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Ultrasound-assisted sample preparation for simultaneous extraction of anionic, cationic and non-ionic surfactants in sediment

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Abstract

Despite their very wide use in various fields, knowledge concerning surfactants in environmental solid matrices is generally poor. One of the difficulties encountered in the analysis of surfactants is their very diverse physicochemical properties which require different extraction techniques.

The objective of this work was therefore to develop an extraction method in sediments that allows the simultaneous analysis of anionic, cationic and non-ionic surfactants. Different extraction techniques (salting-out, ultrasound), solvents and additives were compared. The optimized method, followed by analysis by coupling liquid chromatography with tandem mass spectrometry, was then validated and applied to real samples in which the analytes were quantified by matrix matched calibration.

Optimization of the extraction parameters showed different trends depending on the surfactant family. However, ultrasound assisted extraction with a 90/10 acetonitrile/water mixture at 1% acetic acid and 0.1 M EDTA showed the best results overall. The quantification limits obtained, between 6.4 $\mu\text{g}/\text{kg}$ for linear alkylbenzene sulfonate (LAS) C10 and 158 $\mu\text{g}/\text{kg}$ for 1-laureth sulfate, allow the analysis of traces in sediments. Eighteen of the 27 targeted surfactants were thus detected. The highest concentrations were found for LAS and quaternary ammoniums. Strong correlations between concentrations of different homologues of the same families of surfactants were observed.

Keywords

surfactant; linear alkylbenzene sulfonates ; quaternary ammoniums ; ultrasound; LC-MS/MS; sediment

1. Introduction

Due to their specific physical and chemical properties, surfactants are used in many different fields. The main applications are in the formulation of domestic or industrial detergents (laundry, dishwashing, cleaning products), and cosmetic products (shampoos, shower gels, toothpastes, creams, make-up...). They are also used as auxiliary products in the manufacturing processes of industry and agriculture: in the treatment of textiles and leather, the synthesis and formulation of plastics and paints, the processes of the petroleum industry, the formulation of phytosanitary products, and fertilizers. This very high consumption and these very diverse applications suggest a strong impact of these compounds on the environment, particularly on aquatic related bodies [1].

Their presence in the environment raises 2 major concerns. The first one is related to their ability to solubilize relatively insoluble xenobiotics, making them more bioavailable [2]. Hari et al. [3] and Pan et al. [4] studied the effect of surfactants on the adsorption of pharmaceuticals and perfluorooctanesulfonic acid (PFOS). They revealed that the impact of surfactants was compound-dependent and varied with surfactant concentration. Moreover, cationic surfactants had a much stronger impact than anionic and non-ionic surfactants. The second one concerns their ecotoxicity. Lewis [5] wrote a review on the toxicity of these 3 families of surfactants, on algae. The toxicity varied by 3 orders of magnitude depending on the species of algae studied, and on the same species, it varied by 4 orders of magnitude depending on the surfactant. It is therefore difficult to generalize and extrapolate the results, especially since the analytical verification of the exposure concentration was not often performed. However, in general the cationic molecules were the most toxic, followed by the non-ionic, and finally the anionic. Moreover, the presence of cationic surfactants such as quaternary ammonium could increase the risk of bacterial resistance, as bacteria exposed to quaternary ammoniums have been shown to acquire both quaternary ammonium resistance and antibiotic

resistance [6]. Finally, alkylphenols, the final degradation products of the non-ionic surfactants alkylphenol ethoxylates, are persistent, bioaccumulative, and disrupt endocrine activity [7].

Data on the occurrence of surfactants in the environment are, however, very limited [1]. The latest studies reveal high concentrations of surfactants in wastewater. In particular, anionic surfactants are found in concentrations sometimes exceeding mg/L [8]. Non-ionic surfactants have also been quantified in wastewaters but at concentrations lower than anionic ones; between 0.1 and 10 µg/L [9, 10]. Finally, cationic surfactants were detected at lower concentrations [6, 11]. However, these have the particularity of being in very high concentrations in solid matrices, particularly in sewage sludge [6, 12]. Their positive charge generates ionic interactions with the particles, which result in strong adsorption [13, 14]. Anionic surfactants are also found in solid matrices, at slightly lower concentrations [15-17]. Finally, concentrations of non-ionic surfactants between 50 µg/kg and 5 mg/kg have been reported [18, 19]. These high concentrations suggest a strong impact on the receiving environment, such as river sediments [1].

Due to these possible strong interactions between the analytes and the solid environmental matrices, the extraction of these compounds requires a dedicated efficient methodology to release them from the solid material. Different types of extraction techniques were reported: mechanical agitation (Vortex [15, 19, 20], oscillation with Zirconium beads [6]), temperature (Soxhlet [21]), temperature and pressure (Pressurized Liquid Extraction (PLE) [9, 22-24]) and ultrasound [12, 16, 25-27]. However, in most studies, PLE or Ultrasound-assisted Extraction (UAE) were used. Different parameters explain this choice: short extraction time, low volume of solvent, moderate cost and ease of use. Indeed, the extraction times are very variable, from 10 and 30 minutes respectively for PLE and ultrasound, to 18 hours with the Soxhlet method. Moreover, UAE can be performed using an ultrasonic bath, which is quite inexpensive. However, to our knowledge, only two surfactant analysis methods allowing the extraction of anionic, non-ionic and cationic substances from sediments and sewage sludges have been reported in the literature. Both methods required a purification step, which can be very time consuming.

Gonzalez et al. [24] used PLE followed by solid phase extraction on C18 cartridge. Bergé et al. [20] adapted a QuEChERS method [28], with the addition of a second extraction at acidic pH, followed by purification by SPE on C8 cartridge.

Within this context, the objective of this study was to develop a sensitive and reliable analytical methodology to fill the knowledge gap regarding the occurrence of surfactants in the environment, particularly in sediments. In order to limit the number of analyses, this method must cover a wide range of surfactants, which were chosen based on a previous work [29]. This study focuses on the optimization, validation and application of the developed analytical method. After having compared two types of extraction, salt, and vortex assisted solid-liquid extraction and UAE, different extraction solvents were tested. Then, the results of the validation of the final UAE protocol and analysis by LC-MS/MS are presented. The optimized analytical method was finally applied to 30 French river sediment samples, revealing concentrations higher than 1 mg/kg for some cationic and anionic surfactants.

2. Materials and methods

2.1 Standards and chemicals

Targeted surfactants were chosen from a previous study [29] and comprise 12 families of surfactants: anionic (linear alkylbenzene sulfonate (LAS), alkylethersulfate and alkylsulfate), non-ionic (octylphenol ethoxylate (OP_nEO), cocamides and 2,4,7,9-Tetramethyl-5-decyne-4,7-diol (TMDD)), cationic (benzalkonium chloride (BAC), dialkyldimethyl ammonium chloride (DDAC), alkylpyridinium, triethanolamine esterquat (TEAQ), amidoamine) and amphoteric (cetylbetaine). The suppliers of standards are reported in Table S1. Stock standards solutions were prepared as published elsewhere [29].

LC-MS grade methanol (MeOH) and acetonitrile (ACN) were supplied by Honeywell (Seelze, Germany), while water was purchased from Fisher Chemical (Geel, Belgium). Formic acid (FA), acetic acid (AA) were supplied by Biosolve-chemicals (Dieuze, France), ammonium hydroxide by Fluka (Saint-Quentin Fallavier, France) and ethylenediaminetetraacetic acid (EDTA) by VWR Chemicals (Fontenay-sous-bois, France). Citrate buffers (Part Number: 5982-6650, Agilent Technologies, Avondale, Arizona), consisted of 4 g anhydrous MgSO₄, 1 g sodium citrate, 0.5 g citric disodium salt sesquihydrate, and 1 g NaCl.

2.2 Salt-assisted solid liquid extraction

The salt-assisted solid-liquid extraction (SLE) protocol was based on the work of Bergé et al. [20]. It consists of a double salt-assisted SLE, with acidic conditions: the first with a mild acid and the second with strong acidic conditions. Briefly, 500 mg of sample was introduced into a 50-mL polypropylene centrifuge tube, to which a ceramic homogenizing bar, 10 mL of ACN, and 6 mL of LC-MS water were added. After a 20-s vortex run, 3 mL of heptane was added. Then, after a 40-s vortex run, the citrate buffer was introduced into the tube, which was immediately shaken manually for 20 s and then

40 s by vortex. After centrifugation at 10,000 rpm for 5 min, 4 mL of supernatant was collected in a 12-mL calcined glass tube. 0.5 mL of sulfuric acid was then added to the 1st extraction tube containing the solid sample, and after shaking 30 seconds and centrifugation, 4 mL of supernatant was collected and added to the 1st supernatant. The extracts were evaporated to dryness under nitrogen at 40°C and then reconstituted in 1 mL of the injection solvent, which was composed of acetonitrile, water and a 25% ammonium hydroxide (NH₄OH) solution (see section 2.4).

2.3 Ultrasound-assisted extraction

The UAE protocol was adapted from the method developed by Gago-Ferrero et al. [30] for pharmaceuticals in sludges. It consists in a double UAE extraction. 500 mg of sample were introduced in a 12 mL glass tube, previously calcined at 450°C for 15h. 3 mL of extraction solvent were added and the tube was then vortexed for 15 seconds, ultrasonicated for 15 minutes at 50°C, and centrifuged for 10 minutes at 5000 rpm. The supernatant was collected in a glass tube. A second 3 mL aliquot of solvent was added to the sample tube and vortexed, ultrasonicated, and centrifuged as above. The two supernatants were combined in a glass tube, evaporated to dryness under nitrogen flow at 40°C then taken up with 1 mL of the injection solvent. The tube was vortexed for 15 seconds, then ultrasonicated for 10 minutes, and centrifuged for 5 minutes at 5000 rpm. Finally, the supernatant was collected in a vial for injection. Five extraction solvents were tested: 100% MeOH, MeOH with 1% FA, 90/10 MeOH/water with 0.1 M EDTA, 100% ACN, 90/10 ACN with 1% AA/water at 0.1 M EDTA.

2.4 LC-MS/MS analysis

Analysis was carried out with an Agilent 1290 infinity LC system (Agilent Technologies, Avondale, USA) coupled with a 3200 QTrap (ABSciex, Foster City, USA) triple quadrupole mass spectrometer, with an electrospray ionization (ESI) source. The injection solvent was composed of acetonitrile, water

and a 25% ammonium hydroxide (NH₄OH) solution (30%, 65% and 5%, respectively). The reverse phase LC column was a Poroshell 120 (Agilent) C18 1.9 μm (50 mm x 2.1 mm) protected with a Krudkatcher from Phenomenex (Torrence, California). The injection volume was 20 μL for positive ESI mode and only 10 μL for negative ESI analyses due to high concentrations of LAS. The organic phase (B) was methanol. Aqueous phase (A) consisted in 0.1% formic acid water for positive ESI and 1 mM ammonium acetate for negative ESI. In positive mode, the gradient was a linear ramp from 50% to 100% B over 5 minutes with a 2 minute plateau and a 3 minute equilibration phase. In negative mode, it was a linear ramp from 40% to 100% B over 4 minutes with a 2 minute plateau and a 3 minute equilibration phase. Other LC parameters were the same as already published [29]. Chromatograms are presented in Figure S1.

Two MRM transitions, parent ion > product ion, were recorded for each substance, the most sensitive for quantification (MRM1), and the second most sensitive for confirmation (MRM2). Optimized MS/MS parameters are summarized in Table S2. Temperatures of ESI sources were set to 450 and 500°C, for positive and negative modes respectively.

2.5 Validation of the whole procedure

Matrix-matched calibration was used. The calibration was performed using Fontainebleau sand [31] (VWR chemicals) (calcined at 450°C for 15h) spiked at different concentrations, which underwent the entire analytical protocol. Prior to extraction, an overnight contact time was applied as follows: the tube containing the spiked sample was vortexed for 30 seconds, then the added solvent was evaporated in a hood overnight.

Validation of the analytical method was performed using the same reference matrix. The method limits of quantitation (LOQ) were determined differently, according to the contamination of method blanks: if signal to noise (S/N) was inferior to 10, LOQ was the concentration of analyte that produces a peak signal 10 times higher than the chromatogram background. If S/N was superior to 10, the LOQ was

the concentration that produces a peak area twice as high as the blank peak area. LOQ were validated following the French standard NF T90-210 [32]. Repeatability and trueness experiments were performed using calcined sand at LOQ and 10 times LOQ. Linearity was evaluated between LOQ and 10 times the LOQ. Inter-operator precision was evaluated at the LOQ level and inter-days precision, at 10 times the LOQ level.

2.6 Application and statistical analysis

30 sediments samples, collected in the French territory between September and October 2018, were analysed using the validated method. Their organic carbon concentration was between 2 and 256 mg/g with a mean of 39 mg/g and their dry matter content between 9 and 81% with a mean of 51%. Sediments were first freeze-dried, grinded and sieved. Each sample was spiked with 100 μ L of a solution of surrogate standards (BDDA-d5 (100 μ g/L), HexPyr-d5 (1000 μ g/L), SDS-d25) (1000 μ g/L)) and an overnight contact time was applied before extraction. Identification of surfactants was confirmed following four criteria: MRM 1 with S/N > 10, MRM2 with S/N > 3 and the concordance of retention times and MRM ratios between the sample and calibration standards (Table S2).

Matrix-matched calibration was used for quantification. Each calibration was composed of 6 points corresponding to a method blank and the five concentration levels, 0.5*LOQ, 1*LOQ, 2.5*LOQ, 5*LOQ and 10*LOQ. The 0.5*LOQ level allowed to verify that the signal corresponding to this concentration was higher than the method blank. If this was not the case, clean-ups of the LC-MS/MS analytical system were performed with different solvent mixtures until a background compatible with the LOQ was obtained. Each analytical sequence comprised the calibration standards, samples, quality controls, injection blanks and method blanks. The creation of a correlation matrix [33] of surfactant concentrations and the calculation of the corresponding p-values [34] were performed using R studio.

3. Results and discussion

3.1 Impact of sample preparation on blank contamination

Given the problems of contamination experienced during the development of the analysis of surfactants in surface water [29], initially, method blanks from the different protocols described in sections 2.2 and 2.3 were carried out. For these tests, the reference matrix was Fontainebleau sand calcined at 450°C for 15h. Extraction blank contamination was observed for two cationic surfactants, BAC-C₁₂ and C₁₄, one anionic one, EHS, and two non-ionic ones, TMDD and CMEA, particularly when using the salt-assisted solid-liquid extraction. Among these compounds, a peak with a signal to noise superior to 10 was observed for BAC-C₁₂ and C₁₄ showing that the source of contamination is in the analytical instrument itself and/or in the mobile phase. Regardless of the extraction solvent used, ACN or MeOH, and the additives, areas from UAE were in average 10 times lower than areas from salt-assisted SLE. The highest signals in the extraction blanks were observed for BAC-C₁₂ and EHS, and were on average 3 and 30 times lower using UAE, respectively. One source of contamination was the centrifuge tubes, which were made of polypropylene, in the salt assisted SLE, whereas calcined glass tubes were used for UAE. Migration of different additives from this kind of polymer has already been reported [35]. Further experiments determined that these contaminations came also from the citrate buffers, which were ready-to-use and packaged in foil pouches. Consequently, UAE was selected for the following experiments.

3.2 Ultrasound-assisted extraction optimization

One of the most critical parameters for extracting compounds from environmental solid matrices is the extraction solvent. This one must allow a good solubility of the analytes and break the interactions between the contaminants and the matrix. Considering that surfactants have both hydrophilic and hydrophobic functions, relatively polar organic solvents, MeOH and ACN, were selected. Based on

another work on sludge [20] and literature, these solvents were tested pure or with 10% water to which an acid and/or EDTA was added. All extraction tests were performed in triplicates with Fontainebleau sand. During preliminary experiments, differences of recoveries were observed when samples were spiked with all surfactants together and with cationic and anionic surfactants separately. Consequently, to be as close as possible to real samples, the reference matrix was spiked with cationic, anionic and non-ionic surfactants.

Figure 1 shows the comparison of the extraction recoveries obtained with the different tested conditions. Since the trends are the same for different homologues of the same surfactant family, only the recoveries of one homologue are shown in the figure. For EHS and SDS, recoveries are quite similar whatever the extraction solvent used. The addition of FA and/or EDTA improved the yields of LAS and alkyl ether sulfates. Specifically, the 90/10 acetonitrile with 1% acetic acid (AA)/water and 0.1 M EDTA mixture performed best for alkyl ether sulfates. Improved extraction efficiency with the addition of EDTA has recently been observed, particularly for pharmaceuticals [30] and polar pesticides [36], but, to our knowledge, has never been tested before for surfactant extraction.

Regarding non-ionic surfactants, the trends for these three families of compounds are different. For CMEA, the UAE technique with a 100% organic solvent, MeOH or ACN, gave the best recovery. For TMDD, it was the UAE with 100% acetonitrile. Finally, for OPEO, the extraction with 100% methanol or methanol with EDTA yielded the best result.

For most cationic surfactants, extraction with MeOH and formic acid was the least efficient conditions. The two conditions giving the best performance for most the compounds were 100% ACN and the 90/10 ACN with 1% acetic acid (AA)/water mixture with 0.1 M EDTA. However, the most efficient conditions for extracting BAC-C₁₂ and LaurPyr were with 100% organic solvent, MeOH or ACN. The difference between BAC-C₁₂ and its C₁₄, C₁₆ and C₁₈ homologues may come from its lower

hydrophobicity, making it more soluble in the tested organic solvents. Finally, for cetylbetaine, extraction with 100% MeOH yielded the best result.

In conclusion, except for anionic surfactants, no extraction condition was optimal for all target substances. These experiments show the need to find a compromise when developing multi-residue analytical methods. However, the mixture 90/10 ACN with 1% acetic acid (AA)/water with 0.1 M EDTA was retained for the rest of the study as it gave the highest recoveries regarding anionic surfactants and was the only one that allowed recoveries superior to 70%, except the TEAQ.

3.3 Validation

The optimised analytical method was evaluated in terms of sensitivity, linearity, accuracy, repeatability and intermediate precision, using Fontainebleau sand calcined at 450°C for 15 hours as the reference matrix.

The LOQs ranged from 6.4 µg/kg for LAS C10 to 158 µg/kg for 1-laureth sulfate (Table 1). Compared to the literature, these LOQs are of the same order of magnitude or higher. However, the methods developed in the other studies were specific to some families of surfactants. Concerning the method developed by Sanderson for laureth sulfates [27], the sample mass was 35 g, compared to 500 mg in our method, and the limits of quantification were only estimated and not validated.

The highest LOQs are those of SDS and laureth sulfates. These rather high LOQs are explained by the presence of these compounds in the method blanks. Indeed, 13 substances out of the 27 targeted have a signal-to-noise ratio greater than 10 in the method blanks: LAS C10 to C13, laureth sulfates, SDS, BAC-C₁₂ and C₁₄, DDAC-C₁₀ and TEAQ. The concentrations of these contaminations are highly variable, ranging from 1.6 µg/kg for LAS C10 to 31 µg/kg for SDS. In order to be above this background during the analysis, the LOQ were determined so that the peak area was twice as high as the blank peak area. Finally, extraction recoveries were superior to 80%, except for the cationic

surfactants TEAQ and SADP-DMA. Cationic surfactants are well-known to be difficult to extract from environmental solid matrices, due to polar, hydrophobic and electrostatic interactions with the surfaces of negatively charged particles.

Given these results in terms of recoveries and levels of contamination of the method blanks, matrix-matched calibration was selected. Linearity range, trueness, repeatability and intermediate precision indicators are summarized in Table 2. The correlation coefficients were all higher than 0.991, except for BAC-C₁₆ and C₁₈. These two surfactants are both hydrophobic and cationic, the calibration curves tended toward a quadratic curve pattern. Trueness was evaluated at the LOQ level and at ten times LOQ. In both cases, trueness was higher greater than 75%, showing that matrix-matched calibration effectively corrected for the lower recoveries of TEAQ. Repeatability and intermediate precision were also evaluated at these two concentrations. At the LOQ, the inter-operator precision was evaluated, whereas at 10 times the LOQ, it was the inter-day precision on 3 days. The coefficients of variation (CV) were respectively comprised between 6 and 22% and between 10 and 32% for repeatability and inter-operator precision. Laureth sulfate and TEAQ were the compounds with the most variability, which may have two explanations: high and variable contamination levels and low mass spectrometry response factors. Indeed, the response factors for TEAQ were about ten times lower than for BAC. Overall, these validation data were satisfactory.

Finally, in order to evaluate the matrix effects and to validate the relevance of the calibration in the Fontainebleau sand matrix, three sediment samples were extracted and analyzed, the concentrations of surfactants were calculated by matrix-matched calibration and standard addition. Regarding standard addition, spiking was performed using the same protocol as matrix-matched calibration (see section 2.5). The standard addition calibration comprised 4 points which corresponded to a non-spiked sediment, and the sediments spiked at the expected concentration (determined by matrix-matched calibration) divided by 5, by 2 and by 1. Results of quantification are presented in Table S3. The differences in the concentrations determined through the two calibration methods being less than 25%,

these experiments allowed to validate the calibration in the Fontainebleau sand matrix for the surfactants quantified in these sediments.

3.4 Application to real samples

The 27 surfactants were searched for in 30 sediment samples collected in French rivers, between September and October 2018. Matrix-matched calibration with Fontainebleau sand was used for quantification. Quantification frequencies and mean concentrations are summarized in Table 3. This study was part of a nation-wide monitoring campaign of 53 contaminants of emergent concern in surface water and sediment [37]

Of the 27 surfactants searched for, 9 were not detected: one cationic LaurPyr, one anionic, 2-laureth sulfate, and all targeted nonionic surfactants, OP₇₋₁₁EO, CMEA, and TMDD. These results can be explained either by a low use of these compounds or by a low affinity of these substances for solid particles. In the study by Loyo-Rosales et al. [23], OP₁₋₅EO were looked for in river water and sediments and were very little quantified. In Western Europe, the use of OPEO has decreased following the identification of their main degradation products as endocrine disruptors, and their inclusion in the OSPAR convention and in the list of "substances of very high concern" (SVHC). On the contrary, TMDD has already been detected quite frequently in river waters [29, 38, 39]. The fact that it was not quantified in sediment suggests that this compound has little affinity for the particulate phase.

Considering the anionic surfactants, alkyl and alkyl ether sulfates were found in very few samples, with quantification frequencies between 0 for 2-laureth sulfate and 6% for EHS. SDS and 1-laureth sulfate were quantified in the same sample. Among the alkyl ether sulfate homologues, the major presence in sediments of SDS and 1-laureth sulfate has already been observed [27]. LAS were the most frequently quantified anionic surfactants. Quantification frequencies were between 23% for LAS C14 and 70% for LAS C11 to C13. They were also the surfactants with the highest concentrations, with

average concentrations above mg/kg for LAS C11 to C13. These high levels of contamination are consistent with the literature [22, 24, 25, 40]. The correlation matrix of surfactant concentrations (Figure 2) showed a strong correlation between the four different homologues of LAS (p-value < 0.0001 [34]). This is consistent with the fact that they all are used in the same formulations and have similar behaviours in the aquatic environment.

Quantification frequencies of cationic surfactants were between 3% for SADP-DMA and 90% for DDAC-C₁₀. Cetylbetaine, a zwitterionic surfactant, which had never been quantified in river water, was found in 10% of the sediment samples. Average concentrations ranged from 23.5 µg/kg for TEAQ-C₁₈ to 828 µg/kg for TEAQ-C₁₈ saturated. These results are consistent with the literature that reports a high affinity of cationic surfactants for the particulate phase [13]. To our knowledge, no sediment occurrence data are available for TEAQ, SADP-DMA, and cetylbetaine, although TEAQ are widely used compounds, mainly as softeners [41]. Cetylbetaine concentrations were strongly correlated with concentrations of BAC (p-value < 0.0001) (Figure 2). BAC were quantified in more than 30% of the sediment samples at average concentrations of 84 µg/kg for BAC-C₁₈ and 355 µg/kg for BAC-C₁₂, which is consistent with the literature [21, 40]. Concentrations of DDAC-C₁₀, which was quantified surfactant in 90% of the sediment samples, were also correlated with BAC, particularly with BAC-C₁₄. Finally, concentrations of TEAQ homologues were strongly correlated with each other, which is consistent with the fact that they are present in the same products. More surprisingly, their concentrations also strongly correlated with LAS (p-value < 0.0001). As LAS, TEAQ may be markers of heavily polluted sites.

In conclusion, this application shows that the developed analytical method is efficient enough to obtain a broad view of the surfactant contamination of sediments. However, a compromise was made during the development and it would be necessary to use more class-specific methods to lower the limits of quantification.

4. Conclusion

Since surfactants are present in both dissolved and particulate fractions of rivers, it is essential to develop methods for extracting them from sediments. Two types of extraction, salt- and vortex-assisted, and ultrasound-assisted extraction were compared, first in terms of method blank contamination, then in terms of extraction efficiency. Different organic solvents and the addition of acid and EDTA were also tested. Except for anionic surfactants, no extraction condition was optimal for all target substances which shows the limitation of multi-residue analytical methods. However, the ultrasound-assisted extraction with the mixture 90/10 ACN/water with 1% acetic acid and 0.1 M EDTA yielded globally the highest recoveries and the lowest method blank contamination. The validation of the finalized protocol showed satisfactory performances in terms of sensitivity, linearity, precision and trueness. The limits of quantification obtained, between 6.4 $\mu\text{g}/\text{kg}$ for LAS C10 and 158 $\mu\text{g}/\text{kg}$ for 1-laureth sulfate, are compatible with trace analysis in sediments. Finally, more than half of the targeted surfactants were quantified in river sediment samples. The surfactants with the highest quantification frequencies were BAC, DDAC, and LAS, with mean concentrations between 75 and 4182 $\mu\text{g}/\text{kg}$. These results show that rivers are highly contaminated with different families of surfactants, which would therefore deserve increased monitoring in the environment.

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References

- [1] Jardak, K., Drogui, P. and Daghrir, R. Surfactants in aquatic and terrestrial environment: occurrence, behavior, and treatment processes. *Environmental Science and Pollution Research*. 23 (2016) 3195-3216.
- [2] Dollinger, J., Schacht, V. J., Gaus, C. and Grant, S. Effect of surfactant application practices on the vertical transport potential of hydrophobic pesticides in agrosystems. *Chemosphere*. 209 (2018) 78-87.
- [3] Hari, A. C., Paruchuri, R. A., Sabatini, D. A. and Kibbey, T. C. G. Effects of pH and cationic and nonionic surfactants on the adsorption of pharmaceuticals to a natural aquifer material. *Environmental Science & Technology*. 39 (2005) 2592-2598.
- [4] Pan, G., Jia, C., Zhao, D., You, C., Chen, H. and Jiang, G. Effect of cationic and anionic surfactants on the sorption and desorption of perfluorooctane sulfonate (PFOS) on natural sediments. *Environmental Pollution*. 157 (2009) 325-330.
- [5] Lewis, M. A. chronic toxicities of surfactants and detergent builders to algae - A review and risk assessment. *Ecotoxicology and Environmental Safety*. 20 (1990) 123-140.
- [6] Ostman, M., Lindberg, R. H., Fick, J., Bjorn, E. and Tysklind, M. Screening of biocides, metals and antibiotics in Swedish sewage sludge and wastewater. *Water Research*. 115 (2017) 318-328.
- [7] Acir, I.-H. and Guenther, K. Endocrine-disrupting metabolites of alkylphenol ethoxylates - A critical review of analytical methods, environmental occurrences, toxicity, and regulation. *Science of the Total Environment*. 635 (2018) 1530-1546.
- [8] Freeling, F., Alygizakis, N. A., von der Ohe, P. C., Slobodnik, J., Oswald, P., Aalizadeh, R., Cirka, L., Thomaidis, N. S. and Scheurer, M. Occurrence and potential environmental risk of surfactants and their transformation products discharged by wastewater treatment plants. *Science of the Total Environment*. 681 (2019) 475-487.
- [9] Barber, L. B., Loyo-Rosales, J. E., Rice, C. P., Minarik, T. A. and Oskouie, A. K. Endocrine disrupting alkylphenolic chemicals and other contaminants in wastewater treatment plant effluents, urban streams, and fish in the Great Lakes and Upper Mississippi River Regions. *Science of the Total Environment*. 517 (2015) 195-206.
- [10] Ciofi, L., Ancillotti, C., Chiuminatto, U., Fibbi, D., Pasquini, B., Bruzzoniti, M. C., Rivoira, L. and Del Bubba, M. Fully automated on-line solid phase extraction coupled to liquid chromatography-tandem mass spectrometry for the simultaneous analysis of alkylphenol polyethoxylates and their carboxylic and phenolic metabolites in wastewater samples. *Analytical and Bioanalytical Chemistry*. 408 (2016) 3331-3347.
- [11] Li, W. L., Zhang, Z. F., Sparhamb, C. and Li, Y. F. Validation of sampling techniques and SPE-UPLC/MS/MS for home and personal care chemicals in the Songhua Catchment, Northeast China. *Science of the Total Environment*. 707 (2020) 136038.

- [12] Ruan, T., Song, S., Wang, T., Liu, R., Lin, Y. and Jiang, G. Identification and Composition of Emerging Quaternary Ammonium Compounds in Municipal Sewage Sludge in China. *Environmental Science & Technology*. 48 (2014) 4289-4297.
- [13] Margot, J., Rossi, L., Barry, D. A. and Holliger, C. A review of the fate of micropollutants in wastewater treatment plants. *Wiley Interdisciplinary Reviews-Water*. 2 (2015) 457-487.
- [14] Li, X. and Brownawell, B. J. Analysis of Quaternary Ammonium Compounds in Estuarine Sediments by LC-ToF-MS: Very High Positive Mass Defects of Alkylamine Ions as Powerful Diagnostic Tools for Identification and Structural Elucidation. *Analytical Chemistry*. 81 (2009) 7926-7935.
- [15] Huber, S., Remberger, M., Kaj, L., Schlabach, M., Jorundsdottir, H. O., Vester, J., Arnorsson, M., Mortensen, I., Schwartzon, R. and Dam, M. A first screening and risk assessment of pharmaceuticals and additives in personal care products in waste water, sludge, recipient water and sediment from Faroe Islands, Iceland and Greenland. *Science of the Total Environment*. 562 (2016) 13-25.
- [16] Abril, C., Luis Santos, J., Luis Malvar, J., Martin, J., Aparicio, I. and Alonso, E. Determination of perfluorinated compounds, bisphenol A, anionic surfactants and personal care products in digested sludge, compost and soil by liquid-chromatography-tandem mass spectrometry. *Journal of Chromatography A*. 1576 (2018) 34-41.
- [17] Gonzalez, M. M., Martin, J., Camacho-Munoz, D., Santos, J. L., Aparicio, I. and Alonso, E. Degradation and environmental risk of surfactants after the application of compost sludge to the soil. *Waste Management*. 32 (2012) 1324-1331.
- [18] Andreu, V., Ferrer, E., Rubio, J. L., Font, G. and Pico, Y. Quantitative determination of octylphenol, nonylphenol, alkylphenol ethoxylates and alcohol ethoxylates by pressurized liquid extraction and liquid chromatography-mass spectrometry in soils treated with sewage sludges. *Science of the Total Environment*. 378 (2007) 124-129.
- [19] Koh, Y. K. K., Chiu, T. Y., Paterakis, N., Boobis, A., Scrimshaw, M. D., Lester, J. N. and Cartmell, E. Fate and occurrence of alkylphenolic compounds in sewage sludges determined by liquid chromatography tandem mass spectrometry. *Environmental Technology*. 30 (2009) 1415-1424.
- [20] Berge, A., Giroud, B., Wiest, L., Domenjoud, B., Gonzalez-Ospina, A. and Vulliet, E. Development of a multiple-class analytical method based on the use of synthetic matrices for the simultaneous determination of commonly used commercial surfactants in wastewater by liquid chromatography-tandem mass spectrometry. *Journal of Chromatography A*. 1450 (2016) 64-75.
- [21] Martinez-Carballo, E., Gonzalez-Barreiro, C., Sitka, A., Kreuzinger, N., Scharf, S. and Gans, O. Determination of selected quaternary ammonium compounds by liquid chromatography with mass spectrometry. Part II. Application to sediment and sludge samples in Austria. *Environmental Pollution*. 146 (2007) 543-547.

- [22] Traverso-Soto, J. M., Lara-Martin, P. A., Gonzalez-Mazo, E. and Leon, V. M. Distribution of anionic and nonionic surfactants in a sewage-impacted Mediterranean coastal lagoon: Inputs and seasonal variations. *Science of the Total Environment*. 503 (2015) 87-96.
- [23] Loyo-Rosales, J. E., Schmitz-Afonso, I., Rice, C. P. and Torrents, A. Analysis of octyl- and nonylphenol and their ethoxylates in water and sediments by liquid chromatography/tandem mass spectrometry. *Analytical Chemistry*. 75 (2003) 4811-4817.
- [24] Gonzalez, S., Petrovic, M. and Barcelo, D. Simultaneous extraction and fate of linear alkylbenzene sulfonates, coconut diethanol amides, nonylphenol ethoxylates and their degradation products in wastewater treatment plants, receiving coastal waters and sediments in the Catalonian area (NE Spain). *Journal of Chromatography A*. 1052 (2004) 111-120.
- [25] Lara-Martin, P. A., Gonzalez-Mazo, E. and Brownawell, B. J. Multi-residue method for the analysis of synthetic surfactants and their degradation metabolites in aquatic systems by liquid chromatography-time-of-flight-mass spectrometry. *Journal of Chromatography A*. 1218 (2011) 4799-4807.
- [26] Gonzalez, M. M., Santos, J. L., Aparicio, I. and Alonso, E. Method for the simultaneous determination of the most problematic families of organic pollutants in compost and compost-amended soil. *Analytical and Bioanalytical Chemistry*. 397 (2010) 277-285.
- [27] Sanderson, H., Price, B. B., Dyer, S. D., DeCarvalho, A. J., Robaugh, D., Waite, S. W., Morrall, S. W., Nielsen, A. M., Cano, M. L. and Evans, K. A. Occurrence and hazard screening of alkyl sulfates and alkyl ethoxysulfates in river sediments. *Science of the Total Environment*. 367 (2006), 312-323.
- [28] Gonzalez-Curbelo, M. A., Socas-Rodriguez, B., Herrera-Herrera, A. V., Gonzalez-Salamo, J., Hernandez-Borges, J. and Rodriguez-Delgado, M. A. Evolution and applications of the QuEChERS method. *Trac-Trends in Analytical Chemistry*. 71 (2015) 169-185.
- [29] Wiest, L., Giroud, B., Assoumani, A., Lestremau, F. and Vulliet, E. A multi-family offline SPE LC-MS/MS analytical method for anionic, cationic and non-ionic surfactants quantification in surface water. *Talanta*. 232 (2021) 122441.
- [30] Gago-Ferrero, P., Borova, V., Dasenaki, M. E. and Thomaidis, N. S. Simultaneous determination of 148 pharmaceuticals and illicit drugs in sewage sludge based on ultrasound-assisted extraction and liquid chromatography-tandem mass spectrometry. *Analytical and Bioanalytical Chemistry*. 407 (2015) 4287-4297.
- [31] Al Saadi, F., Wolf, K., Kruijsdijk, C.V. Characterization of Fontainebleau sandstone: quartz overgrowth and its impact on pore-throat framework. *Journal of Petroleum and Environmental Biotechnology*. 7: 328 (2017). doi: 10.4172/2157-7463.1000328.
- [32] AFNOR 2009 NF T90-210 - Water quality - Protocol for the initial method performance assessment in a laboratory - May 2009 - AFNOR, 2009.
- [33] Wei T. and Simko V. (2017). R package "corrplot": Visualization of a Correlation Matrix (Version 0.84). Available from <https://github.com/taiyun/corrplot>.

- [34] Harrell F.E. Jr, with contributions from Charles Dupont and many others. (2020). Hmisc: Harrell Miscellaneous. R package version 4.4-2. <https://CRAN.R-project.org/package=Hmisc>.
- [35] Assoumani, A., Lestremau F., Ferret, C., Lepot, B., Salomon M, et al. Nation-Wide Monitoring Campaign of 53 Contaminants of Emergent Concern in Surface Waters and Sediment (EMNAT 2018): Occurrence and PNEC Exceedance Evaluation. 31. SETAC Europe annual meeting, Jun 2021, Online, Belgium <https://hal.archives-ouvertes.fr/ineris-03273938/>.
- [36] Chamkasem, N. and Harmon, T. Direct determination of glyphosate, glufosinate, and AMPA in soybean and corn by liquid chromatography/tandem mass spectrometry. *Analytical and Bioanalytical Chemistry*. 408 (2016) 4995-5004.
- [37] Pouech, C., Kiss, A., Lafay, F., Leonard, D., Wiest, L., Cren-Olive, C. and Vulliet, E. Human exposure assessment to a large set of polymer additives through the analysis of urine by solid phase extraction followed by ultra high performance liquid chromatography coupled to tandem mass spectrometry. *Journal of Chromatography A*. 1423 (2015) 111-123.
- [38] Guedez, A. A., Froemmel, S., Diehl, P. and Puettmann, W. Occurrence and temporal variations of TMDD in the river Rhine, Germany. *Environmental Science and Pollution Research*. 17 (2010) 321-330.
- [39] Dsikowitzky, L., Botalova, O., Illgut, S., Bosowski, S. and Schwarzbauer, J. Identification of characteristic organic contaminants in wastewaters from modern paper production sites and subsequent tracing in a river. *Journal of Hazardous Materials*. 300 (2015) 254-262.
- [40] Li, X., Doherty, A. C., Brownawell, B. and Lara-Martin, P. A. Distribution and diagenetic fate of synthetic surfactants and their metabolites in sewage-impacted estuarine sediments. *Environmental Pollution*. 242 (2018) 209-218.
- [41] Human and Environmental Risk Assessments (HERA) (2008): Esterquats environmental risk assessment. <http://www.heraproject.com>.

Figure captions

Figure 1: Absolute extraction recoveries with UAE, at 10 times the LOQ, using different solvents and additives: (A) anionic, (B) non-ionic, (C) cationic surfactants

Figure 2: Correlation matrix of surfactant concentrations in sediments (R package « corrplot » [33])

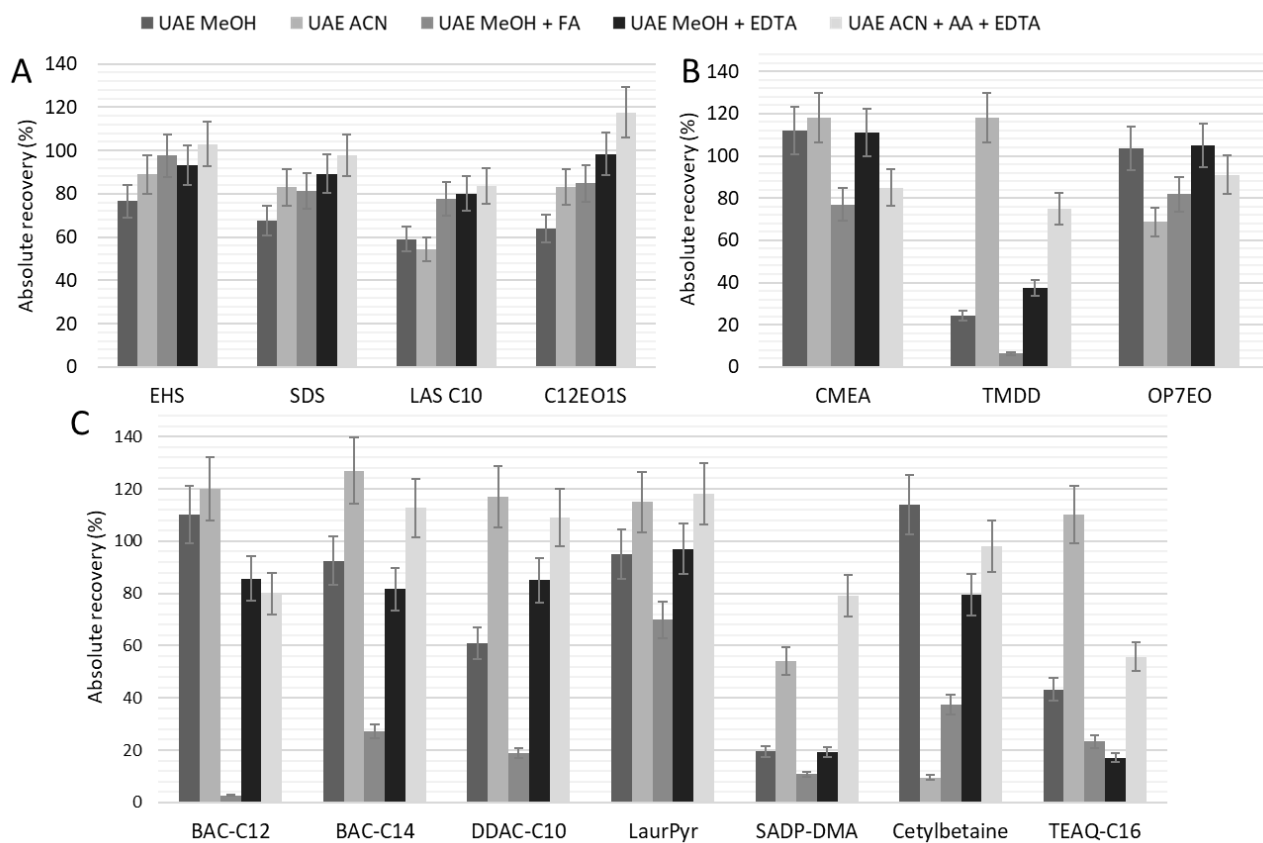


Figure 1

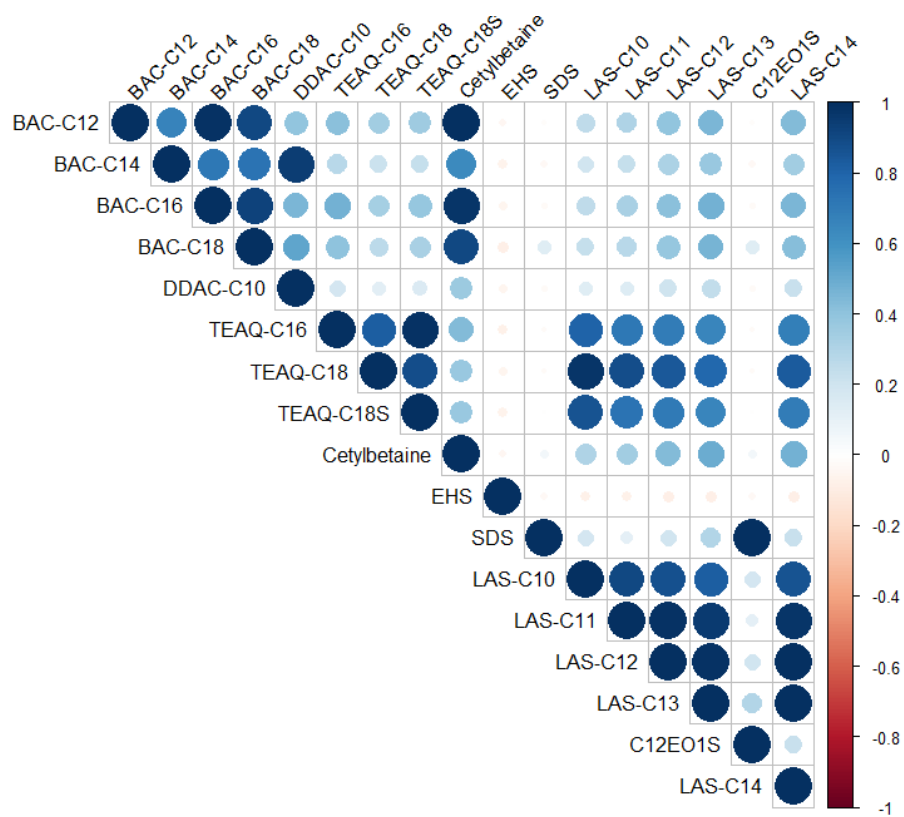


Figure 2

Table 1: Instrument (Instr.) and method limits of quantification (LOQ) compared to the literature, estimated method blank concentration and absolute extraction recoveries

| Substance | Instr. LOQ (µg/L) | Method LOQ (µg/kg) | Literature LOQ (µg/kg) | Ref. | Method blank concentration (µg/kg) | Absolute extraction recovery (%) at 5*LQ |
|-----------------------------------|-------------------|--------------------|------------------------|------|------------------------------------|--|
| LAS C10 | 2 | 6.4 | 9.3 | [25] | 1.6 | 83.7 |
| LAS C11 | 20 | 49 | 27 | [25] | 16 | 98.5 |
| LAS C12 | 15 | 44 | 15 | [25] | 20 | 97.6 |
| LAS C13 | 10 | 31 | 2.7 | [25] | 14 | 97.4 |
| LAS C14 | 0.5 | 32 | ND | | S/N <10 | 97.5 |
| C ₁₂ EO ₁ S | 10 | 158 | 1 (estim.) | [27] | 16 | 117.6 |
| C ₁₂ EO ₂ S | 8 | 124 | 1 (estim.) | [27] | 12 | 109.9 |
| SDS | 30 | 123 | 50 | [16] | 31 | 97.8 |
| EHS | 0.5 | 11 | ND | | S/N <10 | 103.0 |
| OP ₇ EO | 0.8 | 9.6 | 9 | [23] | S/N <10 | 111.3 |
| OP ₈ EO | 0.8 | 9.6 | 9 | [23] | S/N <10 | 119.1 |
| OP ₉ EO | 0.8 | 9.6 | 9 | [23] | S/N <10 | 117.2 |
| OP ₁₀ EO | 0.8 | 9.6 | 9 | [23] | S/N <10 | 107.8 |
| OP ₁₁ EO | 0.8 | 9.6 | 9 | [23] | S/N <10 | 113.7 |
| CMEA | 1 | 13 | ND | | S/N <10 | 107.6 |
| TMDD | 0.2 | 42 | ND | | S/N <10 | 113.6 |
| BAC-C ₁₂ | 5 | 27 | 1 | [21] | 2.7 | 120.8 |
| BAC-C ₁₄ | 4 | 18 | 1 | [21] | 3.0 | 112.7 |
| BAC-C ₁₆ | 0.2 | 28 | 0.7 | [21] | S/N <10 | 111.0 |
| BAC-C ₁₈ | 0.2 | 34 | 2 | [21] | S/N <10 | 113.1 |
| DDAC-C ₁₀ | 1 | 40 | 0.6 | [21] | 15 | 109.1 |
| LaurPyr | 0.3 | 105 | ND | | S/N <10 | 118.0 |
| TEAQ-C ₁₆ | 6 | 59 | ND | | 22 | 55.7 |
| TEAQ-C ₁₈ | 3 | 32 | ND | | 12 | 22.1 |
| TEAQ-C ₁₈ sat. | 1 | 12 | ND | | 4.0 | 94.4 |
| SADP-DMA | 0.5 | 39 | ND | | S/N <10 | 79.0 |
| Cetylbetaine | 0.5 | 21 | ND | | S/N <10 | 98.1 |

EHS: Ethylhexylsulfate; CMEA: Cocamide MonoEthanolAmine; LaurPyr: lauryl pyridinium;

SADP-DMA: StearAmiDoPropyl DiMethylAmine; TEAQ-C₁₈ sat.: saturated TEAQ-C₁₈

ND: No Data

Table 2: Linearity range and their determination coefficient (R^2), trueness, and intra and inter-days precision

| Substance | Linearity range ($\mu\text{g}/\text{kg}$) | R^2 | Trueness (%) at LOQ (n=6) | Intra-day precision CV (%) at LOQ (n = 6) | Inter-operator precision CV (%) at LOQ (n = 6) | Trueness (%) at 10*LOQ (n=6) | Intra-day precision CV (%) at 10*LOQ (n = 6) | Inter-day precision CV (%) at 10*LOQ (3 days) (n = 6) |
|-----------------------------------|---|-------|---------------------------|---|--|------------------------------|--|---|
| LAS C10 | 6.4 - 65 | 0.999 | 107 | 10 | 15 | 105 | 9.3 | 10 |
| LAS C11 | 49 - 490 | 0.998 | 107 | 8.9 | 16 | 106 | 7.1 | 14 |
| LAS C12 | 44 - 440 | 0.999 | 119 | 8.3 | 14 | 115 | 7.6 | 23 |
| LAS C13 | 31 - 310 | 0.996 | 119 | 18 | 20 | 114 | 8.1 | 17 |
| LAS C14 | 32 - 318 | 0.999 | 109 | 6.7 | 16 | 106 | 7.3 | 11 |
| C ₁₂ EO ₁ S | 158 - 1580 | 0.995 | 101 | 15 | 22 | 101 | 22 | 32 |
| C ₁₂ EO ₂ S | 124 - 1240 | 0.995 | 106 | 13 | 25 | 113 | 19 | 30 |
| SDS | 123 - 1226 | 0.999 | 105 | 8.2 | 10 | 103 | 7.5 | 10 |
| EHS | 11 - 107 | 0.999 | 118 | 7.1 | 17 | 113 | 14 | 15 |
| OP ₇ EO | 9.6 - 96 | 0.999 | 91 | 15 | 20 | 96 | 9.3 | 19 |
| OP ₈ EO | 9.6 - 96 | 0.992 | 75 | 12 | 15 | 86 | 11 | 15 |
| OP ₉ EO | 9.6 - 96 | 0.996 | 84 | 15 | 20 | 90 | 12 | 15 |
| OP ₁₀ EO | 9.6 - 96 | 0.994 | 80 | 19 | 25 | 89 | 17 | 18 |
| OP ₁₁ EO | 9.6 - 96 | 0.999 | 82 | 10 | 15 | 89 | 16 | 17 |
| CMEA | 13 - 131 | 0.998 | 101 | 9.6 | 14 | 101 | 5.7 | 13 |
| TMDD | 42 - 416 | 0.999 | 94 | 14 | 18 | 97 | 6.2 | 13 |
| BAC-C ₁₂ | 27 - 266 | 0.999 | 106 | 6.7 | 15 | 104 | 8.7 | 13 |
| BAC-C ₁₄ | 18 - 178 | 0.994 | 115 | 6.8 | 17 | 124 | 12 | 20 |
| BAC-C ₁₆ | 28 - 284 | 0.99 | 118 | 14 | 23 | 111 | 16 | 23 |
| BAC-C ₁₈ | 34 - 244 | 0.99 | 113 | 20 | 25 | 95 | 20 | 28 |
| DDAC-C ₁₀ | 40 - 402 | 0.991 | 112 | 13 | 18 | 117 | 16 | 18 |
| LaurPyr | 105 - 1050 | 0.999 | 105 | 8.6 | 16 | 104 | 10 | 17 |
| TEAQ-C ₁₆ | 59 - 590 | 0.998 | 115 | 19 | 22 | 110 | 17 | 26 |
| TEAQ-C ₁₈ | 32 - 320 | 0.993 | 119 | 12 | 20 | 108 | 16 | 23 |
| TEAQ-C ₁₈ s. | 12 - 125 | 0.993 | 113 | 15 | 18 | 124 | 15 | 27 |
| SADP-DMA | 39 - 392 | 0.999 | 120 | 17 | 21 | 105 | 12 | 22 |
| Cetylbetaine | 21 - 212 | 0.993 | 117 | 10 | 16 | 106 | 8.9 | 16 |

TEAQ-C₁₈ s.: saturated TEAQ-C₁₈

Table 3: Quantification frequency and mean concentration of the targeted surfactants in 30 sediments sampled in France in 2018

| Substance | Quantification frequency (%) | Mean concentration (µg/kg) |
|---|------------------------------|----------------------------|
| DDAC-C ₁₀ | 90 | 526 |
| LAS C13 | 70 | 4182 |
| LAS C11 | 70 | 1515 |
| LAS C12 | 70 | 3066 |
| BAC-C ₁₄ | 63 | 278 |
| BAC-C ₁₂ | 63 | 355 |
| LAS C10 | 57 | 74.6 |
| BAC-C ₁₈ | 37 | 84.2 |
| BAC-C ₁₆ | 30 | 93.3 |
| LAS C14 | 23 | 658 |
| TEAQ-C ₁₆ | 20 | 98.8 |
| TEAQ-C ₁₈ sat. | 17 | 148 |
| Cetylbetaine | 17 | 113 |
| TEAQ-C ₁₈ | 13 | 15.3 |
| EHS | 6 | 20.4 |
| 1-laureth sulfate (C ₁₂ EO ₁ S) | 3 | 412 |
| SDS | 3 | 236 |
| SADP-DMA | 3 | 82.6 |
| TMDD | 0 | |
| 2-laureth sulfate (C ₁₂ EO ₂ S) | 0 | |
| OP ₇₋₁₁ EO | 0 | |
| CMEA | 0 | |
| LaurPyr | 0 | |