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Nation-wide monitoring campaign of 49 biocides and surfactants in surface waters and wastewaters

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Abstract

Despite their intensive use and their impact on ecosystems, biocides and surfactants are still poorly regulated and poorly monitored at large scale. In the frame of the revision of the national regulatory surveillance plan of surface waters, France planned in 2018 a monitoring campaign at national scale focused on these two types of substances of very emerging concern. Forty-nine contaminants (32 biocides and 17 surfactants) were investigated in surface water and sediment samples from 91 sampling sites, and in effluent and sludge samples of 7 wastewater treatment plants (WWTP), 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 the surfactants (up to 91% in water samples and up to 57% in sediment samples for LAS C10-C13) and for the biocides (up to 64% for fipronil in water samples and up to 90% for methyl nonyl ketone in sediment samples). The median concentrations of surfactants were up to 2 µg/L in mainland surface water samples and up to 528 µg/kg in sediment samples, and for biocides, the median concentrations were up to 0.18 µg/L in mainland surface water samples and up to 104 µg/kg in sediment samples. PNEC exceedances in water and sediment were determined for both types of substances. The analysis

of effluent and sludge suggested significant but not total removal of these substances in the WWTP. Temporal and spatial variations of the concentrations of both types of substances in surface water samples were also observed, suggesting both punctual and diffuse contamination sources of the surface water investigated.

Key words: Organic contaminants, aquatic environment, occurrence, PNEC exceedance

1. Introduction

Surface water monitoring in France is regulated by ministerial decree, which is in accordance with the European Water Framework Directive (WFD) (European Commission, 2000). Within the WFD, ecological status is determined for rivers, lakes, and transitional and coastal waters based on biological quality elements and supporting physico-chemical and hydromorphological quality elements. Physico-chemical quality elements generally consist of light and thermal conditions, oxygenation conditions, salinity, nutrient conditions and river basin-specific pollutants (RBSPs). In rivers and lakes, they also include acidification condition. Member States identify RBSPs being substances discharged in significant quantities into a water body. In addition to this criterion for identifying RBSPs, France set a two-phase strategy based on prioritization exercises fueled by data collected through monitoring of substances of emerging concern in the aquatic environment. Each phase of this strategy –one phase by 6-year WFD monitoring cycle- consists in collecting monitoring data and a prioritization exercise that aims at selecting the substances of interest. During the first phase, substances of very emerging concern are monitored during one short campaign on a limited numbers of sampling site at the country scale. This is performed in the frame of the French prospective surveillance network (Staub et al., 2019). The results of this first campaign are then processed in a prioritization exercise to select so-called substances relevant to monitor (SRMs). During the next phase, SRMs are monitored regulatorily for 6 years in 25% of French sites of surveillance monitoring network. The results of this regulatory monitoring are then processed in a prioritization exercise to select RBSPs.

Biocides are largely used in a wide range of products to destroy or prevent the action of any harmful organism by any means other than mere physical or mechanical action. They are added to disinfectants, repellents and baits, algicides, insecticides, rodenticides, human and animal hygiene products, bactericidal antiseptics, wood preservatives, building materials and liquids

used in cooling and manufacturing systems. They are found in wastewaters from households, hospitals, industries and urban areas, and enter the aquatic environment via wastewater treatment plants (WWTP) effluents (Kroon et al., 2020; Margot et al., 2015; Paijens et al., 2020; Saidulu et al., 2021). They also leach from buildings (Bollmann et al., 2014; Paijens et al., 2020), then reach surface waters via runoffs of urban and rural areas, induce negative effects on aquatic life (Kroon et al., 2020; Margot et al., 2015). Despite their impact on ecosystems and intensive use, biocides are still poorly regulated and thus poorly monitored (Geissen et al., 2015). For example, the Water Framework Directive (European Commission, 2013) covers only five biocides (tributyl-tin, diuron, isoproturon, terbutryn and cybutryn). The emissions of biocides from building materials have been widely studied (Bollmann et al., 2017, 2016; Jungnickel et al., 2008; Schoknecht et al., 2009). Many other studies focused on the contamination of receiving waters by biocides, which were mostly used as pesticides (Ccanccapa et al., 2016; Vorkamp et al., 2014; Wick et al., 2010). However, these studies focused on a limited number of biocides or were carried out at local scales.

Surfactants are also largely used in many manufactured products. They are found mainly in washing and cleaning products, cosmetics and personal care products, adhesives and sealants, textile treatment products and dyes, and leather treatment products, in households, hospitals and industries. These substances are then found at high concentrations in wastewater and enter the aquatic environment via wastewater treatment plants (WWTP). Despite their removal rates in WWTP up to 95 %, their concentrations in effluents remain high, at the lower to mid $\mu\text{g/L}$ range (Margot et al., 2015). Surfactants can be considered as “pseudo-persistent” contaminants due to their exceptionally high usage and their continuous introduction into the environment. Therefore, they have the same exposure potential as persistent contaminants (Freeling et al., 2019) and expose a wide variety of aquatic ecosystems to potential risks (Jardak et al., 2016). Surfactants are not regulated yet in water bodies, except for nonylphenols and octylphenols

(European Commission, 2000), although their occurrence in the aquatic environment has been reported in a few studies (Traverso-Soto et al., 2015; Sakai et al., 2017; Li et al., 2020).

Biocides and surfactants have been monitored in some studies at a local scale. However, they have never been investigated in a nation-wide monitoring survey. This study aimed at monitoring 32 biocides and 17 surfactants as substances of very emerging concern, which was carried out in French surface waters in 2018, in order to identify SRMs candidates for the 3rd WFD monitoring cycle. These substances were monitored in surface waters, in sediments, and in WWTP effluents and sludges.

2. Materials and methods

2.1 Target substances

The list of target substances selected for the campaign was set from a list of approximately 1100 candidate substances, compiled from the list of substances established by the European network of experts NORMAN (<https://www.norman-network.net/>), the list of substances recommended by the French Water Agencies (purged of substances already regulated, SRMs or Watch List), and the results of scientific monitoring collected from the literature. In accordance with the prioritization decision tree developed by the French comity of prioritization experts (CPE) (Dulio and Andres, 2013), all candidate substances were evaluated based on information on the amount of monitoring data available and the frequency of quantification, the level of the limits of quantification (LOQ) achieved in relation to the Predicted No Effect Concentration (PNEC) and the existence of experimental data to assess the hazard associated with the substances. Biocides and surfactants were selected because there was a need to conduct screening campaigns, to improve analytical performance and to conduct risk assessment campaigns for such substances. The candidate substances of these two families were prioritized regarding their

tonnage, releases in the environment, and dissemination via broad spectrum uses, and their hazard towards ecosystems and human health, their endocrine disruptor effect, and criteria of persistence, bioaccumulation and toxicity. After prioritization and assessment of the analytical feasibility, a list of 49 substances, including 32 biocides and 17 surfactants, was established. Table 1 presents the target substances selected, their use, the types of products in which they are used and the matrices in which they were investigated during this campaign.

The surfactants targeted in this study included 9 anionic substances, 4 cationic, 3 non-ionic, and one amphoteric for a total of 17 individual substances of 10 families (Table 1) as follows: the anionic surfactants targeted in this study belong to three families (linear alkylbenzene sulfonates (LAS), alkylethersulfates (AES) and alkylsulfates (AS)); the cationic surfactants belong to three families (alkylpyridinium, amidoamines and triethanolamine esterquat (TEAQ)); the non-ionic surfactants belong to three families (octylphenol ethoxylate (OPEO), cocamides and surfynol); finally, one amphoteric surfactant belongs to alkylbetaines. The 32 biocides targeted were 4 benzalkoniums (BAC), 1 dialkyldimethylammonium (DDAC), 2 ethylbenzalkoniums (EBAC), 5 isothiazolinones (IT), 3 pyrethroids, 1 avermectin, 1 sulfamid 1 phenylpyrazols, 3 phenols, 1 pyrrol, 3 4-hydroxycoumarin-type anticoagulants, 1 quaternary ammonium, 1 bisbiguanide compound, and 1 ketone. Table S1 presents the suppliers, reference, CAS numbers and purity of all the target substances purchased for the study. Five of the standards of surfactants consisted of mixes of homologues. Of these, the BAC standard was characterised by the manufacturer as containing 64.9% and 31.2% BAC-C12 and C14 respectively. Since the individual concentrations of LAS, AES, OPEO and TEAQ homologues in these standards were not provided by the manufacturer, an experimental determination of individual homolog concentrations was conducted (Wiest et al., 2021). The surrogate standards were: benzyldimethyldecylammonium-d5 Chloride (BDDA-d5), hexadecylpyridinium-d5 bromide (HexPyr-d5), sodium dodecyl-d25 sulfate (SDS-d25), 4-hydroxybiphenyl d9, triclosan d3,

diflubenzuron d4, simazine d10, supplied by CDN isotopes (purity > 97%), cis-permethrin ¹³C6, supplied by Cambridge Isotope Laboratories (purity > 99%), fipronil ¹⁵N ¹³C, (rac-cis)-z-bifenthrine d5, brodifacoum d4, octylisothiazolinone d17, supplied by Toronto Research Chemical (purity > 96%), trans-cyfluthrin d6, trans-cypermethrin d6, propiconazole d5, DEET d7, diuron d6, supplied by Dr Ehrenstorfer (purity > 96%), and chlorhexidine d8, supplied by Santa Cruz Biotech.

2.2 Solvents and reagents

The reagents were LC-MS grade formic acid (Biosolve-chemicals, Dieuze, France and Merck, Darmstadt, Germany), ammonium acetate (Biosolve-chemicals, Dieuze, France, and Sigma Aldrich, Saint-Quentin-Fallavier, France), LC-MS grade water (Fisher Chemical, Geel, Belgium), LC-MS grade methanol and acetonitrile (Honeywell, Seelze, Germany, and J.T. Baker, Atlantic Labo, Bruges, France), ammonium hydroxide (Merck KGaA, Saint Louis, USA), dichloromethane (Acros Organics, Geel, Belgium), and HPLC grade ethyl acetate (Sharlau, Barcelona, Spain). MilliQ water was produced by a Millipore filtration system. Mineral water packaged in glass bottles was supplied by Evian® (Evian-les-Bains, France). Binder-free glass fiber filters, 0.7 µm pore size, diameter 142 mm were supplied by Merck Millipore Ltd. (Carrigtwohill, Ireland). Glass fiber filters, field sample vials and glass tubes were calcined for 15 h at 450 °C before use.

2.3 Sample types, sampling sites and sampling strategy

Four types of samples were collected during the campaign: surface waters, river sediments, WWTP effluents and WWTP sludges. The sampling campaigns were coordinated by INERIS

in collaboration with the Water Agencies in metropolitan France and Water Offices in overseas regions. Surface waters samples were collected on 84 sampling sites throughout metropolitan and overseas France (i.e., French Guiana, and Guadeloupe, Martinique and La Réunion islands) (Figure 1). Ten of these sites were known from WFD regular monitoring to present low level of contamination and could be considered as reference sites. The rest of the sites were characterized by chemical pressures (rural, urban, industrial, hospital effluents). Sediments were collected on 79 sampling sites, of which 72 were the same as where surface waters were collected. Effluent and sludges were collected from 7 WWTP located in mainland France. The characteristics of the WWTP are presented in Table S2. A total of 98 sites (79 in mainland France and 19 overseas), located in 10 French hydrographic basins, were sampled during the campaign. Among the sampling sites in mainland France, continuums on 7 rivers were investigated. The continuums consisted of 4 to 6 sites on the same rivers on which the 7 WWTP studied in the monitoring campaign were also located. Table S3 presents the details on the sampling sites. Three sampling campaigns were carried out for the surface water samples in 2018 during three seasons, in April-May, September-October, and November-December whereas one sampling campaign was performed for the sediments, in September-October. One sampling campaign was also performed for the WWTP effluents and sludges, from October 2018 to January 2019. Overall, about 250 grab water samples, 70 grab sediment samples, 7 WWTP effluent samples and 7 WWTP sludge samples were collected in 1-L amber glass bottles. All water samples were placed in refrigerated coolers at 4°C as soon as they were collected and sent directly to the analysis laboratories, within 24 h for the waters in metropolitan France and within 72 hours for the overseas regions. Water samples and WWTP effluent samples were filtered with 0.7 µm pore size glass fiber filters within 24 h 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 and sludge

samples were pretreated within 24 h upon arrival at the laboratory. The wet sediments were sieved at 2 mm, freeze-dried, ground at 250 μm , then stored at room temperature until analysis. The sludges were freeze-dried, sieved at 2 mm, ground at 250 μm , then stored at room temperature until analysis.

2.4 Quality controls

Several quality controls were carried out during the campaign: bottle controls, method blanks, LOQ controls and field controls. Contamination originating from the glass bottles used for the sampling was evaluated regarding the targeted substances. Tests were performed on different types of glass bottles and taps, using cleaning procedures (calcination, solvent washing, no treatment) to select the most suitable bottle. For liquid samples, three different types of bottles with taps were tested. The results showed that the water samples tested contained in bottles with PTFE septa in the tap, calcined and washed or just calcined before use, did not show any quantified substances. These bottles were then used calcined at 450°C overnight for the sampling operations. For method blanks regarding water sample analyses, at least three method blanks (Evian® mineral water) per water sampling campaign, for a total of nine method blanks, were performed during the water sample analyses. For wastewater and sediment samples, two method blanks were performed. Method blanks for sediment samples were performed with Fontainebleau sand. LOQ controls were performed on extracted spiked Evian® water samples and analyzed at the beginning and end of each analytical run to ensure compliance with the targeted LOQ when the samples were analyzed. LOQ controls for sediment samples were performed with spiked Fontainebleau sand. A field blank for water sampling was conducted by each sampling team at the start of the campaign (mostly during the 1st campaign). Twenty-four water field blanks were collected and analyzed.

2.5 Stability

Due to longer transport times between the overseas departments and the analysis laboratories located in mainland France, temperatures in the refrigerated cooler sometimes exceeded 4°C. Stability tests on the target molecules were carried then out. The stability assessment method were taken from Lardy-Fontan and Lalère (2006). A type 2 pseudo-isochronous approach, over 7 days, was followed with Evian® mineral water samples spiked at a concentration level corresponding to 10 times the LOQ value of each substance. All samples were prepared in glass vials that had been calcined for 15 hours at 450°C. Stability studies were conducted at 4°C and 12°C, in the dark.

2.6 Analytical methods

Analytical methods 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 liquid and solid samples is described elsewhere (Wiest et al., 2022, 2021). Briefly, surface water and WWTP effluent samples were analysed by off-line solid phase extraction followed by liquid chromatography coupled with tandem mass spectrometry (SPE-LC-MS/MS), and sediment and sludge samples were analysed by ultrasound-assisted extraction (USAE) coupled with LC-MS/MS. Biocides in water samples were analysed by multiple techniques depending on the substances: solid phase micro-extraction followed by gas chromatography coupled with tandem mass spectrometry (SPME-GC-MS/MS), direct injection (DI) LC-MS/MS or SPE-LC-MS/MS. Sediment and sludge samples were analysed by USAE-LC-MS/MS or accelerated solvent extraction (ASE) coupled with GC-MS/MS. Table 2 details the analytical method

employed for all substances in each type of sample, the PNEC in water and in sediment and the target LOQ in surface water samples, WWTP effluent samples, sediment and sludge samples.

2.7 Data treatments

Nearly 14,000 data (including concentrations of quantified contaminants and data lower than the quantification limits) were collected. The produced data were controlled through two steps. First, the data were controlled automatically regarding several criteria, which were the accordance on the GPS coordinates of the sampling site with the actual location of where the samples were collected, the accordance of the LOQ reported by the laboratories that performed that analyses with the target LOQ, the temperature of the samples upon arrival at the laboratories, the date of reception of the samples, the date of the filtration of the surface water and WWTP effluent samples and the outliers (measured concentration larger than 1 µg/L or 100 times the LOQ depending on the target contaminant). The results flagged regarding these criteria or as outliers by the automatic control were then manually reviewed by an expert. The controlled results were then discussed with the laboratories and the French national reference laboratory for the monitoring of the aquatic environment (AQUAREF) for exclusion or inclusion in the final data set.

Validated data were then processed. First, quantification frequencies and levels of concentrations were determined for all sample types. Then for surface water and sediment samples, based on these data, warning indicators, i.e., frequency and degree of PNEC exceedance, were calculated to estimate the criticality of exceedance. 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 therefore considered with caution. The frequency of PNEC exceedance was calculated as the number of

sites for which the maximal concentration was larger than the PNEC over the total number of sites for which this substance had been analyzed. The degree of PNEC exceedance was the ratio of the 95th percentile of the maximal concentrations of all sites and the PNEC. Temporal variability was also addressed by investigating the results of the water samples analyses of the three sampling periods. Spatial variability was studied through the evolution of the target substances concentrations along the 7 continuums. The concentrations of the target substances were also processed regarding the different chemical pressures associated to the sampling sites.

3. Results and discussion

3.1 Quality controls

For the method blanks, the analytical results showed slight contamination of LAS substances during the analytical process (data not shown): of the 42 substances tested, none was quantified in campaign 1, LAS C10 and LAS C11 were quantified in campaign 2, and LAS C10 to LAS C13 were quantified in campaign 3, at levels close to the LOQ. The ratios of the concentrations of the substances in the blanks to the LOQ were between 1.07 and 1.65. No substances were quantified for the two method blanks performed for the sediment samples. The water LOQ controls were satisfactory since the measured concentrations were determined between 80 and 120% of the validated LOQ value in more than 88% of the cases. The water LOQ controls were between 120 and 160% of the validated value in all other cases except for ethylhexyl sulfate, for which the water LOQ control was close to 185% of the validated value. For the sediment samples, the LOQ controls were between 80 and 120% of the validated LOQ value in 89% of the cases (43 substances analysed in two LOQ controls). LOQ controls were in the 120-160% range for the remaining 11% of cases. Ten of the 42 substances analyzed in water were quantified in the surface water field blanks (data not shown). Nine surfactants were quantified,

at frequencies between 4 and 54% and at concentration levels up to 0.8 µg/L. Fipronil was the only biocide quantified in a field blank, at twice the validated LOQ (i.e., 0.0006 µg/L). The frequencies of quantification and average concentrations of the quantified substances in the field blanks varied depending on the sampling team and the sampling technique. Comparison of results for the different sampling techniques showed that sampling from a bridge induced a more frequent quantification of LAS C10 to LAS C13 (between 67 and 83%) and 1- and 2-laureth sulfates (33%). Indeed, this technique implies the use of an intermediary material for sampling and increases the risks of contamination.

3.2 Stability

The stability of the surfactants studied varied from one compound to another (data not shown). The TEAQ were stable at neither 4°C nor 12°C. At 4°C, after 24 hours, we observed already a 30% drop in concentration, then the concentration remained stable for up to 3 days. After 7 days, only 20% of the initial concentration remained. At 12°C, the decrease was even greater after 24 hours. At 4°C, LAS C12, C13 and C14 were stable up to 3 days, and other surfactants were stable for up to 7 days. At 12°C, only Triton X-100, surfynol 104 and ethylhexylsulfate were stable for up to 7 days. The concentrations of the 5 LAS, lauryl pyridinium, comperlan 100 and hexadecylbetaine were stable for up to 3 days. Finally, concentrations of laureth sulfates and incromine sd were stable for up to 48 hours.

Regarding biocides, the concentrations of BAC-C12 and C14, DDAC-C10 were stable for 7 days at 4°C and for up to 3 days at 12°C. Several of the other biocides were not stable after 24 hours at 5°C. So stability of the biocides was investigated at -20°C. Water samples were spiked and stored for a month at -20°C. Waters samples were then defrosted at room temperature and analysed. Analyses results showed that most biocides were stable in water when stored at -

20°C. Only the concentrations of methyl nonyl ketone and EBAC-C12 were 30 % lower after a month.

3.3 Occurrence in surface waters in mainland France

Over the 42 contaminants targeted in the water samples collected in mainland France, 22 were quantified at least once over the three sampling campaigns, including 16 surfactants and 6 biocides (Figure 2). Linear alkylbenzene sulfonates (LAS C10 to C13) were the most frequently quantified surfactants, between 82 and 88%. Fipronil was the most quantified biocide, at 64%. The surfactants concentrations were globally 10 times larger than biocides concentrations. The surfactants median quantified concentrations ranged from 0.04 to 1.3 µg/L and their maximal concentrations ranged from 0.04 to 19 µg/L. The biocides quantified median concentrations ranged from 0.90 ng/L to 0.18 µg/L and maximal concentrations ranged from 12 ng/L to 1.8 µg/L. Figure S1 shows graphical representations of each site in mainland France with the concentrations of each target contaminant quantified at least once in water.

LAS C10 to C14, 1- and 2-laureth sulfates, lauryl sulfate, Incromine sd and fipronil were found in the field blanks. Their median concentrations were between 1.1 and 3.3 times lower than the median concentrations in the samples, except for incromine sd found in just one field blank, with a concentration 1.2 times higher than the median concentration in the samples. The concentrations of these substances quantified in the field blanks are not negligible compared with the concentrations determined in the samples. In view of these results, the quantification frequencies and concentrations of these substances in surface water samples may have been overstated. Caution should therefore be exercised when interpreting the results for these substances. For future monitoring of these substances in water, appropriate sampling and

instrument cleaning practices could reduce or even eliminate the presence of these substances in samples.

LAS are widely present in cleaning products, cosmetics personal care products, and textile treatment products. Their continuous and extensive use implies very high concentrations in the influents, and although they are very effectively eliminated in WWTP, high concentrations are discharged in the aquatic environment through the WWTP effluents (Freeling et al., 2019; Margot et al., 2015). Fipronil is frequently used in insecticides, acaricides and products used against arthropods. In WWTP, fipronil is quite persistent and not very well removed from the influents (Heidler and Halden, 2009). This corroborated their frequent occurrences in the aquatic environment. The concentration levels observed for the surfactants and biocides in this monitoring campaign are in line with previous studies in surface waters (Freeling et al., 2019; Margot et al., 2015; Paijens et al., 2020; Wan et al., 2021).

The quantification frequencies of the targeted substances obtained during campaign #1 (April-May), campaign #2 (September-October) and campaign #3 (November-December) were compared in mainland France (Figure S3). In mainland France, lauryl sulfate, 1-laureth sulfate and 2-laureth sulfate, and, to a lesser extent, the biocide methylisothiazolinone were more frequently quantified during campaign #1 than during campaign #2 and campaign #3. LAS C10 to C13, fipronil, and especially ethylhexyl sulfate and surfynol 104 were quantified slightly more frequently in campaign #3 than in campaigns #1 and #2 (overall additional 10%). For the remaining 11 substances over the 22 quantified, very few differences in quantification frequencies between campaigns were observed. Overall, the investigated substances were quantified slightly more frequently in campaign #3, i.e., in November -December, the coldest and wettest period among the ones investigated. The heavier rainfalls could have resulted in greater runoffs of urban and rural areas and wastewater bypasses and overflows (Lee et al., 2022), and colder water temperatures could imply lower degradation rates of the target

substances, leading to larger concentrations in the receiving waters in winter than in spring or summer.

Principal component analyses (PCA) were performed on the concentrations of the biocides and of the surfactants in water samples for all 3 campaigns. All substances quantified at least once were included in the PCA, and for each included substance, only the quantified concentrations were processed in the PCA. Separate PCA for the two types of substances were performed, because biocide concentration levels were much lower than those of the surfactants, and a single PCA for both types of compounds did not allow to observe any relevant results for the biocides. Along with concentrations, the variables in the PCA were the sampling sites, which were characterized regarding chemical pressures (rural, urban, industrial, hospital effluents). PCA charts of biocides and surfactants are presented in Figure S4 for metropolitan surface waters.

Over the three campaigns, in metropolitan France, fipronil was the most quantified biocide. It is located on the left side of the chart because its concentrations in the water samples were very low. Fipronil is close to the axis 1 because it was quantified in all types of sites. Although they were less frequently quantified than fipronil, methylisothiazolinone and didecyldimethylammonium are on the same right side of the chart since their concentrations were larger than those of fipronil. Methylisothiazolinone and didecyldimethylammonium are separated because they were quantified at their highest concentrations in different sites. Methylisothiazolinone was quantified in urban and industrial sites whereas, besides urban and industrial sites, didecyldimethylammonium was quantified in sites exposed to hospital effluents. For surfactants, the LAS C10 to C13 were quantified in all types of sites. The four homologues are separated on the chart of individuals, especially the LAS C10, because of the differences in the observed concentrations. Median concentrations were ranked as follows: LAS C10 < LAS C13 < LAS C12 < LAS C11; which correlate with the order in which the four homologues are located on the chart from left to right. 1-laureth sulfate, 2-laureth sulfate and

lauryl sulfate are separated from the LAS; they were quantified at their highest concentration only on a few sites of all types, on which LAS were also quantified.

3.4 Occurrence in surface waters in overseas regions

Three biocides and 12 surfactants were quantified at least once over the three sampling campaigns in the water samples collected in overseas regions (Figure S5). LAS C10 to C13 were the most frequently quantified surfactants, between 89 and 98%. Fipronil was the most quantified biocide, at 21%. The surfactants median quantified concentrations, which were between 0.22 and 2 $\mu\text{g/L}$, were 13 times greater than those of biocides, from 1.7 ng/L to 0.15 $\mu\text{g/L}$). The maximal concentrations of surfactants (0.50 to 45 $\mu\text{g/L}$) were globally 70 times greater than those of biocides (from 5.4 ng/L to 0.7 $\mu\text{g/L}$). 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. Figure S1 shows graphical representations of each site in overseas regions with the concentrations of each target contaminant quantified at least once in water.

The comparison of the quantification frequencies of the targeted substances obtained during campaign #1 (April-May), campaign #2 (September-October) and campaign #3 (November-December) is presented in Figure S6. LAS C14, lauryl sulfate, TEAQ-C16 and C18, and fipronil were more frequently quantified during campaign #1 than during campaign #2 and campaign #3. LAS C10, didecyldimethylammonium, 1-laureth sulfate and triton X-100 were more frequently quantified in campaign #2 than in campaigns #1 and #3. Finally, DEET and ethylhexyl sulfate were more frequently quantified during campaign #3 than during campaign #1 and campaign #2. For the remaining 5 substances over the 15 quantified, no significant

differences in quantification frequencies between campaigns were observed. Overall, the target substances were quantified slightly more frequently in campaign #1, i.e., in April-May. In overseas regions, the air temperature remains relatively constant and high (25-32 °C) during the year. Regarding rainfalls, in French Guiana, heavier episodes occur in April-May, which could lead to higher concentrations of the target substances in the surface waters. However, the heavier episode among the investigated periods occurred in September-October in Guadeloupe and Martinique, and in December in La Réunion. This could explain the less contrasted results for the overseas region regarding seasonal variability. Studies on seasonal variations of surfactants and biocides concentrations in surface waters highlighted that rainfalls and concentration of biocides in surface waters could be correlated (Bollmann et al., 2014; Paijens et al., 2020). Traverso-Soto et al. (2015) observed higher LAS concentrations in water samples collected in a lagoon in south-east Spain during winter than during summer. Lower concentrations in summer were explained by a faster biodegradation rate of the LAS in a hotter weather.

PCA charts of biocides and surfactants for overseas regions are presented in Figure S7. fipronil and didecyldimethylammonium were quantified mostly in sites characterized by different chemical pressures. Fipronil was quantified in more urban sites whereas didecyldimethylammonium was quantified in more rural sites. DEET was quantified only three times during the third campaign on three urban stations on which fipronil was quantified. For surfactants, the same pattern was observed. LAS were quantified in almost all sites and 1-laureth sulfate, 2-laureth sulfate and lauryl sulfate were quantified at their highest concentration only on a few urban sites, where LAS were also quantified.

3.5 Occurrence in river sediments in mainland France and in 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 (Figure 3). For biocides, methyl nonyl ketone was the most quantified substance, at 90%. Octylisothiazolinone, didecyldimethylammonium and fipronil were quantified at 50%, 60% and 68%, respectively. For the six least frequently quantified biocides in sediments, the quantification frequencies ranged from 2 to 40%. For surfactants, LAS C10 to LAS C13 were the most frequently quantified, ranging from 40 to 55%. LAS C14, TEAQ-C16 and C18, hexadecyl betaine, ethylhexyl sulfate, lauryl sulfate, 1-laureth sulfate, and incromine sd were quantified at frequencies between 1.9 and 13%. The median and maximal concentrations of surfactants (up to 528 $\mu\text{g}/\text{kg}$ and 26.6 mg/kg , respectively) were 4 times greater than those of most biocides (up to 104 $\mu\text{g}/\text{kg}$ and 6.8 mg/kg). 2-hydroxybiphenyl was quantified once at a quite high concentration level (738 $\mu\text{g}/\text{kg}$). Figure S2 shows graphical representation of each site in mainland France and overseas regions with the concentrations of each target contaminant quantified at least once in sediment.

Fourteen contaminants were quantified in overseas regions samples, including 7 surfactants and 7 biocides (Figure S8). For biocides, methyl nonyl ketone was the most quantified substance at 86%. Bifenthrin, octylisothiazolinone, fipronil, didecyldimethylammonium, dodecyl dimethyl benzyl ammonium and tetradecyl dimethyl benzyl ammonium were quantified at frequencies between 7.1 and 29%. Regarding surfactants, LAS C10 to C13 were the most frequently quantified, between 36 and 57%. LAS C14, triton X-100 and hexadecylbetaine were quantified at a frequency of 7.1% (i.e., only one quantified sample for these substances over 14 samples collected). The median and maximal concentrations of surfactants (up to 1.2 and 17 mg/kg , respectively) were 15 to 170 times greater than those of the biocides (up to 80 and 103 $\mu\text{g}/\text{kg}$). Fewer contaminants were quantified in overseas regions sediment samples in comparison with mainland France sediment samples. Overall, in mainland France and in overseas regions, LAS

C10 to C14 were the most frequently quantified surfactants in sediments, and methyl nonyl ketone was the most frequently quantified biocide.

3.6 Occurrence both in water and sediment samples

Of the 36 substances investigated in both water and sediment samples, 24 substances were quantified in mainland France, including 7 biocides and 17 surfactants. Figure S9 shows the quantification frequencies of these substances in both matrices. It appears that all the biocides except fipronil and 2-hydroxybiphenyl were much more frequently quantified in the sediment, between 38 and 90%, than in the water, between 0 and 5%. Fipronil was quantified at equivalent frequencies in the two matrices (64% in water and 68% in sediment) and 2-hydroxybiphenyl was only quantified in sediment at 2%. To a lesser extent, all surfactants except hexadecylbetaine, TEAQ-C16 and C18, and LAS C14 were more frequently quantified in water, between 5.5 and 88%, than in sediment, between 0 and 55%. Hexadecylbetaine, TEAQ-C16 and C18, and LAS C14 were more frequently quantified in sediment (9.4, 11 and 13%, respectively) than in water (0, 1.0 and 2.5%, respectively). Incromine sd was quantified at equivalent frequencies in the two matrices (1.0% in water and 1.9% in sediment). Comperlan 100 and laurylpyridinium were quantified only in water samples, at 1.0 and 0.50% respectively. The higher quantification frequencies observed in sediment are partly due to the integrative nature of this matrix, the affinity and possibly the persistence of the substances in it.

In overseas regions, over the 36 substances investigated in the water and sediment matrices, 19 substances were quantified in at least one matrix, including 6 biocides and 13 surfactants. Figure S10 shows the quantification frequencies of these substances. Of the 6 biocides quantified in at least one of the two matrices, fipronil and didecyldimethylammonium were slightly more quantified in water. The other 4 biocides were only quantified in sediment. As in mainland

France, surfactants were more frequently, if not exclusively, quantified in water. Only hexadecylbetaine was quantified only in the sediment. 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. The LOQ reached for the target substances in each matrix can explain some of these observations as well as the physical chemical properties, as the hydrophobic substances might be more frequently quantified in sediment than hydrophilic substances.

3.7 Criticality of PNEC exceedance for the contaminants in water and sediments samples

In water samples, 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 S11). LAS C10, 1-laureth sulfate and 2-laureth sulfate (encircled in orange in Figure S11) were ranked as moderately critical (i.e., with the frequency of PNEC exceedance between 5 and 35 % and/or the degree of PNEC exceedance between 10 and 100). In overseas regions water samples, LAS C11, C12 and C13 were identified as highly critical regarding PNEC exceedance (encircled in red in Figure S12). Fipronil, LAS C10, triton X-100, 1-laureth sulfate and 2-laureth sulfate were classified as moderately critical (encircled in orange in Figure S12). Overall, LAS C11, C12 and C13 were the only substances highly critical both in mainland France and in overseas regions.

In sediment samples, in mainland France, LAS C12 and C13, TEAQ-C18, fipronil, octylisothiazolinone and methyl nonyl ketone were ranked as highly critical in sediment samples (encircled in red in Figure S13). LAS C11, 1-laureth sulfate, TEAQ-C16 and bifenthrin

were moderately critical (encircled in orange in Figure S13). In overseas regions, LAS C12 and C13, and methyl nonyl ketone were highly critical contaminants (encircled in red in Figure S14). LAS C10 and C11, triton X-100, bifenthrin, fipronil, and octylisothiazolinone were moderately critical (encircled in orange in Figure S14). LAS C12 and C13 and methyl nonyl ketone were highly critical contaminants in sediment samples from mainland France and overseas regions. The contaminants identified in this study as moderately and highly critical regarding PNEC exceedance will be SRM candidates for the next WFD monitoring cycle, to consolidate the results of environmental impregnation and the criticality of the exceedance of PNEC observed in this study.

A recent study performed with the data produced in this monitoring campaign drew different conclusions regarding the risks that target surfactants might pose to the environment (Briels et al., 2023). The aim and approach of our study differ from this study, for which a mixture approach was adopted as the authors investigated the toxicity contribution of 13 surfactants among over 1000 biocides, pesticides, pharmaceutical, hormones, polycyclic aromatic hydrocarbons, and other types of contaminants in surface waters. In the present study, we focused on surfactants and biocides only, and we adopted a substance-by-substance approach, aiming for prioritization of contaminants to be monitored in the future in France. Substances for which regulation already existed were outside the scope and objective of our study. And the potentially ecotoxic substances that are not yet regulated were discarded in our prioritization process for selecting the substances targeted in our study. The conclusions of this study (Briels et al., 2023) were mostly driven by the value of the ecotoxicological thresholds used for the toxicity assessment. Hazardous concentration for 5% of the species (HC_{5s}) were used in this study whereas we used PNEC. Those HC_{5s} were 2 to 900 times larger than the PNECs we used, leading to lower hazard quotients.

The PNEC used in our study have been chosen according to the Norman prioritization framework (Dulio and von der Ohe, 2013) and on a worst-case basis, for the protection of the aquatic environment, and more precisely fish, invertebrates, and algae. They are proposed based on bibliographic research, and modelled PNEC were chosen in case no experimental PNEC was available. They must then be used with caution as they are provisional PNEC. The PNEC selected referred to many endpoints. Besides effects on mortality and reproduction, the target substances may also have other ecotoxicological effects on biota, such as endocrine disruption and genotoxicity. It is worth mentioning that target LOQ for 7 substances in water or sediment were above the PNEC, biasing the assessment of the criticality of the PNEC exceedance and possibly leading to lower quantification frequencies (Table 2). These substances were methylisothiazolinone for water, and dichlofluanid, triton X-100, 1- and 2-laureth sulfate, and TEAQ-C16 and C18 for sediment. With LOQ equal or lower than the PNEC, the frequencies of quantification and PNEC exceedance for these substances would certainly have been higher, and the MEC95 lower.

3.8 Occurrence in WWTP effluent and sludge samples

The frequency of quantification and the concentrations were determined from the results of analyses of the 7 effluent samples and 7 sludge samples taken from the 7 WWTP under study (1 effluent sample and 1 sludge sample were taken per WWTP). Figure S15 shows the frequency of quantification and the mean concentrations obtained for biocides and surfactants in the wastewater of the 7 WWTP in the mainland France. It should be noted that for all the surfactants and the biocides didecyldimethylammonium, dodecyl dimethyl benzyl ammonium and tetradecyl dimethyl benzyl ammonium, only 6 effluent samples were analyzed. In total, 3 biocides and 9 surfactants were quantified at least once in the effluent samples. Regarding

biocides, fipronil was the most frequently quantified (100%), at an average concentration of 0.02 µg/L. DEET and didecyldimethylammonium were less frequently quantified (in 29 and 17%, respectively), but their concentrations were higher than that of fipronil. These three substances were among the 6 biocides quantified in surface waters at the metropolitan scale. In surface waters, Fipronil was also the most quantified substance (64%), with an average concentration ten times lower than that in the WWTP effluents (0.002 µg/L). Among the nine surfactants quantified at least once, LAS C10 to C13 were quantified in all effluent samples analyzed, with average concentrations ranging from 1.1 to 5.8 µg/L, and surfynol 104 was quantified in 83% of the samples at an average concentration of 0.1 µg/L. All nine surfactants were also quantified in surface waters, with LAS C10 through C13 most frequently quantified (82-88%), at average concentrations ranging from 0.4 to 2.5 µg/L. Surfynol 104 was quantified in 16% of surface waters at an average concentration of 0.3 µg/L, higher than that observed in WWTP effluent waters.

The 3 biocides and 9 surfactants quantified at least once in WWTP effluent samples were also quantified in surface water samples. Among these 12 substances, fipronil, surfynol 104, ethylhexyl sulfate and didecyldimethylammonium were more frequently quantified in surface waters of stations subject to urban pressures. This suggest that WWTP effluents could be a source of contamination of surface waters regarding these surfactants and biocides.

Figure S16 shows the frequency of quantification and the average concentrations obtained for biocides and surfactants in the sludge of the 7 WWTP. All substances were analyzed in the 7 sludge samples. In total, 13 biocides and 12 surfactants were quantified in the sludge samples. Regarding biocides, 7 substances, including fipronil, were quantified in all samples analyzed at average concentrations ranging from 6.6 µg/kg to 123 mg/kg. Bifenthrin was quantified in 71% of the samples at an average concentration of 5.2 µg/kg. The other biocides were quantified in only 14 or 29% of the samples, at concentrations ranging from 0.7 to 19 mg/kg. Among them,

Diclosan, clorophene, and chloroxidine, which were quantified once, have not been found during this campaign in the aquatic environment (neither in water nor in sediment) in mainland France. For surfactants, 8 substances, including LAS C10 to C13, were quantified in all samples analyzed at average concentrations ranging from 1.8 to 122 mg/kg. The remaining four surfactants were quantified in 29 to 71% of the samples at average concentrations ranging from 0.9 to 3.2 mg/kg. The concentrations in WWTP effluents and sludges are in line with those reported in previous studies (Juksu et al., 2019; Margot et al., 2015; Teerlink et al., 2017).

Figure 4 shows the average concentrations of the biocides and surfactants quantified in the effluent water and WWTP sludge among the 36 substances investigated in both matrices. These substances were not completely retained by the sewage sludge, resulting in their presence in the effluent water. Like what was observed in the natural environment for surface water samples and sediment samples, LAS C11 to C13 were the substances present at the highest average concentrations in the sludge and in the effluent. Didecyldimethylammonium was quantified in the sludge at a slightly higher average concentration than LAS C11 to C13, but at a lower concentration in the effluent water. This shows the high affinity of this substance for sludge, as reported by Margot et al. (2015).

Among the 36 substances investigated in sludge and WWTP effluent, 13 substances were found only in sludge: 2-hydroxybiphenyl, dodecyl dimethyl benzyl ammonium, tetradecyl dimethyl benzyl ammonium, octylisothiazolinone, diclosan, clorophene, chlorhexidine, methyl nonyl ketone, lauryl sulfate, 1-laureth sulfate, 2-laureth sulfate, TEAQ-C16, and hexadecyl betaine. In the natural environment, 2-hydroxybiphenyl, methyl nonyl ketone and hexadecylbetaine were found only in the sediment. The other substances, except for diclosan, clorophene and chloroxidine, which were not quantified in the natural environment, were found both in surface water and sediment. In WWTP, it can be assumed that these substances have an additional affinity for sewage sludge, compared to sediment, and therefore a good retention in the

treatment process. Triton X-100 and ethylhexyl sulfate were searched in both matrices and were quantified in the effluent water only. In the natural environment in mainland France, triton X-100 was found only in water, and ethylhexyl sulfate was found in water and sediment. It seems that these two substances have a poor affinity for sewage sludge.

Twelve substances were not found in either matrix. Among these, abamectin, chlorfenapyr, difenacoum, brodifacoum, flocoumafen, (benzothiazol-2-ylthio)methyl thiocyanate, 4,5-dichloro-2-octyl-1,2-thiazol-3(2H)-one, cetylpyridium and metofluthrin were not found in water or in sediment from mainland France. On the other hand, although observed in the water and sediment of the mainland, comperlan 100, incromine sd and laurylpyridinium were not found in the effluent and sludge of the 7 WWTP.

3.9 Concentrations of the target substances along 7 river continuums

The data acquired from the analysis of surface water and WWTP effluent samples were investigated regarding 7 rivers continuums. The number of biocides and surfactants quantified and their total concentrations per site along the Isle River are presented in Figure 5. Up to two biocides per site, fipronil and didecyldimethylammonium, and 4 to 6 surfactants per site, LAS C10, C11, C12, C13 and C14, 1-laureth sulfate, ethyl hexyl sulfate, and Triton X 100, were quantified. High total concentrations per site, from 13 to 60 $\mu\text{g/L}$, were determined along the river. The highest concentration was determined in the Vauclaire WWTP effluent (VAU), which is a small facility located on a hospital site (120 inhabitant equivalent). Total concentrations decreased for sites n° 529, 523 and 530, and then increased for the site n° 526. This might be due to a possible impact of Vauclaire WWTP effluent. Moreover, Périgueux City could also have an impact on total concentrations at site n° 523. The results obtained on the Escaut River continuum are presented in Figure S17. Fipronil was quantified on all sites of the

continuum besides the first one (n° 105). Between 5 and 7 surfactants per site, LAS C10, C11, C12, and C13, 1-laureth sulfate, surfynol 104, ethyl hexyl sulfate and lauryl sulfate, were quantified, with the larger number of substances for the downstream sites (n° 104 and 108) and high total concentrations determined, ranging from 2.9 to 14 µg/L. No clear impact of the Trith St Léger WWTP (TRI) was observed on the target substances concentrations on the site n° 104. However, a possible impact of Cambrai City on concentrations on site n°106, and a possible impact of Valenciennes City on concentrations on sites n° 104 and 108 could be observed. The results obtained on the Loire River continuum are presented in Figure S18. Fipronil was quantified on two sites and in the La Grange David (LAG) WWTP effluent. The biocides were not analysed on site n° 411 water sample. Between 4 and 5 surfactants per site, LAS C10, C11, C12, and C13, surfynol 104, Triton X 100, and lauryl sulfate, were quantified along the Loire River. High total concentrations, ranging from 1.0 to 11 µg/L, were determined. Possible impact of Saint-Etienne City on the water concentrations on the site n° 403 could be observed, as well as a possible large impact of an industrial zone on the water concentrations on site n° 411. The results obtained on the Meuse River continuum are presented in Figure S19. Fipronil was quantified on two sites and in the Charleville-Mézières (MEZ) WWTP effluent. Between 1 and 7 surfactants per site, LAS C10, C11, C12, and C13, surfynol 104, ethyl hexyl sulfate, and TEAQ-C18, were quantified along the Meuse River. No surfactant was quantified on site n° 217 station. Total concentrations were determined, ranging from 0.6 ng/L to 11 µg/L. No impact of the MEZ WWTP effluent on the Meuse River concentration was observed. The results obtained on the Moselle River continuum are presented in Figure S20. One or 2 biocides per site were quantified along the Moselle River, fipronil and didecyldimethylammonium, and 2 to 6 surfactants per site, LAS C10, C11, C12, and C13, surfynol 104, ethyl hexyl sulfate, and Triton X 100 were quantified. Intermediate to high total concentrations, ranging from 0.17 to 13 µg/L, were determined. A possible impact of Nancy City on concentrations on site n° 213

was observed, whereas no impact of the Thionville (THI) WWTP effluent was observed on the water concentrations of the site n° 214. The results obtained on the Arc River continuum are presented in Figure S21. One or 2 biocides per site were quantified along the Arc River, fipronil, DEET and methylisothiazolinone. Four to 9 surfactants per site, LAS C10, C11, C12, and C13, TEAQ-C16 and C18, surfynol 104, ethyl hexyl sulfate, 1- and 2-laureth sulfate and Triton X 100 along the river. High total concentrations were determined, ranging from 2.5 to 32 µg/L, and a possible impact of a large industrial zone on the concentrations of the site n° 634. The results obtained on the Eure River continuum are presented in Figure S22. One or 2 biocides per site, Fipronil and DEET, and 4 to 9 surfactants per site, LAS C10, C11, C12, and C13, lauryl sulfate, surfynol 104, ethyl hexyl sulfate, 1-laureth sulfate and Triton X 100, were quantified along the Eure River. Intermediate to high concentrations, ranging from 0,15 to 9,6 µg/L, were determined, with a possible impact of Chartres City on concentrations on site n° 322, and a possible impact of Dreux City on concentrations on site n° 324 station. These results suggest punctual sources of contamination, such as WWTP effluents, as well as diffuse sources, such as runoffs from urban and industrial areas, along the studied continuums regarding the target biocides and surfactants. This has been pointed out in several field studies (Heidler and Halden, 2009; Singer et al., 2010; Szopińska et al., 2021) and literature reviews (Geissen et al., 2015; Kroon et al., 2020; Margot et al., 2015).

4. Conclusion

A nation-wide prospective campaign targeting 32 biocides and 17 surfactants in water, sediment, wastewater and sludge samples on 98 sites located in mainland France and overseas regions was conducted. 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. The study of temporal variability in the water concentration showed that slightly more target substances were quantified in November-December 2018 in mainland France, and in April-May in overseas regions. A Principal component analysis on the water concentrations showed that some biocides were quantified in different types of sites, suggesting different types of contamination sources. Highly and moderately critical PNEC exceedances in water and sediment were determined for the surfactants LAS C10-C13, TEAQ-C16 and C18, 1- and 2-laureth sulfate, triton X-100, and the biocides fipronil, methyl nonyl ketone, octylisothiazolinone, bifenthrin, and methylisothiazolinone. These data have been used by the French Prioritization Experts Committee for prioritization of the substances relevant to be monitored for the 3rd WFD cycle. Analysis of effluent and sludge samples from 7 WWTP showed larger number of substances and quantification frequencies for biocides and surfactants in sludge, suggesting partial retention of these substances in the WWTP. The analysis of the spatial variations of the number and the concentration of both types of substances along 7 river continuums showed the possible impact of the WWTP plant effluent and the urban and industrial areas on their concentrations.

Biocides and surfactants come from various sources and appear to be widespread in the aquatic environment. As they have might cause adverse effect on the aquatic life, their concentrations in the environment need to be reduced. To this end, efforts should be put on reducing their use or replacing these products in households and hospitals, which would decrease the concentration in WWTP influents and effluents. Moreover, their use in urban, rural and industrial areas should be controlled to limit the impact of runoffs on their concentrations in water streams.

As far as WFD is implemented in France, the SRM parameters identified through this study are to be monitored during the 2022-2027 cycle in hundreds of sites, and recommendations will be

given by AQUAREF so that regulatory monitoring laboratories can manage these measurements adequately. Meanwhile, PNEC for these parameters should be consolidated so that they ultimately may be converted into environmental quality standards, enabling those chemicals to contribute to WFD ecological status assessment of surface water bodies.

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Supporting information

Supporting information containing additional figures and tables are available free of charge via the internet.

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Tables

Table 1. List of substances selected for the monitoring campaign, type of product and relevant matrices monitored

Substance	Abbreviation	CAS number	Usage	Type of product	Relevant matrices monitored
N,N-diethyl-meta-toluamide	DEET	134-62-3	Biocide	Repellents and baits	Water
Methylchloroisothiazolinone	MCIT	26172-55-4	Biocide	Protection of products during storage	Water
Dodecyl dimethyl ethylbenzyl ammonium	EBAC-C ₁₂	774118-92-2	Biocide	Wood preservation products	Water
Tetradecyl dimethyl ethylbenzyl ammonium	EBAC-C ₁₄	Not defined	Biocide	Wood preservation products	Water
Benzisothiazolinone	BIT	2634-33-5	Biocide	Disinfectants and algicides not intended for direct application to humans or animals	Water
Methylisothiazolinone	MIT	2682-20-4	Biocide	Liquid protection products used in cooling and manufacturing systems Human hygiene products	Water
Didecyl dimethyl ammonium	DDAC-C ₁₀	7173-51-5	Biocide	Wood preservation products	Water/Sediment/Sludge
Dodecyl dimethyl benzyl ammonium	BAC-C ₁₂	10328-35-5	Biocide	Disinfectant in human hygiene, animal hygiene. Treatment of roofs, slabs... Disinfection of surfaces in contact with foodstuffs	Water/Sediment/Sludge
Tetradecyl dimethyl benzyl ammonium	BAC-C ₁₄	16287-71-1	Biocide	In liquids, used in cooling and manufacturing systems Anti-biofilm product Taxidermy Cationic surfactant.	Water/Sediment/Sludge
Dichlofluanid		1085-98-9	Biocide	Anti-fouling products	Water/Sediment/Sludge
Abamectin		71751-41-2	Biocide	Insecticides, acaricides and products used to control other arthropods	Water/Sediment/Sludge
Fipronil		120068-37-3	Biocide	Insecticides, acaricides and products used to control other arthropods	Water/Sediment/Sludge
2-Hydroxybiphenyl		90-43-7	Biocide	Products for human hygiene, disinfection, veterinary hygiene Animal feed, product conservation, conservation of working fluids / cutting	Water/Sediment/Sludge
Chlorfenapyr		122453-73-0	Biocide	Wood preservation products	Water/Sediment/Sludge
Difenacoum		56073-07-5	Biocide	Rodenticides	Water/Sediment/Sludge
Brodifacoum		56073-10-0	Biocide	Rodenticides	Water/Sediment/Sludge
Flocoumafen		90035-08-8	Biocide	Rodenticides	Water/Sediment/Sludge
(benzothiazol-2-ylthio)methyl thiocyanate	TCMTB	21564-17-0	Biocide	Protective products for fibers, leather, rubber and polymerized materials	Water/Sediment/Sludge
4,5-dichloro-2-octyl-1,2-thiazol-3(2H)-one	DCOIT	64359-81-5	Biocide	Wood preservation products	Water/Sediment/Sludge
Octylisothiazolinone	OIT	26530-20-1	Biocide	Wood preservation products	Water/Sediment/Sludge
Diclosan		3380-30-1	Biocide	Human hygiene products Disinfectants and algicides not intended for direct application to humans or animals	Water/Sediment/Sludge

Clorofene		120-32-1	Biocide	Disinfectants and algaecides not intended for direct application to humans or animals	Water/Sediment/Sludge
Cetylpyridium		7773-52-6	Biocide	Cationic antiseptic belonging to the quaternary ammonium class	Water/Sediment/Sludge
Metofluthrin		240494-70-6	Biocide	Insecticides, acaricides and products used to control other arthropods	Water/Sediment/Sludge
Chlorhexidine		55-56-1	Biocide	Broad spectrum bactericidal antiseptic	Water/Sediment/Sludge
Methyl nonyl ketone		112-12-9	Biocide	Repellents and baits	Water/Sediment/Sludge
Hexadecyl dimethyl benzyl ammonium	BAC-C ₁₆	10328-34-4	Biocide	Disinfectant in human hygiene, animal hygiene. Treatment of roofs, slabs... Disinfection of surfaces in contact with foodstuffs	Sediment/Sludge
Octadecyl dimethyl benzyl ammonium	BAC-C ₁₈	37612-69-4	Biocide	In liquids used in cooling and manufacturing systems Anti-biofilm product, Taxidermy Cationic surfactant.	Sediment/Sludge
Bifenthrin		82657-04-3	Biocide	Wood preservation products	Sediment/Sludge
1-(4-(2-chloro-a,a-p-trifluorotolyloxy)-2-fluorophenyl)-3-(2,6-difluorobenzoyl) urea	Flufenoxuron	101463-69-8	Biocide	Wood preservation products	Sediment/Sludge
Cyfluthrin		68359-37-5	Biocide	Insecticides, acaricides and products used to control other arthropods	Sediment/Sludge
d-Phenothrin		188023-86-1	Biocide	Insecticides, acaricides and products used to control other arthropods	Sediment/Sludge
Lauryl sulfate	SDS	151-41-7	Surfactant	Anionic surfactant	Water/Sediment/Sludge
1-laureth sulfate	C ₁₂ EO ₂ S	15826-16-1	Surfactant	Anionic surfactant	Water/Sediment/Sludge
2-laureth sulfate	C ₁₂ EO ₂ S	3088-31-1	Surfactant	Anionic surfactant	Water/Sediment/Sludge
Decylbenzene sulfonate	LAS C10	Not defined	Surfactant	Anionic surfactant - washing and cleaning products, cosmetics and personal care products, adhesives and sealants, textile treatment products and dyes and leather treatment products	Water/Sediment/Sludge
Undecylbenzene sulfonate	LAS C11	Not defined	Surfactant		Water/Sediment/Sludge
Dodecylbenzene sulfonate	LAS C12	Not defined	Surfactant		Water/Sediment/Sludge
Tridecylbenzene sulfonate	LAS C13	Not defined	Surfactant		Water/Sediment/Sludge
Tetradecylbenzene sulfonate	LAS C14	Not defined	Surfactant		Water/Sediment/Sludge
Ethylhexyl sulfate	EHS	72214-01-8	Surfactant	Anionic surfactant	Water/Sediment/Sludge
Laurylpyridinium		15416-74-7	Surfactant	Cationic surfactant	Water/Sediment/Sludge
SADP-DMA	Incromine sd	7651-02-7	Surfactant	Cationic surfactant	Water/Sediment/Sludge
C16 Triethanolamine esterquat	TEAQ-C ₁₆	157905-74-3	Surfactant	Cationic surfactant	Water/Sediment/Sludge
C18 Triethanolamine esterquat	TEAQ-C ₁₈	157905-74-3	Surfactant	Cationic surfactant	Water/Sediment/Sludge
2,4,7,9-Tetramethyl-5-decyne-4,7-diol	Surfynol 104	126-86-3	Surfactant	Non-ionic surfactant	Water/Sediment/Sludge
OP7-11EO	Triton X-100	9002-93-1	Surfactant	Non-ionic surfactant	Water/Sediment/Sludge
CMEA	Comperlan 100	68140-00-1	Surfactant	Non-ionic surfactant	Water/Sediment/Sludge
Hexadecylbetaine		693-33-4	Surfactant	Amphoteric surfactant	Water/Sediment/Sludge

Table 2. Analytical methods carried out on surface water, WWTP effluent, sediment and sludge samples

Substance	Abbreviation	Usage	Relevant matrices monitored	PNEC water (µg/L)	Analytical method	LOQ water (µg/L)		LOQ WWTP effluents (µg/L)		PNEC sediment (µg/kg)	Analytical method	LOQ sediment/sludge (µg/kg)	
						Target	Mean	Target	Mean			Target	Mean
N,N-diethyl-meta-toluamide	DEET	Biocide	Water	41	DI-LC-MS/MS	0.1	0.1	1	0.1	-	-	-	-
Methylchloroisothiazolinone	MCIT	Biocide	Water	0.28	DI-LC-MS/MS	0.2	0.2	2	0.2	-	-	-	-
Dodecyl dimethyl ethylbenzyl ammonium	EBAC-C ₁₂	Biocide	Water	1	DI-LC-MS/MS	1	1	10	1	-	-	-	-
Tetradecyl dimethyl ethylbenzyl ammonium	EBAC-C ₁₄	Biocide	Water	1	DI-LC-MS/MS	1	1	10	1	-	-	-	-
Benzisothiazolinone	BIT	Biocide	Water	7.1	DI-LC-MS/MS	5	5	50	5	-	-	-	-
Methylisothiazolinone	MIT	Biocide	Water	0.006	DI-LC-MS/MS	0.05	0.05	0.05	0.05	-	-	-	-
Didecyl dimethyl ammonium	DDAC-C ₁₀	Biocide	Water/Sediment/Sludge	0.2	SPE-LC-MS/MS*	0.2	0.05	0.4	0.05	4848	USAE-LC-MS/MS**	1000	40
Dodecyl dimethyl benzyl ammonium	BAC-C ₁₂	Biocide	Water/Sediment/Sludge	1	SPE-LC-MS/MS*	0.2	0.06	0.4	0.06	13587	USAE-LC-MS/MS**	1000	27
Tetradecyl dimethyl benzyl ammonium	BAC-C ₁₄	Biocide	Water/Sediment/Sludge	1	SPE-LC-MS/MS*	0.2	0.04	0.4	0.04	13587	USAE-LC-MS/MS**	1000	18
Dichlofluanid		Biocide	Water/Sediment/Sludge	-	-	-	-	-	-	0.21	USAE-LC-MS/MS	0.1	1
Abamectin		Biocide	Water/Sediment/Sludge	0.001	DI-LC-MS/MS	0.001	0.001	0.01	0.001	0.28	USAE-LC-MS/MS	0.2	0.2
Fipronil		Biocide	Water/Sediment/Sludge	0.0008	SPME-GC-MS/MS	0.0008	0.0008	0.008	0.0008	0.02	ASE-GC-MS/MS	0.01	0.01
2-Hydroxybiphenyl		Biocide	Water/Sediment/Sludge	0.36	DI-LC-MS/MS	0.3	0.3	3	0.3	122	USAE-LC-MS/MS	100	100
Chlorfenapyr		Biocide	Water/Sediment/Sludge	0.03	SPME-GC-MS/MS	0.03	0.03	0.3	0.03	75	ASE-GC-MS/MS	50	50
Difenacoum		Biocide	Water/Sediment/Sludge	0.002	DI-LC-MS/MS	0.002	0.002	0.02	0.002	5.7	USAE-LC-MS/MS	5	5
Brodifacoum		Biocide	Water/Sediment/Sludge	0.06	DI-LC-MS/MS	0.05	0.05	0.5	0.05	28	USAE-LC-MS/MS	10	10
Flocoumafen		Biocide	Water/Sediment/Sludge	0.09	DI-LC-MS/MS	0.09	0.09	0.9	0.09	6.2	USAE-LC-MS/MS	5	5
(benzothiazol-2-ylthio)methyl thiocyanate	TCMTB	Biocide	Water/Sediment/Sludge	0.0021	DI-LC-MS/MS	0.002	0.002	0.02	0.002	0.36	USAE-LC-MS/MS	0.3	0.3
4,5-dichloro-2-octyl-1,2-thiazol-3(2H)-one	DCOIT	Biocide	Water/Sediment/Sludge	0.062	DI-LC-MS/MS	0.05	0.05	0.5	0.05	7.1	USAE-LC-MS/MS	5	5
Octylisothiazolinone	OIT	Biocide	Water/Sediment/Sludge	0.006	DI-LC-MS/MS	0.005	0.005	0.05	0.005	0.05	USAE-LC-MS/MS	0.05	0.05
Diclosan		Biocide	Water/Sediment/Sludge	0.48	DI-LC-MS/MS	0.4	0.4	4	0.4	157	USAE-LC-MS/MS	100	100
Clorofene		Biocide	Water/Sediment/Sludge	0.54	DI-LC-MS/MS	0.5	0.5	5	0.5	517	USAE-LC-MS/MS	100	100

Cetylpyridium		Biocide	Water/Sediment/Sludge	0.025	DI-LC-MS/MS	0.02	0.02	0.2	0.02	1830	USAE-LC-MS/MS	100	100
Metofluthrin		Biocide	Water/Sediment/Sludge	0.024	SPME-GC-MS/MS	0.02	0.02	0.2	0.02	40	ASE-GC-MS/MS-	10	10
Chlorhexidine		Biocide	Water/Sediment/Sludge	1	DI-LC-MS/MS	0.5	0.5	5	0.5	3602	USAE-LC-MS/MS	1000	1000
Methyl nonyl ketone		Biocide	Water/Sediment/Sludge	0.23	SPME-GC-MS/MS	0.1	0.1	1	0.1	3.8	ASE-GC-MS/MS	3	3
Hexadecyl dimethyl benzyl ammonium	BAC-C ₁₆	Biocide	Water/Sediment/Sludge	-	-	-	-	-	-	1949	USAE-LC-MS/MS**	1000	28
Octadecyl dimethyl benzyl ammonium	BAC-C ₁₈	Biocide	Sediment/Sludge	-	-	-	-	-	-	1949	USAE-LC-MS/MS**	1000	34
Bifenthrin		Biocide	Sediment/Sludge	-	-	-	-	-	-	0.08	ASE-GC-MS/MS	0.1	0.08
1-(4-(2-chloro-a,a-p-trifluorotolyloxy)-2-fluorophenyl)-3-(2,6-difluorobenzoyl) urea	Flufenoxuron	Biocide	Sediment/Sludge	-	-	-	-	-	-	0.05	USAE-LC-MS/MS	0.1	0.05
Cyfluthrin		Biocide	Sediment/Sludge	-	-	-	-	-	-	0.64	ASE-GC-MS/MS	0.5	0.5
d-Phenothrin		Biocide	Sediment/Sludge	-	-	-	-	-	-	19	ASE-GC-MS/MS	10	10
Lauryl sulfate	SDS	Surfactant	Water/Sediment/Sludge	65	SPE-LC-MS/MS*	10	0.5	10	0.5	1131	USAE-LC-MS/MS**	1000	123
1-laureth sulfate	C ₁₂ EO ₁ S	Surfactant	Water/Sediment/Sludge	1	SPE-LC-MS/MS*	1	0.4	1	0.4	7.96	USAE-LC-MS/MS**	7.9	158
2-laureth sulfate	C ₁₂ EO ₂ S	Surfactant	Water/Sediment/Sludge	1	SPE-LC-MS/MS*	1	0.3	1	0.3	7.96	USAE-LC-MS/MS**	7.9	124
2,4,7,9-Tetramethyl-5-decyne-4,7-diol	Surfynol 104	Surfactant	Water/Sediment/Sludge	16	SPE-LC-MS/MS*	16	0.1	20	0.1	59	USAE-LC-MS/MS**	59	42
Decylbenzene sulfonate	LAS C10	Surfactant	Water/Sediment/Sludge	1	SPE-LC-MS/MS*	1	0.02	0.4	0.02	188	USAE-LC-MS/MS**	188	6.4
Undecylbenzene sulfonate	LAS C11	Surfactant	Water/Sediment/Sludge	1	SPE-LC-MS/MS*	1	0.1	0.4	0.1	341	USAE-LC-MS/MS**	340	49
Dodecylbenzene sulfonate	LAS C12	Surfactant	Water/Sediment/Sludge	0.2	SPE-LC-MS/MS*	0.2	0.1	0.4	0.1	124	USAE-LC-MS/MS**	120	44
Tridecylbenzene sulfonate	LAS C13	Surfactant	Water/Sediment/Sludge	0.085	SPE-LC-MS/MS*	0.085	0.1	0.4	0.1	98	USAE-LC-MS/MS**	98	31
Tetradecylbenzene sulfonate	LAS C14	Surfactant	Water/Sediment/Sludge	Not defined	SPE-LC-MS/MS*	0.12	0.1	0.4	0.1	Not defined	USAE-LC-MS/MS**	100	32
OP7-11EO	Triton X-100	Surfactant	Water/Sediment/Sludge	0.28	SPE-LC-MS/MS*	0.2	0.1	0.4	0.1	12	USAE-LC-MS/MS**	10	48
N-(2-hydroxyethyl)dodecanamide	Comperlan 100	Surfactant	Water/Sediment/Sludge	1.35	SPE-LC-MS/MS*	1	0.1	0.5	0.1	18	USAE-LC-MS/MS**	18	13
N-[3-(dimethylamino)propyl]octadecanamide	Incromine sd	Surfactant	Water/Sediment/Sludge	0.51	SPE-LC-MS/MS*	0.5	0.05	0.4	0.05	5339	USAE-LC-MS/MS**	1000	39
Ethylhexyl sulfate	EHS	Surfactant	Water/Sediment/Sludge	11	SPE-LC-MS/MS*	10	0.05	1	0.05	165	USAE-LC-MS/MS**	100	11
C16 Triethanolamine esterquat	TEAQ-C ₁₆	Surfactant	Water/Sediment/Sludge	1	SPE-LC-MS/MS*	1	0.3	0.5	0.3	1.6	USAE-LC-MS/MS**	1.6	44
C18 Triethanolamine esterquat	TEAQ-C ₁₈	Surfactant	Water/Sediment/Sludge	1	SPE-LC-MS/MS*	1	0.2	0.5	0.2	1.6	USAE-LC-MS/MS**	1.6	59
Laurylpyridinium		Surfactant	Water/Sediment/Sludge	0.047	SPE-LC-MS/MS*	0.04	0.03	0.2	0.03	312	USAE-LC-MS/MS**	300	105
Hexadecylbetaine		Surfactant	Water/Sediment/Sludge	1	SPE-LC-MS/MS*	1	0.1	0.2	0.1	353	USAE-LC-MS/MS**	300	21

*Wiest et al., 2021; **Wiest et al., 2022

Figures

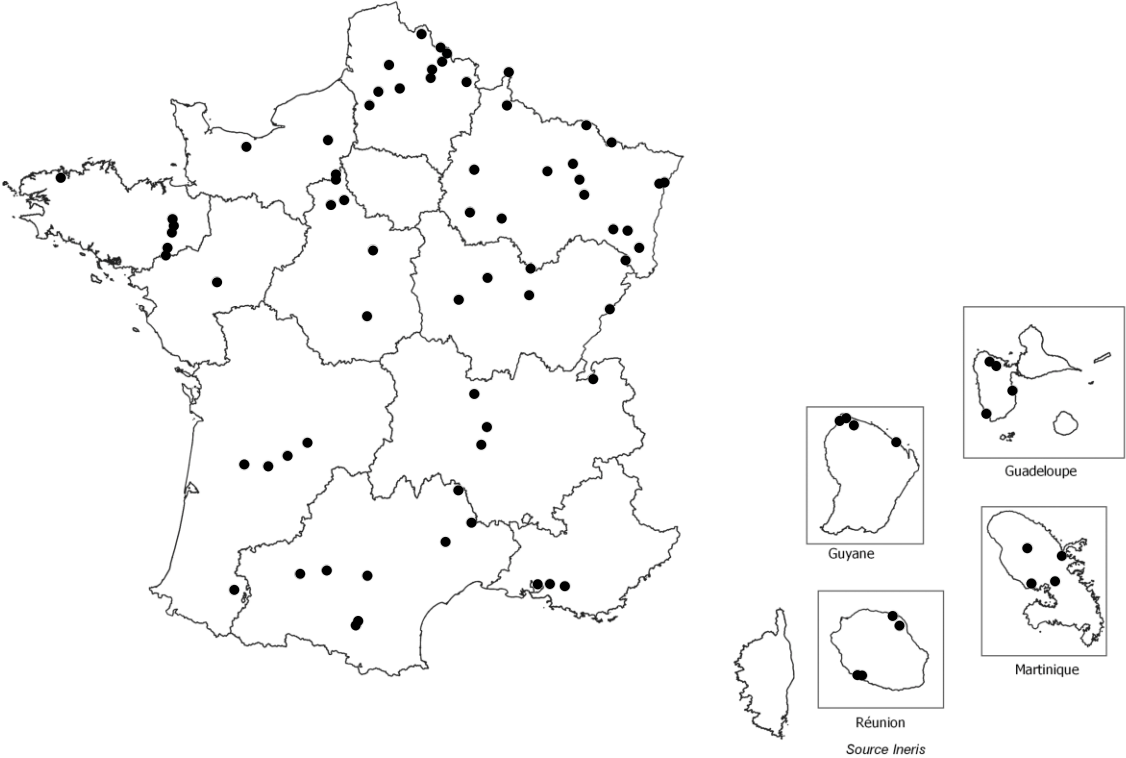


Figure 1. Locations of the sampling sites investigated during the monitoring campaign

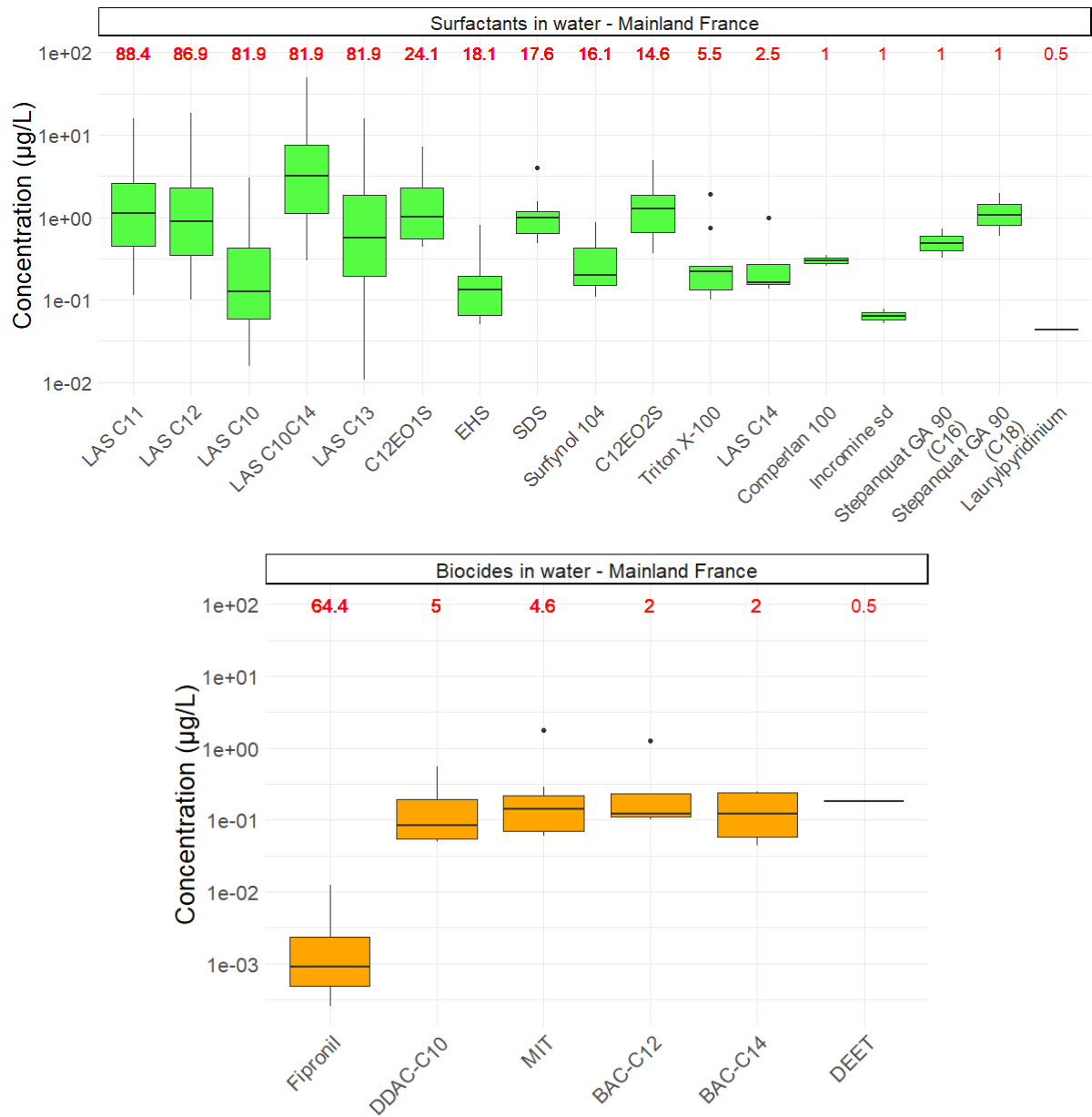


Figure 2. Frequency of quantification and distribution of the concentrations of the surfactants and biocides quantified in metropolitan surface waters

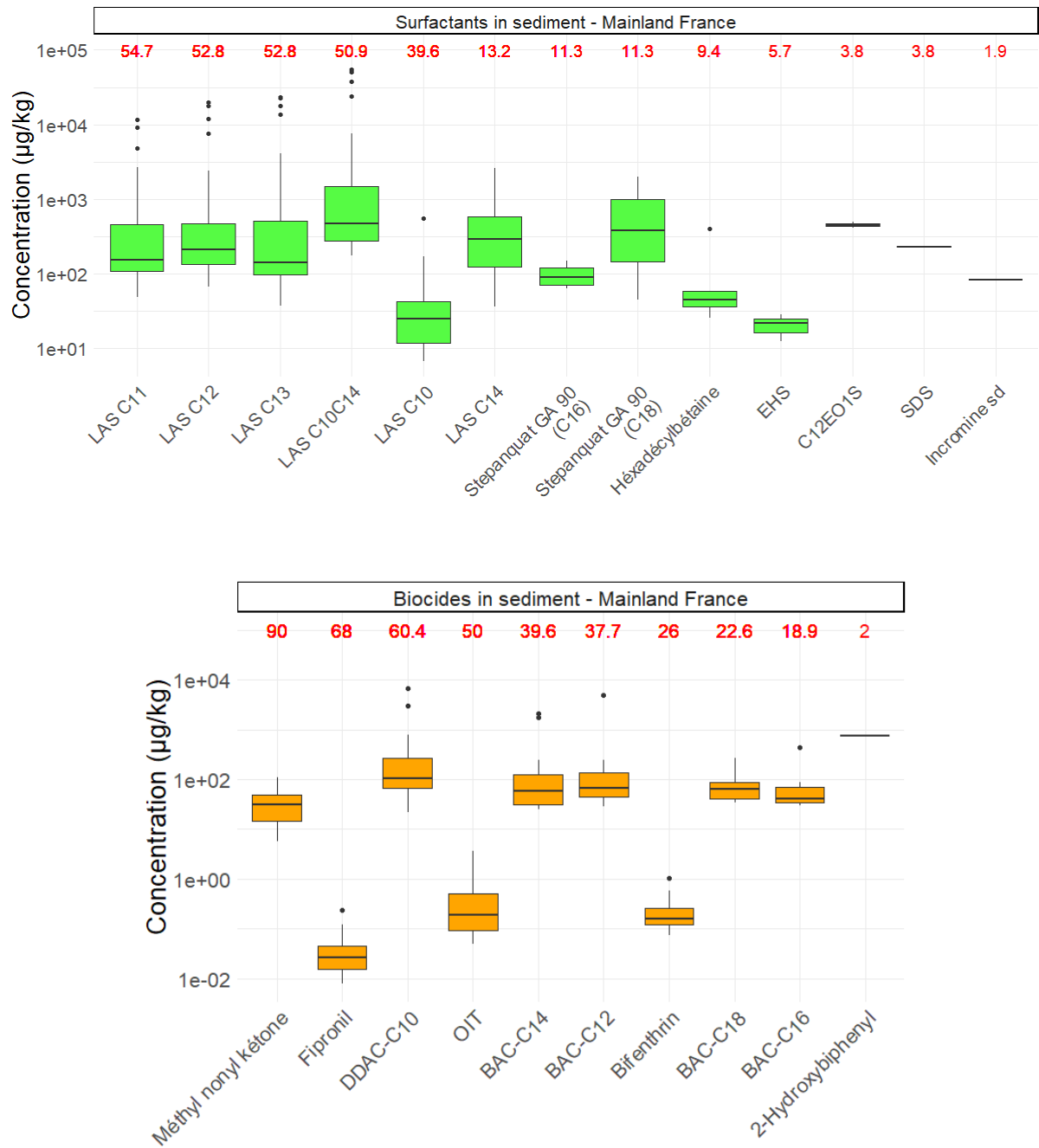


Figure 3. Frequency of quantification and distribution of the concentrations of the surfactants and biocides quantified in metropolitan river sediments

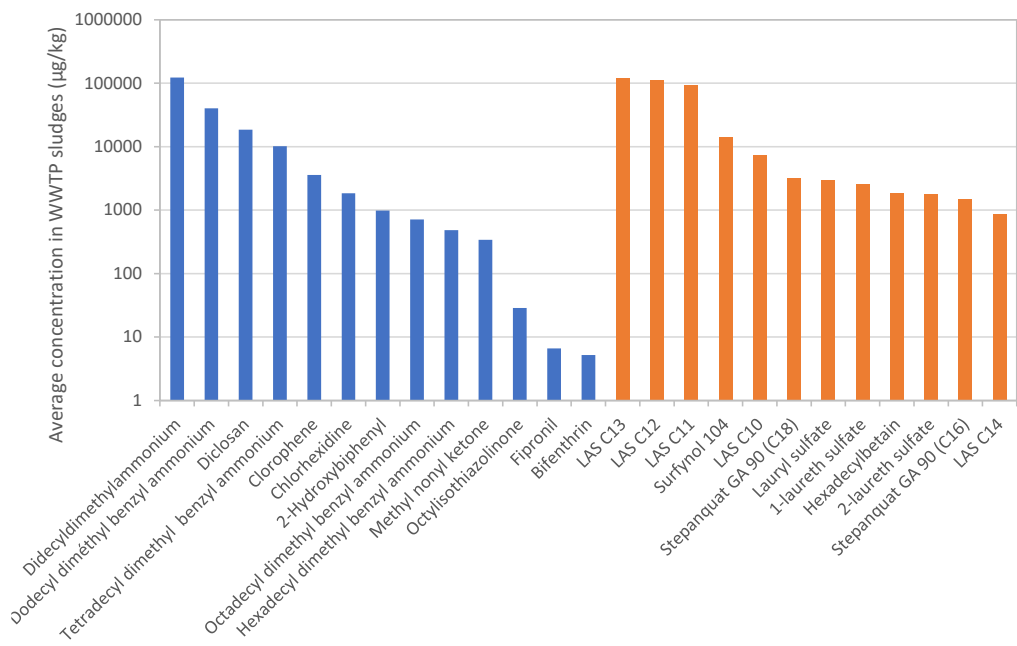
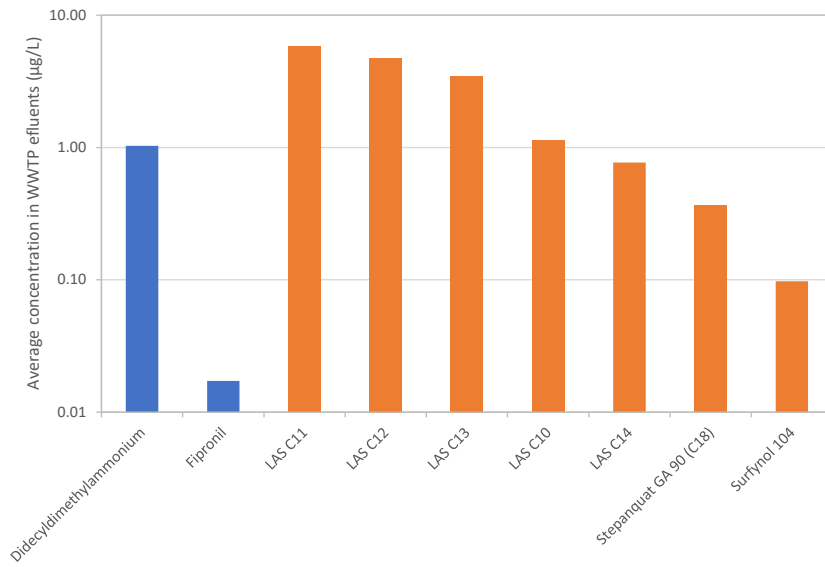


Figure 4. Average concentrations of biocides (blue bars) and surfactants (orange bars) in WWTP effluent (top) and sludge (bottom) samples in the mainland France

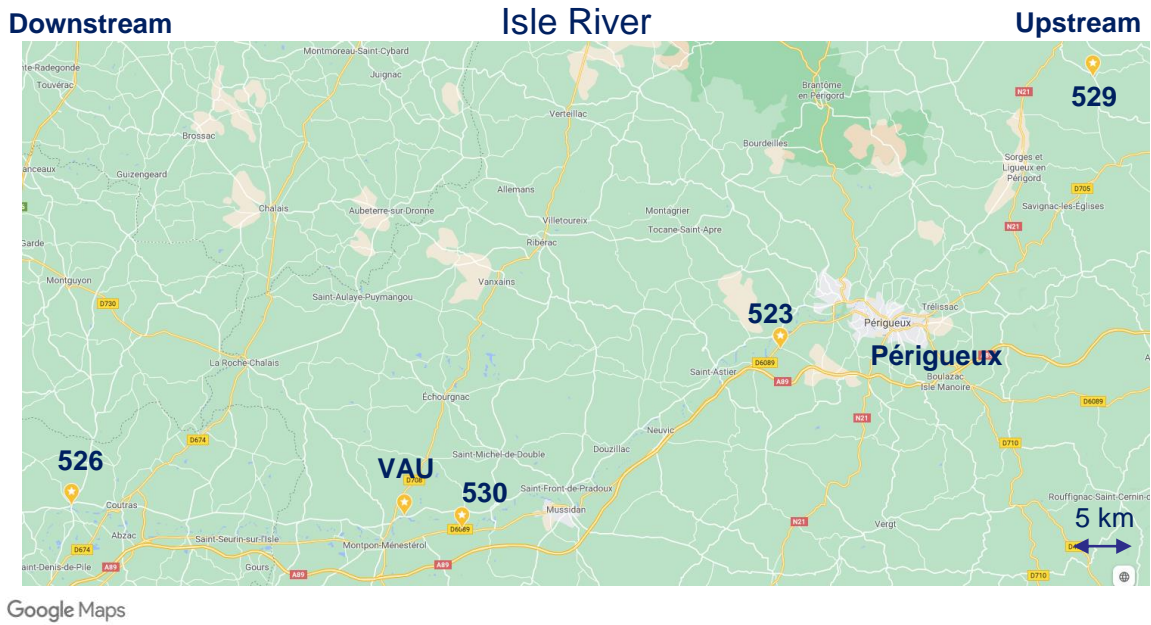
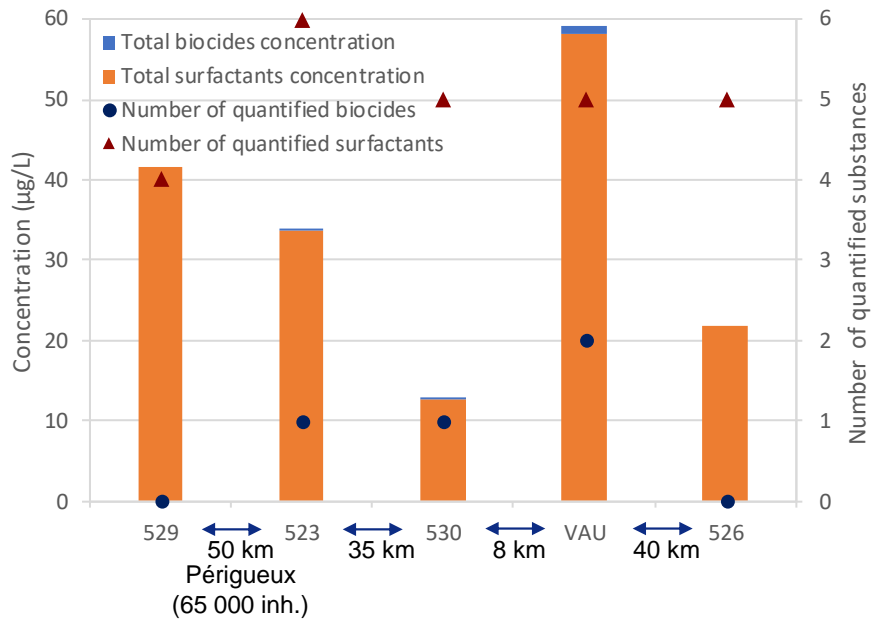


Figure 5. Number and concentrations of biocides and surfactants along the Isle River (up) and location of the sampling sites (down)

Nation-wide monitoring campaign of 49 biocides and surfactants in surface waters and wastewaters

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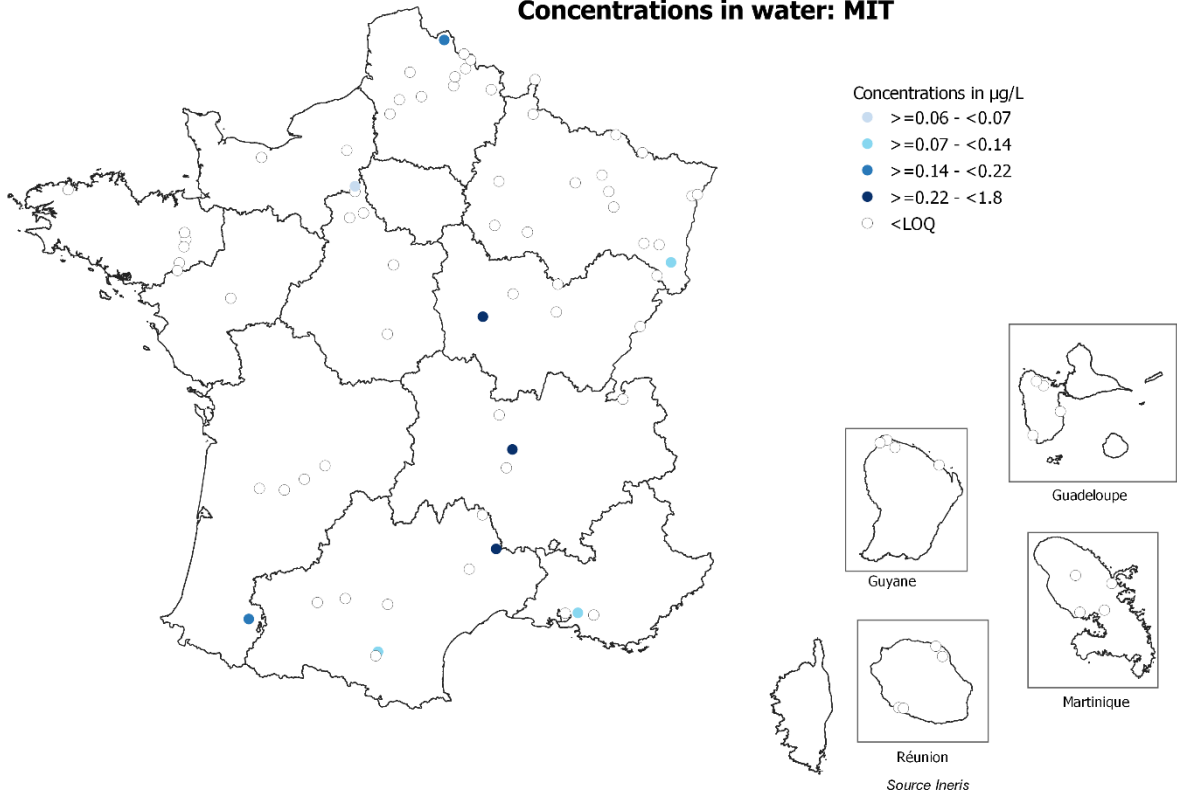
⁷French Biodiversity Agency, Direction of research & scientific support, 94300 Vincennes, France

*Corresponding author: Tel: +33 3 44 61 81 45; Email: azziz.assoumani@ineris.fr

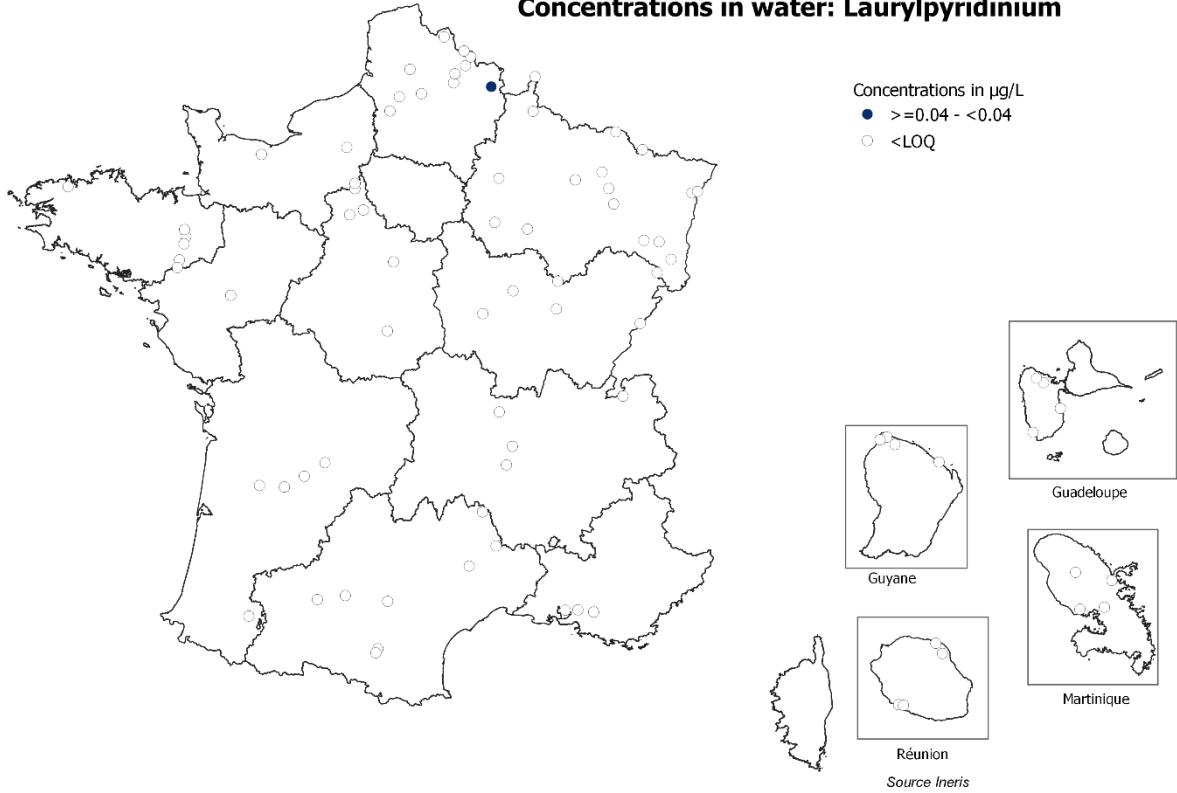
Supplementary Data

Figure S1. Graphical representations of the concentrations of each target contaminant quantified at least once in water

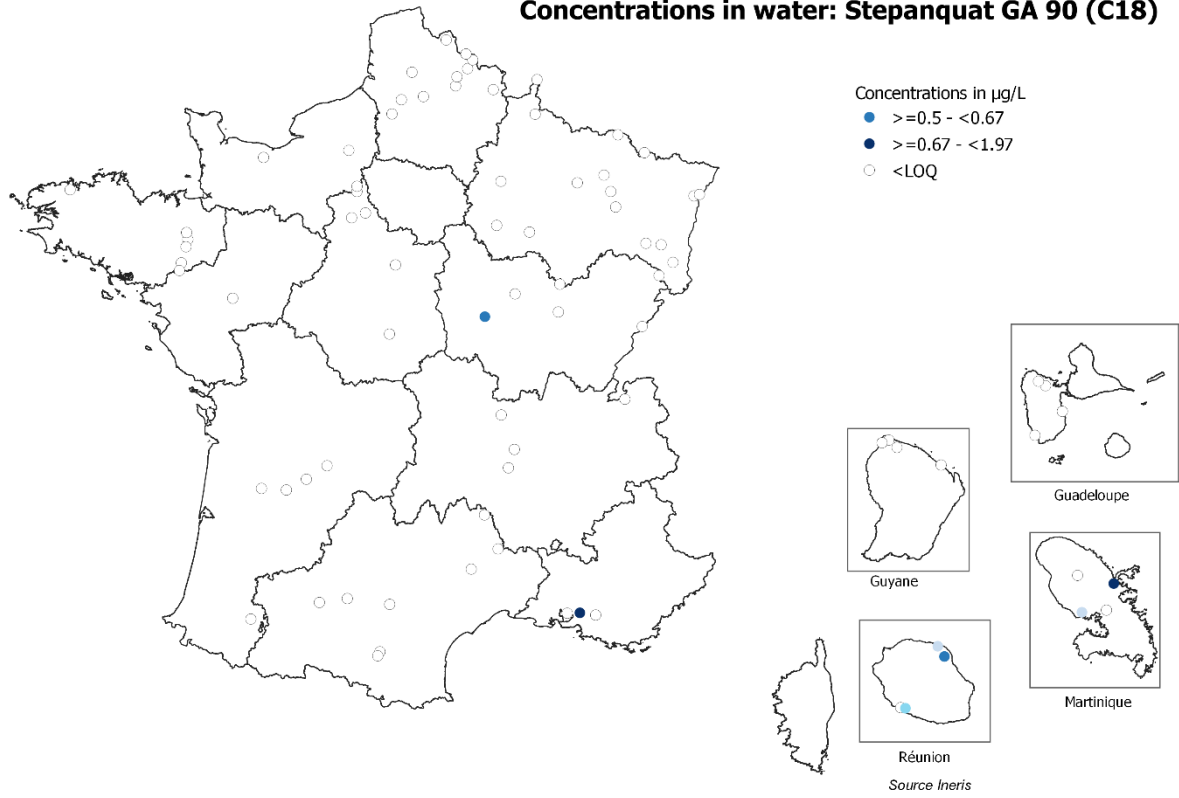
Concentrations in water: MIT



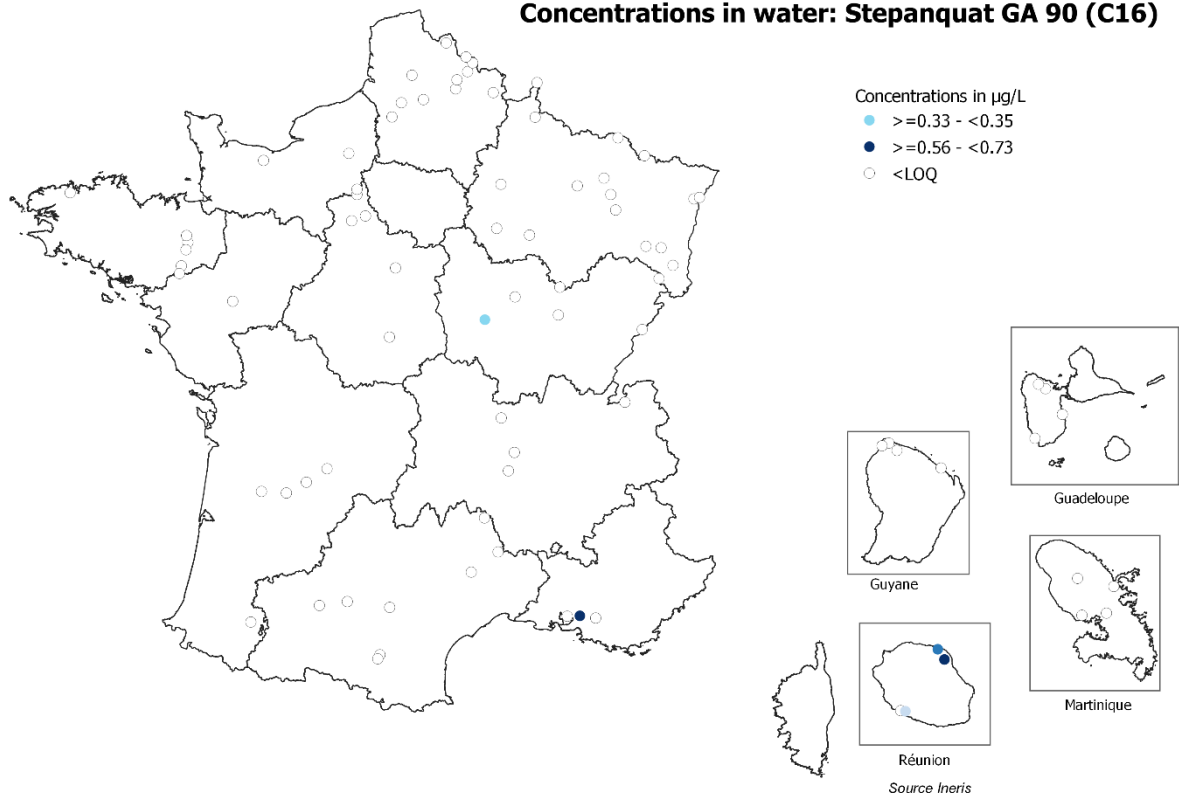
Concentrations in water: Laurylpyridinium



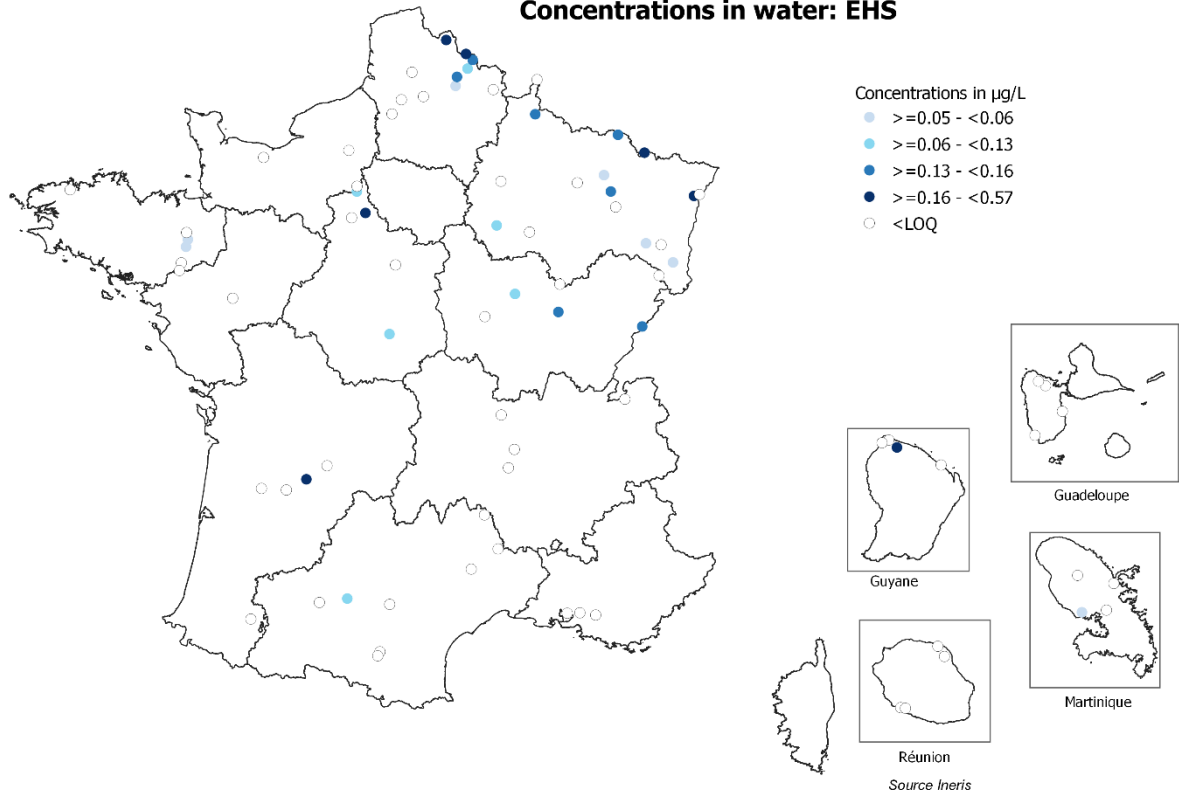
Concentrations in water: Stepanquat GA 90 (C18)



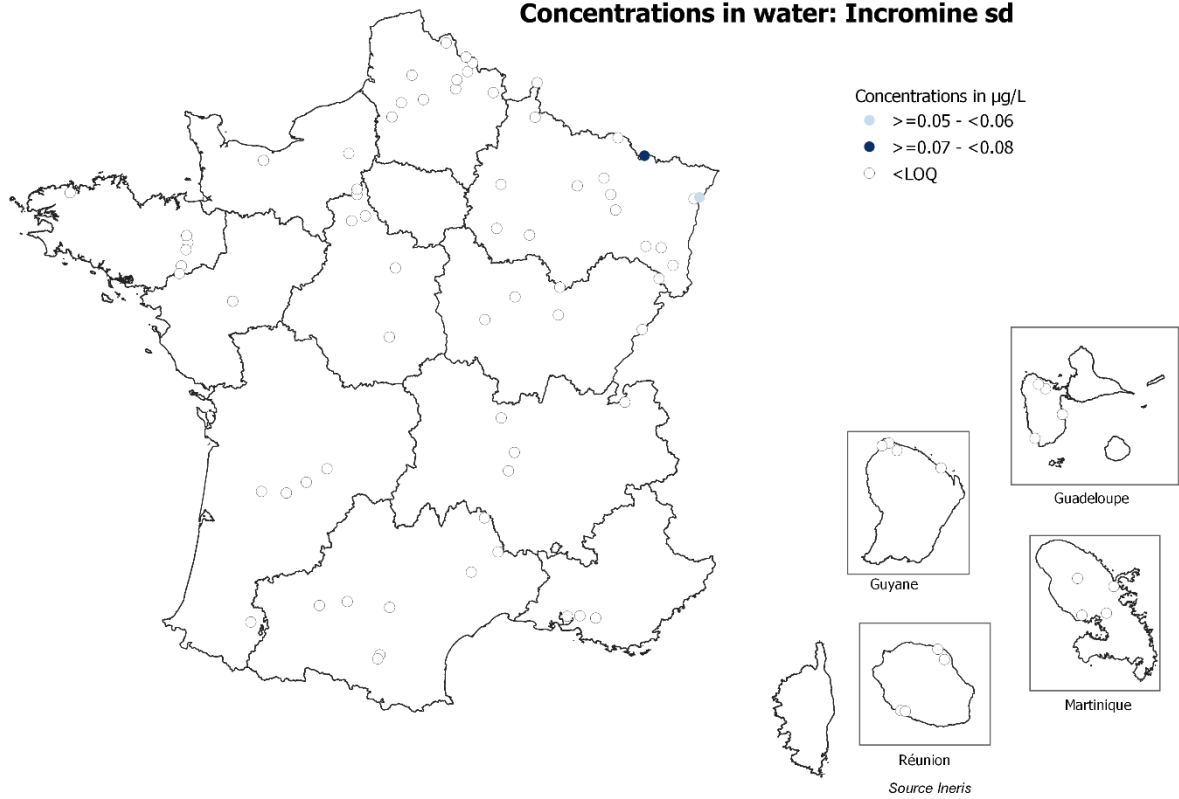
Concentrations in water: Stepanquat GA 90 (C16)



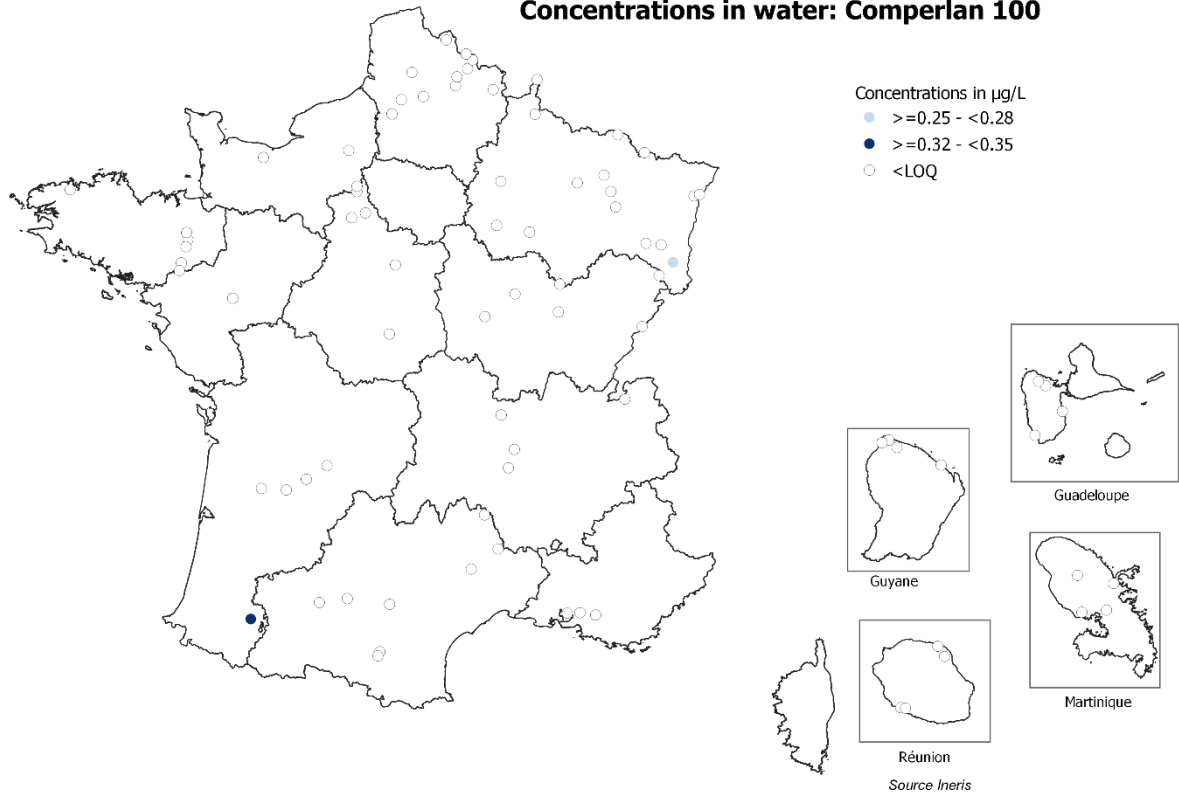
Concentrations in water: EHS



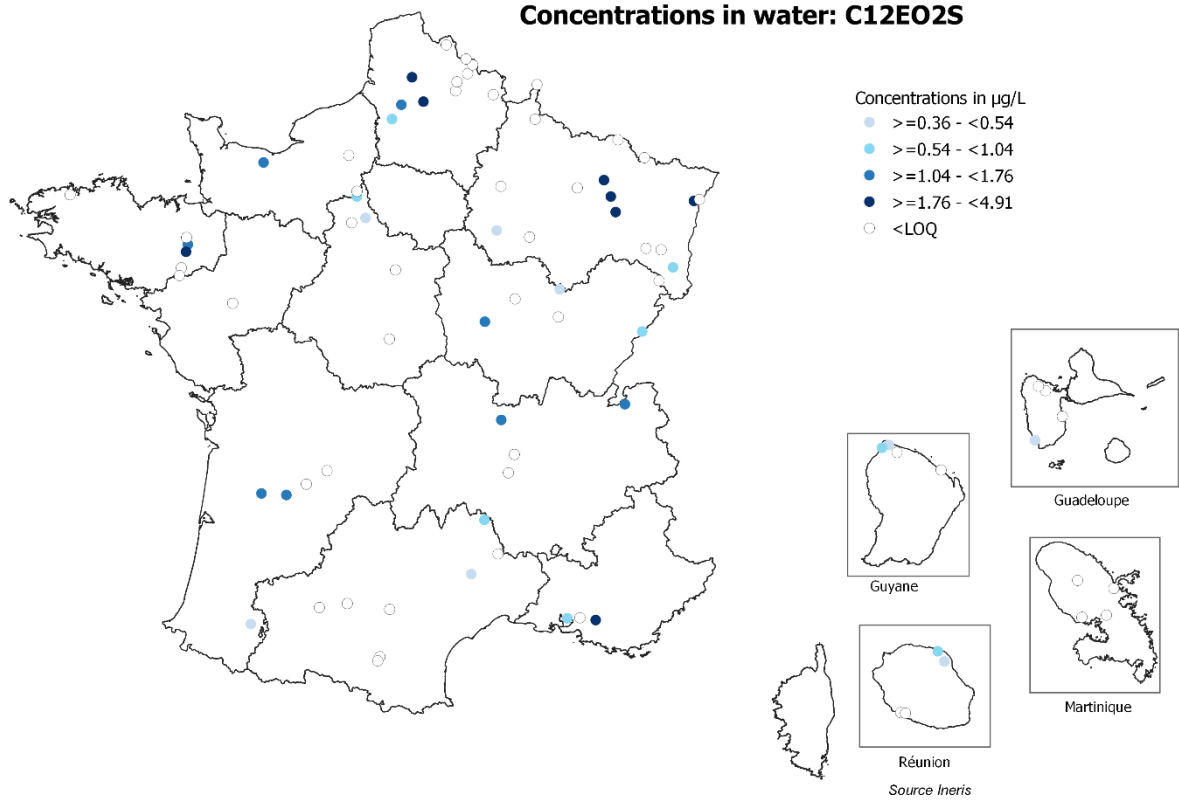
Concentrations in water: Incromine sd



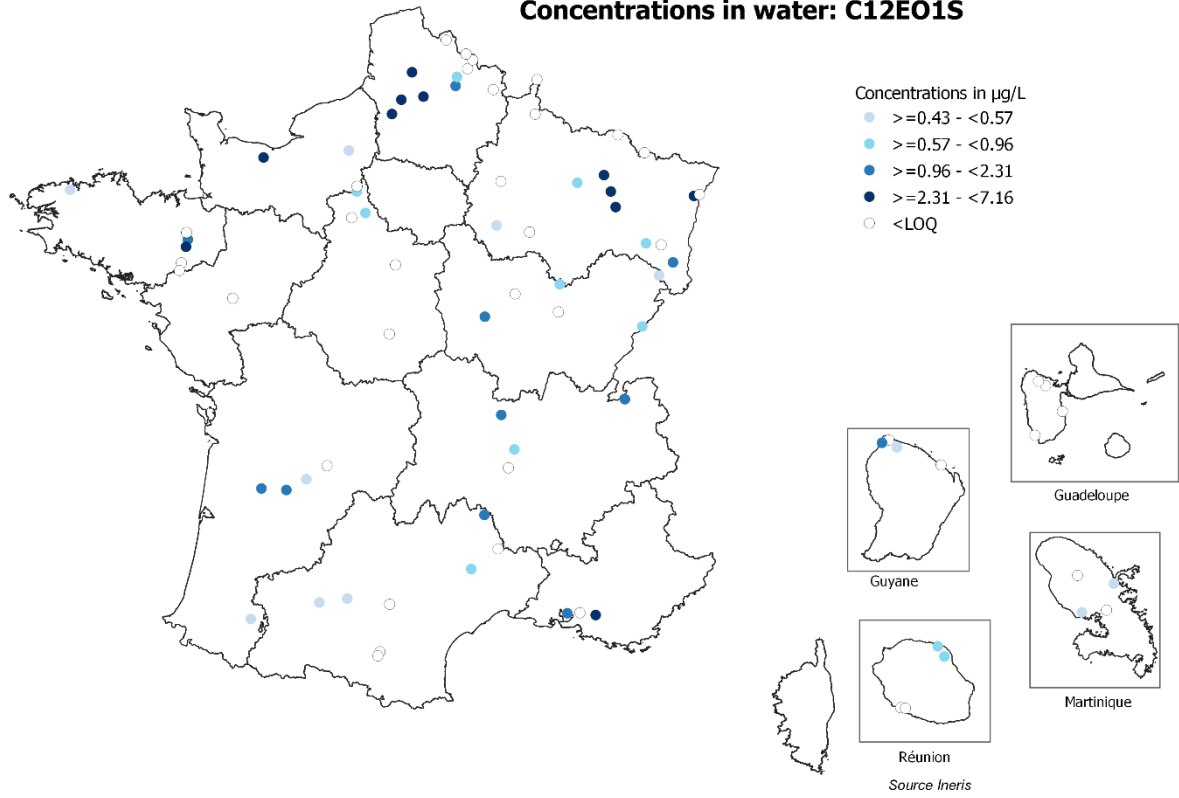
Concentrations in water: Comperlan 100



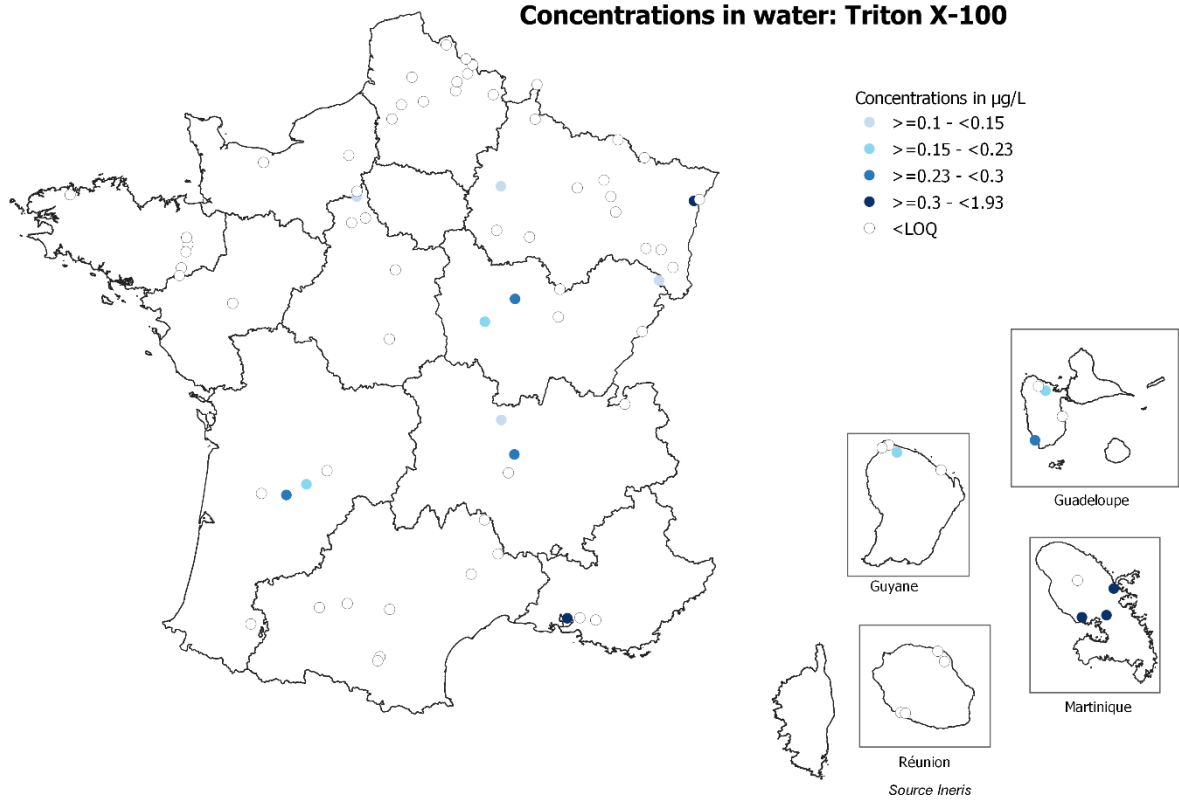
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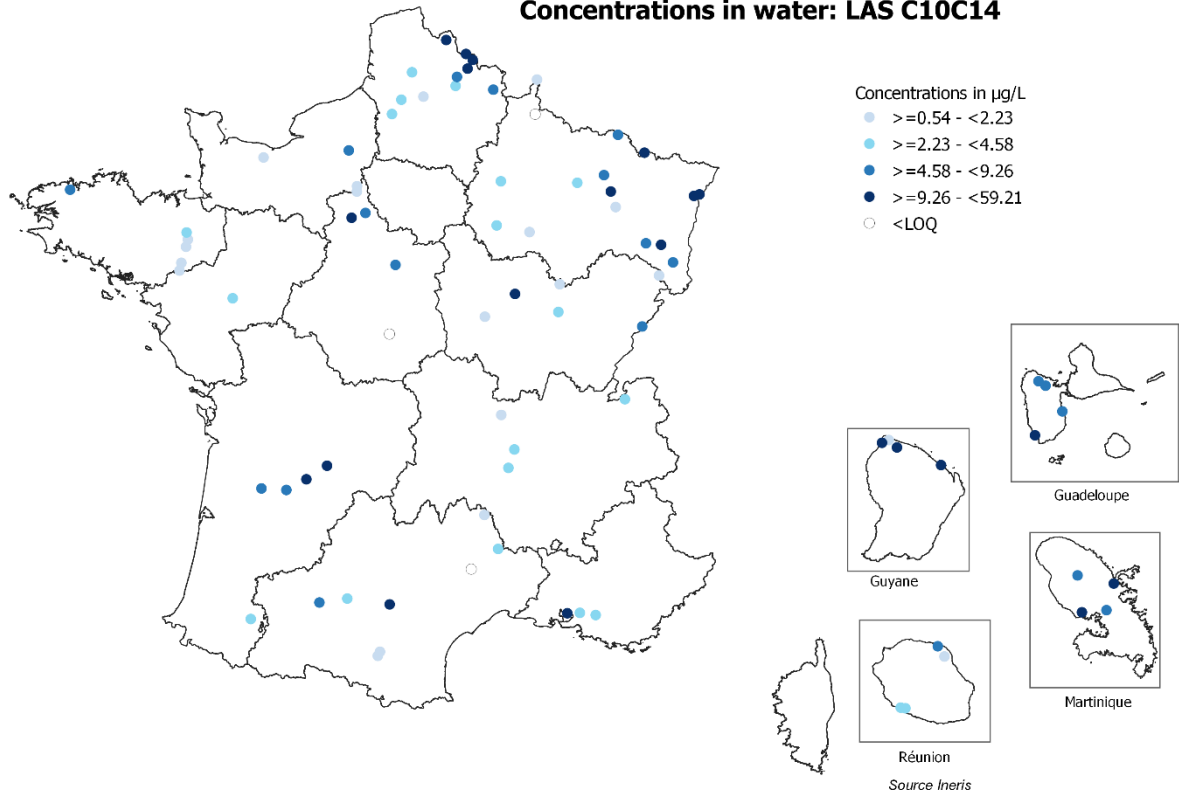
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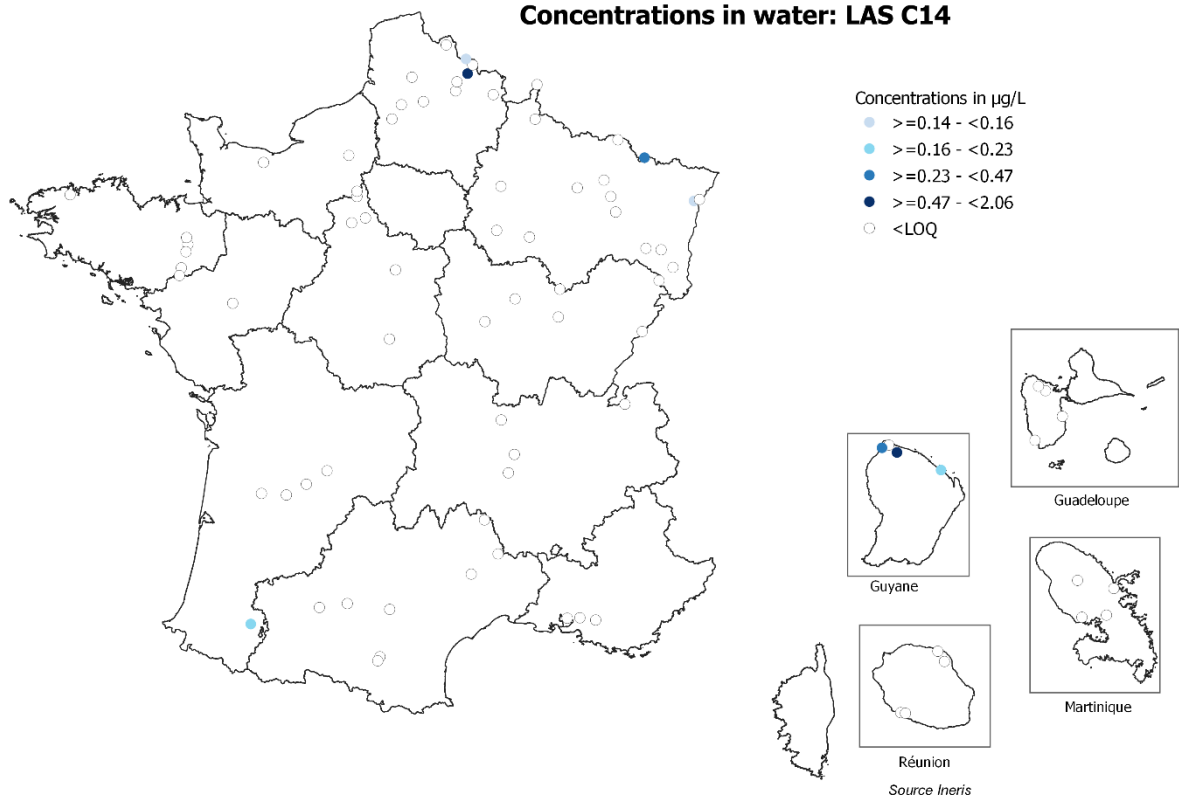
Concentrations in water: Triton X-100



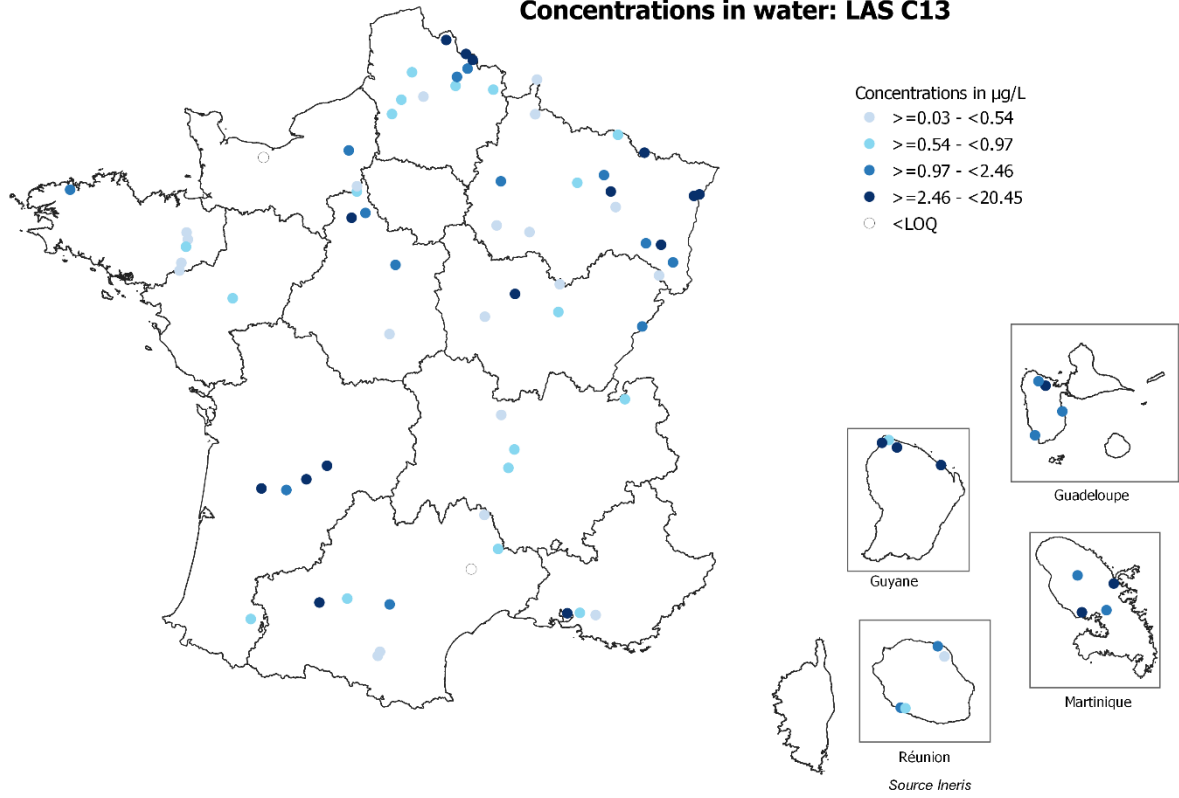
Concentrations in water: LAS C10C14



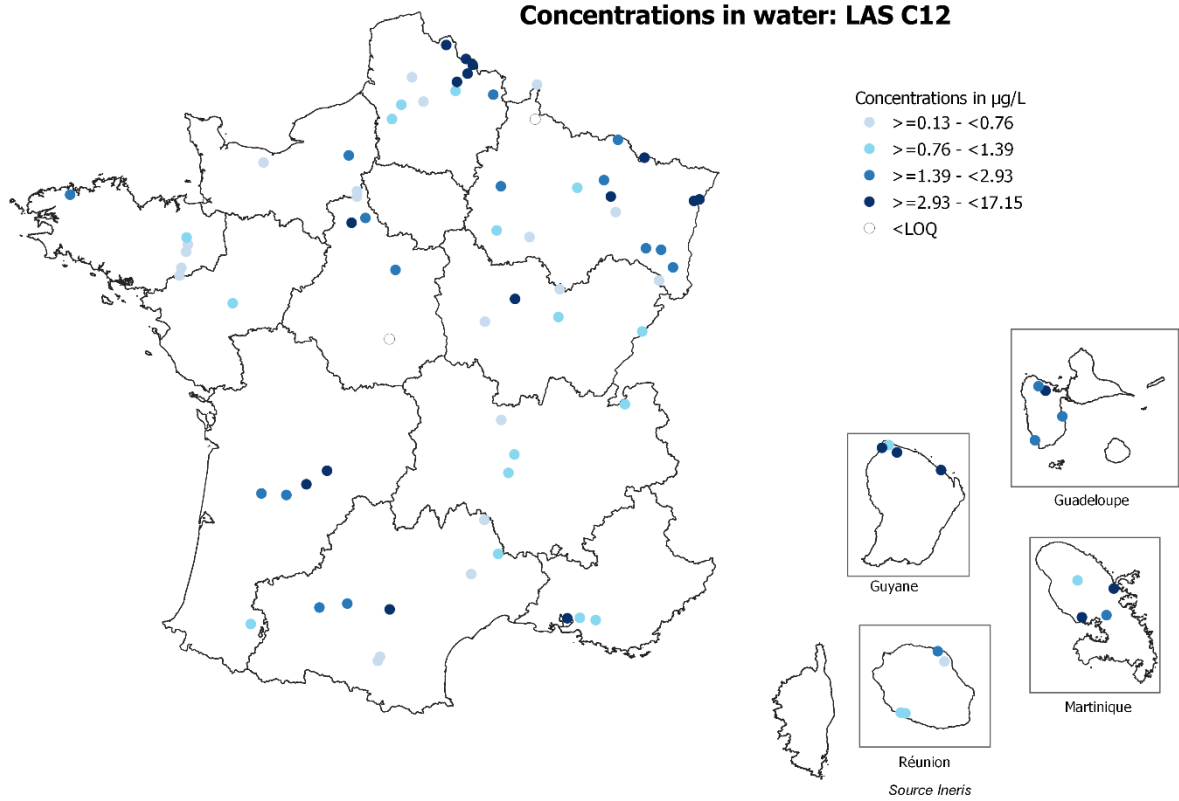
Concentrations in water: LAS C14



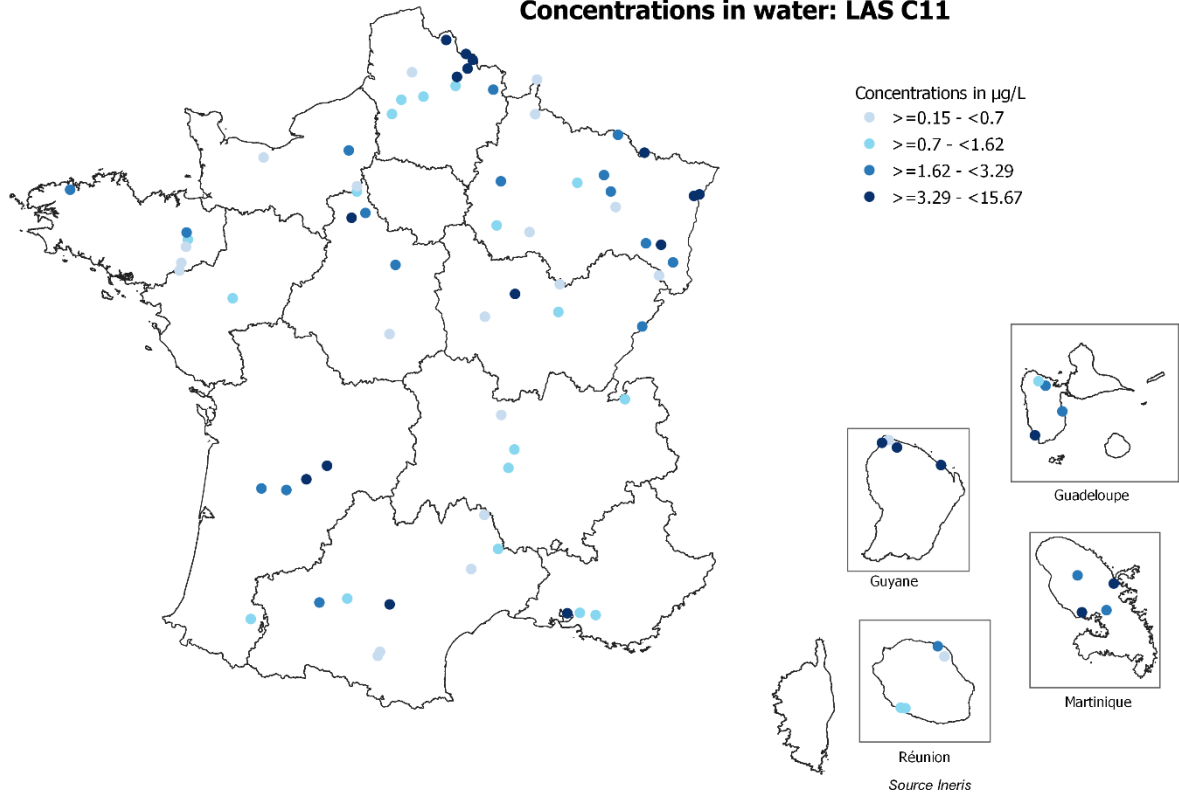
Concentrations in water: LAS C13



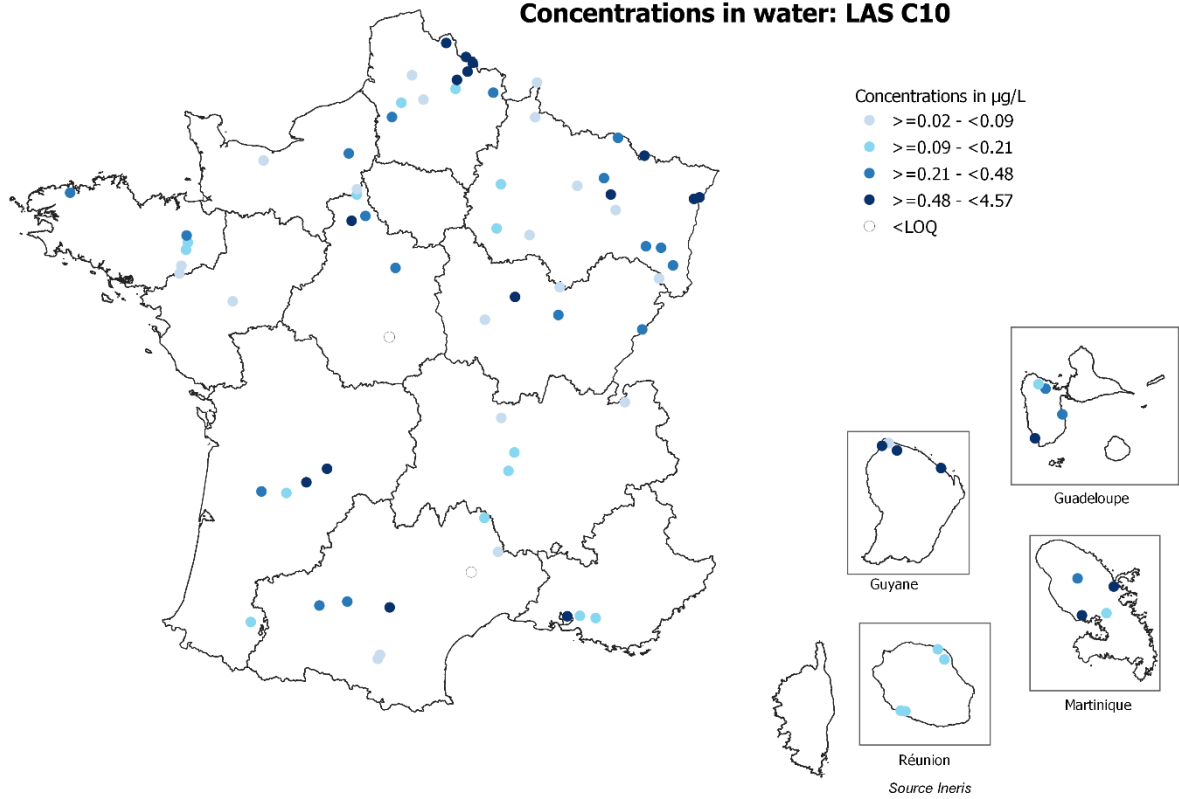
Concentrations in water: LAS C12



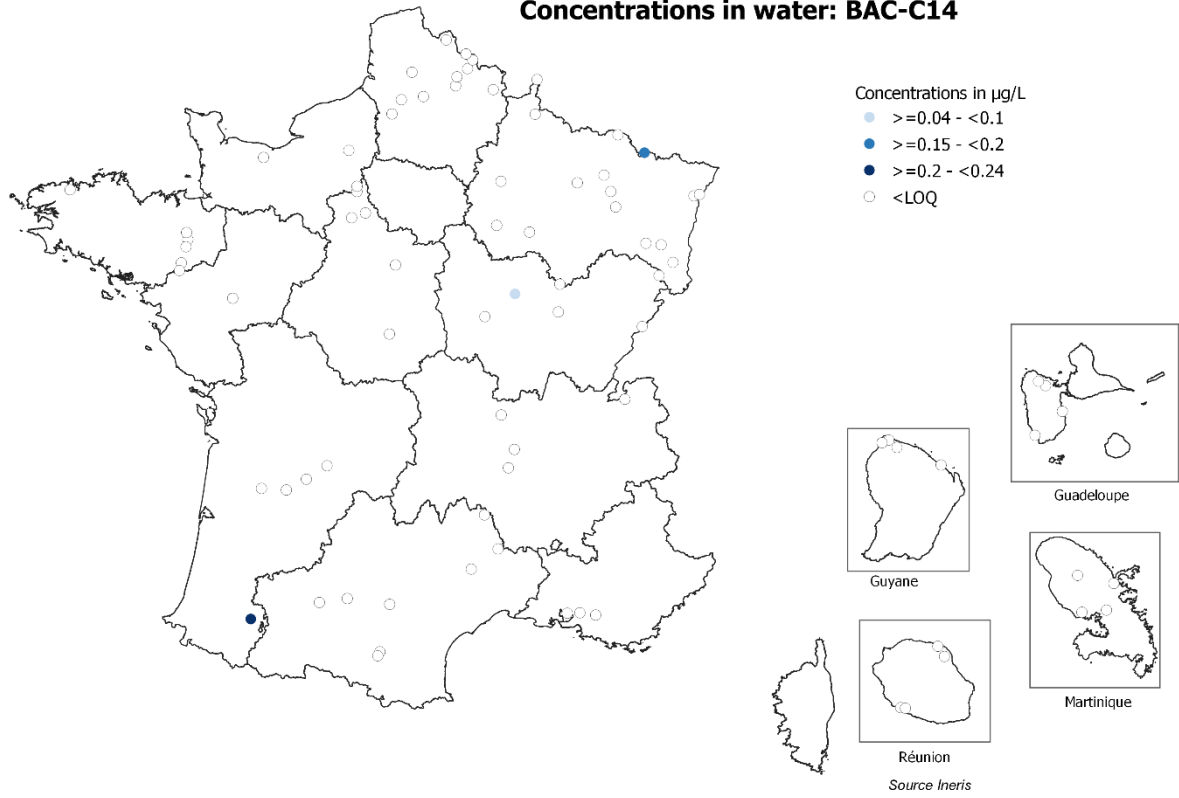
Concentrations in water: LAS C11



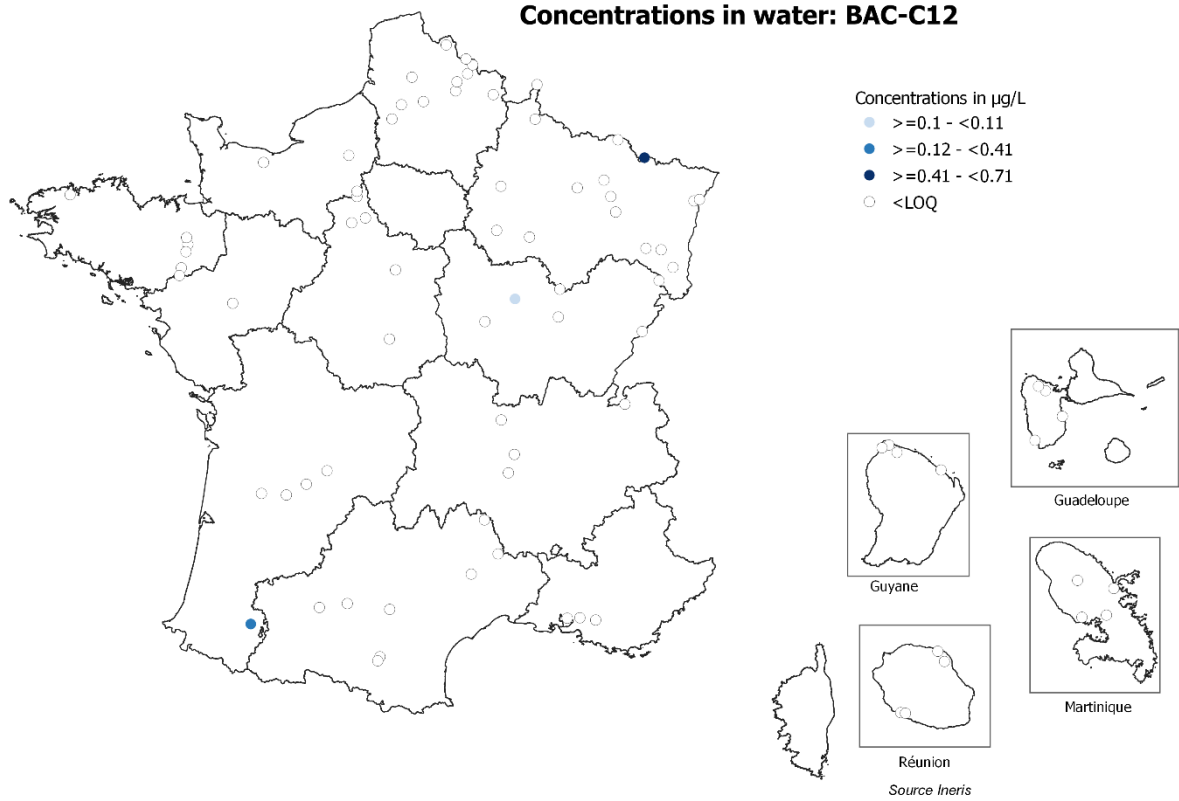
Concentrations in water: LAS C10



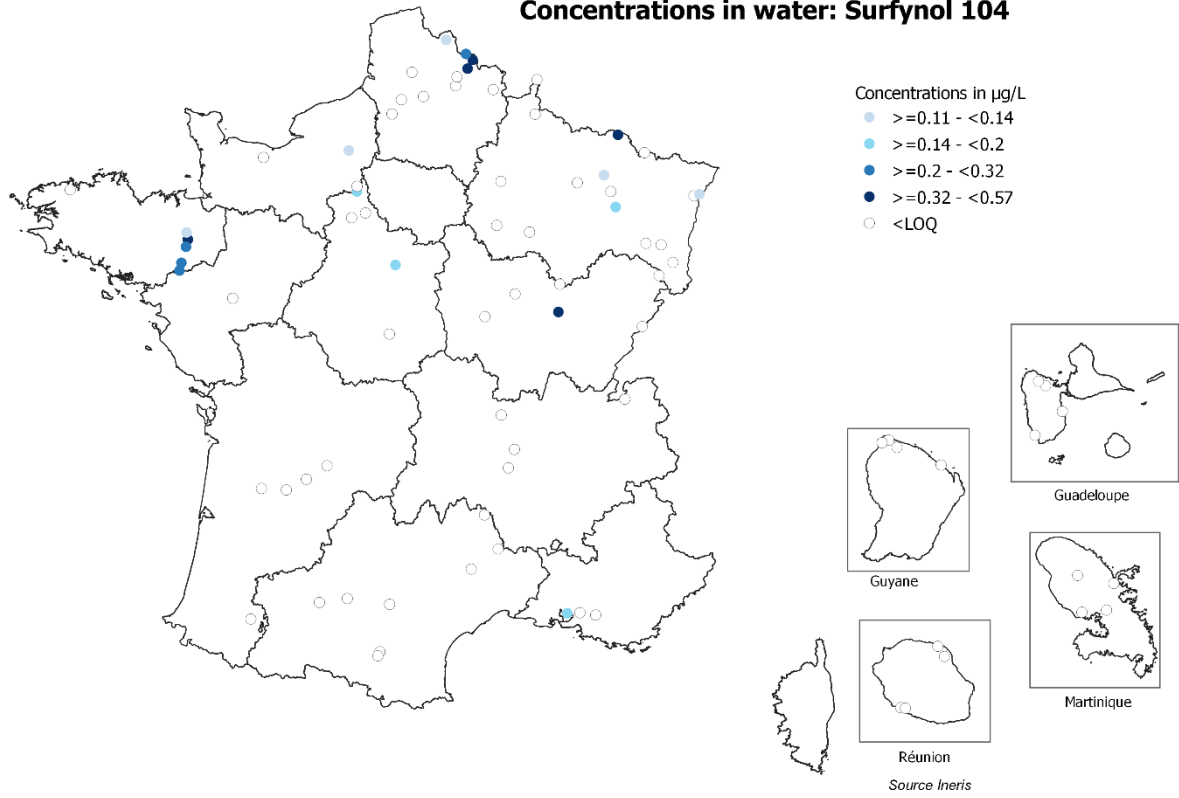
Concentrations in water: BAC-C14



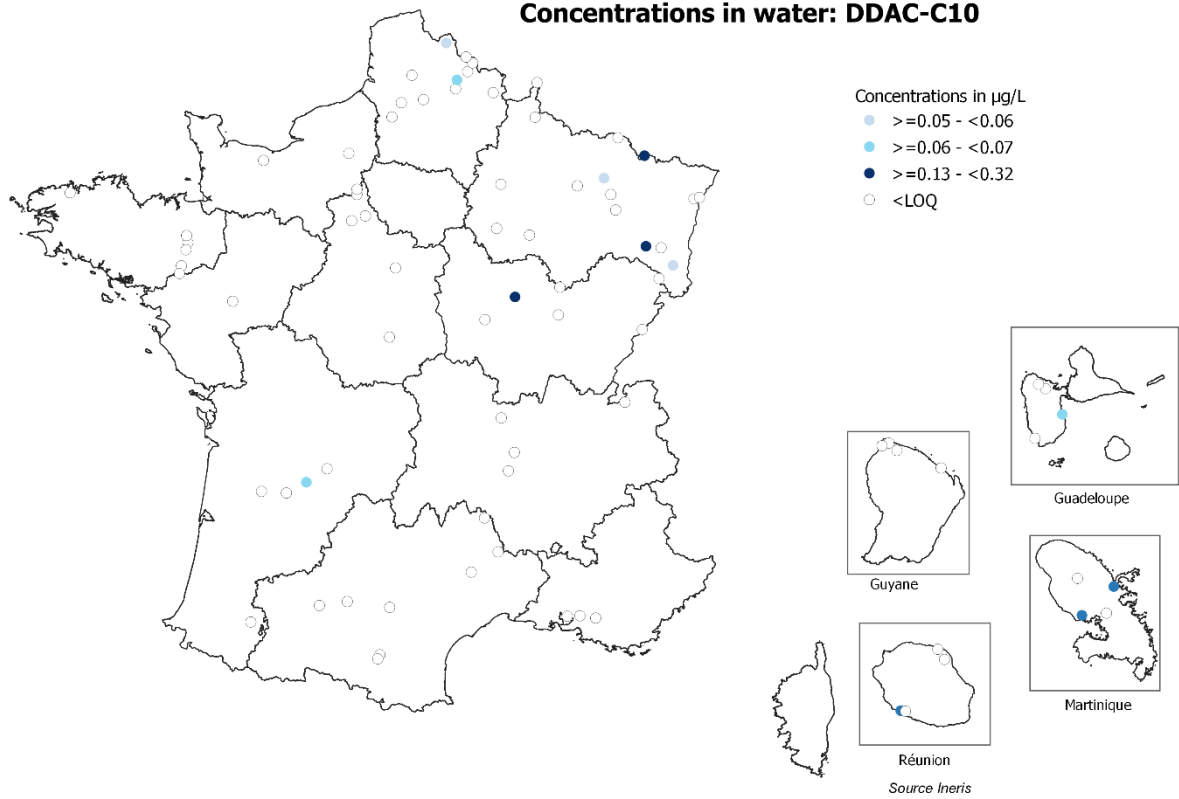
Concentrations in water: BAC-C12



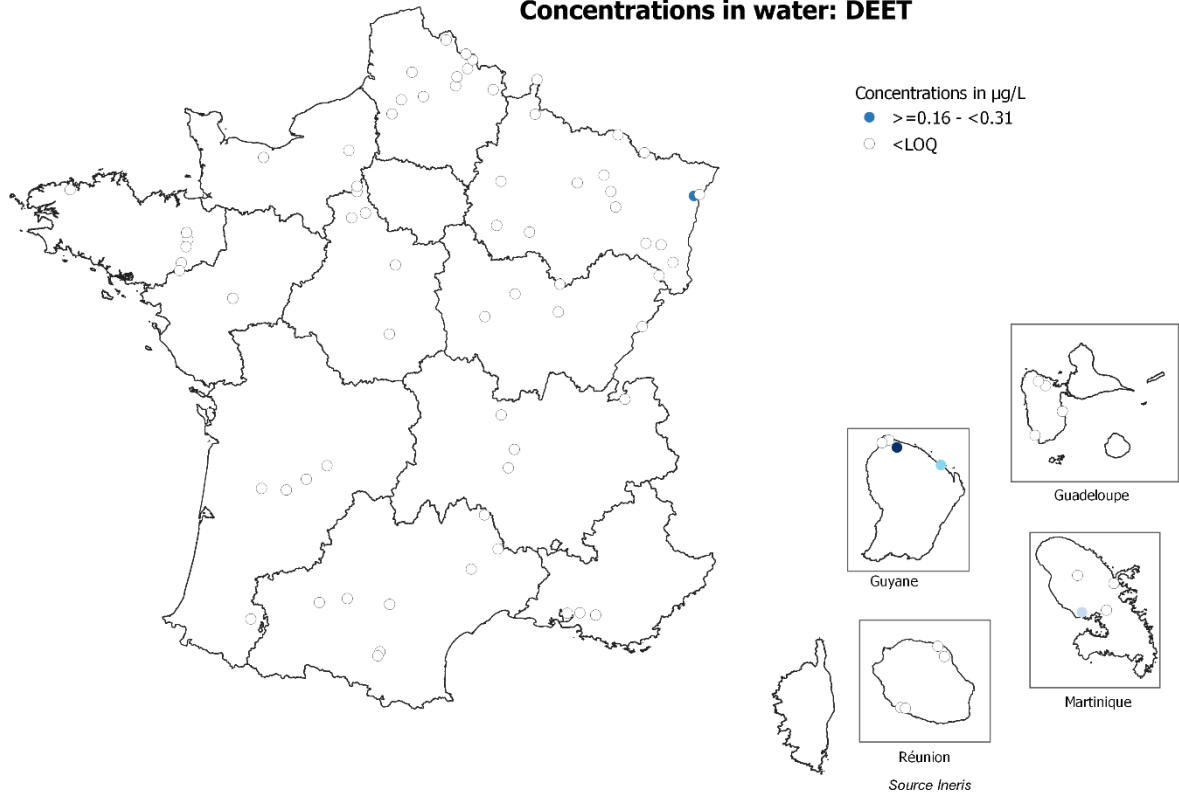
Concentrations in water: Surfynol 104



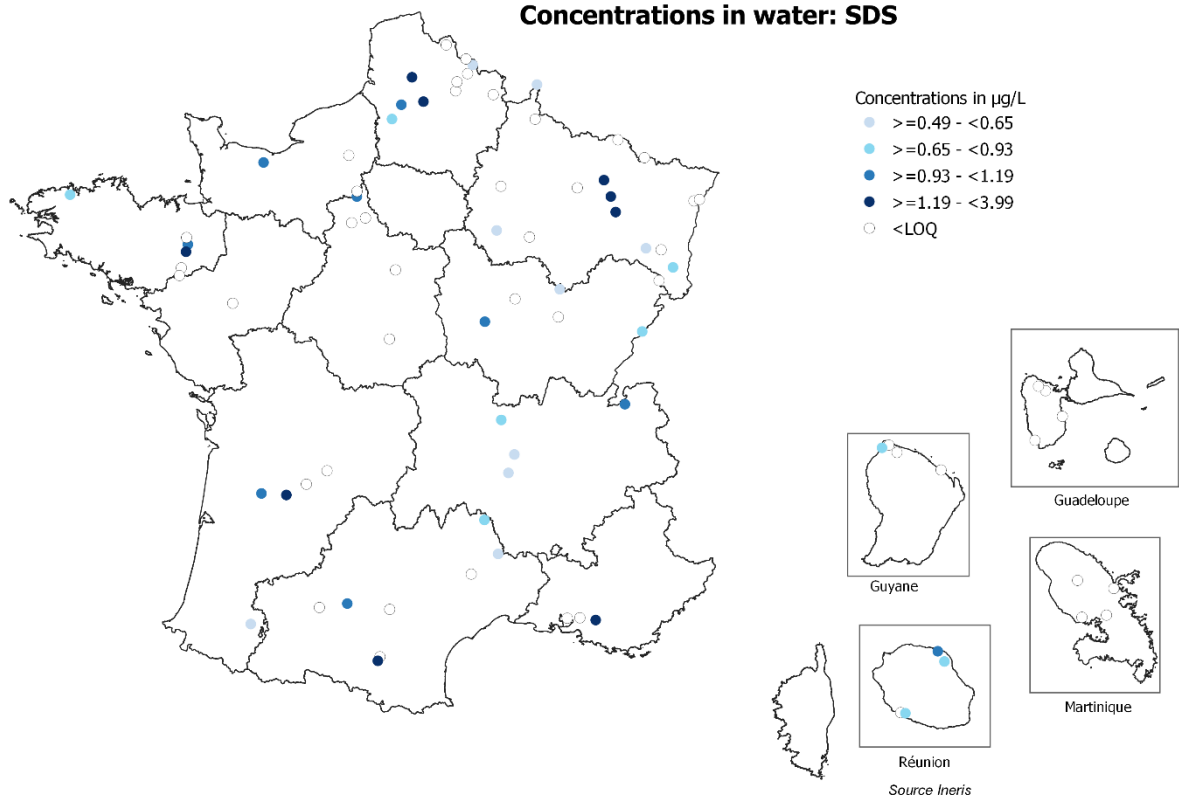
Concentrations in water: DDAC-C10



Concentrations in water: DEET



Concentrations in water: SDS



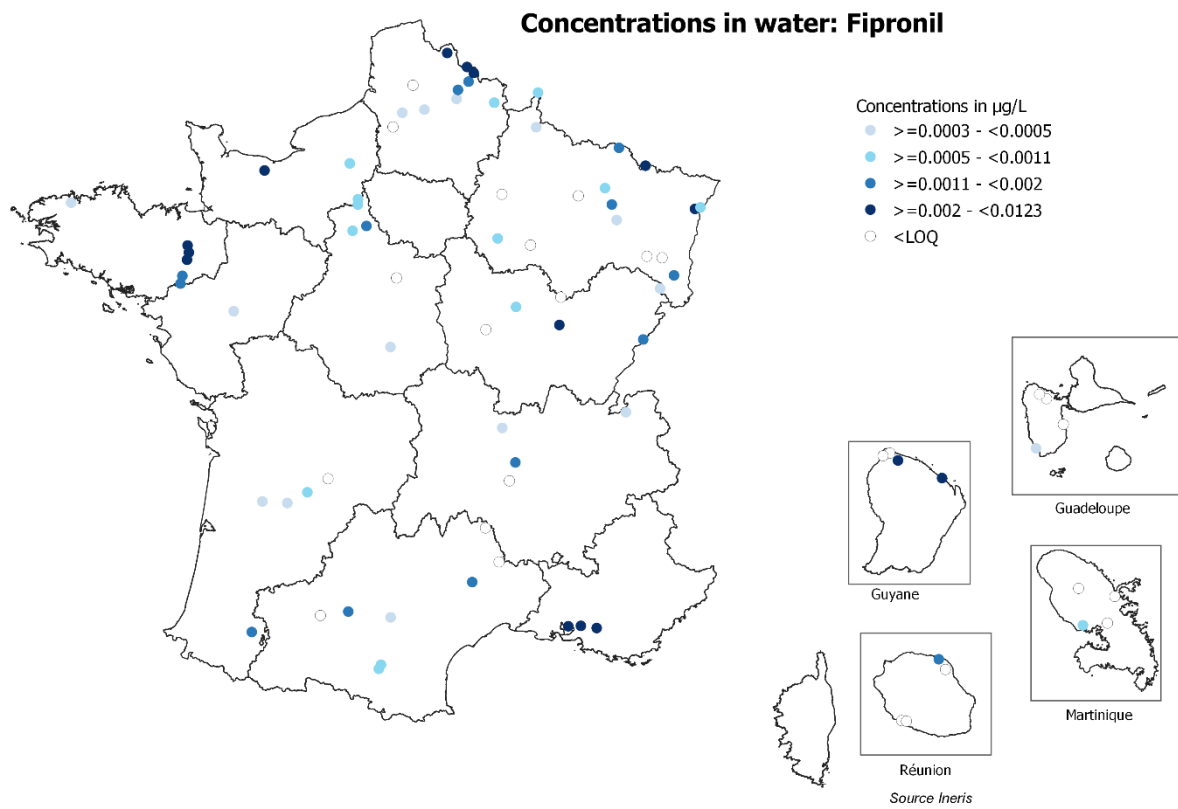
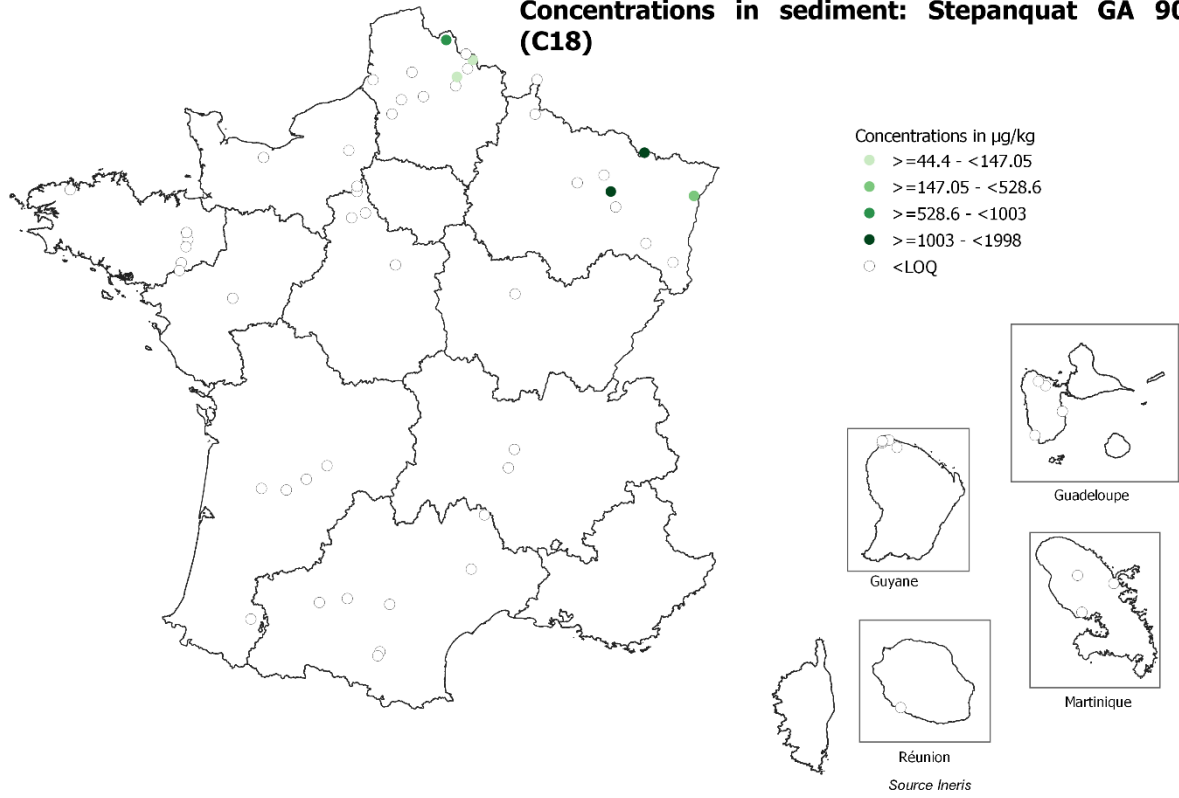
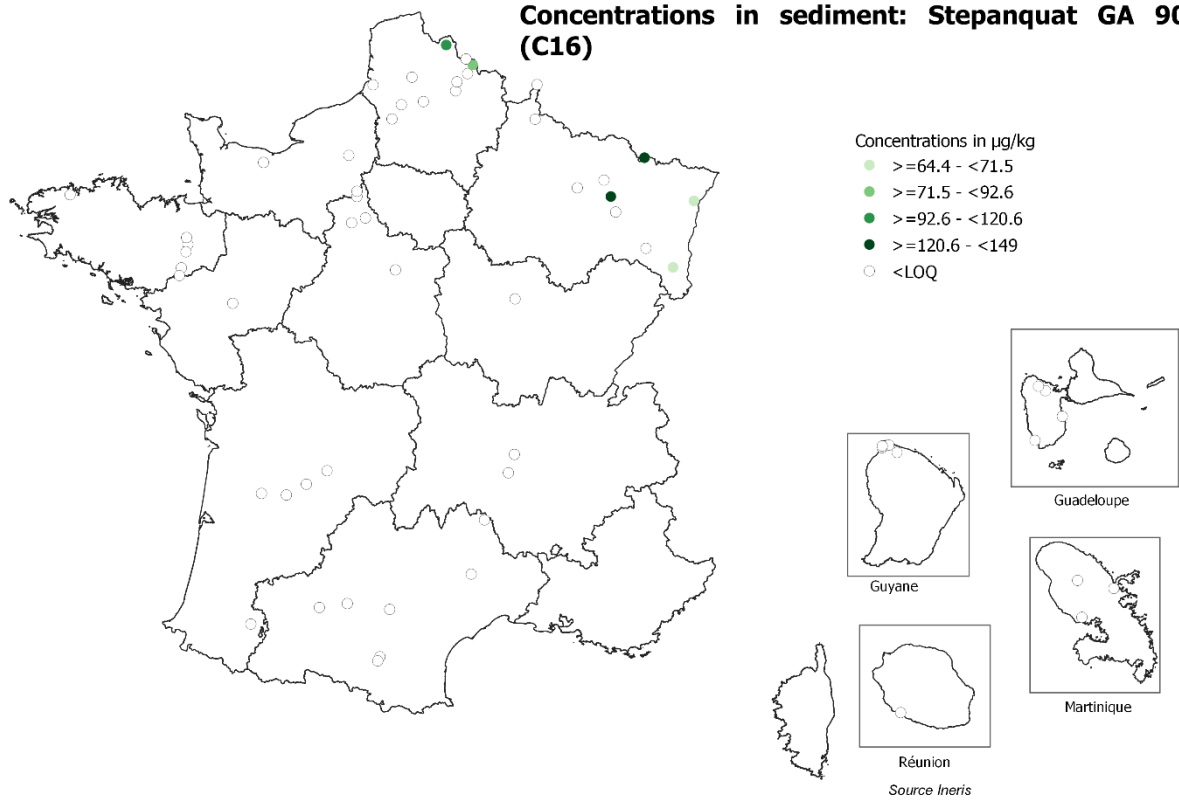


Figure S2. Graphical representations of the concentrations of each target contaminant quantified at least once in sediment

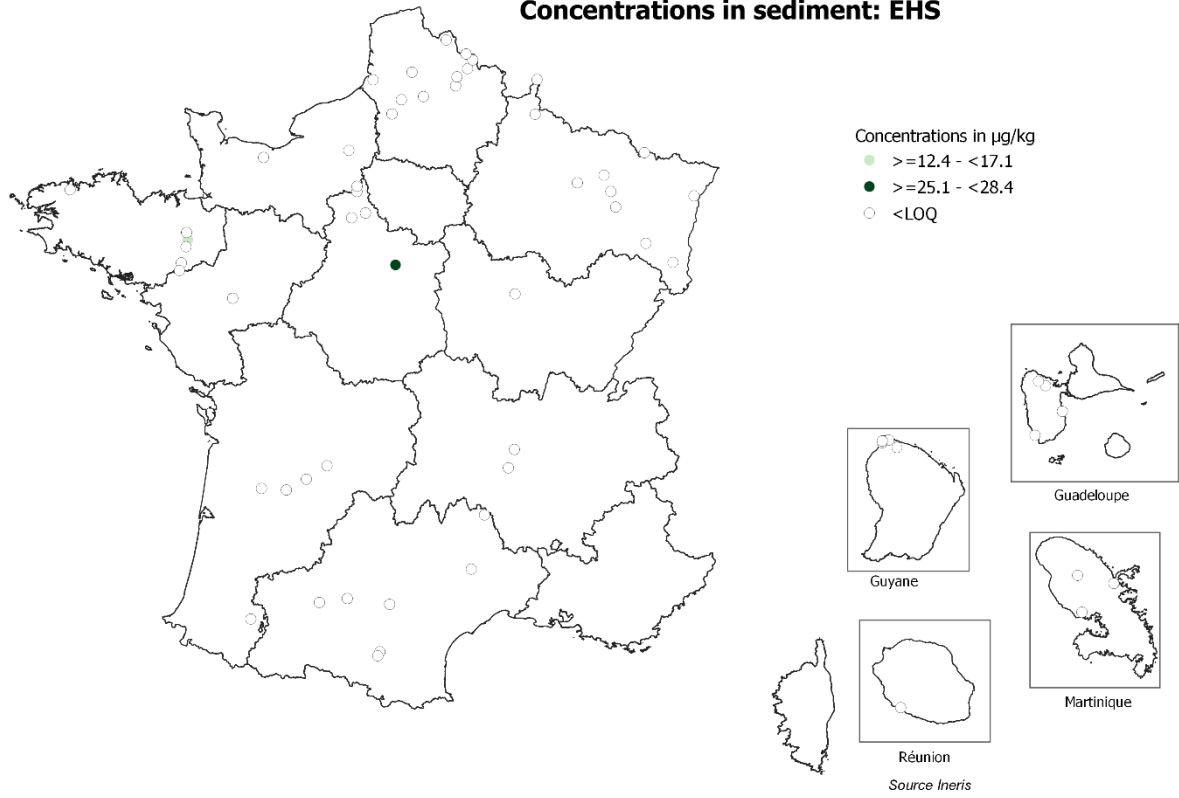
Concentrations in sediment: Stepanquat GA 90 (C18)



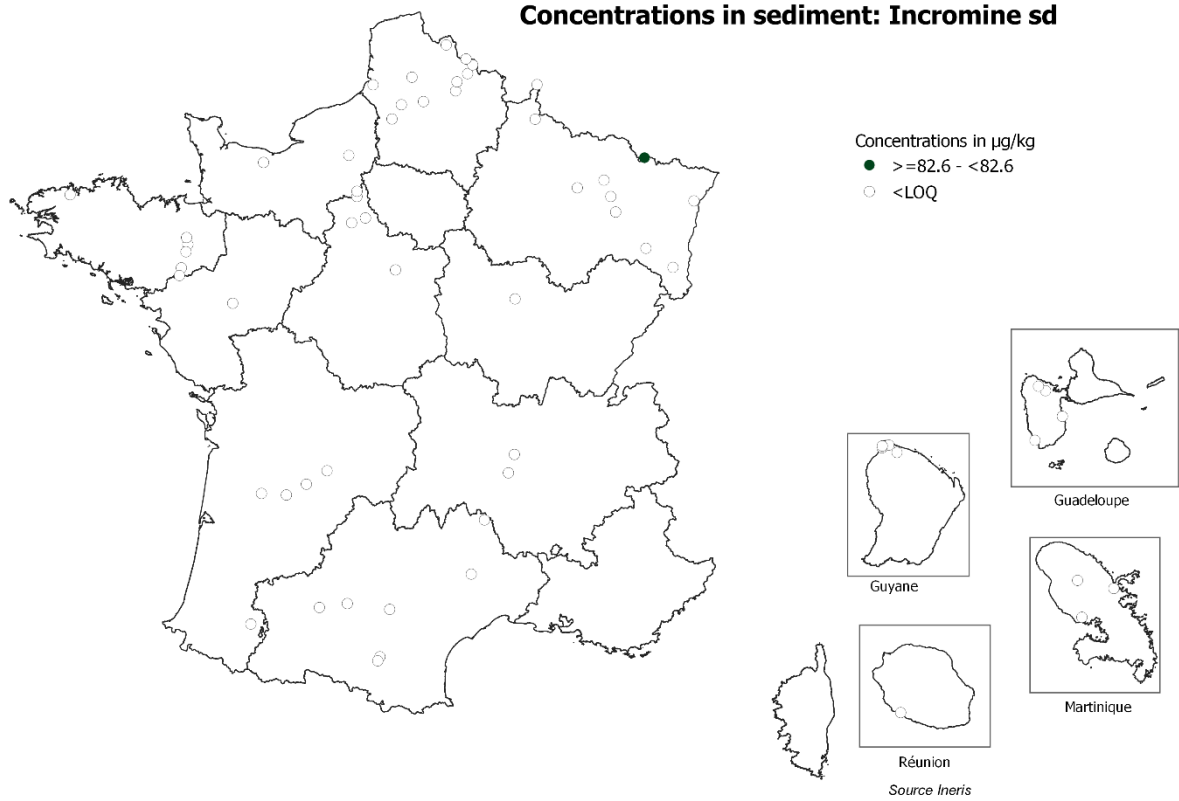
Concentrations in sediment: Stepanquat GA 90 (C16)



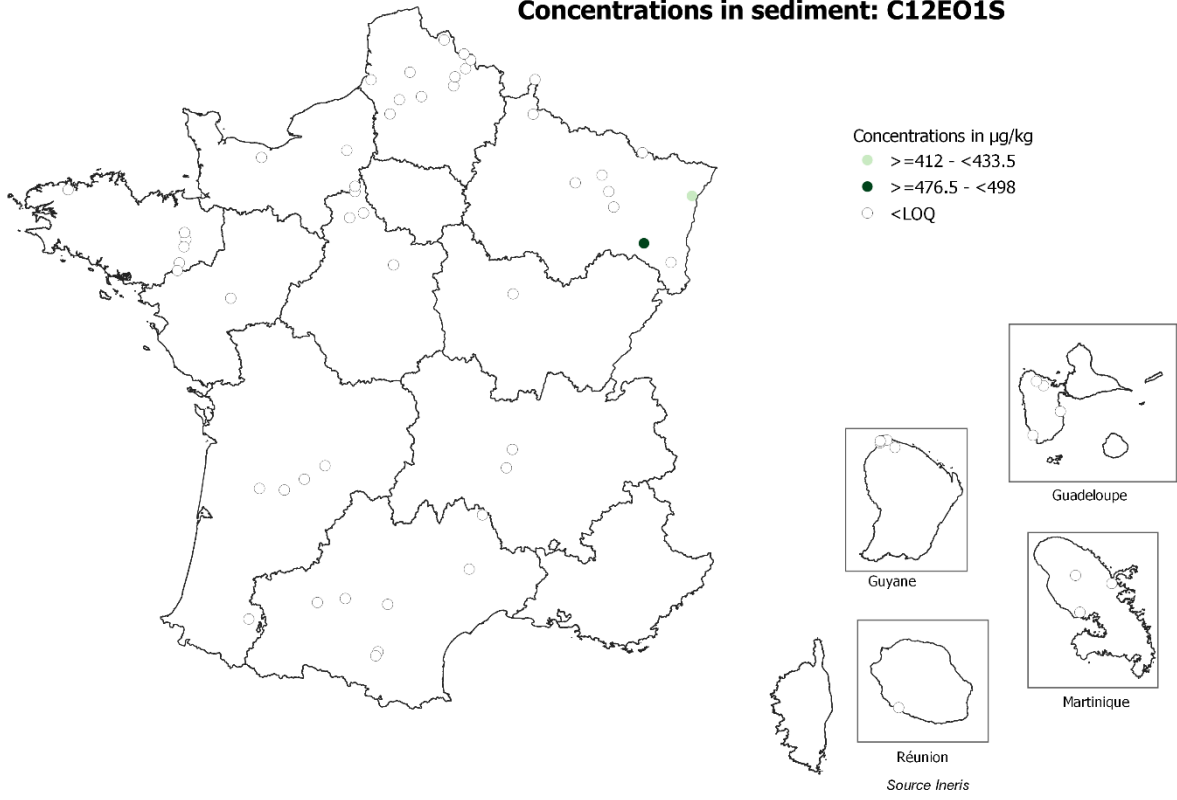
Concentrations in sediment: EHS



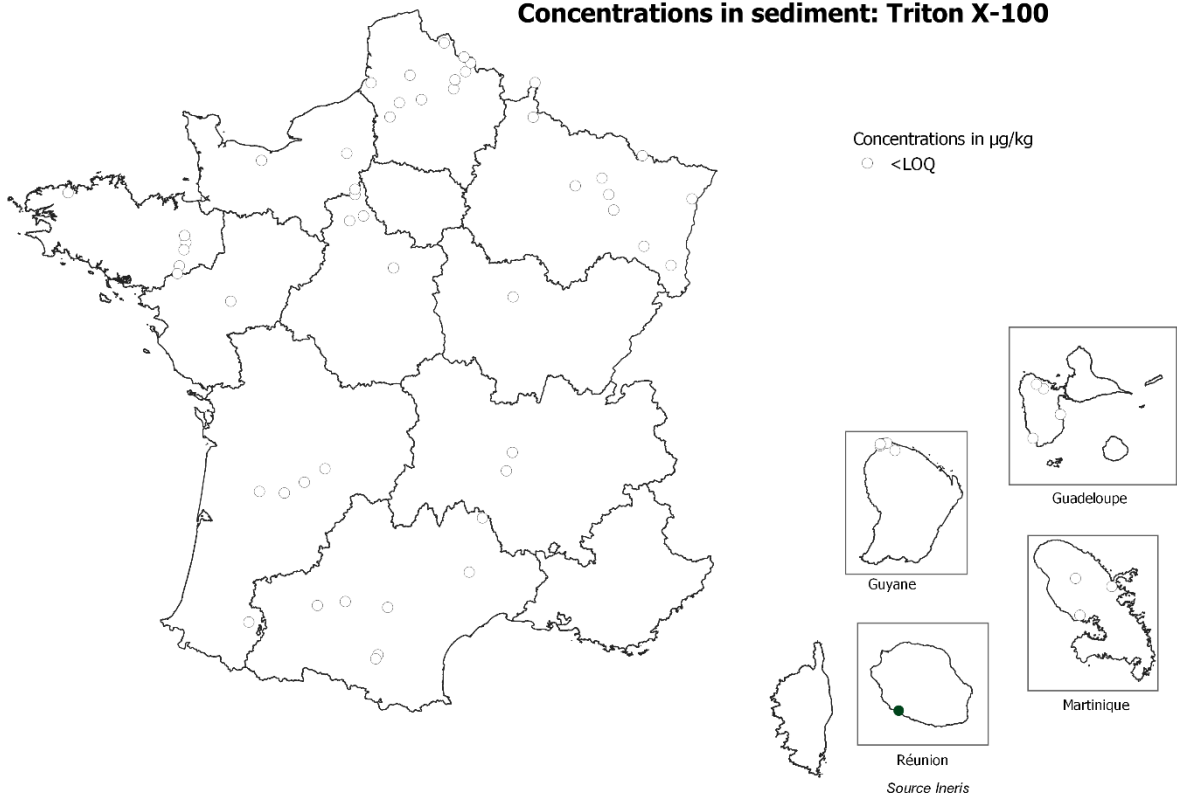
Concentrations in sediment: Incromine sd



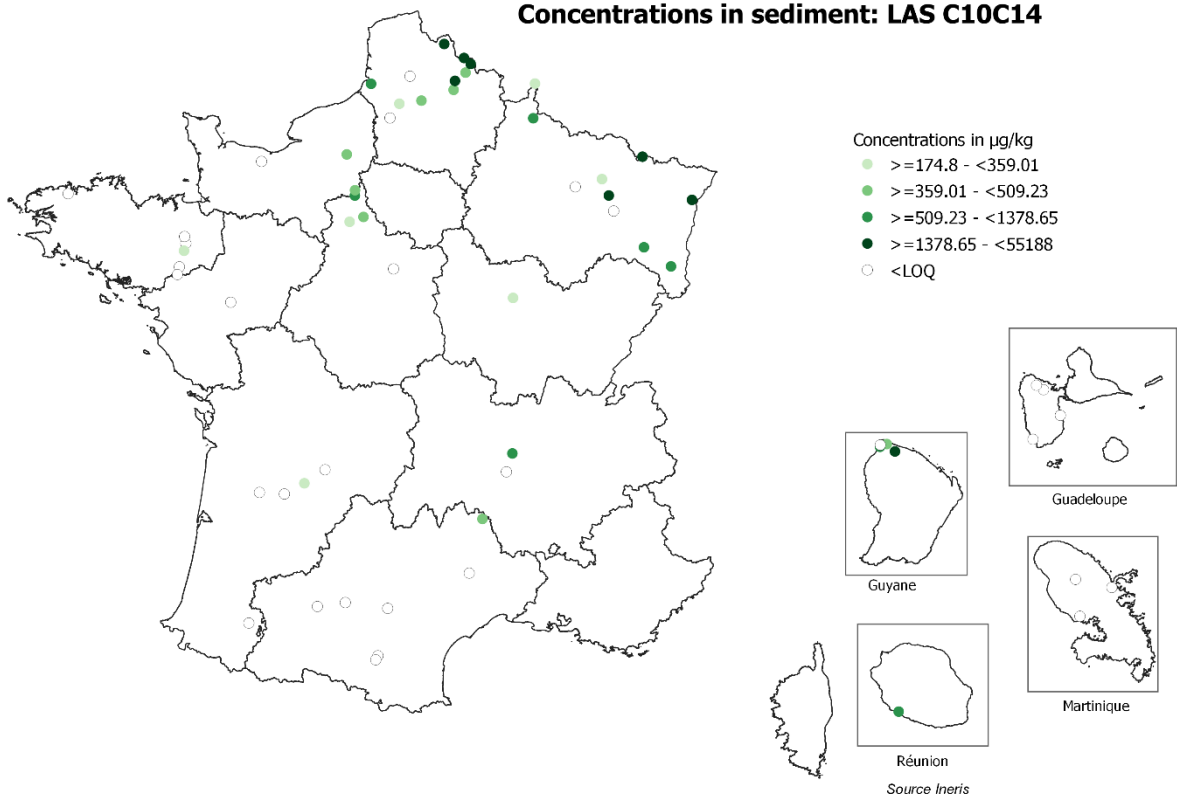
Concentrations in sediment: C12E01S



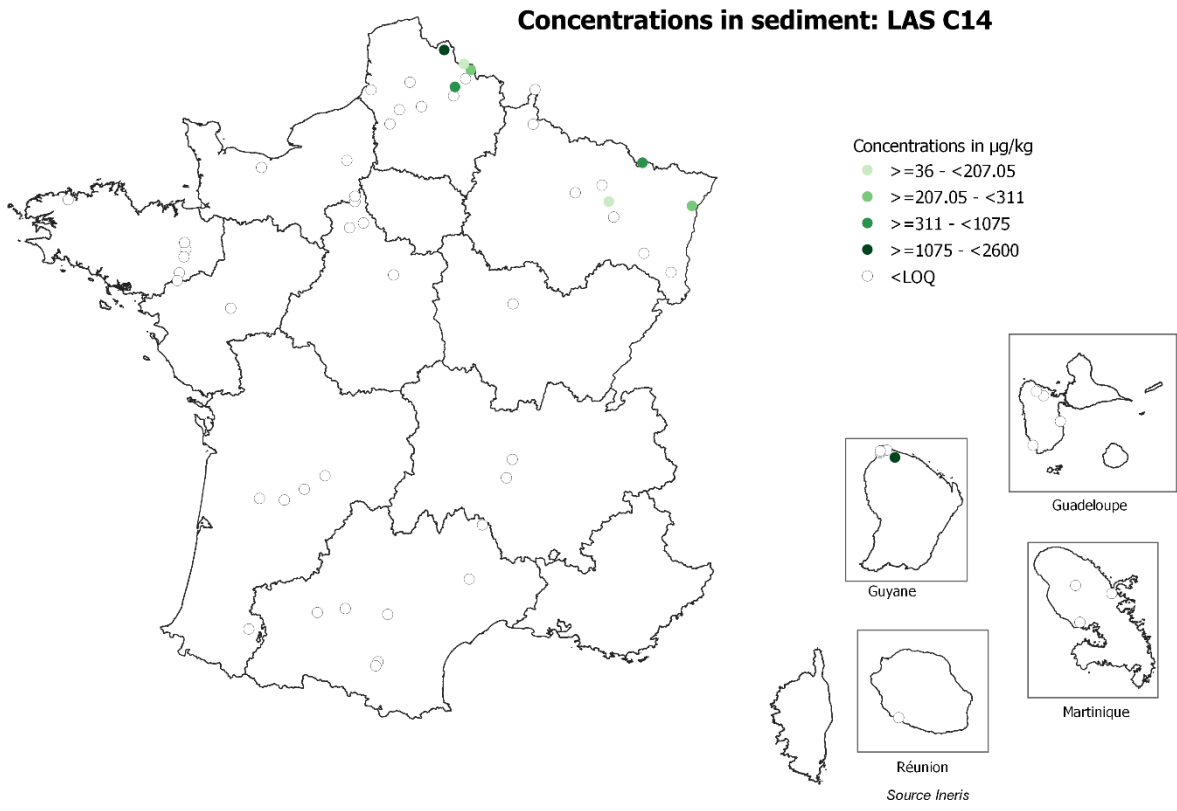
Concentrations in sediment: Triton X-100



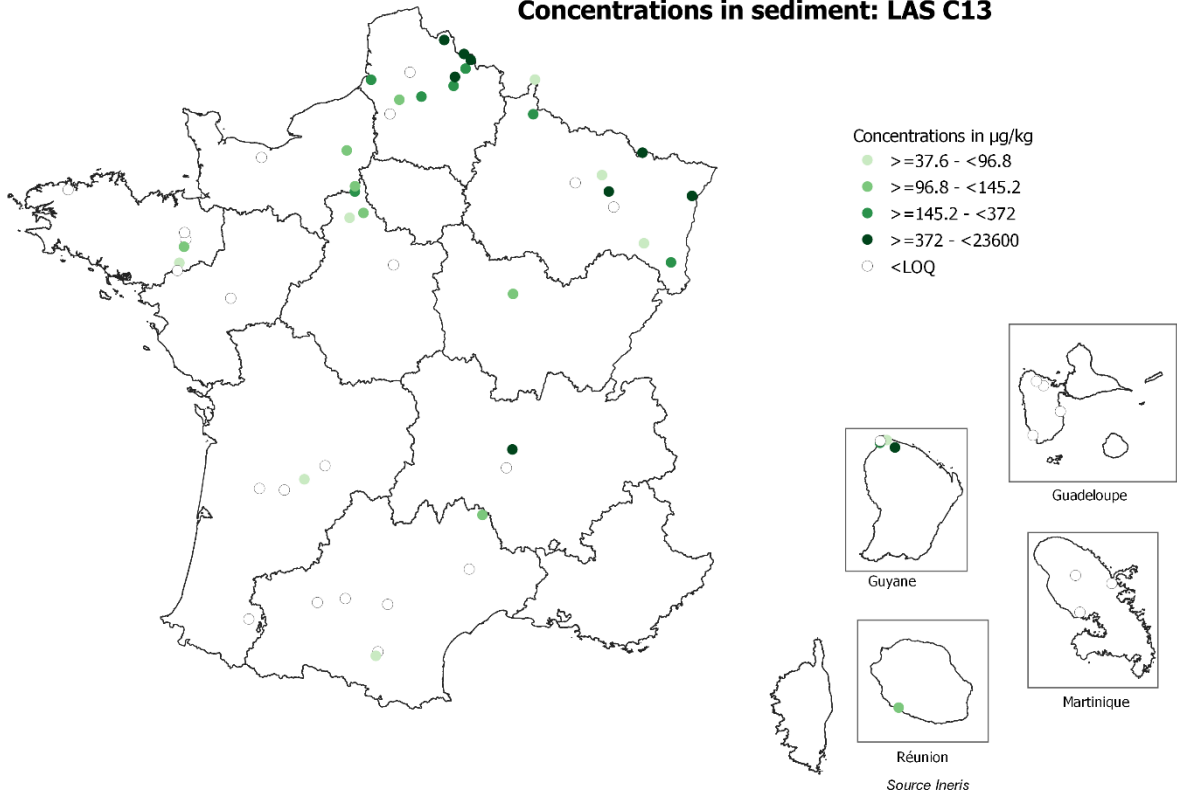
Concentrations in sediment: LAS C10C14



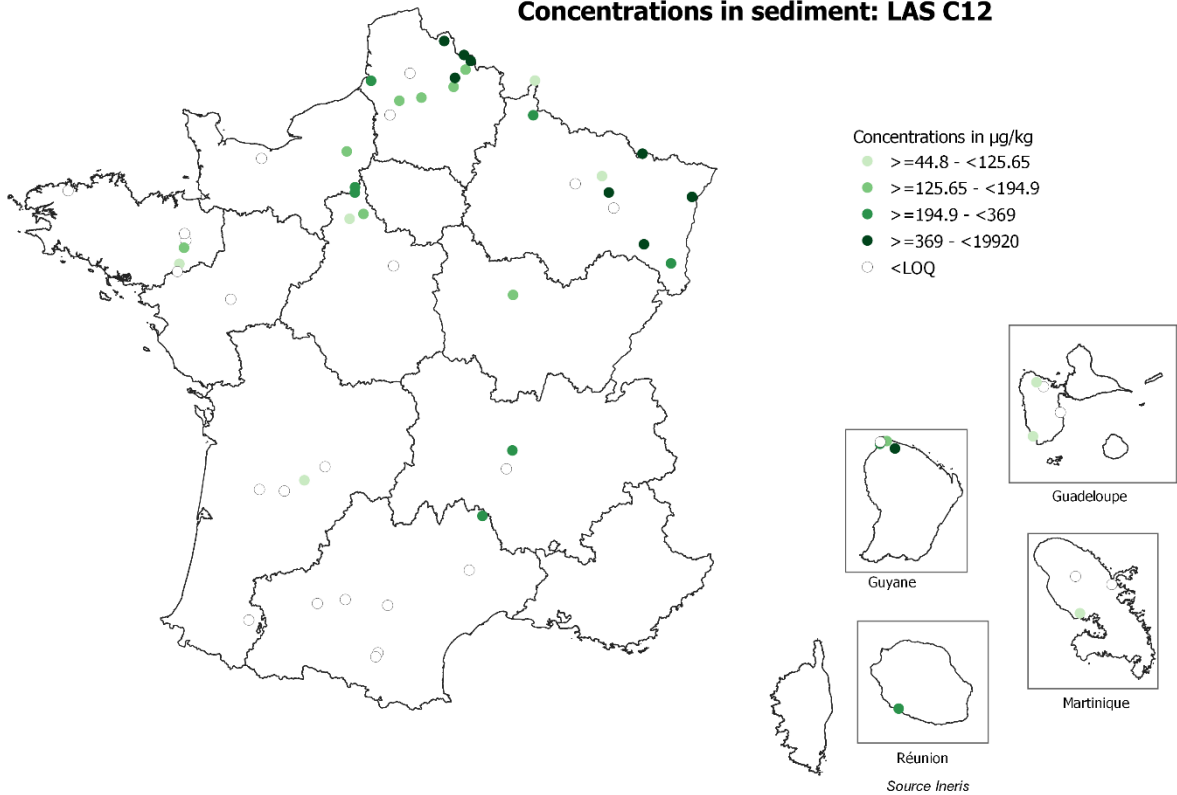
Concentrations in sediment: LAS C14



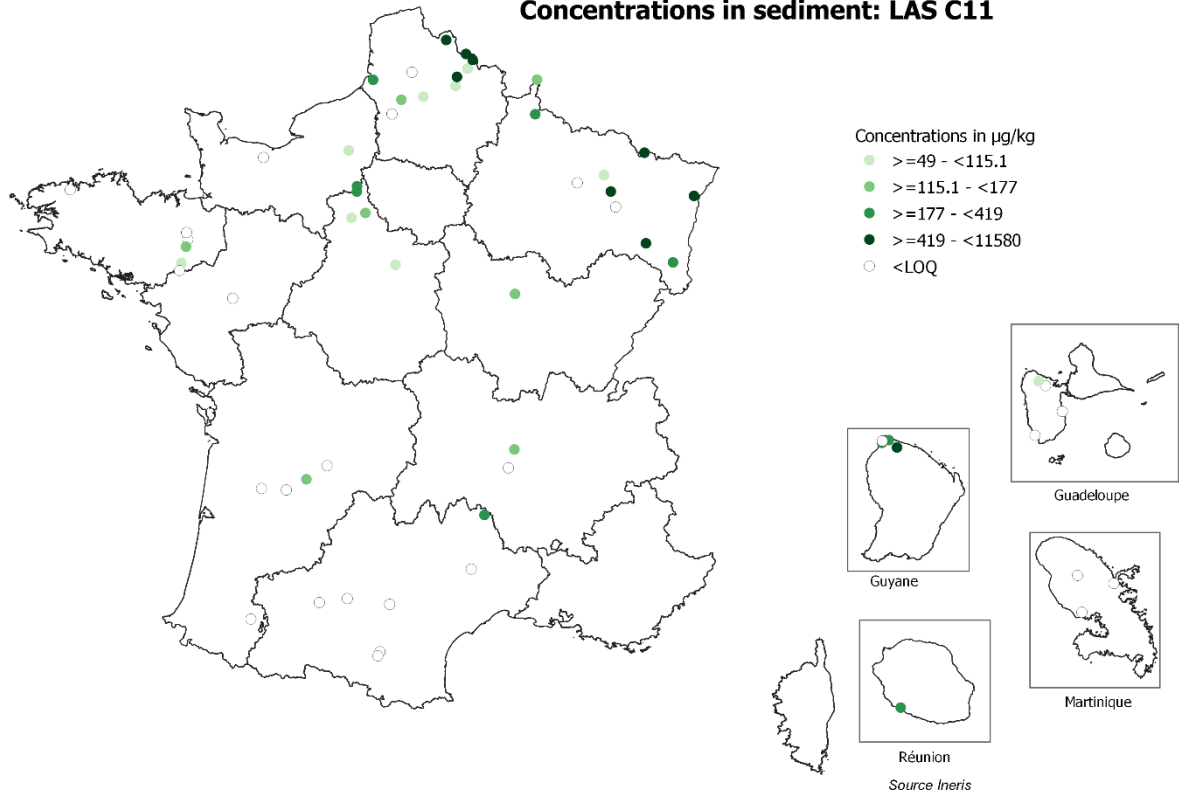
Concentrations in sediment: LAS C13



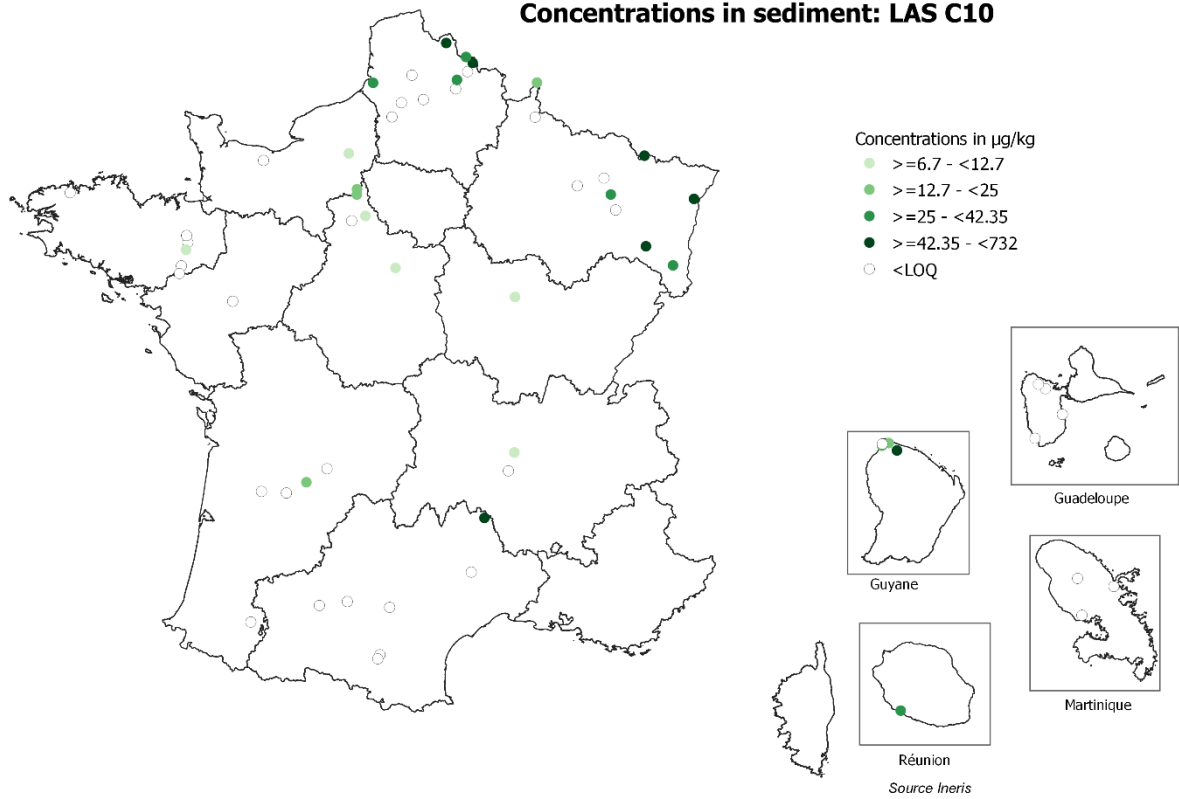
Concentrations in sediment: LAS C12



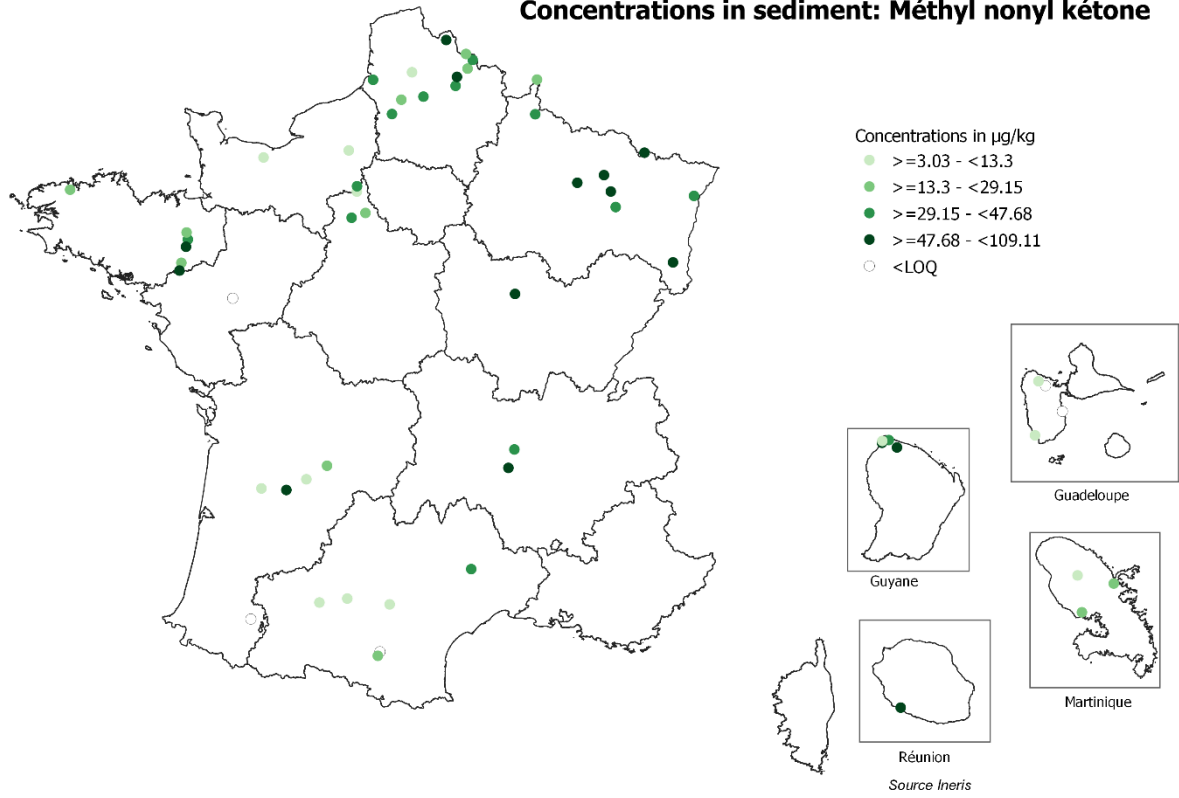
Concentrations in sediment: LAS C11



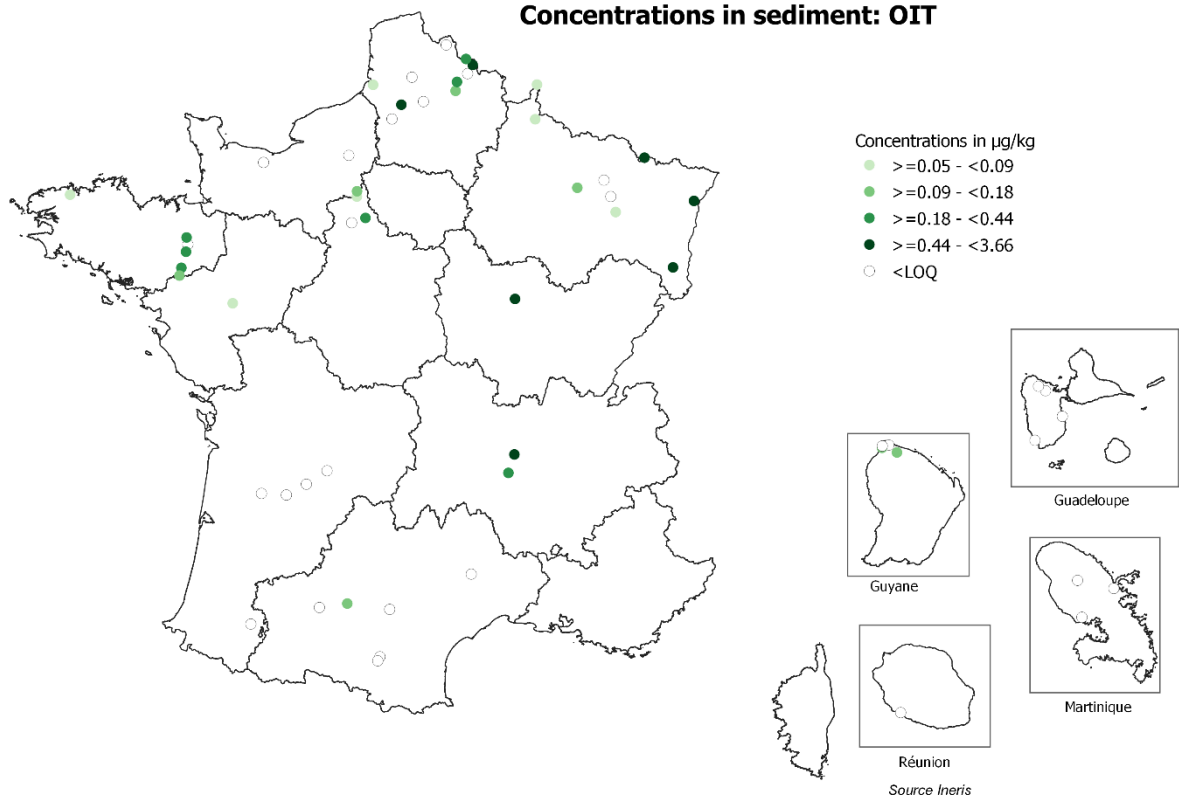
Concentrations in sediment: LAS C10



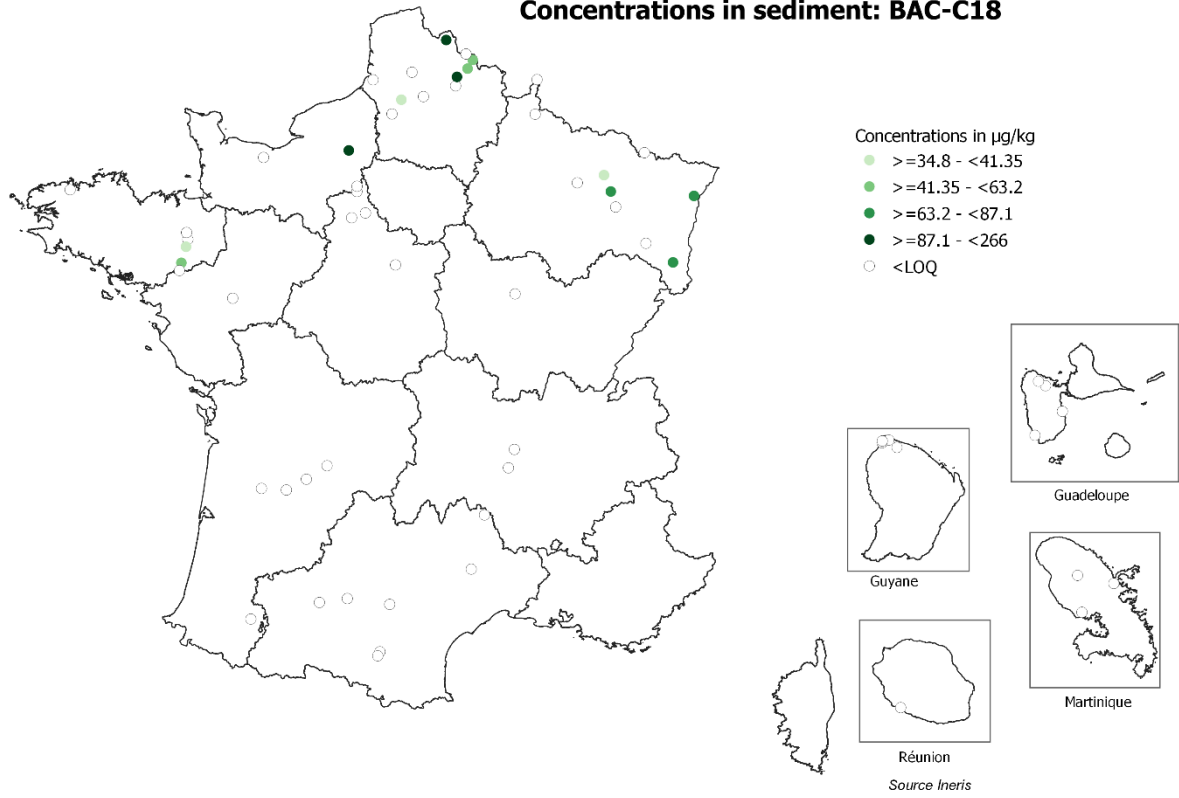
Concentrations in sediment: Méthyl nonyl k tone



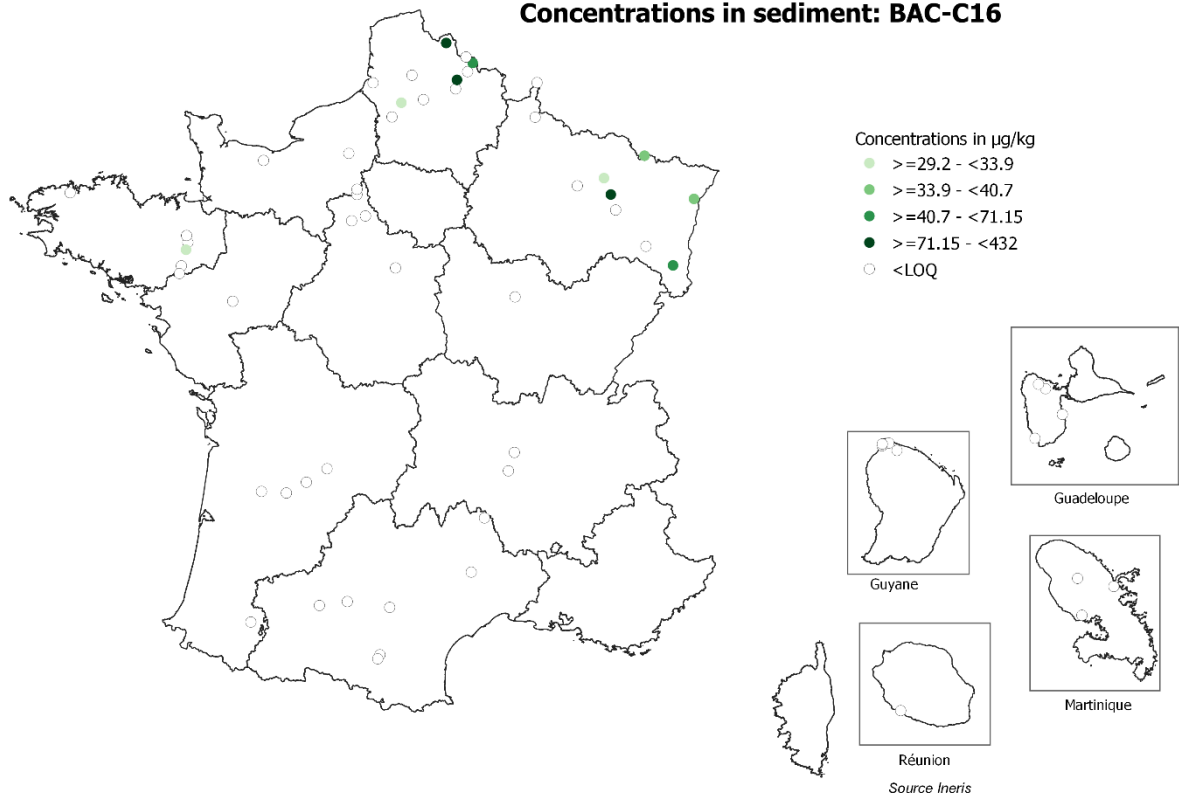
Concentrations in sediment: OIT



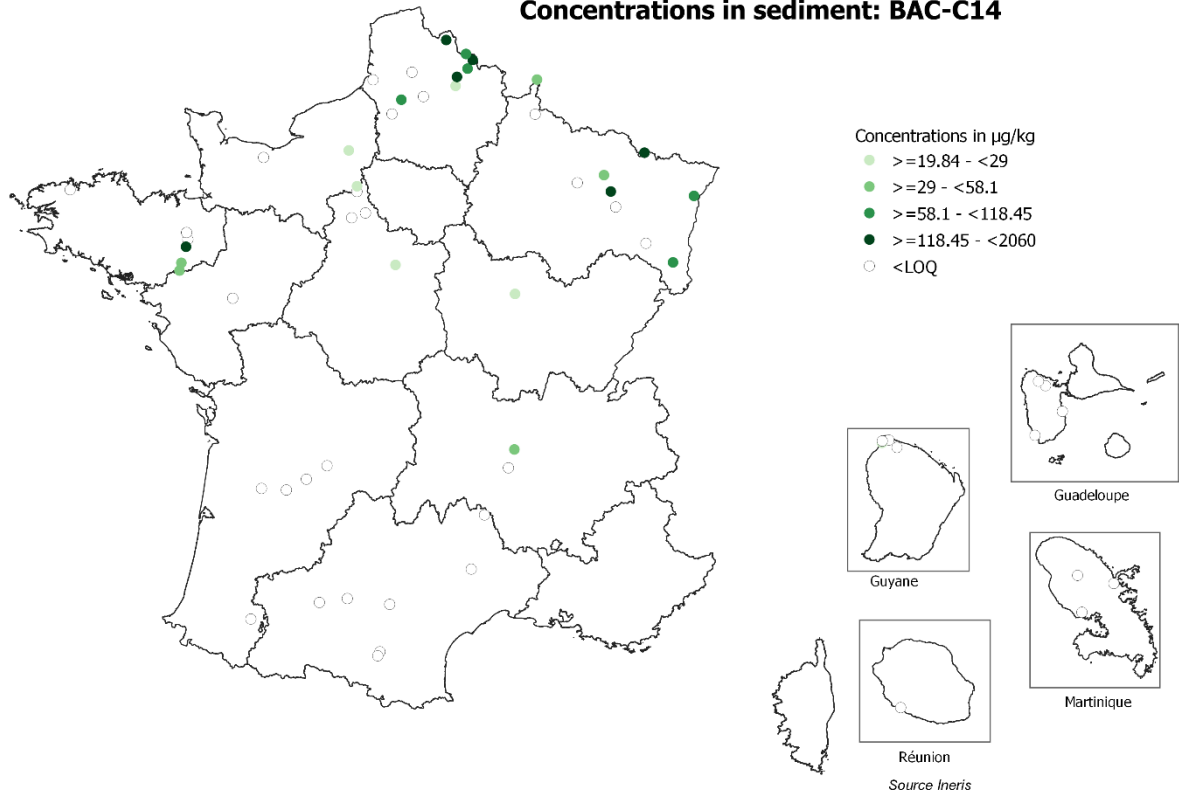
Concentrations in sediment: BAC-C18



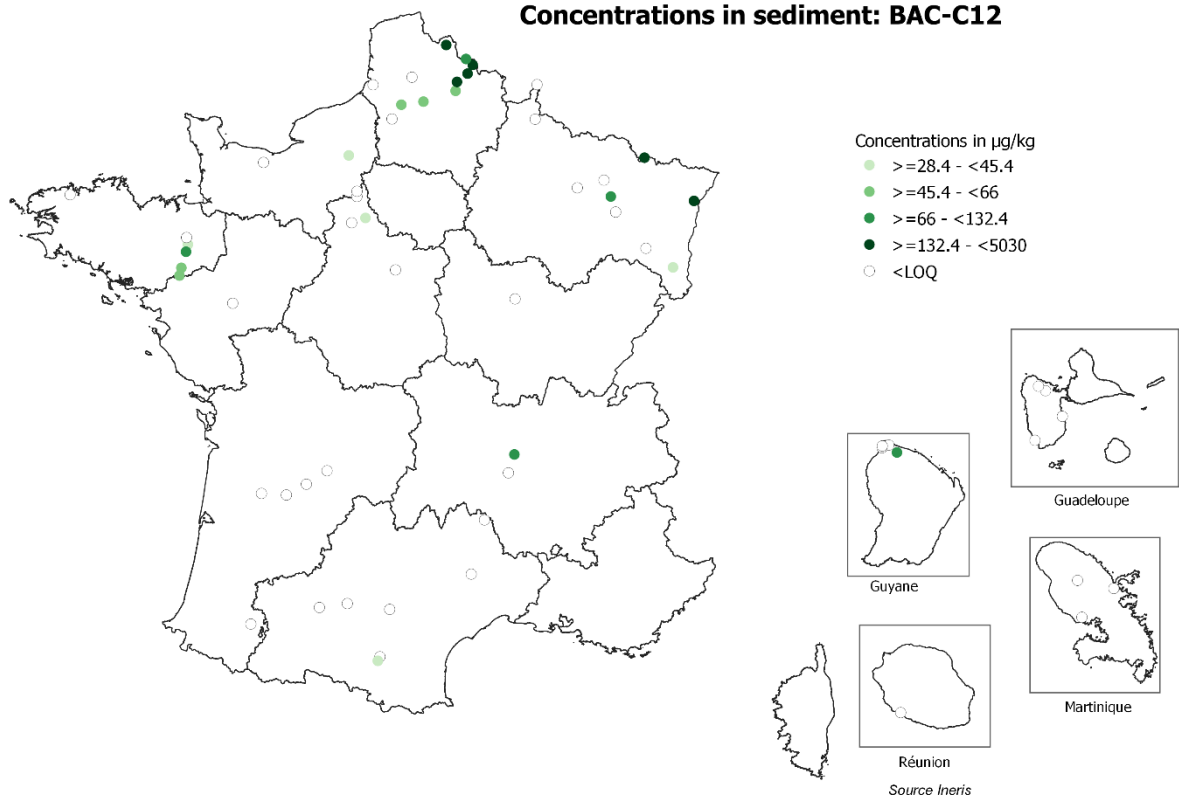
Concentrations in sediment: BAC-C16



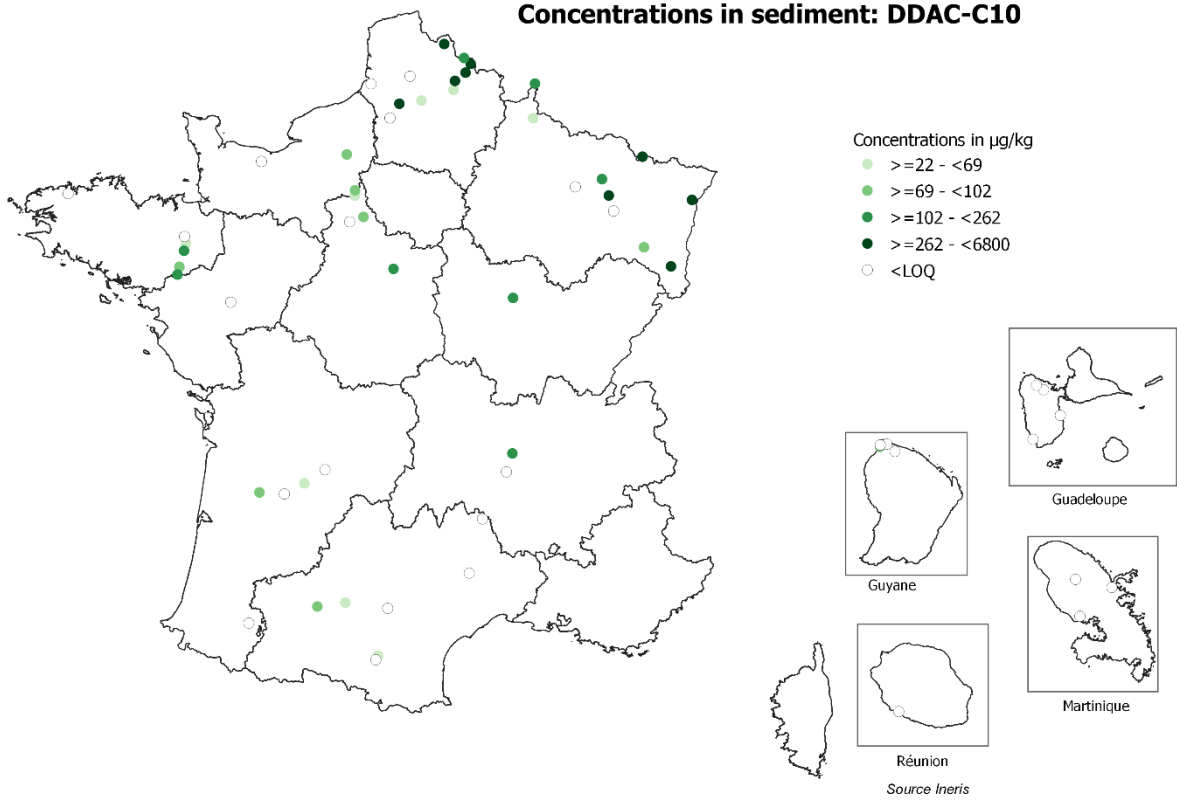
Concentrations in sediment: BAC-C14



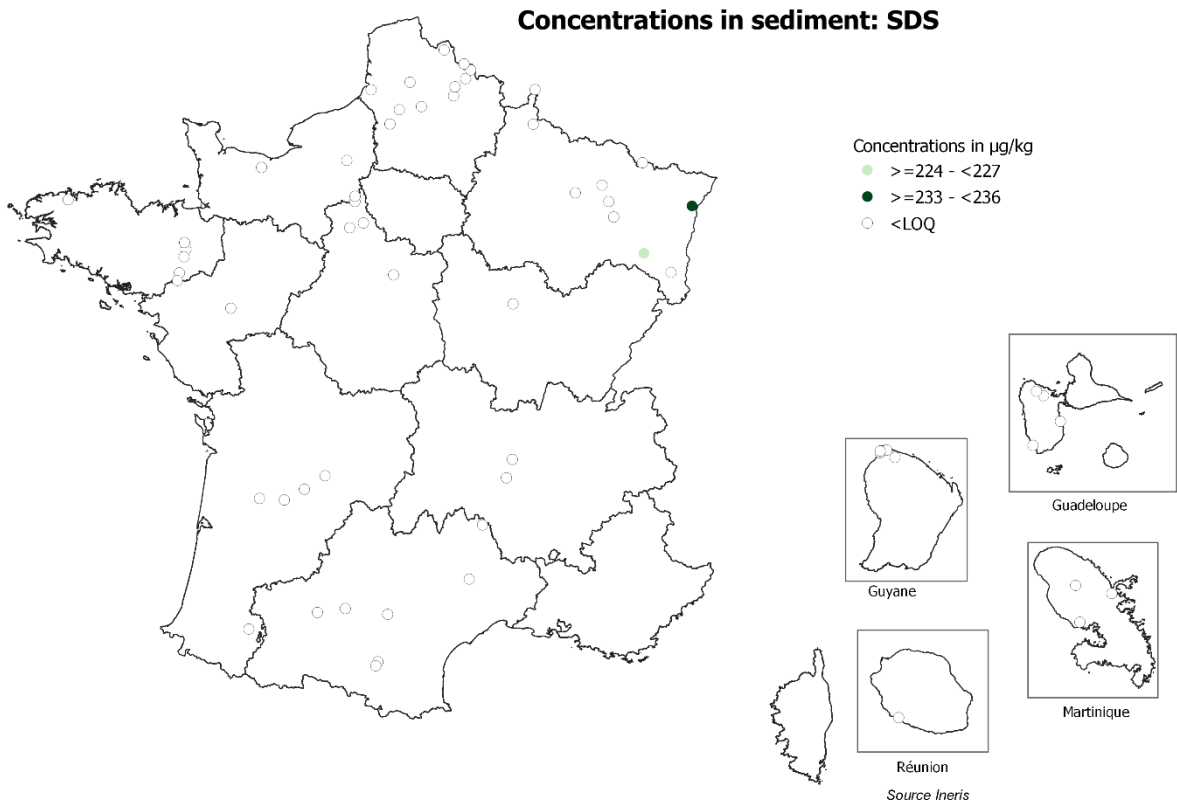
Concentrations in sediment: BAC-C12



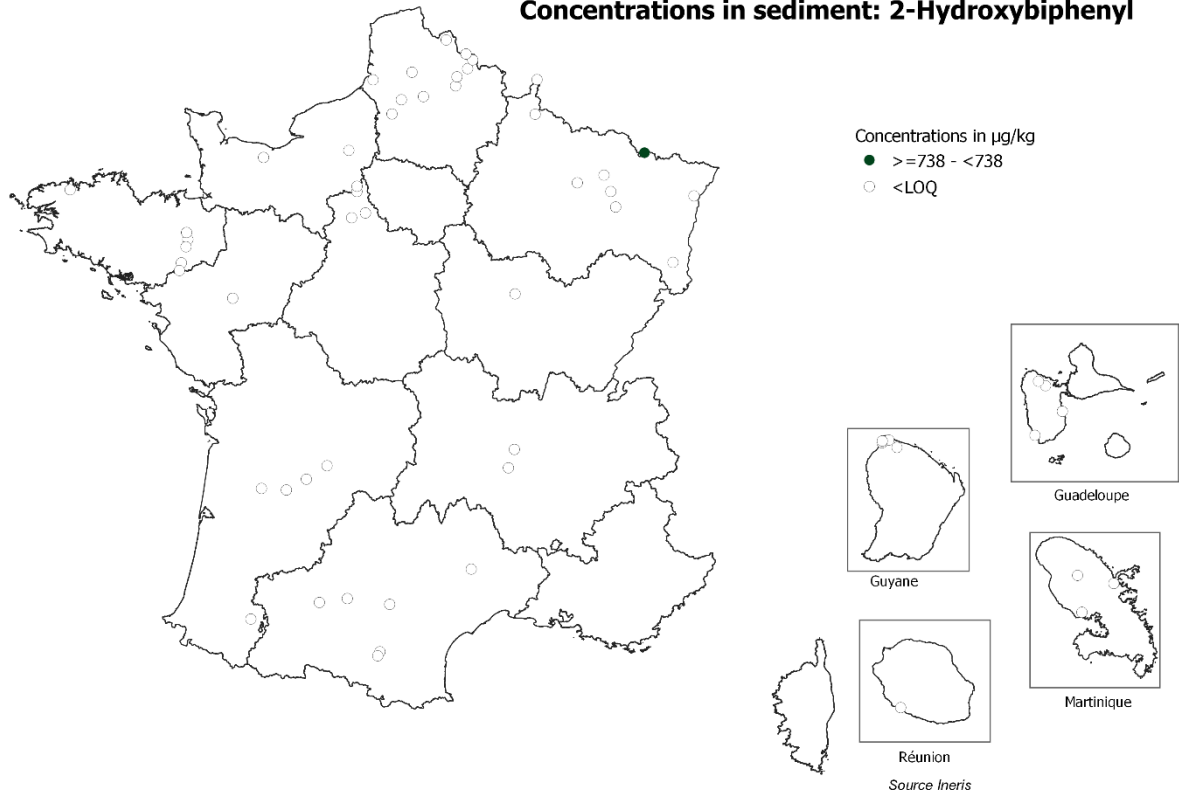
Concentrations in sediment: DDAC-C10



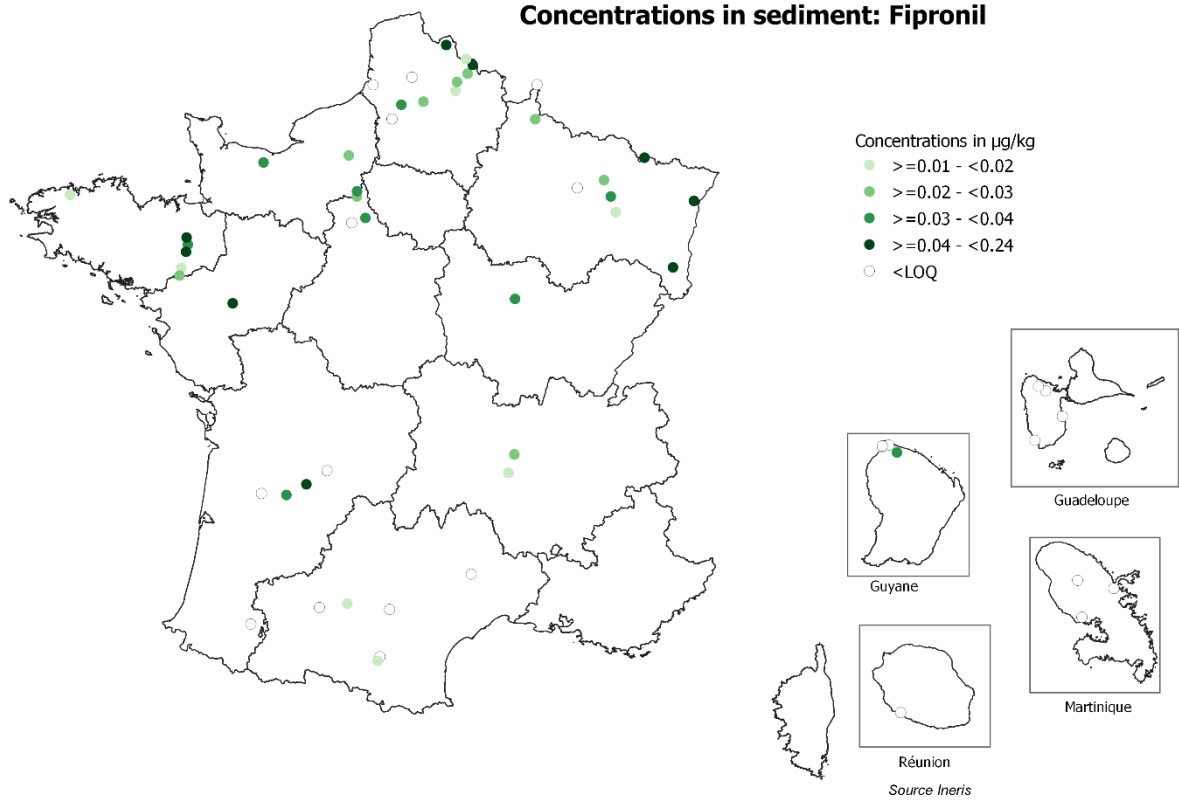
Concentrations in sediment: SDS



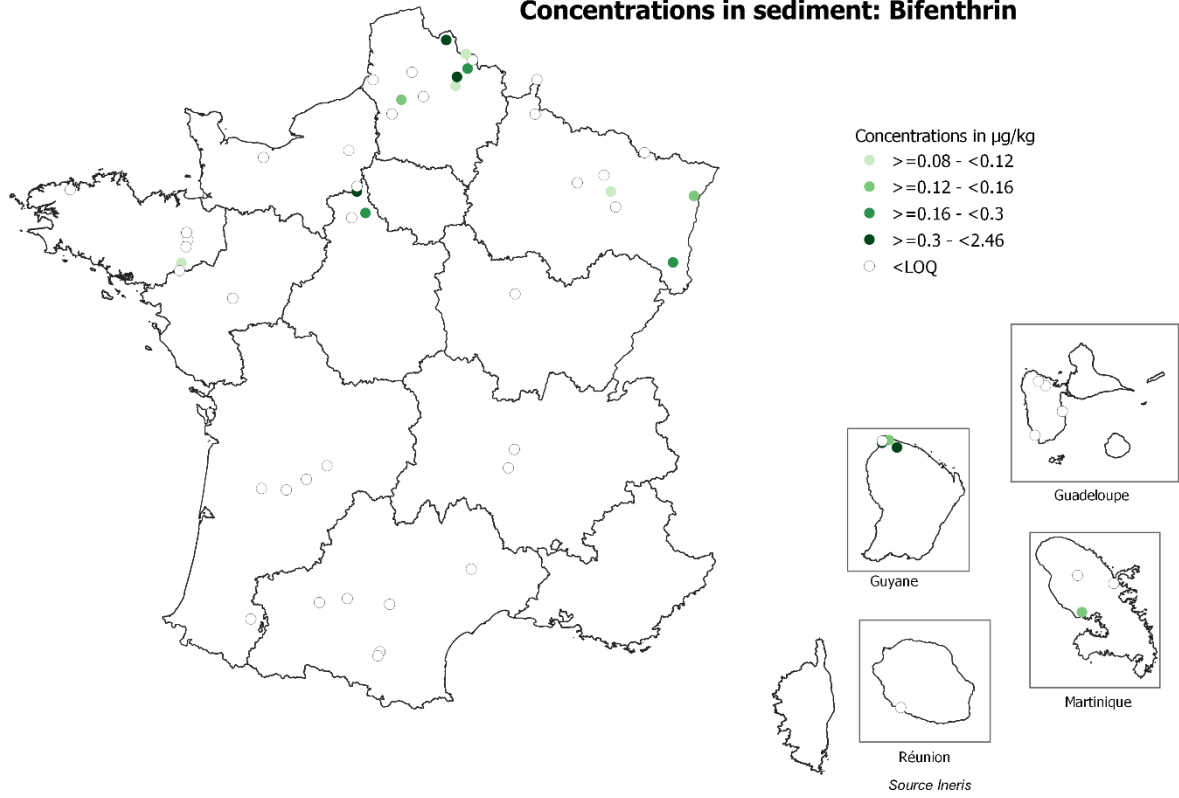
Concentrations in sediment: 2-Hydroxybiphenyl



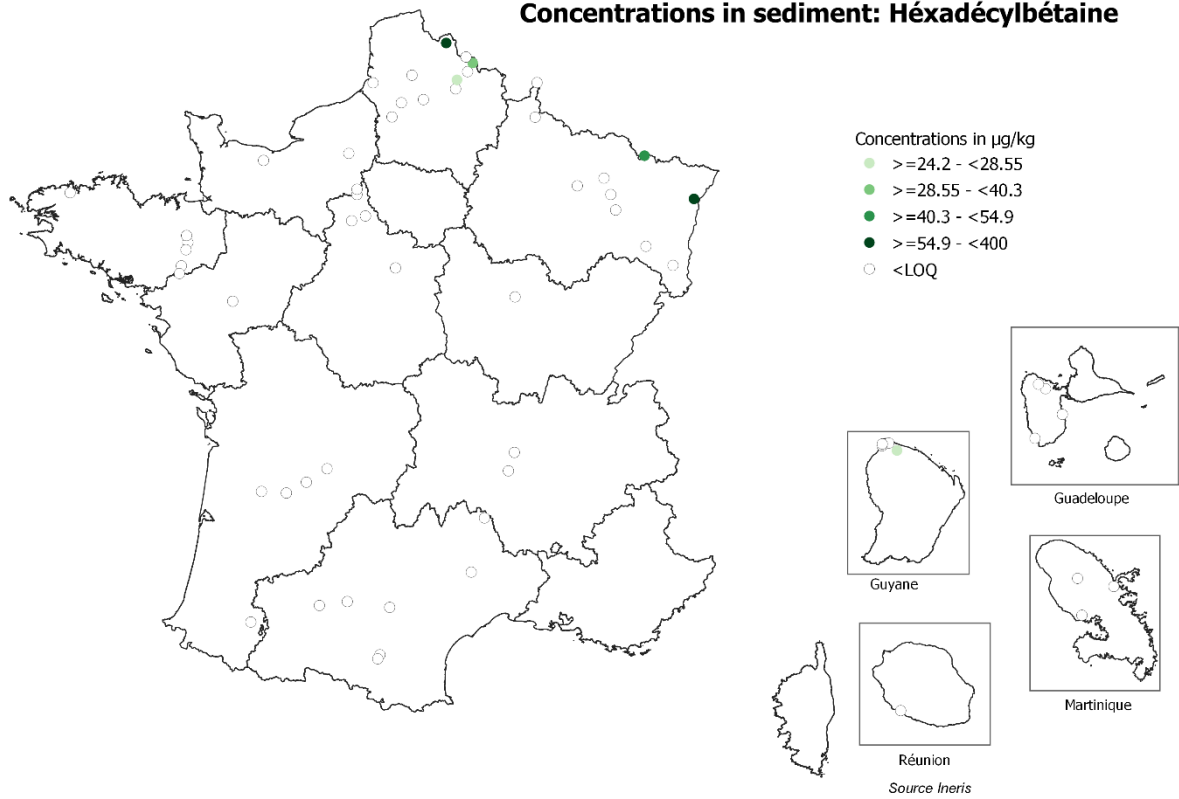
Concentrations in sediment: Fipronil

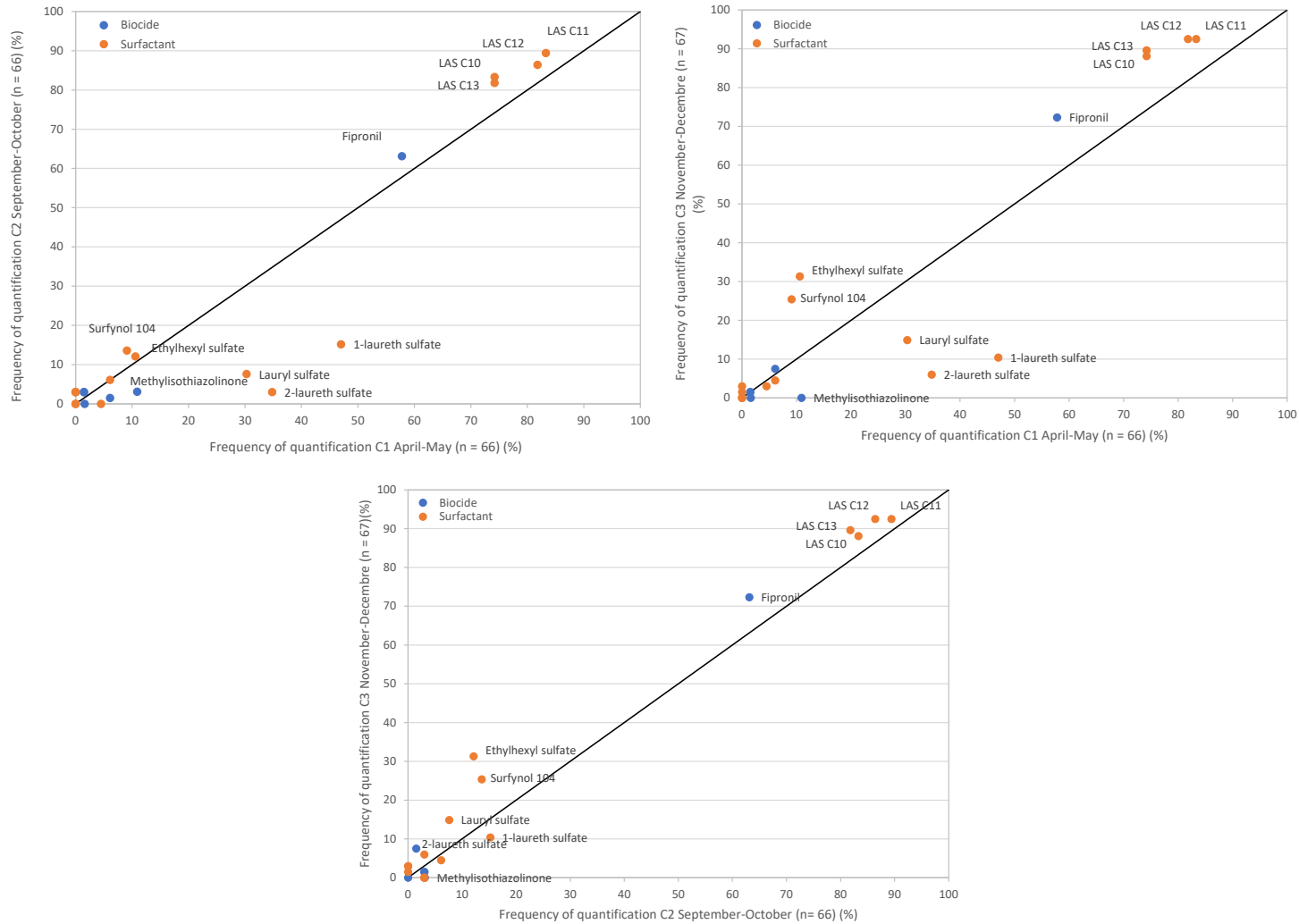


Concentrations in sediment: Bifenthrin



Concentrations in sediment: Héxadécylbétaine





n = number of samples

Figure S3. Comparison of the quantification frequencies of surfactants and biocides in metropolitan water obtained during campaign #1, campaign #2 and campaign #3

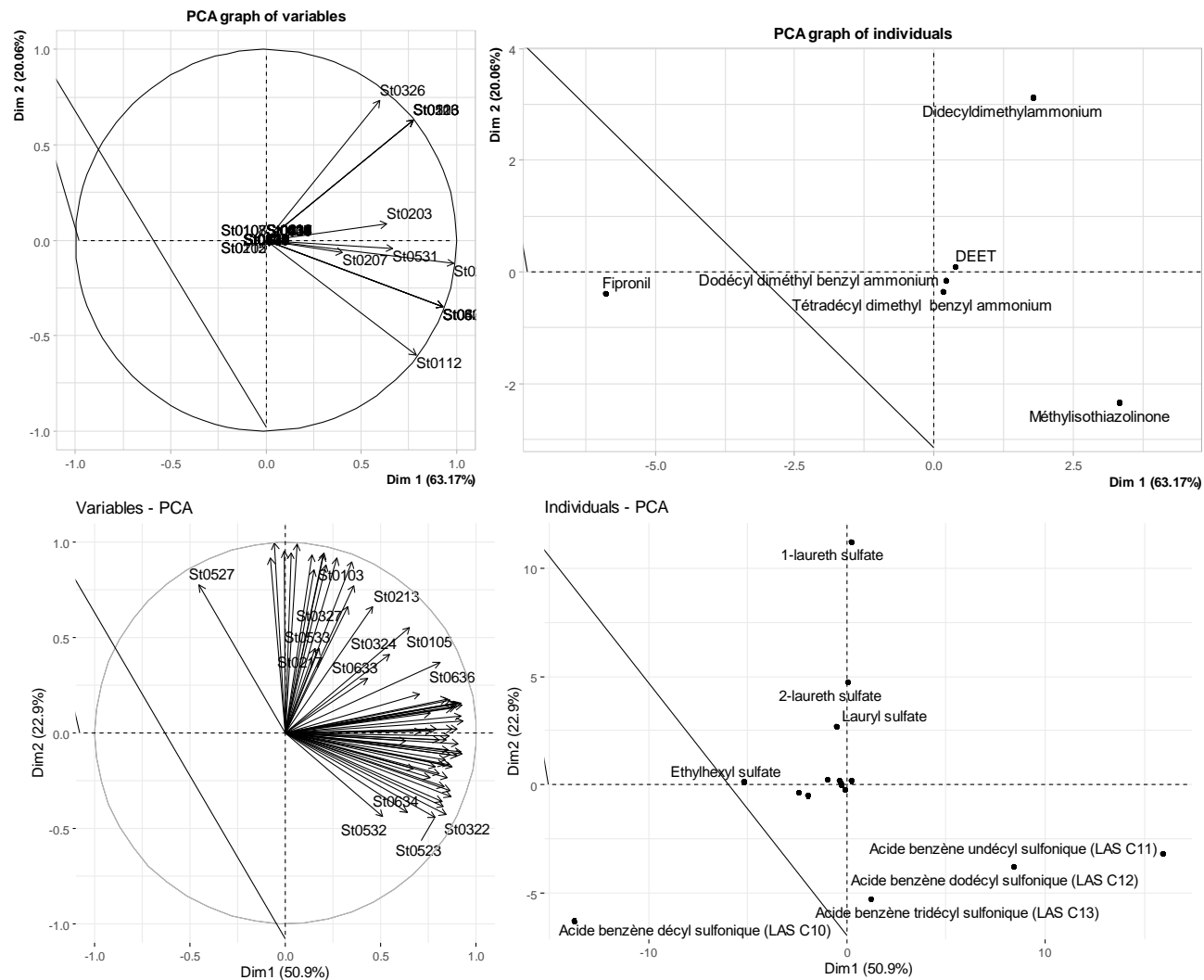


Figure S4. PCA charts of the concentrations of biocides (top) and surfactants (bottom) in metropolitan surface water samples collected during the 3 campaigns

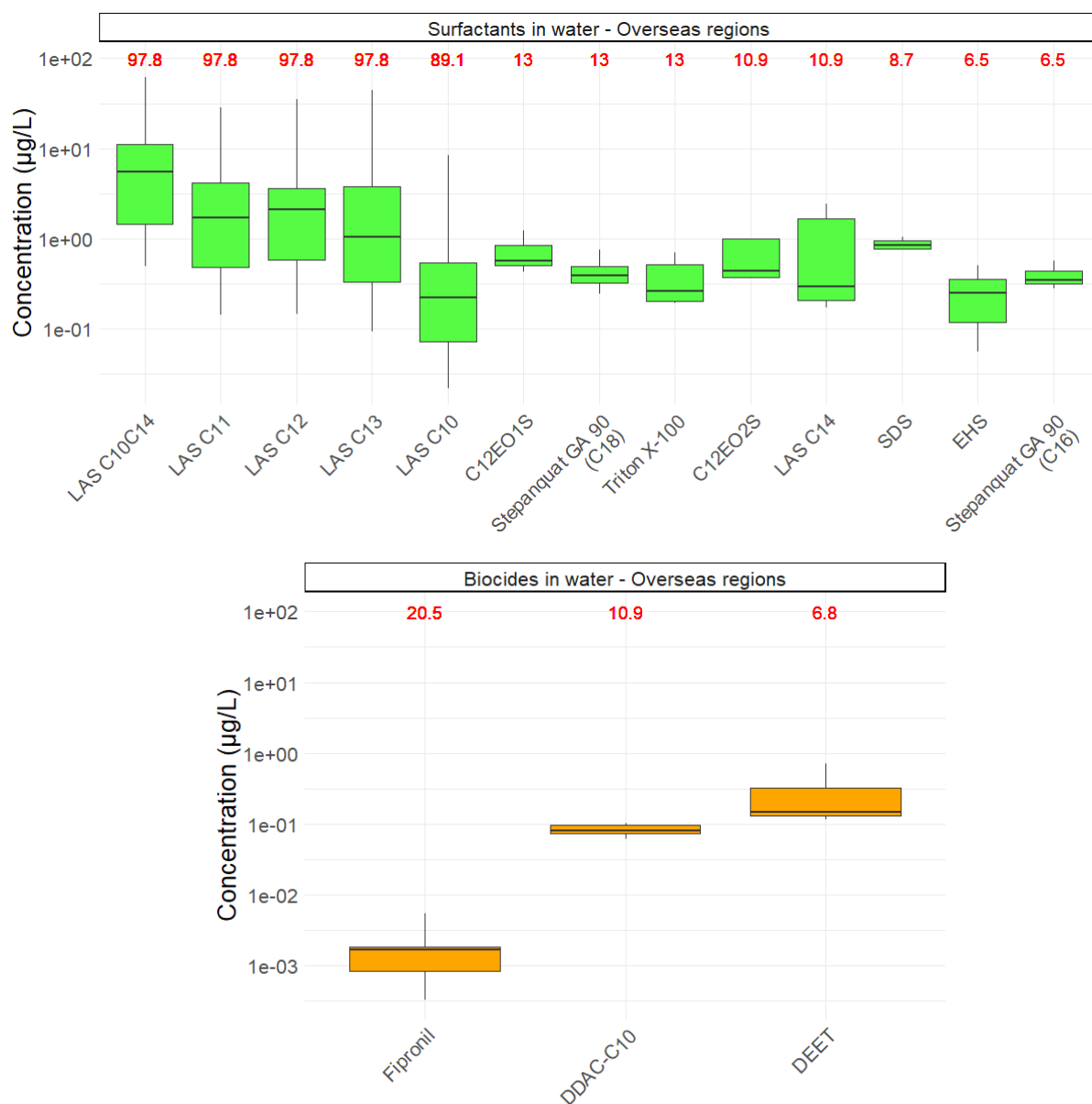


Figure S5. Frequency of quantification and distribution of the concentrations of the surfactants and biocides quantified in overseas regions water samples

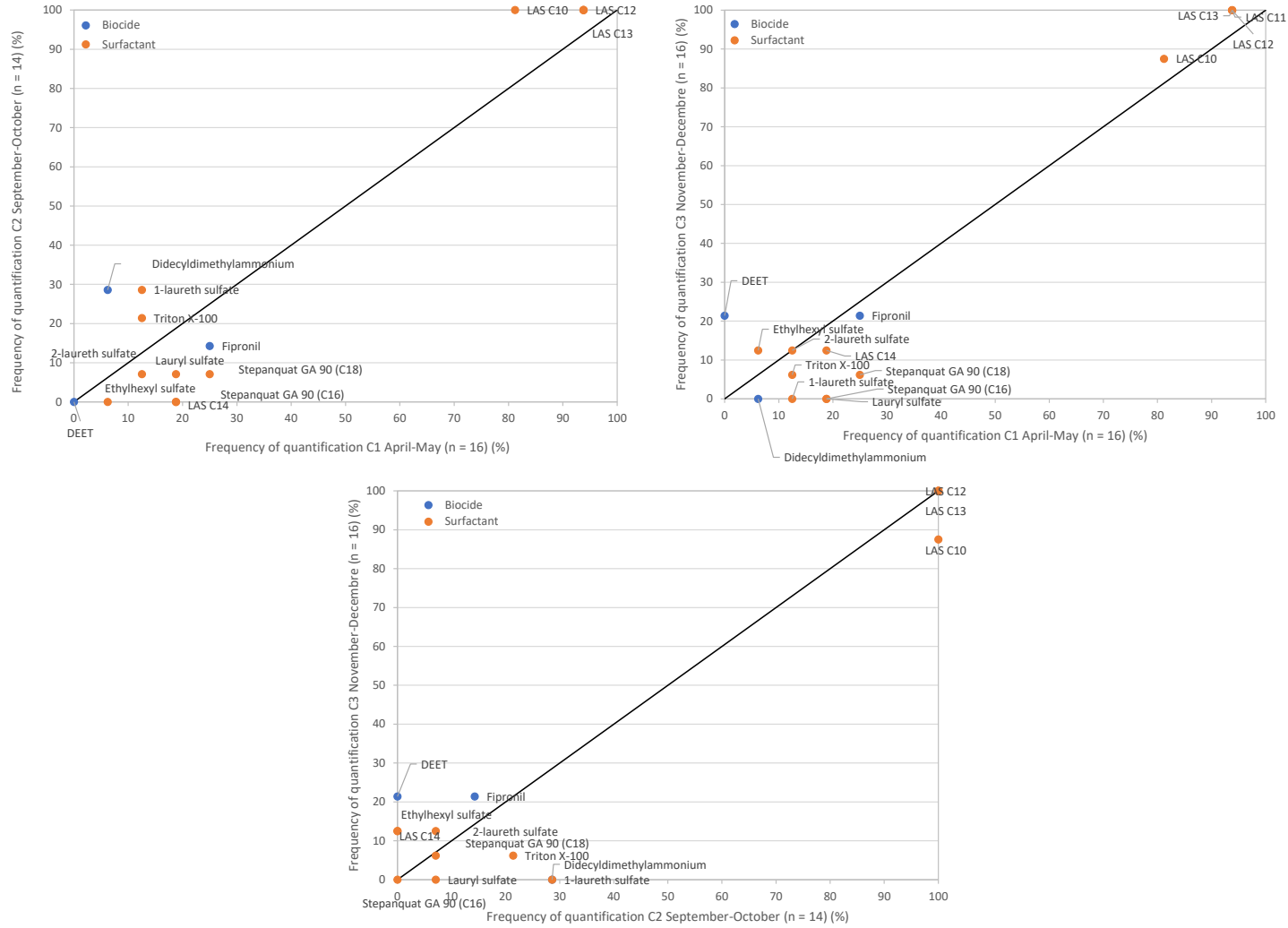


Figure S6. Comparison of the quantification frequencies of surfactants and biocides in overseas regions water obtained during campaign #1, campaign #2 and campaign #3

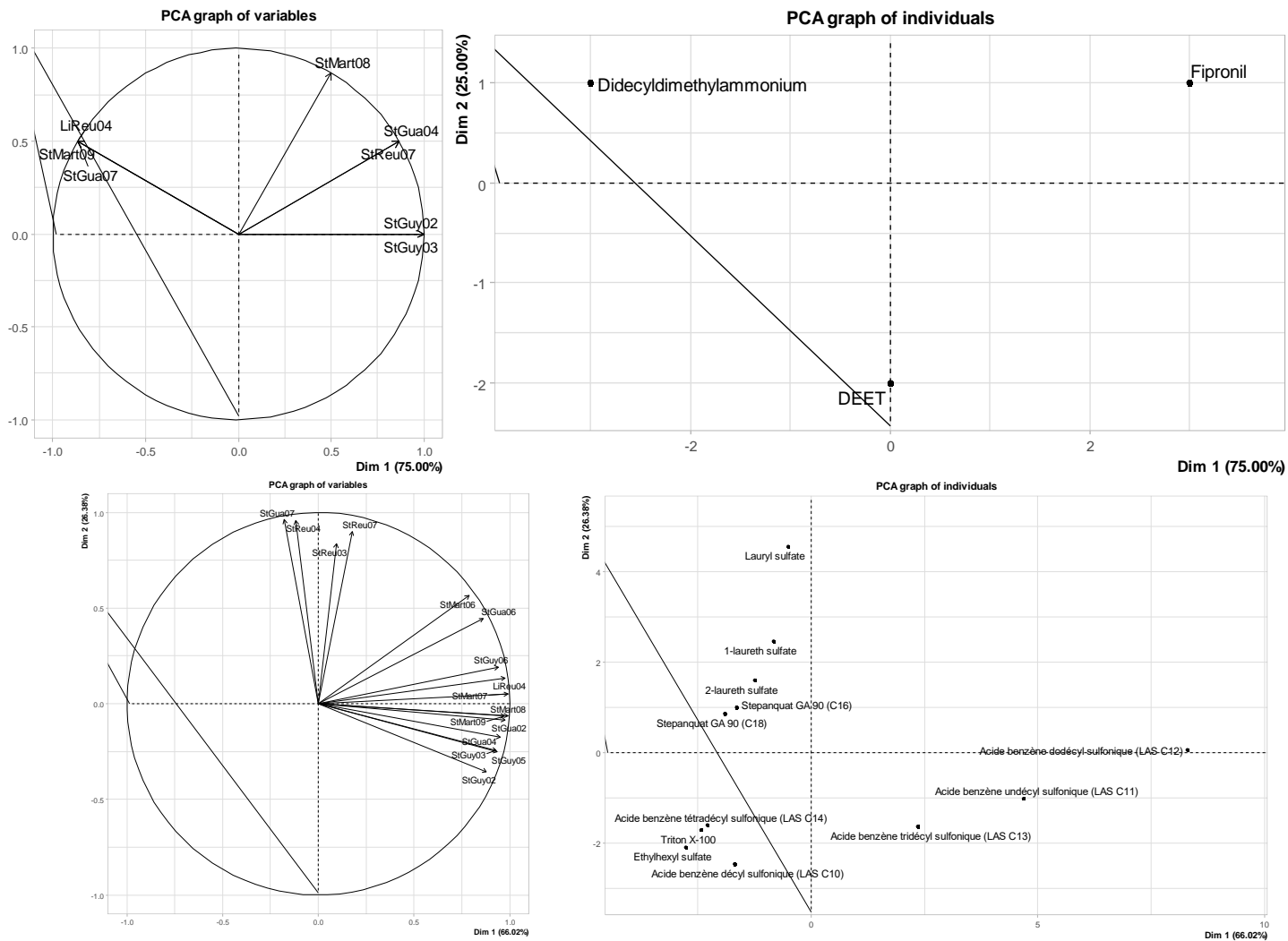


Figure S7. PCA charts of the concentrations of biocides (top) and surfactants (bottom) in overseas regions surface water samples collected during the 3 campaigns

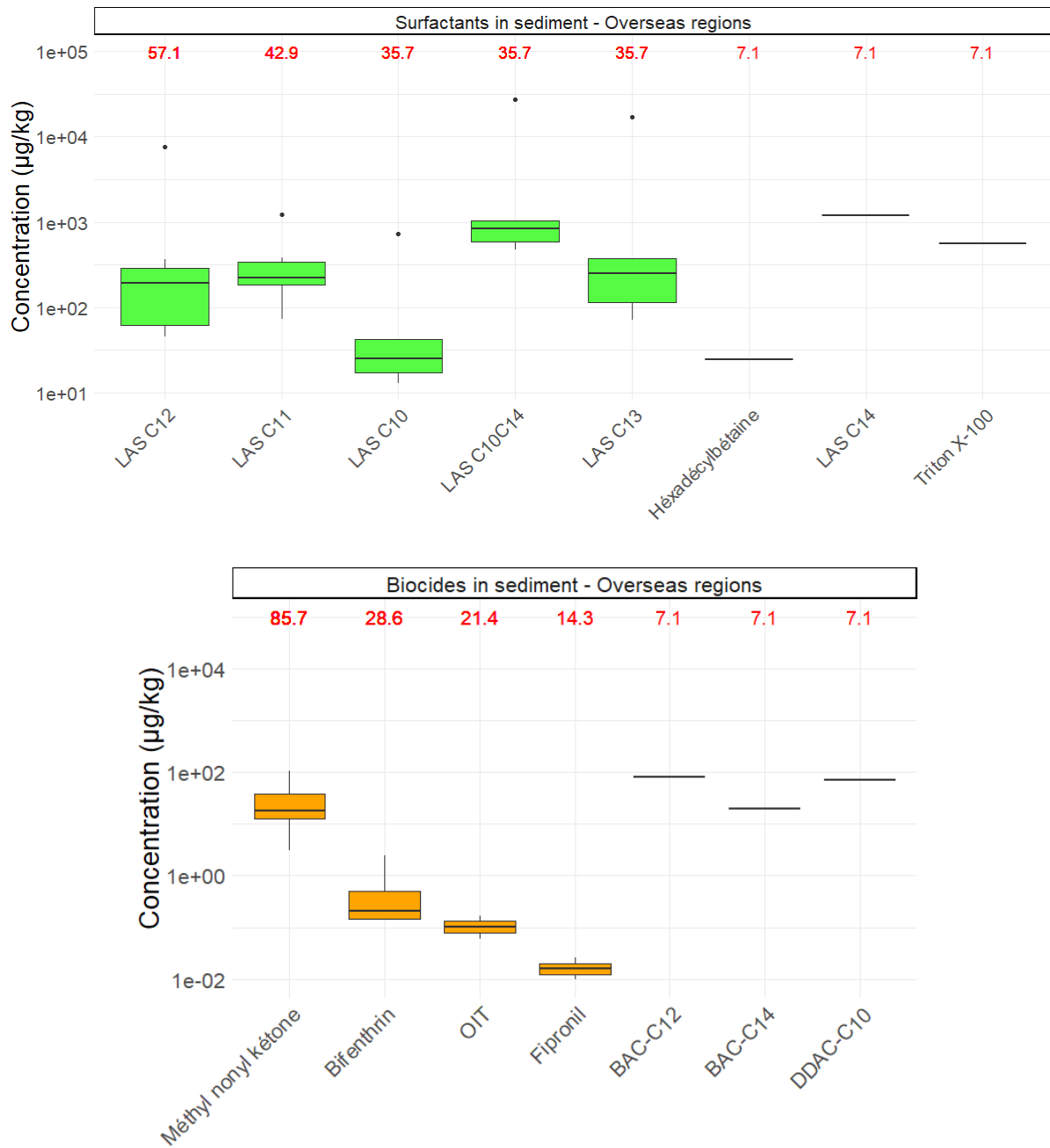


Figure S8. Frequency of quantification and distribution of the concentrations of the surfactants and biocides quantified in overseas regions sediment samples

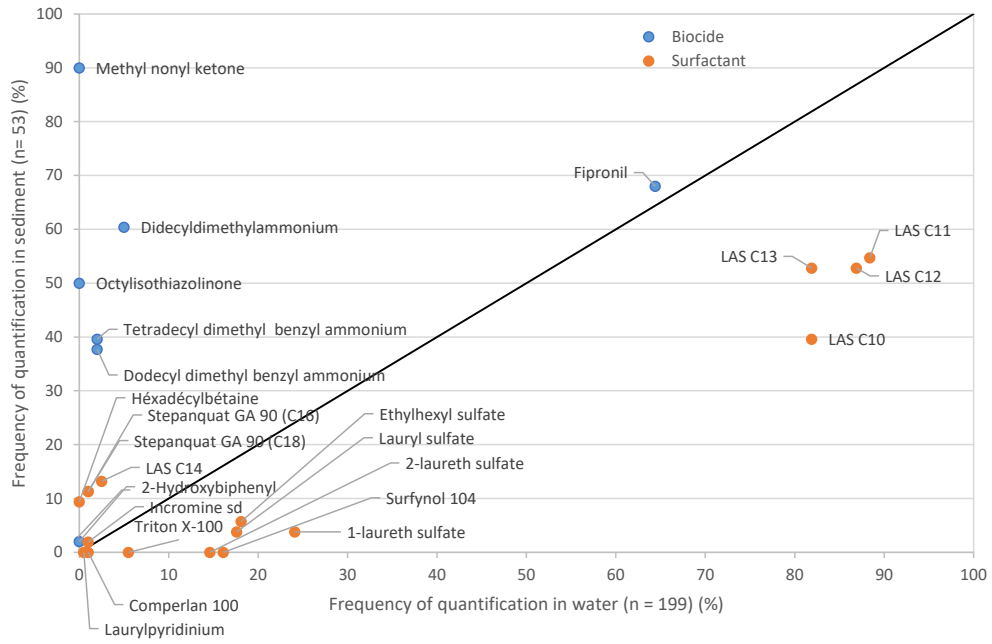


Figure S9. Comparison of the quantification frequencies of surfactants and biocides in water and sediment in mainland France

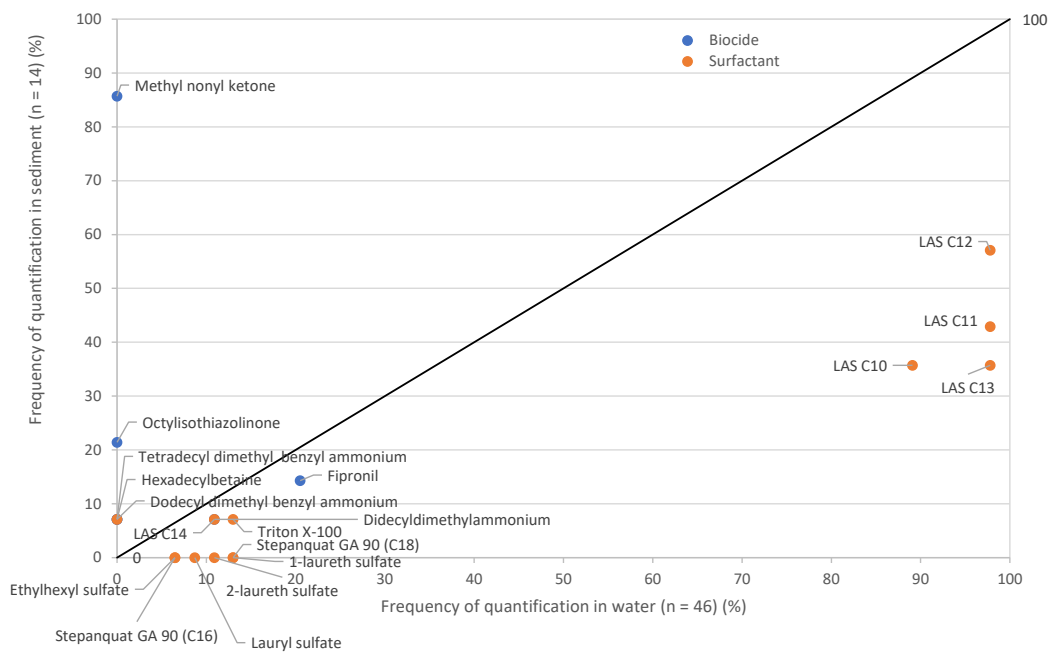


Figure S10. Comparison of the quantification frequencies of surfactants and biocides in water and sediment in overseas regions

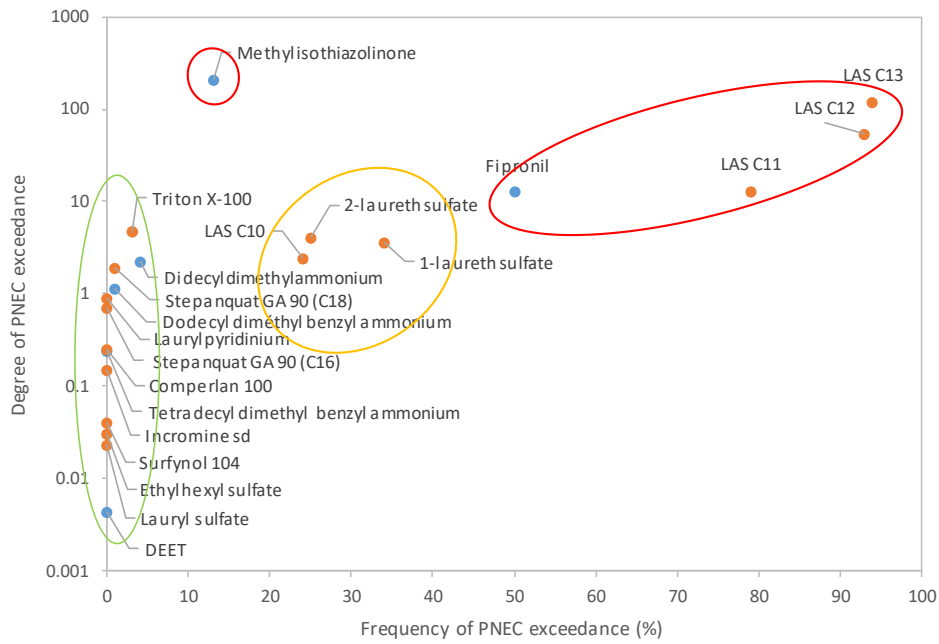


Figure S11. Frequency of PNEC exceedance and degree of PNEC exceedance of the surfactants and biocides targeted in metropolitan water samples

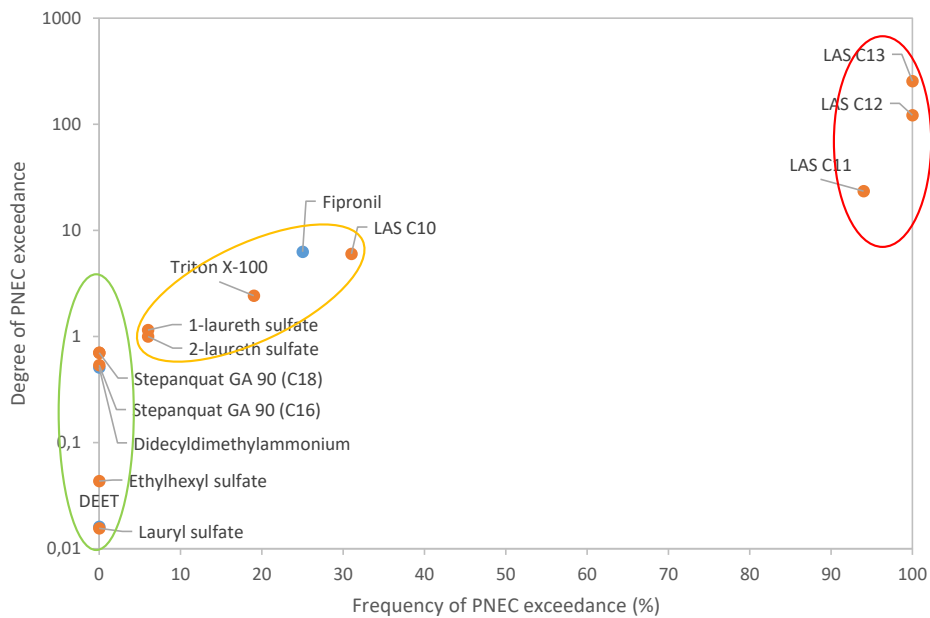


Figure S12. Frequency of PNEC exceedance and degree of PNEC exceedance of the surfactants and biocides targeted in overseas regions water samples

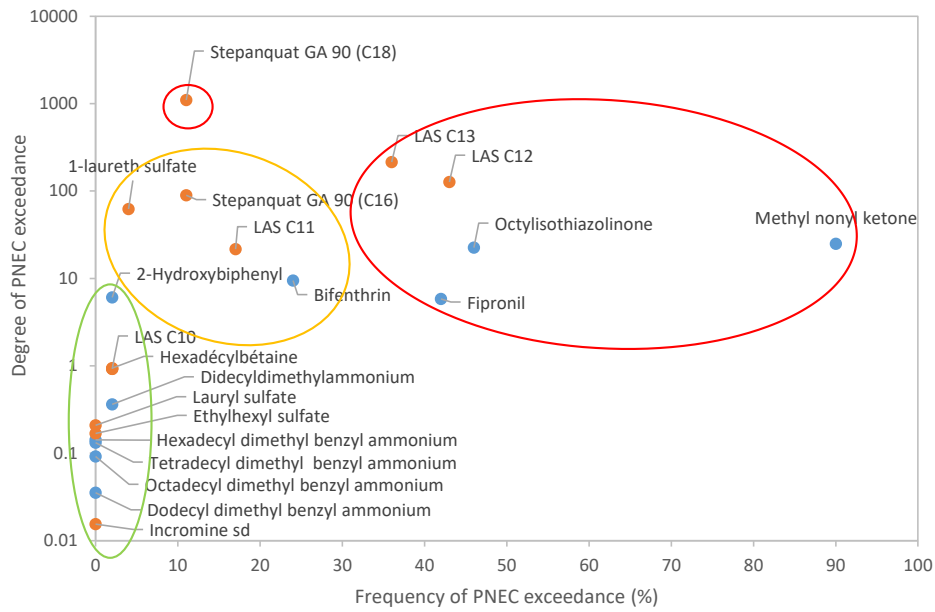


Figure S13. Frequency of PNEC exceedance and degree of PNEC exceedance of the surfactants and biocides targeted in metropolitan sediment samples

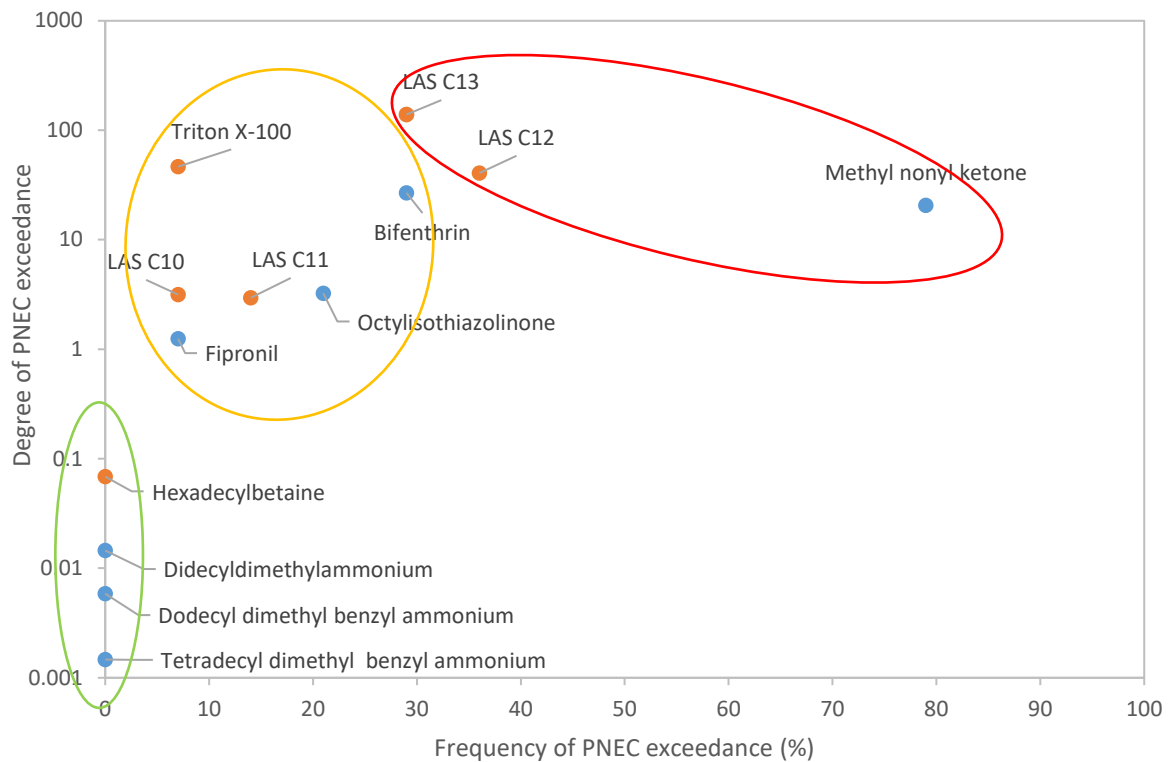


Figure S14. Frequency of PNEC exceedance and degree of PNEC exceedance of the surfactants and biocides targeted in overseas regions sediment samples

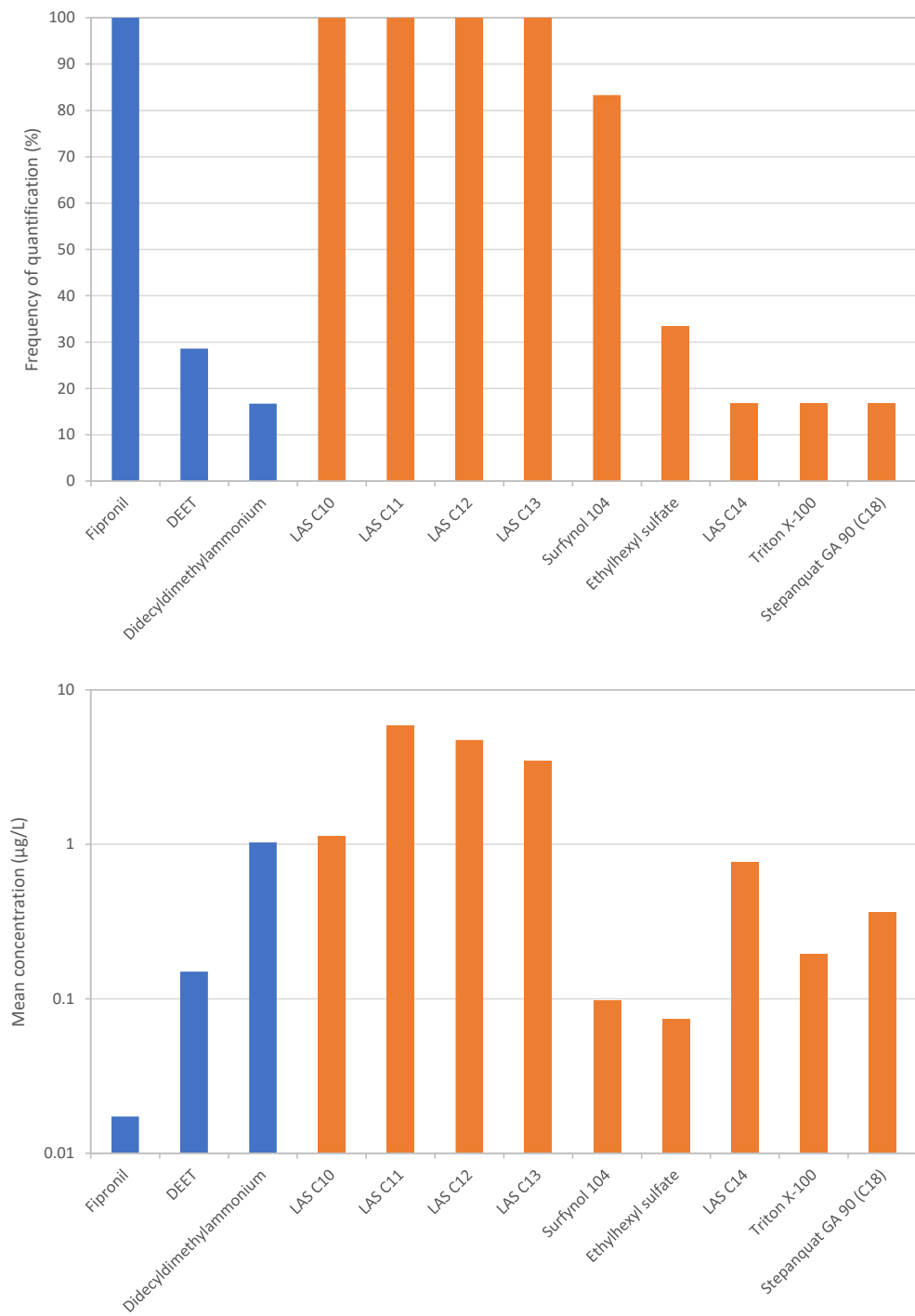


Figure S15. Frequency of quantifications (top) and mean concentrations (bottom) of biocides and surfactants in the effluent samples

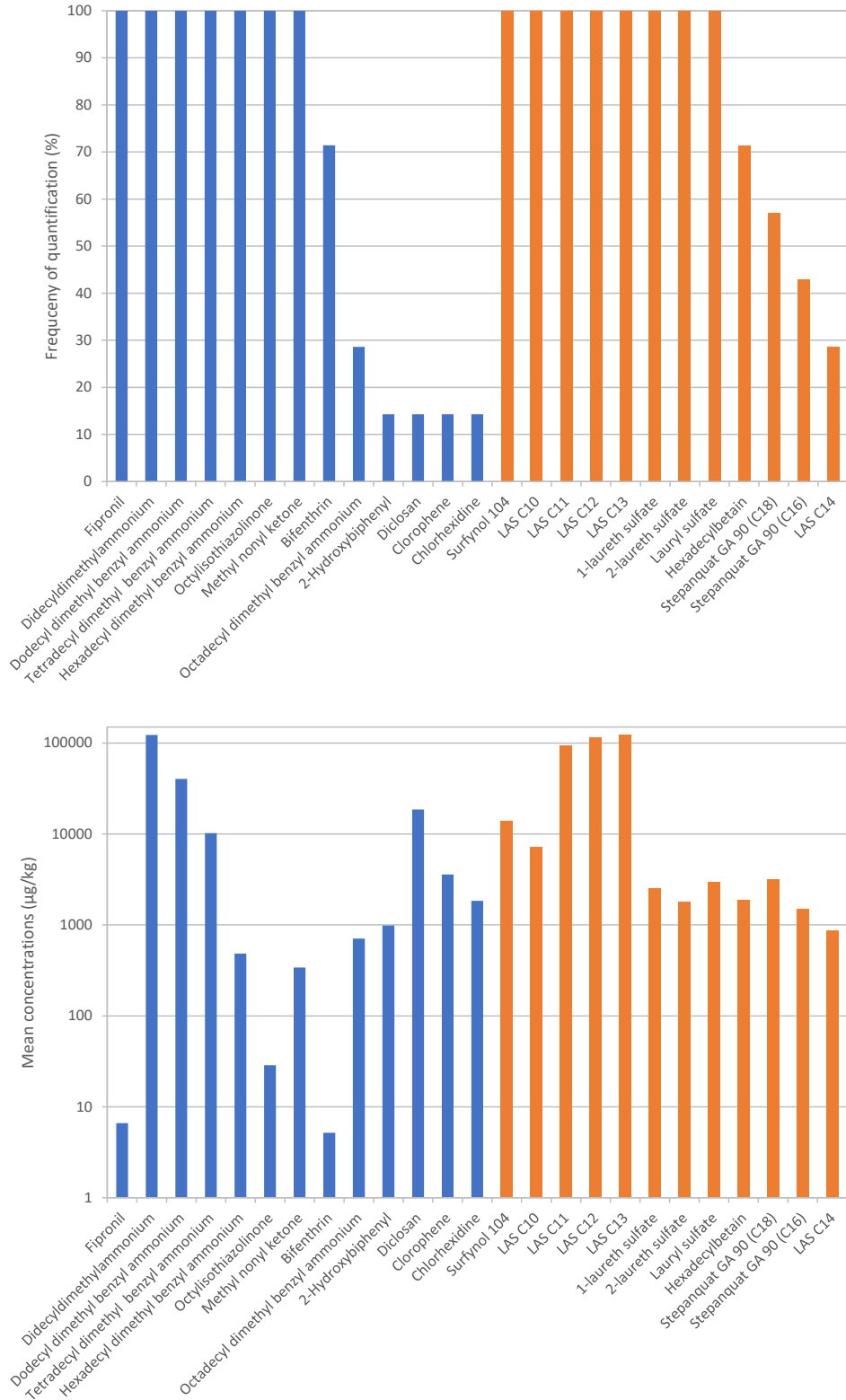


Figure S16. Frequency of quantifications (top) and mean concentrations (bottom) of biocides (blue bars) and surfactants (orange bars) in the sludge samples

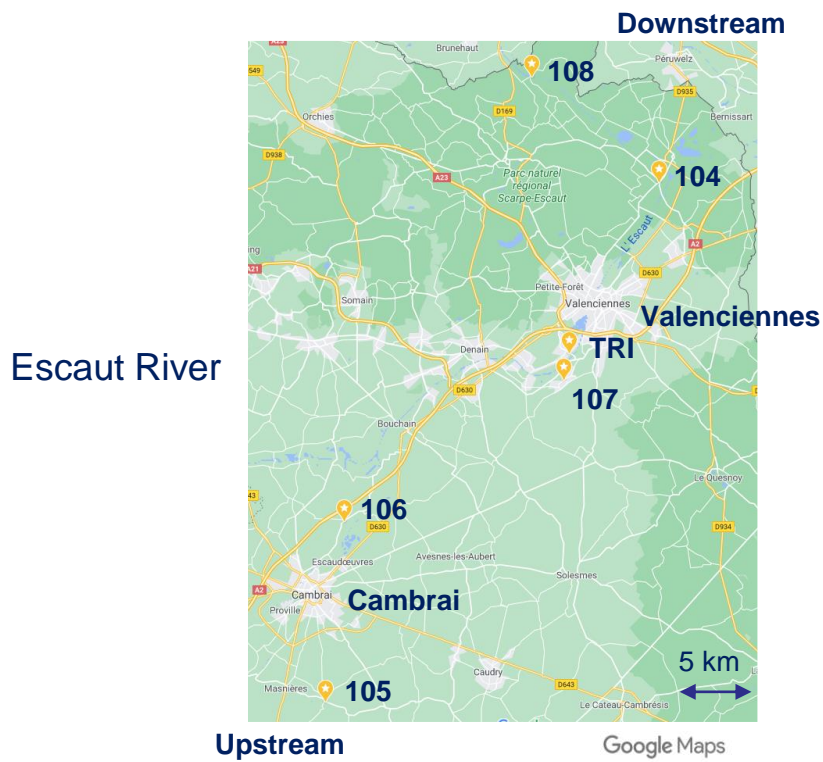
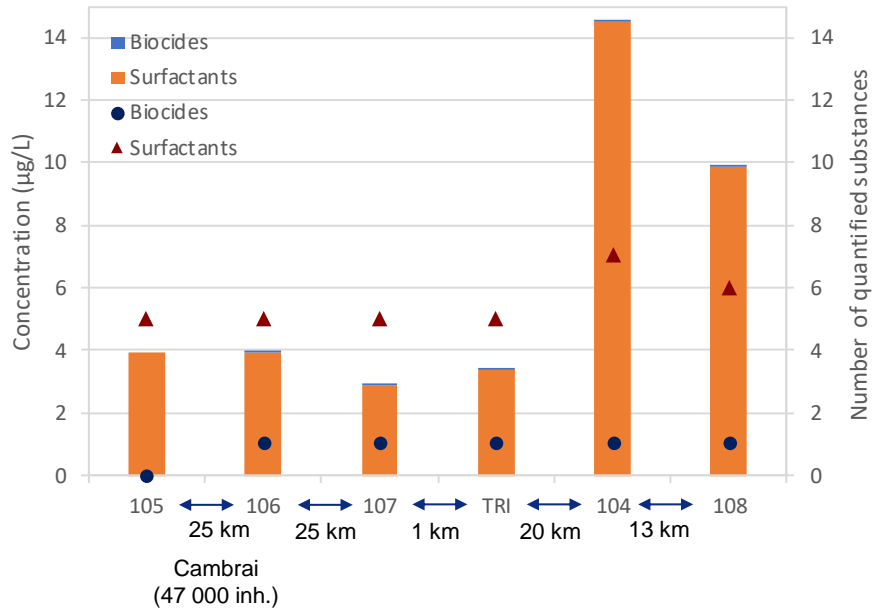
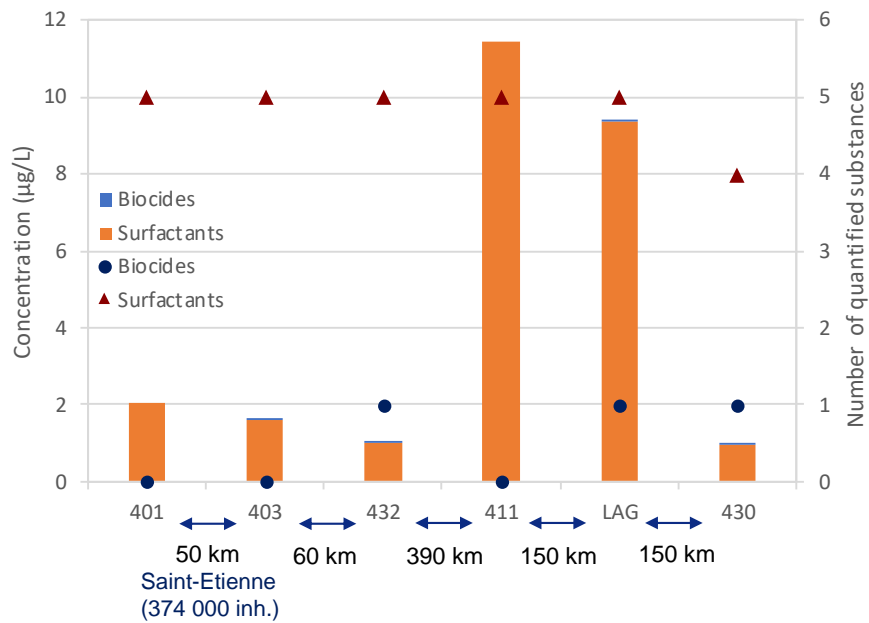


Figure S17. Number and concentrations of biocides and surfactants along the Escaut River (up) and location of the sampling sites (down)



Downstream

Loire River

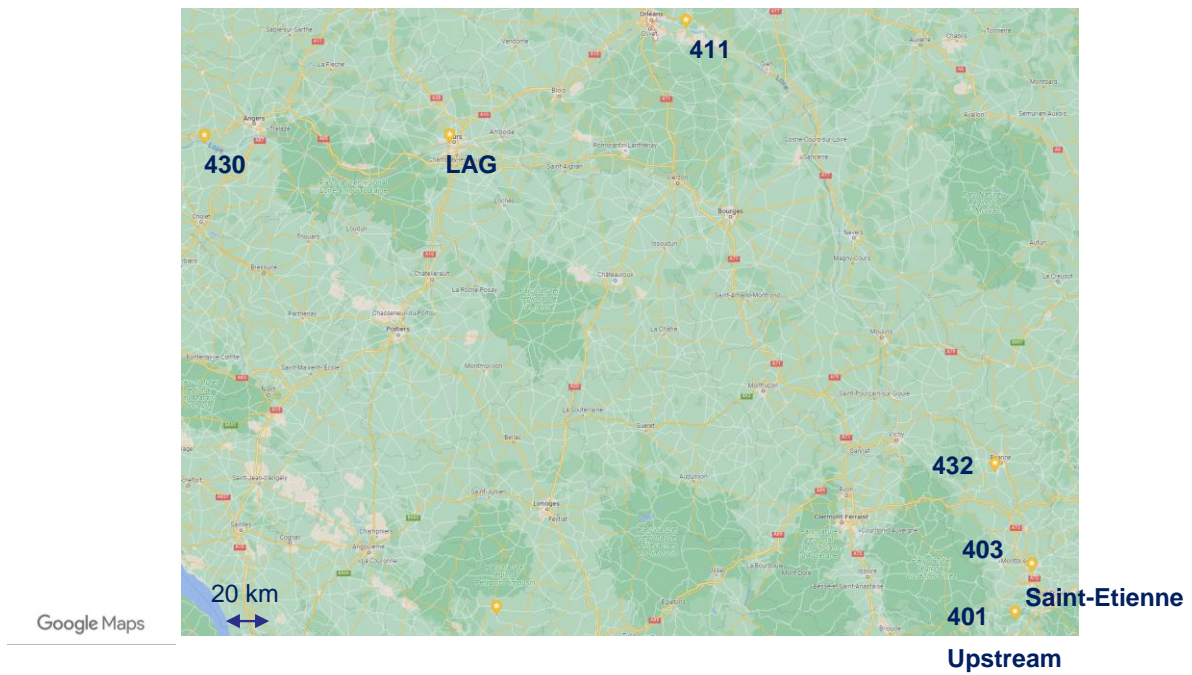
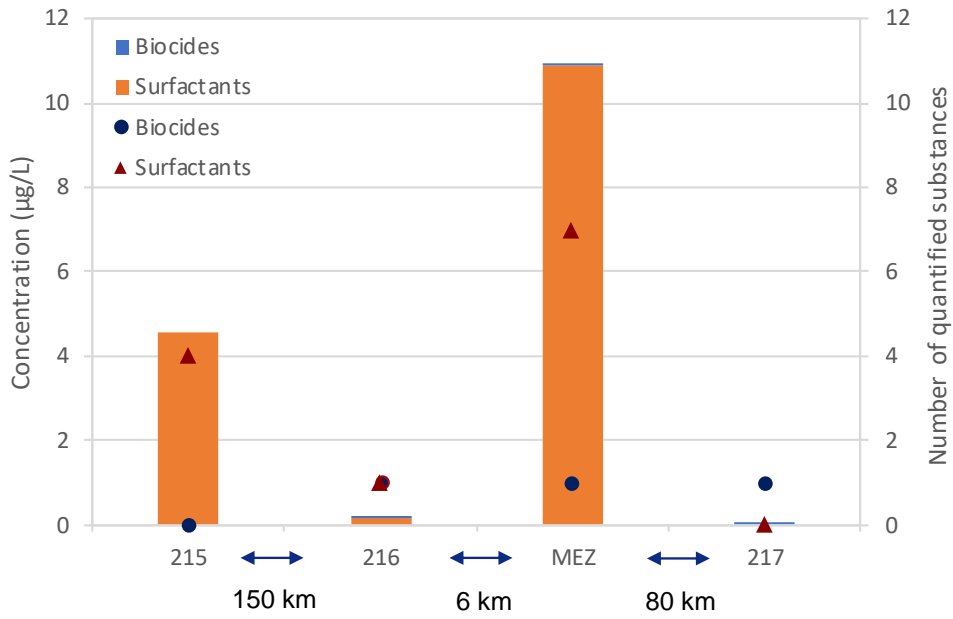
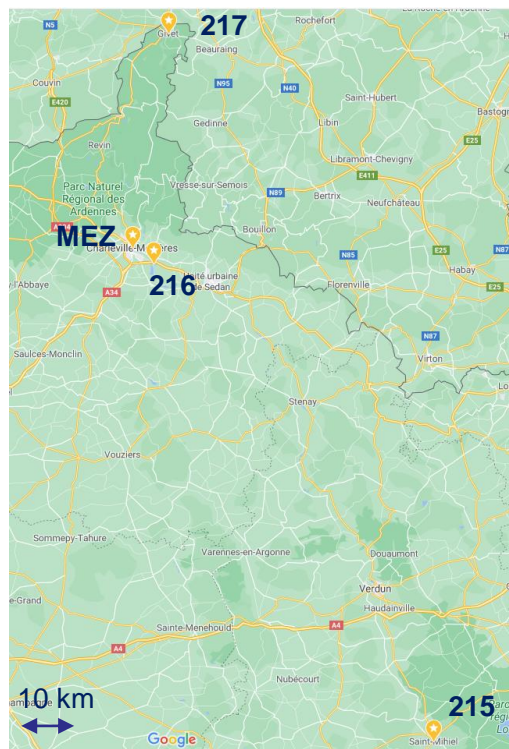


Figure S16. Number and concentrations of biocides and surfactants along the Loire River (up) and location of the sampling sites (down)



Downstream



Meuse River

Google Maps

Upstream

Figure S19. Number and concentrations of biocides and surfactants along the Meuse River (up) and location of the sampling sites (down)

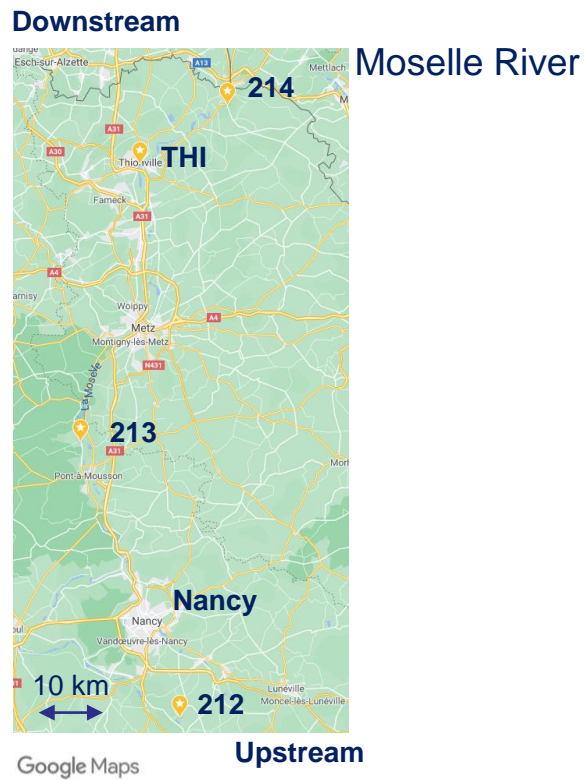
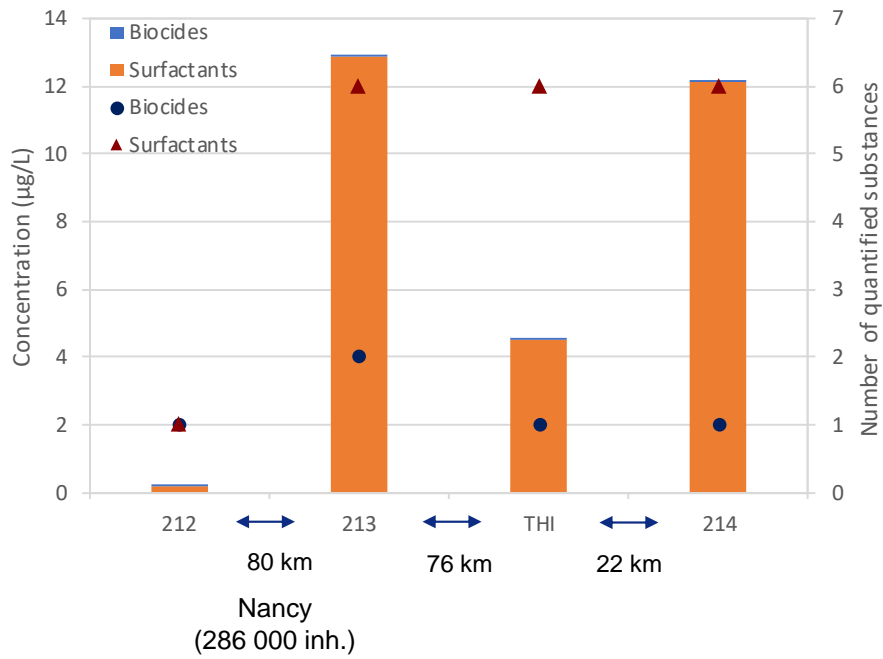


Figure S20. Number and concentrations of biocides and surfactants along the Moselle River (up) and location of the sampling sites (down)

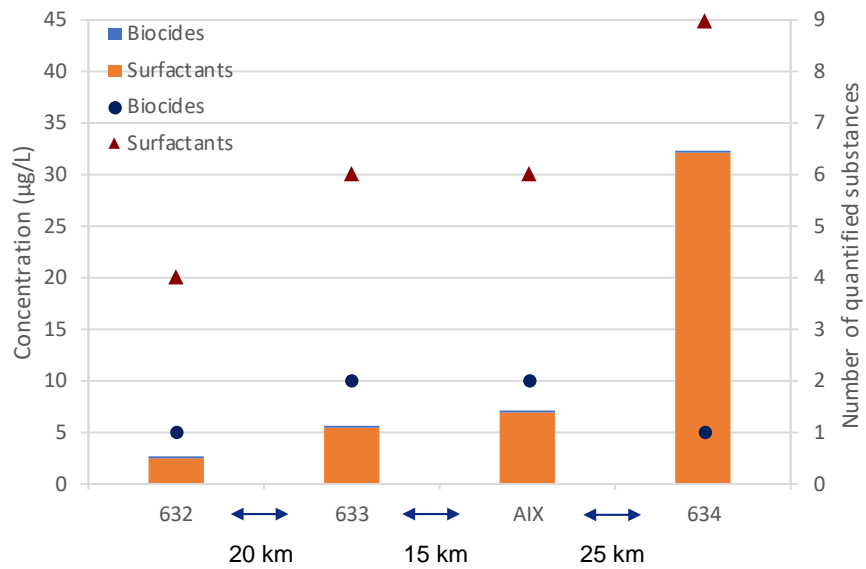


Figure S21. Number and concentrations of biocides and surfactants along the Arc River (up) and location of the sampling sites (down)

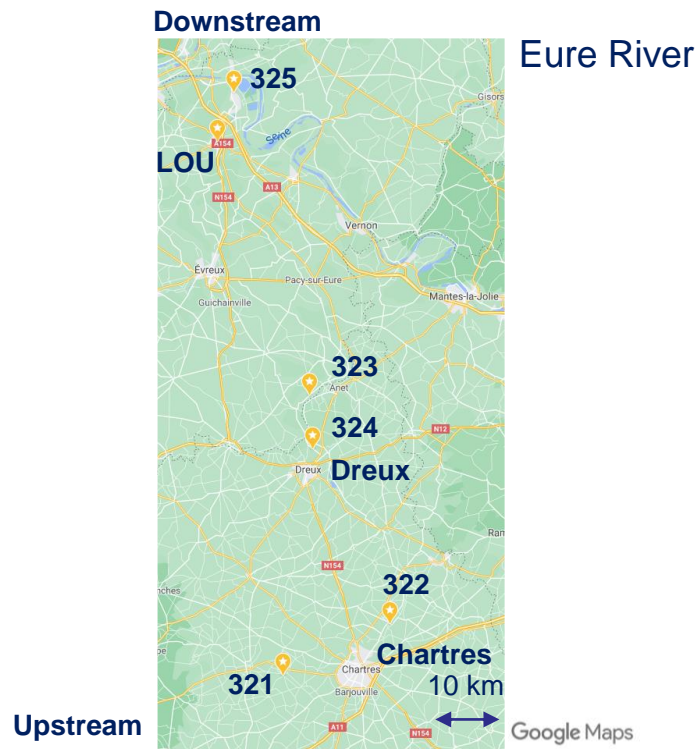
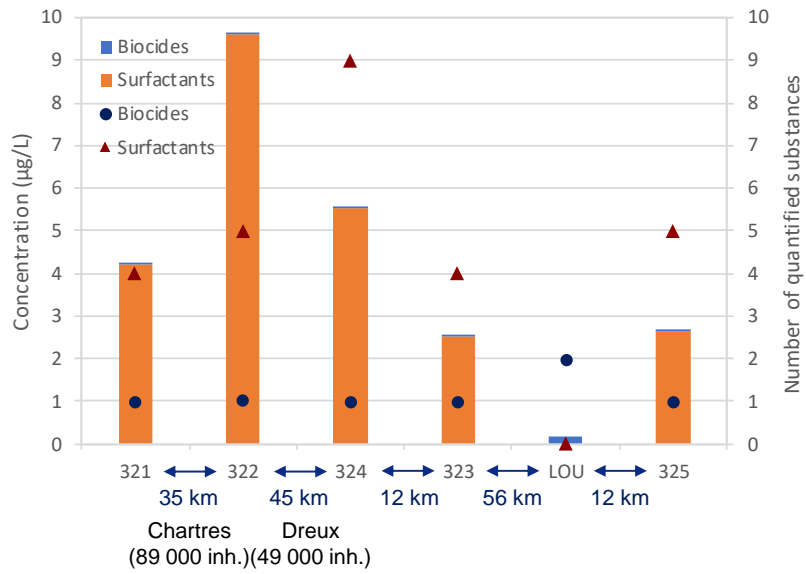


Figure S22. Number and concentrations of biocides and surfactants along the Eure River (up) and location of the sampling sites (down)

Table S1: Suppliers, references and purity of the standard for the substances monitored in this study

Substance	Supplier	Reference	CAS	Purity
				(%)
LAS C10-C13	Fisher Scientific	AC325905000	85536-14-7	96.6
		ACROS Organics		
LAS C14	Sobioda	193-13151 / Wako	28348-61-0	95
C ₁₂ EO ₀₋₂ S	BOC Science	BCH8921-1	9004-82-4	70
Ethylhexyl sulfate	Sigma Aldrich	71220	126-92-1	50
OP ₇₋₁₁ EO	Merck	108603 (Triton X-100)	9036-19-5	85
CMEA	Care Chemicals	Comperlan 100	68140-00-1	56
TMDD	Sigma Aldrich	278386-100G	126-86-3	98
BAC-C ₁₂ and C ₁₄	Sigma Aldrich	12060-60G	63449-41-2	96.1
BAC-C ₁₆	Sigma Aldrich	B4136-25G	122-18-9	97
BAC-C ₁₈	TCI	B1297	122-19-0	98
DDAC-C ₁₀	Sigma Aldrich	34466-250MG	7173-51-5	89
TEAQ-C ₁₆ and C ₁₈	BASF	Basocorr E 1005	157905-74-3	85
Laurylpyridinium	Sigma Aldrich	278602-5G	104-74-5	98
SADP-DMA	Croda	Incromine SD	7651-02-7	95
Hexadecylbetaine	Sigma Aldrich	CDS003288-500MG	693-33-4	90
(benzothiazol-2-ylthio)methyl thiocyanate	A2S	T425P010	21564-17-0	99
1-(4-(2-chloro-a,a,a-p-trifluorotolyloxy)-2-fluorophenyl)-3-(2,6-difluorobenzoyl)urea	Dr Ehrenstorfer	C13712000	101463-69-8	99
1,2-benzisothiazol-3(2H)-one	Techlab (HPC)	676256	2634-33-5	98
2-Hydroxybiphenyl	Sigma Aldrich	24,021-4	90-43-7	> 99
2-methyl-2H-isothiazol-3-one	Techlab (HPC)	675700	2682-20-4	99.9
2-Octyl-3(2H)-isothiazolone	Toronto Research Chemical	O239300	26530-20-1	98

4,5-Dichloro-2-n-octyl-4-isothiazolin-3-one	Techlab (HPC)	678225	64359-81-5	99.9
5-Chloro-2-methyl-4-isothiazolin-3-one (CMI)	Cluzeau Info Labo	11433000	26172-55-4	99
Abamectin	HPC	672896	71751-41-2	96.8
Bifenthrin	Dr Ehrenstorfer	105840000	82657-04-3	99
Brodifacoum	A2S	B086P010	56073-10-0	98.5
Cetylpyridinium	Dr Ehrenstorfer	C193P010	123-03-5	99,00
Chlorfenapyr	A2S	C135P010	122453-73-0	98
chlorhexidine	Sigma Aldrich	28227-1G	55-56-1	99.5
Chlorophen	Cluzeau Info labo	10572000	120-32-1	98
Cyfluthrin	Dr Ehrenstorfer	C11850000	68359-37-5	99.52
Dichlofluanid	Dr Ehrenstorfer	C12300000	1085-98-9	98
Diclosan / 5-chloro-2-(4-chlorphenoxy)phenol	Cluzeau Info Labo	D436620	3380-30-1	98
Difenacoum	Dr Ehrenstorfer	C12608000	56073-07-5	97
d-Phenothrin	Techlab (HPC)	676582	188023-86-1	98
Fipronil	Dr Ehrenstorfer	C13645000	120068-37-3	96
Flocoumafen	Dr Ehrenstorfer	C13662000	90035-08-8	98
Methyl nonyl ketone	Techlab (HPC)	680967	112-12-9	99.8
Metofluthrin	Dr Ehrenstorfer	C142589	240494-70-6	99
N,N-diethyl-meta-toluamide	Santa Cruz Biotech	SC211219	134-62-3	98
Quaternary ammonium compounds, C12-14-alkyl[(ethylphenyl)methyl]dimethyl, chlorides	Sigma Aldrich	32279	85409-23-0	98.4

Table S2: Characteristics of the wastewater treatment plants monitored

Hydrographic basin	WWTP name	Abbreviation	Nominal Capacity (EH)	Type of treatment	Wastewater collecting systems
Adour-Garonne	STEU Centre Hospitalier du Vauclaire	VAU	120	Secondary/biological	
Artois-Picardie	STEU Trith Saint Léger	TRI	13500	Secondary	Combined
Loire-Bretagne	STEU La Grange David	LAG	393330	Secondary	Separate
Rhin-Meuse	STEU Charleville-Mézières	MEZ	117000	Secondary	Combined
Rhin-Meuse	STEU Thionville	THI	80000	Secondary	Combined
Rhône-Méd.-Corse	STEU Aix-en-Provence Ouest	AIX	30000	Secondary	Separate
Seine-Normandie	STEU Louviers	LOU	34000	Secondary	Separate and combined

Table S3. Number and type of sampling sites of the campaign regarding each hydrographic basin

Hydrographic basin	Inland surface water				Wastewater	Coastal water	Number of sites
	Urban sites	Rural sites	River continuum	Reference point			
Artois-Picardie	3	2	5	1	1	1	13
Rhin-Meuse	5	1	6	1	2	0	15
Seine-Normandie	2	3	5	1	1	1	13
Loire-Bretagne	4	2	6	1	1	0	14
Adour-Garonne	4	2	4	1	1	1	13
Rhône-Méd.-Corse	3	2	3	1	1	1	11
Total for Mainland	21	12	29	6	7	4	79
Martinique	3		0	1	0	1	5
Guadeloupe	3		0	1	0	1	5
La Réunion	3		0	1	0	0	4
French Guiana	3		0	1	0	1	5
Total for overseas regions	12		0	4	0	3	19