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Distribution and diagenetic fate of synthetic surfactants and their metabolites in sewage-impacted estuarine sediments☆

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ABSTRACT

Surfactants are high production volume chemicals used in numerous domestic and industrial applications and, after use, the most abundant organic contaminants in wastewater. Their discharge might jeopardize the receiving aquatic ecosystems, including sediments, where they tend to accumulate. This is the first comprehensive study on their distribution and fate in this environmental compartment as we performed simultaneous analysis of the three main classes of surfactants (anionic: LAS; nonionic: NPEO and AEO; cationic: DTDMAC, DADMAC, BAC, and ATMAC) and some of their transformation products (SPC, NP, NPEC, and PEG). To account for spatial and time trends, surface sediments and dated cores were collected from Jamaica Bay, a heavily sewage-impacted estuary in New York City. The concentrations of surfactants in surface sediments were between 18 and > 200 $\mu g\ g^{-1}$ and showed slight variation (<10%) over different sampling years (1998, 2003 and 2008). Cationic surfactants were found at the highest concentrations, with DTDMAC accounting for between 52 and 90% of the total sum of target compounds. Vertical concentration profiles in dated cores from the most contaminated station, in the vicinity of the biggest local sewage treatment plant (STP), indicated two sub-surface surfactant peaks in the mid-1960s (469 $\mu g\ g^{-1}$) and late 1980s (572 $\mu g\ g^{-1}$) coinciding with known STP upgrades. This trend was observed for most target compounds, except for DADMAC, C22ATMAC, and PEG, which showed a continuous increase towards the top of the cores. *In-situ* degradation was studied by comparing sediment core samples taken 12 years apart (1996 and 2008) and revealed a net decrease in PEG and specific surfactants (BAC, ATMAC, NPEO, and AEO) accompanied by growing concentrations of metabolites (SPC, NP, and NPEC). DTDMAC, DADMAC, and LAS, however, remained stable over this period, suggesting recalcitrant behavior under the anaerobic conditions in Jamaica Bay sediments.

Main finding: Chronology of major synthetic surfactants are illustrated in the dated sediment cores, as well as their different diagenetic fates.

1. Introduction

Surfactants are a large class of chemicals that are often classified based on the electric charge as either anionic, cationic, nonionic, or amphoteric. They are typically used as complex mixtures in a large variety of applications such as household cleaning and personal care products (e.g., shampoos and detergents), and in industrial applications as emulsifiers, wetting agents, and additives in hydraulic fracturing fluids (Ying, 2006). Their current production is over 15 billion tons per year and is expected to increase by 4% by 2021 (Acmite Market Intelligence, 2016). Due to their extensive use, wastewater analysis indicates that surfactants are the predominant organic substances in both concentration and frequency (Kolpin et al., 2002). Although most surfactants are efficiently removed in sewage treatment plants (STPs) (McAvoy et al., 1998), concentrations in the order of a few micro grams per liter can be found in receiving surface waters (Lara-Martín et al., 2008a). Their levels increase in sediments as they are natural sinks for surfactants due to the relatively high affinity of these chemicals for particulate organic carbon and/or charged surfaces (Lara-Martín et al., 2008b).

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Because of their widespread use, source specificity, and generally low degradation rate under anaerobic conditions, many surfactants can be employed as molecular indicators in sediments for monitoring contamination caused by human activities (Takada et al., 1997; Ferguson et al., 2001; Corada-Fernández et al., 2011; Li et al., 2014). Environmental behaviors of surfactants, e.g. biodegradation and interactions with other organic contaminants, were well reviewed in previous researches (Haigh, 1996; Ivankovic and Hrenovic, 2010), however, the long-term behavior of these compounds in this environmental compartment is still widely unknown but key to understand their final fate in aquatic systems.

Most studies on the occurrence and distribution of surfactants to date have focused on a few components. The most notable case are linear alkylbenzene sulfonates (LAS), which are the most widely used anionic surfactants. They have been reported in many parts of the world (Trehy et al., 1996; González-Mazo et al., 1998; Eichhorn et al., 2002), with values typically ranging from less than 0.1 to nearly 100 $\mu g\, g^{-1}$ in sediments, depending on their distance from urban sewage sources and the quality of wastewater treatment in the sampling area. Although they are rapidly removed from the water column and transformed into sulfophenylcarboxylic acids (SPC) (León et al., 2004), there is still debate about whether they can be anaerobically biodegraded once they are deposited in sediments (Lara-Martín et al., 2008a). Other extensively researched compounds are nonylphenol ethoxylates (NPEO), nonionic surfactants that breakdown into recalcitrant degradation metabolites with estrogenic properties (Jobling et al., 1996), namely nonylphenol (NP) and nonylphenol ethoxylcarboxylates (NPEC). The use of NPEO is restricted in the European Union as a result of environmental concerns, but no nationwide restrictions exist in the United States. Levels of NP in sediments are comparable to those for LAS (Ying et al., 2002; Lara-Martín et al., 2008b). Regarding other anionic and nonionic surfactants, there are only a few studies available on the occurrence of alkyl ethoxysulfates (AES), secondary alkane sulfonates (SAS), and alcohol ethoxylates (AEO) in surface sediments from Spanish coasts (Lara-Martín et al., 2008b; Baena-Nogueras et al., 2013).

Although having lower production volumes than their anionic and nonionic counterparts, analysis of cationic surfactants such as quaternary ammonium compounds (QACs) has revealed higher levels in sediments. Some of them (e.g. alkyltrimethyl and ditallowdimethylammonium chloride, or ATMAC and DTDMAC, respectively) have been identified as emerging contaminants in sewage sludge and estuarine sediments, reaching concentrations up to thousands of micro gram per gram of sediment (Li and Brownawell., 2010; Ruan et al., 2014). These observed concentrations are so high mostly due to a combination of strong adsorption capacity resulting from their hydrophobic and cationic nature, and minimal microbial degradation in the absence of oxygen (Garcia et al., 2000). Very limited characterization is available for other QACs such as benzylalkyldimethyl ammonium chlorides (BAC) and dialkyldimethyl ammonium chlorides (DADMAC), with shorter n-alkyl chain lengths varying between C8 and C10. Both are used in disinfectants and their potential impacts on microbial communities and on the spread of QAC-resistance genes are unknown (Plante et al., 2008). Furthermore, new types of surfactants such as polyoxyethylene tallow amines, diglycol ether sulfate, and behentrimonium chloride have been reported in the environment (Lara-Martín et al., 2010b; Gago-Ferrero et al., 2015) in recent years due to increased production and use.

The focus of this work was to carry out, for the first time, a comprehensive comparative study on the occurrence, distribution, and final fate of anionic, nonionic, and cationic surfactants and related compounds (including potential degradation intermediates) in sewage-impacted sediments. LAS (anionic), NPEO and AEO (nonionics), DADMAC, BAC, and ATMAC (cationics) were selected since they are among the most widely used surfactants in the United States. Possible degradation products such as SPC, NP, and NPEC, and polyethylene glycols (PEG), used in the synthesis of ethoxylated surfactants, were also measured. Examples of the molecular structures of these compounds are shown in Fig. S1 in the Supporting Information (SI). The concentrations and distribution of these surfactants were compared in surface sediments collected across Jamaica Bay, NY, a heavily sewage-impacted aquatic environment adjacent to New York City (NYC). Furthermore, vertical concentration profiles obtained from two dated sediment cores taken at the same location twelve years apart were compared to understand historical use trends over the last century. Changes in the surfactant mass inventories between both sampling periods were used to assess their relative persistence under realistic anaerobic conditions, which has never been attempted for most of the substances under study.

2. Experimental section

2.1. *Area description and sample collection*

Jamaica Bay is a highly urbanized estuarine setting located on the southwestern shore of Long Island, NY (Fig. 1). It has been the subject of a number of studies focused on wastewater-derived contaminants in sediments and detailed descriptions of this area and its sedimentary environment can be found elsewhere (Ferguson et al., 2001; Ferguson and Brownawell, 2003; Reddy and Brownawell, 2005; Lara-Martín et al., 2010a, 2015). Briefly, the bay has been dredged over 80 years and increased water depth caused increased residence time and stratification of the water column. It is therefore a highly depositional area (Ferguson et al., 2001) where sedimentation rates over 1 cm $year^{-1}$ have been reported. The Jamaica STP, in the vicinity of JFK airport, is the main plant in the region and discharges approximately 360 million liter per day of biologically treated effluent directly into the basin. It was built in 1943 with modified aeration secondary treatment and underwent

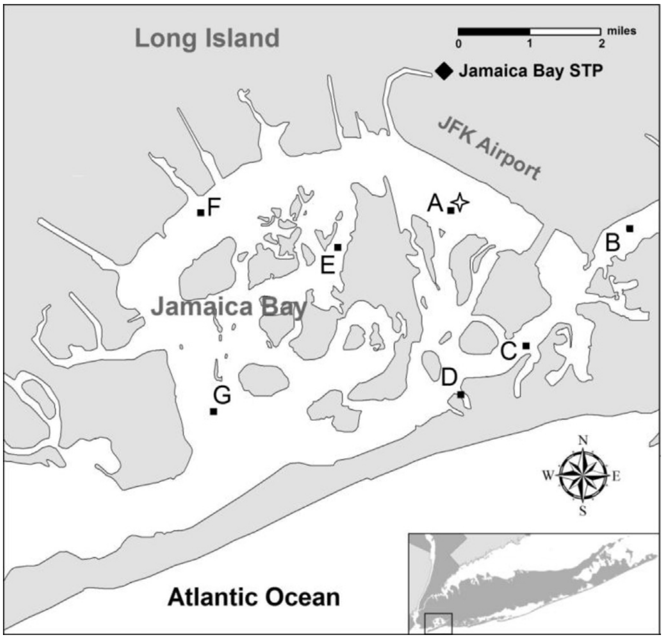

Fig. 1. Map showing the location of the sampling area (Jamaica Bay) in Long Island (NY), the main sewage treatment plant (Jamaica Bay STP), JFK airport, and sampling sites (A-G, including the sediment core location, marked with a star symbol).