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RIVER CONTAMINATION BY BIOCIDES: PASSIVE SAMPLING DEVELOPMENT AND APPLICATION TO PARIS CONURBATION

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1. Purpose

Triclosan (TCS) and triclocarban (TCC) are two emergent pollutants used as antimicrobial in many personal care products (Bedoux et al. 2012) and found in wastewater at high concentrations (Gasperi et al. 2014). They are only removed in a range of 34-99 % by waste water treatment plants (WWTP). As a consequence they are measured in surface waters at concentrations that may induce bioaccumulation and antibiotic resistance (Bedoux et al. 2012; Carey and McNamara 2015). But the monitoring of micropollutants is still a challenge due to their weak concentrations in complex matrix and their temporal variability. Passive samplers have been developed and used for water quality monitoring with two main advantages (i) to improve the temporal representativeness by measuring the “Time Weighted Average (TWA) concentration” and (ii) to measure the “truly dissolved compounds” available for aquatic organisms (Gourlay-Francé et al. 2011). Polymeric membranes are used as passive samplers for hydrophobic contaminants. To determine the TWA concentration in water, the knowledge of the uptake and export constants (k_u and k_e) and the sampler / water partition coefficient (K_{sw}) is needed. The first objective of this research is to optimize a passive sampling protocol for triclosan and triclocarban and to calibrate all parameters. The second objective is to use this method to assess the impact of Paris conurbation on TCS and TCC concentrations in the Seine river.

2. Methodology

Passive sampling protocol development. The passive sampling protocol (type of polymeric membrane, spiking and dialyze solvents) was optimized on the basis of the recuperation rate. This protocol allows a recuperation rate ranging from 93 to 140 %.

Kinetic experiment. Fifteen membranes in PolyDiMethylSiloxane (PDMS) spiked with molecules of interest (TCS, TCC, TCSd3) were placed in a pilot filled with 3.3L of mineral water with fifteen cleaned PDMS membranes. At each sampling time, 1 cleaned membrane and 1 spiked membrane were removed, dialyzed and analyzed by LC/MSMS. Elimination and accumulation were observed respectively for the spiked and cleaned membranes for all the compounds during 15 days to obtain the accumulation and elimination kinetic curves. A first order kinetic exchange model was used to obtain all the constants using the software R for calibration.

Field deployment. PDMS membranes were exposed during 7 days in duplicate at three stations on the Seine River: upstream Paris (Ablon-sur-Seine) and downstream Paris (Bougival and Andrésey). These two last points are respectively downstream and upstream the discharge of the main WWTP of the Paris conurbation.

3. Results

Kinetic experiment. The results obtained from the kinetic experiment are presented in Figure 1 for TCS. Decreasing concentrations in spiked membranes (C_s) were observed over the time with increasing concentrations in unspiked membranes (C_c) until equilibrium was reached. The three

constants were calibrated for TCS ($k_e=0.756\pm 0.049\text{ d}^{-1}$; $k_u=3409\pm 221\text{ d}^{-1}$; $\log K_{sw}=3.65$) and TCC. *Field deployment.* The TCS and TCC accumulation in membranes (Figure 2) highlighted an increase of concentration in the Seine river from upstream to downstream, that means that there is an impact of Paris on its receiving water.

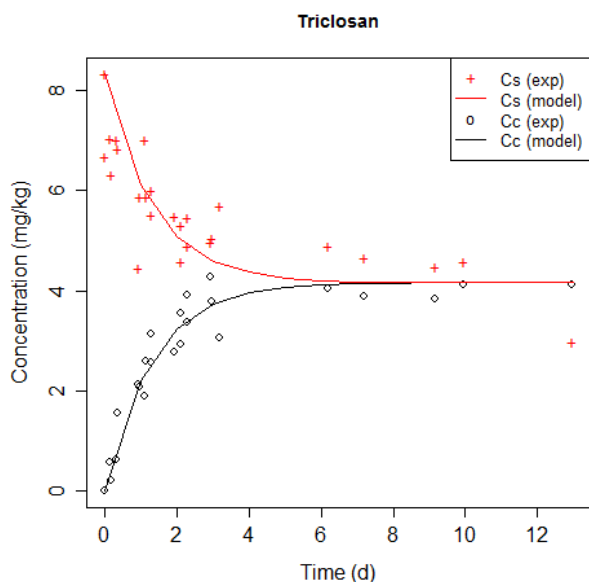


Figure 1. Elimination and accumulation kinetic of TCS (experimental data (exp) and modelisation (model))

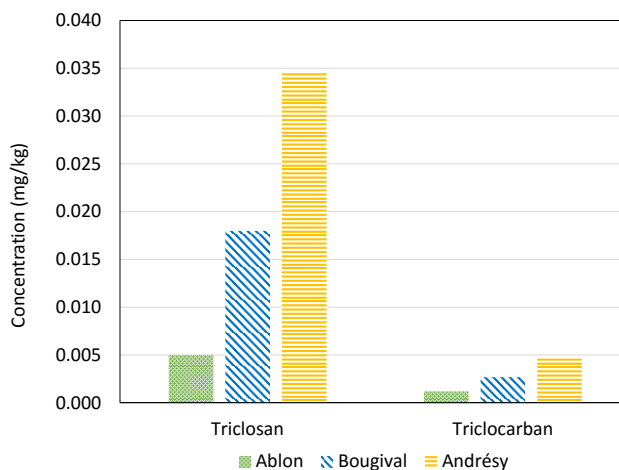


Figure 2. Concentrations of TCS and TCC accumulated in membranes exposed in the Seine river from upstream (Ablon) to downstream (Andrésy)

4. Conclusion

A robust protocol has been developed to use polymeric membranes as passive samplers for TCS and TCC monitoring. All the kinetic and thermodynamic parameters were calibrated for TCS, TCC and TCSd3. The in situ exposition highlighted that the Paris conurbation increases the contamination of the river in these biocides.

Reference

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