



Distribution of anionic and nonionic surfactants in a sewage-impacted Mediterranean coastal lagoon: Inputs and seasonal variations



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HIGHLIGHTS

- Surfactant fluxes in El Albuji3n watercourse show a marked seasonal variability.
- Maximum annual inputs (>400 kg) to Mar Menor lagoon were for LAS and SPC.
- LAS, AEO and NPEO levels were higher in samples collected near the lagoon shore.
- Surfactant concentrations in seawater were lower in summer than in other seasons.

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ABSTRACT

In this work we have monitored the seasonal inputs, occurrence and distribution of the world's most widely used surfactants (linear alkylbenzene sulfonates, LAS, nonylphenol polyethoxylates, NPEOs, and alcohol polyethoxylates, AEOs) in Mar Menor lagoon (SE Spain) and its main tributary (El Albuji3n) for the first time. Concentration of target compounds was determined in both surface waters and sediments after solid phase extraction and pressurized liquid extraction, respectively, followed by liquid chromatography–mass spectrometry (LC–MS). There were significant differences in surfactant fluxes from El Albuji3n towards Mar Menor depending on the season and the day of the week, with maximum estimated annual inputs being detected for LAS (406 kg) and their metabolites, sulfophenyl carboxylic acids (482 kg). Average concentrations of surfactants in the lagoon were between 44 and 1665 µg/kg in sediment, and between 0.3 and 63 µg/L in water. These levels were significantly higher for samples collected near the shore than for those measured inside the lagoon itself. Overall, the occurrence and distribution of surfactants in the system could be explained due to a combination of different sources (surface and groundwater inputs, treated and untreated wastewater effluents, towns, ports, etc.) and simultaneous in-situ physicochemical and biological processes, with a special emphasis on degradation during warmer months.

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1. Introduction

Synthetic surfactants comprise a broad group of organic compounds that are used in large quantities as active ingredients of household and industrial detergents, as well as in the formulation of personal care products, pesticides and pharmaceuticals, among other applications (Ying, 2006). These compounds can be classified, according to their charge, into several main groups, where those of the anionic and nonionic classes account for the highest production volumes. Thus, the European Committee of Organic Surfactants and their Intermediates (CESIO) reported that 1200 kt of anionic and 1400 kt of nonionic

surfactants were manufactured in Europe during the year 2010, which together represent for about 90% of the total European production of synthetic surfactants. Alcohol polyethoxylates (AEOs) are the most representative nonionic surfactants (e.g., 747 kt in Europe in 2000), followed by alkylphenol polyethoxylates (APEOs) and the anionic linear alkylbenzene sulfonates (550 kt both together). Widely used in household and laundry detergents, hand dishwashing liquids, shampoos, and other personal care products (Linear Alkylbenzene Sulfonate, LAS, 2009a), linear alkylbenzene sulfonates (LAS) are commercially available as a mixture containing homologues with alkyl chains ranging from 10 to 14 carbon units, and isomers resulting from the different attachment positions of the phenyl group along that chain. Commercial AEOs consist of a mixture of homologues typically having from 12 to 18 carbon atoms in their alkyl chain, which is bonded to a varying number of ethoxylate (EO) units. NPEOs (nonylphenol polyethoxylates, which

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are the main type of APEOs) are mixtures of a wide range of ethoxymers (from 1 to 20 EO units), and isomers, depending on the degree of branching of the C₉ alkyl chain. Both, AEOs and NPEOs, are widely employed in domestic and industrial applications (Alcohol ethoxylates, AEOs, 2009b) (e.g., detergents, emulsifiers, wetting, antifreeze and dispersing agents, industrial cleaners, textile, pulp and paper processing), although the estrogenic properties shown by some of NPEO degradation intermediates have resulted in restrictions on their production in recent years (Sonneschein and Soto, 1998).

Once used, surfactants and their metabolites enter aquatic environments via treated or untreated wastewater discharges, where these compounds are often found at very high concentrations compared to other targeted analytes (Prats et al., 2006) in spite of their high removal efficiencies (between 85% and 99.9%) in wastewater treatment plants (WWTPs) (González et al., 2004; Morrall et al., 2006). Sewage effluents may contain surfactant concentrations up to 872 µg/L for LAS (González et al., 2004), and from 0.9 to 15.6 µg/L for NPEOs and AEOs (Loyo-Rosales et al., 2007; Morrall et al., 2006). A considerable number of studies have also reported the presence of LAS (Corada-Fernández et al., 2011; Ding et al., 1999; Eichhorn et al., 2002; González-Mazo et al., 1998; Lara-Martín et al., 2008; León et al., 2002; Marcomini et al., 2000) and NPEOs (Belmont et al., 2006; Corada-Fernández et al., 2011; Isobe and Takada, 2004; Jonkers et al., 2003, 2005; Lara-Martín et al., 2008; Lee Ferguson et al., 2001; Maruyama et al., 2000; Petrovic et al., 2002; Zoller, 2006; Zoller and Hushan, 2000) in surface waters all around the world, with values between <50 and >1000 µg/L and between <0.1 and 100 µg/L, respectively. Data on the occurrence of AEOs are more limited in spite of their production volumes being comparable to those for LAS and NPEOs. One of the main reasons for this could be that analysis of AEOs cannot be resolved by conventional protocols based on the use of high performance liquid chromatography (HPLC) coupled to ultraviolet fluorescence detectors and gas chromatography coupled to mass spectrometry, as these compounds do not fluoresce or are nonvolatile (Fendinger et al., 1995; Kiewiet et al., 1995). So far, some authors have reported AEO levels lower than 50 µg/L in marine and fresh water (Corada-Fernández et al., 2011; Lara-Martín et al., 2011, 2008; Petrovic et al., 2002).

In spite of their relatively high solubility, a significant fraction of surfactants ends up in surface sediments due to sorption/precipitation processes. Concentrations in the solid phase are often higher by several orders of magnitude than those measured in water. A wide LAS concentration range (from less than 1000 to more than 200,000 µg/kg, depending on the distance from urban wastewater discharge sources and type of wastewater treatment) has been detected in sediments and suspended solids (Bester et al., 2001; Corada-Fernández et al., 2011; Folke et al., 2003; Lara-Martín et al., 2011, 2008, 2006a; León et al., 2002) from diverse freshwater and marine settings. Among nonionic surfactants, NPEOs have been widely detected in sediments from different sampling areas in Europe (Bester et al., 2001; Corada-Fernández et al., 2011; Jonkers et al., 2003, 2005; Petrovic et al., 2002), Japan (Isobe and Takada, 2004) and the United States (Lara-Martín et al., 2012; Loyo-Rosales et al., 2007) at levels between <10 and 28,500 µg/kg. Extensive datasets on the presence and distribution of NPEO degradation intermediates (nonylphenol and NPE₁₋₃Os) are also available due to their potential estrogenicity, reporting values from less than 100 to 30,000 µg/kg in rivers (Lara-Martín et al., 2006a; Loyo-Rosales et al., 2007; Isobe and Takada, 2004; Jonkers et al., 2003) and the sea bed (Bester et al., 2001; Lara-Martín et al., 2012; Lee Ferguson et al., 2001). A few recent papers have reported AEO levels in sediments (Corada-Fernández et al., 2011; Lara-Martín et al., 2011, 2012; Petrovic et al., 2002; Traverso-Soto et al., 2013), showing total concentrations, comparable to those found for NPEOs, between 7 and 12,200 µg/kg. Several studies have also reported surfactant concentrations in soils treated with sewage sludges, with values up to 15,000 µg/kg (Andreu and Picó, 2004) for LAS, and from 20 to 5000 µg/kg for NPEOs and AEOs (Andreu et al., 2007).

Surfactants in aquatic environments undergo degradation and sorption processes, which affect their removal and transport. As an example, LAS total amount onto particulate matter is commonly below 3% in rivers but from 11% to 59% in coastal waters, its sorption increasing towards higher salinity values (González-Mazo et al., 1998; Lara-Martín et al., 2008). Previous studies also showed relatively fast in-situ degradation of LAS, resulting in the formation of sulfophenylcarboxylic acids (SPCs), which are predominant in the dissolved form (>99%) (Corada-Fernández et al., 2011; Eichhorn et al., 2002; León et al., 2002). Regarding nonionic surfactants, between 25 and 65% of the total mass of NPEOs can be found in suspended solids (Jonkers et al., 2005; Lara-Martín et al., 2008). Their more polar metabolites (nonylphenol ethoxycarboxylates) are only present in the aqueous phase (Isobe and Takada, 2004; Jonkers et al., 2003), whereas those derived from progressive shortening of the ethoxylated chain (e.g., nonylphenol) are more hydrophobic than the parent compound and are strongly attached to sediments (Lee Ferguson et al., 2001; Maruyama et al., 2000). AEOs have also shown high affinity for suspended solids (86% is adsorbed according to Lara-Martín et al., 2008). Their in-situ degradation into polyethylene glycols (PEGs), generated by central fission of the ether bond of the AEO molecule, has been also confirmed at various sampling sites (Lara-Martín et al., 2011; Traverso-Soto et al., 2013). Both degradation and sorption processes, as well as concentrations of surfactants and their metabolites in wastewater and aquatic environments, are strongly dependent on environmental factors such as precipitation, temperature or salinity. Thus, their levels are expected to change depending on the season. As an example, León et al. (2004, 2011) have reported the influence of winter (10 °C) and summer (25 °C) temperatures in the sorption and degradation of LAS in laboratory experiments. This influence has been also observed in field samplings in estuaries (Lara-Martín et al., 2010), where a decrease in the concentrations of anionic surfactants was found in summer, when degradation processes are faster, whereas the highest concentrations were detected during the wet months, as rainwater exceeds the capacity of WWTPs, so untreated wastewater is discharged.

The present study focuses on performing, for the first time, a comparative study on the seasonal occurrence and distribution of LAS and NPEOs, as well as other less studied surfactants such as AEOs, in surface waters and sediments from a Mediterranean lagoon (Mar Menor, SE Spain) and its most relevant tributary (El Albujón watercourse). This setting was selected due to a high variability in physicochemical conditions and anthropogenic activities during the year. Specific objectives are: (i) to characterize the seasonal distribution of target compounds along El Albujón watercourse; (ii) to estimate their daily and annual input to the Mar Menor lagoon through El Albujón watercourse, considering both regular and flash flood periods; and (iii) to determine the presence and compare the seasonal distribution of surfactants in surface waters and sediments from the Mar Menor lagoon, identifying their main inputs along the coast.

2. Material and methods

2.1. Sampling areas and sample collection

The study area is the Mar Menor lagoon (Fig. 1), a hypersaline (42–47 psu) marine environment located in the southeastern coast of Spain that is heavily affected by intensive agriculture, seasonal tourism and recreational nautical activities. Water exchange between the lagoon and the Mediterranean Sea is limited (water residence time is 0.79 years according to Pérez-Ruzafa, 1989), taking place only through three shallow channels and, as a consequence of this, there are high seasonal fluctuations in temperature and salinity. Soils surrounding Mar Menor (Campo de Cartagena) are used for irrigated vegetable and woody crops, and there are also untreated wastewater discharges from farms and isolated houses. The main input of biologically treated

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