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Abstract

Isothiazolinones are ubiquitous in our daily life; they are used as preservatives in cosmetics, household products and in building materials. These biocidal substances may be emitted inside house, inducing a potential risk for health, and released into the environment through wastewater or runoff, thus inducing a potential impact on aquatic ecosystems. The overall objective of this communication was to explore the isothiazolinone contamination of the continuum House-Sewer-River and to assess the induced risks for health and the aquatic life. The experimental results showed the ubiquity of isothiazolinones in indoor dust, urban water discharges and in the Seine River. Annual mass loads discharged into the Seine River were estimated using Monte Carlo method at both the conurbation and annual scales, they showed that wastewater discharges constitute the major entry pathway.

Keywords

Biocide; combined sewer overflow; indoor dust; mass loads; river; wastewater

CONTEXT AND OBJECTIVES

Despite intense use of isothiazolinones in household products (Ducup de Saint Paul *et al.* 2021) and in construction materials (Bollmann *et al.* 2014) and their potential harmful effects for humans and for aquatic receiving environments (Kresmann *et al.* 2018; Kim *et al.* 2021), few studies have documented their presence along the continuum extending from the indoor environment to the river (Paijens *et al.* 2020a). Indeed, isothiazolinones are poorly integrated into monitoring programs. Most studies addressed small-scale emissions in runoff at building scale. This work focused on five isothiazolinones and aimed at (i) collecting data on their occurrence in indoor environment to assess Human exposure; (ii) quantifying their release into the receiving environment through wastewater and combined sewer overflows (CSOs); and (iii) assessing the contamination of surface waters and the associated risk.

METHODOLOGY

Sampling campaigns

This study focused on the continuum House-Sewer-River on the Paris conurbation example. Samples were collected at different levels of this continuum: (i) close to the use of isothiazolinones in the house, *i.e.*, in indoor dust and greywater; (ii) at the level of urban discharges (wastewater treatment plant – WWTP, and CSOs); and (iii) in the aquatic receiving environment.

Sampling inside house: indoor dust and greywater

Indoor dust and greywater were sampled in order to estimate the indoor contamination by biocides linked to their uses in building material and daily products (households, cosmetics etc.). For that purpose, indoor dust was collected with a vacuum cleaner in 12 dwellings from the Paris conurbation. Greywater (cooking water, shower, floor washing, sink) was sampled 6 times in a building of collective catering.

Sampling inside the sewer system

Six sampling campaigns were conducted during dry weather in the influent and effluent of the *Seine centre* WWTP (900,000 inhabitant equivalent, physico-chemical lamellar unit and biofiltration). Eight sampling campaigns were performed during wet weather in the biggest Parisian CSO located in Clichy. For each campaign, composite samples (24 h for WWTP or discharge duration for CSO) were collected by automatic samplers equipped with Teflon® pipes and maintained at 4°C before analysis.

Sampling in the Seine River

The sampling campaigns targeted (i) the Marne and the Seine Rivers before their confluence upstream the Paris conurbation, and the Seine River downstream (10 sampling campaigns covering all hydrological characteristics of the year). At each sampling location, a boat was used to collect 5-L water samples in the middle of the river at a depth of approx. 1 m, thus avoiding the biases related to the uneven flow conditions and incomplete mixing close to the banks. These samples were composited from 5 sub samples kept in cleaned glass bottles and stored at 4°C.

Biocides analysis

Five isothiazolinones 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): methylisothiazolinone (MIT), chloromethylisothiazolinone (CMIT), benzisothiazolinone (BIT), octylisothiazolinone (OIT), dichloro-octylisothiazolinone (DCOIT).

Dust samples were sieved at 100µm. Water samples were filtrated through glass fiber filters (0,7 µm, GF/F Whatman). Particles from water and from dust (~ 100 mg) were solvent extracted by microwaves. Dissolved fractions were solid phase extracted. All the extracted fractions were analyzed by ultra-performance liquid chromatography coupled with tandem mass spectrometry (Paijens *et al.* 2020b).

Data treatment

The method used for the assessment of biocide loads at the annual scale relies on Monte Carlo simulations and aimed at propagating the inherent variability and uncertainties of the measured variables (Paijens *et al.* 2021). For WWTP and CSO results, theoretical distributions were first fitted to the experimental data, to characterize the temporal variability of concentrations. These distributions were then used to randomly reconstruct a 1-year series of daily/event-mean biocide concentrations, to which a Gaussian error term was added. These concentrations, multiplied by the daily flow rates measured during the study period, 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.

RESULTS

Isothiazolinone emissions at home

Table 1 summarizes the frequencies of quantification and contents of isothiazolinones in indoor dust. MIT, BIT and OIT were quantified in all the 12 samples, CMIT in 9 samples and DCOIT in 2 samples out 12. These frequencies of quantification are consistent with two levels of concentrations. MIT, BIT and OIT were measured with respective median contents of: 490 ng/g, 850 ng/g and 260 ng/g. CMIT and DCOIT were measured with respective median contents of: 49ng/g and 34 ng/g. Greywater samples are currently being analysed.

Occurrence of isothiazolinones in the sewer system

MIT, BIT and DCOIT were systematically quantified in WWTP influent and effluent samples as OIT in influent (Table 1), while CMIT was never quantified and OIT two times over six in effluent. Three levels of concentrations could be observed: (i) concentrations of MIT were generally higher than 100 ng/L, (ii) concentrations of BIT ranged between 20 and 60 ng/L, and (iii) concentrations of OIT and DCOIT were lower than 5 ng/L. In CSOs, isothiazolinones were quantified in almost all samples between <0.5 ng/L and 300 ng/L, except DCOIT exhibiting concentrations < 10 ng/L.

In order to discriminate the origins of biocides in CSO discharges (wastewater vs. stormwater), we looked for a trend between concentrations in CSO and proportions of stormwater (estimated from electrical conductivity). The concentrations of MIT and BIT decreased with increasing proportion of stormwater in the CSO, suggesting a dilution of wastewater by stormwater. These compounds are indeed widely used as preservatives in household products. No trends were observed for CMIT, OIT, DCOIT. These compounds thus appear to be contributed in equivalent proportions by wastewater and stormwater, consistent with their use in domestic products and as preservatives in building materials.

Occurrence of isothiazolinones in the Seine River

For the Seine River, the frequencies of quantification were found to be lower. MIT and BIT downstream were always detected, while BIT upstream, OIT and DCOIT were quantified between 5/10 and 7/10, and less than 3/10 for CMIT. Median total concentrations were generally below 10 ng/L, except for MIT (13-21 ng/L). Frequencies of quantification and median concentrations are higher downstream the Paris conurbation than upstream. The risk quotient (RQ ratio between the river concentration and the predicted no effect concentration (PNEC)) was calculated for each substance and each campaign. RQ was high (>1) for 70% of the samples for MIT (PNEC=50 ng/L). CMIT, OIT, DCOIT represented a low to medium risk (0.01 < RQ < 1).

Table 1. Quantification frequencies (F) and median concentrations (min/max) of isothiazolinones in the continuum House-Sewer-River

	Indoor dust		WWTP influent		WWTP effluent		CSO		Seine River upstream		Seine River downstream	
	F	Median conc. min/max ng/g	F	Median conc. min/max ng/L	F	Median conc. min/max ng/L	F	Median conc. min/max ng/L	F	Median conc. min/max ng/L	F	Median conc. min/max ng/L
MIT	12/12	490 59/1,360	6/6	620 (350 / 860)	6/6	150 39/350	8/8	70 9.8/290	9/10	13 <1/150	9/10	21 <1/170
BIT	12/12	890 130/3,500	6/6	320 (210 / 660)	6/6	24 20/55	8/8	32 4.6/64	5/10	3.0 <1.2/6.8	9/10	7.0 <1.4/11
CMIT	9/12	49 12/150	0/6	<13	0/6	<3.7	4/8	14 <9.5/160	3/10	<4.7	2/10	<14
OIT	12/12	260 47/1,300	6/6	5.9 (1.1 / 9.0)	2/6	<1.8 <0.7/2.0	8/8	27 18/46	5/10	0.9 <0.3/1.2	7/10	1.1 <0.3/1.7
DCOIT	2/12	34 31/36	5/6	4.5 (<0.6 / 10)	6/6	1.5 0.5/4.6	6/8	4.6 <0.5/6.3	7/10	1.1 <0.3/2.9	7/10	1.6 <0.4/43

Annual contributions of CSOs and WWTPs at the Paris conurbation scale

Annual biocide loads in WWTP effluents were found to range in the following order: DCOIT (1-10 kg/yr) < BIT (10-100 kg/yr) < MIT (> 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. Therefore, at the annual and city scales, WWTPs seem to constitute the major pathway of isothiazolinones into receiving waters 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.

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