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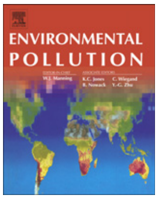

Determination and occurrence of secondary alkane sulfonates (SAS) in aquatic environments

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ABSTRACT

A new methodology has been developed for the determination of secondary alkane sulfonates (SAS), an anionic surfactant, in environmental matrices. Sediment and sludge samples were extracted using pressurized liquid extraction and sonication, whereas wastewater and surface water samples were processed using solid-phase extraction. Extraction recoveries were acceptable for both aqueous (78–120%) and solid samples (83–100%). Determination of SAS was carried out by high or ultra performance liquid chromatography – mass spectrometry using ion trap and time-of-flight detectors. The methodology was applied to samples from Guadalete River (SW Spain), where SAS concentrations below 1 μg L^{-1} were measured in surface water, and from 72 to 9737 μg kg^{-1} in sediments. Differential partitioning was observed for SAS homologues as those having a longer hydrocarbon chain which preferentially sorbed onto particulate matter. A preliminary environmental risk assessment also showed that SAS measured levels were not harmful to the aquatic community in the sampling area.

1. Introduction

Many aquatic ecosystems may be jeopardized because of the presence of diverse organic contaminants originating from human activities. In order to minimize negative effects from these chemicals, sewage from most European cities is treated nowadays in wastewater treatment plants (WWTPs) prior to being discharged. Among the different contaminants in wastewater, surfactants are the xenobiotic organic chemicals showing the highest concentrations as a consequence of their huge worldwide production (>10 million tons per year according to Holmberg et al., 2003); with approximately 60% of this amount belonging to surfactants of the anionic type (Salager, 2002). We have focused our attention in secondary alkane sulfonates (SAS), one of the major anionic surfactants used in dishwashing, laundry and cleaning products (66 000 tons/year in Europe) (HERA Project, 2005). SAS molecular structure consists of a sulfonate group bonded to a linear alkyl chain (linearity >98%) having typically from 14 to 17 carbon units, with an average of 15.9 carbon atoms and an average molecular weight of 328 Da. As with many other surfactants, removal of SAS in WWTPs is often about 95–99% and, according to Field et al. (1995), most of the compound is aerobically degraded in the activated sludge unit (84%), whereas approximately 16% of SAS is transferred to the sludge. Measured influent concentrations are between 598 and 976 μg L^{-1}, decreasing toward 3–14 μg L^{-1} in the effluent. Highest concentrations (509 μg kg^{-1}) have been reported to occur in sludges (Field et al., 1994), where this surfactant appears to remain stable even after anaerobic digestion (removal was only between 5 and 13% after 14 days according to Bruno et al., 2002).

In spite of the efficiency of WWTP removing surfactants from wastewater, significant concentrations of these compounds can be measured in many surface water, sediment and suspended solid samples (Prats et al., 1997; Di Corcia, 1998; Matthijs et al., 1999; Morrall et al., 2006). So far, most of the effort has been put into understanding the distribution and environmental behavior of two surfactants: linear alkylbenzene sulfonates (LAS) and nonylphenol polyethoxylates (NPEO). Under our knowledge, there are no available studies on this topic for SAS, excepting a concentration value of 3 μg L^{-1} that was reported in surface waters from Ruhr River (Germany) (Schröeder, 1995). Therefore, there it is necessary to improve the understanding of the environmental behavior of this surfactant. In this sense, the first step would be developing a reliable analytical method for their determination in environmental matrices at trace levels. Few protocols are available for the isolation and analysis of SAS, and most of them are focused on processing samples from WWTPs. Wastewater samples were extracted by solid phase extraction (SPE) using C18 Empore disks (Field et al., 1992a, 1994, 1995), whereas sewage sludge samples

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were processed using ion-pair/supercritical fluid extraction and conventional liquid solvent extraction (Field et al., 1992b). Bruno et al. (2002) employed a homemade apparatus using pressurized solvents instead. Subsequent separation and quantification of SAS homologues has been carried out by high-resolution liquid chromatography with fluorescence detection (HPLC-FL) (Field et al., 1992a) or coupled to mass spectrometry for the simultaneous analysis of these and other surfactants (Bruno et al., 2002). Derivatization of SAS and later analytes by gas chromatography-mass spectrometry (GC–MS) was also accomplished (Field et al., 1992b, 1994, 1995).

The main objectives of this study are: a) to develop a methodology for the analysis of SAS in surface water and sediment samples at sub-ppb levels, and b) to report for the first time the occurrence and distribution of SAS homologues in estuarine settings.

2. Experimental section

2.1. Material and standards

Formaldehyde, methanol (MeOH), dichloromethane (DCM), acetone (Ac) and ethyl acetate (EA) were of chromatography quality and purchased from Scharlau (Barcelona, Spain), phosphoric acid and sodium sulfate were purchased from Panreac (Barcelona, Spain), and water was Milli-Q quality. The solid-phase extraction (SPE) mini-columns used (500 mg) were supplied by Varian (Bond Elut C_{18}) and by Waters (Oasis HLB). The pure SAS internal standard (C_{12} SAS), the surrogate (C_{10} SAS), and the commercial SAS mixture was supplied by Clariant Produkte, with the following homologue distribution for the commercial mixture: C_{14} (31%), C_{15} (32%), C_{16} (23%) and C_{17} (14%).

2.2. Sampling and pretreatment

Wastewater samples and sludge were taken from a WWTP at Puerto Real (SW Spain), a 40 000 inhabitant town (36°31′29.88″N, 6°14′07.97″O). This WWTP treats an average flow of 8000 $m^3\ d^{-1}$ using primary and biologic treatments, and discharges directly into Bay of Cadiz. Additionally, surface water and sediment samples were collected from Guadalete River, within the same area. This river is 157 km long and flows across the province of Cadiz, entering the sea in the northern part of the Bay of Cadiz. Most of the terrain adjacent to the river is used to irrigate crops, and there are also direct discharges from farms and individual households. Two main pollution sources have been identified in the last stage of the river (Lara-Martín et al., 2008; Corada-Fernandez et al., 2011): a) occasional wastewater discharges from El Puerto de Santa María (80 000 inhabitants), and b) the discharge outlet of a WWTP that serves a town of 200 000 inhabitants (Jerez de la Frontera) located upstream. Surface water samples were collected from this river during a tidal cycle at station G0, using amber glass bottles (Fig. 1). Target compounds were preserved by adding 4% of formaldehyde and keeping the temperature below 4 °C during their transport to the laboratory, where samples were processed immediately. Solid samples were obtained at five different points (G1–G5) by taking the surface layer (1–3 cm) of sediments by means of PVC cores (length = 60 cm, diameter = 6 cm). Later, sediments were dried in a heater at 65 °C until constant weight and milled and strained through a 63 μm sieve.

2.3. Solid phase extraction

First, 200 mL surface water aliquots (100 mL for wastewater) were spiked to 50 $\mu g\ L^{-1}$ using C_{10} SAS as surrogate. Then, these samples (as well as sediment extracts previously redissolved in water) were purified and preconcentrated by C_{18} solid-phase extraction (SPE) mini-columns in an automated SPE Autotrace unit (Zymark). The mini-columns were rinsed with 8 mL of methanol and 5 mL of water before passing the aqueous samples at a flow of 3 mL min^{-1}. They were then washed with 20 mL of water, dried, and eluted with 10 mL dichloromethane/methanol 1:1. The eluate was finally evaporated to dryness and redissolved in 1 mL of methanol. This protocol was developed by spiking Milli-Q water to 100 $\mu g\ L^{-1}$ of a SAS commercial mixture and carrying out several recovery assays for optimizing cartridge type, pH and extraction solvent.

2.4. Ultrasonic extraction and pressurized liquid extraction

Solid samples (sludge and sediment) were extracted using two different techniques: sonication and pressurized liquid extraction (PLE). First, dried and sieved sludge (2 g) and sediment (4 g) samples were spiked to 1 mg kg^{-1} using C_{10} SAS. These amounts were placed inside PLE stainless steel extraction cells (22 mL) and mixed with 20 g of sodium sulfate. Dichloromethane/methanol 1:1 was passed through the heated (100 °C) and pressurized (1500 psi) cells during three cycles of 5 min each using a Dionex ASE 200 unit. Solid samples were also extracted using an ultrasonic bath (Selecta Ultrasons HD 10 L). Glass tubes were filled with 0.5 mL of sample and 10 mL of dichloromethane/methanol 1:1 at 30 °C, extracting SAS homologues during 3 cycles of 30 min each. Solvent was separated from the solid phase by centrifugation during 10 min at 3500 g after the end of each cycle, being replaced before starting a new extraction cycle. In both cases, extracts were evaporated to dryness and redissolved in 5 mL of methanol and 95 mL of Milli-Q prior purification and preconcentration by SPE. These protocols were developed by spiking non polluted sediment between 2 and 50 mg kg^{-1} of SAS and carrying out several recovery assays for optimizing the extraction solvent.

2.5. Liquid chromatography – mass spectrometry

Analysis of SAS was carried out using two different LC-MS systems. First, 100 μL of sample (dissolved in methanol) were mixed with 100 μL of water in 2 mL amber glass vials, and C_{12} SAS was added as internal standard at a concentration of 1 mg L^{-1}. Then, samples were analyzed using high-performance liquid chromatography coupled to ion trap mass spectrometry (HPLC-IT-MS) (LCQ, Thermo Fisher Scientific, Waltham, MA, USA). The injection volume was set to 20 μl. The chromatographic separation was performed on a reverse-phase C18 analytical column (LiChrospher 100 RP-18, Merck) of 250 mm × 2 mm and 3 μm particle size, using methanol and water as solvent at a flow rate of 0.15 mL min^{-1}. The elution gradient started at 45% of methanol and 55% of water. The percentage of methanol was increased linearly to 100% during the first 10 min, and kept at 100% over another 10 min. Total run time was 27 min including a re-equilibration time of 7 min. The determination of the analytes was carried out using an electrospray source operating in negative ionization mode (ESI−) due to the presence of a sulfonate group in the SAS structure. The source temperature was 220 °C and the source gas flow was

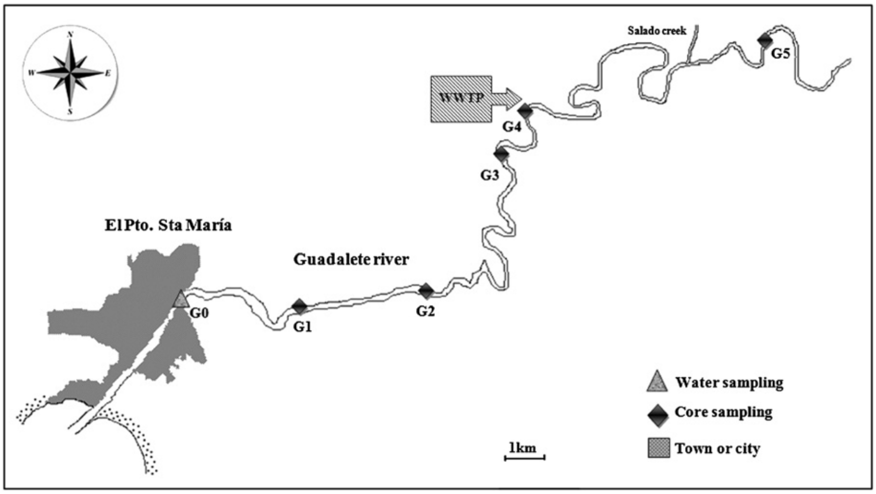

Fig. 1. Map showing the location of the sampling stations (G0–G5) along Guadalete River.