

PERFORCE: PERFLUORINATED ORGANIC COMPOUNDS IN THE EUROPEAN ENVIRONMENT

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Abstract

The PERFORCE project was initiated in July 2004 after a successful application to the NEST-INSIGHT instrument of the EU-FP6 programme. Because of very low levels of contamination and limited knowledge on the possible sources and pathways of perfluorinated organic compounds (PFCs), as well as on their key compound properties, at the stage of the project's initiation it was difficult to estimate the real risk of fluorinated compounds to man and the environment. The project included a large European sampling campaign of the PFCs in environmental media, including surface waters, sediments, sewage treatment plants, air, and biota. Several of the results have been published or submitted in separate journal articles already. This contribution focuses on the most important results found in surface waters, sediments and STPs. It is concluded that PFCs are ubiquitously present in the European environment. Sewage treatment plants probably serve as sources of PFCs both for the aquatic ecosystems (through effluent discharges) and the terrestrial environment (through application of sewage sludge in agriculture).

Introduction

The major objective of the project was to introduce and evaluate new chemical and biological techniques and tools in order to assess the occurrence and distribution of PFCs in the European ecosystems. The project covered a full array of investigations required to correctly assess and model the fate and impact of a new series of anthropogenic compounds. The project work packages included physico-chemical parameters (properties), evaluation of sources and routes in Europe, new chemical and biological measurement techniques, quality assurance, interlaboratory studies, and a European monitoring campaign. The objectives correspond to providing tools for developing a rapid exposure assessment of perfluoro organics. The assessment will enable a better understanding of the problem and can contribute to understand potential dangers. The exposure assessment will, together with ongoing hazard assessment and toxicity testing elsewhere, enable a proper environmental risk assessment of PFCs to be made in the nearby future.

Materials and Methods

The main objective of the chemical analytical work package was to develop and validate trace analytical methods for quantification of PFCs in biota, sediment, water and air. Main target compounds were perfluorinated sulfonates C4 (PFBS) and C8 (PFOS), perfluorocarboxylates C4 (PFBA), C8 (PFOA), C9 (PFNA) and C11 (PFUnA), perfluorooctane sulfonamide (PFOSA), 6:2 fluorotelomer sulfonate (6:2 FTS) as well as 6:2 and 8:2 fluorotelomer alcohols (FTOH). Analytical protocols were optimised and validated and are available at the perforce website www.science.uva.nl/perforce. These include methods for sampling and analysis of water, biological tissues, blood, sediment¹. Air methods have been published elsewhere^{2,3}. The quality assurance program included worldwide interlaboratory exercises on five different matrices, the results of which were presented elsewhere⁴.

In the sampling campaign surface water and sediments were collected from all over Europe (see Fig. 1). To evaluate sewage treatment plants as possible sources of PFCs in Europe, five STPs were selected from 4 countries giving geographical coverage of Europe (Spain, Sweden, The Netherlands, United Kingdom see Fig.1). Four of the STPs (one in each country) served large urban centres (Cadiz, Stockholm, Amsterdam, Lancaster). A second STP in Sweden (Alingsås) served only households and was used as a control for the influence of commercial and industrial activity on PFCs in STPs. An industrial STP was also sampled.

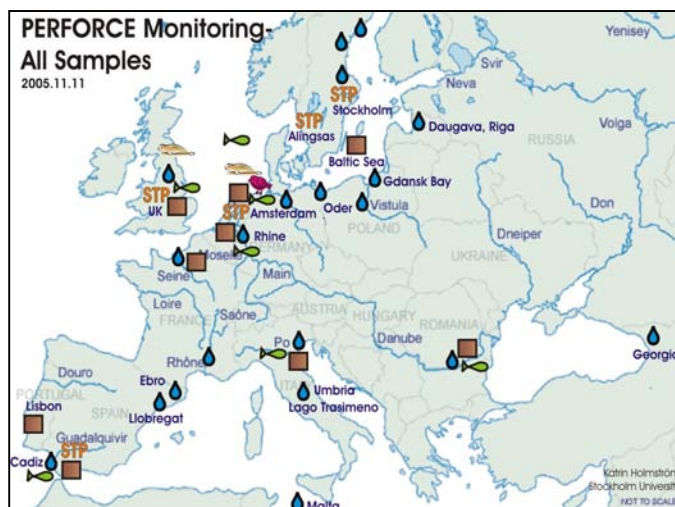


Figure 1. Overview of sampling sites in the monitoring program. Symbols indicate type of sample collected. Blue drops, water samples; brown squares, sediments.

Results and Discussion

Key issues in the analytical chemistry of PFCs identified are (i) blank contamination due to the presence of analytes of interest in e.g. instrument tubings and laboratory materials made from fluoropolymers (e.g., PTFE, PVDF); (ii) purity of standards, which need careful characterisation before use; and (iii) matrix effects, such as signal suppression. Matrix effects can be reduced substantially by applying carbon⁵.

Apart from analytical protocols, specific bio-assays were developed that were able to quantify individual compounds (PFOA and PFOS) but were less promising when applied to extracts from environmental matrices due to cytotoxic side effects¹. Perfluoralkyl compounds show distinct toxicological modes of action *in vitro* that include estrogen-like, mitogen-like properties, membrane and DNA interference, and oxidative stress.

Table 1: Concentrations of PFCAs in European river water (ng/L)

River	PFHxA	PFHpA	PFOA	PFNA
Dalälven	<0.94	0.36	<0.97	<0.14
Vindelälven	<0.58	0.20	<0.65	0.22
Kalix Älv	<0.58	0.26	<0.85	<0.14
Elbe	15.3	2.7	7.6	0.27
Oder	2.2	0.73	3.8	0.73
Vistula	2.3	0.48	3.0	0.36
Po	19	6.6	200	1.5
Danube	3.0	0.95	16.4	0.27
Daugava	<0.90	0.53	<1.37	0.22
Seine	14.5	3.9	10.6	1.43
Loire	3.2	0.87	3.3	0.42
Thames	32	4.1	23	0.79
Rhine	18.2	1.80	11.6	0.55
Guadalquivir	6.2	1.58	4.6	1.02

The perfluorosulfonates could not be quantified in the water samples due to poor and highly variable recoveries of the labeled PFOS internal standard. Despite extensive experience in analysing water with this method in 2 laboratories, this study showed that the method is not sufficiently robust to be applied to a wide range of different waters. In a separate sampling campaign in rivers in The Netherlands concentrations of PFOS were found to range between <10 and 56 ng/L¹. The PFCA concentrations in European river water are summarised in Table 1, those in sediments are presented in Table 2.

The annual loading to the European environment of PFHxA, PFHpA, and PFOA from rivers is estimated to be of the order of 10, 2, and 20 tonnes¹. The Po, Danube and Rhine watersheds are particularly important source regions, whereby the Elbe also makes a significant contribution for PFHxA. In European air, PFOA was often the predominant PFC found in the particulate phase, while 6:2 FTOH and 8:2 FTOH were the prevailing analytes found in the gas phase³. Many other compounds were also present in air³.

Spatial differences were observed particularly in biota. PFOS and PFOSA concentrations were higher in North Sea cod liver than in cod liver from the Kattegat and the Baltic. In marine mammals concentrations of PFOS are higher in species feeding close to the shore or in estuaries than in off shore feeders⁶. A relationship appears to exist between concentrations of PFOS and trophic levels in marine mammals. In these mammals perfluorinated carboxylic acids are relatively low in all species and tissues analysed. PFOS, PFDA and PFOA bioaccumulate in a simple estuarine food chain, PFOA accumulates significantly less.

Table 2: Concentrations of PFCs in sediments collected from Scheldt, Rhine, Po, Danube and Tagus rivers ng/g dwt.

Location	Sulfonates					Carboxylates						
	C4	C6	C8	6:2 FTS	PFOSA	C7	C8	C9	C10	C11	C12	C14
Western Scheldt, ZL08	0.35	<0.10	<0.54	1.07	0.01	<0.22	<1.34	<2.54	0.01	0.08	0.01	0.03
Western Scheldt, S01	<0.39	<0.11	<0.62	0.39	0.25	<0.25	<1.55	<2.94	<0.01	<0.06	<0.02	<0.10
Western Scheldt, S4	0.06	<0.10	<0.57	<0.86	<0.01	0.86	14.5	4.15	0.21	0.08	0.01	0.02
Western Scheldt, S07	<0.33	<0.09	<0.53	0.18	0.00	<0.21	<1.32	<2.50	0.01	<0.05	0.02	<0.09
Western Scheldt, S20	<0.34	<0.10	<0.54	<0.82	<0.04	0.48	16.8	18.28	0.85	0.69	0.08	0.03
Western Scheldt, <90 um, si no. 1144 (BROC)	0.26	0.24	0.59	0.71	0.32	0.10	0.60	<4.17	<0.02	<0.08	0.01	0.01
Western Scheldt 2005	<0.55	<0.16	1.46	2.85	0.05	<0.36	<2.19	<4.14	0.29	0.20	0.06	0.14
Ijmuiden, (Rhine) Netherlands, Nieuwe Waterweg (Rhine)	0.73	0.09	14.0	1.40	0.12	<0.36	<2.21	<4.18	0.29	0.22	0.48	0.09
Danube 1	<0.31	<0.09	<0.50	<0.75	0.02	<0.20	<1.25	<2.36	0.03	<0.05	0.01	0.01
Danube 2	0.09	<0.12	<0.67	0.92	<0.01	<0.27	0.20	<3.19	<0.01	0.10	0.01	<0.11
Italy, Po	<0.30	<0.09	<0.48	0.60	<0.01	<0.20	<1.21	<2.28	<0.01	<0.05	0.01	<0.08
Portugal, Lisbon, Tagus Bay #16	0.15	<0.13	<0.71	2.05	0.05	<0.29	<1.77	<3.34	0.02	0.68	0.02	0.02
Portugal, Lisbon, Tagus Bay #33	<0.57	<0.16	<0.91	<1.37	<0.01	<0.37	<2.28	<4.31	<0.02	<0.09	0.01	0.01
	<0.54	<0.15	<0.86	<1.30	<0.01	<0.35	<2.16	<4.08	<0.02	<0.08	<0.03	0.04

All PFCs analysed were observed in influents, effluents and sewage sludge of STPs. The reference STP in general exhibited the lowest levels of PFCs, but detectable levels of several PFCs were found in both the influent and the effluent of this STP. PFOS (range: 10-200 ng/L), PFOA (20-65 ng/L), PFNA (8-45 ng/L) and FTS (15-300 ng/L) were most abundant in the dissolved phase of the STP influents. The particulate phase of the influents contributed significantly to the overall influent concentration in the case of the carboxylic acids, but less for the sulfonates and for PFOSA. In general, within a specific STP the order of abundance of the sulfonates in (the dissolved phase of) influents was PFOS>6:2FTOS>PFBS>PFHxS. For the carboxylic acids this order was PFOA>PFNA>PFHpA>PFDA> PFUA>PFDoA. Samples from the

industrial STP contained the highest levels of C7-C12 acids. The measurements in the STP effluents showed relatively high concentrations of sulfonates (C4: 2-50 ng/L, C6: 2-50 ng/L, PFOS: 15-200 ng/L) and PFHpA (4-18 ng/L), PFOA (20-110) and PFNA (2-19 ng/L). The highest concentrations of PFCAs (C7-C12), viz. 560 ng/L of PFOA, 380 ng/L of PFNA, and 200 ng/L of PFDA were observed in the effluent of the textile industry-related STP. In general, large differences in removal efficiencies were observed between the STPs. The removal efficiencies for the fully fluorinated sulfonic acids was poor, with mean values ranging between 0 and 11%. For 6:2FTS a somewhat higher removal efficiency was observed (~40%). For the carboxylic acids the removal efficacy of STPs was higher, ranging from 20-80%, showing the following order: C12>C9=C7>C8>C11>C10. For PFOSA large differences in efficiency were observed between STPs, with a mean value of 28%. The general observation is that PFC removal efficacy of STPs is poor to moderate compared to e.g. non-ionic surfactants or estrogenic compounds.

Table 3. Mean removal efficiencies (%) of PFCs in domestic STP plants (n=5)

	C4S	C6S	C8S	PFOSA	6:2FTS	C7A	C8A	C9A	C10A	C11A	C12A	C14A
Mean	10.9	0.6	5.1	27.7	39.1	54.0	48.6	54.7	19.5	42.1	79.8	N.A.
STD	20.1	1.2	9.8	39.5	29.1	33.2	42.3	41.2	24.7	36.6	8.7	N.A.

The results of the sampling campaigns show that PFCs are ubiquitously present in the European environment. Sewage treatment plants probably serve as sources of PFCs both for the aquatic ecosystems (through effluent discharges) and the terrestrial environment (through application of sewage sludge in agriculture). Levels of PFOS in sediments have increased from 1990 to 2005, whereas for PFOSA an initial increase was followed by a possible decreases after 2000.

The PERFORCE study has obviously taken away some of the important knowledge gaps that existed several years ago with regard to the occurrence of the PFCs in the European environment. In particular the exposure levels in Europe are much better known, as a result of the project. Yet, it is obvious that further work is necessary to identify unknown origins, e.g. of PFHxA, to assess the fluxes to the environment from STPs, and to quantify loadings of river water and identify sources. There is also a need to improve our understanding of PFC transfer to as well as removal from the atmosphere, oceanic transport routes, and the mechanisms of bioaccumulation / biomagnification / bioelimination of PFC.

Acknowledgements

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