

ペルフルオロオクタンスルホン酸の危険性の概要

分解性	蓄積性	人健康影響	動植物への影響
<p>【生分解性】 活性汚泥、底質培養物、土壌培養物中での好氣的生分解試験及び下水汚泥での嫌氣的生分解試験では、分解の兆候はまったく示されなかった。</p> <p>【光分解性】 ・直接または間接光分解の証拠は見られなかった(EPA OPPTS プロトコル 835.5270)。 ・25°Cにおける間接光分解の半減期は3.7年以上と算出された。</p> <p>【加水分解性】 ・分解はまったく示されなかった(EPA OPPTS プロトコル 835.2210) ・半減期は41年以上とされた。</p> <p>※PFOSFは水中で速やかに加水分解されPFOSを生成する知見が別途得られている。</p>	<p>【BCF(経鰓的生物濃縮係数)】 ・ニジマス: BCF =2900(肝臓), 3100(血漿) ・丸ハゼ: BCF =約 2400(全魚体) ・ブルーギルサンフィッシュ: BCF_k =2796 ※上記の値は、POPs条約付属書Dの基準値(BCF<5000)以下であるが、PFOSの物性の一つである非脂肪組織中の蛋白質親和性を考慮すると、脂溶性物質を対象に設定されているBCF基準値のPFOSへの適用は不適切な可能性がある。</p> <p>【BMF(経口的生物濃縮係数)】 ・ミルク: BMF=22(魚中の濃度から推計) ・ホッキョクグマ: BMF>160(ホッキョクアザラシ中の濃度から推計) ※人為的発生源から最も遠く離れた北極圏の動物において高濃度のPFOSが検出されていることに留意。魚類・魚食性鳥類など食物連鎖上の低位種においてもPFOSが検出。また、ワシなど捕食生物種は、低位にある鳥類よりも高濃度のPFOSを蓄積することが認められている。このことは、PFOSの残留性と長期蓄積性によるものである。</p>	<p>【反復投与毒性】 アカゲザル(強制経口90日): 4.5mg/kg/dayで全数死亡、 0.5mg/kg/dayで消化管毒性(カリウム塩)</p> <p>ラット(経口90日): 18mg/kg/dayで全数死亡、6mg/kg/dayで半数死亡、 2mg/kg/dayで体重及び臓器重量変化(カリウム塩)</p> <p>カニクイサル(26週): LOEL 0.03mg/kg/day 主な毒性は、胸腺萎縮(♀)、HDL、コレステロール、T3低下</p> <p>ラット(混餌2年): 0.06(♂)、 0.07mg/kg/day(♀)で肝細胞の病理組織的变化</p> <p>【発生毒性】 ラット(二世経口): NOAEL: 0.1mg/kg/day 0.4mg/kg/dayでF1児体重増加量低下、 1.6mg/kg/dayでF1世代生存率低下、母体体重低下等(カリウム塩)</p> <p>ラット(♀): 妊娠17-20日目の 25mg/kgで全児死亡</p>	<p>【慢性毒性】 ユスリカ <i>Chironomus tentans</i> : 10dNOEC=0.0491 mg/L(成長・生存)</p>

・PFOS は疎水性・疎油性であるため POPs に特有な脂肪組織に蓄積するという典型的パターンに該当しない。また、PFOS は物理化学的特性が特異なため、生物蓄積のメカニズムは他の POPs と異なる。



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Geneva, 6–10 November 2006**

Report of the Persistent Organic Pollutants Review Committee on the work of its second meeting

Addendum

Risk profile on perfluorooctane sulfonate

At its second meeting, the Persistent Organic Pollutants Review Committee adopted the risk profile on perfluorooctane sulfonate, on the basis of the draft contained in document UNEP/POPS/POPRC.2/11. The text of the risk profile, as amended, is provided below. It has not been formally edited.

PERFLUOROOCCTANE SULFONATE

RISK PROFILE

Adopted by the Persistent Organic Pollutants Review Committee
at its second meeting

November 2006

CONTENTS

1 INTRODUCTION	4
1.1 Chemical identity of the proposed substance.....	4
1.2 Conclusion of the POP Review Committee on Annex D information	6
1.3 Data sources	7
1.4 Summary of assessment and management under other programs	7
1.5 Status of the chemical under international conventions	8
2 SUMMARY INFORMATION RELEVANT FOR THE RISK PROFILE.....	8
2.1 Sources.....	8
2.1.1 Production and trade	8
2.1.2 Uses.....	9
2.1.3 Releases to the environment	13
2.2 Environmental fate.....	14
2.2.1 Persistence.....	14
2.2.2 Bioaccumulation	14
2.2.3 Long-range environmental transport.....	17
2.3 Exposure	17
2.3.1 Measured environmental levels	18
2.3.2 Bioavailability.....	24
2.4 Hazard assessment for endpoints of concern.....	25
2.4.1 Mammalian toxicity	25
2.4.2 Ecotoxicity	26
3 SYNTHESIS OF THE INFORMATION.....	27
4 CONCLUDING STATEMENT	29
References:.....	30

EXECUTIVE SUMMARY

1 INTRODUCTION

1.1 Chemical Identity of the proposed substance

On July 14, 2005, the government of Sweden made a proposal for listing perfluorooctane sulfonate (PFOS) and 96 PFOS-related substances in Annex A of the Stockholm Convention on Persistent Organic Pollutants (POPs).

Chemical name: Perfluorooctane Sulfonate (PFOS)

Molecular formula: $C_8F_{17}SO_3^-$

PFOS, as an anion, does not have a specific CAS number. The parent sulfonic acid has a recognised CAS number (CAS No. 1763-23-1). Some examples of its commercially important salts are listed below:

Potassium salt (CAS No. 2795-39-3)

Diethanolamine salt (CAS No. 70225-14-8)

Ammonium salt (CAS No. 29081-56-9)

Lithium salt (CAS No. 29457-72-5)

Structural formula:

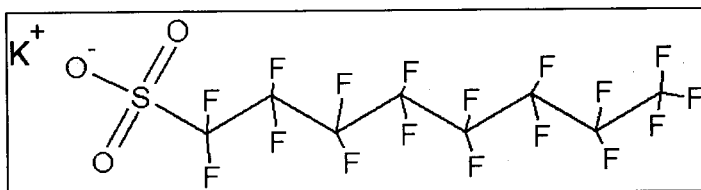


Figure 1. Structural formula of PFOS shown as its potassium salt

PFOS is a fully fluorinated anion, which is commonly used as a salt or incorporated into larger polymers. PFOS and its closely related compounds, which contain PFOS impurities or substances which can give rise to PFOS, are members of the large family of perfluoroalkyl sulfonate substances. In its regulatory measures on PFOS, the EU has addressed all molecules having the following molecular formula: $C_8F_{17}SO_2Y$, where $Y = OH$, metal or other salt, halide, amide and other derivatives including polymers (European Union 2006).

The physical and chemical properties of the potassium salt of PFOS are listed in Table 2.

Table 2. Physical and chemical properties of PFOS potassium salt.
(Data from OECD, 2002, unless otherwise noted).

Property	Value
Appearance at normal temperature and pressure	White powder
Molecular weight	538 g/mol
Vapour Pressure	$3,31 \times 10^{-4}$ Pa
Water solubility in pure water	519 mg/L ($20 \pm 0,5^{\circ}\text{C}$) 680 mg/L ($24 - 25^{\circ}\text{C}$)
Melting point	> 400°C
Boiling point	Not measurable
Log K_{ow}	Not measurable
Air-water partition coefficient	$< 2 \times 10^{-6}$ (3M, 2003a)
Henry's Law Constant	$3,09 \times 10^{-9}$ atm m^3/mol pure water

PFOS can be formed (by environmental microbial degradation or by metabolism in larger organisms) from PFOS-related substances, i.e., molecules containing the PFOS-moiety depicted in Figure 1. Although the ultimate net contribution of individual PFOS-related substances to the environmental loadings of PFOS cannot be predicted readily, there is a potential that any molecule containing the PFOS moiety could be a precursor to PFOS.

The majority of PFOS-related substances are polymers of high molecular weights in which PFOS is only a fraction of the polymer and final product (OECD, 2002). PFOS-related substances have been defined somewhat differently in different contexts and there are currently a number of lists of PFOS-related substances (Table 3). The lists contain varying numbers of PFOS-related substances that are thought to have the potential to break down to PFOS. The lists overlap to varying extents depending on the substances under consideration and the overlap between national lists of existing chemicals.

Table 3. Number of PFOS-related substances as proposed by UK – DEFRA, US – EPA, OECD, OSPAR, and Canada

Source	Number of PFOS-related substances
RPA and BRE (2004)	96
US - EPA (2002, 2006)	88 ¹ + 183 ¹
OECD (2002)	172 ¹ (22 classes of perfluoroalkyl sulfonate substances)
OSPAR (2002)	48
Environment Canada (2006)	57

¹ Perfluorinated substances with different carbon chain lengths are included in the list.

A large number of substances may give rise to PFOS and thus contribute to the contamination problem. DEFRA in the United Kingdom (RPA and BRE, 2004) has recently proposed a list of 96 PFOS-related substances. However, the properties of the 96 substances have not generally been determined. According to 3M (submission to the secretariat of Stockholm Convention (SC), 2006), they may have very different environmental characteristics such as solubility, stability and ability to be absorbed or metabolised. Nevertheless, the document by the United Kingdom infers that all of these substances would give rise to the final degradation product of PFOS (RPA and BRE, 2004).

Environment Canada's ecological risk assessment defines PFOS precursors as substances containing the perfluorooctylsulfonyl ($C_8F_{17}SO_2$, $C_8F_{17}SO_3$, or $C_8F_{17}SO_2N$) moiety that have the potential to transform or degrade to PFOS (Environment Canada, 2006). The term "precursor" applies to, but is not limited to, some 51 substances identified in the ecological assessment. However, this list is not considered exhaustive, as there may be other perfluorinated alkyl compounds that are also PFOS precursors. This information was compiled based on a survey to industry, expert judgement and CATABOL modelling, in which 256 perfluorinated alkyl compounds were examined to determine whether non-fluorinated components of each substance were expected to degrade chemically and/or biochemically and whether the final perfluorinated degradation product was predicted to be PFOS. While the assessment did not consider the additive effects of PFOS and its precursors, it is recognized that the precursors to PFOS contribute to the ultimate environmental loading of PFOS. Precursors may also play a key role in the long-range transport and subsequent degradation to PFOS in remote areas, such as the Canadian Arctic.

1.2 Conclusion of the POP Review Committee on Annex D information

The Persistent Organic Pollutants Review Committee (POPRC) evaluated Annex D information at the First meeting of the POPRC, Geneva, 7-11 November 2005, and concluded that PFOS information meets the screening criteria specified in Annex D (decision POPRC-1/7: Perfluorooctane sulfonate).

1.3 Data sources

This document on PFOS mainly builds on information that has been gathered in the hazard assessment report prepared by the UK and the USA for the OECD, and in the UK risk reduction strategy:

OECD (2002) Co-operation on Existing Chemicals - Hazard Assessment of Perfluorooctane Sulfonate and its Salts, Environment Directorate Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology, Organisation for Economic Co-operation and Development, Paris, 21 November 2002.

RPA AND BRE (2004) Perfluorooctane Sulfonate – Risk reduction strategy and analysis of advantages and drawbacks, Final Report prepared for Department for Environment, Food and Rural Affairs and the Environment Agency for England and Wales.

Recent relevant information from the open scientific literature (up to May 2006) is also included. Data submitted by Parties and observers, which have been considered, are also included in this report when they add new information.

1.4 Summary of assessment and management under other programs

The hazard assessment of PFOS, prepared by the OECD in 2002, concluded that the presence and the persistence of PFOS in the environment, as well as its toxicity and bioaccumulation potential, indicate a cause of concern for the environment and human health.

An environmental risk assessment, prepared by the UK-Environment Agency, and discussed by the EU member states under the umbrella of the existing substances regulation (ESR DIR 793/93) shows that PFOS is of concern.

The final Environment Canada/Health Canada assessments of PFOS, its salts and its precursors were released in July 2006. The ecological risk assessment has concluded that PFOS and its salts are persistent and bioaccumulative, and that PFOS, its salts and its precursors have immediate or long-term harmful effects on the environment (Environment Canada, 2006).

The EU has recently decided on restrictions on the marketing and use of PFOS (European Union, 2006). The measures cover PFOS acid, its salts and PFOS derivatives, including PFOS polymers. The decision prohibits the placing on the market and use of these compounds as a substance or constituent of preparations in a concentration equal to or higher than 0,005% by mass. Furthermore, semi-finished products and articles, containing PFOS more than 0,1% by mass are prohibited. Some derogations are, however, granted in the decision. These include certain uses in photolithography processes, in photographic coatings and in metal plating, hydraulic fluids for aviation and fire fighting foams that have already been placed on the market.

The UK and Sweden have proposed the following classification for PFOS in EU (2005):

T Toxic

R40 Carcinogen category 3; limited evidence of carcinogenic effect

R48/25 Toxic; danger of serious damage to health by prolonged exposure if swallowed

R61 May cause harm to the unborn child

R51/53 Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment has.

Norway is now considering a proposal to prohibit the use of fire fighting foams containing PFOS and PFOS-related compounds, which is the major use of these compounds today in Norway.

The Environmental Protection Agency (EPA) in the USA finalized two Significant New Use Rules (SNURs) in 2002, requiring companies to inform the EPA before manufacturing or importing 88 listed PFOS-related substances. The EPA proposed an additional SNUR under section 5(a)(2) of the Toxic Substances Control Act (TSCA) in March 2006 to include within the scope of this regulation another 183 perfluoroalkyl sulfonates with carbon chain lengths of five carbons and higher. The EPA further proposed an amendment to the Polymer Exemption rule in March 2006 which would remove from exemption polymers containing certain perfluoroalkyl moieties consisting of CF₃- or longer chains, and would require that new chemical notifications be submitted on such polymers.

1.5 Status of the chemical under international conventions

OSPAR: PFOS was added to the list of Chemicals for Priority Action in June 2003.

Persistent Organic Pollutants Protocol to the Long-Range Transboundary Air Pollution Convention ("LRTAP"): The Executive Body of the UNECE LRTAP Convention agreed that PFOS be considered a POP as defined under the Protocol on POPs and requested that the UNECE Task Force on POPs continue with the review of the substance and exploring management strategies.

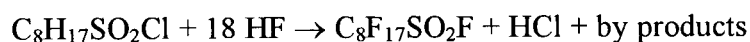
2 SUMMARY INFORMATION RELEVANT FOR THE RISK PROFILE

2.1 Sources

2.1.1 Production and trade

The main production process of PFOS and PFOS-related substances is electro-chemical fluorination (ECF), utilized by 3M, the major global producer of PFOS and PFOS-related substances prior to 2000.

Direct fluorination, electro-chemical fluorination (ECF):



The reaction product, perfluorooctanesulfonyl fluoride (PFOSF)¹ is the primary intermediate for synthesis of PFOS and PFOS-related substances. The ECF method results in a mixture of isomers and homologues with about 35-40% 8-carbon straight chain PFOSF. However, the commercial PFOSF products were a mixture of approximately 70% linear and 30% branched PFOSF derivative impurities. The global production of PFOSF by 3M until the production ceased is estimated to have been 13,670 metric tonnes (1985 to 2002), with the largest yearly production volume, 3700 metric tonnes of PFOS and PFOS related substances, in 2000 (3M, Submission to SC, 2006). PFOSF may be further reacted with methyl- or ethylamine to form *N*-ethyl- and *N*-methyl perfluorooctane sulfamide and subsequently with ethylene carbonate resulting in *N*-ethyl- and -methyl-perfluorooctane sulfamidoethanol (*N*-EtFOSE and *N*-MeFOSE). *N*-EtFOSE and *N*-MeFOSE were the principal building blocks of 3M's product lines. PFOS is formed after the chemical or enzymatic hydrolysis of PFOSF (3M, 1999).

Other production methods for perfluoroalkylated substances are telomerisation and oligomerisation. However, to which extent these methods are applied for production of PFOS and PFOS-related substances is not evident.

¹ In the OECD report, 2002, perfluorooctanesulfonyl fluoride is abbreviated POSF.

On 16 May 2000, 3M announced that the company would phase-out the manufacture of PFOS and PFOS-related substances voluntarily from 2001 onwards. By the end of 2000, about 90 % of 3M's production of these substances had stopped and in the beginning of 2003 the production ceased completely.

3M's voluntary phase-out of PFOS production has led to a reduction in the use of PFOS-related substances. This is due not only to the limited availability of these substances (3M had at the time the greatest production capacity of PFOS-related substances in the world), but also to action within the relevant industry sectors to decrease companies' dependence on these substances.

The US Environmental Protection Agency (US EPA) compiled a list of non-US companies which are believed to supply PFOS-related substances to the global market. Of these (and excluding the plant of 3M in Belgium), six plants are located in Europe, six are located in Asia (of which four are in Japan) and one in Latin America (OECD, 2002). However, this list may not be exhaustive or current.

According to the recent submission from Japan to the secretariat of the Stockholm Convention, 2006, there is one manufacturer in Japan still producing PFOS and with a production amount of 1-10 tonnes (2005). The submission from Brazil states that lithium salt of PFOS is produced but that no quantitative data is available.

2.1.2 Uses

Perfluorinated substances with long carbon chains, including PFOS, are both lipid-repellent and water-repellent. Therefore, the PFOS-related substances are used as surface-active agents in different applications. The extreme persistence of these substances makes them suitable for high temperature applications and for applications in contact with strong acids or bases. It is the very strong carbon-fluorine binding property that causes the persistence of perfluorinated substances.

The historical use of PFOS-related substances in the following applications has been confirmed in the US and the EU.

- Fire fighting foams
- Carpets
- Leather/apparel
- Textiles/upholstery
- Paper and packaging
- Coatings and coating additives
- Industrial and household cleaning products
- Pesticides and insecticides

In the UK study (RPA and BRE, 2004), detailed information has been received from the following sectors that currently use PFOS-related substances:

- Use of existing fire fighting foam stock
- Photographic industry
- Photolithography and semiconductor
- Hydraulic fluids
- Metal plating

The sectors presented above account for the UK but are considered to be representative for EU. However, deviation in the current use pattern between EU countries cannot be excluded.

PFOS and its precursors are not manufactured in Canada but rather are imported as chemicals or products for Canadian uses. They may also be components in imported manufactured articles. It is estimated that the majority of PFOS has been used as water, oil, soil and grease repellents (e.g. on fabric, leather, paper, packaging, rugs and carpets) and as surfactants (e.g. in fire fighting foams and coating additives) (Environment Canada, 2006).

PFOS and its precursors are not manufactured in the US, but can be imported either as chemicals or in products for the specific limited uses that were excluded from regulation. These comprise use as an anti-erosion additive in aviation hydraulic fluids; use as a component of a photoresist substance, including a photo acid generator or surfactant, or as a component of an anti-reflective coating, used in a photomicrolithography process to produce semiconductors or similar components of electronic or other miniaturized devices; use in coatings for surface tension, static discharge, and adhesion control for analog and digital imaging films, papers, and printing plates, or as a surfactant in mixtures used to process imaging films; and use as an intermediate only to produce other chemical substances to be used solely for these uses. Historically, PFOS and its precursors were also used as surfactants in fire fighting foams and in industrial and household cleaning products; in carpet, textile, leather, and paper coatings; and in termite and ant bait insecticide products. Stocks of PFOS and PFOS-containing products that were in existence at the time the US regulations were promulgated in 2002 could continue to be used in any application until they were consumed without violating the regulation, except that the PFOS-related insecticide products are subject to a phase-out agreement prohibiting their use after 2015.

The table below outlines the estimated current demand for PFOS-related substances in these applications in the EU (RPA and BRE, 2004).

Estimated Current (2004) Demand for PFOS Related Substances in the EU	
Industry Sector	Quantity (kg/year)
Photographic industry	1,000
Photolithographic and semi-conductors	470
Hydraulic fluids	730
Metal plating	10,000

In the survey on production and use of PFOS and related substances performed by OECD in 2004 (published 2005), data concerning PFOS were difficult to separate from data on other perfluoroalkyl sulfonates.

Fire Fighting Foams

The fire fighting foams can be grouped in two main categories:

- Fluorine-containing foam types (some of them consist of PFOS-related substances)
- Fluorine-free foam types

Since the announcement of the voluntary cessation of production of PFOS-related substances by 3M, the presence of PFOS in fire fighting foams has gradually decreased (RPA and BRE, 2004).