Perfluorooctane sulphonate and perfluorooctanoic acid in drinking and environmental waters

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Perfluorooctane sulphonate (PFOS) and perfluorooctanoic acid (PFOA) are chemicals that have been used for many years as surfactants in a variety of industrial and consumer products. Owing to their persistent, bioaccumulative and toxic (PBT) characteristics, PFOS has been phased out by its principal producer and the use of PFOA has been reduced. This PBT potential and a number of pollution incidents have led in recent years to an increase in studies surveying the concentrations of PFOS and PFOA in environmental waters worldwide. This paper reviews the results of these studies, as well as the monitoring that was conducted after the pollution incidents. The results of surveys suggest that PFOS and PFOA are found in environmental waters worldwide at low levels. In general, these levels are below health-based values set by international authoritative bodies for drinking water. There have been limited measurements of these chemicals in drinking water, but again these are below health-based values, except in some cases following pollution incidents. Monitoring studies suggested that where PFOS and PFOA were detected, they were at similar levels in both source and drinking water, suggesting that drinking water treatment does not remove these chemicals. However, new data show that PFOS and PFOA are effectively removed by granular activated carbon absorbers in practice. Further research is required on the newer perfluorinated chemicals that appear to be safer, but their degradation products have not as yet been fully studied.

Keywords: perfluorooctane sulphonate; perfluorooctanoic acid; drinking water; environmental waters

1. Introduction

Perfluorooctane sulphonate (PFOS) and perfluorooctanoic acid (PFOA) and related compounds are members of a large family of perfluorinated chemicals (PFCs). Although available for the last 50 years, PFCs have been increasingly used as surfactants in a number of industrial and consumer products, mainly to repel dirt, water and oils (Brooke et al. 2004). Their use has included performance

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chemicals such as photographic film, surfactant in fire-fighting foams, surfactant for alkaline cleaners, emulsifiers in floor polish, mist suppressant for metal plating baths, surfactant for etching acids for circuit boards, pesticides, and dirt-repellent treatments for textiles (e.g., carpets, home furnishings and leather) and paper (e.g., food containers and masking tape). PFOS-related chemicals are manufactured from a precursor material known as perfluorooctanesulphonyl fluoride (POSF).

It has been estimated that the total global production/use (from 1970 to 2002) has been 96000 tonnes of POSF, with total global emissions being 650–2600 tonnes of POSF and 6.5–130 tonnes of PFOS. Most of the environmental release is to water (98%) and the remainder to air (Paul et al. 2009). They are immobile in soil and are non-biodegradable in, for example, activated sewage sludge (Brooke et al. 2004).

It has become clear in the last few years that these compounds are very persistent in the environment. The chemical nature of fluorine means that the carbon–fluorine bond is found to be the strongest in nature, making fluorinated compounds resistant to chemical or biochemical reactions. Fluorinated compounds are stable against many degradation processes found in the environment, such as hydrolysis, photolysis, acid and base attacks, oxidizing and reducing agents, and biodegradation (Lange et al. 2006).

PFCs have been shown to bioaccumulate in animals, including humans. Traces of PFCs are found in blood (where they bind to serum proteins) and organs such as liver and kidneys, as well as in muscle tissue. This is in contrast to other persistent organic pollutants (e.g., polychlorinated biphenols) that tend to accumulate in the fatty tissues. PFCs have been detected globally in the environment, having been found in polar bears in Greenland, giant pandas in China and albatrosses in the middle of the Pacific Ocean (EHP 2007). This suggests atmospheric transport of these compounds, although their potential to volatilize is low. However, PFOS and PFOA seem more prevalent in the more industrial areas such as the Baltic Sea, the Mediterranean, the Great Lakes and along Asian coasts (Lange et al. 2006).

There is some evidence that, in humans, blood concentrations of PFOS and to a lesser extent PFOA may have declined since 2000. Olsen et al. (2007), using plasma samples from Minnesota American Red Cross blood donors, have shown, in a small sample, that PFOS levels have decreased from 2000 (33.1 ng ml\(^{-1}\) geometric mean) to 2005 (15.1 ng ml\(^{-1}\)). The geometric mean for PFOA was 4.5 ng ml\(^{-1}\) in 2000 and 2.2 ng ml\(^{-1}\) in 2005. The decline in PFOS and PFOA levels may be due to the phase-out of POSF by the principal global manufacturer, 3M, in 2000–2002 and the reduction in the use of PFOA.

Although the acute toxicity of PFCs is moderate, their persistence in the body (half-lives for PFOA of up to 8.7 years have been determined in retired production workers) has led to increasing concerns over long-term effects. The toxicity of PFOS and PFOA is not clearly understood at present. Different animal species appear to have different sensitivities to these compounds, which makes interpretation of experiments difficult (e.g., Rhesus monkeys are more sensitive to PFOS than rats, while mice are the least sensitive). The species variability may be due to the different handling of these compounds in the body. At present, it is unclear whether PFOS and PFOA act by the same mechanisms, and high and low doses may differ in their toxic effects. High-dose studies on animals have indicated that cancer, developmental delays, endocrine disruption,
immunotoxicity and neonatal mortality are potential toxic endpoints. Recent research has also suggested that receptor binding may be an important general mechanism. PFOS and PFOA both bind to peroxisomal proliferator-activated receptor. Activation of such receptors may alter fatty acid metabolism and play a role in cancer, foetal growth, hormone and immune function (reviewed in COT 2005; EHP 2007).

In the year 2000, between 3665 and 4500 tonnes of POSF were produced globally, and 3M was the dominant producer. In that year, 3M announced that they would phase out the use of POSF after data revealed that PFCs are extremely persistent in the environment, are bioaccumulative and pose a risk to the environment and human health. Global production and use by 3M ceased in 2001. 3M also phased out production of PFOS, PFOA and related chemicals by 2002. However, other manufacturers have filled the deficit of 300 tonne yr\(^{-1}\) production of the ammonium salt of PFOA.

In 2006, the European Union announced severe restrictions on the use of PFOS, with member states adopting national measures by June 2008. PFOS cannot be placed on the market or used as a substance or constituent of preparations in a concentration equal to or higher than 0.005 per cent by mass, or 0.1 per cent in semi-finished articles or preparations, or 1 µg m\(^{-2}\) in textiles and coated materials (EU 2006). Exemptions to this restriction include its use in anti-reflective coatings for photolithography, mist suppressants for non-decorative hard chromium(VI) plating and hydraulic fuels for aviation. However, any PFOS-containing fire-fighting foams in existence are still permitted for use until mid-2011.

This paper reviews some of the recent studies on the levels of the PFCs, PFOS and PFOA in environmental waters, outlining the impact on levels detected after known contamination incidents and concentrations that have been detected in different types of environmental waters around the world. The more limited studies on the detection of PFOS and PFOA in drinking water are also examined, together with the data on removal of these compounds by the various water treatments.

2. Contamination incidents

The presence of PFCs and in particular PFOS and PFOA in environmental waters has been the subject of much interest in recent years. Important information has emerged following contamination incidents: in the USA at manufacturing plants; in the UK in 2005, following the use of PFOS-containing fire-fighting foams to tackle fires following an oil depot explosion at Buncefield; and in 2006, in the rural area of Sauerland in Germany, where soil improver contaminated with PFOA was spread onto agricultural land.

(a) Little Hocking, West Virginia, USA

PFOA has been detected in the drinking water supply of Little Hocking near Washington, West Virginia, USA (Paustenbach et al. 2007; Tillett 2007). This village is across the Ohio River from and downwind of the Dupont fluoropolymer manufacturing facility. The extent of exposure to residents of the village was assessed by questionnaire and measuring PFOA in blood samples. Levels of PFOA in drinking water averaged 3.55 µg l\(^{-1}\) during 2002–2005. The blood PFOA

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levels were 60–75 times higher than in the general population. Serum PFOA was particularly high in individuals who consumed more home-grown fruit and vegetables. It is unclear whether PFOA was present in the produce itself or in the water used for cooking.

A further study on the exposure of residents living near this facility (Paustenbach et al. 2007) used historical emission records for 52 years to estimate the potential intake of 50,000 residents. PFOA detected in groundwater was deemed to have originated by particulate deposition from air emissions to the soil and then transferred to the water. Maximum concentrations were estimated to occur at up to one mile from the site, with maximum air, surface soil and drinking water levels estimated to be 200 ng m$^{-3}$, 11 μg kg$^{-1}$ and 4 μg l$^{-1}$, respectively.

An independent team of scientists, C8 Assessment of Toxicity Team (CATT), was assembled to conduct human health and ecological risk assessments and to communicate health risk information to the public. Their risk assessment concluded that average daily intake of PFOA within five miles of the plant over a 50 yr time span was 10,000 times less than an intake that was not considered a risk to human health (Paustenbach et al. 2007).

(b) Cottage Grove, Minnesota, USA

3M produced PFCs at a site in Cottage Grove, Minnesota, from the late 1940s until 2002 (ATSDR 2005). During this time, there were air emissions of PFCs, waste from production was deposited in an on-site pit, and wastewater treatment plant effluent containing PFCs was discharged into the nearby Mississippi River. There was also a fire-training area on site where PFC-containing foams were used.

Monitoring indicates that groundwater beneath the site was contaminated with PFOS and PFOA at significant levels (PFOS and PFOA concentrations up to 120 and 105 μg l$^{-1}$, respectively). Much of this contaminated groundwater was then processed through the wastewater plant on site, which was unable to remove PFCs. However, in recent years (approx. 2004 onwards), the addition of a large granular activated carbon (GAC) system has eliminated PFC discharge into the Mississippi River.

(c) Decatur, Alabama, USA

A further 3M PFC production plant is situated in Decatur, Alabama. Monitoring of the nearby Tennessee River upstream and downstream of this plant showed PFOS present throughout the 80-mile stretch of the river studied, with levels of 32 ± 11 ng l$^{-1}$ upstream of the facility and 114 ± 19 ng l$^{-1}$ downstream. Concentrations of PFOA were below the level of detection upstream, but 394 ± 128 ng l$^{-1}$ downstream (Hansen et al. 2004).

(d) Sauerland, Germany

In the summer of 2006, 12 perfluorinated surfactants were sampled in various surface water and drinking waters in Germany (Skutlarek et al. 2006). Surface water sampled included the rivers Rhine, Ruhr and Möhne as well as some of their tributaries, while the drinking water samples were from public buildings.
in the Rhine–Ruhr area. The sum of the seven compounds most frequently found in the River Rhine and its tributaries was less than 100 ng l\(^{-1}\). The highest concentrations of these 12 compounds detected were in the Ruhr River at 94 ng l\(^{-1}\), with PFOA being the major component. However, samples from the rivers Ruhr and Moehne (a tributary of the Ruhr) showed high (446 and 4385 ng l\(^{-1}\), respectively) concentrations in their upper reaches. By tracking these high concentrations, the main source of contamination was localized to an area of agricultural land near Brilon-Scharfenberg in the Sauerland region. The main source of the substantial environmental PFC contamination was concluded to be industrial waste with high concentrations of PFCs that was applied as a ‘soil improver’ on agricultural land. It is estimated that the contamination lasted for several years.

The maximum drinking water concentration of the total PFCs detected in Arnberg Heheim in this area was 598 ng l\(^{-1}\), with PFOA being the most prevalent compound. Drinking water concentrations were comparable to those found in surface water, suggesting that these compounds were not being significantly removed by water treatment, although approximately 50 per cent of the water works on the Ruhr River were equipped with GAC. A further study was conducted on the blood plasma levels of PFCs in adult and children residents of Arnberg Heheim who were exposed to PFC-contaminated drinking water. PFOA was the major PFC in blood, with concentrations being four- to eight-fold higher than in non-exposed controls (Holzer et al. 2008).

A previous study conducted in Germany in 2004 indicated that the normal background levels of perfluorinated surfactants are in the low nanograms per litre range (Lange et al. 2006).

(e) Buncefield Oil Depot, UK

In December 2005, there was an explosion at the Buncefield Oil Depot, north of London. This was the largest post-war explosion in Europe. The use of PFOS-containing fire-fighting foams led to the widespread contamination of the local aquifer and surface waters. In the months following this event, there was continuous monitoring of local waters for PFOS. Boreholes (except for one deep borehole) around the Buncefield site remained contaminated after sampling in June 2006. In general, the surface water sources (the local rivers) remained uncontaminated, with levels below 1 \(\mu g l^{-1}\) and just a few samples above this, the exact source of which remains unexplained. However, there were a number of groundwater sites around Buncefield and in the surrounding area that showed raised levels of PFOS (up to 5.91 \(\mu g l^{-1}\)), starting in April 2006 and continuing until June 2006, and this short-term contamination also remains unexplained. PFOS was not detected in drinking water samples. However, at this time, the methodology used had a limit of detection (LOD) of 1 \(\mu g l^{-1}\), dropping to 0.1 \(\mu g l^{-1}\) after about April 2006 (reported in Atkinson et al. 2008). This relatively high LOD reflects the fact that there was no standard method of detection already developed and available in the UK when the Buncefield incident occurred. This and the large number of samples generated meant that a number of laboratories had to rapidly develop at least some screening technique for detecting PFOS in water. This contrasts with the low LODs (ng l\(^{-1}\)) that have been developed for the planned research-monitoring exercises described in §4.
During June 2006, there was an accidental release of stored contaminated surface water (held following the clean-up of the Buncefield site) from a sewage treatment works into a local river. Monitoring at the nearest downstream water abstraction point some days later detected PFOS for 2 days (0.9 and 0.8 μg l⁻¹), but the sample then returned to below the LOD (<0.1 μg l⁻¹).

(f) Jersey Airport, Jersey, Channel Islands, UK

In the 1990s, foam used by practising fire-fighters at the airport on the island of Jersey, one of the Channel Islands, off the coast of France, polluted the surrounding area. It seriously contaminated local land and boreholes with PFOS that can still be detected at above 10 μg l⁻¹ levels in certain boreholes, ditches and ponds in the area, confirming the persistence of PFOS in the environment. Of nine seriously contaminated sites, four had shown some evidence of decreased PFOS concentrations (reported in Atkinson et al. 2008). Drinking water obtained from boreholes was also seriously contaminated (the highest PFOS level measured in one property was 98 μg l⁻¹, with other samples mainly over 20 μg l⁻¹; most other properties had levels below 1 μg l⁻¹) and affected residents now have mains water or are supplied with bottled water.

3. Drinking water guidelines

In the light of the pollution incidents, a number of authoritative bodies have issued guidance, based on human health effects, for PFOS and PFOA if found in drinking water.

(a) United Kingdom

In 2007, the Drinking Water Inspectorate of England and Wales issued guidance for PFOS and PFOA based on a three-tiered system with values ranging from 0.3 to 9.0 μg l⁻¹ with requirements for increased monitoring through to action to decrease concentrations. This guidance is presented in table 1 (DWI 2007).

Following the use of PFOS-containing foams on the fire at the Buncefield Oil Depot, the Environment Agency and the Department for Communities and Local Government issued a circular to the fire-fighting authorities entitled ‘Guidance on the phasing-out of PFOS-based foams for Class B fires’. This document sought a voluntary ban on the future use of PFOS-based foams by the UK fire and rescue service, and highlighted the ways by which emissions to the environment can be prevented or, if this was not possible, minimized during any further use of such foams (DCLG 2006).

(b) Germany

In June 2006, following the high PFOA contamination of drinking water in Arnsberg Heheim, the Drinking Water Commission of the German Ministry of Health at the Federal Environment Agency issued guidance on maximum values for combined PFOA and PFOS concentrations in drinking water (Wilhelm et al. 2008). This guidance is outlined in table 2. In some ways,
Table 1. Drinking Water Inspectorate (DWI) guidance levels for PFOS and PFOA (DWI 2007).

<table>
<thead>
<tr>
<th>guidance value</th>
<th>drinking water (μg l⁻¹)</th>
<th>duration</th>
<th>value</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOS tier 1</td>
<td>maximum</td>
<td>&gt;0.3</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>PFOS tier 2</td>
<td>maximum</td>
<td>&gt;1.0</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>PFOS tier 3</td>
<td>maximum</td>
<td>&gt;9.0</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td>PFOA tier 1</td>
<td>maximum</td>
<td>&gt;0.3</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>PFOA tier 2</td>
<td>maximum</td>
<td>&gt;10.0</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>PFOA tier 3</td>
<td>maximum</td>
<td>&gt;90.0</td>
<td>c</td>
<td></td>
</tr>
</tbody>
</table>

a Minimum action to be taken: consult with local health professionals; and monitor levels in drinking water.
b Minimum action to be taken: as tier 1 plus: put in place measures to reduce concentrations to below 1.0 μg l⁻¹ (PFOS) or 10 μg l⁻¹ (PFOA) as soon as practicable.
c Minimum action to be taken: as tier 2 plus: ensure consultation with local health professionals takes place as soon as possible; and take action to reduce exposure from drinking water within 7 days.

Table 2. German maximum value guidance for combined PFOA and PFOS concentrations in drinking water (Wilhelm et al. 2008).

<table>
<thead>
<tr>
<th>type of maximum value</th>
<th>abbreviation</th>
<th>value (μg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>health-based precautionary value (long-term minimum quality goal) for non-genotoxic substances</td>
<td>HPV₁</td>
<td>0.1</td>
</tr>
<tr>
<td>strictly health-based guidance value for safe lifelong exposure for all population groups</td>
<td>GV</td>
<td>0.3</td>
</tr>
<tr>
<td>precautionary action value for infants</td>
<td>PAVᵢ</td>
<td>0.5</td>
</tr>
<tr>
<td>precautionary action value for adults</td>
<td>PAVₒ</td>
<td>5.0</td>
</tr>
</tbody>
</table>

These values are similar to the UK values for a single PFOS contamination event. However, for action on PFOA contamination, the German value is more precautionary.

(c) United States of America

For the US States where contamination around production plants has been identified, a site-specific action level of 0.5 μg l⁻¹ (500 ng l⁻¹) has been set for West Virginia, where the Dupont Little Hocking plant is situated. The same value is set for a safe level for PFOA in drinking water in Minnesota, where the 3M Cottage Grove production plant is situated (ACS 2007).
The New Jersey Department of Environmental Protection have recommended a preliminary health-based guideline value for PFOA in drinking water of $0.04\,\text{μg}l^{-1}$ ($40\,\text{ng}l^{-1}$). This value is more precautionary than the action levels set in West Virginia and Minnesota and the German and UK guidance values (ACS 2007).

4. Concentrations of perfluorooctane sulphonate and perfluorooctanoic acid detected in groundwater, surface water and drinking water worldwide

Following the contamination incidents and the heightened interest in PFCs and their persistent, bioaccumulative and toxic (PBT) characteristics, there has been recent global interest in monitoring of environmental water for the presence of PFOS and PFOA, in particular. The recent studies are outlined below and the results are summarized for environmental waters in table 3 and drinking water in table 4. This list may not be comprehensive but does demonstrate the range of concentrations found in the environmental waters of the world. The LODs for these studies appear to vary widely, with some reporting levels less than $1\,\text{ng}l^{-1}$ while older studies, particularly those in the UK that were set up rapidly after the Buncefield Oil Depot fire, have LODs several orders of magnitude higher.

(a) China

A Chinese study has examined the concentrations of 14 perfluorinated compounds (including PFOS and PFOA) in water samples taken from the Pearl and Yangtze Rivers (So et al. 2007). PFOS levels were $0.9–99\,\text{ng}l^{-1}$ and less than $0.01–14\,\text{ng}l^{-1}$ from the Pearl and Yangtze Rivers, respectively, while PFOA concentrations were $0.85–13\,\text{ng}l^{-1}$ and $2.0–260\,\text{ng}l^{-1}$, respectively. Samples from the Yangtze River near Shanghai (the major industrial region in China) had the highest concentrations. Different detection profiles for the compounds analysed were found, and therefore the sources of these compounds in these two rivers were considered to be different.

Fujii et al. (2007) reported tap water levels in China of $1.5–13\,\text{ng}l^{-1}$ and $1.1–109\,\text{ng}l^{-1}$ for PFOS and PFOA, respectively.

(b) Japan

PFOS and PFOA were monitored in the Yodo River basin in Japan (Lein et al. 2008). PFOS and PFOA concentrations were from $0.4$ to $123\,\text{ng}l^{-1}$ and from $4.2$ to $2600\,\text{ng}l^{-1}$, respectively. The highest concentrations were detected in the effluent streams of some sewage treatment works and tributary streams.

PFOS and PFOA have been detected in the sludge from Japanese sewage treatment works in the range of $200–500\,\text{ng}l^{-1}$ (Fujii et al. 2007). The removal of these compounds from contaminated sludge may need to be considered in future.

Senthilkumar et al. (2007) detected PFOA and PFOS concentrations of $7.9–11\,\text{ng}l^{-1}$ and less than $5.2–10\,\text{ng}l^{-1}$, respectively, in water samples from the Kyoto River.

Takagi et al. (2008) monitored raw and tap water from 14 Osaka drinking water treatment plants in summer and winter. PFOS and PFOA were detected in all raw water samples at concentrations ranging from $0.26–22\,\text{ng}l^{-1}$ to $5.2–92\,\text{ng}l^{-1}$.
**Table 3. Levels of PFOS and PFOA in environmental waters.**

<table>
<thead>
<tr>
<th>country</th>
<th>PFOS levels (ng l⁻¹)</th>
<th>PFOA levels (ng l⁻¹)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>USA</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>North Carolina</td>
<td>132</td>
<td>287</td>
<td>Nakayama et al. (2007)</td>
</tr>
<tr>
<td>Kentucky</td>
<td>7.0–149</td>
<td>22–334</td>
<td>Loganathan et al. (2007)</td>
</tr>
<tr>
<td>Georgia</td>
<td>1.8–22</td>
<td>1–227</td>
<td>Loganathan et al. (2007)</td>
</tr>
<tr>
<td><strong>Japan</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Osaka</td>
<td>0.26–22</td>
<td>5.2–92</td>
<td>Takagi et al. (2008)</td>
</tr>
<tr>
<td>Yodo River</td>
<td>0.4–123</td>
<td>4.2–2600</td>
<td>Lein et al. (2008)</td>
</tr>
<tr>
<td>Tsurumi River</td>
<td>180</td>
<td>13–16</td>
<td>Zushi et al. (2008)</td>
</tr>
<tr>
<td>Kyoto</td>
<td>&lt;5.2 to 10</td>
<td>7.9–110</td>
<td>Senthilkumar et al. (2007)</td>
</tr>
<tr>
<td>Other</td>
<td>0.24–37.3</td>
<td>0.10–456</td>
<td>Saito et al. (2004)</td>
</tr>
<tr>
<td><strong>Italy</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lake Maggiore</td>
<td>9</td>
<td>3</td>
<td>Loos et al. (2007)</td>
</tr>
<tr>
<td>River Po</td>
<td>10</td>
<td>60–1300</td>
<td>Loos et al. (2008)</td>
</tr>
<tr>
<td><strong>South Korea</strong></td>
<td>2.4–651</td>
<td>0.9–62</td>
<td>Rostkowski et al. (2006)</td>
</tr>
<tr>
<td><strong>Germany</strong></td>
<td>1–195</td>
<td>0.7–250</td>
<td>Skutlarek et al. (2006)</td>
</tr>
<tr>
<td>United Kingdom</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EA GWᵃ</td>
<td>&lt;100 to 6300</td>
<td>&lt;100 to 600</td>
<td>EA (2007)</td>
</tr>
<tr>
<td>EA SWADᵇ</td>
<td>&lt;100 to 14500</td>
<td>&lt;100 to 340</td>
<td>EA (2007)</td>
</tr>
<tr>
<td>EA TRBMᶜ</td>
<td>&lt;100 to 33900</td>
<td>&lt;100 to 2000</td>
<td>EA (2007)</td>
</tr>
<tr>
<td>WRc</td>
<td>&lt;11 to 208</td>
<td>&lt;24 to 370</td>
<td>Atkinson et al. (2008)</td>
</tr>
<tr>
<td><strong>China</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pearl River</td>
<td>0.99–99</td>
<td>0.85–13</td>
<td>So et al. (2007)</td>
</tr>
<tr>
<td>Yangtze River</td>
<td>&lt;0.01 to 14</td>
<td>2–260</td>
<td>So et al. (2007)</td>
</tr>
</tbody>
</table>

ᵃEnvironment Agency Groundwater monitoring.
ᶜEnvironment Agency Targeted Risk Based Monitoring, mainly sites that monitor effluent from sewage treatment works or rivers receiving such effluent.

**Table 4. PFOS and PFOA levels in drinking water.**

<table>
<thead>
<tr>
<th>country</th>
<th>PFOS (ng l⁻¹)</th>
<th>PFOA (ng l⁻¹)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA—West Virginia</td>
<td>—</td>
<td>3550</td>
<td>Paustenbach et al. (2007)</td>
</tr>
<tr>
<td>Japan</td>
<td>0.16–51</td>
<td>0.7–84</td>
<td>Takagi et al. (2008), Fujii et al. (2007)</td>
</tr>
<tr>
<td>Germany—Rhine-Ruhr</td>
<td>0–22</td>
<td>22–519</td>
<td>Skutlarek et al. (2006)</td>
</tr>
<tr>
<td>Canada</td>
<td>—</td>
<td>0.2</td>
<td>Fujii et al. (2007)</td>
</tr>
<tr>
<td>China</td>
<td>1.5–13.2</td>
<td>1.1–109</td>
<td>Fujii et al. (2007)</td>
</tr>
<tr>
<td>Malaysia</td>
<td>0.1</td>
<td>0.1</td>
<td>Fujii et al. (2007)</td>
</tr>
<tr>
<td>Sweden</td>
<td>0.3, 0.8</td>
<td>1.3</td>
<td>Fujii et al. (2007)</td>
</tr>
<tr>
<td>Thailand</td>
<td>0.1–1.9</td>
<td>0.2–4.6</td>
<td>Fujii et al. (2007)</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>&lt;11 to 45</td>
<td>&lt;24 to 240</td>
<td>Atkinson et al. (2008)</td>
</tr>
</tbody>
</table>
respectively. Concentrations of PFOS and PFOA in potable tap water were 0.16–22 ng l\(^{-1}\) and 2.3–84 ng l\(^{-1}\), respectively, and there was a positive correlation between raw and tap water levels, suggesting that removal by the treatment processes is low.

Zushi \textit{et al.} (2008) has sampled river water and sewage effluent along the Tsurumi River and at a fixed station and monitored PFC levels. With an increase in river flow rate, PFOS and PFOA levels stayed approximately the same. The load of PFCs increased with the rate of river flow, and the load in rain run-off was estimated to be 2–11 times greater than those in sewage treatment effluents discharged into the river. These results suggested the existence of non-point sources with a significant impact on the PFC river load. This is contrary to most other studies where raised PFOS or PFOA concentrations are normally associated with a point source of contamination.

Saito \textit{et al.} (2004) monitored the widespread occurrence of PFOS and PFOA at 78 sites in Japanese rivers and tributaries. The range of PFOS and PFOA concentrations detected was 0.24–37.3 ng l\(^{-1}\) and 0.10–456 ng l\(^{-1}\), respectively. Two contaminated sites were identified: an airport for PFOS and a public water disposal site for PFOA.

\(\text{(c) Italy}\)

An Italian study of PFOS and PFOA concentrations in Lake Maggiore in northern Italy produced low maximum concentrations of 8 and 3 ng l\(^{-1}\), respectively. Drinking water concentrations were reported to be very similar, and the authors concluded that the removal systems of sand filtration and chlorination were inefficient at removing PFOS and PFOA. Lake Maggiore receives municipal, industrial and agricultural discharges (Loos \textit{et al.} 2007).

Loos \textit{et al.} (2008) monitored selected stretches of the River Po and its major tributaries for PFCs. Higher concentrations (approx. 1300 ng l\(^{-1}\)) of PFOA were detected in the Tanaro River close to the city of Alessandria. After this tributary, levels between 60 and 337 ng l\(^{-1}\) were measured in the River Po on several occasions. The PFOA concentration close to the river mouth in Ferrara was between 60 and 174 ng l\(^{-1}\). Using the river discharge flow data of 920 m\(^3\) s\(^{-1}\) for the year 2006, a mass load of approximately 0.3 kg h\(^{-1}\) or 2.6 tonne yr\(^{-1}\) discharged into the Adriatic was calculated. PFOS concentrations in the River Po at Ferrara were approximately 10 ng l\(^{-1}\).

The PFOA concentration for the mouth of the River Po was confirmed by McLachlan \textit{et al.} (2007), who detected a level of 200 ng l\(^{-1}\). This study measured PFCs at the mouth of 13 other rivers in Europe, including the Rhine, Danube, Elbe, Oder, Seine and Loire. The Po accounted for two-thirds of all the PFOA discharge measured, as the other concentrations were in the low nanograms per litre range.

\(\text{(d) South Korea}\)

In South Korea, PFCs were monitored in the streams of the industrial areas on the west coast, near Lake Shihwa and Gyeonggi Bay (Rostkowski \textit{et al.} 2006). The highest concentrations detected were PFOS and PFOA at 2.24–651 ng l\(^{-1}\) and 0.9–62 ng l\(^{-1}\), respectively. Local industrial sources were considered to be the origin of these highest levels.

\textit{Phil. Trans. R. Soc. A} (2009)
In a recent study on the occurrence of PFOS and PFOA in raw and treated waters in England, 20 sites were sampled, comprising five control low-risk sites and 15 perceived high-risk water treatment works (Atkinson et al. 2008). Four sampling sessions were undertaken to account for any seasonal variation. Sites covered a range of lowland and upland surface waters and confined and unconfined groundwater sources as well as a range of different water treatments. The control sites were in rural areas while the high-risk sites were near industrial areas or civil or military airfields.

PFOS was not detected in any of the control sites (LOD 10ngl$^{-1}$). Of the 15 high-risk sites, PFOS was detected at four sites in both raw and final waters (the maximum level being 208, 76, 23 and 28ngl$^{-1}$), with no obvious seasonal differences. One of the sites was in the region of Buncefield Oil Depot and subsequent pollution, while the others were in the neighbourhood of airfields. The conclusions regarding the presence of PFOA were less clear, as it was detected in 18 out of 20 sites (<24 to 370ngl$^{-1}$) but usually only once (or at most twice) out of the four sampling regimes. There did not appear to be widespread background contamination of raw or treated drinking water. Where PFOS was detected, source water originated primarily from unconfined aquifers, as might be expected if resulting from point source contamination events. In addition, there was no apparent correlation between the detection of PFOS or PFOA and any particular water treatment or method of disinfection (chlorine gas or hypochlorite). Where PFOS was detected, there was little difference in concentration between raw and final waters, indicating that the water treatment processes involved did not show any signs of being able to remove the contaminants. However, the GAC treatment that was present at two of the four works had not been generated for at least 2 years and this would probably have affected its ability to remove PFOS and PFOA (see §5). There was no correlation between the presence of PFOS and PFOA in water.

The Environment Agency of England and Wales also carried out a monitoring programme at selected sites, which was published in 2007 (EA 2007). PFCs were detected in 26 per cent (57 out of 219) of the groundwater monitoring sites, with about 14 per cent recording PFOS. Most sites were sampled only once, but when results showed concentrations well above the level of detection (100ngl$^{-1}$), repeat sampling in most cases did not duplicate the results. In cases where detected levels of PFOS were greatly elevated (>3000ngl$^{-1}$), the results were then below the level of detection upon resampling. The range of concentrations detected in groundwater were less than 100–6300ngl$^{-1}$ and less than 100–600ngl$^{-1}$ for PFOS and PFOA, respectively.

Sampling of untreated surface water at drinking water abstraction sites (SWADs, Surface Water Abstraction Directive sites) indicated that PFCs appeared to be widespread but at low levels. PFCs were detected at 52 per cent (22 out of 42) of these sites, but in only 18 per cent of the samples taken. At a single site where PFOS was detected at 14500ngl$^{-1}$, a further sample had a concentration of 500ngl$^{-1}$ and subsequent samples were below the level of detection. The range of concentrations detected in surface water were less than 100–14500ngl$^{-1}$ and less than 100–340ngl$^{-1}$ for PFOS and PFOA, respectively.

Phil. Trans. R. Soc. A (2009)
In targeted monitoring of effluents and rivers (TRBM, targeted risk-based monitoring), PFCs were detected at 67 per cent of the sites and in 32 per cent of samples. The range of concentrations detected in surface water were less than 100–33 900 ng l$^{-1}$ and less than 100–2000 ng l$^{-1}$ for PFOS and PFOA, respectively.

The highest levels seen in this survey of up to 33 900 ng l$^{-1}$ in surface water were higher than those detected in any other survey worldwide. However, subsequent resampling did not confirm these results. The report stated that these results suggest a very transient source of contamination or sampling/analysis problems and that the robustness of their quality control and the pattern of results indicate that variations of PFOS concentrations with time are the most likely cause. However, the extremely high levels seen and the subsequent disappearance have not been seen with other monitoring.

(f) United States of America

Samples from different locations in the Cape Fear River Basin in North Carolina were analysed for PFCs (Nakayama et al. 2007). Detectable levels were found in all samples, with the maximum PFOS at 132 ng l$^{-1}$ and PFOA at 194 ng l$^{-1}$. In general, the lowest levels were detected in the smallest tributaries while the highest levels were found in the middle reaches of the drainage basin. The variability of PFC concentrations suggests a series of source outputs throughout the basin. Twenty-two per cent of the sites had PFOS levels above 43 ng l$^{-1}$, the level the authors estimated as a conservative safe concentration for the protection of avian life, and 32 per cent of the sites had PFOA concentrations above 40 ng l$^{-1}$.

Loganathan et al. (2007) studied levels of PFCs at various stages of wastewater treatment at two wastewater treatment works: one rural works in Kentucky and one in an urban area in Georgia. PFOS levels in the Kentucky works were 8.2–990 ng g$^{-1}$ dry weight in solid samples and 7.0–149 ng l$^{-1}$ in aqueous samples, and for PFOA were 8.3–219 ng g$^{-1}$ and 22–334 ng l$^{-1}$, respectively. In the urban Georgia works, PFOS levels were less than 2.5–77 ng g$^{-1}$ and 1.8–22 ng l$^{-1}$, and PFOA levels were 7.0–130 ng g$^{-1}$ and 1–227 ng l$^{-1}$, respectively. Other PFCs were detected in most samples. Concentrations of some PFCs, particularly PFOA, were slightly higher in effluent than influent samples, suggesting that biodegradation of some precursors contributes to an increase in PFOA concentrations in wastewater treatment processes. No large-scale variation was observed, although the mass flow of PFCs was higher in winter than in summer. In general, samples from the rural Kentucky plant contained greater concentrations of PFCs than those from the urban plant in Georgia.

A recent study in California measured PFCs in recycled water from four wastewater treatment plants that employed tertiary treatment and one that treated primary sewage in a wetland environment (Larabee & Reinhard 2008). Effluent was compared with surface and groundwater from a creek where recycled water was being evaluated as a potential means of increasing flow. PFCs (total 90–470 ng l$^{-1}$) were detected in the recycled water, mainly PFOA (10–190 ng l$^{-1}$) and PFOS (20–190 ng l$^{-1}$). No significant removal of PFCs was observed in the wetlands. Although there was no wastewater discharge into the creek, PFCs were detected in the surface water and underlying groundwater (20–150 ng l$^{-1}$), with PFOA and PFOS again making the largest contribution.
Fujii et al. (2007) list a number of other countries where limited monitoring of tap water for PFOS and PFOA have been carried out. The levels detected are: Canada, 0.2 ng l\(^{-1}\) PFOA; Malaysia, 0.1 ng l\(^{-1}\) PFOS and 0.1 ng l\(^{-1}\) PFOA; Sweden, 0.3–0.8 ng l\(^{-1}\) PFOS and 1.3 ng l\(^{-1}\) PFOA; Thailand, 0.1–1.9 ng l\(^{-1}\) PFOS and 0.2–4.6 ng l\(^{-1}\) PFOA.

5. Removal of perfluorooctane sulphonate and perfluorooctanoic acid by drinking water treatment processes

There is some conflicting evidence from the monitoring studies on the ability of drinking water treatment processes to remove PFCs.

The study of Lake Maggiore in Italy gave similar very low levels of PFOS (3 ng l\(^{-1}\)) and PFOA (9 ng l\(^{-1}\)) in both lake and drinking water and the authors concluded that the treatment (slow sand filtration and chlorination) was ineffective in removing these chemicals (Loos et al. 2007).

The use of reverse osmosis (RO) membranes to remove PFOS from wastewater has been assessed by Tang et al. (2006). PFOS at feed concentrations ranging from 0.5 to 1500 ppm was removed by 90% per cent or more. In a further study, Tang et al. (2007) investigated the use of RO and nanofiltration (NF) to remove PFOS from wastewater. A feed concentration of 10 ppm over 4 days was employed with five RO membranes and three NF membranes. The rejection of PFOS was concurrent with that of sodium chloride. Greater than 99 per cent and 90–99 per cent removal was achieved with RO and NF membranes, respectively.

The installation of GAC into the wastewater treatment system of the PFC production facility in Minnesota, USA, successfully removed PFCs from the effluent discharged into the Mississippi River (ATSDR 2005).

In the monitoring that took place following the contamination in the Sauerland region of Germany, drinking water concentrations were comparable to those found in surface water, which suggested that these compounds were not being significantly removed by water treatment, although approximately 50 per cent of the water works on the Ruhr River were equipped with GAC (Skutlarek et al. 2006). However, a recent publication described a further study on the Mohneberg water works in this region, drinking water from which gave the highest level of PFOA (519 ng l\(^{-1}\)). These works installed GAC filters in June 2006 (Wilhelm et al. 2008). This treatment proved to be effective at removing PFOA, with levels decreasing from 0.9 μg l\(^{-1}\) to below the level of detection (0.01 μg l\(^{-1}\)). However, a steady increase occurred after about three months, with levels exceeding 0.1 μg l\(^{-1}\) after about five months. Exchange of filters and reactivation of the carbon resulted in effective removal of PFOA again. PFOS levels were below the level of detection (<0.01 μg l\(^{-1}\)) except for two occasions (0.034 and 0.025 μg l\(^{-1}\)).

In December 2006, Anglian Water, the local water company in the East Anglia region of the UK, was made aware of the use of fire-fighting foam containing PFOS and other PFCs at an airbase in the region (Markall 2008). Upon sampling at water treatment works adjacent to this airbase, it was discovered...
that raw water contained 3.7 μg l⁻¹ PFOS with lower concentrations of other PFCs. The water treatment works is a groundwater abstraction, shallow chalk aquifer via a single borehole hydraulically downstream of the airbase. It has forced draught aeration and five Chemviron F400 GAC absorbers, orthophosphoric acid dosing and disinfection. The water is blended with other groundwater sources in a contact tank and then passed to a reservoir where it is further blended before being delivered to a Public Water Supply Zone supplying approximately 57,000 people. At the time of the incident, the site was designed to give an empty bed contact time (EBCT) of the water with the GAC of 30 min with a regeneration frequency of 24 months. Besides PFOS, other PFCs were also monitored including PFOA. Owing to the dilution and blending with water from other sources, the final concentration of PFOS in drinking water was never above the lowest guideline value (0.3 μg l⁻¹) set by the Drinking Water Inspectorate (table 1).

The level of PFOS in the raw water has remained at approximately the same level since the incident in December 2006 (ranging from 1.7 to 3.8 μg l⁻¹), showing no evidence of decreasing. PFOA has been detected at levels between 0.2 and 0.5 μg l⁻¹. Perfluorohexane sulphonate has also been detected at approximately 1.5 μg l⁻¹ (maximum concentration, 1.9 μg l⁻¹). These results indicate the persistence of these perfluorinated compounds in water.

The GAC is regenerated by heating at high temperatures in excess of 600 °C, at which PFOS and PFOA are expected to be completely transformed into CO₂ and HF (Fujii et al. 2007).

Pre- and post-filtration sampling indicated that GAC was effective in the removal of PFOS at the levels detected in the raw water. The effectiveness was dependent on the bed life of the carbon, i.e. the period since the last regeneration. The GAC was originally installed to give a minimum EBCT of 30 min with two of the five units out of service for maintenance or washing. Upon detection of PFOS in the raw water, the plant flow was reduced to increase substantially the EBCT to between 65 and 110 min. The GAC regeneration frequency (staggered between the five absorbers) was changed from 24- to 12-monthly. There were approximately 5500 bed volumes between annual regenerations. PFOS and PFOA showed breakthrough after approximately 8000–9000 bed volumes. This was measured prior to the increase in regeneration frequency. Other PFCs showed different breakthrough rates, with perfluorobutane sulphonate showing breakthrough after 8000–9000 bed volumes, perfluorohexane sulphonate after 6000 bed volumes, and 6:2 fluorotelomer sulphonate after 11,000 bed volumes. Perfluorohexanoic acid was least absorbed onto GAC F400 and showed breakthrough after approximately 2000 bed volumes. Figure 1 shows the levels of PFOS detected in one GAC absorber with time and number of bed volumes. The effect on PFOS levels of replacing the GAC in October 2007 is clearly seen.

Other options were also tested in this study including UV and hydrogen peroxide treatment. Results showed no measurable photolysis with UV alone or hydroxyl radical oxidation (from the addition of hydrogen peroxide). Other laboratory studies with extreme conditions using photocatalysis (reaction time up to 3 days) and advance oxidation (with high temperature and pressure) have proved effective in completely degrading PFOS and PFOA to CO₂ and HF (Fujii et al. 2007).
PFOS and PFOA have been found in environmental waters all around the world. However, in general, detected levels have been low, below the values that have been set for drinking water by various international authoritative bodies for the protection of human health of around 300–500 ng l\(^{-1}\). The exception to this was in the survey conducted by the Environment Agency of England and Wales, where occasional concentrations were detected in the micrograms per litre range. However, upon resampling, these results were not repeated. Continuous raised levels were found in specific industrial areas or where known contamination had taken place. In fact, in the Sauerland area of Germany, the specific contamination was identified from the discovery of PFOA in nearby rivers. Therefore, in general, PFOS and PFOA are present in environmental waters due to specific point source pollution.

There are only limited data on the levels of PFOS and PFOA in drinking water. Detection has been mainly confined to pollution incidents, where there is evidence that local environmental water has been contaminated (USA, Germany, UK and Jersey), although data are limited for background levels. Even when groundwater contamination is severe, such as the case following the use of PFOS-containing fire-fighting foams following the Buncefield Oil Depot fire, the amount reaching surface waters and drinking water appears to be limited.
Early studies suggested that levels of PFOS and PFOA in source waters and drinking water were similar and that PFCs were not removed by water treatment, and this appears to be true for sand filtration and chlorination, and also for UV and hydrogen peroxide treatment. However, it now appears from recent careful studies in the UK and Germany that the use of GAC, with long EBCT and appropriate regeneration regimes to prevent breakthrough, is successful in removing both PFOS and PFOA. RO and NF are also successful in removing PFCs from water.

There is some evidence that PFOS levels in the human population may have decreased since the phase-out by 3M in 2000–2002 and that PFOA may also be following, as its use is now being voluntarily reduced. New PFCs are being introduced as replacements, such as perfluorobutane sulphonate (PFBS), which has a much shorter half-life (one month in humans) and is less toxic. The potassium salt of PFBS is more soluble than PFOS and so remains in the water column, but it is less toxic to aquatic organisms, and is persistent but not bioaccumulative (NICNAS 2005). So, while the alternatives may be less bioaccumulative and toxic, they may still be persistent in the environment. As a result, studies on their degradation products and their fate and behaviour will be required, together with their monitoring in environmental water.

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References


COT. 2005 The toxicology of the perfluoroalkyl acids—perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). TOX/2005/07, Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment, UK.


Tillett, T. 2007 (NIEHS News) Beyond the bench: research helps clean up a water supply. Environ. Health Perspect. 115, A134.
