



# Anaerobic degradation of alcohol ethoxylates and polyethylene glycols in marine sediments



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## HIGHLIGHTS

- Anoxic degradation of AEOs/PEG in marine sediments were studied for the first time.
- Methanogenic activity is a good indicator of AEOs and PEG degradation.
- Removal of AEOs and PEG reached up to 99.7 and 93%, respectively (169 days, 30 °C).
- The major fraction on the non-degraded AEOs corresponded to C16 and C18 homologs.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This research is focused on alcohol polyethoxylates (AEOs), nonionic surfactants used in a wide variety of products such as household cleaners and detergents. Our main objective in this work was to study the anaerobic degradation of these compounds and their main aerobic degradation products and precursors (polyethylene glycols, PEGs, which are also used for many other applications) in marine sediments, providing the first data available on this topic. First, we observed that average AEO sediment-water partition coefficients ( $K_d$ ) increased towards those homologs having longer alkyl chains (from 257 L/kg for C<sub>12</sub> to 5772 L/kg for C<sub>18</sub>), which were less susceptible to undergo biodegradation. Overall, AEO and PEG removal percentages reached up to 99.7 and 93%, respectively, after 169 days of incubation using anaerobic conditions in sediments ( $[O_2] = 0$  ppm,  $E_h = -170$  to  $-380$  mV and  $T = 30$  °C). Average half-life was estimated to be in a range from 10 to 15 days for AEO homologs (C<sub>12</sub>AEO<sub>8</sub>–C<sub>18</sub>AEO<sub>8</sub>), and 18 days for PEGEO<sub>8</sub>. Methanogenic activity proved to be intense during the experiment, confirming the occurrence of anaerobic conditions. This is the first study showing that AEOs and PEGs can be degraded in absence of oxygen in marine sediments, so this new information should be taken into account for future environmental risk assessments on these chemicals.

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## 1. Introduction

Alcohol polyethoxylates (AEOs) are an important group of nonionic surfactants that are widely used in domestic and commercial detergents, household cleaners and personal care products (Human and Environmental Risk Assessment on Ingredients of European Household Cleaning Products, 2009). Their sales have increased over the last decade due to recent restrictions by European Union in the use of alkylphenol polyethoxylates (APEOs) in household detergents as their degradation products show estrogenic properties (Sonnenschein and Soto, 1998). Commercial AEOs consist of a mixture of homologs typically having from 12 to 18 carbon atoms in their hydrophobic alkyl chain, which is bonded to a hydrophilic chain of varying degree of ethoxylation. Polyethylene glycols (PEGs), which have been described as the main aerobic degradation metabolites of AEOs (Sparham et al., 2008), are synthetic water-soluble polyethers of ethylene oxide that are also extensively applied in the manufacturing of water-soluble lubricants, cosmetics, pharmaceuticals, plastics and antifreeze agents (Otal and Lebrato, 2003). In fact, several millions of tons of PEGs are annually produced worldwide (Huang et al., 2005). After their use, AEOs and PEGs are ultimately discharged into aquatic ecosystems through both treated and untreated wastewater discharges. Once in the water column, these chemicals are found dissolved and associated with particulate material. Data on the environmental distribution of these compounds are still scarce, but some recent works have shown the wide occurrence of both chemicals (and many other surfactants) in sewage impacted systems (Gago-Ferrero et al., 2015; Lara-Martín et al., 2008; Traverso-Soto et al., 2014; Schymanski et al., 2014) at significant concentrations ( $>1 \text{ mg kg}^{-1}$ ). More specifically for coastal environments, we have reported AEO and PEG levels ranging from 9 to 12,200  $\mu\text{g/kg}$  in marine sediments and suspended solids, whereas total concentrations in surface waters were always below 50  $\mu\text{g/L}$  (Corada-Fernández et al., 2011; Lara-Martín et al., 2011; Traverso-Soto et al., 2013).

AEOs and PEGs are removed with a high efficiency ( $>96\%$ ) in wastewater treatment plants (WWTPs) by a combination of sorption and degradation. Both processes usually take place preferentially over the longer ethoxymers (Lara-Martín et al., 2014; Szymanski et al., 2003; Wind et al., 2006). Once AEOs reach the aquatic environment, their in-situ degradation in the receiving waters is fast, showing a high level of mineralization (60% after 10 days) likely resulted from significant adaptation of microbial communities because of the increased discharge of AEOs to municipal sewers today (Sparham et al., 2008). The most widely accepted aerobic degradation pathway involves the central fission of the ether bond between the alkyl and ethoxylated chain of the AEO molecule, resulting in the formation of fatty acids and PEGs (Marcomini et al., 2000; Sparham et al., 2008). PEGs degrade via hydrolytic shortening and/or generation of carboxylic acids, although this process is slower than for AEOs (Bernhard et al., 2008). However, available data show that a considerable fraction of the total AEOs and PEGs discharged ends up in river and coastal sediments, so their sorption onto particulate matter can be regarded as other of the main processes occurring in the environment (Corada-Fernández et al., 2011; Lara-Martín et al., 2008; Traverso-Soto et al., 2014). Sediments tend to present anaerobic conditions below a topmost layer a few millimeters thick in the case of aquatic areas subjected to pollution. It seems that AEOs and PEGs may be accumulating in these kinds of sediments and other anaerobic environments, especially WWTP sludge (Szymanski et al., 2003; Wind et al., 2006). Previous studies, however, have demonstrated that some surfactants such as nonylphenol polyethoxylates (NPEOs) can be effectively degraded in anaerobic marine sediments, reaching degradation percentages up to 67% after 130 days (Ferguson and Brownawell, 2003). Nowadays, it is generally accepted that the anaerobic degradation pathway for NPEOs during wastewater treatment and after their discharge to the environment (Ferguson and Brownawell, 2003; Ferguson et al., 2003; Paterakis et al., 2012) involves the progressive shortening of the polyethoxylated (EO) chain. This seems also feasible for AEOs according

to results from laboratory experiments performed using sewage sludge (Huber et al., 2000; Mölsche, 2004). On the other hand, sediment cores that our research group collected at several points in an estuary subjected to untreated domestic wastewater discharges (Corada-Fernández et al., 2013) have shown that the length of the EO chain for both NPEOs and AEOs remained fairly stable at anaerobic depths ( $E_h = -380 \text{ mV}$ ), so no evidence for the degradation of these surfactants was found. This disagreement could be explained by changes in the microbial populations in sediments from different areas and the low bioavailability of NPEOs and AEOs in muddy sediments, strongly related to their high partition coefficients. Regarding anaerobic degradation of PEGs, this topic has been researched only in the aqueous phase by using commercial mixtures with molecular weights (MWs) up to 20,000 Da and microorganisms from anaerobic WWTP reactors (Dwyer and Tiedje, 1986; Otal and Lebrato, 2003; Huang et al., 2005). The biodegradation of PEGs in anaerobic seawater was first researched using bacteria from Canale Grande, Venice, Italy (Schink and Stieb, 1983). Further studies showed that the anaerobic cultures in seawater media were able to metabolize PEGs with MWs in a range from 200 to 40,000 Da, yielding acetate, acetaldehyde and ethanol (Straß and Schink, 1986).

There are, therefore, no data available on the anaerobic biodegradation of AEOs and PEGs in anaerobic marine sediments, and some inconsistencies when comparing data from different field and laboratory studies, some of them performed in the early 1980s. In order to improve our knowledge on the final fate of these substances in the marine environment, we have carried out several anaerobic degradation assays using coastal polluted sediments where the disappearance of anionic surfactants has been already confirmed (Baena-Nogueras et al., 2014; Lara-Martín et al., 2007a). The goals of this research were: a) to determine whether AEOs and PEGs are biodegradable or not in absence of oxygen in sewage impacted marine environments; and b) to characterize and compare the biodegradation kinetics for individual components of commercial mixtures (different homologs and/or ethoxymers).

## 2. Material and methods

### 2.1. Chemicals and standards

Formaldehyde, methanol and dichloromethane were of chromatography quality, purchased from Scharlau (Barcelona, Spain). Sodium sulfate and sodium acetate were purchased from Panreac (Barcelona, Spain) and water was Milli-Q quality. The solid-phase extraction (SPE) mini-columns used (6 mL, 500 mg) were supplied by Waters (Oasis HLB).

The  $\geq 98\%$  pure  $\text{C}_{10}\text{AEO}_8$  internal standard, the individual  $>98\%$  pure polyethylene glycols (PEGs) having 1, 2, 3, 6 and 8 EO units, and AEO ethoxymers ( $\text{C}_{12}$ ,  $\text{C}_{14}$ ,  $\text{C}_{16}$  and  $\text{C}_{18}$  homologs having 1, 2, 3, 6 and 8 EO units) were supplied by Sigma-Aldrich (Milwaukee, USA).

### 2.2. Sample collection and pretreatment

Sediment and bottom water samples were collected by means of 50 cm length PVC cores and 2.5 L glass bottles, respectively. The sampling site was located in the central part of Sancti Petri channel ( $36^\circ 28' 20.80'' \text{ N}$ ,  $6^\circ 10' 52.95'' \text{ W}$ ), a shallow tidal marine channel (average depth is between 3 and 6 m) that connects the inner part of the salt marsh environment of the Bay of Cadiz with the Atlantic Ocean (SW Spain). This area has been affected during decades by untreated urban wastewater discharges from an adjacent town (San Fernando,  $>100,000$  inhabitants), recently stopped by the construction of a new WWTP in 2003. Sediment and water samples were previously used to perform anaerobic degradation assays with other surfactants (Lara-Martín et al., 2007a,b, 2010; Baena-Nogueras et al., 2014). Seawater physicochemical properties were:  $\text{pH} = 7.86$ , alkalinity = 2.86 mM, and salinity = 37.5, whereas, in sediment, total organic carbon content was 3.0% and particle distribution size was 14.0% sand and 86.0% silt + clay.

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