

Nation-wide monitoring campaign of 49 contaminants of emerging concern in surface waters and sediments (EMNAT 2018): occurrence and PNEC exceedance evaluation

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Abstract The overall objective of the 2018 survey campaign of contaminants of emerging concern in surface waters (continental and coastal) and sediments known as EMNAT 2018, is to provide monitoring data for the emerging contaminants prioritization exercise, which will allow the update of the list of relevant substances to be monitored (SPAS), as part of the future Water Framework Directive (WFD) monitoring programmes (2022).

This campaign collected nearly 14,000 data regarding 49 contaminants of emerging concern (32 biocides and 17 surfactants) in surface waters and sediments on 98 sites in mainland France and in the French overseas regions.

Linear Alkylbenzene Sulfonic acids (LAS) were the most frequently quantified surfactants and at the highest median concentrations in water and sediment samples, in metropolitan France and in the overseas regions. Fipronil was the most frequently quantified biocide in water samples in metropolitan France and in the overseas regions, but at lower median concentrations than other biocides. Methyl nonyl ketone was the most frequently quantified biocide and at high median concentrations in sediment samples from mainland France and in overseas regions.

Based on the available predicted no effect concentrations (PNEC), several contaminants were identified as highly and moderately critical regarding the PNEC exceedance, and will be considered to be included in the SPAS list for the next WFD cycle.

Keywords: Biocides, surfactants, river waters, coastal waters, ecotoxicological threshold exceedance

1. Introduction

In the framework of the future Water Framework Directive (WFD) (2000) national monitoring programmes, which will be implemented in the next French water body management cycle (2022), the list of relevant substances

to be monitored (SPAS) must be updated. The update of this list is carried out through an exercise of prioritization of contaminants of emerging concern. A nation-wide survey campaign in surface waters (continental and coastal) and sediments, known as EMNAT 2018, has been performed to provide monitoring data regarding this type of contaminants to the prioritization exercise.

2. Materials and methods

During this campaign, 53 contaminants of emerging concern (36 biocides and 17 surfactants) were selected by the French Prioritization Experts Committee (Dulio and Andres, 2012) to be monitored in surface waters and sediments on 98 sites in mainland France and in the French overseas regions. Four contaminants could not be analysed in water samples due to analytical difficulties and stability issues under the storage conditions chosen for the study. Thus, 49 contaminants were analysed in water and/or sediment samples (Table 1).

Three sampling campaigns were carried out in 2018 during three seasons for the water samples, on April-May, September-October, and November-December, and one sampling campaign was performed for the sediments, on September-October. About 250 grab water samples and 70 grab sediment samples were collected in 1-L amber glass bottles. Water samples were filtered with 0.7 µm pore size glass fiber filters within 24h upon arrival at the laboratory. After filtration, the water samples were stored at -18 °C until analysis or extracted by solid phase extraction then stored as extracts at -18 °C until analysis. Sediment samples were pretreated within 24h upon arrival at the laboratory. The wet sediments were sieved at 2 mm, freeze-dried, ground at 250 µm, then stored at -18 °C until analysis.

Analytical methods, involving LC-MS/MS and GC-MS/MS, were developed for all contaminants, and limits of quantification, set at the PNEC (predicted no-effect concentrations) level or lower, were validated according to the French standard NF T90-210 (AFNOR, 2009). The method for the analysis of surfactants in water samples is described elsewhere (Wiest et al., 2021). Nearly 14,000 data (including concentrations of quantified contaminants and data lower than the quantification limits)

were collected. First, quantification frequencies and levels of concentrations were determined. Then, based on these data, warning indicators, *i.e.*, frequency and degree of PNEC exceedance, were calculated to estimate the criticality of exceeding them. They were determined based on provisional PNEC, which were mostly predicted/QSAR PNEC, assessed for each contaminant and for each matrix from a worst-case perspective, and must be considered with caution.

Table 1. List of the contaminants targeted in water and/or sediment samples during the campaign

Usage	Matrix investigated	Target contaminants
Biocide	Water	DEET, Methylchloroisothiazolinone, Dodecyl dimethyl ethylbenzyl ammonium, Tetradecyl dimethyl ethylbenzyl ammonium, Benzisothiazolinone, Methylisothiazolinone
	Water/Sediment	Didecyl dimethyl ammonium, Dodecyl dimethyl benzyl ammonium, Tetradecyl dimethyl benzyl ammonium, Abamectin, Fipronil, 2-Hydroxybiphenyl, Chlorfenapyr, Difenacoum, Brodifacoum, Floccoumafen, (benzothiazol-2-ylthio)methyl thiocyanate, 4,5-dichloro-2-octyl-1,2-thiazol-3(2H)-one, Octylisothiazolinone, Diclosan, Clorophene, Cetylpyridium, Metofluthrine, Chlorhexidine, Methyl nonyl ketone
	Sediment	Dichlofluanid, Hexadecyl dimethyl benzyl ammonium, Octadecyl dimethyl benzyl ammonium, Bifenthrine, Flufenoxuron, Cyfluthrine, d-Phenothrine
Surfactant	Water/Sediment	Lauryl sulfate, 2,4,7,9-Tetramethyl-5-decyne-4,7-diol/ Surfynol 104, LAS C10, LAS C11, LAS C12, LAS C13, LAS C14, OP7-11EO/ Triton X-100, 1-laureth sulfate, 2-laureth sulfate, N-(2-hydroxyethyl)dodecanamide/ Comperlan 100, N-[3-(dimethylamino)propyl] octadecanamide / Incromine sd, Ethylhexyl sulfate, C16 Triethanolamine esterquat / Stepanquat GA 90 (C16), C18 Triethanolamine esterquat / Stepanquat GA 90 (C18), Laurylpyridinium, Hexadecylbetaine

3. Results and discussion

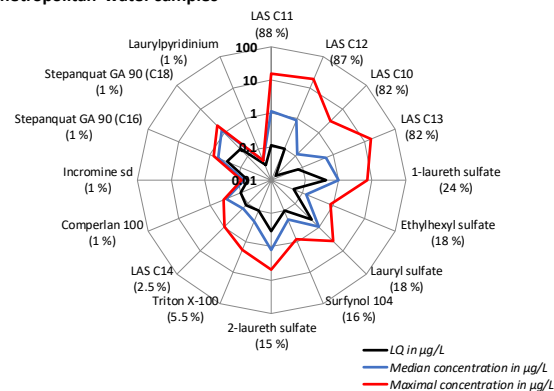
3.1. Occurrence of the contaminants in water in mainland France

Over the 42 contaminants targeted in the water samples collected in mainland France, 22 were quantified at least once, including 16 surfactants and 6 biocides (Figure 1). Linear alkylbenzene sulfonic acids (LAS C10 to C13) were the most frequently quantified surfactants, between 82 and 91 %. Fipronil was the most quantified biocide, at 64 %.

3.2. Occurrence of the contaminants in water in the overseas regions

Three biocides and 12 surfactants were quantified at least once in the water samples collected in overseas regions (Figure 2). LAS C10 to C13 were the most frequently quantified surfactants, between 89 and 98 %. Fipronil was the most quantified biocide, at 21 %. The median concentrations of surfactants (up to 2 µg/L) were 13 times greater than those of biocides (up to 0.15 µg/L). The maximal concentrations of surfactants (up to 45 µg/L) were 64 times greater than those of biocides (up to 0.7 µg/L).

Surfactants in metropolitan water samples



Biocides in metropolitan water samples

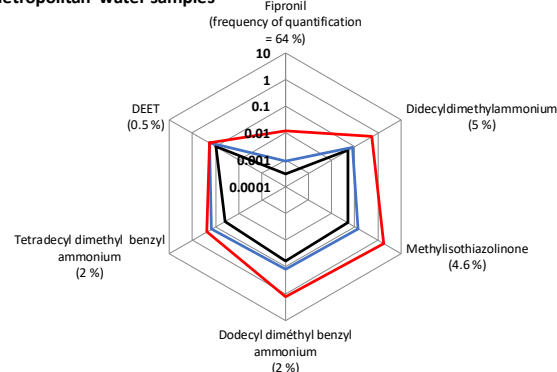
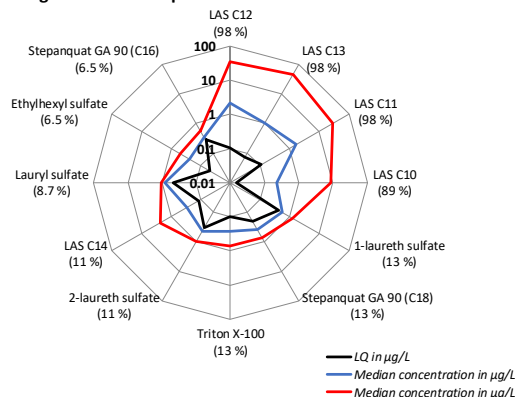


Figure 1. Frequency of quantification, limit of quantification, median and maximal concentrations of the surfactants and biocides targeted in metropolitan water samples

Fewer contaminants were quantified in overseas regions water samples in comparison with mainland France water samples. However, LAS C10 to C13 and fipronil were the most frequently quantified contaminants in the water samples of both territories. LAS are widely present in cleaning products, cosmetics personal care products, and textile treatment products. Fipronil is frequently used in insecticides, acaricides and products used against arthropods.

Surfactants in overseas regions water samples



Biocides in overseas regions water samples

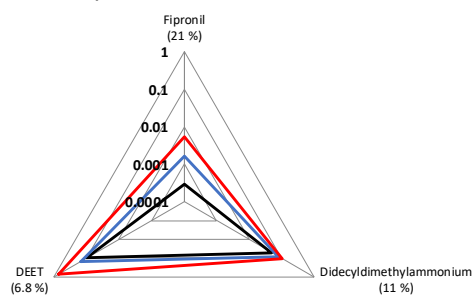


Figure 2. Frequency of quantification, limit of quantification, median and maximal concentrations of the surfactants and biocides targeted in overseas regions water samples

3.3 Criticality of PNEC exceedance for the contaminants in water in mainland France

Based on ecotoxicological data available in the literature, the highly critical contaminants (*i.e.*, those with the frequency of PNEC exceedance greater than 35 % and/or the degree of PNEC exceedance greater than 100) in the metropolitan surface water samples were LAS C11, C12 and C13, fipronil and methylisothiazolinone (encircled in red in Figure 3). LAS C10, 1-laureth sulfate and 2-laureth sulfate (encircled in orange in Figure 3) were moderately critical (*i.e.*, with the frequency of PNEC exceedance between 7 and 35 % and/or the degree of PNEC exceedance between 10 and 100).

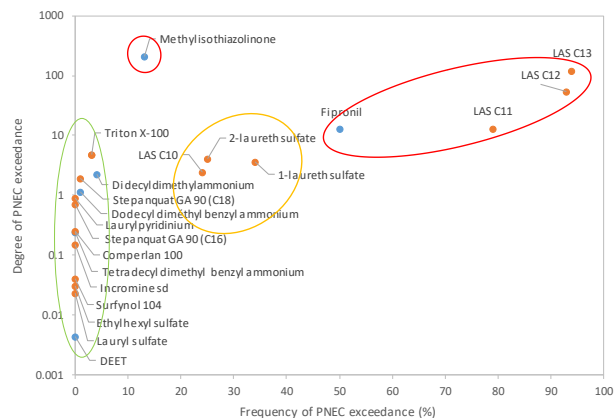


Figure 3. Frequency of PNEC exceedance and degree of PNEC exceedance of the surfactants and biocides targeted in metropolitan water samples

3.4 Criticality of PNEC exceedance for the contaminants in water in overseas regions

In overseas regions water samples, LAS C11, C12 and C13 were identified as highly critical regarding PNEC exceedance (encircled in red in Figure 4). Fipronil, LAS C10 and triton X-100 were classified as moderately critical (encircled in orange in Figure 4). LAS C11, C12 and C13 were highly critical in mainland France and in overseas regions.

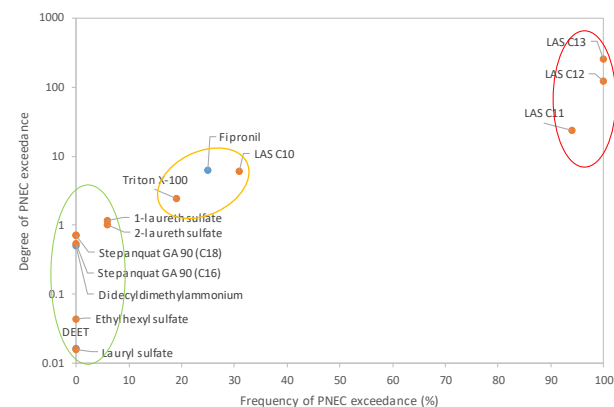


Figure 4. Frequency of PNEC exceedance and degree of PNEC exceedance of the surfactants and biocides targeted in overseas regions water samples

3.5 Occurrence of the contaminants in sediment and criticality of PNEC exceedance in France and overseas regions

Over the 43 contaminants investigated in the sediments, 22 were quantified at least once in mainland France samples, including 12 surfactants and 10 biocides. Fourteen contaminants were quantified in overseas regions samples, including 7 surfactants and 7 biocides (data not shown). In mainland France and in overseas regions, LAS C10 to C14 were the most frequently quantified surfactants, and methyl nonyl ketone was the most frequently quantified biocides. The LAS were the most frequently quantified contaminants both in water and sediment samples because of their widespread use and their amphiphilic properties.

Methyl nonyl ketone was the most frequently quantified biocide in sediments whereas fipronil was the most quantified one in waters. This is probably because methyl nonyl ketone is more hydrophobic than fipronil.

Table 2 presents the contaminants that were moderately and highly critical in sediments in mainland France and overseas regions, alongside with the ones in waters, discussed in the previous sections. In mainland France, LAS C12 and C13, stepanquat GA (C18), fipronil, octylisothiazolinone and methyl nonyl ketone were highly

critical in sediment samples. LAS C11, 1-laureth sulfate, stepanquat GA (C16) and bifenthrin were moderately critical. In overseas regions, LAS C12 and C13, and methyl nonyl ketone were highly critical contaminants. LAS C10 and C11, triton X-100, bifenthrin, fipronil, and octylisothiazolinone were moderately critical.

LAS C12 and C13 and methyl nonyl ketone were highly critical contaminants in sediment samples from mainland France and overseas regions. Methyl nonyl ketone is used in insect and animal repellents.

Table 2. Criticality of PNEC exceedance of the target contaminants in water and sediment samples from mainland France and overseas regions

Criticality of PNEC exceedance	Usage	Mainland		Overseas regions	
		Water	Sediment	Water	Sediment
High	Surfactants	LAS C11	LAS C12	LAS C11	LAS C12
		LAS C12	LAS C13	LAS C12	LAS C13
		LAS C13	Stepanquat GA (C18)	LAS C13	
	Biocides	Fipronil Methylisothiazolinone	Fipronil Octylisothiazolinone Methylnonylketone	-	Methylnonylketone
Moderate	Surfactants	LAS C10	LAS C11	LAS C10	LAS C10
		1-laureth sulfate	1-laureth sulfate	LAS C11	LAS C11
		2-laureth sulfate	Stepanquat GA (C16)	Triton X-100	Triton X-100
	Biocides	-	Bifenthrin	Fipronil	Bifenthrin Fipronil Octylisothiazolinone

3.6 Prospects for the next WFD monitoring cycle

The contaminants identified in this study as moderately and highly critical regarding PNEC exceedance will be considered to be included in the SPAS list for the next WFD monitoring cycle, in order to consolidate the results of environmental impregnation and the criticality of the exceedance of PNEC observed in this study. Table 2 shows that LAS C12 and C13 were highly critical contaminants in mainland France and in overseas regions, both in surface water samples and in sediment samples. LAS are used in manufactured products as a mix of 5 congeners (LAS C10-C14). If the LAS entered the SPAS list for the next monitoring cycle, the five congeners should be considered.

Whenever possible, the PNEC should be consolidated in order to determine more robust PNEC exceedance indicators. Limits of quantification might need to be revised accordingly to ensure robust PNEC exceedance evaluation. Issues related to contaminant stability, blanks, method accuracy and water fractions to be considered for analysis should also be explored.

4. Conclusion

EMNAT 2018 is a nation-wide prospective campaign targeting 49 contaminants in water and sediment samples on 98 sites located in mainland France and overseas regions. Between 33 and 52 % of the target contaminants were quantified at least once in water and sediment. High frequencies of quantification were observed for LAS C10-C13 and fipronil in water samples, and for LAS

C10-C14 and methyl nonyl ketone in sediment samples. Highly and moderately critical PNEC exceedances in water and sediment were determined for the surfactants LAS C10-C13, stepanquat GA C18 and C16, 1- and 2-laureth sulfate, triton X-100, and the biocides fipronil, methyl nonyl ketone, octylisothiazolinone, bifenthrin, and methylisothiazolinone. These data will be used by the French Prioritization Experts Committee for prioritization of the substances relevant to be monitored for the 3rd WFD cycle.

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