Chemosphere 93 (2013) 140–145

Contents lists available at SciVerse ScienceDirect

Chemosphere

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

Formation of perfluorinated surfactants from precursors by indigenous microorganisms in groundwater

Michio Murakami [a,*], Hiroshi Nishikoori [b], Hiroshi Sakai [b], Kumiko Oguma [b], Hideshige Takada [c], Satoshi Takizawa [b]

[a] "Wisdom of Water" (Suntory), Corporate Sponsored Research Program, Organization for Interdisciplinary Research Projects, The University of Tokyo, 7-3-1 Hongo, Bunkyo, Tokyo 113-8656, Japan
[b] Department of Urban Engineering, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo, Tokyo 113-8656, Japan
[c] Laboratory of Organic Geochemistry (LOG), Institute of Symbiotic Science and Technology, Tokyo University of Agriculture and Technology, Fuchu, Tokyo 183-8509, Japan

HIGHLIGHTS

- The formation of PFSs from precursors was measured in incubation tests.
- Indigenous microorganisms in groundwater biodegraded FOSA to PFOS.
- Addition of nutrients and soil promoted the formation of PFOS.
- PFSs were formed from precursors in street runoff by microorganisms in groundwater.
- PFS precursors were more abundant in street runoff than in wastewater effluent.

ARTICLE INFO

Article history:
Received 11 January 2013
Received in revised form 17 April 2013
Accepted 5 May 2013
Available online 5 June 2013

Keywords:
Biodegradation
Diffuse pollution
Groundwater
Non-point source
Perfluorochemical (PFC)
Urban runoff

ABSTRACT

The formation of perfluorinated surfactants (PFSs) from their precursors in waters is of concern. In this study, the formation of PFSs through biodegradation of precursors was measured in incubation tests. Indigenous microorganisms in groundwater were able to biodegrade perfluorooctane sulfonamide (FOSA) to yield perfluorooctane sulfonate (PFOS). The addition of nutrients and soil promoted the formation. A 42-d incubation test using sources of groundwater recharge showed that PFOS, perfluorooctanoate, and perfluorononanoate were significantly and remarkably ($\geqslant 1.5\times$) formed from precursors in street runoff through biodegradation, but not in rainwater or wastewater effluent. Significant formation of PFSs from precursors in street runoff was observed.

1. Introduction

Since the manufacture of perfluorinated surfactants (PFSs), such as perfluorooctane sulfonate (PFOS; $C_8F_{17}SO_3^-$) and perfluorooctanoate (PFOA; $C_7F_{15}COO^-$), began in the late 1940s, PFSs and their precursors have been widely used by various industries in products such as waxes, automotive interiors, windshield fluids, carpet cleaners, fire retardants, apparel, and fluoropolymer manufacture, because of their water repellency and oil repellency (Dinglasan-Panlilio and Mabury, 2006; Prevedouros et al., 2006; Paul et al., 2009). PFSs are water soluble, bioaccumulative (especially long-chain PFSs with $\geqslant 8$ fluorinated carbons), and environmentally persistent (Kauck and Diesslin, 1951; Conder et al., 2008). Owing to these features, PFSs are globally and ubiquitously detected in various waters, organisms, and humans (Giesy and Kannan, 2001; Kannan et al., 2004; Yamashita et al., 2005). Since some PFSs are suspected to be carcinogenic, chronic toxicants, and reproductive toxicants (Biegel et al., 2001; Nakayama et al., 2005; Lopez-Espinosa et al., 2011), their adverse effects on humans and animals are of concern. In response to concerns, the United States Environmental Protection Agency and eight manufacturers reduced emissions of PFOA. PFOS and perfluorooctane sulfonyl fluoride were added to the listing of the Stockholm Convention on Persistent Organic Pollutants in 2009. Yet PFSs are still detected in environments.

In addition to the direct discharge of PFSs from point sources (e.g., wastewater) and non-point sources (e.g., urban runoff), the formation of PFSs from their precursors is a significant route of

* Corresponding author. Tel.: +81 3 5841 6263.
E-mail address: michio@env.t.u-tokyo.ac.jp (M. Murakami).

0045-6535/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.chemosphere.2013.05.010

entry to waters: concentrations or mass loadings of PFSs were increased after wastewater treatment, possibly owing to biodegradation of their precursors (Schultz et al., 2006; Murakami et al., 2009b; Guo et al., 2010). Six PFS precursors (N-ethyl perfluorooctane sulfonamido ethanol, N-ethyl perfluorooctane sulfonamido acetate, N-ethyl perfluorooctane sulfonamide, perfluorooctane sulfonamido acetate, perfluorooctane sulfonamide [FOSA; $C_8F_{17}SO_2NH_2$], and potassium perfluorooctane sulfinate [PFOSI]) in activated sludge were eventually transformed to PFOS (Rhoads et al., 2008). Fluorotelomer alcohols and acids were biodegraded to perfluorocarboxylic acids (PFCAs) such as PFOA in microbial systems (Dinglasan et al., 2004; Myers and Mabury, 2010). The degradation of fluorotelomer polymers also proved a significant source of PFSs in soil microcosms (Russell et al., 2008). PFOS was more abundant in groundwater in Tokyo than in river water, possibly owing to its production from the degradation of precursors (Murakami et al., 2009a). This origin was supported by a column test in which PFOS in street runoff increased during soil infiltration (Murakami et al., 2008b). Nevertheless, knowledge of the occurrence of PFS precursors in waters is limited, because there are several types of precursors (e.g., sulfonamide-containing PFSs; fluorotelomer sulfonates, alcohols, and acids; polyfluoroalkyl phosphate mono- and di-esters; fluorotelomer polymers), including compounds that are difficult to analyze. A method to measure the overall formation of PFSs from the various precursors in waters is needed.

In this study, the formation of PFSs from precursors through biodegradation was measured in incubation tests. Although a chemical oxidation conversion method was recently developed to measure overall PFS precursors (Houtz and Sedlak, 2012), this study focused on microbiological transformation. First, an incubation test was set up to confirm that FOSA is biodegraded to PFOS by indigenous microorganisms in groundwater. Nutrients and soil were added to investigate whether they promote formation. Second, a 42-d incubation test was performed to evaluate the formation of PFSs from precursors in sources of groundwater recharge (street runoff, rainwater, and wastewater effluent).

2. Materials and methods

2.1. Chemicals

R2A nutrient medium was purchased from Nihon Pharmaceutical Co. Ltd. It contained peptone 0.16 g g^{-1}, yeast extract 0.16 g g^{-1}, casamino acids 0.16 g g^{-1}, glucose 0.16 g g^{-1}, amylogen 0.16 g g^{-1}, dibasic potassium phosphate 0.10 g g^{-1}, magnesium sulfate 0.016 g g^{-1}, and sodium pyruvate 0.10 g g^{-1}. 8:2 Fluorotelomer unsaturated carboxylate (8:2 FTUCA; $C_8F_{16}CHCOO^-$) was purchased from Wellington Laboratories. Details of other chemicals are reported elsewhere (Murakami et al., 2008a; Nishikoori et al., 2011).

2.2. Sample collection

Groundwater was collected twice in 2011 from a well on the campus of The University of Tokyo for the two incubation tests. A clayey loam soil sample (29.9% clay, 51.9% silt, 18.2% sand) had been collected at 4.0–6.5 m below ground level from the same site in 2007 and air-dried. Street runoff, rainwater, and wastewater effluent were collected in 2011. The first flush of street runoff was collected from the gutter of National Route 122 (45 249 vehicles d^{-1} in 2010) in Tokyo. Rainwater was taken from a rainwater tank, which collects runoff from 5035 m^2 of asphalt and concrete roof, in Sumida Ward, Tokyo. Wastewater effluent was collected from a sewage treatment plant (temporal trends of PFSs were reported in Murakami et al. (2011)). The samples were filtered through prebaked glass fiber filters (pore size, 0.3 μm; Advantec) and stored at 5 °C before analysis.

2.3. Incubation test 1 (FOSA biodegradation test)

With reference to previous studies (Ang and Abdul, 1992; Organisation for Economic Co-operation and Development, 1992; Myers and Mabury, 2010), six treatments were compared to confirm biodegradation of FOSA to PFOS by indigenous microorganisms in groundwater and to reveal the role of nutrients and soil in the formation:

C1 (groundwater + soil): 8.5 mL groundwater + 2 g soil in a 20-mL prebaked glass bottle.
C2 (groundwater + soil, sterilized): as in C1 and sterilized in an autoclave.
C3 (groundwater + soil + nutrients): as in C1 + 1 mL 4 g L^{-1} R2A.
C4 (groundwater + nutrients): 8.5 mL groundwater + 1 mL 4 g L^{-1} R2A.
C5 (groundwater): 8.5 mL groundwater only.
C6 (distilled water): 8.5 mL distilled water only.

FOSA (500 μL of 2 mg L^{-1}) was added into each bottle. Nine bottles were prepared for each treatment except C6 to supply samples at 1, 4, 9, 14, 21, 28, 35, 42, and 49 d. Samples of C6 were analyzed at 28 and 49 d. All bottles were shaken at 40 rpm in the dark at 20 °C in aerobic condition. The incubated water was mixed with methanol at 1:1 (v/v) and filtered through a 0.2-μm nylon filter (Pall). The soil was freeze-dried for later analysis. Suspended solids (SS) in 5 mL of supernatant were collected on a 0.3-μm glass fiber filter. Although SS were not present in C6, PFSs retained on the glass fiber filter were analyzed. For samples without soil (C4, C5, and C6), the remaining particles were flushed with 1 mL of distilled water, and 5 mL of methanol was then added to the bottle, which was sonicated to extract PFSs adsorbed on the bottle. The addition of 5 mL of methanol and sonication were performed twice and the extracts were mixed.

2.4. Incubation test 2 (PFS formation test)

The conditions for the second incubation test were based on the results of the first with some modifications. To confirm whether PFS precursors are biodegraded, 50 mL of groundwater (as an inoculum of microorganisms), 450 mL of distilled water, and 5 mL of 40 g L^{-1} R2A were mixed in a prebaked bottle and then FOSA and 8:2 FTUCA were spiked to achieve a final concentration of 40 ng L^{-1} each, and the bottles were incubated for 42 d. In addition, three treatments were tested to evaluate the formation of PFS from precursors in street runoff, rainwater, and wastewater effluent:

A (with nutrients): 450 mL water sample + 50 mL groundwater + 5 mL 40 g L^{-1} R2A in a 1-L prebaked glass bottle.
B (with nutrients, sterilized): as in A with 1 g L^{-1} sodium azide (final concentration) for sterilization.
C (without nutrients): 450 mL water sample + 50 mL groundwater in a 1-L prebaked glass bottle.

Treatments A and B were tested on all three samples, and treatment C on street runoff only. All bottles were shaken at 40 rpm in dark at 20 °C in aerobic condition for 42 d. PFSs in street runoff, rainwater, wastewater effluent and groundwater samples were analyzed in triplicate to calculate the concentrations at $t = 0$. Treatments A–C were run in triplicate batches (three different bottles). After incubation, samples were filtered through 0.3-μm glass fibers filters to obtain filtrate and SS. Methanol (10 mL) was added to each bottle, which was sonicated to extract PFSs adsorbed on the bottle. This was performed twice and extracts were mixed.