

Historically, in Canada, the most significant imports of PFOS, itself, were in the form of the potassium salt, used for fire-fighting foams (Environment Canada, 2006). Canada has also identified that existing stocks of PFOS-containing fire fighting foams could be a continued significant source of releases.

An industry survey conducted in the US by the Fire Fighting Foam Coalition in 2004 reported that the total inventory of aqueous film-forming foam in the US was approximately 9.9 million gallons, of which about 45% was PFOS-based stocks produced before 2003, with the other 55% comprised of telomer-based foams.

Textile, Carpet and Leather Protection

PFOS-related substances have been used to provide soil, oil and water resistance to textiles, apparels, home furnishings and upholstery, carpets, and leather products. Since 3M's withdrawal from the market, PFOS-related substances are used to a much smaller extent for these applications (RPA AND BRE, 2004).

Paper and Packaging Protection

PFOS-related substances have been used in the packaging and paper industries in both food packaging and commercial applications to impart grease, oil and water resistance to paper, paperboard and packaging substrates. According to 3M, fluorochemicals were used for both food contact applications (plates, food containers, bags and wraps) and non-food applications (folding cartons, containers and carbonless forms and masking papers). Since 3M's withdrawal from the market, PFOS related substances are used to a much smaller extent for these applications (RPA and BRE, 2004).

Coatings and Coating Additives

3M indicates that prior to its voluntary phase-out of PFOS production, the company would sell fluorochemical polymer coatings and coating additives which were used undiluted or diluted with water or butyl acetate to impart soil or water repellence to surfaces (including printing circuit boards and photographic film) (RPA and BRE, 2004). These polymers contained fluorocarbon residuals at a concentration of 4% or less. Other applications for aqueous coatings are to protect tile, marble and concrete. It is unclear which of these products were actually based on PFOS-related substances.

A survey in the UK among members of the British Coatings Federation (BCF) showed that the use of PFOS-related substances for these purposes is very limited (RPA and BRE, 2004).

Industrial and Household Cleaning Products (Surfactants)

3M PFOS-based products were sold in the past to a variety of formulators to improve the wetting of water-based products marketed as alkaline cleaners, floor polishes (to improve wetting and levelling), denture cleansers and shampoos. Several of these products (alkaline cleaners, floor polishes, shampoos) were marketed to consumers; some products were also sold to janitorial and commercial services. A number of the alkaline cleaners were spray-applied.

With regard to the UK cleaning products industry, the responses received do not indicate the use of PFOS-related substances in industrial and household cleaning products. Based on information provided in product registers, the Swedish National Chemicals Inspectorate (KemI) has indicated that PFOS-related substances are still being used in Sweden for both industrial and household use (RPA and BRE, 2004).

Photographic Industry

PFOS-based chemicals are used for the following purposes in mixtures, in coatings applied to photographic films, papers, and printing plates (RPA and BRE, 2004):

- Surfactants
- Electrostatic charge control agents;

- Friction control agents;
- Dirt repellent agents; and
- Adhesion control agents

Photolithography and Semiconductors

Photoresist

Semiconductor manufacturing comprises up to 500 steps, of which there are four fundamental physical processes:

- Implant
- Deposition
- Etch
- Photolithography

Photolithography is the most important step towards the successful implementation of each of the other steps and, indeed, the overall process. It shapes and isolates the junctions and transistors; it defines the metallic interconnects; it delineates the electrical paths that form the transistors; and joins them together. Photolithography reportedly represents 150 of the total of 500 steps mentioned above. Photolithography is also integral to the miniaturization of semiconductors (RPA and BRE, 2004).

PFOS is used as a photoacid generator (PAG) in a mechanism called chemical amplification that increases the sensitivity of photoresist to allow etching images smaller than wavelength of light.

Antireflective Coatings

A number of resist suppliers sell antireflective coatings (ARC), subdivided into Top (TARC) and Bottom (BARC) coatings and used in combination with deep ultra violet (DUV) photoresist. The process involves placing a thin, top coating on the resist to reduce reflective light, in much the same way and for the same purposes that eyeglasses and camera lenses are coated.

Hydraulic Fluids for the Aviation Industry

Hydraulic fluids were initially used in aircraft to apply brake pressure. As larger and faster aircraft were designed, greater use of hydraulic fluids became necessary. An increase in the number of hydraulic fluid fires in the 1940s necessitated work towards developing fire resistant fluids. The first of these fluids was developed around 1948, when fire resistant hydraulic fluids based on phosphate ester chemistry were developed.

Perfluorinated anions act by altering the electrical potential at the metal surface, thereby preventing the electrochemical oxidation of the metal surface under high fluid flow conditions (RPA and BRE, 2004). As a result, hydraulic fluids based on phosphate ester technology and incorporating additives based on perfluorinated anions are used in all commercial aircraft, and in many military and general aviation aircraft throughout the world, as well as by every airframe manufacturer (RPA and BRE, 2004).

Metal Plating

The main uses of PFOS-related substances in metal plating are for chromium plating, and anodising and acid pickling. PFOS related substances lower the surface tension of the plating solution so that mist containing chromic acid from the plating activity is trapped in solution and is not released to air (RPA and BRE, 2004).

Other

There is information on other historical or current PFOS applications such as in pesticides, medical applications, mining and oil surfactants, flame retardants and in adhesives. Based on current understanding, these applications represent a minor part of known PFOS applications and are therefore not further elaborated in this profile.

2.1.3 Releases to the environment

There is to date very limited information regarding the emissions and pathways of PFOS to the environment. The occurrence of PFOS in the environment is a result of anthropogenic manufacturing and use, since PFOS is not a naturally occurring substance.

Releases of PFOS and its related substances are likely to occur during their whole life cycle. They can be released at their production, at their assembly into a commercial product, during the distribution and industrial or consumer use as well as from landfills and sewage treatment plants after the use of the products (3M, 2000).

Manufacturing processes constitute a major source of PFOS to the local environment. During these processes, volatile PFOS-related substances may be released to the atmosphere. PFOS and PFOS-related substances could also be released via sewage effluents (3M, 2000). High local emissions are indicated by one study that showed extremely high concentrations of PFOS in wood mice collected in the immediate vicinity to 3M's fluorochemical plant in Antwerpen, Belgium (Hoff et al., 2004). High concentrations of PFOS were also found in liver and blood from fish collected in the Mississippi River at the immediate vicinity of another 3M fluorochemical plant at Cottage Grove in Minnesota (MPCA, 2006).

Fire training areas have also been revealed to constitute a source of PFOS emissions due to the presence of PFOS in fire-fighting foams. High levels of PFOS have been detected in neighbouring wetlands of such an area in Sweden (Swedish EPA, 2004) as well as in groundwater in the US close to a fire-training area (Moody et al., 2003).

An investigation on the uses of PFOS and PFOS-related compounds in Norway in 2005 shows that approximately 90% of the total use is in fire extinguishers (Submission to SC, 2006). Estimated releases of PFOS related to fire extinguishers are at least 57 tonnes since 1980 to 2003 (2002; 13-15 tonnes). Remaining quantities of fire extinguisher foam in Norway are estimated to be a minimum of 1.4 million litres, which corresponds to an amount of approximately 22 tonnes PFOS. Releases from the municipal sector in Norway, 2002, were estimated to be 5-7 tonnes (Submission to SC, 2006).

The use of PFOS in semiconductors is estimated to result in a release of 43 kg per year in the EU, according to the Semiconductor Industry Association (SIA) (SIA, Submission to SC, 2006). This corresponds to 12 % of the total PFOS use in this application. PFOS released in the USA from semiconductors is estimated to be in the same range (SIA, 2006).

The releases of sulfonated perfluorochemicals, including PFOS or PFOS-related substances, from different product usages have been estimated (3M Speciality Materials, 2002). For example, garments treated with home-applied products, are expected to lose 73 % of the treatment during cleaning over a 2-year life span. A loss of 34 % to air is expected from spray can products during use, while up to 12.5 % of the original content may be remaining in the cans at the time of disposal.

One route for PFOS and PFOS-related substances to the environment may be through sewage treatment plants (STPs) and landfills, where elevated concentrations have been observed compared to background concentrations. Once released from STPs, PFOS will partially adsorb to sediment and organic matter. A substantial amount of PFOS may also end up in agricultural soil, due to the

application of sewage sludge. The primary compartments for PFOS are therefore believed to be water, sediment and soil (RIKZ, 2002).

Dispersion of PFOS in the environment is thought to occur through transport in surface water, or oceanic currents (Yamashita *et al.*, 2005, Caliebe *et al.*, 2004), transport in air (volatile PFOS-related substances), adsorption to particles (in water, sediment or air) and through living organisms (3M, 2003a).

One major obstacle when trying to estimate the releases of PFOS to the environment is that PFOS can be formed through degradation of PFOS-related substances. The rate and the extent of that formation are presently unknown. In a study on Swedish STPs, higher concentrations of PFOS were found in the effluents compared to incoming sewage water, which could indicate that PFOS was formed from PFOS-related substances (Posner and Järnberg, 2004).

2.2 Environmental fate

2.2.1 Persistence

PFOS is extremely persistent. It does not hydrolyse, photolyse or biodegrade in any environmental condition tested (OECD, 2002).

A study on the hydrolysis of PFOS in water has been performed following US-EPA OPPTS protocol 835.2210. The study was conducted at pH varying from 1.5 – 11.0 and at a temperature of 50°C, to facilitate hydrolysis, but did not indicate any degradation of PFOS. The half-life of PFOS was set to be greater than 41 years.

A study on the photolysis of PFOS in water following US-EPA OPPTS protocol 835.5270 has been conducted. No evidence of direct or indirect photolysis was observed under any of the conditions tested. The indirect photolytic half-life of PFOS at 25°C was calculated to be more than 3.7 years.

Biodegradation of PFOS has been evaluated in a variety of tests. Aerobic biodegradation of PFOS has been tested in activated sewage sludge, sediment cultures and soil cultures in several studies. Anaerobic biodegradation has been tested in sewage sludge. None of the studies demonstrated any signs of biodegradation.

Modelling with a simulator program of microbial degradation, the CATABOL system, and expert judgment predicted that of 171 studied perfluorinated substances over 99% would biodegrade to extremely persistent perfluorinated acids. Of them, 109 substances were predicted to end up as perfluorinated sulfonic acids, including PFOS, and 61 as perfluorinated carboxylic acids (Dimitrov *et al.*, 2004).

The only known condition whereby PFOS is degraded is through high temperature incineration under correct operating conditions (3M, 2003a). Potential degradation at low temperature incineration is unknown.

2.2.2 Bioaccumulation

It should be noted that PFOS does not follow the “classical” pattern of partitioning into fatty tissues followed by accumulation, which is typical of many persistent organic pollutants. This is because PFOS is both hydrophobic and lipophobic. Instead, PFOS binds preferentially to proteins in the plasma, such as albumin and β -lipoproteins (Kerstner-Wood *et al.*, 2003), and in the liver, such as liver fatty acid binding protein (L-FABP; Luebker *et al.*, 2002). Because of the unusual physical-chemical characteristics of PFOS, the mechanism of bioaccumulation probably differs from other POPs.

In a study following OECD protocol 305, the bioaccumulation of PFOS in bluegill sunfish (*Lepomis macrochirus*) has been tested. The whole-fish kinetic bioconcentration factor (BCFK) was determined to be 2796 (3M, 2002).

In another study on rainbow trout (*Oncorhynchus mykiss*), a bioconcentration factor (BCF) in liver and plasma was estimated to be 2900 and 3100, respectively (Martin, *et al.*, 2003).

When strictly looking at the BCF values, it is clear that these values are below the numeric BCF criteria in Stockholm Convention Annex D (the reported BCF values are below 5000) but, in this particular case, as noted above, the BCF numeric criteria may not adequately represent the bioaccumulation potential of the substance. Monitoring data from top predators at various locations show highly elevated levels of PFOS and demonstrate substantial bioaccumulation and biomagnification (BMF) properties of PFOS. It is notable that the concentrations of PFOS found in livers of Arctic polar bears exceed the concentrations of all other known individual organohalogenes (Martin *et al.*, 2004a). Based on the concentration of PFOS in predators (e.g., the polar bear) in relation to the concentration in their principal food (e.g., seals), hypothetical BMF values can be calculated. Such data are reported in Table 4. It should be noted that there are uncertainties in these comparisons. Even if either liver or blood concentrations are compared in two species, species differences in specific protein binding in that particular compartment may affect the concentration in the organ without having affected the whole-body concentration of the substance.

Table 4. Measured concentrations of PFOS in biota from various locations. Calculated BMF is shown where applicable.

Species and Location	Concentrations of PFOS	Reference
• Polar Bear, Canadian Arctic	<ul style="list-style-type: none"> - Concentrations of PFOS in liver (1700 – > 4000 ng/g) exceeding all other individual organohalogenes. - BMF > 160 based on concentrations in Arctic seals. 	Martin <i>et al.</i> , 2004a.
• Arctic fox, Canadian Arctic	<ul style="list-style-type: none"> - Very high concentrations of PFOS in liver (6.1 - 1400 ng/g) 	Martin <i>et al.</i> , 2004a.
• Mink, US	<ul style="list-style-type: none"> - Very high concentrations of PFOS in liver (40 - 4870 ng/g). - BMF = 22 based on data from fish in the same area. - nother mink study also show very high concentrations of PFOS in liver (1280 - 59 500 ng/g, mean 18 000 ng/g,) - BMF ~145 to ~4000 based on data from their prey such as crayfish (whole body), carp (muscle) and turtles (liver 	Giesy and Kannan, 2001 Kannan <i>et al.</i> , 2005

• Bald Eagle, US	- Very high concentrations of PFOS in plasma (1 – 2570 ng/g).	Giesy and Kannan 2001.
• Dolphin, US	- Very high concentrations of PFOS in liver (10 – 1520 ng/g).	3M, 2003a.
• Seal in the Bothnian Sea, Finland	- Very high concentrations of PFOS in liver (130 – 1100 ng/g). - BMF > 60 based on data from salmon in the same area.	Kannan et al., 2002

In a study by Kannan et al. (2005), the whole body BCF for round gobies (*Neogobius melanostomus*) was calculated to be approximately 2400, which is comparable with laboratory data. PFOS concentrations in fish (whole body of round gobies) compared to concentrations in liver of salmon results in BMFs of approximately 10-20. In bald eagles, the mean PFOS concentration in the livers, 400 ng/g ww, gives a BMF of four to five when compared to fish at higher trophic levels in the study. For mink, BMFs from 145 to 4000 can be calculated when based on the mean liver concentration, 18 000 ng/g ww, compared to their prey items such as crayfish (whole body), carp (muscles) and turtles (liver).

In general, data show that animals at higher trophic levels have higher concentrations of PFOS than animals at lower trophic levels, indicating that biomagnification is taking place. For instance, a trophic magnification factor (TMF) of 5,9 was calculated for PFOS based on a pelagic food web including: one invertebrate species, Mysis; two forage fish species, rainbow smelt and alewife; and a top predator fish species, lake trout. A diet-weighted bioaccumulation factor of approximately 3 was determined for the trout (Martin et al., (2004b).

Morikawa *et al.* (2005) showed a high bioaccumulation in turtles. Results from a study performed by Tomy *et al.* (2004a) indicated that PFOS biomagnified in an eastern Arctic marine food web (liver concentrations of PFOS were used for seabirds and marine mammals). Houde *et al.* (2006) showed PFOS biomagnification in the Atlantic Ocean bottlenose dolphin food web.

A study by Bossi *et al.* (2005a) further supports that biomagnification is taking place. In this study, a preliminary screening of PFOS and related compounds has been performed in liver samples of fish, birds and marine mammals from Greenland and the Faroe Islands. PFOS was the predominant fluorochemical in the biota analyzed, followed by perfluorooctane sulfonamide (PFOSA). The results from Greenland showed a biomagnification of PFOS along the marine food chain (shorthorn sculpin < ringed seal < polar bear).

It is assumed that the main and most relevant route of exposure to PFOS for birds is through the diet as biomagnification in bird tissues can occur this way. BMFs above one are reported for several bird species collected in the Gulf of Gdansk (Gulkowska *et al.* 2005). Kannan *et al.* (2005) reported a BMF of 10 to 20 in bald eagles (relative to prey items). Tomy *et al.* (2004a) calculated a trophic level BMF for black-legged kittiwake:cod of 5.1 and a BMF for glaucous gull:cod of 9.0. Newsted *et al.* (2005) indicated that PFOS has relatively shorter half-lives in blood and liver tissue in birds compared to mammals. For example, the estimated elimination half-life for PFOS from serum is 13.6 days in male mallards whereas in male rats, it is greater than 90 days. A recent study has suggested that PFOS is excreted relatively rapidly from birds (Kannan *et al.*, 2005). However, if birds are chronically exposed to PFOS in their diet, biomagnification can still occur.

Environmental monitoring of birds in northern parts of their range in fact indicates accumulation of PFOS.

The fact that PFOS binds to proteins leads to the relevant question -- *at what concentrations of PFOS will the binding sites on these proteins be saturated?* Serum albumin is most likely the binding pool of PFOS (Jones *et al.*, 2003) and several studies have been carried out with regard to bioconcentration in plasma. In Ankley *et al.* (2005), the bioconcentration in fish was studied at concentrations of PFOS in water up to 1 mg/L; the concentration of PFOS in water and plasma followed an almost linear relationship in the doses tested up to 0.3 mg/l without any signs of saturation (1 mg/l was not tested due to mortality at that dose). This is far above environmentally relevant concentrations.

In a study by 3M (2003a), the bioconcentration factor (BCF) in whole fish was determined to be approximately 2800 at a PFOS concentration of 86 µg/l, based on calculations of uptake and depuration of PFOS. Steady-state levels were attained after 49 days of exposure. Depuration occurred slowly and 50% clearance for whole fish tissues was estimated to be 152 days. Due to mortality, a BCF could not be calculated for the other concentration used, 870 µg/l. Thus, it is not likely that saturation of serum protein binding sites will limit the bioconcentration of PFOS in fish. In Cynomolgus monkeys, cumulative doses of PFOS (0,03, 0,15, or 0,75 mg/kg/day, orally, for 182 days) showed a linear increase in plasma at the low- and mid-dose groups while a nonlinear response was showed in the high-dose group (Covance Laboratories, Inc. 2002a). We are not aware of similar data in other mammals, but considering the high level of bioaccumulation observed in mammals, and that mammalian serum contains high concentrations of protein, binding sites are not likely to limit the bioaccumulation of PFOS in environmentally exposed mammals.

2.2.3 Long-range environmental transport

The potassium salt of PFOS has a measured vapour pressure of 3.31×10^{-4} Pa (OECD, 2002). Due to this vapour pressure and a low air-water partition coefficient ($< 2 \times 10^{-6}$), PFOS itself is not expected to volatilise significantly. It is therefore assumed to be transported in the atmosphere predominantly bound to particles, because of its surface-active properties, rather than in a gaseous state.

Some of the PFOS-related substances have a considerably higher vapour pressure than PFOS itself, and are as a result more likely to be volatile. The vapour pressures of precursors, such as N-EtFOSEA and N-MeFOSEA, may exceed 0.5 Pa (1000 times greater than that of PFOS) (Giesy and Kannan 2002). Other PFOS precursors considered volatile include N-EtFOSE alcohol, N-MeFOSE alcohol, N-MeFOSA and N-EtFOSA (3M, 2000). These precursors to PFOS could evaporate into the atmosphere and be more widely transported through air than is possible for PFOS itself. Once in the atmosphere, they can remain in gas phase, condense on particles present in the atmosphere and be carried or settle out with them, or be washed out with rain (3M, 2000). Martin *et al.* (2002) measured the air in Toronto and Long Point, Ontario, for some precursors of PFOS. They found an average N-MeFOSE alcohol concentration of 101 pg/m³ in Toronto and 35 pg/m³ at Long Point. The average concentrations of N-EtFOSE alcohol were 205 pg/m³ in Toronto and 76 pg/m³ in Long Point.

For precursors released to water, the vapour pressure may be significant enough to allow the substance to enter into the atmosphere. For N-EtFOSE alcohol, the tendency to leave the water phase is indicated by its relatively high Henry's law constant (1.9×10^3 Pa·m³·mol⁻¹) (Hekster *et al.* 2002). It has been reported that when these PFOS precursors are present as residuals in products, they could evaporate into the atmosphere when the products containing them are sprayed and dried (3M, 2000).

PFOS has been detected in rainwater from an urban center in Canada with a concentration of 0.59 ng/L. Whether or not PFOS originates from precursors either being transported and subsequently wet deposited and degraded to PFOS, or atmospherically degraded and then wet deposited, is unclear. Measurements of potential precursors for PFOS were not performed in this study (Loewen *et al.*, 2005)

The atmospheric half-life of PFOS is expected to be greater than two days. This statement, while not specifically tested, is based on the fact that PFOS has exhibited extreme resistance to degradation in all tests performed. However, an atmospheric half-life of 114 days has been calculated for PFOS using an AOP computer modeling program v1.91 (Environment Agency,, 2004). The indirect photolytic half-life of PFOS at 25°C has been estimated to be more than 3.7 years (OECD, 2002).

How perfluoroalkyl acid substances have come to be globally disseminated in the environment has been the key question, since, for example, the vapour pressure and Henry's law constant of PFOS indicates it is too involatile and therefore unlikely to enter directly into the atmosphere (Stock *et al.* 2004). Therefore it has been hypothesized that PFOS must be globally distributed via more volatile, neutral airborne contaminants that undergo long-range transport and then degrade to yield the free acids.

In support, Stock *et al.* (2004) have recently reported that polyfluorinated sulfonamides are widely distributed throughout the North American troposphere. Mean concentrations ranged from 22-403 pg/m³ with the dominant polyfluorinated contaminant dependent on the sampling location.

High mean concentrations of N-methyl perfluorooctane sulfonamidoethanol (NMeFOSE) of 359 pg/m³, were identified in the air of Griffin, Georgia. The authors speculate that, as Griffin is located in the midst of the main carpet manufacturing and treatment zone of the US, it probably is entering the environment from carpet treatment products, many of which consist of fluorinated molecules linked to polymeric materials. For example, it is possible that free chemical may be left in the carpet fibres, with publicly available information on 3M produced products indicating the concentration of free polyfluorinated sulfonamides is typically 1-2% or less. Alternatively, it is postulated that chemically bound NMeFOSE may also be released from carpets due to chemical, physical, and/or biological degradation processes.

Support for this hypothesis comes from Shoeib *et al.* (2004), who measured both NMeFOSE and the related N-ethyl perfluorooctane sulfonamidoethanol (NEtFOSE) in both indoor and outdoor air. Mean indoor air concentrations for these were 2590 and 770 pg/m³, respectively, and the ratios between indoor and outdoor air were 110 and 85, respectively. Again carpets were identified as a possible source of NMeFOSE, and high usage of paper in the building as a possible source of NEtFOSE. Paper products were also suggested by Stock *et al.* (2004) as a possible source for the high levels of NEtFOSE in the air of Reno, Nevada.

Recently Dinglasan-Panlilio and Maybury (2006) have demonstrated that residual fluorinated substances detected in materials, including 0.39% of a perfluoroalkyl sulfonamido alcohol present in a commercially available carpet protector product, are the likely sources for these volatile precursors. Further N-methyl perfluorobutane sulfonamidoethanol (NMeFBSE) has been demonstrated in the laboratory to degrade to perfluorobutane sulfonate (PFBS), albeit in low yield (D'eon *et al.*, 2006).

PFOS has been measured in a wide range of biota in the Northern Hemisphere such as the Canadian Arctic, Sweden, the US and the Netherlands. In a study by Martin *et al.* (2004a), the levels of PFOS were measured in liver samples from biota in the Canadian Arctic and were found in the vast majority of the species examined. The presence of PFOS in Arctic biota, far from anthropogenic sources, demonstrates the potential of PFOS for long-range transport. The mechanisms of this transport are not known, but it could be due to the transport of volatile PFOS-related substances that eventually degrade to PFOS.

While precursors will undergo degradation once released to the environment, transformation rates may vary widely. Precursors that reach a remote region through the atmosphere or other media may be subject to both abiotic and biotic degradation routes to PFOS (Giesy and Kannan 2002a; Hekster *et al.* 2002). The mechanisms of this degradation are not well understood. When rats metabolize N-MeFOSE-based compounds, several metabolites have been confirmed in tissue samples, including PFOS and N-MeFOSE alcohol (3M Environmental Laboratory 2001a, 2001b). PFOS appears to be the final product of rat and probably other vertebrate metabolism of POSF-based substances.

A recent study performed with rainbow trout (*Onchorhynchus mykiss*) liver microsomes has demonstrated that *N*-ethyl perfluorooctanesulfonamide (N-EtPFOSA) is a precursor of PFOS in fish (Tomy *et al.*, 2004b). These findings combined with the recent measurements of concentrations up to 92.8 ± 41.9 ng/g wet weight of N-EtPFOSA in aquatic organisms from Arctic regions (Tomy *et al.*, 2004a) strengthen the hypothesis that perfluorinated sulfonamides are one of the volatile precursors of PFOS transported over long distances to the Arctic. However, the hypothesis that these volatile precursors reach the Arctic latitudes by atmospheric transport has not yet been confirmed by atmospheric measurements (Bossi *et al.*, 2005b)

2.3 Exposure

2.3.1 Measured environmental levels

A screening study was assigned by the Swedish Environmental Protection Agency (Swedish EPA) and performed by ITM, Institute of Applied Environmental Research, on the levels of PFOS in the Swedish environment (Swedish EPA, 2004). The results showed highly elevated levels of PFOS in a wetland in the vicinity of a fire drill area with a declining gradient out in the adjacent bay (2.2 – 0.2 µg/L). Elevated levels were also detected outside sewage treatment plants (STPs) and landfills. Effluents from STPs contained levels of PFOS up to 0.020 µg/L and leachate levels from landfills were between 0.038 – 0.152 µg/L.

The occurrence of PFOS and other perfluoroalkyl sulfonate substances in open ocean waters such as the Atlantic and the Pacific Ocean have been investigated. The detection of PFOS in oceanic waters suggests another potential long-range transport mechanism to remote locations such as the Arctic. The results showed that PFOS is present in central to western Pacific Ocean regions in concentrations ranging from 15 – 56 pg/L, comparable to the concentrations in the mid-Atlantic ocean. These values appear to be the background values for remote marine waters far from local sources (Taniyasu *et al.*, 2004). PFOS was also detected in oceanic waters in several coastal seawaters from Asian countries (Japan, China, and Korea) at concentrations ranging from 1.1 - 57 700 pg.L⁻¹ (Jin *et al.*, 2004; Yamashita *et al.*, 2005). PFOS was also observed in the North Sea (estuary of the river Elbe, German Bight, southern and eastern North Sea) (Caliebe *et al.*, 2004).

In a study in cities across China, PFOS was detected in all water samples (surface and sea water, groundwater, municipal and industrial effluents and tap water), showing that PFOS pollution existed generally in water compartments in China. Concentrations were generally at levels of approximately 1 ng/L (Jin *et al.*, 2004).

Studies in the US have identified the presence of PFOS in surface water and sediment downstream of a production facility, as well as in wastewater treatment plant effluent, sewage sludge and landfill leachate at a number of urban centres in the US (3M Multi City study, reviewed in OECD (2002) and 3M (2003a). Four of the cities (Decatur (AL), Mobile, Columbus (GA), Pensacola) were cities that have manufacturing or industrial use of fluorochemicals; two of the cities (Cleveland (TN), Port St. Lucie) were control cities that do not have significant fluorochemical activities. The ranges of PFOS levels in these cities are provided in Table 5.

Table 5. Environmental Levels of PFOS in Six US Urban Centres in the US (from OECD, 2002)

Medium	Range of PFOS levels ($\mu\text{g/L}$ or $\mu\text{g/kg}$)
Municipal wastewater treatment plant effluent	0.041 - 5.29
Municipal wastewater treatment plant sludge	0.2 - 3.120 (dry weight)
Drinking water	ND - 0.063
Sediment	ND - 53.1 (dry weight)
Surface water	ND - 0.138
'Quiet' water	ND - 2.93

Note: ND: not detected

The control cities' samples generally inhabited the lower end of the above ranges, except for the municipal wastewater treatment plant effluent and sludge findings for one of the control cities (Cleveland), which were intermediate in their ranges, and the 'quiet' water samples at control city (Port St. Lucie), which were the highest. In Canada, suspended sediment samples were collected annually at Niagara-on-the-Lake in the Niagara River over a 22 year period (1980-2002). PFOS concentrations ranged from 5 to 1100 $\text{pg}\cdot\text{g}^{-1}$ (Furdui *et al.*, 2005). Preliminary findings suggest that PFOS concentrations increased during the study period from $< 400 \text{ pg}\cdot\text{g}^{-1}$ in the early 1980s to $> 1000 \text{ pg}\cdot\text{g}^{-1}$ in 2002.

Samples of effluent from fifteen representative industry sectors have been analysed for PFOS (Hohenblum *et al.*, 2003). The industry sectors were printing (1 site), electronics (3), leather, metals, paper (6), photographic and textiles (2). The PFOS levels ranged from 0-2.5 $\mu\text{g/L}$ (2.5 $\mu\text{g/L}$ for leather, 0.120 $\mu\text{g/l}$ for metal, 0.140-1.2 $\mu\text{g/l}$ at four paper sites, 1.2 $\mu\text{g/l}$ for photographic, not found in textiles or electronics).

Groundwater from below an air force base in Michigan, US, has been sampled (Moody *et al.*, 2003). Fire fighting foams containing PFOS had been used there in training exercises from the 1950s to 1993 when the base was decommissioned. The groundwater was found to contain PFOS, at levels from 4 - 110 $\mu\text{g/l}$.

Sixteen Great Lakes water samples (eight locations) were analysed for perfluorooctane surfactants. PFOS was present in all samples with a concentration range of 21-70 ng/L . Three PFOS precursors were also found in the water samples. N-EtFOSAA (4.2-11 ng/L) and PFOSA (0.6 -1.3 ng/L) were present in nearly all samples while PFOSulfinate was identified at six out of eight locations (2.2-17 ng/L) (Boulanger *et al.*, 2004). PFOS was detected in surface water as a result of a spill of fire-fighting foam from the Toronto International Airport into nearby Etobicoke Creek. Concentrations

of PFOS ranging from <0.017 to $2210 \mu\text{g}\cdot\text{L}^{-1}$ were detected in creek water samples over a 153-day sampling period. PFOS was not detected at the upstream sample site (Moody *et al.* 2003).

PFOS and related fluorochemicals have been detected in animals in a number of studies in a variety of locations around the globe. Generally, the highest concentrations are found in top predators in food chains containing fish. The highest North American or circumpolar concentration of PFOS in mammal tissue reported in the published literature is $59\,500 \mu\text{g}\cdot\text{kg}^{-1}$ ww in mink liver from USA (Kannan *et al.*, 2005a).

Martin *et al.* (2004a) measured the levels of PFOS in liver samples from biota in the Canadian Arctic. PFOS was found in the vast majority of the samples and higher levels were found in animals at the top of the food chain. The highest levels were found in polar bear, with a mean level of 3100 ng/g from seven animals (maximum value $> 4000 \text{ ng/g}$). The concentrations of PFOS in polar bear are 5-10 times higher than the concentration of all other perfluoroalkyl substances and were higher than any other previously reported concentrations of persistent organochlorine chemicals (e.g., PCBs, chlordane or hexachlorocyclohexane) in polar bear fat (Martin *et al.*, 2004a). PFOSA, a precursor to PFOS, was also found in most of the samples. The concentration of PFOSA was higher than that of PFOS in fish, but not in mammals. This could indicate that PFOSA has been metabolised to PFOS in mammals and the high concentrations may be the result of both direct exposure to PFOS and metabolism from PFOSA.

PFOS is found in birds worldwide. In North America, PFOS has been found in eagles in the Great Lakes, mallards in the Niagara River, loons in northern Quebec, gulls in the Arctic and in Canadian migratory species in the United States (e.g., common loon in North Carolina). In Canadian or Canada-US migratory species, concentrations have been measured in liver ranging from not detectable to 1780 ng/g for loon in northern Quebec and bald eagle in Michigan, in blood plasma ranging from <1 - 2220 ng/g blood plasma in bald eagles, and in eggs and egg yolk ranging from 21 - 220 ng/g in double-crested cormorant in Manitoba. In several monitoring studies, piscivorous water birds were found to have some of the highest liver and serum PFOS concentrations compared to other species (Newsted *et al.*, 2005). In a study of birds in the Niagara River Region, piscivorous birds (common merganser, bufflehead) contained significantly greater PFOS concentrations than non-piscivorous birds (Sinclair *et al.*, 2006). Preliminary data on temporal trends show an increase in bird PFOS concentrations, in two Canadian Arctic species (thick-billed murre and northern fulmars) from 1993 to 2004 (Butt *et al.*, 2005). It is noted that concentrations of PFOS in plasma have been reported in eagle, gulls and cormorants around the Great Lakes and in the Norwegian Arctic ranging from $<1 \text{ ng/g}$ to 2220 ng/g .

Kannan and Giesy (2002b) have summarised results of analyses on archived tissue samples. The tissues analysed came from marine mammals, birds, fish, reptiles and amphibians from around the world, including the Arctic and Antarctic Oceans. Samples collected in the 1990s were used. Around 1700 samples were analysed, with concentrations in liver, egg yolk, muscle or blood plasma determined. The detection limit varied from 1 ng/g to 35 ng/g wet weight. A summary of the results is shown in Table 6.

Table 6. Maximum concentrations of PFOS in various species as well as frequency of detection. Based on Kannan and Giesy (2002a)

Species	Maximum concentration (ng/g ww)	Frequency of detection
Marine mammals	1520	77%
Mink and otter	4900	100%
Birds	2570	60%
Fish	1000	38%

PFOS was detectable in most of the samples, including those from remote marine locations, at concentrations >1 ng/g. The authors compared the results from remote areas with those from more industrial locations and noted that PFOS is widely distributed in remote regions, including the Polar Regions, but that the levels found in more urban and industrial areas (e.g. the Baltic, Great Lakes) are several times higher. The tissues of fish-eating birds in Canada, Italy, Japan and Korea all contained detectable levels of PFOS, suggesting that they are exposed through the fish they consume. A summary of several studies is given in Table 7.

Table 7. Monitored levels of PFOS in animals (data from selected studies, based on OECD, 2002)

Description	Reference	Reported Highest Concentrations (Max, Mean)	Location
Global monitoring survey of marine mammals (Florida, California, Alaska, northern Baltic Sea, Mediterranean Sea, Arctic, Sable Island (Canada))	A	Bottlenose dolphin (liver, n = 26): Max: 1520 ng/g wet wt. Mean: 420 ng/g wet wt.	Florida
		Ringed seal (liver, n = 81): Max: 1100 ng/g wet wt. Mean: 240 ng/g wet wt.	Northern Baltic Sea
Survey of mammals, birds and fish in the Canadian Arctic	B	Polar bear (liver, n = 7): Max: > 4000 ng/g wet wt. Mean: 3100 ng/g wet wt.	Canadian Arctic