Factsheet

<u>Chain of Contamination: The Food Link</u>

PERFLUORINATED CHEMICALS (PFCs) (INCL. PFOS & PFOA)

Background

Note: As information on many of the perfluorinated chemicals is limited, the content of this fact sheet is based mainly on information available for PFOS and PFOA.

PFOS (perfluorooctane sulfonate) and PFOA (perfluorooctanoate or perfluorooctanoic acid) are man-made perfluorinated chemicals (PFCs). PFCs are compounds characterised by chains of carbon atoms of varying lengths, to which fluorine atoms are strongly bonded (Boulanger, et al., 2005a, Dinglasan et al., 2004, Dinglasan-Panlilio & Mabury, 2006, Lehmler, 2005). PFOS and PFOA are both industrially synthesised chemicals, produced in large amounts, and can also be formed by the degradation (breakdown) of other perfluorinated precursor compounds (Lehmler, 2005, OECD, 2002, US EPA, 2003).

PFCs are heat stable, extremely resistant to degradation and environmental breakdown, and repel both water and oil (Dinglasan-Panlilio & Mabury, 2006, Lehmler, 2005, OECD, 2002). It is these properties that are exploited in their numerous different applications, which include the manufacture of non-stick coatings for kitchenware, stain and water repellent treatments for carpets, furniture and clothing, paper coatings, surfactants, pesticide formulations, fire-fighting foams, cleaning products, floor polishes, shampoo and food packaging materials (Boulanger et al., 2005a, Lehmler, 2005, OECD, 2002). Brand names of stain prevention or non stick treatments that are, or have been, associated with PFCs include: Teflon, Gore-tex, Stainmaster, Scotchgard, Guardsman, (EWG, 2006), although Scotchgard, for example, has now been reformulated to avoid these chemicals.

PFCs are persistent, bioaccumulative and toxic chemicals (Dinglasan et al., 2004). The properties that make PFCs so effective in their numerous applications are also those that result in their long-lived persistence in the environment (Lehmler, 2005, OECD, 2002, Prevedouros et al., 2006). Due to their resistance to photolysis, hydrolysis and biological breakdown (biodegradation) (OECD, 2002, US EPA, 2003), PFCs persist in the environment for long periods of time (years, decades), perhaps "forever" (EWG, 2006). Research has revealed that PFOS, PFOA (and other PFCs[1]) are now ubiquitous environmental contaminants (e.g. Boulanger et al, 2004, 2005a, Prevedouros et al., 2006, Sinclair et al., 2006, So et al., 2004, Yamashita et al., 2005) which are bioaccumulating in wildlife and humans all over the world (e.g. Giesy & Kannan, 2001, Inoue et al., 2004, Kannan et al., 2004, Martin et al, 2004a,b, Tomy et al., 2004).

PFCs have been detected in surface waters - lakes (Boulanger et al., 2004) and oceans (So et al., 2004, Yamashita et al., 2005) - sediments (Higgins et al., 2005), sewage sludge (Boulanger et al., 2005b), soil

[1] Other commercially used PFCs that can occur in the environment include perfluorooctanesulfonamide (PFOSA), perfluorohexanesulfonate (PFHS), perfluorobutanesulfonate (PFBS), and perfluorononanoic acid (PFNA) (So et al., 2004).

(Prevedouros et al., 2006), rainwater (Loewen et al., 2005) indoor and outdoor air (Shoieb et al., 2004, 2005, Stock et al., 2004) and household dust (Kubwabo et al., 2005, Moriwaki et al., 2003).

PFOS, PFOA and other PFCs have been detected in numerous and varied wildlife species from around the globe including polar bears in the Arctic (Smithwick et al., 2005), dolphins in the Mediterranean (Kannan et al., 2002a) and Florida (Houde et al., 2006), seals in the Baltic and Wadden Seas (Kannan et al., 2002a, Van de Vijver et al., 2005), sea turtles off the SE coast of the US (Keller et al., 2005), mink and river otters across the US (Kannan et al., 2002b), bald eagles from the mid western US and albatross from the mid-Pacific (Kannan et al, 2001), and wood mice from a Belgian nature reserve (Hoff et al., 2004). Levels of PFCs such as PFOS have also been shown to be increasing in wildlife species, particularly those from polar regions and northern latitudes (Bossi et al., 2005, Holmstrom et al., 2005, Smithwick et al., 2006).

PFOS, PFOA and other PFCs have been measured in human blood from countries across Europe, Asia and the USA (Calafat et al., 2006a,b, Falandysz et al., 2006, Fromme et al., 2006, Guruge et al., 2005, Kannan et al., 2004, Olsen et al., 2004, Taniyasu et al., 2003, Yeung et al., 2006). PFCs have also been found in umbilical cord blood (Inoue et al., 2004). Studies of archived human blood samples have also shown increasing levels of PFCs (PFOS, PFOA) over time (Harada et al., 2006, Olsen et al., 2005). PFCs, including PFOS and PFOA have also been found in human breast milk (So et al., 2005, 2006), although they do not seem to accumulate to the same extent as in serum (Kuklenyik et al., 2004), perhaps due to a preference for binding to protein rather than lipid (Jones et al., 2003). Estimates of the half-lives of PFOS and PFOA in serum vary, but are reported to be in the region of 4-8 years (Lehmler, 2005, OECD, 2002, US EPA, 2003). PFOA is also a "suggested carcinogen" according to the U.S. Environmental Protection Agency (EPA) (US EPA, 2005), although an expert panel advising the EPA recently concluded this should be strengthened to "likely human carcinogen" (EWG, 2006, US EPA, 2006).

Voluntary and legislative action on PFCs (and particularly PFOS and PFOA) is ongoing. Following intense regulatory pressure from the US EPA, PFOS, the active ingredient used for decades in the original formulation of 3M's popular Scotchgard™ products, was taken off the market in 2000 (EWG, 2006). Shortly thereafter, 3M also ceased manufacture of PFOA. This was due to grave concerns over the widespread distribution and persistence of PFOS, PFOA and other PFCs and their breakdown products in wildlife and humans. In December 2005 Dupont were fined U$16.5million for failing to report "substantial risk information" to the US EPA. The regulatory agency said that the company had known since 1981 and should have reported that the chemical PFOA builds up in the body and can be passed to foetuses in pregnant women. Information on the settlement can be found here http://www.epa.gov/compliance/resources/cases/civil/tsca/dupont121405.html. In January 2006, the US EPA invited PFC manufacturers to participate in a global stewardship program on PFOA, PFOA precursors, and related chemicals, asking them to commit towards eliminating these chemicals from emissions and products by 2015 (US EPA, 2006 - http://www.epa.gov/oppt/pfoa/). Signatories to this voluntary agreement included the companies Dupont, Solvay, 3M and Ciba Specialty Chemicals.

Regulatory pressure has also increased in Europe. In 2004, the UK signalled its intention to implement a unilateral legislative ban on some uses of PFOS (http://www.defra.gov.uk/news/2004/041019a.htm), which was then superseded by a proposal from the European Commission in December 2005, to ban PFOS in many applications including in the treatment of carpets, textiles, upholstery, leather, clothing, paper and packaging (UK, CSF, 2006). However, the Commission proposed exemptions for the following – critical applications in photolithography processes and photography, mist suppressants in cadmium plating, aviation hydraulic fluids and fire fighting foams. The UK Government considered that that these proposals did not go far enough (UK CSF, 2006), a view shared by WWF.

Other countries have also recognised the need for urgent action. For example, Norway and Sweden are taking action on PFOS and related compounds (SFT, 2005, KEMI, 2004) and the Canadian government (Environment Canada - EC) has also proposed regulations to ban four fluorotelomer polymers (Renner 2006a). Sweden has also proposed that PFOS should be put under global control and added to the list of persistent organic pollutants controlled under the UN Stockholm convention.

Major uses

PFCs are widely used as industrial surfactants and emulsifiers and their stain/water resistant properties have meant that they have found themselves employed in numerous consumer products. Non-stick pans, carpets, furniture, household cleaners, shampoos, shoes/clothing and convenience food packaging are just some of the products that can contain PFCs or are manufactured using them. A vast array of industrial products and processes also make use of the heat stable, non-stick properties of PFCs.

PFOS and PFOS related compounds have been in commercial use for approximately 50 years (Lehmler, 2005) in a wide range of applications in three broad categories - surface treatments, paper coatings and performance chemicals (OECD, 2002). Surface treatment applications provide soil, oil, and water resistance to clothing, carpets and furniture. PFOS-related chemicals are also used in consumer treatments for clothing, upholstery, carpet, and car interiors. Paper coatings include those for food packaging (containers, bags, and wraps). Other applications of PFOS chemicals include fire fighting foams, mining and oil well surfactants, acid mist suppressants for metal plating and electronic etching baths, photolithography, electronic chemicals, hydraulic fluid additives, alkaline cleaners, floor polishes, photographic film, denture cleaners, shampoos, chemical intermediates, coating additives and carpet spot cleaners, and insecticides (OECD, 2002). For example, PFOS containing fire-fighting foam was recently used to contain a large oil fire at Buncefield fuel depot in the UK, but the resulting firewater and oil was so contaminated with PFOS that it could not be released to wastewater treatment plants for fear of contamination of groundwater supplies (ENDS, 2006b). However, PFOS usage, particularly in consumer products, has been reduced in advance of impending regulatory action.

PFOA is primarily used as a reactive intermediate, while its salts are used as processing aids in the production of fluoropolymers, fluorotelomers and surfactants (US EPA, 2003, 2006). Fluorotelomer products are used to treat a variety of consumer articles (e.g., clothing and carpeting), primarily to impart stain and soil resistance, while fluoropolymers are films e.g. on nonstick cookware, or membranes (e.g. on waterproof, breathable clothing) (Washburn et al., 2005). While these materials may contain small amounts of PFOA as impurities from the manufacturing process, they are not PFOA itself. Fluoropolymers are also employed in hundreds of other uses in almost all industry segments, including the aerospace, automotive, building/construction, chemical processing, electrical and electronics, semiconductor, and textile industries (US EPA, 2006).

How do perfluorinated chemicals get into the environment (and food chain)?

There are numerous studies reporting the occurrence of PFCs in the environment, wildlife and humans (see above), but knowledge and understanding of the routes by which these contaminants enter the environment, and their fate and transport once in the environment, is still very limited. The process(es) by which breakdown products of PFCs, used as surfactants and coatings in consumer products, end up in human blood and wildlife in remote polar regions is a puzzle that is only now being slowly unravelled.

Direct emission or accidental escape of PFCs to the environment can occur during their manufacture and application to consumer articles (Prevedouros et al., 2006, Stock et al., 2004). Research has also suggested that residual, unwanted PFCs left over from the manufacture of fluorinated surfactants and polymers, remain in their industrial and consumer applications and escape during use to be broken down in the environment to compounds such as PFOS and PFOA (i.e. the leftover PFCs act as precursor compounds) (Dinglasan-Panlilio & Mabury, 2006). An important source of PFCs into the environment is thought to be the discharge of wastewater from sewage treatment works, as the cleaning and care of surface-treated products (from clothing to carpets) by consumers and use in industrial processes are believed to release these compounds to municipal wastewater treatment systems (Boulanger, 2005a, Higgins et al., 2005). PFCs can then enter the aquatic environment and find their way into aquatic food webs. Discarded consumer articles containing PFCs may also contribute PFCs to the environment by leaching from landfills (Boulanger, 2005a, Stock et al., 2004). Direct use of firefighting foams might also contribute PFCs to the environment (ENDS, 2006b, Prevedouros et al., 2006, Simcik & Dorweiler, 2005). Due to the presence of PFCs in sewage sludge, application of sludge to agricultural land could be a potential source of PFCs to the terrestrial environment i.e. soil (Higgins et al., 2005, Prevedouros et al., 2006). Precipitation of PFCs in rainwater may also contribute these compounds to soils, and it is thought that soil may be a very important environmental sink for PFCs (Renner et al, 2006b)

There still remains the question, however, of how PFCs such as PFOA and PFOS can be found in Arctic wildlife, when the properties of these chemicals suggest that they should not undergo long range transport to these remote ecosystems. It is theorized that the most significant source is the fluorotelomer alcohols (FTOHs) used to make stain-repellent coatings (see above). FTOHs are volatile compounds and when emitted from factories or consumer products, they undergo atmospheric transport from industrialised nations to cold northern latitudes and are broken down (oxidised) to form PFOA, PFO and related PFCs (Dinglasan et al., 2004, Ellis et al., 2004, Stock et al., 2004, Wallington et al., 2006).which are then precipitated (Loewen et al., 2005, Simcik & Dorweiler, 2005). Although it is estimated that atmospheric transport is the main mechanism, research also suggests that PFCs (the legacy of past releases) reside in the oceans and are transported by oceanic currents to the Arctic (Prevedouros et al., 2006).

How are people exposed to perfluorinated chemicals?

Although PFCs are being found consistently in studies of human blood, the routes of human exposure to PFCs are still not fully understood (US EPA, 2003, Calafat et al., 2006a, Lehmler, 2005).

The use of consumer articles containing PFCs have been suggested as potential routes (Kannan et al., 2004., Prevedouros et al., 2006), although more work is needed in this area. Kannan et al. (2004) state that "prolonged use of perfluorochemicals for a wide variety of applications, such as paper and packing products, residential and mill-applied carpet spraying, stain resistant textiles, and cleaners, may be a major source of human exposure to these compounds" and suggest the variation in the levels of PFOS in human blood seen in different countries is due to different patterns of use of consumer articles containing PFCs. For example, the use of carpets and fast food packaging is widespread in developed nations such as the United States, whereas it is minimal in India. The authors also suggest a specific route of exposure to PFOSA (perfluorooctanesulfonamide) from the use of N-ethyl perfluorooctanesulfonamide, commonly known as Sulfluramid, an insecticide used to control cockroaches, termites, and ants. PFOSA is one of the metabolic breakdown products of this chemical, so occurrence of PFOSA in serum samples may indicate recent exposure to it (Kannan et al., 2004).

Inhalation of indoor air and dust containing PFCs released from consumer products is another likely human exposure route (Shoieb et al., 2004, 2005, Kubwabo et al., 2005, Moriwaki et al., 2003, Kannan et al., 2004) particularly for infants and young children who tend to ingest more household dust than adults (Shoeib et al., 2005). Inhalation of precursor PFCs can lead to the formation of the highly persistent PFOS and PFOA via metabolic degradation. Recent research has also shown that greaseproof fast food packaging such as microwave popcorn bags and pizza boxes can be a source of human exposure to precursor fluorotelomers, which can then be slowly metabolized to compounds like PFOA (Begley et al., 2005, Renner, 2006c). PFOA itself has also been found on microwave popcorn bag paper (Begley et al., 2005). It appears that the use of non-stick pans is not a major route of exposure to PFCs (Renner, 2006c, Washburn et al., 2005) although residues of PFOA have been found on PTFE (Teflon™) coated cookware (Begley et al., 2005).

Perfluorinated chemicals in food

Information on levels of PFCs in food is limited (UK FSA, 2006, Gulkowska et al., 2006) but it is likely that diet is an important source of PFCs in humans. In addition to exposure via food packaging, the widespread contamination of the environment and food chain with PFCs (see above) means there is potential for human exposure to occur through the consumption of contaminated foodstuffs, particularly seafood (shellfish, marine and freshwater fish) (Falandysz et al., 2006, Lehmler, 2005) (see table 1). For example, in a study of Baltic fishermen, individuals who declared a high fish intake in their diet (mainly Baltic fish) contained the highest levels PFCs in their blood when compared with the other subpopulations (Falandysz et al., 2006). Levels of PFCs in breast milk (which is itself a vitally important food source for the developing infant) have been positively correlated with increased fish consumption (So et al., 2006). Exposure via contaminated drinking water is also a possibility (Harada et al., 2003).

Food item(s)	**Reference(s)**	**Comments**
Various (UK Total Diet samples incl. bread, vegetables, meat, eggs, milk, nuts, poultry, sugar)	Food Standards Agency UK (June 2006) – Fluorinated chemicals: UK dietary intakes http://www.food.gov.uk/science/surveillance/	PFOS, PFOA and related PFCs analysed in food groups from 2004 Total Diet Survey. PFOS found in potatoes, canned vegetables, eggs, sugars and preserves food groups. PFOA detected only in the potatoes group, which included fresh and processed products including chips, crisps etc. 10 different PFCs detected in potatoes. Other PFCs detected only occasionally.
Fish (cod) and Eider duck from the Baltic Sea	Falandysz J, et al. (2006). Environ Sci Technol., 40(3), pp748-51.	Baltic cod (*Gadus morhua*) and eider duck (*Sommateria mollisima*) were analysed with human blood samples for 10 PFCs. Residues of 9 of the 10 PFCs analysed were detected, including PFOA, PFOS, PFOSA, PFDA, PFNA.
Fish and shellfish (incl. fish, squid, crabs, lobster, shrimp, mussels, oysters)	Gulkowska et al. (2006). Environ Sci Technol., 40(12), pp3736-41.	Analysis of seafood collected from fish markets in two coastal cities of China for 9 PFCs, including PFOS, PFUnDA, PFDA, PFNA and PFOA. PFOS predominated and was found in all 27 seafood samples. Highest concentration of PFOS found in mantis shrimp.
Beef	Guruge et al., (2004). Organohalogen Compounds, 66, pp4029-4034.	Analysis of PFCs in beef cattle
Various (3M MultiCity study) incl. bread, ground beef, green beans, apples.	3M (2001). Analysis of PFOS, FOSA, PFOA from various food matrices… http://www.ewg.org/reports/pfcworld/pdf/food_full.pdf	Analysis of PFCs in food items from 6 US cities, 3 of which had fluorochemical plants (test cities) and 3 that did not (control cities). 8 of 12 samples containing PFCs were from test cities. PFOS found in 4 whole milk samples (3 tests) and ground beef sample (test). PFOA found in 2 ground beef (controls), 2 bread (1 test), 2 apple (test) and 1 green bean (test).

Table 1: Perfluorinated chemicals in food items – examples from the literature

What health effects are associated with exposure to perfluorinated chemicals?

The majority of the information on the toxicity of PFCs (mainly PFOS and PFOA) comes from animal studies and information on adverse health effects in humans is limited to a small number of occupational studies (Calafat et al, 2006a). For a brief overview of the toxic effects of PFOS and PFOA see Lehmler et al., (2005). Despite the limited number of human studies, there are serious health concerns over the widespread exposure of human populations to PFCs, especially considering their highly persistent and bioaccumulative nature and increasing evidence of their potential developmental effects (e.g. Lau et al., 2004).

Exposure to PFOS results in accumulation mostly in the serum and liver, causing hepatotoxicity (damage to the liver), the formation of adenomas (non cancerous tumours) in liver and thyroid tissues, decreases in serum cholesterol and lipid depletion in rodent and primate studies (OECD, 2002). Postnatal survival studies on rats have shown that *in utero* (during pregnancy) exposure to PFOS increases mortality in newborn pups and developmental effects are also reported in prenatal developmental toxicity studies in the rat and rabbit (OECD, 2002). Significant decreases in foetal body weight and significant increases in external and internal abnormalities have been observed in rats exposed *in utero* to PFOS (OECD, 2002).

These toxic effects have raised considerable concern, although it is presently unclear whether such findings are relevant to humans. Medical surveillance of fluorochemical production workers has not shown hepatotoxicity or substantial changes in serum cholesterol or lipoproteins, which are some of the toxic effects of PFCs seen in animals (Calafat et al., 2006a). However, mortality studies have shown increased risk of some cancers (neoplasms of the male reproductive system, bladder cancer) among fluorochemical production workers (OECD, 2002). Alterations in thyroid hormone levels have also been observed in workers occupationally exposed to PFOS (OECD, 2002), and altered thyroid hormone levels have also been reported in exposed monkeys, raising the tentative suggestion that thyroid disruption may be the critical effect of PFOS exposure (COT UK, 2006). The thyroid system is crucial for brain development and proper growth. PFOS (as well as PFOSA and PFHA - perfluorohexane sulfonic acid) has also been shown to inhibit gap junctional intercellular communication (GJIC) in cells, which is an important mechanism by which cells communicate with each other, and is thus important for normal cell growth and function (Hu et al., 2002).

Reliable data on the human health effects of exposure to PFOA are limited (US EPA, 2003). For example, a mortality study on workers at a 3M plant in the US indicate an increased prostate cancer risk that was significantly associated with the length of employment, i.e. of exposure to PFOA, but much more work is needed in this area to clarify such findings (Lehmler, 2005, US EPA, 2005). Rodent studies report reduced birth weight, increased postnatal mortality, delayed sexual maturation, hepatotoxicity and haematological (blood) effects in rats (US EPA, 2003, 2005). The developmental toxicity of PFOA is reviewed by Lau et al., (2004). There is evidence that PFOA is carcinogenic in rodents (see above), inducing tumours in the liver, Leydig cells (in the testis) and pancreas in male rats, but the relevance of this to humans in unclear (US EPA, 2005). PFOA also appears to be immunotoxic, at least in mice – dietary exposure to PFOA resulting in adverse affects on the thymus and spleen and suppressed immune responses (US EPA, 2005).

How can exposure to perfluorinated chemicals be reduced?

In light of the fact that human exposure routes to PFCs are still not fully understood, there are uncertainties inherent in any advice on avoiding exposure to these compounds. Avoiding the use of stain/waterproofing products to treat furniture, carpets, shoes and clothing could be one way to reduce exposure to perfluorinated precursor compounds that might ultimately degrade to compounds such as PFOS or PFOA. Asking retailers if their products have been treated with any waterproof or stainproof surfactants or coatings, and then avoiding such products that have been, is another possible way to reduce potential exposure.

Minimising convenience food and fast foods in the diet could also be an effective way to reduce PFC exposure (as well as exposure to other man-made compounds which can accumulate in fatty, animal derived foods) as these foods can be packaged in materials coated with PFCs (see above). Evidence for the migration of PFCs from non-stick cookware into food is limited (Begley et al., 2005), but it is reasonable to suggest that minimising the use of such items might help reduce any possible exposure. PFCs (and many other pollutants) can frequently be found as contaminants in fish and shellfish. The UK Food Standards Agency issues advice regarding the consumption of fish and other foods on the basis of their pollutant levels (www.food.gov.uk).

As PFCs can be found in household dust (along with other man-made chemicals such as phthalates and brominated flame retardants) regular vacuuming can help to keep dust levels, and any potential resulting inhalation, to a minimum. Regarding the use of personal care products (toiletries and cosmetics), it is difficult to avoid exposure to PFCs via these routes unless there are words such as "fluoro" or "perfluoro" listed on the ingredients.

Further information

http://www.ewg.org/reports/pfcworld/index.php
http://www.oecd.org/dataoecd/23/18/2382880.pdf
http://www.epa.gov/oppt/pfoa

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