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Vertical distribution profiles and diagenetic fate of synthetic surfactants in marine and freshwater sediments

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HIGHLIGHTS

- Distribution of surfactants depended on type and proximity of wastewater sources.
- Sorption capacity was lower for anionic surfactants, thus being more bioavailable.
- Anaerobic degradation of LAS into SPC was observed in anoxic estuarine sediments.
- Nonionic surfactants were persistent in sediments under most conditions.

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ABSTRACT

This manuscript deals with the presence and degradation of the most commonly-used surfactants, including anionic (linear alkylbenzene sulfonates, LAS, and alkyl ethoxysulfates, AES) and non-ionic (alcohol polyethoxylates, AEOs, and nonylphenol polyethoxylates, NPEOs) compounds, in sediments and pore water from several aquatic environments (Southwest, Spain). Different vertical distributions were observed according to the respective sources, uses, production volumes and physicochemical properties of each surfactant. Levels of nonionics (up to 10 mg kg^{-1}) were twice as high as anionics in industrial areas and harbors, whereas the opposite was found near urban wastewater discharge outlets. Sulfophenyl carboxylic acids (SPCs), LAS degradation products, were identified at anoxic depths at some sampling stations. Their presence was related to in situ anaerobic degradation of LAS in marine sediments, whereas the occurrence of these metabolites in freshwater sediments was attributed to the existence of wastewater sources nearby. No significant changes in the average length of AEO and NPEO ethoxylated chains were observed along the sediment cores, suggesting that their biodegradation was very limited in the sampling area. This may be directly related to their lower bioavailability, as their calculated sediment–pore water distribution coefficients (log K_{sw}), which showed that non-ionic surfactants examined in this study had greater sorption affinity than the anionic surfactants (e.g., 2.3 ± 0.3 for NPEOs).

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1. Introduction

Many aquatic systems are subjected to the influence of both urban and industrial wastewater discharges, which are among the main sources of organic contaminants in the environment. Among many other chemicals, synthetic surfactants can be found at relatively high concentrations in wastewater due to their extensive use in a wide variety of applications: paints, pesticide formulations, wetting agents, personal care products, and, especially, active ingredients of detergents in cleaning products (Ying, 2006). In recent decades there have been several studies focused not only on understanding their distribution, behavior and fate once they are introduced into aquatic environments (Lara-Martín et al., 2008a), but also on their the effects on the cell membranes, on the activity of enzymes, on the binding to various proteins and to other cell components (Cserhatí et al., 2002). Special attention has been paid to anionic and non-ionic surfactants, which account for up to 90% of overall production of these chemicals. Data on the presence and concentrations of linear alkylbenzene sulfonates (LAS) (Ding et al., 1999; Eichhorn et al., 2002; González-Mazo et al., 1998; León et al., 2002; Takada and Ogura, 1992) and nonylphenol polyethoxylates (NPEOs) (Ahel et al., 1994; Ding et al., 1999; Isobe and Takada, 2004; Jonkers et al., 2003; Lee Ferguson et al., 2001) in the water column, and, to some extent, surface sediments, are available for a considerable number of aquatic settings from the United States and Europe. Relatively high concentrations of both surfactants (on the order of several ppm) can be found in river and coastal sediments impacted by sewage (Corada-Fernández et al., 2011; Lara-Martín et al., 2008b; Petrovic et al., 2002; Takada and Ogura, 1992), which act as sinks due to the affinity of these compounds to be sorbed onto suspended solids.

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The diagenetic fate of surfactants once they are buried is still not fully understood. It is often assumed, not only for surfactants but also for many other organic contaminants, that they may be preserved during years due to their low bioavailability and the absence of oxygen a few millimeters below the surface. There are some reports describing historical profiles of regulated contaminants such as polycyclic aromatic hydrocarbons (PAHs) or polychlorinated biphenyls (PCBs) (Eganhouse et al., 2000; Li et al., 2001; Lima et al., 2003; Pavoni et al., 1987; Rinawati et al., 2012; Santschi et al., 2001; Yamashita et al., 2000) in sediments. In some occasions, however, disappearance of contaminants by means of mechanisms such as reductive dechlorination has been observed in chlorinated chemicals such as chlorinated hydrocarbons and chlorofluorocarbons (CFCs). More recently, it has been also reported that reduced sulfur species, iron (II), and/or natural organic matter present in sediment pore water may be capable of promoting the in situ transformation of recalcitrant organic contaminants such as pesticides (Zeng et al., 2011, 2012). Regarding the biogeochemistry of surfactants, available data are still scarce. Sediment cores have been collected from a few points in harbors from Europe (Lara-Martín et al., 2006a, 2006b; León et al., 2001; Marcomini et al., 2000; Reiser et al., 1997), Canada (Shang et al., 1999), USA (Lee Ferguson et al., 2003) and Japan (Isobe et al., 2001; Yamashita et al., 2000), measuring vertical profiles for NPEOs and LAS, as well as some of their biodegradation intermediates (nonylphenol, NP, and sulfophenylcarboxylic acids, SPCs). Results from these studies show serious disagreements depending on the sampling area: some of them state that these compounds persist in the sedimentary column (Reiser et al., 1997; Shang et al., 1999) whereas others suggest that anaerobic degradation processes may take place as a reduction in the levels of these surfactants has been observed (Isobe et al., 2001; Lara-Martín et al., 2006a; Lee Ferguson et al., 2003; León et al., 2001; Marcomini et al., 2000).

Results from degradation laboratory assays performed under anaerobic conditions also show discrepancies. Thus, LAS is not biotransformed in sewage sludge as it has been detected at high concentrations (of the order of several g/kg) after anaerobic digestion (Federle and Schwab, 1992; García et al., 2005; Wagener and Schink, 1987). On the other hand, degradation of this surfactant into SPC has been confirmed (Lara-Martín et al., 2007a, 2007b) in laboratory experiments using anoxic marine sediments where significant concentrations of SPCs at anoxic depths ($E_h = -380$ mV) had been previously observed in pore water (González-Mazo et al., 1997; Lara-Martín et al., 2006a; León et al., 2001).

Degradation mechanisms of NPEOs during wastewater treatment and after discharge to the environment have been the subject of sometimes heated debate in the literature as well (Lee Ferguson et al., 2003; Shang et al., 1999). Today, it is generally accepted that both aerobic and anaerobic degradation processes (Ahel et al., 1994; Lee Ferguson et al., 2003; Lee Ferguson and Brownawell, 2003; Paterakis et al., 2012) involve the shortening of the polyethoxylated chain by progressive reduction in the number of ethoxylated units (EO) until NP is formed. Oxidation of this chain has been also observed, leading to the generation of nonylphenol ethoxycarboxylates (NPECs).

The main objective of this work was to shed some light on this topic by sampling sediment cores in different aquatic systems (estuaries, rivers and water reservoirs) and analyzing and comparing the vertical distributions of LAS and NPEOs. The research has been also extended to alkyl ethoxysulfates (AES) and alcohol ethoxylates (AEOs), two widely used surfactants previously detected by our group in water and surface sediments (Corada-Fernández et al., 2011; Lara-Martín et al., 2008b) that have received less attention from the scientific community. Concentrations of these chemicals in sediment samples and pore water have been measured along the sedimentary column, making it possible to calculate their sediment–pore water partitioning coefficients. Possible occurrence of in situ anaerobic degradation processes have been considered by determining the presence of SPCs in the case of LAS, and the loss of EO units for ethoxylated surfactants (NPEOs and AEOs).

2. Experimental

2.1. Study area

Six sediment cores (60 cm length × 6 cm diameter) were sampled between 2004 and 2008 from different aquatic systems at SW Spain. The location of these systems (water reservoir at Bornos, and the middle stretch and the estuary of the Guadalete River) and the sampling points are shown in Fig. 1. The first sediment core (C3) was sampled at the Bornos water reservoir, which has a water capacity of 200 hm^3 and is surrounded by a protected area employed only for recreational activities (hiking, kayaking and fishing). Treated wastewater is discharged from Bornos, an adjacent town of 8000 inhabitants. Next sampling points (G2, G3 and G7) are located 50 km downstream. A small creek (Salado Stream) flows directly into the Guadalete River at sampling point G7 after collecting sewage from small isolated urban areas (Lomopardo, Estella del Marqués and Torremelgarejo). Another sediment core was taken at sampling point G12, located 1 km away from the discharge outlet of a sewage treatment plant (STP) that receives wastewater from Jerez de la Frontera (a city of 200000 inhabitants). There is a small dam at this point that prevents the tidal wave going upstream, so the presence of seawater is discarded from station G12 to C3. Finally, the last sediment core was sampled at station G13, adjacent to El Puerto de Santa María, a town of 80000 inhabitants with small but active fishermen docks and several other industrial facilities located at the mouth of the river.

2.2. Sample pre-treatment

Sediment columns were sampled by using PVC cores with a scuba diver's help. They were maintained in a vertical position and at a temperature of 4 °C during their transfer to the laboratory, where they were frozen and stored until the time of analysis. Later, the frozen cores were sectioned taking slices of 1–3 cm from a length of 30–40 cm. These slices were centrifuged at 10000 g for 30 min to extract pore water. The sediment was then dried in a heater at 65 °C until a constant weight was reached, then milled using a zirconium oxide ball mill (Fristch) and passed through a 0.063 mm sieve. Porosity and redox potential (E_h) (See Supplementary Information, Figure S1) were determined along the sedimentary column, as well as C/N ratio (See Supplementary Information, Table S1).

2.3. Determination of target compounds

Analysis of LAS, AES, NPEOs, AEOs, NPECs and SPCs was performed according to the methodology previously described by Lara-Martín et al. (2006b). Briefly, target compounds were extracted from sediments in 20 min using pressurized liquid extraction (PLE) at 120 °C and 1500 psi with methanol as solvent. The methanolic extracts were evaporated to 1 mL and re-dissolved in 100 mL of Milli-Q water. Later, purification and preconcentration of these extracts as well as pore water samples were carried out by solid phase extraction (SPE) with octadecylsilica cartridges conditioned with methanol and eluted with a mixture of acetone/methanol 1:1 and ethyl acetate/dichloromethane 1:1. Recoveries were in the range from 70% to 107% for most homologues and the standard deviations were less than 14%.

Chromatographic separation of target compounds was performed by high performance liquid chromatography (HPLC) using a reversed–phase C-18 analytical column (Lichrospher 100 RP-18, Merck) and an elution gradient with methanol and water containing 5 mM of acetic acid and 5 mM of triethylamine. Finally, simultaneous identification and quantification of target compounds were performed by mass spectrometry (MS) (LCQ, Thermo) using an electrospray interface (ESI) operating in mix-mode ionization (negative ion mode for LAS, AES, SPCs and NPECs, whereas positive ionization was required for NPEOs and AEOs). Calibration curves were prepared using external standards

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