COHIBA

CONTROL OF HAZARDOUS SUBSTANCES
IN THE BALTIC SEA REGION

COHIBA GUIDANCE DOCUMENT NO. 4

MEASURES FOR EMISSION REDUCTION OF PFOS AND PFOA IN THE BALTIC SEA AREA

COHIBA Project Consortium

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Lead author:
Eve Menger-Krug

Co-authors:
Hanna Andersson, Swedish Environmental Research Institute Ltd. (IVL)
Zita Dudutyte, Baltic Environmental Forum Lithuania
Janusz Krupanek, IETU Institute for Ecology of Industrial Areas
Ülle Leisk, Tallinn University of Technology
Frank Marscheider-Weidemann, Fraunhofer Institute for Systems and Innovation Research ISI
Cindy Mathan, Federal Environment Agency of Germany (UBA)
Jukka Mehtonen, Finnish Environment Institute SYKE
Päivi Munne, Finnish Environment Institute SYKE
Ulf Nielsen, DHI
Simon Siewert, Federal Environment Agency of Germany (UBA)
Laura Stance, Baltic Environmental Forum Lithuania
Felix Tettenborn, Fraunhofer Institute for Systems and Innovation Research ISI
Valters Toropovs, Baltic Environmental Forum Latvia
Jenny Westerdahl, Swedish Environmental Research Institute Ltd. (IVL);

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Lead organizations of the Consortium for this activity:

Federal Environment Agency of Germany (UBA)
Wörlitzer Platz 1, DE-06844 Dessau- Roßlau
Tel. +49 340-2103-2780
www.umweltbundesamt.de

supported by
Fraunhofer Institute for Systems and Innovation Research ISI
Breslauerstr. 48, DE-76139 Karlsruhe
www.isi.fraunhofer.de

Finnish Environment Institute (SYKE)
P.O.Box 140, FI-00251 Helsinki, Finland
Tel. +358 20 610 123
www.environment.fi/syke/cohiba

Baltic Marine Environment Protection Commission (Helsinki Commission)
Katajanokanlaituri 6B, FI-00160 Helsinki, Finland
Tel. +358 207 412 649
www.helcom.fi and www.cohiba-project.net

Preface

The Baltic Sea ecosystem is particularly at risk from hazardous substances, due to its natural characteristics, such as slow water exchange, and due to a long history of urbanization and industrialization at the shores and in the catchment area. The ecosystem status of nearly all open-sea and coastal areas of the Baltic Sea is considered to be “disturbed by hazardous substances” (HELCOM 2010). Therefore, HELCOM identified 11 hazardous substances of special concern, amongst them perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) and laid down environmental targets in the Baltic Sea Action Plan (BSAP) for a Baltic Sea with life undisturbed by hazardous substances and all fish safe to eat.

To achieve the targets of BSAP, measures for emission reduction are needed.

This report analyses and compares different measures for reducing emissions of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in order to contribute to a knowledge base for decision making. It starts with a review of chemical properties (chapter 2), production and use, emission sources and environmental fate (chapter 3), followed by an overview of existing regulations and an analysis of regulatory gaps (chapter 4). The main part of the report deals with the selection and analysis of emission reduction measures (chapters 5 and 6) and concludes with a comparison of measures (chapter 7) and final conclusions (chapter 8).

This report is part of a series of COHIBA guidance documents, dealing with each of the 11 hazardous substances of special concern to the Baltic Sea as identified by HELCOM. Concerning recommendations for cost-effective strategies for reducing emissions of all 11 hazardous substances, please also refer to the Recommendation Report. This report and other outputs of the COHIBA project are available on the project website (www.cohiba-project.net).

COHIBA

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Baltic Sea Region
Programme 2007–2013

This document is part of a series of COHIBA WP5 Guidance Documents on Hazardous Substances of special concern to the Baltic Sea (available for download www.cohiba-project.net)	
Dioxins (PCDD), furans (PCDF) & dioxin-like polychlorinated biphenyls	
2. Organotin compounds	2a. Tributyltin compounds (TBT)
	2b. Triphenyltin compounds (TPhT)
3. Brominated diphenyl ethers	3a. Pentabromodiphenyl ether (pentaBDE)
	3b. Octabromodiphenyl ether (octaBDE)
	3c. Decabromodiphenyl ether (decaBDE)
4. Perfluoroalkylated substances	4a. Perfluorooctane sulfonate (PFOS)
	4b. Perfluorooctanoic acid (PFOA)
5. Hexabromocyclododecane (HBCDD)	
6. Nonylphenols	6a. Nonylphenols (NP)
	6b. Nonylphenol ethoxylates (NPE)
7. Octylphenols	7a. Octylphenols (OP)
	7b. Octylphenol ethoxylates (OPE)
8. Chlorinated paraffins (or chloroalkanes)	8a. Short-chain chlorinated paraffins (SCCP, C_{10-13})
	8b. Medium-chain chlorinated paraffins (MCCP, C_{14-17})
9. Endosulfan	
10. Mercury (Hg)	
11. Cadmium (Cd)	

Content

1 Introduction to PFOS and PFOA

Perfluorinated compounds (PFCs), such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), have been used in a range of industrial and consumer applications and products since the 1950s. Perfluorinated surfactants, for example, are surface active substances. They repel grease, dirt, as well as water, and they are stable in industrial processes even under harsh conditions.

Perfluorinated substances are of anthropogenic origin, they are not formed naturally (UBA 2007). Perfluorinated compounds retain the unique properties that make them valuable for industrial and consumer applications also after being emitted to the environment, making them practically non-degradable under environmentally relevant conditions, and are therefore very persistent (Buser and Morf 2009).

During 60 years of use, PFCs, especially perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), have achieved a worldwide distribution, including even remote areas like the Arctic, as many studies[1] have reported. They are found in wildlife such as fish, birds and marine mammals, as well as in human blood samples. They were detected in surface water and also tap water samples in several countries, for example in the vicinity of production sites for perfluorinated compounds in the USA.

PFOS and PFOA are toxic, the predominant toxic effects[2] include developmental toxicity, hormonal effects and carcinogenic potential (Lau *et al.* 2007). Due to their persistence, PFOS and PFOA can accumulate in the environment. PFOS and PFOA can also bioaccumulate in living organisms[3]. The risks posed to ecosystems and human health by long term exposure, continuing bioaccumulation and combined effects of “cocktails” of different chemicals are very difficult to predict. But once persistent substances are released into the environment, it is almost impossible to remove them again. Therefore, whatever the potential effects of these substances on ecosystems and wildlife, they are irreversibel.

2 Description of chemical properties

Substances within the group of perfluorinated substances are characterised by their fully fluorinated carbon chain. All hydrogen atoms are exchanged for fluorine atoms (Kissa 2001, OECD 2007b). The perfluorinated carbon chain has both hydrophobic and lipophobic

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[1] See review in e.g. Buser and Morf 2009.

[2] A review of the toxicology of PFOS and PFOA can be found in Lau *et al*. (2007). In animal studies, hepatotoxicity, developmental toxicity, immunotoxicity, hormonal effects and carcinogenic potential are the predominant effects of concern.

[3] Even though PFOA does not fulfill the REACH criteria for bio-accumulation, see Chapter 2

properties. The chemical structure of PFOS and PFOA is shown in Figure 1. A table listing important physico-chemical properties is presented in the annex.

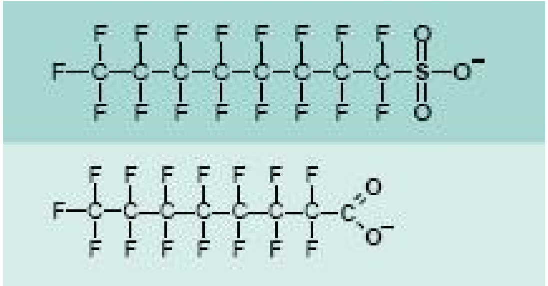

Figure 1: Chemical structure of PFOS and PFOA (UBA 2008)

Carbon-fluorine bonds are very strong chemical bonds. They can only be broken by high energy inputs (e.g. high temperature incineration). PFOS is classified as vPBvT-substance (very persistant, bioaccumulative and very toxic) and PFOA as vP T-substance (very persistant and toxic) under REACH[4]. PFOA does not fulfill the REACH criteria for bioaccumulation[5]. But chemical biomonitoring data indicate that PFOA is bioaccumulative and magnifies in food webs (Houde et al, 2006). Critics say that the testing method applied is too limited[6] (see Reineke 2010). Due to long-range transport characteristics and occurrences in biota and wildlife, PFOA might be of equivalent concern as PBT-substances (van der Putte et al. 2010).

There are a vast number of PFOS-related compounds[7], i.e. derivatives containing PFOS moiety and PFOS salts. PFOA also exists in a number of forms of which the most commonly used is an ammonium salt called APFO (KemI 2004a,b). The OECD lists 165 PFOS-related compounds and 30 PFOA related-compounds[8]. In the annex commonly used abbreviations are explained and the CAS numbers of PFOS, PFOA and some related compounds are listed.

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[4] Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH, Regulation (EC) No 1907/2006, annex XVII), amended by Commission Regulation 552/2009.

[5] The criteria for a substance to be bioaccumulative under REACH is a bioconcentration factor (BCF) higher than 2000, measured as n-octanol/water partition coefficient(see: http://eur-lex.europa.eu/

[6] PFOA binds to blood proteins and not lipids and therefore has a low bioconcentration factor in the current testing method (see Reineke 2010).

[7] 165 substances are listed under “PFOS and Related Compounds” and 30 substances under “PFOA and Related Compounds” in the OECD document “Lists of PFOS, PFAS, PFOA, PFCA, Related Compounds and Chemicals that may degrade to PFCA”, 2007 revision (OECD 2007a)

[8] Andersson *et al.*, p. 32 and p. 32, 2011

There is a large number of potential precursor substances[9] for PFOS and PFOA. Longer chain perfluorinated compounds (PFCs) can break down to PFOS or PFOA in the environment or during waste water treatment. The chemical characteristics, use patterns and environmental fates, including potential for long range transport, of these potential precursor substances are largely unknown, which adds to the uncertainty about the environmental distribution of PFOS/PFOA.

3 Inventory of Inputs to the Baltic Sea

3.1 Production and use

Manufacture of PFOS and PFOS-related compounds is banned in the EU and the US (see Chapter 4) but China started large-scale production of PFOS-related compounds in 2003[10]. There is no production of PFOS in the European catchment area of the Baltic Sea.

Manufacture of PFOA/APFO is still allowed in the EU, but there is a voluntary agreement to eliminate emission of PFOA and PFOA content of products by 2015 (see also Chapter 4). There is no production of PFOA in the European catchment area of the Baltic Sea.

Industrial applications of PFOS in metal (chromium) plating, manufacture of semiconductors and manufacture of photographic material are still allowed in the EU. These industries exist in the European catchment area of the Baltic Sea.

Industrial applications of PFOA include fluoropolymer manufacture and fluoropolymer dispersion processing, manufacture of semi-conductors and manufacture of photographic material. These industries exist in the European catchment area of the Baltic Sea.

PFOS and PFOA have been used in the past in high performance fire fighting foams, but by 2011 all stocks have to be used up or destroyed. Besides industrial and commercial use, an important focus is PFOS and PFOA in household products for private use. Prior to the phase-out of PFOS in 2006 and the PFOA stewardship programme launched in 2005 (see Chapter 4), both substances were used in a wide range of products in much higher concentrations than today. These products (depending on use pattern and lifetime) can still contribute to the urban stock. Emissions from urban stock can continue long after cessation of use. These emissions are channelled through urban infrastructure systems (MWWTPs, ur-

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[9] 146 substances (PFOS) and 469 substances (PFOA) are listed by OECD as potential precursors (OECD 2007a).

[10] 15 Chinese enterprises have been producing more than 200 tof POSF per year, about 100 t/year of which were for export (MEP 2008).

ban run-off, waste disposal/incineration sites as point sources), or occur as diffuse urban emissions[11].

Historical uses of PFOS/PFOA in household products include impregnated carpets, impregnated leather/apparel, impregnated textiles/upholstery, impregnated paper and packaging, industrial and household cleaning products.

Ongoing use of PFOS as impregnation agent is allowed in the EU up to a limit value of 1 µg/m² (see Chapter 4), which can continue to contribute to the urban stock. Ongoing use of PFOA as manufacturing aid in the production of fluoropolymers can also continue to contribute to the urban stock, as products with fluoropolymers can contain trace amounts of PFOA as impurity. These products have a vast range of applications, including non-stick cookware (e.g. Teflon ®), textiles (e.g. Goretex ®), wire and cables coating, electronics, semiconductors, etc. (OECD 2007b, also see annex for list of products). Due to a voluntary commitment by industries, substantial reductions in PFOA impurities in products were forecasted for 2010 (Armitage *et al.* 2006). Besides products from within the EU, imported products can also contribute to urban stocks of PFOS/PFOA, but it is unknown to what extent.

Two recent OECD surveys (from 2006 and 2010)[12] give an overview of global production of PFOS/PFOA and related compounds. They show markedly decreasing trends in emissions from industrial sources. This increases the relative importance of emissions from urban stock.

3.2 Emission sources in the Baltic Sea catchment area

COHIBA WP4 identified the sources of emissions of PFOS and PFOA to the Baltic Sea, based on substance flow analysis (SFA) and review of literature. This chapter gives a short overview of results from COHIBA WP4[13]. Total input of PFOS/PFOA to all environmental compartments in the Baltic Sea catchment area amounts to 300-600 kg/year (see Figure 1). Approximately 40% of the total load is emitted to water.

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[11] flows not captured by urban infrastructure systems, e.g. surface run off directly to surface water, emission via air or airborne particles, illegal (off site) dumping, illegal (off site) waste water disposal and illegal (off site) incineration of waste, or losses from sewers.

[12] The results of the OECD surveys (OECD 2007 and 2011) do not provide a complete picture of the global production and use of perfluorinated chemicals, due to limited responses. The survey also includes other PFCs (precursor substances).

[13] for more details, please refer to the project website

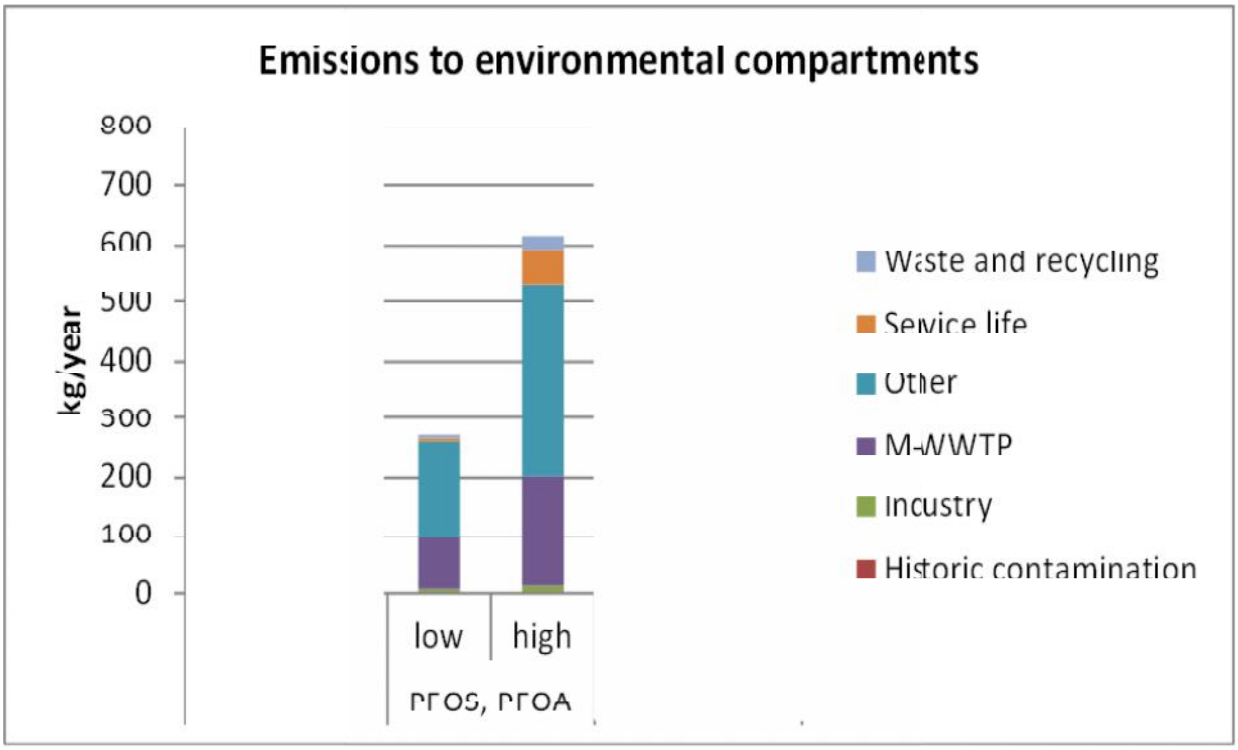

Figure 1: Results from COHIBA WP4: sources of emissions of PFOS and PFOA to the Baltic Sea (all environmental compartments)

Industrial sources seem to be less important for PFOS/PFOA, they account for about ~1-5% of the total load. But there are data gaps introducing high uncertainties into the quantification of industrial sources. The availability of information on production volumes and emissions of industries is low, due to the problem of confidential business information. Data gaps exist for PFOA in particular. As PFOA is not regulated (see chapter 4), there are no reporting duties for industries.

The contribution of emissions from MWWTP to the total load is in the range of 30%. This includes direct emissions to water via MWWTP effluent, as well as emissions to (agricultural) land via sewage sludge. The load in municipal waste water originates from urban stock (products), as well as from indirect dischargers, for example metal plating facilities.

The largest contribution to the total load of PFOS/PFOA comes from “other” sources (>50%). These “other” sources are mainly use of fire fighting foam containing PFOS (and PFOA as impurity). This emission estimate is subject to high uncertainty, since the load emitted to the environment (mainly to land) depends on the incidence of fires and the fate of used fire fighting foam. This use of PFOS has been banned in the EU since 2008, the remaining stocks have to be used or destroyed by mid 2011 (see Chapter 4). Therefore, emissions from this source can be expected to decline sharply after 2011.

3.3 Environmental Fate

PFOS and PFOA are persistent in the environment. There are no known degradation mechanisms under environmentally relevant conditions (Buser and Morf 2009).

PFOS/PFOA are stable end products of a large number of potential precursor substances[14]. This becomes evident in waste water treatment, where effluent concentrations of PFOS/PFOA are often higher than influent concentrations, due to degradation of precursors. These precursors may have very different environmental fates (e.g. FTOH: transport via air) and add to the uncertainty concerning emission sources. The contribution of degradation of precursors to total emission of PFOS/PFOA is under discussion in the scientific community[15].

The water phase is likely the most important pathway for PFOS/PFOA. PFOA has a higher solubility than PFOS, and is likely more mobile in matrices, e.g. landfill leachate has higher concentrations of PFOA than PFOS, maybe due to higher mobility (Buser and Morf 2009).

PFOS/PFOA partly adsorb to particles. PFOS has a higher affinity to particles than PFOA. In waste water treatment, partitioning of PFOS/PFOA between effluent (water phase) and sewage sludge (solid phase) can be observed, but partitioning rates are subject to high uncertainties[16].

Transport via air may be contributing to long range transport, but this aspect is still under discussion in the scientific community.

An important environmental sink for PFOS/PFOA are surface waters, oceans, and groundwater, due to high water solubility and persistence (Prevedouros et al. 2006, Armitage et al. 2006 and 2009). Biota are also possible sinks for PFOS/PFOA, due to their bioaccumulative properties (PFOS > PFOA). Via food chain, they can also bioaccumulate in humans.

4 Existing regulations

Table 1 shows existing regulations at international, EU, HELCOM and national level for PFOS and PFOA. Additional information can be found in the annex.

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[14] see Chapter 2

[15] For PFOA, it is estimated that precursor degradation accounts for about 10% of total emission of PFOA. More information can be found in (Prevedouros *et al.* 2006, Armitage *et al.* 2006 and 2009*)*

[16] In a study by Schultz et al. (2006), PFOS flows 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. These data were presented in a recent review article on the chemical fate of chemicals in WWTPs (Heidler and Halden 2008).
Buser and Morf (2009), taking into account recent studies (Schultz et al. 2006, Heidler and Halden 2008; Sinclair & Kannan 2006, Loganathan et al. 2007, Huset et al. 2008) estimated a best guess emission factor to hydrosphere of 1.2 (range 0.8–2) and a best guess transfer coefficient to sewage sludge of 2.2 (range 0.5–20).
The authors state that the substance flow of PFOS into sewage sludge seems not to be directly related to the mass in the influent. As sludge has a longer residence time in WWTPs than water and the microbial conditions are considerably different, the potential for 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 NMeFOSE, 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 (Buser and Morf 2009)

Table 1: Existing regulations for PFOS and PFOA (in brackets: date of implementation)

Existing regulations	PFOS	PFOA
International level	Stockholm Convention on Persistent Organic Pollutants (2009)	US EPA PFOA stewardship program (voluntary) UNEP and OECD activities
EU level	Directive 2006/122/EC (2008) REACH PBT substance Not a WFD priority substance[17]	None Not a REACH PBT substance[18] Not a WFD priority substance
HELCOM	HELCOM Rec. 19/5 Helcom objective with regard to hazardous substances	
National level	National regulatory activities e.g.[19] in Canada, United States, Australia, United Kingdom, Germany, Norway, Latvia	

Stockholm Convention on Persistent Organic Pollutants. The substance PFOS was proposed for listing in Annex A of the Stockholm Convention on Persistent Organic Pollutants in 2005. The risk management evaluation was adopted for PFOS in November 2007 (UNEP 2007). In May 2009, PFOS, its salts and perfluorooctane sulfonyl fluoride (POSF) were listed under Annex B of the Stockholm Convention (Stockholm Convention Secretariat 2009[20]).

EU Directive on PFOS. Directive 2006/122/EC amending Directive 76/769/EEC restricts the marketing and use of perfluorooctane sulfonates[21] in the European Union (EC 2006a). The directive became effective in 2008 and applies to substances and preparations with concentrations 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, the directive provides some exceptions:

- manufacture of semiconductors: photoresists or anti reflective coatings for

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[17] Under the Water Framework Directive (2000/60/EC), PFOS is a candidate for the new priority substances list. A final advice for the European Commission is expected by September 2010 (from http://www.rivm.nl/bibliotheek/rapporten/601714013.pdf)

[18] see Chapter 2 Description of chemical properties

[19] Full list in Annex (chapter A.2 Additional information on existing regulations on page 38)

[20] see Buser and Morf 2010

[21] defined by the generic molecular formula $C_8F_{17}SO_2X$ (X = OH, metal salt (O−M+), halide, amide and other derivatives including polymers

- photolithography processes
- photographic coatings applied to films, papers or printing plates
- metal plating: 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
- BAT (best available techniques)
- hydraulic fluids for aviation
- existing stocks of fire-fighting foams (until 2011)

Water Framework Directive: PFOS is listed in annex III of the daughter directive (2008/105/EC) to the Water Framework Directive (2000/60/EC) as a substance subject to review for possible identification as a priority substance (or priority hazardous substance). This review process is currently ongoing [22]

PFOA is not regulated at EU or international level. As it does not fulfill the bioaccumulation criteria of REACH (see Chapter 2), it is not classified as PBT substance (only as vP T substance). Therefore, a regulatory gap for PFOA can be determined.

Even though there is no international regulation of PFOA, there is a voluntary commitment by industry to achieve a reduction in PFOA emissions (US EPA PFOA stewardship program). 8 large fluorotelomer producers participate[23]. Participation in the stewardship program requires voluntary corporate commitment to two goals (US EPA 2006): To commit to achieve 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, no later than 2010. In 2015, the voluntary phase out should be completed.

National regulatory activities are ongoing in some countries around the Baltic Sea (e.g. Germany: Limit values for PFOS/PFOA in sewage sludge and fertilizer (planned) and nomination of PFOA for REACH, in Latvia PFOA regulation is in progress). In addition to that, there is an initiative by Germany and Norway to place PFOA on the list of substances of very high concern (SVHC).

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[22] Under the Water Framework Directive (2000/60/EC), PFOS is a candidate for the new priority substances list. A final advice for the European Commission is expected by September 2010 (from http://www.rivm.nl/bibliotheek/rapporten/601714013.pdf)

[23] http://www.epa.gov/opptintr/pfoa/pubs/stewardship

5 Measures for Emission Reduction

5.1 Evaluation methodology

In order to identify appropriate measures for reducing emissions of hazardous substances to the Baltic Sea a pragmatic approach is applied. In view of the multitude of possible sources and measures, source-measure combinations promising a large reduction potential are preselected. For the identification of large reduction potentials two criteria are considered: firstly the load at the source and secondly the effectiveness of the applied measure (chapter 5.2).

In a second step these pre-selected measures are analyzed in detail and compared (chapters 6 and 7). If appropriate data on effectiveness and costs are available a quantitative assessment of the cost-effectiveness of measures is performed by using the following evaluation criteria:

Effectiveness

The effectiveness of a measure at a given source relates to the reduction it achieves in the emissions of a given hazardous substance. The effectiveness of technical measures is usually expressed as elimination rate in percent. In combination with the load of the respective source, the effectiveness can be expressed as load reduction in kilogramme.

Costs

The evaluation of costs is subdivided in direct costs and running costs. Whilst direct costs include initial expenditures (e.g. construction costs, investment costs, costs for developing a substitute, rule making costs), running costs comprise ongoing expenditures (e.g. operation and maintenance costs, (additional) costs for using a substitute, costs for implementation and enforcement). In order to adapt the costs to local circumstances, they are further broken down into costs for labour, energy and material, if data are available.

Cost-Effectiveness Analysis

The cost effectiveness of different measures is expressed by the ratio of cost to the reduced load of hazardous substances. As there are large uncertainties, different scenarios – a worst case scenario (low load reduction effectiveness – high costs) and best case scenario (high load reduction effectiveness – low costs) - are used for the calculation of cost effectiveness.

The quantitative assessment is complemented by a comprehensive qualitative evaluation to include sustainability aspects, which is mainly based on experts' estimates rather than on empirical data. For this additional assessment the following qualitative evaluation parameters are used:

Secondary environmental effects

Besides the direct effects on emissions of the targeted hazardous substance, measures can have a wide array of positive or negative secondary environmental effects (e.g. effects on emission reduction of other hazardous substances or nutrients, effects on waste production which requires deposition on landfills, effects on climate change through energy consumption or effects on land use).

Technical feasibility

The technical feasibility describes the ease of technical implementation of the respective measure under different boundary conditions. This touches on aspects like practical experiences (emerging, pilot or existing technology), necessary process modifications, or impact on ongoing processes. These can present limitations for the application of the respective measure. One indicator of technical feasibility is e.g. the time needed for (technical) implementation of the measure.

Secondary socio-economic effects

Besides the primary costs of a measure, there are also secondary socio-economic effects (including indirect costs) of a measure. Possible secondary socio-economic effects of a measure include indirect costs, effects on employment, on job qualification (e.g. qualification needed for operation and maintenance of advanced technologies) and on product prices including the question whether industries pass on higher costs to consumers. An important aspect is which stakeholders are affected, who pays for the measures and who benefits from them.

Geographical and time scale of effects

Another additional parameter to describe measures is the geographical and time scale of effects. Some measures are effective on a local or watershed level and other measures show effects on a national or international level. The time scale of effects varies from immediate effects to long lag times until the measure becomes effective (e.g. varying time spans of effects due to different technical lifetimes for certain measures).

Political enforceability

The political enforceability of measures depends on how well the measure is aligned with other political targets, on the national financial scopes (e.g. compensation payments), on possible conflicting interests and on their acceptance by existing interest groups. The political enforceability is also influenced by the other parameters, such as effectiveness, costs, technical feasibility and secondary environmental and socio-economic effects.

5.2 Overview of measures

COHIBA WP5 preselected and prioritized source-measure combinations promising a large reduction potential[24] as described in chapter 5.1. Measures at industrial sources and at urban sources (MWWTPs) were included in the evaluation of measures.

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[24] This is a pragmatic approach chosen in view of the multitude of possible sources and measures. In terms of science, excluding source-measure combinations from analysis confines the evaluation to the measures that were analysed. With this approach, we cannot draw any conclusions on which is the best measure, only which is the best from the analysed range of measures.

For PFOS, the remaining industrial sources excepted from the EU ban were selected for analysis: Metal (chromium) plating, Manufacture of semiconductors and Manufacture of photographic material. For each of these industrial sources, the measure “substitution” was investigated. Based on available information, metal (chromium) plating shows the highest emission factor of reviewed industries. Due to high emission factors, the measures “Improvement of BAT and revision of BREF document for metal surface treatment” and an additional end of pipe technology (AC filter) were also evaluated. The proven technology “AC filter” was chosen because it is available and shows good cost effectiveness, as confirmed by a German study which compares different end of pipe technologies for waste water from metal (chromium) plating[25].

This selection of source-measure combinations is subject to high uncertainties. As accurate information is not available, this selection is based on approximations of size of sources, emission factors, effectiveness and costs of measures. Obtaining accurate information is hindered by dynamic change in emission patterns due to recent regulation and confidential business information (CBI).

For PFOA, there is even less information available on the size of industrial sources and corresponding emission factors. PFOA is not regulated on EU or international level (see Chapter 4); therefore there are no reporting duties.

As there is a voluntary agreement to phase out the use of PFOA in fluorotelomer manufacture and dispersion processing by 2015, this source was excluded from analysis. For the industrial sources “manufacture of photographic material” and “manufacture of semiconductors” the measure “substitution” was investigated.

Besides the industrial sources of emission of PFOS/PFOA, urban sources are major emitters. With better regulation of industrial sources, the total load to the environment is reduced and the relative importance of urban sources increases, as also confirmed by recent OECD studies (OECD 2010). Therefore measures to reduce emissions from urban sources were included in the analysis.

These emissions from urban areas are channelled mainly through the urban infrastructure systems for waste, waste water and run off. One of the most important pathways are municipal waste water treatment plants (MWWTP). This is also due to the fact that the effluent of MWWTPs represents a direct discharge to surface water bodies[26]. MWWTPs receive waste water from households (for household products containing PFOS/PFOA, see Chapter 3.1) as well as from industrial indirect dischargers, such as metal plating facilities. In addition to that, MWWTPs often receive landfill leachates. Therefore, additional end of pipe measures at MWWTPs are considered to be important for PFOS/PFOA emission reduction and were

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[25] Fath 2008: Minimierung des PFT Eintrags in die Galvanikabwässer – Minimizing PFT emission to galvanizing waste water

[26] PFOS/PFOA are very mobile in the water phase (see chapter 0)

selected for further analysis. Oxidative technologies such as ozonation are not effective against PFOS/PFOA, due to their very high persistence. Instead, the absorption based technology AC treatment was chosen for further analysis, since this technology is proven to be effective at MWWTPs and has a broadband effect on many pollutants in municipal waste water, such as heavy metals, pharmaceuticals, and other organic micropollutants.

PFOS/PFOA can also be found in urban runoff, landfill leachate and sewage sludge, but no measures are analysed for these sources, due to high uncertainties in load estimation. Generally, the load from urban sources is subject to high uncertainties and may be very variable in time and space.

Other potential sources of PFOS/PFOA are excluded from analysis, because firstly the substances have been phased out in the EU for these uses, such as impregnation of textiles, paper and packaging, use in pesticides and other agrochemical products, paints and varnishes, soap and detergents, cleaning and polishing preparations, and fire fighting foam[27]; and secondly because available data are insufficient for quantifications and uncertainties concerning possible loads are very high, such as atmospheric deposition, mist suppressing agents in the mining industry and manufacture of liquids for hydraulic transmission.

Table 2 gives an overview of the selected measures for PFOS/PFOA. In the next chapter (chapter 6), measures are described and analysed according to the framework laid out in chapter 5.1. A comprehensive comparison between the selected and analysed set of measures is presented in chapter 7.

Table 2: Overview of analysed measures and corresponding sources of PFOS/PFOA

No.	Measure	Relevant sources
1a	Substitution of PFOS in metal (chromium) plating	Metal (chromium) plating (only PFOS)
1b	Substitution of PFOS/PFOA in semi-conductor industry	Manufacture of semi-conductors
1c	Substitution of PFOS/PFOA in photographic industry	Manufacture of photographic material
2	Improvement of BAT and revision of BREF document for metal surface treatment[28]	Metal (chromium) plating (only PFOS)
3	Advanced waste water treatment - AC	Metal (chromium) plating (industrial waste water,

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[27] The diffuse source "Use of PFOS containing fire fighting foam" is excluded from analysis, as remaining stocks have to be used by 2011.

[28] Best Available Techniques (BAT) are defined in reference documents, called BREFs, compiled by the European IPPC Bureau. BREFs are the main reference documents used by competent authorities in Member States when issuing operating permits for relevant installations (http://eippcb.jrc.es)

	treatment of industrial waste water	only PFOS)
4	Advanced waste water treatment - AC treatment of municipal waste water	MWWTPs (municipal waste water)
5	Public awareness raising	PFOS/PFOA in products
6	Awareness raising for enterprises	industrial/commercial users

6 Description and Analysis of Measures

6.1 Measure 1a: Substitution of PFOS in metal (chromium) plating

6.1.1 Description of source

PFOS is used as mist suppressant for non-decorative hard chromium (VI) plating and as wetting agent for use in controlled electroplating systems. These applications are exempted from the EU ban, if “the amount of PFOS released into the environment is minimised, by fully applying relevant best available techniques[29]”.

Metal plating facilities are regulated by the integrated pollution prevention and control Directive (IPPC[30]), if the bath volume exceeds 30 m³. But there are many small and medium-sized enterprises (SMEs) in this sector[31], which may not be covered by the IPPCDirective.

The main applications for the final product are heavy duty engines (marine, etc.), rolling mill bearings (steel and non-ferrous metal), rollers (in paper mills), aerospace undercarriage and control components, medical equipment, automotive shock absorbers (ACEA, 2004, cited in STM BREF 2006), but also e.g. sanitary applications, such as water taps (see e.g. Fath 2008)[32].

PFOS is used as process aid in metal plating, but the final product does not contain any PFOS, and therefore does not contribute to urban stock via products. But many facilities

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[29] Review of BAT can be found in chapter 6.4 Measure 2:

[30] Integrated pollution prevention and control (IPPC Directive), Directive (2008/1/EC)

[31] Surface treatment of metals and plastics, which also comprises chromium plating, is carried out in more than 18 300 installations (both IPPC and non-IPPC) in Europe, ranging from small private companies to facilities owned by multinational corporations. The large majority are small or medium-sized enterprises (SMEs, [61, EC, 2002]). Around half of the installations are surface treatment shops within another installation typically also an SME. The installations are very diverse (CETS, 2002, 104, UBA, 2003, cited in STM BREF 2006).

[32] Fath 2008: Minimierung des PFT Eintrags in die Galvanikabwässer – Minimizing PFT emission to galvanizing waste water

seem to be indirect dischargers to MWWTPs (after pre-treatment to remove metals, see e.g. Fath 2008).

6.1.2 Description of measures

In this chapter, different options for substitution of PFOS in metal plating are reviewed: substitution with polyfluorinated substances and substitution with non fluorine substances. Both are drop in substitutes and require no change in process design

In chrome plating PFOS works by lowering the surface tension and forming a single foamy film barrier of a thickness of about 6 nm on the surface of the chromic acid bath, and thus reduces airborne loss of chromium-VI from the bath and decreases exposure of workers to this carcinogenic agent[33] (POPRC 2010). Therefore the performance of the substitute is a crucial issue for workplace safety.

Other bottlenecks to substitution are resistance against a corrosive environment (caused by the chromium acidic electrolyte) and stability of the mist suppressing property (Bruinen de Bruin et al. (2010)[34]). Considering the extreme chemical properties needed for this application, another bottleneck to substitutes is a significant better environmental performance than PFOS.

Adaptation of processes: According to industry information, switching to trivalent chrome electroplating (process oriented measure) is not possible for hard chrome plating (POPRC 2010). Physical barriers for aerosol forming (balls or nets), as well as adapted ventilation are being investigated, but are possibly not as effective and may therefore compromise workplace safety (POPRC 2010). Future physical solutions, in the form of adapted ventilation and other mechanical measures, would have the advantage of avoiding use and emissions of chemicals (PFOS or substitute), but further research is needed on this emerging measure. The crucial point for evaluation of this measure is workplace safety (performance against aerosol formation).

Drop-in substitutes are available for hard chrome electroplating. Often polyfluorinated[35] substances are used as substitutes. In a recent study from Denmark (Poulsen *et al.* 2011) a polyfluorinated substitute was found, based on 1H,1H,2H,2H-perfluorooctane sulfonic acid (H4PFOS), equal to PFOS in performance and price. These results are also supported by a German study (Fath et al. 2010).

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[33] Class 1 carcinogen (ref)

[34] Bruinen de Bruin et al. 2010: Estimation of emissions and exposures to PFOS used in industry - An inventory of PFOS used in metal plating and fire fighting in NL, National Institute for Public Health and the Environment, RIVM Report 601780002/2009

[35] ”Poly” means that many of the hydrogen atoms in the alkyl chain have been replaced with fluorine; ”per” means that all the hydrogen in the alkyl chain has been replaced with fluorine.

6.1.3 Secondary environmental effects

Polyfluorinated substances such as 1H, 1H, 2H, 2H-perfluorooctane sulfonic acid are an improvement compared to PFOS in terms of toxicity and bioaccumulation potential. This is most probably due to the lower number of highly stable C-F bonds in these molecules (van Putte 2010). The perfluorinated part of the substance is not degradable, but the non-fluorinated part can be degraded. It can be expected that the stable non degradable end product of 1H,1H,2H,2H-perfluorooctane sulfonic acid is a C6-perfluorinated substance, which is likely 10-1000 times less toxic and bioaccumulative than PFOS with its C8-chain (Poulsen *et al.* 2011).

In spite of this improvement compared to PFOS, the viability of polyfluorinated substances as environmentally compatible substitutes is often questioned, on account of their great stability and possible contamination of groundwater and drinking water (UBA 2009)[36]. The environmental and health performance of substitutes has to be assessed carefully in targeted studies by industry and the research community. A full assessment is outside the scope of this study. Also potentially important aspects such as increased amounts of substitute necessary for comparable performance or decreased effectiveness of end-of-pipe measures for the substitute have to be taken into account. This is especially important in cases of high emission factors.

Concerning future physical solutions the crucial point for evaluation is workplace safety (performance against aerosol formation).

6.1.4 Technical feasibility

Polyfluorinated substitutes are commercially available (reference year 2010) and reports from long term tests are available (Poulsen *et al.* 2011, Fath *et al.* 2010). Future physical solutions are an emerging measure, but targeted research is needed.

6.1.5 Secondary socio-economic effects (including indirect costs)

No secondary socio-economic effects are expected, since available substitutes seem to be moderately priced (same as PFOS based products) and can be operated as drop in. Workplace safety and health of workers seem to be maintained at high standards. For future physical solutions workplace safety (performance against aerosol formation) is crucial.

6.1.6 Geographical and time scale of effects

According to the document “Implementation of the restriction on PFOS under the Directive 2006/122/EC – electroplating applications and fire fighting foams containing PFOS stocks”

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[36] UBA 2009, UBA Background paper “Do without Per- and Polyfluorinated Chemicals and Prevent their Discharge into the Environment“: http://www.umweltdaten.de/publikationen/fpdf-l/3818.pdf

issued by the European Commission on 29 January 2010, only Germany, Sweden and Finland reported use of PFOS in metal plating. The use in Denmark is confirmed by Poulsen *et al.* 2011. The remaining EU countries in the Baltic Sea catchment area reported that they do not use PFOS.

6.1.7 Political enforceability

National or regional regulations can be effective for individual installations and the relevant EU directive foresees a review process for the exemptions.

6.1.8 Cost-effectiveness analysis

For cost effectiveness analysis, two different scenarios for cost and effectiveness of the measure are applied, based on the approach presented in the preceding chapters. These are combined with approximated load reductions to give ranges of cost effectiveness.

The following assumptions are made: The used amount in EU is assumed to be 4 t/a (2010)[37], emission factor to water is assumed to be medium to high (5% - 50%[38]) and the total load from this source in EU is estimated to be 200-2000 kg per year. Generally the uncertainties for these assumptions are high.

In scenario M1 for polyfluorinated drop in substitute the formulations containing H4PFOS have costs comparable to those with PFOS (Poulsen *et al.* 2011, Fath *et al.* 2010). The cost effectiveness of this substitution is estimated to be 100-1000 €/kg to account for potential enhanced need for surveillance.

In scenario M2 concerning future physical solutions, an estimate from Canada gives a cost of 3.9 M USD/a (5.4 M€/a[39]) needed for improved ventilation and other mechanical measures (discounted over 25 years, Canada 2007 cited in POPRC 2007). Scaling this estimate to the EU using population as proxy[40] results in a cost estimate of 80 M€/a. Based on this cost approximation, a cost effectiveness of 40-400 T€/kg is estimated.

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[37] European Commission. 29 January 2010. Implementation of the restriction on PFOS under the Directive 2006/122/EC – electroplating applications and fire fighting foams containing PFOS stocks.

[38] Lower estimate: emission factor stated in reporting to EC (European Commission. 29 January 2010. Implementation of the restriction on PFOS under the Directive 2006/122/EC – electroplating applications and fire fighting foams containing PFOS stocks)
Higher estimate according to Buser and Morf 2009. This substance flow analysis (SFA) uses 45% (20-80%) as emission factor, RPA (2004) and Bruinen de Bruin et al. 2010 use emission factors of 99% (Bruinen de Bruin et al. 2010: Estimation of emissions and exposures to PFOS used in industry - An inventory of PFOS used in metal plating and fire fighting in NL, National Institute for Public Health and the Environment, RIVM Report 601780002/2009)

[39] For USD to EUR a factor of 1.39 is used (baseline 2008)

[40] Canada 33 739 900 inhabitants, EU population 497.5 million, Lanzieri 2008 gives a scaling factor of 14.75.

6.2 Measure 1b: Substitution of PFOS/PFOA in manufacture of semi-conductors

6.2.1 Description of source

According to industry information reported in POPRC (2007) and Van Putte et al. (2010), PFOS or PFOA are used in anti-reflective coatings in combination with photoresists. In this high tech sector the performance of the chemical is crucial for product quality. Chemical formulation of photolithography[41] products occurs under highly automated, largely closed system conditions. The same process for electronics fabrication is similarly automated, with a low volume of PFOS or PFOA used, and use of protective equipment. Chemical isolation is also an intrinsic part of quality control procedures. Emission factors are relatively low, as enclosed processes are employed and most waste is incinerated. There is no residual PFOS or PFOA compound present in manufactured products and therefore no contribution to urban stock.

6.2.2 Description of measure

According to industry information, there is no substitute available for PFOS or PFOA for manufacture of semi conductors (POPRC 2007). The costs for development of a future substitute are estimated in (POPRC 2007). It is likely that this substitute would be based on polyfluorinated substances.

6.2.3 Secondary environmental effects

As the substitute would likely be based on polyfluorinated substances, see chapter 6.1.3.

6.2.4 Technical feasibility

No substitutes are commercially available (reference year 2010). Therefore, it is an emerging measure.

6.2.5 Secondary socio-economic effects (including indirect costs)

As semi-conductors are a “high quality – high price” product, negative secondary socio-economic effects may be minor. On the other hand, global competition exists and production may be outsourced to countries with less regulation.

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[41] etching of conductors

6.2.6 Geographical and time scale of effects

According to industry, innovation cycles may take up to 15 years.

6.2.7 Political enforceability

National or regional regulations can be effective for individual installations and the relevant EU directive foresees a review process for the exemptions.

6.2.8 Cost-effectiveness analysis

Based on information from industries (POPRC, 2007) development costs for a new photoresist system can be estimated to add up to 700 MUSD (973 M€) over a 5-year development period. The time span for analysis is 25 years and for emission reduction over 20 years. No additional running costs were assumed.

The following assumptions are made: The used amount in EU is assumed to be 0.5 – 1 t per year for PFOS in critical applications (uncritical uses ended in 2007 according to industry information[42]) and emission to water is assumed to be approximately 5-10% (6 kg/a[43] to 50[44] kg/a). As there is no information available on used amount of PFOA (other than confirmation of use (van Putte et al. 2010)), the same rough estimate as for PFOS is used for PFOA.

In scenario S1, assuming that PFOS and PFOA are substituted individually, the emission reduction (over 20 years) equals 120-1000 kg of PFOS and 120-1000 kg of PFOA. Cost effectiveness lies in the range of 1-8 M€/kg PFOS and 1-8 M€ of PFOA.

In Scenario S2, assuming that PFOS and PFOA are replaced by a single substitute, emission reduction (over 20 years) equals 240-2000 kg of PFOS and PFOA. Cost effectiveness lies in the range of 0.5-4 M€/kg of PFOS and PFOA.

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[42] (WSC 2008)

[43] (WSC 2008)

[44] (SIA 2006a quoted in POPRC 2006)

6.3 Measure 1c: Substitution of PFOS/PFOA in manufacture of photographic material

6.3.1 Description of source

In the photo industry PFOS-related substances (tetraethylammonium perfluorooctane sulfonate and perfluorooctyl sulfonamidopropyl quaternary ammonium iodide) have been used in manufacturing film, paper and plates. These PFOS-related compounds function as dirt rejecters and friction control agents and they reduce surface tension and static electricity. Imaging materials that are very sensitive to light (e.g. high-speed films) benefit particularly from the properties provided by PFOS-based materials. The concentration of PFOS-related substances in coatings of films, paper and plates is in the range of 0.1–0.8 $\mu g/cm^2$ (POPRC 2010). World consumption of PFOS for colour film production fell from 23 tonnes in 2000 to 8 tonnes in 2004, due to the spread of digital photography. Current annual consumption in the European Union's photographic industry is 1 tonne (POPRC 2010, RPA 2004).

According to van Putte et al. (2010), PFOS and PFOA have comparable critical applications in the photographic industry. According to I&P Europe (2010), the photo imaging industry has already discontinued all non-critical uses of PFOA-related substances. The remaining uses accounted for 2 t per year in 2008. Both PFOS and PFOA remain in the (coated) product[45] and may therefore contribute to emissions from urban stock (e.g. via MWWTP) or from recycling facilities.

6.3.2 Description of measure

According to industry information, there is no substitute available for PFOS or PFOA in the manufacture of photographic material (POPRC 2007). The costs for future development of a substitute are estimated in POPRC (2007). It is likely that this substitute would be based on polyfluorinated substances.

Properties that alternatives must have in order to match the quality of PFOS or PFOA compounds include dynamic surface tension capability, antistatic property, solubility, photoinactivity and stability against heat and chemicals. According to the I&P Europe - Imaging and Printing Association (Michiels 2010[46]) PFOS/PFOA-related substances also provide important safety features due to their antistatic properties preventing product damage and controlling fire and explosion hazards. Other important properties include lack of photoac-

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[45] coating of films, paper and plates is in the range of 0.1–0.8 $\mu g/cm^2$ (limit value 1 $\mu g/cm^2$). Results from Germany, reported in Buser and Morf (2009), show high concentrations of PFOS in effluent from a recycling plant for photographic material

[46] I&P Europe - Imaging and Printing Association 2010: Use of PFOA in critical photographic applications, Workshop on " PFOA and its Ammonium salt. Production, use, risk"– 4 May 2010, presentation by Michiels

tivity (no interference with the imaging process), control of surface wetting properties, and prevention of build-up of particles that can clog magnetic strip readers.

According to industry information, special products in particular, such as high-speed films and X-ray film[47] for photo imaging for medical and industrial uses (e.g. non-destructive testing), benefit from the properties provided by PFOS- and PFOA-based materials.

6.3.3 Secondary environmental effects

As the substitute would likely be based on polyfluorinated substances, see chapter 6.1.3.

6.3.4 Technical feasibility

According to industry information compiled by van Putte at al. (2010) for the European Commission, there are as yet no substitutes ready for market for the remaining critical application and no information about the cost of substitution is available. Therefore, this substitution is considered to be an emerging measure.

6.3.5 Secondary socio-economic effects (including indirect costs)

As photographic material is a “high quality – high price” product, negative secondary socio-economic effects may be minor. On the other hand, global competition exists and production may be outsourced to countries with less regulation.

6.3.6 Geographical and time scale of effects

After the development period, the measure becomes effective in eliminating emissions of PFOS and PFOA.

6.3.7 Political enforceability

National or regional regulations can be effective for individual installations. In addition to that, the relevant EU directive foresees a review process for existing exemptions.

6.3.8 Cost-effectiveness analysis

For cost-effectiveness calculations the following assumptions were made: Use in EU is assumed to be 1 t per year for PFOS (worldwide use was 23 t in 2000 and 8 t in 2004) and 2 t

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[47] Wet film processing of medical film represents worst case for emission to environment (van Putte et al. 2010).

per year for PFOA (POPRC 2010). Emissions to water are assumed to be 1-2 kg per year (0.1% for PFOS and PFOA, respectively) due to low factors for emission to water[48].

Scenario P1, which is based on previous cost estimates by RPA (2004), shows costs of US$20-40 M for reduction of roughly 15 t (worldwide in uncritical applications 2000-2004). Based on this estimate, POPRC (2007) estimates further reductions to cost more than twice as much, up to US$5 M per tonne of substitute used. For substitution of 1 t of PFOS used in the EU, the annual costs are 7 M€; for 2 t of PFOA used in EU, the annual costs are 14 M€. Cost effectiveness lies in the range of 7 M€/kg PFOS resp. PFOA.

6.4 Measure 2: Improvement of BAT and revision of BREF document for metal surface treatment

6.4.1 Description of source

See chapter 6.1.1

6.4.2 Description of measure

“Best Available Techniques” (BAT) are defined in “BAT reference documents” (BREFs) compiled by the European IPPC Bureau. BREFs are the main documents which competent authorities in member states use as a basis for issuing operating permits for installations[49].

The BREF document which defines current BAT in metal surface treatment dates from 2006[50]. As the document was written before the EU ban (Directive 2006/122/EC), it contains only few references to PFOS, giving rather general advice on PFOS emission reduction, such as closing water cycles, minimizing drag out, economic use of PFOS by measuring surface tension in the baths. In particular, the BREF document does not contain any definite reference on which waste water treatment technologies are effective for PFOS. For example AC treatment is mentioned as an option, but so is sand filtration, which is not effective for PFOS. Therefore, even with full implementation of BAT metal plating facilities

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[48] Submission of Annex E Information on PFOS and Its Precursors by the International Imaging Industry Association, the European Photo and Imaging Association, and the Photo-sensitized Materials Manufacturers’ Association (31.01.06): releases of PFOS to water and air, worldwide, were estimated to be 1.6 and 0.1 kg/year, respectively. PFOS emissions in the EU were estimated to be 1.1 kg (both air and water), see also COHIBA SFA report on PFOS and PFOA

[49] http://eippcb.jrc.es

[50] http://eippcb.jrc.ec.europa.eu/reference/brefdownload/download_STM.cfm

can have very high emission factors for PFOS[51]. Additionally, metal plating facilities with bath volumes <30 m³ are not IPPC regulated.

The revised BREF should include references to substitutions as well as to end-of-pipe technologies for metal plating facilities which are effective in eliminating PFOS. The issue of polyfluorinated substitutes should also be addressed, including possible EoP technologies for elimination of polyfluorinated substitutes.

6.4.3 Cost-effectiveness analysis

The cost for revision of the BREF should be covered from the funds made available for the regular review cycle; there is no information on costs for an earlier review.

6.5 Measure 3: Advanced waste water treatment - AC treatment of industrial waste water

6.5.1 Description of source

See chapter 6.1.1

6.5.2 Description of measure

Activated carbon (AC) filtration of industrial waste water from metal plating facilities is a promising EoP measure. A recent study from a large German facility (Fath 2010) recommends an AC filter for PFOS containing waste water (after chrome reduction). As part of this measure the spent AC is incinerated in order to ultimately destroy included PFOS.

6.5.3 Secondary environmental effects

Negative environmental side effects are low (additional energy use for operation of filter, transport and incineration of spent material). Elimination of other (organic) pollutants from waste water flow streams may contribute to positive environmental side effects.

6.5.4 Technical feasibility

Activated carbon (AC) filtration is a proven technology. Feasibility (and costs) depends on individual process design, such as availability of space for filtration step, existing storage tanks and separation or mixing of flow streams.

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[51] A recent study uses emission factors of 45% (20-80%) (Buser and Morf 2009), RPA (2004) and Bruinen de Bruin et al. 2010 use emission factors of 99%. On the other hand, industry associations report 2.7% as emission factor (ZVO 2010)

6.5.5 Secondary socio-economic effects (including indirect costs)

No information available on secondary social effects.

6.5.6 Geographical and time scale of effects

After implementation of activated carbon (AC) filtration, the measure becomes effective immediately. For geographical aspects, see chapter 6.1.6.

6.5.7 Political enforceability

Activated carbon (AC) filtration could be included in BREF document as BAT.

6.5.8 Cost-effectiveness Analysis

A recent study from a large German facility (Fath 2010) estimated investment costs of 30-60 T€ and running costs of 20-30 T€. The effectiveness of this measure is reported to be 85% (from 5.5 to 0.7 kg/a). The resulting cost effectiveness lies in the range of 5-10 T€/kg eliminated PFOS. The study stresses that costs and effectiveness are very site specific, but nevertheless the reported value is included in calculations for orientation.

6.6 Measure 4: Advanced waste water treatment - AC treatment of municipal waste water

6.6.1 Description of source

Most of the emissions from urban stock are channelled through MWWTPs, urban runoff and landfills. The types and loads of pollutants in waste water are dependent on local conditions in the urban area served, e.g. pattern of indirect dischargers[52], product use pattern, user behaviour and pollutant load from urban surfaces (roofs, streets etc.) in case of combined sewer systems.

The types and loads of pollutants in waste water vary greatly between different cities/districts/MWWTPs and can also vary markedly in time. Therefore, predicting type and load of pollutants at MWWTPs has a very high uncertainty.

In case of PFOS and PFOA, the uncertainty is heightened by the fact that precursor substances can be transformed to PFOS and PFOA during conventional[53] waste water treatment. Effluent concentrations in MWWTPs therefore often exceed influent concentrations

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[52] Industrial and commercial sites discharging to municipal sewers and MWWTP.

[53] Centralized plant with activated sludge (with/without nutrient elimination).

(Schultz et al. 2006, Sinclair & Kannan 2006, Becker et al. 2008, Bossi et al. 2008, Huset et al. 2008). The identity of precursors and their emission sources and environmental fate processes are largely unknown. Another factor adding to the uncertainty for this source is the rate of partitioning between water and solid phase (e.g. between effluent and sewage sludge[54]) (Buser and Morf 2009), as well as emissions to atmosphere (e.g. during aerobic treatment) (Ahrens *et al.* 2011).

6.6.2 Description of measure

Activated Carbon (AC) treatment for removal of pollutants from wastewater is a proven technology. AC has a large surface area and is an effective sorbant for many substances. Different technical systems are commercially available (e.g. powder (PAC) and granular activated carbon (GAC)). The technical prerequisite for the use of AC treatment is a well-functioning MWWT with low concentrations of suspended solids and dissolved organics (BOD and COD). After waste water treatment, PFCs cannot be removed from activated carbon (LANUV 2008). Therefore, in order to avoid possible releases and to ultimately destroy PFCs, the spent activated carbon must be incinerated.

6.6.3 Effectiveness

The effectiveness of AC filters at MWWTPs for elimination of PFOS/PFOA depends on the concentration range of the pollutant, technical parameters and the matrix. At well maintained MWWTPs reduction rates of 20%-75%[55] for PFOS and PFOA can be observed. At higher PFC concentrations, in the µg-range, reduction rates of up to >95% were observed.

6.6.4 Costs

Economic analysis in the Swiss project “StrategyMicroPoll”[56] found costs of 10-60 € per person and year, including discounted investment costs and running costs. However, specific costs are strongly dependent on the size of the MWWTP (e.g. due to economies of scale, large WWT show low specific costs).

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[54] In one study, the emission factor to the hydrosphere was 1.43 and the transfer coefficient to sewage sludge was 0.55 (Schultz et al. 2006), other studies found 0.73–3.89 and 4.0–40 (Loganathan et al. 2007), respectively, and 1.87 and 1.53 (Becker et al. 2008).

[55] Vecitis et al. 2009, citing earlier studies by 3M, report an efficiency of >90% for removal of PFOS and PFOA from municipal waste water by granular activated carbon GAC. A German study found a removal rate of 99% for PFOS and 95% for PFOA for spiked municipal waste water (10 µg/l). AC treatment was the most effective treatment, compared to oxidative treatment, RO, NF and others (Schröder et al. 2010). But preliminary results from COHIBA WP3 show low efficiencies (~20%). This shows that removal efficiency strongly depends on technology specificities, matrix effects, concentrations and other (local) boundary conditions

[56] http://www.bafu.admin.ch/gewaesserschutz/03716/index.html; http://www.eawag.ch/forschung/eng/schwerpunkte/abwasser/strategie_micropoll/index

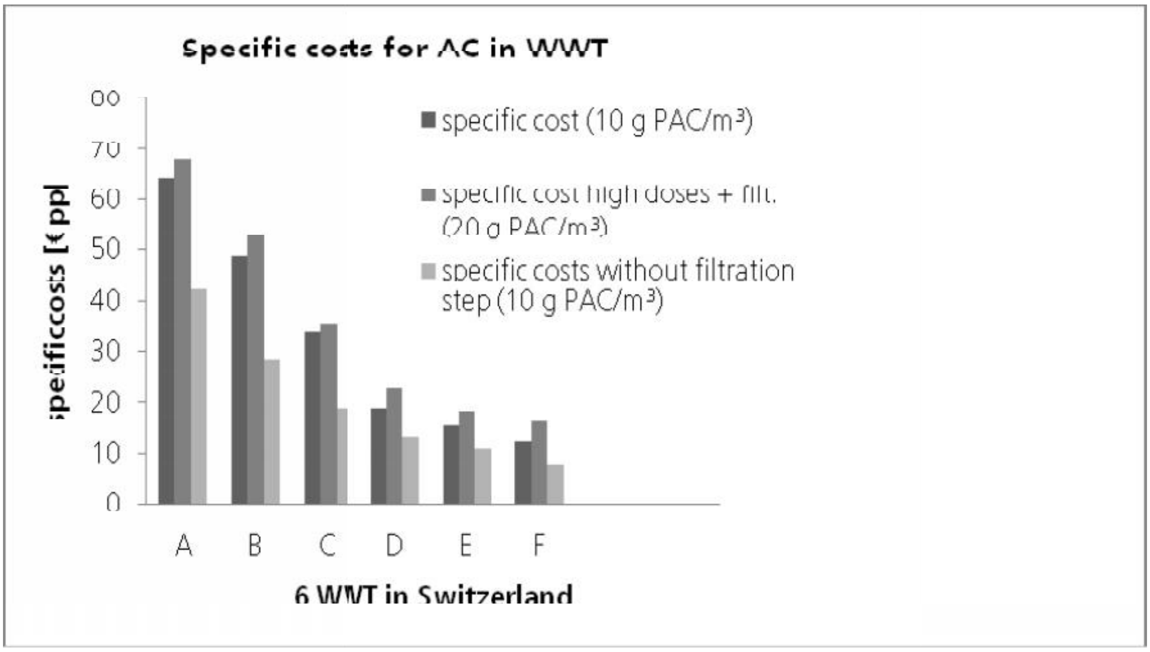

Figure 2: Specific costs per person in 6 MWWTP in Switzerland, economic data from Strategy-MicroPoll

6.6.5 Secondary environmental effects

AC filtration at MWWTPs, which is sometimes called the 4th stage of waste water treatment, affects PFOS and PFOA emissions as well as the emissions of the other 11 HS of special concern to the Baltic Sea, which are typically present in municipal waste water in very low concentrations. AC filtration also potentially has major positive secondary environmental effects on other pollutants, such as heavy metals, organic micropollutants (which are not on the HELCOM list), pharmaceuticals and their metabolites or endocrine disrupters. But also negative secondary environmental effects can be assumed in terms of increased energy use and GHG emissions through both, construction and operation of AC treatment, and through the manufacture of activated carbon[57].

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[57] Weighing environmental advantages and disadvantages of advanced wastewa-ter treatment of micro-pollutants using environmental life cycle assessment. Water Sci Technol. 2008;57(1):27-32. Wenzel H, Larsen HF, Clauson-Kaas J, Høibye L, Jacobsen BN.).

6.6.6 Technical feasibility

AC treatment is a proven technology, but the technical prerequisite is a well-functioning MWWT with low concentrations of suspended solids and dissolved organics (BOD and COD). Also skilled personnel is required for operation and maintenance (O&M) although this is likely not different from O&M of large MWWTPs.

6.6.7 Secondary socio-economic effects (including indirect costs)

If large MWWTPs are equipped with a "4th treatment stage" the question is who pays for it. One option is that the respective MWWTPs charge the cost to their clients (large MWWTPs often have lower per capita costs than smaller MWWTPs). The other option is to have the costs paid by all citizens (e.g. via taxes), as the whole community benefits from a non-toxic environment. The latter option was put into practice in Switzerland, where total costs of waste water treatment rose by 6%.

6.6.8 Geographical and time scale of effects

This measure becomes effective immediately and has a technical life span of 80 years. It seems to be suitable for large plants because of economy of scale effects. In BSR approximately 50% of the total waste water flow runs through large MWWTPs. In the context of the COHIBA project, especially MWWTPs near the shore are interesting targets.

6.6.9 Political enforceability

The political enforceability is good, for example in Switzerland it has been mandatory for large MWWTPs to eliminate hazardous substances since 2010.

6.6.10 Cost-effectiveness analysis

Two scenarios are derived to describe per-capita load ranges for PFOS and PFOA in MWWTP effluent: For PFOS a low load of 0.66 mg/cap*a[58] and a high load of 6.9 mg/cap*a[59] is assumed. For PFOA a low load of 0.7 mg/cap*a [60] and a high load of 4.9

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[58] Based on the concentration of PFOS in STP effluents (Lilja et al. (2010) (9.0 ng/l (n=7)), the standard volume of wastewater generated per capita (200 l d-1 eq-1, ECB 2003) and the EU population in 2008 (approximately 497.5 million, Lanzieri 2008), the yearly load in the EU is calculated to be 300 kg; see also COHIBA SFA report on PFOS and PFOA

[59] The load per capita (27 µg/day) found in an EU-wide monitoring campaign by JRC (Pistocchi and Loos 2009) gives the upper boundary level? of discharge via waste water to surface water. But this figure also includes other pathways to surface water: leaching and erosion from land, atmospheric deposition on rivers, and discharge via urban runoff or losses from sewerage system (including wrongly connected pipes). The contribution of emissions from MWWTP is assumed to be 50%. This estimate is backed up by MWWTP studies, which often show even higher loads per capita. Studies in Switzerland and Germany found MWWTPs to be the major source of PFC river pollution (Huset *et al.* 2008 and Becker *et al.*2008)

mg/cap*a[61] is assumed. The effectiveness of AC treatment in removing PFOS and PFOA from municipal waste water is assumed to be 25%-75%[62].

“Scenario WW” is based on cost approximations from the Swiss project strategy Micro-Poll[63] which estimated costs for AC treatment of 15 €/cap*a for large MWWTPs[64]. With higher efficiency of the measure (75%), cost effectiveness lies in the range of 4-40 M€/kg for PFOS and 5-38 M€/kg for PFOA. With lower efficiency of the measure (20%), costs for reduction of 1 kg are much higher, in the range of 14-150 M€/kg for PFOS and 20-143 M€/kg for PFOA.

As the measure has cross substance effects on multiple hazardous substances, the combined cost effectiveness lies in the range of 1.7-14 M€/ kg PFOS plus PFOA resulting in a higher efficiency of the measure (75%). With lower efficiency of the measure (20%), the combined cost effectiveness lies in the range of 3-40 M€/ kg PFOS plus PFOA.

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[60] Based on the concentration of PFOA in STP effluents (Lilja et al. (2010) (9.0 ng/l (n=7)), the standard volume of wastewater generated per capita (200 l d-1 eq-1, ECB 2003) and the EU population in 2008 (approximately 497.5 million, Lanzieri 2008), the yearly load in EU is calculated to be 300 kg (see also COHIBA SFA report on PFOS and PFOA)

[61] The load of PFOA per capita (19 µg/day PFOA per capita, in absence of industrial point sources), found in an EU-wide monitoring campaign by JRC (Pistocchi and Loos 2009) gives the upper boundary level of discharge via waste water to surface water, analogous to the estimate for PFOS. The contribution of emission from MWWTP is assumed with 70%. This estimate is backed up by MWWTP studies, from the U.S. and Switzerland with 11 resp. 12 µg/day per capita (representing 60%), and 30 µg/day per capita in Bayreuth, Germany (representing 160%); also see COHIBA SFA report on PFOS and PFOA.

[62] Vecitis et al. 2009, citing earlier studies by 3M, report an efficiency of >90% for removal of PFOS and PFOA from municipal waste water by granular activated carbon GAC. A German study found a removal rate of 99% for PFOS and 95% for PFOA for spiked municipal waste water (10 µg/l). AC treatment was the most effective treatment, compared to oxida-tive treatment, RO, NF and others (Schröder et al. 2010). But preliminary results from COHIBA WP3 show low efficiencies (~20%). This shows that removal efficiency strongly depends on technology specificities, matrix effects, concentrations and other (local) boundary conditions

[63] detailed cost study from swiss project Strategy MicroPoll (discounted at 30 years); SFr. to EUR assumed with factor 0.69

[64] >100 000 population equivalents (p.e.)

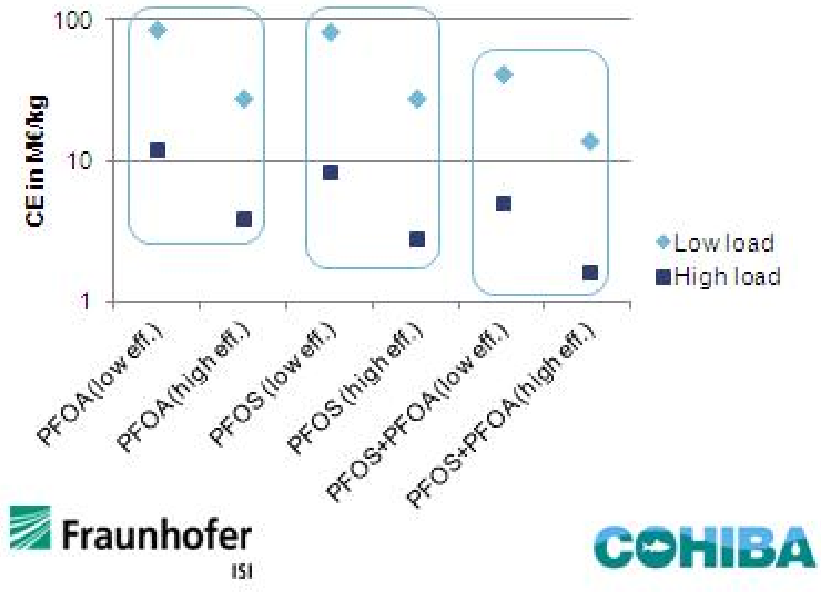

Figure 2: Comparison of cost effectiveness of measure: AC treatment of municipal waste water for elimination of PFOS, PFOA and PFOS+PFOA. Scenarios for different loads and rates of effectiveness of the measure.

6.7 Measure 5: Public awareness raising

6.7.1 Description of source

PFOA and PFOS are contained in products for “private” use in very low concentrations, for example in impregnated textiles. The total volume of these products is referred to as urban stock. Emissions from urban stock are mainly channelled through MWWTPs. The urban stock also includes products manufactured before the EU ban and voluntary industry agreements became effective. These products contain much higher concentrations of PFCs and may still contribute to emissions from “recent” urban stock, depending on technical life span of the product.

6.7.2 Description of measure

The measure “Public awareness raising” mainly targets emissions from urban stock. Consumer awareness [in the field of of hazardous substances in products is generally rather low, which can be due to the complexity of the issue. The pathways of hazardous substances in modern societies are tangled and hard to follow. Nevertheless, it can be expected that people desire to live in non-toxic cities”[65].

Awareness raising can have several positive effects:

- Consumers prefer to buy products which are labelled as non-toxic
- (e.g. teflon pans without PFOA). Via reduced demand, emissions from production can be reduced.
- Consumers buy less of certain products (“chromium” water taps or car parts) as
- they are aware that this is a specialized product (whose production requires
- hazardous substances) and that the functionality of the product is not required in the foreseen application (e.g. impregnated jackets for everyday use).
- Improved public acceptance of measures which have to be paid for by the
- community (e.g. AC treatment of waste water, see chapter 6.5)

There are no data available to quantify the costs or effectiveness of this measure.

6.8 Measure 6: Awareness raising for enterprises

6.8.1 Description of source

PFOA and PFOS are also contained in products for industrial or commercial use. Examples are mist suppressant formulations for metal plating, hydraulic fluids for aviation or fire fighting foams (until 2011). Some industrial or commercial users may discharge their waste water to public sewer systems (indirect dischargers).

6.8.2 Description of measure

Enterprises may have low awareness of how to appropriately discharge waste water or dispose of unused products as well as of possible substitutes. Therefore offering and disseminating information may contribute to reducing emissions from this source (e.g. information leaflets for enterprises or workshops[66]).

There are no data available to quantify the costs or effectiveness of this measure.

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[65] see campaign from Stockholm: Stockholm – towards a non-toxic environment http://www.stockholm.se/Global/Stads%C3%B6vergripande%20%C3%A4mnen/Klimat%20&%20Milj%C3%B6/Kemikalier%20och%20miljogifter/Nya%20gifter%20-%20nya%20verktyg/0906_towards_nontoxic_environment.pdf

[66] e.g. COHIBA seminars in eastern Baltic Sea Region (see www.cohiba-project.net)

7 Comparison of measures

A comparison of cost effectiveness of the measures described above shows “metal (chromium) plating” to be the source with the lowest costs for emission reduction [€/kg] (Scenario M1-3 left-hand side in Figure 3), followed by manufacture of semi conductors (Scenario S1-2), manufacture of photographic material (Scenario P) and measures at MWWTPs (Scenario WW1-2). The source “metal (chromium) plating” is only relevant for PFOS (PFOA is not used).

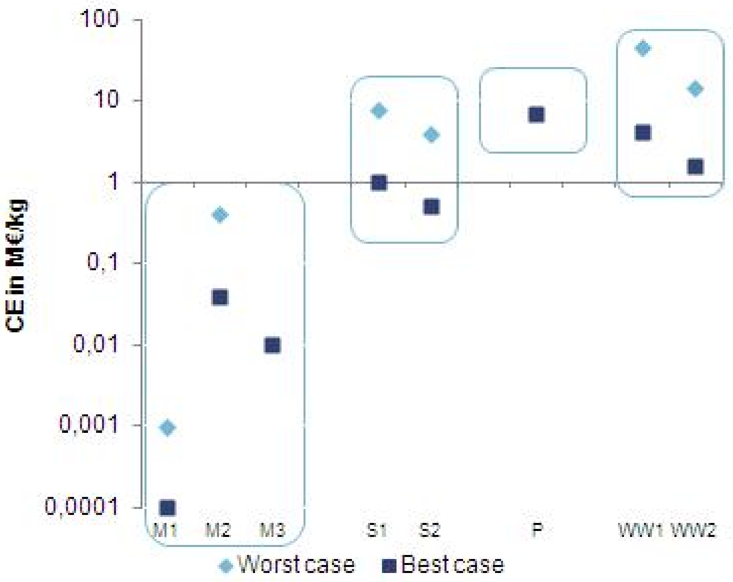

Figure 3: Comparison of the cost effectiveness of measures to reduce emissions of PFOS/PFOA. M Scenarios: Measures for metal (chromium) plating, S Scenarios: Measures for manufacture of semi conductors; P Scenarios: Measures for manufacture of photographic material; WW Scenarios: Measures for MWWTP

The following measures for reduction of PFOS emission from the industrial source “metal (chromium) plating” were evaluated (PFOA is not used in this sector): Substitution with polyfluorinated drop in substitute (M1), future physical measures (M2) (see chapter 6.1) and AC filtration as end of pipe measure (M3) (see chapter 6.5).

For this sector, the lowest costs for emission reduction [€/kg] were found for polyfluorinated drop in substitutes (Scenario M1 left-hand side in Figure 3). As these drop in substitutes are available and are markedly less toxic and bioaccumulative than PFOS, there is no reason that PFOS should continue to be exempted from the EU ban for this application. But even though they are the most cost effective measure, polyfluorinated substitutes can only be a short term solution, as they also give cause for environmental and health concerns (see chapter 6.1.3). Especially with regard to high emission factors in this sector, a better long term solution would be to additionally introduce appropriate end of pipe measures, such as AC filters, to reduce emissions of polyfluorinated substitutes. The technology is available for elimination of PFOS (Scenario M3, see also chapter 6.5) and it can be expected to be similarly cost effective in eliminating polyfluorinated substitutes[67]. These end of pipe measures for emission reduction can be implemented by improving BAT and revising the relevant BREF document (see chapter 6.4).

As many metal (chromium) plating plants are indirect dischargers to municipal sewer systems, this measure may have a downstream effect on MWWTPs. Usually, it is much more cost effective to eliminate loads of hazardous substances close to the (industrial) source. This is illustrated in Figure 4 by a comparison between treatment of industrial waste water from metal plating and treatment of municipal waste water (activated carbon). In this example, the factor is in the range of 1000-10 000. Therefore, if high loads of hazardous substances are found in MWWTPs, analysis of indirect dischargers is advisable before additional measures at MWWTP are implemented.

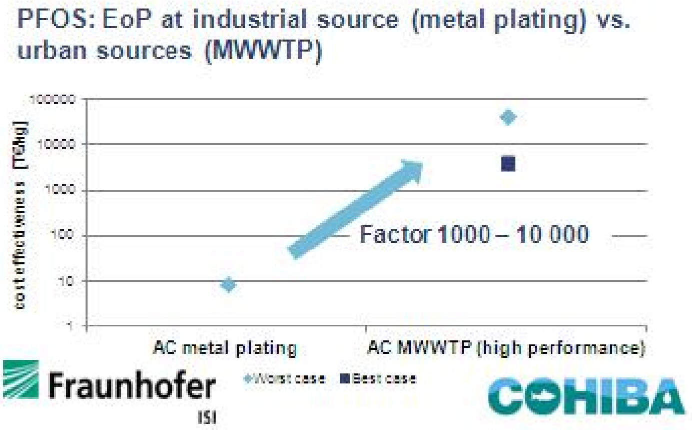

Figure 4: Comparison of the cost effectiveness of end of pipe measures for PFOS at industrial source (metal (chromium) plating) and at MWWTP

Another long term solution would be to develop physical measures to avoid aerosol formation (Scenario M3, see also chapter 6.1). This measure would avoid emissions of both PFOS and the polyfluorinated substitute. As this is an emerging measure, the uncertainties are high. The crucial point for evaluation of this future measure is workplace safety.

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[67] As the elimination efficiency may be lower due to shorter chain lengths, the process may need to be modified (e.g. longer contact time)

Compared to measures at the industrial source “metal (chromium) plating” (M1 and M3), measures at the other industrial sources: manufacture of semi conductors (Scenario S1-2, see chapter 6.2) and manufacture of photographic material (Scenario P, see chapter 6.3), have markedly higher costs per kg emission reduction. The cost effectiveness of substitution in these latter sectors lies in the range of 0.5-10 M€/kg, which is higher by a factor of 100-1000 (compared to M1 and M3). As PFOA is not used in metal (chromium) plating, the most cost effective measure for this substance is substitution in manufacture of semi conductors (Scenario S1-2), especially if a single (combined) substitute can be developed for PFOS/PFOA (Scenario S2). As this is an emerging measure, the uncertainties are high.

These substitutes for PFOA in the manufacture of semi conductors (Scenario S1-2, see chapter 6.2) and manufacture of photographic material (Scenario P, see chapter 6.3) are not yet available. As these are emerging measures, uncertainty is high and targeted research is needed. The substitutes will likely be based on polyfluorinated substitutes, which are also a cause of concern (see chapter 6.1.3). Therefore, the emission factors to the environment of these future polyfluorinated substitutes should be kept as low as possible. Emission factors to water are reported to be 0.1% for manufacture of photographic material and 10% for manufacture of semi conductors. No additional end of pipe technologies for these industrial sources have been evaluated in this study.

Photographic material may contribute to emissions of PFOS/PFOA from urban stock or recycling facilities, as the chemicals stay in the coated products. As it was not possible to quantify these emissions, they are not included in the calculation of cost effectiveness. Inclusion may significantly lower the costs per kg emission reduction.

Besides measures at industrial sources, measures at urban sources can also reduce emissions of PFOS/PFOA, such as advanced treatment of municipal waste water by activated carbon (see chapter 6.6). Municipal waste water contains hazardous substances originating from urban stock (products) and indirect dischargers, e.g. metal plating facilities. Standard waste water treatment is not effective for PFOS and PFOA (see chapter 0).

The cost effectiveness of advanced treatment of municipal waste water by activated carbon is subject to high uncertainties, even though technology is available and proven. This is mainly due to uncertainties about the load of PFOS and PFOA (and precursor substances) in municipal waste water and its dynamics (timeline of emissions from urban stock). Large uncertainties are also due to differences in the elimination efficiency of the measure, which depends on concentrations of hazardous substances and the presence and concentrations of other organic substances (matrix effects).

Therefore, to evaluate the cost effectiveness of advanced treatment of municipal waste water by activated carbon, we used two different scenarios for loads of PFOS and PFOA in municipal waste water and two different scenarios for elimination efficiency (high: 75% elimination efficiency, low: 25% elimination efficiency, for scenario description and cost calculations, see chapter 6.6). For the individual substances the cost effectiveness lies in the range of 5-50 M€/kg with high effectiveness and 10-100 M€/kg with low effectiveness.

From a single-substance specific perspective, the costs per kg emission reduction tend to be higher compared to treatment at the industrial sources themselves, especially for PFOS. But as there are many hazardous substances in municipal waste water and activated carbon has a broadband effect, a cross substance perspective is needed. For example, adding up the effect on PFOS and PFOA improves the cost effectiveness, because the (combined) load of hazardous substances is higher. Besides the 11 hazardous substances which are the focus of

BSAP, the measure also reduces the emission loads of other pollutants such as pharmaceutical substances and their metabolites.

The dependency of the cost effectiveness on the combined load of hazardous substances is illustrated in Figure 5. Figure 5 shows that the costs per kg emission reduction decrease exponentially with higher loads per person and year in MWWTP influent. With high elimination efficiency, cost effectiveness is below 1 M€/kg when the combined load of hazardous substances in MWWTP influent is higher than 20 mg per person and year (60 mg with low elimination efficiency).

Therefore, when taking into account its effect on all 11 hazardous substances, it may be worthwhile to consider making advanced treatment of municipal waste water an element of a cost effective strategy for reducing emissions of hazardous substances in the BSR. This is discussed in the COHIBA recommendation report.

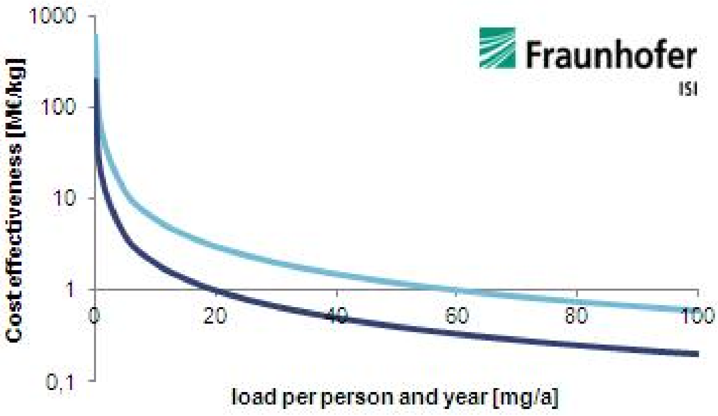


Figure 5: Cost effectiveness of AC treatment of municipal waste water as a function of the load of hazardous substances in waste water influent (assumed costs 15 € per person and year at large MWWTPs; upper curve (light blue): 25% elimination efficiency, lower curve (dark blue): 75% elimination efficiency

The described measures to reduce PFOA and PFOS emissions should be flanked by awareness raising measures. Public awareness of the issue of hazardous substances is in general rather low, which can be due to its complexity. The pathways of hazardous substances in modern societies are tangled and hard to follow. Everyday products contain a multitude of hazardous substances in very low concentrations, and little is known about their chronic and combined (cocktail) effects. But it can be expected that people desire to live in "toxfree cities". Awareness raising can have several effects, including improved acceptance of measures which have to be paid for by the community, such as advanced treatment of municipal waste water. Besides public awareness raising, awareness raising among enterprises is also important, especially for enterprises not regulated by the IPPC Directive, such as recycling facilities or small to medium metal plating facilities. There are no data available to quantify the costs or effectiveness of these measures.

Table 3: Comparison of measures for emission reduction of PFOS and PFOA

Measures	**Effectiveness**	**Cost**	**Secondary environmental effects**	**Technical feasibility**	**Secondary socio-economic effects**	**Geographical/time scale of effects**	**Political enforceability**	**Cost effectiveness**
Substitution of PFOS in metal (chromium) plating	+++	+++	-/+	+++	+	+++, DE, DK, . SE, FI	+++	+++
Substitution of PFOS/PFOA in semi-conductor industry	+++	+	-/+	+	+	++	+++	+
Substitution of PFOS/PFOA in photographic industry	+++	+	-/+	+	+	++	+++	+
Improvement of BAT and revision of BREF document for metal surface treatment	+++	+++	+	+++	+	+++ DE, DK, . SE, FI	+++	++
Advanced waste water treatment - AC treatment for industrial waste water	+++	++	++	+++	+	+++ DE, DK, . SE, FI	+++	++
Advanced waste water treatment - AC treatment for municipal waste water	++	+	+++	+++	+	++	+	+
Public awareness raising	?	++	+++	+++	+	++	+++	?
Awareness raising for enterprises	?	++	+++	+++	+	++	+++	?

Key

+	Only limited effectiveness	Very high costs	Negative secondary environmental effects	Technology not yet available or very new management option	Negative or no socio-economic effect	Only long-term realization, > >10 years	Strong political opposition expected	Costs per kg (or per Teq) emission reduction high
++	Partially effective	Moderate costs	Several positive secondary environmental effects	Pilot process or transferrable non-technical measures available	Some positive socio-economic effects	Medium-term realization, approx. 3 -10 years	Political opposition expected	Costs per kg (or per Teq) emission reduction medium to high
+++	Substantial effects	Low costs	Numerous positive	proven and available	Many positive socio-	Rapid realization poss-	Political support	Costs per kg (or per Teq)

			secondary environmental effects	technology	economic effects	ible, 1-3 years	expected	emission reduction medium to low

8 Conclusion

In the preceding chapter, different measures for reduction of PFOS and PFOA emissions were compared. From a single-substance specific perspective, the most cost effective measure for reducing PFOS emissions was determined to be substitution by polyfluorinated drop in systems in metal (chromium) plating (Scenario M1 left side in Figure 3).

As these drop in substitutes are available and are markedly less toxic and bioaccumulative than PFOS, there is no reason that PFOS should continue to be exempted from the EU ban for this application. But even though they are the most cost effective measure, polyfluorinated substitutes can only be a short term solution, as they also give cause for environmental and health concerns (see chapter 6.1.3). A more sustainable long term solution would be to additionally introduce appropriate end of pipe measures, such as AC filters, to reduce emission of polyfluorinated substitutes. These end-of-pipe measures for emission reduction can be implemented by improving BAT and revising the metal surface treatment BREF, which is one of the recommendations of this guidance document (see chapter 6.4).

For PFOA, substitution of PFOA in manufacture of semi conductors (Scenario S1-2) was found to be the most cost effective measure, especially if a single (combined) substitute can be developed for PFOS/PFOA (Scenario S2). As this is an emerging measure, the uncertainties are high and development time is needed before the measure can become effective. As these future substitutes will likely be based on polyfluorinated substances, the same reasoning as above applies. In case of high emission factors, appropriate end of pipe measures should additionally be researched and applied to avoid high loads of the substitutes to environment.

Besides measures at industrial sources, measures at urban sources can also reduce emission of PFOS/PFOA, such as advanced treatment of municipal waste water by activated carbon (see chapter 6.6). Even though this technology is available and proven, its cost effectiveness is subject to high uncertainties. The cost effectiveness of advanced treatment of municipal waste water is strongly dependent on the combined load of hazardous substances per person and year in incoming municipal waste water and the removal efficiency of the measure.

Therefore, before introducing advanced waste water treatment, the combined load of hazardous substances per person should be assessed on individual facility level for large MWWTPs to decide whether the cost effectiveness of the measure is competitive. It can be expected that the combined load will vary for different urban areas, due to different user behaviour and different patterns of indirect dischargers. But on the other hand, if high loads of one hazardous substance are found in incoming municipal waste water, analysis of indirect dischargers to this MWWTP is advisable. Generally, it is more cost effective to reduce emissions close to their industrial sources. In the presented example, the factor for PFOS is in the range of 1000-10 000.

From a single substance specific perspective treatment at MWWTPs tends to be more costly per kg of reduced emissions than treatment at the industrial sources themselves, especially for PFOS. However, a cross substance perspective is needed for evaluation, as there are many hazardous substances in municipal waste water and activated carbon has a broadband effect. Therefore, when taking into account the effect on all 11 hazardous substances, it may be worthwhile to consider making advanced treatment of municipal waste water an element of a cost effective strategy for reducing emissions of hazardous substances in the BSR. This issue is discussed in COHIBA recommendation report.

The described measures for reduction of PFOA and PFOS emissions should be flanked by awareness raising measures for the public and enterprises, since these measures are relevant for all 11 hazardous substances which are the focus of BSAP.

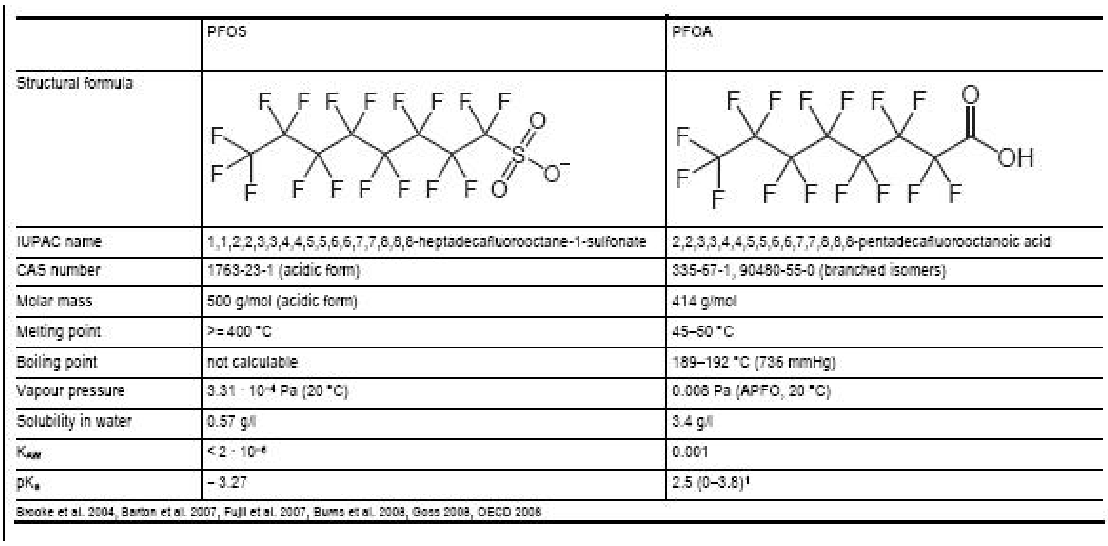
Table 3 gives an overview of evaluated parameters for measures for emission reduction of PFOS and PFOA. Cost effectiveness is an important criteria for selection of measures for emission reduction, but other criteria, such as secondary environmental effects, technical feasibility or political enforceability are also important.

Information in Table 3 is based on the data presented in the respective chapters. The data has inherently large uncertainties. As accurate information is not available, the evaluation is based on approximations of size of sources, emission factors, effectiveness and costs of measures.

One of the main challenges in evaluating reduction measures is the lack of reliable and up to date information on loads to the environment. As accurate information is not available, the evaluation is based on approximations of size of sources, emission factors, effectiveness and costs of measures. Obtaining accurate information is hindered by dynamic change in emission patterns due to recent regulation of PFOS and issues with confidential business information (CBI). For PFOA, there is even less information available especially on industrial sources and corresponding emission factors. PFOA is not regulated at EU or international level (see Chapter 4), therefore there are also no reporting duties. This regulatory gap for PFOA should be addressed.

A Additional background information

A.1 Additional information on chemical properties



	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

Figure 6: Important physico-chemical properties of PFOS and PFOA (from Buser and Morf 2009)

Table 4: Commonly used abbreviations (from Andersson 2010)

Abbreviation	Explanation
APFO	Ammonium salt for PFOA, the most commonly used salt of PFOA
Fluoropolymers	Fluorocarbon based polymers, *e.g.* polytetrafluoroethylene (PTFE)
Fluorotelomers	Fluorocarbon based telomers
PFAS	perfluorinated alkyl sulfonates
PFO	perfluorooctanoate
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
PFOSA	perfluorooctane sulfonic acid
POSF	perfluorooctane sulfonyl fluoride (CAS nr: 307-35-7); starting material for PFOS-related chemicals
xFOSAs	perfluorooctane sulfonamides (N-methyl and N-ethyl FOSA; xFOSAs)
xFOSEs	N-methyl or N-ethyl sulfonamidoethanols

Table 5: Selected CAS numbers for PFOS and PFOA as listed in Mehtonen 2009

Compound	CAS number	Comment
PFOS		The anion does not have a CAS number and is not commercially available (KemI 2004)
Perfluorooctane sulfonic acid	1763-23-1	
Potassium salt for perfluorooctane sulphonic acid	2795-39-3	
Diethanolamine salt for perfluorooctane sulphonic acid	70225-14-8	
Ammonium salt for perfluorooctane sulfonic acid	29081-56-9	
Lithium salt for perfluorooctane sulfonic acid	29457-72-5	
PFOA	335-67-1	
Ammonium salt for PFOA, APFO	3825-26-1	
Sodium salt for PFOA	335-95-5	
Potassium salt for PFOA	2395-00-8	
Silver salt for PFOA	335-93-3	
Fluoride salt for PFOA	335-66-0	
Methyl ester for PFOA	376-27-2	
Ethyl ester for PFOA	3108-24-5	

A.2 Additional information on existing regulations

This chapter gives additional information to Chapter 4 Existing regulations on page 10.

A.2.1 Directive 2006/122/EC (PFOS)

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 $\mu g/m^2$ 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.

A.2.2 Stockholm Convention on Persistent Organic Pollutants

In 2005, the Swedish government proposed PFOS for listing in Annex A of the Stockholm Convention on Persistent Organic Pollutants. The Persistent Organic Pollutants Review Committee (POPRC) adopted the risk management evaluation for PFOS in November 2007 and recommended 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, PFOS, its salts and perfluorooctane sulfonyl fluoride was listed under Annex B of the Stockholm Convention (Stockholm Convention Secretariat 2009).

A.2.3 PFOA stewardship program (PFOA)

PFOA is not regulated on EU or international level. It does not fulfill the bioaccumulation criteria of REACH, and therefore is not classified as PBT substance (only P T-substance, see Chapter 2).

Even though there is no regulation of PFOA, there is a voluntary commitment of industry to achieve reduction of emission of PFOA (US EPA PFOA stewardship program). 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.3 Important links and further reading

List from OECD portal on PFCs[68] (published by OECD 2010)

Canada

Perfluorooctane Sulfonate and its Salts and Certain Other Compounds Regulations: http://www.ec.gc.ca/CEPARegistry/regulations/DetailReg.cfm?intReg=107

Action Plan for the Assessment and Management of Perfluorinated Carboxylic Acids and their Precursors: http://www.ec.gc.ca/Publications/default.asp?lang=En&xml=2DC7ADE3-A653-478C-AF56-3BE756D81772

Proposed Regulations Amending the Prohibition of Certain Toxic Substances Regulations, 2005 (Four New Fluorotelomer-based Substances) (Long Chain PFCA Precursors): http://www.gazette.gc.ca/archives/p1/2006/2006-06-17/html/reg2-eng.html

PFOS Summary Page: http://www.ec.gc.ca/toxiques-toxics/Default.asp?lang=En&n=98E80CC6-1&xml=ECD5A576-CEE5-49C7-B26A-88007131860D

PFCA Summary Page: http://www.ec.gc.ca/toxiques-toxics/Default.asp?lang=En&n=6B9B6B28-1&xml=F68CBFF1-B480-4348-903D-24DFF9D623DC

Four New Fluorotelomer-based Substances (Long Chain PFCA Precursors) Summary Page: http://www.ec.gc.ca/toxiques-toxics/Default.asp?lang=En&n=98E80CC6-1&xml=0593FBA5-FFCA-4B9D-8D6D-70EAC1094008

United Kingdom

The UK risk reduction strategy document for Perfluorooctane Sulphonate (PFOS) has been published in 2004 and is available via this link to the UK's Department for Environment, Food & Rural Affairs Chemicals web site:

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[68] http://www.oecd.org/document/28/0,3746,en_21571361_44787844_44798236_1_1_1_1,00.html

http://www.defra.gov.uk/environment/quality/chemicals/documents/pfos-riskstrategy.pdf

Chemicals Policy
http://www.defra.gov.uk/environment/quality/chemicals/ukpolicy.htm

United States

Action Plan on long chain perfluorinated chemicals:
http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/pfcs.html

Provisional health advisories for PFOA and PFOS:
http://epa.gov/oppt/pfoa/pubs/activities.html#advisories

Significant New Use Rules on perfluoroalkyl sulfonates:
http://epa.gov/oppt/pfoa/pubs/pfas.html

Perfluorinated Acid (PFOA) and Fluorinated Telomers

http://www.epa.gov/oppt/pfoa/

Germany

German Federal Environment Agency proposes threshold values for the sake of environment and health:

http://www.umweltbundesamt.de/uba-info-presse-e/2009/pe09-046_perfluorinated_compounds_avoid_inputs_protect_the_environment.htm

Background document:

http://www.umweltdaten.de/publikationen/fpdf-l/3818.pdf

Norway
Action plan on perfluorinated substances

PFOS in textiles, impregnatingagents and fire fighting foam are banned according to the Norwegian product regulations

Proposal for a ban on PFOA in consumer products

Hazard and Risk Assessments

Canada Environment: Ecological Screening Assessment Report on Perfluorooctane Sulfonate, Its Salts and Its Precursors that Contain the C8F17SO2, C8F17SO3 or C8F17SO2N Moiety: http://www.ec.gc.ca/CEPARegistry/documents/subs_list/PFOS_SAR/PFOS_TOC.cfm

Canada Environment: State of Science Report for a Screening Health Assessment - Perfluorooctane Sulfonate, Its Salts and Its Precursors that Contain the C8F17SO2 or C8F17SO3 Moiety: http://www.ec.gc.ca/CEPARegistry/subs_list/FinalAssess.cfm

Canada Environment: Risk Assessments on Four New Fluorotelomer-based Substances (Long Chain PFCA Precursors): http://www.ec.gc.ca/subsnouvelles-newsubs/default.asp?lang=En&n=6F22A1D6-1

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RPS Advies B.V. 26 January 2010. Analysis of the risks arising from the industrial use of Perfuorooctanoic acid (PFOA) and Ammonium Perfluorooctanoate (APFO) and from their use in consumer articles. Evaluation of the risk reduction measures for potential restrictions on the manufacture, placing on the market and use of PFOA and APFO. Final Report to the European Commission, Enterprise and Industry Directorate-General.

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UK COT (Committee on toxicity of chemicals in food, consumer products and the environment). July 2009. Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment. Update statement on the tolerable daily intake for perfluorooctanoic acid.

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Technical Reports

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http://www.rivm.nl/bibliotheek/rapporten/601780002.html

Research activities at the US-EPA's Office of Research and Development

http://epa.gov/oppt/pfoa/pubs/activities.html#ord

Outcome of the UNEP Workshop on Managing Perfluorinated Chemicals and Transitioning to Safer Alternatives, Geneva, Switzerland, February 2009.
http://www.chem.unep.ch/unepsaicm/cheminprod_dec08/PFCWorkshop/default.htm

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