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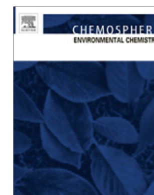

Fluorotelomer ethoxylates: Sources of highly fluorinated environmental contaminants part I: Biotransformation

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ABSTRACT

Polyethoxylated 2-perfluoroalkylethanols ('fluorotelomer ethoxylates', F–(CF_2–CF_2–)$_x$–(CH_2–CH_2–O)$_y$–H, FTEO) are an important class of non-ionic fluorinated surfactants, which have been disregarded as potential source of per- and polyfluorinated organic pollutants despite their high production and application amounts.

A commercial mixture of FTEO with a perfluoroalkyl chain length between 6 and 10 carbon atoms and an ethoxymer distribution between 0 and 13 was subjected to a biodegradation test. Monitoring of the aerobic biotransformation process by HPLC–ESI-MS/MS showed that FTEO are rapidly transformed with a half-life of approximately 1 d.

Structural elucidation of the biotransformation products with the help of hybrid quadrupole – linear ion trap tandem mass spectrometry revealed oxidation to the respective carboxylic acid followed by sequential shortening of ethoxylate units which led to FTEO carboxylates (FTEOC). The conversion rate of FTEOC was found to diminish with decreasing number of ethoxylate units and virtually ceased for compounds with seven intact ethoxy units. These short-chain FTEOC were not further degraded within 48 d.

Nonetheless, perfluorohexanoic acid (PFHxA) and perfluorooctanoic acid (PFOA) were detected, whose formation is ascribed to degradation of residual fluorotelomer alcohols present in the commercial product.

This article represents the first of two parts of a series concerning FTEO. Whilst this part is clearly focused on results of a biodegradation study of FTEO, part two will pinpoint analytical aspects, synthesis of biotransformation products and first evidence of environmental presence of the biotransformation products.

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1. Introduction

Ever since the global and ubiquitous detection of several perfluorinated carboxylic and sulfonic acids at the beginning of the millennium (Giesy and Kannan, 2001; Moody et al., 2001; Olsen et al., 2003), fluorinated organic substances have forged ahead to some of the most extensively investigated organic pollutants. While primary focus has obviously been set on perfluorinated compounds and their environmental behavior, only few reports on the fate and presence of less fluorinated organic substances are available. Most of these articles cover fluorotelomer alcohols (FTOH), which are used as intermediates in manufacturing processes of polymers such as acrylates (Russell et al., 2008), but also of lower molecular weight sulfonates, phosphates, betaines and polyethoxylates. FTOH have been proven to be a source of perfluorinated carboxylic acids (PFCA) by microbial degradation (Dinglasan et al., 2004; Wang et al., 2005a,b, 2009; Liu et al., 2007) and atmospheric chemical reactions (Ellis et al., 2004; Prevedouros et al., 2006).

The number of articles describing the environmental fate of commercial FTOH-based low molecular weight fluorosurfactants is very low. Very recently, polyfluoroalkyl phosphoric acid diesters were detected in human blood sera as well as in wastewater treatment plant sludge (D'Eon et al., 2009). The same authors described that metabolism of these fluorotelomer phosphates in rats also leads to PFCA (D'Eon and Mabury, 2007), which suggests that intake of such chemicals, which were used in food contact paper products, may finally result in human exposure to PFCA. This implies that fluorotelomer-based chemicals may be enzymatically biotransformed to the respective fluorotelomer alcohol and thus represent a source of PFCA.

The herein presented polyethoxy-1H,1H,2H,2H-perfluoroalkanols ('fluorotelomer ethoxylates', FTEO) may represent a significant source of fluorinated substances due to their high production and application amounts. It is known that commercial FTEO products

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as well as other FTOH based chemicals may contain residual unreacted FTOH of various chain lengths, as reported by Dinglasan and Mabury (2006). Therefore, these products may represent a source of PFCA as well as of other non-perfluorinated substances that were discovered to be dead-end metabolites of FTOH degradation (Wang et al., 2009). However, very little is known about the fate of FTEO in the environment. One article tentatively describes the formation of carboxylic acid species from FTEO, although it lacks information on degradation kinetics and comparison of FTEO with different perfluoroalkyl and ethoxylate chain lengths (Schröder, 2003). The fluorinated moiety of these compounds was obviously not attacked as inorganic fluoride concentration did not increase. The results gathered in that study seemed unsatisfactory considering the significance of these fluorinated species. The fate of the fluorinated moiety is of particular interest as these highly fluorinated molecules often exhibit high ecotoxicological (Boudreau et al., 2003) and toxicological (Lau et al., 2007) potential as compared with their non-fluorinated counterparts.

So far, no data are available as to evaluate the fate of FTEO and their biotransformation products in the aquatic environment. In case all ethoxylate functions could be degraded, FTEO might pose another important source of PFCA. In the present study, biotransformation rates and biotransformation products of FTEO are described.

We will publish a separate paper on the analytical aspects gathered during this study, which will cover mass spectrometric measurements of the parent surfactant and its biotransformation products as well as synthesis of two biotransformation products and first evidence of their environmental presence.

In the following sections, acronyms of FTEO and their oxidized metabolites will be based upon the respective FTOH, e.g. 6:2-$FTEO_2$ represents the 6:2-FTOH which has been doubly ethoxylated. Consequently, oxidation of 6:2-$FTEO_2$ will lead to 6:2-$FTEO_2C$. If no degree of ethoxylation is given, all ethoxymers of a distinct perfluoroalkyl chain length are referred to.

2. Experimental section

2.1. Chemicals

All solvents used were of the highest purity available and were from Merck (Darmstadt, Germany). ^{13}C labeled standards were *n*-perfluoro-[1,2-^{13}C]-octanoic acid (M2PFOA) and *n*-perfluoro-[1,2-^{13}C]-hexanoic acid (MPFHxA) purchased from Wellington laboratories (Ontario, Canada).

The commercial FTEO mixture was Zonyl® FSH from DuPont de Nemours (Neu-Isenburg, Germany). The fluorosurfactant fraction is 50%, the remainder consisting of water and dipropylene glycol methyl ether in equal shares (DuPont Company, 2001). The perfluorocarbon chain length was found to be at least between 4 and 12 carbon atoms and the degree of ethoxylation was at least 0–18. Due to the relatively low fractions of other congeners and very high adsorption of compounds with a long perfluorocarbon chain length, this study will only be focused on FTEO with a perfluorocarbon chain length of six and eight carbon atoms and a degree of ethoxylation between 0 and 13.

Stock solutions were prepared at a concentration of 1 mg mL^{-1} in acetone (FTOH and Zonyl FSH) or MeOH (all other chemicals). Working solutions were regularly prepared at concentrations of 0.1 ng μL^{-1}, 1 ng μL^{-1}, 10 ng μL^{-1} or 100 ng μL^{-1} by dilution with the respective solvent. All solutions were stored at −20 °C.

2.2. Biodegradation

Biodegradation experiments were carried out at approximately 25 °C in amber 1 L glass bottles filled with 1 L of unfiltered effluent water of the municipal waste water treatment plant Beuerbach (Hesse, Germany). Aerobic conditions were maintained by aerating the bottles regularly (1–2 h per day) with an aquarium pump. Permanent aeration was not chosen in order to reduce potential volatilization of metabolites. In order to distinguish microbial degradation from adsorption to particles or the glass surface, additional experiments were carried out in waste water spiked with 10 g L^{-1} sodium azide, analogous to OECD guideline 309 (Organisation for Economic Co-Operation and Development, 2004). The bottles were spiked with 9.5 mL of a solution containing 1.2 mg mL^{-1} Zonyl FSH in MilliQ water, resulting in an effective FTEO concentration of 5.7 mg L^{-1}. Blank bottles containing WWTP effluent only were also prepared. Sample intervals decreased from daily in the beginning of the experiment to weekly after several weeks had passed.

For FTEO analysis, 100 μL of the fresh samples were mixed with 500 μL of a 10 mM aqueous ammonium acetate solution, 380 μL acetonitrile and 20 μL of internal standard solution (nonylphenol diethoxylate ($NPEO_2$), 10 ng μL^{-1} in acetonitrile). The samples were vortex-shaken and filtered through a 0.2 μm nylon membrane filter (Carl Roth, Karlsruhe, Germany). For metabolite analysis, 500 μL of the samples were mixed with 300 μL 10 mM aqueous ammonium acetate solution, 180 μL acetonitrile and 20 μL of internal standard solution (MPFHxA and M2PFOA, 100 pg μL^{-1} in methanol).

2.3. Instrumental analysis

The instrumental chromatographic setup consisted of two Series 200 Micro Pumps, a Series 200 vacuum degasser, and a Series 200 autosampler (Perkin Elmer, Norwalk, CT, USA). Separations were carried out on a HALO C_{18} column (Advanced Materials Technology, Wilmington, DE, USA), 50 × 2.1 mm, 2.7 μm particle size (2.2 μm solid core), 90 Å pore size. Mobile phases were A: water/acetonitrile (95/5; V/V) and B: water/acetonitrile (20/80; V/V) both containing 5 mM ammonium acetate.

The chromatograph was coupled to a hybrid triple quadrupole linear ion trap tandem mass spectrometer Q Trap 3200 (Applied Biosystems, Foster City, CA, USA) using a Turbo Ionspray interface in electrospray mode ("Turbo Spray"). Nitrogen was used as curtain gas (172 kPa), nebulizer gas (379 kPa), turbo gas (448 kPa) and collision activated dissociation (CAD) gas (five arbitrary units on a scale of 1–12). Optimization of MRM parameters was carried out automatically with the help of the 'Quantitative Optimization' tool included in the Analyst Software (Version 1.4.2, build 1346, Applied Biosystems).

2.4. FTEO analysis

Chromatography was carried out with a binary gradient, starting with 60% A, held for 0.5 min, followed by a linear decrease to 0% A within 5.5 min. The column was rinsed at 0% A for 3 min, brought back to 60% A within 4 min and reequilibrated for 5 min. The flow rate was 300 μL min^{-1} and the injection volume was 50 μL.

The MS was operated in multiple-reaction monitoring (MRM) mode. FTEO were measured as their ammonium adducts in positive electrospray mode. The MRM transitions and the compound-dependent parameters are given in Table 1.

The Ionspray voltage was set to 4.5 kV, the Entrance Potential (EP) was 10 V and the Collision Cell Exit Potential was 3 V.

Semi-quantification was performed by the internal standard method. Nonylphenol diethoxylate ($NPEO_2$) (m/z 326.5 → 183.3) was used as the internal standard. It was chosen because of similar retention time to the target analytes, and it can likewise be measured as its ammonium adduct. Thus, it is suited to overcome

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