Addendum to the PFOS dossier
Room document prepared by Sweden

The addendum should be read in conjunction with the original dossier “PERFLUOROOCTANE SULFONATE (PFOS)”, prepared in support for a nomination of PFOS to the UN-ECE LRTAP Protocol and the Stockholm Convention, dated August 2004.

Introduction
This addendum contains an update of the scientific literature published during the period June 2004 to October 2005, and also includes a few studies missed in the original dossier. As PFOS as an environmental pollutant is a burning issue today, this update contains some 80 studies (see appendix), building up new knowledge regarding the POP-related properties of this substance/group of substances. The references are listed in order of decreasing importance, with the most important studies described in detail, and less important studies not described at all (but the full reference including the title is given).

The new studies reported herein support the previous conclusions in our PFOS dossier (August 2004) that PFOS fulfills all the POP-criteria. However, as PFOS not formally fulfills the BCF-criteria, while the new studies present further evidence of bioaccumulation, this update gives us a chance to further elaborate on the bioaccumulation properties of PFOS.

Bioaccumulation
Thus, although PFOS may not formally fulfill the BCF-criteria (the reported BCF-values are below 5000) all monitoring data published show that PFOS bioaccumulates in the food webs. However, because of the unusual physical-chemical characteristics of this substance, the mechanism of bioaccumulation probably differs from other POPs.

Thus, PFOS does not follow the “classical” pattern of partitioning into fatty tissues, but does instead bind 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).

The fact that PFOS does bind to proteins leads to the relevant question at what concentrations of PFOS the binding sites on these proteins will 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 concentration of PFOS in water up to 1 mg/L and where 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 another study, the bioconcentration factor (BCF) in whole fish was determined to approximately 2800 at a concentration of 86 µg/l based on calculations of uptake and depuration of PFOS (3M, 2003). Steady-state levels were attained after 49 days of exposure. Depuration occurred slowly and 50% clearance for whole fish tissues was estimated to 152 days. Due to mortality, 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. We are not aware of similar data in mammals, but considering the high level of bioaccumulation observed in mammals, and that mammalian serum contains high concentrations of protein, one may speculate that saturation of binding sites are not likely to limit the bioaccumulation of PFOS in mammals either.

In general, data show that animals at higher trophic levels have higher concentrations of PFOS than animals at lower trophic levels, displaying that biomagnification is taking place. At the time of writing the dossier, very limited data were available regarding BCFs based on non-laboratory studies, as well as on biomagnification factors (BMFs) in general. However, recently published monitoring studies provide complementary data.

In Kannan et al., 2005, the whole body-BCF for round gobies was calculated to approximately 2400, which is comparable with laboratory data. Concentrations in fish (whole body of round gobies, 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 Martin et al. (2004), a trophic magnification factor (TMF) of 5,9 was calculated for PFOS based on one invertebrate species, Mysis, two forage fish species, rainbow smelt and alewife and a top predator fish species, lake trout, from a pelagic food web. A diet weighted bioaccumulation factor of approximately 3 was determined for the trout.

Morikawa et al. (2005) shows a high bioaccumulation in turtles, and studies by Tomy et al. (2004) and Bossi et al. (2005) support that biomagnification is taking place.

**Conclusion**
In conclusion, the new data supports that PFOS fulfills all POP-criteria, including the bioaccumulation criteria.
APPENDIX

1. Supplementary references of interest but not previously cited in the PFOS-dossier

We appreciate the comments we have received that have made us aware of these studies.


  An article describing the global distribution of PFOS as tissue measurements of wildlife, including, fish, birds and marine mammals such as bald eagles, polar bears, albatrosses and seals. Samples were collected from urbanized areas in North America and Europe as well as from a number of more remote, less urbanized locations such as the Arctic and the North Pacific Oceans. The results demonstrated a widespread occurrence of PFOS in the environment and concentrations of PFOS in animals from relatively more populated and industrialized regions were greater than those in animals from remote marine locations. Fisheating, predatory animals such as mink and bald eagles contained concentrations of PFOS greater than the concentrations in their diets, suggesting that PFOS can bioaccumulate to higher trophic levels of the food chain.


  Tissue samples from 15 species of marine mammals collected from North American coastal waters; the northern Baltic Sea; the Arctic (Spitsbergen); and Sable Island in Canada were analyzed for PFOS. PFOS was detected in liver and blood of marine mammals from most locations. The greatest concentrations of PFOS found in liver and blood were 1520 ng/g wet wt in a bottlenose dolphin from Sarasota Bay, FL, and 475 ng/mL in a ringed seal from the northern Baltic Sea (Bothnian Sea), respectively. No age-dependent increase in PFOS concentrations in marine mammals was observed in the samples analyzed.


  PFOS was measured in samples of liver, kidney, blood, or egg yolk from 21 species of fish-eating water birds collected in the United States, including albatrosses from the central North Pacific Ocean. Concentrations of PFOS in the blood plasma of bald eagles ranged from 13 to 2220 ng/mL. Among the liver samples, Brandt’s cormorant contained the greatest concentration of PFOS (1780 ng/g, wet wt). PFOS was also found in the sera of albatrosses from the central North Pacific Ocean at concentrations ranging from 3 to 34 ng/mL.

An article describing temporal trends in the concentrations of PFOS and PFOA in the Baltic Sea marine environment, using archived guillemot eggs. Samples collected from Stora Karlso (Sweden) between 1968 and 2003 were received from an environmental specimen bank and concentrations of PFOS (and PFOA). There was an almost 30-fold increase in PFOS concentrations in the guillemot eggs during the time period, from 25 ng/g in 1968 to 614 ng/g in 2003 (wet weight). A significant trend, increasing on average between 7 and 11% per year was observed.


An article comparing isomer patterns of perfluorocarboxylates (PFCAs) in livers of polar bears in the Canadian Arctic with polar bears in eastern Greenland. The article does not concern PFOS


The kinetics of the reactions of Cl atoms and OH radicals with a series of fluorotelomer alcohols was studied. The conclusion was that the atmospheric lifetime is determined by reaction with OH radicals and is approximately 20 d. The article does not concern PFOS precursors.


PFOS (and PFOA) were evaluated for their toxicity to the aquatic midge, Chironomus tentans. A definitive 10-d assay with PFOS concentrations ranging from 1 to 150 µ/L produced an EC50 for growth of 87.2 µg/L. A chronic life-cycle test using a nominal concentration range of 1 to 100 µg/L showed that three of the four endpoints measured—survival, growth, and emergence—were significantly affected, with EC50 values of 92.2, 93.8, and 94.5 µg/L, respectively. Reproduction was not affected.


Groundwater from wells around a fire-training area at an airforce base were analysed for PFOS and other perfluorinated surfactants. The result showed that PFOS was still present in groundwater, at concentrations of 8 - 110 µg/l, five or more years after its last known use.


A field evaluation was conducted in outdoor microcosms to assess the toxicological risk associated with exposure to PFOS. A community-level NOEC of 3.0 mg/L was determined for the 35-day study. The persistence of PFOS was tested over 285 d in
microcosms under natural conditions. The study showed no drastic reduction in any treatment microcosm over the entire study period.


2. Recently published references (June 2004 to October 2005)

The references are listed in order of decreasing importance, with the most important studies described in detail, and less important studies not described at all (but the full reference including the title is given).


The trophic transfer of PFOS (and other perfluorinated compounds) was examined at three locations in the Great Lakes benthic food web. The levels examined included water-algae-mussels- goby- bass. PFOS (together with other perfluorinated compounds) was also measured in livers and eggs of salmon and lake whitefish as well as in muscle tissue of carp and eggs of trout. Also, frog livers, turtle plasma, mink livers and bald eagle tissues were analyzed to determine the concentrations in higher trophic-level organisms in the food chain.

The result showed that the bioconcentration factor (BCF) of PFOS was approximately 1000 in benthic invertebrates. A BCF of approximately 2400 was calculated in gobies, based on the water concentration of PFOS (3.5 ng/L) and their mean whole body PFOS concentration of 8.3 ng/g ww. (6.6 – 11.2, n = 3). This result is similar to results obtained in laboratory studies in e.g. rainbow trout (martin et al., 2003). The concentrations of PFOS in gobies were two- to fourfold higher that in their prey species, mussels and crayfish, suggesting a biomagnification factor (BMF) of two to four between these. Livers of salmon contained concentrations of PFOS approximately 10 to 20-fold higher compared to whole body concentrations of PFOS in gobies. For lake whitefish, concentrations of PFOS were higher in eggs than in livers showing maternal transfer of PFOS possibly via binding to egg albumin.

High concentrations of PFOS were found in top predators. The mean concentration of PFOS in liver from male mink was 18 000 ng/g ww. (1280 – 59 500, n = 7), giving BMFs from ~130 to ~7500 when compared to their prey items such as crayfish (whole body), carp (muscles) and turtles (liver). Among the mink liver samples, the highest concentration of PFOS reported so far for any aquatic species was measured, 59 500 ng/g.
The concentrations of PFOS in the livers of mink were $1 \times 10^6$ fold greater than the PFOS concentration in the water from that location. Plasma samples from turtles ranged from 105 to 169 ng/ml in males and from <1 to 8.8 ng/ml in females, suggesting oviparous transfer of PFOS similar to that of fish. Mean concentrations in bald eagles was 400 ng/g (26.5 – 1740 ng/g, n = 7) which is four- to fivefold greater than in several higher trophic-level fish in the study. Higher trophic-level organisms have a greater capacity to metabolize environmental contaminants than do lower trophic-level organism, which could lead to that some precursor molecules to PFOS, such as FOSA, may contribute to the body burden of PFOS in higher trophic-level organisms and thereby constitute a source of error for the estimation of BMF in the study.


The bioconcentration factor (BCF) of PFOS (and PFOA) was investigated in two species of turtles in the heavily PFOA-contaminated Ai river system in Japan. Water samples were collected at 10 locations (including reference sites) and plasma concentrations of PFOS were determined in turtles at the respective sites, from where a BCF could be calculated. The result showed that the BCF of PFOS varied from a factor of 8000 – 38000 with a geometrical mean of 11000. The water concentrations ranged from 2.9 – 37.1 ng/l and the mean plasma concentrations in turtles from each site varied between 25.1 – 398 µg/l.


PFOS (together with other perfluorinated compounds) was analysed in various organisms from a food web of Lake Ontario, Canada. The sampled organisms included a top predator fish, lake trout, three forage fish species including rainbow smelt, slimy sculpin and alewife and two invertebrates Diporeia and Mysis. High concentrations was detected in the benthic species Diporeia and sculpin suggesting that a major source of PFOS to the food web was the sediment, not the water. There was evidence for biomagnification among the pelagic fish species where the trophic magnification factors (TMF) was 5.88 for PFOS.by accounting for the known diet composition of lake trout, a bioaccumulation factor (BAF) of 2.9 was calculated. A portion of the increase may be due to metabolism of FOSA, which showed an overall decreasing trend with increasing trophic levels. Archived lake trout samples collected between 1980 and 2001 showed that mean whole body PFOS concentrations increased from 43 to 180 ng/g over this period, but not linearly, and may have been indirectly influenced by the invasion and proliferation of zebra mussels through effects on the population and ecology of forage fishes.

In this study, spatial and temporal trends in the concentrations of PFOS and other selected perfluorinated compounds (PFCs) were measured using archived liver samples of ringed seal from East and West Greenland. The samples were collected in four different years at each location, between 1986 and 2003 in East Greenland and between 1982 and 2003 in West Greenland. PFOS was the major contributor to the burden of PFCs in samples. Regression analysis of PFOS median concentrations indicated a significant temporal trend with increasing concentrations at both locations. PFOS concentrations in liver of ringed seals east Greenland showed an annual increase in median concentrations of 8.2% whereas seals from western Greenland showed an annual increase in median concentrations of 4.7%. A spatial trend in PFOS concentrations was observed between the two sampling locations, with significantly higher concentrations in seals from East Greenland.


An eastern Arctic marine food web was analyzed for PFOS and other perfluorinated compounds to examine the extent of bioaccumulation. PFOS was detected in all species analysed, and mean concentrations ranged from 0.28 ng/g wet wt in clams (whole body) to 20.2 ng/g wet wt in liver of glaucous gulls. A positive linear relationship was found between PFOS concentrations and trophic level, resulting in a trophic magnification factor of 3.1. TL-corrected biomagnification factor estimates for PFOS ranged from 0.4 to 9. The results indicate that PFOS biomagnifies in the Arctic marine food web when liver concentrations of PFOS are used for seabirds and marine mammals. Transformation of N-EtPFOSA and PFOSA and potential other perfluorinated compounds to PFOS may contribute to PFOS levels in marine mammals and may inflate estimated biomagnification values. The presence of perfluorinated compounds in seabirds and mammals provides evidence that trophic transfer is an important exposure route of these chemicals to Arctic biota.


PFOS and other perfluoralkylated substances were measured in hepatic tissue of polar bears collected in East Greenland, to compare with other populations and to examine effects of age and gender on concentrations of these contaminants. PFOS was the major contaminant and concentrations found in samples from East Greenland (mean = 2,470+/−1,320 ng/g wet weight) were similar to Hudson Bay, Canada. Both populations had significantly greater concentrations than those reported for Alaska, suggesting a spatial trend. Male bears showed a marginally significant increase in concentrations up to the age six.


Concentrations of PFOS and other perfluoroalkyl substances were determined in liver
tissues and blood of polar bears from five locations in the North American Arctic and two locations in the European Arctic. PFOS concentrations were significantly correlated with age at four of seven sampling locations, while gender was not correlated to concentration for any compound measured. Populations in South Hudson Bay (2000-2730 ng/g wet wt), East Greenland (911-2140 ng/g wet wt), and Svalbard (756-1290 ng/g wet wt) had significantly higher PFOS concentrations than western populations such as the Chukchi Sea (435-729 ng/g wet wt).


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). PFOS was found at concentrations above LOQ (10 ng/g wet weight) in 13 out of 16 samples from Greenland and in all samples from the Faroe Islands. The results from Greenland showed a biomagnification of PFOS along the marine food chain (shorthorn sculpin < ringed seal < polar bear). The greatest concentration of PFOS was found in liver of polar bear from east Greenland (mean: 1285 ng/g wet weight, n = 2). The geographical distribution of perfluorinated compounds in Greenland was similar to that of persistent organohalogenated compounds (OHCs), with the highest concentrations in east Greenland, indicating a similar geographical distribution to that of OHCs, with higher concentrations in east Greenland than in west Greenland.


The toxicity and bioconcentration of PFOS was assessed in the fathead minnow where sexually mature fish were exposed via the water to 0, 0.03, 0.1, 0.3 or 1 mg PFOS/l for 21 days. Effects on reproductive capacity and endocrinology were assessed as well as possible developmental effects. A concentration of 1 mg PFOS/L was lethal to adults within two weeks. The 21-d 50% effect concentration for effects on fecundity of the fish was 0.23 (0.19-0.25) mg PFOS/L. Adult fathead minnows readily accumulated PFOS from the water. The highest concentrations of PFOS were detected in blood, followed by liver and then gonad; for all tissues. Females accumulated higher concentrations than males.


Air-borne concentrations of PFOS (and PFOA) were evaluated in two Japanese cities, Oyamazaki (O) and Morioka (M). Air-dust particles were collected at several time-points on particle filters at sampling stations located 1,5 meter over ground level in the close vicinity of a road in the respective cities. Approximately 1400 m³ and 1000 m³ of air were collected at O and M sampling stations respectively, over a 24-hour period. The result
showed that the mean level of PFOS in air varied between 5.2 pg/m³ in O to 0.7 pg/m³ in M. The mean concentration of PFOS in dust was 72.2 ng/g in O. No distinction with regard to particle size was made.


A paper summarising the results from the Northern Contaminants Program from 1998 to 2003 with respect to terrestrial animals in the Canadian Arctic. PFOS was most abundant in arctic fox and least abundant in mink. However, no spatial or temporal trends regarding PFOS were mentioned in the paper.


A review summarising data generated on mercury and persistent organic pollutants (POPs) in Canadian Arctic marine biota since the first Canadian Arctic Contaminants Assessment Report (CACAR) was published in 1997. PFOS was found, but there is insufficient information to assess species differences, spatial patterns or food web dynamics.


A paper showing surface water concentrations of PFOS and other PFCs in urban surface waters with presumably both atmospheric and non-atmospheric sources, remote waters with only atmospheric sources and Lake Michigan. PFOS concentrations ranged from nondetect to 1.2 ng/L and from 2.4 to 47 ng/L in remote and urban surface waters, respectively. The authors conclude that the major source of PFOS was non-atmospheric.


Rainwater samples was collected in Winnipeg, Canada, and analysed for PFOS and other perfluorinated compounds (PFCs). PFOS was deposited in rainwater with a concentration of 0.59 ng/l. According to the authors it is unclear in the study whether the concentrations of PFOS were a result of precursors being transported and subsequently wet deposited followed by degradation to PFOS, or by atmospheric degradation of precursors followed by wet deposition.


• Verreault, Jonathan; Houde, Magali; Gabrielsen, Geir W.; Berger, Urs; Hauks, Marianne; Letcher, Robert J.; Muir, Derek C. G. Perfluorinated Alkyl Substances in Plasma, Liver, Brain, and Eggs of Glaucous Gulls (Larus hyperboreus) from the Norwegian Arctic. Environ Sci and Technol (2005), 39(19), 7439-7445.


• So MK, Taniyasu S, Lam PK, Zheng GJ, Giesy JP, Yamashita N. Alkaline Digestion and Solid Phase Extraction Method for Perfluorinated Compounds in Mussels and Oysters from South China and Japan. Arch Environ Contam Toxicol. 2005 Sep 16; [Epub ahead of print]


• Oakes KD, Sibley PK, Martin JW, MacLean DD, Solomon KR, Mabury SA, Van Der Kraak GJ. Short-term exposures of fish to perfluorooctane sulfonate: acute effects on fatty


Pelley J. Canada moves to eliminate PFOS stain repellents. Environ Sci Technol. 2004 Dec 1;38(23):452A.


Fricke, Marc; Lahl, Uwe. Risk evaluation of perfluorinated surfactants as a contribution to the current debate on the EU Commission's REACH document. Umweltwissenschaften und Schadstoff-Forschung (2005), 17(1), 36-49. General Review written in German.


• Guruge, Keerthi Siri; Taniyasu, Sachi; Miyazaki, Shigeru; Yamanaka, Noriko; Yamashita, Nobuyoshi. Age dependent accumulation of perfluorinated chemicals in beef cattles. Organohalogen Compounds (2004), 66 (Dioxin 2004).

• Van Wouwe, Nathalie; Covaci, Adrian; Kannan, Kurunthachalam; Gordon, John; Chu, Andrew; Eppe, Gauthier; De Pauw, Edwin; Goeyens, Leo. Levels of contamination for various pollutants present in Belgian human plasma. Organohalogen Compounds (2004), 66 (Dioxin 2004), 2784-2790.

• Kaerrman, Anna; van Bavel, Bert; Jaemberg, Ulf; Hardell, Lennart; Lindstroem, Gunilla. Levels of perfluoroalkylated compounds in whole blood from Sweden. Organohalogen Compounds (2004), 66(Dioxin 2004), 4008-4012.

• Yang, Jae-Ho; Kannan, Kurunthachalam; Kim, Sun-Young; Shin, Im-Hee. Levels of perfluorooctanesulfonate and related fluorochemicals in human blood from the general population of Korea. Organohalogen Compounds (2004), 66(Dioxin 2004), 3991-3995.

• Corsolini, Simonetta; Kannan, Kurunthachalam. Perfluorooctanesulfonate and related fluorochemicals in several organisms including humans from Italy. Organohalogen Compounds (2004), 66 (Dioxin 2004), 4029-4035.


