



HAL
open science

Mise en évidence des rejets urbains de biocides à travers la contamination des eaux de surface de l'agglomération parisienne

Damien Tedoldi, Claudia Paijens, Bertrand Frère, Régis Moilleron, Adèle Bressy

► To cite this version:

Damien Tedoldi, Claudia Paijens, Bertrand Frère, Régis Moilleron, Adèle Bressy. Mise en évidence des rejets urbains de biocides à travers la contamination des eaux de surface de l'agglomération parisienne. Novatech 2023, Jul 2023, Lyon, France. hal-04184780

HAL Id: hal-04184780

<https://hal.science/hal-04184780>

Submitted on 22 Aug 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Urban discharges of biocides evidenced by surface water contamination in the Paris conurbation

Mise en évidence des rejets urbains de biocides à travers la contamination des eaux de surface de l'agglomération parisienne

Damien Tedoldi¹, Claudia Paijens^{2,3}, Bertrand Frère³, Régis Moilleron², Adèle Bressy²

¹Univ Lyon, INSA Lyon, DEEP, EA7429, 69621 Villeurbanne, France (damien.tedoldi@insa-lyon.fr)

²LEESU, Ecole des Ponts, Univ Paris Est Creteil, Marne-la-Vallée, France (moilleron@u-pec.fr, adele.bressy@enpc.fr)

³Laboratoire Central de la Préfecture de Police (LCPP), Paris, France

ABSTRACT

Urban uses of biocidal substances are numerous, leading to the contamination of urban waters and, consequently, to discharges into the receiving environment. In this study, an indirect approach was carried out to evidence these urban inputs of biocides, by sampling and analyzing surface waters up- and downstream of the Paris conurbation. Most of the substances under consideration were consistently quantified at all sampling locations, with frequent exceedance of the Predicted No Effect Concentration for benzalkonium compounds. The biocides reported to be stormwater-borne in urban areas (because of outdoor uses and leaching during wet weather) displayed higher concentrations in the river during or after a rainy period, while no differences were visible between dry and wet weather for wastewater-borne substances. The Seine River was found to carry mass loads of biocides between a few tens of grams per day and several kilograms per day depending on the compound. For several molecules, a significant increase in daily mass loads was observed between the upstream and downstream sampling locations; in the case of benzisothiazolinone, this increase was of the same order of magnitude as the average mass load discharged from the two wastewater treatment plants in the study area. Overall, identifying the main pathways of urban biocides into surface waters is a first step towards the implementation of effective and concerted mitigation solutions.

RÉSUMÉ

Les usages de substances biocides en ville sont nombreux, conduisant à la contamination des eaux urbaines et, par conséquent, à des rejets vers le milieu récepteur. Cette étude propose une approche indirecte pour mettre en évidence ces apports urbains de biocides, en échantillonnant et analysant les eaux de surface en amont et en aval de l'agglomération parisienne. La plupart des substances ciblées ont été systématiquement quantifiées sur tous les sites, avec un dépassement fréquent de la concentration prédite sans effet pour les benzalkoniums. Les biocides véhiculés principalement par les eaux pluviales (en raison de leur utilisation sur/dans les matériaux du bâti et de leur lessivage par temps de pluie) présentaient des concentrations plus élevées dans les rivières pendant ou après une période de pluie ; à l'inverse, aucune différence n'était visible entre temps sec et temps de pluie pour les substances véhiculées principalement par les eaux usées. Les flux de biocides dans la Seine ont été estimés entre quelques dizaines de grammes par jour et plusieurs kilogrammes par jour selon le composé. Pour plusieurs molécules, une augmentation significative des flux journaliers a été observée entre les sites amont et aval. Dans le cas de la benzisothiazolinone, cette augmentation est du même ordre de grandeur que le flux moyen rejeté par les deux stations d'épuration de la zone d'étude. Ce travail d'identification des principales voies d'introduction des biocides urbains dans les eaux de surface constitue une première étape vers la mise en œuvre de solutions d'atténuation efficaces et concertées.

KEYWORDS

Biocides, Emerging contaminants, Impacts, Stormwater, Urban river

1 INTRODUCTION

Although the presence of biocidal substances in surface waters has been a matter of concern for a long time, most research efforts have been devoted to agricultural pesticides, while the contribution of urban areas as sources of such compounds has been comparatively overlooked (Merel *et al.*, 2018) – except for the well documented case of biocide leaching from building materials (Gromaire *et al.*, 2015; Linke *et al.*, 2021). Urban uses of biocidal substances other than pesticides or building protection products are nevertheless relatively numerous, including, but not limited to, fungicides, insecticides, and preservatives in household products and cosmetics. As a result, urban discharges – stormwater discharges, effluents from wastewater treatment plants (WWTPs), as well as combined sewer overflows (CSOs) – represent potential introduction pathways for these compounds into the receiving environment (Bollmann *et al.*, 2014), and may lead to comparable or even greater loads of certain molecules than agricultural losses (Wittmer *et al.*, 2011). This is notably the case for substances that have been banned as pesticides, the concentrations of which showed a marked decrease in surface waters, but stabilized at a non-negligible background level (Figure 1), possibly attributable to urban inputs.

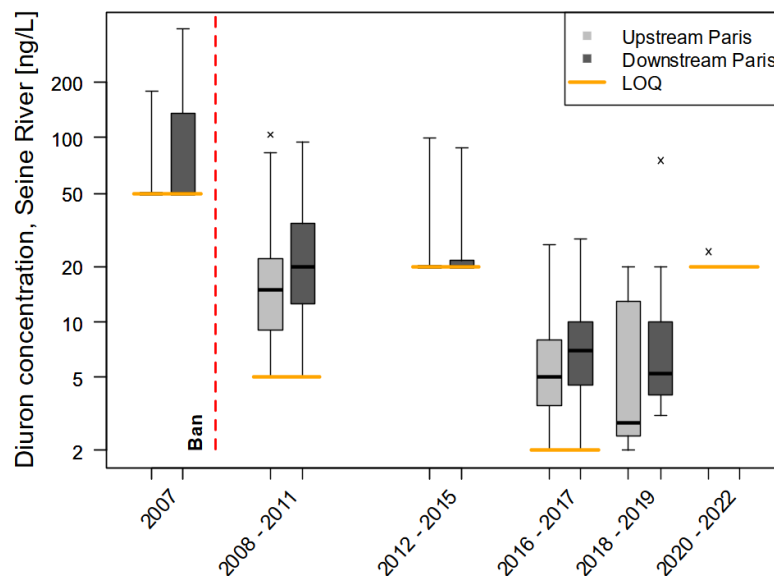


Figure 1 – Long-term evolution of diuron concentrations in the Seine River (updated from Paijens *et al.*, 2022).

Various approaches have been implemented to gain insight into the urban emissions and pathways of biocidal substances, such as pilot-scale leaching experiments (*e.g.*, Gromaire *et al.*, 2015), *in situ* sampling or elution experiments at selected small-scale infrastructures (Linke *et al.*, 2021), stormwater sampling at the outlet of small catchments with contrasting land uses (Wicke *et al.*, 2021), influent sampling in a WWTP under different weather conditions (Bollmann *et al.*, 2014), or effluent and CSO sampling (Paijens *et al.*, 2021). The present assessment consists of targeting the main receiving environment at the scale of the Paris megacity, *viz.* the Marne and Seine Rivers, in order to collect some evidence of the urban contribution to surface water contamination. Emphasis will be placed on three groups of biocides depending on their main transport pathways, as evidenced by previous studies (Bollmann *et al.*, 2014; Paijens *et al.*, 2021): (i) isothiazolinones, which are largely used in household products and therefore mostly wastewater-borne; (ii) diuron, isoproturon and terbutryn, the outdoor uses of which result in a predominance in stormwater; and (iii) the ubiquitous benzalkonium compounds.

2 MATERIALS & METHODS

2.1 Study area and sampling sites

The Paris conurbation is characterized by a high degree of urbanization (~6 000 000 inhabitants on approximately 1000 km²) and a high impervious surface (around 40%). The central area is mainly drained by a combined sewer system, while the peripheral suburbs are drained by a mixed network. The conurbation is crossed by two major rivers, the Seine River and the Marne River (interannual average flow rate: 218 and 110 m³/s, respectively), the confluence of which is located a few kilometers upstream of the inner city of Paris. Surface waters were sampled (i) upstream of Paris, in the Marne River at Saint-Maurice and in the Seine River at Alfortville, and (ii) downstream of Paris, in the Seine

River at Conflans-Sainte-Honorine. Upstream of Saint-Maurice and Alfortville, both rivers run for approx. 30 km starting from the edge of the Paris conurbation, which already includes several urban discharges. Between the upstream and downstream points (~80-km stretch of river), the effluents from two WWTPs (900 000 and 5 000 000 population equivalents) and several CSOs are discharged into the river.

2.2 Water sampling and analysis

Ten sampling campaigns were carried out in each river location between March 2018 and May 2019, covering all hydrological characteristics of the year, during both dry and wet weather. A boat was used to collect 5-L composite water samples at approx. 1 m depth in the middle of the river. Sampling campaigns were systematically carried out on the same day in Saint-Maurice and Alfortville; however, synchronizing the campaigns to account for the transport time between the up- and downstream locations was not always feasible. The samples were stored in cleaned glass bottles at 4 °C pending filtration and analysis. Eighteen biocides were analyzed in both the dissolved and particulate fractions using high performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS); the method is fully described in a previous publication (Paijens *et al.*, 2020). For the present paper, the focus will be on methylisothiazolinone (MIT), benzisothiazolinone (BIT), octylisothiazolinone (OIT), diuron, isoproturon, terbutryn, and benzalkonium chlorides (BZK C12–C16).

3 RESULTS & DISCUSSION

3.1 Variability of biocide concentrations

All reported substances were almost consistently quantified in the water samples from the three locations, with the exception of BIT (whose frequency of quantification increased from 5–7/10 upstream to 9/10 downstream), OIT (5/10 to 7/10), and BZK C16 (3–4/10 to 6/10). Different orders of magnitude were observed for total concentrations (Figure 2), ranging from several ng/L (BIT, OIT, isoproturon, terbutryn, BZK C16) to several tens of ng/L (MIT, diuron, BZK C14) to several hundreds of ng/L (BZK C12). As expected from the biocides' hydrophilicity, the dissolved fraction was predominant for these compounds, generally amounting to > 80% of the total concentrations. Dissolved concentrations of BZK C12 and C14 often exceeded Predicted No Effect Concentrations (62 and 43 ng/L, respectively, according to the data gathered from the Norman network); this occurred for diuron in one sample only.

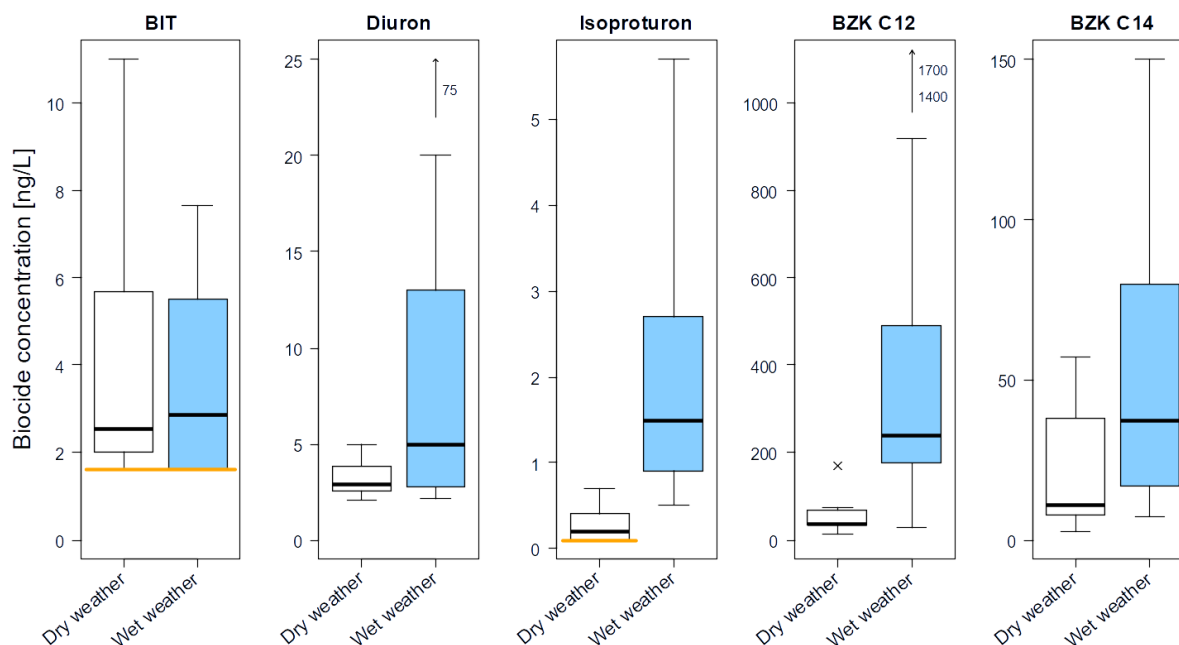


Figure 2 – Concentrations of selected biocides (all sampling points merged) during dry and wet weather.

From one campaign to another, some biocides showed concentrations spanning more than one order of magnitude (*e.g.*, from 10 ng/L to 1.7 µg/L for BZK C12). So as to better understand this variability, samples were categorized according to the weather conditions during the 4 days preceding the sampling dates (Figure 2). Interestingly, the substances proven (according to our previous study – Paijens *et al.*, 2021) to be stormwater-borne (diuron, isoproturon, terbutryn), or with an equivalent contribution of

sources (benzalkonium chlorides), presented significantly higher concentrations in both rivers during/after a rainy period than in dry weather – even after “small” rainfall events (< 5 mm). Contrariwise, for isothiazolinones, which are usually found in higher amounts in wastewater, no difference was visible in surface waters between the two weather conditions.

3.2 Upstream/downstream variations

In order to further explore the potential impact of the Paris conurbation on surface water quality, daily mass loads of biocides transiting in the rivers were computed upstream and downstream of the study area. For each site and sampling campaign, total concentrations were multiplied by the corresponding daily flow rate in the river; then, for the two upstream points, the contributions of the Seine and Marne Rivers were summed to obtain total upstream daily loads. As a result of the contrasting concentration levels presented above, river-borne biocide loads ranged from several tens of g/day (BIT, OIT, isoproturon, terbutryn) to several hundreds of g/day (diuron, MIT, BZK C14) to ≥ 1 kg/day (BZK C12).

Statistical distributions of upstream and downstream mass loads were compared using a non-paired Wilcoxon test (since the campaigns were not always synchronized). For terbutryn and BIT, the differences between the two locations were hardly consistent with the hypothesis of the same parent distribution ($p = 0.001$ and 0.029 , respectively). This test also provided a 95% confidence interval for the shift between up- and downstream distributions, which for BIT was 30–153 g/day: noteworthy, this range included the average BIT load previously estimated for the two WWTPs within the study area (~50 g/day, Paijens *et al.*, 2021). Although this result by no means represents a “mass balance closure”, it supports the idea that wastewater (even after treatment) is the primary transport pathway for this compound. For the other biocides under consideration, no particular upstream/downstream trend could be evidenced from the current dataset.

4 CONCLUSIONS & PERSPECTIVES

In this study, an indirect approach has been carried out to evidence urban discharges of biocides, by sampling and analyzing surface waters up- and downstream of the Paris conurbation. The contribution of wet weather discharges was thus identified for most compounds, with the notable exception of the wastewater-borne isothiazolinones. Uncovering the links between biocide uses, pathways, and impacts, allows mitigation solutions to be proposed. Current research perspectives include the potential use of vegetated, infiltration-based systems as sinks for biocides, the fate of these hydrophilic albeit degradable molecules within the soil, and the possible threat they would represent for groundwater quality.

REFERENCES

- Bollmann, U.E., Tang, C., Eriksson, E., Jönsson, K., Vollertsen J. and Bester, K. (2014). *Biocides in urban wastewater treatment plant influent at dry and wet weather: Concentrations, mass flows and possible sources*, Water Res., 60, 64-74.
- Gromaire, M.-C., Van de Voorde, A., Lorgeoux, C. and Chebbo, G. (2015). *Benzalkonium runoff from roofs treated with biocide products – In situ pilot-scale study*, Water Res., 2015, 81, 279-287.
- Linke, F., Olsson, O., Preusser, F., Kümmerer, K., Schnarr, L., Bork M. and Lange, J. (2021). *Sources and pathways of biocides and their transformation products in urban storm water infrastructure of a 2ha urban district*, Hydrol. Earth Syst. Sci., 25, 4495-4512.
- Merel, S., Benzing, S., Gleiser, C., Di Napoli-Davis, G. and Zwiener, C. (2018). *Occurrence and overlooked sources of the biocide carbendazim in wastewater and surface water*, Environ. Pollut., 239, 512–521.
- Paijens, C., Frère, B., Caupos, E., Moilleron, R. and Bressy, A. (2020). *Determination of 18 Biocides in Both the Dissolved and Particulate Fractions of Urban and Surface Waters by HPLC-MS/MS*, Water, Air, Soil Pollut., 231, 210.
- Paijens, C., Bressy, A., Frère, B., Tedoldi, D., Mailler, R., Rocher, V., Neveu, P. and Moilleron, R. (2021). *Urban pathways of biocides towards surface waters during dry and wet weathers: Assessment at the Paris conurbation scale*. J. Hazard. Mater., 402, 123765.
- Paijens, C., Tedoldi, D., Frère, B., Mailler, R., Rocher, V., Moilleron, R., and Bressy, A. (2022). *Biocidal substances in the Seine River: contribution from urban sources in the Paris megacity*. Environ. Sci.: Water Res. Technol., 8, 2358-2372.
- Wicke, D., Matzinger, A., Sonnenberg, H., Caradot, N., Schubert, R.-L., Dick, R., Heinzmann, B., Dünnbier, U., von Seggern, D. and Rouault, P. (2021). *Micropollutants in Urban Stormwater Runoff of Different Land Uses*, Water, 13, 1312.
- Wittmer, I.K., Scheidegger, R., Bader, H.-P., Singer, H. and Stamm, C. (2011). *Loss rates of urban biocides can exceed those of agricultural pesticides*, Sci. Total Environ., 409, 920-932.