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# > Substance flow analysis for Switzerland

*Perfluorinated surfactants perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA)*

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# > Abstracts

A substance flow analysis was carried out for the perfluorinated surfactants perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) for Switzerland for the year 2007. Both substances are chemicals with several unique properties making them beneficial for many applications on one hand, but on the other hand pollutants that are persistent in the environment. The use of PFOS has been restricted in the EU, whereas the industry has agreed to reduce the residual contents of PFOA in products. The substance flow analysis serves a valuable base for the definition of risk reduction measures. The results will also allow the control of the efficiency of measures taken in the future.

Keywords:
Chemicals,
substance flow analysis,
perfluorinated surfactants,
perfluorooctanesulfonate,
perfluorooctanoic acid,
PFOS, PFOA

Für die perfluorierten Tenside Perfluoroctansulfonat (PFOS) und Perfluoroctansäure (PFOA) wurde eine Stoffflussanalyse mit Systemgrenze Schweiz für das Jahr 2007 durchgeführt. Bei den beiden Substanzen handelt es sich einerseits um Chemikalien mit etlichen hervorragenden Eigenschaften für viele technische Anwendungen, aber andererseits um in der Umwelt persistente Schadstoffe. Der Einsatz von PFOS wurde in der EU bereits stark eingeschränkt, während sich die Industrie auf freiwilliger Basis verpflichtet hat, die Gehalte von PFOA in Produkten zu senken. Die Stoffflussanalyse schafft eine Grundlage, auf deren Basis Risikoreduktionsmassnahmen getroffen werden können. Anhand der Resultate wird später eine Erfolgskontrolle von allfälligen Massnahmen möglich sein.

Stichwörter:
Chemikalien, Stoffflussanalyse,
perfluorierte Tenside,
Perfluoroctansulfonat,
Perfluoroctansäure,
PFT, PFOS, PFOA

La Suisse a conduit une analyse des flux de substances pour 2007, portant sur deux agents tensioactifs perfluorés, le sulfonate de perfluorooctane (SPFO) et sur l’acide perfluorooctanoïque (APFO). Il s’agit dans les deux cas de produits chimiques ayant des propriétés idéales pour de multiples applications techniques, mais aussi de polluants organiques persistants. L’utilisation du SPFO est déjà soumise à des restrictions sévères dans l’Union européenne tandis que l’industrie s’est engagée à limiter volontairement la teneur des produits en APFO. L’analyse des flux de substances fournit les éléments nécessaires pour prendre des mesures de réduction des risques. Elle permettra également de procéder à un contrôle des résultats des mesures qui seront mises en œuvre.

Mots-clés:
Produits chimiques,
analyse des flux de substances,
agents tensioactifs perfluorés,
sulfonate de perfluorooctane,
acide perfluorooctanoïque,
SPFO, APFO

In Svizzera è stata effettuata un'analisi dei flussi di sostanze rilevati nel 2007 relativi a due tensioattivi perfluorurati (PFT), il perfluorottano sulfonato (PFOS) e l’acido perfluorottanico (PFOA). Si tratta in ambedue i casi di agenti chimici con numerose proprietà uniche idonee per molte applicazioni tecniche, i quali sono al contempo anche degli inquinanti persistenti nell’ambiente. L’UE ha già notevolmente limitato l’impiego dei PFOS, mentre l’industria si è impegnata di sua iniziativa a ridurre il tenore di PFOA nei prodotti. L’analisi dei flussi di sostanze crea una base che permette di adottare misure di riduzione dei rischi. I risultati permetteranno poi di effettuare un controllo dell’efficienza delle misure che saranno adottate in futuro.

Parole chiave:
agenti chimici,
analisi dei flussi sostanze,
tensioattivi perfluorurati,
perfluorottano sulfonato,
acido perfluorottanico,
PFOS, PFOA

# > Foreword

Perfluorinated compounds (PFCs) have unique physicochemical properties, which make them useful in a wide range of applications in both industry and the consumer product sector. Unfortunately, some of these properties such as poor degradability and mobility are a problem for the environment. Among the PFCs, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) with a chain length of 8 carbon atoms are considered particularly problematic. The large number of precursor substances which can form PFOS or PFOA when partially degrading in the environment and the variety of possible uses present additional challenges for any estimate of substance flows and environmental exposure.

The goal of this substance flow analysis is to identify the main applications for PFOS and PFOA and to clarify how PFOS and PFOA enter the environment from the different products and in what quantities. This data is the basis for any risk reduction measures implemented in Switzerland. The information also forms a useful basis for implementation of the obligations entered into by Switzerland as a Party to the Stockholm Convention.

There are very few specialists with detailed knowledge of the complex field of PFOS and PFOA and they are nearly all to be found among the members of SGCI Chemie Pharma Schweiz. For this study it was possible to set up a small working group of highly specialised experts with specific knowledge of perfluorinated compounds. At this point I would like to thank the representatives from the working group most sincerely for making this study possible through their active cooperation.

Georg Karlaganis
Head of Substances, Soil and Biotechnology Division
Federal Office for the Environment (FOEN)

# > Vorwort

Perfluorierte Verbindungen (PFCs) haben einzigartige physikalisch-chemische Eigenschaften. Deshalb sind sie in einem weiten Anwendungsbereich nützlich, sowohl in der Industrie als auch in Konsumentenprodukten. Leider sind einige dieser Eigenschaften wie zum Beispiel die schlechte Abbaubarkeit und die Mobilität problematisch für die Umwelt. Unter den PFCs gelten insbesondere Perfluoroctansulfonsäure (PFOS) und Perfluorooctancarbonsäure (PFOA) mit einer Kettenlänge von 8 Kohlenstoffatomen als problematisch. Zusätzliche Herausforderungen für die Abschätzung von Stoffflüssen und Umweltexposition sind die grosse Zahl der Vorläuferstoffe, bei deren Teilabbau in der Umwelt PFOS oder PFOA gebildet werden können und die vielen Anwendungsmöglichkeiten.

Ziel der vorliegenden Stoffflussanalyse ist es, die wichtigsten Anwendungsgebiete für PFOS und PFOA zu identifizieren und abzuklären, auf welchen Wegen und in welchen Mengen PFOS und PFOA aus den verschiedenen Produkten in die Umwelt gelangen. Diese Kenntnisse sind eine Grundlage für allfällige Massnahmen zur Risikoreduktion in der Schweiz. Auch dienen die Informationen als wertvolle Grundlage für die Umsetzung der Verpflichtungen, welche die Schweiz als Vertragspartei der Stockholm-Konvention eingegangen ist.

Es gibt nur wenige Spezialistinnen und Spezialisten, welche dieses komplexe Gebiet der PFOS und PFOA überblicken. Diese findet man fast ausschliesslich unter den Mitgliedern der SGCI Chemie Pharma Schweiz. Es war möglich, für diese Studie eine kleine Arbeitsgruppe hochspezialisierter Expertinnen und Experten mit spezifischen Kenntnissen über perfluorierte Verbindungen zu bilden. An dieser Stelle möchte ich mich bei den Vertreterinnen und Vertretern der Arbeitsgruppe herzlich bedanken, welche durch ihre aktive Mitarbeit diese Studie überhaupt erst ermöglicht haben.

Georg Karlaganis
Chef der Abteilung Stoffe, Boden, Biotechnologie
Bundesamt für Umwelt (BAFU)

# > Avant-propos

Les composés perfluorés (PFC) possèdent des propriétés physico-chimiques uniques, raison pour laquelle ils sont utiles dans de nombreux domaines d'application, dans l'industrie comme dans les produits destinés aux consommateurs. Malheureusement, certaines de leurs propriétés, comme par exemple leur mauvaise biodégradabilité et leur capacité de propagation, sont problématiques pour l'environnement. C'est le cas en particulier de deux PFC, le sulfonate de perfluorooctane (SPFO) et l'acide perfluorooctanoïque (APFO), dont la chaîne de carbone compte huit atomes. L'estimation des flux de substances et de l'exposition à laquelle est soumis l'environnement est compliquée par le grand nombre de précurseurs de ces substances, dont la décomposition partielle dans l'environnement peut produire du SPFO et de l'APFO, et par leurs multiples possibilités d'application.

La présente analyse des flux de substances a pour but d'identifier les principaux domaines d'application du SPFO et de l'APFO et de déterminer comment et combien de SPFO et d'APFO les différents produits concernés relâchent dans l'environnement. Ces connaissances apportent les éléments nécessaires pour prendre d'éventuelles mesures de réduction des risques en Suisse. Elles constituent également des informations précieuses pour mettre en œuvre les engagements que la Suisse a contractés en devenant partie à la Convention de Stockholm.

Il n'existe que très peu de spécialistes capables d'avoir une vue d'ensemble de ce domaine complexe que constituent le SPFO et l'APFO. On les trouve presque exclusivement parmi les membres de la Société suisse des industries chimiques (SSCI). Il a été possible de réunir pour la présente étude un petit groupe de travail d'experts hautement spécialisés, ayant des connaissances spécifiques des composés perfluorés. Qu'il me soit permis de remercier ici chaleureusement les membres de ce groupe de travail, sans la participation active desquels la présente étude n'aurait pas pu voir le jour.

Georg Karlaganis
Chef de la division Substances, sols, biotechnologie
Office fédéral de l'environnement (OFEV)

# > Prefazione

I composti perfluorurati (PFC) hanno delle proprietà fisico-chimiche uniche che ne permettono un'ampia utilizzazione sia in ambito industriale che nella fabbricazione di beni di consumo. Purtroppo, molte di queste caratteristiche, come ad esempio il basso tasso di degradabilità e la mobilità, creano problemi all'ambiente. Per quanto riguarda i PFC, sono considerati problematici soprattutto il perfluorottano sulfonato (PFOS) e l'acido perfluorottanico (PFOA) con una catena di 8 atomi di carbonio. Una sfida supplementare per la valutazione dei flussi di sostanze e per l'esposizione ambientale è costituita dall'elevato numero di precursori, il cui degrado parziale nell'ambiente può condurre alla formazione di PFOS e PFOA, e le numerose possibilità di applicazione che tali composti offrono.

L'obiettivo della presente analisi dei flussi di sostanze è quello di identificare i maggiori settori di applicazione dei PFOS e dei PFOA e di chiarire lungo quali vie e in quali quantità giungano nell'ambiente partendo da diversi prodotti. Queste conoscenze costituiscono una base per l'eventuale adozione di misure volte a ridurre i rischi in Svizzera. Le informazioni servono inoltre come basi preziose per attuare gli impegni sottoscritti dalla Svizzera in quanto Parte contraente della Convenzione di Stoccolma.

Sono solo pochi gli specialisti che hanno una visione d'insieme del complesso settore costituito da PFOS e PFOA. Tali specialisti sono da cercare quasi esclusivamente fra i membri della SSIC Società Svizzera delle Industrie Chimiche. Per questa ricerca è stato possibile formare un piccolo gruppo di lavoro di esperti altamente qualificati, con conoscenze specifiche in materia di composti perfluorurati. Vorrei cogliere l'occasione per ringraziare i rappresentanti del gruppo di lavoro, il cui contributo ha permesso la realizzazione del presente studio.

Georg Karlaganis
Capo della divisione Sostanze, suolo, biotecnologia
Ufficio federale dell'ambiente (UFAM)

# > Summary

### Background

Perfluorinated compounds such as perfluorinated surfactants have been used in a range of industrial and consumer applications and products for several decades. Perfluorinated surfactants are surface active substances with an extremely low surface tension and a high resistance to oxidation. Hence, they repel grease, dirt, as well as water, and they are stable in industrial processes even under harsh conditions. However, in the past years, increased awareness has risen over these chemicals as they started being considered as a new type of persistent organic substances. Perfluorinated compounds keep the unique properties that make them valuable for industrial and consumer applications also after their emission to the environment making them practically non-degradable substances. They have been found ubiquitary in the environment, even in remote areas, in wildlife and in humans. Among these substances, perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) have attracted the most interest from scientists, authorities and non-government organisations due to their levels in human blood, breast milk and the environment as well as their persistence, bioaccumulation and toxicity. PFOS has been listed under the Stockholm Convention on Persistent Organic Pollutants since May 2009.

### Question addressed

The currently available sparse data on the production, import and usage of perfluorinated substances in Switzerland does not provide a sound basis for an early-recognition of specific problems associated with these chemicals nor does it allow the evaluation of regulatory or technical measures to be taken. Within the scope of this report, the available database for PFOS and PFOA has been studied and discussed and a substance flow analysis (SFA) for these substances has been applied for Switzerland for the year 2007. This analysis allows depicting a holistic view of the flows and stocks in the anthroposphere and the environment in order to define efficient risk reduction measures. In the future, the results will also allow controlling the efficiency of measures possibly taken.

### Methodical procedure

The methodology of substance flow analysis established two decades ago was adopted as a basis. The complex real situation involving a multitude of processes and interconnections was simplified using the method of system analysis in order to get a manageable model. The geographical boundary of the system was set to be the political border of Switzerland and the temporal boundary was set for the year 2007. The following relevant application areas were considered in the SFA in order to account for any behavioural differences in the processes (different stages of the use and in waste management):

- Metal plating
- Fire-fighting foams (AFFF)
- Photolithography and semiconductors
- Photography
- Hydraulic fluids for aviation
- Textile protection
- Leather protection
- Carpet protection
- Paper and paperboard protection
- Coating of metals and ceramics
- Cleaning products, wax and polish
- Paints and lacquers
- Impregnation agents

The SFA was carried out for the two substances PFOS and PFOA. In addition, the contribution of four selected precursor substances to the occurrence of PFOS and PFOA in the environment was simulated semi-quantitatively using a simplified SFA model.

### Data acquisition

Due to the large amount of data required, data acquisition constituted a major part of the study. Important sources referred to include peer-reviewed journal papers, books, reports and conference abstracts. The international network established through several conferences attendances was used as a resource for additional (unpublished) data. Two sets of questionnaires were sent to domestic and international producers as well as selected downstream users in order to get improved and updated data on the domestic production and use compared to the OECD surveys. The first questionnaire focussed on PFOS, PFOA and selected precursors, whereas the second was on fluorotelomer-based polymers and fluoropolymers. A number of additional companies were contacted by phone and e-mail. Only aggregated data are stated in the report as it was assured to the companies to treat the provided data as confidential business information.

### Results

Consumption and stocks in the anthroposphere

A substantial consumption of PFOS in 2007 occurred only in a few application areas. The main consumer process was metal plating, while the amounts used in products and processes for photography and photolithography were estimated to be markedly smaller. The application of a certain fraction of the stock of approximately 13 t in stored fire-fighting foams, which is continuously decreasing, also contributes significantly to the use of PFOS. The historical consumption of PFOS in other application areas has led to a stock build up in potential long-term emission sources such as in the service life and in landfills.

The consumption of PFOA as a residual content in products was more evenly distributed among the different application areas compared to PFOS. The largest amounts were estimated to be imported to Switzerland as constituents of products used in fire-fighting foams, coating of metals and ceramics, textile and carpet protection as well as impregnation agents. The stock in the service life was simulated to be approximately 500 kg and decreasing. It was mainly accumulated due to the historically higher residual contents of PFOA in products.

Emissions

The simulated total emissions of PFOS to the Swiss environment are approximately 500 kg/year. Over 90 % of these emissions are to the hydrosphere, whereas the emissions to soil and especially to the atmosphere are markedly lower. The total emissions of PFOA were simulated to be an order of magnitude lower, i.e. approximately 35 kg/year. The shares of these emissions to the atmosphere, hydrosphere and soil are pretty similar to the shares for PFOS. The wastewater pathway was shown to be most important for the emissions of both substances. Approximately 90 % of the emissions to hydrosphere originate from this pathway. The application areas of metal plating and AFFF contribute the majority to the emissions of PFOS, whereas carpet protection, AFFF and textile protection were simulated to be most relevant for the emissions of PFOA.

Contribution of precursors

The atmospheric degradation of two FOSE derivatives only contributes to a minor extent to the occurrence of PFOS in the environment, as their emissions as well as the degradation yield of PFOS are low. Their contribution to the increase in the substance flows of PFOS in WWTPs, however, might be larger. On the other hand, the contribution of the atmospheric degradation of the two selected FTOH derivatives to the occurrence of PFOA in the environment was simulated to be higher (70 kg/year) than direct emissions of PFOA. The atmospheric degradation of the FOSE derivatives yields more PFOA than PFOS, but the amounts were still simulated to be less than 1 kg/year.

Environmental concentrations

The predicted environmental concentration (PEC) of PFOS in water, sediment and soil are 9 ng/L, 0.07 ng/g w.w. and 0.009 ng/g w.w., respectively. The few field data on surface water from Switzerland range between 2 ng/L and 93 ng/L. Considering that the highest concentrations were found in the Glatt River, i.e. a highly populated watershed, there is a reasonable agreement of the PEC and field data. The PEC in sediment seems to be somewhat lower than the field data, but the database is too week to draw a conclusion. The concentrations in soil were supposed to have a high spatial variability, because only certain soils are influenced by the application of AFFF nearby or sewage sludge as a fertiliser. No field data that were considered representative for Switzerland are known.

The PEC for PFOA (taking into account the contribution of the selected precursors) in water, sediment and soil are 2 ng/L, 0.005 ng/g w.w. and 0.008 ng/g w.w., respectively. For water, there is a good agreement with the field data from Switzerland that range from < 2 ng/L to 12 ng/L. Based on the few sediment data available and appropriate for Switzerland, it seems that the PEC derived for the year 2007 is approximately one order of magnitude smaller than the reported concentrations. As for PFOS, there are no appropriate field data for soil.

## Conclusions

Based on the available data, only a rough picture of the use, stocks, flows, emissions and PEC could be drawn in this substance flow analysis. The results are associated with a considerable degree of uncertainty originated mainly from the uncertainty of the amounts consumed in Switzerland as well as the behaviour of the substances during their application and in wastewater treatment plants (transfer coefficients, emission factors). Despite these constraints, the results such as the total emissions, the contributions of the individual application areas or emission pathways offered a better insight on the situation in Switzerland and provide a valuable basis for further work regarding risk reduction. There are currently few analyses of goods and products, waste streams and environmental concentrations in Switzerland. The database for Switzerland is expected to be improved further by the third OECD survey on PFCs that will be carried out in the summer of 2009 and by an on-going PhD thesis focussing on the occurrence in the environment, goods, waste streams and transport pathways to the environment.

# 1 > Introduction

## 1.1 Initial situation and aims

Perfluorinated compounds (PFCs) such as perfluorinated surfactants have been used in a wide range of industrial processes and products due to their unique physico-chemical properties. Members of this class, particularly perfluorooctanesulfonate (PFOS) and perfluoroocanoic acid (PFOA), are environmentally persistent and have been detected in a variety of matrices, in humans and in wildlife across the globe. However, there is only sparse information on the production, import and usage of perfluorinated substances in Switzerland. Knowledge on the most important substance flows, stocks and emissions establishes a basis for assessments and a benchmark for a comparison of changes in the future. The objective of the study is to carry out a substance flow analysis (SFA) for PFOS and PFOA in Switzerland. The project is embedded in national and international activities. The outcomes of the SFA and the survey among producers and selected downstream users support work in the framework of OECD, the Stockholm Convention and the revision of the Ordinance on Risk Reduction related to Chemical Products (ORRChem).

## 1.2 Objectives

The objective of the study was to carry out a substance flow analysis for two perfluorinated compounds – PFOS and PFOA – in Switzerland. Based on the available knowledge, the SFA was performed as comprehensively as possible. The consumption amounts and the uses were also determined for some selected, so called, precursor substances, for which the degradation to PFOS or PFOA is established and which are of high relevance. The emission sources to the environment were estimated for these precursors. However, the number of precursors was limited between three and five. Furthermore, no full SFA for these substances was carried out. Other known important precursors were listed and their importance and open questions were discussed.

Two surveys among producers and downstream users was carried out in order to get information on the current uses of perfluorinated compounds. No self-conducted measurements have been carried out in the scope of this study. However, data published in literature and available through contacts within the network in Switzerland and abroad and other projects on a similar topic were accessed.

## 1.3 Fundamentals on perfluorinated chemicals

### 1.3.1 Background

Substances within the group of perfluorinated substances are characterised by their fully fluorinated carbon chain; all hydrogen atoms in that part of the chain are exchanged for fluorine atoms (Kissa 2001). The perfluorinated carbon chain has both hydrophobic and lipophobic properties. Carbon-fluorine bonds are the strongest in organic chemistry. Perfluorinated substances such as perfluoroalkyl sulfonates (PFAS, Fig. 1) and perfluorocarboxylic acids (PFCA, Fig. 2) have surface active properties and high resistance to oxidation, which make them very useful for a wide field of applications. Several hundred poly- and perfluoroalkyl substances are known today. Industrial and consumer products containing these substances include detergents or impregnation agents marketed under trade names such as Gore-Tex®, Scotchgard®, Zonyl®, Stainmaster®, Baygard® and many more.

**Fig. 1 > Perfluoroalkyl sulfonates**

*Structural formula of perfluorooctane sulfonate (PFOS) as an example of perfluoroalkyl sulfonates. The chain length is variable.*

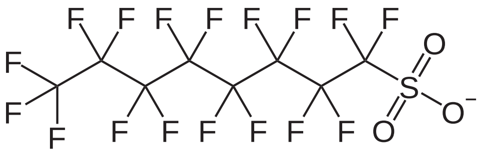
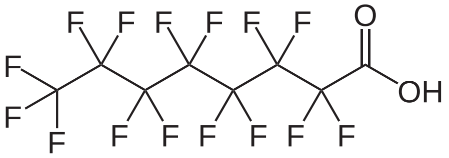


**Fig. 2 > Perfluorocarboxylic acids**

*Structural formula of perfluorooctanoic acid (PFOA) as an example of perfluorocarboxylic acids. The chain length is variable.*



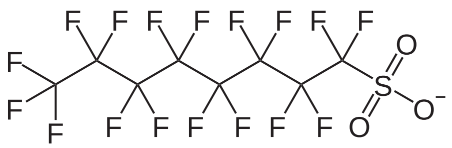
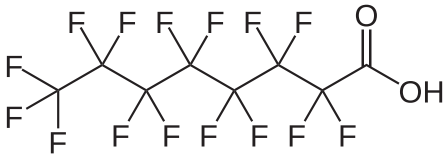
### 1.3.2 Characterisation of the selected substances

The two substances perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) were selected for the substance flow analysis. In this report, the terms PFOS and PFOA are defined as follows:

- > Perfluorooctanesulfonic acid and its salts, e.g. potassium (CAS number 2795-39-3), lithium (29457-72-5), ammonium (29081-56-9) or diethanolamine salts (70225-14-8). In contrast to the term "PFOS-related/PFOS based substances" as defined in the *OECD Hazard Assessment of Perfluorooctane Sulfonate (PFOS) and its Salts* (OECD 2002, OECD 2007a), polymers that contain PFOS only as a portion of the entire polymer are not included. PFOS
- > Perfluorooctanoic acid and its salts. Out of the "PFOA-related substances" as defined by OECD (2007a) only the acid and salts of PFOA, e.g. sodium, potassium or ammonium are included. Polymers that contain PFOA only as a portion of the entire polymer are not included. PFOA

Selected physico-chemical properties of PFOS and PFOA are given in Tab. 1.

**Tab. 1 > Physico-chemical properties of PFOS and PFOA**

| | PFOS | PFOA |
|---|---|---|
| Structural formula |  |  |
| IUPAC name | 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctane-1-sulfonate | 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoic acid |
| CAS number | 1763-23-1 (acidic form) | 335-67-1, 90480-55-0 (branched isomers) |
| Molar mass | 500 g/mol (acidic form) | 414 g/mol |
| Melting point | >= 400 °C | 45–50 °C |
| Boiling point | not calculable | 189–192 °C (736 mmHg) |
| Vapour pressure | $3.31 \cdot 10^{-4}$ Pa (20 °C) | 0.008 Pa (APFO, 20 °C) |
| Solubility in water | 0.57 g/l | 3.4 g/l |
| $K_{AW}$ | $< 2 \cdot 10^{-6}$ | 0.001 |
| $pK_a$ | $-3.27$ | 2.5 (0–3.8)[1] |

Brooke et al. 2004, Barton et al. 2007, Fujii et al. 2007, Burns et al. 2008, Goss 2008, OECD 2008

The selection of the precursors to be included qualitatively or semi-quantitatively in the SFA was based on

- > the evidence that they contribute to the occurrence of PFOS or PFOA in the environment
- > the amount used in processes and products or contained as impurities in products as well as the occurrence indoors and in the environment
- > the current knowledge on the substance

Fluorotelomer alcohols (FTOHs) have been used in a wide range of products. They were extracted from textiles at higher rates compared to other PFCs (Berger & Herzke 2006). The volatile substances 8:2 fluorotelomer alcohol (8:2 FTOH) and 10:2 fluorotelomer alcohol (10:2 FTOH) have been detected at high levels in indoor and outdoor air (Jahnke et al. 2007, Shoeib et al. 2007). 8:2 FTOH was shown to degrade to PFOA (Ellis et al. 2004). 10:2 FTOH that can degrade to PFOA after two “unzipping cycles” (i.e., its chain length is reduced by sequential loss of $COF_2$) was also selected as a precursor.

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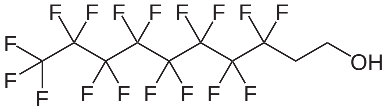
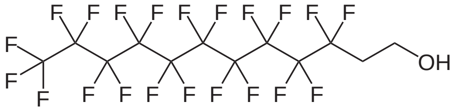
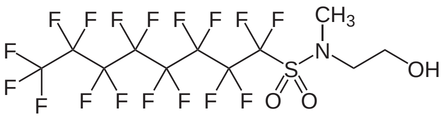
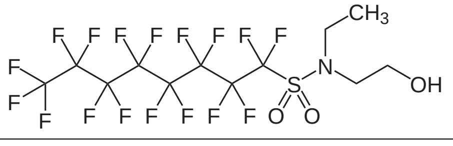
[1] The value of the $pK_a$ determined differs markedly among different studies. Therefore, the peer-reviewed value of 2.5 from the Screening Information DataSheet (SIDS) Initial Assessment Profile was considered.

Tab. 2 > Properties of selected precursors (1)

| | 8:2 FTOH | 10:2 FTOH |
|---|---|---|
| Structural formula |  |  |
| IUPAC name | 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecan-1-ol | 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluorododecan-1-ol |
| CAS number | 678-39-7 | 865-86-1 |
| Molar mass | 464.12 g/mol | 564.13 g/mol |
| Use 2006 (OECD survey) | – | – |
| Producers/importers (ESIS) | – | – |
| Degradation products | PFOA | PFOA |

*N*-methylperfluorooctanesulfonamidoethanol (*N*-MeFOSE) and *N*-ethylperfluorooctanesulfonamidoethanol (*N*-EtFOSE) are common intermediates for producing POSF-based chemicals. They have been predicted by CATABOL modelling and/or expert judgment to degrade to PFOS (Greg Hammond, Environment Canada, personal communication). PFOS was also observed experimentally as a product of the degradation of FOSE derivatives (D'eon et al. 2006). FOSE derivatives can degrade to PFOA, too (D'eon et al. 2006, Schenker et al. 2008). *N*-MeFOSE was found as a residual in Scotchgard (Dinglasan-Panlilio & Mabury 2006). Both substances are also detected in lower concentrations in the gas phase than FTOHs but exhibit higher levels in the particulate phase (Jahnke et al. 2007). Both chemicals including their degradation products 2-(*N*-methylperfluorooctanesulfonamido) acetic acid (*N*-MeFOSAA) and 2-(*N*-ethylperfluorooctanesulfonamido) acetic acid (*N*-EtFOSAA) are also suspected to degrade to PFOS in wastewater treatment plants (Schultz et al. 2006, Becker et al. 2008).

Tab. 3 > Properties of selected precursors (2)

| | *N*-MeFOSE | *N*-EtFOSE |
|---|---|---|
| Structural formula |  |  |
| IUPAC name | 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(2-hydroxyethyl)-*N*-methyloctanesulfonamide | 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(2-hydroxyethyl)-*N*-ethyloctanesulfonamide |
| CAS number | 24448-09-7 | 1691-99-2 |
| Molar mass | 557.23 g/mol | 571.25 g/mol |
| Use 2006 (OECD survey) | – | – |
| Producers/importers (ESIS) | – | 3M, Belgium |
| Degradation products | PFOS, PFOA | PFOS, PFOA |

## 1.3.3 History

The production of PFOA by the electrochemical fluorination method started in 1947 by the company 3M (Prevedouros et al. 2006). DuPont started using PFOA in the manufacturing of fluoropolymers in 1951 (Emmett et al. 2006). Perfluorooctanesulfonyl fluoride (POSF) and its derivatives, which can ultimately degrade to PFOS, have also been in commercial use for approximately 50 years (Giesy & Kannan 2002, Lehmler 2005). In 1961, DuPont performed studies showing hepatomegaly in mice that were fed with PFOA (Arneson 1961, Clapp et al. 2006). Organofluorine contamination was detected in blood serum of consumers in 1968 and in 1976 it was suggested that the substance detected was likely to be PFOA (Kennedy et al. 2004). Four years later, PFOA was identified as the primary organofluorine present in the blood serum of fluorochemical production workers (Ubel et al. 1980). After that, several studies on the toxicity of PFOS and PFOA and their occurrence in humans, animals and the environment have been conducted (e.g. Olsen et al. 1999, Giesy & Kannan 2001). The Environmental Protection Agency of the United States (US EPA) began investigating perfluorinated chemicals in 1999 after having received data on the global distribution and toxicity of PFOS. US EPA expanded investigation in 2000 to PFOA and fluorinated telomers (Dominiak 2003). For these reasons, in May 2000, 3M announced the phase-out of the production of PFOA, PFOS and POSF-based products. Regarding PFOA, 3M had manufactured the compound primarily for commercial sale to other companies. As a result of its phase-out decision, 3M no longer manufactures or sells PFOA. 3M completed its phase-out of PFOS production in 2002 (3M 2008). Meanwhile research demonstrating the ubiquity, toxicity and links to human effects has increased attention towards PFOS. Additionally, advances in analytical chemistry in recent years have allowed the routine detection of low- and sub-ppb levels of PFOS and PFOA in water, food, wildlife and humans (Lau et al. 2004).

### 1.3.3.1 US EPA stewardship program

In January 2006, US EPA invited eight companies to participate in a voluntary program to reduce global emissions and use of PFOA by 2010/2015. All eight fluoropolymer and telomer manufacturers have agreed to participate in EPA’s global stewardship program for PFOA. Participation in the stewardship program required voluntary corporate commitment to two goals (US EPA 2006):

- To commit to achieve, no later than 2010, a 95 % reduction, measured from a year 2000 baseline, in both: facility emissions to all media of PFOA, precursor chemicals that can break down to PFOA, and related higher homologue chemicals, and product content levels of PFOA, precursor chemicals that can break down to PFOA, and related higher homologue chemicals.
- To commit to working toward the elimination of PFOA, PFOA precursors, and related higher homologue chemicals from emissions and products by five years thereafter, or no later than 2015.

A summary of the achievements of the stewardship program is presented in section 2.5.1.3.

### 1.3.3.2 OECD surveys

Switzerland takes part in the activities coordinated by the OECD. The first OECD survey in Switzerland was carried out by FOEN and the Federal Office of Public Health (FOPH) in 2000. This survey confirmed that there was no noteworthy domestic production of PFOS. A second survey was carried out through cooperation with OECD in 2004 and focused primarily on researching FOPH's product register. Only sparse information originated from selective surveys with industries and commerce and no detailed information on the current use of PFCs in processes and products in Switzerland could be acquired due to: a) possibility of entries in the product register that were not in use anymore, but had not been deleted in the database, b) highly aggregated entries (e.g. "fluorinated substance" instead of a CAS number), c) no standardised acquisition process (selection and definition of the substances). However, the results showed that it had to be assumed that POSF-based substances were still in use even after the production stop of 3M. The OECD tried to improve the data with an additional survey in 2006. The results of this survey are summarised in section 2.5.1.2. OECD initially planned to carry out another survey in 2008. The present study was indented to provide additional information for that survey and vice versa, the SFA could have benefited from data received from answers from industries and commerce. However, it was decided to postpone the survey to 2009 in order to allow more time to revise the lists of chemicals and the survey questionnaire.

### 1.3.3.3 Issues concerning chemical analyses

There are several problems associated with the analytical chemistry of perfluorinated compounds (PFCs). These issues include diverse aspects such as unique physicochemical properties, lack of reliable standards, impurities, complicated mixtures of isomers and congeners, ion suppression and contamination during all stages of the analytical procedure. Contamination, especially for PFOA, is likely to happen during sampling (clothes such as raincoats or shoes, equipment) and from laboratory, including instrumental sources (e.g. Teflon caps of vials). State-of the-art analysis involves either direct or ion-paired extraction of the compounds from environmental media, followed by LC-MS(/MS) or GC-MS (for neutral compounds) (de Voogt & Saez 2006, Bücking et al. 2008, Ungewiss 2008). Because of these problems, a certain proportion of measurements resulted in incorrect concentrations, especially in older publications. A lot of work has been done to address the problems mentioned above. The first worldwide interlaboratory study on the analyses of 13 PFCs in three environmental and two human samples indicates a varying degree of accuracy in relation to the matrix or analyte determined. The PFCs which were reported most frequently by the 38 participating laboratories from 13 countries and assessed with the most satisfactory agreement were PFOS and PFOA. In general, the level of agreement between the participating laboratories decreased in the following order: PFC standard solution – human blood – human plasma – fish liver extract – water – fish tissue. Hence, a relative good agreement between laboratories was obtained for the study of standard and human matrices. For the fish extract, most laboratories underestimated the actual PFOS concentration due to matrix effects. The results for the fish tissue and water were also poor, indicating that the extraction and cleanup steps require further improvement. It was concluded that the

PFC determinations in various matrices have not yet been fully mastered (Van Leeuwen et al. 2006).

## 1.3.4 Production

### 1.3.4.1 Production process

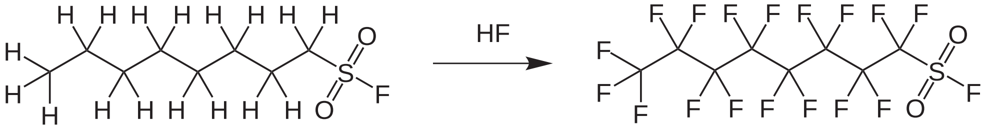
Historically, there have been four major production methods of perfluorinated surfactants: electrochemical fluorination (ECF), fluorotelomer iodide oxidation, fluorotelomer olefin oxidation and fluorotelomer iodide carboxylation (Prevedouros et al. 2006). PFOS has been produced by ECF, while PFOA can be produced by ECF as well as fluorotelomer iodide oxidation. The other two methods have been used to produce perfluorononaoic acid PFNA. Telomerisation is a production method of polyfluorinated surfactants such as fluorotelomer alcohols that has gained a lot of importance in recent years. In contrast to the other methods, the ECF process gives both linear and branched substances, while the others lead to linear substances only. The substances formed in all these processes can then be further processed to different derivatives and polymers (Kissa 2001).

Electrochemical fluorination

The electrochemical fluorination (ECF, also called "Simons Electrochemical Fluorination") was developed by J. H. Simons and co-workers in 1941. In this process, the organic substrate is dissolved in anhydrous hydrofluoric acid at 0 °C and a current is passed through the solution at a potential of 4.5–6 V. ECF provided, for the first time, at a reasonable cost, commercial quantities of technically important fluorochemicals such as trifluoroacetic acid or perfluorooctyl sulfonic acids (Kirsch 2004). Fig. 3 shows the electrochemical fluorination of 1-octanesulfonyl fluoride that yields perfluorosulfonyl fluoride (POSF, sometimes also abbreviated as PFOSF), a chemical intermediate in the synthesis of PFOS as well as *N*-alkylperfluorooctanesulfonamide (FOSA) and *N*-alkylperfluorooctanesulfonamide (FOSE) derivatives. The potassium salt of PFOS can be synthesized by hydrolysis of the fluoride with aqueous potassium hydroxide (Lehmler 2005).

**Fig. 3 > Synthesis of POSF by electrochemical fluorination**

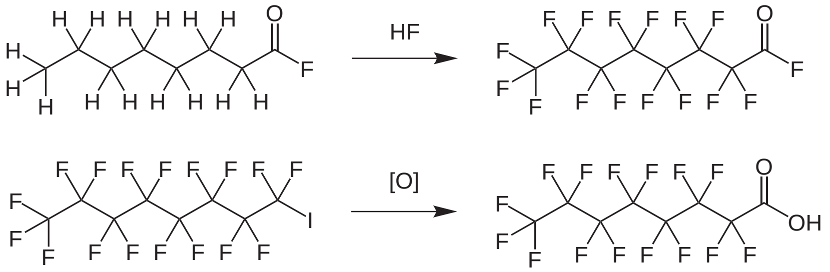
*Electrochemical fluorination of 1-octanesulfonyl fluoride to give perfluorooctanesulfonyl fluoride (POSF). POSF is a chemical intermediate in the synthesis of PFOS as well as FOSA and FOSE derivatives.*



The ECF process was used worldwide to manufacture the majority of ammonium perfluorooctanoate (APFO) between 1947 and 2002 (Fig. 4). In 2000, the fraction of this process was estimated to be between 80 % and 90 %. The products contained homologues ranging from four to thirteen carbons and as much as 30 % by weight of branched isomers. The remaining 10–20 % of APFO was manufactured starting from about 1975 by direct oxidation of perfluorooctyl iodide (Prevedouros et al. 2006).

**Fig. 4 > Synthesis of PFOA by electrochemical fluorination and by fluorotelomer iodide oxidation**

*The two synthesis routes of PFOA: (above) Electrochemical fluorination of octanoyl fluoride to give perfluorooctanoyl fluoride; this substance is reacted further to APFO. (below) Fluorotelomer iodide oxidation of perfluorooctyl iodide yields PFOA.*

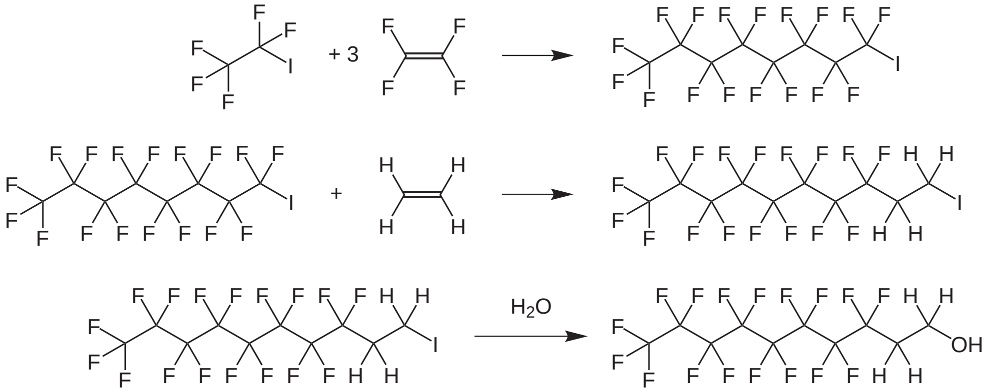


Telomerisation

Fluorotelomer alcohols (FTOHs) are synthesized by a process called telomerisation. This is a radical process by which a telogen such as perfluoroethyl iodide reacts with one or more unsaturated molecules called taxogens, e.g. tetrafluoroethene. A simplified telomerisation process is outlined in Fig. 5 for 8:2 FTOH. The first step (not shown in the figure) is the synthesis of the telogen, perfluoroethyl iodide, by reacting tetrafluoroethylene with $IF_5$ and $I_2$ (Kissa 2001). Telomerisation of tetrafluoroethylene with perfluoroethyl iodide results in a mixture of even-carbon-numbered telomers. The chemistry of the resulting perfluoroalkyl iodides is limited and further functionalisation to intermediates useful for the synthesis of surfactants (e.g. alcohols or amines) is not possible. The perfluoroalkyl iodides are, therefore, reacted in a radical coupling with ethylene resulting in perfluoroalkyl ethyl iodides. These iodides are converted into fluorotelomer alcohols. Olefins, fluorinated carboxylic acids and other fluorinated intermediates are also possible products (Lehmler 2005).

**Fig. 5 > Synthesis of 8:2 fluorotelomer alcohol using telomerisation**

*Synthesis of 8:2 fluortelomer alcohol:*
*(above) The telogen perfluoroethyl iodide reacts with three taxogen units (tetrafluoroethene) and yields perfluorooctyl iodide.*
*(middle) The insertion of ethene results in 8:2 fluorotelomer iodide.*
*(bottom) 8:2 fluorotelomer iodide is hydrolysed to 8:2 fluorotelomer alcohol*



### 1.3.4.2 Production volumes

PFOS

Quantitative historical data on PFOS production exist only for the USA (i.e. for 3M's operations). In 1997, 1848 t/year of POSF were manufactured or imported into the USA with the figure slightly lower at 1820 t/year for the year 2000. During the same year, the total global POSF production by 3M was estimated to be around 3665 t/year. However, the vast majority of POSF was used to manufacture fluoropolymers or functionally derivatised fluoroorganic molecules. Less than 91 metric tonnes of PFOS and its salts were commercialised as finished products (OECD 2002, RPA 2004). The total historical worldwide production of POSF was estimated to be 96 000 t (or 122 500 t, including unusable wastes) between 1970 and 2002 in a paper published shortly prior to the publication of this report (Paul et al. 2009).

In the last quarter of the year 2000, the production of POSF-based substances by 3M was around 1135 tonnes. Due to the phase-out, the production volumes dropped markedly during 2001 and 2002. By 2003, there was no more production of POSF-based substances by 3M. Since then, the Italian company Miteni has been the world’s largest producer of PFCs manufactured using the ECF method by its own statement (Umweltbundesamt 2007). China stated that the large-scale production of POSF-based chemicals began in 2003. Before 2004, total production was less than 50 t/year. From 2005 on, while production in developed countries was restricted, China’s annual output has grown due to the increase of PFOS' application fields and demands overseas. According to 2006 statistics, 15 Chinese enterprises have been producing more than 200 t/year of POSF, about 100 t/year of which were for export to EU, Brazil and Japan (MEP 2008).

PFOA

Prevedouros et al. (2006) estimated the global production of PFOA and APFO between 1951 and 2004 to be 3600–5700 t. In 2005, there were four producers of APFO: Miteni, DuPont, Daikin and a Chinese producer. The annual production of APFO during 1995–2002 was estimated to be 200–300 t/year (OECD 2007b).

Fluorotelomers

The largest producers of fluorotelomers are DuPont, Daikin, Clariant and Asahi Glass. During 2004, an estimated 72 000 tonnes of products were sold containing 11 250–13 500 tonnes of active fluorotelomer ingredients. Another source estimates that the production of fluorotelomer alcohols is 12 000 tonnes per year. Additional sources indicate that the production and use of fluorotelomer alcohols are more in the order of 6000 tonnes per year (OECD 2007b).

The results of the OECD survey on “production and use of PFOS, PFAS and PFOA, related substances and products/mixtures containing these substances” are summarised in section 2.5.1.2.

## 1.3.5 Use

Perfluorinated substances are used in many types of products where their capacity to form smooth water, oil, grease, and stain repellent surfaces is desirable.

Fluorotelomers are the compounds most widely used in products. They are used either as independent active ingredients (e.g. in fire fighting foam) or as a component in more complex structures (e.g. impregnating agents). The main areas of use of fluorotelomers include fire fighting foam, water-resistant and dirt-resistant textiles, grease-repellent paper, surface treatments for tiles, flooring materials, etc. (NERA 2006).

PFOS and PFOS derivatives were used in many of these same applications prior to the recent phase-out of most POSF-based products. Historically, the use of these substances has been confirmed for the EU in the following applications (RPA 2004):

- carpets
- leather/apparel
- textiles/upholstery
- paper and packaging
- coatings and coating additives
- industrial and household cleaning products
- pesticides and insecticides

On-going usage of POSF-based substances has been confirmed for five sectors, representing industrial and professional uses (RPA 2004):

- metal plating
- POSF-based fire fighting foams, where these foams are held in current stocks
- photographic industry
- semiconductors and in photolithography
- hydraulic fluids for the aviation industry

The main use of PFOA is as a processing aid in the production of fluoropolymers, e.g. polytetrafluoroethylene (PTFE). Another PFCA, perfluorononanoic acid (PFNA), is used in a similar way, mainly in the production of polyvinylidene fluoride (PVDF) (Prevedouros et al. 2006). Fluoropolymers are typically used in non-stick cookware, electronics, textiles, wire and cables coating, semiconductors, etc. (OECD 2007b). Historically, PFCA has been used in many different products. As early as 1966, the following areas of use were described in literature: metal cleaning, electrolytic surface treatment, floor polish, cement, fire-fighting foams, paints, lubricants, petrol, and treatment of paper, leather and textiles (KemI 2006, Prevedouros et al. 2006).

### 1.3.6 Emissions

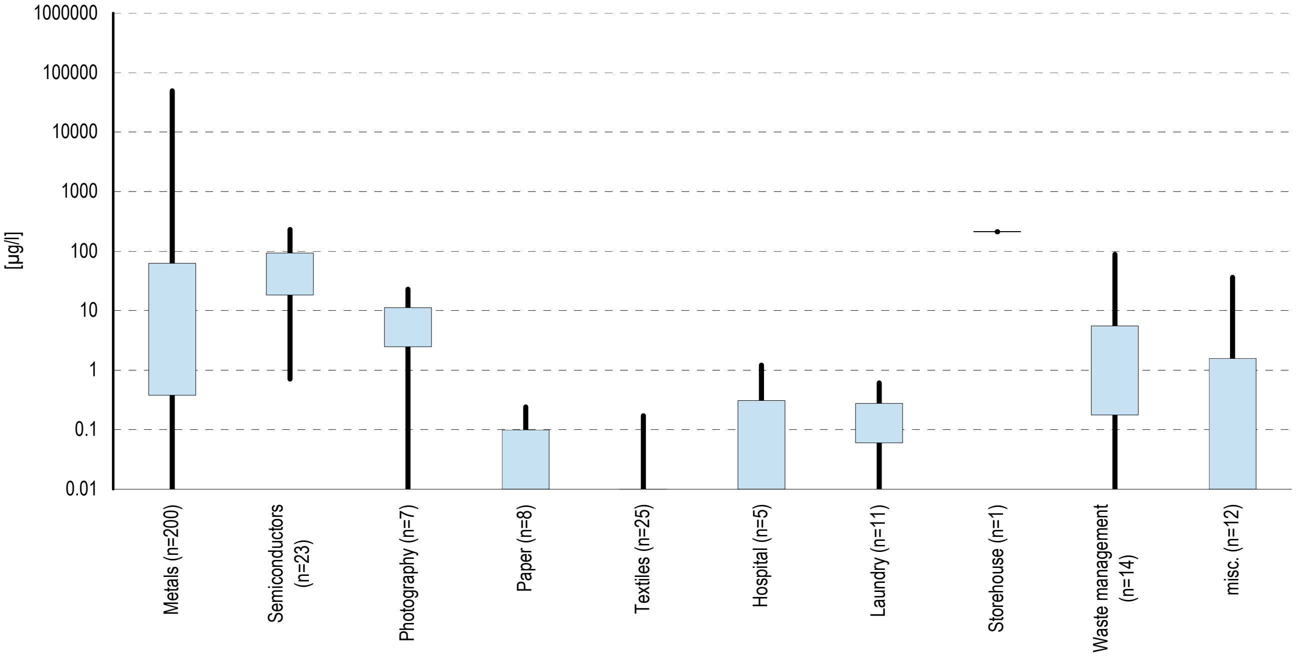
Wastewater treatment plants (WWTPs) play an important role in mitigating pollutant releases from municipalities to aquatic and terrestrial environments. Their contribution as point sources to PFCs' burdens has recently been studied in the greater context of the watershed of the Glatt River, a populated and industrialised area in Switzerland. The mass flows of PFCs from seven WWTPs that discharge effluent into the Glatt River were measured during a one week period and compared to the measured mass flows within the river. It was concluded that, other than WWTPs, there are no apparent unaccounted sources of PFCs along the 35 km Glatt River. Effluents from WWTPs and Glatt River water were dominated by PFOS, which was detected in all samples, followed by PFHxS and PFOA. The per-capita discharges of PFCs calculated from the populations served by the WWTPs studied were 57 µg/day/person for PFOS and 12 µg/day/person for PFOA. While the per-capita discharge of PFOS was higher compared to three studies done in the USA, the discharge of PFOA was comparable to two of the studies, and more than one order of magnitude lower than the third one (Huset et al. 2008).

During the past two years, a lot of analyses have been performed in North Rhine-Westphalia (NRW) in order to identify the sources of PFCs in the environment and to take measures where appropriate. More than 400 wastewater samples from industrial indirect dischargers were taken during 2007 and 2008. While only the linear isomers of PFOS and PFOA were analysed in the beginning, the analytical methods were changed later in order to determine the sum of all isomers. The concentrations determined based on the second method are occasionally more than 30 % higher. No interlaboratory studies for industrial wastewater have been conducted yet. However, most chemical analyses have been performed in official laboratories of LANUV, especially for samples with high concentrations (see section 1.3.3.3) and there are currently no standardised methods (LANUV 2008). Due to the larger number of samples analysed for linear isomers only and since the year 2007 was chosen for the SFA, these results are presented in Fig. 6 and Fig. 7 in an aggregated form. The figures with the concentrations of all isomers are shown in the appendix. All samples below the limit of detection were set as 0.01 µg/L in the figures and are represented by the lowest line of the logarithmic scale. More than half of the samples were taken from different companies in the metal business. Their fields include e.g. metal plating such as copper/nickel/chromium-plating, plastic electroplating, galvanising, anodising as well as the manufacture of instruments, needles, rims and furniture. The concentration of PFOS in the wastewater of these companies ranged between 0.005 µg/L and 49 000 µg/L (i.e. seven orders of magnitude). Two companies that are copper/nickel/chromium-plating plastic surfaces were identified as main source of PFOS in the receiving WWTPs. The substance flow was determined to be approximately 26 g/day (LANUV 2008) which corresponds to 8 kg/year if a constant release throughout the year is assumed. High concentrations were also analysed in wastewater of semiconductor manufacturers (0.7–230 µg/L) and recyclers of old films (2–23 µg/L). A particularly high concentration was detected in the wastewater of a large chemical storehouse. Consultation of the company revealed that the periodical testing of the fire sprinkling system was responsible for the concentrations of 60 000 µg/L and 770 000 µg/L in the wastewater (see Fig. 23 in the appendix). The volume of AFFF released during one test was 600–800 L (LANUV 2008). If assuming that the storehouse did not produce much additional wastewater prior to sampling, the amount of PFOS released to wastewater during one test would have been 30–600 g.

Similar measurements were also carried out in Austria and Bavaria (Clara et al. 2008, Sengl 2008). The number of companies in these studies was smaller than in NRW, yet they corroborate the main finding from NRW: The highest concentrations of PFOS were found in wastewater from a metal plating company in both studies.

**Fig. 6 > PFOS concentrations found in indirect dischargers**

*Concentrations of PFOS (linear isomer) in indirect dischargers of different industries. The samples were taken in North Rhine-Westphalia in the years 2007 and 2008. The lines represent the concentration range, while the boxes indicate the range between the 25th and the 75th percentile. Note the logarithmic scale.*

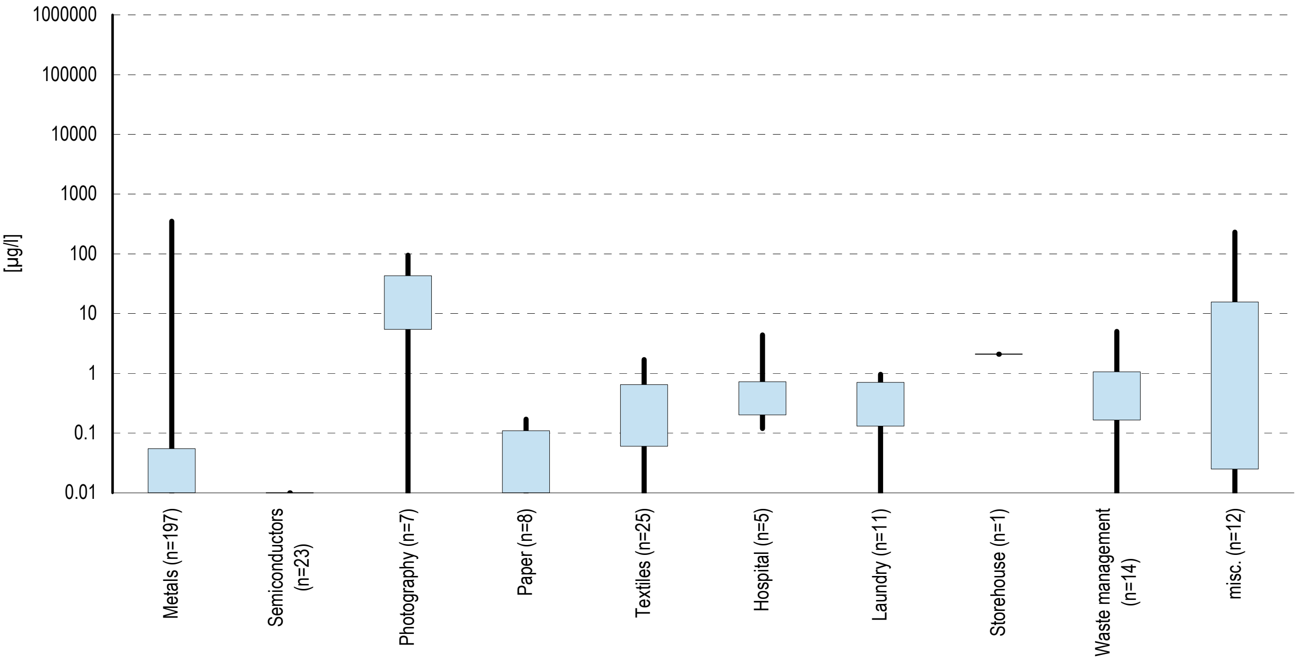


LANUV 2008

The concentrations of PFOA were generally somewhat lower and the differences between the individual industries were smaller. Except for a few outliers, all concentrations in samples from metalworking industries were below 1 µg/L, of which most were markedly lower. All concentrations in wastewater from semiconductor manufacturers were below the limit of detection. On the other hand, comparable concentrations to PFOS were also analysed in wastewater recyclers of old films (up to 95 µg/L). The concentrations in wastewater from the textile industry, from hospitals, laundries and waste management companies were all around 1 µg/L, while it was lower for the paper industry. The latter, however, produces large volumes of wastewater. As for PFOS, there were also high concentrations of PFOA in two wastewater samples from a large storehouse of chemicals (1700 µg/L and 20 000 µg/L) (see Fig. 24 in the appendix). Making the same assumptions as above, the amount of PFOA released to the wastewater during one test would have been 1–16 g.

**Fig. 7 > PFOA concentrations found in indirect dischargers**

*Concentrations of PFOA (linear isomer) in indirect dischargers of different industries. The samples were taken in North Rhine-Westphalia in the years 2007 and 2008. The lines represent the concentration range, while the boxes indicate the range between the 25th and the 75th percentile. Note the logarithmic scale.*



LANUV 2008

Armitage et al. (2006), estimated based on previous work (Prevedouros et al. 2006), that 2700–5900 tons of PFOA have been emitted between the years 1950 and 2004. The largest single source contribution (72 % of the total) originated from fluoropolymer manufacturing followed by APFO manufacturing (12 %) and fluoropolymer dispersion processing (7 %). Direct sources were estimated to be approximately an order of magnitude larger than indirect sources. Projected cumulative emissions between 2005 and 2050 (480–950 t) were forecast to be at least 80 % lower than the estimated cumulative emissions between 1950 and 2004. Both the already achieved emission reductions and the industry commitment to a 95 % reduction in emissions by the year 2010 from a 2000 baseline were reflected in these estimates. As Tab. 4 shows, 85 % of emissions after 2004 were attributed to the use of APFO in fluoropolymer manufacturing followed by fluoropolymer dispersion processing (9 %) and APFO manufacturing (4 %). Due to the projected reductions of PFOA impurities in products, only 1 % of total PFO emissions was forecast to originate from indirect sources over the period 2005–2050 (Armitage et al. 2006). It has to be emphasized that no fluoropolymer manufacturing using APFO or APFN and also no manufacturing of these substances takes place in Switzerland. Hence, a top-down estimate from the global emissions based on a per-capita approach would undoubtedly be inappropriate.

**Tab. 4 > Estimated global historical and future PFOA emissions**

| Emission source | 1950–2004 [t] | Percentage of total emission | 2005–2050 [t] | Percentage of total emission |
|---|---|---|---|---|
| Direct sources | | | | |
| Fluoropolymer manufacturing (APFO) | 2060–4090 | 72.3 % | 410–815 | 86.0 % |
| APFO manufacturing | 370–590 | 11.8 % | 20–40 | 4.2 % |
| Fluoropolymer dispersion processing (APFO) | 215–340 | 6.8 % | 45–75 | 8.7 % |
| AFFF manufactured with ECF | 50–100 | 1.8 % | 0 | 0 % |
| Fluoropolymer manufacturing (APFN) | 3–10 | 0.1 % | < 1–2 | 0.1 % |
| Consumer and industrial products | 2–10 | 0.1 % | 0 | 0 % |
| APFN manufacturing | 1–2 | 0 % | < 1 | 0 % |
| PVDF (APFN) | < 1 | 0 % | < 1 | 0 % |
| Σ direct sources | 2700–5140 | 92.9 % | 475–932 | 99 % |
| Indirect sources | | | | |
| POSF raw material degradation | 4–585 | 5.0 % | 0 | 0 % |
| POSF impurities | 14–110 | 1.2 % | 0 | 0 % |
| AFFF based on POSF | 2–23 | 0.2 % | 0 | 0 % |
| Fluorotelomer raw material degradation | 3–60 | 0.6 % | 1–14 | 0.8 % |
| Fluorotelomer impurities | < 1–17 | 0.1 % | < 1–4 | 0.2 % |
| Σ indirect sources | 23–795 | 7.1 % | 1–18 | 1.0 % |
| Total | 2723–5935 | 100.0 % | 476–950 | 100.0 % |

Armitage et al. 2006

### 1.3.7 Occurrence and fate in the environment, and toxicology

In the last years, many studies have reported ubiquitous distribution of PFCs, especially PFOS and PFOA in the environment, particularly in wildlife such as fish, birds and marine mammals, but also in human samples. Surface water and also tap samples in several countries were found to be contaminated. Concentrations in animals from relatively more industrialized areas were greater than those from the less populated and remote locations. The bioconcentration factors (BCFs) of PFOS in fish were in the range of 10 000 or above, while the BCF of PFOA in fish was below 200. Blood samples of occupationally exposed people and the general population in various countries were found to contain PFOS and PFOA (e.g. Giesy & Kannan 2002, Houde et al. 2006, Fujii et al. 2007, Lau et al. 2007). PFOS and PFOA are persistent in the environment, as available data indicate that there are no known degradation mechanisms under environmentally relevant conditions. The toxicology of PFOS and PFOA was extensively reviewed by several groups, including Lau et al. (2007). In animal studies, hepatotoxicity, developmental toxicity, immunotoxicity, hormonal effects and carcinogenic potential are the predominant effects of concern. The most sensitive endpoint of many PFCs is oxidative stress by inducing peroxisomal proliferation. However, this mechanism does not seem to be relevant for humans. A long serum/plasma elimination half-life of several years in humans was also notable (Wilhelm et al. 2008). The German Federal Institute for Risk Assessment has recently concluded that based on the latest scientific findings available, a health risk from the dietary intake of PFOS and PFOA is unlikely in conjunction with their levels in foods detected up to now (BfR 2008).

Through the investigation of mass flows in the Glatt Valley in Switzerland, it was found that the mass flows of PFCs emanating from WWTPs were conserved within the 35 km of river length. This indicates that input from the WWTPs is additive and that removal within the Glatt River is not significant (Huset et al. 2008).

A case of criminal mismanagement of several thousand tons of sludge and waste materials containing PFCs and the consequential contamination of agricultural sites in Germany resulted in a high public awareness and initiated a lot of administrative and research activities in Germany. The leachate and runoff from some of these sites contaminated tributary rivers of the Ruhr River. This contamination resulted in elevated concentrations in the Ruhr River and associated drinking water supplies. The population in the area with the highest drinking water contamination (approx. 500 ng/L PFOA) showed highly elevated PFOA concentrations in the blood (around 25 µg/L) compared to the German background contamination (around 5 µg/L) (Skutlarek et al. 2006b, Kröfges et al. 2007). However, it was found that there are other sources contributing markedly to the occurrence of PFCs in the environment (see previous section).

PFOA has been found in remote ocean water and Arctic samples even though it has not been used in significant quantities in remote areas. Two main scenarios for the contamination of the Arctic by PFOA have been suggested (Schenker et al. 2008): a) emissions of volatile precursor substances that are transported and oxidised in the atmosphere to form PFOA, which is subsequently deposited to the Arctic (Andersen et al. 2006) and b) direct emissions of PFOA and oceanic transport to the Arctic (Prevedouros et al. 2006, Wania 2007). Recently, aerosol-mediated transport of PFOA from water bodies to the atmosphere and the subsequent emission of gas-phase PFOA have been hypothesised as an additional mechanism for the occurrence of PFOA in remote regions (McMurdo et al. 2008, Renner 2008).

## 1.4 Existing regulatory framework

### 1.4.1 European Union

On 12 December 2006, the Directive 76/769/EEC was amended by the European Parliament and the Council of the European Union in Directive 2006/122/EC (EC 2006a). Therein, the marketing and use of perfluorooctane sulfonates, which are defined by the generic molecular formula $C_8F_{17}SO_2X$ (X = OH, metal salt ($O^-M^+$), halide, amide and other derivatives including polymers) were restricted in the European Union. This regulation became effective on 27 June 2008 and applies to substances and preparations with concentrations of equal to or higher than 0.005 % by mass. Semi-finished products, articles or parts thereof may not be placed on the market if the concentration of perfluorooctane sulfonates is equal to or higher than 0.1 % by mass. For textiles or other coated materials, the limit is 1 µg/m² of the coated material. However, based on the fact that there are no substitutes available for perfluorooctane sulfonates, there are some exceptions made by the regulation:

> photoresists or anti reflective coatings for photolithography processes
> photographic coatings applied to films, papers or printing plates
> mist suppressants for non-decorative hard chromium (VI) plating and wetting agents for use in controlled electroplating systems where the amount of PFOS released into the environment is minimised, by fully applying relevant best available techniques
> hydraulic fluids for aviation

Member States had to adopt and publish, no later than 27 December 2007, laws, regulations and administrative provisions necessary to comply with this Directive. They were to communicate to the Commission the text of those measures and a table showing the correlation between the measures and the Directive. Fire-fighting foams that have been placed on the market before 27 December 2006 can be used until 27 June 2011. The existing stocks of fire-fighting foams containing PFOS had to be established by the Member States and communicated to the Commissions not later than 27 December 2008.

During the work on the European Directive 2006/122/EC there have been requests from several parties for enacting the same restrictions as on PFOS also on PFOA. However, the restrictions were not regarded as appropriate since PFOA has different application patterns. The final wording in the Directive is as follows:

"Perfluorooctanoic acid (PFOA) and its salts are suspected to have a similar risk profile to PFOS, and consequently there is a need to keep under review the ongoing risk assessment activities and the availability of safer alternatives and to define what kind of risk reduction measures, including restrictions on marketing and use, if appropriate, should be applied within the European Union."

### 1.4.2 Switzerland

The marketing and use of PFOS and PFOA have not been restricted in Switzerland so far. However, the Swiss Federal Institute for the Environment (FOEN) is currently revising the Ordinance on Risk Reduction related to Chemical Products (ORRChem). In line with the regulation from the European Union on PFOS that became effective on 27 June 2008 and its addition to the Stockholm Convention (see below), the Swiss authorities focus on PFOS in a first step.

### 1.4.3 Convention on Long-range Transboundary Air Pollution and Stockholm Convention

PFOS has been nominated and is currently under negotiations to restrict its use to a few specific applications under the Protocol on Persistent Organic Pollutants of Convention on Long-range Transboundary Air Pollution (UN ECE). In 2005, the Swedish government proposed PFOS for listing in Annex A of the Stockholm Convention on Persistent Organic Pollutants. The Swedish government argued that PFOS is extremely persistent in the environment, is bioaccumulative, has a long-range transport potential and is associated with serious harmful effects in mammals and aquatic organisms. The Persistent Organic Pollutants Review Committee (POPRC) adopted the risk management evaluation for PFOS in November 2007 and recommended to the Conference of Parties (COP) to list PFOS acid, its salts and perfluorooctane sulfonyl fluoride in Annex A or Annex B of the Stockholm Convention while specifying the related control measures (UNEP 2007). In May 2009, the COP decided to list PFOS, its salts and perfluorooctane sulfonyl fluoride under Annex B of the Stockholm Convention (Stockholm Convention Secretariat 2009).

# 2 > Methodical procedure

## 2.1 Method adopted

In the present report, the methodology of substance flow analysis established in Baccini and Brunner (1991) and “Stoffflussanalyse Schweiz” (BUWAL 1996) was adopted as a base. As in the report, the flows of substances are first determined in subordinate systems and then aggregated to form the whole system.

## 2.2 System analysis

The method of system analysis was used to establish a simulated system of reality. This was done by simplifying the complex real situation involving a multitude of processes and interconnections (flows of goods) to produce a cohesive and manageable model. The latter was reduced to its principal components and tailored to suit the objectives and stated boundaries of the study. System analysis involves three steps:

- limitation of the system in space and time
- establishment of the internal structure of the system: choice and definition of processes and their input and output goods, and determination of interconnections
- definition of the substances to be studied

### 2.2.1 System definition

The system comprises the transport and transformation processes as well as stocks of two selected PFCs, PFOS and PFOA, in the Swiss anthroposphere.

#### 2.2.1.1 Geographical border and investigated time period

The geographical boundary of the system is identical to the political border of Switzerland. The year 2007 was selected as a temporal boundary of the system. However, in order to estimate the accumulated stocks in the anthroposphere, some data for temporal trends and historic consumptions were also required.

#### 2.2.1.2 Selected application areas

The different goods containing PFCs have been split up in the following application areas:

- Metal plating
- Fire-fighting foams (AFFF)
- Photolithography and semiconductors

- Photography
- Hydraulic fluids for aviation
- Textile protection
- Leather protection
- Carpet protection
- Paper and paperboard protection
- Coating of metals and ceramics
- Cleaning products, wax and polish
- Paints and lacquers
- Impregnation agents

#### 2.2.1.3 Selected subsystems

The system is divided into the three subsystems production and use, waste management and environment.

Tab. 5 shows the three subsystems comprising the selected processes. The environmental compartments atmosphere, hydrosphere and soil are considered to lie outside the system boundary.

**Tab. 5 > Selected subsystems and processes**

| Subsystem | Process |
|---|---|
| Production and use | AFFF storage |
| | Application |
| | Service life |
| | End-of-life |
| Waste management | Sewerage |
| | Wastewater treatment plant (WWTP) |
| | Recycling |
| | Incineration |
| | Landfill |
| Environment | Atmosphere |
| | Hydrosphere |
| | Soil |

### 2.2.1.4 Definition of processes and flows

In Tab. 6, the selected processes in the system are defined. The processes *AFFF storage*, *service life* and *landfill* include a stock where the substances may accumulate. It was assumed that the other processes do not include a stock because the residence times are much shorter and can be neglected in a first-order approximation.

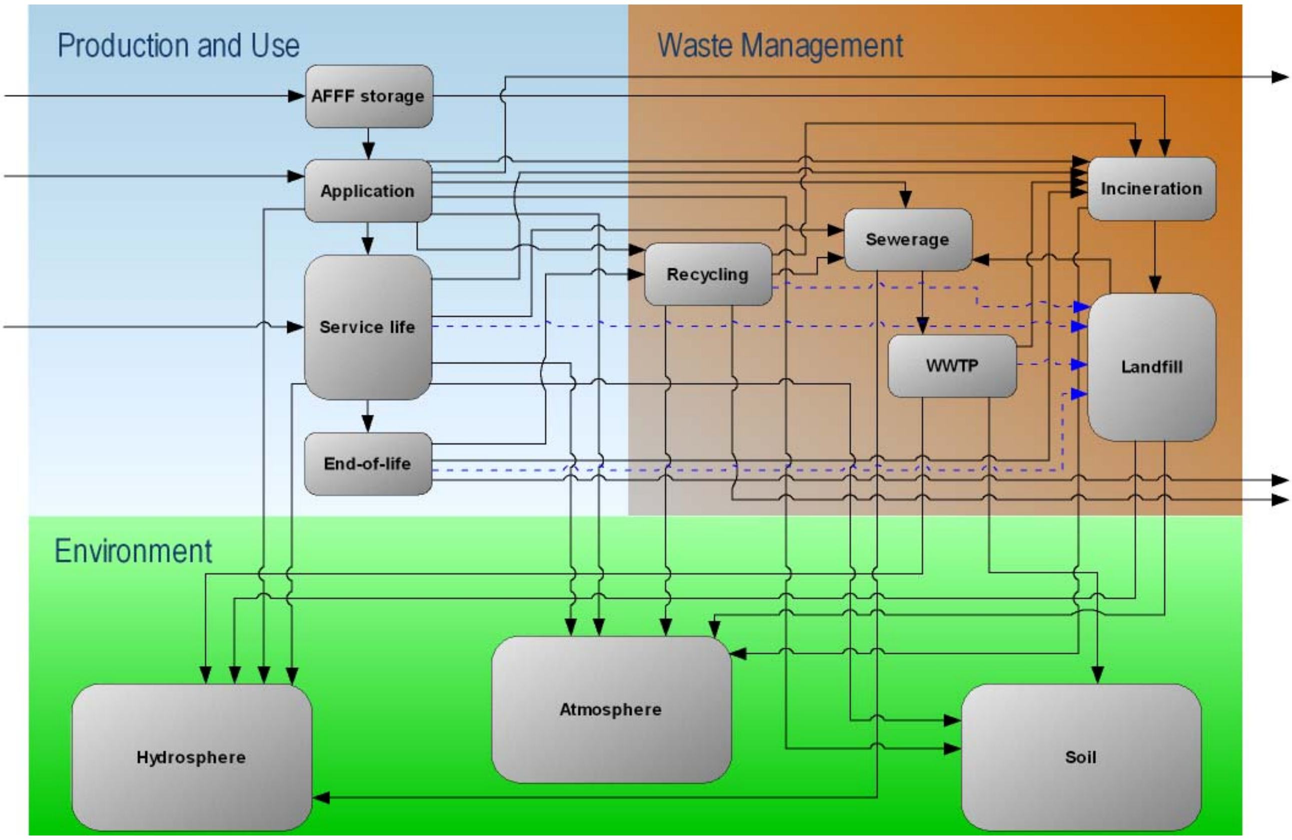
**Tab. 6 > Definition of the processes**

| Process | Description |
|---|---|
| AFFF storage | The process comprises the PFCs in stored aqueous film-forming foam (AFFF). |
| Application | The process comprises the application of industrial or consumer products that contain the PFCs under study. |
| Service life | The process comprises the stock of PFCs in products. |
| End-of-life | The process comprises PFCs containing products that reach the end of their service life and are disposed. |
| Sewerage | The process comprises the sewer system in which wastewater is collected, transported and delivered to the WWTP. |
| WWTP | The process comprises treatment of municipal wastewater in wastewater treatment plants in Switzerland. It contains wastewater from private households as well as from production sites. |
| Recycling | The process comprises the mechanical and manual treatment of goods in recycling facilities. |
| Incineration | The process comprises the incineration processes in municipal waste incineration plants, sludge incineration plants, fluid bed incineration and cement works. |
| Landfill | The process comprises landfills where waste containing PFCs under study is disposed of. |
| Atmosphere | The compartment comprises an air volume of a height of 1000 m and the area of Switzerland. |
| Hydrosphere | The compartment comprises the surface water in rivers and lakes including sediment and aquatic organisms. The mean residence time of water considered is 850 h. |
| Soil | The compartment comprises the soil in Switzerland with a mean thickness of 10 cm. |

The system comprising the processes and substance flows used in this substance flow analysis is illustrated in Fig. 8. Fire-fighting foams do not have a service life after application as is the case for other application areas. However, they are stored in the process *AFFF storage* until usage or shelf life is reached.

**Fig. 8 > System used for the substance flow analysis**

*The system used in the substance flow analysis with three subsystems, eleven processes and a number of substance flows. Note that the dotted blue arrows indicate substance flows before 2007.*



### 2.2.1.5 Selection of substances to be studied

The substances selected for the substance flow analysis are (for details see section 1.3.2 on page 16):

- Perfluorooctanesulfonic acid and its salts (PFOS)
- Perfluorooctanoic acid and its salts (PFOA)

The following substances were included as precursors of PFOS and PFOA:

- *N*-methylperfluorooctanesulfonamidoethanol (*N*-MeFOSE)
- *N*-ethylperfluorooctanesulfonamidoethanol (*N*-EtFOSE)
- 8:2 fluorotelomer alcohol (8:2 FTOH)
- 10:2 fluorotelomer alcohol (10:2 FTOH)

## 2.3 Mathematical model

### 2.3.1 Equations

Balance equations serve as a base for the system of equations. Parameters used in the equations are substance flows, transfer coefficients and emission factors. A transfer coefficient is defined as the ratio of the substance flow in an output and the total input flow into the investigated process. The sum of the transfer coefficients of all process outputs is equal to one. If a substance flow gets into the environment, the coefficient is denoted as emission factors (EF). For processes within the anthroposphere, the coefficients are named transfer coefficients (TC).

### 2.3.2 Uncertainty estimation

For most of the parameters used in the model, there were no data series or other information, from which it would have been possible to calculate a domain of uncertainty. Therefore, so called, best guess values were considered. However, the uncertainty was estimated as a range in order to derive estimated minimum and maximum substance flows.

## 2.4 Data acquisition

A large amount of data was required for this study. The data were gathered by reviewing peer-reviewed literature published in journals, conference abstracts, reports and books. The existing and recently established international network (industry, research and authorities) was used to get additional data. These contacts were important as no self-conducted measurements were carried out in the scope of this project and the quantity of data in Switzerland was limited at the time of the study. In accordance with the planned OECD survey, two surveys were sent to selected manufacturers and downstream users in order to get information on the current uses of perfluorinated compounds. Initially, it was planned to do a combined survey, i.e. for OECD and the substance flow analysis, but the OECD survey was then postponed to 2009. The first survey mainly dealt with PFOS, PFOA and their precursor substances, while the second survey focused on the import of fluoropolymers and their residual concentrations. The number of recipients in the second questionnaire was smaller as there is only a limited number of fluoropolymer manufacturers relevant not only to the Swiss market but also worldwide. A number of additional companies were also contacted by phone and e-mail. As it was assured to the companies that the data they provided would be treated as confidential business information, only aggregated data are presented in the report, and the names of individual companies are not stated. For the same reason, a list of the companies contacted is not provided here as that might allow inferring the information provided by an individual company.

## 2.5 Data input for the model

### 2.5.1 Use

#### 2.5.1.1 Product register

According to the Ordinance on Protection against Dangerous Substances and Preparations, manufacturers have to submit information on substances or products they put in the Swiss market; this information is included in the product register. The product register, however, does not contain information on amounts. If there are changes concerning a substance or a product, they must be notified within three months. However, if a substance or a product is withdrawn from the market, the entries are not always deleted. Therefore, the entries of PFOS and PFOA including their salts shown in Tab. 7 do not necessary reflect the current situation of their use. It is unlikely that PFOS salts' uses other than in electroplating and photo imaging are still happening. In addition to these substances, there are derivatives of PFOS, PFCs with a longer or shorter perfluorinated chain length and polymeric substances in the product register. Among these chemicals, there are three potential precursor substances of PFOS. Potassium *N*-ethylperfluoro-1-octanesulfonamidoacetate (potassium salt of *N*-EtFOSAA) is one of PFOS' precursors and has entries for 206 products used in impregnation and cleaning agents, care products for leather and shoes, floors and cars, paints, emulsions, adhesives, fillers, sealants and disinfectants. The two other PFOS' precursor substances are chlorine and iodine salts of quaternary ammonium derivatives of FOSA with two entries in the product register for each substance.

**Tab. 7 > Entries in the Swiss product register**

*PFOS and PFOA including salts that are registered for the use in specific products in the Swiss product register. The entries may remain in the product register if they are not deleted, even though they might not be in use anymore.*

| Simplified name | CAS number | Number of entries | Registered uses |
|---|---|---|---|
| PFOS potassium salt | 2795-39-3 | 4 | Electroplating, anti-corrosive protection, metal care, wood care, floor care, impregnation agent |
| PFOS lithium salt | 29457-72-5 | 3 | Photographic chemical, laboratory chemical |
| PFOS tetraethylammonium salt | 56773-42-3 | 35 | Electroplating, photographic chemical, paint/lacquer, adhesive, car care, sealant, filler, auxiliary substance |
| PFOS diethylamine salt | 70225-14-8 | 8 | Electroplating, surface treatment, thinner, pickling agent, remover, solvent, degreaser |
| PFOA | 335-67-1 | 3 | Textile cleaning, fluxing agent, common chemical |
| APFO (PFOA ammonium salt) | 3825-26-1 | 3 | Coating composition, paint, auxiliary substance |

### 2.5.1.2 Overall use of PFOS and PFOA

2006 OECD survey

The results of the 2006 OECD survey are shown in Tab. 8. However, due to limited responses, the survey results do not provide a complete picture of the global production and use of perfluorinated chemicals. The manufacture and import volumes were summarised as 74–175 t/year for PFOS and 69–320 t/year for PFOA. It has to be emphasised that the amount of PFOS given in the survey includes precursors such as POSF and *N*-EtFOSA. For Switzerland, no information on import volumes of PFOS and PFOA was received in that survey, but it was confirmed that no domestic manufacture of these substances takes place.

**Tab. 8 > Results of the 2006 OECD survey for PFOS and PFOA including their salts and related substances**

| (Simplified) name | CAS | Group | Global import/ manufacture [t/year] |
|---|---|---|---|
| POSF | 307-35-7 | PFOS | up to 70 |
| PFOS tetraethylammonium salt | 56773-42-3 | PFOS | up to 30 |
| PFOS potassium salt | 2795-39-3 | PFOS | up to 20 |
| *N*-EtFOSA | 4151-50-2 | PFOS | 17 |
| PFOS | 1763-23-1 | PFOS | 1–10 |
| PFOS lithium salt | 29457-72-5 | PFOS | 1–10 |
| PFOS ammonium salt | 29081-56-9 | PFOS | < 1 |
| *N*-[3-(dimethylamino)propyl]perfluorooctanesulfonamide | 13417-01-1 | PFOS | < 1 |
| *N*-[3-[[(perfluorooctyl)sulfonyl]amino]propyl]trimethylammonium iodide | 1652-63-7 | PFOS | < 1 |
| *N*-ethylperfluoro-*N*-[3-(trimethoxysilyl)propyl]octanesulfonamide | 61660-12-6 | PFOS | < 1 |
| α-[2-[[(perfluorooctyl)sulfonyl]propylamino]ethyl]-ω-hydroxy-poly(oxy-1,2-ethanediyl) | 52550-45-5 | PFOS | < 1 |
| APFO | 3825-26-1 | PFOA | up to 260 |
| PFOA | 335-67-1, 90480-55-0 | PFOA | up to 10 |
| PFOA sodium salt | 335-95-5 | PFOA | up to 10 |

OECD 2006c

Current information on the manufacture and import in Switzerland

Almost all companies contacted either by a questionnaire, by phone or by e-mail stated that they did not manufacture or import PFOS, PFOA or the selected precursor substances. Only one company stated that they imported PFOS potassium salt and APFO for industrial use in Switzerland. The volumes, however, were both in the low kg range. Another company asserted that they imported fluorotelomer intermediates, which were used for the production of fluorotelomer-based polymer dispersions and totally consumed in the polymerisation step. The volume was in the range of several tens of tons per year. Neither the imported fluorotelomer used exclusively as raw material, nor the end polymer dispersions, were put in the Swiss market.

### 2.5.1.3 Overall use of fluoropolymers

Fluoropolymer world production volumes

The world consumption of fluoropolymers was estimated to be 133 000 t/year in 2004. The estimated annual growth from 2004 to 2009 is 6.0 % for PTFE, while it is 5.3 % for other fluoropolymers (Will et al. 2005). Hence, according to these data, the extrapolated world consumption has been estimated to be between 150 000 and 160 000 t/year in 2007. On the other hand, PlasticsEurope estimates the world market for fluoropolymers to be between 80 000 and 90 000 t/year. This represents just 0.1 % of all plastics (PlasticsEurope, undated). In 2004, PTFE held a share of about 60 %, followed by PVDF with approximately 15 % (Will et al. 2005). As part of their commitment to the US EPA 2010/15 PFOA Stewardship Program, the eight participating companies agreed to submit annual progress reports on their reductions of PFOA, PFOA precursors and higher homologues in facility emissions and product content. By 31 October 2007, they submitted the annual reports for the reporting year 2006. The reports of some companies also contained the production volume of fluoropolymer dispersions and other fluoropolymers (see Tab. 9). However, the information provided by the companies only included ranges. Hence, it can only be concluded that all these companies produce more than 3000 t/year each for fluoropolymer dispersions and other fluoropolymers.

**Tab. 9 > Production volumes of fluoropolymer dispersions and other fluoropolymers**

*Reported production volumes of fluoropolymer dispersions and other fluoropolymers for the reporting year 2006 provided by the companies participating in the US EPA's 2010/15 PFOA Stewardship Program.*

| Company | Fluoropolymer dispersions [t/year] | Other fluoropolymers [t/year] |
|---|---|---|
| 3M/Dyneon | > 1000 | Not reported |
| Arkema | 10–100 | > 1000 |
| Asahi Glass | > 1000 | > 1000 |
| Ciba | Not reported | Not reported |
| Clariant | Not reported | Not reported |
| Daikin | Not reported | Not reported |
| DuPont | Not reported | Not reported |
| Solvay Solexis | > 1000 | > 1000 |

US EPA 2008

2006 OECD survey

The volume of PFCA precursors as called by OECD (i.e. fluoropolymers) identified in the 2006 OECD survey was 700–7000 t/year (OECD 2006c). For Switzerland, a volume of 28 t/year fluoropolymers (called "products/mixtures containing PFCA or PFCA-related substances" in the survey) was received.

Import to Switzerland

There are no data on the import or export of PFOS or PFOA available in the statistics of the Swiss Federal Customs Administration. However, these statistics exist for fluoropolymers (see Tab. 10). The "primary forms" in the statistics, however, were suspected to contain a high percentage of semi-finished products such as sheets, rods or molded parts. The amounts corresponded reasonably with the information concerning imports of fluoropolymers to Switzerland in 2007 received from the relevant fluoropolymer manufacturers as confident business information. Even though not all of the companies contacted returned the questionnaire (return rate 67 %), the received information was considered valuable. The total imports volumes were estimated to be around 2000 t/year (d.w.). The import included dispersions as well as solid forms such as pellets or powders. PTFE (approx. 20–30 %), PVDF (approx. 30–45 %) together with FEP, PFA and ECTFE make up the majority of the import volumes.

**Tab. 10 > Import and export statistics of fluoropolymers for the year 2007**

| Tariff heading | Description of goods | Import [t/year] | Export [t/year] |
|---|---|---|---|
| 3904.6100 | Polytetrafluoroethylene in primary forms | 975 | 217 |
| 3904.6900 | Fluoro-polymers in primary forms, excl. polytetrafluoroethylene | 1438 | 319 |

FCA 2008

Residual concentrations in fluoropolymers

PFOA, in the form of the ammonium salt (APFO, CAS number 3825-26-1), is used as an emulsifier in the polymerisation of some product families of fluoropolymers. These product families are sold as liquid dispersion products and/or dry resin products. The end uses of PTFE dispersions are numerous due to the convenience of coating techniques. Most important product types and applications include low friction and non-stick surfaces, yarns, fabric and filter cloth, gaskets, laminates, electrical insulation, etc. (Ebnesajjad & Khaladkar 2004). There are dozens of PTFE dispersions due to the variety of their uses. The solid content of the aqueous PTFE dispersions manufactured by DuPont, Dyneon, Solvay Solexis and Daikin is generally about 60 % (McKeen 2006). The aqueous emulsion polymerisation process is conducted in a stirred, pressurized, temperature controlled reactor. The resultant emulsion (or dispersion) is transferred through a filter. If the fluoropolymer emulsion produced is destined to be sold as a liquid fluoropolymer dispersion product, it is concentrated, stabilized and packaged at this point; however, if it is destined to be sold as a dry fluoropolymer product, then the filtered emulsion is separated into solid polymer particles (“agglomerate”) and an aqueous phase. The wet agglomerate is then washed repeatedly with water to remove the remaining polymerisation ingredients, including APFO. The majority of the APFO used in the polymerisation step is contained in these aqueous phases. The clean wet agglomerate is then dried (3M/Dyneon 2007).

**Tab. 11 > Product content of PFOA**

*Reported product content of PFOA for the reporting year 2006 provided by the companies participating in the US EPA's 2010/15 PFOA Stewardship Program.*

| Company | Facility location | Dispersions (ppm, wet-weight basis) | Other fluoropolymers (ppm, dry-weight basis) |
|---|---|---|---|
| 3M/Dyneon | Non-US<br>US | 130<br>0 | Not reported<br>Not reported |
| Arkema | Non-US<br>US | Not applicable<br>> 500–1000 | > 70–150<br>> 70–150 |
| Asahi Glass | Non-US<br>US | 1144 (< 30–2900)<br>500–1570 | 18<br>0.12 |
| Ciba | Non-US<br>US | 30 kg (total for emissions and product content)<br>0.05 kg (total for emissions and product content) | |
| Clariant | All | – | – |
| Daikin | Non-US<br>US | 480<br>280 | 120<br>Plastics: 2; Elastomers: 300 |
| DuPont | Non-US<br>US | 775<br>547 | Elastomers: 0<br>Elastomers: 69 |
| Solvay Solexis | US | 600–700 | 170–200 |

US EPA 2008

Dyneon reported that a small amount (< 5 %) of the total PTFE dispersion manufacturing volume, made at the beginning of the year, had the same APFO concentration as reported for 2000; an average of 1500 ppm. All the rest of the PTFE dispersion manufacturing volume was "Reduced APFO dispersions", with typical concentrations of 10 ppm. 2006 was a transition year for fluoroplastic dispersions made at Gendorf, Germany. Some dispersions manufactured at the beginning of the year had the same average APFO concentration as reported for 2000, an average of 2000 ppm. By the end of the year, all fluoroplastic dispersions manufactured were "Reduced APFO dispersions", with typical concentrations of 50 ppm (3M/Dyneon 2007). Due to the company's success in inventing a replacement for PFOA, 3M and its subsidiary Dyneon stated to be able to accelerate their commitment under the EPA PFOA Stewardship Program. The company planned to stop using PFOA by the end of 2008 as Dyneon has announced finding a replacement for PFOA (3M 2008).

According to confidential business information received from fluoropolymer manufacturers relevant for the Swiss market, the residual concentrations of PFOA were between 0 and < 100 ppm. Products with 0 ppm included PVDF where PFNA is used as a process aid, ECTFE as well as some PTFE, PFA and ETFE products. Highest residual concentrations were indicated to be in PFA and FEP. The total amount of PFOA in residuals of fluoropolymers imported to Switzerland was estimated to be approximately 2–10 kg/year. The total residual amount of PFNA in PVDF imported to Switzerland could be one order of magnitude or higher according to information received by a manufacturer. Applications of PVDF include lining of tanks and reactors, containers for chemicals, pulp and paper industries, semiconductor process equipment and medical devices.

Analyses of several industrial and consumer liquid products containing fluoropolymers or fluorotelomers have been carried out. The results are summarised in Tab. 12 (no analyses of solid products such as packaging or frying pans are listed here). PFOA was found in all samples where this substance was analysed in concentrations between 1 and 160 ppm. Note that most samples were taken before US EPA had initiated the stewardship program in January 2006, which resulted in a reduction of the residual concentrations by the industry.

Precursors selected for the substance flow analysis were detected in variable amounts. FTOHs were present in samples including dispersions of fluorotelomer polymers and other fluorosurfactants. Concentrations of 8:2 FTOH (750–16 000 ppm) were higher by a factor of 2–5 compared to 10:2 FTOH (200–3000 ppm). Compared to PFOA, the residual contents of FTOHs were approximately two orders of magnitude higher. *N*-EtFOSE was detected in a commercial fabric protector from the year 1995 manufactured from POSF at 0.6 ppm (Boulanger et al. 2005). *N*-MeFOSE, stated to be the major constituent in such products, was not analysed in this study, but it was detected in a concentration of 3900 ppm in another study (Dinglasan-Panlilio & Mabury 2006).

**Tab. 12 > Residual concentrations of PFOS, PFOA and selected precursors analysed in industrial and commercial products**

*All concentrations are given as ppm. Note that concentrations were specified either based on dry weight (d.w.) or wet weight (w.w.); n.a. = not available, n.d. = not detected.*

| Product | PFOS | PFOA | *N*-MeFOSE | *N*-EtFOSE | 8:2 FTOH | 10:2 FTOH | Reference |
|---|---|---|---|---|---|---|---|
| Scotchgard, commercial fabric protector (1994), w.w. | 0.2 | 13 | n.a. | 0.6 | n.a. | n.a. | Boulanger et al. 2005 |
| Scotchgard, rug and carpet protector, d.w. | n.a. | n.a. | 3900 | n.a. | n.d. | n.d. | Dinglasan-Panlilio & Mabury 2006 |
| Teflon Advance, carpet protector, d.w. | n.a. | n.a. | n.d. | n.a. | 1900 | 1000 | Dinglasan-Panlilio & Mabury 2006 |
| Zonyl FSO 100, ethoxylated non-ionic fluorosurfactant for the incorporation into caulks, paints, coatings and adhesives, d.w. | n.a. | n.a. | n.d. | n.a. | 2800 | 1500 | Dinglasan-Panlilio & Mabury 2006 |
| Zonyl FSE, water-soluble, anionic phosphate fluorosurfactant for the use in floor waxes and coatings, d.w. | n.a. | n.a. | n.d. | n.a. | 16 000 | 3000 | Dinglasan-Panlilio & Mabury 2006 |
| Motomaster, commercial windshield washer fluid with Teflon, d.w. | n.a. | n.a. | n.d. | n.a. | 750 | 200 | Dinglasan-Panlilio & Mabury 2006 |
| Perfluoro paper coatings, w.w. | n.a. | 88–160 | n.a. | n.a. | n.a. | n.a. | Begley et al. 2005 |
| Fabric protector, spray application consumer product (~ 2000), d.w. | n.d. | 5 | n.a. | n.a. | n.a. | n.a. | Prevedouros et al. 2006 |
| Protector for leather, spray application consumer product (~ 2000), d.w. | n.d. | 78 | n.a. | n.a. | n.a. | n.a. | Prevedouros et al. 2006 |
| Cleaner for rugs and carpets, spray application consumer product (~ 2000), d.w. | 500 | 9 | n.a. | n.a. | n.a. | n.a. | Prevedouros et al. 2006 |
| Cleaner for fabric and upholstery, spray application consumer product (~ 2000), d.w. | 450 | 5 | n.a. | n.a. | n.a. | n.a. | Prevedouros et al. 2006 |
| Solution for mill-carpeting, w.w. | n.a. | 30–80 | n.a. | n.a. | n.a. | n.a. | Washburn et al. 2005 |
| Carpet-care solution, w.w. | n.a. | 1–50 | n.a. | n.a. | n.a. | n.a. | Washburn et al. 2005 |
| Industrial floor waxes and wax removers, w.w. | n.a. | 5–120 | n.a. | n.a. | n.a. | n.a. | Washburn et al. 2005 |
| Latex paint, w.w. | n.a. | 50–150 | n.a. | n.a. | n.a. | n.a. | Washburn et al. 2005 |
| Home and office cleaners, w.w. | n.a. | 50–150 | n.a. | n.a. | n.a. | n.a. | Washburn et al. 2005 |
| Aqueous dispersion of fluoroacrylate polymer, commercial stain and soil repellent for textiles, w.w. | n.a. | 10 | n.a. | n.a. | 1200 | 650 | Russell et al. 2008 |

### 2.5.1.4 Metal plating

PFOS is widely used in metal finishing processes as a foam suppressant and surfactant to reduce surface tension. It prevents mist being formed by gas evolution at electrodes during plating, especially in alkali non-cyanide/zinc baths and hexavalent chromium electroplating, in order to reduce the workplace air concentration of hexavalent chromium. It is also used in a similar way in anodising and acid pickling. Surface finishing is also used in (RPA 2004, EC 2006c):

- copper plating, preventing haze by regulating foam and improving bath stability while improving brightness and adhesion
- nickel plating, as non-foaming surfactants, to reduce the surface tension and increase strength of the electroplate by eliminating pinholes, cracks and peeling
- tin plating producing a uniform coating thickness
- imparting a positive charge to fluoropolymer particles and to aid electroplating of polymers such as PTFE onto steel

Availability of substitutes and possibly measures

By 2007, there were no substitutes for PFOS in Cr(VI) plating and pickling because of its strong resistance to oxidation. PFOS is also used in alkali cyanide-free zinc processes to reduce spray, as well as zinc alloy plating, some anodising and strong acid gold processes. In situations where PFOS has been used, such as Cr(VI) plating, other measures may be taken to prevent Cr(VI) mist reaching MAC levels in the workplace, such as use of floating insulation, lids on tanks and/or redesigned and/or upgraded ventilation, substitution by a less harmful process. Where PFOS is used, it is BAT (best available technique) to minimise its emission to the environment by material conservation techniques such as closing the material loop. Cr(VI) plating can be run on a closed loop system. Other processes can utilise drag-out and rinsing techniques to minimise the release of PFOS. The use of PFOS can also be minimised by controlling its addition (or its containing solutions) using surface tension measurements. In anodising plants, it is BAT to use PFOS-free surfactants, while in other processes, it is BAT to seek phasing out PFOS (EC 2006c). However, accurate implementation of BAT is unknown.

The German Central Association of Surface Treatment Professionals e.V. (Zentralverband Oberflächentechnik e.V., ZVO) changed its opinion concerning the availability of substitutes for PFOS in November 2007 (ZVO 2007). ZVO's opinion in the most recent position paper in September 2008 (ZVO 2008) can be summarised as follows: There are a) products free of PFOS and perfluorinated surfactants as well as b) fluorine-free products. However, there is no long-term experience yet. Fluorine-free products have been used in the hard and decorative chromium plating. Their use in pickling solutions for plastic chromium plating is currently (September 2008) under investigation. ZVO also emphasised that the use of fluorine-free products require higher technical efforts compared to the use of PFOS. In summary, ZVO remains convinced that there is need for PFOS, but the industrial sector will continue to reduce the use of PFOS and replace it by alternatives where possible.

Use in the domestic industry

The specific substance used in metal plating is the tetraethylammonium salt of PFOS (structural formula, see Fig. 10 on page 50). An import of 560 kg or more tetraethylammonium PFOS could be derived from data accessible to the Federal Office for the Environment (FOEN 2009) for the years 2007 and 2008 together. The amount of PFOS alone (80 % by weight) during one year was thus approximately 220 kg or more. Therefore, a best guess consumption of 300 kg/year (200–500 kg/year) was estimated (Tab. 13). The use of PFOS in the EU was estimated for chromium plating as 10 000 kg/year and anodising and acid pickling as 20–30 kg/year (RPA 2004). Converting this number on a per-capita basis as a cross-check, the consumption for Switzerland would be approximately 150 kg/year. Considering the differences in industrial composition, higher per-capita consumption in Switzerland was considered realistic.

There is potential for residual concentrations of PFOA in the PFOS products used in metal plating. The concentrations of PFOA in wastewater samples from the metal plating industry, however, are much lower than the concentrations of PFOS. The concentration of PFOS in wastewater from a company conducting the processes of pickling, galvanising, nickel/chromium-plating and anodising was 8400 ng/L, while it was only 20 ng/L for PFOA (Clara et al. 2008). PFOS concentrations were also higher by generally two to three orders of magnitude in wastewater samples taken from companies in NRW (LANUV 2008). The amounts of PFOA in products for metal plating applications were thus estimated to be small and were not considered in the substance flow analysis.

**Tab. 13 > Estimated domestic consumption of PFOS and PFOA in metal plating**

| Substance | Use in 2007 [kg/year] | | Historical use [kg/year] | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| PFOS | 300 | 200–500 | 300 | 200–500 |
| PFOA | – | – | – | – |

Historical use

Consultation with companies in the UK and in Germany by RPA indicated that no significant changes had been observed in market trends in the last five years and that the companies did not envisage any changes to the market (RPA 2004). As there was no specific information available, it was assumed that the historical use in Switzerland was equal to the use in 2007.

#### 2.5.1.5 Fire-fighting foams

Poly- and perfluorinated surfactants have been widely used as a film forming agent in fire fighting foam (aqueous film-forming foam, AFFF) concentrates against hydrocarbon and polar liquid fires. Foam fire protection has been utilized e.g. in the aviation industry for many years to provide vital fire protection at airports. Fluoroprotein-based foams have been the standard for many years. In the 1960s, chemists at the 3M Company developed agents that provided surface tension properties that enable the formation of an aqueous film that is distributed over the whole surface of the hydrocarbon. In the 1970s, a substantial improvement was made in the effectiveness of foam fire protection with the development of fluorosurfactant-based foams. The fluorosurfactants are unique in their ability to reduce surface tension of aqueous solutions (Scheffey & Hanauska 2002, Pabon & Korzeniowski 2005). AFFF was claimed to be responsible for the consumption of 3 % of perfluorinated substances (Prall 2007). According to the Fire Fighting Foam Coalition, 5 % of fluorotelomer-based products manufactured worldwide are used in the production of fire fighting foams (Renner 2007).

Foam concentrates come in 6 %, 3 % and 1 % products, being mixed with 94 %, 97 % and 99 % water, respectively. The foam solution that is formed generally contains the following (Scheffey & Hanauska 2002):

- Water, 98–99 %
- Surfactants (fluorosurfactants and hydrocarbon surfactants), 0.03–0.45 %
- Glycol ether, 0.5–1.1 %
- Ethylene glycol (not in all formulations), 0.34–0.60 %
- Urea (not in all formulations), 0.2–0.4 %
- Xantham gum (in alcohol resistant formulations)

Because of the presence of large quantities of flammable liquids, municipalities (i.e., fire departments), the hydrocarbon-processing industry (i.e., oil refineries), and military sectors utilize AFFFs. In 1985, the U.S. market for AFFF products (i.e., 3 % and 6 % concentrates) was 6.8 million litres, with the military comprising 75 % of the total market, whereas the municipal entities and hydrocarbon-processing industry represent 13 % and 5 %, respectively (Moody & Field 2000).

No production or formulation of AFFF occurs in Switzerland and the concentrates are imported. In 2007, there was no more import of POSF-based AFFF. However, as a result of their long storage lives, there are still considerable amounts of PFOS in stock. Through consultations with fire brigades, the army, Alcosuisse and the relevant industry, an estimation of the stored volume of AFFF was made for the year 2005. Based on the fraction of POSF-based AFFF and a mean content of 1 % PFOS contained in these foams, a stock of approximately 15–18 t was estimated for that year (Tab. 14). Because of the continuous replacement of AFFF concentrates stored by PFOS-free alternatives, the PFOS in stock was estimated to have decreased between 2005 and 2007 by 15–20 %. Hence, the stock of PFOS in AFFF concentrates was approximately 12–15 t in 2007.

**Tab. 14 > Estimation of the stocks of AFFF and PFOS therein in Switzerland for the year 2005**

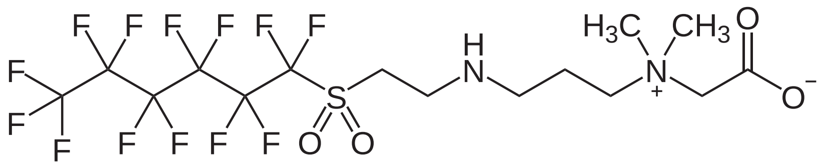
| Location | Number of locations | Stored volume of AFFF per location | Stored volume of AFFF | Fraction of AFFF with PFOS | Stored volume of PFOS |
|---|---|---|---|---|---|
| Tank farms of combustibles and fuels | 30 | 5–40 t | 400 t | 80 % | ~ 3 t |
| Army (mobile reserves) | | | 300 t | 65 % | ~ 2 t |
| Tank farms of Alcosuisse | 2 | 16–25 t | 41 t | 100 % | ~ 0.5 t |
| Industrial plants with fire-extinguishing systems | 200 | 3–5 t | 600–1000 t | 80 % | 5–8 t |
| Supporting fire stations | 200 | 4 t | 800 t | 50 % | 4 t |
| Portable fire extinguishers | 300 000 | 0.00023 t | 68 t | 100 % | ~ 0.5 t |
| Total | | | 2200–2600 t | | ~ 15–18 t |

UVEK 2008

Subsequent to the phase-out of PFOS by 3M after 2000, fluorotelomer-based substances became the standard fluorosurfactant used in AFFF. The primary building block for currently manufactured fluorotelomer surfactants has been the 6:2 fluorotelomer backbone (IFJ 2007). An example of a fluorotelomer-based structure is the perfluoroalkyl betaine derivative shown in Fig. 9. Due to their more complex structure compared to PFOS, the production of fluorotelomer-based structures is more expensive (Prall 2007). 6:2 fluorotelomer sulfonate (6:2 FTS) is likely the primary breakdown product of the six-carbon fluorosurfactants contained in fluorotelomer-based AFFF, which should ultimately degrade to perfluorohexanoic acid (PFHxA) by a partial dehydrofluorination process based on chemical principles. However, this breakdown pathway has not been directly demonstrated experimentally yet (IFJ 2007, Renner 2007, Herzke et al. 2008a).

**Fig. 9 > Structural formula of perfluoroalkyl betaine**

*Structural formula of a perfluoroalkyl betaine that has been used as a film forming surfactant in AFFF; IUPAC name: 2-[dimethyl-[3-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-sulfonylamino)propyl]azaniumyl]acetate, CAS number: 34455-29-3*



POSF-based AFFF is known to contain PFCA impurities in products (IFJ 2007). The concentrations of PFOS and PFOA after a fire incidence in Germany in wastewater sampled at the local WWTP amounted to 17–18 µg/L and 3.6–5.5 µg/L, respectively. The concentrations dropped to 2.2 µg/L and 0.045 µg/L, respectively, about two weeks after the fire. The ratio of the peak concentrations of PFOS and PFOA after another fire in Germany was approximately 10:1. The background concentrations were elevated by two orders of magnitude or more in the sampled streams (LANUV 2008). On the other hand, in another study, no PFOA was found: Samples were taken from two sedimentation basins on a fire drill site in Norway, where fire safety and emergency preparedness courses take place. Average concentrations of PFOS and 6:2 FTS were 30.1 and 82.7 µg/kg, while the concentration of PFOA was below the limit of detection (Herzke et al. 2008b).

Concentrations of PFOA found in four tested AFFF concentrates ranged between 0.015 and 0.066 % w.w. (150–660 ppm), while the concentration in the fifth concentrate could not be quantified (Krop et al. 2008). Samples of two different AFFF concentrates were analysed following a fire incident in Germany in 2008. The first AFFF not containing PFCs according to the manufacturer was found to contain 0.35 ppm of PFOS (sum of all isomers), whereas the concentrations of PFOA and the other eight PFCs analysed were all < 0.15 ppm. The second AFFF analysed contained 0.53 ppm PFOA (sum of all isomers), but PFOS was < 0.15 ppm (LANUV 2008). This concentration is significantly lower than in four of the five AFFF tested in the other study. It was concluded, that the residual concentration of PFOA in AFFF ranges widely. Based on the volume of AFFF stored in Switzerland (2200–2600 t), the amount of PFOA contained was estimated to be 0.1–2 t. Considering the mean of the above mentioned seven AFFF analysed (180 ppm), a stock of 0.4 t was estimated. On the other hand, based on the PFOS:PFOA ratio of peak concentrations that could clearly be attributed to the use of AFFF and that were 10:1 or even lower, the stock would be estimated to be 1–3 t. As a best guess, 1 t was considered (Tab. 15).

**Tab. 15 > Estimated stock of PFOS and PFOA in AFFF in Switzerland in 2007**

| | PFOS | | PFOA | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| Stock [kg] | 13 000 | 12 000–15 000 | 1 000 | 100–3 000 |

Some fluorine-free alternatives to fluorotelomer-based AFFF exist for class B fires, (e.g. Sthamer 2004, LFV Bayern 2008, Sthamer 2008). However, for the year 2007 no substantial replacement of fluorotelomer-based AFFF was assumed to have taken place as its performance has been shown to be better compared to its alternatives (Prall 2007). The import of PFOA in AFFF was thus estimated to be equal to the amount used and disposed of after having reached its shelf life. The best guess estimate was thus the sum, i.e. 77 kg/year for PFOA, while the import of PFOS was estimated to be zero (Tab. 16).

**Tab. 16 > Estimated imports of PFOS and PFOA in AFFF to Switzerland in 2007**

| | PFOS [kg/year] | | PFOA [kg/year] | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| Import | 0 | – | 77 | 10–200 |

#### 2.5.1.6 Photolithography and semiconductors

POSF-based substances are used in a number of functions within the semiconductor industry. These relate to photolithography, a process by which the circuits are produced on the semiconductor wafers. This process uses photoresists, materials whose composition is altered on exposure to light, making them either easier or more difficult to remove, thus allowing structures to be built up in the wafer. The POSF-based substances can form part of the photoresist itself, acting as a photoacid generator in the chemical amplification of the effect of exposure. They can also be used to add a thin coating to the resist to reduce reflections either to the top (top anti-reflective coatings, TARC) or to the bottom (bottom anti-reflective coatings, BARC). POSF-based substances may also be used as surfactants in developers or in ancillary products such as edge bead removers (EBRs). Industry stated that the manufacture of advanced semiconductor devices is not currently possible without the use of PFOS in critical applications such as photoresists and antireflective coatings (see Tab. 17). Some alternatives to PFOS have been created for non-critical uses such as developers or edge bead removers (Brooke et al. 2004, SIA 2008b). In May 2006, the global semiconductor industry through the World Semiconductor Council (WSC) agreed to curtail the use of POSF-based chemicals where they are not critical to the manufacturing process (SIA 2006).

ESIA (European Semi-Conductor Industry Association) and SEMI (Semiconductors Equipment & Materials International) have provided the information on the use of POSF-based substances in the EU in 2002 (status 2005). As shown in Tab. 15 total consumption accounted for 436 kg/year. Information on the use in 2005 is also available on a global level: critical applications summed up to 5000 kg/year, whereas non-critical applications accounted for 750 kg/year. Industry affirmed that the Semiconductor Industry Associations in Europe, Japan and Korea eliminated non-critical uses during 2007 (SIA 2008a). Therefore, it was assumed that figures for non-critical applications could be reduced by 50 % taking into account the whole year 2007. There are around 80 production sites in the semiconductor industry in Western Europe (ESIA 2004), while there are two large and several small production sites in Switzerland. Assuming that the use of POSF-based substances is equally distributed among the production sites, Switzerland accounts for 3–5 % of the use in Western Europe. Hence, the consumption in domestic semiconductor industry was estimated to be 9–15 kg/year.

**Tab. 17 > Consumption of POSF-based substances in critical and non-critical applications in photolithography in the European Union**

| Critical applications | EU use in 2002 [kg/year] | Non-critical applications | EU use in 2002 [kg/year] |
|---|---|---|---|
| Photoresists | 45 | Developers | 195 |
| Top anti-reflective coatings (TARCs) | 104 | Edge bead removers (EBRs) | 85 |
| Bottom anti-reflective coatings (BARCs) | 7 | Spin-on-glass (SOGs) | – |

SIA 2005, SIA 2008a

There is little information about the specific substances used in this area, and the involved companies are reluctant to identify them (Brooke et al. 2004). OECD listed acid catalyst for photoresists and surfactants for etching acids for circuit boards as being of the PFOS salt type (OECD 2002). In another OECD document, it is stated that chemicals used for photoresists in the photolithography process for semiconductor manufacturing include e.g. poly(hexafluorobutylmethacrylate) and polyfluoroalkylmethacrylates (chain length not specified) (OECD 2004e). Due to the lack of more reliable data, it was estimated that PFOS makes up between 10 % and 90 % by mass of the POSF-based substances used in the semiconductor industry. Hence, the estimated use in 2007 was between 1–14 kg/year and a best guess of 6 kg/year was considered. The historical use (nineties and beginning of the current decade) was estimated with the non-reduced amounts in non-critical applications (Tab. 18).

**Tab. 18 > Estimated consumption of PFOS and PFOA in the domestic semiconductor industry**

| Substance | Use in 2007 [kg/year] | | Historical use [kg/year] | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| PFOS | 6 | 1–14 | 10 | 2–22 |
| PFOA | – | – | – | – |

### 2.5.1.7 Photography

POSF-based chemicals have been used for the following purposes in mixtures used in coatings applied to x-ray films, photographic films, papers and printing plates (EPCI 2003 cited in RPA 2004):

- surfactants
- electrostatic charge control agents
- friction control agents
- dirt repellent agents
- adhesion control agents

EPCI indicate that the main area of use for PFOS-related substances is in the medical area (x-rays), with 85 % of EU use in this sector (Brooke et al. 2004). The photo imaging industry argued that it does not use PFOS itself, but POSF-based substances play an essential role in manufacturing and performance of certain traditional and digital imaging products because they provide critical antistatic, surfactant, friction control and dirt repellent qualities. These substances also provide important safety features by controlling the build-up and discharge of static electricity and preventing employee injury, operating equipment, product damage, as well as fire and explosion hazards (Guest 2007a).

Six different POSF-based chemicals have been reported as being used by the photographic industry in Europe (EPCI 2003 cited in RPA 2004): The two salts shown in Fig. 10 and Fig. 11 as well as four different polymeric substances or mixtures. Tetraethylammonium perfluorooctanesulfonate that is a PFOS salt has been used in the manufacture of photographic film. 3-(perfluorooctylsulfonylamino)propyl-trimethylazanium iodide is a derivative of FOSA and a potential precursor substance of PFOS. This substance has been used in the manufacture of photographic film, paper and plates.

**Fig. 10 > Structural formula of tetraethylammonium perfluorooctanesulfonate**

*Structural formula of tetraethylammonium perfluorooctanesulfonate that has been used in the manufacture of photographic film. CAS number: 56773-42-3*

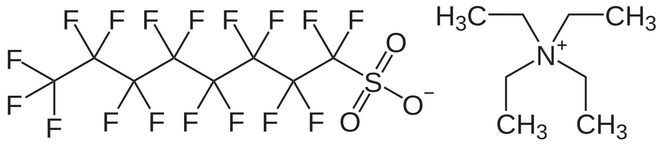
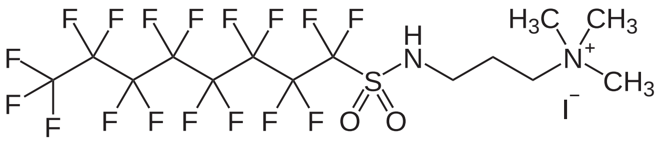


**Fig. 11 > Structural formula of 3-(perfluorooctylsulfonylamino)propyl-trimethylazanium iodide**

*Structural formula of 3-(perfluorooctylsulfonylamino)propyl-trimethylazanium iodide that has been used in the manufacture of photographic film, paper and plates. CAS number: 1652-63-7*



The trend in imaging has been towards the development of digital products that are processed dry. This has increased demands for static control and tended to increase the use of POSF-based substances. Thus, until the mid-1990s, the historical use of PFOS materials was one-half to one-third of the level used in 2000 when 3M announced its voluntary PFOS phase-out. Since 2000, the use of POSF-based chemicals for imaging purposes has declined markedly and it was estimated that the total reduction in tonnage was as high as 83 % (EPCI 2003 cited in RPA 2004). A decrease in the worldwide usage of POSF-based substances in the manufacture of traditional and digital imaging products from about 25 000 to less than 10 000 kg/year, between 2000 and 2004 through voluntary replacement initiatives was estimated by industry organisations. Additional decreases in use have occurred since 2004. Even though replacements do not currently exist for the remaining critical product applications, further reductions are expected as the transition continues towards digital imaging technologies (Guest 2007a, Guest 2007b). Some uses have been discontinued totally by the industry. Such uses include:

- defoamer in the production of processing chemicals for films, papers and printing plates
- PAG (photo-acid generator) in the manufacture of printing plates
- surfactant in photolithographic processing solutions in the manufacture of printing plates
- surfactant in photographic processing solutions in the processing of films and papers

According to industry, restrictions on the remaining uses of POSF-based substances would have a severe impact on the photo imaging industry's ability to manufacture a number of important imaging products, including diagnostic medical products, industrial X-ray for non-destructive testing and graphic printing (printing mask) (Guest 2007a).

The demand for POSF-based chemicals was expected to be 1500 kg/year in the EU in 2004, from which, less than 50 kg/year were used for paper products and less than 150 kg/year for printing plates, with the remainder being used for various types of film products. Tetraethylammonium perfluorooctanesulfonate that was considered as PFOS (80 % by weight of that salt is PFOS) has only been used in the manufacture of photographic films. 1300 kg/year were accounted for this use in 2004. The polymeric substances and mixtures were assumed to contain 1 % of PFOS as residuals (Brooke et al. 2004). Assuming that the consumption in the EU did not decrease much between 2004 and 2007 and that each of the six substances or formulations used in the manufacture of photographic film hold an equal share, the consumption of tetraethylammonium perfluorooctanesulfonate could be estimated to be approximately 200 kg/year. This corresponds to 160 kg/year of PFOS in the EU. Converting this number on a per-capita basis, the consumption for Switzerland would be 2.5 kg/year. This estimate is only related to imports as no domestic manufacturer of photographic or x-ray films is known.

Information from EPCI indicates a concentration of POSF-based substance in film of 0.1–0.8 µg/cm². The most common backing material for film is PET (polyethylene terephthalate). The material has a density of 1.39 g/cm³. The depth of film was suggested to be 45 µm. Hence, the mass per unit area is $6.3 \cdot 10^{-3}$ g/cm². In the import and export statistics of the Customs Authorities (Tab. 19), there is no distinction between photographic plates and film. Assuming that films account for approximately half by weight, i.e. 2000 t/year, the area of film would approximately be $3 \cdot 10^{11}$ cm²/year. Taking into account the concentration of POSF-based substances in film mentioned above, they would amount to 30–240 kg/year.

**Tab. 19 > Domestic import and export statistics of photographic materials for the year 2007**

| Tariff heading | Description of goods | Import [t/year] | Export [t/year] |
|---|---|---|---|
| 3701 | Photographic plates and film in the flat, sensitized, unexposed, of any material other than paper, paperboard or textiles; instant print film in the flat, sensitized, unexposed, whether or not in packs | 4265 | 876 |
| 3702 | Photographic film in rolls, sensitized, unexposed, of any material other than paper, paperboard or textiles; instant print film in rolls, sensitized, unexposed | 749 | 421 |
| 3703 | Photographic paper, paperboard and textiles, sensitized, unexposed | 865 | 81 |
| 3704 | Photographic plates, film, paper, paperboard and textiles, exposed but not developed | 38 | 45 |
| 3705 | Photographic plates and film, exposed and developed, other than cinematographic film | 57 | 13 |
| 3706 | Cinematographic film, exposed and developed, whether or not incorporating sound track or consisting only of sound track | 182 | 82 |
| 3707 | Chemical preparations for photographic uses (other than varnishes, glues, adhesives and similar preparations); unmixed products for photographic uses, put up in measured portions or put up for retail sale in a form ready for use | 3299 | 2745 |

FCA 2008

Hence, the amount of PFOS is approximated to be 4–30 kg/year assuming the same share of tetraethylammonium perfluorooctanesulfonate and the same residual concentration of PFOS in polymers. Thus, there is a reasonable agreement between the estimates based on the breakdown of European data and Swiss market statistics. A best guess import of PFOS of 4 kg/year and a range of 1–30 kg was considered (Tab. 20). There might also be a residual content of PFOA in these products. However, as the concentrations are most likely in the range of some to a few hundreds of ppm, the amounts of PFOA were estimated to be a few grams per years. Therefore, this application area was not considered for PFOA. The historical import was estimated based on the two statements of decreased in the use of POSF-based substances since 2000 (83 % and 60 %, see above).

Since 2000, the use of POSF-based chemicals for imaging purposes has declined markedly with a total reduction in tonnage estimated to be as high as 83 % (EPCI 2003 cited in RPA 2004). A reduction of the worldwide usage of POSF-based substances by more than 60 % since 2000 through voluntary replacement initiatives was estimated by industry organisations.

**Tab. 20 > Estimated amounts of PFOS and PFOA in imports for the domestic photographic industry**

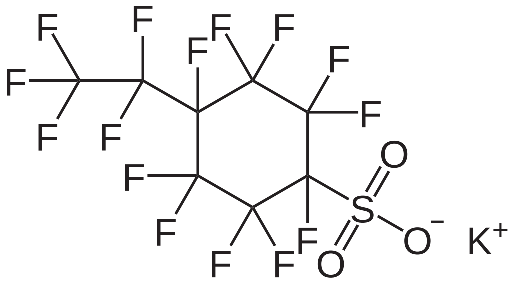
| Substance | Use in 2007 [kg/year] | | Historical use [kg/year] | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| PFOS | 4 | 1–30 | 15 | 2–180 |
| PFOA | – | – | | – |

### 2.5.1.8 Hydraulic fluids for aviation

Potassium perfluoroethylcyclohexylsulfonate (Fig. 12) has been used as a component of fire-resistant hydraulic fluids in aircrafts. It acts to inhibit erosion and damage to parts of the hydraulic systems and is present in the fluids at ppm levels (< 500 ppm). Hydraulic fluids containing this substance have been used in all commercial transport aircrafts. The world-wide use was estimated to be 2.2 t/year, of which one third was assumed to be used in the EU each year (Boeing 2001, Brooke et al. 2004, RPA 2004). Converted on a per-capita basis (assuming a similar commercial transport aircraft density compared to the situation in the EU), the use in Switzerland would amount to 10 kg/year. 3M has included ethylcyclohexyl derivatives in the products they have discontinued. It has been supposed that if the ethylcyclohexyl derivatives should become unavailable, the only known substitute is the potassium salt of PFOS (RPA 2004). Potassium perfluoroethylcyclohexylsulfonate is on the “Lists of PFOS, PFAS, PFOA, PFCA, Related Compounds and Chemicals that may Degrade to PFCA” (OECD 2007a). Hydraulic fluids for aviation are covered in the appendix of the Directive 2006/122/EC, paragraph 3d (EC 2006a). However, as the molecular formula of potassium perfluoroethylcyclohexylsulfonate is $C_8HF_{15}O_3S^-K^+$, it is not covered by the generic molecular formula defined as $C_8F_{17}SO_2X$ (X = OH, metal salt ($O^-M^+$), halide, amide and other derivatives including polymers). Hence, it is also not a precursor of PFOS. Hydraulic fluids for aviation were not included in the substance flow analysis since their contribution to the occurrence of PFOS in the environment was unexpected.

**Fig. 12 > Structural formula of potassium perfluoroethylcyclohexylsulfonate**

*Structural formula of potassium perfluoroethylcyclohexylsulfonate that has been used in hydraulic fluids; IUPAC name: potassium 1,2,2,3,3,4,5,5,6,6-decafluoro-4-(pentafluoroethyl)cyclohexane-1-sulfonate; CAS number: 335-24-0*



### 2.5.1.9 Textile protection

General information

Easy-to-clean textiles are desired for many applications (upholstery, table-cloths, curtain material, bed linen, car seats, etc.) or the textiles must be waterproof but breathable (e.g. tents, ski clothes, rain jackets, shoes). When applied as a finish to certain textiles, such as polyester and polyamide garments, treatments with fluorotelomer-based polymers give water, oil and soil repellence and a soft handle. In technical textiles, they impart or enhance properties such as resistance to water, mechanical loads and intense heat. Furthermore, PTFE-based membranes are often used in rain coats due to their water resistance and ability to breathe. However, these membranes are not strong enough to be employed as outer layers of outdoor clothes and are attached on the inside to a robust textile, which is often additionally surface treated with fluorinated polymers or co-polymers (Hekster et al. 2002, RPA 2004, Berger & Herzke 2006).

Commercial fluorochemical repellents are mostly copolymers of fluoroalkyl acrylates and methacrylates. Marketed formulations contain the active agent together with emulsifiers and other by-products which are often solvents. The success of these agents, despite their high cost compared to other types of water repellents, is especially due to the fact that they are permanent and they provide both oil and water repellency (Umweltbundesamt 2003). The perfluoroalkyl sulfonates (PFAS) that were, in general, used for textile (and carpet) surface treatment applications are the acrylate, adipate and urethane polymers produced from the ECF intermediate, *N*-MeFOSE and *N*-Et-FOSE (RPA 2004). By poundage, *N*-MeFOSE based intermediates and products slightly predominated over *N*-EtFOSE-based materials (3M 1999).

PFOS

According to information received from industry and textile manufacturers, the use of products based on ECF process has been discontinued in the domestic textile market several years ago. One large textile manufacturer stated that they replaced Scotchgard made by 3M between 1994 and 1995 with fluorotelomer-based products that do not contain PFOS. The year in which other Swiss textile manufacturers switched to fluorotelomer-based products is unknown. However, the Scotchgard product line was changed from the ECF-based C8- to C4-based substances after the phase-out of the

PFOS-chemistry by 3M. Hence, the ultimate degradation product is PFBS and not PFOS. Overall, there is no indication of a use of POSF-based products by domestic manufacturers in 2007. However, clothes and other textiles containing these substances might be imported from abroad, especially from outside the European Union. China e.g. stated that more than 10 000 t/year of fluorine-containing textile finishing agents were imported for the treatment of high-quality clothing. Estimated 1.5 billion meters of the total 50 billion meters of dyed and finished textiles were treated with such agents (MEP 2008).

Fluorotelomer-based polymers

Fluorotelomer-based acrylate polymers, copolymers with perfluorooctylethylacrylate (8:2 FTA) and perfluorooctylethylmethacrylate (8:2 FTMA), have been used as active components for textile finishing (Malner 2002). They are applied to outdoor clothes, upholstery fabric, curtain material, umbrellas, car seat covers, protective clothing, mechanics' overalls, etc. The production of high quality curtains and upholstery was estimated to represent the largest use (RPA 2004).

According to confidential business information received from fluorotelomer and textile manufacturers, the volumes of fluorotelomer-based polymer dispersions used in 2007 were approximately 150–250 t. The solid content therein was approximately 30–60 t. One large domestic textile manufacturer claimed that it used C8-based fluorotelomer polymer dispersions in 2007. The same company used C6-based fluorotelomer polymer dispersions only in small quantities for experiments at that time. On the other hand, one large supplier of Swiss textile manufacturers informed that in 2007 all of its textile products were mainly based on C6[2] chemistry. The residual concentrations PFOA in these fluorotelomer-based polymer dispersions were stated to be below 2 ppm. Another company stated that their fluorotelomer-based products contain less than 1 ppm of PFOA. No information on PFOA residual concentrations was received from other producers or from textile manufacturers. In a 2005 study, the residual PFOA content in fluorotelomer product formulations were analysed. The concentrations ranged between not detected (< 1 mg/L) and 40 mg/L (Washburn et al. 2005). The amount of PFOA in fluorotelomer-based polymer dispersions used by domestic textile manufacturers was therefore calculated to be < 0.15–10 kg/year. On one hand, the producers of fluorotelomer-based polymer dispersions have worked to reduce the PFOA content since the study was performed. On the other hand, import of products that were not “reduced content” at that time or production by companies that do not take part in the US EPA Stewardship Program might have also taken place. Therefore, an amount of 1 kg/year was considered as a best guess. Residuals of 8:2 FTOH and 10:2 FTOH in an aqueous dispersion of a fluoroacrylate polymer used commercially as a stain and soil repellent for textiles were analysed. Concentrations were 1200 and 650 ppm (w.w.), respectively (Russell et al. 2008). Based on the fluoroacrylate polymer content of 24–28 % given, concentrations were calculated to be approximately 4500 and 2500 ppm. Considering the 30–60 t/year fluorotelomer-based polymers uses by the domestic industry, the amount of 8:2 FTOH and 10:2 FTOH would account for approximately 130–300 kg/year and 70–150 kg/year.

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[2] The main active ingredients are C6 chains, but the products contain a distribution in chain length which will include C8, C10, etc.

Historical use

One Swiss company informed that, historically, it used 5–7 t/year of Scotchgard products with a solid content of 1–1.5 t/year. Even though the market share of the company in the nineties is not exactly known, an historical use of 3–15 t/year of POSF-based substances was estimated. A sample of a commercial fabric protector from a 1994 can of Scotchgard was analysed and the amount of different PFCs present as residual compound in the polymeric product was quantified. The concentrations on a wet weight basis were 13 ppm PFOA, 0.2 ppm PFOS and those of the PFOS precursors *N*-EtFOSE, *N*-EtFOSA and FOSA 0.6 ppm, 0.2 ppm and 1.3 ppm, respectively (Boulanger et al. 2005). These concentrations were claimed to be low. However, the dominant fluorinated material used in surface protection in this product line was *N*-MeFOSE, which was apparently not analysed in their study (Dinglasan-Panlilio and Mabury 2006). If the solid content of the commercial product analysed is assumed to be 1 %, residual concentrations are on a dry weight basis 1300 ppm, 20 ppm and 60 ppm for PFOA, PFOS and *N*-EtFOSE, respectively. In their own study, Dinglasan and Mabury found the residual concentration of *N*-MeFOSE in a rug and carpet protector to be 3900 ppm (d.w.). Four spray application consumer products purchased at retail prior to phase-out of POSF-based products by 3M were analysed. The concentration of PFOS was 450 and 500 ppm d.w., respectively, whereas the concentrations were below limit of detection in the two others (Prevedouros et al. 2006). It was assumed that the residual concentrations of PFOS and the selected FOSE derivatives in POSF-based used for the protection of apparel, leather and carpets were similar relating to the dry weight. The consumption figure estimates derived from these data are shown in Tab. 21. The work of the fluoropolymer and fluorotelomer manufacturers that has joined the US EPA stewardship program was estimated to have led to a decrease of PFOA present in residuals, even though historical use volumes of fluoropolymers and fluorotelomers were somewhat lower than in 2007. Hence, the historical use was estimated to be tenfold higher than what it was in 2007. The historical use of FTOHs was assumed to be equal to the present use. On one hand, recent efforts by the industry were estimated to have resulted in lowered emissions (Armitage et al. 2006, Yarwood et al. 2007). On the other hand, annual fluorotelomer production was estimated to have more than doubled from the period 1980–1994 to 1995–2004 (Prevedouros et al. 2006). As a rough estimation, a constant use was considered.

**Tab. 21 > Estimated consumption of PFOS, PFOA and selected precursors in the domestic textile industry**

| Substance | Use in 2007 [kg/year] | | Historical use [kg/year] | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| PFOS | 0 | – | 2 | 0.1–8 |
| PFOA | 1 | 0.1–10 | 10 | 1–100 |
| *N*-MeFOSE | 0 | – | 30 | 10–60 |
| *N*-EtFOSE | 0 | – | 0.2 | 0.1–1 |
| 8:2 FTOH | 200 | 130–300 | 200 | 130–300 |
| 10:2 FTOH | 100 | 70–150 | 100 | 70–150 |

Imports in clothing and textiles

Berger and Herzke (2006) analysed the amount of different PFCs that are freely extractable from textile samples. The samples included e.g. several kinds of rain and sports jackets, trousers, overalls, synthetic and cotton textiles as well as a PTFE tablecloth. Tab. 22 also includes the results of samples taken in Sweden, but also analysed in the laboratories of NILU as the samples mentioned above.

**Tab. 22 > Freely extractable amounts of fluorinated substances from textile samples**

*Statistical dataset of two studies analysing 11 and 6 textile samples taken in Norway and Sweden. Concentrations are given in ng/g of textile.*

| | PFOS | PFOA | *N*-MeFOSE | *N*-EtFOSE | 8:2 FTOH | 10:2 FTOH |
|---|---|---|---|---|---|---|
| Mean | 22 | 98 | 31 | 5.4 | 8000 | 360 |
| Median | 0.2 | 66 | 2.8 | < 3 | 490 | 250 |
| Minimum | < 0.1 | 2.0 | < 0.3 | < 0.3 | < 23 | < 25 |
| Maximum | 350 | 420 | 280 | 70 | 120 000 | 1300 |
| % detected | 82 % | 100 % | 65 % | 41 % | 94 % | 94 % |

Berger & Herzke 2006, Schulze & Norin 2006, SFT 2006

Total sales of the Swiss textile and clothing industry were worth CHF 4.3 billion in 2007, of which CHF 2 billion were made up by clothing and CHF 125 million by textile finishing. However, no detailed statistics are available for the domestic production or consumption volumes. Imports of textiles amounted to 190 000 t or CHF 2.5 billion, whereas exports were 170 000 t or CHF 2.2 billion, respectably, in 2007. The corresponding numbers for clothing were: import 100 000 t (CHF 6.2 billion), export 11 000 t (CHF 2.2 billion). 86 % by value of the imports came from EU and another 10 % from Asia (TVS 2008). The import of textiles and clothing that were suspected to potentially contain PFCs was approximately 16 000 t (CHF 120 million) and 8000 t (CHF 320 million) according to statistics made by the Swiss Federal Customs Administration and own assumptions. For an estimation of the amounts in imported goods, it was assumed that the concentrations measured in clothing (Tab. 22) apply to the import of 24 000 of textile and clothing. The maximum concentrations were considered for the upper boundary of the range, whereas for the lower boundary, a tenth of the mean was taken into account. The mean was considered for the estimation of the best guess (Tab. 23). The historical imports were estimated based on the same assumptions made on the consumption in the domestic industry. In addition, a tenfold higher historic import of PFOS and the two selected precursors were assumed due to the lack of data.

**Tab. 23 > Estimated amounts of PFOS, PFOA and selected precursors in textiles and clothing imported to Switzerland**

| Substance | Use in 2007 [kg/year] | | Historical use [kg/year] | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| PFOS | 0.5 | 0.05–8 | 5 | 0.5–80 |
| PFOA | 2 | 0.2–10 | 20 | 2–100 |
| *N*-MeFOSE | 0.7 | 0.07–7 | 7 | 0.7–70 |
| *N*-EtFOSE | 0.1 | 0.01–1.5 | 1 | 0.1–15 |
| 8:2 FTOH | 200 | 20–2800 | 200 | 20–2800 |
| 10:2 FTOH | 9 | 0.9–30 | 9 | 0.9–30 |

### 2.5.1.10 Leather protection

Fluorinated surfactants are used in various leather manufacturing processes and repellent treatments of tanned leather. They improve the efficiency of the process, reduce the processing time and increase the quality of the product (Kissa 2001).

Fluorotelomer-based polymers

The amounts of fluorotelomer-based polymer dispersions used for the treatment of leather products in the domestic market were 1–3 t in 2007 according to confidential business information received. The solids amounted to 0.3–1 t/year only. Assuming the PFOA residual content as half the specified maximum concentration (i.e. 2 ppm), the amount of PFOA is only 1 g/year or less. Even if the PFOA content in some products from manufacturers that did not participate in the survey would be somewhat higher, the amount would still be very low in this application area. The same residual concentrations of 8:2 FTOH and 10:2 FTOH on a solid weight basis as in a fluoroacrylate polymer stain and soil repellent for textiles in the section above were assumed: 4500 and 2500 ppm. Considering the 0.3–1 t/year fluorotelomer-based polymers used by the domestic industry, the amounts of 8:2 FTOH and 10:2 FTOH account for approximately 1–5 kg/year and 0.7–3 kg/year. Also, as revealed by the information from Germany, Austria and the UK, there was no indication of a use of POSF-based substances in Switzerland in 2007. There is an entry in the Swiss product register for a product used for leather, which contained a potassium salt of a glycine derivative of *N*-EtFOSA (CAS number 2991-51-7). However, this product is probably not in use anymore.

Historical use

The historical use of POSF-based acrylate, adipate and urethane polymers produced from the intermediate substance *N*-EtFOSE was estimated to be 15 tonnes for apparel and leather (Brooke et al. 2004). Assuming that a per-capita approach is appropriate and that leather made up half of the use, the historical consumption of POSF-based polymers in Switzerland was estimated as approximately 1 t/year. The same concentrations of PFOS, *N*-MeFOSE and *N*-EtFOSE based on dry weight as in the section on textiles above were considered. Hence, the amounts of these substances in products were roughly estimated as 0.02–0.5 kg/year of PFOS, 4 kg/year of *N*-MeFOSE and 0.06 kg/year of *N*-EtFOSE, respectively. Due to the lack of multiple measurements, an estimated range was added to the latter two substances. The historical consumption of PFOA and the two FTOHs was estimated in the same manner as in the previous sections (Tab. 24).

**Tab. 24 > Estimated consumption of PFOS, PFOA and selected precursors in the domestic leather industry**

| Substance | Use in 2007 [kg/year] | | Historical use [kg/year] | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| PFOS | 0 | – | 0.2 | 0.02–0.5 |
| PFOA | 0.001 | 0–0.01 | 0.01 | 0–0.1 |
| *N*-MeFOSE | 0 | – | 4 | 1–10 |
| *N*-EtFOSE | 0 | – | 0.6 | 0.1–2 |
| 8:2 FTOH | 3 | 1–5 | 3 | 1–5 |
| 10:2 FTOH | 1.5 | 0.7–3 | 1.5 | 0.7–3 |

Import in shoes

According to the statistics of the Swiss Federal Customs Administration, 20 million pairs of leather shoes were imported with a weight of 16 000 t in 2007. The exports were roughly tenfold lower (FCA 2008). Also the domestic production of shoes was estimated to be markedly smaller than the import. As there are no other data available, the amount of PFOA in technical textiles estimated by Washburn et al. (2005) as 0–0.034 mg/kg was considered for this study. Hence, the import of PFOA in leather shoes would be up to 0.5 kg/year. However, not all leather shoes imported are treated with fluorinated substances. Danish EPA assumed that mainly boots, especially those for children, are coated with PTFE (Jensen et al. 2008). PTFE is probably used as a membrane in an internal layer of the shoes. In addition to shoes, fluorinated substances have been used to protect other types of leather products such as leather coats or furniture. Despite these uncertainties, the amounts of PFOA imported were still roughly estimated. In order to get a very rough estimate for the other substances, it was assumed that the import of leather products is one order of magnitude higher than the domestic production. Therefore, the imported amounts of these substances were considered to be tenfold of the domestic consumption while keeping the lower boundary of the range (Tab. 25).

**Tab. 25 > Estimated amounts of PFOS, PFOA and selected precursors leather products imported to Switzerland**

| Substance | Use in 2007 [kg/year] | | Historical use [kg/year] | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| PFOS | 0 | – | 2 | 0.2–5 |
| PFOA | 0.2 | 0.05–1 | 2 | 0.5–10 |
| *N*-MeFOSE | 0 | – | 40 | 1–100 |
| *N*-EtFOSE | 0 | – | 6 | 0.1–20 |
| 8:2 FTOH | 30 | 1–50 | 30 | 1–50 |
| 10:2 FTOH | 15 | 0.7–30 | 15 | 0.7–30 |

### 2.5.1.11 Carpet protection

Fluorinated substances have been used to treat carpet fibres to prevent the adherence of oil, liquid spills, stains and grit to the surface. They have also been used as carpet spot cleaners in which they provide stain resistance (RPA 2004). However, commercially available impregnation agents applied by privates were not considered here but were included in section 2.5.1.16 (impregnation agents). Information RPA received from the European Carpet Association indicates that stain and soil repellent products based on fluorinated polymers are used by its members. It was stated that currently all fluorinated chemicals used in anti-stain/anti-soil preparations are prepared via the telomerisation route (RPA 2004).

According to the Swiss Federal Customs Administration 22 400 tons of carpets were imported and 11 300 tons were exported in 2007. A Swiss carpet manufacturer estimated that the imports of carpets are markedly higher than the domestic production.

Half of the domestic production or slightly more is used in Switzerland. The 21 tariff headings were split up in carpets made of natural and synthetic fibres according to the descriptions and information provided by one carpet manufacturer (Tab. 26). Six carpet manufacturers and one carpet finisher were contacted, four of which were willing to provide information. Two of them did not manufacture carpets in Switzerland in 2007. One company applies stain repellents to 3 % of its production volume. However, the products used do not contain fluorinated substances. The other company does not use stain repellent agents in domestic production. However, yarns pre-treated are imported for the manufacture of carpets in Switzerland. No information was provided on the products used to pre-treat the yarns abroad.

**Tab. 26 > Domestic import and export statistics of carpets**

*Aggregated statistics of different carpet categories for the year 2007 [t/year].*

| Number of tariff headings | Description | Import [t/year] | Export [t/year] |
|---|---|---:|---:|
| 12 | Carpets made of natural fibres | 5 200 | 2 100 |
| 9 | Carpets made of synthetic fibres | 17 200 | 9 200 |
| 21 | Total | 22 400 | 11 300 |

FCA 2008

None of the polymer manufacturer participating in the survey on imports of fluorotelomers and fluoropolymers claimed the import products to be used by Swiss carpet manufacturers. Hence, no domestic use of fluorinated products could be confirmed. This finding is in contrast to information provided by two large carpet manufacturers in Denmark. One company impregnates all of the carpets produced with a fluorinated DuPont product. About 20 % of the carpets manufactured by the other company are impregnated with a Zonly product. The company also stated that only specific fibres are being impregnated: While nylon fibres are always impregnated, carpets based on wool fibres are never impregnated. Primarily, carpets for use in offices are treated with stain repellents (Jensen et al. 2008). Also information collected in a Norwegian study suggests that carpets made of natural fibres such as wool are normally not impregnated. On the other hand, a substantial part of carpets made of synthetic fibres are impregnated with fluorinated compounds during manufacturing (SFT 2007).

Imports

It was thus assumed that only the synthetic carpets imported into Switzerland contain fluorinated compounds and that the fraction treated with them is 30–80 %. Based on an estimated concentration of PFOA in carpet fibres of 0.2–2 mg/kg (Washburn et al. 2005), the amount of PFOA in imported carpets derived accounted for 1–30 kg/year. The weight per unit area of carpets made of synthetic fibres was assumed to be 1.5–2.5 kg/m$^2$ based on a web search performed. Hence, the import of synthetic carpets was approximately to be between 7 and 12 million m$^2$ in 2007. Considering the content of fluorinated compounds in carpets to be 0.1–2 g/m$^2$ as estimated by Jensen et al. (2008) and considering that 30–80 % of imported carpets are being treated, the amount of fluorinated compounds sums up to 0.2–20 t/year. The assumption that PFOA residual concentration is between 1 and 100 ppm yields a very wide range of 0.0002–2 kg/year.

A best guess of 5 kg/year in imported carpets was considered based on the two different estimation methods (Tab. 25).

Estimates for POSF-based substances (only used historically) and FTOHs were made based on residual concentrations measured in a range of products (see Tab. 12 on page 42). 8:2 FTOH and 10:2 FTOH contents on a dry weight basis were determined as 1900 ppm and 1000 ppm, respectively (Dinglasan-Panlilio & Mabury 2006). Based on the amount of fluorinated compounds above, the imports are estimated to be 0.4–40 kg/year and 0.2–20 kg/year, respectively. As in the sections above, it was assumed that the amounts of FTOHs remained stable over time, whereas for PFOA, historically, a tenfold higher import was assumed. For PFOS, residual concentrations on a dry weight basis were determined as 20–5000 ppm. The approximate figure for the historical use of POSF-based polymers in the UK was estimated to be 23 t/year (Brooke et al. 2004). The amount of 3 t/year converted on a per-capita approach to Switzerland is consistent with the estimate above (0.2–20 t/year). The amounts historically imported in carpets were estimated using the residual contents of PFOS (20–500 ppm), *N*-MeFOSE (3900 ppm) and *N*-EtFOSE (60 ppm) analysed in different carpet and rug protectors (Boulanger et al. 2005, Dinglasan-Panlilio and Mabury 2006, Prevedouros et al. 2006). The resulting amounts are shown in Tab. 27.

**Tab. 27 > Estimated amounts of PFOS, PFOA and selected precursors in carpets imported to Switzerland**

| Substance | Use in 2007 [kg/year] | | Historical use [kg/year] | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| PFOS | 0 | – | 2 | 0.01–10 |
| PFOA | 5 | 0.01–30 | 50 | 0.1–300 |
| *N*-MeFOSE | 0 | – | 12 | 0.8–80 |
| *N*-EtFOSE | 0 | – | 0.6 | 0.01–2 |
| 8:2 FTOH | 8 | 0.4–40 | 8 | 0.4–40 |
| 10:2 FTOH | 4 | 0.2–20 | 4 | 0.2–20 |

Use in the domestic industry

As stated above, a use of fluorotelomers or fluoropolymers for the protection of carpets by the Swiss industry could not be corroborated based on the survey among relevant polymer manufacturers and interviews with domestic carpet manufacturers. However, as it was not possible to get a reply from all companies contacted, a use cannot be excluded. Based on the information that the domestic production is markedly smaller than the imports and the estimated market share of the companies not providing any information, an estimate was made in relation to the amounts in imported carpets. As both of the factors were assumed as 0.5, the maximum of the use in the domestic production was estimated as a fourth of the imported amounts (Tab. 28).

**Tab. 28 > Estimated consumption of PFOS, PFOA and selected precursors in the domestic carpet industry**

| Substance | Use in 2007 [kg/year] | | Historical use [kg/year] | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| PFOS | 0 | – | 0.5 | 0.003–3 |
| PFOA | 1 | 0–8 | 12 | 0.03–80 |
| *N*-MeFOSE | 0 | – | 3 | 0.2–20 |
| *N*-EtFOSE | 0 | – | 0.2 | 0.003–0.5 |
| 8:2 FTOH | 2 | 0–10 | 2 | 0.1–10 |
| 10:2 FTOH | 1 | 0–5 | 1 | 0.05–5 |

#### 2.5.1.12 Paper and paperboard protection

Fields of use

PFCs have been incorporated into coatings used on paper products to impart grease, oil and water resistances to paper and packaging substrates. Such products have been used for both food contact applications (plates, food containers, bags and wraps) and non-food applications (folding cartons, containers, carbonless forms and masking papers). PFCs might find applications in the following products (RPA 2004):

- liner board (for packaging machine parts, rope, twine, meat)
- folding cartons (for snack foods, fast food, cake mixes, margarine, confectionery and bakery products, and pet foods)
- multiwall bags (snack foods, cake mixes, pet food)
- moulded pulp products for plates and food containers
- flexible packaging (fast food and confectionery wrappings)
- flexible or lightweight papers primarily for bags, wraps and micro flute containers
- support cards (confectionery and bakery products)
- business and specialty papers for carbonless forms and masking papers

PFOS

High molecular weight phosphate ester produced using *N*-EtFOSE and an acrylate copolymer based on *N*-MeFOSEA have been applied to paper and paperboard (3M 1999, RPA 2004). According to the TGD, surface coating, e.g. wax, polyurethanes pigmented coatings are added at a rate of 0.1–0.8 % to paper. For cardboard, a use of 8–15 g per side is given (ECB 2003). Fluoroalkyl compounds are often present in these paper products in the tens of milligrams per gram of dry weight of fibre range. Any small molecular weight manufacturing residuals or breakdown products of the larger fluoroalkyl compounds could potentially emit from the coated paper (Tittlemier et al. 2006). According to information from the UK paper industry, in 2004 there was no more interest in POSF-based substances (RPA 2004). The majority of the POSF-based substances seem to have been replaced by non-POSF-based fluorochemical alternatives. There was no indication that POSF-based substances were used in Switzerland in 2007.

Fluorotelomer-based polymers

Fluorotelomer-based polymers such as phosphate esters or acrylates have been used instead. Typically, these fluorotelomer paper coatings/additives are either very low molecular weight fluorotelomers, which are mixtures of C6-, C8-, C10- and C12-

perfluorinated chemicals or high molecular weight polymers with fluorotelomer-based side chains (Begley et al. 2005, D'eon & Mabury 2007). The domestic use of fluorotelomer-based polymers was estimated to amount to approximately 30–120 t/year according to confidential business information received from relevant polymer manufacturers.

Another way to estimate the amounts of fluorotelomer-based polymers used was derived from the statistics of the Swiss paper industry. Assuming that only the two categories–folding box board and packaging paper in Tab. 29–have been impregnated with polymers and 1 kg is used per ton (SFT 2007), the use in the domestic paper industry would amount to approximately 130 t/year. The order of magnitude of this amount could be confirmed by the consultation mentioned above. Similarly, the consumption in paper products in Switzerland (i.e. sum of production and import minus export) would be around 190 t/year. A market survey carried out in the Netherlands in 2000 indicated that 6000–7000 t/year of coated paper were sold annually. Hekster et al. (2002) estimated that for these types of papers 1.0–1.5 % d.w. fluoroalkyl phosphates are needed to achieve the protection. This would correspond to an annual use of 60–105 t of fluoroalkyl phosphates in the Netherlands.

**Tab. 29 > Domestic production, import, export and consumption statistics of paper and paperboard**

*Statistics of different paper and paperboard categories for the year 2007 [t/year].*

| | Production | Import | Export | Consumption |
|---|---|---|---|---|
| Newsprint | 341 000 | 121 000 | 157 000 | 304 000 |
| Wood containing graphic paper, uncoated | 3 000 | 40 000 | 2 000 | 41 000 |
| Wood containing graphic paper, coated | 168 000 | 158 000 | 150 000 | 177 000 |
| Woodfree graphic paper, uncoated | 132 000 | 194 000 | 66 000 | 260 000 |
| Woodfree graphic paper, coated | 382 000 | 144 000 | 341 000 | 184 000 |
| Sanitary and household paper | 77 000 | 111 000 | 27 000 | 161 000 |
| Corrugated board | 305 000 | 168 000 | 187 000 | 285 000 |
| Folding box board | 108 000 | 126 000 | 76 000 | 159 000 |
| Packaging paper | 21 000 | 40 000 | 20 000 | 40 000 |
| Other cardboard | 60 000 | 35 000 | 40 000 | 54 000 |
| Other paper (special paper) | 108 000 | 12 000 | 105 000 | 14 000 |
| Total paper and cardboard | 1 705 000 | 1 147 000 | 1 172 000 | 1 680 000 |

ZPK 2008a

PFOA

Fluorotelomer-based paper coating/additive formulations may before application onto paper have had PFOA content as high as 88–160 ppm w.w., but during normal application rates this amount of PFOA is diluted by about 300 times on the final paper product. Therefore, the PFOA content on finished paper was in the few hundred ppb range at that time (Begley et al. 2005). However, the industries participating in the stewardship program made substantial progress to reduce the PFOA residual levels in the last couple of years. According to information received from the industry, the residual concentration of PFOA in polymers used in the manufacture of impregnated paper was < 2 ppm or < 10 ppm d.w. in 2007. For calculation purposes, half of the given maximum concentrations were considered. Hence, the amount of PFOA in fluorotelomer-based polymers used in the domestic industry was estimated to be 0.1–0.7 kg/year in 2007.

Concentrations in industrial wastewater

To crosscheck the estimates made above, an approach based on data on amounts of wastewater and concentrations of PFOS and PFOA therein was used. The water consumption of the Swiss paper manufacturers (13 companies including one pulp mill) was 41 million $m^3$ (excluding cooling water) in 2006. This corresponds approximately to a usage of 24 $m^3$ per ton of manufactured paper (ZPK 2008b). The concentrations measured in wastewater of the paper mills in North Rhine-Westphalia and Austria (Clara et al. 2008, LANUV 2008) ranged between below detection limit and 170 ng/L for PFOA and below detection limit and 240 ng/L for PFOS. The mean concentrations were 67 ng/L and 73 ng/L, respectively. Assuming that these concentrations were appropriate for the situation in Switzerland, the releases to wastewater would account for approximately $< 1$–7 kg/year for PFOA and $< 1$–10 kg/year for PFOS. The corresponding use could be higher as only a limited fraction is released into the wastewater but also be smaller because of precursor degradation. The estimated amount of PFOS released using data from Germany and Austria is surprising as there was no indication of a domestic use of POSF-based substances or polymers in 2007. The situation in Germany and Austria might not differ too much from the one in Switzerland. As the releases came from paper mills, the possibility that PFOS was imported in finished products from abroad can be excluded. Hence, the origin of the PFOS remains an open gap.

Precursors

The concentration of 8:2 FTOH found in a popcorn packaging paper before and after cooking was $1.7 \pm 0.2$ ng/$cm^2$ and $3.4 \pm 0.5$ ng/$cm^2$, respectively, whereas the concentration was below limit of detection ($< 1.6$ ng/$cm^2$) in the second sample. FTOHs may be produced from fluorotelomer-based coating during microwave cooking, but the difference may also result from the difficulties in the analyses (Sinclair et al. 2007). Assuming a mean density of packaging paper and paperboard of 100–200 g/$m^2$ and the same categories in Tab. 29 as above, the potentially treated area would be approximately $1\text{–}2 \cdot 10^9$ $m^2$. The resulting amount of 8:2 FTOH of 17–68 kg/year was considered to probably be too high as coated with fluorotelomer-based polymers. Therefore, a best guess of 20 kg/year and a range between 5 and 70 kg were considered.

Historical use

The total historical use of POSF-based substances in the EU was estimated to be 160 t/year (RPA 2004), which would correspond to 2.5 t/year in Switzerland assuming that a per-capita approach was valid. In the RPA report, it was assumed that the polymeric compounds used contain 1 % of manufacturing residuals according to information by 3M. Analyses of different POSF-based products were used to estimate the approximate residual content of the substances studied on a dry weight basis, as it is known that paper and packaging protection products had also been made with FOSE derivatives, mainly acrylates, phosphate esters and copolymers (OECD 2002). It was therefore assumed that residual contents in textile, carpet and rug protectors were similar to products for the protection of paper and paperboard. In a first order approximation, the same contents as of textiles (section 2.5.1.9) were considered: 20–500 ppm, 3900 ppm and 60 ppm for PFOS, *N*-MeFOSE and *N*-EtFOSE, respectively. As there were only single measurements for the latter two substances, a variance was taken into consideration. The historical consumption of PFOS was estimated to be 0.05–1 kg/year based on these numbers. Considering the concentrations mentioned above and a range yields an estimated historical use of 3–30 kg/year of *N*-MeFOSE and 0.05–0.5 kg/year of *N*-EtFOSE. For PFOA, the consumption estimate based on the non-reduced formulations as they were used before the industry committed to the stewardship program (considered concentration range 88–160 ppm w.w., see above) accounted for approximately 0.5–8 kg/year. The historical use of FTOHs was assumed to be equal to the present use as it was made for other application areas.

**Tab. 30 > Estimated consumption of PFOS, PFOA and selected precursors in the domestic paper and paperboard industry**

| Substance | Use in 2007 [kg/year] | | Historical use [kg/year] | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| PFOS | 0 | – | 0.5 | 0.05–1 |
| PFOA | 0.5 | 0.1–1 | 4 | 0.5–8 |
| *N*-MeFOSE | 0 | – | 10 | 3–30 |
| *N*-EtFOSE | 0 | – | 0.2 | 0.05–0.5 |
| 8:2 FTOH | 20 | 5–70 | 20 | 5–70 |

### 2.5.1.13 Coating of metals and ceramics

Metal and ceramic surfaces are coated with PTFE dispersions to protect them from corrosion and create non-stick surfaces. These objectives can be accomplished by using filled and unfilled coatings. Unfilled PTFE forms a smoother and less porous surface, whereas filled formulations lead to a harder surface that wears at slower rate than the unfilled coating. Examples of applications include household and commercial cookware and industrial equipment (Ebnesajjad & Khaladkar 2004). Also other types of fluoropolymer dispersions as well as powders are in use.

According to confidential business information received by the relevant manufacturers and selected users, the consumption of fluoropolymers was approximately 80–150 t (d.w.) in the year 2007. Only aggregated data may be presented here due to confidentiality reasons. Dispersions clearly prevailed over powders. PTFE was the most important fluoropolymer followed by PFA, but also other types such as ECTFE and FEP were imported to the domestic market. The residual contents of PFOA ranged between 0 ppm (not used in the manufacturing of a polymer) and < 100 ppm (d.w.). According to personal information by a Swiss coating company, a small fraction of the fluoropolymer dispersion imported to the domestic market to be used for the coating of metals and ceramics was of non-reduced PFOA type in 2007. Considering half of the number given as maximum concentrations and this information, the total content in imported fluoropolymers in this application area was estimated to be 1–10 kg/year with a best-guess estimate of 4 kg/year (Tab. 31).

Historically, dispersions typically contained residual PFOA concentrations of 1500–2000 ppm, in some cases up to 7000 ppm (Prevedouros et al. 2006, 3M/Dyneon 2007). This is significantly higher than the concentrations in the dispersions imported to Switzerland in 2007. On the other hand, there was an increased usage of fluoropolymers during the past two decades. It was estimated that the former effect clearly prevailed, especially in the more recent past. This is supported by estimates on temporal trends of emission from fluoropolymer processing (Armitage et al. 2006, Prevedouros et al. 2006). There was no known use of PFOS or a precursor substance that was considered in the substance flow analysis.

**Tab. 31 > Estimated domestic consumption of PFOS and PFOA in the coating of metals and ceramics**

| Substance | Use in 2007 [kg/year] | | Historical use [kg/year] | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| PFOS | 0 | – | 0 | – |
| PFOA | 4 | 1–10 | 40 | 10–100 |

### 2.5.1.14 Cleaning products, wax and polish

Fluorotelomer-based surfactant products are added to acrylic/wax floor polish formulations to improve wetting and levelling (important for spreading and gloss), and re-wetting characteristics (e.g. the second coat is smooth and level) (Washburn et al. 2005). POSF-based substances (probably different salts) 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 cleaning services. These substances have been used in low concentrations (0.01 %) in film making water based floor polish products (3M 1999, RPA 2004). The Swedish trade association, Industrial and Institutional Hygiene, asked its member companies if they use any of the compounds which are included in Sweden's proposal for the banning of PFOS. The results showed that none of the compounds appears to be used (KemI 2006). As there was also no indication for a use of PFOS and POSF-based chemicals in Switzerland, the use in 2007 was considered negligible.

Unfortunately, no information such as volumes was received from relevant companies in Switzerland. An import of < 1 t/year of different perfluoroalkanes to be used in wax or in polish could be derived from the questionnaires returned by fluorotelomer and fluoropolymer manufacturers. The import of waxes and polishes accounted for 6200 t and 2300 t, respectively, in 2007 (Tab. 32).

**Tab. 32 > Domestic import and export statistics of waxes and polish for the year 2007**

| Tariff heading | Description of goods | Import [t/year] | Export [t/year] |
|---|---|---|---|
| 3404.2000 | Artificial waxes and prepared waxes of poly(oxyethylene) (polyethylene glycol) | 1100 | 50 |
| 3404.9000 | Artificial waxes and prepared waxes: other | 5200 | 1000 |
| 3405.1000 | Polishes, creams and similar preparations for footwear or leather | 440 | 90 |
| 3405.2000 | Polishes, creams and similar preparations for the maintenance of wooden furniture, floors or other woodwork | 1500 | 300 |
| 3405.3000 | Polishes and similar preparations for coachwork, other than metal polishes | 400 | 340 |

FCA 2008

Floor polish

The fluorotelomer-based surfactant product is added in an amount between 100 and 500 mg of product/kg of wax or wax remover. Based on a PFOA concentration of 5–120 ppm in the fluorotelomer-based product, the estimated concentration of PFOA in industrial floor waxes and wax removers was estimated to be 0.0005–0.06 mg/L solution when applied to surfaces (Washburn et al. 2005). Assuming that the 1500 t/year in Tab. 32 correspond approximately to the domestic use, the estimated amount of PFOA in these products would be 0.001–0.1 kg/year. Few analyses for precursor substances have been performed. A water-soluble anionic phosphate fluorosurfactant for the use in floor waxes and coatings was found to contain 8:2 FTOH and 10:2 FTOH in levels of 16 000 ppm and 3000 ppm (d.w.), respectively (Dinglasan-Panlilio & Mabury 2006). Considering the 100–500 mg/kg from above, the concentrations in the liquid would have been approximately 1.6–8 ppm and 0.3–1.5 ppm. The Danish EPA analysed eight wax and floor polishes in 2002. In one of the products (wash and care agent for vinyl, cork linoleum, etc.) a concentration of 9 mg/L *N*-EtFOSE was detected, whereas no PFOS or PFOS precursors were found in any of the products. PFOA and FTOHs were not analysed (Vejrup & Lindblom 2002). Based of these number and the frequency detected, the amounts of 8:2 FTOH, 10:2 FTOH and *N*-EtFOSE in products were estimated to be 2–12 kg/year, 0.4–2 kg/year and 0.5–5 kg/year, respectively. The latter was considered to be a historical use only, whereas both FTOHs were considered as present and historical use. As it remained unclear if PFOS salts have been used historically in Switzerland, their use in this application area was not considered in the substance flow analysis.

Car polish and wax

Fluorinated substances have been used in car polish and waxes. Assuming that car polish and waxes contain 25–1000 ppm of fluorosurfactants (Jensen et al. 2008), a market share of 5–50 % of products which contain such substances and the 400 t/year imported in 2007 (Tab. 32) correspond approximately to the domestic use resulting in a 0.5–200 kg/year estimate of fluorinated substances. Considering a PFOA residual content of 5–120 ppm as made above, the amount of PFOA would be < 0.001–0.01 kg/year. As a comparison, the amount of PFOA in waxes (of all types) in Norway was estimated to be 0.0003–0.03 kg/year (SFT 2007). No information on contents of FTOHs and historical contents of PFOS and the selected precursors was available for these products. However, considering the same mean contents as in floor polish, the amounts of 8:2 FTOH, 10:2 FTOH and *N*-EtFOSE in products would account for 0.5–3 kg/year, 0.1–0.5 kg/year and 0.1–1 kg/year, respectively. *N*-EtFOSE was only considered as a historical use. A car care product containing the tetraethylammonium salt of PFOS is listed in the Swiss product register (see Tab. 7 on page 37). As there was no information available on its historical use volumes, it was assumed that the use of the tetraethylammonium salt of PFOS was equal to *N*-EtFOSE while considering a tenfold higher maximum range.

Cleaning products

A windshield washer fluid available at common hardware and retail stores, which was stated to contain PTFE, was examined. Levels of 8:2 FTOH and 10:2 FTOH found were 750 ppm and 200 ppm (d.w.), respectively (Dinglasan-Panlilio & Mabury 2006). Hence, the concentration is more than one order of magnitude lower than for the fluorosurfactant mentioned above. In a Danish study, it was concluded that ordinary glass cleaning products seem not to contain fluorinated substances. It was uncertain whether glass cleaning products that are based on nanotechnology contain such substances (Jensen et al. 2008). Washburn et al. (2005) estimated the concentration of PFOA in office and home cleaning products as 0.05–0.005 ppm (w.w.). The consumption of cleaning agents in Switzerland accounted for 20 000 t in 2007 (SKW 2008). The use of PFOA would account for 0.1–1 kg/year if it is assumed that all cleaning agents contain fluorinated substances. This is, however, not the case and the fraction of such cleaning agents was estimated to be rather small. Therefore, it was assumed that the amounts of PFOA in this application area were negligible. As the amount of FTOHs is also probably low and information is not sufficient, it was decided not to include this particular use to the substance flow analysis.

Ski wax

PFCs used in ski wax are synthesised with the general formula $F(CF_2)_n–(CH_2)_mH$, with $n = 2–16$ and $m = 14–24$. During synthesis a lot of by-products are produced and purification is not easy (Plassmann & Berger 2008). There exists a Norwegian company that produces one type of wax based on 80–100 % of perfluorohexadecane. As this wax is very expensive, it is only used by professional skiers (SFT 2007, Jensen et al. 2008). The production volume was just below 1 t/year. According to OECD, this substance is not a precursor of PFOS or PFOA (OECD 2007a); thus, it was not considered in the substance flow analysis. Different kinds of PFCs have also been used in fluorinated wax for mountaineering ropes (Spierings et al. 2008), but the use might be limited. The amounts of PFOA in residuals in ski wax and wax for mountaineering ropes were assumed to be negligible.

**Tab. 33 > Estimated domestic consumption of PFOS, PFOA and relevant precursors in waxes and polish**

| Substance | Use in 2007 [kg/year] | | Historical use [kg/year] | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| PFOS | 0 | – | 0.5 | 0.1–10 |
| PFOA | 0.05 | 0.001–0.1 | 0.5 | 0.01–1 |
| *N*-EtFOSE | 0 | – | 2 | 0.6–6 |
| 8:2 FTOH | 5 | 2–15 | 5 | 2–15 |
| 10:2 FTOH | 1 | 0.5–3 | 1 | 0.5–3 |

### 2.5.1.15 Paints and lacquers

Fluorotelomer-based surfactants are added to latex paints to improve flow, wetting, levelling, and can also reduce surface defects such as craters. Latex paint is a suspension of finely divided synthetic resins in water. Commonly called “water-based paint” includes resins such as acrylics, vinyls and epoxies. Latex paints contain four basic components: a) resins, which form a film or coating on the surface, b) solvents, which keep the resins liquefied until the paint is applied, c) pigments, which provide the colour and d) additives, which are used as driers, thickeners or antifoam agents. Fluorotelomer-based surfactants are added to latex paints in an amount between 300 and 500 mg of product/kg of paint.

The concentration of PFOA in latex paints was estimated to be 0.02–0.08 mg/L paint, as applied to surfaces, based on a PFOA concentration of 50–150 ppm in the fluorotelomer-based product (Washburn et al. 2005). The import of paint, lacquers and inks that potentially contain PFCs was estimated to be 40 000 t/year according to statistics from the Swiss Federal Customs Administration. Water-based acrylic paint made up approximately half of that volume (FCA 2008). An amount of PFOA imported in paints, lacquers and inks was estimated to be 0.5–3 kg/year from these numbers when assuming that the imported volumes are approximately the same as the domestic consumption and that all products contain fluorinated substances. However, this is most probably not the case. The information received from different suppliers within the paint and varnish industry suggests that fluorinated surfactants in general are much more expensive alternatives compared to other surfactants. Therefore, fluorosurfactants are only used for special purposes where low surface tension is necessary and when other (non-fluorinated) alternatives fail, e.g. in a product in which an extremely smooth surface is necessary (Poulsen et al. 2005). Hence, the amount estimated above was assumed to be reduced by approximately one order of magnitude. The import of fluoropolymers for paints, lacquers and inks to Switzerland was approximately 1–3 t/year in 2007 according to confidential business information. Residual contents of PFOA were stated to be < 1 ppm to < 10 ppm for the different products. Based on these data and assuming the contents as half of the given maximum concentration, the amount of PFOA imported in these products was 0.001–0.02 kg/year. The difference between this amount and the amount estimated above is a result of the significant decrease of residual concentrations by the fluoropolymer manufacturers in recent years.

Residual concentrations of 2800 ppm 8:2 FTOH and 1500 ppm 10:2 FTOH (both d.w.), respectively, were determined in an ethoxylated non-ionic fluorosurfactant for the incorportation into caulks, paints, coatings and adhesives (Dinglasan-Panlilio and Mabury 2006). Based on the 300–500 mg/kg fluorotelomer-based surfactants added to paints, the concentration of FTOHs in paints was estimated to be 0.8–1.5 ppm and 0.5–0.8 ppm. With these numbers and an assumed market share of products containing fluorotelomer-based substances, amounts of 30–60 kg/year 8:2 FTOH and 20–30 kg/year 10:2 FTOH were derived. There was no indication of a use of PFOS or its precursors in paints, lacquers or inks in 2007. These substances are no longer in use in Denmark, but this application area was stated to be a former major use area (Poulsen et al. 2005). The historical use of POSF-based substances in coatings was estimated to be 18 t/year in the UK. One particular substance identified was a potassium salt of a glycine derivative of *N*-EtFOSA (CAS number 2991-51-7). Several products including paints containing this substance are also listed in the Swiss product register. The substance was, however, not selected as a precursor for the substance flow analysis. Additionally, the tetraethylammonium salt of PFOS was also registered for the use in paints and lacquers in Switzerland (see Tab. 7 on page 37). Assuming that a per-capita approach is appropriate and that the fraction of the ethylammonium salt (80 % by weight of PFOS) accounted for 10–50 %, the historical use of PFOS would have accounted for approximately 0.1–0.6 t/year.

**Tab. 34 > Estimated domestic consumption of PFOS, PFOA and relevant precursors in paints and lacquers**

| Substance | Use in 2007 [kg/year] | | Historical use [kg/year] | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| PFOS | 0 | – | 200 | 100–600 |
| PFOA | 0.01 | 0.001–0.02 | 0.1 | 0.01–0.2 |
| 8:2 FTOH | 45 | 30–60 | 45 | 30–60 |
| 10:2 FTOH | 25 | 20–30 | 25 | 20–30 |

#### 2.5.1.16 Impregnation agents

The Swiss production of aerosol cans was estimated to be 37.5 million units in 2007. The estimated consumption in Switzerland was slightly higher: 41.5 million units. Approximately 50 % are used as cosmetic products, 16 million (~ 40 %) in households and commerce, while the consumption by the pharmacy and food sectors were considerably smaller. The mean content of an aerosol can is approximately 300 ml (Assoziation der Schweizerischen Aerosolindustrie, personal communication). Hence, the consumption in households and commerce amounts to about 4.8 million litres per year. The percentage of aerosol cans for the impregnation of textiles, shoes, carpets, etc. is unknown. It was assumed that the amount consumed in the sum of polyurethane foam, paint, bicycle chains, insecticide sprays, etc. was markedly higher. The percentage of impregnation sprays was therefore assumed to be 10–25 %. Hence, the consumption of these cans accounts for roughly 0.5–1.2 million litres annually. 1 million L/year was chosen as a best guess value.

**Tab. 35 > Concentrations of fluorinated substances extracted from several commercial impregnation agent products**

*All concentrations are given in µg/L.*

| | Sum PFCA | Sum PFAS | Sum FTOH | Sum FOSA/FOSE | Sum FTS/FTCA |
|---|---|---|---|---|---|
| Mean | 1 500 | 12 | 1 400 000 | n.d. | 5 |
| Median | 220 | n.d. | 220 000 | n.d. | n.d. |
| Minimum | n.d. | n.d. | n.d. | n.d. | n.d. |
| Maximum | 8 400 | 81 | 9 400 000 | n.d. | 59 |

Norin & Schulze 2007

The amounts of fluorinated substances that can be extracted from commercial impregnation agent products were recently measured (Tab. 35). The FTOHs were found to have the highest concentrations ranging from not detected to as high as 9 g/L. Concentrations of 8:2 FTOH averaged at 0.9 g/L, whereas the median and the maximum were 0.16 g/L and 5.7 g/L, respectively. The corresponding concentrations for 10:2 FTOH were 0.45 g/L, 0.07 g/L and 3.7 g/L. PFCA were detected in eight out of thirteen samples with maximum concentrations three orders of magnitude lower than for FTOHs. The highest concentration of PFOA detected was 0.7 mg/L, while the mean was 0.1 mg/L. Concentrations of PFAS and FTS/FTCA were approximately another two orders of magnitude lower than PFCA. PFOS concentrations averaged at 0.01 mg/L, while the highest concentration was 0.07 mg/L. FOSA and FOSE were not detected at all (Norin & Schulze 2007). Four care products for shoes (impregnation agents) were analysed in double determination for eight specific PFCs. Components could only be determined in one impregnation product where the PFOA concentration was 0.36 mg/kg (Engelund & Sørensen 2005). Few products (impregnation of textiles, shoes, furniture, tents, etc,) of a Norwegian company were analysed for PFOA. Concentrations of 0.73 mg/kg and 4.0 mg/kg were found (SFT 2007). These values correspond well with the above mentioned concentrations of PFCA. In order to estimate the PFOA mass flow in Switzerland, a mean concentration of 2 mg/L and a range of 0.1–4 mg/L were assumed. Hence, the Swiss consumption of PFOA in impregnation aerosol cans accounts to approximately 1 kg/year (range 0.05–5 kg/year). The consumption of PFOS, 8:2 FTOH and 10:2 FTOH were estimated accordingly. While the amount of PFOS lies in the grams range, the amount of FTOHs could be in the low tons range. As in the sections above, the historical use of FTOHs was assumed to be similar to the use in 2007.

Thirteen impregnating agents for shoes and textiles were tested for PFAS and precursors by the Danish EPA. No PFOS was found in any of these consumer products, but two of them contained 212 mg/L perfluorodecanesulfonate (PFDS) and 3.5 mg/L FOSA, respectively (Vejrup & Lindblom 2002). The former is a longer homologue of PFOS and not a precursor, while the latter was not included as a precursor in the study. On the other hand, the analyses of four spray application consumer products purchased prior to the phase-out of POSF-based products by 3M showed concentrations of 454 and 500 ppm d.w. PFOS in two products. No PFOS was detected in the other products (Prevedouros et al. 2006). Assuming a solid content of 0.5–1.5 % in the products, the amount of PFOS would account for up to 10 kg/year. However, as no PFOS was found in the two other products and in any of the products analysed in Denmark, a best guess of 1 kg/year was considered to be more realistic for the historical use (Tab. 36). Like in the sections above, the historical consumption of PFOA was assumed to be tenfold higher, as the residual concentrations were significantly higher.

Tab. 36 > Estimated domestic consumption of PFOS, PFOA and relevant precursors in impregnation agents

| Substance | Use in 2007 [kg/year] | | Historical use [kg/year] | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| PFOS | 0.05 | 0.005–0.1 | 1 | 0.2–10 |
| PFOA | 1 | 0.05–5 | 10 | 0.5–50 |
| 8:2 FTOH | 900 | 70–7000 | 900 | 70–7000 |
| 10:2 FTOH | 400 | 30–4000 | 400 | 30–4000 |

## 2.5.2 Residence times

The consideration of the residence times of the selected substances in the anthroposphere can be of importance in certain cases. This applies to situations where the residence times are long and the losses are estimated on a per-time basis or if the use of a substance varies significantly over time. The second case is particularly true for PFOS that is not used in many applications anymore to date. Tab. 37 lists the service lives (i.e. the number of years in use) for various articles.

Tab. 37 > Service lives of different articles

| Application area | Article | Service life (years) | Reference |
|---|---|---|---|
| Photography | Patient documents | ~ 10 | EDÖB, undated |
| Textile protection | Clothes on contact with skin | 1 | Ciba 2001 cited in OECD 2004f |
| | Other clothes and bed linen | 2–5 | Ciba 2001 cited in OECD 2004f |
| | Trekking jackets, rain coats | 6–10 | Pfitzner & Wilken 2003 |
| | Household linen | 5–10 | Ciba 2001 cited in OECD 2004f |
| | Bedding (mattress) | 10 | Ciba 2001 cited in OECD 2004f |
| | Sunblind | 8–15 | Ciba 2001 cited in OECD 2004f |
| | Tents | 5–20 | Ciba 2001 cited in OECD 2004f |
| | Awnings | 2 | Ciba 2001 cited in OECD 2004f |
| | Personal cars | 14 | Reinhardt & Richers 2004 |
| Leather protection | Jogging, tennis, soccer shoes | 2–4 | Pfitzner & Wilken 2003 |
| | Snowboard boots | 4–8 | Pfitzner & Wilken 2003 |
| Paper protection | Paper | 1 | Pfitzner & Wilken 2003 |
| | Food contact applications | < 1 | Own estimate |
| Carpet protection | Carpets | 8–20 | Ciba 2001 cited in OECD 2004f |
| | Carpeting | 11 | The Old House Web, undated |
| | Wall-to-wall carpets | 5–30 | Ciba 2001 cited in OECD 2004f |
| Paints and lacquers | Finishes used for waterproofing: Paint, plaster and stucco | 3–5 | The Old House Web, undated |
| Cleaning products, wax and polish | Finishes used for waterproofing: sealer, silicone and waxes | 1–5 | The Old House Web, undated |

## 2.5.3 Transfer coefficients and emission factors

### 2.5.3.1 Primary production of substances and manufacture of polymers

According to information by Swiss industry representatives, there is neither a production of the substances PFOS, PFOA, nor the manufacture of PTFE and other fluoropolymers using PFOA as a processing aid taking place in Switzerland.

### 2.5.3.2 Application

The application phase is only considered for application areas, where industrial or consumer products containing PFCs are used in a specific process over a short period. The long term usage is described in the *service life* in the following section.

Metal plating

Most of the PFOS used in chromium plating, anodising and acid pickling finally gets into wastewater. In the “Risk reduction strategy and analysis of advantages and drawbacks” (RPA 2004), it was estimated that 0.2 % are emitted to the air, while the rest goes to wastewater. Losses from the treatment tank can occur through drag-out, i.e. solution remaining on the metal articles as they are removed from the tank. The drag-out is removed from the metal by rinsing, so this substance is diluted in the rinse water. It was estimated that the fraction sticking to the metals after rinsing was negligible. In order to recover the metals, the treatment of the streams containing metal in the system essentially precipitates the dissolved metal ions as insoluble compounds. Hexavalent chromium compounds are difficult to precipitate and are normally reduced to trivalent chromium, which are subsequently precipitated as Crc) hydroxide on neutralisation (EC 2006c). The thresholds defined in the Swiss Water Protection Ordinance (0.1 mg/L Cr(VI) or 0.5 mg/l total chromium in daily average) have to be fulfilled.

In Germany, both on-site and off-site disposal is made (ZEA 2008). The fractions of process baths treated on-site and off-site in Switzerland are not known. It was assumed that half of the process baths were disposed on-site in 2007. This value is important to determine the emission pathways, but the impact on the total emissions to the environment is reduced by the fact that the fraction released during on-site and off-site treatment probably does not differ largely. It was not possible to derive the disposal pathways of process baths that are not treated on-site from the hazardous waste statistics by the FOEN (BAFU 2009). Wastes are probably contained in several of the imprecisely defined subcategories of the waste code 11 01 00 (“wastes from chemical surface treatment and coating of metals and other materials (for example galvanic processes, zinc coating processes, pickling processes, etching, phosphating, alkaline degreasing, anodising)”). However, a rough allocation to the different disposal pathways was possible using the 2005 statistics, where the old VVS code system was applied: 459 t/year of acid wastewaters, baths and sludge containing chromium were characterised as hazardous waste in 2005. 4 % of this amount was incinerated, 3 % was exported, while the remainder came to a physico-chemical treatment. One third of the 540 t/year of acids containing Cr(VI) was exported, while the remainder was physico-chemically treated in Switzerland. Less than 1 % was incinerated (BAFU 2007b).

The German Central Association of Surface Treatment Professionals e.V. (ZVO) stated in a template letter for its member companies published on www.zvo.org that according to preliminary results of investigations commissioned by ZVO, the release of PFOS used to the wastewater pathway is only 2 %. This small fraction was doubted by a range of chemists and environmental scientists asked (e.g. LANUV 2008). No reply was received from ZVO on questions concerning the investigations they commissioned. However, a study was carried out by the Zentrale Entsorgungsanlage (ZEA) in Iserlohn in 2008, because all previously known methods have been shown to be ineffective in removing PFOS from wastewater. For this reason, process baths with PFOS have been stored intermediately until the conclusion of the investigations. Prior to the storage, high levels of PFOS have been detected in the receiving WWTP in Iserlohn as well as in wastewater samples from metal plating companies taken in NRW (see section 1.3.6 on page 24) (LANUV 2008). These facts confirmed the doubt that only small fractions of PFOS get into public sewer. A combination of different methods was finally found to be able to effectively remove PFOS from wastewater. However, the confirmation of the effectiveness on the large-scale is currently being investigated (ZEA 2008). Problems have been arisen from the fact that the activated carbon used is destroyed by the presence of the strong oxidising agent chromium(VI) oxide and sulfuric acid, which affects its ability to absorb perfluorinated surfactants. Additionally, as PFOS cannot be removed from the activated carbon, it has to be incinerated (LANUV 2008). As no effective methods to remove PFOS from wastewater were available by 2007, a release of 90 % PFOS from the rinsing water and the process baths treated on-site was estimated as a best guess. The remainder was estimated to be incinerated with wastes or as a left-over in packaging. For simplification reasons, melting processes of recovered metals were also considered as a form of incineration. In combination with the disposal pathways of process baths not treated on-site and the share of on-site and off-site treatment, the emission factor and transfer coefficients shown in Tab. 38 were estimated. The physico-chemical treatment is considered in the process recycling.

**Tab. 38 > Transfer coefficients and emission factors for metal plating at the process *application***

| | Best guess | Range |
|---|---|---|
| EF atmosphere | 0.002 | 0.0005–0.01 |
| TC wastewater | 0.45 | 0.2–0.8 |
| TC recycling | 0.40 | 0.1–0.7 |
| TC incineration | 0.06 | 0.03–0.2 |
| TC export | 0.09 | 0.05–0.2 |

Fire-fighting foams

The use rate of AFFF in tank farms and industrial plants is low. Estimates from the UK indicate that a large proportion of AFFF is not used during the 15 years shelf life (RPA 2004). Between 1991 and 2002 there were 27 accidents in industrial buildings causing business interruptions following fire or explosions for more than 24 hours in the UK. The event rate was 0.025 per location and year. For larger fires, this rate amounted to 0.0015. In the canton of Berne, 39 000 fires on buildings occurred during the period from 1986 to 1995. Only 15 of these were in industrial buildings and resulted in a loss of more than 1 000 000 Swiss Francs (Fontana et al. 1999). There are approximately 18 000 damages on buildings caused by fires annually according to Swiss fire statistics. The fraction of chemical and plastics industry affected was 0.1 % each (IRV 2008). The most notable fire incident in Switzerland in 2007 was probably the fire incident on 25 Mai in Steinhausen in the building of a manufacturer of plastic products such as insulation panels. 3600 L of AFFF were used together with 2 million L of water to fight the fire. The fire water that was not vapourised by the fire was collected and directed to a WWTP according to official information (AFU 2007). Other data were available from a large fire in St. Wendel, Germany, at a storage building of a recycling company on 17 Mai 2007. During more than forty hours, 30 t of an AFFF containing PFOS were applied (Schlummer et al. 2008). Such large fires were considered to happen once a year or less in Switzerland.

Considering the rate for large fires and the 232 locations from Tab. 14 (p. 46), it can be concluded that 0.35 large fires occur annually. Based on the data on the stored volume of AFFF per location in Tab. 14 and assuming that all AFFF in stock is used in case of a large fire, 3–40 t of AFFF or 30–400 kg of PFOS are used in case of a large fire. Hence, the annual usage would be 1–14 t of AFFF or 10–140 kg of PFOS, respectively. Based on these numbers, the annual use rate would be 0.1–1 % for tank farms and industrial plants alone. In the UK, the fraction of the stock of foams (all types) used in 2002 was 15 %, while the fraction of POSF-based foams used was only 0.5 % (RPA 2004). There is a good agreement between the 0.5 % and the 0.1–1 % estimated for Swiss tank farms and industrial plants. It has been documented in Germany that AFFF containing PFOS and PFOA were released to the sewer system during the periodical testing of the fire sprinkling system of a large storehouse (see section 1.3.6). Even though this should not happen, such cases cannot be excluded for Switzerland. The use rate for portable fire extinguishers was estimated to be also rather low and was assumed to be equal to the rate above. However, AFFF stored at supporting fire stations was estimated to have a higher use rate. This foam is either used in case of a large fire in a tank farm or an industrial plant when the stock in the location is not sufficient, which was the case during the major fire in Steinhausen described above, where additional AFFF was gotten from the airport fire station in Kloten (SF 2007). The foam is also used for other large fires if appropriate, when no AFFF is in stock locally. The use of AFFF containing PFOS for training purposes will be prohibited by December 1 2009 (UVEK 2008). Hence, the use rate was assumed to be somewhat higher than for tank farms and industrial plants and a range of 0.5–5 % (i.e. up to a third of the 15 % indicated for all types of foam) was considered with 1 % as a best guess. Generally, the army was supposed to use PFOS-free (but not PFCs-free) AFFF for exercise; however, a certain percentage of POSF-based foam was assumed to be used, especially in case of an emergency. As no data were available, the same use rate as for supporting fire stations was assumed. The overall use rate was assumed to be variable as it is closely related to the number of incidences in a particular year. The overall use rate was estimated to be 0.7 % (0.2–3 %) based on the individual use rates and the proportions of the stocks.

In the RPA report, two scenarios for the release to the environment are considered as possible extremes. In the first, there is no containment of the foam and water, and so 50 % of the release goes to surface water without treatment and 50 % to the soil. In the second scenario, it is assumed that the foam and water are collected and passed to a WWTP (RPA 2004). In the case of the fire in Steinhausen, it was reported that a considerable fraction of the water was vapourised and the rest was passed to a WWTP (AFU 2007). However, a certain percentage might still get directly to surface water. This was observed e.g. subsequent to the fire in St. Wendel, where runoffs from this area were flowing into fish ponds and receiving waters. The highest concentrations of PFOS and PFOA in water were 610 µg/L and 67 µg/L, respectively. Half a year later, concentrations had dropped by three orders of magnitude (LANUV 2008, Schlummer et al. 2008). A certain fraction of PFOS and PFOA is decomposed by the heat. Other fractions are incorporated in debris that is disposed either to incineration plants or landfills. However, only the pathways to WWTP, to hydrosphere and to the soil were considered. It was assumed that approximately 70 % of the AFFF can be directed to a WWTP in average and the remaining 30 % are emitted directly to hydrosphere and soil. A transfer coefficient of 0.07 was derived from the estimated shelf life of 15 years (Tab. 39).

**Tab. 39 > Transfer coefficients and emission factors of AFFF in stock (per year)**

| | Best guess | Range |
|---|---:|---:|
| TC incineration | 0.07 | 0.05–0.1 |
| TC wastewater | 0.005 | 0.001–0.02 |
| EF hydrosphere | 0.001 | 0.0003–0.005 |
| EF soil | 0.001 | 0.0003–0.005 |

Photolithography and semiconductors

PFOS is a process chemical that does not remain in the final product – the semiconductor device (SIA 2008b). The organisations ESIA and SEMI carried out a mass balance of PFOS during the industrial application where it was estimated that the PFOS used in developers entirely goes to wastewater, whereas it ends in the solvents and is then incinerated in the case of EBRs. For photoresists and BARCs, more complex substance flows within the production process are indicated. 1 % of PFOS in photoresists initially remains on produced parts but still ends in the incineration plant. The transfer coefficients of the different applications are summarised in Tab. 40.

**Tab. 40 > Transfer coefficients of the individual applications in the semiconductor industry**

| Application | Photoresists | TARCs | BARCs | Developers | EBRs |
|---|---:|---:|---:|---:|---:|
| Characterisation | Critical | Critical | Critical | Non-critical | Non-critical |
| TC wastewater | 0.005 | 0.40 | 0.005 | 1.00 | |
| TC incineration | 0.995 | 0.60 | 0.995 | | 1.00 |

SIA 2005

Overall transfer coefficients were derived from the transfer coefficients of the individual applications and the mass fraction of each (see Tab. 17 and page 48). A 50 % reduction of the use in non-critical applications was assumed for the situation in 2007 (Tab. 41).

**Tab. 41 > Overall transfer coefficients in the semiconductor industry**

| | Use in 2007 [kg/year] | | Historical use [kg/year] | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| TC product | 0 | – | 0 | – |
| TC wastewater | 0.47 | 0.40–0.55 | 0.54 | 0.50–0.60 |
| TC incineration | 0.53 | 0.45–0.60 | 0.46 | 0.40–0.50 |

Photography

No domestic manufacture of photographic or x-ray films is known. Also a search in a Swiss classified directory for companies in the x-ray film business listed only wholesaler or retailers (WLW 2008b). Processing was considered here instead of the manufacture of the film.

There is little information on the fraction of substances released from the film when it is processed. Only default release factors of 0 and 1 are given in Emission Scenario Document for the photographic industry (OECD 2004d). EPCI commented that approximately 5–10 % of one of the POSF-based substances used in imaging is released from film into film developer. However, none of the other substances would be expected to be released during developing. It was stated that these substances are intended to remain in the film in order to perform their function. It was assumed that the substance being released into the developer at the given percentage is the tetraethylammonium PFOS salt (Fig. 10). Four different waste categories from photographic industry are listed in the statistics on hazardous waste: In 2005, there were 2435 t/year of waste from developing baths, of which 7 % was incinerated, 27 % was physico-chemically treated and 0.1 % was recycled, while the majority was exported. All waste (111 t/year) from developing baths for the manufacture of offset litho plates was incinerated, while 99 % of the 3318 t/year of miscellaneous photographic wastewater was also incinerated. 96 % of the waste from non-desilvered fixing baths (730 t/year) was physico-chemically treated, while the remainder was incinerated (BAFU 2007b). Statistics for 2007 were not available. From above, especially the data for developing baths and non-desilvered fixing baths were considered as appropriate for x-ray and photographic films. Approximately 30–50 % was assumed to be physico-chemically treated, 5–30 % to be incinerated and the remaining 40–60 % to be exported. The physico-chemical treatment process was not included in the substance flow analysis as its own process, but it was considered in a basis manner in the process *application*. A release of 30–90 % of the PFOS present in the developing or fixing baths was assumed to be released to wastewater during physico-chemical treatment. The remainder of PFOS present in the physico-chemical treatment process was assigned to be incinerated. The resulting transfer coefficients are shown in Tab. 42.

Tab. 42 > Transfer coefficients and emission factors for photography at the process *application*

| | Best guess | Range |
|---|---|---|
| TC product | 0.92 | 0.84–0.97 |
| TC wastewater | 0.02 | 0.005–0.04 |
| TC incineration | 0.02 | 0.005–0.06 |
| TC export | 0.04 | 0.02–0.06 |

Textile protection

Fluorochemical repellents are usually applied in combination with other finishing auxiliaries by a pad-dry-cure process. In many cases they are applied with “extenders” which perform as repellents themselves (Umweltbundesamt 2003). Foulard application is the most common way to apply a fluorotelomer-based polymer formulation in the textile industry. There, the finishing substances are used in aqueous solutions and fixed to the material. The main process is immersion dipping and usually the application of chemical additives takes place by continuous “padding” (impregnating and pressing out again). Chemical finishes are usually followed by fixation steps, i.e. drying, curing and cooling. Besides this impregnation method with the help of padding devices, spraying or printing techniques as well as exhaustion processes and foam application are common in textile finishing (ECB 2003, OECD 2004f). There are no data on the degree of fixation of residual PFCs during the finishing process. The estimated degree of fixation for different types of dyes, processes and fibres in the TGD ranges from 70 % to 100 %. Brooke et al. (2004) estimated an emission factor of 1.4 % for “PFOS-related chemicals”, amongst which polymers were also counted. As a residual content of 1 % PFOS was considered there, the emission factor for PFOS alone would become much higher. The sum of the release of polymers to wastewater and the amounts cut off lost as solid waste were estimated to be 10 % (3M 2000 cited in Hekster et al. 2002). Considering the chemical properties of PFOS and PFOA compared to fluorotelomer-based polymers or other substances, its degree of fixation was assumed to be closer at the lower boundary. Losses to wastewater were assumed to be twice the 10 % losses estimated for polymers (see Tab. 43). Similar transfer coefficients to wastewater were assumed for the volatile precursors, namely 8:2 FTOH, 10:2 FTOH, *N*-MeFOSE and *N*-EtFOSE. As there was no intention to perform a full quantitative substance flow analysis for these substances, the reasonable worst case scenario of an atmospheric emission of the remainder was considered. Chemical analyses have shown that a certain fraction remains in the product. It probably gases off during service life, and emissions to the hydrosphere and soil are thus likely (e.g. washing out by rain, abrasion). Similar assumptions were made in other application areas.

Tab. 43 > Transfer coefficients and emission factors for textile protection at the process *application*

| | Non-volatile substances: PFOS, PFOA | | Volatile precursor substances | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| TC product | 0.8 | 0.6–0.9 | 0 | – |
| TC wastewater | 0.2 | 0.1–0.4 | 0.2 | – |
| EF atmosphere | 0 | – | 0.8 | – |

Leather protection

Fluorinated surfactants have been used in hydrating, bating, pickling, degreasing and tanning processes. Treatments are applied to leather and suede to give oil, water and stain repellence. This treatment is normally used on hides that require high levels of oil and water repellence throughout the thickness of the leather (e.g. in upholstery grades). The techniques suitable for applying fluorinated surfactants to leather after tanning are a) tumbling in a drum, in which the leather sorbs the fluorinated surfactant from an emulsion, suspension or solution, b) spraying and c) cast coating. Tanning treatments react with the leather during the process and on subsequent drying. On losing water, they release hydrochloric acid and react with the proteins in the leather (Kissa 2001, RPA, 2004). There are no data on the degree of fixation of residual PFCs in the tanning process. In the TGD, the estimated degree of fixation for different types of dyes ranges from 65 % to 100 % (ECB 2003). The degree of fixation of PFOS and PFOA was assumed to be at the lower boundary, considering its chemical properties (Tab. 44). Like for volatile precursors in textiles, the reasonable worst case assumption of an atmospheric emission of the remainder not being released to wastewater was made here too.

**Tab. 44 > Transfer coefficients and emission factors for leather protection at the process *application***

| | Non-volatile substances: PFOS, PFOA | | Volatile precursor substances | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| TC product | 0.7 | 0.5–0.9 | 0 | – |
| TC wastewater | 0.3 | 0.1–0.5 | 0.3 | – |
| EF atmosphere | 0 | – | 0.7 | – |

Carpet protection

According to *Gemeinschaft umweltfreundlicher Teppichboden*, the section responsible for technical issues in the European Carpet Association (GuT 2003 cited in RPA 2004), there are three main ways in which preparations can be applied to the carpet fabric in the mill: foam applications, dye-bath applications and spray applications. Carpets are dried after the application of the finishing. *Gemeinschaft umweltfreundlicher Teppichboden* stated that releases to wastewater are unknown (GuT 2002 cited in Hekster et al. 2002). No fixation rates applicable are given in this case in the ESD from OECD (OECD 2004a), either. While the fixation rates for dyes range between 65 % and 97 %, only the default value of 0 % is given for other types of chemicals. Therefore, it was assumed that the transfer coefficients estimated for textile protection are also applicable for carpet protection (Tab. 45). The same reasonable worst case assumption of an atmospheric emission of the remainder not being released to wastewater as in the sections above is considered for volatile precursors present in carpet finishing products.

**Tab. 45 > Transfer coefficients and emission factors for carpet protection at the process *application***

| | Non-volatile substances: PFOS, PFOA | | Volatile precursor substances | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| TC product | 0.8 | 0.6–0.9 | 0 | – |
| TC wastewater | 0.2 | 0.1–0.4 | 0.2 | – |
| EF atmosphere | 0 | – | 0.8 | – |

Paper and paperboard protection

Fluorotelomer-based polymers are considered to be mainly applied during the paper making process rather than being added to finished paper in subsequent operations (Brooke et al. 2004). The loss to wastewater in the paper making process was estimated for different types of additives in the TGD (ECB 2003). For “Surface coating, e.g. wax, polyurethanes pigmented coating”; however, no numbers but only the general process leading to loss, “spillages and intermittent washout” is given. For dyes, the degree of fixation given ranges between 40 % and 99 %. In the ESD of the OECD, a fixation range of 1–20 % was assumed for water soluble substances in general (OECD 2006a). For POSF-based substances, transfer coefficients to the atmosphere and to wastewater were estimated as zero and 0.05, respectively, based on TGD as they are intended to remain in the paper (Brooke et al. 2004). For residual PFOA in polymers applied to paper, the emission factor was estimated to be higher corresponding to their chemical properties. Hence, a transfer coefficient to wastewater of 0.1 was assumed (Tab. 46). The remainder of volatile precursors not released to wastewater was assumed to be emitted entirely to the atmosphere as a reasonable worst case (see also sections above).

**Tab. 46 > Transfer coefficients and emission factors for paper and paperboard protection at the process *application***

| | Non-volatile substances: PFOS, PFOA | | Volatile precursor substances | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| TC product | 0.9 | 0.7–0.95 | 0 | – |
| TC wastewater | 0.1 | 0.05–0.3 | 0.1 | – |
| EF atmosphere | 0 | – | 0.9 | – |

Coating of metals and ceramics

Coated goods are subject to various levels of heat treatment up to and including temperatures that decompose all or most of the PFOA present (Prevedouros et al. 2006, Kämpf 2008). The Fluoropolymer Manufacturing Group has carried out a mass balance for aqueous fluoropolymer dispersions, where the following average transfer coefficient and emission factors for PFOA were found (Prevedouros et al. 2006):

- 62 % decomposed in dispersion processing
- 16 % emissions to atmosphere
- 5 % releases to wastewater
- 5 % disposed as solid waste
- 12 % undetermined

According to estimates received from a Swiss coating company, 70 % of the PFOA present in impurities of fluoropolymer dispersions are destroyed during coating operations. The remaining 30 % was stated to be disposed of as solid waste. A specialised company takes care of the waste in that particular case. It was suspected that this company has a higher standard than average in this line of business. Atmospheric emissions from four PTFE-coating plants in Norway were determined as 7–8 g/year (SFT 2007), so 16 % of the emissions to the atmosphere were considered as being on the upper limit of the emission factor. The residual content of PFOA in PTFE cookware analysed was 0.004–0.075 ppm (Begley et al. 2005). Compared to residual contents in fluoropolymer dispersions, this concentration is approximately three orders of magnitude lower. Hence, the transfer coefficient into coated metals and ceramics was estimated to be 0.001. The other transfer coefficient and emission factors were estimated based on the data provided by the Fluoropolymer Manufacturing Group and the interviewed Swiss coater (Tab. 47).

**Tab. 47 > Transfer coefficients and emission factors for coating of metals and ceramics at the process *application***

| | PFOS | | PFOA | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| TC product | No use in 2007 | – | 0.001 | 0.0001–0.01 |
| TC decomposition | No use in 2007 | – | 0.70 | 0.5–0.9 |
| TC wastewater | No use in 2007 | – | 0.05 | 0.01–0.1 |
| TC incineration | No use in 2007 | – | 0.20 | 0.05–0.3 |
| EF atmosphere | No use in 2007 | – | 0.05 | 0.01–0.2 |

Cleaning products, wax and polish

Cleaning products, polishes and waxes are used in a wide range of applications. In many cases, these products are directly released to wastewater. However, polish might remain on flooring materials for a few years. During that time, the floor may be polished or cleaned and a new layer of polish applied. This works for a number of years and then all the polish is removed and new polish is applied. When the film of polish is removed, the PFCs end up in wastewater. Some of the film is worn away and forms particles which may be deposited in washing water, mop materials, vacuum cleaners etc. It is also possible that perfluorinated substances migrate through the film and are released into the air (KemI 2006). However, as the amounts used in this application area are small, only a rough assumption for the emission factors was made. It was assumed that 80 % of the non-volatile substances are released to wastewater during application while the fraction in vacuum cleaner bags disposed of as solid waste was assumed to be negligible. The remainder was assumed to stay on the surface. For volatile substances, it was assumed that 50 % each are emitted to the atmosphere and released to wastewater as a reasonable worst case.

**Tab. 48 > Transfer coefficients and emission factors for cleaning products, wax and polish at the process *application***

| | Non-volatile substances: PFOS, PFOA | | Volatile precursor substances | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| TC product | 0.2 | 0.1–0.5 | 0 | – |
| TC wastewater | 0.8 | 0.5–0.9 | 0.5 | – |
| EF atmosphere | 0 | – | 0.5 | – |

Paints and lacquers

In order to estimate the emissions during application, it was assumed that the default emission factors for paints, lacquers and coatings in the Technical Guidance Document can be applied. Assuming the paints are water-based, the emission factors are zero to air and 0.005 to wastewater (RPA 2004). Volatile substances were estimated to be released completely during application and probably shortly after as a reasonable worst case. However, the whole release was accounted to the application process because the individual fractions are unknown and the aggregated emissions are similar anyway.

**Tab. 49 > Transfer coefficients and emission factors for paints and lacquers at the process *application***

| | Non-volatile substances: PFOS, PFOA | | Volatile precursor substances | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| TC product | 0.995 | 0.99–0.999 | 0 | – |
| TC wastewater | 0.005 | 0.001–0.01 | 0 | – |
| EF atmosphere | 0 | – | 1 | – |

Impregnation agents

Impregnation of textiles and shoes by privates is usually performed outside. In contrast, impregnation of carpets or upholstery is mostly done inside. The fraction of the spray that does not deposit on the impregnated fabric is called overspray. Vernez et al. (2006, as cited in Horowitz 2007) found that the fraction of overspray in the total mass of emitted product was only 0.1 % in average. This fraction was assumed to apply when the spray is directed precisely to the fabric. However, especially when impregnating smaller articles like shoes or during spraying the border of a textile, the fraction of the impregnation agent that does not get onto the fabric was estimated to be much higher. It has been assumed that 96 % of the liquid sprayed sticks on the treated surface in average. For carpets and other fabrics sprayed indoor, this fraction was considered to be higher and lower for fabrics sprayed outside. 2 % each were estimated to be emitted to the atmosphere and soil. FTOHs were assumed to be emitted entirely to the atmosphere as a reasonable worst case.

**Tab. 50 > Transfer coefficients and emission factors for impregnation agents at the process *application***

| | Non-volatile substances: PFOS, PFOA | | Volatile substances: FTOHs | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| TC product | 0.96 | 0.9–0.99 | 0 | – |
| EF atmosphere | 0.02 | 0.005–0.05 | 1 | – |
| EF soil | 0.02 | 0.005–0.05 | 0 | – |

### 2.5.3.3 Service life

Hydraulic fluids for aviation

Even though hydraulic fluids for aviation were not expected to contribute to the occurrence of PFOS in the environment, some basic information related to the emissions of hydraulic fluids is given: the latter were taken from an Emission Scenario Document on Lubricants and Lubricant Additives (OECD 2004c). Losses are most likely to occur during installation into equipment, maintenance and removal for disposal. Due to the type of equipment used, hydraulic fluid systems are generally efficiently sealed, losses during use are generally very low apart from major but temporary losses arising from leakages from burst pipes, etc. An emission factor of 0.02 to environment was estimated, of which 0.014 go to soil and 0.006 to the hydrosphere (Brooke et al. 2004).

Photography

Emissions from x-ray or photographic films or releases to wastewater during service life were assumed to be negligible.

Textile protection

It is known that the washing permanence of textile coatings is dependent on the degree of copolymerisation and crosslinking (Malner 2002). A Swedish textile company tested one of its products which was treated with fluorinated compounds and found that the full effect remained even after 100 washes. However, no analyses were carried out on what disappeared with the washing water (KemI 2006). Additionally, while the polymers are responsible for maintaining the effects, the residuals of small molecules such as PFOS, PFOA or FTOHs are not required for that function and could have washed out completely. Experiments on the extractable amount of PFOA from textiles revealed that it is extracted even by pure water but at a slower rate than with other solvents (Mawn et al. 2005). As there was no additional specific information on the loss of PFCs from clothes, furniture and textiles in vehicles, the information on carpets (see below) was used as the basis for the assumptions. Clothes are probably washed more frequently than carpets are steam cleaned, while upholstery, interior textiles in cars and other textiles might be cleaned in a comparable frequency (Brooke et al. 2004). The releases from clothes might be somewhat higher than from steam cleaning of carpets, but on the other hand, the releases from the cleaning of other textiles could be lower. Overall, the transfer coefficient to wastewater was therefore assumed to be higher than for carpets. The degree of wear was assumed to be less than that for carpets and was taken as half of that figure. As treated textiles are also worn outside and e.g. emissions from textiles in vehicles are more readily released to the outdoor environment, the proportion of the emissions to solid waste (vacuum cleaner bags), was assumed to be similar to the sum of emissions to the hydrosphere and soil. The transfer coefficients and emission factors were assumed to be the same for PFOS and PFOA (Tab. 51). For the volatile substances (FOSE derivatives and FTOHs), it was considered that all residuals are emitted to the atmosphere during the service life as a reasonable worst case.

**Tab. 51 > Transfer coefficients and emission factors for textiles during service life**

| | Best guess | Range |
|---|---|---|
| TC wastewater | 0.5 | 0.3–0.7 |
| TC incineration | 0.13 | 0.08–0.25 |
| EF soil | 0.09 | 0.03–0.15 |
| EF hydrosphere | 0.03 | 0.01–0.05 |

Leather protection

As there was no specific information available about the loss of PFCs from leather, the information on carpets was again used as the basis for the assumptions. Wear was expected to be lower than it is for carpets and was assumed to be half of that (Brooke et al. 2004). Most leather products such as boots, coats and furniture are not washed. They are however cleaned in different ways. In the ESD of the OECD, it is stated that for articles subject to cleaning, substantial releases to wastewater can be assumed (OECD 2004b). The use of boots and coats outdoors leads to some direct releases to the environment. These emissions were assumed to be larger than they are for textiles and carpets, while the releases to solid waste and wastewater were expected to be lower. The latter was assumed to be markedly lower than for textiles. As a best guess, a release of 20 % to each wastewater, solid waste and the environment was assumed. As shown in Tab. 52 the emissions to the environment were split up in the same manner as for carpets (75 % to soil, 25 % to hydrosphere, see below). Similarly to textiles, it was assumed that all residuals of the volatile precursors selected are emitted to the atmosphere during the service life as a reasonable worst case.

**Tab. 52 > Transfer coefficients and emission factors for leather during service life**

| | Best guess | Range |
|---|---|---|
| TC wastewater | 0.2 | 0.1–0.4 |
| TC incineration | 0.2 | 0.1–0.4 |
| EF soil | 0.15 | 0.06–0.3 |
| EF hydrosphere | 0.05 | 0.02–0.1 |

Carpet protection

Releases during the service life of carpets may arise from cleaning (vacuuming or washing) or through mechanical wear. Hekster et al. (2002) quote 3M as providing a worst case estimate of 95 % loss of PFOS from carpets over their service life, with 50 % through abrasion from walking and vacuuming and 45 % through steam cleaning. The total of the releases from steam cleaning was assumed to go to wastewater. The use of vacuum cleaners leads to removal in solid waste and consequently incineration.

No information was provided concerning the proportion of the losses resulting from walking over carpets and vacuuming. It was assumed that clearly more than half was vacuumed. The remainder was assumed to be carried over to outside on shoes, clothes, etc. In Existing Substances Regulation risk assessments, the loss of particulates due to wear from plastics has been considered as ‘waste remaining in the environment’ and distributed as 75 % to soil and 25 % to hydrosphere (Brooke et al. 2004). The same assumption was applied here: the best guess emission factors and transfer coefficients considered in the SFA are somewhat lower than the worst case estimate by 3M (Tab. 53).

Extractable amounts of PFOA from mill-treated and carpet-care solution treated carpeting were determined as < 0.002–0.2 mg/m² and 0.3–0.5 mg/m² (Washburn et al. 2005). Based on the PFOA concentration present in carpet fibres estimated in the same study (0.2–0.6 and 0.2–2 mg/kg) and a weight per unit area of 1.5–2.5 kg/m², the fraction released was derived as < 0.03–1 and 0.1–1 for mill-treated and carpet-care solution treated carpeting, respectively. The fraction released could not be determined more precisely and there was no other information concerning the emissions of PFOA from carpets available. Therefore, as the transfer coefficients and emission factors were assumed to be comparable to PFOS, the same values were applied for both substances (Tab. 53). The reasonable worst case of a total emission to the atmosphere was considered for the volatile precursor substances (FOSE derivatives and FTOHs), in the same manner it was done for textiles and leather products.

**Tab. 53 > Transfer coefficients and emission factors for carpets during service life**

| | Best guess | Range |
|---|---:|---:|
| TC wastewater | 0.35 | 0.25–0.45 |
| TC incineration | 0.3 | 0.2–0.4 |
| EF soil | 0.09 | 0.05–0.15 |
| EF hydrosphere | 0.03 | 0.01–0.1 |

Levels in house dust do not necessarily originate from carpets. Despite of this, a rough estimate based on measurements was performed in order to have a comparison. Concentrations of PFOS and PFOA found in house dust in Bavaria had medians (ranges) of 16 ng/g (3–342 ng/g) and 11 ng/g (2–141 ng/g), respectively (Fromme et al. 2008). These concentrations were similar or up to one order of magnitude lower than in house dust from Canada, Japan, Norway and the USA analysed earlier (Moriwaki et al. 2003, Kubwabo et al. 2005, Nakata et al. 2007, Huber et al. 2008, Strynar & Lindstrom 2008). Dust deposition rates of 3.7 ± 1.3 mg/m²/day in summer and 2.2 ± 1.3 mg/m² /day in winter were determined in an American study (Edwards et al. 1998). In a study carried out in Germany, a dust deposition rate of 6.2 mg/m²/day was measured (Krause 1991). By multiplying these rates with the Swiss population and an average living area of 44 m²/person (BFS 2008), the amount of house dust generated was estimated to be 200–800 t/year. The amounts of PFOS and PFOA in house dust were thus estimated to be 0.001–0.3 kg/year and 0.001–0.1, respectively, considering the whole concentration range found in the German study.

Paper and packaging protection

No emissions during service life were considered in the RPA report (RPA 2004) for PFOS and its precursors because this period is short. However, atmospheric emissions were suspected to be possible. They were only considered for 2007, as they do not contribute to the stock in landfills. Hence, as there was no use of PFOS and its precursors in that year, no emissions of these substances were considered at that stage. However, PFOA and its precursors were present in paper and packaging in 2007. An experiment with microwave popcorn bags revealed that PFOA and FTOHs can emit into the air (Sinclair et al. 2007). However, the fraction emitted during cooking in a microwave oven for 3 min was 0.2 %. For 8:2 FTOH the fraction derived from the amounts in the package and emitted was 8 %. On one hand, the heat conditions were considered to be harsher than for most coated paper. Heat significantly increases the vapour pressure and FTOHs may be produced from fluorotelomer-based coating during microwave cooking. On the other hand, the experiment was carried out over a short period. Hence, emissions could be significantly higher over service life. It was assumed that the latter effect was stronger. As a reasonable worst case, it was assumed that all 8:2 FTOH was emitted to atmosphere over service life. For PFOA, the atmospheric emission factor was estimated to be negligible due to the low vapour pressure under normal conditions. Migration into oily food has been shown (Begley et al. 2005), but this process was estimated to have an significant contribution to emissions into the environment.

Coating of metals and ceramics

Although, it was determined that only a very small fraction of the PFOA in fluoropolymer dispersions gets into coated products, an estimate was made for the atmospheric emission factor. As stated above, the residual content of PFOA in PTFE cookware analysed was 0.004–0.075 ppm (Begley et al. 2005). This number can be converted to a concentration per unit area by considering a PTFE density of 2.2 g/cm³ and a film thickness of 75 µm, which results in 66–1200 pg/cm². Sinclair et al. (2007) determined a release of 11–503 pg/cm² during an experiment carried out at 250 °C for 20 minutes. The fraction emitted during one run was thus between 1 % and 100 %, but a figure of approximately one third seemed to be most appropriate. Although in one sample the mass of off-gassed PFOA released was observed to decrease following multiple uses, PFOA was measurable in the gas phase on the fourth use of both brands of frying pans. The authors concluded that further analysis was needed to determine whether cookware represents a continuous emission source of PFOA. The worst case of a total release was considered as possible. However, an emission factor of 0.7 was selected as a best guess for the substance flow analysis (Tab. 54).

**Tab. 54 > Transfer coefficients and emission factors for coatings during service life**

| | Best guess | Range |
|---|---|---|
| TC product | 0.3 | 0–0.99 |
| EF atmosphere | 0.7 | 0.1–1 |

Cleaning products, wax and polish

Products in this application area require their surfaces treated with waxes, polish or cleaning products, i.e. cars or floors, normally have a long service life of one to several decades. It was assumed that virtually all PFOS or PFOA is removed from the surface before end-of-life. Substances in car waxes were assumed to be washed out by rain and to either enter wastewater (on sealed ground in cities with combined wastewater systems) or soil. While substances in products applied to indoor surfaces were assumed to entirely get to wastewater, releases from outside surfaces may go to both wastewater and soil. Overall, it was assumed that 70 % is released to wastewater (Tab. 55).

**Tab. 55 > Transfer coefficients and emission factors for cleaning products, wax and polish during service life**

| | Best guess | Range |
|---|---:|---:|
| TC wastewater | 0.7 | 0.4–0.9 |
| EF soil | 0.3 | 0.1–0.6 |

Paints and lacquers

There would also be the possibility of emissions of the PFCs from the painted surfaces during the course of their service life. However, no information on these possible releases is available. As PFOS and PFOA have a very low vapour pressure, it was considered reasonable not to take into account this emission. All volatile precursors were assumed to have been emitted to the atmosphere previously.

Impregnation agents

Impregnation agents are applied to fabrics such as textiles, clothing, leather and carpets. It was assumed that emission factors and transfer coefficients during service life are equally composed by the respective numbers of the individual application areas (Tab. 56).

**Tab. 56 > Transfer coefficients and emission factors for impregnation agents during service life**

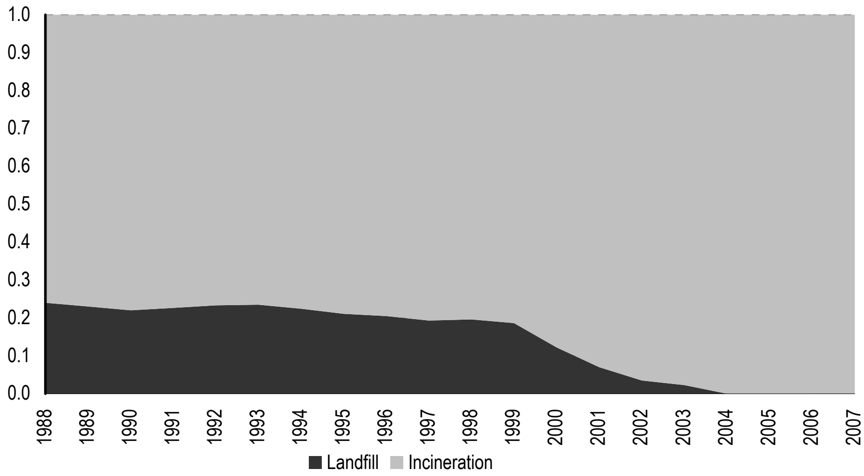
| | Best guess | Range |
|---|---:|---:|
| TC wastewater | 0.35 | 0.22–0.52 |
| TC incineration | 0.21 | 0.13–0.35 |
| EF soil | 0.11 | 0.05–0.20 |
| EF hydrosphere | 0.04 | 0.01–0.06 |

### 2.5.3.4 End-of-life

Temporal trend of disposal routes for solid waste

In order to estimate the stock accumulated on landfills during the past twenty years, the temporal trends of the disposal routes needed to be considered, even though the present study is not a dynamic SFA. The temporal trend of the fraction of the solid waste disposed of to landfills and incineration plants was taken from the national waste statistics for burnable waste (BUWAL 1998, BUWAL 2002, BUWAL 2004). During the nineties approximately 20–25 % of this waste was landfilled. At the end of the nineties the ratio decreased drastically, so that in 2005 there was no more direct landfilling of untreated waste (Fig. 13).

**Fig. 13 > Temporal trends of disposal routes for solid waste**



BUWAL 1998, BUWAL 2002, BUWAL 2004

**Metal plating**

As it was assumed that negligible proportions of the PFCs used for metal plating adhere to the products, there are also negligible amounts in the end-of-life products.

**Fire fighting foams**

Fire fighting foams that have to be replaced without being used are considered hazardous waste. It was assumed that they are incinerated in municipal solid waste incineration plants only. Additionally, it was assumed that there was no landfilling during the past twenty years. Hence, fire fighting foams did not contribute to the stocks on landfills.

**Photography**

Photographic films are mostly returned to the customer after processing, where they are either stored for some time or directly disposed of as solid waste. Waste prints and negatives are disposed of to municipal waste streams. The major concern of both light-sensitive material manufacturers and the companies who deal with waste of photographic film is to extract silver efficiently (ECB 2003). Kodak states that both types of modern film base (acetate and polyester) can be recovered, though the facilities for doing so may not exist in all locations. If local recovery is not possible, de-silvered film should be disposed of by incineration with energy recovery (Kodak, undated). Considering a Swiss classified directory, there are at least three recycling companies that do film recycling as one of their businesses (WLW 2008a). X-ray films that were estimated to be responsible for the largest fraction of the PFOS consumption are delivered to the recyclers in order to extract the silver content (AWEL 2007a). It is difficult to derive accurate transfer coefficients based on the available information. Export to foreign recyclers is possible but was not considered due to the lack of data. As x-ray films seem to be recycled in most cases and they represent the most important application, a transfer coefficient to recycling of 0.4–0.8 was considered, even though a smaller proportion of photographic films are recycled (Tab. 57). It was assumed in a first order approximation that the transfer coefficients were constant over time as silver recovery has also been done during the past two decades.

**Tab. 57 > Transfer coefficients for photography at end-of-life estimated for 2007**

| | Best guess | Range |
|---|---|---|
| TC recycling | 0.6 | 0.4–0.8 |
| TC incineration | 0.4 | 0.2–0.6 |

Hydraulic fluids for aviation

The total of hydraulic fluids was incinerated in 2005 (BAFU 2007b). No more recent statistics were available, but it was assumed that there was no change in the disposal routes until 2007.

Textile protection

After end-of-life, textiles are either disposed of as municipal solid waste, bulky waste or they are collected. Texaid, the largest organisation, collected 19 000 t of used clothes, shoes and home textiles in 2007 (Texaid 2008a). The amount (street and container collection) collected by the four leading organisations, Contex, Satex, SoliTex and Texaid, was 42 000 t in 2007 (U. Fischer, Contex, personal information). Other collection systems account for 5 000 t/year (BAFU 2007a). The collection quote of all discarded items is 50–55 %. After manual sorting, wearable clothes are predominantly sold to Western and Eastern Europe and Africa. Texaid is the only organisation that sorts collected textiles partially in Switzerland. The other organisations export unsorted textiles to be sorted abroad (Texaid 2008b). Wool and cotton clothes that are not wearable anymore are used as shoddy wool or as a cleaning rag material by the industry, respectably. Other textile materials are then reprocessed as insulating materials (AWEL 2003). The breakdown for textiles collected by Texaid is approximately as follows: 55 % wearable clothes, 20 % raw materials for the textile and paper industry, 15 % raw materials for the production of cleaning rags, 5 % is incinerated and 5 % is unaccounted (Texaid 2008b). However, impregnated textiles such as raincoats or protecting clothing are either exported to be reused or incinerated if they are damaged. There is no recycling of textiles from raincoats and similar clothes (U. Fischer, Contex, personal information). Therefore, approximately 60 % of the textiles (excl. upholstery and car seat covers) containing PFCs disposed of in Switzerland are incinerated and 40 % are exported.

Furniture with textile parts such as upholstered furniture are either brought to second-hand stores and are subsequently reused or disposed of as municipal solid waste or bulky waste, respectively. Reuse was assumed to extend the residence time in the use phase but not to change the fact that in 2007 the total is incinerated in Switzerland.

Vehicles including the textiles in interior decoration are either sent to domestic automobile recyclers or are exported. Out of 230 000 passenger cars taken out of circulation in Switzerland in 2007, 130 000 (57 %) were exported and 100 000 (43 %) processed in domestic recycling plants (Swiss Auto Recycling Foundation 2008a). According to the Swiss Auto Recycling Foundation (personal communication) most of the lorries at end-of-life are exported. Disused trains are about forty years old and are recycled in Switzerland (SBB, personal communication). In contrast to trains, a large proportion of tramways and buses are exported at their end-of-life. Airplanes were assumed to be mostly exported. Due to the fact that the PFCs flows in passenger cars were assumed to be by far bigger than the flows in the other vehicle types like lorries, buses, agricultural vehicles, caravans, motorbikes, trains, ships, airplanes or helicopters, the same share of the export was applied as for passenger cars. The temporal trend for the past twenty years is shown in the appendix in Fig. 25.

The transfer coefficients for the sum of disposed textiles are based on the disposal routes for clothes, furniture and vehicles. As the use of PFCs in upholstery and curtains was estimated to represent the most important application area (see section 2.5.1.6), furniture was weighted double. The resulting transfer coefficients are listed in Tab. 58. The temporal trend of the transfer coefficients required to estimate the stock accumulated on landfills was derived from the disposal routes of clothes, furniture and vehicles as well as from the disposal routes of burnable waste (see Fig. 13 on page 87). Textile products except of car seat covers not collected were assumed to be included to 100 % in the municipal solid waste or in the bulky waste. For clothes and other textiles collected, the data were based on statistics (BAFU 2007a) and information by the four organisations on when they started with the collection. Overall, the fraction dumped on landfills was 12–17 % during the nineties and dropped to a negligible fraction by the middle of the current decade (see Fig. 26 in the appendix).

**Tab. 58 > Transfer coefficients for textiles at end-of-life estimated for 2007**

| | Best guess | Range |
|---|---:|---:|
| TC recycling | 0.11 | 0.05–0.15 |
| TC incineration | 0.65 | 0.50–0.75 |
| TC export | 0.24 | 0.15–0.40 |

Leather protection

Shoes are collected in the same collection system as clothes. The mass fraction of shoes in the street collection system is roughly 16–18 %. Approximately, 10 000 t of clothes and shoes were collected in this manner in 2007. In the container collection system (33 000 t in 2007), the mass fraction of the shoes is lower and was estimated to be 8 % (U. Fischer, Contex, personal information). Hence, approximately 4000 t of shoes were collected in 2007. There was no information on the fraction of shoes collected or the amount of shoes disposed of. However, the import of shoes accounted for 16 000 t in 2007, while the export was a tenfold lower (FCA 2008). Assuming that the domestic production of shoes is markedly smaller than the import and that the consumption corresponds to approximately the amount of shoes disposed of, the fraction of shoes collected was roughly 20 % in 2007. All organisations but Texaid export the collected shoes to foreign countries, where approximately 70 % can be sold and 30 % are disposed of as waste. Other leather articles treated with fluorinated products are assumed to be either collected as textiles or to be disposed of in the solid waste. It was assumed that a mean 20 % export fraction was appropriate for leather articles containing PFCs and the temporal trend in the collection quote was parallel to the one for textiles (see Tab. 59). These assumptions apparently bear a considerable uncertainty. However, only the temporal trend of the disposal on landfills, where the uncertainty is smaller, is of importance (see Fig. 27 in the appendix).

**Tab. 59 > Transfer coefficients for leather products at end-of-life estimated for 2007**

| | Best guess | Range |
|---|---|---|
| TC incineration | 0.8 | 0.7–0.9 |
| TC export | 0.2 | 0.1–0.3 |

Carpet protection

Recycling techniques for carpets exist, e.g. falling film crystallisation to recover polyamides and plants practising such techniques exist in Germany. According to Gugerli and Rubli (2003) and information received from industry, these techniques are however not used in Switzerland. It was therefore assumed that carpets are disposed of like bulky waste (Tab. 60). Hence, the temporal trend of the disposal on landfills is equal to the one in Fig. 13 (page 87).

**Tab. 60 > Transfer coefficients for carpets at end-of-life estimated for 2007**

| | Best guess | Range |
|---|---|---|
| TC incineration | 1.0 | – |

Paper and paperboard protection

The collection rate of paper and paperboard was 79 % in 2007. This corresponds to 1 324 000 t/year, while the import and export of recovered paper and paperboard amount to 131 000 t/year and 519 000 t/year, respectably (ZPK 2008a). Hence, the net export of the recovered paper and paperboard is 29 %, which corresponds to 23 % of the total. The remainder that was not collected was assumed to be disposed of with the municipal solid waste. However, it is not known if the collection rate for paper and paperboard in general also applies for coated papers such as food wraps, folding cartons or packaging. As some of these products get dirty during use, it was assumed that a higher percentage was disposed of as waste in incinerators. A collection rate of 50 % was used as a best guess. The export share was assumed to be similar as for all paper and paperboard–29 % of the collected amount. The resulting transfer coefficients are listed in Tab. 61. It was assumed that the temporal trend in the collection quote of coated paper was parallel to the one for all paper and paperboard (BAFU 2007a). Because only the temporal trend of the disposal in landfills is needed, the fraction collected was not split up into recycling and export (see Fig. 28 in the appendix). As mentioned above, these assumptions bear a considerable uncertainty.

**Tab. 61 > Transfer coefficients for paper and paperboard at end-of-life estimated for 2007**

| | Best guess | Range |
|---|---|---|
| TC recycling | 0.35 | 0.25–0.50 |
| TC incineration | 0.50 | 0.30–0.60 |
| TC export | 0.15 | 0.10–0.25 |

Coating of metals and ceramics

At end-of-life coated products such as frying pans, baking trays or parts of machines are collected as scrap metal in order to be recycled. A small proportion is disposed of as municipal waste. However, there are no data on the distribution to these two disposal routes. It was assumed that roughly 90 % was recycled and the remainder was incinerated (Tab. 62).

**Tab. 62 > Transfer coefficients for coatings at end-of-life estimated for 2007**

| | Best guess | Range |
|---|---|---|
| TC recycling | 0.9 | 0.7–1 |
| TC incineration | 0.1 | 0–0.3 |

Paints and lacquers

It was assumed that paints and lacquers applied to surfaces are disposed of as solid waste at end-of-life (Tab. 63).

**Tab. 63 > Transfer coefficients for paints and lacquers at end-of-life estimated for 2007**

| | Best guess | Range |
|---|---|---|
| TC incineration | 1.0 | – |

Impregnation agents

Similarly to the service life, transfer coefficients of the application areas *textile protection*, *leather protection* and *carpet protection* were averaged as a first order approximation, as these fabrics may all contain PFCs applied by impregnation agents. The resulting transfer coefficients were not rounded (Tab. 64).

**Tab. 64 > Transfer coefficients for impregnation agents at end-of-life estimated for 2007**

| | Best guess | Range |
|---|---|---|
| TC recycling | 0.04 | 0.02–0.05 |
| TC incineration | 0.81 | 0.73–0.88 |
| TC export | 0.15 | 0.08–0.23 |

### 2.5.3.5 Recycling

Metal plating

As stated in detail in section 2.5.3.2 (page 72 ff.), no efficient method to remove PFOS from wastewater during physico-chemical treatment was known by 2007. The same best guess estimate, 90 % release to public sewer, was also made here (Tab. 65).

**Tab. 65 > Transfer coefficients of metal plating in the process *recycling***

| | Best guess | Range |
|---|---|---|
| TC wastewater | 0.9 | 0.8–0.95 |
| TC incineration | 0.1 | 0.05–0.2 |

Photography

X-ray and reprographic films are shredded after delivery to recycling companies and before the photographic layer is removed. The films are then washed in water containing enzymes in order to separate the gelatine from the plastic foil. As a result, the residues in the films are removed, while the underlying foil consisting of PET material, is freed for recycling in pure source quality (NAVEG 2008). It is unknown if there are also other types of recycling techniques. There are no transfer coefficients available for PFOS in this recycling process. It is assumed that a considerable fraction of PFOS is removed from the layer and gets into wastewater. A substantial part might also end in the solid waste fraction. The possibility of re-entering to the material flow of silver or PET was not considered. In the absence of any data, the transfer coefficients were roughly estimated and a large range was considered (Tab. 66).

**Tab. 66 > Transfer coefficients of photography in the process *recycling***

| | Best guess | Range |
|---|---|---|
| TC wastewater | 0.7 | 0.3–0.9 |
| TC incineration | 0.3 | 0.1–0.7 |

Textile protection

Discarded vehicles are first treated by an automobile recycler, where liquids are removed and batteries, tyres and catalytic converters are dismantled and passed on for recycling. Metals are sorted out in shredder works. Finally, around 25 % vehicle automobile shredder residue (ASR) of an end-of-life vehicle remains (Swiss Auto Recycling Foundation 2008a). ASR consists essentially of plastic materials (60 %), glass/sand, i.e. mineral substances (15 %), textiles/leather/wood (10 %), paint dust/rust (10 %) and residual metals (5 %) (Swiss Auto Recycling Foundation 2008b). In 2007, the shredder works delivered a total of 55 000 t/year of ASR to the incineration plants. Swiss MSWIPs processed 24 500 t/year, i.e. 45 % and the remaining part was exported (Swiss Auto Recycling Foundation 2008a) as shown in Tab. 67. Fig. 29 (appendix) reveals the transfer coefficients for the past twenty years. The landfilling of ASR was the sole disposal route until 1995 and occurred until 2000.

**Tab. 67 > Transfer coefficients of textiles in automobiles in the process *recycling***

| | Best guess | Range |
|---|---|---|
| TC incineration | 0.45 | 0.4–0.5 |
| TC export | 0.55 | 0.5–0.6 |

Paper and paperboard protection

It was assumed that the same portion of the substances which is retained on the fibre during the papermaking process is retained on the sludge when the recovered paper gets re-pulped (ECB 2003). Hence, the fraction lost to wastewater was assumed to be 10 % (see Tab. 46 on page 79). Depending on the type of paper or paperboard recycled, between 4 % and 40 % becomes solid waste in recovered paper mills (OECD 2006b). A mean proportion of 20 % was assumed and it was further assumed that the temporal trend of the disposal was similar to the one for solid waste in general (see Fig. 13). The remainder was assumed to be contained in the recycled paper product. However, this loop was not considered in the SFA for simplification reasons.

**Tab. 68 > Transfer coefficients of paper in the process *recycling***

| | Best guess | Range |
|---|---|---|
| TC wastewater | 0.1 | 0.05–0.3 |
| TC incineration | 0.2 | 0.04–0.4 |

Coating of metals and ceramics

In absence of any data on emission factors in the melting process, it was assumed that the atmospheric emission factors were the same as those of municipal solid waste incineration plants in a first order approximation (see Tab. 72). It was further assumed that the rest of PFCs was destroyed during this process and no residuals remained in the molten metal.

Impregnation agents

As only a fraction of textiles, but not of leather products or carpets, enter recycling processes (see section 2.5.3.4 above), the same transfer coefficients as in Tab. 67 were considered.

#### 2.5.3.6 Sewerage

Sewer systems are designed to collect and transport the municipal and industrial wastewaters from residences, commercial buildings, industrial plants and institutions to WWTPs. Two loss mechanisms of substances from the sewer system are considered in this report:

- Combined sewer overflows caused by strong or long-lasting precipitation events
- Sewage exfiltration from leaking pipes of house connections and public sewer systems

Sewer overflows

In combined wastewater systems, the sewage and the storm water are transported in the same sewer pipe. The combined sewage surpasses the treatment capacity of the sewage treatment plant during storm water peak flow and therefore has to be partially discharged without treatment to receiving water such as rivers and lakes. In modern sewage systems in Central Europe with infrastructure for temporary storage and rough treatment of sewage and storm water, sewer overflow occurs in only about 2 % of the time (Brombach et al. 1999, Gujer 1999). During the overflow events, only about 50 % of the diluted wastewater is discharged (Krejci et al. 2000). The estimated pollution load is therefore about 1 % of the annual load of the raw sewage (Ternes & Joss 2006).

Sewer exfiltration

Over the years, many sewer systems have experienced major infrastructure deterioration due to inadequate preventive maintenance programs and insufficient planned system rehabilitation and replacement programs. These conditions have resulted in deteriorated pipes, manholes and pump stations that allow sewage to exit the systems (exfiltration) and contaminate adjacent ground and surface waters (Amick et al. 2000). The magnitude of exfiltration due to sewer leakage is unclear. There are currently two contradictory viewpoints concerning the amount and impact of exfiltration in the scientific discussion (Rutsch et al. 2008): On one hand, it has been argued that loss volumes are generally negligible and despite some extreme, exceptional cases of loss, there is little if any evidence that sewer leakage endangers groundwater resources on a large scale. A considerable self-sealing of sewer damages has been observed in some cases. On the other hand, exfiltrating wastewater from sewers has been shown to be a major source of groundwater contamination (e.g. Bishop et al. 1998). One possible explanation for this knowledge gap is that the impact of exfiltrating wastewater on groundwater is strongly variable in both time and space (Rutsch et al. 2008).

The extent of sewer exfiltration in the literature is subject to large uncertainties, partly caused by the influence on the method applied and different areas investigated. Based on different methods, losses from public sewer systems have been estimated as 1–11 % (Schluep et al. 2006, Ternes & Joss 2006). Since the private sewer system (house connections) are generally considered to be in a worse condition than the better controlled public sewer system, the total loss by sewer exfiltration must be substantially higher and could reach 20–25 % (Ternes & Joss 2006).

The knowledge on the conditions of the private sewer system is limited and large deficiencies are supposed to exist in several areas (Franz 2007). The overall exfiltration rate in Switzerland was therefore roughly estimated to be in the range of 1 % to 15 % with a medium value of 5–8 % (J. Rieckermann, Eawag, personal communication). A large proportion of the PFOS and PFOA in the sewer system originates from industry and commerce, whose private sewer systems are controlled occasionally, whereas there are normally no controls of those of households. Therefore, a 5 % loss of PFOS and PFOA was considered as a best guess for the exfiltration from the Swiss sewer system.

Emission factors and transfer coefficients derived for the process ***sewerage***

The total of the losses by sewer overflows and sewer exfiltration was not assumed to be emitted to hydrosphere. Even though PFOS and PFOA were also found to be easily transported in ground water and showed a low sorption rate (Hoehn et al. 2007), a certain amount is probably still retained in the underground. Considering both loss mechanisms, an emission factor of 0.05 was selected as a best guess with a range of 0.02–0.15 (see Tab. 69). Even though the uncertainty is large for the losses from the sewer system, their impact on the emissions of PFOS and PFOA to the hydrosphere was not estimated to be high. As the substance flows are not reduced in WWTPs efficiently (see section 2.5.3.7), the influence of that uncertainty is considerably smaller than it would be for substances eliminated efficiently in WWTPs.

**Tab. 69 > Emission factors and transfer coefficients at the process *sewerage***

| | PFOS | | PFOA | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| TC WWTP | 0.95 | 0.85–0.98 | 0.95 | 0.85–0.98 |
| EF hydrosphere | 0.05 | 0.02–0.15 | 0.05 | 0.02–0.15 |

### 2.5.3.7 WWTP

PFOS

It has been shown in several studies that wastewater treatment plants (WWTPs) are unable to reduce the concentrations of PFCs in the effluent significantly compared to the concentrations in the influent. In several studies, even an increase in concentrations or mass flows from the influent to the effluent has been found and attributed to the degradation of precursor substances (Schultz et al. 2006, Sinclair & Kannan 2006, Becker et al. 2008, Bossi et al. 2008, Huset et al. 2008). However, the data from different WWTP vary significantly. Results from studies on substance flows and a comprehensive investigation from Switzerland based on flow-proportional 24 h composite samples of WWTP influents and effluents collected daily for seven consecutive days are summarized in Tab. 78 (appendix, page 130). There are only three studies investigating the substance flows including sewage sludge. In the first one (Schultz et al. 2006), the substance flows of PFOS in the effluent and in sewage sludge were 143 % and 55 % relative to the influent, i.e. the emission factor to the hydrosphere was 1.43 and the transfer coefficient to sewage sludge was 0.55. This data were selected in a recent review article on the chemical fate of chemicals in WWTPs (Heidler and Halden 2008). In the second study, the analyses were repeated in each season. The emission factors and transfer coefficients were 0.73–3.89 and 4.0–40, respectively (Loganathan et al. 2007). In the third study, the numbers equaled 1.87 and 1.53 (Becker et al. 2008). It has to be noted however that there is a high uncertainty for the values obtained in the second and third studies as only grab samples and not composite samples were taken and since the concentrations in influent and effluent are subject of a considerable fluctuation. The emission factor of PFOS to the hydrosphere, including the other studies (Sinclair & Kannan 2006, Loganathan et al. 2007, Huset et al. 2008), ranges between 0.56 and 3.89. Based on the mean (1.29), geometric mean (1.14), median (1.09) and the differences in sampling quality and therefore accuracy, a best guess emission factor of 1.2 and a range of 0.8–2 were selected for the model. It seems that the substance flow of PFOS into sewage sludge is not directly related to the mass in the influent. As the residence time in WWTPs is longer for sludge than for water and the microbial conditions are considerably different, the potential of the formation of PFOS by degradation from precursors is higher. The substance flow into sewage sludge might therefore be strongly dependent on the presence of precursor substances such as *N*-MeFOSE, *N*-EtFOSE, FOSAA, *N*-MeFOSAA or *N*-EtFOSAA (Schultz et al. 2006, Sinclair & Kannan 2006, Loganathan et al. 2007, Rhoads et al. 2008) in wastewater. Because of the large variation (two orders of magnitude and up to a factor of 40) of the substance flow increase in sewage sludge compared to the influent, it is difficult to make an appropriate estimation. The transfer coefficient of 0.55 derived in the sole study applying composite samples is the lowest obtained. Because of the higher accuracy, this value was weighted as much as the other values together. The resulting geometric mean, 2.2, was considered as a best guess. As the highest increases could be a result of sampling artefacts, a range of 0.5–20 was considered.

PFOA

For PFOA, the results of the three substance flow studies including sewage sludge differ significantly. While the emission factors and transfer coefficients determined in the first one (Schultz et al. 2006) were 0.75 for the effluent and $<0.01$ for sewage sludge, they were 20 and 0.75 in the second one (Becker et al. 2008). In the third study, the emission factors and transfer coefficients were 0.95–6.33 and 0.29–9, respectively. It has to be emphasized that the two latter studies were based on grab samples only, i.e. could be influenced strongly by a variable input. The emission factors to hydrosphere for PFOA ranged between 0.81 and 5.71 in the other studies (Sinclair & Kannan 2006, Loganathan et al. 2007, Huset et al. 2008). The value of 20 was considered as an outliner in order to calculate the mean (2.2), geometric mean (1.78) and median (1.51). Based on that and the differences in sampling quality and therefore accuracy, a best guess emission factor of 1.8 and a range of 0.7–6 were considered in the model. Precursors that potentially contribute to that increase substance flow include fluorotelomer alcohols, especially 8:2 FTOH (Wang et al. 2005, Sinclair & Kannan 2006). For sewage sludge, the value of 9 was considered as an outliner for the calculation of the mean (0.6), geometric mean (0.22) and median (0.68). As the lowest transfer coefficient was obtained in the study with composite samples and therefore the highest accuracy, a best guess transfer coefficient of 0.2 was assumed with a range from 0.002 to 1.3.

Atmospheric emissions

At pH values occurring in WWTPs, only negligible proportions of PFOS ($pK_a \approx -3.3$, see Tab. 1 on page 17) and PFOA ($pK_a \approx 2.5$) are present in the neutral form. It was thus assumed that the gaseous emissions to the atmosphere were negligible. This is supported by the fact that an emission to air is not taken into account in any of the publications on the fate of PFCs in WWTPs.

Disposal of sewage sludge

Most of the fraction of the PFCs that is adsorbed to sewage sludge was incinerated in 2007. The most recent data on the disposal routes of sewage sludge are for the year 2006. In that year, 89 % of the sewage sludge was incinerated (44 %, sludge incineration plants and similar, 23 % municipal solid waste incineration plants, 22 % cement plants), 10 % was used in agriculture and 1 % was exported. The export was only made for WWTPs in border areas, proportionally to the connected inhabitants (BAFU 2008). It was thus assumed that there is no export of sewage sludge originating from Swiss households or industry. Beginning October 1st 2006, the usage of sludge in the agriculture was prohibited in principle. However, cantons had the possibility of a further usage in the agriculture during a transitional period of two years (vegetable and feed crops as well as groundwater protection zones excluded; appendix 2.6 paragraph 5.3 ORRChem). According to FOEN, few cantons exercised that option for small WWTPs in rural areas. Based on this information and in the absence of data, the proportion of sewage sludge used in agriculture in 2007 was estimated to be 1–3 % (best guess 2 %).

Emission factors and transfer coefficients derived for the process ***WWTP***

The best guess emission factors and transfer coefficients estimated and the ranges are shown in Tab. 70. The transfer coefficients to soil and incineration were calculated by multiplying the transfer coefficients to sewage sludge and the proportion of sludge that is incinerated or used in agriculture in the year 2007.

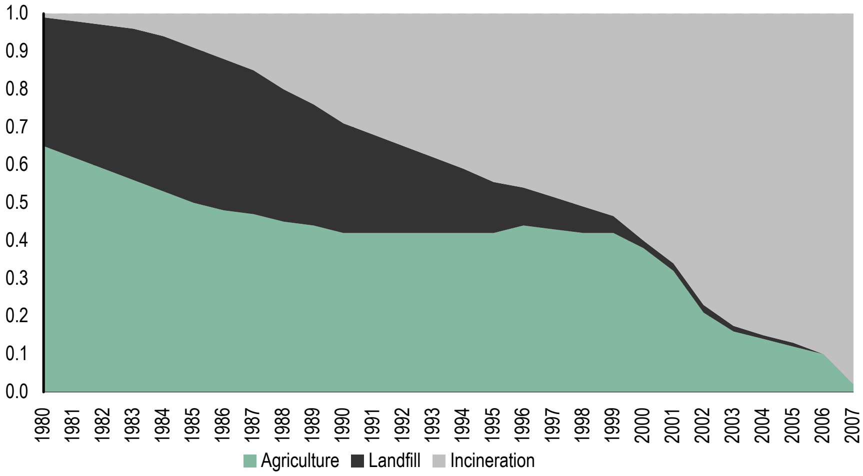
**Tab. 70 > Emission factors and transfer coefficients at the process *WWTP***

| | PFOS | | PFOA | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| TC incineration | 2.2 | 0.5–20 | 0.2 | 2.0E−02 – 1.3E−00 |
| EF soil | 4.4E−02 | 0.5E−03 – 6.0E−01 | 4.0E−03 | 2.0E−04 – 3.9E−02 |
| EF hydrosphere | 1.2 | 0.8–2.0 | 1.8 | 0.7 – 6.0 |

In order to estimate the amount of PFOS and PFOA that has accumulated on landfills where sewage sludge was dumped, the disposal routes since 1980 were compiled from the literature and some own assumptions. The temporal trend is shown in Fig. 14.

**Fig. 14 > Disposal routes of sewage sludge.**

*Fraction of the individual disposal routes of sewage sludge between 1980 and 2007: "agriculture", "landfill" and "incineration".*



Külling et al. 2002, Laube & Vonplon 2004, BAFU 2008

#### 2.5.3.8 Incineration

Few studies investigating the fate of PFOS and PFOA during incineration of waste and the few emissions from incineration plants have been carried out. One study investigated the thermal degradation of a polyester/cellulose fabric treated with a fluorotelomer-based acrylic polymer under laboratory conditions. The temperature where 99.9 % is destroyed during combustion was found to be 725 °C for the treated article and 1000 °C for the investigated polymer, respectively. No detectable amount of PFOA was formed under typical municipal incineration conditions. The authors therefore concluded that textiles and paper treated with such a fluorotelomer-based acrylic polymer disposed of in municipal waste and incinerated are destroyed and are not a significant source of PFOA in the environment (Yamada et al. 2005).

An experiment in a pilot-scale rotary kiln incinerator simulator was carried out using treated and untreated carpet materials as well as carpeting deliberately doped with high concentrations of a commercially available PFC mixture. A limited number of PFCs were found in trace levels in the stack. In all cases, most PFCs were either not detected or were at such low concentrations to not be quantifiable. PFHxA and PFOA were the most consistently detected species and were both at levels well below 1 $\mu g/m^3$. The concentrations were relatively independent of kiln feed, which was interpreted by the authors as the result of effective destruction of PFCs even under mild combustion conditions. The trace levels that were found were due to either trace contamination of the sampling duct with fluorinated compounds due to the historical use of PTFE and other fluoropolymers or sampling artefacts (Lemieux et al. 2007). No emission factors could be derived from these measurements.

The combustion efficiency of PFOS was tested in a laboratory-scale thermal degradation study at 600 °C and 900 °C. 450 µg PFOS ($K^+$ salt) were gasified and combusted at 600 °C for two minutes. The sum of the amounts extracted from the two PUF sample cartridges in the exhaust was 2.2 µg. 0.33 µg PFOS of the 500 µg combusted at 900 °C were extracted from the two cartridges. Combustion experiments of two perfluorosulfonamides (named FC-807A and FC-1395) resulted in no PFOS emissions above the detection limit of 10 ng/ml (Taylor & Yamada 2003). The atmospheric emission factors for PFOS at these temperatures that could be calculated from this experiment are 0.0049 and 0.00066, respectively. The latter experiment is considered as being more realistic, as 900 °C are normally reached during combustion duration in an incineration plant. However, since there was no flue gas cleaning in the experiment in contrast to a full-scale incineration plant, these emission factors were not directly applicable for the SFA. The factor 0.00066 is three times greater than the maximum atmospheric emission factors for PFOS ($< 0.0002$) derived from the analyses at the sludge incineration plant (see below).

Emissions during the incineration of sewage sludge were analysed in Germany. The concentrations in all flows leaving the plant were below the detection limit for PFOS as well as for PFOA: $< 15$ ng/$Nm^3$ in the flue gas, $< 10$ µg/kg d.w. in fly ash, in spray dryer product and in gypsum, respectively. The incinerator was fed with 7 tons of sewage sludge (d.w.) per hour. The sludge with the highest concentrations of PFCs was a 1:1 mixture of contaminated (120 µg/kg d.w. PFOA, 580 µg/kg d.w. PFOS) and normal (< 10 µg/kg d.w. PFOA, 530 µg/kg d.w. PFOS) sewage sludge (Geueke 2007). This study was criticised by an NGO concerning the use of a non-standardised method for the analyses of flue gas, which results in a half-quantitative detection limit (Kröfges 2007). In spite of this and for lack of other data, *maximum* emission factors and transfer coefficients were calculated from the data given: The atmospheric emission factors were < 0.0002 for PFOS and < 0.002 for PFOA. The transfer coefficients into fly ash, spray dryer product and gypsum were < 0.01, < 0.0003 and < 0.0005 for PFOS and due to the smaller input ten times higher for PFOA.

In a study carried out in Georgia (USA), the substance flows of PFCs in wastewater throughout a WWTP including the incineration of sewage sludge were investigated (Loganathan et al. 2007). The incineration was performed at temperatures of 600 °C and above (K. Kannan, personal communication). 600 °C are however not sufficient to destroy C–F bonds of PFCs to a satisfactory extent. According to best available techniques, sewage sludge should be incinerated at furnace temperatures of around 850 °C (EC 2006b). Typical temperatures in Swiss sewage sludge incineration plants are 800–850 °C. In one plant, for example, the flue gas is kept for at least 4 seconds at 800 °C. Even though this difference in combustion temperature (600 °C vs. 800–850 °C) might strongly influence the destruction efficiency of PFOS and PFOA, the transfer coefficients to ash were also calculated applying the data from Loganathan et al. (2007) as a worst case and as a comparison to the results derived from the German study. Mechanically dewatered sludge has a solids content of 25–35 % (AWEL 2007b). Assuming that 30 % the mass of the solid fraction decreased from 20.6 t/day to 5.6 t/day during incineration. The transfer coefficients to ash derived from the concentration changes and the decrease of mass are listed in Tab. 71.

**Tab. 71 > Concentration changes in sewage sludge and transfer coefficients to ash during incineration**

*Concentrations in sewage sludge from a WWTP in Georgia before and after incineration. The operating temperatures were 600 °C and above. The transfer coefficients to ash were calculated based on the assumption of a solids content of 30 % in sewage sludge before incineration.*

| | Cake before burning | Cake after burning | TC to ash |
|---|---|---|---|
| PFOS | 38 | 50 | 3.5E−01 |
| PFOS | 61 | 35 | 1.5E−01 |
| PFOS | 77 | < 2.5 | < 8.7E−03 |
| PFOA | 64 | 35 | 1.5E−01 |
| PFOA | 130 | 9.7 | 2.0E−02 |
| PFOA | 47 | 7 | 4.0E−02 |

Loganathan et al. 2007

Emission factors and transfer coefficients derived for the process ***incineration***

Half of the maximum atmospheric emission factor derived from the detection limit in the German study (Geueke 2007), which is 3.3 times lower than the emission factor derived from the laboratory-scale incineration plant without flue gas cleaning, was considered as a reasonable best guess for PFOS (see Tab. 72). A range from a tenth of that value to the maximum emission factor (laboratory-scale study) was selected for the SFA. The fact that the maximum atmospheric emission factor for PFOA derived from the study in Germany is ten times greater is caused by the smaller concentrations in the sewage sludge incinerated. Since the behaviour of PFOA during combustion was assumed to be comparable to PFOS, the same value was selected as a best guess. However, the maximum value considered was the maximum atmospheric emission factor for PFOA. The transfer coefficient to landfill was derived from the maximum transfer coefficients into fly ash, spray dryer product and gypsum in the German study. Similarly to the atmospheric emission factor, half of the maximum was selected as a realistic best guess value. The transfer coefficient for PFOA was also assumed to be equal to PFOS and the ranges were chosen as described for the atmospheric emission factors. After comparing the results to the values obtained from the German study and considering the low combustion temperatures, the (worst case) results from Georgia (USA) were considered inappropriate for Switzerland.

Measurements in cleaned wastewater of incineration plants were carried out in Germany. The concentrations of PFOS and PFOA in wastewater of a municipal solid waste incineration plant in North Rhine-Westphalia were below the limit of detection of 100 ng/L (LANUV 2008). The concentrations were also below the limit of detection (25 ng/L) in the scrubber water of a sludge incineration plant, except in one sample for PFOS, where the concentration was 27 ng/L (Geueke 2007). Considering that approximately 300 L of water are used per ton of solid waste and 3 million t/year of solid waste, the volume of cleaned wastewater form incineration plants is approximately 1 billion L/year. Based on the limits of detection of 25 ng/L (PFOS detected above once) and 100 ng/L (no measurements above), it was concluded that the emissions from incineration plants to the hydrosphere are < 0.1 kg/year. This substance flow was thus not included in the substance flow analysis.

**Tab. 72 > Emission factors and transfer coefficients at the process *incineration***

| | PFOS | | PFOA | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| TC landfill | 5.0E−03 | 5.0E−04 – 1.0E−01 | 5.0E−03 | 5.0E−04 – 1.0E−01 |
| EF atmosphere | 1.0E−04 | 1.0E−05 – 2.0E−04 | 1.0E−04 | 1.0E−05 – 2.0E−03 |

Several studies have shown that small fluorinated molecules such as tetrafluorosilane or fluorinated alkenes such as tetrafluoroethylene, hexafluoropropylene, perfluoroisobutylene or fluorobenzene can be formed during combustion of PFCs such as PFOS and PFOA or PTFE. Some of them are corrosive and highly toxic (e. g. Waritz 1968, Taylor & Yamada 2003, Yamada et al. 2005, Ochi et al. 2008). However, a detailed consideration of these substances is beyond the scope of this study. Nevertheless, this might need further investigation.

### 2.5.3.9 Landfill

Atmospheric emissions

Three different types of atmospheric emissions may occur on landfills: emissions during unloading, emissions of dust caused by operations done on landfills and wind as well as gaseous emissions.

No data on emissions during unloading on landfills were available. Therefore, an emission factor was derived by considering a study on emissions from an opencast coal mining in India (Chaulya et al. 2002) as a worst case situation. A mean emission rate of overburden and coal unloading, given in grams per second, was divided by the capacity of the unloader and the frequency of unloading. The emission factors determined are 11 g/t for overburden unloading and 8 g/t for coal unloading. The drop height on the coalmine for overburden and coal unloading was around 13 m and 3 m, respectively. The drop heights during unloading on landfills are normally less than 3 m. Moreover, not all fractions dumped on landfills are dusty. APC residues are dumped in underground landfills. Therefore, it was assumed that the emission factor in landfills is one order of magnitude lower than in a coal mine. An emission factor of 5.0E−06 was considered as a worst case for the model, whereas 1.0E−06 was selected as a best guess (see Tab. 73). The annual emissions of dust from landfills in Switzerland due to operations and wind might be relatively low. As none of the landfill operators contacted was able to provide data or rough estimates, an assumption of 1 g annually released per ton in the landfill was used for the model. Gas condensate samples from a landfill in Minnesota were analysed for PFOS and PFOA. The concentrations found were 29.9 µg/L and 83.8 µg/L, respectively (Oliaei et al. 2006). The concentrations were higher than in the leachate samples from the same landfill (see Tab. 79 in the appendix on page 131). However, the gas condensate volumes were assumed to be much lower than the leachate volumes. As the pH in landfills usually ranges between 5 and 8, only a very small proportion of PFOS ($pK_a \approx -3.3$, see Tab. 1 on page 17) and PFOA ($pK_a \approx 2.5$) is present in the neutral form. As ionic molecules are not volatile, it was assumed that the gaseous emissions were negligible compared to emissions with dust being stirred up.

Landfill leachates

There is limited data available to date for studies of PFCs in landfill leachates. The first known study on PFCs in landfill leachates was carried out by 3M in 1999 and 2000 (3M 2001). One landfill sampled was in Decatur (Alabama), where 3M operates a plant manufacturing fluorochemicals. The landfill was used for disposal of industrial biological wastewater treatment sludge and other nonhazardous materials prior to 1998. The concentrations of PFOS and PFOA in the leachate of this landfill were both at approximately 50 000 ng/L. Concentrations in landfill leachates from cities with some textile and carpets manufacturing (Columbus, Georgia) or no known significant industrial use of fluorochemicals (Port St. Lucie, Florida) were two or more orders of magnitude lower (see Tab. 79 in the appendix on page 131).

PFCs in landfill leachates were also monitored in Minnesota in 2005. The landfill received sewage sludge from a 3M plant beginning in about 1975, but it also receives mixed municipal solid waste. PFOA was found in the highest concentrations of any PFCs at an average of 62 ppb consistent with its apparent greater mobility through solid matrices. PFHxA, was found in the next highest concentration at an average of 25 ppb, which may be also related to greater mobility, particularly in the landfill's more acidic environment. PFOS was found at an average of 20 ppb in the leachate. The author concluded that it appeared that the primary source of PFCs in the landfill leachate was related to the deposition of the 3M sludge and not consumer products containing PFCs. The relatively high levels of PFCs are comparable to the Decatur, Alabama landfill leachate which received 3M sludge from the 3M fluorochemical plant (Oliaei et al. 2006).

Concentrations of several fluorochemicals were analysed in landfill leachates in the USA (Huset 2007). Perfluorocarboxylates (C4–C10) were the dominant species observed. The short chained carboxylates, PFBA and PFPA, were discovered to be the most concentrated of the analytes assayed in eight of the twelve leachates (maximum concentrations of 1700 ng/L and 1500 ng/L, respectively). The low tendencies for these short chained analytes to sorb on solid materials make it unlikely that they would be retained in the landfill, and conversely, make it very likely that they would become enriched in the aqueous phase. PFOA was found in all leachates. The concentrations ranged from 130 to 1100 ng/L. Fluorotelomer sulfonates were measured in all landfill leachate samples. Concentrations of 8:2 FTS found were 8–210 ng/L (Huset 2007).

PFOS was also detected in all samples at concentrations of 38–160 ng/L (see Tab. 79 in the appendix), including those from sites that received waste only after the 2002 phase out of PFOS, indicating that PFOS is still being released from consumer products post phase out. Concentrations of PFBS and PFHxS exceeded those of PFOS (maximum concentrations of 2300 ng/L and 700 ng/L, respectively). Fluoroalkyl sulfonamides, which are precursors to PFOS, were also detected in leachate, often in concentrations exceeding those of their degradation product. Concentrations of Me-FOSAA, which is indicative of the chemicals used in textile and carpet treatments, ranged from ND to 290 ng/L, while concentrations of Et-FOSAA, which is associated with polymeric paper coating applications, ranged from 7 to 480 ng/L (Huset 2007).

Time may be indicative of either biodegradation, a change in input, or both. However, no correlation between PFCs concentrations and time (the year a landfill opened) was found for PFOS and PFOA. The only significant correlation was found for 6:2 FTS. There are many other factors possibly affecting PFCs concentrations in landfill leachates such as the origin of refuse and acceptance of sewage sludge (Huset 2007).

Landfill leachates were analysed in Norway and Finland. PFOS concentrations ranged from 30 to 187 ng/L, while they were 168–516 ng/L for PFOA. The authors concluded that these results indicate that landfill effluents were contributing as important anthropogenic sources for the release of PFCs into the environment (Kallenborn et al. 2004). The concentrations found are comparable to those analysed by Huset (2007). Recently, leachates from two Danish landfills were analysed (Bossi et al. 2008). These concentrations, however, were significantly lower than in the other Scandinavian countries. PFOS and PFOA concentrations were between LOD and 3.8 ng/L or 5.8 ng/L, respectively. The leaching of PFCs from a landfill was also investigated at a site in Norway with an average annual leachate discharge for the years 2003–2006 of 480 000 m$^3$. In the sediment samples taken from the pump ditch at the landfill site, the total PFCs concentrations summing compounds detected were within the range of 5.2–17.2 µg/kg with PFOS (3.8–7.5 µg/kg) and PFHxS (0.4–0.9 µg/kg) being found in all samples and PFOA (4.6 µg/kg), PFNA (3.3 µg/kg), PFTrA (5.1 µg/kg), PFTA (5.0 µg/kg), 6:2 FTS (2.4 µg/kg), PFDS (0.15–0.17 µg/kg) and PFBS (0.13 µg/kg) being found in two or fewer samples (Herzke et al. 2008b).

Recently, also landfill leachates were analysed in North Rhine-Westphalia. The concentrations were 70–190 ng/L for PFOS and 1100–5100 ng/L for PFOA (LANUV, personal communication, 2008).

It can be concluded that the concentrations in landfill leachates vary by several orders of magnitude. There are not enough data to draw general conclusions on different parameters such as the geographical distribution, except for the dumping of sewage sludge from fluorochemical industry. In consequence of the technical ordinance on waste ("Technische Verordnung über Abfälle", TVA) (Schweizerischer Bundesrat 1990) and the restrictions on the disposal of combustible waste including sewage sludge on landfills, the proportion of PFOS and PFOA to be dumped on landfills has decreased in recent years. However, concentrations in leachates of landfills that have been closed for ten of fifteen years are not markedly lower than leachates of operating landfills. Therefore, the concentrations in leachates of Swiss landfills were assumed to be most likely comparable with medium or low values measured in the USA and Europe.

Releases to leachates

There are currently no studies determining the mass balance of PFCs in landfills. There are two possible methods for the estimation of the transfer coefficients to sewerage and the emission factor to the hydrosphere:

> Estimating the fraction released annually based on the mobility of the substances derived from physicochemical properties and measurements
> Indirectly by dividing the substance flows (i.e. leachate volume multiplied with the concentrations) by the amount of PFOS and PFOA, respectively, stored in landfills

First method

In the first method, the fraction of PFOS and PFOA released from landfills had to be estimated based on known data and analogy observations. Studies determining the extractable PFOA in water, sweat simulant, saliva simulant and methanol from textile and carpet samples revealed that a total extraction is achieved with all solvents (Mawn et al.2005). However, in landfills a certain fraction of the substances may be bound to or incorporated in materials, so that it is not being leached out. As mentioned above PFOS and PFOA are both present in the ionic form in landfills. Solid/solution distribution coefficients, $K_d$, were calculated from adsorption experiments with various solid materials. $K_d$ values for PFOS ranged from 2.8 to 8.9 L/kg in one study and averaged to 6.15 L/kg in another, which is lower than for many persistent organic pollutants of similar molecular weight, indicating a greater tendency to stay in the aqueous phase (Johnson et al. 2007). PFOA is more mobile in soil than PFOS and its averaged $K_d$ was determined as 1.3 kg/L. PFOA was found to elutriate easily from a highly contaminated agricultural crop land in Brilon-Scharfenberg (Bergmann et al. 2008). PFOS and PFOA were also found to be important groundwater contaminants, to be easily transported in surface and ground water and to show a low sorption rate (Hoehn et al. 2007). A transport from soils into plants was shown for PFOS and PFOA (Stahl et al. 2007). In consideration of the fact that PFOS and PFOA are still leaching from landfills that were closed in 1988 and 1993 (see Tab. 79 in the appendix), the annual loss is probably not higher than 30 %. However, the possible contribution from precursors contributes additionally to the uncertainty here. Based on the available knowledge, the fraction of PFOS annually released from landfills was estimated to be 10 % (range 5–20 %), whereas the estimate for PFOA was 20 % (range 10–30 %), because of its higher mobility. The percentage of landfill leachates caught and introduced to sewer system was estimated to be 90 % for sanitary landfills (von Arx 2006). The percentage of leachates getting into surface or groundwater is markedly larger for other types of landfills, but no data were available. As most of the materials containing PFCs (sewage sludge, ash, consumer goods) were probably dumped in sanitary landfills, the overall percentage was estimated to be 70 %. The emission factors and transfer coefficients resulting from these estimates are given in Tab. 73.

Second method

In the second method, the volume estimate was done as follows: The area of sanitary landfills was estimated as 300 ha, whereas the area of other types of landfills such as old domestic refuse dumps and multifills was estimated as 5000–10 000 ha. The leachate flow rate was estimated as 0.13 L/s/ha for sanitary landfills, while the estimates for the other types range between 0.04 L/s/ha and 0.16 L/s/ha (von Arx 2006). The annual leachate volume thus is approximately 1.2E + 09 L/year and 6.3E+09–50E +09 L/year, respectively. The total corresponds to 0.3–2 % of the wastewater volume produced in Switzerland (Schluep et al. 2006). If assuming that the concentrations in leachate found in the USA and other European countries (except the hot spots associated with the fluorochemical industry) would also apply to Switzerland, a rough estimate of the PFOS and PFOA substance flow can be done: Taking into account concentrations of 1–400 ng/L and 1–5000 ng/L, the substance flows (total of flows to hydrosphere and sewerage) would be < 1–20 kg/year PFOS and < 1–250 kg/year PFOA, respectively. The best guess substance flows of PFOS determined in the substance flow analysis (24 kg/year and 56 kg/year, see section 3.1.1) moderately exceed the range estimated with the second method based on the few available data from abroad (excluding hot spots), while they correspond well with the estimate for PFOA (10 kg/year). The transfer coefficients and emission factors estimated with the first method were not changed. However, the maximum of the worst case substance flows were set as five times the upper boundary of the estimate based on the second method.

**Tab. 73 > Emission factors and transfer coefficients at the process *landfill***

Emission factors and transfer coefficients derived for the process landfill

| | PFOS | | PFOA | |
|---|---|---|---|---|
| | Best guess | Range | Best guess | Range |
| TC sewerage | 0.07/year | 0.035/year – 0.14/year | 0.14/year | 0.07/year – 0.21/year |
| EF atmosphere (unload) | 1.0E−06 | 2.0E−07 – 5.0E−06 | 1.0E−06 | 2.0E−07 – 5.0E−06 |
| EF atmosphere (diffuse) | 1.0E−06/year | 1.0E−07/year – 1.0E−05/year | 1.0E−06/year | 1.0E−07/year – 1.0E−05/year |
| EF hydrosphere | 0.03/year | 0.015/year – 0.06/year | 0.06/year | 0.03/year – 0.09/year |

# 3 > Results and discussion

## 3.1 Substance flows in the anthroposphere and emissions to the environment

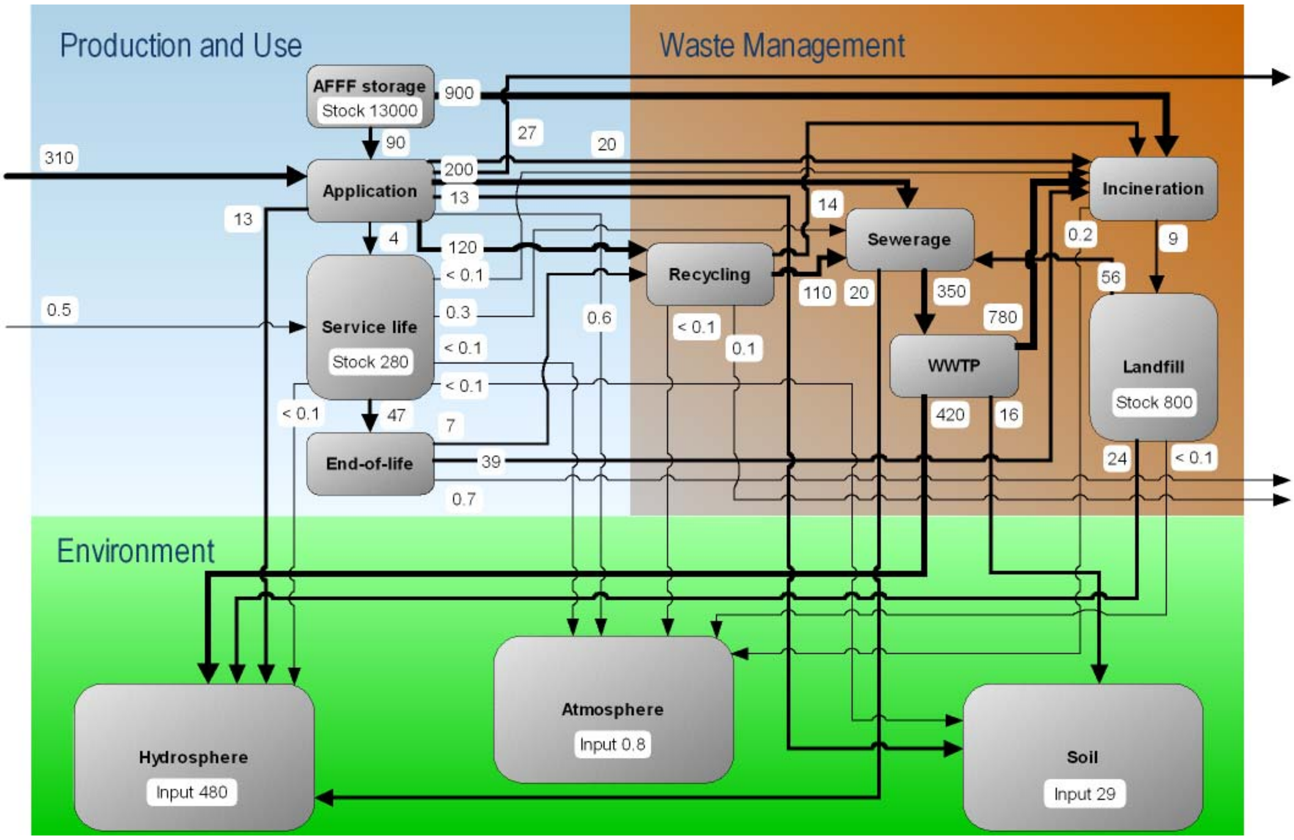
### 3.1.1 PFOS

The import of PFOS to the process *application* was estimated as 310 kg (uncertainty range of 200–550 kg) in 2007 (Fig. 15) with metal plating contributing 300 kg. The stock of PFOS in stored AFFF was estimated as 12 000–15 000 kg. Approximately 900 kg/year is disposed of in incineration plants in AFFF having reached its shelf-life. 90 kg/year are used (flow to process *application*) and then enters wastewater or is emitted to the hydrosphere and soil. In the process *application* approximately 13 kg/year (4–75 kg/year) were estimated to be emitted to each hydrosphere and soil, while the simulated atmospheric emissions are below 1 kg/year. 200 kg/year were released to wastewater, whereas approximately 120 kg/year entered the process *recycling* (physico-chemical treatment of process baths). The stock in the process *service life* was modelled as 280 kg (80–2000 kg), which is approximately fifty times lower than the stock of PFOS in stored AFFF. By far, the largest proportion of this stock originates from the historical uses of PFOS before 2002. Losses during service life account for less than 1 kg/year. At end-of-life, most PFOS is incinerated, whereas smaller proportions enter recycling processes or are exported. Almost the total of PFOS entering recycling processes was simulated to be either released to wastewater or finally disposed of in incineration plants. Incineration plants emitted a simulated amount of 0.2 kg/year (up to 5 kg/year) to the atmosphere, while approximately 9 kg/year contained in ash were dumped in landfills. The stock in landfills was modelled as approximately 800 kg, most of which originates from the historical use of POSF-based products. The simulated substance flows in leachates to the sewerage system and the hydrosphere were 56 kg/year and 24 kg/year, respectively. The substance flows from landfills might be somewhat too high compared to an estimate based on concentrations in leachates available for other countries (see section 2.5.3.9). Emissions from the sewerage system to the hydrosphere caused by sewage exfiltration or combined sewer overflows were simulated as 20 kg/year (2–180 kg/year). 350 kg/year (60–1200 kg/year) get into WWTPs, where the PFOS substance flow was shown to increase due to the degradation of precursors (see section 2.5.3.7 on page 95). The modelled emissions to the hydrosphere are 420 kg/year (50–2700 kg/year). It has to be emphasised that the given ranges of substance flows have to be regarded as spans from the best best case to the worst worst case, as they result from multiplying best case consumption with best case transfer coefficient(s) and/or emission factor(s). Approximately 16 kg/year and 780 kg/year of PFOS in sewage sludge get to soil and incineration plants, respectively. The uncertainty is particularly high for these two substance flows because the transfer coefficient of PFOS in WWTP influent to sewage sludge ranged over two orders of magnitude among the different studies conducted.

The largest proportion of the substance flows to waste management end in incineration plants. The process *incineration* with an input of approximately 2 t/year and a simulated output of 10 kg/year is an important sink for the substance flows of PFOS. The wastewater pathway is responsible for more than 90 % of the emissions to the hydrosphere even though only approximately 17 % of the flows to waste management get into the sewer system. Overall, approximately 94 % of the emissions to the environment are to the hydrosphere and 6 % to soil, while atmospheric emissions contribute about 0.2 %.

**Fig. 15 > Substance flows and stocks of PFOS in 2007**

*Substance flows and stocks of PFOS in the anthroposphere.*
*Numbers in kg and rounded to two significant digits*[3] *or one if below 10 kg.*



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[3] The numbers are rounded to two significant digits only in order to allow retracing allocation to the different substance flows. In respect of the uncertainty, only one significant digit should be given for all substance flows.

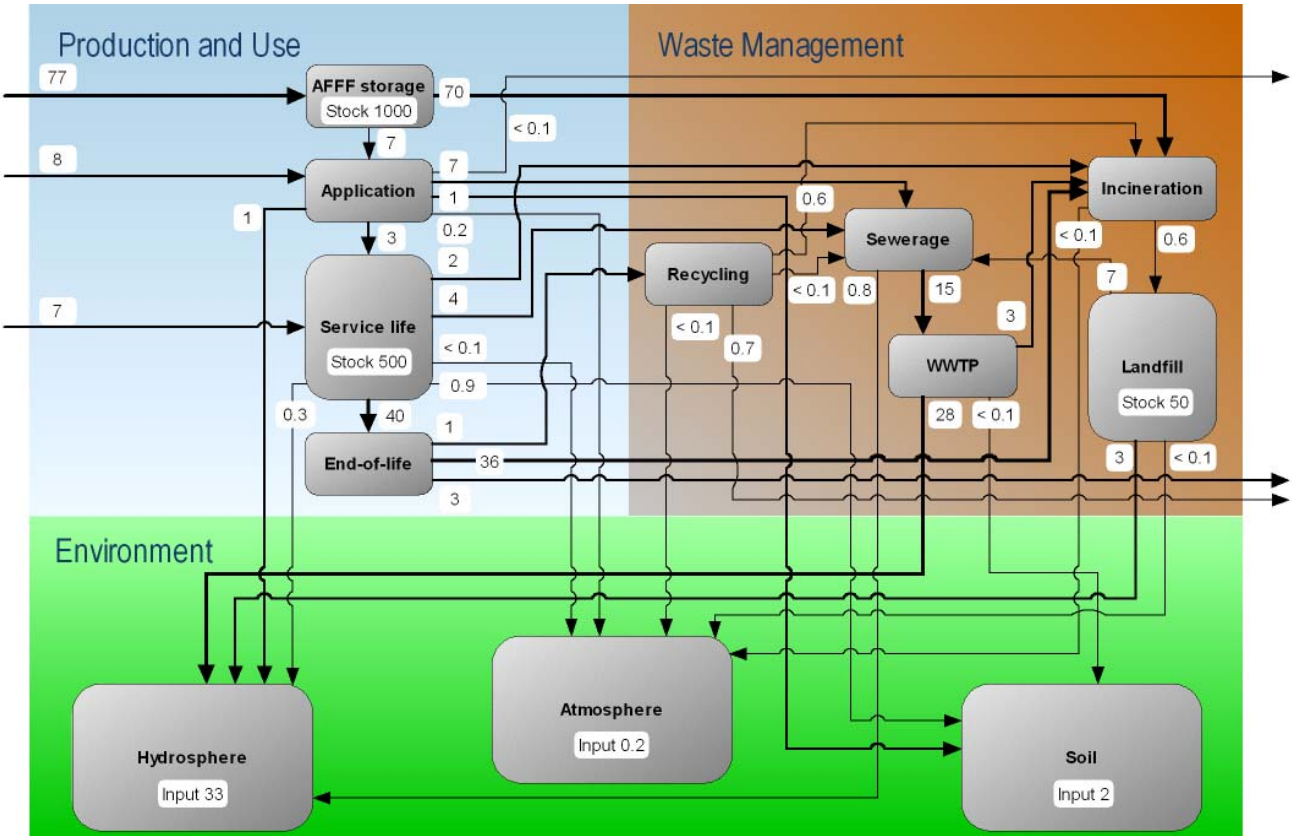
### 3.1.2 PFOA

The estimated imports of PFOA in products to the processes *application* and *service life* (contained in finished goods) accounted for approximately 8 kg and 7 kg in 2007 (maximum estimates are 120 kg and 40 kg, respectively). The imports of PFOA in AFFF were estimated to be 77 kg/year, i.e. compensating the losses from the process *AFFF storage*. The releases from the application (including the use of stored AFFF) to sewerage and incineration were simulated as 70 kg/year and 7 kg/year (Fig. 16). Simulated emissions to the atmosphere were 0.2 kg/year (< 0.1–2 kg/year) and 1 kg/year (< 0.1–15 kg/year) to each the hydrosphere and soil. Approximately 3 kg/year add to the stock in the process *service life*, being 500 kg (14–2300 kg) and originating mostly from the period where the residual levels of PFOA were markedly higher than at present. Releases to sewerage and incineration during service life were modelled as 4 kg/year (0.1–33 kg/year) and 2 kg/year (< 0.1–22 kg/year), respectively. Simulated emissions to the atmosphere, hydrosphere and soil were < 0.1 kg/year, 0.3 kg/year (< 0.1–3 kg/year) and 0.9 kg/year (< 0.1–10 kg/year), respectively. Approximately 40 kg/year (2–180 kg/year) were disposed of at end-of-life, mostly to incineration plants. Simulated emission to the atmosphere and releases to wastewater from recycling processes are both < 0.1 kg/year, whereas approximately 0.6 kg/year and 0.7 kg/year are incinerated and exported, respectively. Incineration plants emitted a simulated amount of < 0.1 kg/year (up to 2 kg/year) into the atmosphere, while approximately 0.6 kg/year was dumped in landfills. The stock in landfills was modelled to be 50 kg (3–900 kg). Whereas emissions to the atmosphere were negligible, emissions to the hydrosphere and releases to the sewerage system were simulated to be 3 kg/year and 7 kg/year, respectively. The modelled total input from all processes to the sewerage system is 16 kg/year (0.4–290 kg/year). Emissions from the sewerage system to the hydrosphere caused by sewage exfiltration or combined sewer overflows were simulated as 0.8 kg/year (< 0.1–40 kg/year), whereas 15 kg/year (0.3–280 kg/ year) get into WWTPs. As it has been shown in section 2.5.3.7 (page 95) the substance flows of PFOA can increase in WWTPs due to the degradation of precursors. However, the extent of the increase as well as the partitioning to sewage sludge (large range among the different studies, see Tab. 78 in the appendix) is subject of a considerable uncertainty. The simulated emissions to the hydrosphere are 28 kg/year (0.3–1700 kg/year), while approximately < 0.1 kg/year and 3 kg/year of PFOA in sewage sludge get to soil and incineration plants, respectively.

Similar to PFOS, the largest percentage of the PFOA substance flows to waste management finally get to incineration plants. Having a simulated input of > 100 kg/year and an output of < 1 kg/year, incineration plants are an important sink for the substance flows of PFOA. Approximately 12 % of the substance flows to waste management get into the sewer system, but the wastewater pathway is responsibly for about 87 % of the emissions to the hydrosphere. Overall, approximately 93 % of the emissions to the environment are to the hydrosphere and 6 % to soil, while atmospheric emissions contribute by 0.7 %.

**Fig. 16 > Substance flows and stocks of PFOA in 2007**

*Substance flows and stocks of PFOA in the anthroposphere.*
*Numbers in kg and rounded to two significant digits*[4] *or one if below 10 kg.*



## 3.2 Emissions to the environment from different application areas

### 3.2.1 PFOS

Metal plating and fire-fighting foams (AFFF) were simulated to contribute to approximately 71 % and 25 %, respectively, to the emissions of PFOS (excluding the degradation of precursors in the environment), whereas modelled emissions from photography (2 %), photolithography and semiconductors (1 %), textile protection (0.4 %), as well as paints and lacquers (0.2 %) contributed to smaller extents (Fig. 17). The other application areas were simulated to contribute to 0.1 % or less to the emissions. The shares of the individual application areas for the simulated emissions to the hydrosphere (representing 94 % of the emissions to the environment) are similar to the ones for the emis-

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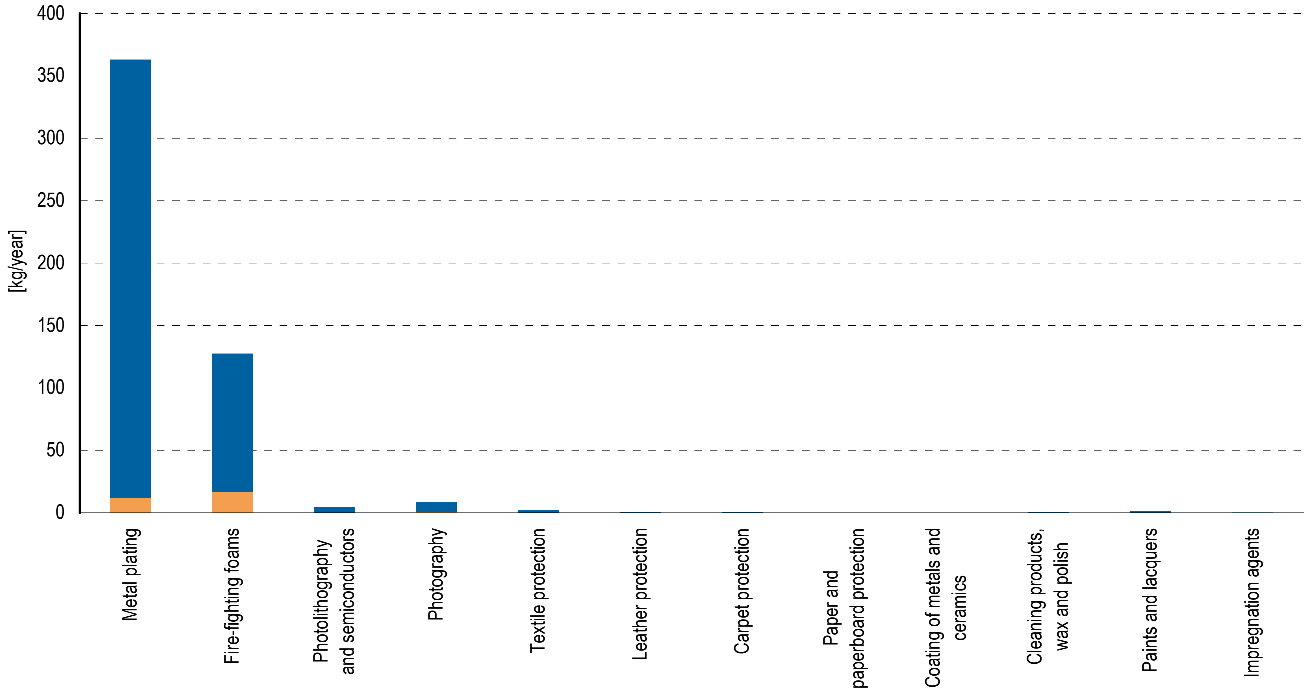
[4] The numbers are rounded to two significant digits only in order to allow retracing allocation to the different substance flows. In respect of the uncertainty, only one significant digit should be given for all substance flows.

sions to the environment. For soil, AFFF alone makes up approximately 57 % of the emissions that are caused by this kind of application. Atmospheric emissions only contribute to 0.2 % to the emissions to the environment and are thus not visible in Fig. 17. It has to be noted that in the model, the increase in the substance flow in the process *WWTP* due to the degradation of precursors was accounted to the individual application areas according to the share of the substance flow of PFOS to this process. However, the contribution of the individual application areas to precursors being degraded to PFOS in WWTPs might in fact differ markedly from their share of PFOS released to wastewater. As a consequence, the emission shares of application areas releasing primarily PFOS to wastewater, but only low amounts of precursors, are overestimated to a certain extent.

Emissions from AFFF do most likely exhibit a large temporal and spatial variability, depending on the occurrence of mayor fires. Emissions from other application areas, especially those with a high proportion of the release of PFOS to wastewater in industrial processes and a limited number of locations (particularly metal plating), do primarily show a spatial variability.

**Fig. 17 > Simulated emissions of PFOS in 2007**

*Emissions of PFOS to the atmosphere (bright blue, almost invisible), hydrosphere (blue) and soil (brown) from the individual application areas.*



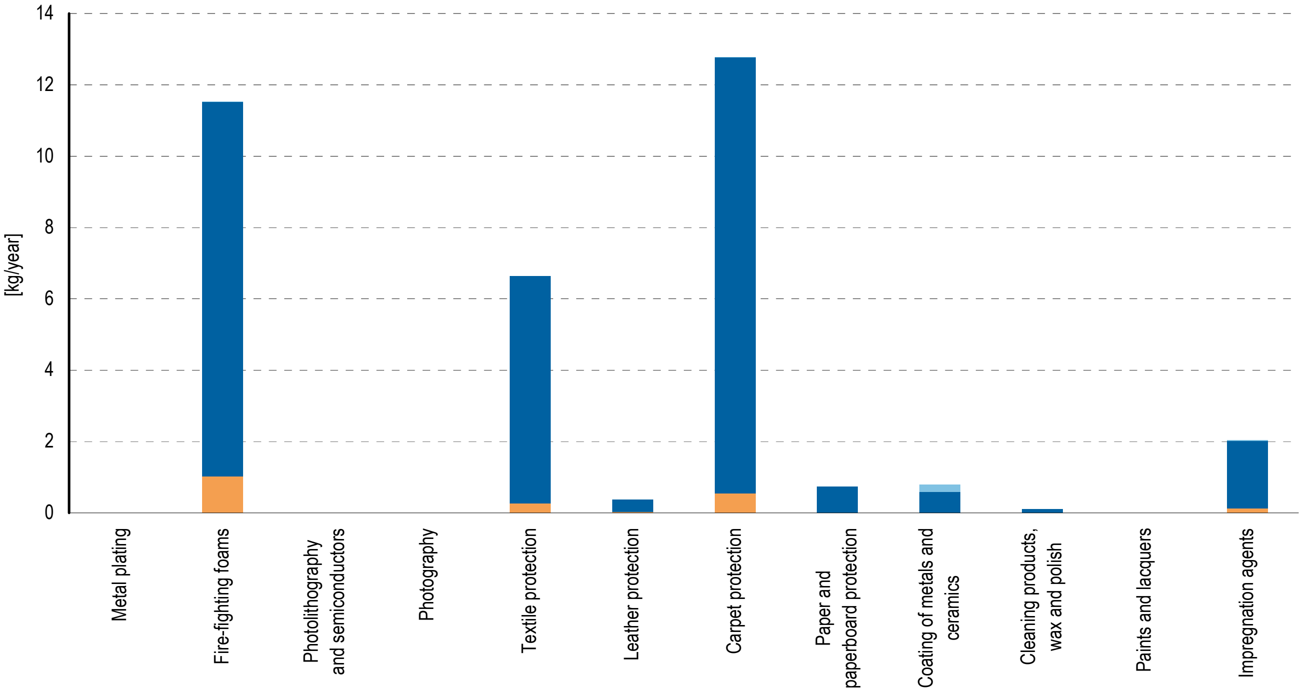
## 3.2.2 PFOA

In contrast to PFOS, the simulated emissions of PFOA to the environment are composed by more application areas contributing to a substantial extent. According to the modelling results, carpet protection emitted approximately 37 %, AFFF 33 % and textile protection 19 %. Impregnation agents (6 %), coating of metals and ceramics (2 %), paper and paperboard protection (2 %), leather protection (1 %) as well as cleaning products, wax and polish (0.3 %) contributed to a lower extent to the emissions to the environment as shown in Fig. 18. Analogous to PFOS, the shares of the individual application areas of the emissions to the hydrosphere are similar to the ones to the environment. However, AFFF was simulated to be responsible for approximately half of the emissions to soil, whereas also carpet protection (27 %), textile protection (13 %) and impregnation agents (7 %) contribute to significant extents. As for PFOS, it has to be emphasised that in the model there is the possibility that the increase in the substance flow in the process *WWTP* due to the degradation of precursors was not attributed appropriately to the individual application areas.

In contrast to PFOS, emissions of PFOA are considered to be more evenly composed by different application areas as well as from processes contributing significantly (e.g. service life or landfills) and are thus likely to be less variable in both time and space.

**Fig. 18 > Simulated emissions of PFOA in 2007**

*Emissions of PFOA to the atmosphere (bright blue, almost invisible), hydrosphere (blue) and soil (brown) from the individual application areas.*



## 3.2.3 Contribution of precursors

### 3.2.3.1 PFOS

Atmosphere

The use and emissions of the four selected precursors were roughly estimated. As no full substance flow analyses were performed for the substances, the atmospheric emissions were derived from best guess estimates on the use and reasonable worst case estimates for the emission factors. A use of *N*-MeFOSE and *N*-EtFOSE for the year 2007 was only considered for imported textiles and clothing. The respective estimated amounts were 0.7 kg (0.07–7 kg) and 0.1 kg (0.01–1.5 kg), respectively. As the emissions based on these numbers would be small, the simulated historical emissions are shown in Fig. 19. Precursors contained in historically used products can still contribute to the occurrence of PFOS in the environment, either by (lagged) emissions from goods during their service life, landfill leachates emitted to the hydrosphere or released to wastewater or the degradation of historical emissions of precursors in the environment. The simulated historical atmospheric emissions of *N*-MeFOSE are approximately 80 kg/year, of which textile and leather protection made up the largest proportion, followed by carpet protection as well as paper and cardboard protection. It is possible that also impregnation agents contained relevant amounts of *N*-MeFOSE. There were however not enough data to make accurate estimates. Simulated atmospheric emissions of *N*-EtFOSE are approximately one order of magnitude lower than for *N*-MeFOSE, with leather protection as the most important application area.

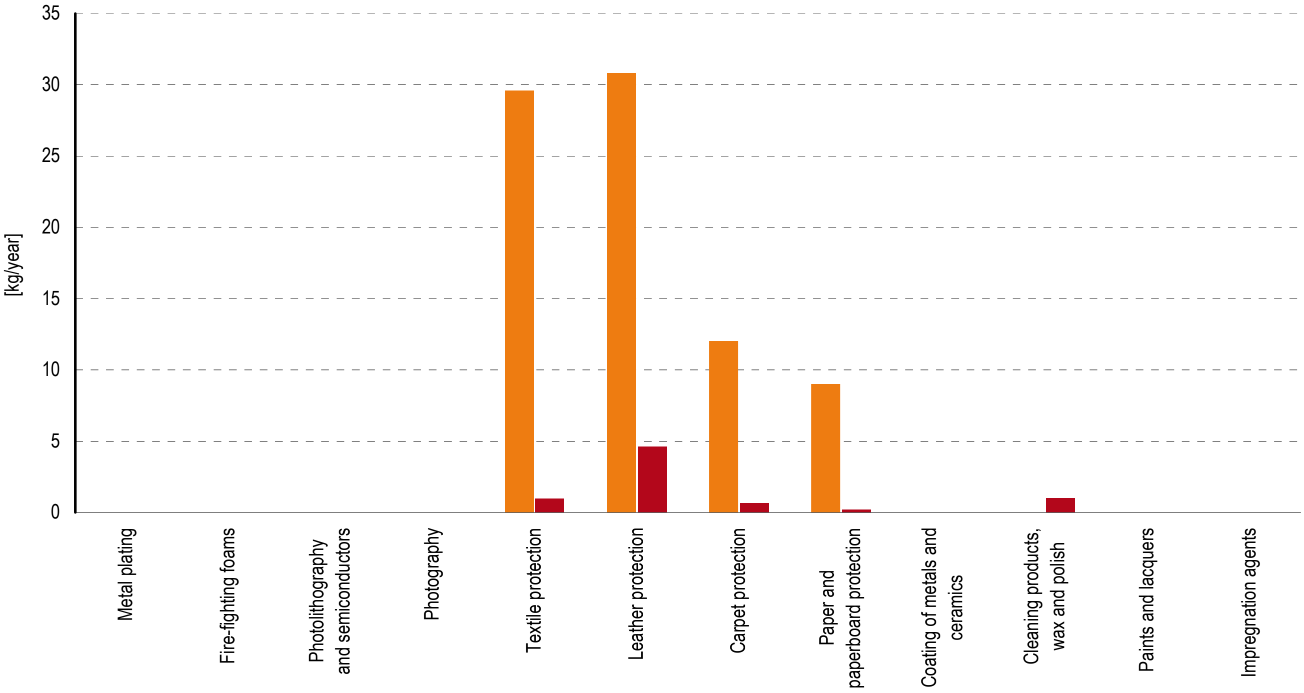
A degradation of *N*-MeFOSE, *N*-EtFOSE or *N*-MeFOSA and *N*-EtFOSA in the atmosphere to PFOS has not been measured yet. However, the degradation of shorter homologues (C4) to PBFS was investigated and it was assumed that the results were also valid for the C8-homologues investigated in this study (i.e. *N*-MeFOSE and *N*-EtFOSE). The yield of PFBS was tenfold lower than of PFCAs in one study (D'eon et al. 2006), whereas in the other, PFBS was not detected above the level of the blank in any sample (Martin et al. 2006). Therefore, a degradation yield of 0.01 from these precursors to PFOS was considered. The contribution of *N*-MeFOSE and *N*-EtFOSE to the environmental occurrence by their degradation in the atmosphere was thus estimated to be less than 1 kg/year. A minor contribution of the aerobic transformation after deposition is possible, but the wastewater pathway seems to be of most importance (see below).

Wastewater

The contribution of precursors to the increased substance flows of PFOS in WWTPs has already been taken into account by the transfer coefficients and emission factors applied for this process (see section 2.5.3.7 on page 95). A yield of PFOS from the aerobic transformation of *N*-EtFOSE in activated sludge over four to five intermediate substances was experimentally determined as 0.06–0.1 after ten days, while the model predicted a yield of 0.12. The model also predicted that air stripping removes 76 % of *N*-EtFOSE in WWTPs (Rhoads et al. 2008). The historical releases of *N*-MeFOSE and *N*-EtFOSE to wastewater were estimated to be 25 kg/year (3–80 kg/year) and 3 kg/year (0.4–13 kg/year), respectively. If we only consider the use in 2007, the releases would be < 1 kg/year, but releases are partially time-delayed as mentioned above. Nonetheless, the simulated substance flow increase in WWTPs by approximately 900 kg/year cannot be fully explained by the two selected precursors. Other precursors such as the potassium salt of a glycine derivative of *N*-EtFOSA (CAS number 2991-51-7, see sections 2.5.1.10 and 2.5.1.15) might contribute to the increasing PFOS substance flows to a considerable extent, too. However, as there is a high uncertainty in the behaviour of PFOS in WWTPs, no detailed conclusions can be made.

**Fig. 19 > Simulated reasonable worst case atmospheric emissions of *N*-MeFOSE and *N*-EtFOSE before 2002**

*Historical emissions of N-MeFOSE (orange bars) and N-EtFOSE (red bars) from the individual application areas to the atmosphere simulated based on best guess use figures and reasonable worst case emission factors.*



### 3.2.3.2 PFOA

Atmosphere

The atmospheric emissions of the two fluorotelomer alcohols (derived from best guess estimates on the use and reasonable worst case estimates for the emission factors) were simulated for 2007. As it was assumed that the use of these substances in products remained constant over the last years, the simulated emission figures do also apply for the past. The simulated emissions are considerably higher than for the two FOSE derivatives. The model results for the emissions of 8:2 FTOH and 10:2 FTOH are 1300 kg/year (200–9000 kg/year) and 500 kg/year (100–4000 kg/year), respectively. As shown in Fig. 20, the application areas contributing principally to these emissions are impregnation agents and textile protection.

A yield of PFOA from the atmospheric degradation of 8:2 FTOH of 0.05 (0.01–0.1) as modelled by Wallington et al. (2006) and used by Schenker et al. (2008) was considered. After two unzipping cycles, 10:2 FTOH degrades into PFO, while 8:2 FTOH degrades into PFOA without perfluorinated chain unzipping. It was assumed in a first order approximation that the yield ratio of PFOA to PFDA (chain length: 10) from the degradation of 10:2 FTOH was similar to the yield ratio of PFHxA (chain length: 6) to PFOA from the degradation of 8:2 FTOH. The latter was experimentally determined as 0.16 (Ellis et al. 2004, Yarwood et al. 2006). Hence, the degradation yield of PFOA from the atmospheric degradation of 10:2 FTOH was assumed as 0.01 (0.001–0.02). Applying these yields to the simulated emissions, the derived transformation rates are 65 kg/year and 5 kg/year PFOA from 8:2 FTOH and 10:2 FTOH. The combined uncertainty range of the sum however is large: 2–980 kg/year. As shown in section 1.3.2 on page 16, also FOSE derivatives can degrade to PFOA in the atmosphere. Schenker et al. (2008) have estimated the degradation yield as 0.05 as for 8:2 FTOH (see above). Considering the historical use, the best guess transformation rate would be 1–2 kg/year, but as the emissions have been decreased in recent years, the yield of the transformation to PFOA is probably lower than 1 kg/year.

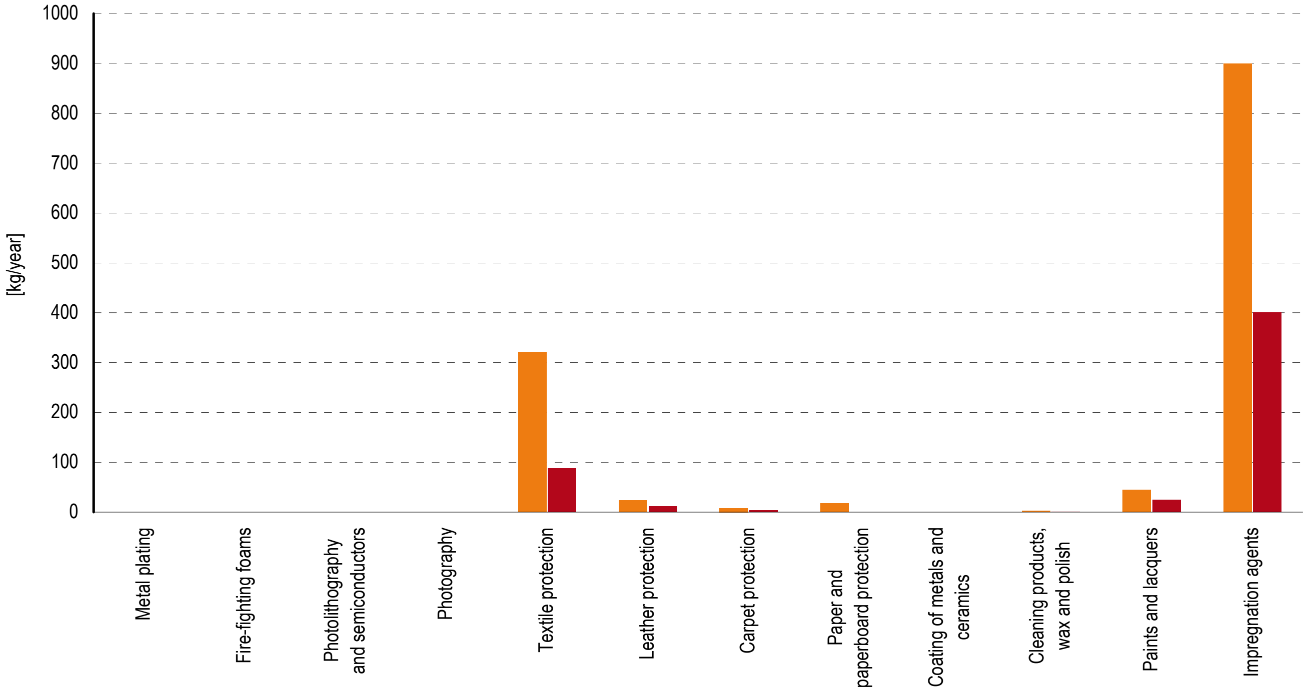
Wastewater

The contribution of precursors to the substance flow increase of PFOA in WWTPs has already been taken into account by the transfer coefficients and emission factors, as it was mentioned above. The releases of 8:2 FTOH and 10:2 FTOH to wastewater simulated in a simplified substance flow analysis are given in order to compare them with the substance flow increase of PFOA in WWTPs. For 8:2 FTOH, the model result is 100 kg/year (30–700 kg/year), while it is 30 kg/year (10–50 kg/year) for 10:2 FTOH.

The yield from aerobic biodegradation of FTOH mixtures and 8:2 FTOH was experimentally determined as 0.06–0.07 and 0.03, respectively (Lange 2002, Dinglasan et al. 2004). The increase in the substance flows of PFOA in WWTP was simulated to be approximately 15 kg/year. Hence, the input of 8:2 FTOH and 10:2 FTOH to wastewater might contribute to it significantly.

**Fig. 20 > Simulated reasonable worst case atmospheric emissions of 8:2 FTOH and 10:2 FTOH in 2007**

*Emissions of 8:2 FTOH (orange bars) and 10:2 FTOH (red bars) from the individual application areas to the atmosphere in 2007 simulated based on best guess use figures and reasonable worst case emission factors.*



## 3.3 Data quality and uncertainty

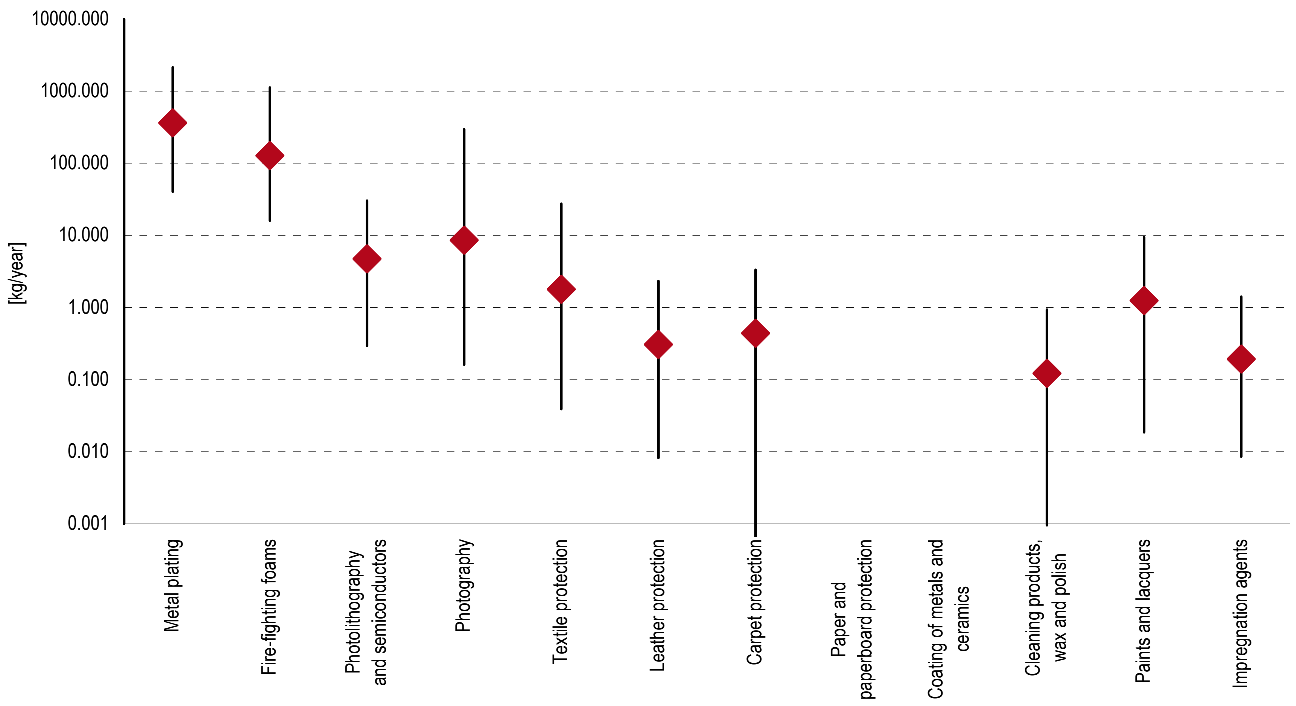
The data input to the substance flow analysis is associated with a considerable uncertainty, with its extent dependent on the parameters. The form of the uncertainty distribution and also the probability that a specific parameter is in the estimated range are unknown. Hence, the uncertainty distribution of e.g. emissions to the environment cannot be calculated based on regular error propagation. Therefore, the uncertainly ranges presented in Fig. 21 and Fig. 22 as well as in Tab. 74 and Tab. 75 show the span from the best best case (multiplication of minimum estimates for use and transfer coefficients and emission factors) to the worst worst case (multiplication of maximum estimates). These ranges are as large as two to three orders of magnitude, but the extremes are considered to be unlikely to be realistic.

## 3.3.1 PFOS

Consideration of the uncertainty ranges of the emissions from different application areas reveals that metal plating and AFFF contribute to the emissions of PFOS even in the best best case to a considerable extent (Fig. 21). Emissions of more than 10 kg/year were also simulated to be possible from the application areas *photolithography and semiconductors*, *photography* as well as *textile protection*. Leather protection, carpet protection, paints and lacquers as well as impregnation agents may contribute to more than 1 kg/year, while emissions above this level are excluded based on the model results for the remaining application areas. Paper and paperboard protection may however contribute to the occurrence of PFOS in the environment by the degradation of precursors (see section 3.2.3).

**Fig. 21 > Uncertainty of the PFOS emissions from individual application areas to the environment**

*The figure shows the range of emissions from the individual application areas. The rhombuses mark the emissions derived from best guess estimates. The lines represent the range of emissions derived from minimum and maximum estimations of the use as well as transfer coefficients and emission factors.*



In order to distinguish which parameters, i.e. their uncertainty, are responsible for the majority of the uncertainty range of the emissions to atmosphere, hydrosphere and soil, the range was omitted for three sets of parameters: consumption and import as well as transfer coefficients and emission factors in the processes *application* (including the proportion of the AFFF storage used), *WWTP* and *incineration* (Tab. 74). For the atmospheric emission, the emission factor in the process *application* is of most importance for the reduction of the maximum emissions, followed by the transfer coefficient describing the fraction of the PFOS input to WWTPs that is finally incinerated with sewage sludge. However, the atmospheric emission factor in incineration plants has a lower impact. Omitting the uncertainty range of the parameters in the process *application* increases the minimum emission to the hydrosphere by a factor of three and lowers the maximum emission by almost half. The transfer coefficients to wastewater for both metal plating and AFFF were identified to be responsible for most of the uncertainty in this process. The parameters in the process *WWTP* as well as consumption and import reduce the maximum emission to the hydrosphere by approximately one third each, whereas the uncertainly in the parameters in the process *incineration* is of no relevance here. In the case of emissions to soil, the large range between minimum and maximum model results is mainly caused by the parameters in the processes *WWTP* and *application*. The former is caused by the large uncertainty of how much of the PFOS enters sewage sludge (including the contribution of precursors) and finally to soil, whereas for the latter, the emission factor of AFFF to soil is the main reason for triggering the extent of uncertainty.

**Tab. 74 > Uncertainty of PFOS emissions and influence of different parameter sets**

*Uncertainty of emissions to the atmosphere, hydrosphere and soil. The influence of different parameters is shown by omitting any range in a) the consumption and import, b) the transfer coefficients and emission factors in the process application, c) the transfer coefficients and emission factors in WWTPs and d) the transfer coefficients and emission factors in incineration plants.*

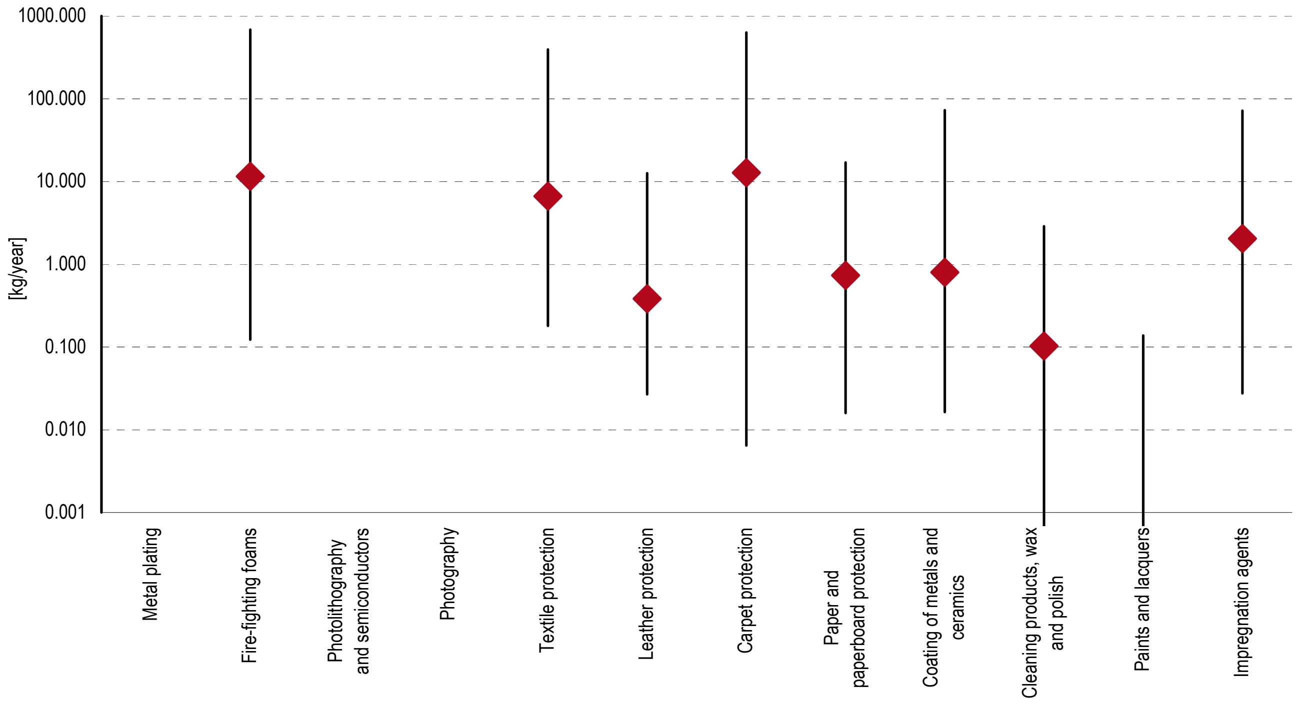
| Model results | Emissions to atmosphere [kg/year] | | | Emissions to hydrosphere [kg/year] | | | Emissions to soil [kg/year] | | |
|---|---|---|---|---|---|---|---|---|---|
| | Best guess | Min | Max | Best guess | Min | Max | Best guess | Min | Max |
| | 0.8 | 0.11 | 10.6 | 480 | 50 | 2700 | 29 | 3.6 | 790 |
| Omitting range in | | | | | | | | | |
| Consumption and import parameters | 0.8 | 0.16 | 6.6 | 480 | 80 | 1800 | 29 | 3.9 | 530 |
| TC/EF application parameters | 0.8 | 0.41 | 4.2 | 480 | 170 | 1500 | 29 | 12.0 | 410 |
| TC/EF WWTP parameters | 0.8 | 0.11 | 6.0 | 480 | 80 | 1700 | 29 | 6.4 | 130 |
| TC/EF incineration parameters | 0.8 | 0.17 | 7.9 | 480 | 50 | 2700 | 29 | 3.6 | 790 |

### 3.3.2 PFOA

The uncertainty ranges of the PFOA emissions from different application areas are generally larger than for PFOS (Fig. 22). However, the ranges represent best best and worst worst cases. It was considered that emissions are unlikely to be as low or as high as the extremes. Based on the model results, emissions of more than 100 kg/year cannot be excluded for AFFF, textile protection and carpet protection. For the application areas *leather protection*, *paper and paperboard protection*, *coating of metals and ceramics* as well as *impregnation agents*, emissions above 10 kg/year are possible, whereas simulated emissions from the remaining application areas are below this level or no use was considered at all. The very wide range for emissions from carpet protection is mainly caused by the large range of the consumption and in the imports.

**Fig. 22 > Uncertainty of the PFOA emissions from individual application areas to the environment**

*The figure shows the range of emissions from the individual application areas. The rhombuses mark the emissions derived from best guess estimates. The lines represent the range of emissions derived from minimum and maximum estimated of the use as well as transfer coefficients and emission factors.*



In contrast to PFOS, the parameters responsible for the majority of the simulated uncertainty range of PFOA emission are the consumption in products used in Switzerland and the import in goods (Tab. 75). Only for the emissions to the hydrosphere, where the contribution of precursors results in an increased substance flow of PFOA, the parameters characterising the process *WWTP* are of equal importance. On the contrary, the uncertainty of the parameters in the processes *application* and *incineration* were determined to have a much lower effect on the uncertainty range of the emissions to the hydrosphere. For soil, the emission factor in the process *application* (mostly AFFF) contributes the second most to the uncertainty in the emissions after consumption and import.

**Tab. 75 > Uncertainty of PFOA emissions and influence of different parameter sets**

*Uncertainty of emissions to the atmosphere, hydrosphere and soil. The influence of different parameters is shown by omitting any range in a) the consumption and import, b) the transfer coefficients and emission factors in the process application, c) the transfer coefficients and emission factors in WWTPs and d) the transfer coefficients and emission factors in incineration plants.*

| Model results | Emissions to atmosphere [kg/year] | | | Emissions to hydrosphere [kg/year] | | | Emissions to soil [kg/year] | | |
|---|---|---|---|---|---|---|---|---|---|
| | Best guess | Min | Max | Best guess | Min | Max | Best guess | Min | Max |
| | 0.2 | 0.01 | 4.0 | 33 | 0.3 | 1800 | 2 | 0.05 | 36 |
| Omitting range in | | | | | | | | | |
| Consumption and import parameters | 0.2 | 0.05 | 1.3 | 33 | 6.6 | 430 | 2 | 0.60 | 9 |
| TC/EF application parameters | 0.2 | 0.05 | 1.9 | 33 | 0.7 | 1300 | 2 | 0.10 | 20 |
| TC/EF WWTP parameters | 0.2 | 0.01 | 3.4 | 33 | 0.7 | 430 | 2 | 0.05 | 26 |
| TC/EF incineration parameters | 0.2 | 0.01 | 2.4 | 33 | 0.4 | 1300 | 2 | 0.05 | 33 |

## 3.4 Predicted environmental concentrations

The predicted environmental concentrations (PEC) were derived by entering the simulated emissions in a level III environmental fate model based on work by Mackay et al. (Mackay et al. 1996) by P. Dimmler, G. Geiseler, T. Hofstetter & M. Scheringer, adapted for Switzerland (see Tab. 6 on page 34). No import of substances in the atmosphere from abroad was considered. The physicochemical properties such as water solubility and vapour pressure used are given in Tab. 1 on page 17. The log $K_{OC}$ of PFOS and PFOA (anionic forms) considered were 2.57 and 2.06, respectively (Higgins & Luthy 2006). The PEC resulting from the simulated emissions in 2007 are summarised in Tab. 76:

**Tab. 76 > Predicted environmental concentrations**

*PEC of PFOS and PFOA without and with the contribution of the degradation of selected precursors based on the emissions in 2007. Concentrations are in ng/L and ng/g w.w. (rounded to one significant digit).*

| | Water | | | Sediment | | | Soil | | |
|---|---|---|---|---|---|---|---|---|---|
| | Best guess | Min | Max | Best guess | Min | Max | Best guess | Min | Max |
| PFOS | 9 | 1 | 60 | 0.07 | 0.007 | 0.5 | 0.009 | 0.001 | 0.3 |
| PFOS including precursors | 9 | 1 | 60 | 0.07 | 0.007 | 0.5 | 0.009 | 0.001 | 0.3 |
| PFOA | 0.7 | 0.01 | 30 | 0.002 | 0.00002 | 0.08 | 0.0003 | 0.00001 | 0.005 |
| PFOA including precursors | 2 | 0.04 | 50 | 0.005 | 0.0001 | 0.1 | 0.008 | 0.0002 | 0.1 |

Water

The PEC of PFOS in water is 9 ng/L (best best and worst worst case 1 ng/L and 60 ng/L). As shown in Tab. 76, the atmospheric degradation of the selected precursors does not significantly affect the PEC. Compared with the concentrations measured in the Glatt River (Tab. 77), the best guess is up to one order of magnitude lower. However, the watershed of the river is highly populated and the proportion of river water originating from WWTPs is high. This might explain the difference. The concentrations found in the rivers Aare and Rhine as well as in Lake Maggiore range between 2 ng/L and 8.6 ng/L, which are similar or slightly lower that the PEC. Overall, there is a reasonable agreement with the few measurements available for Switzerland.

The atmospheric degradation of the selected precursors was simulated to have a significant influence to the PEC of PFOA in water: The PEC of PFOA alone is 0.7 ng/L (0.01–30 ng/L), while it is 2 ng/L (0.04–50 ng/L) taking the selected precursors into consideration. The PEC corresponds well with the concentrations measured in Switzerland, bearing in mind that the Glatt River is affected by the dense population in its watershed. The PEC is also within the range of concentrations of PFOA in fourteen European rivers being between < 0.65 ng/L and 16.4 ng/L, with the exception of River Po, where 200 ng/L were analysed (McLachlan et al. 2007).

Sediment

The PEC of PFOS in sediment determined with the environmental model is 0.07 ng/g w.w. (0.007–0.5 ng/g w.w.). Note that referring to dry weight, the values would be approximately two to three times higher. The only sediment samples known from Switzerland (in fact from the Austrian part of Lake Constance) were taken in shallow water and in harbours. PFOS was detected below the limit of quantification (0.9 ng/g d.w.) in three out of five samples, while the remaining two samples as well as samples taken from mountain lakes in the Vorarlberg region were below limit of detection (0.5 ng/g d.w.). Globally, sediment from remote Arctic Lakes and from temperate regions such as the Great Lakes, US coastal areas and Japan have been analysed for concentrations of PFOS and PFOA. PFOS concentrations were reported as < 0.1–0.9 ng/g d.w. in the Danube River (Weiss et al. 2007), 0.2–4 ng/g d.w. in surface sediment from the US (Higgins et al. 2005), < 1.4–11 ng/g d.w. in river sediments of Kyoto (Senthilkumar et al. 2007), 0.09–0.14 ng/g d.w. in the sediments from the Ariake Sea (Japan) (Nakata et al. 2006). Considering the available data from Switzerland and abroad, the best guess PEC of PFOS in sediment seems to be somewhat lower than the available field data. However, the database of analyses is still week, especially for Switzerland. A significant fraction of the concentrations in sediments could also be remnants from historically higher emissions of PFOS. Additionally, there could be a significant contribution of precursors that were not accounted for this study.

The PEC of PFOA in sediment derived from the environmental fate model is 0.002 ng/g w.w. (0.0002–0.08 ng/g w.w.) and 0.005 ng/g w.w. (0.001–0.1 ng/g w.w.) without and with the contribution of the atmospheric degradation of the selected precursors, respectively. Concentrations measured in Lake Constance, mountain lakes in Vorarlberg and in Danube River were 0.2–0.8 ng/g d.w., < 0.1–0.3 ng/g d.w. and < 0.1–2.8 ng/g d.w., respectively (Weiss et al. 2007). Other analyses were in a similar range, e.g. < 0.1–0.6 ng/g d.w. in surface sediment from the US (Higgins et al. 2005), 1.3–3.9 ng/g d.w. in river sediments of Kyoto (Senthilkumar et al. 2007), 0.8–1.1 ng/g d.w. in the sediments from the Ariake Sea (Japan) (Nakata et al. 2006). Based on the few data available and appropriate for Switzerland, it seems that the PEC derived for the year 2007 is approximately one order of magnitude smaller than the reported concentrations. Note that some of the measurements were conducted before or shortly after the agreement of the industry to the PFOA stewardship program, which caused the use and the emissions of PFOA to decrease. Additionally, some locations sampled such as harbours are potential hot spots and the PEC of PFOA in sediment is sensitive for the $K_{OC}$ used. However, the difference could also be an indication of unaccounted contribution by precursor substances.

Soil

The PEC of PFOS in soil estimated with the environmental fate model is 0.009 ng/g w.w. (0.001–0.3 ng/g w.w.). The atmospheric degradation of the selected precursors contributes only small amounts to the occurrence of PFOS in soil. It was supposed that the concentrations have a high spatial variability because only certain soils are influenced by the application of AFFF nearby or sewage sludge as a fertiliser. The emissions to agricultural soil have been markedly higher in the past since the fraction of the sewage sludge used as a fertilizer decreased to almost zero in 2007 (see Fig. 14 on page 97). However, due to its persistence, PFOS from earlier immissions to soil can remain for a long time in soils, even though it has a high mobility for a POP substance that causes the leaching of a certain fraction. There are very few studies reporting the concentrations of PFOS and PFOA in soil. Soil was analysed for these substances after the use of highly contaminated fertiliser in Germany (see section 1.3.7 on page 29), but these levels (up to > 1000 ng/g d.w.) (Bergmann et al. 2008) are not representative for Switzerland.

For PFOA, the PEC in soil is only 0.0003 ng/g w.w. (0.00001–0.005 ng/g w.w.) if the contribution of the atmospheric degradation of the selected precursors is not included. The inclusion of this process raises the PEC to 0.008 ng/g w.w. (0.0002–0.1). The span from the best best to the worst worst case is especially large in this case. The statements made for PFOS above are also valid here: supposed high spatial variability of the concentration due to the application of AFFF and sewage sludge as a fertiliser, significantly higher historical immissions to soil with sewage sludge applied to crops, persistence in soils, no monitoring data appropriate for Switzerland. The contribution of precursor degradation other than from atmospheric degradation of the selected substances and the increase in the substance flow in WWTP might result in higher concentrations than simulated here. The aerobic biotransformation of 8:2 FTOH to PFOA as reported by Wang et al. (2005) or other precursor substances in sewage sludge after being applied to soil could have added to the environmental concentrations of PFOA. A main source of PFOA was predicted to be the degradation of fluorotelomer acrylate polymers present in the environment in the far future (van Zelm et al. 2008). This estimation is based on a biodegradation half-life of 1200–1700 years that was calculated from the rate of formation of PFOA in aerobic soils over two years to assess whether the FTOH side chains covalently bonded to the polymer backbone may be transformed. However, virtually all of the PFOA formed during the study was generated from the degradation of residuals initially present in the test substance (Russell et al. 2008).

**Tab. 77 > Measurements of PFOS and PFOA in the Swiss and neighboring countries' environment**

*Summary of environmental concentrations found in Switzerland. Concentrations for water samples given in ng/L, for sediment in ng/g d.w. and for fish in ng/g fresh weight. Note that the samples from Lago Maggiore and Lake Constance were taken in the Italian and Austrian part, respectively.*

| Location | Media | PFOS | PFOA | Reference |
|---|---|---:|---:|---|
| Glatt River (three sites) | River water | 27–93 | 3–12 | Huset et al. 2008 |
| Aare River, Koblenz | River water | 8 | 2 | Skutlarek et al. 2006a |
| Rhine River, Neuhausen | River water | 2 | < 2 | Skutlarek et al. 2006a |
| Rhine River, Stein | River water | 6 | < 2 | Skutlarek et al. 2006a |
| Lake Maggiore | Lake water | 7.2–8.6 | 1.8–2.9 | Loos et al. 2007 |
| Hard, Lange Erlen (Basel) | Groundwater | 8–17 | 2–4 | IWB 2007 |
| Lake Constance | Lake sediment | n.d. – < 0.5 | 0.2–0.8 | Weiss et al. 2007 |
| Lake Geneva | Fish, different species | 7–94 | < 0.2 | CIPEL 2008 |

# 4 > Conclusions

## 4.1 Stocks, flows and emissions

In 2007, approximately 0.3 t of PFOS were used in products in the application areas of *metal plating*, *photography* and *photolithography and semiconductors*. Additionally, there is a stock of 12–15 t in AFFF. In contrast, the stock of PFOS in the service life of goods mainly originating from historical uses of PFOS was simulated to be significantly smaller and accounting for 0.3 t. The most relevant (ultimate) emission source determined was WWTPs. This finding agrees with conclusions made in other studies. Other important emission sources identified are the application of products containing PFOS and landfills. The simulated best guess emissions in 2007 are 0.8 kg/year to the atmosphere, 480 kg/year to the hydrosphere and 29 kg/year to soil. Even though no dynamic SFA model was applied in this study, it was concluded that there was a decrease in the emissions of PFOS to the environment caused by both the phase-out by 3M and changes in the waste management. The latter includes the fact that the fractions of sewage sludge put to soil and dumped in landfills have decreased drastically over the past two decades. Incineration plants are thus important sinks for the substance flows of PFOS. According to the simplified SFA model used for the selected precursors, their atmospheric emissions and consecutive degradation do not markedly contribute to the occurrence of PFOS in the environment. Precursors in wastewater do however contribute significantly to the emissions to the hydrosphere, but it is unknown which proportion can be attributed to the selected FOSE derivatives.

Carpet protection, textile protection and AFFF have been identified as the application areas contributing the most to the occurrence of PFOA in the environment. As for PFOS, the most relevant (ultimate) emission source determined was WWTPs, followed by landfills and the application of products containing a PFOA residual content. The best guess emissions to the atmosphere, the hydrosphere and soil simulated are 0.2 kg/year, 33 kg/year and 2 kg/year, respectively. Because of the reduction of the residual concentrations of PFOA in products as well as changes in the waste management in Switzerland (see above), the emissions were estimated to have decreased during the past years. The atmospheric degradation of precursors was determined to contribute significantly to the occurrence of PFOA in the environment. The application areas with the highest estimated emissions are impregnation agents and textile protection. The most relevant precursor was simulated to be 8:2 FTOH.

Huset et al. (2008) estimated the per-capita discharge of PFOS and PFOA in the Glatt Valley based on their sampling conducted in 2006 as 57 µg/day/person and 12 µg/day/person, respectively. Assuming that the discharge per person was the same in all parts of Switzerland, the total releases to surface waters would be approximately 160 kg/year PFOS and 30 kg/year PFOA. This might not be a valid assumption as the releases of

WWTPs have been shown to differ significantly (Huset et al. 2008, Sun et al. 2008), which might be caused by the type and number of industries involved. The location of metal plating industries and recycling plants (physico-chemical treatment of process baths) as well as of major fire incidents has a large impact on the occurrence of PFOS in the environment. However, there is a high chance for the order of magnitude estimated from the study in Glatt Valley to be accurate. Despite the uncertainty of spatial and temporal variability, it may be concluded that the simulated (best guess) emissions to the hydrosphere, 480 kg/year PFOS and 33 kg/year of PFOA, are in a reasonable agreement with the numbers derived from the measurements in the Glatt Valley.

In Norway, the annual maximal emissions of PFOA from a range of consumer products were estimated to be 15 kg/year, of which carpets were estimated to be the most important source. The total of the direct and indirect sources of PFOA including long-range transport in the atmosphere and in oceans as well as degradation of 8:2 FTOH was estimated to be 130–380 kg/year (SFT 2007). Bearing the population and the area of Norway in mind, the estimate was considered comparable to the model result for Switzerland.

## 4.2 Concentrations in the environment

The PEC of PFOS and PFOA in water correspond quite well to the few field data available for Switzerland. The PEC of PFOS is somewhat lower than the analyses in the Glatt River but in good agreement with the sparse other field data for Switzerland. The elevated concentrations in the Glatt River compared to other rivers and lakes in Switzerland might be explained by its highly populated watershed. The PEC of PFOA in water is in reasonable correspondence with all Swiss data. Simulated concentrations in sediments and soils are all low (< 1 ng/g w.w.). Compared with the few field data for sediments from areas close to Switzerland, the PEC of PFOS and PFOA could be underestimated. However, the PEC generated in the environmental fate model is only a function of the emission rate in 2007 and does not include (higher) historical emissions. For soil, no field data are known except the analyses of crops in Germany where highly contaminated fertiliser was used. Hence, no conclusion on the agreement of PEC to field data was possible.

## 4.3 Data gaps

Only a rough picture of the use, stocks, flows and emissions could be drawn by this substance flow analysis because there are major data gaps. As shown in section 3.3, the main contributors to the overall uncertainty of the emissions are the uncertainties in a) the amounts of PFOS and PFOA in products used in Switzerland as well as in imported goods and the transfer coefficients and emission factors in the processes b) *application* and c) *WWTP*. Other data such as the transfer coefficients and emission factors in the process *incineration* contribute to a lower extent to the uncertainty. This indicates that further information on the use and these processes would help to improve the overall picture obtained by this study. The change (decrease) of the residual concentrations of PFOA in recent years after the agreement to the PFOA stewardship program adds to the uncertainty as some data are not valid anymore and as there are differences in the progress among the producers. Studies investigating the fate of PFOS and PFOA in WWTP in consideration of the contribution of individual precursors are currently in progress. In addition to the factors mentioned above, the emissions and the degradation yield of the FTOH precursors selected contribute markedly to the uncertainty of the PEC of PFOA. An open gap would also exist for the source of PFOS in the wastewater of paper mills measured in North Rhine-Westphalia and Austria (see section 2.5.1.12 on page 61) if these findings would be confirmed by analyses in Switzerland.

In this study, only four precursor substances (the different salts of PFOS and PFOA are not counted) that were selected by their likeliness to contribute to the levels of PFOS and PFOA in the environment were considered. However, 165 substances are contained in the section "PFOS and Related Compounds", 30 substances in the section "PFOA and Related Compounds" and 146 + 469 substances in the two parts of section "Fluorinated Chemicals that Potentially Degrade to PFCA" of the OECD document "Lists of PFOS, PFAS, PFOA, PFCA, Related Compounds and Chemicals that may degrade to PFCA" revised in 2007 (OECD 2007a). Some of these substances might also contribute to the levels of PFOS and especially of PFOA in the environment. PFOS, its salts and perfluorooctane sulfonyl fluoride have been listed to the Annex B of the Stockholm Convention shortly prior to publication of this report (see section 1.4.3 on page 31).

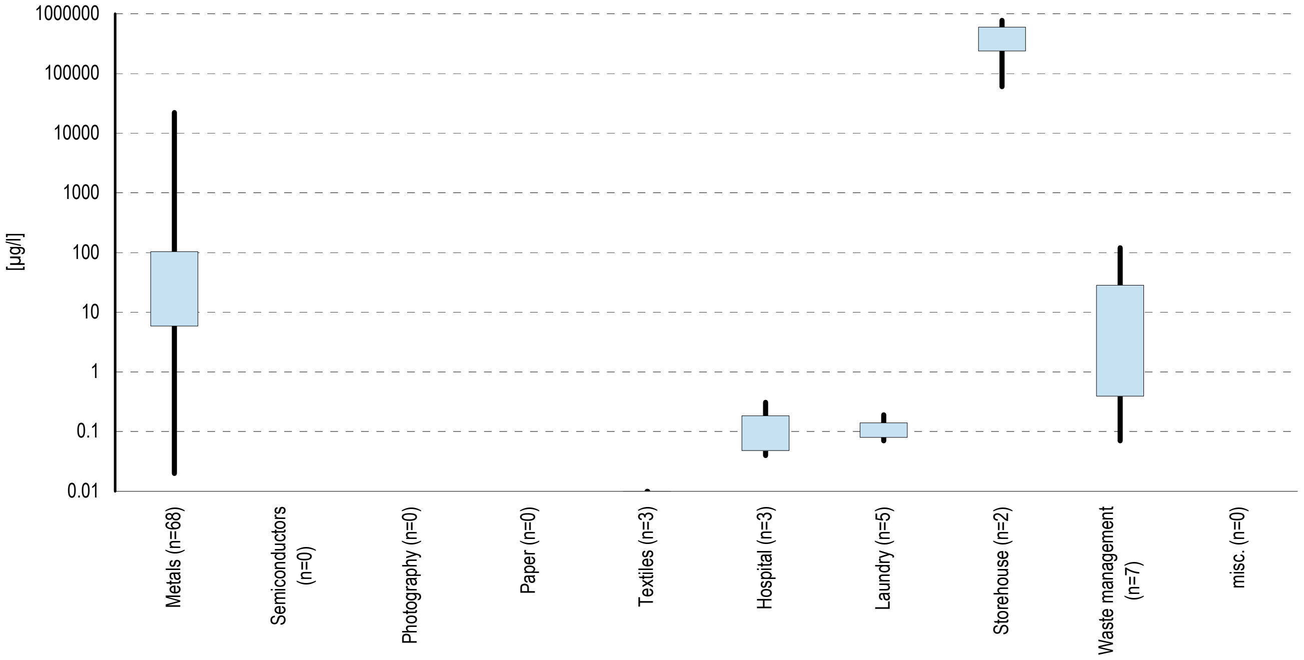
There are currently few analyses of goods and products, waste streams and environmental concentrations in Switzerland. Better data are expected from a new release of the OECD survey on PFCs that will be carried out in 2009. A PhD thesis focussing on the occurrence in the environment (surface water, groundwater, atmosphere, sediments and soils), goods, waste streams (wastewater, sewage sludge) and transport pathways to the environment has started at Empa in 2008. The data that will be generated in the OECD survey and the PhD thesis will allow improving the knowledge on the use, substance flows and emissions to the environment.

# > Appendix

## A1 Concentrations in indirect dischargers

**Fig. 23 > PFOS concentrations found in indirect dischargers**

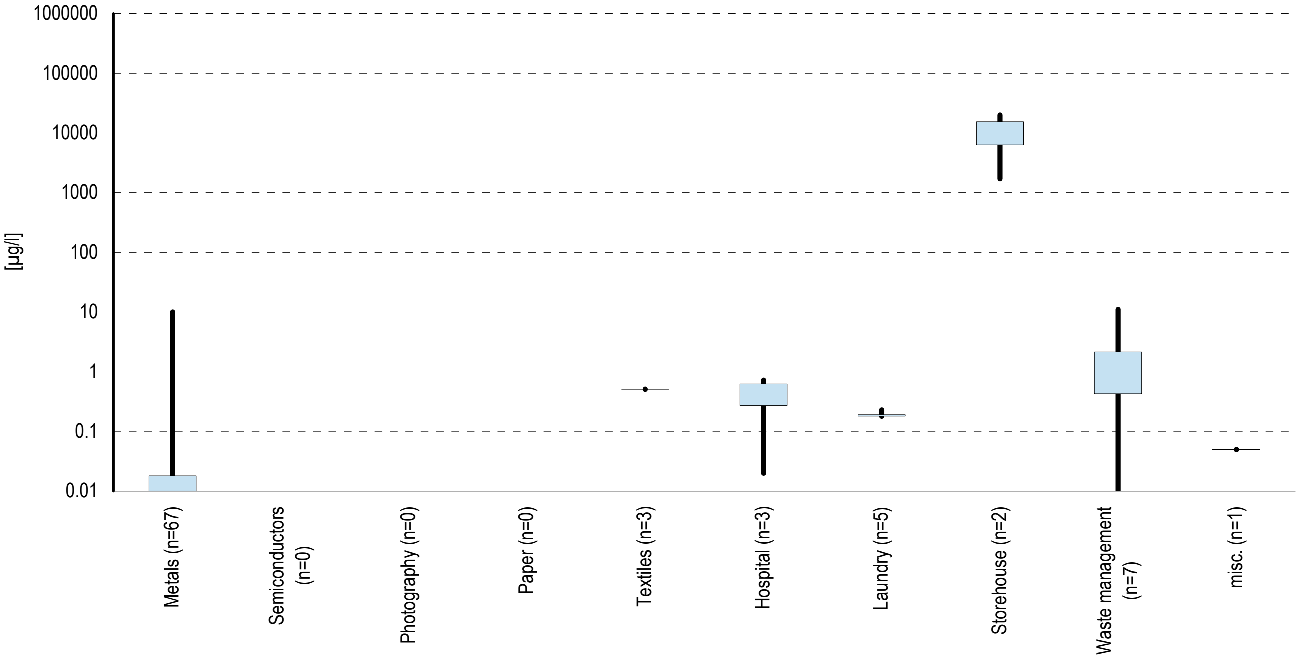
*Concentrations of PFOS (all isomers) in indirect dischargers of different industries. The samples were taken in North Rhine-Westphalia in the years 2007 and 2008. The lines represent the concentration range, while the boxes indicate the range between the 25th and the 75th percentile. Note the logarithmic scale.*



LANUV 2008

**Fig. 24 > PFOA concentrations found in indirect dischargers**

*Concentrations of PFOA (all isomers) in indirect dischargers of different industries. The samples were taken in North Rhine-Westphalia in the years 2007 and 2008. The lines represent the concentration range, while the boxes indicate the range between the 25th and the 75th percentile. Note the logarithmic scale.*



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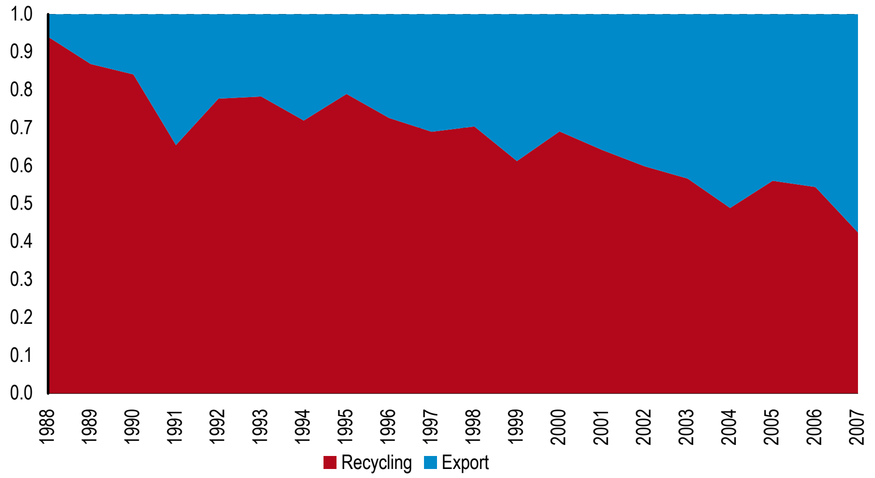
## A2 Temporal trends of transfer coefficients

Fig. 25 > Estimated temporal trend of transfer coefficients of textiles in automobiles at end-of-life



Swiss Auto Recycling Foundation 2008a

Fig. 26 > Estimated temporal trend of transfer coefficients of textiles (all uses)

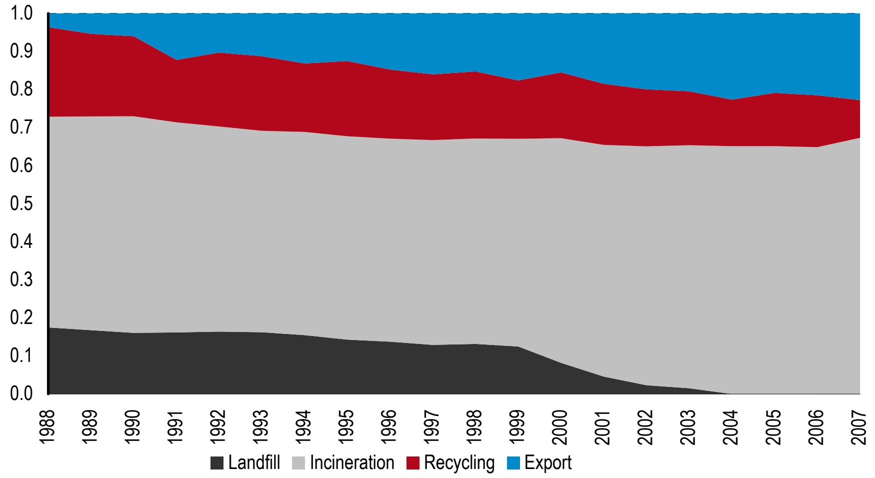


Fig. 27 > Estimated temporal trend of transfer coefficients of leather products at end-of-life

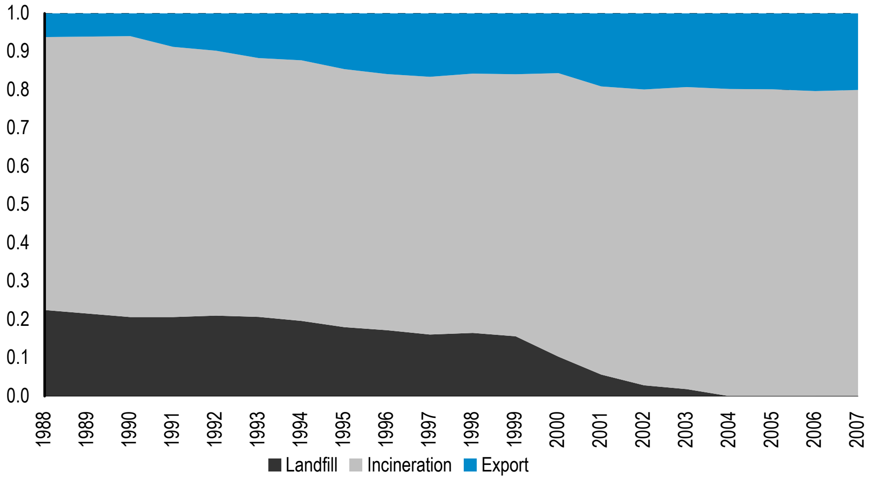


Fig. 28 > Estimated temporal trend of transfer coefficients for paper and paperboard products at end-of-life

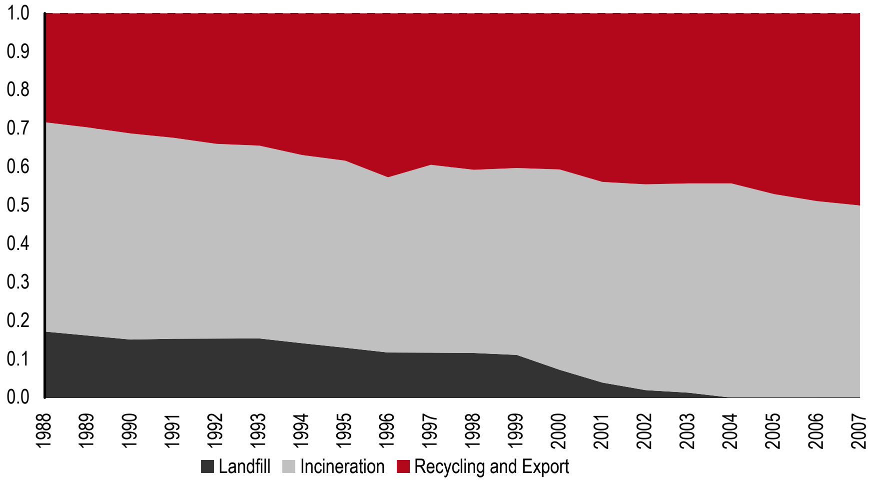
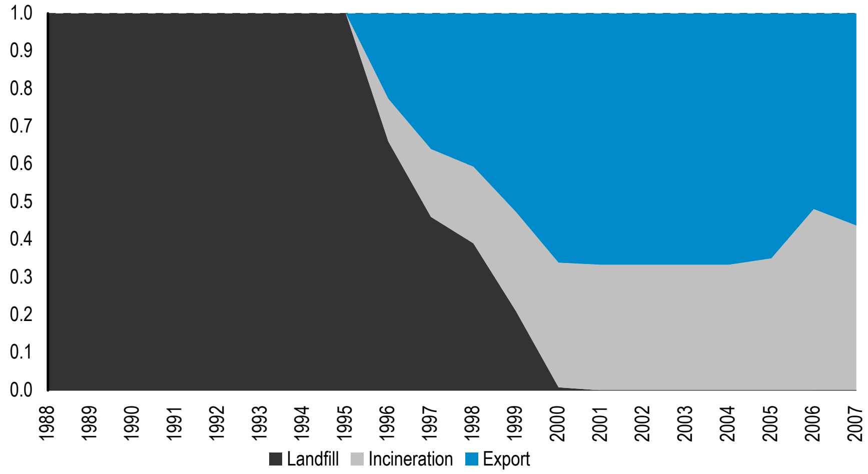


**Fig. 29** **> Estimated temporal trend of transfer coefficients of textiles in automobiles in the process *recycling***



Swiss Auto Recycling Foundation 2008a and earlier annual reports

## A3 Wastewater treatment plants

**Tab. 78 > Substance flows and concentrations in WWTP from Switzerland and abroad**

*Available studies on substance flows in WWTPs abroad (composite and grab sampling) and concentrations measured in Swiss WWTPs (composite sampling)*

| | Influent | Effluent | Sewage sludge | EF hydrosphere | TC sewage sludge | Reference |
|---|---|---|---|---|---|---|
| PFOS [mg/day] (comp. s.) | 420 ± 130 | 600 ± 110 | 230 ± 60 | 1.43 | 0.55 | Schultz et al. 2006 |
| PFOS [mg/day] (comp. s.) | 570 ± 150 | 1170 ± 380 | n.a. | 2.05 | n.a. | Sinclair & Kannan 2006 |
| PFOS [mg/day] (comp. s.) | 390 ± 40 | 380 ± 70 | n.a. | 0.97 | n.a. | Sinclair & Kannan 2006 |
| PFOS [mg/day] (grab s.) | 129 | 208 | 5165 | 1.61 | 40.04 | Loganathan et al. 2007 |
| PFOS [mg/day] (grab s.) | 168 | 122 | 5990 | 0.73 | 35.65 | Loganathan et al. 2007 |
| PFOS [mg/day] (grab s.) | 258 | 195 | 2330 | 0.76 | 9.03 | Loganathan et al. 2007 |
| PFOS [mg/day] (grab s.) | 111 | 432 | 445 | 3.89 | 4.01 | Loganathan et al. 2007 |
| PFOS [mg/day] (grab s.) | 534 | 705 | n.a. | 1.32 | n.a. | Loganathan et al. 2007 |
| PFOS [mg/day] (grab s.) | 527 | 492 | n.a. | 0.93 | n.a. | Loganathan et al. 2007 |
| PFOS [mg/day] (grab s.) | 171 | 95 | n.a. | 0.56 | n.a. | Loganathan et al. 2007 |
| PFOS [mg/day] (grab s.) | 1500 | 2800 | 2300 | 1.87 | 1.53 | Becker et al. 2008 |
| PFOS [ng/L] (weekly av.) | 71 ± 36 | 103 ± 32 | n.a. | 1.45 | n.a. | Huset et al. 2008 |
| PFOS [ng/L] (weekly av.) | 18 ± 10 | 16 ± 3 | n.a. | 0.89 | n.a. | Huset et al. 2008 |
| PFOS [ng/L] (weekly av.) | 449 ± 200 | 303 ± 120 | n.a. | 0.67 | n.a. | Huset et al. 2008 |
| PFOS [ng/L] (weekly av.) | 134 ± 50 | 119 ± 37 | n.a. | 0.89 | n.a. | Huset et al. 2008 |
| PFOS [ng/L] (weekly av.) | 76 ± 30 | 92 ± 30 | n.a. | 1.21 | n.a. | Huset et al. 2008 |
| PFOS [ng/L] (weekly av.) | 33 ± 23 | 23 ± 6 | n.a. | 0.70 | n.a. | Huset et al. 2008 |
| PFOS [ng/L] (weekly av.) | 117 ± 38 | 144 ± 46 | n.a. | 1.23 | 0.55 | Huset et al. 2008 |
| PFOA [mg/day] (comp. s.) | 400 ± 90 | 300 ± 40 | 1 ± 2 | 0.75 | < 0.01 | Schultz et al. 2006 |
| PFOA [mg/day] (comp. s.) | 7600 ± 1100 | 15000 ± 3900 | n.a. | 1.97 | n.a. | Sinclair & Kannan 2006 |
| PFOA [mg/day] (comp. s.) | 4700 ± 1200 | 7100 ± 740 | n.a. | 1.51 | n.a. | Sinclair & Kannan 2006 |
| PFOA [mg/day] (grab s.) | 1329 | 2350 | 11970 | 1.77 | 9.00 | Loganathan et al. 2007 |
| PFOA [mg/day] (grab s.) | 2929 | 2774 | 860 | 0.95 | 0.29 | Loganathan et al. 2007 |
| PFOA [mg/day] (grab s.) | 1596 | 1857 | 1080 | 1.16 | 0.68 | Loganathan et al. 2007 |
| PFOA [mg/day] (grab s.) | 358 | 2265 | 450 | 6.33 | 1.26 | Loganathan et al. 2007 |
| PFOA [mg/day] (grab s.) | 2043 | 5400 | n.a. | 2.64 | n.a. | Loganathan et al. 2007 |
| PFOA [mg/day] (grab s.) | 3400 | 2740 | n.a. | 0.81 | n.a. | Loganathan et al. 2007 |
| PFOA [mg/day] (grab s.) | 134 | 354 | n.a. | 2.64 | n.a. | Loganathan et al. 2007 |
| PFOA [mg/day] (grab s.) | 400 | 8000 | 300 | 20.00 | 0.75 | Becker et al. 2008 |
| PFOA [ng/L] (weekly av.) | 4.9 ± 9.8 | 28 ± 12 | n.a. | 5.71 | n.a. | Huset et al. 2008 |
| PFOA [ng/L] (weekly av.) | 5.1 ± 3.5 | 17 ± 6.6 | n.a. | 3.33 | n.a. | Huset et al. 2008 |
| PFOA [ng/L] (weekly av.) | 35 ± 11 | 35 ± 8.8 | n.a. | 1.00 | n.a. | Huset et al. 2008 |
| PFOA [ng/L] (weekly av.) | 25 ± 21 | 27 ± 15 | n.a. | 1.08 | n.a. | Huset et al. 2008 |
| PFOA [ng/L] (weekly av.) | 8.9 ± 8.3 | 12 ± 9.7 | n.a. | 1.35 | n.a. | Huset et al. 2008 |
| PFOA [ng/L] (weekly av.) | 9.0 ± 11 | 27 ± 16 | n.a. | 3.00 | n.a. | Huset et al. 2008 |
| PFOA [ng/L] (weekly av.) | 9.0 ± 8.0 | 13 ± 9.4 | n.a. | 1.44 | n.a. | Huset et al. 2008 |

## A4 Landfills

**Tab. 79 > Concentrations in landfill leachates**

| Location | Years of operation | Accepts sewage sludge | PFOS [ng/L] | PFOA [ng/L] | Reference |
|---|---|---|---:|---:|---|
| USA, Decatur, Alabama | n.a. | Yes | 52300–53100 | 46800–48100 | 3M 2001 |
| USA, Columbus | n.a. | n.a. | < 2 | < 25–28 | 3M 2001 |
| USA, Port St. Lucie | n.a. | n.a. | 329–429 | 939–1030 | 3M 2001 |
| USA, Minnesota | 1971–present | Yes | 3140–31400 | 14200–81800 | Oliaei et al. 2006 |
| USA, Gulf Coast | 1998–present | Yes | 160 ± 17 | 490 ± 15 | Huset 2007 |
| USA, Pacific Northwest | 1996–present | Yes | 100 ± 08 | 1000 ± 85 | Huset 2007 |
| USA, West Coast | 2003–present | Yes | 97 ± 13 | 910 ± 40 | Huset 2007 |
| USA, Mid-Atlantic States | 1982–1988 | Yes | 56 ± 17 | 380 ± 33 | Huset 2007 |
| USA, Mid-Atlantic States | 1988–1993 | Yes | 91 ± 06 | 480 ± 27 | Huset 2007 |
| USA, Mid-Atlantic States | 1993–1999 | Yes | 120 ± 11 | 400 ± 39 | Huset 2007 |
| USA, Mid-Atlantic States | 1993–1999 | Yes | 88 ± 04 | 430 ± 05 | Huset 2007 |
| USA, Mid-Atlantic States | 1999–present | Yes | 140 ± 09 | 720 ± 28 | Huset 2007 |
| USA, Southeast | 2006 | n.a. | 100 ± 10 | 1100 ± 53 | Huset 2007 |
| USA, West Coast | 1999–present | No | 110 ± 14 | 140 ± 12 | Huset 2007 |
| USA, Mid-Atlantic States | 2004–present | Yes | 38 ± 13 | 130 ± 01 | Huset 2007 |
| USA, Mid-Atlantic States | 1990–present | Yes | 120 ± 02 | 760 ± 07 | Huset 2007 |
| Finland, Espoo | n.a. | n.a. | 30.2–34.7 | 300–399 | Kallenborn et al. 2004 |
| Norway, Spilhaug | n.a. | n.a. | 33.0 | 91.3–93.5 | Kallenborn et al. 2004 |
| Norway, Støleheia | n.a. | n.a. | 108 | 516 | Kallenborn et al. 2004 |
| Norway, Gålås | n.a. | n.a. | 56.4 | 293 | Kallenborn et al. 2004 |
| Norway, Røyken | n.a. | n.a. | 187 | 367 | Kallenborn et al. 2004 |
| Norway, Spilhaug | n.a. | n.a. | 75.1 | 168 | Kallenborn et al. 2004 |
| Denmark, site 1 | n.a. | n.a. | < 1.5 | 5.8 | Bossi et al. 2008 |
| Denmark, site 2 | n.a. | n.a. | 0.8–3.8 | < 2.0 | Bossi et al. 2008 |
| Germany, NRW | n.a. | n.a. | 70–170 | 1100–5100 | LANUV 2008 |

# > Index

## Glossary

**6:2 FTS**
6:2 fluorotelomer sulfonate

**8:2 FTA**
Perfluorooctylethylacrylate

**8:2 FTMA**
Perfluorooctylethylmethacrylate

**8:2 FTOH**
8:2 fluorotelomer alcohol

**10:2 FTOH**
10:2 fluorotelomer alcohol

**AFFF**
Aqueous film-forming foam

**APFO**
Ammonium perfluorooctanoate

**EF**
Emission factor

**ESD**
Emission Scenario Document

**ESIS**
European chemical Substances Information System

**Fluoropolymers**
Polymers that have fluorine attached to the majority of carbon atoms which comprise the polymer chain backbone

**Fluorotelomers**
Even carbon number length oligomers created by the reaction of tetrafluoroethylene with perfluoroethyl iodide

**FTOHs**
Fluorotelomer alcohols

**IUPAC**
International Union of Pure and Applied Chemistry

**$K_{AW}$**
Air water partitioning coefficient

**$K_d$**
Solid/solution distribution coefficient

**LANUV**
Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westfalen

***N*-EtFOSE**
*N*-ethylperfluorooctanesulfonamidoethanol

***N*-MeFOSE**
*N*-methylperfluorooctanesulfonamidoethanol

**OECD**
Organisation for Economic Co-operation and Development

**PFCs**
Perfluorinated compounds

**PFBS**
Perfluorobutanesulfonate

**PFNA**
Perfluorononanoic acid

**PFOA**
Perfluorooctanoic acid; pentadecafluorooctanoic acid (not distinguished between neutral form and anion)

**PFOS**
Perfluorooctanesulfonate

**PTFE**
Polytetrafluoroethylene

**PVDF**
Polyvinylidene fluoride

**SFA**
Substance flow analysis

**TC**
Transfer coefficient

**TGD**
Technical Guidance Document on Risk Assessment

**WWTP**
Wastewater treatment plant

## Figures

## Tables

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