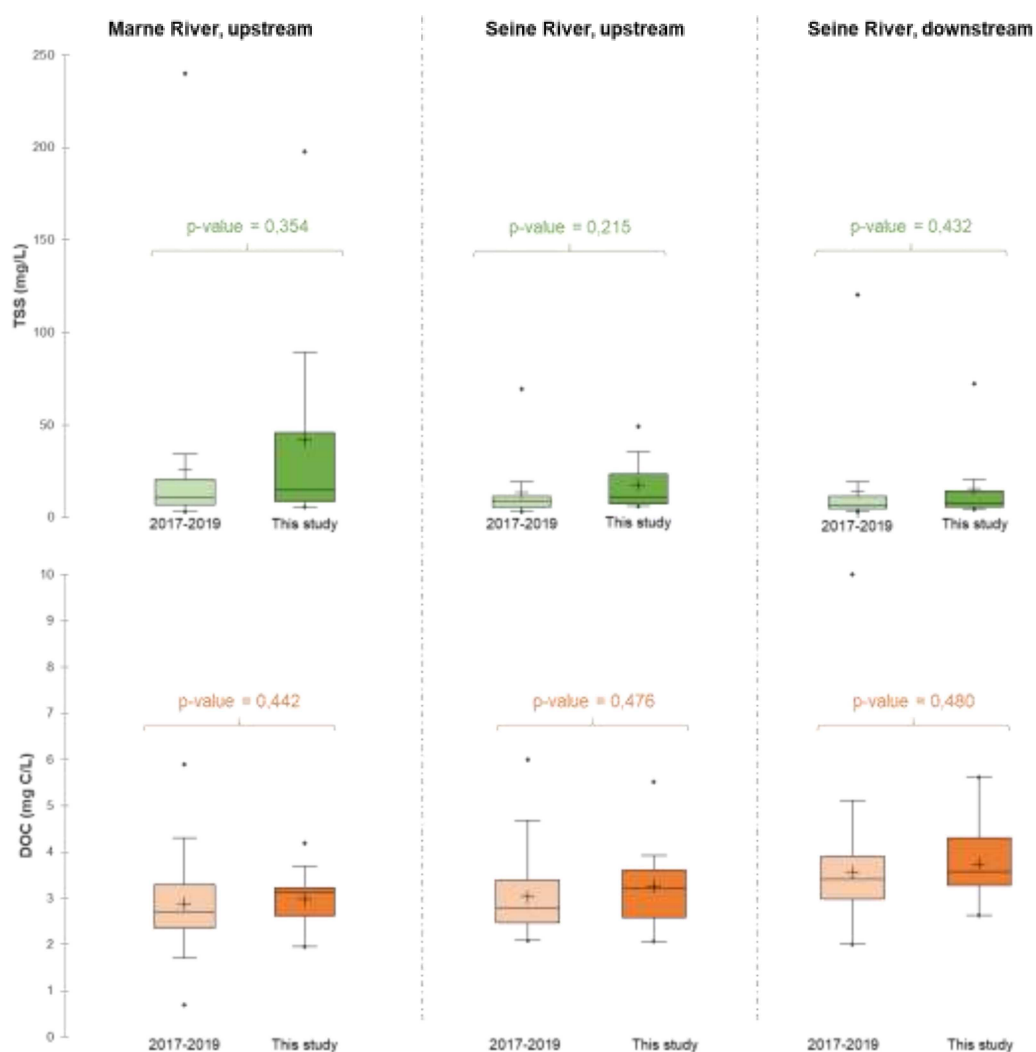


Fig. S2. Representativeness of the sampling campaigns: comparison of water quality parameters (TSS and DOC). The bottom of the box represents the 1st quartile and the top the 3rd quartile. The horizontal line represents the median value and the cross the mean value. The two data sets were compared using a Mann-Whitney test. The resulting p-values are indicated on the figure.

Table S2. Information on the 18-targeted biocides

Biocide	Abbreviation	CAS number	Formula	MW (g/mol)	Log Kow	pKa	logD*	EQS ^a (µg/L)(average / max)	PNEC (µg/L)	DT50 ^b in fresh waters (day)
Diuron		330-54-1	C ₉ H ₁₀ Cl ₂ N ₂ O	233.1	2.85		0.13	0.2 / 1.8	0.07 ^c	113-2190
Isoproturon		34123-59-6	C ₁₂ H ₁₈ N ₂ O	206.3	2.5		2.45	0.3 / 1	0.32 ^d	30-1560
Methylisothiazolinone	MIT	2682-20-4	C ₄ H ₅ NOS	115.2	-0.49		-0.23		3.39 ^e	18-30
Benzisothiazolinone	BIT	2634-33-5	C ₇ H ₅ NOS	151.2	0.64		1.41		4.03 ^e	>50
Chloro-methylisothiazolinone	CMIT	26172-55-4	C ₄ H ₄ ClNOS	149.6	0.4		1.12		0.049 ^e	3-6.6
Octylisothiazolinone	OIT	26530-20-1	C ₁₁ H ₁₉ NOS	213.3	2.45		2.99		0.0071 ^e	>30
Dichloro-octylisothiazolinone	DCOIT	64359-81-5	C ₁₁ H ₁₇ Cl ₂ NOS	282.2	3.59		4.43		0.034 ^e	<1
Benzyl dimethyl dodecyl ammonium chloride	BZK C12	139-07-1	C ₂₁ H ₃₈ ClN	304.5	1.7				0.062 ^c	30
Benzyl dimethyl tetradecyl ammonium chloride	BZK C14	139-08-2	C ₂₃ H ₄₂ ClN	346.6	2.5				0.043 ^c	30
Benzyl dimethyl hexadecyl ammonium chloride	BZK C16	122-18-9	C ₂₅ H ₄₇ ClN	388.7	3.2				0.043 ^c	30
Terbutryn		886-50-0	C ₁₀ H ₁₉ N ₅ S	241.4	3.7	4.3	1.38	0.065 / 0.34	0.065 ^c	354
Cybutryn (Irgarol 1051)		28159-98-0	C ₁₁ H ₁₉ N ₅ S	253.4	3.7	4.1	3.21	0.0025 / 0.016	0.0025 ^c	30
Terbuthylazine		5915-41-3	C ₉ H ₁₆ ClN ₅	229.7	3.0	2	2.99		0.06 ^d	77
Carbendazim		10605-21-7	C ₉ H ₉ N ₃ O ₂	191.2	1.5	4.2	1.61		0.15 ^d	42-350
Iodopropynyl butylcarbamate	IPBC	55406-53-6	C ₈ H ₁₂ INO ₂	281.1	2.8		3.2		0.168 ^c	7-139
Thiabendazole		148-79-8	C ₁₀ H ₇ N ₃ S	201.2	2.4	4.7 & 12	2.39		1.2 ^d	203
Tebuconazole		107534-96-3	C ₁₆ H ₂₂ ClN ₃ O	307.8	3.7	5	3.74		0.24 ^c	28
Mecoprop		93-65-2	C ₁₀ H ₁₁ ClO ₃	214.6	0.1	3.7	-0.65		0.9 ^c	31

MW: molecular weight / PNEC: predicted no effect concentration

*ChemSpider

^a Environmental quality standards from ECHA; ^b Half-life in fresh waters from Pajjens et al. (2020b); ^c Norman, 2022; ^d AA-EQS FW; ^e ECHA 2022

Table S3. Limits of detection (LOD_d) and quantification (LOQ_d) in the dissolved fraction of urban waters in ng/L

	River	
	LOD _d (ng/L)	LOQ _d (ng/L)
Diuron	0.27	0.66
Isoproturon	0.11	0.11
MIT	5	9.9
BIT	0.28	2.1
CMIT	1.6	8
OIT	0.21	0.52
DCOIT	0.04	0.45
BZK C12	5	17
BZK C14	4.7	16
BZK C16	3.6	12
Terbutryn	0.13	0.13
Cybutryn	0.14	0.14
Terbuthylazine	0.11	0.11
Carbendazim	0.17	0.17
IPBC	1.2	2.4
Thiabendazole	0.15	0.15
Tebuconazole	0.08	0.08
Mecoprop	1.5	2

Table S4. Limits of detection (LOD_p) and quantification (LOQ_p) (min-max) in the particulate fraction of waters in ng/g (dry weight)

	River	
	LOD _p (ng/g)	LOQ _p (ng/g)
Mass of particles (min-max in mg)	8.5 - 103	
Diuron	1.0-1.2	2.4-30
Isoproturon	0.5-5.9	0.5-5.9
MIT	2.4-30	4.9-59
BIT	1.0-12	7.3-89
CMIT	4.9-59	24-296
OIT	1.0-12	2.4-30
DCOIT	0.5-5.9	4.9-59
BZK C12	7.3-89	24-296
BZK C14	7.3-89	24-296
BZK C16	7.3-89	24-296
Terbutryn	1.0-12	1.0-12
Cybutryn	0.5-5.9	0.5-5.9
Terbuthylazine	0.5-5.9	0.5-5.9
Carbendazim	0.5-5.9	0.5-5.9
IPBC	4.9-59	9.7-118
Thiabendazole	0.5-5.9	0.5-5.9
Tebuconazole	1.0-12	1.0-12
Mecoprop	7.3-89	9.7-119

Table S5. Management of < LOD or < LOQ values for data treatment

Data treatment	
Case 1: one fraction (1 - dissolved or particulate) was $\geq \text{LOQ}_1$ and the other (2) was $> \text{LOD}_2$ and $< \text{LOQ}_2$, <i>i.e.</i> , the total concentration was between $C_{\text{determined}} + \text{LOD}_2$ and $C_{\text{determined}} + \text{LOQ}_2$.	The indeterminate term was approximated by $\max(\text{LOD}_2, \text{LOQ}_2/2)$.
Case 2: One fraction (1) was $\geq \text{LOQ}_1$ and the other was $< \text{LOD}_2$, <i>i.e.</i> , the total concentration was between $C_{\text{determined}}$ and $C_{\text{determined}} + \text{LOD}_2$.	The indeterminate term was considered equal to zero.
Case 3: Both fractions were $< \text{LOQ}$ or $< \text{LOD}$.	Concentrations in these samples were reported as “< M”, where M was calculated from the corresponding LOQ_i or LOD_i . When this applied to more than half of the dataset, the median value was reported as “< M”, and no attempt was made to perform further statistics on the data.
Particulate proportion (f_{part}) calculation	
Case 1: the substance was quantified in both C_d and C_p fractions (both expressed in ng/L).	$f_{\text{part}} = \frac{C_p}{C_d + C_p}$
Case 2: the concentration in the particulate fraction C_p was lower than the limit of quantification LOQ_p (resp. of detection LOD_p).	An upper limit of the f_{part} proportion was estimated by replacing the unquantified (resp. detected) value with the LOQ_p (resp. LOD_p): $C_p < \text{LOQ}_p \Rightarrow f_{\text{part}} < \frac{\text{LOQ}_p}{C_d + \text{LOQ}_p}$
Case 3: the dissolved C_d concentration was below the limit of quantification LOQ_d (resp. of detection LOD_d).	A lower bound on the proportion f_{part} was estimated by replacing the unquantified (resp. non-detected) value by LOQ_d (resp. LOD_d): $C_d < \text{LOQ}_d \Rightarrow f_{\text{part}} > \frac{C_p}{\text{LOQ}_d + C_p}$
Case 4: the substance was not quantified in any fraction.	f_{part} was not calculated.

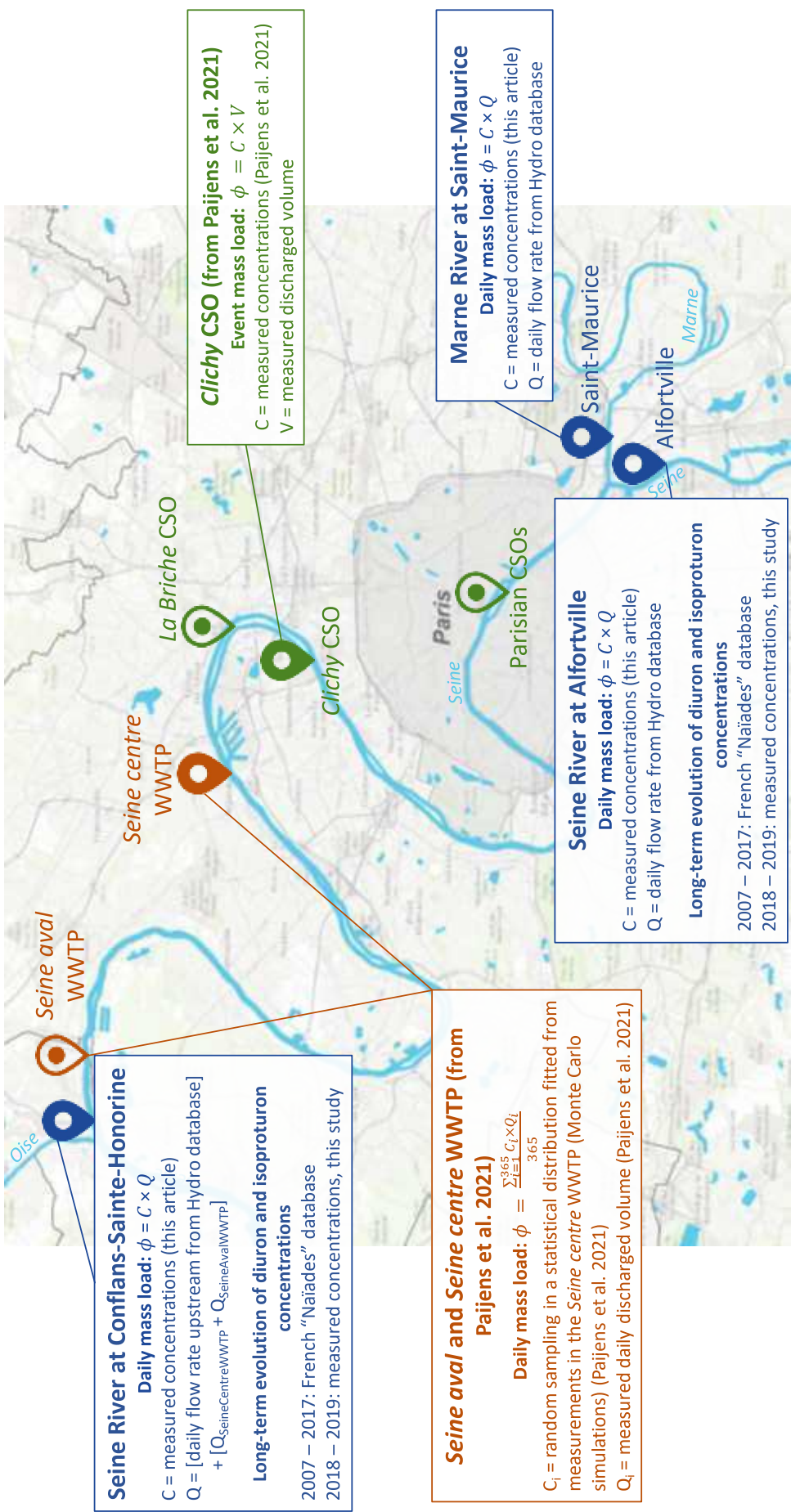


Fig. S3. Overview of the overall estimation approach to estimate daily mass loads and to study long-term evolutions of diuron and isoproturon concentrations

Table S6. Particulate contents measured in the Marne and the Seine Rivers up- and downstream the Paris conurbation (quantification frequencies, median contents (min-max))

Compound	Marne River (Saint-Maurice)		Seine River upstream (Alfortville)		Seine River downstream (Conflans-St-Honorine)	
	Number of quantification	Median content (ng/g) (min – max)	Number of quantification	Median content (ng/g) (min – max)	Number of quantification	Median content (ng/g) (min – max)
Diuron	0/10	-	1/10	<2.0 – 2.9	1/10	<3.0 – 51
Isoproturon	5/10	1.6 (<0.5 – 6.9)	4/10	<1.1 – 10	3/10	<1.7 – 44
MIT	9/10	78 (<6.6 – 1,100)	9/10	170 (<15 – 2,300)	8/10	140 (<13 – 3,600)
BIT	3/10	<7.3 – 12	3/10	<13 – 22	8/10	7.9 (<0.9 – 110)
CMIT	3/10	<13 – 270	3/10	<11 – 350	1/10	<6.0 – 1,900
OIT	0/10	-	1/10	<4.3 – 3.6	1/10	<3.0 – 63
DCOIT	0/10	-	0/10	-	0/10	-
BZK C12	10/10	83 (18 – 24,000)	10/10	630 (36 – 40,000)	9/10	2,200 (<90 – 11,000)
BZK C14	9/10	38 (<3.5 – 870)	10/10	770 (27 – 5,400)	9/10	170 (<42 – 2,000)
BZK C16	2/10	<2.4 – 9.0	3/10	<43 – 150	5/10	17 (<7.3 – 130)
Terbutryn	7/10	3.0 (<0.5 – 7.1)	7/10	3.8 (<1.1 – 100)	2/10	<1.7 – 5.8
Cybutryn	0/10	-	0/10	-	0/10	-
Terbuthylazine	8/10	2.6 (<0.5 – 5.7)	5/10	3.0 (<2.6 – 8.0)	4/10	<1.8 – 41
Carbendazim	7/10	1.9 (<1.3 – 9.0)	3/10	<1.1 – 4.2	3/10	<1.7 – 6.0
IPBC	7/10	37 (<11 – 150)	5/10	130 (<20 – 160)	9/10	76 (<31 – 170)
Thiabendazole	7/10	2.0 (<1.3 – 12)	5/10	3.6 (<1.1 – 16)	5/10	4.0 (<1.7 – 36)
Tebuconazole	10/10	11 (3.7 – 42)	9/10	7.9 (<3.4 – 34)	10/10	6.6 (1.9 – 63)
Mecoprop	0/10	-	0/10	-	0/10	-

Table S7. Daily/event loads of biocides discharged by the sewer system through WWTP effluents and CSOs, and transiting in the river upstream (Marne + Seine Rivers) and downstream (Seine River) the Paris conurbation: data presented as min-max (median), except for WWTPs (95% confidence interval about the mean value). NC: not calculated.

	WWTP effluents (<i>Seine aval + Seine centre</i>) (Paijens et al. 2021)	Clichy CSO discharges)	Marne + Seine Rivers, upstream	Seine River, downstream
	g/day	g/event	g/day	g/day
Diuron	32 ± 2	3 – 290 (20)	28 – 870 (100)	55 – 1020 (160)
Isoproturon	2.7 ± 0.2	<1 – 12 (1)	<1 – 200 (20)	<1 – 280 (32)
MIT	290 ± 20	1 – 240 (20)	<10 – 3200 (480)	<10 – 4800 (500)
BIT	47 ± 3	1 – 54 (7)	<10 – 200 (50)	<60 – 450 (140)
CMIT	NC	<1 – 30 (<5)	<20 – 240 (<70)	<50 – 820 (<80)
OIT	NC	1 – 38 (8)	<2 – 41 (15)	<2 – 120 (20)
DCOIT	3.9 ± 0.3	<1 – 8 (1)	<4 – 130 (17)	<1 – 620 (24)
BZK C12	1460 ± 130	63 – 3000 (700)	270 – 27000 (7100)	730 – 43000 (3700)
BZK C14	NC	26 – 2200 (230)	50 – 6300 (660)	170 – 3800 (980)
BZK C16	NC	<10 – 250 (40)	<70 – 2200 (<300)	<80 – 4000 (450)
Terbutryn	31 ± 2	1 – 66 (10)	5 – 160 (36)	30 – 200 (58)
Cybutryn	NC	<1 – 5 (<1)	<1 – 10 (<3)	<1 – 120 (<3)
Terbutylazine	1.9 ± 0.2	<1 – 8 (1)	<3 – 2000 (23)	<1 – 630 (26)
Carbendazim	32 ± 3	2 – 190 (15)	28 – 740 (110)	<10 – 760 (150)
IPBC	7.6 ± 0.5	<1 – 9 (<1)	<15 – 330 (22)	<20 – 150 (25)
Thiabendazole	23 ± 2	<1 – 26 (3)	<3 – 65 (30)	25 – 250 (60)
Tebuconazole	14 ± 1	1 – 67 (10)	20 – 5100 (60)	30 – 1200 (100)
Mecoprop	56 ± 4	<10 – 140 (40)	<20 – 790 (60)	<25 – 340 (160)