Marine Pollution Bulletin xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Evaluation of the levels of alcohol sulfates and ethoxysulfates in marine sediments near wastewater discharge points along the coast of Tenerife Island

C. Fernández-Ramos [a], O. Ballesteros [a,*], A. Zafra-Gómez [a], F.J. Camino-Sánchez [a], R. Blanc [a], A. Navalón [a], J.P. Pérez-Trujillo [b], J.L. Vílchez [a]

[a] *Research Group of Analytical Chemistry and Life Sciences, Department of Analytical Chemistry, Faculty of Sciences, University of Granada, Campus of Fuentenueva, E-18071 Granada, Spain*

[b] *Department of Analytical Chemistry, University of La Laguna, E-38204 Tenerife, Spain*

A R T I C L E I N F O

Keywords:
Marine sediments pollution
Alcohol sulfates
Alcohol ethoxysulfates
Principal Components Analysis
Urban pollution
LC–MS/MS

A B S T R A C T

Alcohol sulfates (AS) and alcohol ethoxysulfates (AES) are all High Production Volume and 'down-the-drain' chemicals used globally in detergent and personal care products, resulting in low levels ultimately released to the environment via wastewater treatment plant effluents. They have a strong affinity for sorption to sediments. Almost 50% of Tenerife Island surface area is environmentally protected. Therefore, determination of concentration levels of AS/AES in marine sediments near wastewater discharge points along the coast of the Island is of interest. These data were obtained after pressurized liquid extraction and liquid chromatography–tandem mass spectrometry analysis. Short chains of AES and especially of AS dominated the homologue distribution for AES. The Principal Components Analysis was used. The results showed that the sources of AS and AES were the same and that both compounds exhibit similar behavior. Three different patterns in the distribution for homologues and ethoxymers were found.

1. Introduction

Tenerife Island is located in the Canary Archipelago, in the Atlantic Ocean, and lies just over 300 km from the coast of Africa. It is the largest island of the archipelago with a total coastline amounting to 342 km, a surface area of 2034 km^2 and a population of 906,854 (INE, 2011). Agriculture and tourism are the principal economic resources, and the island has little industry. Some small industrial areas and one oil refinery located in Santa Cruz are the main sources of industrial wastewaters. Due to its geographic location, climatic conditions and the limited industrial activity pollution levels are expected to be very low. Almost 50% of its surface area is environmentally protected, for this reason, more effective methods to fight pollution are needed.

Coastal ecosystems receive large amounts of a wide range of organic pollutants from urban wastewater which are discharged treated or untreated. Among these pollutants, surfactants constitute one of the major categories. Surfactants are widely used for both industrial and domestic purposes accounting for over 3 million tonnes per year in Western Europe (CESIO, 2011). The surface-active properties of surfactants are responsible for their extensive usage and wide variety of applications, mainly as ingredients of laundry and cleaning products, cleaners for hard surfaces, shampoos, emulsifiers, pesticides, adjuvants, and wetting agents. Approximately 41% of this production corresponds to anionic surfactants. Linear alkylbenzene sulfonates (LAS) are the main component of anionic surfactants, with an estimated annual production of 400 million kg in Europe (HERA, 2004). European production of alcohol ethoxysulfates (AES) and alcohol sulfates (AS) together reaches 378 million kg per year (HERA, 2002a,b), so it is second after LAS by a narrow margin. AS and AES include a molecular structure containing a hydrophilic portion, which provides them with high water solubility, and a hydrophobic portion, usually from a long alkyl chain, that contributes to the surfactant properties needed in detergents. AS and AES are produced by sulfonation of alcohol ethoxylates, which are composed of a long-chain fatty alcohol with an ether linkage to a chain of ethylene oxide (EO) units. In the case of AES, the EO group typically has 3–4 EO units (zero for AS), while the alkyl chain length has between 12 and 16 carbon units. These compounds are typically highly water soluble and surface active, which may lead them to partition to suspended particles that become incorporated into sediments in the environment, where the highest exposure to these substances is expected (Marchesi et al., 1991). In addition, biodegradation rates and pathways of organic compounds, including some detergent ingredients,

---

* Corresponding author. Tel.: +34 958 243326; fax: +34 958 243328.
E-mail address: oballest@ugr.es (O. Ballesteros).

0025-326X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.marpolbul.2013.12.031

Please cite this article in press as: Fernández-Ramos, C., et al. Evaluation of the levels of alcohol sulfates and ethoxysulfates in marine sediments near wastewater discharge points along the coast of Tenerife Island. Mar. Pollut. Bull. (2014), http://dx.doi.org/10.1016/j.marpolbul.2013.12.031

may be altered by the anoxic conditions (Swisher, 1987; Schröder, 2001) that take place in sediments, leading to a potential increase in exposure. The concentration range of AS/AES in wastewater treatment plant effluents is 3–164 μg L^{-1} and 19–71 μg L^{-1} for LAS (DK-EPA, 2001; Matthijs et al., 1999). However, there have been relatively few assessments of the bioavailable fraction of these compounds, especially AS/AES, up- and downstream of wastewater treatment plants on a homologue specific basis (Sanderson et al., 2006a). Under anoxic conditions, deposition of surfactants in sediments may occur (Swisher, 1987; Schröder, 2001). In addition, in some situations, continued input to the environment (e.g., via wastewater treatment plant effluent, other known and unknown point sources, runoff) of compounds that biodegrade rapidly may result in a chronic low exposure. In this respect, several studies have been conducted in recent decades to obtain a better understanding of the distribution, behavior and fate of anionic surfactants in the environment; they are examined in a review article by Ying (2006).

Partitioning to sediments has only been reported under controlled laboratory conditions, with AS/AES and LAS having a similar high tendency to partition to sediments. Distribution coefficients (K_d) for AS/AES range from 70 to 350 L kg^{-1}, and are higher for alkyl chain-length from C_{12} to C_{14} (LAS C_{12} = 330 L kg^{-1}) (Marchesi et al., 1991). Despite having a similar volume of use and partitioning behavior to LAS, there are limited data regarding the levels, fate, and effects of AS/AES in the environment. The referred data for LAS have been summarized in the OECD report (LAS SIAP, 2005). The measured surface water concentrations of LAS were generally below 50 μg L^{-1}, total concentrations from river sediments were generally less than 1–2 mg kg^{-1} dry weight (LAS SIAP, 2005), and total concentrations from marine sediment were generally from 0.1 to 70 mg kg^{-1} dry weight (Cantarero et al., 2012). The monitoring data on AS/AES are limited to studies on removal in wastewater treatment facilities where effluent concentrations of all combined AS/AES homologues were between 5.7 and 21 μg L^{-1} (Sanderson et al., 2006b). The behavior of AS/AES in sediments has been recently researched and some studies have been carried out in cities such as Cadiz (Spain), Mississipi, Ohio and Glendale (USA) (Lara-Martín et al., 2005, 2006a,b; Sanderson et al., 2006b). A total concentration from 0.11 to 0.24 mg kg^{-1} for AS, and a total concentration from 0.02 to 0.59 mg kg^{-1} for AES were found in marine sediments from the Bay of Cadiz (Lara-Martín et al., 2005, 2006a,b).

The current paucity of field measurements of AS and AES, particularly in sediments, may be partially attributed to the complex nature of commercial AES mixtures sometimes containing more of 36 ethoxymers (this composition reflects the selection of aliphatic alcohol feedstock and the average degree of ethoxylation) and to the lack of suitable analytical methodology. Sanderson et al. (2006b) adapted the analytical method for the determination of AS/AES homologues in river waters and sediments and reported a low aquatic risk associated to these compounds. However, they also concluded that additional monitoring with more sampling locations, in combination with assessment of potential perturbations on biota and habitat up- and downstream of wastewater treatment plants, was needed to better elucidate the potential risks more comprehensively. To assess the environmental hazard of AS/AES, it is important to determine their concentration in waters and sediments and apply this information to estimate the effects on both aquatic and sediment dwelling organisms. We focused our studies on sediments because they are considered to play an important environmental role acting as a sink for these pollutants. Moreover, because of their widespread use, source specificity and low degradation rate under anaerobic conditions, surfactants in sediments can be usefully employed as molecular indicators of human-caused contamination (Reiser et al., 1997).

The main objective of the work is to study the levels and superficial distribution of AS/AES in the sediments of the continental platform near the nine wastewater discharge points of Tenerife Island (Spain). AS/AES concentrations were obtained after pressurized liquid extraction and liquid chromatography coupled to triple quadrupole mass spectrometry (LC–MS/MS) analysis. The Principal Components Analysis (PCA) was used to determine and establish the relationship between the concentration levels of AS/AES and discharge points/population. Therefore, the presented results could be employed to establish background levels for future environmental investigations, in this or other areas.

All reagents were of analytical grade unless otherwise specified. Individual standard of sodium dodecyl sulfate (AS-C_{12}) (purity 99%) was supplied by Fluka (Madrid, Spain), sodium 1-tetradecyl sulfate (AS-C_{14}), sodium n-hexadecyl sulfate (AS-C_{16}) and sodium n-octadecyl sulfate (AS-C_{18}) (purity 95–99%) were supplied by Alfa Aesar (Barcelona, Spain). The commercial mixture of AES was supplied by Sasol (COSMACOL AES 70-2-24) as an aqueous solution of the sodium salt with an AES (AES-C_xE_n) content of 70.0% (w/w) with the following homologue distribution: AES-C_{12} (55.0%) and AES-C_{14} (45.0%) and an average number of EO units of 2.0. The internal standard, 2-Octylbenzene sulfonic acid sodium salt (2ØC$_8$-LAS; 81%, w/w) was supplied by Cepsa Química S.A. (Madrid, Spain). Stock solutions of AS and AES (100 mg L^{-1}) were prepared in methanol. The solutions were stored at 4 °C in the dark, remaining stable for at least 6 months. Working standards were prepared immediately before use by dilution in methanol. Methanol and acetonitrile (both HPLC-grade) used as mobile phase were supplied by Merck (Darmstadt, Germany). LC–MS grade water, triethylamine, acetic acid and formaldehyde were supplied by Sigma–Aldrich (Madrid, Spain). Methanol (PAI grade) used in the extraction and clean up were supplied by Panreac (Barcelona, Spain). Water (18.2 MΩ cm) was purified with a Milli-Q plus system (Millipore, Bedford, MA, USA). Before the injection into the LC system, the samples were filtered through regenerated non sterile cellulose filters (pore size, 0.20 μm, and 4 mm in diameter) supplied by Sartorius (Goettingen, Germany).

Sediment samples were extracted with an ASE 200 pressurized liquid extraction system (Dionex Corp, Sunnyvale, CA, USA). A centrifuge, model Universal 32, from Hettich (Tuttlingen, Germany) was used to separate solid and liquid phases. Analyses were performed using an Agilent 1200 series (Agilent Technologies Inc., Palo Alto, CA, USA) high-performance liquid chromatography system equipped with a binary pump, a vacuum membrane degasser, a thermostated column compartment, an automatic autosampler and connected “on line” to an API 2000 (Applied Biosystems, Foster City, CA, USA) triple quadrupole mass spectrometer system that can use either atmospheric pressure chemical ionization (APCI) or electrospray ionization (ESI) interfaces. Analyst software version 1.4.2 was used for instrument control and for data acquisition and analysis. Statgraphics 5.0 software package (2000) was used for statistical and regression analysis.

Regarding the sampling process, two published guides were followed, the TBT Assessment Project (Simpson et al., 2005) and the EPA Recommended Guidelines for sampling marine sediment, water column, and tissue in Puget Sound (US-EPA, 1997). A total of 36 sediment samples were collected from the nine wastewater discharge points of Tenerife Island. All discharges of wastewater to the sea, from land, through those outfalls have been previously subjected to the treatments listed in the Order of July 13, 1993 the Ministry of Public Works and Transport of the Government of Spain (Official State Bulletin, BOE July 13, 1993). Four samples were collected at each sampling point: one right at the outlet of the discharge point and the rest at a distance of 20 m surrounding the outlet. Fig. 1 shows the sampling points and Table 1 the location, the coordinates of each

Please cite this article in press as: Fernández-Ramos, C., et al. Evaluation of the levels of alcohol sulfates and ethoxysulfates in marine sediments near wastewater discharge points along the coast of Tenerife Island. Mar. Pollut. Bull. (2014), http://dx.doi.org/10.1016/j.marpolbul.2013.12.031