



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 $\mu\text{g g}^{-1}$ 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 $\mu\text{g g}^{-1}$) and late 1980s (572 $\mu\text{g g}^{-1}$) 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.

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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 $100 \mu\text{g g}^{-1}$ 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 ethoxycarboxylates (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 ditalowdimethylammonium 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 behen-trimonium 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 underw-

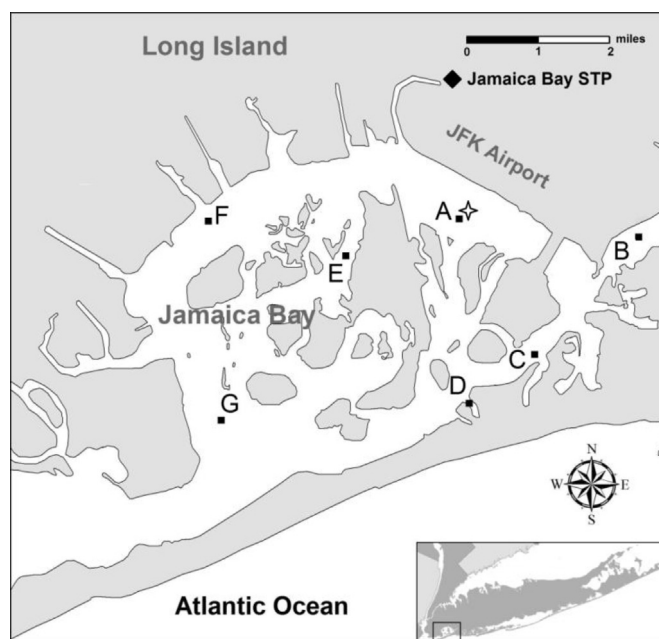


Fig. 1. Map showing the location of the sampling area (Jamaica Bay) in Long Island (NY), the main sewage treatment plant (Jamaica Bay STP), JFK airport, and sampling sites (A-G, including the sediment core location, marked with a star symbol).

two different upgrades (1963 and 1978) to increase its capacity and to implement activated-sludge. Over the last 30 years, both the population in the area (Queens and Brooklyn boroughs) and the sewage treatment conditions have remained fairly stable.

Surface muddy sediments (0–2 cm) were selected for this study, and their physicochemical properties, aluminum, and total organic carbon (TOC) contents are shown in Table S1 in SI. Seven sites (A–G) were sampled using a Van Veen grab sampler during the summers of 1998 and 2003 as part of an EPA sponsored Regional Environmental Monitoring and Assessment Program (REMAP) (Adams and Benyi, 2003), and were resampled in 2008 by our research group. Additionally, two gravity cores, JB16 in 1996, and JB4 in 2008, were taken from less than 100 m from station A, sectioned at 2–4 cm intervals, and freeze-dried and stored at -20°C pending analysis. Sedimentation rates were estimated by the analysis of ^{137}Cs and ^7Be using γ -counter, and detailed information have been reported elsewhere (Ferguson et al., 2001; Lara-Martín et al., 2015).

2.2. Analytical methodology

The surfactants were analyzed following the methodologies previously developed by our research group (Li and Brownawell, 2010; Lara-Martín et al., 2011, 2012). Briefly, surfactants and their metabolites were extracted from freeze-dried sediments in an ultrasonic bath using either methanol (anionic and nonionic compounds) or methanol with 1M HCl (cationic surfactants). After purification of the extracts, high performance liquid chromatography - time-of-flight - mass spectrometry (HPLC-ToF-MS) was used for the identification and quantification of most target compounds, except for NP and shorter ethoxymers (1-3EO) of NPEO and AEO. Ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) was used for these compounds to improve sensitivity. Available standards included different homologues and/or ethoxymers of linear alkylbenzene sulfonates (C10-C13LAS), sulfophenylcarboxylic acids (C4-C13SPC), nonylphenol ethoxylates (NP1-15EO), nonylphenol (NP), nonylphenol ethoxycarboxylates (NP1-2EC), alcohol ethoxylates (C12-16A1-10EO), polyethylene glycols (PEG4-13), benzylalkyldimethyl ammonium chlorides (C12-C18BAC), alkyltrimethyl ammonium chlorides (C16-C22ATMAC), dialkyldimethyl (C8:C10 and C10:C10DADMAC), and ditallowdimethyl ammonium chlorides (C14:14-C18:C18DADMAC). Further information on different aspects of the analytical methods used (e.g., extraction recoveries, limits of detection, internal standards, purification steps, etc.) are presented in the aforementioned references as well as in the Supporting Information.

3. Results and discussion

3.1. Distribution and composition of surfactant classes in surface sediments

The concentrations of target compounds in Jamaica Bay surface sediments are shown in Fig. 2, while the complete dataset is given in Table S2 in SI. Since only QACs were measured at site G in 2003, information on the levels of other contaminants is not available for this site; hence, this site was not included in the following calculations. The concentration range for all surfactants combined was between 18 and $> 200 \mu\text{g g}^{-1}$ (Fig. 2a). There was a slight variation ($< 10\%$, except for sites E and F) over the sampling years (1998, 2003, and 2008) and maximum values were always observed at site A. Previous studies of specific surfactants (NPEO metabolites and ATMAC) and other particle reactive wastewater contaminants such as natural steroid estrogens found similar spatial distributions in concentrations across Jamaica Bay (Ferguson et al., 2001; Reddy and Brownawell, 2005; Lara Martín et al., 2010a). The higher

concentrations of surfactants found at sampling station A, located in the northeast corner of Jamaica Bay within a depositional basin known as Grassy Bay, could be attributed to the presence of the nearby Jamaica Bay STP (Fig. 1). After the discharge of treated sewage, chemicals with low to medium polarity are quickly removed from the water column due to the combination of high sorption onto sewage and/or suspended particles together with the rapid settling of these particles within Grassy Bay. High burial rates ($> 1 \text{ cm year}^{-1}$), virtually no benthic infauna, little biological or physical mixing, and anoxic or hypoxic conditions prevailing in the near-bottom waters are expected to minimize the degradation of surfactants in sediments, which has been found to be significantly slower than in aerobic environments such as surface waters (Lara-Martín et al., 2008a).

Among the analyzed compounds, DTDMAC had the highest contribution to the total concentration of surfactants in Jamaica Bay surface sediments (52–90%), with values between 2 and $140 \mu\text{g g}^{-1}$ (Fig. 2i). The high abundance of these chemicals in sediments was expected as they are not significantly biodegraded in sludge under similar anoxic conditions (Cross and Singer, 1994; Garcia and Ribosa, 2001), where values up to $9200 \mu\text{g g}^{-1}$ have been reported (Gerike et al., 1994). Consequently, DTDMAC has been voluntarily phased out in the European Union in fabric softeners, in where they are mostly used (Fernández et al., 1996). This is not the case of United States, where a recent study (Li and Brownawell, 2010) has shown that they are widely detected in sediments at concentrations that are frequently higher than other well-known contaminants such as polycyclic aromatic hydrocarbons (PAHs). Other cationic surfactants considered in the present work were also detected in all sampling sites, though at much lower concentrations: ATMAC ($0.4\text{--}6.3 \mu\text{g g}^{-1}$) $>$ BAC ($0.2\text{--}4.2 \mu\text{g g}^{-1}$) $>$ DADMAC ($0.1\text{--}1.0 \mu\text{g g}^{-1}$) (Fig. 2j–l). These chemicals have lower production volumes as they are used for more specific applications such as hair softeners and disinfectants (Schaeufele, 1984). Since they only have one alkyl chain in their molecular structure, their hydrophobicity and corresponding sorption capacity are also lower as compared to DTDMAC.

The second most abundant class of target compounds were nonionic surfactants (NPEO and AEO) and their degradation products. The sum of NPEO, NP, and NPEC accounted for up to 29% of the total amount of surfactants in surface sediments, achieving maximum concentrations of 26, 29, and $19 \mu\text{g g}^{-1}$ for NPEO, NP, and NPEC, respectively (Fig. 2d–f). The distribution of NPEO and NP in Jamaica Bay was previously assessed by Ferguson and co-workers (Ferguson et al., 2001). Halogenated NPEOs, presumably derived from wastewater treatment, were also included in that study, although their levels were always lower than $0.1 \mu\text{g g}^{-1}$. The occurrence of carboxylated metabolites (NPEC) was not investigated then, and, despite their higher polarity, their importance is reflected in our data, as they can contribute with up to 46% of the total concentration of NPEO and related compounds in surface sediments. Regarding AEO, they were always found at concentrations lower than $2 \mu\text{g g}^{-1}$ in Jamaica Bay (Fig. 2g). AEO levels, however, were comparable to those of NPEO in other aquatic systems such as Cadiz Bay (SW Spain) (Lara-Martín et al., 2008b). This divergence might be related to their different uses of AEO in the European Union, where they have replaced NPEO in many applications such as detergents, and also influenced by their higher biodegradability compared to NPEO (Federle and Schwab, 1992). In contrast, concentrations of PEG were significantly higher than AEO, between 0.7 and $30 \mu\text{g g}^{-1}$ (Fig. 2h), and comparable to those of NPEO. The occurrence of these chemicals in the environment has rarely been reported. They are used in many applications from industrial manufacturing to medicine, including the synthesis of ethoxylated surfactants such as NPEO and AEO. The relatively high

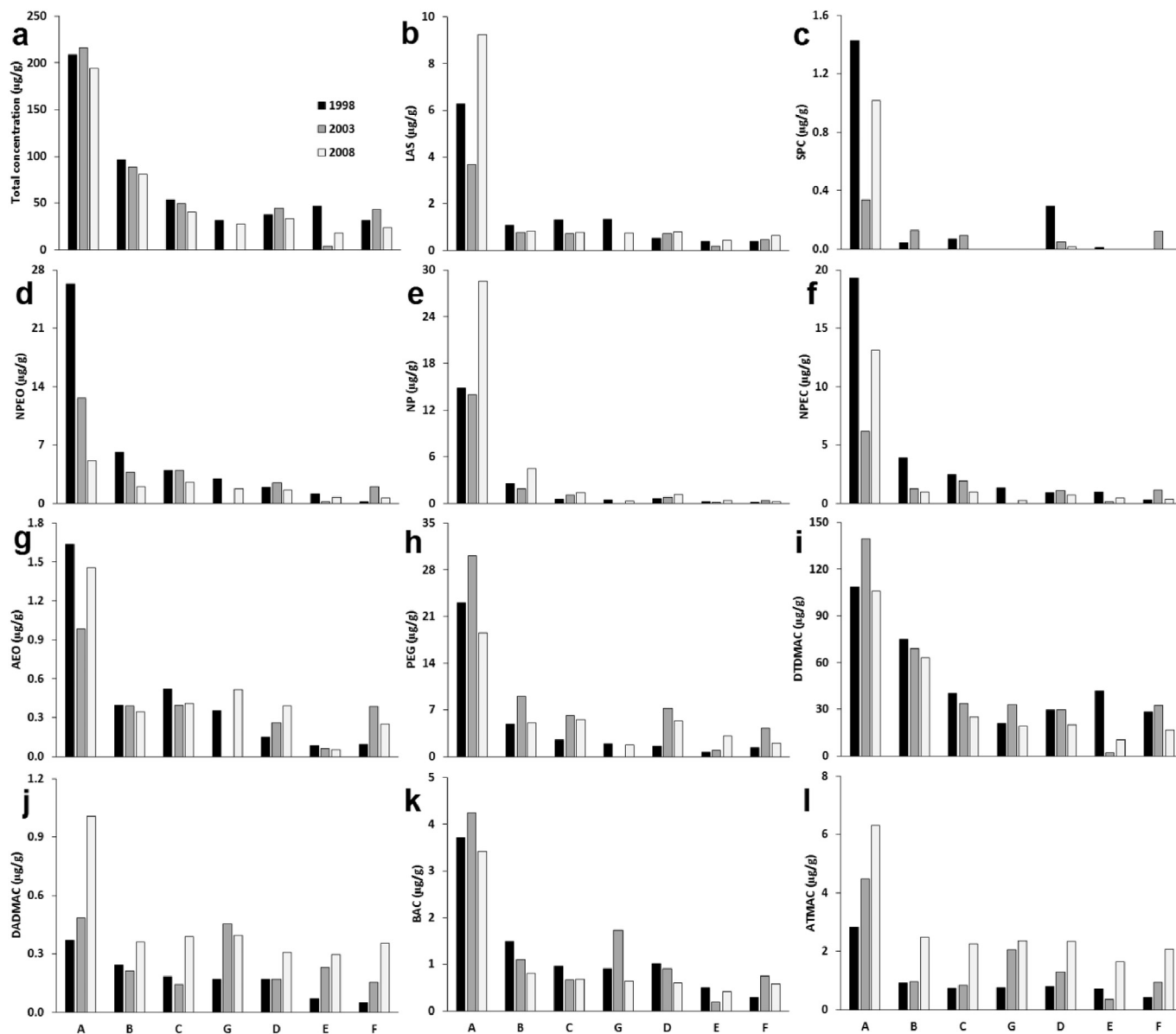


Fig. 2. Concentrations of surfactants ($\mu\text{g g}^{-1}$) in surface sediments from Jamaica Bay (sampling sites A–G; years 1998, 2003 and 2008): (a) total concentration, (b) LAS, (c) SPC, (d) NPEO, (e) NP, (f) NPEC, (g) AEO, (h) PEG, (i) DTDMAC, (j) DADMAC, (k) BAC, and (l) ATMAC. Sampling sites are arranged from higher (A) to lower (F) total organic carbon content, as noted in Fig. S2a in SI. Note the different scales for concentration ranges, ranging from 0 to $250 \mu\text{g g}^{-1}$ for total concentration to $0\text{--}1.2 \mu\text{g g}^{-1}$ for DADMAC.

levels measured in Jamaica Bay are probably due to a combination of sewage discharges, where they were identified with higher intensities in mass spectrometry analysis of wastewater (Gago-Ferrero et al., 2015), and runoff from the JFK airport (Fig. 1), as PEG are major components in aircraft deicing fluids and lubricants (Corsi et al., 2006). Additionally, the *in-situ* aerobic degradation of nonionic surfactants and other ethoxylated chemicals can also be a secondary source of PEGs in aquatic systems (Marcomini et al., 2000).

Finally, anionic compounds were present at lower concentrations than nonionic and cationic surfactants in surface sediments, between 0.2 and $9.2 \mu\text{g g}^{-1}$ for LAS and $<1.5 \mu\text{g g}^{-1}$ for SPC (Fig. 2b and c). The levels of these surfactants in sediments are within the range reported for highly contaminated areas in the United States (Trehy et al., 1996) and Europe (González-Mazo et al., 1998; Corada-Fernández et al., 2011; Lara-Martín et al., 2008b). Their relatively lower concentrations compared to other surfactants analyzed in

this work is in contrast to their high production volume (over 4 million tons per year worldwide, the most widely used synthetic surfactant) and abundance in effluent wastewater and surface water (e.g., $>100 \mu\text{g L}^{-1}$ reported in the United States) (Trehy et al., 1996). The lower abundance in sediment is related to LAS being negatively charged and, hence, having lower affinity towards negatively charged particulate matter, in comparison with the significantly less used but positively charged QACs (Brownawell et al., 1990). Detection of very polar LAS metabolites, SPC, in surface sediments is indicative of the strong influence of nearby wastewater discharges from Jamaica Bay STP, where they can be found at the same levels as the parent compounds (Lara-Martín et al., 2014).

The spatial variability of all target compounds was similar, as evidenced by a significant positive correlation amongst the analytes (Table S3 in SI) using the Spearman's correlation coefficient ($r = 0.8$, $\alpha < 0.05$). This correlation was stronger for surfactants and

metabolites belonging to the same class. For example, both $r > 0.95$ between LAS and SPC, and $r > 0.99$ among NPEO, NP, and NPEC suggest commonalities in their sources, and in the processes involved in their transport, deposition, and preservation in Jamaica Bay sediments. The correlation between surfactant concentrations and the physicochemical properties of sediments (TOC and aluminum) was also positive ($r = 0.46$ – 0.96) and significant except for SPC (Table S3). This correlation was stronger for QACs ($r > 0.7$) than for other target compounds due to their higher hydrophobicity and positive charge, denoting a stronger affinity of these surfactants towards organic matter and negatively charged clays in fine grain particles. In fact, QACs showed a higher degree of dispersion across Jamaica Bay (Fig. S2a in SI) when comparing site A, which is adjacent to the main sewage source (Jamaica Bay STP), to the rest of the sites. On average, the relative amount of cationic surfactants increased by almost 30% when moving out of Grassy Bay, whereas it decreased by 46–49% for less particle-reactive anionic and nonionic compounds (Fig. S2b in SI). Considering these data, super hydrophobic and positively charged DTDMAC could be an especially good tracer for sewage-affected sediments, and sources and fate of other particle reactive contaminants (Li and Brownawell, 2010; Li et al., 2014).

Fig. 3 shows the average composition of different surfactant mixtures in surface sediments from sampling site A. The resulting profiles were remarkably constant among sites (Table S2) and could be explained by the combination of the relative amount of each component in the commercial mixtures and the influence of environmental processes (mainly sorption and degradation) (Lara-Martín et al., 2008a) remaining consistent across the Bay. Alkyl chain homologues with a higher number of carbon atoms were present at higher concentrations. This is clearly observed in all QACs, where the most hydrophobic homologues such as C18 BAC

and C18:C18 DTDMAC represented more than 50% of the total concentration in sediment. Other surfactants such as LAS and AEO were enriched in long chain homologues when their distributions were compared with those typically found in commercial products (González-Mazo et al., 1998; Lara-Martín et al., 2008b). This was expected considering that interactions with organic matter in sediments are favored for these components (Westall et al., 1999). The composition of ethoxylated surfactants (NPEO and AEO) in terms of EO chain length is given in Fig. 3. In general, there was a shift towards short-chain ethoxylates, with those with a single EO unit (NP1EO and A1EO) accounting for over 40% of the total amount. Levels of nonylphenol, where the ethoxylated chain has been completely degraded, were comparable to those for NP1EO. This is directly related to the degradation mechanism of these substances (*in-situ* and/or during wastewater treatment), which usually involves the progressive loss of EO units (Ferguson et al., 2003). Resulting metabolites are more abundant in the environment, and have higher hydrophobicity, which explain their predominance in the samples. Hydrophilic interactions between the EO chain and the surface of sediments, however, cannot be ruled out since such interactions are relevant and often enhanced towards longer chain ethoxymers (Droge and Hermens, 2007). In that context, the average EO chain length distribution for PEG in sediments was centered around 8–9 ethoxylated units and depleted in very polar and soluble shorter components (<6 EO). Lastly, the distribution of SPC and NPEC components in sediments was directly related to their relative abundance in the STP effluents and receiving waters. Previous studies have reported NP2EC as the most abundant NPEO-related compound in wastewater (Petrovic et al., 2003) and mid-chain length SPC (C6 to C9) are often the only LAS biodegradation products detected in marine sediment and seawater (González-Mazo et al., 1997) due to the high reactivity of

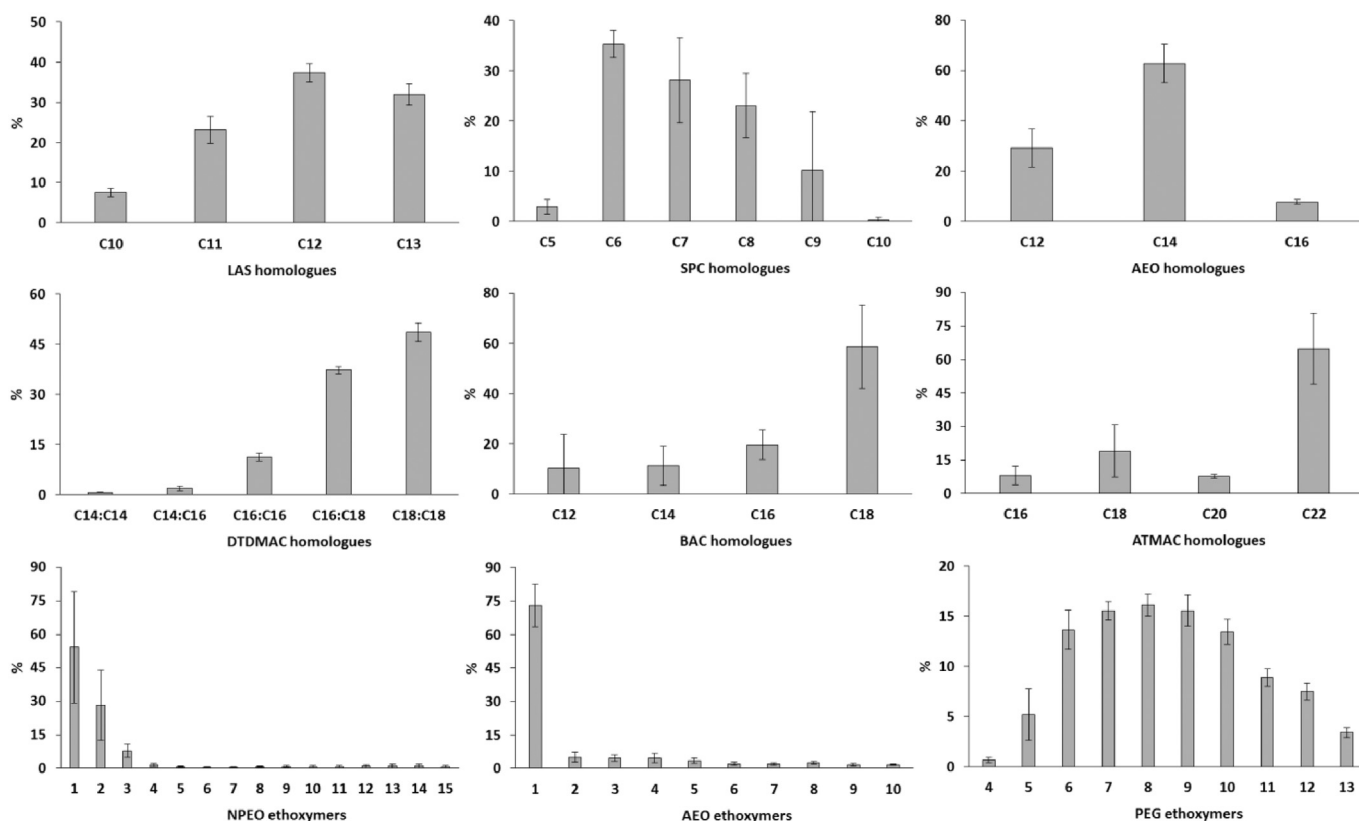


Fig. 3. Average composition of surfactant mixtures in the surface sediments from Jamaica Bay (sampling site A; years 1998, 2003 and 2008).

longer homologues.

3.2. Vertical concentration profiles of surfactants in sediment cores

The vertical concentration profiles of total surfactants and each individual surfactant class as a function of estimated age in the sediment core collected in 2008 are shown in Fig. 4. Raw data are given in Table S4 in SI. The vertical profile of total surfactants (Fig. 4a) shows two sub-surface peaks in the mid-1960s and late 1980s with concentrations of 469 and 572 $\mu\text{g g}^{-1}$, respectively. The levels decreased to around 184 $\mu\text{g g}^{-1}$ in the top layer of the sediment core, in agreement with the concentration detected in the nearby site A. As seen in surface sediments (Fig. S2), cationic compounds, especially DTDMAC, were the largest contributors to the total amount of surfactants, with similar subsurface maximum concentrations of 380 and 510 $\mu\text{g g}^{-1}$ around the same time periods (Fig. 4i). Concentrations of DTDMAC in the top layer were approximately 20% of the subsurface maximum from the late 1980s, probably due to a shift towards the use of biodegradable classes of “esterquats” in fabric softeners (Gerike et al., 1994; Fernández et al., 1996; Radke et al., 1999). This is reflected in the historical production of DTDMAC (Fig. S3) in the United States. Historic production in Europe followed a similar pattern, with a 20-fold drop in DTDMAC concentrations in sewage sludge samples collected in Switzerland between 1991 (2570–5870 $\mu\text{g g}^{-1}$) and 1994 (150–300 $\mu\text{g g}^{-1}$) (Fernández et al., 1996). Similarly, a significant drop was observed when comparing DTDMAC concentrations in the 1994 Swiss sludge with those collected in 2004 from Austrian WWTPs (30 $\mu\text{g g}^{-1}$ for total QACs) (Martínez-Carballo et al., 2007). BAC and C16–C18 ATMAC (Fig. 4k and l, respectively) showed two subsurface peaks during the same time periods as DTDMAC, suggesting similar input patterns and post-depositional fate. Among other surfactants, higher relative levels of DTDMAC, BAC, and ATMAC are shown in the sediment records between 1960 and 1975. Ferguson et al. (2003) observed a similar pattern in NPEO distributions around the same period and attributed it to a combination of increased surfactant production and direct discharge of untreated sewage during the Jamaica Bay WWTP upgrades in 1963 (Ferguson et al., 2003). There was, however, an exponential increase in the concentration of C22 ATMAC and DADMAC, which may reflect an increase in their production and application in industrial and commercial products. C22 ATMAC (Fig. 4l), named as behentrimonium chloride or behentrimonium methosulfate in formulations, was introduced in the 1980s as a partial replacement to C16–C18 ATMAC in selected personal care products such as hair conditioners (Lara Martín et al., 2010a). DADMAC (Fig. 4j), which are newer generation of disinfectants sometimes referred to as “twin chain QACs”, were first reported in environmental samples collected from the Jamaica Bay by our group (Li and Brownawell, 2009). These disinfectants were introduced in the late 1950s and their environmental levels have consistently increased, reaching concentrations up to 0.62 $\mu\text{g g}^{-1}$ in the most recent samples.

Regarding nonionic surfactants, the NPEO profile analyzed in this research (Fig. 4d) is in line with Ferguson's work, with a maximum concentration of 137 $\mu\text{g g}^{-1}$ in 1963. NPEO metabolites, NP and NPEC, were also detected (Fig. 4e and f, respectively), and their levels increased since their first appearance in the early 1960s until approximately year 2000 (up to 78.5 $\mu\text{g g}^{-1}$ for NP and 28.2 $\mu\text{g g}^{-1}$ for NPEC), followed by a decrease. Their vertical concentration profiles in the most recent decade increase with depth, in contrast to decreasing concentrations of NPEO with depth. This may suggest degradation of the parent compound in the upper layer of the sediment. This confirms the Ferguson's work (Ferguson et al., 2003), which presented evidence for conversion of NP1EO to NP, and the loss of NP in the upper sections of their core. The

decrease in NP up to 5-fold was more rapid than the change in NPEO loading to Jamaica Bay STP over the corresponding period (Ferguson et al., 2003), and was attributed to anaerobic transformation of the surfactant. Similar results were also reported in coastal marine sediments from Cadiz Bay (SW Spain) (Lara-Martín et al., 2006). The possibility of in-situ anaerobic degradation of the surfactants is discussed in more detail in the following section.

The first appearance of AEO, another nonionic surfactant, was in the early 1960s (Fig. 4g) and their concentrations reached their maximum a few years later (5.6 $\mu\text{g g}^{-1}$), after which AEO levels remained relatively constant (<2 $\mu\text{g g}^{-1}$) until present. The annual consumption of AEO in the United States over the last 20 years have been fluctuating between approximately 300 and 400 k tons (Cowan-Ellsberry et al., 2014). In contrast, PEG were first detected in the 1950s, after which concentrations steadily increased to 40 $\mu\text{g g}^{-1}$ in surface sediments (Fig. 4h). As we commented in the previous section, these chemicals are not only possible metabolites formed during the aerobic biodegradation of nonionic surfactants (for which they are also precursors) but they are also used in different applications such as pharmaceuticals, coatings, inks, and hydraulic fracturing fluids. The current global production of PEG is approximately 500 000 tons per year and has been continuously growing over the last decades (Grand View Research, 2015). PEG properties such as non-toxicity, wear resistance, and solubility in organic solvents make them particularly useful as lubricating solutions in the pharmaceutical industry, which drives the PEG market with >40% of total sales. In fact, the vertical distribution of PEG in Jamaica Bay sediments agrees with previously detected pharmaceutical concentrations (Lara-Martín et al., 2015), with a correlation coefficient of 0.92 between both datasets (Fig. S4 in SI).

Last, the anionic surfactant LAS first appeared in the sediment core in the mid-1960s. During that time they began to be used as substitutes for their non-biodegradable counterparts, branched alkylbenzene sulfonates (BAS), mostly consisting on tetrapropylene benzenesulfonate (TPS) (Reiser et al., 1997). The transition from one chemical to another is evident in Fig. 4b, and supports the dating of the sediment column. The peak of BAS concentrations in the sediment core and subsequent decline in concentrations is in line with the time frame of the ban of BAS in Europe and the United States (Reiser et al., 1997). Concentrations of LAS in sediments reached their maximum of 178 $\mu\text{g g}^{-1}$ a few years later. They were reduced to approximately 10 $\mu\text{g g}^{-1}$ from late 1960s to 1980, and remained relatively constant since then. The annual consumption of LAS in the United States over the last 20 years has been fluctuating between approximately 300 and 400 ktons (Cowan-Ellsberry et al., 2014). LAS biodegradation intermediates, SPC, however, followed a different vertical concentration profile (Fig. 4c), which is more in line with that of NPEO metabolites. The maximum level of 43.3 $\mu\text{g g}^{-1}$ was observed in 1986. The occurrence of SPC in sediment columns has been reported in both marine (León et al., 2001; Lara-Martín et al., 2006) and freshwater (Corada-Fernández et al., 2011) systems, and could be attributed either to direct input via treated/untreated wastewater discharges or anaerobic degradation of LAS in sediments, similar to NP and NPEC.

3.3. In-situ diagenetic transformation of surfactants

The biogeochemical behavior of surfactants in Jamaica Bay sediments was evaluated using matched cores. This approach is based on the comparison of vertical concentration profiles of contaminants in cores from a single highly depositional site (such as our sampling area, > 1 cm year⁻¹) taken several years apart. Date-matched sediment core horizons obtained from a single core site represent endpoints of an *in-situ* incubation. The differences in organic contaminant concentrations in matched horizons from

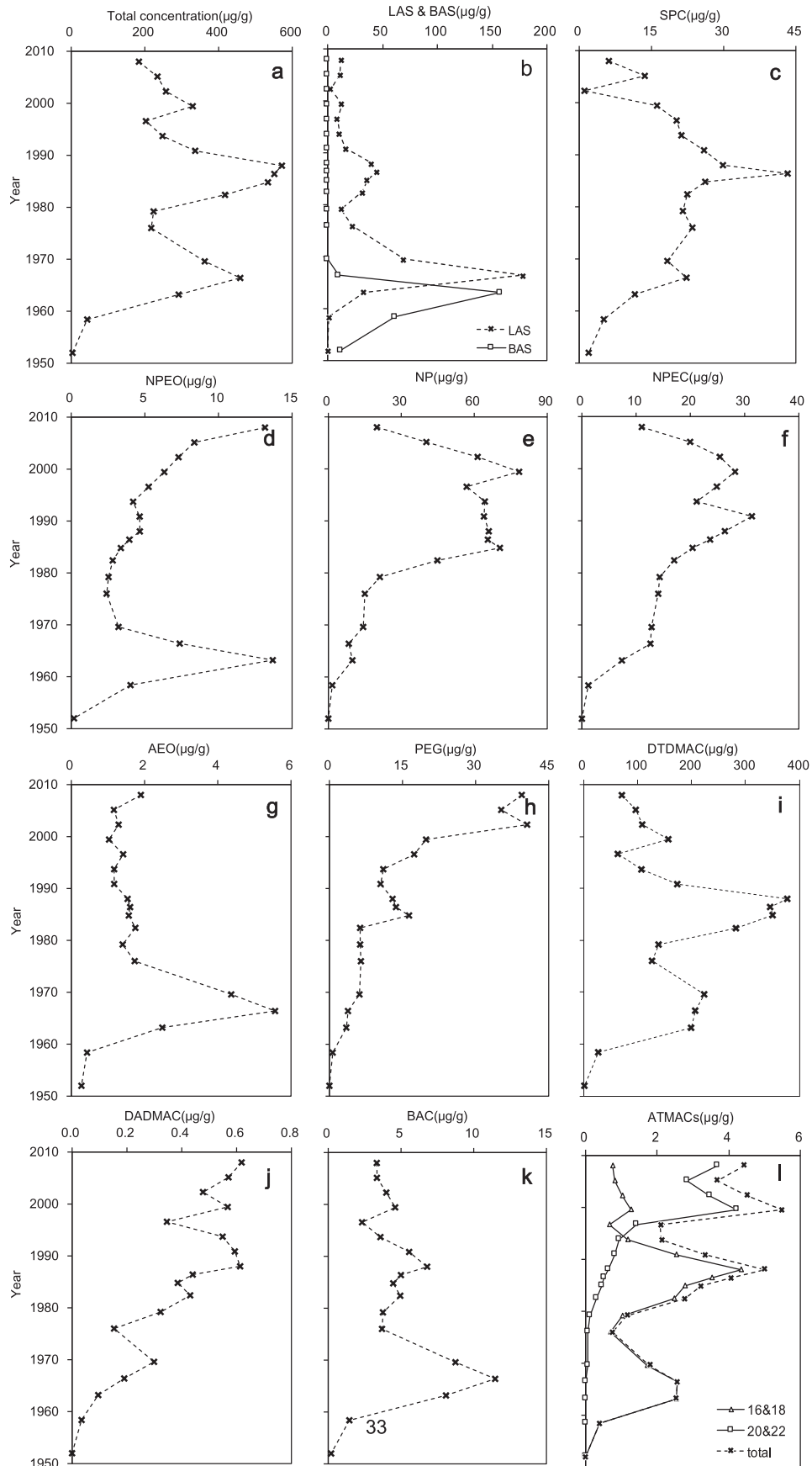


Fig. 4. Vertical concentration profiles (µg g⁻¹) of target compounds in a sediment core from Jamaica Bay taken in 2008: (a) total concentration, (b) LAS and BAS, (c) SPC, (d) NPEO, (e) NP, (f) NPEC, (g) AEO, (h) PEG, (i) DTDMAC, (j) DADMAC, (k) BAC, and (l) C16-C18 and C22ATMAC.

different cores reflect any modification to the contaminant within the sediment over the time between core collections. This strategy has been previously applied to study the depositional chronology of NPEO (Ferguson et al., 2003) and pharmaceuticals (Lara-Martín et al., 2015). The profiles of the two matched cores collected in 1996 (Table S5) and 2008 (Table S4) at the same location are shown in Fig. S5 in SI. Mass inventories of the surfactants (Table 1) in both cores were defined as the mass of total target compounds per unit area, that is $\sum C_i \rho_B d$, where C_i is the concentration of target compounds in sediment layer i , ρ_B (g cm^{-3}) is the density of the dry sediment, and d (cm) is the thickness of the sediment layer i . The mass of compounds for those intervals that were not analyzed was estimated by linear interpolation of adjacent measured intervals.

Differences in the mass inventories for the total surfactants were only 5.7% between the core collected in 2008 and the one taken in 1996, suggesting that these substances have remained fairly stable over the twelve-year period. This is especially relevant for DTDMAC, which are the major components in sediments ($>20\,000\text{ mg m}^{-2}$), and DADMAC, which share a similar molecular structure. Previous studies on the removal and mass balance of these compounds in the sewage sludge suggest that DTDMAC are not appreciably biodegradable within wastewater treatment plants (WWTPs) due to their strong sorption and hydrophobicity, a function of their twin alkyl chain structure, higher total number of carbons, and positive charge (Van Ginkel and Kolvenbach, 1991; Clara et al., 2007). Our previous work found that the compositional pattern of DTDMAC homologues in estuarine sediments was identical to that in the sewage sludges collected in the adjacent WWTPs, indicating their persistency during sedimentation (Li and Brownawell, 2010; Li et al., 2014). Similarly, the compositional patterns of both DTDMAC and DADMAC (Fig. S6 in SI) did not change between 1996 and 2008 cores. BAC and ATMAC, on the other hand, showed an appreciable decrease of 39% and 55%, respectively, in their inventories (Table 1). Compared to DTDMAC and DADMAC, BAC and ATMAC are more biodegradable and more soluble given their single alkyl chain (Van Ginkel and Kolvenbach, 1991). Additionally, biodegradation seems to be more effective for shorter alkyl chain homologues, as a significant increase of 5–20% was observed in the relative percentage of longer BAC and ATMAC homologues such as C18BAC and C18ATMAC at the same depths in the sediment cores after twelve years (Fig. S7 in SI). This suggests the highest recalcitrance of these long alkyl chain components, in agreement with the findings by Garcia and coworkers (Garcia et al., 1999), who reported degradation of up to 38% for C12ATMAC, 23% for C14ATMAC, and 19% for C16ATMAC in sludge after 200 days of anaerobic incubation.

Both nonionic surfactants, NPEO and AEO, had a reduction in the total inventories between 21 and 39% (Table 1). The anaerobic

biodegradation of NPEO has been more extensively studied than any other cationic and nonionic surfactants. It is generally accepted that the parent compound slowly undergoes de-ethoxylation that yields lower ethoxymers (Lu et al., 2009) and, ultimately, leads to the formation of nonylphenol. A previous study on the sediment core collected in 1996 suggested that this pathway occurs only in the first 20 cm, and NPEO remains reasonably stable in deeper layers (Ferguson et al., 2003). The recalcitrance of this surfactant ($t_{1/2} > 60$ years) was reported by Shang et al. (1999) in sediments from Canada. According to the vertical profiles in our work, transformation of NPEO into NP was evident in Jamaica Bay in the sedimentary layers corresponding between the 1960s and 2008 (Figs. S5 d and e in SI). The total mass inventory of NP increased by 85% over 12 years, whereas there was a reduction in the average length of the ethoxylated chain of the parent compound (Fig. S8 in SI). Furthermore, NPEC concentrations increased by 48% over that same time frame. This could be attributed to *in-situ* generation of these metabolites, which has not been reported in the field but observed in previous laboratory experiments conducted with anaerobic sediments (Ferguson and Brownawell, 2003). However, analysis of the NPEC composition pattern (Fig. S8 in SI) revealed an increase in the relative amount of NP2EC compared to NP1EC between 1996 and 2008, suggesting that the contribution of other sources such as Jamaica Bay STP sewage discharges may have affected these sediments. This possibility will be discussed in more detail as similar patterns were observed for other carboxylic metabolites (SPC).

The decrease in the AEO mass inventory (Fig. S5g in SI) was accompanied by a progressive increase in the relative percentage of longer chain homologues and ethoxymers with depth in the sediment core (Fig. S9 in SI). According to previous data from laboratory incubations, these surfactants can be transformed either by successive de-ethoxylation (Huber et al., 2000) (under anaerobic conditions) and/or by central cleavage of the molecule yielding PEG (Marcomini et al., 2000) (under aerobic conditions). The first degradation pathway was expected to occur in Jamaica Bay sediments but was not supported, however, by our field data as the changes in the average length of the ethoxylated chain were not significant between 1996 and 2008. Instead, an increase in the relative amount of C16AEO compared to shorter alkyl chain homologues was observed. This is in agreement with BAC and ATMAC, which showed enhanced biodegradability and solubility in the shorter chained homologues. The possible degradation of ethoxylated compounds by successive de-ethoxylation was confirmed for PEG, as their concentrations decreased by 40% (Fig. S5h in SI) over the same period due to an enrichment of short chain ethoxymers (4–7 EO) (Fig. S10 in SI), as was also observed for NPEO. Though AEO and PEG were reasonably well degraded in Jamaica Bay sediments, this process was much slower than has been observed in previous laboratory experiments, where the degradation rates reached as high as 100% after 25 days for AEO (Huber et al., 2000) and up to 50% after 9 days for PEG (Huang et al., 2005).

Regarding the degradation of LAS, we did not observe any significant changes in their vertical concentration profiles (Fig. S5b in SI) and relative homologue distributions (Fig. S11) in the 2008 and 1996 cores. This is in agreement with the results from previous laboratory experiments conducted in river sediments and STP sludge (Federle and Schwab, 1992; Garcia et al., 2005). On the other hand, *in-situ* degradation of LAS and their precursors, linear alkylbenzenes (LABs), was found to occur in other coastal sediments (León et al., 2001; Lara-Martín et al., 2006; Eganhouse and Pontolillo, 2008). The apparent persistence of LAS in Jamaica Bay, however, was in contrast to the increase in the overall concentration of SPC in the 2008 core (+230%) compared to the one taken in 1996 (Fig. S5c in SI). The occurrence of these intermediates in

Table 1
Mass inventories (mg m^{-2}) from 1955 to 1996 and relative variations for total surfactants, the different classes of surfactants, and their metabolites in the two sediment cores collected in 1996 and 2008.

	1996 core	2008 core	Relative variation (%)
Total	33700	35600	5.7
LAS	3290	4690	43
SPC	713	2340	230
NPEO	892	542	-39
NP	1770	3280	85
NPEC	1130	1680	48
AEO	323	256	-21
PEG	1390	821	-40
DTDMAC	22800	21100	-6.8
DADMAC	30	32	8.0
BAC	1030	631	-39
ATMAC	452	203	-55

marine sediments was already reported in other sampling areas (León et al., 2001; Lara-Martín et al., 2006) and could be indicative of the anaerobic oxidation of LAS via fumarate addition (Lara Martín et al., 2010b). The absence of changes in LAS inventories over time suggests that SPC may have been derived from an external source, likely from Jamaica Bay STP sewage discharges, and later deposited into the seafloor, where they may have experienced diffusion towards deeper layers in the sediment. This has been previously observed in sediment cores taken near STP outfalls in SW Spain (Corada-Fernandez et al., 2013), where relatively high SPC levels were measured in pore water ($>1000 \text{ ng mL}^{-1}$) (León et al., 2001) but no decrease in LAS concentrations was found. This hypothesis is reinforced by the increase in the relative amount of longer alkyl chain SPC homologues between 1996 and 2008 cores (Fig. S11 in SI), indicative of “fresh” sewage inputs over that period.

4. Conclusions

This work represents the first attempt to compare the distribution and *in-situ* biodegradability of the main surfactant classes in sediments. Their presence in our sampling area (Jamaica Bay, NYC) was directly related to urban wastewater discharges from an adjacent STP. Overall, cationic surfactants prevailed over nonionic and anionic compounds due to a combination of higher sorption capacity and poor anaerobic biodegradation, reaching concentrations above $100 \mu\text{g g}^{-1}$. The environmental relevance of surfactants is derived from their wide use and predominance in the environment in comparison to other contaminants of emerging concern such as pharmaceuticals, also measured in the same area at levels below $0.1 \mu\text{g g}^{-1}$. Some of the target compounds are potential endocrine disruptors (e.g., NP) or present strong antimicrobial activity (e.g., BAC), whereas others show apparent persistence after deposition (e.g., DTDMAC and LAS) or increasing concentrations over the last decades (e.g., PEG and DADMAC). Further monitoring of the last group of contaminants is encouraged, as available information on their environmental occurrence is almost non-existent and their levels are on the rise. Additionally, more research is necessary to fully understand the different degradation mechanisms for LAS and other surfactants in anaerobic sediments, and to evaluate the role of environmental factors such as changes in the microbial populations, organic carbon content, and sediment texture, which can have a significant impact on the degradation kinetics.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at

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