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

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

1. Introduction



Etymologically, **biocidal substances** refer to a wide variety of compounds designed or used to "kill life". While 75 years ago, DDT was presented as "a benefactor of all humanity" (Figure 1), the widespread use of biocidal substances is now recognized as a major environmental threat. Over the last decades, huge emphasis has been placed on **pesticides** and their impact on the quality of aquatic environments: various mitigation actions have been implemented, including the ban or substitution of certain compounds, and the overall reduction of the quantities used.

The example of diuron (Figure 2) shows that the ban on this substance as a pesticide has led to a tenfold reduction in its concentrations in the Seine River within 10 years. Nevertheless, diuron concentrations stabilized at a non-negligible background level, which raises concerns about the **contribution of urban areas** as additional sources of biocides^{1,2}.

Various approaches have been implemented to gain insight into the urban emissions and pathways of biocides, such as pilot-scale leaching experiments³, *in situ* sampling or elution experiments at small-scale infrastructures⁴, stormwater sampling at the outlet of different catchments⁵, WWTP influent sampling under different weather conditions⁶... As a complementary approach, 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.

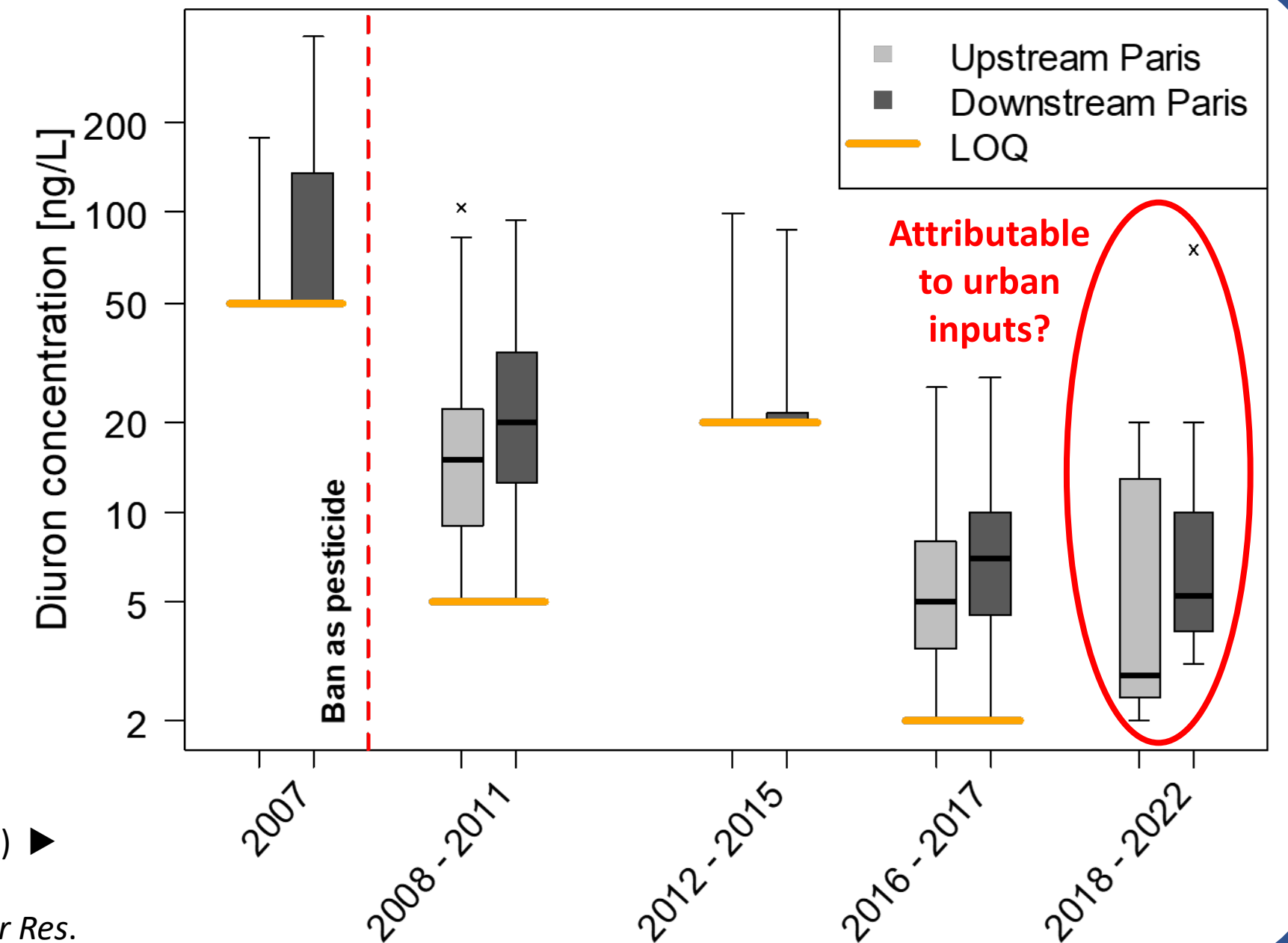


Figure 2 – Long-term evolution of diuron concentrations in the Seine River, up- and downstream the Paris conurbation (data from "Naiades" database) ▶

Figure 1 – Advertisement for Pennsalt DDT products. Time Magazine, June 30, 1947

References: ¹Wittmer et al., 2011, *Sci. Total Environ.* ²Merel et al., 2018, *Environ. Pollut.* ³Gromaire et al., 2015, *Water Res.* ⁴Linke et al., 2021, *Hydrol. Earth Syst. Sci.* ⁵Wicke et al., 2021, *Water.* ⁶Bollmann et al., 2014, *Water Res.*

2. Materials & Methods

Sampling of surface waters

- Alfortville (upstream, Seine River)
- S^t-Maurice (upstream, Marne River)
- Conflans-S^t-Honorine (downstream)

Biocide analysis (HPLC-MS/MS)

Focus on biocides with different uses in urban areas:

- Compounds mainly used in household products: isothiazolinones (methyl-, benz-, and octylisothiazolinone – MIT, BIT, and OIT, respectively)
- Compounds with mostly outdoor uses: diuron, isoproturon, terbuthryn
- Widespread compounds: benzalkonium chlorides (BZK), thiabendazole

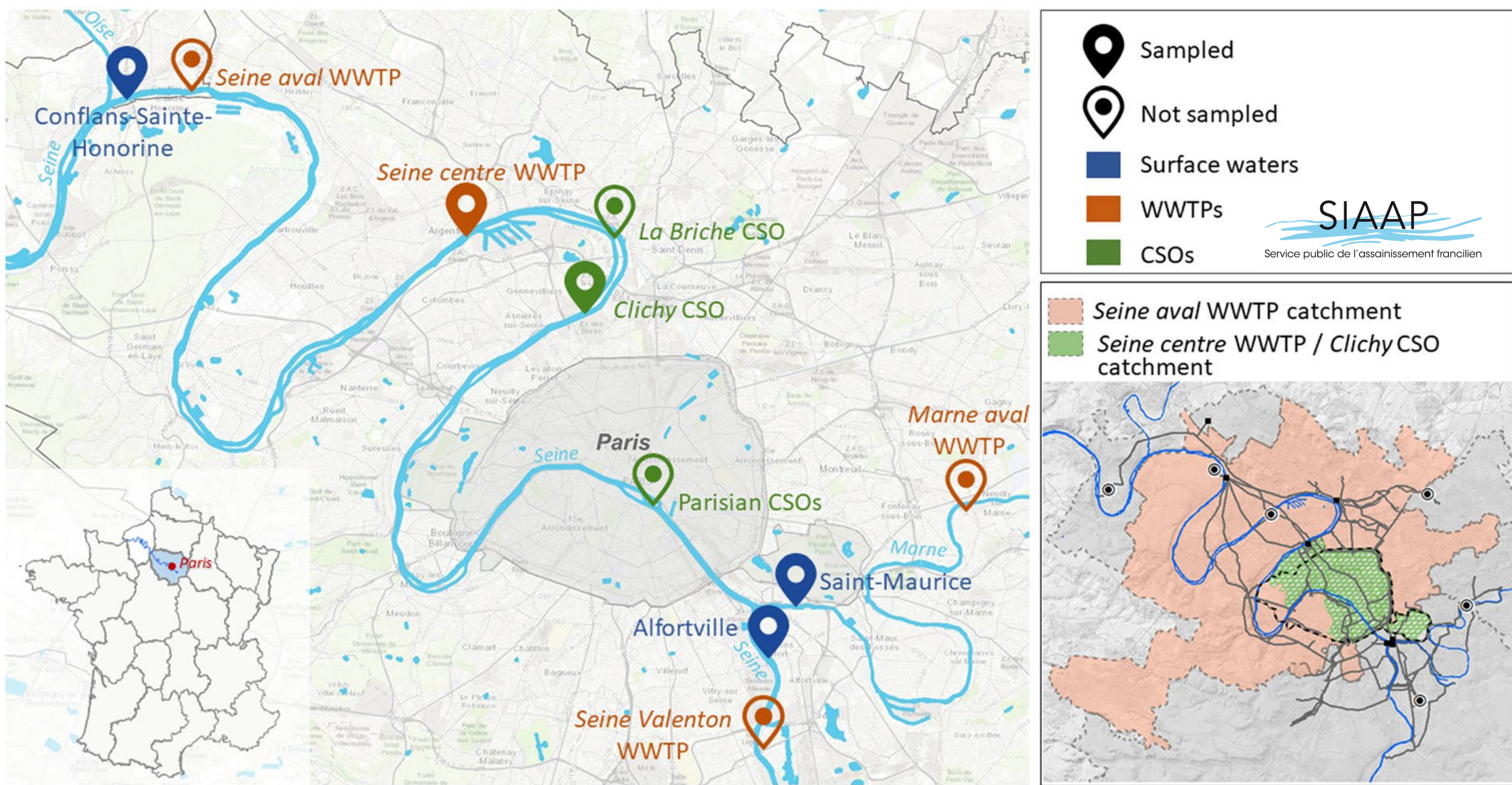


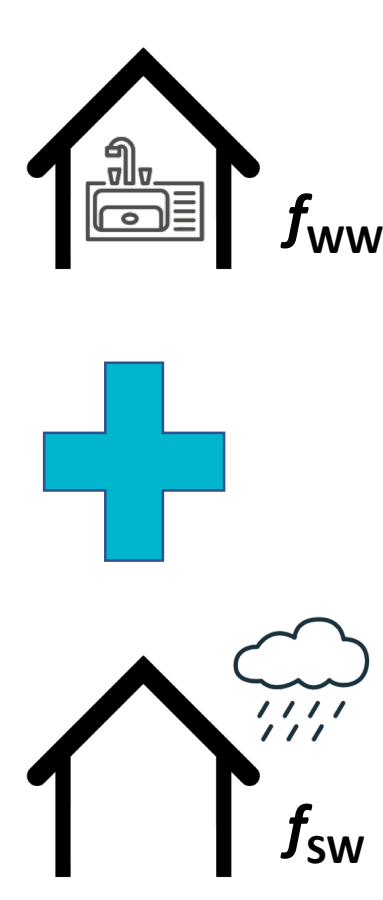
Figure 3 – Presentation of the study area (~ 6 000 000 inhabitants on approximately 1000 km²) with the major urban sources of biocides, as well as the different sampling locations.

Sampling of urban effluents

in collaboration with SIAAP

- Wastewater Treatment Plant: Seine centre
- Combined Sewer Overflow: Clichy

3. Evidencing the main pathways of biocides

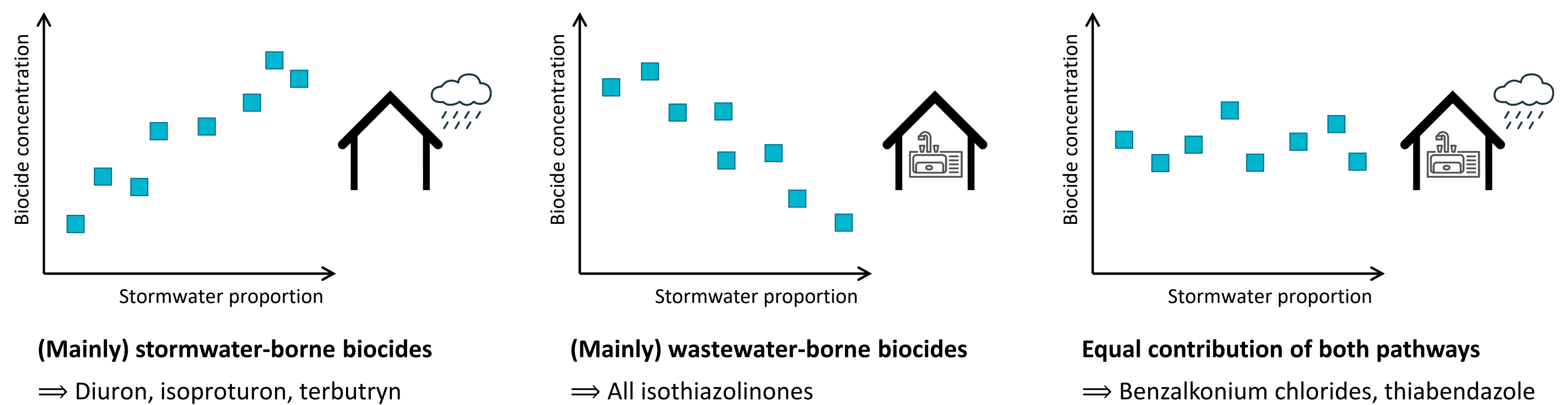


Estimation of the stormwater proportion (f_{sw}) in CSOs

$$\text{Conductivity}_{\text{CSO}} = f_{\text{WW}} \times \text{Conductivity}_{\text{WW}} + f_{\text{SW}} \times \text{Conductivity}_{\text{SW}}$$

$$\Rightarrow f_{\text{SW}} = \frac{\text{Conductivity}_{\text{WW}} - \text{Conductivity}_{\text{CSO}}}{\text{Conductivity}_{\text{WW}} - \text{Conductivity}_{\text{SW}}}$$

Relationship between f_{sw} and biocide concentrations? Three possible patterns (Δ mock data):



4. Influence of wet weather



From one campaign to another, some biocides showed concentrations spanning more than one order of magnitude in surface waters (e.g., from 10 ng/L to 1.7 μg/L for benzalkonium C12). So as to better understand this variability, samples were categorized according to the weather conditions during the four days preceding the sampling campaigns (Figure 4).

The substances proven to be stormwater-borne, or with an equivalent contribution of pathways, presented significantly **higher concentrations in surface waters during/after a rainy period** than in dry weather, showing the impact of stormwater discharges. Contrariwise, for isothiazolinones (mainly wastewater-borne), no difference was visible in surface waters between the two weather conditions.

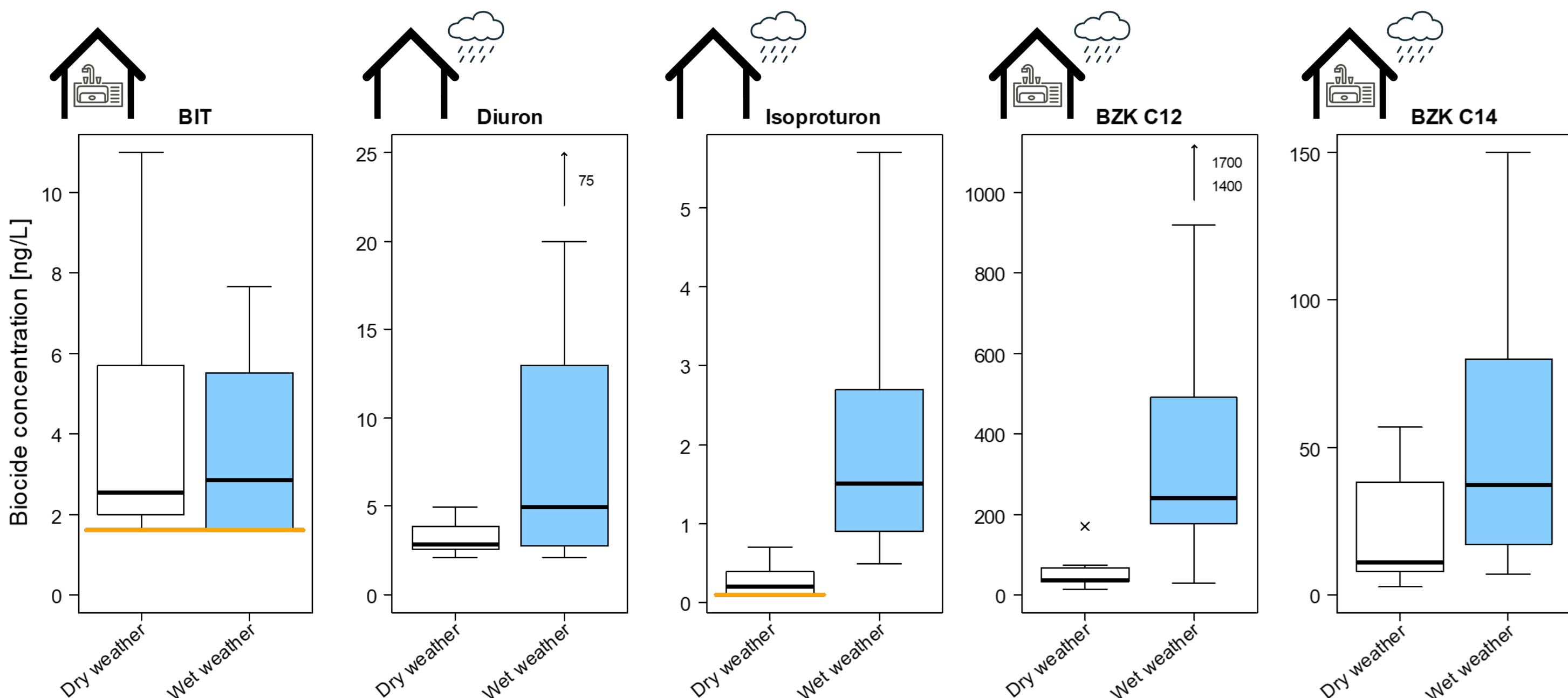


Figure 4 – Statistical distributions of different biocide concentrations (all sampling points merged) as a function of the weather conditions during the 4 days preceding the sampling campaigns. The orange line indicates the limit of quantification.

5. Upstream-downstream differences



Daily mass load of biocide = Biocide concentration × Daily flow rate

× 3 sampling locations and N campaigns
Upstream campaigns were synchronized, allowing for summation

For several biocides, a **significant increase was evidenced between up- and downstream mass loads**. Figure 5 indicates a 95% confidence interval for the shift between the two distributions, which for BIT (wastewater-borne) included the estimated average load in WWTP effluents (~ 50 g/day, Paijens et al., 2021). This result by no means represents a "mass balance closure" but supports the idea that wastewater (even after treatment) may contribute to river contamination by biocides.

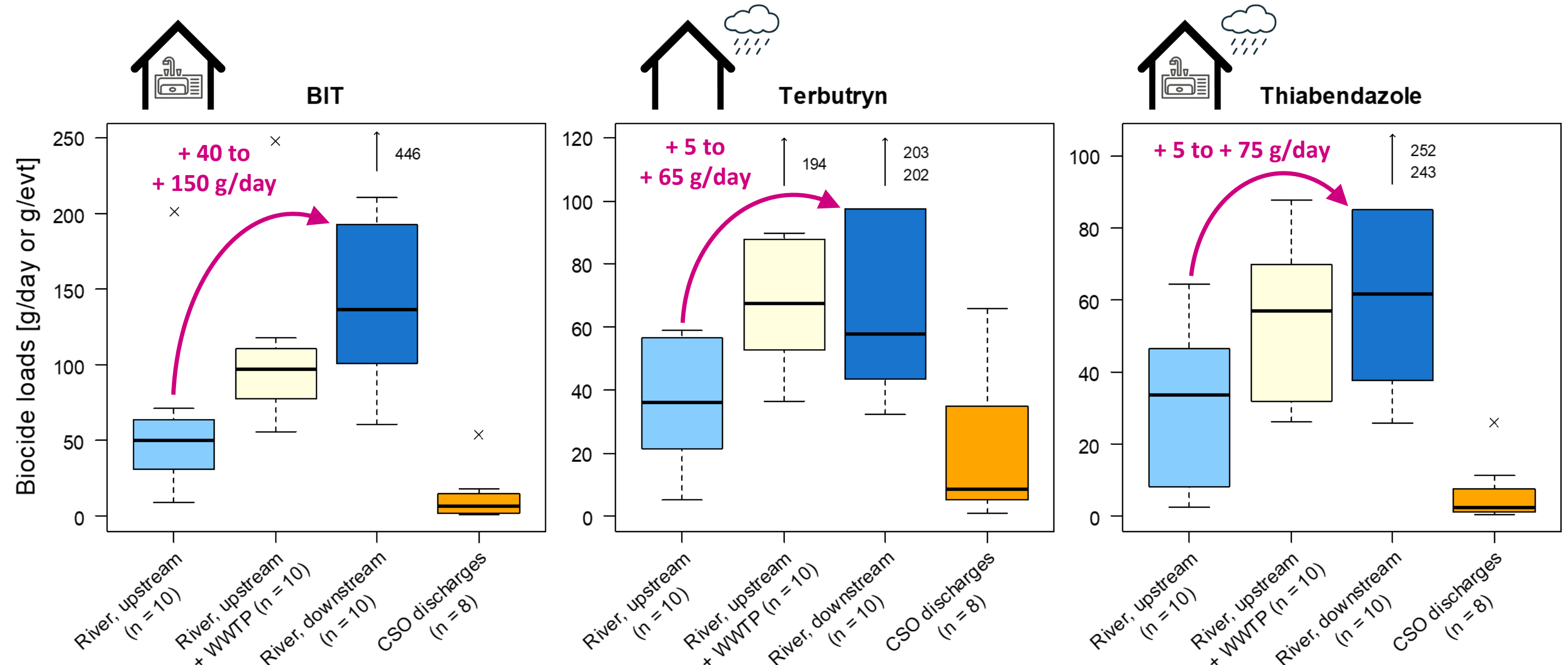


Figure 5 – Statistical distributions of the daily biocide loads in the river up- and downstream the Paris conurbation; 95% confidence interval for the shift between the two distributions, as determined from a Wilcoxon-Mann-Whitney test; comparison with urban discharges.

For more information:

- C. Paijens, A. Bressy, B. Frère, D. Tedoldi, R. Mailler, V. Rocher, P. Neveu and R. Moilleron, Urban pathways of biocides towards surface waters during dry and wet weathers: Assessment at the Paris conurbation scale, *J. Hazard. Mat.*, 2021, 420 ▶
- C. Paijens, D. Tedoldi, B. Frère, R. Mailler, V. Rocher, R. Moilleron and A. Bressy. Biocidal substances in the Seine River: contribution from urban sources in the Paris megacity. *Environmental Science: Water Research & Technology*, 2022, 10