Perfluorinated Surfactants in Surface and Drinking Waters

Dirk Skutlarek, Martin Exner and Harald Färber*

University of Bonn, Institute for Hygiene and Public Health (IHÖG), Department of Water Chemistry, Sigmund-Freud-Strasse 25, 53105 Bonn, Germany

* Corresponding author (harald.faerber@ukb.uni-bonn.de)

Abstract

Goal, Scope and Background. In this paper recent results are provided of an investigation on the discovery of 12 perfluorinated surfactants (PS) in different surface and drinking waters (Skutlarek et al. 2006 a, Skutlarek et al. 2006 b). In the last years, many studies have reported ubiquitous distribution of this group of perfluorinated chemicals, especially perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in the environment, particularly in wildlife animal and human samples (Giesy and Kannan 2001, Houde et al. 2006, Prevedouros et al. 2006). Perfluorinated surfactants (e.g. PFOS and PFOA) have shown different potentials for reproductive interference and carcinogenicity in animal experiments as well as partly long half-lives in humans (Guruge et al. 2006, FSA UK 2006a, FSA UK 2006b, 3M 2005, OECD 2002, Yao and Zhong 2005). They possess compound-dependent extreme recalcitrance against microbiological and chemical degradation and, in addition, they show variable potentials for bioaccumulation in animals and humans (Houde et al. 2006).

Methods. Surface and drinking water samples were collected from different sampling sites:

- Surface waters: samples taken from the rivers Rhine, Ruhr, Moehne and some of their tributaries. Further samples were taken from the Rhine-Herne-Canal and the Wesel-Datteln-Canal.
- Drinking waters: samples taken in public buildings of the Rhine-Ruhr area.

After sample clean-up and concentration by solid-phase extraction, the perfluorinated surfactants were determined using HPLC-MS/MS.

Results. All measured concentrations (sum of seven mainly detected components) in the Rhine river and its main tributaries (mouths) were determined below 100 ng/L. The Ruhr river (tributary of the Rhine) showed the highest concentration (94 ng/L), but with a completely different pattern of components (PFOA as major component), as compared with the other tributaries and the Rhine river. Further investigations along the Ruhr river showed remarkably high concentrations of PS in the upper reaches of the Ruhr river and the Moehne river (tributary of the Ruhr) (Ruhr: up to 446 ng/L, Moehne: up to 4385 ng/L). The maximum concentration of all drinking water samples taken in the Rhine-Ruhr area was determined at 598 ng/L with the major component PFOA (519 ng/L).

Discussion. The surface water contaminations most likely stem from contaminated inorganic and organic waste materials (so-called ‘Abfallgemisch’). This waste material was legally applied to several agricultural areas on the upper reaches of the Moehne.

Conclusions. The concentrations found in drinking waters decreased with the concentrations of the corresponding raw water samples along the flow direction of the Ruhr river (from east to west) and were not significantly different from surface water concentrations. This indicates that perfluorinated surfactants are at present not successfully removed by water treatment steps.

Recommendations and Perspectives. Because of their different problematic properties (persistence, mobility, toxicity, bioaccumulation), the concentrations of specific perfluorinated surfactants and their precursors in drinking waters and food have to be minimised. Therefore, it is of utmost importance to take the initiative to establish suitable legal regulations (limitations/ban) concerning the production and use of these surfactants and their precursors. Furthermore, it is indispensable to protect water resources from these compounds. A discussion on appropriate limit values in drinking water and foodstuffs is urgently needed. Concerning the assumed soil contamination, the corresponding regulation (Bioabfall-Verordnung 1998 – Regulation on Organic Waste 1998) should be extended to allow the control of relevant organic pollutants.

Keywords: Drinking water; HPLC-MS/MS; organic waste; perfluorinated chemicals; perfluorinated surfactants; PFOA; PFOS; soil; surface water

Introduction

Perfluorinated surfactants (PS), especially perfluorinated carboxylates and sulfonates, represent special chemicals with specific technological properties (Fricke and Lahl 2005): They show high thermal and chemical stability, possess a high polarity and are not bio-degradable. They are used for coatings of textiles, papers and carpets to achieve oil, stain and water repelling properties. Furthermore, they are employed as performance chemicals in fire-fighting foams and ingredients in consumer products such as floor polishes and shampoos (Begley et al. 2005, Moody et al. 2003, Yamashita...
Major compounds like perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), but also components with varying chain lengths from C2–C12, were found in different environmental samples, even in polar regions (Berger et al. 2004, Kannan et al. 2005, Taniyasu et al. 2003, Taniyasu et al. 2004). The described concentrations of perfluorinated surfactants may not be acutely toxic, but these compounds can be enriched in humans (blood, liver), which raises the concern of long-term metabolic effects of these celluly recognised xenobiotics (Flaherty et al. 2005, Harada et al. 2004, Inoue et al. 2004, Kudo and Kawashima 2003). Because of the multiple toxicities of PS (coupled with bioaccumulation and biomagnification in the food web), different risk assessments on PFOS and PFOA have been undertaken in the last years (OECD 2002, US EPA 2005, Swedish Chemical Inspectorate 2006, FSA UK 2006a, FSA UK 2006b). In 2005, an international symposium on fluorinated alkyl organics in Toronto, Canada summarised the current research results about PS (FLUOROS 2005). Recent research studies (Jernbro et al. 2006) indicate that PFOS increases the effect of genotoxic substances like cyclophosphamide in the micronucleus test, which adds a new dimension of concern to the toxicology of perfluorinated surfactants and other perfluorinated compounds.

It is assumed that the main sources of human intake concerning perfluorinated surfactants, especially PFOS and PFOA, are foods and beverages, which are either primarily contaminated or secondarily contaminated by food packaging materials (Begley et al. 2005); however, drinking water can also contribute to the daily uptake. In the last years, several results on detected contaminations of ground, surface and drinking waters have been published. After an incident, the Tennessee River showed concentrations of PFOA up to 598 ng/L (Hansen et al. 2002). In the Osaka Bay area, PFOA and PFOS were detected in surface waters with maximum concentrations of 67,000 ng/L and 526 ng/L, respectively (Saito et al. 2004). The occurrence of PFOA and PFOS in several German surface waters was described in 2004 (Lange et al. 2004).

In our study, the concentrations of 12 different perfluorinated surfactants in German rivers (Rhine river and its main tributaries, as well as Moehne river), canals and drinking waters of the Ruhr catchment area are presented. Furthermore, the main contamination source was identified as an agricultural area on the upper reaches of the Moehne river, which is an important tributary of the Ruhr river.

At present, 23 water works use raw water of the Ruhr river for the supply of about 5 million people with drinking water.

1.1 Chemicals and standards

Standards of perfluorobutanoic acid (PFBuA, chemical purity 97.2%), perfluoropentanoic acid (PFPeA, 97.1%), perfluorohexanoic acid (PFHxA, 98.9%), perfluorohexanoic acid (PFHxA, 98.8%), perfluorooctanoic acid (PFOA, 98.9%), perfluorododecanoic acid (PFDoDA, 97.2%), perfluorobutane sulfonate potassium salt (PFBS, 98.0%), perfluorohexane sulfonate potassium salt (PFHxS, 99.9%) and perfluorooctane sulfonate potassium salt (PFOS, 99.9%) were purchased from Sigma-Aldrich (Taufkirchen, Germany). 1,2,3,4,13C5-labelled PFOA and 1,2,3,4,13C5-labelled PFOS were obtained as internal standards from Campro scientific (Berlin, Germany). All solvents used were ultra-residual analysed or LC-MS grade (Sigma-Aldrich), ammonium acetate was LC-MS grade (Sigma-Aldrich).

1.2 Water sampling

Surface and drinking water samples were collected from rivers, canals and public buildings in several campaigns from March (Rhine) to May (Ruhr area and Moehne) 2006. Every 250 mL-sample was collected in a glass bottle with glass stopper. In order to minimise sample contamination, sampling bottles were prepared by rinsing with deionised water and acetone additionally after dishwasher cleaning. Samples were stored at ambient temperature.

1.3 Solid-phase extraction

100 mL of the sample (pH adjusted to 7.0–8.0) were spiked with the internal standards (13C1-PFOA and 13C2-PFOS). A Strata-x column with 200 mg solid-phase material (Phenomenex, Aschaffenburg, Germany) was consecutively conditioned with 1x2 mL (acetone/acetonitrile/formic acid, 50/50/1, v/v/v) and 3x2 mL water (pH 8.0). The sample was passed through the column at a flow rate of 2.5 mL/min. The cartridges were then dried for 30 min with nitrogen and eluted four times with 2 mL (acetone/acetonitrile/formic acid, 50/50/1, v/v/v). All extracts were reduced to dryness in a gentle nitrogen stream and then reconstituted with 0.5 mL LC-Solvent A (see LC-MS conditions).

1.4 LC-MS conditions

The analyses were carried out using an Agilent 1100 HPLC-System (Agilent Technologies, Waldbronn, Germany) interfaced to an API 2000 triple-quadrupole mass spectrometer (Applied Biosystems, Darmstadt, Germany). The mass spectrometer was operated in turbo ion spray negative ion mode using multiple reaction monitoring (MRM).

The chromatographic column was a NUCLEODUR SPHINX-RP 2.0 x 150 mm, 3 μm particle size (Macherey-Nagel, Düren, Germany). The extracted compounds (injection volume: 50 μL) were separated by liquid chromatography at a flow rate of 0.3 mL/min (column temperature: