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Environmental risk limits for PFOS

A proposal for water quality standards in accordance with the Water Framework Directive

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Rapport in het kort

Milieurisicogrenzen voor PFOS
Het RIVM heeft wetenschappelijke milieurisicogrenzen afgeleid voor perfluoroctaansulfonaat (PFOS) in zoet en zout oppervlaktewater. Gemeten concentraties in Nederland en andere Europese landen overschrijden de in dit rapport berekende waarden voor alledrie de beschermingsdoelen: de mens (rekening houdend met visconsumptie), waterorganismen en visetende vogels en zoogdieren. De overschrijding wijst op een potentieel risico voor het waterecosysteem. Het risico voor de gemiddelde consument van vis is vanwege de veiligheidsmarges gering.

Bij de in dit rapport afgeleide waarden is uitgegaan van de methodiek behorend bij de Kaderrichtlijn Water. Bij verdere besluitvorming over PFOS op nationaal en Europees niveau worden deze waarden als uitgangspunt gebruikt, maar zijn ook andere aspecten en overwegingen van belang. In Nederland stelt de Stuurgroep Stoffen de uiteindelijke milieukwaliteitsnormen voor stoffen vast op basis van dit advies en andere overwegingen. De overheid gebruikt de milieukwaliteitsnormen voor de uitvoering van het nationaal stoffenbeleid.

Als standaard worden het ‘maximaal toelaatbaar risiconiveau’ (MTR) en het daar rekenkundig mee samenhangend ‘verwaarloosbaar risiconiveau’ (VR) bepaald. Het MTR is het niveau waarbij geen schadelijke effecten te verwachten zijn, gebaseerd op jaargemiddelde concentraties. Het MTR wordt bepaald op basis van de drie bovengenoemde beschermingsdoelen; de laagste waarde, in dit geval de consumptie van vis door de mens, bepaalt het uiteindelijke MTR voor zoetwater (0,65 nanogram per liter). Deze waarde is gebaseerd op een consumptie van 115 gram zoetwatervis per persoon per dag. Dit is ruim hoger dan de gemiddelde visconsumptie van mensen in Nederland.

PFOS wordt gebruikt in producten zoals blusschuim, schoonmaakmiddelen, lijmen en papier. De stof breekt slecht af in het milieu. PFOS hoopt zich op in organismen en is zelfs in afgelegen gebieden in zoogdieren aangetroffen. De productie en het gebruik van PFOS is recent door een aantal internationale regelingen sterk aan banden gelegd. PFOS mag alleen nog onder bepaalde voorwaarden worden toegepast in een beperkt aantal producten waarin het onmisbaar wordt geacht. Uiteindelijk wordt naar een algeheel verbod gestreefd.

Trefwoorden:
milieurisicogrenzen, PFOS, maximaal toelaatbaar risiconiveau, verwaarloosbaar risiconiveau, maximaal aanvaardbare concentratie

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Abstract

Environmental risk limits for PFOS
The National Institute for Public Health and the Environment (RIVM) has derived scientific Environmental Risk Limits (ERLs) for perfluorooctane sulfonate (PFOS) in fresh and marine surface waters. Measured concentrations in the Netherlands and other European countries exceed the ERLs for humans through fish consumption, as well as for water organisms and fish-eating birds and mammals. This indicates a potential risk for the water ecosystem. The risks for the average fish consumer are low because sufficient safety margins have been applied in the derivation.

RIVM used the methodology as required by the European Water Framework Directive for the derivation of the ERLs in this report. ERLs are scientifically derived advisory values. They serve as a scientific background for the decisions to be taken at the national and European level, where other aspects will be taken into account as well. In the Netherlands, environmental quality standards are set by the Dutch Steering Committee for Substances, based on this advice and other considerations. The Dutch government uses environmental quality standards when implementing the national policy on substances.

The MPC (maximum permissible concentration) is the level at which no harmful effects are expected, based on annual average concentrations. This MPC is based on three routes: direct ecotoxicity, secondary poisoning, and consumption of fish by humans. The lowest of these three routes determines the overall MPC. For PFOS, the consumption of fish by humans is the most critical route, which results in an MPC of 0.65 ng/L for freshwater. This route is based on a consumption of 115 grams of fish per day, which is seen as a conservative estimate.

PFOS is a surfactant and is used in a variety of products such as fire-fighting foams, cleaners, adhesives and paper. Due to the physicochemical properties of PFOS, it does not degrade well and has been found to accumulate in biota, also in mammals even in remote areas. Production and use of PFOS are strongly restrained as a result of international regulations, with a complete ban as the ultimate goal. Restricted use of PFOS is allowed in a limited number of products for which it is deemed indispensible. Its use in these products will also eventually be phased out.

Key words:
environmental risk limits, PFOS, maximum permissible concentration, maximum acceptable concentration

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The results of the present report have been discussed in the scientific advisory group INS (WK-INS). The members of this group are acknowledged for their contribution.

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List of abbreviations

BAF	Bioaccumulation Factor
BCF	Bioconcentration Factor
BMF	Biomagnification Factor
EC_x	Concentration at which x% effect is observed
ERL	Environmental Risk Limit
EU	European Union
INS	International and National Environmental Quality Standards for Substances in the Netherlands
LOEC	Lowest Observed Effect Concentration
MAC_{eco}	Maximum Acceptable Concentration for ecosystems
$MAC_{eco, water}$	Maximum Acceptable Concentration for ecosystems in freshwater
$MAC_{eco, marine}$	Maximum Acceptable Concentration for ecosystems in the marine compartment
MATC	Maximum Acceptable Toxicant Concentration, geometric mean of NOEC and LOEC
MPC	Maximum Permissible Concentration
MPC_{water}	Maximum Permissible Concentration in freshwater
MPC_{marine}	Maximum Permissible Concentration in the marine compartment
$MPC_{eco, water}$	Maximum Permissible Concentration in freshwater based on ecotoxicological data
$MPC_{eco, marine}$	Maximum Permissible Concentration in the marine compartment based on ecotoxicological data
$MPC_{sp, water}$	Maximum Permissible Concentration in freshwater based on secondary poisoning
$MPC_{sp, marine}$	Maximum Permissible Concentration in the marine compartment based on secondary poisoning
$MPC_{hhfood, water}$	Maximum Permissible Concentration in freshwater based on consumption of fish and shellfish by humans
$MPC_{hhfood, marine}$	Maximum Permissible Concentration in the marine compartment based on consumption of fish and shellfish by humans
$MPC_{dw, water}$	Maximum Permissible Concentration in freshwater based on abstraction of drinking water
NC	Negligible Concentration
NC_{water}	Negligible Concentration in freshwater
NC_{marine}	Negligible Concentration in the marine compartment
NOEC	No Observed Effect Concentration
PBT	Persistent Bioaccumulative Toxic
POP	Persistent Organic Pollutant
SRC_{eco}	Serious Risk Concentration for ecosystems
$SRC_{eco, water}$	Serious risk concentration for freshwater and marine ecosystems
TDI	Tolerable Daily Intake
TGD	Technical Guidance Document
TMF	Trophic Magnification Factor
WFD	Water Framework Directive (2000/60/EC)

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Summary

Environmental risk limits for PFOS
In 2008, a large spill of PFOS occurred during an incident at Schiphol airport. Because of this, the Ministry of VROM commissioned RIVM to derive ERLs for water. The National Institute for Public Health and the Environment (RIVM) has derived Environmental Risk Limits (ERLs) for perfluorooctane sulfonate (PFOS) in fresh and marine surface waters. Measured concentrations exceed these ERLs for humans through fish consumption, as well as for water organisms and fish-eating birds and mammals.

The ERLs in this report are scientifically derived advisory values. They can be used for further decision making on PFOS at the national and European level. In the Netherlands, environmental quality standards are set by the Dutch Steering Committee for Substances, based on this advice and other considerations. The Dutch government uses environmental quality standards when implementing the national policy on substances. RIVM used the methodology as required by the European Water Framework Directive for the derivation of the ERLs in this report. Using this methodology, potential risks for humans as well as effects on the aquatic ecosystem are taken into account.

PFOS is a surfactant, and is used in a variety of products such as fire-fighting foams, cleaners, adhesives and paper. Due to the physicochemical properties of PFOS, it does not degrade well and has been found to accumulate in biota, also in remote areas. PFOS has recently been assigned to be a persistent organic pollutant (POP) and has been added to Annex B of the Stockholm convention. Within the European Union, PFOS is a persistent, bioaccumulative and toxic (PBT-) compound. Because of these international regulations, production and use are strongly restrained, with a complete ban as the ultimate goal. Under certain circumstances, PFOS can be applied in a limited number of products for which it is deemed indispensible. Its use in these products will also eventually be phased out.

An overview of the derived ERLs is given in Table 1. The MPC (maximum permissible concentration) is the level at which no harmful effects are expected, based on annual average concentrations. This MPC is based on three routes: direct ecotoxicity, secondary poisoning, and consumption of fish by humans. The lowest of these three routes determines the overall MPC. For PFOS, the consumption of fish by humans is the most critical route, which results in an MPC of 0.65 ng/L for freshwater. Calculations are based on a consumption of 115 grams of fish per day, which is seen as a conservative estimate. Other environmental risk limits include the negligible concentration (NC), maximum acceptable concentration for ecosystems (MAC_{eco}), and serious risk concentration for water ecosystems (SRC_{eco}). The relevance of these latter two is limited, since the MAC_{eco} and SRC_{eco} do not take food chain transfer to predators and humans into account. In addition, the MAC_{eco} is based on acute data, whereas a single peak will automatically lead to long-term exposure. Since effects of PFOS will become mainly apparent in the long-term, short-term toxicity tests are not a good basis for risk evaluation. No risk limits were derived for the sediment compartment because this was outside the scope of this project.

Measurements show that in the Netherlands and other European countries, PFOS is detected in fresh surface waters in concentrations above the MPC. This is not only the case for the overall MPC, which is based on consumption of fish by humans, but also for the MPC based on secondary poisoning. In a number of cases, the MPC for direct ecotoxicity is also exceeded. The fact that MPCs are exceeded for all three exposure routes points at a potential risk for exposure via surface water.

The currently derived ERLs clearly underpin the ongoing efforts to eventually phase out the use of PFOS. Regular monitoring of PFOS is needed to investigate the potential risks for the aquatic ecosystem and to evaluate the (inter) national regulatory measures.

Table 1 Derived MPC, MAC_{eco}, NC, and SRC_{eco} values for PFOS

ERL	**MPC**		**MAC_{eco}**	**NC**		**SRC_{eco}**
	µg/L	**ng/L**	**µg/L**	**µg/L**	**ng/L**	**µg/L**
Freshwater	6.5×10^{-4}	0.65	36	6.5×10^{-6}	0.0065	930
Surface water intended for drinking water abstraction	0.53	530	n.a.	n.a.	n.a.	n.a.
Marine water	5.3×10^{-4}	0.53	7.2	5.3×10^{-6}	0.0053	930

n.a. = not applicable

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1 Introduction

1.1 Project Framework

In this report, environmental risk limits (ERLs) for surface water (freshwater and marine) are derived for perfluorooctane sulfonate (PFOS) in the context of the project 'Standard setting for other relevant substances within the WFD'. This project is closely related to the INS-project ('International and national environmental quality standards for substances in the Netherlands').

The following ERLs are considered (VROM, 2004):

- negligible concentration (NC) – concentration at which effects to ecosystems are expected to be negligible and functional properties of ecosystems must be safeguarded fully. It defines a safety margin that should exclude combination toxicity. The NC is derived by dividing the MPC (see next bullet) by a factor of 100.
- maximum permissible concentration (MPC) – concentration in an environmental compartment at which:
  1. no effect to be rated as negative is to be expected for ecosystems;
  2a no effect to be rated as negative is to be expected for humans (for non-carcinogenic substances);
  2b for humans no more than a probability for cancer incidence of 10^{-6} per year can be calculated (for carcinogenic substances). Within the scope of the Water Framework Directive, a probability of 10^{-6} on a lifetime basis is used.

  Within the scope of the Water Framework Directive the MPC is specifically referring to long-term exposure.
- maximum acceptable concentration ($MAC_{eco, water}$) – concentration protecting aquatic ecosystems for effects due to short-term exposure or concentration peaks;
- serious risk concentration (SRC_{eco}) – concentration at which possibly serious ecotoxicological effects are to be expected.

The results presented in this report have been discussed by the members of the scientific advisory group for the INS-project (WK-INS). It should be noted that the Environmental Risk Limits (ERLs) in this report are scientifically derived values, based on (eco)toxicological, fate and physicochemical data. They serve as advisory values for the Dutch Steering Committee for Substances, which is appointed to set the Environmental Quality Standards (EQSs). **ERLs should thus be considered as preliminary values that do not have an official status. It should be noted that there are several international frameworks in which PFOS is considered (see section 1.2.2 below). The ERLs as derived in this report also serve as a scientific background for the decisions to be taken within the context of, e.g., the selection of priority substances under the Water Framework Directive. The outcome of these processes is not clear as yet and may influence the decisions to be taken on the final choice of the EQS.**

1.2 Background information on PFOS

1.2.1 Substance information

PFOS is a fluorinated anion that belongs to a large group of perfluorinated substances. The PFOS anion does not have a specific CAS number but is available as a sulfonic acid and as various salts (Table 2).

Table 2 PFOS and its salts

CAS Number	Common name	Chemical name	Molecular formula	Mol. weight
N/A	PFOS anion Perfluorooctane sulfonate	1-Octanesulfonate, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-	$C_8F_{17}SO_3^-$	499.1
1763-23-1	PFOS acid Perfluorooctane sulfonic acid PFOSH	1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-	$C_8F_{17}SO_3H$	500.1
2795-39-3	PFOS potassium (K^+) salt	1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, potassium salt	$C_8F_{17}SO_3K$	538.2
29081-56-9	PFOS ammonium (NH_4^+) salt	1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, ammonium salt	$C_8F_{17}SO_3NH_4$	517.1
29457-72-5	PFOS lithium (Li^+) salt	1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, lithium salt	$C_8F_{17}SO_3Li$	506
70225-14-8	PFOS diethanol-amine (DEA) salt	1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, compd. with 2,2-iminobis[ethanol] (1:1)	$C_8F_{17}SO_3NH(CH_2CH_2OH)_2$	604.1
56773-42-3	PFOS tetraethyl-ammonium salt	1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, tetraethylammonium salt	$C_8F_{17}SO_3C_8H_{20}N$	629.1
251099-16-8	PFOS didecyldimethyl-ammonium salt	1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, didecyldimethylammonium salt	$C_8F_{17}SO_3C_{22}H_{48}N$	825.1

PFOS is a surfactant and is used in a variety of products which can be divided into three main categories of use (OECD, 2002):

- Surface treatments
    - PFOS-related chemicals produced for surface treatment applications provide soil, oil, and water resistance to personal apparel and home furnishings. Specific applications in this use category include protection of apparel and leather, fabric/upholstery and carpets.

- Paper protection
    - PFOS-related chemicals produced for paper protection applications provide grease, oil and water resistance to paper and paperboard as part of a sizing agent formulation. Specific applications in this use category include food contact applications (plates, food containers, bags, and wraps), as well as non-food contact applications (folding cartons, containers, carbonless forms and masking papers).
- Performance chemicals
    - PFOS-related chemicals in the performance chemical category are used in a variety of specialised industrial, commercial, and consumer applications. This category includes various salts of PFOS that are commercialised as finished products. Specific applications in this category include fire fighting foams, mining and oil well surfactants, acid mist suppressants for metal plating and electronic etching baths, photolithography, electronic chemicals, hydraulic fluid additives, alkaline cleaners, floor polishes, photographic film, denture cleaners, shampoos, chemical intermediates, coating additives, carpet spot cleaners and as an insecticide in bait stations.

1.2.2 International regulatory context

Due to its physicochemical properties, PFOS does not degrade well and has been found to accumulate in biota, also in remote areas (OSPAR, 2006). Within the context of the Stockholm Convention, it was decided in 2009 by the Conference of Parties to classify PFOS as a POP substance and add PFOS to Annex B of the Convention, which includes a restriction on production and use with the ultimate aim to phase out PFOS (http://chm.pops.int). As a result of the international negotiations a relatively large number of specific uses are, however, still allowed. The decision becomes effective in August 2010.
In the European Union, PFOS is considered as Persistent, Bioaccumulative and Toxic (PBT). Its use is severely restricted by Commission Regulation (EC) No 1907/2006 of the European Parliament and of the Council. Based on this regulation PFOS has been added to Annex XVII of the Regulation on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) on 22 June 2009 (EC, 2009). The restrictions under REACH Annex XVII have been taken forward in the implementation of the Stockholm treaty into the EU POP regulation 850/2004/EC by August 24, 2010.
In the EU, the use of PFOS as mist suppressants/wetting agents in industrial chromium plating is derogated from the restriction until technically and economically feasible alternatives are available. The use of PFOS in fire-fighting foams is no longer allowed as from June 27, 2011. Recently, Bruinen de Bruin et al. (2009) made an estimation of the total stocks of PFOS in the Netherlands available for use for these purposes. Based on sales data, market shares and an inventory among users, it was estimated that 390 kg PFOS/year is used for non-decorative hard chromium plating, while the total stored volume of PFOS-containing fire-fighting foams on airports and industrial locations is about 18540 m^3. In view of the coming ban on the use in fire-fighting foams, owners have been informed to consider alternatives in due time. The exact way of an environmentally sound removal of stockpiles is under discussion. In conclusion, elimination of point sources is expected for the future, but this may take considerable time. In addition, PFOS-treated (consumer) articles will remain a potential emission route.
Within the context of 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.

1.2.3 Need for environmental risk limits

In the Netherlands, there are no officially authorised environmental risk limits for PFOS. In 2008, a large spill of PFOS occurred during an incident at Schiphol airport. In an evaluation report of the Transport and Water Management Inspectorate in the Netherlands on this incident (IVW, 2008), reference is made to standards of 10 and 25 µg/L. These values were supplied by RIVM and Waterdienst, based on a quick data screening. The Dutch Food and Consumer Products Safety

Authority, refers to the value of 25 µg/L as an indicative MPC in an advice concerning fish consumption from the affected area (VWA, 2008). Although referred to as "standard" and "indicative MPC", these values were supplied to facilitate acute incident management and should not be regarded as official environmental risk limits.

As stated above, long-term presence of PFOS in the environment can be expected even when phasing out will have been completed. PFOS is also present on the Dutch priority substances list and as such, environmental risk limits are still needed by local authorities. In view of the hazardous properties of PFOS, the Ministry of VROM requested the derivation of ERLs for PFOS.

Compounds that are used as replacements for PFOS (e.g., perfluorobutane sulfonate, PFBS, and perfluorobutanoate, PFBA) are also suspected of posing a potential risk to the environment and ERLs for these compounds may have to be derived in the future.

2 Methods for derivation of ERLs

2.1 General method used

The methodology for the data selection and derivation of ERLs is described in detail in Van Vlaardingen and Verbruggen (2007), further referred to as the 'INS Guidance'. This guidance is in accordance with the guidance of the Fraunhofer Institute (FHI; Lepper, 2005) and prepared within the context of the WFD.

The process of ERL-derivation contains the following steps: data collection, data evaluation and selection, and derivation of the ERLs on the basis of the selected data. Specific items will be discussed below.

2.2 Data collection, evaluation and selection

In accordance with the WFD, data of existing evaluations were used as a starting point. The OECD (2002) evaluation was used, together with the environmental risk evaluation reports from the British Environment Agency (Brooke et al., 2004) and OSPAR (2006).
Because of the known bioaccumulative properties of PFOS, it was anticipated that secondary poisoning and exposure of humans via consumption of fish are the determining routes for the derivation of ERLs. Therefore, physicochemical data were taken from the above-mentioned reports and only a quick literature scan on additional ecotoxicity data was performed. Emphasis was put on performing a thorough literature search on bioconcentration and biomagnification studies.

Ecotoxicity studies were screened for relevant endpoints (i.e., those endpoints that have consequences at the population level of the test species). Toxicity data that were deemed 'good' or 'acceptable' in the OECD report were used without any further validity evaluation, and other ecotoxicity studies from scientific literature were only quickly evaluated. All bioaccumulation studies were thoroughly evaluated with respect to their validity (scientific reliability), using the criteria of Klimisch et al. (1997).

After data collection and validation, toxicity data were combined into an aggregated data table with one effect value per species according to section 2.2.6 of the INS-Guidance. When for a species several effect data were available, the geometric mean of multiple values for the same endpoint was calculated where possible. Subsequently, when several endpoints were available for one species, the most relevant or if this cannot be determined, the lowest of these endpoints (per species) is reported in the aggregated data table.

To facilitate the comparison of toxicity data, all results are recalculated to concentrations of the anion. Hence, also the ERLs are expressed as anion concentrations.

2.3 Derivation of ERLs – deviations from guidance

Two ERLs are derived not completely in line with the present guidance: the ERL for drinking water (and the way it is compared to the other ERLs for surface water) and the maximum acceptable concentration (MAC) for marine waters. The deviations from the guidance are discussed below.

2.3.1 Surface water intended for drinking water abstraction

The INS-Guidance includes the MPC for surface waters intended for the abstraction of drinking water ($MPC_{dw, water}$) as one of the MPCs from which the lowest value should be selected as the general MPC_{water} (see INS-Guidance, section 3.1.6 and 3.1.7). According to the proposal for the daughter directive Priority Substances, however, the derivation of the AA-EQS (= MPC) should be based on direct exposure, secondary poisoning, and human exposure due to the consumption of fish. Drinking water was not included in the proposal and is thus not guiding for the general MPC_{water} value. The MPC_{water} is thus derived considering the individual MPCs based on direct exposure ($MPC_{eco, water}$), secondary poisoning ($MPC_{sp, water}$) or human consumption of fishery products ($MPC_{hh\ food, water}$). The $MPC_{dw, water}$ is reported separately. For derivation of the $MPC_{dw, water}$, it is assumed that the compound is not removed upon treatment.

2.3.2 $MAC_{eco, marine}$

In this report, the $MAC_{eco, marine}$ value is based on the $MAC_{eco,water}$ value

- with no additional assessment factor when acute toxicity data for at least two specific marine taxa are available,
- using an additional assessment factor of 5 when acute toxicity data for only one specific marine taxon are available,
- using an additional assessment factor of 10 when no acute toxicity data are available for specific marine taxa (analogous to the derivation of the MPC according to Van Vlaardingen and Verbruggen, 2007).

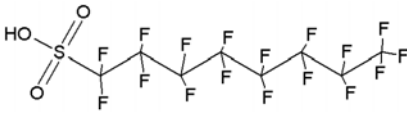
It has to be noted that this procedure is currently not agreed upon. Therefore, the $MAC_{eco, marine}$ value needs to be re-evaluated once an agreed procedure is available.

3 Derivation of environmental risk limits

3.1 Identification, physico-chemical properties, fate and distribution

3.1.1 Identity

Table 3 Identification of PFOS acid and its most important salt

Common name	PFOS	PFOS K^+ salt
CAS number	N.A.	2795-39-3
EC number	N.A.	220-527-1
Annex I Index number	607-624-00-8	607-624-00-8
Structural formula	Acid: 	Salt: 
Molecular formula	$C_8F_{17}SO_3H$	$C_8F_{17}SO_3K$

3.1.2 Physico-chemical properties

Physico-chemical properties of PFOS are summarised in Table 4 below.

Table 4 Physico-chemical properties of PFOS

Parameter	Unit	Value	Remark	Reference
Molecular weight	[g/mol]	499	PFOS ion	OECD, 2002
		500	PFOS acid	
		538	PFOS K^+ salt	
Water solubility	[mg/L]	570	Pure water	OECD, 2002
		370	Freshwater	
		12.4	Unfiltered seawater	
		25	Filtered seawater	
p*K*a	[-]	-3.27	Calculated value; PFOS is a strong acid and in the environment only present in the ionised form	Brooke et al., 2004
log K_{OW}	[-]	Not possible to measure/calculate		OECD, 2002
log K_{OC}	[-]	5.0	Overall geometric mean of reported values	OECD, 2002 Möller, 2009
Vapour pressure	[Pa]	3.31×10^{-4}	20 ºC	OECD, 2002
Melting point	[ºC]	> 400		OECD, 2002
Boiling point	[ºC]	Not calculable		OECD, 2002
Henry's law constant	[atm.m^3/mol]	4.34×10^{-7}		OECD, 2002

3.1.3 Behaviour in the environment

PFOS is an acid and in the environment, it is only present in the ionised form. Hydrolysis and photolysis of PFOS are insignificant, with a hydrolysis half-life of ≥ 41 years and a photolysis half-life of > 3.7 years (OECD, 2002). Because virtually no aerobic nor anaerobic biodegradation of PFOS occurs, PFOS is highly persistent in the environment.

3.2 Bioconcentration and biomagnification

In this section, an overview is given of the bioconcentration, bioaccumulation and biomagnification data. For derivation of the risk limits for secondary poisoning and human fish consumption, the accumulation of substances by aquatic organisms from the aqueous phase (bioconcentration) and accumulation in the food chain (biomagnification) has to be taken into account. These are represented by a laboratory bioconcentration factor (BCF) and biomagnification factors (BMF). A bioaccumulation factor (BAF) represents the total accumulation in the field relative to the exposure concentration in water, including bioconcentration and biomagnification. A BAF is thus equal to the product of BCF and BMF. In general, biomagnification, and thus total bioaccumulation, increases with increasing bioconcentration potential. The TGD (EC, 2003) recommends relying on experimental data for selection of the BMF. In case such data are not available, defaults are suggested that are related to the BCF (i.e., BMF 2 kg/kg for compounds with BCF 2000-5000 L/kg, 10 kg/kg for BCF > 5000 L/kg). It should be noted, however, that these defaults apply to lipophilic organic compounds, whereas PFOS primarily binds to proteins (see also 3.2.3).

In the following, the bioconcentration factors from laboratory experiments are discussed first in section 3.2.1. These values serve as basis for selection of the BCF. Second, bioaccumulation factors (BAF) from field data are discussed in section 3.2.2. In the field, exposure is not only via the water phase, as in laboratory BCF studies but via the food as well. The BAF values thus represent a combination of bioconcentration and biomagnification. Because biomagnification (uptake through food) depends on trophic level, BAF values are dependent on trophic level as well, if biomagnification occurs. Third, an overview of biomagnification studies is presented in section 3.2.3. An emphasis is put on trophic magnification studies in which a regression between the logarithm of the concentrations in organisms and the corresponding trophic level of these organisms is established. These so-called trophic magnification factors (TMF) are considered to be the most reliable representation of the biomagnification factors (BMF), because they are normalised to trophic level and cancel out fluctuations in biomagnification between individual species by regression over several trophic levels. For the purpose of deriving risk limits for secondary poisoning and human fish consumption, a biomagnifaction factor for the pelagic food chain has to be derived (see section 3.2.3.1). This factor, which is referred to as the first biomagnification factor BMF_1, describes the biomagnification from small fish to larger fish, which in turn is eaten by predators (including humans). Next to that, for deriving a risk limit for secondary poisoning in the marine environment, an additional biomagnification factor has to be derived to account for accumulation in birds and mammals (e.g., seals, dolphins, seabirds) that serve as food for top predators (e.g., polar bears and killer whales). This factor, called BMF_2,is derived see section 3.2.3.2. Last, based on the BCF, BAF and BMF (TMF) data, a value for BCF, BMF_1, and BMF_2 will be selected in section 3.2.4, based on a weight of evidence approach.

The BCF and BMF values are used to calculate a safe concentration in surface water starting from a safe concentration for humans or predatory birds and mammals according to the methods described in Van Vlaardingen and Verbruggen (2007). In short, the MPC for humans, expressed as a concentration in fish ($MPC_{hh\ food}$ in $mg/kg_{biota\ ww}$), is calculated from the human-toxicological threshold (TDI in

mg/kg_{bw}/d), assuming a body weight of 70 kg, a daily intake of 115 g fish, and a maximum contribution of 10% to the TDI. The equation used is: $MPC_{hh\ food} = 0.1 \times TDI \times 70/0.115$. The accompanying $MPC_{hh\ food\ water}$ (in mg/L) is calculated by dividing the $MPC_{hh\ food}$ by the product of BCF (in L/kg) and BMF_1 (in kg/kg) as $MPC_{hh\ food,\ water} = MPC_{hh\ food}/(BCF \times BMF_1)$.
The MPC in water that accounts for secondary poisoning of predatory birds or mammals ($MPC_{sp,\ water}$), is derived by dividing the lowest MPC from bird or mammal toxicity studies ($MPC_{oral,\ min}$, in mg/$kg_{biota\ ww}$) by the product of BCF and BMF_1. In formula: $MPC_{sp,\ water} = MPC_{oral,\ min} / (BCF \times BMF_1)$. The additional BMF_2 is applied to calculate the MPC for the marine environment: $MPC_{sp,\ marine} = MPC_{oral,\ min} / (BCF \times BMF_1 \times BMF_2)$.

3.2.1 Bioconcentration – laboratory data

The BCF value in a laboratory study is determined by exposing aquatic organisms to the substance dissolved in water. The BCF is calculated as the ratio between the concentration in the organisms and in the water determined at equilibrium. The standard guideline to perform bioconcentration tests with fish is the OECD 305 guideline.

The reported BCF values vary widely (for detailed data see Appendix 1, Table A1.1). Whole body BCF-values are much lower than values based on liver concentrations (e.g., Martin et al., 2003). The final value of 2796 L/kg selected in the 3M report (3M, 2003) is the whole body (wet weight) BCF for bluegill sunfish exposed to 86 µg/L PFOS. This is different from the value mentioned in the OECD assessment, which refers to the same study (OECD, 2002). According to the OSPAR assessment (OSPAR, 2006) this is because an inappropriate kinetic method was used in the OECD report, which was amended later in the 3M report. The only other BCF-value based on whole body concentrations is the study with carp (*Cyprinus carpio*) performed by the Japanese Kurumi laboratory, also mentioned in the OECD assessment (OECD, 2002). These values are, however, concentration ratios after 58 days, at which time point a steady state was apparently not reached. If the reported concentration ratios at different time intervals are extrapolated to steady state, the BCF-values are 818 L/kg at 20 µg/L and 2180 L/kg at 2 µg/L. The latter value is comparable to the (rounded off) value of 2800 L/kg for bluegill sunfish.

3.2.2 Bioaccumulation – field data

Bioaccumulation factors (BAFs) are presented in many of the reported field studies or can be deduced from these studies. In general, BAFs appear to be significantly higher than the BCF-values obtained in laboratory studies, which is a clear indication of contribution of uptake via the food and of biomagnification. The BAFs in fish that were obtained from the literature are tabulated in Appendix 1 (Table A1.2). BAF-values range from about 2500 to 95000 L/kg for freshwater fish, and from 1600 to 10000 L/kg for marine fish. The highest BAF of 95000 L/kg refers to sculpin, which is a small bottom feeder. For lake trout, which is considered more representative for human consumption, the BAF is 16000 L/kg. From a recent study (Houde et al., 2008) it must be noted that the bioaccumulation factor for linear PFOS is about 2.5 times as high as for the sum of the isomers.

Additional studies are available in which BAFs are presented based on serum and liver concentrations. In a study from Japan, 94 freshwater turtles (*Trachemys scripta elegans* and *Chinemys reevesii*) were caught (and killed). The concentration of PFOS in blood serum was determined, together with the water concentration in a simultaneously sampled 2-L volume of water. The geometric mean of the bioaccumulation factor based on serum concentrations was 11000 L/kg (Morikowa et al., 2006).
From another study in Japan, in which fish and water were sampled simultaneously at three locations (Tokyo Bay, Osaka Bay, and Lake Biwa), BAFs based on liver concentrations were derived that range from 274 to 41600 L/kg, with an average of 8540 L/kg (Taniyasu et al., 2003). From the presented data

it can be concluded that the BAF based on blood concentrations is on average about twice as high. The BAF-values for liver and blood from this Japanese field study are thus about 1 to 4 times as high as the BCF-values for liver and blood based on laboratory experiments with aqueous exposure only (Martin et al., 2003; see Appendix 1, Table A1.1).
Much higher bioaccumulation factors of 6300 to 125000 L/kg based on liver concentrations were reported as well (Moody et al., 2002). However, these concentrations were based on measurements 7 months after a spill of PFOS. Given the very slow depuration kinetics of PFOS from fish, the concentrations in fish may have stayed relatively constant while the water concentrations might have dropped significantly by dilution as a result of current. These BAF-values should therefore be considered unreliable.
Based on the data presented in a study on the food chain of bottlenose dolphins, the bioaccumulation factors based on serum concentrations of bottlenose dolphins are 76000 and 380000 L/kg for the Charleston Harbor area and the Sarasota Bay, respectively. Based on estimated whole body concentrations, the values are 12000 and 60000 L/kg (Houde et al., 2006).

3.2.3 Biomagnification – trophic magnification from field studies

In general, the most reliable data on biomagnification originate from trophic magnification studies. In such studies the levels of contaminants in several species in an ecosystem are measured and expressed as a function of the trophic level. The trophic level is mostly derived from stable nitrogen isotope ratios and a regression is made between contaminant concentration and trophic level. The contaminant values should preferably be normalised to the fraction in the organisms that contains the substance ***e.g.*** lipids in the case for lipophilic organic chemicals. However, PFOS partitions to proteins and a normalisation to protein content seem not possible at this moment (Haukås et al., 2007).

Several trophic magnification studies are available, in which the accumulation of PFOS through the food web is followed (Tomy et al., 2004; Martin et al., 2004; Houde et al., 2006). Detailed data can be found in Appendix 1 (Table A1.3 and A1.4). To calculate the final concentration in food for the predator or top predator, the biomagnification process has to be based on whole body concentrations. For many higher organisms (e.g., mammals) only plasma or liver concentrations are reported. This can lead to substantially different biomagnification factors (Houde et al., 2006). If no correction could be made and only liver samples were available, studies have not been taken into account.

3.2.3.1 BMF_1

In aquatic food webs excluding mammals and birds, the samples are almost solely whole body homogenates. Therefore, the TMF can be considered as a good representative of the biomagnification in the aquatic environment (e.g., between fish and larger fish), which is representative of the first biomagnification factor BMF_1 (e.g., biomagnification in the food of humans and predators such as herons and otters in the freshwater environment and seals, dolphins and seabirds in the marine environment).

A trophic magnification study in the aquatic food chain of Lake Ontario was performed in 2001-2002 (Martin et al., 2004). The study showed a good correlation between the logarithm of the PFOS concentrations and trophic level for the pelagic species. For the slimy sculpin (*Cottus cognatus*), which feeds partly on the benthic macroinvertebrate *Diporei hoyi*, higher concentrations were found. This could be explained by the high concentrations in *Diporeia*, which suggests that sediment is a major source of PFOS in this food web. For the pelagic species a TMF of 5.88 kg/kg was determined. It should be mentioned that the results were based on earlier measurements of stable nitrogen isotope, which makes the reliability of the trophic magnification uncertain, because trophic positions may be different for individual organisms and trophic position was determined on other samples.

In a follow-up study, the biomagnification of individual PFOS congeners was studied in Lake Ontario (Houde et al., 2008). For this purpose, additional samples were taken for *Diporeia* in September 2003, and zooplankton was collected in July 2004 and in July 2006. Further, the lake trout samples seem to be different as well, with the ones in the current study dating from September 2002. The first samples of *Mysis* were already taken in September 2001, while the remaining samples were collected in October 2002. Further, the exact sampling location is not similar for all species. Therefore, the results of the study can only be considered as indicative. In this study, the trophic levels for the species considered differ from those reported in the former study (Martin et al., 2004). From the data in the supporting information, it can be concluded that the stable nitrogen isotopes were measured for this follow-up study, which could mean that the measured PFOS concentrations and the reported trophic positions refer to the same individuals. A major conclusion from the study is that especially the linear PFOS isomer biomagnifies to the largest extent, about a factor of 2.5 more than the methyl isomers. The dimethyl isomers do not biomagnify at all.

In a study in a lake in Beijing, China, which receives water from a wastewater treatment plant, zooplankton (mainly *Moina* species) and five species of fish were sampled from December 2005 to April 2007 (Li et al., 2008). For fish, blood or serum were analysed and concentrations were expressed as serum concentrations, while for zooplankton whole body concentrations were measured. A positive relationship between PFOS concentration and trophic level was observed when tilapia (*Oreochromis niloticus*) was excluded from the regression analysis. Tilapia is a rather benthic species and should for that reason not be included in the regression analysis for pelagic species. The data for fish are expressed as serum concentrations, which were calculated as twice the blood concentrations. From the study by Martin et al. (2003), it appears that the BCF in blood is almost four times higher than the concentration in the carcass and as such, the reported BAF-values for fish are not representative for whole body homogenates. Based on the serum data for the four remaining fish, the TMFs would be 6.0 kg/kg, but it is not clear to what extent the differences in serum concentrations between the fish species are representative of the differences in whole body concentrations.

For the aquatic part of the food chain in the Canadian arctic, data are reported for several species sampled in 2000-2002 in David Strait and Frobisher Bay. No biomagnification between zooplankton (mainly *Calanus* species) and arctic cod (*Boreogadus saida*) was observed. However, concentrations in clams and shrimps were much lower than in zooplankton. Since these species are associated to the sediment to a larger extent, this suggests that in this marine environment exposure occurs through the water column (Tomy et al., 2004).

Data are reported for the aquatic part of the food chains in the Sarasota Bay (Florida, USA) sampled in 2004 and Charleston Harbor (South Carolina, USA) sampled in 2002-2004 (Houde et al., 2006). For the Sarasota Bay, zooplankton was sampled as well next to several fish species. TMFs could be calculated from the presented data. Considering the fish species only, the values are 1.3 kg/kg for the Sarasota Bay and 1.4 kg/kg for the Charleston Harbor area. Thus, no significant biomagnification occurs among the fish species, but the span in trophic level was only 1.3 and 0.9 for these areas respectively. If zooplankton is included, the TMF in the Sarasota Bay is 5.1 kg/kg.

In a study from the Western Scheldt estuary, biomagnification with trophic level was measured and compared with modelling results (De Vos et al., 2008). Biomagnification factors were based on whole body wet weight concentrations. Organisms were classified in four trophic levels, which are herbivores (level 2, suspended solids being level 1), primary carnivores (level 3), primary-secondary carnivores (level 3.5), and secondary carnivores (level 4). The assignment in trophic levels is less accurate than on

basis of stable nitrogen isotopes. However, an overall TMF for the food chain in the aquatic environment of 2.6 kg/kg could be derived from the presented data.

There are several uncertainties related to the studies presented above, mainly related to the time span over which sampling was performed, the use of liver or serum levels instead of whole body concentrations, and the assignment of trophic levels. However, with estimated TMFs ranging from 1.3 to 6.0 kg/kg, it can be concluded that biomagnification of PFOS in fish is relevant.

3.2.3.2 BMF_2

A second biomagnification factor BMF_2, that is representative for the accumulation of larger fish to mammals and birds, is used as an additional biomagnification step in the derivation of risk limits for the marine environment (where, e.g., seals serve as food for top predators such as polar bears and killer whales).

Some trophic magnification studies are performed for the bottlenose dolphin (*Tursiops truncatus*) from Charleston Harbor area, South Carolina, USA and Sarasota Bay, Florida, USA. (Houde et al., 2006) and for beluga (*Delphinapterus leucas*) and narwhal (*Monodon monoceros*) from the arctic (Tomy et al., 2004). Because the latter data were based on liver concentrations, whole body concentrations for the beluga and narwhal were estimated and the trophic magnification factor were recalculated based on whole body estimates (Houde et al., 2006). The arctic biomagnification study (Tomy et al., 2004) can however not be considered as a reliable study, because of the spread in both the sampling times (1996-2002) and the sampling location (vast area in the eastern Canadian arctic). Still, the recalculated BMF-value for the arctic food web based on whole body concentrations of 1.7 kg/kg is well in line with the values for the bottlenose dolphin of 1.4-1.8 (see Table A1.4).
To exclude the influence of biomagnification in the aquatic environment the chosen values for the biomagnification factors (BMFs) were also expressed on the basis of single fish species and dolphins separately. The BMFs based on whole body concentrations of bottlenose dolphins for the Sarasota Bay area were 9.6, 18, 16, 11, and 6.2 kg/kg for striped mullet, pigfish, sheepshead, pinfish, and seatrout, respectively. It is also stated that pinfish makes up 70% of the diet for the bottlenose dolphins in this area. Normalised to the measured trophic levels, these BMF values become 5.6, 18, 18, 14, and 16 kg/kg. For the Charleston Harbor area the reported BMF values were 2.6, 4, 1.2, 2.2, 0.8, and 0.9 kg/kg for striped mullet, pinfish, red drum, Atlantic croaker, spotfish, and seatrout, respectively. However, the data as tabulated in Houde et al. (2006) do not match with the data as presented in the figure from this paper. Moreover, the ratio between the whole body concentrations and the plasma concentrations in dolphins for the Charleston Harbor area is different from that for the Sarasota Bay. The data from the figure do present the same ratio between these concentrations for both areas. The presented BMF values for the Charleston Harbor area are probably underestimated by a factor of 2. Another uncertainty in these data is that the trophic position of pinfish, which makes up 70% of the diet in dolphins in the Sarasota Bay area, only differs by 0.1 from the trophic positions of dolphins in the Charleston Harbor area, whereas this difference is 0.8 in the Sarasota Bay area. A further complication in the study is that the calculation of whole body concentrations in dolphins from plasma concentrations cannot be reproduced from the presented data. This makes the validity of the biomagnification data for birds and mammals for the whole study more or less unassignable.

In the study from the Western Scheldt estuary (De Vos et al., 2008), the biomagnification from aquatic species to eggs of the common tern (secondary carnivore) was also determined. For primary carnivores to secondary carnivores the biomagnification factor was 2.4 kg/kg. For primary-secondary carnivores to secondary carnivore the biomagnification factor was 2.1 kg/kg, with a difference in trophic level of 0.5. The BMF normalised for trophic level is then 4.4 kg/kg. In view of the low difference in trophic

level this value is less reliable. In addition, the sampled tissue of the common tern is not the bird itself, but its eggs. Therefore, the relevance for quantification of the biomagnification factor to birds and mammals is unclear.

In stranded marine mammals at the Dutch, Belgian, and French part of the North Sea both PFOS and trophic position were measured (Van de Vijver et al., 2003). If the natural logarithm of the hepatic PFOS concentration in these stranded mammals is plotted against the nitrogen stable isotope ratio, a TMF of 2.3 kg/kg can be calculated. The value of this factor is limited, because the only trophic level taken into account is that of the predator, the time span of the samples is between 1995 and 2000, all data are from liver homogenates, and the samples are from a relatively large area. However, the obtained value is of the same magnitude as the values from the dolphins from Florida and South Carolina.

In an Arctic study, the biomagnification in the food chain sea ice amphipod (*Gammarus wilkitzkii*), polar cod (*Boreogadus saida*), black guillemot (*Cepphus grylle*) and glaucous gull (*Larus hyperboreus*) was determined. Results were based on liver concentrations for fish and birds, but on whole organism concentrations for the amphipods (Haukås et al., 2007). The BMFs, normalised to trophic level, were 0.32 from amphipod to cod (which in fact is a BMF_1), 1.54 from amphipod to black guillemot, 10.1 from cod to black guillemot, 38.7 from cod to glaucous gull, and 27.0 from black guillemot to glaucous gull (all kg/kg). Further, for the black guillemot and the glaucous gull, composition of the diets was estimated. For the black guillemot this consisted of 80% polar cod and 20% amphipods. For the glaucous gull this diet was 20% black guillemot, 30% polar cod and 20% amphipods. The BMFs based on these diets, were 5.66 and 11.3 for the black guillemot and the glaucous gull, respectively. Apparently no biomagnification from amphipods to polar cod was observed, but as the amphipods are not having the same habitats, the difference in trophic position might rather reflect a difference in nitrogen sources. When considering cod and the two bird species, the TMF based on liver concentrations that can be read from the figure presented in the study, is about 13 kg/kg.

Upon finalisation of this report, two new articles were published on trophodynamics of PFOS. Kelly et al. (2009) reported a protein-normalised TMF value of 11.0 kg/kg over the entire marine food web from the Hudson Bay area (Canada) including microalgae, capelin, cod, salmon, eider duck, white winged scoter and beluga whale. The species were collected between 1999 and 2003. On wet weight basis this value was 17.4 kg/kg, but the concentrations in birds and partly in whales were from liver samples. The TMF value normalised to protein content for the piscivorous food web only was 2.2 kg/kg.
Tomy et al. (2009) reported a liver-based TMF for PFOS of 6.3 kg/kg in a food web from the western Canadian Arctic containing the copepod *Calanus hyperboreus*, the amphipod *Themisto libellula*, cisco (a herring-like fish), pacific herring, arctic cod, beluga and ringed seal. Species were collected over the period 2004-2007.

As for the studies presented in section 3.2.3.1 for BMF_1, there are several uncertainties related to the BMF_2-data because of the sampling schemes, choice of trophic levels and the use of liver or serum concentrations. Although the individual studies are thus less reliable, in combination the range of BMFs of 1.4 to 17 kg/kg shows that biomagnification in predatory birds and mammals is relevant.

3.2.4 Selection of BCF and BMF values

For lipophilic organic chemicals, data on bioaccumulation can be normalised to the percentage lipids of the organisms. This strongly reduces variability for these substances. As PFOS does not bind to lipids, but to proteins, normalisation is not possible at this moment (Haukås et al., 2007). This causes a high

residual uncertainty especially in estimating the biomagnification potential of PFOS, which is reflected in the high variability of the data.
Several field bioaccumulation studies are available from the literature (see Appendix 1, Table A1.2). Houde et al. (2006) report BAF-values between 1600 and 10000 for marine fish (geometric mean 4500 L/kg; Houde et al., 2006), while for freshwater fish BAF between 2500 and 95000 L/kg are observed with a geometric mean of about 17000 L/kg (Kannan et al., 2005; Houde et al., 2008). BAF-values for the linear PFOS isomer may even be 2.5 times as high (Houde et al., 2008). It appears that BAF-values for predators such as dolphins can reach values as high as 60000 L/kg (Houde et al., 2006). Additional studies do not allow for a reliable quantification of whole body BAFs, because liver or serum concentrations were used instead of whole body values. Nevertheless, they show that considerable accumulation occurs.
Because biomagnification depends on trophic level, the reported experimental BAF-values depend on trophic level as well. This partly explains the variation in the observed data. Since not all trophic levels are relevant for human consumption, it is not justified to take the geometric mean, but picking out a single value does not cover the range of fish potentially consumed by humans. Therefore, it is considered most appropriate to rely on the reliable laboratory BCF-value of 2800 L/kg for bluegill sunfish and apply a fixed value for BMF_1 and BMF_2, instead of using an experimental BAF.
If the BCF-value of 2800 L/kg is selected as the most reliable value for further calculations, the values for the first and second biomagnification step should not be less than 5 kg/kg. The resulting product of BCF and BMF_1 of 14000 L/kg adequately covers the BAF-values obtained for relevant fish species in field studies (e.g., 16000 L/kg for lake trout, 19000 L/kg for alewife). Moreover, the additional factor of for BMF_2 leads to a BAF of 70000 L/kg that is similar to the value of 60000 L/kg obtained for the bottlenose dolphin. The choice of the BMF of 5 is also supported by many of the above reported BMF and TMF-studies, although they are individually less reliable and is comparable to the maximum BMF of 5.88 mentioned in the ecological screening assessment of PFOS and related compounds by Environment Canada (2006).
A stated above, the TGD (EC, 2003) proposes a default BMF of 2 kg/kg in case the BCF is between 2000 and 5000 L/kg. It should be realised, however, that the bioaccumulation potential of PFOS is not adequately predicted from the laboratory BCF and associated default BMF. As stated above in section 3.2, the defaults apply to lipophilic organic compounds, while PFOS primarily binds to proteins. In other words, the BAF will be underestimated when using the product of laboratory BCF and default BMF. This was also recognised in the preliminary risk profile that was prepared by the Swedish KemI and EPA for the nomination of PFOS as a POP under the Stockholm Convention (KemI/Swedish EPA, 2004). In that document, a calculated hypothetical BMF of 22–160 kg/kg is mentioned, based on part of the literature references that were evaluated for the present report. These BMF-values, however, are most likely too high, since they cover more trophic levels than should be included for the derivation of standards according to the WFD.
In conclusion, the data presented above and the special characteristics of PFOS biomagnification in the food chain support to deviate from the default value of 2 kg/kg proposed in the TGD (EC, 2003). Based on a weight of evidence (WoE) approach the chosen BCF value is 2800 L/kg, the value for BMF_1 is 5 kg/kg and the BMF_2 is 5 kg/kg (Table 5).

Table 5 Selected bioaccumulation and biomagnification values for PFOS

Parameter	Unit	Value	Remark	Reference
BCF (fish)	L/kg	2800	experimental, whole body value	3M, 2003
BMF_1	kg/kg	5		
BMF_2	kg/kg	5		

3.3 Human toxicological threshold limits and carcinogenicity

PFOS has the following risk-phrases: Carc. Cat. 3; R40 - Repr. Cat. 2; R61 - T; R48/25 - X; R20/22 - R64 - N; R51-53. From a subchronic study in Cynomolgus monkeys, the EFSA identified 0.03 mg/kg_{bw} per day as the lowest no-observed-adverse-effect level (NOAEL) and considered this a suitable basis for deriving a Tolerable Daily Intake (TDI) of 150 ng/kg_{bw} per day by applying an overall uncertainty factor (UF) of 200 to the NOAEL (EFSA, 2008).

3.4 Trigger values

This section reports on the trigger values for ERLwater derivation (as demanded in WFD framework).

Table 6 Collected properties for comparison to MPC triggers for PFOS

Parameter	Unit	Value	Method/Derived at section
Log $K_{p,\ susp\text{-}water}$	[-]	4.0	$K_{OC} \times f_{OC,susp}$[1]; log K_{OC} = 5.0; (see section 3.1.2)
BCF	[L/kg]	2800	3.2
BMF	[kg/kg]	5 (BMF_1) 5 (BMF_2)	3.2
Log K_{OW}	[-]	Not available	3.1.2
R-phrases	[-]	R40; R61; R48/25; R20/22; R64; R51-53	3.3
A1 value	[mg/L]	Not available	
DW standard	[mg/L]	Not available	

[1] $f_{OC,susp}$ = 0.1 kg_{OC}/kg_{solid} (European Commission (Joint Research Centre), 2003).

- PFOS has a log $K_{p,\ susp\text{-}water}$ > 3; derivation of $MPC_{sediment}$ is triggered. However, this is beyond the scope of this report.
- PFOS has a log $K_{p,\ susp\text{-}water}$ > 3; expression of the MPC_{water} as $MPC_{susp,\ water}$ is required. However, this is beyond the scope of this report.
- PFOS has a BCF > 100 L/kg; assessment of secondary poisoning is triggered.
- PFOS has a BCF > 100 L/kg is classified as a carcinogenic cat. 3 and has the R-phrases R40, R61, R48/25, R20/22, R64, R51-53. Therefore, an MPC_{water} for human health via food (fish) consumption ($MPC_{hh\ food,\ water}$) has to be derived.
- For PFOS, no compound-specific A1 value or Drinking Water value standard is available from Council Directives 75/440, EEC and 98/83/EC, respectively.

3.5 Aquatic toxicity data

To facilitate comparison of results, all toxicity data that are based on nominal concentrations have been recalculated into the concentration of the anion. Measured data are used as such, assuming that the anion is measured.

3.5.1 Laboratory toxicity data

An overview of the selected freshwater toxicity data for PFOS is given in Table 7. Marine toxicity data[1] are given in Table 8. Detailed toxicity data for PFOS are tabulated in Appendix 2. In a number of studies, effects were observed at the lowest test concentrations. NOECs could thus not be derived from these studies but in view of the very low level of the LOECs, these are included in Table 7 and further discussed below.

Table 7 Selected toxicity data for PFOS for freshwater species

Chronic[a]			**Acute**[a]		
Taxonomic group	**NOEC/EC10 [mg/L]**	**[µg/L]**	**Taxonomic group**	**L(E)C50 [mg/L]**	[µg/L]
Algae			**Algae**		
Chlorella vulgaris	8.2[b]	8200	*Chlorella vulgaris*	82[b]	82000
Navicula pelliculosa	191	191000	*Navicula pelliculosa*	283	283000
Pseudokirchneriella subcapitata	53[c]	53000	*Pseudokirchneriella subcapitata*	120[c]	120000
Cyanobacteria			**Cyanobacteria**		
Anabaena flos-aqua	94	94000	*Anabaena flos-aqua*	176	176000
Macrophytes			**Macrophyta**		
Lemna gibba	6.6[d]	6600	*Lemna gibba*	31[d]	31000
Myriophyllum sibiricum	0.56	560	**Crustaceans**		
Myriophyllum spicatum	3.2	3200	*Daphnia magna*	48[i]	48000
Crustaceans			*Daphnia pulicaria*	124	124000
Daphnia magna	7.0[e]	7000	*Moina macrocopa*	18	18000
Moina macrocopa	0.40[f,m]	400	*Neocaridina denticulate*	9.3	9300
Insects			**Platyhelmintes**		
Chironomus tentans	$< 2.3 \times 10^{-3}$[m]	< 2.3	*Dugesia japonica*	18[j]	18000
Enallagma cyathigerum	$< 1.0 \times 10^{-2}$[m]	< 10	**Mollusca**		
Fish			*Physa acuta*	165	165000
Oryzias latipes	$< 1.0 \times 10^{-2}$[m]	< 10	*Unio complamatus*	59	59000
Pimephales promelas	2.8×10^{-2}[g]	27	**Fish**		
Amphibians			*Lepomis macrochirus*	6.4	6400
Xenopus laevis	5.0[h]	5000	*Pimephales promelas*	6.6[k]	6600
			Oncorhynchus mykiss	13[l]	13000

[a] For detailed information see Appendix 2. For a description of LOEC values see main text.
[b] Most sensitive endpoint (cell density).
[c] Preferred endpoint (growth rate), preferred exposure time (72 h).
[d] Most sensitive endpoint (wet weight).
[e] Most sensitive endpoint (reproduction); geometric mean of 12, 25, 6.5 and 1.25 mg/L.
[f] Preferred endpoint (population growth rate)
[g] Most sensitive endpoint (spawning).
[h] Most sensitive endpoint (growth); geomean of 4.82 and 5.25 mg/L).
[i] Geometric mean of 61.0; 25.0; 53.8; 67.2; 37.4 and 58.4 mg/L
[j] Geometric mean of 15.8 and 21.3 mg/L
[k] Geometric mean of 9.5 and 4.6 mg/L
[l] Geometric mean of 7.2 and 22 mg/L
[m] See comment in text below

[1] Species living and tested in water with salinity > 0.5‰.

In Ji et al. (2008) a NOEC of 0.1 mg/L is reported for reproduction and a LOEC of 0.01 mg/L for larval survival of *Oryzias latipes*. At the level of the LOEC the effect percentage is 80%. Based on a rough estimation, the EC10 for larval survival would be in the order of 20 ng/L.

Ji et al. (2008) also report a LOEC value of 0.3125 mg/L for number of young per adult of the crustacean *Moina macrocopa*. This value is lower than the reported NOEC for adult survival of 1.25 mg/L and the NOEC for number of young per brood and broods of young per adult of 0.3125 mg/L. No significant effect was observed for the days to first brood. However, the population growth rate, which incorporates all of these parameters is also reported. An EC10 of 0.40 mg/L can be calculated from the presented data. Therefore, the LOEC value for number of young per adult is considered less relevant and the value of 0.40 mg/L is taken over.

MacDonald et al. (2004) report a NOEC of < 0.0023 mg/L (= LOEC 0.0023 mg/L) for total emergence of the insect *Chironomus tentans*. At this level, total emergence was decreased by 32% as compared to the control. The authors also report an EC10 of 0.089 mg/L for total emergence. When taking a closer look at the data, however, this EC10 seems to be rather uncertain and preference is given to the NOEC.

In Bots et al. (2010), a LOEC of 0.01 mg/L is reported for metamorphosis of the insect *Enallagma cyathigerum*, with an effect percentage of 18%. The NOEC for foraging success and larval survival. is 0.01 mg/L.

Table 8 Selected toxicity data for PFOS for marine species

Chronic[a]			**Acute**[a]		
Taxonomic group	**NOEC/EC10 [mg/L]**	**[µg/L]**	**Taxonomic group**	**L(E)C50 [mg/L]**	**[µg/L]**
Crustaceans			**Crustaceans**		
Americamysis bahia	0.25	250	*Americamysis bahia*	3.6	3600
			Artemia sp.	8.3	8300
			Fish		
			Oncorhynchus mykiss[b]	13	13000

[a] For detailed information see Appendix 2.
[b] Acclimated to 30‰ salinity

There are a number of valid marine toxicity data with 'higher-than values' due to the low solubility of PFOS in seawater. These include acute and chronic toxicity data for algae (*Skeletonema costatum*) and acute data for mollusca (*Crassostrea virginica*) and fish (*Cyprinodon variegatus*). For detailed information see Appendix 2.

3.5.2 Treatment of fresh- and marine toxicity data

According to Lepper (2005), data obtained for freshwater and marine species should be pooled unless there are indications that sensitivity of species differs between the two compartments. There are not enough data to make a sound comparison and the data are combined.

3.5.3 Model ecosystem toxicity data

Two microcosm studies are available, both focusing on effects on the zooplankton community. An extensive summary of both studies is presented in Appendix 4.

Sanderson et al. (2002) exposed 30 L indoor microcosms to 1, 10 or 30 mg/L PFOS in a 35-day experiment. Measured concentrations in water were consistent with nominal and remained constant throughout the study. Clear effects on zooplankton were apparent at 10 and 30 mg/L, with elimination of the copepods *Cyclops diaptomus* and *C. canthocampus staphylinus* and the cladoceran *Daphnia magna* and reductions in total abundance and species diversity. Rotifers showed a variable response, with some species decreasing and others increasing. Due to variability between replicates, it was not possible to determine with statistical confidence whether or not treatment related effects were present at 1 mg/L. The NOEC for zooplankton from this study is considered to be < 10 mg/L.

Boudreau et al. (2003) performed an outdoors experiment in which 12000 L-systems were exposed to 0.3, 3, 10 or 30 mg/L PFOS for 35 days. Actual concentrations in the water phase were in line with nominal and remained constant during the study. A total of 92 species was collected during the study, of these 68 species belonging to the Rotifera, Copepoda and Cladocera were used to determine effects on the zooplankton community using multivariate analysis (Principal Response Curve). The PRC-analysis indicated significant community effects at 10 and 30 mg/L. The PRC was dominated by two rotifer species that showed an increase in abundance. In contrast, 21 species displayed an opposite response. Among these were the cladoceran *Simocephalus vetulus*, copepod nauplii, the rotifers *Trichocerca* sp., *Cephalodella* sp., *Lecane monostyla* and *Lepadella* sp., and the copepod *Macrocyclops albidus*. The total number of species was significantly reduced by 74% at 30 mg/L and by 45% at 10 mg/L. Based on these results, the NOEC for the zooplankton community is considered to be 3.0 mg/L.

Sanderson et al. (2004) further elaborated on the results of the two above-mentioned studies and performed a power analysis in order to determine the LOECs. They concluded that the tentative LOEC in the indoor microcosm experiment was most likely closer to 1 than to 10 mg/L. Given the experimental set-up of the outdoor experiment, the deviations from the control should be 83% for abundance and 43% for species richness to be regarded as a true effect. The tentative LOEC based on the outdoor experiment would be between 10 and 30 mg/L.

3.6 Derivation of the MPC_{water} and MPC_{marine}

3.6.1 $MPC_{eco, water}$ and $MPC_{eco, marine}$

3.6.1.1 Assessment factor method

The acute base set is complete (algae, *Daphnia* and fish present). Eleven NOEC/EC10 values are available for the combined freshwater and marine datasets, the lowest of which is 27 µg/L for *Pimephales promelas*. According to the guidance, an assessment factor of 10 will normally be applied to the lowest NOEC when long-term NOECs are available from at least three species across three trophic levels. This is only sufficient, however, if the species tested can be considered to represent one of the more sensitive species groups. As can be seen from Table 7, there are several LOECs that are far below the lowest NOEC, and substantial effects are observed at the level of these LOECs. Applying an assessment factor of 10 on the lowest NOEC of 27 µg/L would lead to an $MPC_{eco, water}$ of 2.7 µg/L. This value is highly underprotective, since considerable effects on emergence of *Chironomus tentans* were present at 2.3 µg/L. Moreover, 18% effect on metamorphosis of the insect *Enallagma cyathigerum* and 80% effect on larval survival of *Oryzias latipes* were observed at 10 µg/L (Ji et al., 2008; Bots et al., 2010). Therefore, an assessment factor of 100 is put on the lowest available endpoint

(the LOEC of 2.3 µg/L) and the $MPC_{eco, water}$ using the assessment factor method becomes 2.3 / 100 = 0.023 µg/L = 23 ng/L. This $MPC_{eco, water}$ is not conservative, considering the estimated EC_{10} of around 20 ng/L for larval survival of *O. latipes*.

No true longer-term studies for species representing additional marine taxa are available. However, there is a 96-hour study with the pacific oyster *Crassostrea virginica* (EC50 > 3.0 mg/L). Shell deposition is a very sensitive parameter, which can be considered as representative of chronic effects. With one additional marine taxon, an additional assessment factor of 5 can be applied to the LOEC of 2.3 µg/L (total assessment factor 500). Thus, the $MPC_{eco, marine}$ becomes 2.3 / 500 = 0.0046 µg/L = 4.6 ng/L

3.6.1.2 Species sensitivity distribution method

The dataset does in principle fulfil the requirements for performing a species sensitivity distribution with respect to number and type of species tested, however all LOECs are for species that appear to be sensitive to PFOS and for which no NOECs are available in the dataset. For this reason, the lower end of the species sensitivity distribution cannot be estimated. It is therefore not considered justified to derive an $MPC_{eco, water}$ by statistical extrapolation.

3.6.1.3 Microcosm studies

Since constant chronic exposure was maintained in the experiments, the results of the experiments are in principle useful for derivation of the $MPC_{eco, water}$. Both studies are consistent in that clear effects on zooplankton are present at 10 and 30 mg/L, but the NOEC of 3.0 mg/L established in the outdoor experiment is probably not protective in view of the results of the first experiment. In addition, both studies were restricted to rotifers, copepods and cladocerans and did not take those species groups into account that on the basis of the laboratory data are potentially most sensitive (e.g., insects, fish). It is therefore not considered justified to adapt an $MPC_{eco, water}$ on the basis of the NOEC from the microcosm experiments.

3.6.1.4 Final choice for $MPC_{eco, water}$ and $MPC_{eco, marine}$

The $MPC_{eco, water}$ is 0.023 µg/L (23 ng/L) and the $MPC_{eco, marine}$ is 0.0046 µg/L (4.6 ng/L), and both derived using the assessment factor method.

3.6.2 $MPC_{sp, water}$ and $MPC_{sp, marine}$

Detailed bird and mammal toxicity data and corresponding MPC_{oral} are reported in Appendix 3.

The lowest $MPC_{oral, min}$ is 0.037 $mg/kg_{biota\ ww}$ for rabbits. This value is based on a NOAEL of 0.1 $mg/kg_{bw}/d$ for maternal weight gain from a teratogenicity study where exposure lasted from gestation day 6 to 20. The applied assessment factor was 90. Normally, the factor of 90 is applied to subchronic toxicity studies with an exposure duration of 90 days. From similar studies with rats exposed during the gestation period compared with full chronic studies, it can be concluded that the assessment factor of 90 can also be applied to teratogenicity studies. The extra assessment factor in comparison with a full chronic toxicity is 3.
Subsequently, the $MPC_{sp, water}$ can be calculated using the BCF of 2800 L/kg and the BMF_1 of 5 kg/kg (section 3.2) and becomes 0.037 / (2800 × 5) = 2.6×10^{-6} mg/L = 0.0026 µg/L = 2.6 ng/L.

For the marine environment, an extra biomagnification factor (BMF_2) should be used, which is also 5 (see section 3.2). Thus, the $MPC_{sp, marine}$ becomes 3.7×10^{-2} / (2800 × 5 × 5) = 5.3×10^{-7} mg/L = 0.00053 µg/L = 0.53 ng/L.

3.6.3 $MPC_{hh\ food,\ water}$ and $MPC_{hh\ food,\ marine}$

The $MPC_{hh\ food,\ water}$ and $MPC_{hh\ food,\ marine}$ represent the concentrations in water that will be protective for humans upon consumption of fishery products. First, the maximum permissible concentration in fish ($MPC_{hh\ food}$) is calculated based on the TDI of 1.5×10^{-4} $mg/kg_{bw}/d$ (see section 3.3), assuming a body weight of 70 kg, a daily intake of 115 g fish, and a maximum contribution to the TDI of 10%. The $MPC_{hh\ food}$ is then $(0.1 \times 1.5 \times 10^{-4} \times 70) / 0.115 = 9.1 \times 10^{-3}$ mg/kg = 9.1 $\mu g/kg_{biota\ ww}$.

Subsequently, the $MPC_{hh\ food}$ is converted to equivalent concentrations in water using the BCF and BMF as derived in section 3.2.4. The resulting $MPC_{hh\ food,\ water}$ and $MPC_{hh\ food,\ marine}$ are calculated as $9.1 \times 10^{-3} / (2800 \times 5) = 6.5 \times 10^{-7}$ mg/L = 0.00065 µg/L = 0.65 ng/L.

3.6.4 Selection of the MPC_{water} and MPC_{marine}

The MPC_{water} and MPC_{marine} are set to the lowest value derived for either direct exposure ($MPC_{eco,\ water}$), secondary poisoning ($MPC_{sp,\ water}$), or human exposure ($MPC_{hh\ food,\ water}$).

The $MPC_{eco,\ water}$ is 0.023 µg/L, the $MPC_{sp,\ water}$ is 0.0026 µg/L and the $MPC_{hh\ food,\ water}$ is 0.00065 µg/L. The final MPC_{water} is set equal to the $MPC_{hh\ food,\ water}$ and becomes 0.00065 µg/L = 0.65 ng/L.

The $MPC_{eco,\ marine}$ is 0.0046 µg/L, the $MPC_{sp,\ marine}$ is 0.00053 µg/L and the $MPC_{hh\ food,\ marine}$ is 0.00065 µg/L. The final MPC_{marine} is set equal to the $MPC_{sp,\ marine}$ and becomes 0.00053 µg/L = 0.53 ng/L.

3.7 Derivation of the $MPC_{dw,\ water}$

A provisional drinking water standard can be calculated using the TDI assuming 10% of the TDI may be taken up through drinking 2 litres of water and a bodyweight of 70 kg. The provisional drinking water standard then becomes $(0.1 \times 1.5 \times 10^{-4} \times 70) / 2 = 0.00053$ mg/L = 0.53 µg/L. This value is used as the MPC for surface water intended for the abstraction of drinking water.

3.8 Derivation of the MAC_{eco}

3.8.1 $MAC_{eco,\ water}$

The base set of acute toxicity data is complete. LC50s are available for a number of taxa. However, because no acute insect toxicity data are available, the requirements to perform an SSD are not met. Besides that, chronic toxicity data show that insects are among the most sensitive species.

The lowest LC50 is 3.6 mg/L for the marine crustacean *Americamysis bahia*. Given the following arguments:

- the bioconcentration factor is higher than 100 and fish are amongst the most sensitive species;
- the mode of action is unknown (although PFOS is suspected to have endocrine disrupting effects);
- the variation is not too high in view of the large number of data;

an assessment factor of 100 is used and the $MAC_{eco,\ water}$ becomes 3.6 / 100 = 0.036 mg/L = 36 µg/L.

Please note that the derivation of a MAC value for PFOS is mainly theoretical. Because of the physico-chemical properties of the compound (almost no degradation), a high peak will automatically lead to high long-term concentrations and consequently a high chronic exposure. Short-term toxicity tests are thus not a good basis for risk evaluation, which is also shown in the large acute to chronic ratios obtained from the toxicity test results for a number of species (see Table 7). PFOS is a typical compound for which effects will become mainly apparent in the long-term. Moreover, the $MAC_{eco, water}$ does not take food chain transfer into account.

3.8.2 $MAC_{eco, marine}$

For the marine compartment, an additional assessment factor of 5 should be used since one typically marine taxon is present in the acute dataset (the mollusc *Crassostrea virginica*). Thus, the $MAC_{eco, marine}$ becomes 3.6 / 500 = 0.0072 mg/L = 7.2 µg/L.

3.9 Derivation of the NC_{water} and NC_{marine}

The NC_{water} and NC_{marine} are set to 1/100 of the respective MPCs, and are 6.5×10^{-6} and 5.3×10^{-6} µg/L (6.5 and 5.3 pg/L).

3.10 Derivation of $SRC_{eco, water}$

The geometric mean of all chronic data without the LOECs is 3.3 mg/L. However, with the LOECs included for the three species for which no NOECs could be established, the geometric mean is considerably lower and is 0.93 mg/L. It could be argued that the geometric mean would even be lower if for these three species NOECs would have been established. Therefore, the lower value of 0.93 mg/L is used as basis for the SRC_{eco}. Because more than three NOECs are available, no comparison has to be made with the geometric mean of the acute data. Thus, the $SRC_{eco, water}$ and the $SRC_{eco, marine}$ are set at 0.93 mg/L = 930 µg/L. It should be noted that since food chain transfer is not taken into account, the relevance of the $SRC_{eco, water}$ to express potential risks for the aquatic ecosystem is limited. In may be considered to adapt the methodology to be able to include secondary poisoning in future SRC-derivations when the compound characteristics give rise to concern for predators.

3.11 Overview of derived ERLs

An overview of the derived MPCs for surface water is given in Table 9, based on the three routes direct ecotoxicity, secondary poisoning, and consumption of fish by humans. The lowest of these determines the final MPC. The final MPC for freshwater is based on the MPC for human consumption of fishery products, while the MPC for marine waters is based on the MPC for secondary poisoning.

Table 9 Derived MPC values for PFOS (in µg/L) in surface water

Freshwater			Marine water		
	µg/L	**ng/L**		**µg/L**	**ng/L**
$MPC_{eco, water}$	0.023	23	$MPC_{eco, marine}$	0.0046	4.6
$MPC_{sp, water}$	0.0026	2.6	$MPC_{sp, marine}$	0.00053	0.53
$MPC_{hh\ food, water}$	0.00065	0.65	$MPC_{hh\ food, marine}$	0.00065	0.65

Table 10 summarises the final ERLs. The relevance of the MAC_{eco} and SRC_{eco} for fresh and marine waters is limited, since these risk limits do not take food chain transfer to predators and humans into account. In addition, the MAC_{eco} is based on acute data, whereas a single peak will automatically lead to chronic exposure and long-term effects.

Table 10 Derived MPC, NC, MAC_{eco} and SRC_{eco} values for PFOS

ERL	**MPC**		**MAC_{eco}**	**NC**		**SRC_{eco}**
	µg/L	**ng/L**	**µg/L**	**µg/L**	**ng/L**	**µg/L**
Freshwater	0.00065	0.65	36	6.5×10^{-6}	0.0065	930
Surface water intended for drinking water abstraction	0.53	530	n.a.	n.a.	n.a.	n.a.
Marine water	0.00053	0.53	7.2	5.3×10^{-6}	0.0053	930

n.a. = not applicable

At first sight, it may seem strange that the MPC for surface water intended for the abstraction of drinking water is much higher than those for fresh and marine water. Both values refer to exposure of humans, taking the TDI as a starting point. Intuitively one might expect that direct intake of drinking water leads to higher exposure as compared to indirect exposure via fish. For a compound such as PFOS, however, this is not the case. PFOS accumulates in aquatic organisms and because of this, concentrations increase along the food chain. At similar concentrations in water, consumption of fish therefore leads to a much higher uptake than consumption of drinking water. Starting from the maximum permissible concentrations in fish based on the TDI, equivalent concentrations in water should thus be lower.

3.12 Comparison of derived ERLs with standards from other countries

3.12.1 Drinking water

The US EPA derived a provisional drinking water limit of 0.2 µg/L (US EPA, 2009). The German Federal Environmental Agency recommends for drinking water a precautionary value of 0.10 µg/L and a long-term toxicological threshold value of 0.30 µg/L (Drinking Water Commission, 2006; Roos et al., 2008). The Health Protection Agency of the United Kingdom advises that the maximum acceptable concentration of perfluorooctane sulfonate (PFOS) in drinking water is 0.3 µg/L (UK HPA, 2007). Recently, Schriks et al. (2010) proposed a drinking water limit of 0.5 µg/L. These values are all well in line with the proposed $MPC_{dw, water}$ of 0.53 µg/L.

3.12.2 Surface water

In 2004, the United Kingdom Environment Agency published a risk evaluation report on PFOS (Brooke et al., 2004). The Predicted No Effect Concentration (PNEC) for the aquatic ecosystem is set to 25 µg/L, by putting an assessment factor of 10 on the NOEC of 0.25 mg/L for the mysid shrimp *Americamysis bahia* (formerly known as *Mysidopsis bahia*). This endpoint is also included in the present evaluation (see Table 8), but much lower endpoints were retrieved from the recent literature. As argued in section 3.6.1.1, an assessment factor of 10 on the lowest NOEC is highly underprotective. With respect to secondary poisoning of birds and mammals, the UK evaluation is based on the same BCF as reported here (2796 L/kg, here rounded off to 2800 L/kg) and a biomagnification factor of 2 kg/kg (TGD default for BCF 2000 – 5000 L/kg), leading to an estimated bioaccumulation factor of 5600 L/kg. As already discussed in section 3.2.4, this value is considered too low. The PNEC for vertebrates is set to 0.0167 mg/kg$_{food}$, an alternative PNEC of 0.067 mg/kg$_{food}$ is also used. The MPC$_{oral}$ of 0.037 mg/kg$_{biota\ ww}$ that is used in the present report (see 3.6.2) is in this range. A risk for secondary poisoning is identified for several use patterns of PFOS, but a standard expressed as concentration in water is not derived. Human risks are not evaluated.

In 2006, Environment Canada published an ecological screening assessment report on PFOS and related compounds (Environment Canada, 2006). The critical toxicity value selected for standard derivation is the 10-days NOEC of 0.0491 mg/L for *Chironomus tentans* from a study by MacDonald et al. (2004). With an assessment factor of 100, the estimated no effect value is 0.491 µg/L (491 ng/L). The study of MacDonald et al. (2004) was also evaluated for the present report (see Appendix 2, table A2.3), and it appears that lower endpoints are reported in this study, i.e., a 20-day NOEC for growth of 0.022 mg/L (22 µg/L) and a 36-days NOEC for emergence of < 0.0023 mg/L (< 2.3 µg/L), associated with 32% effect. The study of Ji et al. (2008), published after finalisation of the Canadian assessment report, shows 80% effect on larval survival of *Oryzias latipes*, with an estimated EC10 of 20 ng/L. In view of this, the value of 491 ng/L is not considered sufficiently protective. Risk evaluations for birds and mammals are based on liver concentrations, which cannot be compared directly with our values.

In the USA, Stevens and Coryell (2007) derived surface water quality criteria for PFOS for the Minnesota Pollution Control Agency. They calculate an LC50 of 170 µg/L for 10-days survival of *Chironomus tentans* using a study that is most likely the aforementioned study of MacDonald et al. (2004). This value is divided by an acute/chronic ratio (ACR) of 9.12, resulting in a chronic quality standard of 19 µg/L. No further assessment factor has been applied in this derivation. It should be noted that the ACR is calculated as the ratio of L/EC50 and MATC (Maximum Acceptable Toxicant Concentration), the latter being the geometric mean of NOEC and LOEC. The ACR based on a comparison of L/EC50 and NOEC is thus higher. Furthermore, only two individual ACRs are used, 22.2 for fish and 1.9 for *Daphnia magna* to calculate the geometric mean and it is unknown whether this value is applicable to *Chironomus tentans* or other sensitive taxa. The authors point at the fact that it is unknown whether this value is protective for frogs, since a LOEC of 30 µg/L for foot development was determined in one study. They do not mention, however, that the endpoint for emergence of *C. tentans* is even lower, although the NOEC of < 2.3 µg/L is included as valid in their dataset. Recent data on fish and insects, with severe effects at 10 µg/L, also show that the chronic quality standard of 19 µg/L is not protective.
Stevens and Coryell (2007) also include human health-based water quality standards, based on fish consumption, of 12 and 6 ng/L for rivers and lakes, respectively. The methodology is similar to the WFD-method used in the present report (see section 3.6.3), but the input values differ. Starting point is a reference dose of 75 ng/kg$_{bw}$/d, which is a factor of 2 lower than the TDI of 150 ng/kg$_{bw}$/d derived by EFSA (2008) that is used in our calculations (see section 3.3). The same bodyweight of 70 kg is used, however, fish consumption is set to 30 g/d instead of the WFD-default of 115 g/d. Furthermore, the

contribution to the human risk limit is 20% instead of the WFD-default of 10%. BAFs of 2800 and 5737 L/kg are used for rivers and lakes, respectively, based on samples from Lake Cahon and River Mississippi. A BAF of 2800 L/kg is considered very low, taking into account that the laboratory BCF is also 2800 L/kg, without taking bioaccumulation into account. Starting from the laboratory BCF of 2800 L/kg, a BAF of 5737 L/kg would be reached using a BMF of 2 kg/kg. As argued above in section 3.2.4, this value is considered too low and does not cover the field BAFs obtained from the literature. However, the differences in the human risk limit (factor of 2) and bioaccumulation estimates (factor of 2.5) more or less outweigh each other. The 9-fold difference in the resulting water quality standard (6 ng/L vs. 0.65 ng/L) can thus merely be attributed to the differences in defaults for fish consumption (30 g/d vs. 115 g/d, factor of 3.8) and contribution to the TDI (20% vs. 10%, factor of 2).

From the above it can be concluded that the risk limits for water that are derived in this report are lower than those obtained by others. This is mainly due to inclusion of recent literature data in which considerable effects are observed at concentrations below the lowest NOEC reported so far. Accordingly, we apply a higher assessment factor to account for uncertainty with respect to protection of sensitive species. However, the critical MPC-value, which is derived based on the consumption of fish by humans is supported by the standard derived for the Minnesota Pollution Control Agency by Stevens and Coryell (2007). The difference in the resulting values is caused by the choices that are made within the context of the WFD with respect to (fixed) input values for fish consumption and contribution to the TDI.

3.13 Comparison of derived ERLs with monitoring data

In this section, some monitoring data are presented on PFOS concentrations in fish and surface water. It should be noted that a full inventory on monitoring data is beyond the scope of this report. The data presented here are thus merely the result of a quick screening of readily available data, but are still considered useful as a first indication whether the newly derived ERLs will be exceeded.

3.13.1 Fish

After the fire fighting foam incident at Schiphol airport in 2008, the Dutch Food and Consumer Products Safety Authority (“Voedsel en Warenautoriteit”, VWA), concluded that PFOS-concentrations in fish from the Ringvaart were too high (400 – 1500 µg/kg as compared to 30 µg/kg in fish caught upstream from the incident location) and consumption was advised against (VWA, 2008). This ‘background’ concentration of 30 µg/kg in fish is in agreement with data from Van Leeuwen and De Boer (2006; cited in Bakker and Te Biesebeek, 2009), who measured levels of PFOS in fish caught in the Netherlands. Reported concentrations are 93 and 230 $\mu g/kg_{ww}$ for flounder (Western Scheldt and Waddensea), 40 and 150 $\mu g/kg_{ww}$ for perch (Hollands Diep and IJsselmeer) and 6 to 57 $\mu g/kg_{ww}$ for eel (six locations, including Rivers Rhine and Meuse, IJsselmeer and Ketelmeer).
These data show that concentrations in wild fish may be well above the $MPC_{hh\ food}$ of 9.1 µg/kg fish. It should be noted, however, that this $MPC_{hh\ food}$ cannot be considered as a product safety standard, but relates to the WFD-definition of good water quality. This is based on a lifetime daily human consumption of fishery products of 115 g per day. In addition, fish consumption is allowed to contribute to the TDI for at most 10%. Using consumption patterns for the average Dutch population (10 g fish per day) and measured concentrations in various food items, including fish, Bakker and Te Biesebeek (2009) conclude that the overall intake of PFOS will be below the TDI of 150 ng/kg_{bw} per day. A similar conclusion was reached by EFSA, although it was noted that individuals with a high exposure due to specific food consumption patterns, may exceed the TDI (EFSA, 2008).

3.13.2 Water

A measured water concentration of 3 µg/L is reported after a large fire where fire-fighting foams containing PFOS were used (Schrap et al., 2004).

In 2006 and 2007, PFOS was monitored monthly in the Lekkanaal at Nieuwegein (RIWA, 2007 and 2008), with measured concentrations varying from 5.0 to 26 ng/L, and an annual average concentration of 13 ng/L in 2006 and 8.6 ng/L in 2007. In 2006, PFOS was also monitored monthly in the Amsterdam-Rijnkanaal at Nieuwersluis (RIWA, 2007), with measured concentrations varying from below the detection limit (once) to 26 ng/L. The annual average at that location was 14 ng/L.

In a recently published EU-wide survey, polar organic persistent pollutants were analysed in unfiltered water samples collected in 2007 at 122 sampling stations in streams and rivers in 27 European countries (Loos et al., 2009). PFOS was detected in 93% of the samples (reporting limit 1 ng/L). The maximum level was 1371 ng/L, found in the river Krka in Slovenia. The average and median were 39 and 6 ng/L, respectively, the 90th percentile was 73 ng/L. Relatively high concentrations were found in the River Scheldt in Belgium (154 ng/L) and the Netherlands (110 ng/L), which is higher than the data of Möller (2009) presented below. This may be due to differences in the time of sampling and the exact sampling locations. Fluorochemical industry has been active upstream (Hoff et al., 2004; Dauwe et al., 2007), which probably influences the measured concentrations. Other rivers with a relatively high PFOS concentrations were the rivers Seine in France (97 ng/L), Severn in the UK (238 ng/L), Rhine in Germany (32 ng/L at Wesel) and some smaller streams in Spain.

Möller (2009) measured the concentrations of a range of poly- and perfluoroalkyl compounds in samples taken in September and October 2008 along the River Rhine from the Lake Constance to the North Sea including important tributaries (e.g., River Ruhr, River Main) and delta rivers (*e.g.* River Scheldt, River Meuse). For the Dutch part of the Rhine-Meuse delta (excluding the River Scheldt), dissolved concentrations of PFOS were between 1.1 and 25 ng/L (minimum detection limit 0.23 ng/L). Relatively high concentrations are reported for the River Scheldt and the Canal Ghent-Terneuzen (14-25 ng/L) and the Noordzeekanaal (12 ng/L) and River Waal (7.2 ng/L). Concentrations between 1.1 and 4.3 ng/L were found at the other sampling stations, including the rivers Rhine, Meuse, IJssel and associated rivers and lakes, and the Western Scheldt. For the latter, concentrations of 4.6 to 8.4 ng/L were measured in 2007 (Martine van den Heuvel-Greve, personal communication).
For several sampling points in the North Sea, Möller (2009) reports concentrations between 0.13 and 0.70 ng/L, concentrations tend to decline with increasing distance from the shore.

From September till December 2008, samples from several locations in the Noordzeekanaal were analysed for PFOS. Concentrations over that time period were between 19 and 52 ng/L. In samples taken from spring to autumn 2008 at Kampen, Lobith and Maassluis, PFOS was present at the level of the detection limit for that method (9-10 ng/L), in a few cases concentrations of 20 ng/L were found (data obtained via Helpdesk Water, http://www.helpdeskwater.nl/, 30 September 2009).

The monitoring data confirm the widespread occurrence of PFOS in surface water. Although concentrations may vary over time, the reported data indicate that it is likely that annual average concentrations in the Netherlands will exceed the newly derived MPC_{water} of 0.65 ng/L for freshwater. As stated above in section 3.13.1 for concentrations in fish, it should be noted that the MPC_{water} is based on the $MPC_{hh\ food,\ water}$. According to the definitions of the WFD, the $MPC_{hh\ food,\ water}$ represents good water quality which allows humans to consume 115 g fish per day without exceeding 10% of the TDI. In this way, the WFD aims to protect all situations including those locations where local fishermen consume self-caught fish on a daily basis. The current average fish consumption in the

Netherlands is lower. Bakker and Te Biesebeek (2009) used 10 g fish per day based on a food consumption inventory. In the advise on the Schiphol incident, the Dutch Food and Consumer Products Safety Authority used 25 g per week for the average consumer and 400 g per week (57 g per day) for people that specifically like fish (VWA, 2008). In that sense, the MPC_{water} based on human consumption of fish can be considered as a conservative risk limit. However, the $MPC_{sp, water}$ of 2.6 ng/L and probably the $MPC_{eco, water}$ of 23 ng/L may be exceeded as well, and the few available measurements for the North Sea are at the level of the MPC_{marine}. As a whole, this points at a potential risk for the aquatic ecosystem and higher organisms that depend on freshwater fish as a food source.

4 Conclusions

In this report, the risk limits negligible concentration (NC), maximum permissible concentration (MPC), maximum acceptable concentration for ecosystems (MAC_{eco}), and serious risk concentration for ecosystems (SRC_{eco}) are derived for PFOS in water. No risk limits were derived for the sediment compartment because this was outside the scope of this project. The ERLs that were obtained are summarised in the table below.

Recent freshwater monitoring data indicate that annual average concentrations in freshwater will likely exceed the MPC_{water} of 0.65 ng/L, which is based on human consumption of fish. According to the definitions of the WFD, this value represents good water quality which allows humans to consume 115 g fish per day without exceeding 10% of the TDI. The current average fish consumption in the Netherlands is lower, and the MPC_{water} based on human consumption of fish can be considered as a conservative risk limit. However, the $MPC_{sp, water}$ of 2.6 ng/L and probably the $MPC_{eco, water}$ of 23 ng/L and MPC_{marine} of 0.53 ng/L may be exceeded as well, which points at a potential risk for the aquatic ecosystem and higher organisms that depend on freshwater fish as a food source.

The relevance of the MAC_{eco} and SRC_{eco} is limited, since these risk limits do not take food chain transfer into account. In addition, the MAC_{eco} is based on acute data, whereas a single peak will automatically lead to long-term exposure. Since effects of PFOS will become mainly apparent in the long-term, short-term toxicity tests are not a good basis for risk evaluation.

The currently derived ERLs clearly underpin the ongoing efforts to eventually phase out the use of PFOS. They can be used for further decision making on PFOS at the European level and for setting environmental quality standards by the Dutch Steering Committee for Substances. Regular monitoring of PFOS, using sufficiently sensitive analysis methods, is needed to investigate the potential risks for the aquatic ecosystem and to evaluate the (inter)national regulatory measures.

Table 11 Derived MPC, NC, MAC_{eco}, and SRC_{eco} values for PFOS

ERL	MPC		MAC_{eco}	NC		SRC_{eco}
	µg/L	ng/L	µg/L	µg/L	ng/L	µg/L
Freshwater	6.5×10^{-4}	0.65	36	6.5×10^{-6}	0.0065	930
Surface water intended for drinking water abstraction	0.53	530	n.a.	n.a.	n.a.	n.a.
Marine water	5.3×10^{-4}	0.53	7.2	5.3×10^{-6}	0.0053	930

n.a. = not applicable

rivm

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Appendix 1. Information on bioconcentration and biomagnification

Table A1.1 Aquatic bioconcentration data for PFOS

Species	Species properties	Test substance	Substance purity [%]	Analysed	Test type	Test water	pH	Hardness/ Salinity [g/l]	Exp. time [d]	Temperature [°C]	Exp. conc. [µg/L]	BCF [L/kg_{ww}]	BCF type	Method	RI	Notes	Reference
Oncorhynchus mykiss	juvenile, 5-10 g, 8.4 g at start of depuration	KPFOS tested in mixture	86.4	LC-MS	CF	am			12 d + 33 d	12	0.35±26%	1100±150	Carcass	k1 implied by fitted k2, growth corrected	2	1	Martin et al., 2003b
Oncorhynchus mykiss	juvenile, 5-10 g, 8.4 g at start of depuration	KPFOS tested in mixture	86.4	LC-MS	CF	am			12 d + 33 d	12	0.35±26%	4300±570	Blood	k1 implied by fitted k2, growth corrected	2	1	Martin et al., 2003b
Oncorhynchus mykiss	juvenile, 5-10 g, 8.4 g at start of depuration	KPFOS tested in mixture	86.4	LC-MS	CF	am			12 d + 33 d	12	0.35±26%	5400±860	Liver	k1 implied by fitted k2, growth corrected	2	1	Martin et al., 2003b
Lepomis macrochirus	7 m, 62 (56-66) mm and 2.70 (2.03-3.32) g at end of test	KPFOS (n-octane isomer)	86.9	LC-MS	CF	nw	8.1 (7.9-8.2)	130 (128-132)	62 d + 56 d	21.7-22.0	86	1124	Edible		2	2,3	3M, 2003
Lepomis macrochirus	7 m, 62 (56-66) mm and 2.70 (2.03-3.32) g at end of test	KPFOS (n-octane isomer)	86.9	LC-MS	CF	nw	8.1 (7.9-8.2)	130 (128-132)	62 d + 56 d	21.7-22.0	86	4013	Non-edible		2	2,3	3M, 2003
Lepomis macrochirus	7 m, 62 (56-66) mm and 2.70 (2.03-3.32) g at end of test	KPFOS (n-octane isomer)	86.9	LC-MS	CF	nw	8.1 (7.9-8.2)	130 (128-132)	62 d + 56 d	21.7-22.0	86	2796	Whole fish		2	2,3	3M, 2003
Lepomis macrochirus	7 m	KPFOS (n-octane isomer)	86.9	LC-MS	CF	nw	8.1 (7.9-8.2)	130 (128-132)	35 d	21.7-22.0	870				3	3,4	3M, 2003
Pimephales promelas	males								21 d			1167-1300	Plasma	ratio, non-equilibrium	3		Ankley et al., 2005
Pimephales promelas	females								21 d			1600-1750	Plasma	ratio, non-equilibrium	3		Ankley et al., 2005
Pimephales promelas	males								21 d			250-400	Liver	ratio, non-equilibrium	3		Ankley et al., 2005
Pimephales promelas	females								21 d			900-1333	Liver	ratio, non-equilibrium	3		Ankley et al., 2005
Pimephales promelas	males								21 d			167-367	Gonads	ratio, non-equilibrium	3		Ankley et al., 2005
Pimephales promelas	females								21 d			800-1000	Gonads	ratio, non-equilibrium	3		Ankley et al., 2005
Cyprinus carpio	6.4-9.6	KPFOS	100	LC-MS	CF	gw	7.6-7.8	111	58 d + 37 d	25.0-25.8	20	720	Whole fish		3	5,6	Kurume Laboratory (2001)
Cyprinus carpio	6.4-9.6	KPFOS	100	LC-MS	CF	gw	7.6-7.8	111	58 d + 37 d	25.0-25.8	20	1000-1400	Tegument		3	5,6	Kurume Laboratory (2001)
Cyprinus carpio	6.4-9.6	KPFOS	100	LC-MS	CF	gw	7.6-7.8	111	58 d + 37 d	25.0-25.8	20	1100-1400	Head		3	5,6	Kurume Laboratory (2001)
Cyprinus carpio	6.4-9.6	KPFOS	100	LC-MS	CF	gw	7.6-7.8	111	58 d + 37 d	25.0-25.8	20	2200-2700	Viscera		3	5,6	Kurume Laboratory (2001)

Species	Species properties	Test substance	Substance purity [%]	Analysed	Test type	Test water	pH	Hardness/ Salinity [g/l]	Exp. time [d]	Temperature [°C]	Exp. conc. [µg/L]	BCF [L/kg_{ww}]	BCF type	Method	RI	Notes	Reference
Cyprinus carpio	6.4-9.6	KPFOS	100	LC-MS	CF	gw	7.6-7.8	111	58 d + 37 d	25.0-25.8	20	1900-2300	Liver		3	5,6	Kurume Laboratory (2001)
Cyprinus carpio	6.4-9.6	KPFOS	100	LC-MS	CF	gw	7.6-7.8	111	58 d + 37 d	25.0-25.8	20	320-380	Remainder parts		3	5,6	Kurume Laboratory (2001)
Cyprinus carpio	6.4-9.6	KPFOS	100	LC-MS	CF	gw	7.6-7.8	111	58 d + 37 d	25.0-25.8	20	818	Whole fish	kinetic ratio from presented data	2	5,6	Kurume Laboratory (2001)
Cyprinus carpio	6.4-9.6	KPFOS	100	LC-MS	CF	gw	7.6-7.8	111	58 d + 37 d		2	200-1500	Whole fish		3	5,6	Kurume Laboratory (2001)
Cyprinus carpio	6.4-9.6	KPFOS	100	LC-MS	CF	gw	7.6-7.8	111	58 d + 37 d		2	2400-2800	Tegument		3	5,6	Kurume Laboratory (2001)
Cyprinus carpio	6.4-9.6	KPFOS	100	LC-MS	CF	gw	7.6-7.8	111	58 d + 37 d		2	2400-2900	Head		3	5,6	Kurume Laboratory (2001)
Cyprinus carpio	6.4-9.6	KPFOS	100	LC-MS	CF	gw	7.6-7.8	111	58 d + 37 d		2	3800-5100	Viscera		3	5,6	Kurume Laboratory (2001)
Cyprinus carpio	6.4-9.6	KPFOS	100	LC-MS	CF	gw	7.6-7.8	111	58 d + 37 d		2	3900-4700	Liver		3	5,6	Kurume Laboratory (2001)
Cyprinus carpio	6.4-9.6	KPFOS	100	LC-MS	CF	gw	7.6-7.8	111	58 d + 37 d		2	720-930	Remainder parts		3	5,6	Kurume Laboratory (2001)
Cyprinus carpio	6.4-9.6	KPFOS	100	LC-MS	CF	gw	7.6-7.8	111	58 d + 37 d		2	2180	Whole fish	kinetic ratio from presented data	2	5,6	Kurume Laboratory (2001)

Notes
1 initial loading 8 g/L, 2.5 in control
2 initial loading ≤3 g/L
3 The robust summary in the OECD hazard assessment has different values to those used in the main OECD text (which are those cited here). The 3M (2003) report explains that the original study used an inappropriate method to estimate the kinetic BCF values, and that those were revised in a later amended study report. This is assumed to explain the different values in the OECD robust summary, as the BCF values in the main report and the 3M report agree.
4 100% mortality after 35 d
5 initial loading less than 4 g/L
6 Chemicals Evaluation and Research Institute, Japan. Test number: 51520.

Table A1.2 Aquatic field bioaccumulation data for PFOS

Species common name	Latin name	Location	Year	Property/trophic level	BAF [L/kg]	Compartment	Reference
striped mullet	*Mugil cephalus*	Sarasota Bay	2002	2.4	6333	Marine	Houde et al., 2006
pigfish	*Orthopristis chrysoptera*	Sarasota Bay	2002	3.1	3444	Marine	Houde et al., 2006
sheepshead	*Archosargus probatocephalus*	Sarasota Bay	2002	3.2	3778	Marine	Houde et al., 2006
pinfish	*Lagodon rhomboides*	Sarasota Bay	2002	3.3	5333	Marine	Houde et al., 2006
spotted seatrout	*Cynoscion nebulosus*	Sarasota Bay	2002	3.7	9778	Marine	Houde et al., 2006
striped mullet	*Mugil cephalus*	Charleston Harbor area	2002-2004	3.4	2500	Marine	Houde et al., 2006
pinfish	*Lagodon rhomboides*	Charleston Harbor area	2002-2004	4.3	1583	Marine	Houde et al., 2006
red drum	*Sciaenops ocellatus*	Charleston Harbor area	2002-2004	3.9	5583	Marine	Houde et al., 2006
Atlantic croaker	*Micropogonias undulatus*	Charleston Harbor area	2002-2004	4.2	2833	Marine	Houde et al., 2006
spotfish	*Leiostomus xanthurus*	Charleston Harbor area	2002-2004	4.2	7667	Marine	Houde et al., 2006
spotted seatrout	*Cynoscion nebulosus*	Charleston Harbor area	2002-2004	4.3	7500	Marine	Houde et al., 2006
lake trout	*Salvelinus namaycush*	Lake Superior	2001	4 y, (4.9; Martin et al. 2004)	19953	Fresh	Furdui et al., 2007
lake trout	*Salvelinus namaycush*	Lake Huron	2001	4 y, (4.9; Martin et al. 2004)	15849	Fresh	Furdui et al., 2007
lake trout	*Salvelinus namaycush*	Lake Erie	2001	4 y, (4.9; Martin et al. 2004)	25119	Fresh	Furdui et al., 2007
lake trout	*Salvelinus namaycush*	Lake Ontario	2001	4 y, (4.9; Martin et al. 2004)	7943	Fresh	Furdui et al., 2007
lake trout	*Salvelinus namaycush*	Lake Michigan	2001	4 y, (4.9; Martin et al. 2004)	6310	Fresh	Furdui et al., 2007
round goby	*Neogobius melanostomus*	Raisin River, MI, USA	1998-2001		2456	Fresh	Kannan et al., 2005
round goby	*Neogobius melanostomus*	St. Clair River	1998-2001		4354	Fresh	Kannan et al., 2005
alewife	*Alosa pseudoharengus*	Lake Ontario	2001-2002		19000	Fresh	Houde et al., 2008
sculpin	*Cottus cognatus*	Lake Ontario	2001-2002		95000	Fresh	Houde et al., 2008
lake trout	*Salvelinus namaycush*	Lake Ontario	2001-2002		16000	Fresh	Houde et al., 2008

Table A1.3 Trophic magnification factors from field studies –BMF1

Sampling period	Sampling area	Species included	Trophic Magnification Factor (TMF) [kg/kg]	Ri	Reference
2001–2002	Niagara-on-the-Lake, Lake Ontario, ON, Canada	*Mysis relicta*, alewife (*Alosa pseudoharengus*), rainbow smelt (*Osmerus mordax*), lake trout (*Salvelinus namaycush*)	5.88	4	Martin et al., 2004
2001–2006	Lake Ontario, ON, Canada	zooplankton, *Mysis relicta*, alewife (*Alosa pseudoharengus*), rainbow smelt (*Osmerus mordax*), lake trout (*Salvelinus namaycush*)	4.2 L-PFOS: 3.9 MM-PFOS: 2.8 DM-PFOS: 0.77	3	Houde et al., 2008
2001–2006	Lake Ontario, ON, Canada	zooplankton, *Diporeia hoyi*, *Mysis relicta*, alewife (*Alosa pseudoharengus*), rainbow smelt (*Osmerus mordax*), slimy sculpin (*Cottus cognatus*), lake trout (*Salvelinus namaycush*)	3.8 L-PFOS: 3.7 MM-PFOS: 3.0 DM-PFOS: 0.87	3	Houde et al., 2008
2005–2007	Lake in Beijing	common carp (*Cyprinus carpio*), crucian carp (*Carassius auratus*), leather catfish (*Clarias lazera*), white semiknife carp (*Hemiculter leucisculus*)	6.0	3	Li et al., 2008
May–August 2005	Western Scheldt, Terneuzen, Netherlands	herbivores: lugworm (*Arenicola marina*) primary carnivores: brown shrimp (*Crangon crangon*), sprat (*Sprattus sprattus*), sandeel (*Ammodytes* sp.) primary-secondary carnivores: green crab (*Carcinus maenas*), sole (*Solea solea*), plaice (*Pleuronectes platessa*), bib (*Trisopterus lucus*), eel (*Anguilla anguilla*), sea bass (*Dicentrarchus labrax*)	2.6	4	De Vos et al., 2008

Table A1.4 Trophic magnification factors from field studies – BMF2

Sampling period	Sampling area	Species included	trophic magnification factor (TMF) [kg/kg]	Ri	Reference
2002–2004	Charleston Harbor and surrounding waters, SC, USA	striped mullet (*Mugil cephalus*), pinfish (*Lagodon rhomboides*), red drum (*Sciaenops ocellatus*), Atlantic croaker (*Micropogonias undulatus*), spotfish (*Leiostomus xanthurus*), spotted sea trout (*Cynoscion nebulosus*), bottlenose dolphin (*Tursiops truncatus*)	1.8	4	Houde et al., 2006
2004	Sarasota Bay, FL, USA	striped mullet (*Mugil cephalus*), pinfish (*Lagodon rhomboides*), red drum (*Sciaenops ocellatus*), Atlantic croaker (*Micropogonias undulatus*), spotfish (*Leiostomus xanthurus*), spotted sea trout (*Cynoscion nebulosus*), bottlenose dolphin (*Tursiops truncatus*)	1.4	4	Houde et al., 2006
1996–2002	Eastern Canadian arctic	zooplankton, clams (*Mya truncata*; *Serripes groenlandica*), shrimp (*Pandalus borealis; Hymenodora glacialis*), Arctic cod (*Boreogadus saida*), redfish (*Sebastes mentella*), walrus (*Odobenus rosmarus*), narwhal (*Monodon monoceros*), beluga (*Delphinapterus leucas*)	1.7	3	Tomy et al., 2004
May–August 2005	Western Scheldt, Terneuzen	primary carnivores: brown shrimp (*Crangon crangon*), sprat (*Sprattus sprattus*), sandeel (*Ammodytes* sp.) Secondary carnivores: common tern eggs (*Sterna hirundo*)	2.4	4	De Vos et al., 2008
May–August 2005	Western Scheldt, Terneuzen	primary-secondary carnivores: green crab (*Carcinus maenas*), sole (*Solea solea*), plaice (*Pleuronectes platessa*), bib (*Trisopterus lucus*), eel (*Anguilla anguilla*), sea bass (*Dicentrarchus labrax*) Secondary carnivores: common tern eggs (*Sterna hirundo*)	4.6	4	De Vos et al., 2008

Appendix 2. Detailed aquatic toxicity data

Table A2.1 Acute toxicity data for freshwater species

Scientific Name	Substance	Purity [%]	A y/n	Test Type	Temp [°C]	pH	DO [mg/L]	Exp. Time	Endpoint	Criterion	Conc. [mg/L]	Conc. ion [mg/L]	Ri[a]	Notes	Reference
Algae															
Chlorella vulgaris	K+ salt	95	n	-	23+/- 1			96 h	Cell density	IC50	81.6	81.6	2	1,2	Boudreau et al., 2003b
Chlorella vulgaris	K+ salt	95	n	-	23+/- 1			96 h	Chlorophyll a	IC50	88.1	88.1	2	1,2	Boudreau et al., 2003b
Navicula pelliculosa	K+ salt			s				96 h	growth rate	EC50	305	283	1 (OECD)	3	3M (2001), ref 38 in OECD, 2002
Pseudokirchneriella subcapitata	K+ salt	95	n		23+/- 1			96 h	Cell density	IC50	48.2	48.2	2	1,2	Boudreau et al., 2003b
Pseudokirchneriella subcapitata	K+ salt	95	n		23+/- 1			96 h	Chlorophyll a	IC50	59.2	59.2	2	1,2	Boudreau et al., 2003b
Pseudokirchneriella subcapitata	K+ salt	90.49	y	s	23.6-25.8	7.5-8.1		72 h	Cell density	EC50	70	70	1 (OECD)	4	Wildlife Int. (2000b), ref 2 in OECD, 2002
Pseudokirchneriella subcapitata	K+ salt	90.49	y	s	23.6-25.8	7.5-8.1		96 h	Cell density	EC50	71	71	1 (OECD)	4	Wildlife Int. (2000b), ref 2 in OECD, 2002
Pseudokirchneriella subcapitata	K+ salt	90.49	y	s	23.6-25.8	7.5-8.1		72 h	area under curve	EbC50	74	74	1 (OECD)	4	Wildlife Int. (2000b), ref 2 in OECD, 2002
Pseudokirchneriella subcapitata	K+ salt	90.49	y	s	23.6-25.8	7.5-8.1		96 h	area under curve	EbC50	71	71	1 (OECD)	4	Wildlife Int. (2000b), ref 2 in OECD, 2002
Pseudokirchneriella subcapitata	K+ salt	90.49	y	s	23.6-25.8	7.5-8.1		72 h	Growth rate	ErC50	120	120	1 (OECD)	4	Wildlife Int. (2000b), ref 2 in OECD, 2002
Pseudokirchneriella subcapitata	K+ salt	90.49	y	s	23.6-25.8	7.5-8.1		96 h	Growth rate	ErC50	126	126	1 (OECD)	4	Wildlife Int. (2000b), ref 2 in OECD, 2002
Pseudokirchneriella subcapitata	K+ salt		n	s				96 h	cell density	EC50	82	76	2 (OECD)	4	3M (1981), ref 13 in OECD, 2002
Cyanobacteria															
Anabaena flos-aqua	K+ salt		y	s				96 h	growth rate	EC50	176	176	1 (OECD)	3	3M (2001), ref 36 in OECD, 2002
Macrophyta															
Lemna gibba	K+ salt		n	-	25+/- 1			7 d	frond number	EC50	59.1	59.1	2	1,2	Boudreau et al., 2003b
Lemna gibba	K+ salt		n	-	25+/- 1			7 d	wet weight	EC50	31.1	31.1	2	1,2	Boudreau et al., 2003b
Crustaceans															
Daphnia magna	K+ salt		y	s				48 h	Immobility/mortality	EC50	61	61	1 (OECD)	5	3M (2000), ref 3 in OECD, 2002
Daphnia magna	K+ salt			s				48 h	Immobility/mortality	EC50	27	25	2 (OECD)	6	3M (1984), ref 15 in OECD, 2002
Daphnia magna	K+ salt			s				48 h	Immobility/mortality	EC50	<210	<195	2 (OECD)	7	3M (2000), ref 17 in OECD, 2002
Daphnia magna	K+ salt			s				48 h	Immobility/mortality	EC50	58	54	2 (OECD)	8	3m (2001), ref 33 in OECD, 2002
Daphnia magna	K+ salt	95	n		21+/- 1			48 h	Immobility/mortality	EC50	67.2	67.2	2	1,2,9	Boudreau et al., 2003b
Daphnia magna	Mixture of didecyldimethyl ammonium PFOS salt (~ 35%) and water with 5% residual perfluorochems	35	n	s	20.9-21.0	8.04-8.11	8.0-9.1	48 h	Immobility/mortality	EC50	4	2.4	2 (OECD)	10	Asci (1996), ref 29 in OECD, 2002
Daphnia magna	PFOS acid			s	21+/- 1			48 h	Immobility/mortality	EC50	37.4	37.4	2	11	Ji et al., 2008
Daphnia magna	K+ salt	>98		s	25+/- 1		7.8-7.9	48 h	Mortality	LC50	63	58	2	5	Li, 2009
Daphnia pulicaria	K+ salt	95	n		21+/- 1			48 h	Immobility/mortality	EC50	134	124	2	1,2,9	Boudreau et al., 2003b
Moina macrocopa	PFOS acid			s	25+/- 1			48 h	Immobility/mortality	EC50	18	18	2	11	Ji et al., 2008

Scientific Name	Substance	Purity [%]	A y/n	Test Type	Temp [°C]	pH	DO [mg/L]	Exp. Time	Endpoint	Criterion	Conc. [mg/L]	Conc. ion [mg/L]	Ri[a]	Notes	Reference
Neocaridina denticulate	K+ salt	>98		s	25+/- 1			96 h	Mortality	LC50	10	9.3	2	12	Li, 2009
Platyhelmintes															
Dugesia japonica	K+ salt	>98		s	25+/- 1			96 h	mortality	LC50	17	15.8	2		Li, 2008
Dugesia japonica	K+ salt	>98		s	25+/- 1			96 h	Mortality	LC50	23	21.3	2		Li, 2009
Mollusca															
Physa acuta	K+ salt	>98		s	25+/- 1			96 h	Mortality	LC50	178	165	2		Li, 2009
Unio complamatus	K+ salt		y	r	21.4-23.7	8.0-8.5	5.8-8.6	96 h	Mortality	LC50	59	59	1 (OECD)		Wildlife Int. (2000h), ref 5 in OECD, 2002
Fish															
Lepomis macrochirus	diethanolamine (DEA) salt	n	s	22	8.2-8.3		5.8-8.4	96 h	Mortality	LC50	7.8	6.4	2 (OECD)	13,14	AB Laboratories (1979), ref 20 in OECD, 2002
Pimephales promelas	K+ salt		y	s	20.4-22.1	8.3-8.6	7.8-9.0	96 h	Mortality	LC50	9.5	9.5	1 (OECD)	14,15	Wildlife Int. (2000a), ref 1 in OECD, 2002
Pimephales promelas	lithium salt		n	s				96 h	Mortality	LC50	4.7	4.6	2 (OECD)	15	3M (1994), ref 16 in OECD, 2002
Pimephales promelas	Mixture of didecyldimethyammonium PFOS salt (~ 35%) and water with 5% residual perfluorochems	n	s					96 h	Mortality	LC50	200	121	2 (OECD)	10,14	3M (2001), ref 28 in OECD, 2002
Oncorhynchus mykiss	K+ salt		n		15	7.4-8.7	8.0-10.4	96 h	Mortality	LC50	7.8	7.2	2 (OECD)	16	Beak (1985a), ref 31 in OECD, 2002
Oncorhynchus mykiss	K+ salt	86.7	y	s				96 h	Mortality	LC50	22	22	2 (OECD)	14	3M (2002), ref 42 in OECD, 2002

a: Reliability Index according to Klimisch et al., 1997.

Notes:
1 According to ASTM protocols
2 Reported concentration based on the anion
3 According to OPPTS 850.5400 protocol
4 According to OECD 201 protocol
5 According to OECD 202 protocol
6 According to ASTM 1981 and OECD 1981 protocol
7 Stock solution was prepared at a concentration that exceeded water solubility, therefore exposure concentrations are likely to be lower than nominal.
8 According to ISO 1982 protocol
9 Hardness 200-225 mg/L of $CaCO_3$
10 Endpoint calculated assuming 35% of substance in mixture.
11 According to US EPA 2002 protocol
12 According to Taiwan EPA standard protocol (2005)
13 Nominal exposure concentrations expressed relative to concentration of test substance (~25% PFOS DEA salt and 75% water). Results divided by 4 to PFOS DEA salt concentration based on reported 96 hour LC50 31 mg/L and NOEC of 18 mg/L.
14 According to OECD 203 protocol
15 Nominal exposure concentration expressed relative to concentration of test substance (24.5% PFOS Li salt and 74.5% water). Test result divided by 4 to express 96 h LC50 in terms of PFOS Li salt concentration.
16 According to Standard Procedures of Environment Canada

Table A2.2 Acute toxicity data for marine species

Scientific Name	Substance	Purity [%]	A y/n	Test Type	Temp [ºC]	pH	DO [mg/L]	Exp. Time	Endpoint	Criterion	Conc. [mg/L]	Conc. ion [mg/L]	Ri[a]	Notes	Reference
Algae															
Skeletonema costatum	K+ salt		y	s	20.2-21.4	8.0-8.4		96 h	Growth rate	EC50	>3.2	>3.2	1 (OECD)	1	Wildlife Int. (2001b), ref 39 in OECD, 2002
Crustaceans															
Americamysis bahia	K+ salt		y	s	24.2-25.4	8.1-8.2	6.8-7.4	96 h	Mortality	LC50	3.6	3.6	1 (OECD)	2	Wildlife Int. (2000e), ref 7 in OECD, 2002
Artemia sp.	K+ salt		n	s	21	8.0-8.2	>6.0	48 h	Mortality	LC50	8.9	8.3	2 (OECD)	3	Beak (1985b), ref 32 in OECD, 2002
Molluscs															
Crassostrea virginica	K+ salt		y	s	21.8-22.7	7.6-8.1	6.1-7.7	96 h	Shell Growth	EC50	>3.0	>3.0	1 (OECD)	4	Wildlife Int. (2000f), ref 4 in OECD, 2002
Fish															
Oncorhynchus mykiss	K+ salt		n	r	15	7.2-8.0	8.0-10.3	96 h	Mortality	LC50	13.7	12.7	2 (OECD)	5	Beak (1985c), ref 30 in OECD, 2002
Cyprinodon variegatus	K+ salt	86.7	y	r	22.1-23.1	7.9-8.3	1.7-7.6	96 h	Mortality	LC50	>15	>15	2 (OECD)	6	Wildlife Int. (2002), ref 43 in OECD, 2002

a: Reliability Index according to Klimisch et al., 1997.

Notes:
1 According to OPPTS 850.5400 protocol
2 According to OPPTS 850.1035 protocol
3 Sample purity not characterised; according to draft ISO 1981 protocol
4 According to OPPTS 850.1025 protocol
5 According to Standard Procedures of Environment Canada; acclimated to 30‰ salinity
6 Results reported as a.i; according to OECD 203 protocol

Table A2.3 Chronic toxicity data for freshwater species

Scientific Name	Substance	Purity [%]	A y/n	Test Type	Temp [°C]	pH	DO [mg/L]	Exp. Time	Endpoint	Criterion	Conc. [mg/L]	Conc. ion [mg/L]	Ri[a]	Notes	Reference
Algae															
Chlorella vulgaris	K+ salt	95	n	-	23+/- 1			96 h	Cell density	EC10	8.2	8.2	2	1	Boudreau et al., 2003b
Chlorella vulgaris	K+ salt	95	n	-	23+/- 1			96 h	Chlorophyll a	EC10	9.6	9.6	2	1	Boudreau et al., 2003b
Navicula pelliculosa	K+ salt			s				96 h	growth rate	NOEC	206	191	1 (OECD)	2	3M (2001), ref 38 in OECD, 2002
Pseudokirchneriella subcapitata	K+ salt		n	s				96 h	Cell density	EC10	10	9.3	2 (OECD)	3	3M (1981), ref 13 in OECD, 2002
Pseudokirchneriella subcapitata	K+ salt		n	s				14 d	Cell density	EC10	16	15	2 (OECD)	3	3M (1981), ref 13 in OECD, 2002
Pseudokirchneriella subcapitata	K+ salt	95	n	-	23+/- 1			96 d	Chlorophyll a	EC10	16.6	17	2	1	Boudreau et al., 2003b
Pseudokirchneriella subcapitata	K+ salt	95	n	-	23+/- 1			96 h	Cell density	EC10	5.3	5.3	2	1	Boudreau et al., 2003b
Pseudokirchneriella subcapitata	K+ salt	90.49	y	s	23.6-25.8	7.5-8.1		72 h	Growth rate	EC10	53	53	1 (OECD)	4	Wildlife Int. (2000b), ref 2 in OECD, 2002
Pseudokirchneriella subcapitata	K+ salt	90.49	y	s	23.6-25.8	7.5-8.1		72 h	Cell density	EC10	37	37	1 (OECD)	4	Wildlife Int. (2000b), ref 2 in OECD, 2002
Pseudokirchneriella subcapitata	K+ salt	90.49	y	s	23.6-25.8	7.5-8.1		72 h	Area under the curve	EC10	46	46	1 (OECD)	4	Wildlife Int. (2000b), ref 2 in OECD, 2002
Pseudokirchneriella subcapitata	K+ salt	90.49	y	s	23.6-25.8	7.5-8.1		96 h	Growth rate	EC10	59	59	1 (OECD)	4	Wildlife Int. (2000b), ref 2 in OECD, 2002
Pseudokirchneriella subcapitata	K+ salt	90.49	y	s	23.6-25.8	7.5-8.1		96 h	Cell density	EC10	49	49	1 (OECD)	4	Wildlife Int. (2000b), ref 2 in OECD, 2002
Pseudokirchneriella subcapitata	K+ salt	90.49	y	s	23.6-25.8	7.5-8.1		96 h	Area under the curve	EC10	49	49	1 (OECD)	4	Wildlife Int. (2000b), ref 2 in OECD, 2002
Cyanobacteria															
Anabaena flos-aqua	K+ salt		y	s				96 h	growth rate	NOEC	94	94	1 (OECD)	2	3M (2001), ref 36 in OECD, 2002
Macrophytes															
Lemna gibba	K+ salt		n	-	25+/- 1			7 d	frond number	EC10	29.2	29.2	2	1	Boudreau et al., 2003b
Lemna gibba	K+ salt		n	-	25+/- 1			7 d	wet weight	EC10	6.6	6.6	2	1	Boudreau et al., 2003b
Lemna gibba G3	K+ salt		y	s		7.9-8.9		7 d	Inhibition of frond production	NOEC	15.1	15.1	1 (OECD)	5	Wildlife Int. (2001a), ref 37 in OECD, 2002
Myriophyllum sibiricum	K+ salt							42 d	biomass	EC10	0.6	0.56	2	6	Hanson et al., 2005
Myriophyllum spicatum	K+ salt							42 d	biomass	EC10	3.5	3.2	2	6	Hanson et al., 2005
Crustaceans															
Daphnia magna	K+ salt		y	r	19.4-20.1	8.1-8.5	8.3-8.9	21 d	Survival	NOEC	12	12	1 (OECD)	7	Wildlife Int. (2000g), ref 9 in OECD, 2002
Daphnia magna	K+ salt		y	r				21 d	Reproduction	NOEC	12	12	1 (OECD)	7	Wildlife Int. (2000g), ref 9 in OECD, 2002
Daphnia magna	K+ salt		y	r				21 d	Growth	NOEC	12	12	1 (OECD)	7	Wildlife Int. (2000g), ref 9 in OECD, 2002
Daphnia magna	K+ salt	95	n	-	21+/- 1			21 d	adult survival	NOEC	25	25	2	1	Boudreau et al., 2003b
Daphnia magna	K+ salt	95	n	-	21+/- 1			21 d	days to first brood	NOEC	25	25	2	1	Boudreau et al., 2003b
Daphnia magna	K+ salt	95	n	-	21+/- 1			21 d	number of young/adult or brood	NOEC	25	25	2	1	Boudreau et al., 2003b
Daphnia magna	K+ salt	95	n	-	21+/- 1			21 d	adult survival	EC10	5.3	5.3	2	1	Boudreau et al., 2003b
Daphnia magna	K+ salt		n	r				28 d	Reproduction	NOEC	7	6.5	2 (OECD)	8	3M (1984), ref 15 in OECD, 2002
Daphnia magna	PFOS acid			s	21+/- 1			21 d	adult survival	NOEC	≥ 5	≥ 5	2	7	Ji et al., 2008
Daphnia magna	PFOS acid			s	21+/- 1			21 d	days to first brood	NOEC	1.25	1.25	2	7	Ji et al., 2008
Daphnia magna	PFOS acid			s	21+/- 1			21 d	number of young/adult	NOEC	1.25	1.25	2	7	Ji et al., 2008

Scientific Name	Substance	Purity [%]	A y/n	Test Type	Temp [°C]	pH	DO [mg/L]	Exp. Time	Endpoint	Criterion	Conc. [mg/L]	Conc. ion [mg/L]	Ri[a]	Notes	Reference
Daphnia magna	PFOS acid			s	21+/- 1			21 d	number of young/brood	NOEC	1.25	1.25	2	7	Ji et al., 2008
Daphnia magna	PFOS acid			s	21+/- 1			21 d	number of broods/adult	NOEC	≥ 5	≥ 5	2	7	Ji et al., 2008
Daphnia magna	PFOS acid			s	21+/- 1			21 d	adult survival	EC10	1.1	1.1	2	7	Ji et al., 2008
Daphnia magna	PFOS acid			s	21+/- 1			21 d	number of young/adult	EC10	1.1	1.1	2	7	Ji et al., 2008
Daphnia magna	PFOS acid			s	21+/- 1			21 d	number of young/brood	EC10	1.7	1.7	2	7	Ji et al., 2008
Daphnia magna	PFOS acid			s	21+/- 1			21 d	number of broods/adult	EC10	3.7	3.7	2	7	Ji et al., 2008
Daphnia magna	PFOS acid			s	21+/- 1			21 d	population growth rate	EC10	1.0	1.0	2	7	Ji et al., 2008
Moina macrocopa	PFOS acid			s	25+/- 1			7 d	adult survival	NOEC	1.25	1.25	2	9	Ji et al., 2008
Moina macrocopa	PFOS acid			s	25+/- 1			7 d	days to first brood	NOEC	≥ 5	≥ 5	2	9	Ji et al., 2008
Moina macrocopa	PFOS acid			s	25+/- 1			7 d	number of young/adult	LOEC	0.3125	0.3125	2	9	Ji et al., 2008
Moina macrocopa	PFOS acid			s	25+/- 1			7 d	number of young/brood	NOEC	0.3125	0.3125	2	9	Ji et al., 2008
Moina macrocopa	PFOS acid			s	25+/- 1			7 d	number of brood/adult	NOEC	0.3125	0.3125	2	9	Ji et al., 2008
Moina macrocopa	PFOS acid			s	25+/- 1			7 d	adult survival	EC10	1.1	1.1	2	9	Ji et al., 2008
Moina macrocopa	PFOS acid			s	25+/- 1			7 d	number of young/adult	EC10	0.079	0.079	2	9	Ji et al., 2008
Moina macrocopa	PFOS acid			s	25+/- 1			7 d	number of young/brood	EC10	0.17	0.17	2	9	Ji et al., 2008
Moina macrocopa	PFOS acid			s	25+/- 1			7 d	number of broods/adult	EC10	0.29	0.29	2	9	Ji et al., 2008
Moina macrocopa	PFOS acid			s	25+/- 1			7 d	population growth rate	EC10	0.40	0.40	2	9	Ji et al., 2008
Insects															
Chironomus tentans	K+ salt	95	y	r	21-23		>5.0	36 d	Total Emergence	NOEC	<0.0023	<0.0023	2	10,17	MacDonald et al., 2004
Chironomus tentans	K+ salt	95	y	r	21-23		>5.0	36 d	Total Emergence	EC10	0.089	0.089	2	10	MacDonald et al., 2004
Chironomus tentans	K+ salt	95	y	r	23		>5.0	20 d	Growth	NOEC	0.022	0.022	2	10	MacDonald et al., 2004
Chironomus tentans	K+ salt	95	y	r	23		>5.0	20 d	Growth	EC10	0.088	0.088	2	10	MacDonald et al., 2004
Chironomus tentans	K+ salt	95	y	r	23		>5.0	20 d	Survival	NOEC	0.095	0.095	2	10	MacDonald et al., 2004
Chironomus tentans	K+ salt	95	y	r	23		>5.0	20 d	Survival	EC10	0.086	0.086	2	10	MacDonald et al., 2004
Chironomus tentans	K+ salt	95	y	r	23		>5.0	10 d	Growth	NOEC	0.049	0.049	2	10	MacDonald et al., 2004
Chironomus tentans	K+ salt	95	y	r	23		>5.0	10 d	Growth	EC10	0.049	0.049	2	10	MacDonald et al., 2004
Chironomus tentans	K+ salt	95	y	r	23		>5.0	10 d	Survival	NOEC	0.049	0.049	2	10	MacDonald et al., 2004
Chironomus tentans	K+ salt	95	y	r	23		>5.0	10 d	Survival	EC10	0.108	0.108	2	10	MacDonald et al., 2004
Enallagma cyathigerum	tetraethylammonium salt	98	n	r	21			120 d	foraging success	NOEC	0.01	0.01	4	11	Van Gossum et al., 2009
Enallagma cyathigerum	tetraethylammonium salt	98	n	r	21			15 d	hatching	NOEC	1	1	2		Bots et al., 2010
Enallagma cyathigerum	tetraethylammonium salt	98	n	r	21			20 d	larval survival	NOEC	0.1	0.1	2		Bots et al., 2010
Enallagma cyathigerum	tetraethylammonium salt	98	n	r	21			120 d	larval survival	NOEC	0.01	0.01	2		Bots et al., 2010
Enallagma cyathigerum	tetraethylammonium salt	98	n	r	21			120 d	metamorphosis	NOEC	< 0.01	< 0.01	2	18	Bots et al., 2010
Fish															
Lepomis macrochirus	K+ salt		y					62 d	Survival	NOEC	0.086-0.87	0.086-0.87	1 (OECD)	12	3M (2001), ref 41 in OECD, 2002
Oryzias latipes	PFOS acid			r	25+/- 1			14 d	reproduction	NOEC	0.1	0.1	2		Ji et al., 2008
Oryzias latipes	PFOS acid			r	25+/- 1			14 d	survival of larvae	NOEC	<0.01	<0.01	2		Ji et al., 2008
Pimephales promelas	K+ salt	>98	y	f	25+/- 1	7.3	6.2	21 d	Spawning	NOEC	0.0276	0.0276	2	13	Ankley et al., 2005
Pimephales promelas	K+ salt	>98	y	f	25+/- 1	7.3	6.2	21 d	Hatching success	NOEC	>0.281	>0.281	2	13	Ankley et al., 2005
Pimephales promelas	K+ salt	>98	y	f	25+/- 1	7.3	6.2	24 d	Survival	NOEC	>0.281	>0.281	2	13	Ankley et al., 2005

Scientific Name	Substance	Purity [%]	A y/n	Test Type	Temp [°C]	pH	DO [mg/L]	Exp. Time	Endpoint	Criterion	Conc. [mg/L]	Conc. ion [mg/L]	Ri[a]	Notes	Reference
Pimephales promelas	K+ salt		y	f	24.4-24.7	8.0-8.4	7.6-8.2	42 d	Post-hatch survival	NOEC	0.3	0.3	1 (OECD)	14	Wildlife Int. (2000c), ref 8 in OECD, 2002
Pimephales promelas	K+ salt		y	f	24.4-24.7		7.6-8.4	42 d	Post-hatch growth	NOEC	0.3	0.3	1 (OECD)	14	Wildlife Int. (2000c), ref 8 in OECD, 2002
Pimephales promelas	K+ salt		y	f				30 d	ELS	NOEC	1	1	2 (OECD)		3M (2000), ref 14 in OECD, 2002
Pimephales promelas	K+ salt	86	y	s	16.6-29.2	8.9-10.9	6.3-12.4	28 d	Mortality	LC10	3.5	3.5	2	15	Oakes et al., 2005
Amphibians															
Xenopus laevis	K+ salt		y			7.0-7.7	7.0-8.5	96 h	Growth	NOEC	4.82	4.82	2 (OECD)	16	UM-WREC (2001), ref 40 in OECD, 2002
Xenopus laevis	K+ salt		y			7.0-7.7	7.0-8.5	96 h	Growth	NOEC	5.25	5.25	2 (OECD)	16	UM-WREC (2001), ref 40 in OECD, 2002
Xenopus laevis	K+ salt		y			7.0-7.7	7.0-8.5	96 h	Malformation	EC10	3.91	3.91	2 (OECD)	16	UM-WREC (2001), ref 40 in OECD, 2002
Xenopus laevis	K+ salt		y			7.0-7.7	7.0-8.5	96 h	Malformation	EC10	4.98	4.98	2 (OECD)	16	UM-WREC (2001), ref 40 in OECD, 2002
Xenopus laevis	K+ salt		y			7.0-7.7	7.0-8.5	96 h	Malformation	EC10	7.02	7.02	2 (OECD)	16	UM-WREC (2001), ref 40 in OECD, 2002
Xenopus laevis	K+ salt		y			7.0-7.7	7.0-8.5	96 h	Mortality	EC10	12.05	12.05	2 (OECD)	16	UM-WREC (2001), ref 40 in OECD, 2002
Xenopus laevis	K+ salt		y			7.0-7.7	7.0-8.5	96 h	Mortality	EC10	7.67	7.67	2 (OECD)	16	UM-WREC (2001), ref 40 in OECD, 2002
Xenopus laevis	K+ salt		y			7.0-7.7	7.0-8.5	96 h	Mortality	EC10	7.49	7.49	2 (OECD)	16	UM-WREC (2001), ref 40 in OECD, 2002

a: Reliability Index according to Klimisch et al., 1997.

Notes:
1 Reported concentrations based on the anion; according to ASTM protocols
2 According to OPPTS 850.5400 protocol
3 Result not expressed relative to growth rate. According to OECD 201; US EPA 600/9-78-018 and ASTM -E-35.23 protocol.
4 According to OECD 201 protocol
5 According to OPPS 850.4400 protocol
6 Microcosm study with sediment (13.9% OC). Results based on average measured concentrations; a number of endpoints are reported, biomass was selected as most relevant parameter
7 According to OECD 211 protocol; EC10 values derived by evaluator from presented data with log-logistic dose-response relationship
8 According to ASTM 1981/OECD 1981 protocol
9 According to Oh (2007) protocol, cited in ref; EC10 values derived by evaluator from presented data with log-logistic dose-response relationship
10 According to US EPA and ASTM protocols; test organisms exposed in clean sand
11 Larvae were used
12 Bioconcentration study (OECD 305)
13 Hardness 46 mg/L as $CaCO_3$; alkalinity 40 mg/L as $CaCO_3$; 16:8 hour light : dark
14 According to OECD 210 protocol
15 Microcosm experiment with sediment. Concentrations based on anion. Alkalinity 89.9-148.8 mg $CaCO_3$/L.
16 FETAX test. In-life phases were not subject to GLP
17 total emergence read from figure 50% as compared to 73% in the control (32% decrease)
18 successful metamorphosis 75.5% at 10 µg/L as compared to 92.5% in control (18% decrease)

Table A2.4 Chronic toxicity data for marine species

Scientific Name	Substance	Purity [%]	A y/n	Test Type	Temp [°C]	pH	DO [mg/L]	Exp. Time	Endpoint	Criterion	Conc. [mg/L]	Conc. ion [mg/L]	Ri[a]	Notes	Reference
Algae															
Skeletonema costatum	K+ salt		y	s	20.2-21.4	8.0-8.4		96 h	Growth rate	NOEC	>3.2	>3.2	1 (OECD)	1	Wildlife Int. (2001b), ref 39 in OECD, 2002
Crustaceans															
Americamysis bahia	K+ salt		y	f	24.5-25.2	8.2-8.4	5.9-6.4	35 d	Reproduction	NOEC	0.25	0.25	1 (OECD)	2	Wildlife Int. (2000d), ref 10 in OECD, 2002
Americamysis bahia	K+ salt		y	f	24.5-25.2	8.2-8.4	5.9-6.4	35 d	Growth	NOEC	0.25	0.25	1 (OECD)	2	Wildlife Int. (2000d), ref 10 in OECD, 2002
Americamysis bahia	K+ salt		y	f	24.5-25.2	8.2-8.4	5.9-6.4	35 d	Survival	NOEC	0.55	0.55	1 (OECD)	2	Wildlife Int. (2000d), ref 10 in OECD, 2002

a: Reliability Index according to Klimisch et al., 1997.

Notes:
1 According to OPPTS 850.5400 protocol
2 According to OPPTS 850.1350 protocol

Appendix 3. Mammal and bird toxicity data

Table A3.1 Mammal and bird toxicity data

Species	Species properties	Substance	Duration[b]	Route	Criterion	Endpoint	Result $mg/kg_{bw}/d$	BW/DFI[c]	Result diet mg/kg_{diet}	AF	MPC_{oral} $mg/kg_{biota\ ww}$	Ri[a]	Original reference
Rats			GD 6-15	gavage	NOAEL	maternal toxicity, developmental toxicity	5	20	100	90	1.11	2	Gortner, 1980
Rats			GD 6-15	gavage	NOAEL	maternal toxicity, developmental toxicity	1	20	20	90	0.22	2	Wetzel, 1983
Rats	Sprague-Dawley	KPFOS	GD2-21	gavage	NOAEL	maternal weight gain	1	10	10	90	0.11	2	Thibodeaux et al., 2003
Rats	Sprague-Dawley	KPFOS	GD2-21	gavage	NOAEL	foetal weight	5	10	50	90	0.56	2	Thibodeaux et al., 2003
Rats	Sprague-Dawley	KPFOS	GD2-21	gavage	NOAEL	foetal malformations	3-5	10	30-50			2	Thibodeaux et al., 2003
Rats	Sprague-Dawley	KPFOS	GD2-21	gavage	NOAEL	foetal malformations	1	10	10	90	0.11	2	Thibodeaux et al., 2003
Rats	Sprague-Dawley	KPFOS	GD2-21	gavage	NOAEL	foetal malformations	5	10	50	90	0.56	2	Thibodeaux et al., 2003
Rats	Sprague-Dawley	KPFOS	GD2-21	gavage	NOAEL	survival, growth, development	1	10	10	90	0.11	2	Lau et al,. 2003
Rats	Crl:CD®(SD)IGS VAF/Plus®	KPFOS	6 w prior mating - PD4	gavage	NOAEL	gestation length, pup viability	0.37	20.0	7.4	90	0.08	2	Luebker et al. 2005
Rats	CD	KPFOS	90 d	diet	NOEC	body weight, mortality food consumption	2	(15)	30	90	0.33	2	Goldenthal et al. 1978a
Rats	Sprague Dawley, Crl:CD† (SD) IGS BR	KPFOS	14 w	diet	NOEC	body weight	>1.5	(13.3)	>20			2	Seacat et al., 2003
Rats	Crl:CD(SD)IGS BR	KPFOS	chronic	diet	NOEC	carcinogenicity study	0.14	(14.3)	2	30	0.07	2	Thomford, 2002
Rats		KPFOS	two generation	gavage	NOAEL	survival, body weight F1	0.4	20	8	30	0.27	2	Christian et al. 1999
Rats		KPFOS	two generation	gavage	NOAEL	birth weight F2	0.1	20	2	30	0.07	2	Christian et al. 1999
Mice	CD-1	KPFOS	GD1-18	gavage	NOAEL	maternal weight gain	15	8.3	124.5	90	1.38	2	Thibodeaux et al., 2003
Mice	CD-1	KPFOS	GD1-18	gavage	NOAEL	foetal weight	5	8.3	41.5	90	0.46	2	Thibodeaux et al., 2003
Mice	CD-1	KPFOS	GD1-18	gavage	NOAEL	foetal malformations	1-15	8.3	8.3-124.5			2	Thibodeaux et al., 2003
Mice	CD-1	KPFOS	GD1-18	gavage	NOAEL	sternal defects	1	8.3	8.3	90	0.09	2	Thibodeaux et al., 2003
Mice	CD-1	KPFOS	GD1-18	gavage	NOAEL	cleft palate	10	8.3	83	90	0.92	2	Thibodeaux et al., 2003
Rabbit	New Zealand white	KPFOS	GD6-20	gavage	NOAEL	birth weight, ossification	1	33.3	33.3	90	0.37	2	Case et al. 2001
Rabbit	**New Zealand white**	**KPFOS**	**GD6-20**	**gavage**	**NOAEL**	**maternal weight gain**	**0.1**	**33.3**	**3.33**	**90**	**0.037**	2	**Case et al. 2001**
Rhesus monkeys		KPFOS	90 d	gavage	NOAEL	survival	1.5	20	30	90	0.33	2	Goldenthal et al., 1978b
Rhesus monkeys		KPFOS	90 d	gavage	NOAEL	severe gastrointestinal effects, trembling; monkeys were euthanized to prevent further suffering	0.5	20	10	90	0.11	2	Goldenthal et al., 1978b
Cynomolgus monkeys	2.4-4.4 kg	KPFOS	183 d	intubation	NOAEL	body weight, mortality	0.15	20	3	30	0.10	2	Seacat et al., 2002
mallard ducks		KPFOS	21 w	diet	NOEC	body weight, reproduction	1.49	6.7	10	30	0.33	2	Newsted et al., 2007
northern bobwhite quail		KPFOS	21 w	diet	NOEC	body weight, reproduction	0.77	13	10	30	0.33	2	Newsted et al., 2007

a: Reliability Index according to Klimisch et al., 1997.
b: GD = Gestation day
c: Conversion factor body weight/daily food intake (see Van Vlaardingen and Verbruggen, 2007)

Appendix 4. Description of microcosm studies

Study 1

Reference	Sanderson H, Boudreau TM, Mabury SA, Cheong W-J, Solomon KR. 2002. Ecological impact and environmental fate of perfluorooctane sulfonate on the zooplankton community in indoor microcosms. Ecotoxicol Environ Chem 21: 1490-1496
Species; Population; Community	zooplankton, gastropods, macoinvertebrates, macrophytes, insects
Test Method	indoor microcosm
System properties	30 L; natural water and sediment
Test substance	K salt of PFOS
Exposure regime	1, 10 and 30 mg/L (expressed as anion); single application, mixing
Analysed	Yes, on days 1, 8 and 35
Temperature [°C]	18 °C
pH range	8.28-8.37 (mean 8.3)
Hardness [mg $CaCO_3$/L]	not specified
Exposure time	35 days
Criterion	NOEC
Test endpoint	zooplankton
Value [mg/L]	< 10 mg/L (expressed as anion)
GLP	not specified
Guideline	not specified
Ri	2

DESCRIPTION

Test system. Indoor microcosms of PVC, 46 x 26 x 26 cm, 30 L, natural pond water (pH 8.3) and sediment. Temperature 18 °C, 12:12 h L:D (2852 lumen). Constant aeration, DO 6 mg/L.
The zooplankton community consisted of *Cyclops diaptomus*, *C. strenuous*, *Canthocamptus staphylinus*, *Daphnia magna*, *Keratella quadrata*, *Phyllopoda* sp., *Echinorhynchus* sp., *Ostracoda* sp., and *Rotifera* sp. In addition, pond snails and occasional macrophytes (*Elodea canadensis* and *Myriophyllum spicatum*) and larger invertebrates (*Ephemeroptera* sp., *Asellus aquaticus*) were also present. Phytoplankton (*Scenedesmus acutus*) were added each week to prevent food deficiency.
Test concentrations 1, 10 and 30 mg/L (as anion) and control, five replicates per treatment. Test solutions were added to the systems and water was hand-mixed.
Water sampling. Water samples were taken after 1, 8 and 35 days. Analysis of PFOS by HPLC-ion chromatography with conductivity detector. Range of calibration curve 0.6-70 mg/L.
Monitoring of pH, P and total N on days 1, 14 and 35.
Biological sampling. Sampling of zooplankton 24 hours before and after treatment, and after 2, 4, 7, 14, 21, 28 and 35 days using funnel traps. Traps were installed for 24 hours, a volume of 30 mL was analysed and counted. Chlorophyll *a* was sampled at study termination.
Statistical analysis
ANOVA on dominant zooplankton species, total zooplankton abundance, number of species and end stock of chlorophyll *a*.

RESULTS

Chemical analysis. Initial measured concentrations were between 113 and 133% of nominal. Concentrations remained constant with 12% decline on average. Geometric means of the reported measured concentrations were 1.2, 12.0 and 31.7 mg/L.

Water quality. Overall mean nitrate was 5.3 mg/L (2.2-13.5), total P < 2 µg/L. No difference between treatments and control. pH 8.3 (8.28-8.37). Chlorophyll a was not
Biological observations.

- Copepods. *Cyclops diaptomus* and *C. canthocamptus* were absent at 30 mg/L after one week and at 10 mg/L after two weeks, control abundance remained constant. At 1 mg/L, numbers of *C. diaptomus* were lower than in the control. Numbers declined towards very low levels after 35 days, but differences were already present pre-treatment and differences were not significant. An increase of *C. canthocampus* was observed after one week at 1 mg/L, abundance was constant thereafter.
- *Daphnia magna*. *D. magna* was almost entirely reduced at 10 and 30 mg/L, but differences were only significant at days 7, 14 and 21 because of low statistical power due to control variability.
- Rotifers. Abundance of total rotifers at 1 mg/L was always higher than in the control (not significant). Abundance of smaller and tolerant rotifer species increased, abundance in the control was temporarily significantly lower than in the treatments. Larger rotifers decreased.
- Ephemeroptera. Mayflies were absent at 10 and 30 mg/L. At 1 mg/L, three mayflies emerged after three weeks, otherwise there were none. Mayfly abundance in the control was higher (n=5, 4 and 3 after three, four and five weeks, respectively).
- Species diversity. The total number of species was significantly reduced at 10 and 30 mg/L. At 1 mg/L, the number of species was lower than in the control as from 14 days after treatment, differences were not significant.
- Total abundance. Total abundance of zooplankton at 10 and 30 mg/L was significantly different from the control after one and two weeks. Numbers started to decline after 1 to 4 days and remained constant at a low level from 7 days onwards. Abundance at 1 mg/L was also lower, but levels remained constant and the difference with the control was already present before treatment.
- Chlorophyll *a*. There was a significant increase in chlorophyll *a* with increasing PFOS concentrations, indicative of an indirect effect resulting from decreased grazing activity.

There were no significant differences at 1 mg/L as compared to the control, but the authors conclude that it is not possible to define this treatment as the NOEC because statistical power was too low. For instance, an effect of 25% on number of species was not detected as significant.

Evaluation of the scientific reliability of the field study and the suitability for ERL-derivation

The reliability and usefulness of the study for derivation of ERLs is evaluated according to the following criteria:

1. Does the test system represent a realistic freshwater community?
   Yes/No. The zooplankton community consisted of several representative species groups. Sampling was restricted to zooplankton. For the other groups mentioned (snails, macrophytes, larger invertebrates), it is not clear whether distribution was comparable between replicates and treatments (presence of macrophytes is described as “occasional”). Potential effects on these groups were not included in the study, mayflies are mentioned in the discussion. Fish were not present.
2. Is the description of the experimental set-up adequate and unambiguous?
   Yes.
3. Is the exposure regime adequately described?
   Yes. Measured concentrations at start were close to nominal and remained more or less constant throughout the study.
4. Are the investigated endpoints sensitive and in accordance with the working mechanism of the compound?
   No. From the available laboratory data it appears that insects, fish and macrophytes are the

potentially most sensitive species groups on a chronic scale. Except for mayflies, these were not included in the present study.

5. Is it possible to evaluate the observed effects statistically?
   No. Results are presented for selected zooplankton species only, results for rotifers are only given for the phylum as a whole. From the graphs it appears that there was considerable pre-treatment variation, especially considering abundance of total zooplankton, *Cyclops diaptomus* and *Daphnia magna*. For total abundance and *C. diaptomus*, pre-treatment deviation from the control was highest for the 1 mg/L-treatment. It is not clear if and how this was accounted for in the statistical analysis. The authors use the term "$NOEC_{community}$" in their discussion of endpoints, but since the evaluation is not based on a PRC, the NOECs refer to selected zooplankton groups.

Based on the criteria listed above, the study is considered to be less reliable mainly due to the restriction to specific zooplankton species and the uncertainty with respect to statistical methods. It is clear, however, that the NOEC for zooplankton is < 10 mg/L (Ri 2). In view of the constant exposure conditions, the endpoint should in principle be considered for derivation of the $MPC_{eco, water}$. However, information from laboratory studies indicates that zooplankton may not represent the most sensitive species groups, which limits the usefulness of the endpoint for ERL-derivation.

Study 2

Reference	Boudreau TM, Wilson CJ, Cheong W-J, Sibley PK, Mabury SA, Muir DCG, Solomon KR. 2003. Response of the zooplankton community and environmental fate of perfluorooctane sulfonic acid in aquatic microocsms. Ecotoxicol Environ Chem 22: 2739-2745
Species; Population; Community	zooplankton, periphyton, phytoplankton, benthic invertebrates, algae, small plants, macrophytes; caged fish
Test Method	outdoor microcosm
System properties	12000 L; natural water and sediment
Test substance	K salt of PFOS
Exposure regime	0.3, 3, 10 and 30 mg/L (expressed as anion); single application, subsurface injection and mixing
Analysed	Yes, regularly over 285 days
Temperature [°C]	16-20 °C
pH range	8.3-8.8
Hardness [mg $CaCO_3$/L]	292–300 mg/L
Exposure time	35 days (zooplankton community; start on August 21, 2000) 42 days (bioassay *Lemna gibba*, start on May 21, 2001)
Criterion	NOEC
Test endpoint	zooplankton community
Value [mg/L]	3
GLP	not specified
Guideline	not specified
Ri	2
Notes	Results of the fish bioassays are reported separately in Oakes et al. (2005) Results of the Myriophyllum bioassays are reported in Hanson et al. (2005) These references are included in the single-species data tables in Appendix 2

DESCRIPTION

Test system. Outdoor microcosms, 11.95 m2, 1.05 m depth, 12000 L. Natural pond water (pH 8.3-8.8) and sediment (1:1:1 mixture of sand, loam and manure as OM, 13.9% OC; data from Hanson et al., 2005). Average temperature 16-20 °C, DO 7.2-8.8 mg/L.

Natural water from a spring-fed irrigation pond was circulated among the microcosms for 10 days prior to application (22 August, 2000). The community consisted of zooplankton, periphyton, phytoplankton, benthic invertebrates, algae, small plants. Additional macrophytes *Myriophyllum spicatum* and *M. sibiricum* were planted in holding trays, caged fathead minnows (*Pimephales promelas*) were introduced.

A separate 42-days study with *Lemna gibba* was started in May 2001. Laboratory cultured *L. gibba* were exposed in enclosures starting 1 hour after PFOS-application. Three compartments per microcosm, each compartment contained four plants with three fronds each. Plants were observed on days 7, 14, 21, 28, 35 and 42. Endpoints mean plant number, mean frond number and physical appearance.

Application. Test concentrations 0.3, 3, 10 and 30 mg/L (as anion) and control, three replicates per treatment, application on August 22, 2000. Test solutions were added to the systems by sub-surface injection followed by 15 min. circulation.

Water sampling. Water samples were taken at regular intervals for 42 days (PFOS data reported for 285 days). Analysis of PFOS by HPLC-ion chromatography with conductivity detector. The 0.3 mg/L-treatment was < LOD and not included. Water quality parameters (temperature, DO, pH, alkalinity and hardness) were monitored.

Biological sampling. Sampling of zooplankton one day before treatment, 1 h after treatments, and after 1, 2, 4, 7, 14, 21, 28 and 35 days using funnel traps. Traps (2 per cosms) were installed for 24 hours. Zooplankton was identified to species level where possible. Chlorophyll *a* was determined as surrogate for total phytoplankton.

Statistical analysis

Data were ln- or square root transformed when assumptions of homogeneity of variances and normality were not met. Scaling was applied to deal with zero values. ANOVA to test treatments versus control. Analysis of community effects by PRC using CANOCO, followed by Monte Carlo permutation tests. The $NOEC_{community}$ from the PRC was derived using William's test. Mean total zooplankton abundance analysed using multivariate Dunnett's test. IC10 and IC50 for growth inhibition of *L. gibba* determined by linear interpolation.

RESULTS

Chemical analysis. Average initial concentrations (1 h post-treatment) differed by 1.8 ± 8.7% from nominal. Measured concentrations during toxicological evaluations deviated by 2.2 ± 2.7% from nominal. Time weighted average concentrations were between 75 and 104% of initial measured. All endpoints were expressed on the basis of nominal concentrations.

Water quality. No differences were observed between treatments and control.

Biological observations. There were no significant differences in species abundance between replicates before treatment. A total of 92 zooplankton species was collected (Rotifera, Cladocera, Copepoda, macroinvertebrates and Ostracoda), the statistical analysis was performed on 68 species belonging to the first three groups.

- PRC. A significant change in the zooplankton community was present at 10 and 30 mg/L, where an increase in abundance occurred as compared to the control. The $NOEC_{community}$ was 3 mg/L on days 4, 7, 21 and 28, and 0.3 mg/L on day 35. A $NOEC_{community}$ could not be established for day 14, due to low power. The major part (43%) of the total variance could be explained by treatment, 23% by sampling day. From the species weight diagram it appeared that the positive trend was caused by two out of a total of 68 species: the rotifers *Bdelloidea* sp. and *Polyartha vulgaris* which had a positive weight of +0.6. In contrast, 21 organisms showed an opposite response (i.e. a decline), indicated by species weights < -0.6. The remaining 45 species either had insignificant roles or changed little over the duration of the study. The most prominent opposite response was displayed by the cladoceran *Simocephalus*

vetulus and copepod nauplii (larvae) with species weights of -3.5 and -3.0. Other species with an opposite response were the rotifers *Trichocerca* sp., *Cephalodella* sp., *Lecane monostyla* and *Lepadella* sp., and the copepod *Macrocyclops albidus*.

- Rotifers. At 30 mg/L, total abundance of rotifers was decreased by ≥ 89% between days 1 and 21, but differences were only significant on days 4, 21 and 35. A 100-fold increase in abundance was observed at 10 mg/L from day 14 to 28.
- Copepods. Total copepods at 30 mg/L were significantly reduced after day 2 until day 35. At 10 mg/L, a maximum decrease was seen after 14 days (significant), but numbers increased thereafter to control levels by day 28.
- Cladocerans. Response of total cladocerans at 30 mg/L was similar to that of copepods with a significant decrease after two days and no signs of an increase thereafter.
- Number of species. A significant reduction in species number was observed at 30 mg/L from day 1 onwards, mean reduction was 74.3% as compared to the control. The 10 mg/L-treatment showed a significant reduction in species number between 14 and 35 days, mean reduction was 45%. No significant differences were seen at 0.3 and 1 mg/L.
- Chlorophyll *a*. There was a high temporal variation in chlorophyll a concentrations in the PFOS-treated microcosms as compared to the control. A significant increase was present at 10 mg/l at day 4 and 14. Otherwise, no significant differences were observed, statistical power was generally low.
- *Lemna gibba*. Acute toxicity was evident at 30 mg/L. Frond number at 0.3 and 3 mg/L was decreased as compared to the control. Frond number at 10 mg/L was not significantly different at 10 mg/L, but visual signs of toxicity were present. The 42-days IC50 was reported to be 19.1 mg/L for frond number and 20.9 mg/L for plant number. The NOEC (IC10) for frond number was reported as 0.2 mg/L. Visual signs of toxicity were present as from day 4.

The authors conclude that the $NOEC_{community}$ for zooplankton is 3.0 mg/L.

Evaluation of the scientific reliability of the field study and the suitability for ERL-derivation

The reliability and usefulness of the study for derivation of ERLs is evaluated according to the following criteria:

1. Does the test system represent a realistic freshwater community?
   Yes/No. Microcosms contained a representative zooplankton community, but analysis was performed on rotifers, cladocerans and copepods only. The results on macrophytes and fish are reported separately in Hanson et al. (2005) and Oakes et al. (2005) and are included in the data tables in Appendix 2.
2. Is the description of the experimental set-up adequate and unambiguous?
   Yes/No. The description is adequate with respect to the August 2000 study on zooplankton, but not with respect to the *Lemna* test. The bioassay was started on 21 May, 2001, 1 h after treatment. It is not clear whether a second PFOS application was made to the microcosms that already had been treated in August 2000, or that other microcosms were used.
3. Is the exposure regime adequately described?
   Yes. Measured concentrations at start were close to nominal and remained more or less constant throughout the study.
4. Are the investigated endpoints sensitive and in accordance with the working mechanism of the compound?
   No. From the available laboratory data it appears that insects, fish and macrophytes are the potentially most sensitive species groups on a chronic scale. Results for these groups are not reported.
5. Is it possible to evaluate the observed effects statistically?
   Yes/No. The statistical analysis includes a PRC and the major zooplankton groups are discussed separately. Although the William's test resulted in a lowest $NOEC_{community}$ of 0.3 mg/L after 35 days, it is considered justified to set the overall $NOEC_{community}$ for zooplankton

to 3.0 mg/L in view of the PRC-diagram and analyses of separate taxa. The validity of the reported NOEC and EC50 for frond number of *Lemna gibba* is not clear, since frond number at 10 mg/L was comparable to the control.

Based on the criteria listed above, the results for *Lemna gibba* are not considered reliable. The study is considered to be reliable with respect to the NOEC for the zooplankton community, which is considered to be 3.0 mg/L (Ri 2). In view of the constant exposure conditions, the endpoint should in principle be considered for derivation of the $MPC_{eco, water}$. However, information from laboratory studies indicates that zooplankton may not represent the most sensitive species groups, which limits the usefulness of the endpoint for ERL-derivation.

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