

OCCURRENCE OF PERFLUORINATED CHEMICALS (PFCs) IN THE SEWAGE SYSTEM OF A LARGE GERMAN CITY

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Abstract

Perfluorinated chemicals (PFCs), especially perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are ubiquitous distributed in the aquatic environment. Due to the harmful persistent organic pollutant properties and as a consequence of a present water scandal in Germany sewage water and sludge samples have to be monitored for PFCs all over the country. Target values for the sum of PFOS and PFOA in water samples (300 ng/l) and sludge samples (100 µg/kg dry mass) have been established by competent authorities. Therefore, Eurofins / GfA has established an approved analytical method for the determination of individual PFC compounds in environmental samples using HPLC-MS/MS. This study focussed on the PFC monitoring of a series of influent and sludge samples from the sewage system of large German city. The results indicate that PFCs are detectable in most aquatic samples. Furthermore, PFC concentrations above the target levels can be found in sewage samples from industrialized areas, which could be traced back to local contamination sources.

Introduction

Perfluorinated chemicals (PFCs) have been used widely as surfactants, lubricants, paper and textile coatings, polishes, food packaging and fire-retarding foams over the past fifty years. PFCs occur in the environment primarily as the stable perfluorooctane sulfonate (PFOS) and long chained perfluorocarboxylic acids (PFCAs) with seven to fourteen carbon atoms. Emission of PFCs occur during production or use and disposal of the above-mentioned consumer products. Several studies have shown that these compounds are globally distributed and environmentally persistent. They have been found in wild animal samples around the world.^{1,2} Due to the harmful persistent organic pollutant properties and risks related to the continuing production and use, global action is necessary to eliminate the pollution caused by PFOS.³ With Directive 2006/122/EC the marketing and use of PFOS as well as of PFOS containing preparations and articles is now prohibited.⁴

European water companies have already recognized perfluorinated surfactants as potential contaminants in drinking water sources, as highlighted in a review published by the Dutch Association of River Water Companies in 2006.⁵ The separate analysis of water and particulate phase from waste water treatment plants (WWTPs) indicated that PFCs are mainly found in the water phase. For some compounds, particularly PFOS and PFOA, the concentration in the effluent water can be higher than in the influent water.⁶ In the summer of 2006 scientist in Germany reported high concentrations of perfluorinated surfactants in the River Moehne. A lot of fears were evoked and local authorities were eager to trace back the source of contamination. The contamination turned out to originate from local fields treated with a fertilizer containing mislabeled waste. In surface waters, PFC levels of up to 439 ng/l were determined and corresponding drinking waters showed PFC concentrations of up to 60 ng/l, with perfluorooctanoic acid (PFOA) the most abundant.⁷

As a consequence of this water scandal, responsible authorities in the German federal state of North Rhine-Westphalia have established target values for the sum of PFOS and PFOA (Σ -PFOS/PFOA) of 300 ng/l for municipal waste waters and 100 µg/kg dry mass for agriculturally used sewage sludges. Sewage matrices have to be monitored since December 2006. In this survey, PFCs were monitored in influent and sludge samples from the municipal sewage system of a large German city with much more than half a million inhabitants. The focus was on a case study including a series of potential waste water polluters, which contribute to a significant PFOS contamination of sewage sludge.

Material and Methods

Sample preparation and extraction

In total 84 influent water samples and 9 sewage sludge samples from several WWTPs were collected by the local authorities. After spiking with a $^{13}\text{C}_4$ -labelled PFOS and PFOA standard, all water samples were extracted by C18 solid phase cartridges (SPE) and elution by 6 ml methanol. The extract was evaporated to dryness and reconstituted in the HPLC mobile phase.

For homogenisation the sludge samples were freeze-dried and after addition of the above-mentioned internal standards twofold extracted with methanol in an ultrasonic bath. The combined extracts were concentrated and cleaned-up by means of a carbon cartridge (Supelclean-Envicarb, Supelco).

Instrumental analysis

Instrumental determination of individual PFCs was accomplished by an Agilent HP1100 liquid chromatograph (Agilent Technologies) interfaced with a SCIEX API 4000 hybrid mass spectrometer (Applied Biosystems) operated in electrospray negative ion mode. In Table 1 the PFC compounds analysed and the corresponding fragment ions are listed. 10 μl of the sample was injected onto a Luna C8 (5 μm ; 2.0 x 100 mm) column (Phenomenex). The column temperature was set at 50°C. Eluents used for separation were a 2 mM ammonium acetate solution in water/methanol (90/10, v/v) and 2 mM ammonium acetate solution in methanol (100, v); the adapted gradient profile is programmed stepwise. The LODs for PFOS and PFOA were in the range of 1.5 to 3.5 ng/l for water samples and 0.5 to 1.5 $\mu\text{g}/\text{kg}$ dry mass for sludge samples. The recovery rates of the internal standards varied between 80 and 110 % for aqueous matrices and 70 and 120 % for solid matrices. The standard deviation values calculated for this method were 4.7 % for PFOS and 12.1 % for PFOA.

Table 1: PFC congeners measured in the study and the corresponding fragment ions (MS-MS parameters)

PFC compound	Structure	Parent Ion (m/z)	Quantifier (m/z)	Qualifier (m/z)
Perfluorhexanoic acid (PFHxA)	$\text{C}_5\text{F}_{11}\text{COO}^-$	313	269	119
Perfluorheptanoic acid (PFHpA)	$\text{C}_6\text{F}_{13}\text{COO}^-$	363	319	169
Perfluoroctanoic acid (PFOA)	$\text{C}_7\text{F}_{15}\text{COO}^-$	413	169	169
Perfluorononanoic acid (PFNA)	$\text{C}_8\text{F}_{17}\text{COO}^-$	463	419	219
Perfluordecanoic acid (PFDA)	$\text{C}_9\text{F}_{19}\text{COO}^-$	513	469	219
Perfluorbutane sulfonate (PFBS)	$\text{C}_4\text{F}_9\text{SO}_3^-$	299	80	99
Perfluorhexane sulfonate (PFHxS)	$\text{C}_6\text{F}_{13}\text{SO}_3^-$	399	80	99
Perfluoroctane sulfonate (PFOS)	$\text{C}_8\text{F}_{17}\text{SO}_3^-$	499	80	99
Perfluoroctane sulfonamide (PFOSA)	$\text{C}_8\text{F}_{17}\text{SO}_2\text{NH}_2$	498	78	78

Results and Discussion

For the considered sewage sludge 140 $\mu\text{g}/\text{kg}$ dry matter for Σ -PFOS/PFOA has been quantified and the pattern illustrated in Figure 1 shows that PFOS is the dominant compound (96 %). Additionally, only a small amount of PFOA (6.0 $\mu\text{g}/\text{kg}$ dry matter) and no further PFC compound could be determined in the sludge. Thus, the cited target value for sewage sludge (100 $\mu\text{g}/\text{kg}$ dry weight) was exceeded and the source of contamination has to be traced back. Consequently, also 22 influent samples have been monitored and the resulting pattern of the mean values is illustrated in Figure 1. Also in the water phase PFOS is the predominant PFC compound (76 %), but additionally, several influent samples showed elevated levels of PFHxS and PFOA. PFHxA, PFHpA and PFBS could be detected in small concentrations only in a few waste water samples of this series.

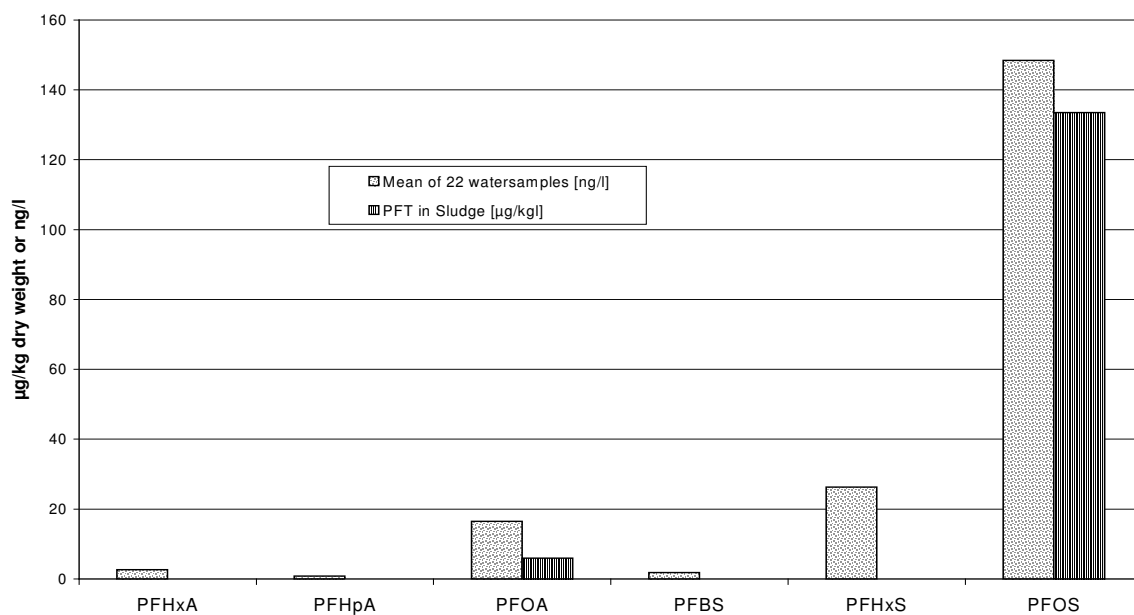


Figure 1: Concentration profile of selected PFCs in the sewage sludge and in the influent water (mean values)

The individual results of the 22 influent water samples are illustrated in Figure 2. The contamination levels vary in a wide range with a maximum concentration of 959 ng/l for the sum of PFOS and PFOA. In total, four influent water samples exceed the above-mentioned target value of 300 ng/l significantly and in all these cases the PFOS concentration is above one order of magnitude higher than the PFOA concentration.

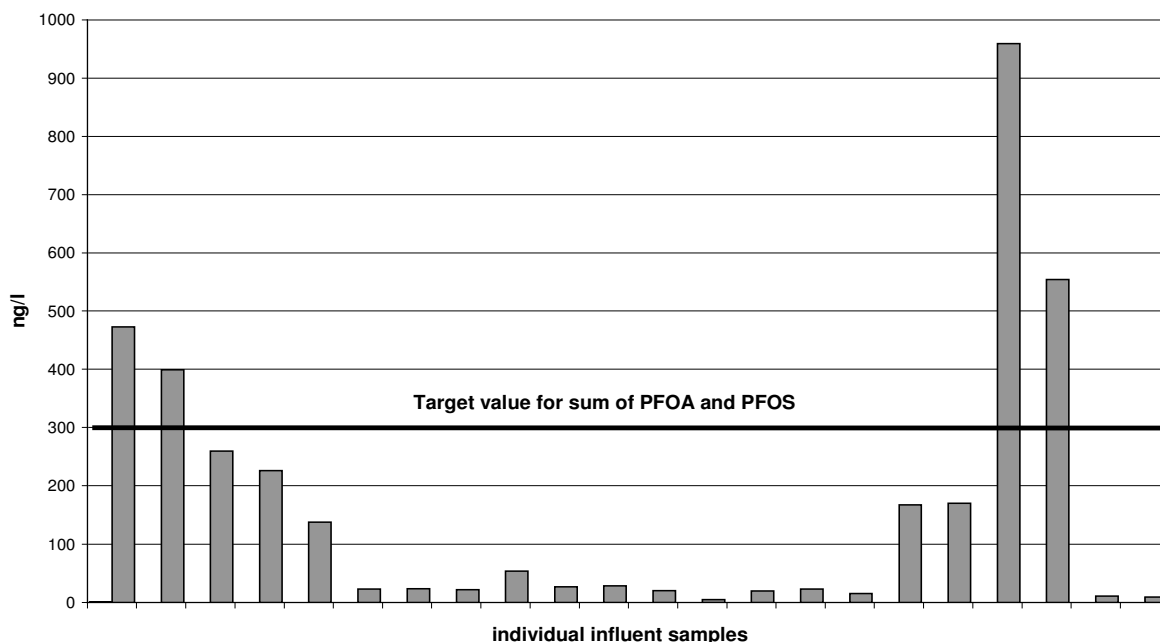


Figure 2: Concentration of Σ -PFOS/PFOA in 22 influent water samples

The results of the present study indicate that there is a diffuse background contamination with PFCs in the freshwater environment. Additionally in industrialized areas predominant primary sources (hot spots) can result in local contamination with perfluorinated surfactants. Nevertheless, the discussion on PFCs should not be limited to drinking water only. Various further entrance paths into the human body (e. g. food, household dust and clothing) should be included in future monitoring programmes.

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