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Perfluorooctane surfactants in waste waters, the major source of river pollution

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Abstract

Perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) are persistent and widely distributed in the environment. Recently, the discharge of municipal waste water has been shown to be an important route of such perfluoroalkyl surfactants into the aquatic environment.

The aim of this study was to assess the mass flow of PFOA and PFOS from typical waste water treatment plants (WWTPs) into surface waters. Samples were collected at different stages of treatment of four WWTPs in Northern Bavaria, Germany, and from the rivers receiving the treated waste waters (WW).

The outflow of PFOA from the WWTPs to the rivers was 20-fold higher than the inflow to the plants; about a tenth was removed with the sludge. For PFOS, the increase from inlet to outlet was about 3-fold; almost half of it was retained in the sludge. Both surfactants were released into river water from the WWTP of a medium-sized city with domestic, industrial and commercial waste waters; in domestic waste waters the surfactants were found at much lower levels.

Keywords: Surface waters; Waste waters; Sewage sludge; Mass flow; Perfluorinated surfactants

1. Introduction

The perfluoroalkyl surfactants (PFS) perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) are persistent environmental contaminants; they are globally distributed and are found in humans and in wildlife, even at remote locations (Houde et al., 2006). PFOA is also a degradation product of fluorotelomer alcohols (Lange, 2002; Dinglasan et al., 2004), PFOS of perfluorooctane sulfonamides (Lange, 2001); precursors such as 2-(*N*-ethyl perfluorooctane sulfonamido) ethanol or 2-(*N*-ethyl perfluorooctane sulfonamido) acetic acid are transformed into PFOS (Lange, 2000; Boulanger et al., 2005).

Their unique molecular properties, chemical and thermal stability, their water- and fat-repellent properties have made them and their derivatives particularly suitable for treatment of textiles and paper, for cosmetics and insecticide formulations, for fire fighting foams, and in the production of fluoropolymers (Kissa, 2001).

The discharge of municipal waste waters (WW) is one of the principal routes of introducing these chemicals into the aquatic environment, as reported for various water treatment plants (WWTPs) in the United States (3M, 2001; Boulanger et al., 2005; Schultz et al., 2006a, b; Sinclair and Kannan, 2006). Studies on their mass flow were reported by Sinclair and Kannan (2006) and Schultz et al. (2006b). In 2006 a severe pollution of some rivers in Germany due to inappropriate disposal of PFS-containing wastes was reported (Skutlarek et al., 2006) resulting in contamination of drinking water in the same region.

Usually, the origin of PFOA and PFOS in WW is from cleaning and care of surface-treated products (clothing and carpets), by use of cosmetics containing such PFS, from industrial activities and by leaching from plastic products

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(Boulanger et al., 2005). PFOA and PFOS are persistent during WW treatment (Lange, 2000) and they partition between aqueous and solid waste streams (Higgins et al., 2005; Sinclair and Kannan, 2006) as shown for some WWTPs in the USA. The aim of this study was to assess the range of mass flows of PFOA and PFOS from typical WWTPs in Germany.

2. Materials and methods

2.1. Chemicals and equipment

Perfluorooctanoic acid (95%, Lancaster Eastgate, UK), perfluorooctane sulfonate potassium salt (98%, Fluka, Buchs, Germany), acetic acid (100%, Merck, Darmstadt, Germany), aqueous ammonium hydroxide solution (25%, Merck, Darmstadt, Germany), ammonium acetate (99%, Fluka, Buchs, Germany), and methanol (picograde, Promochem, Wesel, Germany) were used as obtained. All equipment was pre-cleaned as described previously (Weremiuk et al., 2006); Teflon equipment was avoided.

2.2. Sampling sites

Grab samples were collected from the different stages of the treatment process of the WWTPs: Bayreuth, (A, river Roter Main), Kulmbach (B, river Weißer Main), Ramsenthal (C, river Trebgast), and Himmelkron (D, river Weißer Main), Northern Bavaria, Germany. These WWTPs have average daily flows of 40000, 20000, 2200 and 2300 $m^3 d^{-1}$. Plant A serves 72000 inhabitants including breweries, food, plastics and tobacco industries, B 45000 inhabitants with breweries, food and cosmetics industries; in both cases, approximately two thirds of WW come from commercial and industrial sources. Plant C receives domestic WW from 14000 inhabitants and, to a small extent, from industrial sources (tire recycling, iron works); plant D receives exclusively domestic waste water from 11000 inhabitants.

In all four plants, WW is treated similarly, starting with a mechanical step in which large objects (paper, bottles, and branches) are removed by a grate. Passing an aerated grit chamber, sand and gravel are removed. Next, the water enters the aerated primary treatment tank, followed by a slurry tank to allow sedimentation of suspended solids as primary sludge (PS); about half of the latter is pumped to digestion towers. In the following biological stage, phosphate elimination, nitrification and denitrification takes place and aero–anaerobic microorganisms form aggregates. These settle in the final clarification basin; the clear overflow is discharged into the river. The microorganism-rich underflow from the clarification tanks is returned to the active-sludge treatment tank as recirculated activated sludge (RAS); a tenth (waste-activated sludge, WAS) is transferred to a sludge holding tank, mixed with primary sludge, fermented for 4 weeks, dewatered, the water is returned to the active-sludge treatment tank, and the sewage sludge (SS) is incinerated.

Surface water samples were collected from the rivers receiving the WWTP-effluents. The average river flows are 270000 (Roter Main), 90000 (Weißer Main), and 50000 (Trebgast) $m^3 d^{-1}$.

2.3. Sample collection

Samples were collected on 06 April and 06 July 2005 from plant A and the Roter Main (Table 1), and on 13 July (plant B), 20 July (plant C), 27 July 2005 (plant D) from the WWTPs and the rivers. Average temperatures during these days were between 12 and 20 °C. There was no rainfall 3 days before or during sampling. Effluent samples were collected twice, i.e. on the same day (effluent 1) as the inlet water and 48 h later (effluent 2), the duration of the treatment process. At plant A, deactivated and dewatered sewage sludge samples were collected. A third sampling was performed on 15–17 March 2006 from plant A and the river (Table 1); ambient temperatures were between −5.0 and −2.0 °C, without precipitation during sampling or the 3 days prior to it.

WW samples were stored in 2.0 l polypropylene (PP) bottles at 4.0 °C in the dark. They were allowed to reach room temperature, particulate matter was removed by centrifugation (High-Performance Centrifuge, Avanti J-25, Beckman, USA) at 12000 rpm for 10 min in 250 ml screw-cap PP-bottles. Removed particulate matter was freeze dried in pre-cleaned (hexane and methanol) aluminium boxes (189 × 86 mm, 540 ml), ground with a pestle, transferred to 50 ml PP-tubes and stored at room temperature until analysis.

Sewage sludge was collected in PP-bags, freeze-dried in pre-cleaned aluminium boxes, ground with mortar and pestle, transferred to PP-bottles and stored at room temperature until analysis.

2.4. Sample preparation

Waste and river water samples were extracted as described before (Weremiuk et al., 2006). First, they were filtered using folded paper filters ($597^1/_2$, Schleicher & Schuell, Dassel, Germany). Aliquots (250 ml) were passed through C18 cartridges (200 mg, 6.0 ml, Oasis HLB Waters Corp., Milford, USA) preconditioned with methanol and deionised water. The waste-water-loaded cartridges were washed with deionised water/methanol (60:40, vol%), dried under vacuum (0.4 bar), and the analytes were eluted with 4.0 ml methanol at a flow rate of one drop s^{-1} and collected in PP-tubes. The extracts were dried under a gentle nitrogen stream, the residues were dissolved in 500 µl each of a mixture of aqueous ammonium acetate, 10 mM/acetonitrile (50:50, vol%), the solutions were filtered (membrane filters, 0.45 µm, Roth, Karlsruhe, Germany) and transferred to PP snap ring vials (0.75 ml, Supelco, Bellefonte,