



Simultaneous determination of (*N*-ethyl perfluorooctanesulfonamido ethanol)-based phosphate diester and triester and their biotransformation to perfluorooctanesulfonate in freshwater sediments[☆]

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ABSTRACT

While (*N*-ethyl perfluorooctanesulfonamido ethanol)-based phosphates (SAmPAPs) have been proposed as a group of perfluorooctanesulfonate (PFOS) precursors, investigation of their occurrence and fate has been limited to SAmPAP diester. In this study, SAmPAP diester and triester were simultaneously determined in freshwater sediment from Taihu Lake using a newly developed UPLC-MS/MS method, and their biotransformation to PFOS in lake sediment was investigated. SAmPAP diester and triester were detected in sediments with a detection frequency of 56% and 88%, and their mean concentrations were 0.24 ± 0.11 ng/g dry weight (dw) and 0.12 ± 0.03 ng/g dw, respectively. The SAmPAP diester/triester ratio in sediment was 1.1 ± 4.2 , much lower than that (6.7) observed in the technical product, and the positive correlation was found between the concentrations of SAmPAP diester and PFOS in sediments ($r^2 = 0.45$, $p = 0.01$), suggesting that SAmPAP diester would be biotransformed to PFOS in the lake sediment. The microbial degradation test in the lake sediments further clarified that SAmPAP diester was biodegraded to PFOS, but SAmPAP triester was highly recalcitrant to microbial degradation. This study suggests that the occurrence of SAmPAP diester in freshwater lake sediments may be an important precursor of PFOS.

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1. Introduction

Perfluorooctane sulfonate (PFOS) has been widely applied in commercial and industrial products, such as surfactants, anti-erosion additives, anti-reflective coatings, food packaging, etc. (Paul et al., 2009). As a result of the great use of these products as well as its water solubility and persistence, PFOS has been widely detected in the aquatic environment (Ye et al., 2014; Yu et al., 2015; Habibullah-Al-Mamun et al., 2016; Sammut et al., 2017). It has been demonstrated that PFOS can cause a wide range of adverse effects on both mammalian (Hu et al., 2002; Lau et al., 2007) and aquatic organisms (MacDonald et al., 2004; Boudreau et al., 2003). Based on a reference dose derived from a developmental toxicity study in

rats (Luebker et al., 2005), a lifetime drinking water health advisory (70 ng/L) has been recommended by the U.S. Environmental Protection Agency (US EPA) in 2016.

While water contamination by PFOS is partially caused by its direct use and emissions, biological degradation of some PFOS precursors are proposed as the potential source (Lange, 2000; Liu and Avendano, 2013). Perfluorooctane sulfonamide-based phosphate surfactants have recently been highlighted as precursors of PFOS due to existing, large historical reservoirs. The (*N*-ethyl perfluorooctanesulfonamido) ethanol-based phosphate esters (SAmPAPs) have been manufactured since 1974 for using in food contact paper and packaging by 3M Co. and sold as FC-807 (a commercial SAmPAP formulation), and represented the largest amount of “PFOS equivalents” of all PFOS-containing products by 3M Co. in 1997 (Benskin et al., 2012). Although these perfluorooctane sulfonyl fluoride-based products were voluntarily phased out by 3M Co. in 2002 (U.S. Environmental Protection Agency (USEPA), 2002), 6 manufacturing facilities located at Wuhan (2), Wenzhou,

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Hangzhou, Handan and Jinzhou in China are producing SAmPAPs as wetting agent, defoamer, oil and water-proof strengthener for paper industry (Guidechem Chemical Network, 2017). The commercial SAmPAP formulations were dominated by SAmPAP diester (85%), followed by SAmPAP monoester (10%), and SAmPAP triester (5%) (Lee and Mabury, 2009). As the major constituent of commercial SAmPAP formulations, SAmPAP diester has been detected in marine sediments from Vancouver, Canada with concentrations comparable to those of PFOS (Benskin et al., 2012). Considering that SAmPAP diester is likely biodegraded and would contribute to the occurrence of PFOS, its biodegradation has been investigated in urban marine sediment following a 120-day exposure, and no degradation was observed (Benskin et al., 2013). However, it is important to investigate whether SAmPAP diester could be biodegraded in freshwater sediment, due to potential differences in microbial activity, as exemplified by the relatively rapid biodegradation of organic carbon in inland waters compared to marine systems (Catalán et al., 2016). In addition, although SAmPAP triester is a minor component in the technical product, it is expected to preferentially partition to sediment due to its relatively high octanol/water partition coefficient ($\log K_{ow} = 19.3$), which is greater than that ($\log K_{ow} = 12.6$) of SAmPAP diester (estimated with QSPRs in EPI Suite™ software). Thus, we hypothesize that SAmPAP triester would be accumulated in sediment, and then also biotransformed to PFOS in the aquatic environment. To our best knowledge, no study has yet attempted to determine SAmPAP triester and investigate its biodegradation in environment.

In this study, concentrations of SAmPAPs and their potential biodegradation products including PFOS, perfluorooctane sulfonamide (PFOSA), 2-(perfluorooctane sulfonamido) acetic acid (FOSAA), *N*-Ethyl perfluorooctane sulfonamide (EtFOSA), *N*-ethyl perfluorooctane sulfonamido acetate (EtFOSAA) and *N*-ethyl perfluorooctanesulfonamido ethanol (EtFOSE) were measured in sediments from Taihu Lake, the third largest freshwater lake in China. A microbial degradation test in freshwater sediments was conducted to identify whether SAmPAP diester and triester could be biodegraded and produce PFOS in freshwater sediments. The results obtained in this study will be helpful to assess the potential risk of SAmPAPs and PFOS.

2. Materials and methods

2.1. Chemicals and reagents

The mixture standards of native perfluoroalkylcarboxylic acids (PFCAs) including perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnDA), perfluorododecanoate (PFDoDA), perfluorotridecanoate (PFTriDA) and perfluorotetradecanoate (PFTeDA)) and perfluoroalkylsulfonates (PFASs) including perfluorohexanesulfonate (PFHxS), perfluoroheptanesulfonate (PFHpS), and PFOS, the mixture of mass-labeled PFCAs and mass-labeled PFASs standards including $^{13}\text{C}_2$ -PFHxA, $^{13}\text{C}_4$ -PFOA, $^{13}\text{C}_5$ -PFNA, $^{13}\text{C}_2$ -PFDA, $^{13}\text{C}_2$ -PFUnDA, $^{13}\text{C}_2$ -PFDoDA, $^{18}\text{O}_2$ -PFHxS, and $^{13}\text{C}_4$ -PFOS, PFOSA, EtFOSA, FOSAA, EtFOSAA, EtFOSE and PFDA, and stable isotope labeled standards including $^{13}\text{C}_4$ -PFOS, EtFOSAA- d_5 and $^{13}\text{C}_4$ -bis (1H, 1H, 2H, 2H) perfluorooctyl phosphate ($^{13}\text{C}_4$ -8:2 diPAP) were purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada). Isotope labeled monoisononylphthalate (^{13}C -MiNP) was supplied from Cambridge Isotope Laboratories (Andover, Massachusetts, USA). Tris (2-ethylhexyl)- d_{51} phosphate (TEHP- d_{51}) was purchased by Hayashi Pure Chemical Ind. Ltd. (Osaka, Japan). The standard of SAmPAP diester was purified in our previous study (Peng et al., 2014). The standard of SAmPAP triester was purified from FC-

807, supplied from Hengxin Co. (Wuhan, Hubei, China), as described in Supporting Information (SI) and in accordance with the method reported in our previous article (Peng et al., 2014). The purified SAmPAP triester was characterized by the Ultimate 3000 UHPLC system (Dionex, Sunnyvale, California, USA) coupled to a Q-Exactive MS (Thermo Scientific, Rockford, Illinois, USA). NMR spectra (19F NMR) were taken on a Bruker Avance III (1H, 500 MHz) spectrometer (Fig. S1). The purity of SAmPAP triester was tested by ultraperformance liquid chromatography tandem mass spectrometry (UPLC-MS/MS) and estimated to be >97%. All solvents, including methanol and dichloromethane, were of HPLC grade and were purchased from Fisher Chemicals Co. (Beijing, China). The ammonia solution (NH_4OH , 28%) was purchased from Alfa Aesar (Tianjin, China), and ammonium acetate (HPLC, 99.5%) was purchased from Dikma (Lake Forest, California, USA). Water was obtained from purification of deionized water by a Millipore, Milli-Q synthesis water purification system (Bedford, Massachusetts, USA). The Oasis WAX (150 mg, 6 mL) solid phase extraction cartridges were supplied from Waters (Milford, Massachusetts, USA). Supelclean™ Envi-Carb cartridges (1 mg, 1 mL) were purchased from Supelco (Bellefonte, Pennsylvania, USA).

2.2. Sample collection

In August 2014, 41 surface sediment samples (0–30 cm depth) were collected from the north area of Taihu Lake, including Zhushan Bay, Meiliang Bay and Gonghu Bay in which environmental pollution is greater due to domestic and industrial discharge (Bai et al., 2009; Cao et al., 2012). Samples were collected using a steel bottom sampler and placed into polyethylene (PE) bags before storage at -20°C . Fig. S2 showed the sampling sites which were located with the aid of a global positioning system (GPS).

2.3. Microbial degradation in fresh sediments

Lake sediments used to test the microbial degradation of SAmPAP diester and triester were collected from Taihu Lake. The sediments were stored at 4°C after sampling and used for microbial degradation test within 24 h. 5 g of fresh sediment and 5 mL of deionized water were mixed in a 50 mL polypropylene (PP) centrifuge tube. The sediments were incubated with 50 ng of SAmPAP diester or 50 ng of SAmPAP triester. PFDA and ^{13}C -MiNP have been used to assess loss during incubation period and microbial activity of incubation sediments in previous paper (Benskin et al., 2013). In this study, 50 ng of PFDA and 50 ng of ^{13}C -MiNP were spiked to the sediment as an internal negative control and an internal positive control, respectively. Methanol remained at less than 0.1% in all incubations. Inactivated sediments were autoclaved twice prior to the incubation. After spiking, centrifuge tubes were shaken at 100 rpm at 25°C . Target compounds were monitored on days 0, 7, 21, 35, 49, 63, 77, 91 and 105. All incubation samples were performed in triplicate, and triplicate blank sediments (spiked 30 μL MeOH) were also monitored at the same time.

A 3M, Petrifilm™ Aerobic Count (AC) Plate (St. Paul, Minnesota, USA) was used to assess variation in microbial activity during the 105-day experiment in active/inactive sediments. Microbial activities in sediments on days 0, 21, 49, 77, 91 and 105 of the experiment were assessed. The procedures of the test were described in the SI.

2.4. Sample extraction and cleanup

For chemical analysis, samples of sediment from Taihu Lake were freeze-dried, ground, and sieved through a 0.2 mm mesh.

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