PFOS/PFOA CONTAMINATED MEGASITES IN GERMANY POLLUTING THE DRINKING WATER SUPPLY OF MILLIONS OF PEOPLE

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Abstract
A criminal mismanagement of several thousand tons of sludge and waste materials, contaminated with perfluorinated surfactants (PS; including PFOS/PFOA), caused the contamination of hundreds of sites (agricultural fields, forests and grazing areas) in Germany. Approximately 1000 areas are suspected to be contaminated and are presently being evaluated.

The leachate and runoff of PS from some of these contaminated and contaminate tributary rivers of the Ruhr river (e.g. the main tributary river called Möhne), which services the raw water source for the drinking water supply of ca. 5 million people. This contamination resulted in elevated concentrations in the Ruhr river and associated drinking water supplies.

The population in the area with the highest drinking water contamination (approx. 500 ng/L PFOA) showed five to eight times elevated PFOA concentrations in the blood (around 25 μg/L) after only ca. 3 years exposure, compared to the German background contamination (around 5 μg/L).

Trials to decontaminate the leachate from one high impact area (of the possibly hundreds of contaminated sites) of the Möhne river using drainage and carbon filtration of the leaching rainwater has commenced. After ca. 2 months operation of the remediation a breakthrough of PS in the activated carbon filters was observed and the filters had to be exchanged.

Introduction
It is assumed that the main sources of human intake of perfluorinated surfactants (PS), mainly PFOS and PFOA, are foods and beverages, which are either primarily contaminated or secondarily contaminated by food packaging materials1a, 1b and other PS treated items of daily use1b (e.g. the German Environmental Agency recommended to avoid the purchase of PS treated furniture, textiles and carpets2).

Another contamination source can be drinking water, in particular when impacted by production facilities and PS processing industries: In the past years, PS production and processing industries were revealed having contaminated several ground- and surface water sites3-11. The related contamination of drinking water4-11 lead in some cases to high contamination of the surrounding population6,7,9.

In 2006 Skutlarek et al.1 reported on perfluorinated surfactant contamination of the German rivers Ruhr (up to 446 ng/l) and tributary rivers Möhne (up to 4385 ng/l) and Elpe (4268 ng/l) and their tributary greeks (up to 43000 ng/l). PFOA was/is the main contaminant accounting in most cases for ca 80% of the PS. The authors demonstrated that the drinking water in this area was contaminated with PS up to 598 ng/l (PFOA 519 ng/l) in the most affected areas8. Some agricultural fields on the upper reaches of the Möhne river were identified as the main emission source. However the dimension of the contamination could not been assessed at that time and the origin of the contamination of the agricultural fields could not be revealed8.

The present paper reports on follow-up findings of this PS contaminated site case with preliminary information on the chronology of the contamination and some aspects on it’s origin, a summary on the activities of responsible authorities, the preliminary German regulations established for PS contaminated drinking water and information on initial remediation attempts.

Materials and methods
The history of the case including the management and authorisation of the contaminated sludge was investigated and documented by the BUND11 (Bund für Umwelt und Naturschutz Deutschland – Union for Environment and Nature protection, a German NGO belonging to the international network of Friends of the Earth (FoE)).

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) and separated on NUCLEODUR SPHINX-RP column (2.0 x 150 mm, 3 μm particle size; Macherey-Nagel, Dueren, Germany). Analytical details on the measurement methods are reported elsewhere.

Results and Discussion

Chronology of events and origin of the contaminating sludge
In spring 2002 several claims from the public regarding smelly sludge distributed on agricultural fields from the company GW Umwelt (GW Environment!!) resulted in requests by the NGO BUND to the local authority in Soest for investigation\(^8\). The local authority Soest replied that the sludge is classified as bio-waste and is controlled and screened under the German bio-waste regulation. This waste regulation includes however only limit values for some heavy metals and phosphate.

The sludge was applied for about four more years on agricultural fields until the investigations of Skutlarek et al.\(^8\) finally revealed the treated area as contamination source in May 2006\(^8\). After these results were published and were also confirmed by further measurements, the public prosecutor’s office started investigations. In this investigation it was revealed that the material was imported from a hazardous waste from The Netherlands in accordance with the EU Waste Shipment Regulation (EEC 259/93)\(^12\) to the company GW Umwelt that stated that they can treat/decontaminate the sludge. However in a criminal act they then declared the sludge as bio-waste and sold it as “soil improver” to farmers (see above). No PS contaminated material was found in the storage of GW Umwelt however in a leaching water reservoir on the companies land high concentration of PS were detected confirming that GW Umwelt has managed and distributed the PS contaminated material.

In September 2006 the BUND accused the company GW Umwelt and also the local authority Soest\(^11\) GW Umwelt immediately proclaimed bankruptcy after the contamination was revealed. For ca. 3 month the former owner and the CEO of GW Umwelt went to prison and are currently on bail awaiting the trial. Meanwhile, investigations on the detailed origin of the materials by the public prosecutor’s office are ongoing.

Contamination of surface water and drinking water
The comparison of PS surface and drinking water contamination showed that the PS were not sufficiently eliminated for most water works (Table 1) and a higher reduction could be observed only for some water works, either caused by ground water dilution or by using new activated carbon (Table 1). The observed parallelism of the PS concentrations in surface water and drinking waters indicate that present water treatment steps used (even) in industrialized countries do not effectively eliminate perfluorinated surfactants, although approximately 50% of the waterworks at the Ruhr river are equipped with activated carbon filters. The filter efficiency is dependant on the type of activated carbon used and particularly, on the age of the filter beds used. As far as we know at present, the filter material has to be changed after approx. 6 months, depending on different parameters.

<table>
<thead>
<tr>
<th>City:</th>
<th>Surface water</th>
<th>Drinking water</th>
<th>Surface water</th>
<th>Drinking water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mülheim</td>
<td>48</td>
<td>31</td>
<td>94</td>
<td>63</td>
</tr>
<tr>
<td>Essen</td>
<td>60</td>
<td>58</td>
<td>97*</td>
<td>104*</td>
</tr>
<tr>
<td>Bochum</td>
<td>58</td>
<td>53</td>
<td>91*</td>
<td>96*</td>
</tr>
<tr>
<td>Witten</td>
<td>75</td>
<td>50</td>
<td>147</td>
<td>91</td>
</tr>
<tr>
<td>Hagen</td>
<td>91</td>
<td>65</td>
<td>152</td>
<td>118</td>
</tr>
<tr>
<td>Schwerte</td>
<td>178</td>
<td>146</td>
<td>280</td>
<td>234</td>
</tr>
<tr>
<td>Neheim (Möhne)</td>
<td>646</td>
<td>520</td>
<td>765</td>
<td>609</td>
</tr>
</tbody>
</table>

*The slightly higher PS values in drinking water compared to surface water in some measurements might be explained by PS variation in the Ruhr in combination with the time demand of 3 to 11 days for surface water processing to drinking water (filtration) (the small differences are however also within the measurement uncertainty of ca. 5 to 10%).

Activities of authorities
The population of the affected area was highly concerned regarding the health effects of the high PS concentrations in their drinking water. However, no evaluation or recommendation was possible at first since no drinking water guideline values for perfluorinated surfactants (including PFOS and PFOA) existed worldwide and also no risk assessment for highly contaminated drinking water could be undertaken.
The regional authorities approached the German Health Agency for clarification and help (05/2006). On 21st June 2006 the German Health Agency published a preliminary recommendation for drinking water limits for PFOS with target values, health guiding values, precautionary values and action levels (Table 2). During June/July 2006 infants and pregnant women of the high impacted area (city of Arnsberg-Neheim) were provided with PFOS-free bottled drinking water. From July 2006 on large activated carbon filters were installed in some of the water works to decontaminate the drinking water in the affected area. However after about 6 months a breakthrough of PS was observed and the activated carbon had to be renewed.

Table 2: Preliminary recommendation of German Health Agency for PS in drinking water

<table>
<thead>
<tr>
<th>Type of Limits</th>
<th>$\Sigma$PFOS+PFOA**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target value (long term minimum quality target; general precautionary value for $\Sigma$PFOS, PFOA and other PS)</td>
<td>$\leq 0.1 \mu g/l$</td>
</tr>
<tr>
<td>Lifelong health tolerable guiding value for all population groups</td>
<td>$\leq 0.3 \mu g/l$</td>
</tr>
<tr>
<td>Precautionary action value for infants</td>
<td>0.5 $\mu g/l$</td>
</tr>
<tr>
<td>Action value for adults (Not to use for nutrition purposes)</td>
<td>5 $\mu g/l$</td>
</tr>
</tbody>
</table>

**And possibly other perfluorinated surfactants

Contamination of population

The population in the area with the highest drinking water contamination (520 ng/l PFOA in March 2006, table 1) showed after only ca. 3 years exposure five to eight times elevated PFOA concentrations in the blood plasma – children 4.5-fold (median 22.1 $\mu g/l$), men 4.7-fold (median 27.4 $\mu g/l$) and mother 8.4-fold (24.9 $\mu g/l$) – compared to background cohorts in areas with non impacted drinking water. The maximum value of an individual was 99.7 $\mu g/l$. The observed PS concentrations in blood could be correlated to the individual drinking water consumption. The elevated human levels indicate that the proposed German drinking water guidelines (table 2) are too high.

Preliminary evaluation of the dimension of the contamination and of releases

One of the heavy contaminated area (ca. 100,000 m$^2$) at the upper reaches of the Möhne river treated with about 650 t of "Soil Improver" had contamination levels of 6.3 mg/kg PFOS/PFOA in soil layers up to 60 cm depth. The total load of PFOS/PFOA in this area alone is estimated to ca. 400 kg at the time of the measurement. From the present data, at least 15,400 tons of contaminated "Soil Improver" was distributed on agricultural land, grazing fields and forests in different areas in Germany on approx. 1000 sites. Assuming a similar degree of contamination of all "Soil Improver" would lead to an estimated 12000 kg applied PFOS/PFOA. However since some "Soil Improver" were not highly contaminated this can be seen as a conservative estimate (most of the presently evaluated ca. 100 areas had PFOS/PFOA contaminations below 1 mg/kg soil and only a few sites had higher values). The Möhne Reservoir (reserve drinking water reservoir for the approx. 5 million people of the Ruhr area) with a volume of approximately 134.5 million m$^3$, was contaminated with $\Sigma$PS of 822 ng/l (654 ng/l PFOA) equivalent to a total load of ca. 110.5 kg PS (88 kg PFOA). The water release from this reservoir is now managed together with two non-contaminated reservoirs supplying the Ruhr river. This results in dilution of PS concentrations in the Ruhr below 300 ng PFOS/PFOA (the proposed German tolerable guiding value, table 2).

Start of remediation and securing activities

2000 t of suspected sludge were still stored and the local government has started processing this waste in a sewage sludge incinerator without any emission monitoring. The BUND questioned the destruction efficiency of the sewage sludge incinerator (operated around 850°C) and requested monitoring. The regional authority then stopped the incineration activities (however 1600 t had already been processed) and investigated PS emissions to air, solids (ash, adsorbents) and liquids in test runs. Unfortunately, none of the highly contaminated materials were used for these tests.

In November 2006 the first activities for securing/decontamination of leachate from one of the most contaminated area (among the hundreds of contaminated sites) have commenced. At one side of this area the drainage water is collected and cleaned by carbon filtration with a set-up cost of ca. 2 million EURO. After 2 months operation of the activated carbon filters a breakthrough of PS was observed and the filters had to be exchanged.
Detection of other contaminated sites
In addition to the ongoing investigations of the other 1000 potentially contaminated sites related to the “Soil Improver”, a screening has started on PFOS/PFOA contamination in German rivers and water works. In course of this screening several other contaminated surface waters/releases were revealed.

Conclusions
The present case demonstrates that the mismanagement of one waste stream from PS-producing or PS-application industries can contaminate hundreds of sites and the drinking water of millions of people. Therefore in addition to contaminated sites around PS producing and application industry, the waste streams of these industries can become a serious contamination pathway for humans via contaminated drinking water. Therefore the mass flow and waste management of fluorinated organics in the technosphere (perfluorinated surfactants producing and application industries) has to be severely controlled by national authorities. It has to be guaranteed that the PS and PS precursor contaminated waste and waste streams (including PS containing products) are managed and finally destroyed in an environmentally sound manner. The responsibilities of the waste management and related damages have to stay with the PS producers (strict extended producer responsibility). Regulations in this respect should be developed as a matter of urgency along with legal regulations/limitations concerning the general production and use of fluorinated surfactants and their precursors. If the industry cannot demonstrate that PS can be managed in closed cycles and the products containing PS and precursors can be managed in an environmental sound manner, a general ban of PS and precursors should be considered similar to the ban for PFOS and precursors in the EU15.

References
2. German Environmental Agency (UBA), Perflouierte Verbindungen - Falscher Alarm oder berechtigte Sorge 01/2007 p 11.