SINGLE APPLICATION OF FIRE FIGHTING FOAM HAS INCREASED LEVELS OF PERFLUOROOCTANESULFONATE (PFOS) IN RECEIVING WATERS AND FISH

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Introduction

During fire-extinguishing measures in St. Wendel, Germany, in May 2007, 30 tons of fire fighting foam (FFF) were applied, which contained significant levels of perfluorooctanesulfonate (PFOS). Runoffs from FFF-charged areas were flowing into fish ponds and receiving waters. Fish in the first receiving fish pond died due a significant decrease of oxygen levels, whereas no fish lethality was observed in the following waters. Geography of the area is shown in Figure 1.

Several authors describe the effective bioconcentration of PFOS from contaminated waters. Bioconcentration factors (BCF) between 2,400 and 5,400 were reported.[1,2] Furthermore, biomagnification of PFOS was observed in aquatic food webs.[3,4] Therefore, increased levels of PFOS in waters, fish and aquatic ecosystems were suspected.

In order to provide and evaluate data on PFOS levels in the FFF-charged area the Environmental Protection Agency of Saarland, Germany, decided to perform a screening program on perfluorinated compounds (PFC) in affected waters and fish samples.

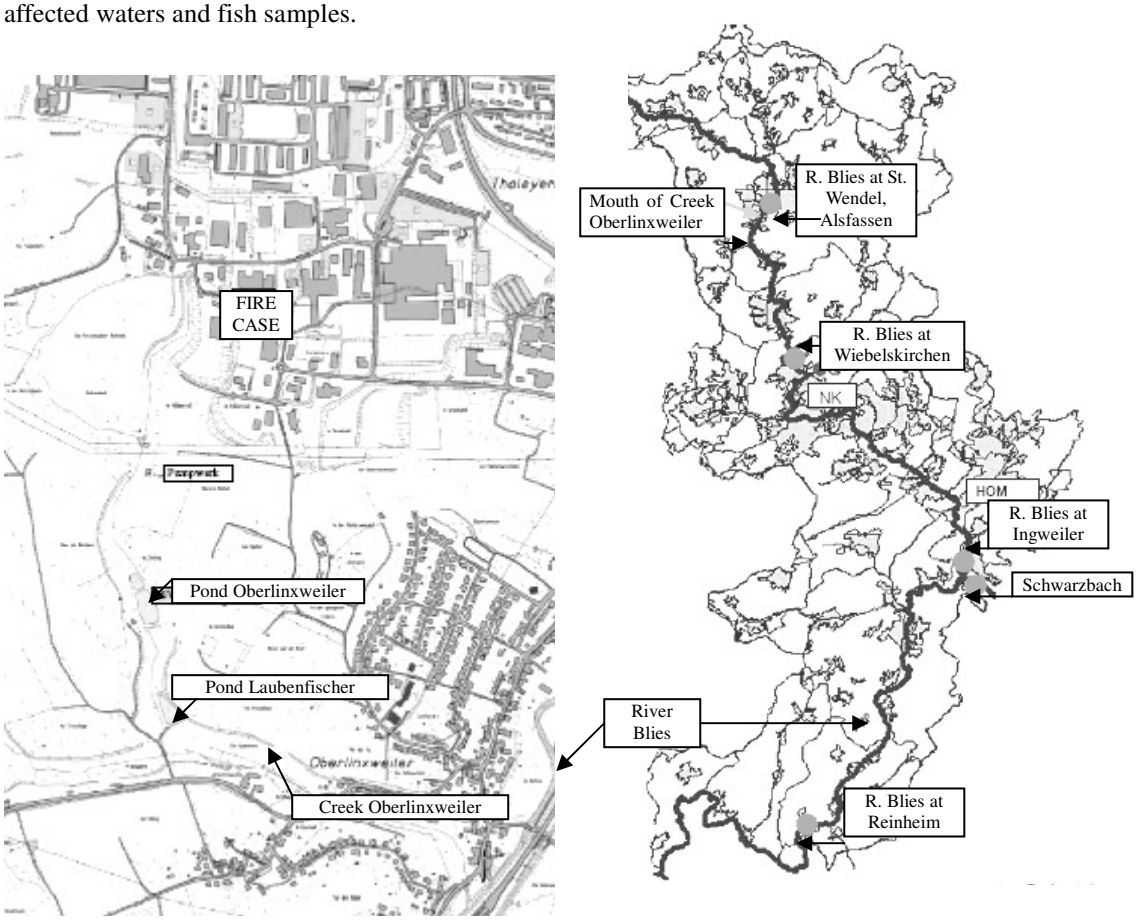

Figure 1. Left: Fish ponds and Creek Oberlinxweiler, the first receiving waters affected by PFOS-containing fire fighting foams. Right: River Blies and sampling sites along the River. (Distance St. Wendel to Reinheim: ~65 km)

Materials and Methods

Water samples were taken from 10 sites on up to 7 dates between December 2006 and September 2007. They were collected in PP bottles and transferred to the laboratory of the DVGW water technology center, Karlsruhe for further analysis.

Water analysis was based on solid-phase extraction of the target compounds onto Bakerbond spe™ SDB 1 extraction cartridges (0.2 g, 6 ml, Mallinckrodt-Baker, Griesheim, Germany). The cartridges were preconditioned with 5 ml of methanol followed by 5 ml of Milli-Q water. A 500 ml aliquot of water sample was spiked with the internal standards MPFHxA, MPFOA, and MPFOS and then loaded onto the cartridge at a flow of 10-20 ml/min. The cartridges were dried with nitrogen. Subsequently, the PFCs were eluted with methanol. The residue was dissolved in 75 µl methanol followed by 75 µl Milli-Q water and transferred into an autosampler glass vial with crimp cap.

Separation of PFCs was performed using an Agilent 1090 high-performance liquid chromatograph (HPLC). 20 µl aliquots of the extracts were injected onto a 250 mm x 2.1 mm (5 µm particle size) MZ-Aqua Perfect C18 column (MZ-Analysentechnik, Mainz Germany). The mobile phase consisted of (A) 5 mM ammonium acetate in water and (B) 5 mM ammonium acetate in methanol. At a flow rate of 200 µl/min and a temperature of 40°C the separation proceeded from initial conditions of 50% B to 90% B at 29 min before returning to 50% B at 30 min. Post run equilibration time was 9 min. For quantitative determination, the HPLC was interfaced to an Applied Biosystems API 2000 tandem mass spectrometer (MS/MS). The MS/MS was operated in electrospray negative ionization mode (ESI). The heater temperature in the ESI interface was held at 250°C. Analyte ions were monitored using multiple reaction monitoring (MRM) mode. MS parameters were optimized for the ion transitions of each analyte.

At least 10 fish per species were caught from each of 7 sites in May, June and August, 2007, by electrofishing. Muscle tissues were collected from the fish. Tissues of the same fish species and sampling site were pooled and shipped to the Fraunhofer-Institute IVV, Freising, for further analysis.

The analytical method based on a pressurized liquid extraction (ASE 200, Dionex) as described elsewhere.[5] Briefly, wet samples of fish muscle were mixed with silica, spiked with $^{13}C_4$-PFOS and $^{13}C_4$-PFOA (Wellington) and filled into ASE cartridges. Extraction was performed with methanol/water (1/1;v/v) at 100°C and 100 bar in three static cycles of 15 minutes each. Extracts were diluted with the 3-fold amount of water and passed through a syringe filter before further clean-up. Weak anion exchange SPE cartridges were preconditioned with 2 ml of methanol and water, respectively, and the diluted extracts as well as the pretreated blood samples were passed through the preconditioned cartridges. The cartridges were then washed with methanol/water (1/1; v/v) and eluted with 1% NH_4OH in methanol. SPE eluates were evaporated under a gentle stream of nitrogen and diluted with water to a final volume of 1 ml.

Identification and quantification of perfluorinated substances was performed on a Surveyor Plus HPLC connected to a Quantum Ultra AM mass spectrometer (both Thermo, Dreieich, Germany). Chromatographic separation was achieved by a Fusion RP phase (20 x 2 mm, 2 µm, Phenomenex, Aschaffenburg, Germany). Gradient HPLC was performed with methanol and 5mM ammonia acetate in water (pH 3.5), increasing methanol from 20 to 100% within 10 minutes. Mass spectrometry was performed by electron spray ionization in the negative ion mode and subsequent single reaction monitoring (MS/MS).

Results and Discussion

As displayed in Table 1, PFOS levels in the investigated water samples ranged from 8 to 610,000 ng/L. Highest values were measured in May 2007 at Oberlinxweiler, where the FFF entered the receiving waters. However, by September 2007 PFOS levels decreased by three orders of magnitude in this highly contaminated area. In comparison, at sampling sites further downstream the initial PFOS levels and their decline are much lower. Interestingly, from July to September 2007 an increase of PFOS by factor 2-3 was observed in the River Blies at the sites Ingweiler, Schwarzbach, and Reinheim. However, these PFOS levels between 8-32 ng/L are in the typical "background" range[6] and may be influenced by other diffuse sources (e.g. varying effluent from waste water treatment plants).[7]

Analysis of fish muscle tissues revealed elevated PFOS levels upstream from Wiebelskirchen ranging from 63.1 to 3,990 ng/g wet weight and indicate a significant bioaccumulation of PFOS (Table 2). Fish caught in the effluent of pond Oberlinxweiler on 19 May 2007 were dead and their PFOS levels between 41.5 and 52.5 ng/g wet weight are lower than expected from above cited BCF. This is probably due to the short time these fish survived the high

discharge of FFF into the pond, which did not allow them to reach a steady state PFOS concentration. In comparison, fish caught in pond Laubenfischer survived the initial flush of FFF and accumulated highest portions of PFOS. They contained 2,180 and 3,990 ng/g wet weight. Fish caught downstream of Wiebelskirchen contained PFOS levels between 13.8 and 54.1 ng/g wet weight. These levels are comparable to previously reported German values in fish muscle tissues.[5]

Table 2 shows differences in PFOS accumulation of fish caught at the same time and place. As indicated by data from Wurzelbach, Wiebelskirchen and Reinheim trout levels exceed regularly concentrations in chub. This trend might be attributed to a varying accumulation potential or varying mobility of different fish species.

Time lines of PFOS levels in water and fish are presented in Figure 2 for three water sampling sites along the River Blies downstream the fish ponds, namely the sites Wiebelskirchen, Ingweiler and Reinheim. They show a significant decline of PFOS concentrations in the water samples from May to September. Fish samples from the same sites sampled in June and August, however, show only slightly differences, ranging from a 13% decline (chub at Wiebelskirchen) to a 92% increase (chub at Ingweiler) (Figure 2).

For an interpretation of these time lines BCF were calculated from the latest measured water and fish muscle concentrations. For chub BCF accounted for 574 L/Kg, 2459 L/kg and 431 L/kg at Wiebelskirchen, Ingweiler and Reinheim respectively. For trout we calculated BCF of 1127 L/kg and 1050 L/kg at Wiebelskirchen and Reinheim, respectively. All BCF are in the same order of magnitude and are well comparable to laboratory data.[1,2]

This indicates, that fish muscle levels measured about 15 km downstream the fire case are mainly determined by the low water levels measured about three month after the fire case and not by the initial high concentrations.

Acknowledgements

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Table 1: PFOS levels in investigated water samples from 10 sites within the FFF-charged area.

PFOS, ng/L	19-May-07	29-May-07	23-Jul-07	17-Sep-07
St.Wendel, Alsfassen	n.d.	n.d.	25	n.d.
River Blies, upstream of Wurzelbach	n.d.	350	46	n.d.
Pond Oberlinxweiler, influent	610,000	12,000	2,100	750
Pond Oberlinxweiler, effluent	430,000	56,000	4,000	1,100
Pond Laubenfischer	n.d.	n.d.	11,000	n.d.
Creek Oberlinxweiler	110,000	n.d.	n.d.	n.d.
River Blies at Wiebelskirchen	n.d.	1,100	110	n.d.
River Blies Ingweiler	n.d.	410	8	22
Creek Schwarzbach	n.d.	9	11	24
River Blies at Reinheim	n.d.	99	11	32

Table 2: PFOS levels in investigated fish samples caught at 7 sites within the FFF-charged area.

PFOS, ng/g	Fish species	19-May-07	05-Jun-07	28-Aug-07
St.Wendel, Alsfassen	Trout	n.d.	n.d.	16.1
River Blies, upstream of Wurzelbach	Trout	n.d.	43.8	38.8
	Chub	n.d.	37.3	29.5
Pond Oberlinxweiler, effluent	Carp	41.5	n.d.	n.d.
	Perch	52.5	n.d.	n.d.
	Rudd	48.7	n.d.	n.d.
Pond Laubenfischer	Roach	n.d.	2,180	3,990
River Blies at Wiebelskirchen	Trout	n.d.	112	124
	Chub	n.d.	72.9	63.1
River Blies Ingweiler	Chub	n.d.	28.1	54.1
River Blies at Reinheim	Chub	n.d.	14	13.8
	Trout	n.d.	n.d.	33.6

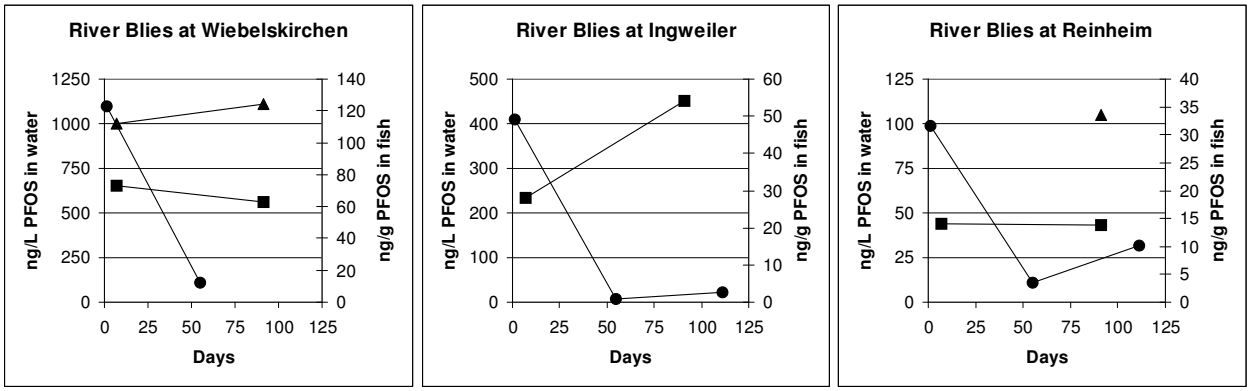

Figure 2: Time lines of PFOS levels in water (ng/L) and fish (ng/g wet weight). Water levels are displayed as circles, chub levels as squares, and trout levels as triangles.