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Occurrence and risk screening of alcohol ethoxylate surfactants in three U.S. river sediments associated with wastewater treatment plants ☆

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ABSTRACT

Alcohol ethoxylates (AE) are high production volume (HPV) chemicals globally used in detergent and personal care products and are truly a work-horse for the household and personal care industries. Commercial AE generally consist of a mixture of several homologues of varying carbon chain length and degree of ethoxylation. Homologues that are not ethoxylated are also known as aliphatic alcohols or simply fatty alcohols (FA). This group of homologues represents a special interest in the context of environmental risk, as these are also abundant and ubiquitous naturally occurring compounds (*e.g.* animal fats and in human feces). Hence, in a risk assessment one needs to distinguish between the natural (background) concentrations and the added contribution from anthropogenic activities. We conducted a weight-of-evidence risk assessment in three streams, documenting the exposure and predicted risk, and compared these to the habitat and *in situ* biota. We found that the parameters (*e.g.*, habitat quality and total perturbations hereunder total suspended solids (TSS) and other abiotic and biotic stressors) contributed to the abundance of biota rather than the predicted risk from AE and FA. Moreover, the documented natural *de novo* synthesis and rapid degradation of FA highlight the need to carefully consider the procedures for environmental risk assessment of naturally occurring compounds such as FA, *e.g.* in line with the added risk concept known from metal risk assessment.

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1. Introduction

Alcohol ethoxylates (AE) are high production volume (HPV) chemicals used widely as 'down-the-drain' chemicals globally in detergent and personal care products. These workhorse surfactants' annual use in the U.S. alone was 381,000 metric tons in 2008 (Blagoev and Gubler, 2009). Commercial AE generally consist of a mixture of several homologues (114) of varying carbon chain length (C_x) and degree of ethoxylation (EO_n). Homologues that are not ethoxylated (C_xEO_0) are also known as aliphatic alcohols or simply fatty alcohols (FA). AE conform to the general structure:

$$CH_3(CH_2)_n(OCH_2CH_2)_yOH, \text{ where n is generally 11–15, 17 and y is 0–18.}$$

A conventional shorthand notation for a material is "C_xEO_n" where x is the alkyl chain-length and n is the degree of ethoxylation. FA are the special case to the formula where $n = 0$ (C_xEO_0). In most consumer product applications, the saturated alkyl group is essentially linear with a very small amount of branching. FA represent a special interest in the context of environmental risk, as these are also abundant and ubiquitous naturally occurring compounds (*e.g.* animal fats and in human feces; Mudge et al., 2012). Since these are lipophilic compounds, they inherently have the potential to partition into fats. Mudge et al. (2012) recently published that long chain alcohols can be sourced from both natural and anthropogenic sources. Hence,

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understanding the potential for bioaccumulation is dependent upon alcohol sourcing. Soluble alcohols correspond to an acute narcosis mechanism of action, increasing toxicity until they are insoluble and therefore not readily available to exert a non-specific disruption of the cell membrane (Schäfers et al., 2009).

The major disposal route of AE is down-the-drain through sewage systems and municipal wastewater treatment plants (WWTP) into receiving surface waters. This makes the fate and effects of residual AE in treated sewage effluent of interest to industry and regulators alike. AE are extensively biologically degraded by WWTP in excess of 95–99% (van de Plassche et al., 1997; Wind et al., 2006; Federle and Itrich, 2006). Nevertheless, as with all biological degradation processes, residuals do remain resulting in low levels which are ultimately released to the environment *via* WWTP effluent. Concentrations of total AE in WWTP effluents range from 1 to 23 μg L^{-1} in Europe, Canada and the United States (Matthijs et al., 1999; Eadsforth et al., 2006; Morrall et al., 2006). Sorption onto activated sludge particles is an important process in removing surfactants from sewage, with significant fractions of effluent AE found associated with effluent suspended solids. AE are the subject of several environmental risk assessments including those of Little (1977), Goyer et al. (1981), Talmadge (1994), and van de Plassche et al. (1999). These assessments are becoming increasingly sophisticated with numerous advancements in understanding analytical methods, exposure, fate, and effects in the environment. These surfactants have a strong affinity for sorption to solids such as activated sludge, river water solids and, ultimately, sediments (Kiewiet et al., 1996; Cano and Dorn, 1996; McAvoy and Kerr, 2001). A predictive equation for sorption coefficients for individual homologues has been reported (Kiewiet et al., 1996) and expanded by van Compernolle et al. (2006). This allows the extension of risk assessments to account for the bioavailable fraction using sorption data (Belanger et al., 2006). These risk assessments address the aquatic environment in WWTP receiving waters. Interest is now extending to the fate and effects of sorbed AE on the sediment domain at and below WWTP discharges. Moreover, in 2009 a special edition of *Ecotoxicology and Environmental Safety* was published based on the HPV assessment for the OECD of long chained aliphatic alcohols documenting the hazard profile of these compounds, which belong to the AE family (Sanderson et al., 2009). Dyer et al. (2006) conducted an assessment of AE in sediment samples, along with an example environmental risk assessment in which the approach as well as validated sediment analytical methods were introduced.

This study applied and extended those methods to a survey of three small stream systems in the mid-west of the US with the objective of characterizing the occurrence and risk of AE up- and down-stream of WWTPs in surface water, porewater and sediment. The streams are effluent dominated and their selection was based on type of wastewater treatment system, its wastewater characteristics (no or low industrial discharge), and sampling accessibility (see Section 2.2).

The aims of the study were the following:

1) Describe the finger-print (homologue distribution) of AE up and down-stream from three WWTPs;
2) Assess the ratio between FA (EO_0) and AE EO_{n+1};
3) Compare modeled exposure predictions to measured concentrations;
4) Assess the predicted risk to aquatic organisms;
5) Compare the predicted risk to observed biota *in situ* in a weight-of-evidence assessment.

2. Materials and methods

2.1. Analytical methods

The analytical methods and instrumentation applied in this study are described in detail in Dyer et al. (2006). There were 114 possible AE and FA ethoxymers in the range of interest (E_xO0 to E_xO18). Due to the great expense in quantifying all ethoxymers (alcohols and AEs with EO of 1 or more), a subset of 38 components was selected that represents both the shape and most toxic portion of the distribution. For alkyl chain lengths of 12 (C12), ethoxylates (EOs) of 0, 1, 2, 3, 6, 9, 12, 15 were measured. For chain lengths of C13, 14, 15, 16, and 18, EOs of 0, 1, 2, 6, 9, and 15 were measured. Ethoxylates of 0, 1, 2, 6, 9, and 15 were also measured for the deuterated internal standard.

2.1.1. Standard and reference materials

The following materials were used as standards and to spike sediments: NEODOL® 25-9 (an alcohol ethoxylate with alkyl chain lengths of C12 through C15 and an average ethoxylate number of 9), Shell Chemical LP (Geismar, USA), 7 GENAPOL® T110 (an alkyl ethoxylate with alkyl chain lengths of C16 and C18 and an average ethoxylate number of 13, Shell Chemical, LP), C12 linear alcohol (99%) from Chem Service (West Chester, USA) C13 and C14 (97%) individual linear alcohols from Sigma-Aldrich (St. Louis, USA), and C15, C16, and C18 individual linear alcohols (99%) from Sigma-Aldrich. A deuterated alcohol ethoxylate, provided by Shell Chemical LP, was used as internal standard. This AE consisted of a single alkyl chain length with the alkyl chain deuterated (C13D27) with an average ethoxylate number of nine.

2.1.2. Reagents and solvents

All solvents were HPLC grade purchased from Honeywell Burdick and Jackson (Morristown, USA) and included methanol, dichloromethane, acetone, acetonitrile, tetrahydrofuran, and ethyl acetate. Water was obtained from a Millipore Milli-Q Plus water system. Triethylamine (99%) was purchased from Fisher Scientific USA (Waltham, USA) formic acid (95–97%) from Sigma-Aldrich (USA), formalin (ACS grade, 37% formaldehyde) from VWR (Radnor, USA), and the derivatization agent, 2-fluoro-N-methyl pyridinium p-toluenesulfonate (>99%, Pyr+) was purchased from Sigma-Aldrich (USA). All reagents and solvents were used as received.

2.1.3. Solid phase extraction cartridges

Varian Mega Bond Elut C-2 (2 g) 12 mL Part No. 1225-6056 Lot 032811, Varian HF Mega Bond Elut SAX (2 g) 12 mL Part No. 1425-6021 Lot 780700, Varian Mega Bond Elut SCX (2 g) 12 mL Part No. 1425-6019 Lot 772209 were used (Palo Alto, USA).

2.1.4. Optimized Sediment Extraction and Derivatization Procedure

An optimized procedure for extraction and derivatization of sediment samples was developed and reported by Morrall et al. (2006) and Dyer et al. (2006), as summarized below. All glassware was cleaned by sequential rinses with hot tap water (~55 °C), deionized water, methanol, acetone, dichloromethane, acetonitrile, and Milli-Q water. The glassware was then autoclaved at 110–120 °C for at least 1 h and stored in cleaned (as described for the glassware above) aluminum foil until used. Care was also taken to avoid contact with latex gloves, paper products, bare skin, or any other item potentially contaminated with soap or surfactants. For each sediment sample, approximately 20 g of wet sediment was freeze dried and then extracted with 30 mL of acetonitrile by manual shaking (2 min) and sonication (5 min), followed by centrifugation (5 min) at 874 *g* to separate the mixture. The supernatant was decanted and 30 mL of acetonitrile was added to the solids and re-extracted as before. The two extracts were combined and labeled as Fraction 1. The sediments were further extracted (twice) with a mixture of 30 mL methanol/ethyl acetate/water (78/20/2, v/v/v) using the same procedure as above. These extracts were combined and labeled as Fraction 2. SPE cartridges were set up in series, C2/SCX/SAX, and pre-conditioned by eluting with 100 mL Milli-Q water, 30 mL of acetonitrile, 10 mL (methanol/ethyl acetate/water (78/20/2, v/v/v)), 50 mL methanol,

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