ENVIRONMENTAL RISK EVALUATION REPORT: PERFLUOROOCTANESULPHONATE (PFOS)

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This report summarises the environmental hazards and risks of PFOS based on its recent and current use pattern in the EU. The information will be used by the Chemicals Policy function of the Agency and the Department of Environment, Food & Rural Affairs to inform decisions on the need for risk management.

Keywords
PFOS, perfluorooctane sulphonate, perfluoroalkylated, hazard, risk, PBT

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Foreword

Perfluorooctane sulphonate (PFOS) is a fully fluorinated anion, the related compounds of which are members of the large family of perfluoroalkylated substances (PFAS). The term PFOS-related substances is used in this document to represent any substance containing the PFOS moiety ($C_8F_{17}SO_2$) with the potential to degrade to PFOS in the environment.

In 2000, 3M (a major global producer of PFOS based in the United States) announced that the company would phase out the production of PFOS voluntarily from 2001 onwards. Production by 3M has now ceased. At a meeting of the OECD Task Force on Existing Chemicals following this announcement, several OECD countries agreed to work together informally to collect information on the effects of PFOS on the environment and on human health to allow hazard assessment to be produced. This hazard assessment concluded that the presence and persistence of PFOS in the environment, as well as its toxicity and bioaccumulation potential, indicate a cause for concern for the environment and for human health.

In response to these findings, the Environment Agency has commissioned this study to review the risks arising from current uses of PFOS-related substances. This work is being undertaken in tandem with a study commissioned by the Department for Environment, Food and Rural Affairs (Defra) to prepare a Risk Reduction Strategy for PFOS-related substances, including an analysis of the advantages and drawbacks of potential risk reduction options. This Risk Reduction Strategy will follow the provision of the EU Existing Substances Regulation according to which, where controls on the marketing and use of the substances in question are proposed, an analysis of the advantages and drawbacks of the substance should be undertaken.

A PBT assessment has been carried out as part of this risk evaluation. Although this PBT assessment concludes that PFOS is a PBT, calculations to allow a PEC:PNEC comparison have also been conducted to help establish priorities for the risk reduction strategy.

This risk evaluation report (RER) has been prepared in accordance with the principles of Council Regulation (EEC) 793/93 on the evaluation and control of the risks of "existing" substances (the "Existing Substances Regulation" or "ESR") and the methods laid down in Commission Regulation (EC) 1488/94[1] which is supported by a technical guidance document (TGD)[2]. The layout follows the format of an ESR RAR with a few small modifications, so that a reader familiar with such assessments can quickly find the information in which they are interested. It has been produced using publicly available data gathered and assessed by the contractor for the Environment Agency. Additional information has been submitted by various organisations and companies as part of the information gathering and consultation for the preparation of the Risk Reduction Strategy. Comments received during a consultation on a draft version of this report in June 2004 have also been taken into account.

Peer review process: The Environment Agency wishes to ensure that the data used in this report are as complete and accurate as possible. Original reports have been obtained and assessed for reliability where possible (it is clearly indicated where this is not the case), except where this has already been done for OECD SIDS purposes. In addition, results from the robust summaries in the 3M assessment (3M, 2003) have been included on the basis of the

[1] O.J. No. L 161, 29/06/1994 p. 0003 – 0011

[2] Technical Guidance Document, (First edition), Part I-V, ISBN 92-827-801[1234] and Second Edition, Parts I-IV, EUR 20418 EN/1-4

validity markings given in them. The report is currently under discussion by stakeholders with the aim of reaching consensus. However, it has not been possible to obtain as much industry-specific information as initially hoped. The information contained in this report does not, therefore, necessarily provide a sufficient basis for decision-making regarding the hazards, exposures or the risks associated with the substance.

In order to avoid possible misinterpretations or misuse of the findings in this draft, anyone wishing to cite or quote this report is advised contact the Environment Agency beforehand.

The Environment Agency would like to thank those who contributed information to the Risk Reduction Strategy and hence to this risk evaluation.

Date of Last Literature Search: **February 2004**

Executive Summary

PFOS is the perfluorooctane sulphonate anion and is not a substance as such. It is or was commercially available in the form of salts, derivatives (PFOS-substances) and polymers (PFOS-polymers). The PFOS moiety is very stable, and has been found in biota in large parts of the world. This evaluation has been produced to support the development of a risk reduction strategy for PFOS, and has been carried out using the methods of the EU Technical Guidance Document.

The term PFOS-related substance is used to refer to any or all of the substances which contain the PFOS moiety (defined as the $C_8F_{17}SO_2$ group) and may break down in the environment to give PFOS. PFOS, the substances and the polymers are made from a common source material. The major producer of the substances, 3M, has voluntarily ceased production. Hence the use in some areas has reduced significantly or even stopped, although the potential market for use remains since there are other known suppliers.

The major uses for the PFOS-related substances were in providing grease, oil and water resistance to materials such as textiles, carpets, paper and in general coatings. The substances used in these areas were largely PFOS-polymers for fabrics and PFOS-substances for paper treatment and coatings. Other smaller volume uses, which are continuing for the present, are in chromium plating, photolithography, photography and in hydraulic fluids for aviation. One further use in fire-fighting foams is discussed; the inclusion of PFOS-related substance in new foams has ceased, but stockpiles of foams containing PFOS still exist and may be used.

In order to simplify the calculations and evaluation, the use areas have been treated as if they use one or more of: PFOS itself; an example PFOS substance; or a hypothetical polymer. Estimates of emissions from each use area have been made, including for those uses which are considered to have reduced or ceased (as it is possible that other suppliers could provide products for use in these areas). The estimates are made on the basis of a mixture of information from industry, emission scenario documents and the default values from the Technical Guidance Document. The emission estimates are for emissions of PFOS, PFOS-substance or PFOS-polymer as appropriate. The calculations of the environmental distribution and concentrations have been made using the EUSES 2 program, considering various combinations of the use patterns and different rates at which the substances and polymers may break down to PFOS in the environment.

PFOS is not degradable, either abiotically or through aerobic or anaerobic biodegradation. It has low volatility. It accumulates in fish, with a measured bioconcentration factor of 2796. Measured sorption coefficients show moderate sorption in soils, less in sediment.

The ecotoxicity data for PFOS have been reviewed. Although limited, the data do not show any obvious differences in toxicity between different salts. PFOS is moderately toxic to aquatic organisms, with acute toxicity values ($L(E)C_{50}$) in the range 1 - 10 mg/l. Coupled with the lack of degradability, this indicates that it would be classified as dangerous for the environment, with the risk phrases R51 (toxic to aquatic organisms) and R53 (may cause long term adverse effects on the aquatic environment). There are several long term test results with aquatic organisms available, the lowest no effect concentration being 0.25 mg/l for Mysid shrimp. The PNECs for freshwater and marine water are derived from this value as 25 μg/l and 2.5 μg/l respectively.

Mammalian toxicity data have not been reviewed for this evaluation; instead the evaluation carried out for the OECD hazard assessment has been used. The key study reviewed for the OECD report was a two-year feeding study with rats which had a no observed adverse effect level of 0.5 ppm for liver effects in male rats. This has been used to give a PNEC for secondary poisoning of 0.0167 mg/kg wwt. An alternative PNEC of 0.067 mg/kg has also been considered.

A PBT assessment shows that PFOS meets the P (and likely the vP), B and T criteria. Strictly this means that a conventional risk evaluation through a PEC:PNEC comparison is not required. However, it was considered useful to carry out such a comparison in order to assist in the setting of priorities for the risk reduction strategy. The risk evaluation shows possible risks for secondary poisoning for all use areas in all of the scenarios used to examine the effects of different rates of break down and different combinations of releases. Risks are also indicated for secondary poisoning through exposure to the calculated regional background concentrations, for the freshwater and marine food chains. The same is true when using the alternative PNEC value. As both the PNECs are based on long term studies, possible refinement of the evaluation seems most likely through revision of the emission estimates. For freshwater, the regional emissions would need to be reduced to less than one twelfth of the estimated values in order to remove the risk at the regional level (assuming a similar distribution of emissions), or to less than one third if the alternative PNEC is used. There are also indications of possible effects from the releases of fire fighting foams to water. Again the PNEC is unlikely to be revised upwards; here, the release estimates are necessarily arbitrary to some degree, as they relate to the use in fighting fire.

There are a number of areas of uncertainty in the evaluation, in particular in relation to the degradation of PFOS-substances to PFOS in the environment (both the rate and the yield). A number of different assumptions about this have been included in the evaluation. Although some of the alternative assumptions result in a reduction in the PEC/PNEC ratios, in most cases the risks for secondary poisoning remain. A comparison of the PNEC(s) with concentrations measured in aquatic biota suggests that levels of concern may be present in some areas.

N.B. No assessment of risk to humans has been carried out.

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1 GENERAL SUBSTANCE INFORMATION

1.1 IDENTIFICATION OF THE SUBSTANCE

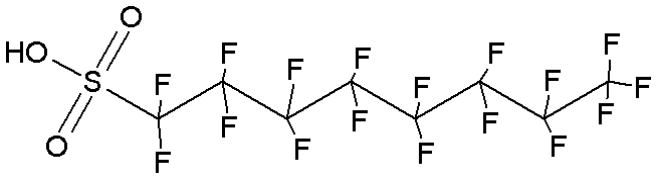
The subject of this risk evaluation is not a discrete substance and does not have a CAS number. It is the perfluorooctane sulphonate anion, known as PFOS. The parent sulphonic acid and some of its commercially important salts are:

Perfluorooctane sulphonic acid (CAS No. 1763-23-1)
Potassium salt (CAS No. 2795-39-3)
Diethanolamine salt (CAS No. 70225-39-5)
Ammonium salt (CAS No. 29081-56-9)
Lithium salt (CAS No. 29457-72-5)

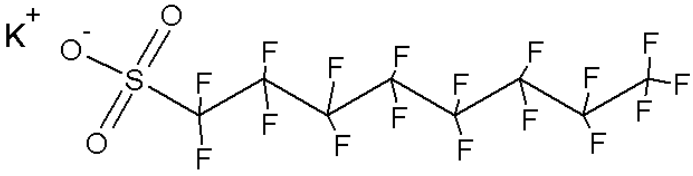
The following sections deal with the properties of this group of substances, generally determined for the potassium salt. The risk evaluation also considers possible releases of PFOS from other products, either directly or from the breakdown of other substances. Section 2 discusses the production of these substances and the properties necessary for assessing their environmental behaviour are discussed in Section 3. Some issues relating to the purity and composition are considered in the current section.

For the purpose of this evaluation, all substances (simple or polymeric) which contain the PFOS moiety ($C_8F_{17}SO_2$-) are termed PFOS-related substances.

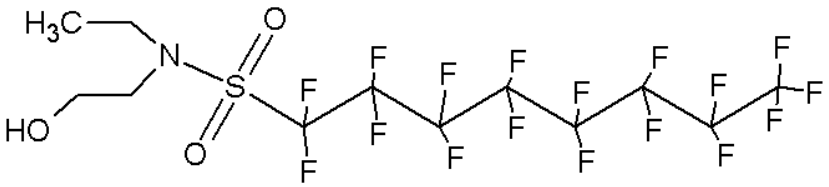
Structure



PFOS acid



Potassium salt



Example amido derivative, N-EtFOSE (n-ethylperfluorooctanesulphonamidoethanol)

It is expected that the anion will be the form present in the environment, probably associated with metal cations (3M, 2003).

1.2 PURITY/IMPURITIES, ADDITIVES

1.2.1 Composition

The production processes for PFOS-related substances are described in Section 2. Although the starting material is n-octane sulphonyl fluoride, this will contain some non-linear C_8 compounds. The fluorination process is expected to lead to some fragmentation of the chain. Thus the product of the fluorination step will contain linear and non-linear chains, mostly C_8 but with other chain lengths present. RIKZ (2002) quote 3M as reporting a final product (as PFOSF, see Section 2) of approximately 70% n-PFOSF and 30% branched impurities including odd and even chain lengths. An alternative description of the content is 90% of C_8 molecules, of which 25% are branched, with 5-10% C_6 compounds and the remainder C_7 (2-5%) and C_5 compounds. A similar distribution is assumed to apply to all products based on the ECF process (see Section 2.1.1), whether produced by 3M or by other companies. No specific information on other companies' products has been identified.

These figures relate to the major precursor of PFOS-related substances, and are assumed to apply to the products made from this. For the purpose of this evaluation, the presence of differing chain lengths is ignored. The quantities of PFOS-related substances produced and used are assumed to relate to the C_8 moiety, recognising that this may lead to some over-estimation of releases.

Other issues relating to the composition of substances and polymers made from the precursor are considered in Section 2, in particular in relation to the presence of residual monomers or unreacted substances in products.

1.2.2 Additives

No information on possible additives has been located.

1.3 PHYSICO-CHEMICAL PROPERTIES

This section discusses the properties relevant to the PFOS anion, mainly in the form of the potassium salt. Data are taken largely from the OECD hazard assessment (OECD, 2002) and the 3M assessment (3M, 2003). The original sources of these data have not been reviewed; in many cases they are 3M reports, which are summarised in the robust summaries in the 3M (2003) document.

1.3.1 Physical state (at ntp)

The potassium salt of PFOS is a white powder at normal temperature and pressure.

1.3.2 Melting point

No indications of melting were seen with the potassium salt at up to 400°C, which was the maximum temperature specified for the instrument used. A value of >400°C will be used in this evaluation.

1.3.3 Boiling point

In view of the high melting point, no attempts have been made to measure the boiling point.

1.3.4 Relative density

The relative densities (specific gravities) of the salts are given in the OECD assessment as: potassium ~0.6; lithium ~1.1; ammonium ~1.1; diethanolamine ~1.1.

1.3.5 Vapour pressure

A vapour pressure of 3.31×10^{-4} Pa has been measured for the potassium salt, using the spinning rotor method (OECD 104). A note in the 3M assessment comments that this result is thought to be due to volatile impurities in the substance. This is supported to some extent by a calculated vapour pressure of 1.9×10^{-9} Pa using the modified Grain method in the MPBPVPWIN (v 1.41) program, with a melting point of 400°C selected. Calculated values for other substances range from 3.1×10^{-11} Pa for the diethanolamine salt to 0.85 Pa for the acid. The measured value will be used in this evaluation, recognising its limitations.

1.3.6 Water solubility

The OECD assessment quotes a value of 570 mg/l in pure water from 3M (1999) reports. The more recent 3M assessment (2003) has the results of two determinations. Both involved the equilibration of an excess of the substance with pure water at 30°C, followed by equilibration at a lower temperature (either 20°C or 24-25°C). Solutions in the 24-25°C experiment were centrifuged before sampling and analysis, this process was not noted for the 20°C experiment. The results were 519 mg/l at 20±0.5°C, and 680 mg/l at 24-25°C. The 3M assessment takes a mean value of 600 mg/l. Both studies are given a validity rating of 1 and so are considered fully valid. For this evaluation the value at 20°C, 519 mg/l, will be used as closer to environmental conditions.

Solubility has also been determined in salt waters (3M, 2003), and is reduced from that in pure water. In natural seawater a solubility of 12.4 mg/l at 22-23°C was measured. A value of 20.0 mg/l was obtained for a sodium chloride solution at 3.5% salinity, the same as the natural seawater.

1.3.7 n-Octanol-water partition coefficient

The surface active properties of the substance make a direct determination of the octanol-water partition coefficient impossible. In a preliminary study reported by 3M an inseparable emulsion was formed. 3M determined the solubility of PFOS in octanol as 56 mg/l, and calculated the log Kow from the ratio of solubilities, giving a value of -1.08. The study summary notes that this is not a real value.

Using the KOWWIN program, a value of 4.13 is calculated for log Kow for the potassium salt, and a value of 6.28 for the acid. The reliability of this program for substances of this type is unknown.

The octanol-water partition coefficient is often used to estimate other properties such as bioconcentration factors and sorption coefficients. The lack of a reliable measured value for this substance means this cannot be done here. However, a number of the required properties have been measured directly, and although there are limitations to these measurements they will be used in the evaluation. Where values for properties have not been measured, a surrogate value for the log Kow will be estimated from suitable measured data. These values will be discussed in Section 3.

1.3.8 Henry's Law constant

3M report a study designed to measure air-water partitioning directly. Although a non-standard method, it was considered suitable for substances with low air-water partition coefficients (K_{aw}). The conclusion from the study was that PFOS was essentially non-volatile, significantly less so than water, which has a K_{aw} of $2x10^{-5}$ (Henry's law constant of 0.044 Pa m^3/mole).

From the solubility and vapour pressure values above, the Henry's Law constant can be calculated as the ratio, at $3.19x10^{-4}$ Pa m^3/mole ($K_{aw} = 1.35x10^{-7}$). This value will be used in the evaluation as an indication of the properties of the substance.

1.3.9 pKa

No direct measurement of the pKa of the acid has been located. A calculated value of -3.27 has been provided in comments from Finland, obtained from the ACD/I-Lab Web Service. 3M (personal communication) confirm that the substance is considered to be a strong acid. The value indicates that PFOS will be present in the environment completely in the ionised form, and that all determination of properties here which involve the substance in solution relate to the anionic form.

1.3.10 Summary of physico-chemical properties

A summary of the physico-chemical data used for the risk assessment is given in Table 1.1.

Table 1.1 Physico-chemical properties

Property	Value and comment
Physical state at ntp	Solid
Molecular weight	500 for acid; 538 for potassium salt
Vapour Pressure	$3.31x10^{-4}$ Pa
Water solubility	519 mg/l
n-Octanol-water partition coefficient (K_{ow})	Not possible to measure
Henry's Law constant	$3.19x10^{-4}$ Pa m^3 $mole^{-1}$ – from vapour pressure/solubility ratio
Acid dissociation constant (pKa)	-3.27 (calculated)

From the very low pKa value, all properties involving solution relate to the ionised form.

2 GENERAL INFORMATION ON EXPOSURE

Information in this Section and Section 3 has been taken from a number of sources. Where these are published sources, this has been indicated. In some cases the information was obtained as part of the consultations carried out for the production of the Risk Reduction Strategy report, which included consultation on aspects required for this risk evaluation. Reference to "the consultation" in this report is intended to cover these cases. More detail can be found in the Risk Reduction Strategy report in some cases.

2.1 PRODUCTION

It is understood that production of significant quantities of PFOS-related substances has never taken place in the UK. All such substances have been imported. Therefore this life cycle step is not considered further in this evaluation in terms of quantities produced or emissions. However, a description of the production processes is needed to explain the source of the different types of substances considered in this evaluation, and to contribute to the basis on which they are later grouped.

2.1.1 Production process

Information in this section is taken from the 3M assessment (3M, 2003) and the OECD hazard assessment (OECD, 2002). PFOS-related substances are manufactured by a process known as Simons Electro-Chemical Fluorination (ECF). In this process, organic feedstocks are dispersed in liquid anhydrous hydrogen fluoride, and an electric current is passed through the solution, leading to the replacement of all of the hydrogen atoms in the molecule with fluorine atoms.

The starting feedstock for this process is 1-octanesulphonyl fluoride, and the initial product is perfluorooctanesulphonyl fluoride (PFOSF). This product is sold commercially to some extent, but is mainly used as an intermediate in the production of other substances. The simplest of these is PFOS itself, produced by hydrolysis of PFOSF. The various salts are then produced from this.

The majority of PFOSF is reacted first with either methylamine or ethylamine to give either N-methyl- or N-ethyl perfluorooctane sulphonamide. These intermediates can be used to make various amides, oxazolidinones, silanes, carboxylates and alkoxylates which are available commercially.

The sulphonamide derivatives can be reacted with ethyl carbonate to form either N-methyl- or N-ethylperfluorooctanesulphonamidoethanol (N-MeFOSE and N-EtFOSE). These then form the basis of adipates, phosphate esters, fatty acid esters, urethanes, copolymers and acrylates as commercialised products. The majority of the PFOSF-related products made by 3M were from this group of products.

It should be noted that the secondary reactions producing the various products are single or sequential batch reactions, and do not necessarily lead to pure products. There may be varying amounts of fluorochemical residuals (unreacted or partially reacted starting materials or intermediate products) carried forward into the final product. According to 3M these residues are present at around 1% or less in the final commercial products. Where information has been provided on fluorochemical residuals for this evaluation, it has been assumed that it relates to these unreacted materials. Possible releases of these residuals are

considered along with releases of the products themselves in Section 3, with an assumed content of 1% if no more specific information is available.

Figure 2.1 shows the flow of PFOS-related substances from initial production to final products.

2.2 GROUPING OF PFOS-RELATED SUBSTANCES

As part of the work in developing the Risk Reduction Strategy, a list of substances containing the PFOS moiety was produced (Appendix 1). These substances are considered to have the potential to lead to releases of PFOS to the environment. These include salts of PFOS, simple derivatives and polymeric materials. In attempting to assess the emissions of PFOS-related substances to the environment, it is neither practical nor realistic to attempt to assess the release and fate of each individual substance. Rather, these substances have been grouped in a way that takes account of the apparent relative ease with which PFOS could be produced. This has been done on a fairly subjective basis, as there is little information on the breakdown of these substances in the environment. In grouping these substances, the general type and description of the PFOS-related substances used in each sector have been used to select the relevant group for the substances. A three way division has been employed on the above basis.

The first group includes substances which are effectively PFOS itself, in the form of salts of perfluorooctane sulphonic acid - salts with potassium, lithium, sodium, ammonium (including quaternary ammonium) and diethanolamine. The use of products containing these substances can lead to the direct emission of PFOS to the environment. The properties of PFOS salts have been used as far as possible in estimating emissions and behaviour in the environment. Measured property values have been used as far as possible, rather than the usual estimates from QSAR approaches - in particular, measurements of sorption coefficients and bioaccumulation. For the purpose of estimating releases and environmental behaviour, these substances will be called **PFOS-salts** (salts rather than acids as the species will be fully ionised in water in the environment).

In the second group are individual substances which are made from perfluorooctane sulphonyl fluoride (PFOSF) in a parallel route to the production of PFOS. These are the FOSA and FOSE-type substances, together with their relatively simple derivatives. These are considered to be potential sources of PFOS in the environment through degradation. There is some evidence for this with the substance N-EtFOSE, but little or none for any other substance. The 3M report (3M, 2003) comments that no production of PFOS was seen through hydrolysis or aqueous photolysis of a number of compounds; formation of PFOS was only seen through biodegradation, largely in studies on N-EtFOSE. Thus assumptions about the extent to which this happens, and the rate, have been made in the model calculations in Section 3. It is not possible to treat each substance of this group individually, so a generic set of properties has been used to estimate emissions and behaviour. There is also little information on the properties of these substances. Most of the information available relates to N-EtFOSE, and this will be used as the basis for these calculations. For the purpose of estimating releases, these substances will be called **PFOS-substances**.

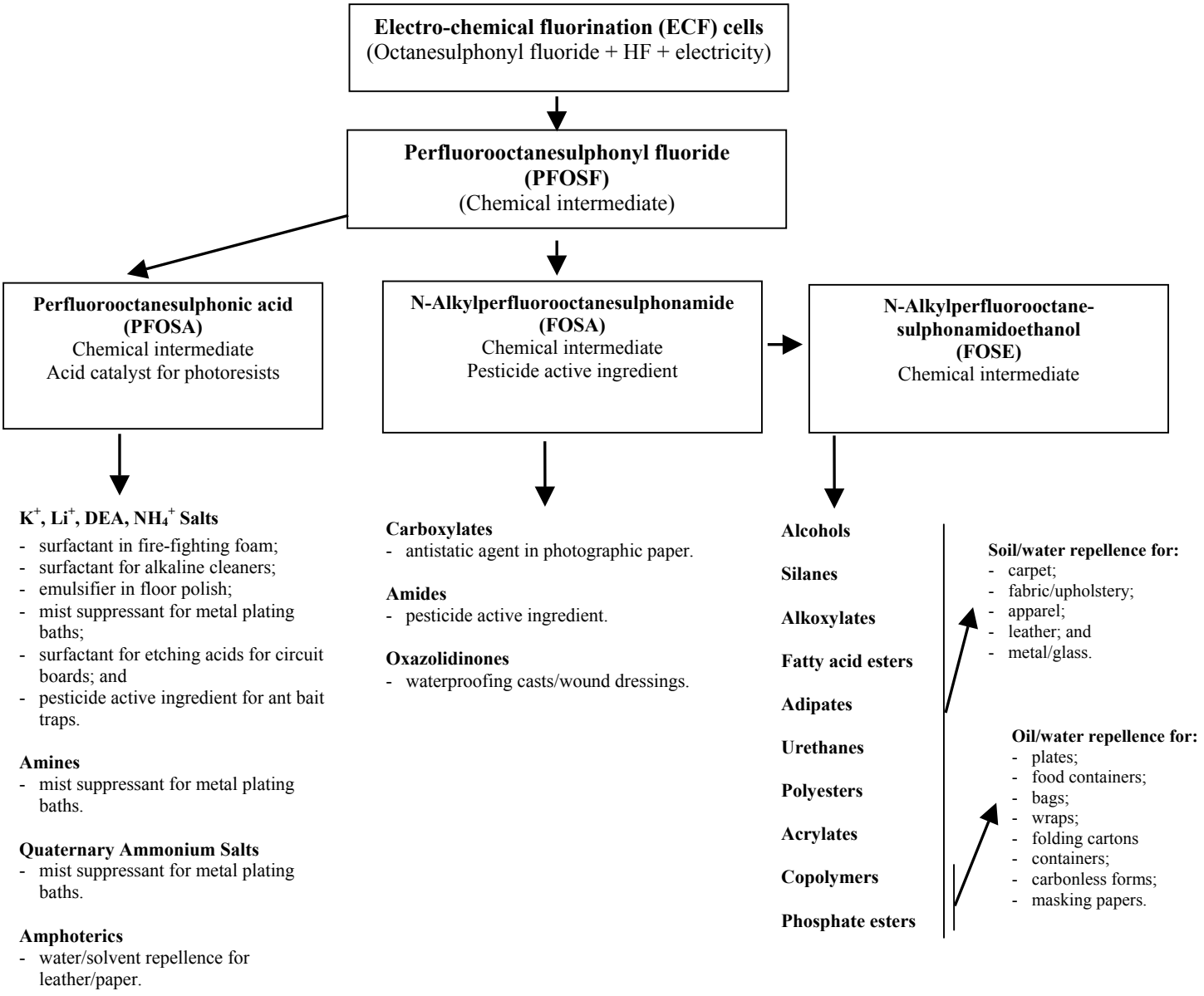


Figure 2.1 Major Product Categories and Applications for Perfluorooctyl-sulphonates (OECD, 2002)

The third group are polymeric materials, higher molecular weight polymers derived largely from the FOSE-type substances. These have also been suggested as potential sources of PFOS in the environment. RIKZ (2002) assumed that all of the PFOS contained in these substances was released. 3M in contrast considered that the polymers were non-degradable. No specific evidence on this has been located. The properties of these polymers may vary over a considerable range, and generic values will be needed. It has been assumed that they have low vapour pressures, low solubilities and a higher affinity for solid phases in the environment. Assumptions have been made about the extent to which they will break down to PFOS in the environment in the model calculations in Section 3. These substances may contain residual PFOS-substances, and releases of these will also be considered. This group of substances will be called **PFOS-polymers**.

It has been assumed throughout that only substances and polymers derived originally from PFOSF have the potential to degrade to PFOS in the environment. Hence telomer-derived substances and materials are not included, nor are perfluorooctanoic acid (PFOA) related substances. It should however be noted that in some areas, it is not always possible to tell which specific type of material is being used. Similarly, the distinctions between the three groups (PFOS-salts, PFOS-substances and PFOS-polymers) are not always clear, and hence in some cases materials may be incorrectly allocated. In some cases the allocation has been simplified by assuming that all of the material used in a particular area is of one group, where the reality may be that substances from different groups are used.

2.3 USES

2.3.1 General information on uses

The use pattern for PFOS-related substances in the UK and the EU has changed significantly since 3M announced their intention to cease the manufacture of a range of these substances. Information collected during the consultation indicates that their use in a number of the major areas has effectively ceased, as users have moved to different types of substance to provide a similar function.

The discussion of uses will initially address those uses expected to continue after the cessation of manufacture by 3M, either because there are no alternatives available at present[3], or where there are stocks of PFOS-related substances to use up. These include:

- metal plating;
- semi-conductors;
- photographic;
- aviation; and
- fire fighting foams stock.

Uses which have taken place in the UK in the past but which are not considered to be relevant at present will also be considered, especially where products treated with PFOS-related substances may be in use from some time. These include:

[3] Although 3M have ceased production of these substances, there are other potential suppliers for continuing uses. Consultation identified a number of possible suppliers to the UK, for more details see the Risk Reduction Strategy. The EA review of perfluoroalkylated substances (EA, 2001) also has some information on potential other producers of PFOS-related substances, in the confidential project record.

- carpets;
- leather/apparel;
- textiles/upholstery;
- paper and packaging; and
- coatings and coating additives.

Other uses which are not considered relevant to the UK or the EU will be mentioned.

In order to provide a common baseline, usage data from 2000 have been used in the evaluation wherever possible. These are largely from information supplied by 3M on the amounts of PFOS-related substances imported into the UK.

2.3.2 Metal (chromium) plating

PFOS-related substances are used to lower the surface tension of metal plating solutions to prevent the formation of mists containing potentially harmful components from the baths. As such they are used in chromium plating, in anodising and in acid pickling. The substances used are of the PFOS-salt type. Four companies supplying mist suppressants containing PFOS-related substances in the UK and the EU indicated the use of the tetraethylammonium salt of PFOS for this purpose.

The amount used in the UK has been estimated as <0.5 tonnes per year from information collected during the consultation. This level of use is considered to have been stable for the last few years. The Risk Reduction Strategy estimated that there were around 300 chromium platers in the UK. A company in Germany estimated that the EU market was 8.6 - 10 tonnes per year for PFOS-related substances, and this level of use will be used in the estimations.

2.3.3 Photolithography (semi-conductors)

PFOS-related substances are used in a number of functions within the semi-conductor industry. These relate to photolithography, which is the process by which the circuits are produced on the semi-conductor wafers. This process uses photoresists, materials whose composition is altered on exposure to light, making them either easier or more difficult to remove and so allowing structures to be built up in the wafer. The PFOS-related substances can form part of the photoresist itself, acting as a photoacid generator in the chemical amplification of the effect of exposure. They can also be used to add a thin coating to the resist to reduce reflections, either to the top (top anti-reflective coatings, TARC) or bottom (bottom anti-reflective coatings, BARC). PFOS-related substances may also be used as surfactants in developers, or in ancillary products such as edge bead removers (EBRs). ESIA (European Semi-Conductor Industry Association) and SEMI (Semiconductors Equipment & Materials International) have provided information on the use of PFOS-related substances in the EU in 2002 and this is presented in Table 2.1. The total use is 470 kg per year.

Table 2.1 Typical Concentrations and EU Consumption of PFOS Related Substances in Preparations Used in Semiconductor Applications

Application	PFOS Concentration	EU Consumption (kg/y)
Photoresists	0.02 - 0.1%	46
EBR	Not available	86
TARCs	ca. 0.1%	136
BARCs		8
Developers (surfactant)	ca. 0.01%	195

There is little information about the specific substances which are used in this area, and the companies involved are reluctant to identify them. For the purpose of this evaluation, it is assumed that they are all PFOS-substance type. This assumption will result in greater emissions of PFOS than if they were assumed to be polymers.

2.3.4 Photography

Information collected through the consultation indicates that PFOS-related substances are used in coatings applied to photographic films, papers and printing plates. The substances were also used in developing solutions in the past, but recent information from EPCI (European Photographic Chemicals Industry) states that they have been removed from such products. The main function of the substances is to act as anti-static agents. This is to prevent static discharge, both for the possible effects on workers handling the material, and from the possible exposure of photographic materials to the discharge. The substances also help in reducing friction, thereby improving transport in cameras, printers and projectors, and are essential to the laying down of multiple thin layers of photographic material on film, creating coatings of high complexity in a highly consistent and rapid manner. EPCI indicate that the main area of use for PFOS-related substances is in the medical area (x-rays), with 85% of EU use in this sector.

In the course of the consultation, six substances which are used in this area were identified. Of these, one is of the PFOS-salt group, one of the PFOS-substance group and the other four are PFOS-polymers. The OECD assessment indicates that the carboxylate derivatives of N-alkyl-perfluorooctane sulphonamide are used as anti-static agents. For these calculations the substances used in this area are assumed to be PFOS-salt for the production of film step, and PFOS-polymers for subsequent steps. The polymers are assumed to contain 1% of PFOS-substances as residuals. Information on the relative proportions of the various types would allow the estimates to be improved.

EPCI have provided data on the use of PFOS-related substances in the EU. The amount of PFOS-related substance used in the production of film in the EU is estimated to be 850 kg per year. In addition to this, finished articles containing PFOS-related substances imported into the EU add a further 150 kg per year. Exports of articles containing PFOS-related substances account for 250 kg per year. Hence the overall amount of PFOS-related substance in film used in the EU is 750 kg per year.

Information from EPCI indicates a concentration of PFOS-related substance in film of 0.1 - 0.8 $\mu g/cm^2$. According to the emission scenario document on the photographic industry in the Technical Guidance document (TGD), x-ray film has a double coating of photographic material. As this is the main use area of PFOS-related substances according to the information from EPCI, the high end of the composition range will be used in the calculations. Using this, the amount of film which would contain 750 kg is $9.4x10^{11}$ cm^2. For comparison, the amount of x-ray film used in the EU according to the ESD is $7.9x10^{11}$ cm^2, which is in good agreement.

2.3.5 Aviation

PFOS-related substances are used as a component of fire-resistant hydraulic fluids in aircraft. They act to inhibit erosion and damage to parts of the hydraulic systems and are present in the fluids at ppm levels. The specific substance used in these fluids is potassium perfluoroethylcyclohexyl sulphonate, rather than the perfluorooctane sulphonate which is

PFOS. Nevertheless they are included in this evaluation, as the perfluorooctane salt may be the replacement should the ethylcyclohexyl substance become unavailable. The ethylcyclohexyl compound has also been identified by other regulatory agencies in the US and Canada, and 3M have also included this in the products which they have discontinued.

The manufacture of these fluids takes place outside the EU, and so this step is not considered in the evaluation. The world-wide use of PFOS-related substances in this area is estimated to be 2.2 tonnes per year (information collected through the consultation). For the purpose of this evaluation, it is assumed that one third of this, or 0.73 tonnes, is used in the EU each year. The substance is of the PFOS-salt type.

2.3.6 Fire-fighting foams

Foams have been developed to assist in fighting fires involving flammable liquids, where the use of water is unable to extinguish the fire and may contribute to its spread. Fluorocarbon surfactants are a component of such foam concentrates, along with synthetic foaming agents, solvents and other substances. In use these foam concentrates are mixed with water and aspirated with air to produced the finished foam. In aqueous film-forming foams, the fluorinated surfactants move to the solution-air interface and produce a very thin film which spreads over the liquid fuel fire. They are also used in alcohol-resistant foams for fires involving more polar solvents, which tend to disintegrate conventional foams. Information on foam products provided during the consultation indicates that the PFOS-related substances used are of the PFOS-salt type.

From the consultation, the majority of fluorocarbon surfactants included in foams produced currently are derived from the alternative telomer based technology, and so will not give rise to PFOS (the substances involved in the telomer products are largely based on C_6 chains rather than C_8). However, PFOS-related substances have been used in such foams and so the production and use of these foams is included in this evaluation.

In terms of quantities, it has to be considered that the foam concentrates are stockpiled by potential users, to be used as and when needed. There are two types of holders of such stocks within the UK, the Fire Authorities (FA) and major installations (which hold stocks for their own use and as part of mutual agreements between FAs and industry for provision of fire cover at major accidents). Information on the current size of such stockpiles at each of these holders has been gathered for the Risk Reduction Strategy. The resulting figures are ~76,000 litres of PFOS-based foam concentrate held by Fire Authorities, and 2,367,000 litres by major installations (in the UK).

The stocks held by major installations are not considered in this evaluation. These will be used in the event of a major incident, and such use is not considered to be part of the ‘normal’ use of the substances. The frequency of use by Fire Authorities is expected to be much higher. The average use of fire fighting foams in general by Fire Authorities in the UK has been estimated as 15% per year.

The estimate of use of PFOS-based foams is therefore based on the amounts held by Fire Authorities. Assuming a density of 1, there are 76 tonnes of foam concentrate in the UK, which at a content of 1% of PFOS corresponds to 760 kg. Based on a use rate of 15%, the use of PFOS-related substances in foams is 114 kg per year. Taking the UK as 20% of the EU, the total use is 570 kg per year, with 57 kg in the region.

The production of foam concentrates can be considered to be a formulation process. There are a limited number of companies producing foams of this type - ten are reported for the European Economic Area, with none in the UK. Information on the quantity produced is only available for one company, this will be used to estimate local emissions. The use of PFOS-related substances at this site was 40 tonnes per year, which at a concentration of 1% in the foam concentrate made a total of 4,000 tonnes of concentrate. Note that these are historical data, as the company no longer uses PFOS-related substances in its foams.

2.3.7 Protective coatings for fabrics (carpets, textiles and leather)

PFOS-related substances have been used on a range of fabrics and other materials to provide soil, water and oil resistance. They have generally been applied as a coating to the surface, to create a protective barrier. The types of PFOS-related substances are the acrylate, adipate and urethane polymers produced from the intermediate substance N-ethylperfluorooctane sulphonamido ethanol. Therefore, for the purpose of this evaluation they are considered to be PFOS-polymers. As such, they contain residual levels of low molecular weight substances from the manufacturing processes. This residual material is assumed to be PFOS-substances, and is present at a level of 1% of the polymer (information provided for the consultation).

The treatment of fabrics with PFOS-related substances is no longer thought to take place in the UK. For the purpose of this evaluation, the possible emissions from the treatment process will be considered as an example calculation. Although no longer produced in the UK, treated fabrics are in use at present and will be so for some time, as at least some of the treated product (carpets, upholstery) have significant lifetimes. Therefore estimates are made of the possible releases of polymers and of PFOS-substances from such materials in use.

Information on the use of PFOS-related substances in this area was obtained through the consultation exercise. The approximate figure for use in the UK was 48 tonnes of PFOS-related substance (as polymer), with 23 tonnes on carpets, 15 tonnes on apparel and leather, and 10 tonnes on upholstery. These figure have been used to make estimates of the possible emissions from this area. Assuming that the UK accounts for 20% of EU use, the total for the EU would be 240 tonnes.

2.3.8 Paper treatment

PFOS-related substances have been used to treat a range of paper types and products. As for fabrics, the main function is to impart grease, oil and water resistance. Such products have been used in food contact applications. The major type of substance used appears to be phosphate derivatives of N-EtFOSE (3M, 1999), and they are therefore considered to be PFOS-substances for this evaluation. They are consider to be mainly applied during the paper making process, rather than being added to finished paper in subsequent operations. The approximate use of PFOS-related substances in this area in 2000 was 32 tonnes; assuming that the UK accounts for 20% of the use then the EU total would be 160 tonnes.

Releases from the paper making process are estimated in Section 3. For paper, there is the possibility of recycling. However, the nature of the use of these treated papers (food wrapping etc) suggests that they are more likely to be disposed of in household or municipal waste rather than entering the recycling streams. Therefore a paper recycling scenario is not considered.

2.3.9 Coatings

Perfluorinated substances (as a more general class than PFOS-related) have been indicated as being used in a wide range of areas in the coatings industries. Some of these areas overlap with areas covered above, such as textiles. No information on specific uses of PFOS-related substances has been found in this area, and it may be that such uses are no longer relevant for the UK. For the purpose of this evaluation, it is assumed that the use was in paints, and that PFOS-substances were used. The amount used in the UK in 2000 was 18 tonnes; assuming the UK to account for 20% of the EU gives an EU total of 90 tonnes. The content of PFOS-related substances in coatings is indicated as 0.1 - 1.0% from the consultation information; assuming an average of 0.55% means that 3,273 tonnes of coating were produced in the UK per year, and 16,346 tonnes in the EU.

2.3.10 Other uses

2.3.10.1 Industrial and household cleaning products

A wide range of applications of fluorosurfactants in the household and personal care and industrial cleaning areas has been identified in the consultation for the Risk Reduction Strategy. For more details, see the Risk Reduction Strategy report. As far as PFOS-related substances are concerned, specific mention is made of products marketed as alkaline cleaners, floor polishes, denture cleaners and shampoos. These products may have been used by consumers as well as in industrial contexts. PFOS-related substances have been found in floor polishes and waxes in a survey in Denmark (this might also be considered as a coating use). There is no information on the amounts used in these areas, and so it is not possible to make any emission estimates.

2.3.10.2 Pesticides

The use of PFOS-related substances in the manufacture of baits against ants and beetles has been described by 3M. The consultation exercise found one company in the EU producing such baits, using 0.5 tonnes of PFOS-related substances (PFOS-salt type) per year. No such use has been identified in the UK. There are no scenarios available for emissions from the use of such baits. If all of this quantity were released to the environment then it could make a significant contribution, but no information on the fate of component in such baits is available.

2.3.11 Summary

Table 2.2 summarises the quantities estimated as being used in the EU from the information in the preceding sections. Note that these figures relate largely to the situation before some of the PFOS products were removed from the market.

Table 2.2 Estimated EU use for each area

Use area	EU quantity (tonnes/year)	Substance type	Notes
Chromium plating	10	acid	Estimate from German company
Photolithography	0.47	substance	ESIA/SEMI estimate
Photography	0.85	acid	EPCI estimate, production of film
	0.75	polymers	EPCI estimate, use of film
Aviation	0.73	acid	One third of world use estimate
Fire fighting foams	0.57	acid	From UK estimate of foam use
Fabric treatment	240	polymer	From UK estimate of 48 tonnes, assuming UK is 20% of EU
Paper treatment	160	substance	From UK estimate of 32 tonnes, assuming UK is 20% of EU
Coatings	90	substance	From UK estimate of 18 tonnes, assuming UK is 20% of EU

2.4 TRENDS

The major world producer of PFOS-related substances was 3M. Quantitative data on production are only available for this company, but it is considered that the combined capacity of the other producers was very much less than that of 3M. The EA review of perfluoroalkylated substances (Environment Agency, 2001) indicated that 3M had the vast majority of the market for PFOS-based substances. In 2000, 3M produced around 3,665 tonnes of PFOSF, the precursor for PFOS-related substances. In 2003 this had been reduced to zero following 3M's decision to cease manufacturing.

As a result, the level of use in many areas has decreased significantly over the last two or three years, in some cases to zero. Users have moved to alternative fluorine-based products (telomer based) in some areas, and to other technologies in other areas. Details of these changes are included in the Risk Reduction Strategy report. The main areas where use is continuing at present are included in the first list in Section 2.3.1. It is expected that the use in fire-fighting foams will reduce further and eventually stop when existing stocks are used up or exceed their shelf life (unless they are disposed of without being used). The level of use in the other areas may depend on the outcome of the risk reduction strategy.

2.5 LEGISLATIVE CONTROLS

There is currently no legislation on the use of PFOS-reported substances in the EU directly related to their potential environmental and/or human health effects.

As noted above, the main producer of PFOS-related substances, 3M, voluntarily decided to phase out the production of these substances in 2000. A number of industry sectors have taken voluntary measures to reduce the potential emissions and risks from PFOS-related substances. More details of these are included in the Risk Reduction Strategy.

There have been a number of international initiatives. The US EPA introduced a significant new use rule (SNUR), requiring companies to inform them before manufacturing or importing any listed PFOS chemicals. There have been two such SNURs, listing 88 substances and allowing some derogations for essential uses (so that the rule does not apply to substances for these uses). Work is being carried out under the auspices of OSPAR to identify groups of PFOS substances which should be added to the OSAPR list of Chemicals for Priority Action.

3 ENVIRONMENTAL EXPOSURE

The evaluation of PFOS is complicated by the number of substances involved and the lack of information about the degree to which they act as sources of PFOS in the environment. As described in Section 2, the PFOS-related substances have been grouped into three types to simplify the evaluation. The approach taken here is to estimate the emissions of each of these three groups in the form that they used - acid, substance or polymer. Information on the fate and behaviour of PFOS is considered, along with any similar information for the substances or polymers. The evaluation considers the effect of different assumptions about the rate at which the substances and polymers break down in the environment on the predicted levels of PFOS. Various combinations of uses are also considered, to provide indications of possible levels from past uses and possible levels if certain uses were to continue.

3.1 ENVIRONMENTAL RELEASES

3.1.1 General introduction

Emissions have been estimated using a range of different sources of information. It is preferable to use information related to the specific substance and the specific area of use. In this evaluation there are specific estimates of PFOS-related substance emissions from photolithography, and some information on losses of polymeric materials from treated fabrics. For the other areas, use has been made of emission scenario documents (ESDs) where these are relevant. Documents used come from the Technical Guidance document, and also drafts from the OECD Task Force on Environmental Exposure Assessment. Where there is no suitable ESD, the default A and B tables from the Technical Guidance document have been used.

Releases have been estimated for local sources on a daily basis where appropriate. Larger scale emissions are presented on an annual basis. A large number of assumptions have had to be made in the course of this evaluation. In order to allow some comparison between the different use areas, the standard assumption of 10% activity in the region has been used as the basis for the regional emission estimates (with the exception of some formulation steps). This has been maintained even where there is specific information about the level of use in the UK.

3.1.2 Metal (chromium) plating

The substances used in this area are considered to be of the PFOS-salt type. Information from the consultation indicates that any formulation step for these products is likely to be simple dilution, and so only emissions from their use are considered here.

Emissions to water are estimated using the approach taken in the risk assessment for chromium (VI) compounds under the Existing Substances Regulation[4]. This approach was in turn based on an Emission Scenario Document on Metal Finishing (Environment Agency, 1997). It is assumed that a large scale processor treats 40 m^2 of metal per hour, over a 12 hour day for 240 days per year. Losses can occur from the treatment tank through solution remaining on the metal articles as they are removed from the tank – this is called drag-out. For a rack deposition system, the typical drag-out rate is 5 litres per 100 m^2 of surface treated. Hence for the site above, the drag-out rate would be 2 litres per hour. Information received

[4] Draft risk assessment report available from the European Chemicals Bureau at http://ecb.jrc.it/existing-chemicals/, search on ESIS for substance name sodium dichromate

indicates that PFOS-salt substances are present in the treatment bath at ppm levels (personal comm.). Assuming a level of 10 ppm, then the removal rate for PFOS would be 20 mg per hour. Chromium plating takes place at ~40°C, and consequently there is some evaporation of water from the tank. This allows some of the drag out or rinse water to be returned to the treatment tank. The ESD suggests that 25% of the drag-out can be returned in this way, and so the amount lost is reduced by 25%, to 15 mg per hour. The drag out is removed from the metal by rinsing, so this substance is diluted in the rinse water, but the rate of loss is not affected by this. For a 12 hour day, the daily loss to water is therefore 180 mg/day. Over 240 days the annual loss is 43 g/year.

There may also be the possibility of emissions to air from this process. This should be low, as the function of the substance is to prevent mist formation during the plating process, and the substance has a low vapour pressure. An approach to estimating such emissions is to consider the maximum limit for chromium (VI) in air of 0.05 mg/m^3, and to assume that all components of the treatment bath are present in any mist at their 'working' concentrations. From the ESD, the concentration of chromium (VI) in a hard hexavalent chromium bath is ~130 g/l. The volume containing 0.05 mg is therefore 3.8×10^{-7} litres. At a concentration of 10 ppm, this contains 3.8×10^{-6} mg of PFOS, hence the air concentration of PFOS is 3.8×10^{-6} mg/m^3. No specific information on air flow rates in chromium plating works is available, but a rate of 7,200 m^3/hour has been used for large lubricant blending sites (Environment Agency 1997a) and is used here as an illustration. For a 12 hour day, this gives a daily removal of air of 86,400 m^3, and hence a release of PFOS of 0.33 mg/day. For a 240 day year, this is an annual emission of 79 mg.

From the calculations, the overall emission from the site is 43 g/year. This appears to be too low to account for the amount of PFOS used in this industry in the UK, which is estimated at 500 kg per year (Section 2.3.2). It would require over 10,000 sites of the size for which the calculation has been performed to account for this amount of PFOS, whereas in Section 2.6.6 there are estimated to be around 300 platers in the UK. The reasons for this difference are not clear. Consultation with the UK Health and Safety Executive (HSE) has indicated that the mist suppressant is added periodically to the tanks every two weeks, which suggests that the ability of the substance to provide the suppressant function is lost or reduced over this length of time. However, no specific information on amounts added is available. Losses of the substance are also possible when the contents of plating baths are disposed of, but information from the ESD and from industry is that such baths are maintained in use over long periods of time without disposal. Bath solutions can be cleaned up by filtration and ion exchange to remove particulates and other metals, but these methods are unlikely to remove PFOS. For this evaluation, the daily emissions estimated above will be used to estimate local concentrations. On the larger scale, it will be assumed that all of the substances sold for use in this area in a year are released to waste water during the course of a year. Emissions to air on this scale are neglected.

Total use in the EU was estimated in Section 2.3.2 to be 10 tonnes per year. Releases are assumed to be 10% (1 tonnes) to the region and 90% (9 tonnes) to the continent, to waste water. Table 3.1 below provides a summary of emissions from chromium plating.

Table 3.1 Summary of Emissions from Chromium Plating

Local (mg/day)	Regional (kg/year)	Continental (kg/year)
180 (waste water) 0.33 (air)	1000 (waste water)	9000 (waste water)

Note: all releases are of PFOS-salt.

3.1.3 Photolithography

For this sector, use has been made of a draft Emission Scenario Document on photoresist use in semiconductor manufacturing produced by the United States Environmental Protection Agency. This document has been reviewed by the OECD Task Force on Environmental Exposure Assessment, and is intended for publication in the OECD Environmental Health and Safety Publications series on Emission Scenario Documents.

The PFOS-related substances used in this industry are considered to be PFOS-substances (see Section 2.3.3).

The Emission Scenario Document (ESD) has information on the use of photoresists at sites in the USA, with up to 36 kg being used on site per day for larger sites, and for up to 360 days per year. These figures have been used here[5]. From information provided for the Risk Reduction Strategy, the content of PFOS-substances in the photoresists is up to 0.1%, hence the amount used per day would be up to 36 g. This assumes that all photoresists used at the site contain PFOS-substances; although this may not be the case, as there is no information relating to this the worst case assumption has thus been taken. This level of use over 360 days corresponds to an annual use of up to 13 kg. This would appear to fit reasonably with the total use of PFOS-substances in the EU, which is given as 471 kg/year in Table 2.2. However, this overall figures covers use in a range of areas and the specific use in photoresists only accounts for 46 kg/year. The estimated site use is still consistent with this, but may be a high estimate. For the calculation of releases on the regional and continental scales in this section, an overall EU use of 500 kg/year is applied.

The ESD estimates emissions from semiconductor manufacturing for a series of processes:

- packaging/container residuals: the loss from this step is estimated as 0.6%, with the losses gong to landfill or to incineration. For a use of 36 g/day, the loss is 0.22 g/day. For a use of 500 kg in the EU the overall loss is 3 kg/year, with 0.3 kg to the region and 2.7 kg to the continent;

- equipment cleaning: losses from this step are estimated as 1% again to landfill and incineration. The estimated loss for the site is 0.358 g/day. The total EU loss is 4.98 kg/year, with 0.498 kg to the region and 4.482 kg to the continent;

- application excess: an amount of resist is applied to the semiconductor wafer which is then spun. The percentage of resist adhering to the wafer is considered to range from 1% to 7%; an average of 4% is used here, hence 96% of the application goes as waste. For the site, the estimated waste is 34 g, which goes to incineration. The total waste for the EU is estimated as 472 kg/year, with 47.2 kg to the region and 425 kg to the continent;

- loss in developer: the ESD assumes that 50% of the resist on the wafer is removed in the developer. The amount released at the site is 0.72 g/day, this is considered to go to waste water. The total loss for the EU is 9.94 kg/year, with 0.994 kg to the region and 8.946 kg to the continent; and

[5] For comparative purposes, the ESD has information from Germany that suggests a use of 11.25 kg photoresist per day, somewhat lower than the value chosen.

- loss on etching and stripping: the ESD assumes that the rest of the resist is removed at this stage. As 50% was removed at the previous stage, the emissions at this step are the same as those for developing: 0.72 g/day to water at the local site, 9.94 kg/year for the EU, 0.994 kg/year for the region and 8.946 kg/year for the continent. These emissions are to waste water or to recycling, release to waste water has been assumed as a worst case.

Table 3.2 below provides a summary of emissions based on the ESD.

Table 3.2 Summary of emissions for photolithography based on ESD

Step	Local emission (g/day)	EU (kg/year)
Container residual (l/i)	0.22	3
Equipment clean (l/i)	0.358	4.98
Application excess (l/i)	34	472
Developer (ww)	0.72	9.94
Etching/stripping (ww)	0.72	9.94

Notes: l/i – landfill/incineration ww – waste water

The overall breakdown of the fate of the PFOS-substances according to the ESD is ~20 kg to waste water and 480 kg to incineration/landfill. This is based on the use of 500 kg per year. ESIA and SEMI estimated a mass balance for the EU based on a use level of 471 kg per year, and concluded a larger proportional release to water, 251 kg/year to waste water and 218 kg/year to incineration. Examining the mass balance, the differences arise largely through the use of PFOS-substances in areas other than as photoresists. For the anti-reflective coatings, the mass balance assumes 40% is present on the wafer when it goes to the developing step, whereas the ESD has only 4% of the photoresist material. On developing, all of the remaining anti-reflective coating is removed, thus entering the waste water stream rather than going to incineration as in the ESD. Part of the PFOS-substances are used in the developer in the EU, and this is considered to go directly into waste water according to the mass balance. The net effect is that a greater proportion of the PFOS-substances used go into waste water.

The mass balance is considered to be more relevant for the EU, and so the overall emissions from this will be used for the regional and continental emissions.

These give 25 kg/year to waste water on the regional scale, and 226 kg/year to waste water on the continental scale. For the local scale, the emissions estimated with the ESD will be used, but with the addition of a release for the use of PFOS-substances in the developer. It is assumed that the site uses developer and resist materials containing PFOS-substances in the same proportions. The site used for calculations uses 13 kg of PFOS-substance as resists etc, from a total of 276 kg for this type of use (or 4.7%). The amount of PFOS-substance in developers is therefore 4.7% of the total in developer (195 kg/year), or 9.2 kg/year. For 360 days of use, this is 25.6 g/day. Combined with the estimated releases from resist materials of 1.43 g/day, the local emission is 27 g/day. Table 3.14 below provides a summary of emissions from photolithographic processes.

Table 3.3 Summary of emissions from photolithography

Local (g/day)	Regional (kg/year)	Continental (kg/year)
27	25	226

Note: All emissions are to waste water and are of PFOS-substances.

In comments on the consultation for the risk reduction strategy, ESIA/SEMI indicated that the use of PFOS-related substances in developers is not a critical use (in contrast to the use in resists) and so could be replaced. The effect of phasing out the use of PFOS-related substances in this area is considered in Appendix 3.

3.1.4 Photography

From Section 2.3.4, both PFOS-salts and PFOS-polymers may be used in this area. For the purpose of these calculations, it will be assumed that they are PFOS-salt for the production of film step, and PFOS-polymers for subsequent steps. The polymers are assumed to contain 1% PFOS-substance. Information on the relative proportions of the various types would allow the estimates to be improved.

The use of PFOS-related chemicals for the production of film in the EU is estimated in Section 2.3.4 as 850 kg/year. The Technical Guidance Document for the Existing Substances Regulation in the EU has been used to estimate releases from the production of film, considered as a formulation step. The emission factors for a substance used in the production of films etc are 0.0001 to air (for vapour pressures below 1 Pa) and 0.002 to water (for any function other than control of crystal growth). The content of PFOS-related substances in film is 0.1 – 0.8 $\mu g/cm^2$. Taking the highest value as representative of use in medical applications, which account for 85% of use in this area, and assuming the use of 850 kg per year, a total of $1.06x10^{12}$ cm^2 of film containing PFOS-related substances could be produced.

The most common backing material for film is PET (polyethylene terephthalate), according to Kirk-Othmer (1994). The material has a density of 1.39 g/cm^3. The depth of film in Kirk-Othmer is suggested as 45 µm, with 10µm of base layer (backing) and 35µm of coating. In the absence of other information, the density will be assumed to apply to the whole film. The mass per unit area is then given as 1.39 x $45x10^{-4}$ or $6.3x10^{-3}$ g/cm^2. For a production of $1.06x10^{12}$ cm^2 this gives 6,630 tonnes of film. This quantity of film can be used in the B tables of the TGD (Table B2.8) to estimate the amount produced at one site and the number of days of operation. This gives a fraction of 0.4 used at one site, applied to the total tonnage, and use over 300 days. The amount of PFOS-related substances used in the EU is 850 kg, so 40% is 340 kg, at 1.13 kg/day. From the emission factors above, the releases to air are 0.11 g/day and to waste water 2.27 g/day. Overall EU emissions are 0.085 kg/year to air and 1.7 kg/year to waste water. As the site accounts for 40% of emissions, these are used for the regional releases. So the regional releases are 0.034 (air) and 0.68 (waste water) kg per year, and the continental releases are 0.051 (air) and 1.02 (waste water) kg per year.

There is little information on whether any of the substances are released from the film when it is processed. EPCI commented that approximately 5-10% of one PFOS material may be released from film into film developer. None of the other PFOS materials used in imaging would be expected to be released on developing. The substances are intended to remain in the film, in order to perform their function. The Emission Scenario Document on the photographic industry in the TGD has a default release factor of 1 in the absence of information, i.e. all of a substance is removed on processing, but this is considered to be inappropriate for these substances. For the purpose of this evaluation, it will be assumed that any PFOS-substance present will be released on developing, and that polymeric material will remain in the film.

From the Emission Scenario Document, the amount of film (taken as x-ray film) processed in one day at a representative site is 110 m^2. The concentration of PFOS-polymer in the film is 0.8 $\mu g/cm^2$, or $8x10^{-6}$ kg/m^2. Hence the amount of PFOS-polymer in the film processed in

one day is 0.88 g. The amount of PFOS-substance is 1% of this, or 8.8 mg, and this is assumed to be released to water. Across the EU, the 750 kg of PFOS-related substance in films used in this area would give rise to 7.5 kg of PFOS-substance released to waste water, with 0.75 kg to the region and 6.75 kg to the continent.
The polymers not released at this time will remain in the film or other material and may be kept for considerable periods of time. At the end of their use, X-ray film, movie film and commercial films are typically collected by brokers, and sold for secure disposal (movie film) or recycling of silver and/or PET polymer. These usually result in the incineration of residual materials.

Table 3.4 below provides a summary of emissions from the photographic industry.

Table 3.4 Summary of Emissions from Photographic Industry

Step	Local (g/day)	Regional (kg/year)	Continental (kg/year)
Film production (formulation)	0.11 (air) 2.27 (waste water)	0.034 (air) 0.68 (waste water)	0.051 (air) 1.02 (waste water)
Film development (processing)	0.0088 (waste water)	0.75 (waste water)	6.75 (waste water)

Note: formulation emissions are of PFOS-salt; processing emissions are of PFOS-substance.

3.1.5 Aviation

PFOS-related substances are used in hydraulic fluids in the aviation industry (Section 2.3.5). These are considered to be PFOS-salt for these calculations (see note on composition in Section 2.3.5). The manufacture of these fluids takes place outside the EU, so there is no need for a formulation step.

Information relating to emissions of hydraulic fluids is taken from an Emission Scenario Document on Lubricants and Lubricant Additives (Environment Agency, 1997a). Losses are most likely to occur on installation into equipment, during maintenance and on removal for disposal. Aviation systems are expected to be well sealed and so losses during use are expected to be low. It is assumed that all of the substances sold during a year go to replace the fluids lost during the same period, as the suggested replacement or reconditioning frequency for these types of fluids is one year. The suggested fate of the fluids is 2% loss to the environment (1.4% to soil, 0.6% to water) over the service life and 98% taken to chemical disposal from which no significant emissions are expected.

The world use of PFOS-related substances in this area is 2.2 tonnes, the EU is assumed to use one third of this, or 0.73 tonnes. The losses in the EU are therefore 4.4 kg/year to water and 10.2 kg/year to soil. In other work it has been assumed that 10% of the EU releases could relate to one large airport. Hence the local and regional annual emissions are 0.44 kg to water and 1.02 kg to soil. The local site emissions are assumed to take place over 300 days, hence the daily emissions are 1.5 g/day to waste water and 3.4 g/day to soil.

Table 3.5 below provides a summary of emissions from hydraulic fluids used in the aviation industry.

Table 3.5 Summary of aviation releases

Local (g/day)	Regional (kg/year)	Continental (kg/year)
1.5 (waste water) 3.4 (soil)	0.44 (waste water) 1.02 (soil)	3.94 (waste water) 9.2 (soil)

Note: all as PFOS-substances

3.1.6 Fire-fighting foams

3.1.6.1 Formulation

This calculation has been included to indicate possible releases from the formulation of fire-fighting foams containing PFOS-related substances. Such foams are not thought to be produced in the UK any longer.

Section 2.3.6 presented information relating to a producer of foams, which gave a use level of 40 tonnes of PFOS-related substances per year (the company no longer uses PFOS-based products). At a concentration of 1% in the foams this would make 4,000 tonnes of concentrate. This seems high in comparison to the UK stock figures below – these indicate a total stock of all foams (not just those with PFOS) of just under $4x10^6$ litres, or 4,000 tonnes assuming a density of 1 g/cm^3. Nevertheless this tonnage is used as an illustration.

There are no specific data regarding emissions from the production of the foams, so the default values from the Technical Guidance Document are used, treating the process as a formulation. The relevant emission factors are 0.001 to air and 0.02 to water, with production over 300 days per year. The resulting emissions are 0.13 kg/d to air and 2.7 kg/d to water. As noted in the next section, these are considered to be PFOS-salt. Larger scale emissions are not considered for this use pattern, as full release on use is included in the next section.

3.1.6.2 Use

The fraction of the stock of foams (all types) used by fire services in 2002 was 15%, although the fraction of PFOS-containing foams used was only 0.5%. For the purposes of these calculations it will be assumed that the higher rate of use is the normal rate, and that the remaining stock will be used at this rate[6]. The shelf life of the foams, based on information from the fire services through the consultation, is 10-20 years; a use rate of 15% would use up the existing stock within this time frame, whereas the reduced use rate would leave much of the stockpile to be disposed of. If the PFOS-containing foam is not used then the releases below will be over-estimates. The volume of PFOS-containing foam concentrates stockpiled in the UK is estimated as 76,000 litres (Section 2.3.6).

Confidential information on the quantities and compositions of formulations imported into the UK in the past has been provided. From this, it is reasonable to assume a concentration of 1% PFOS related substance in the foams as stored (i.e. corresponding to the volumes above). From the information provided the major part of the PFOS containing material was of the PFOS-salt type, and so this will be assumed for these calculations.

Assuming a density of 1 kg/l for the concentrates, the amount of foam is 76 tonnes, containing 760 kg of PFOS-salt. At a use rate of 15% per year, this is a use of 114 kg per year for the UK. It is assumed that all of this is released to the environment. As every fire will have different characteristics, there is probably no such scenario as a typical fire. As an illustrative calculation, it is assumed that 1% of this total is used at a fire[7]. Two scenarios for the release to the environment are considered, as possible extremes. In the first (use A), there

[6] An alternative calculation assuming use of only 0.5% of PFOS-containing foams is included in Appendix 4 and is considered in the risk evaluation.

[7] Foams may also be used in training exercises. As the assumption of 1% release is only for illustration, the scenario can be considered to cover use in large training exercises. As the water and foam from such exercises is likely to be collected, then use B may be more relevant to the training situation.

is no containment of the foam and water, and so 50% of the release (0.57 kg) goes to surface water without treatment and 50% (0.57 kg) to soil. In the second (use B), it is assumed that the foam and water are collected and passed to a waste water treatment plant, hence 1.14 kg to waste water treatment. The release is assumed to take place over one day.

The UK emissions are assumed to be 20% of those for the EU for these calculations, hence the EU release is 570 kg/year. This is assumed to be split evenly between surface water and soil. The regional emissions are 28.5 kg/year to surface water and to soil, and the continental emissions are 257 kg/year to surface water and to soil.

Table 3.6 below provides a summary of emissions from use of fire fighting foams from fire service use.

Table 3.6 Summary of Emissions from Use of Fire Fighting Foams

Local (kg/day)	Regional (kg/year)	Continental (kg/year)
Use A: 0.57 (drain) 0.57 (soil) Use B: 1.14 (wwtp)	28.5 (surface water) 28.5 (soil)	257 (surface water) 257 (soil)

Note: all emissions are of PFOS-salt

These calculations do not specifically address the possible releases from the use of foams on offshore installations, or in fire protection systems on ships. No specific information on these areas of use has been located for this evaluation, although Norway indicated that PFOS-containing foams were used in these areas. As the amounts used at a fire as estimated above are based on an arbitrary choice, it is suggested that in the first instance these may also be considered for the evaluation of offshore use. The calculations for the marine environment would be the most relevant (for Use B, the marine calculation will assume direct emission to the sea without passing through a wwtp) .

3.1.7 Fabric treatment

3.1.7.1 Treatment step

A number of different types of fabric have been treated with PFOS-related substances. For the estimation of releases from the treatment step, the treatment of textiles will be used as an example. Releases from the treatment of other materials may differ to some extent.

To estimate emissions from this treatment step, information from the risk assessment of decabromodiphenyl ether (EC 2002) and a draft Emission Scenario Document on textile processing produced by the Umweltbundesamt in Germany were used. This ESD has been reviewed by the OECD Task Force on Environmental Exposure Assessment, and is intended for publication in the OECD Environmental Health and Safety Publications series on Emission Scenario Documents. The substances used here are considered to be PFOS-polymer, with a residual 1% content of PFOS-substance.

The assessment of decabromodiphenyl ether considers losses from the backcoating of textiles, and this will be taken as being similar to the treatment of textiles with PFOS-related substances. The loss estimated was of 1 kg of formulation per batch used. This was lost to waste water from the setting up and washing down of the coating equipment. It was also assumed that a representative site would process five batches per day, hence the daily loss would be 5 kg of formulation. From data on products imported to the UK, the average content

of PFOS-related substances in formulations for apparel, carpets and fabrics was ~27%. Hence the daily emissions to waste water from the site would be 1.35 kg/day.

From Section 2.3.7, the amount of PFOS-related substances used in the apparel, carpet and fabric areas was 48 tonnes. At an average content of 27% this equates to ~180 tonnes of formulation. RIKZ (2002) indicated that a content of 2-3% by weight of perfluoro product was required in the fabric, which indicates that ~1900 tonnes of fabric could be treated.

From the ESD on textiles, the suggested realistic worst case amount of fabric treated at a site per day is 13 tonnes, with 225 days production giving 2,925 tonnes of fabric treated per year. As it is unlikely that all of a site's production each day will be of only one finish on one fabric type, a factor of 0.3 is used to adjust these figures. The result is 3.9 tonnes of fabric treated with a specific finish per day, and 878 tonnes per year. This yearly figure is just under half of the total estimated above for the whole of the UK, which may indicate that the substances are used over a smaller number of days, or that the amount used on a site is less than estimated.

Taking the 3.9 tonnes per day, at a content of 2.5% PFOS-related substance the amount of PFOS-related substance used per day would be 97.5 kg. The estimated release per day was 1.35 kg, giving an emission factor of 1.4%. Applying this to the UK use level of 48 tonnes gives an annual emission of 672 kg. Taking the UK as 20% of the EU, the total EU emissions would be 3,360 kg. The regional emission would be 336 kg/year, and the continental emission 3,024 kg/year. These values relate to the PFOS-polymer. Assuming a 1% content of PFOS-substance, the releases of PFOS-substance would be 3.4 kg/year (regional) and 30 kg/year (continental).

3.1.7.2 Service life releases

As noted earlier, the use of PFOS-related substances in treatment of fabrics has effectively ceased in the UK. However, there are materials currently in use in articles which contain PFOS-related substances from earlier treatments, and these may contribute to releases of PFOS during the course of the service life of the articles. The possible emissions from these articles are estimated in this section.

The substances used in treating fabrics were for the most part polymeric materials, i.e. PFOS-polymers. They also contained a small amount of residual PFOS-substances. For these calculations, it is assumed that the level of residual material is 1% (based on the information provided for the consultation exercise).

The relevant quantities of substances for these calculations are assumed to be those which were used annually on fabric treatment up until 2000. The use in the different areas was presented in Section 2.3.7, and is 23 tonnes in carpets, 15 tonnes in apparel/leather and 10 tonnes in fabrics (upholstery).

Carpets

Releases during the service life of carpets may arise from cleaning (vacuum or washing) or through wear. RIKZ (2002) quote 3M as providing a worst case estimate of 95% loss of PFOS from carpets over their working life, with 50% through abrasion from walking and vacuuming, and 45% through steam cleaning.

Walking and vacuuming losses may be considered to go to land or to water. The use of vacuum cleaners would probably be expected to lead to removal to solid waste and disposal with household refuse and consequently landfill or incineration. However there is no information to apportion losses to walking (wear) and to vacuuming, so it will be assumed that releases are to the environment as a worst case. In ESR assessments the loss of particulates as wear from plastics has been considered as 'waste remaining in the environment' and distributed as 75% to soil and 25% to water. Assuming a similar distribution for these releases gives 37.5% to soil and 12.5% to water. Releases from steam cleaning are assumed to go to water, hence 45% to water. The overall releases are therefore 57.5% to water and 37.5% to soil. The amount remaining on the carpet at the end of the lifetime is assumed to be disposed of with the carpet, to landfill or to incineration.

The loss factors are estimated over the whole working life. As such they can be applied to the annual use level (this assumes a constant level of use). For a tonnage of 23 tonnes, the UK emissions would therefore be 13.2 tonnes to water and 8.6 tonnes to soil. As before, it is assumed that the UK accounts for one fifth of the EU, so the overall totals are 66 tonnes to water and 43 tonnes to soil. The regional emissions are 6.6 tonnes (water) and 4.3 tonnes (soil), the continental emissions are 59.4 tonnes (water) and 38.7 tonnes (soil). The above are emissions of polymeric material, and would be expected to be mostly associated with particulate material worn from the fabric.

The polymers are considered to contain 1% of PFOS-substances, so the releases of these are: regional 66 kg/year (water), 43 kg/year (soil); continental 0.59 tonnes/year (water), 0.39 tonnes/year (soil).

Upholstery and Furnishing Fabrics

There is no specific information on losses of PFOS-related substances from these materials so the information on carpets will be used as the basis for the assumptions. These materials will be cleaned, although probably not frequently, and so the loss through washing is taken as the same as that for steam cleaning of carpets, i.e. 45% to water. The degree of wear is assumed to be less than that for carpets, and is taken as half of that figure, i.e. 25%. As for carpets this is split between water and soil in the ratio 25:75, although some would be to solid waste. The overall emission factors are therefore 51.25% to water and 18.75% to soil. The amount remaining on the fabrics at the end of the lifetime is assumed to be disposed of with the fabric to landfill or to incineration.

From a tonnage of 10 tonnes per year, the UK emissions would be 5.1 tonnes to water and 1.9 tonnes to soil. Assuming the UK is 20% of the EU, the total emissions would be 25.5 tonnes to water and 9.5 tonnes to soil. The regional emissions are 2.6 tonnes (water) and 0.95 tonnes (soil), the continental emissions are 23 tonnes (water) and 8.6 tonnes (soil). These are emissions of polymeric substances, probably in association with particulate material. As before, taking the content of PFOS-substances as 1% the emissions of these substances are: regional 26 kg/year (water), 9.5 kg/year (soil); continental 0.23 tonnes/year (water), 0.09 tonnes/year (soil).

Apparel and Leather

These two areas are treated together as use in treating clothing. There is no specific information about the loss of PFOS-related substances from clothes, so the information on carpets has again been used as the basis for the assumptions. Clothing will be washed more frequently than carpets or upholstery, although the purpose of the treatment is to reduce the

staining of fabrics. Against this, the lifetime of most clothing is much shorter than that of the two categories above. Washing losses are therefore taken as half of those above, i.e. 22.5%. Wear is expected to be less than for carpets, and is taken as the same as for fabrics above, i.e. 25%. This is again split as 75% to soil, 25% to water, or 18.75% to soil and 6.25% to water. The overall emission factors are therefore 28.75% to water and 18.75% to soil. From a tonnage of 15 tonnes per year, the UK emissions would be 4.3 tonnes to water and 2.8 tonnes to soil. Assuming the UK is 20% of the EU, the total emissions would be 21.5 tonnes to water and 14 tonnes to soil. The regional emissions are 2.15 tonnes (water) and 1.4 tonnes (soil), the continental emissions are 19.4 tonnes (water) and 12.6 tonnes (soil). These are emissions of polymeric substances, probably in association with particulate material. As before, taking the content of PFOS-substances as 1% the emissions of these substances are: regional 22 kg/year (water), 14 kg/year (soil); continental 0.19 tonnes/year (water), 0.13 tonnes/year (soil).

Tables 3.7 below provides a summary of emissions from treatment of fabrics (carpets, upholstery and leather).

Table 3.7 Summary of Emissions from Treatment of Fabrics

Area	PFOS-polymer		PFOS-substance	
	Regional (tonnes/year)	Continental (tonnes/year)	Regional (kg/year)	Continental (kg/year)
Carpets	6.6 (w) 4.3 (s)	59.4 (w) 38.7 (s)	66 (w) 43 (s)	594 (w) 387 (s)
Upholstery & Furnishing Fabrics	2.6 (w) 0.95 (s)	23 (w) 8.6 (s)	26 (w) 9.5 (s)	230 (w) 86 (s)
Apparel & Leather	2.15 (w) 1.4 (s)	19.4 (w) 12.6 (s)	22 (w) 14 (s)	194 (w) 126 (s)
Total	11.35 (w) 6.65 (s)	101.8 (w) 59.9 (s)	114 (w) 66.5 (s)	1018 (w) 599 (s)

3.1.8 Paper treatment

PFOS-related substances have been used to treat a range of paper types and products (grease proof paper, food cartons etc.). The major type of substance used appears to be phosphate derivatives of N-EtFOSE, and these will be considered here as PFOS-substances. They are considered to be applied mostly during the paper making process, rather than as a coating in subsequent operations.

A level of use of 1 – 1.5% by weight of paper is indicated (RIKZ, 2002). The approximate usage in the UK was 32 tonnes, so that 2,100-3,200 tonnes of paper could be treated. For the EU, assuming the UK accounted for 20% of use, the figures would be 160 tonnes of substances, and 10,700-16,000 tonnes of paper.

The Appendices in the Technical Guidance document have been used to estimate the emissions from paper. The substances are intended to remain in the paper, so the main category is 2, use resulting in inclusion into a matrix. The use category is 31 (impregnating agent). The resulting emission factors are zero to air and 0.05 to waste water.

The information in Section 2.3.8 suggests there were only a few users for this type of treatment. Large companies is chosen as the category for the B table, which results in a fraction of main source of 0.333 and 300 days production. The fraction of main source is applied to the UK tonnage in this case, as this gives a result in keeping with the information

available. This results in the use of 10.7 t of PFOS-substance at the site per year, or 35.7 kg/day. The estimated release to waste water is 1.8 kg/day.

From above, the total use in the EU was estimated as 160 tonnes per year. The release is therefore estimated as 8 tonnes per year, with 800 kg to the region and 7.2 tonnes for the continent. These are releases of PFOS-substance to waste water.

The possibility of emissions from paper in use could be considered. However, the lifetime of such papers is not expected to be very long. On disposal, such papers as food wrappings etc might be expected to be disposed of with household waste rather than entering the paper recycling streams. Hence most of the substances used are likely to be disposed of to landfill or incineration.

3.1.9 Coatings

A range of possible uses in coatings of various kinds is described in Section 2.3.9. In some cases there appears to be some overlap with areas which have already been addressed. In order to obtain some indication of the possible emissions from this area, it has been assumed that the default emission factors for paints, lacquers and coatings in the Technical Guidance Document can be applied.

A use of ~18 tonnes for the UK is assumed for these calculations. The content of PFOS-related substances in coatings is indicated to be 0.1-1.0%; taking an average of 0.55% gives a quantity of coating containing PFOS-related substances of 3,270 tonnes per year.

The substances are treated as PFOS-substances for simplicity, and are considered to be surface active agents, use category 50. Assuming the paints are water based, the emission factors are zero to air and 0.005 to waste water. Considering the UK as 20% of the EU, the amount of paints containing PFOS-substances in the EU would be 16,364 tonnes. From the B tables this indicates a fraction of main source of 0.1, or use of 1,636 tonnes per year at the representative site. This would be over 300 days, and equates to the use of 9 tonnes of PFOS-substance at the site. Using the factor of 0.005, the emission to waste water would be 45 kg/year, or 0.15 kg/day. The total emissions for the EU would be 450 kg/year, with 45 kg to the region and 405 kg to the continent. These are emissions of PFOS-substances to waste water.

There would also be the possibility of emissions of the PFOS-substances from the coatings during the course of their service life. No information on these possible releases is available, and so no estimates are possible at this time.

3.1.10 Summary

The releases estimated in Sections 3.1.2 to 3.1.9 are summarised in Table 3.8.

3.2 ENVIRONMENTAL FATE AND DISTRIBUTION

3.2.1 Atmospheric degradation

There are no experimental data. The AOP program (v1.91) estimates a rate constant for the reaction of PFOS (as the acid) with OH radicals of 1.4×10^{-13} cm^3 $molec^{-1}s^{-1}$. With a

concentration of $5x10^5$ molec cm^{-3}, this gives a half life of 114 days. Combined with the low volatility, this indicates that degradation in the atmosphere is not likely to be significant.

The PFOS-substance N-EtFOSE is calculated to be more reactive, with a half life of 16 hours. This is almost entirely due to hydrogen abstraction from the amide substituent group, and may indicate that this part of the substance may break down to leave the PFOS backbone.

Table 3.8 Summary of Emissions from PFOS-salts, PFOS-substances and PFOS-polymers

Use area	Compartment	Local (per day)	Regional (per year)	Continental (per year)
PFOS-salts				
Chromium Plating	air	0.33 mg		
	waste water	180 mg	1000 kg	9000 kg
Photographic	air	0.11 g	0.034 kg	0.051 kg
	waste water	2.27 g	0.68 kg	1.02 kg
Aviation	waste water	1.5 g	0.44 kg	3.94 kg
	soil	3.4 g	1.02 kg	9.2 kg
Fire fighting foams - formulation	air	0.13 kg		
	waste water	1.07 kg		
Fire fighting foams – use (alternative local)	surface water	0.57 kg	28.5 kg	257 kg
	soil	0.57 kg	28.5 kg	257 kg
	waste water	1.14 kg		
PFOS-substances				
Photolithography	waste water	27 g	25 kg	226 kg
Photographic	waste water	8.8 mg	0.75 kg	6.75 kg
Fabrics – treatment	waste water	13.5 g	3.4 kg	30 kg
Fabrics – service life	water		114 kg	1018 kg
	soil		66.5 kg	599 kg
Paper treatment	waste water	1.8 kg	800 kg	7.2 tonnes
Coatings	waste water	0.15 kg	45 kg	405 kg
PFOS-polymers				
Fabrics – treatment	waste water	1.35 kg	336 kg	3024 kg
Fabrics – service life	water		11.35 tonnes	101.8 tonnes
	soil		6.65 tonnes	59.9 tonnes

Notes: Waste water - all releases treated in wwtp.
Surface water - release direct to surface water and not treated.
Water - releases split 80:20 wwtp:direct to surface water.

3.2.2 Aquatic degradation

3.2.2.1 Abiotic degradation

3.2.2.1.1 Hydrolysis

The hydrolysis of the potassium salt of PFOS has been studied over a wide range of pH values, from 1.5 to 11 (3M, 2003). Tests were carried out at 50°C to accelerate any reaction. No loss of PFOS was seen in any of the experiments. Based on the limit of quantification, and adjusting for the higher temperature of the tests, the half life at 25°C was estimated to be >41 years.

RIKZ (2002) quote 3M studies showing that some PFOS-related substances can undergo hydrolysis. The acrylate derivative of N-EtFOSE and N-MeFOSE have half lives of 35 and 99 days respectively at pH 7 and 25°C. The products of hydrolysis were not identified, but RIKZ suggested that they were likely to include acrylic acid and N-EtFOSE and N-MeFOSE.

Longer half life times of 6.3 years for N-MeFOSE and 7.3 years for N-EtFOSE are also quoted by RIKZ from 3M reports.

3.2.2.1.2 Photolysis

The possible photolysis in water of the potassium salt of PFOS has been studied in various test matrices, allowing for both direct and indirect photolysis (3M, 2003). No evidence of direct or indirect photolysis of PFOS was observed under any of the conditions tested. From the limit of quantitation of loss of PFOS, the minimum half life for photolysis in water was estimated to be >3.7 years.

RIKZ (2002) quote a 3M study showing no photolysis of N-EtFOSE.

3.2.2.2 Biodegradation

3.2.2.2.1 Aerobic

The OECD Hazard Assessment (OECD, 2002) and the 3M assessment (3M, 2003) concluded that PFOS was not biodegradable. Information on the main studies reviewed in these assessments is presented below.

A MITI test (Kurume Lab, 2002, quoted in OECD 2002) found zero removal as measured by oxygen demand, 3% by removal of parent compound and 6% by reduction in total organic carbon. These values indicated no significant degradation.

The OECD assessment includes a study summary for a 35-day biodegradation test. Activated sludge from a municipal waste water treatment plant was used , with 50 ml of settled sludge added per litre of mineral salts medium used. The concentration of PFOS (as the potassium salt) was 2.582 mg/l. The study found no evidence of degradation over the 35 day period. The recovery of PFOS from the sludge was good.

The summary also indicates that a number of other compounds were also quantified. None were detected. The majority of the substances listed are other PFOS-related substances, which may break down to give PFOS. It appears unlikely that any of these might be produced from the degradation of PFOS. These would seem to relate better to other work on the degradation of N-EtFOSE, which is considered below.

The 3M (2003) assessment includes a summary of an 18 day biodegradation test on PFOS (potassium salt). The experimental details are similar to those reported for the 35 day study above, except that the activated sludge was allowed to settle for five weeks rather than two days after collection, and the exposure concentration was 2.45 mg/l. No degradation of PFOS was measured in this study. As above, a group of other PFOS-related substances was also quantified, and none were detected. A note in the summary relates to a previous study to evaluate the biodegradation of N-EtFOSE over 35 days and to determine its metabolites. This seems a more relevant study for the determination of the other substances. There is no further information on this study in the documentation available, but Cahill and Mackay (2002) made use of this information in a recent study (see below).

Further experiments on the biodegradation of PFOS are included in study summaries in the 3M assessment (3M, 2003). An inoculum was produced from a mix of activated sludge from two waste water treatment plants, with material from a rotating biological contactor plant, sediment from below a water treatment plant outfall, and sandy soil. The test medium

included the inoculum, primary influent from one of the waste water treatment plants, and OECD 301A medium. The initial PFOS concentration was 20.8 mg/l. At weekly intervals, 70% of the bioreactor contents were removed and replaced with fresh medium including freshly collected waste water treatment plant effluent and inoculum, and additional PFOS. The final concentration of PFOS was 28.4 mg/l. There were no indications of biodegradation in this study. The PFOS was associated primarily with the biomass at the end of the study.

After 12 weeks of acclimation, activated sludge from the above study was added to OECD 301A medium, with PFOS at two concentrations, and placed in closed serum vials. The vials were sampled at intervals of up to 63 days. No clear evidence of the biodegradation of PFOS was seen in this study.

Other substances

RIKZ (2002) presented a degradation pathway for N-EtFOSE in waste water sludge, taken from two 3M reports. The ultimate products are shown as PFOS (anion) and perfluorooctanoic acid (PFOA). There is no indication of the rate of biodegradation, the overall yield of the two products or any intermediate product, or the relative amount of the two products formed. RIKZ (2002) considered that it was likely that N-MeFOSE would follow a similar degradation pathway. They quote a 3M report as stating that the likely endpoints of aerobic biodegradation of ECF-products are PFOS and PFOA. In the sequence of studies carried out by 3M (3M, 2001), the initial products of aerobic biodegradation of N-EtFOSE were identified, and then tested in further aerobic biodegradation tests. The process of identifying and testing products was continued with eventual tests on five intermediates products, PFOS and PFOA. Each of the intermediate products was biodegradable to some degree in the 18-day studies. PFOS and PFOA were not degradable and so represent the end of the chain. These were produced at intermediate stages as well as from degradation of the last intermediate product. The extent of degradation varied between the different substances tested.

Cahill and Mackay (2002) reported the development of a multi-species model, with PFOS-related substances being used in demonstrating the model. For the degradation of N-EtFOSE they used a rate constant of 0.014 – 0.0014 h^{-1}. The upper value was derived from a 3M study (3M (2000),assumed to be that referred to above), the lower rate was taken as 10-fold lower to reflect the lower densities of microbial communities in the environment compared to the test. This lower rate will be used in the modelling calculations later in this evaluation, along with other illustrative degradation rates, in the absence of more specific information. Cahill and Mackay (2002) also quote the same 3M report (3M, 2000) as reporting preliminary results showing that the microbial degradation of N-EtFOSE and M-EtFOSE predominantly resulted in PFOS formation (92%), with 8% of PFOA. In the executive summary for the completed studies (3M, 2001) there are no comments on the overall extent of production of PFOS from the biodegradation of N-EtFOSE. For the main calculations in this evaluation, complete conversion of PFOS-substances to PFOS through biodegradation in the environment will be assumed, recognising that this is a worst case assumption. Alternative assumptions will be considered in the later discussion on uncertainties in the evaluation (Section 5.6).

3.2.2.2.2 Anaerobic

A study on the degradation of PFOS (potassium salt) under anaerobic conditions is summarised in 3M (2003). The inoculum was derived from the anaerobic digestor of a waste

water treatment plant, and exposures took place for 56 days in the dark. The concentration of PFOS in the test was 20.8 mg/l (nominal). No apparent degradation was seen in the study.

The 3M report (3M, 2003) also summarises a study using four pure microbial cultures to try to degrade PFOS (potassium salt). None of the species appeared able to degrade PFOS.

In contrast to these results, Schroder (2003) observed the disappearance of PFOS spiked into a laboratory-scale closed-loop bioreactor using columns filled with glass foam beads. PFOS was added initially at 5-10 mg/l; the inoculum was taken from the anaerobic sludge stabilisation tank of the Aachen-Soers STP, Germany. Anaerobic conditions were maintained and monitored. After two days the concentration of PFOS had fallen to below the detection limit. PFOA remained stable during this period, but following the reduction in the PFOS the level of PFOA also fell, to below the detection limit after 25 days. The fluoride ion concentration was monitored during the experiments and showed no increase, indicating that complete mineralization was not occurring. This may indicate some potential for degradation under certain conditions, however at present this will not be included in the evaluation due to the lack of information on the relevance to an environmental evaluation.

3.2.3 Degradation in soil

The degradation of PFOS, potassium salt, has been studied in a mixed soil and sediment culture (study summarised in 3M, 2003). Soils were obtained from three locations in the USA, sediments were taken from a brackish site below a waste water treatment plant outfall and from one other location. Soil and sediment samples were air dried, sieved and mixed in equal dry weight proportions. A nutrient mixture, containing sterile potting soil extract, trace mineral salts, yeast extract and water, was added to the soil/sediment mixture, to 75% of water holding capacity. Tests were conducted in the dark at 22°C for 20 weeks. No PFOS degradation was observed in the test system (by parent compound analysis).

3.2.4 Evaluation of environmental degradation data

None of the tests carried out show any indication of the biodegradation of PFOS in aquatic systems, under either aerobic or anaerobic conditions. There are also no indications of abiotic degradation in water. The rate estimated for reaction with hydroxyl radicals in air is slow. The one available study in soil also shows no degradation.

The limited information on other PFOS-related substances indicates that N-EtFOSE can be biologically degraded and that one of the products is PFOS. For the purpose of this evaluation, it will be assumed that PFOS is not degradable. For PFOS-substances, it will be assumed that they can be degraded to PFOS. This degradation will be assumed to take place in water, aerobic sediment and in soil. In the absence of more specific information it will be assumed as a worst case that this transformation is quantitative, i.e. one mole of PFOS-substance gives rise to one mole of PFOS. The effect of considering different rates for this process will be considered in the modelling section.

3.2.5 Environmental distribution

3.2.5.1 Adsorption

For most substances, adsorption is predicted on the basis of the log Kow value. As a value for this property cannot be measured for PFOS, this is not possible. Measurements are available

on the sorption of PFOS to soils, sediment and sludge, and these will be used in this evaluation.

Sorption of the potassium salt of PFOS to three types of soil, a sediment and a sludge from a domestic waste water treatment plant has been measured using a method based on OECD 106 (3M, 2003). Adsorption occurred rapidly in all cases, and the concentrations remained fairly constant after 16 hours. Desorption was also investigated - again, the desorption which occurred took place rapidly, and after eight hours the concentration in water did not vary significantly. Values for the sorption and desorption coefficients were calculated. These are presented in Table 3.9

Table 3.9 Sorption and desorption coefficients for various matrices

Matrix type	Kd (L/kg)	Kdes (L/kg)	Mean
Clay soil	18.3	47.1	32.7
Clay loam soil	9.72	15.8	12.8
Sandy loam soil	35.3	34.9	35.1
River sediment	7.42	10	8.7
WWTP sludge			1028

Note: mean values are mean of sorption and desorption coefficients. For sludge, value is the mean of the Freundlich coefficients for sorption and desorption, as direct values are only reported as limit values.

Mean values from sorption and desorption have been used in this evaluation. The average value from the three soils, 26.9, has been used for soil. The value for sediment has been used for both sediment and suspended sediments The single sludge value has been used to represent the different types of sludge in the EUSES calculations. The $K_{comp\text{-}water}$ values derived from these measurements using the TGD methods are: sediment, 5.11; suspended sediment, 3.08; soil, 40.6.

For comparison, a soil Kd value of 25, similar to that derived from the measurements, would be estimated from a log Kow value of 3.7 using the default QSAR equation from the Technical Guidance document. The corresponding estimated sediment and suspended sediment values would be 62.6 and 125 respectively, which are somewhat larger than the value from the measurements. For sludge, the estimated values would be 375 and 413, which are of a similar order but a little lower than that from the measurements.

It is recognised that these measured values are not necessarily representative of the environment. They also do not give any indication of the environmental factors which may affect the sorption of PFOS. As there is no reliable value for log Kow, no comments can be made on whether the sorption behaviour is different from that normally assumed, relating to organic carbon, or whether other processes are significant. However, they are considered to give at least an indication of the probable sorptive behaviour of PFOS.

3.2.5.2 Volatilisation

PFOS is not expected to volatilise significantly. It has a low vapour pressure and a solubility of ~500 mg/l. Attempts to measure the air-water partition coefficient using the potassium salt are reported in 3M (2003). The substance did not volatilise to any measurable extent. On the basis of the result, the value for the air-water partition coefficient was considered to be $<2x10^{-6}$, and to be essentially zero. A value of $1.35x10^{-7}$ is used in this evaluation, derived from the estimated Henry's Law constant (Section 1.3.8). Note that some of the PFOS-substances have considerably higher vapour pressure and are more likely to be volatile to some extent. This may allow the wider transport of potential PFOS-precursors through the air than is possible for PFOS itself.

3.2.5.3 Precipitation

The low vapour pressure and volatility means that PFOS is not expected to be found in air to any great extent. Hence precipitation is not considered to be a significant factor, unless PFOS is formed in air through the breakdown of PFOS-related substances in air. There is no available information on this.

3.2.5.4 Distribution in waste water treatment plant

The distribution of PFOS in waste water treatment plants has been modelled with the SimpleTreat model included in the EUSES 2 program. There is no degradation in the plant. The results are:

To air	4.5×10^{-4}%
To water	72.1%
To sludge	27.9%

3.2.5.5 Distribution in environment

The distribution of PFOS in the environment has been estimated using the EUSES 2 program using the partitioning and degradation data presented in the preceding sections and the physico-chemical data from Section 1. The program was run with a fixed release to air, to water and to soil in turn to examine the fate of releases to different compartments. The results from these calculations are in Table 3.10. It should be noted that the properties of PFOS, in particular the partitioning behaviour, mean that this type of model may not be as appropriate as for other substances. The use of directly measured properties for partitioning should help to compensate for this to some extent. However the results here, and the predicted environmental concentrations in the following sections, should be considered to be indicative.

Table 3.10 Distribution of PFOS in the model environment (releases to individual compartments)

Compartment	Release to		
	Air	Water	Agricultural soil
Freshwater	0.38%	83.18%	0.26%
Seawater	0.04%	9.06%	0.03%
Air	<0.01%	<0.01%	<0.01%
Soil (combined)	99.55%	3.42%	99.7%
Freshwater sediment	0.02%	4.20%	0.01%
Marine sediment	<0.0%1	0.14%	<0.01%

The results show that releases to air are eventually found almost completely in the soil, through deposition, with a small amount in water. Releases to water remain for the most part in the water (either freshwater or seawater) with some found in sediment and some in soil. Releases to soil remain almost completely in soil.

The distribution of PFOS has also been obtained from the calculations for predicted environmental concentrations, i.e. the distributions from the EUSES model using the estimated emissions (see Section 3.3.1). The results for the seven scenarios are presented in Table 3.11. The emissions included in the different scenarios are described in Section 3.3.1.3.

Table 3.11 Distribution of PFOS in seven scenarios

Compartment	Scenario						
	1	2	3	4	5	6	7
Freshwater	2.08%	2.06%	1.07%	1.29%	0.51%	0.55%	1.97%
Seawater	0.23%	0.23%	0.12%	0.14%	0.06%	0.06%	0.22%
Air	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%
Soil (combined)	97.59%	97.60%	98.75%	98.50%	99.40%	99.37%	97.71%
Freshwater sediment	0.10%	0.10%	0.05%	0.06%	0.03%	0.03%	0.10%
Marine sediment	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%

For all scenarios the majority of the PFOS is found in the soil (combined for the three types, but mostly in the agricultural soil, through sludge application). The remainder is mostly in the water compartment. These results reflect the fact that the estimated emissions of PFOS-salt are mainly to waste water, and hence result in emissions to surface water and soil (through sludge) after water treatment. Indirect emissions through the degradation of PFOS-substances or PFOS-polymers are significant only for soil and/or air, and so ultimately contribute mainly to the soil compartment.

The EUSES 2 model also includes three environments on global scales, for the arctic, temperate and tropical zones. For PFOS, the majority of the substance at steady state is found in the water compartments in these environments, i.e. it has been removed from the regional and continental environments. Together, the water compartments of the three global environments account for 98.3 % of the total burden at steady state.

3.2.6 Bioaccumulation and metabolism

3.2.6.1 Aquatic

There are a limited number of studies available on bioaccumulation of PFOS. A flow-through study on bluegill sunfish (*Lepomis macrochirus*) is cited in both 3M and the OECD assessment. The bioconcentration factors for edible tissues, non-edible tissues and whole fish were calculated from the rates of uptake and depuration because steady state had not been reached after 56 days of exposure.[8] The values obtained were 1124 (edible), 4103 (non-edible) and 2796 (whole fish). The exposure concentration was 0.086 mg/l.

A flow-through study on carp (*Cyprinus carpio*) resulted in lower values of 720 at 20 µg/l exposure and 200-1500 at 2 µg/l exposure. Higher values of 6,300 - 125,000 have been reported (for bioaccumulation factors) for in situ measurements at the scene of a spill of fire fighting foam, but these were considered to be due to the uptake of derivatives which were then metabolised to PFOS, hence the values were over-estimated.

Martin et al (2003) measured BCF values in rainbow trout plasma and liver of 2900 and 3100 respectively following exposure in a flow-through system to a combination of perfluorinated acids (both carboxylates and sulphonates).

The value of 2796 will be used as the bioconcentration factor in fish in this evaluation. The Technical Guidance Document indicates a biomagnification factor of 2 for this BCF value,

[8] The robust summary in the OECD hazard assessment (2002) 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.

and this is also used in the calculation of levels in biota for the assessment of secondary poisoning.

Martin et al (2003a) studied the uptake of PFOS from food in juvenile rainbow trout (Oncorhynchus mykiss). Fish were fed food spiked with a mixture of perfluorinated substances - PFOS and its butyl and hexyl analogues, C_5-C_{14} perfluoroalkanoic acids (excluding C_{13}). The concentration of PFOS in the food was 0.54 μg/g. The exposure period was 34 days, and was followed by a depuration period of 41 days. Fish were fed in such a way that the food was consumed rapidly after addition, to minimise the possible transfer of substances from food to water. Water samples were taken before and after feeding on day 30 to confirm that the water concentrations remained low. Fish were sampled at intervals during the uptake and depuration periods.

The measured concentrations in fish were corrected for the growth of the fish. The assimilation efficiency for PFOS calculated from the results was 120±7.9%, the depuration half life was 13±1.8 days, the bioaccumulation factor (BAF) was 0.32±0.05 and the time to steady state was estimated as 43 days. The results show that PFOS will not biomagnify from food in juvenile trout. The authors suggest caution in extrapolating these results to larger fish, e.g. mature trout, as the half lives of other substances have been shown to increase by up to a factor of 10 times in mature fish compared to juveniles. They also considered that these results did not mean that PFOS would not accumulate in higher organisms from food. Elimination through the gills is an important route for fish which is not available to birds for example, and elimination from the lungs is expected to be much lower in view of the low vapour pressure. In view of these comments the default BMF value from the TGD is used.

In the course of a study on the toxicity of PFOS to freshwater mussels (*Unio complamatus*) the concentration of PFOS in the mussel tissues was measured. The toxicity study was reviewed for the OECD assessment, the results are included in this evaluation. The measured concentrations in water and in mussel tissues are in Table 3.12

Table 3.12 Accumulation of PFOS in mussel tissue

Mean measured exposure concentration (mg/l)	% mortality at 96 hours	Mean measured tissue concentration (μg/g)	Calculated BCF
5.3	0	3.69	0.7
12	0	5.22	0.44
20	0	7.33	0.37
41	5	11.85	0.29
79	90	88.8	1.12

As no mortality was seen in the lower concentrations over the exposure period, the results at these concentrations can be considered suitable to determine bioconcentration factors. The average of the three results is 0.5.

3.2.6.2 Terrestrial

A 14-day toxicity study with earthworms has been reported (3M, 2003, see Section 4.2.1). The concentrations in worms were measured at the end of the exposures. The worms were allowed to clear soil from their guts before the concentrations were measured. These levels can be used together with the concentrations in the soil to calculate bioaccumulation factors. The data are in Table 3.13.

Table 3.13 Bioaccumulation in worms

Soil concentration (mg/kg wwt)	Worm concentration (mg/kg wwt)	BCF
77	195	2.5
141	203	1.4
289	252	0.87
488	1105	2.3

Effects were seen on the earthworms in the test at all concentrations above 77 mg/kg, so the factor used in this evaluation will be taken from the 77 mg/kg exposure.

The BCF for earthworms as used in the revised Technical Guidance is based on the pore water concentration. Using the $K_{soil\text{-}water}$ partition coefficient of 40.6, the pore water concentration at 77 mg/kg in soil is 3.22 mg/l. The BCF based on this concentration is 60.5 l/kg wwt.

An alternative approach to a BCF value for worms could be to derive a surrogate log Kow from the fish bioconcentration value. Using the default QSAR equation from the TGD, the fish BCF value of 2796 would be predicted from a log Kow value of 4.88. Using this surrogate log Kow value, a BCF for worms of 911 would be predicted. This is much higher than the value obtained from the measured levels. The measured value will be used in the evaluation.

There are limited data for uptake into plants. As part of a study on the toxicity of PFOS (potassium salt) to seven plant species (Section 5.4.2.1), concentrations of PFOS in plant tissues were measured. The concentrations in plant vegetative tissues were generally in the range of 1-2 times the concentration in soil. The values around twice the soil level were found at lower exposure concentrations, where the plants were less likely to be affected by the exposure. Concentrations in fruit were lower, less than 10% of the soil level. No specific data were located on transfer to meat or milk, processes which are considered in the estimation of exposure to humans through the environment. There are limited measurements of levels in food, which are discussed in Section 3.3.5. In the absence of specific data, uptake and accumulation factors for these are usually estimated from the log Kow value. For the purpose of this evaluation, the surrogate log Kow value estimated above from the fish data will be used. This is a log Kow value of 4.88.

3.2.6.3 Absorption in mammals

PFOS appears to be well absorbed in mammals following ingestion. After a single oral dose in solution of 4.2 mg/kg bw to rats using labelled PFOS, at least 95% of the 14-C label was systematically absorbed after 24 hours (Johnson et al (1979a), in OECD 2002). Approximately 86% of this dose was found in the carcass at 24-48 hours. There was some excretion of total carbon-14 in urine, 1-2% per day. The half life for elimination from plasma was estimated to be 7.5 days. The same authors (Johnson et al (1979b),in OECDE 2002) also gave the same dose intravenously. After 89 days, the mean urinary excretion was ~30%, and the mean faecal excretion was 12.6%.

3.3 ENVIRONMENTAL CONCENTRATIONS

3.3.1 Background to calculations

The calculation of predicted environmental concentrations for PFOS is complicated by a number of factors. One is that some of the uses have effectively ceased, while others are being reduced, so that the use pattern is changing. This is addressed in this evaluation by defining a number of scenarios to include or exclude various sources. The baseline situation is taken to be use as it was in the UK around 2000, so before the removal of products from the market.

A second factor is the possible contribution of PFOS-substances and PFOS-polymer materials to the levels of PFOS in the environment. The rate and extent to which these breakdown and produce PFOS is not known. Therefore a number of calculations based on various assumptions about this degradation have been included.

The EUSES 2.0 model has been used for the calculations in this evaluation. It should be noted that the regional concentrations calculated in the model relate to the steady-state situation. For a persistent substance such as PFOS, the steady state may take a considerable time to be reached, and so to some extent the calculated concentrations may be projections of the concentrations expected in the future, assuming that the emissions in the calculation remain constant.

3.3.1.1 Substance properties for modelling

3.3.1.1.1 PFOS-salt

The physico-chemical properties of the potassium salt, as described in Section 1, are used for this group. As noted in the relevant sections, it is not possible for this substance to predict properties from the log Kow value, and measured values have been used where possible. The full set of values as used in the model is presented in Table 3.14.

There are a number of other factors related to uptake in plants, crops and cattle which are used in the estimation of exposure of humans through the environment. These are usually estimated from the log Kow value. For the purpose of this evaluation, the surrogate log Kow value of 4.88 has been used (for explanation, see Section 3.2.6.2).

Table 3.14 Properties of PFOS-salt for modelling

Property	Value	Section
Molecular weight	538	Table 1.1
Vapour pressure	3.31×10^{-4} Pa	Table 1.1
Water solubility	519 mg/l	Table 1.1
Henry's law constant	3.19×10^{-4} Pa m^3 $mole^{-1}$	Table 1.1
$K_{sed\text{-}water}$	5.16	Section 3.2.5.l
$K_{susp\text{-}water}$	3.08	Section 3.2.5.1
$K_{soil\text{-}water}$	40.6	Section 3.2.5.1
BCF fish	2,796	Section 3.2.6.1
BCF worm	60.5	Section 3.2.6.2
BMF_1, BMF_2	2	Section 3.2.6.2
Biodegradation	Not biodegradable	Section 3.2.4
Photodegradation in air	114 d half life	Section 3.2.1
Other abiotic processes	EUSES defaults	

3.3.1.1.2 PFOS-substances

Although there are a large number of substances which are included in this group, specific property values are not available for the majority. Some data are available for the most widely used, and of these N-EtFOSE (CAS 1691-99-2) has the most extensive data set. This has been used as the model compound for this group. The properties of this group are shown in Table 3.15 below.

Table 3.15: Summary of property values for PFOS-substances (RIKZ, 2002)

Property	Value Used
Molecular weight	571.25
Melting point	57°C
Solubility	0.15 mg/l
Vapour pressure	0.5 Pa
Log Kow	4.4

A degradation half life in air of 16 hours was estimated in Section 3.2.1. For biodegradation, a rate constant of 0.0014 h^{-1} will be used (see Section 3.2.2.2.1). This rate will be used for water, soil and aerobic sediment in the model. This is assumed to be the rate of disappearance of the substance, and may therefore over-estimate the rate of formation of PFOS. An alternative half life of one year, to allow for the possible slower degradation of other substances, is also used in the same way. In all media the final product of degradation is assumed to be PFOS (see Section 3.3.1.2). Further consideration of the rate of degradation and the degree of production of PFOS is included in Appendices 3 and 5.

The fraction of N-EtFOSE adsorbed to particulates in air was measured as 65% in outdoor air samples (see Section 3.3.4.2). This value is used in the calculations rather than estimating this percentage from the log Kow value.

It is recognised that other substances considered in this group may have somewhat different properties. These calculations are intended to give a rough idea of possible behaviour. It should be noted that the possible accumulation and effects of the substances themselves are not considered in this evaluation.

3.3.1.1.3 PFOS-polymers

There are no data on the properties of the polymeric substances. Therefore properties have been chosen to represent the expected behaviour, i.e. low volatility, low solubility, and tendency to be associated with solid phases as shown in Table 3.16 below. The effect of higher values for the log Kow value is considered in Appendix 6.

Table 3.16 Summary of values for PFOS-polymers

Property	Value Used
Molecular weight	10000
Melting point	treated as a solid (100°C used)
Solubility	10^{-6} mg/l
Vapour pressure	10^{-6} Pa
Log Kow	6
Henry's Lax constant	10^{-4} Pa m^3 $mole^{-1}$

There are no data on degradation rates for the polymers, or on the extent to which PFOS may be produced, so again values have been selected to represent possible outcomes. The half lives for polymers are expected to be longer than those for the substances, so a half life of

30 years has been used. This is an arbitrary value. Note that the residual fluorocarbons present in the polymers have been treated as PFOS-substances and so this rate does not apply to them.

3.3.1.2 Releases of PFOS to environment

The emission estimates from Section 3.1.10 are used. The PFOS-salt emissions are considered as emissions of PFOS itself, and are entered directly. For the PFOS-substances, the approach depends on the assumptions made about the breakdown of the substances to PFOS. The first assumption is that the PFOS-substances effectively break down immediately to PFOS on release (or are converted to PFOS before release). In this case the emissions of PFOS-substance are converted to PFOS-salt emissions. It is assumed that the degradation proceeds to PFOS with no by-products, so that the yield is 100%. The relative molecular weights for the chosen representative substances mean the yield is 0.94 kg for 1 kg of PFOS-substance. The resulting emissions are added to those of PFOS-salt direct.

Where the degradation of the PFOS-substances is assumed to take a longer time, the emissions of PFOS-substance are modelled using the properties for PFOS-substance above to allow for the effect of movement of air and water in the model. From the concentrations predicted and the appropriate degradation half lives the rate of degradation of PFOS-substance in each environmental compartment at steady state can be calculated. As above, degradation is assumed to proceed to PFOS with no by-products, so that 1 kg/day degradation of PFOS-substance is assumed to give 0.94 kg/day PFOS. Hence the rates of degradation of PFOS-substance are converted to rates of production of PFOS in each compartment, and these are added to the direct releases of PFOS-salt. The results presented in the tables are for the combined releases as appropriate to the particular scenario. This is done for both half lives chosen. The rates of production of PFOS from the breakdown of PFOS-substances for these scenarios are included in Appendix 2.

It is recognised that the assumption of 100% production of PFOS from the PFOS-substances is a worst case assumption (although Cahill and Mackay (2002) quote an estimated yield of 92% from N-EtFOSE). Other possible assumptions are considered in Appendix 3.

The approach for PFOS-polymer is similar to that for the substances. From the information on polymer composition provided for the Risk Reduction Strategy consultation, the PFOS moiety makes up on average about 30% of the polymer by weight, so a yield of 30% by weight has been used. The production rates of PFOS from polymer degradation are included in Appendix 2.

3.3.1.3 Scenarios

The baseline scenario is considered to be the situation in 2000. This includes all of the uses for which emission estimates have been made in Section 3.1, including the service life of treated fabrics. In order to consider the possible contributions of PFOS-substances and PFOS-polymers, calculations have been carried out with and without these included. Hence there are five scenarios using the baseline emissions:

1 - PFOS-salt releases only
2 - PFOS-salt plus PFOS-substances, assuming instant degradation to PFOS.
3 - PFOS-salt plus PFOS-substances, assuming a 20 day half life for degradation to PFOS.
4 - PFOS-salt plus PFOS-substances, assuming a 1 year half life for degradation to PFOS.

5 - PFOS-salt, PFOS-substances with 20 day half life, PFOS-polymer with 30 year half life degradation to PFOS.

There are no data for the breakdown of PFOS-polymers, and so the fifth scenario is considered to be much more speculative than the others. A 30 year half life is assumed, with complete release of the PFOS moiety from the polymer on this time scale. It should be noted that all of these scenarios reflect the situation in the past as far as emissions are concerned.

Two further scenarios have been used to try to consider the 'current' situation and a possible future. For the 'current' scenario (Scenario 6), continuing use in chromium plating, photolithography, photography and aviation has been assumed, with use of stocks of fire fighting foam and continuing release from fabrics in use. These last two uses will only continue for a number of years, whereas the calculations assume a continuous use to steady state, and so will overestimate.

The future scenario (Scenario 7) is that where the use of stocks of PFOS foams has been completed and the fabrics have reached the end of their service lives.

Local concentrations have been calculated for all releases of PFOS-salt substances where there is a local source. Local concentrations have also been calculated for releases of the PFOS-substances where instant conversion to PFOS has been assumed (in Scenario 2). For other scenarios, the breakdown of the PFOS-substances (or PFOS-polymer) occurs after dispersion in the environment and so local scenarios are not appropriate. Appendix 7 shows the contribution of each use area to the total regional emissions for each scenario.

3.3.2 Aquatic compartment (surface water, sediment and wastewater treatment plant)

3.3.2.1 Estimated aquatic environmental concentrations

The predicted concentrations in the freshwater compartment and for sediment for the seven scenarios are in Tables 3.17 and 3.18.

Table 3.17 Predicted environmental concentrations in freshwater (mg/l)

Use area	Scenario number						
	1	2	3	4	5	6	7
Chromium plating	$4.52x10^{-5}$	$8.1x10^{-5}$	$5.45x10^{-5}$	$5.16x10^{-5}$	$9.46x10^{-5}$	$8.63x10^{-5}$	$4.36x10^{-5}$
Photography - formulation	$1.21x10^{-4}$	$1.56x10^{-4}$	$1.3x10^{-4}$	$1.27x10^{-4}$	$1.7x10^{-4}$	$1.62x10^{-4}$	$1.19x10^{-4}$
- processing	NA	$7.48x10^{-5}$	NA	NA	NA	NA	NA
Aviation	$9.28x10^{-5}$	$1.29x10^{-4}$	$1.02x10^{-4}$	$9.91x10^{-5}$	$1.42x10^{-4}$	$1.34x10^{-4}$	$9.12x10^{-5}$
Fire fighting foams -formulation	0.0973	0.0974	0.0973	0.0973	0.0974	NA	NA
- use A	0.0285	0.0286	0.0285	0.0285	0.0286	0.0286	NA
- use B	0.0411	0.0412	0.0411	0.0411	0.0412	0.0412	NA
Photolithography	NA	$9.75x10^{-4}$	NA	NA	NA	NA	NA
Fabrics - application	NA	$5.32x10^{-4}$	NA	NA	NA	NA	NA
Paper treatment	NA	0.0613	NA	NA	NA	NA	NA
Coatings	NA	$1.6x10^{-3}$	NA	NA	NA	NA	NA
Regional	$3.87x10^{-5}$	$7.45x10^{-5}$	$4.8x10^{-5}$	$4.51x10^{-5}$	$8.81x10^{-5}$	$7.98x10^{-5}$	$3.71x10^{-5}$

Table 3.18 Predicted environmental concentrations in sediment (mg/kg wwt)

Use area	Scenario number						
	1	2	3	4	5	6	7
Chromium plating	$1.21x10^{-4}$	$2.17x10^{-4}$	$1.46x10^{-4}$	$1.38x10^{-4}$	$2.53x10^{-4}$	$2.31x10^{-4}$	$1.17x10^{-4}$
Photography - formulation	$3.23x10^{-4}$	$4.18x10^{-4}$	$3.47x10^{-4}$	$3.4x10^{-4}$	$4.55x10^{-4}$	$4.33x10^{-4}$	$3.18x10^{-4}$
- processing	NA	$2.0x10^{-4}$	NA	NA	NA	NA	NA
Aviation	$2.48x10^{-4}$	$3.44x10^{-4}$	$2.73x10^{-4}$	$2.65x10^{-4}$	$3.8x10^{-4}$	$3.58x10^{-4}$	$2.44x10^{-4}$
Fire fighting foams -formulation	0.26	0.261	0.261	0.261	0.261	NA	NA
- use A	0.0764	0.0765	0.0764	0.0764	0.0765	0.0765	NA
- use B	0.11	0.11	0.11	0.11	0.11	0.11	NA
Photolithography	NA	$2.61x10^{-3}$	NA	NA	NA	NA	NA
Fabrics - application	NA	$1.42x0^{-3}$	NA	NA	NA	NA	NA
Paper treatment	NA	0.164	NA	NA	NA	NA	NA
Coatings	NA	$4.28x10^{-3}$	NA	NA	NA	NA	NA
Regional	$1.7x10^{-4}$	$3.27x10^{-4}$	$2.1x10^{-4}$	$1.98x10^{-4}$	$3.86x10^{-4}$	$3.5x10^{-4}$	$1.63x10^{-4}$

The calculated concentrations in the effluent from waste water treatment do not depend on the regional background and so are not affected by the differences between the scenarios. The resulting concentrations are in Table 3.19.

Table 3.19 Predicted effluent concentrations

Use area	Concentration (µg/l)	Notes
Chromium plating	0.065	PFOS-salt
Photography (formulation)	0.82	PFOS-salt
Photography (processing)	0.003	PFOS-substance, assumed instant conversion
Aviation	0.54	PFOS-salt
Fire fighting foams (formulation)	973	PFOS-salt
Fire fighting foams (use B)	570	PFOS-salt
Photolithography	9.0	PFOS-substance, assumed instant conversion
Fabrics application	4.6	PFOS-substance, assumed instant conversion
Paper treatment	613	PFOS-substance, assumed instant conversion
Coatings	15.2	PFOS-substance, assumed instant conversion

3.3.2.2 Measured aquatic environmental concentrations

Studies have identified the presence of PFOS in surface water and sediment downstream of a production facility, as well as in wastewater treatment plant effluent, sewage sludge and landfill leachate at a number of urban centres in the US (3M Multi City study, various reports reviewed in OECD (2002) and 3M (2003)). Four of the cities (Decatur, Mobile, Columbus, Pensacola) were cities that have manufacturing or industrial use of fluorochemicals; two of the cities (Cleveland, Port St. Lucie) were control cities that do not have significant fluorochemical activities. The ranges of PFOS levels in these cities are provided in Table 3.20.

The control cities' samples generally inhabited the lower end of the above ranges, except for the municipal wastewater treatment plant effluent and sludge findings for one of the control cities (Cleveland), which were intermediate in their ranges, and the 'quiet' water samples at control city (Port St. Lucie), which were the highest.

Hansen *et al* (2002) reported concentrations of PFOS measured from surface water samples taken from the Tennessee River upstream and downstream of the outfall from the fluorochemical manufacturing facility of 3M at Decatur. Upstream of the facility the average concentration of PFOS was 32 ± 11 ng/L; the downstream concentrations were observed to increase at a point approximately six miles below the outfall; the average PFOS concentration from that point downstream was 114 ± 19 ng/L.

Table 3.20 Environmental Levels of PFOS in Six US Urban Centres in the US (from OECD, 2002)

Medium	Range of PFOS levels
Municipal wastewater treatment plant effluent	0.041 - 5.29 ppb
Municipal wastewater treatment plant sludge	0.2 - 3,120 ppb (dry weight)
Drinking water	ND - 0.063 ppb
Sediment	ND - 53.1 ppb (dry weight)
Surface water	ND - 0.138 ppb
'Quiet' water	ND - 2.93 ppb

Source: OECD, 2002
Note: ND: not detected

3M (2003) included measured levels from the vicinity of the facility outfall at Decatur for 2001. The mean concentration in water for seven sites (one sample from each) was 61 µg/l. The corresponding sediment concentration was 2,740 µg/kg dwt.

The first environmental survey of PFOS and related substances in Japan (which followed a Japanese study that showed measurable levels of PFOS in human blood) found the highest concentration in surface water in Tokyo Bay at 59 ng/L (mean: 26 ng/L). The concentrations of PFOS in surface water were similar to those of polyaromatic hydrocarbons (PAHs) and much higher than those of PCBs, dioxins and furans (Taniyasu *et al*, 2002).

Saito et al (2003) determined the PFOS concentrations in surface water samples from 142 locations in Japan (single samples from each location). The geometric mean concentration for river waters (126 samples) was 2.37 ng/l (geometric standard deviation 4.13), the median was 1.68 ng/l, the range 0.3 - 157 ng/l. For coastal water samples, the geometric mean concentration was 1.52 ng/l (SD 4.14), median 1.21 ng/l and range 0.2 - 25.2 ng/l. The authors comment that the levels are much lower than those reported for the US, with the exception of two rivers where 135 and 157 ng/l were measured.

Samples of effluent from fifteen representative industrial branches were analysed for PFOS, perfluoroalkyl carboxylates and perfluoroalkyl sulphonates (Hohenblum et al, 2003). The industry branches were printing (1 site), electronics (3), leather, metals, paper (6), photographic, textiles (2). The PFOS levels found ranged from below the detection limit (25 ng/l) to 2,500 ng/l (2,500 ng/l for leather, 120 ng/l for metal, 140-1200 ng/l at four paper sites, 1,200 ng/l for photographic, not found in textiles or electronic).

Groundwater from below the Wurtsmith Air Force Base in Michigan, US was sampled (Moody et al, 2003). Fire fighting foams containing PFOS had been used there in training exercises from the 1950s to 1993 when the base was decommissioned. The groundwaters were found to contain PFOS, at levels from 4 to 110 µg/l. The C6 (hexyl) analogue of PFOS was also found, as was PFOA and its C6 analogue.

3.3.2.3 Comparison of measured and estimated aquatic concentrations

There are limited measured data available to compare with the predicted concentrations, and in a number of cases it is not possible to allocate the measured data to the relevant scale, local, regional or continental. Hansen et al (2002) reported a concentration of 32 ng/l in an area upstream of a discharge and not considered to be affected by specific sources. The calculated regional background concentrations are in the range 40 – 90 ng/l.

Saito et al (2003) found lower levels in Japan in general, with a median value of 1.2 ng/l. They remarked that the levels were much lower than those found in the United States. This may reflect different patterns of use. Taniyasu et al (2002) found the highest level of PFOS in Tokyo Bay, at 59 ng/l, which is similar to the freshwater background levels but higher by about an order of magnitude than the regional marine concentration (see Section 5.5.2.1). (The value is similar to some of the local concentrations for the marine environment.)

Values up to 2.93 µg/l (ppb) were reported from the 3M Multi-City study. The calculated local values (apart from those for fire fighting foams) are around 0.1 µg/l and so are lower than the highest value. The calculated values are closer to those measured some distance downstream of the production site. The highest calculated concentration is for the formulation of foams, at up to 0.1 mg/l depending on the scenario. This is of a similar order to the levels measured in the vicinity of the production facility outfall, but these are presumably different processes.

The effluent concentrations calculated for chromium plating (65 ng/l) and photography (820 ng/l) agree well with the measured values in effluents reported by Hohenblum et al (2002). The predicted value for paper, 0.6 mg/l, is much higher then the 1200 ng/l reported as the highest measured value. The calculated value is based on the release of PFOS-substance and assumes instant conversion to PFOS before the treatment plant, and so may be expected to over-estimate the concentration of PFOS. Similarly, a concentration of 4.6 µg/l was calculated for fabric treatment, while PFOS was not detected in textile effluents – again the calculated value is based on PFOS-substance release and instant conversion to PFOS. The measurements may indicate a lower presence of PFOS in the effluents from these areas at the point of release. There may have been PFOS-substances present in the effluents, but only one (n-ethylperfluorooctanesulphonamide) was analysed for in the samples – it was not detected in any. The calculated and measured values are therefore not on the same basis and are difficult to compare.

For some of the use areas the calculated effluent concentrations are in reasonable agreement with the range of values reported from the 3M Multi-City study. Higher values are calculated for uses where the PFOS-substances are assumed to be converted instantly to PFOS. Higher values are also calculated for the formulation of PFOS-containing foams (which is a default estimate) and for Use B, which is a use pattern not likely to have been included in the 3M study (use of foams in a fire).

3.3.3 Terrestrial compartment

3.3.3.1 Estimated soil concentrations

The predicted concentrations in the terrestrial compartment for the seven scenarios are in Table 3.21 (concentrations in soil at 30 days after application of sludge) and Table 3.22 (concentrations in groundwater under agricultural soil at 180 days after application of sludge).

Table 3.21 Predicted concentrations in soil (mg/kg wwt, agricultural soil, after 30 days)

Use area	Scenario number						
	1	2	3	4	5	6	7
Chromium plating	$8.52x10^{-4}$	$8.57x10^{-4}$	$1.37x10^{-3}$	$1.45x10^{-3}$	$1.41x10^{-3}$	$9.8x10^{-4}$	$8.47x10^{-4}$
Photography - formulation	0.0107	0.0107	0.0112	0.0113	0.0112	0.0108	0.0107
- processing	NA	$4.92x10^{-5}$	NA	NA	NA	NA	NA
Aviation	$7.06x10^{-3}$	$7.07x10^{-3}$	$7.59x10^{-3}$	$7.66x10^{-3}$	$7.62x10^{-3}$	$7.19x10^{-3}$	$7.08x10^{-3}$
Fire fighting foams - formulation	12.7	12.7	12.7	12.7	12.7	NA	NA
- use A	$5.05x10^{-6}$	$1.01x10^{-5}$	$5.26x10^{-4}$	$6.03x10^{-4}$	$5.61x10^{-4}$	$1.32x10^{-4}$	NA
- use B	5.36	5.36	5.37	5.37	5.37	5.36	NA
Photolithography	NA	0.118	NA	NA	NA	NA	NA
Fabrics - application	NA	0.0598	NA	NA	NA	NA	NA
Paper treatment	NA	8.0	NA	NA	NA	NA	NA
Coatings	NA	0.199	NA	NA	NA	NA	NA
Regional (natural)	$5.05x10^{-6}$	$1.01x10^{-5}$	$5.26x10^{-4}$	$6.03x10^{-4}$	$5.61x10^{-4}$	$1.32x10^{-4}$	$1.77x10^{-5}$

Table 3.22 Predicted concentrations in groundwater under agricultural soil (mg/l, after 180 days)

Use area	Scenario number						
	1	2	3	4	5	6	7
Chromium plating	$3.56x10^{-5}$	$3.58x10^{-5}$	$5.74x10^{-5}$	$6.07x10^{-5}$	$5.89x10^{-5}$	$4.09x10^{-5}$	$3.61x10^{-5}$
Photography - formulation	$4.48x10^{-4}$	$4.46x10^{-4}$	$4.68x10^{-4}$	$4.71x10^{-4}$	$4.69x10^{-4}$	$4.51x10^{-4}$	$4.47x10^{-4}$
- processing	NA	$2.05x10^{-6}$	NA	NA	NA	NA	NA
Aviation	$2.95x10^{-4}$	$2.45x10^{-4}$	$3.17x10^{-4}$	$3.2x10^{-4}$	$3.18x10^{-4}$	$3.0x10^{-4}$	$2.95x10^{-4}$
Fire fighting foams - formulation	0.53	0.53	0.53	0.53	0.53	NA	NA
- use A	$2.12x10^{-7}$	$4.24x10^{-7}$	$2.31x10^{-5}$	$2.53x10^{-5}$	$2.35x10^{-5}$	$5.56x10^{-6}$	NA
- use B	0.224	0.224	0.224	0.224	0.224	0.224	NA
Photolithography	NA	$4.91x10^{-3}$	NA	NA	NA	NA	NA
Fabrics - application	NA	$2.49x10^{-3}$	NA	NA	NA	NA	NA
Paper treatment	NA	0.334	NA	NA	NA	NA	NA
Coatings	NA	$8.31x10^{-3}$	NA	NA	NA	NA	NA
Regional	$3.28x10^{-5}$	$6.27x10^{-5}$	$7.66x10^{-5}$	$5.91x10^{-5}$	$2.93x10^{-4}$	$2.49x10^{-4}$	$3.4x10^{-5}$

3.3.3.2 Measured soil environmental concentrations

No measurements of concentrations of PFOS in soils have been located. Concentrations of PFOS in groundwater under a US Air Force Base are included in Section 3.3.2.2, and range from 4 – 110 µg/l. These are of the same order as those calculated for the use of fire fighting foams in Use B, and for the formulation of foams (default calculation). All other calculated concentrations are much lower than these measurements.

3.3.4 Atmospheric compartment

3.3.4.1 Estimated air concentrations

The predicted concentrations in the atmospheric compartment for the seven scenarios are in Table 3.23.

Table 3.23 Predicted concentrations in air (mg/m^3)

Use area	Scenario number						
	1	2	3	4	5	6	7
Chromium plating	$1.1x10^{-11}$	$8.13x10^{-11}$	$1.09x10^{-9}$	$1.25x10^{-9}$	$1.16x10^{-9}$	$2.75x10^{-10}$	$3.71x10^{-11}$
Photography - formulation	$2.51x10^{-8}$	$2.52x10^{-8}$	$2.62x10^{-8}$	$2.64x10^{-8}$	$2.63x10^{-8}$	$2.54x10^{-8}$	$2.52x10^{-8}$
- processing	NA	$2.09x10^{-11}$	NA	NA	NA	NA	NA
Aviation	$1.22x10^{-11}$	$2.26x10^{-11}$	$1.09x10^{-9}$	$1.25x10^{-9}$	$1.16x10^{-9}$	$2.76x10^{-10}$	$3.84x10^{-11}$
Fire fighting foams - formulation	$2.97x10^{-5}$	$3.04x10^{-5}$	$2.97x10^{-5}$	$2.97x10^{-5}$	$2.97x10^{-5}$	NA	NA
- use A	$1.05x10^{-11}$	$2.09x10^{-11}$	$1.09x10^{-9}$	$1.25x10^{-9}$	$1.16x10^{-9}$	$2.74x10^{-10}$	NA
- use B	$1.43x10^{-11}$	$2.51x10^{-11}$	$1.09x10^{-9}$	$1.25x10^{-9}$	$1.17x10^{-9}$	$2.78x10^{-10}$	NA
Photolithography	NA	$5.39x10^{-11}$	NA	NA	NA	NA	NA
Fabrics - application	NA	$3.14x10^{-11}$	NA	NA	NA	NA	NA
Paper treatment	NA	$1.89x10^{-9}$	NA	NA	NA	NA	NA
Coatings	NA	$6.74x10^{-11}$	NA	NA	NA	NA	NA
Regional	$1.05x10^{-11}$	$2.09x10^{-11}$	$1.09x10^{-9}$	$1.25x10^{-9}$	$1.16x10^{-9}$	$2.74x10^{-10}$	$3.66x10^{-11}$

3.3.4.2 Measured air concentrations

Sasaki et al (2003) measured the levels of PFOS in dust samples from two locations in Japan, monthly samples taken over a 12 month period. The PFOS concentration expressed as a concentration in air ranged from zero to 2.12 pg/m^3 at one location (geometric mean level 0.6 pg/m^3) and from 2.32 to 21.8 pg/m^3 (geometric mean 5.3 pg/m^3) at the other. The amounts of dust in the air were measured. The mean concentrations of PFOS in dust at the two locations were 19.2 ng/g and 97.4 ng/g.

Moriwaki et al (2003) measured the concentration of PFOS in vacuum cleaner dust in Japan. One sample contained 2,500 ng/g, the other 15 samples were below 140 ng/g.

Shoeib et al (2004) measured the total concentration of the PFOS-substances N-EtFOSE and N-MeFOSE in outdoor air from locations described as semi-urban. They found levels of 31.7 and 16 pg/m^3 for N-MeFOSE, and 9.79 and 8.47 pg/m^3 for N-EtFOSE. They also separated the contributions from the vapour and particulate phases. They found 75% of N-MeFOSE associated with particulates and ~65% of N-EtFOSE. These values are much higher than would be expected from the measured octanol-air partition coefficients or from the sub-cooled liquid vapour pressure values, both of which give reasonable predictions for many organic substances.

3.3.4.3 Comparison of measured and estimated atmospheric concentrations

The highest calculated concentration in air is around 1 pg/m^3, which is similar to some of the measured values. However, the number of measurements is limited and their relation to sources is unknown. Hence a comparison is not particularly meaningful.

3.3.5 Food chain exposure

3.3.5.1 Estimated environmental concentrations

Four different situations for food chain exposure are considered in the evaluation. These are: predator feeding on freshwater fish; marine predator feeding on fish; marine top predator; and terrestrial food chain (feeding on worms). The concentrations in the food organisms in each case are derived from combinations of the local and regional exposures of the organisms to PFOS according to the methods in the Technical Guidance Document. In addition, concentrations have been calculated for food organisms assuming that they are exposed only to the regional background concentration (so without any local contribution). These are

included in the tables as regional concentrations. The calculated concentrations in freshwater fish, marine fish, marine predator and worms are presented in Tables 3.24 to 3.27. (The marine concentrations have been included here to allow comparison with the measured levels.)

Table 3.24 Predicted concentrations in freshwater fish (mg/kg wwt)

Use area	Scenario number						
	1	2	3	4	5	6	7
Chromium plating	0.217	0.428	0.268	0.252	0.493	0.446	0.208
Photography - formulation	0.405	0.604	0.456	0.44	0.681	0.634	0.396
- processing	NA	0.417	NA	NA	NA	NA	NA
Aviation	0.361	0.541	0.413	0.397	0.638	0.591	0.353
Fire fighting foams -formulation	224	224	224	224	224	NA	NA
- use A	0.435	0.635	0.487	0.47	0.711	0.665	NA
- use B	0.531	0.731	0.583	0.567	0.807	0.761	NA
Photolithography	NA	2.9	NA	NA	NA	NA	NA
Fabrics - application	NA	1.21	NA	NA	NA	NA	NA
Paper treatment	NA	141	NA	NA	NA	NA	NA
Coatings	NA	3.92	NA	NA	NA	NA	NA
Regional	0.214	0.411	0.265	0.249	0.486	0.440	0.205

Table 3.25 Predicted concentrations in marine fish (mg/kg wwt)

Use area	Scenario number						
	1	2	3	4	5	6	7
Chromium plating	0.0216	0.0432	0.0267	0.0251	0.0484	0.0439	0.0207
Photography - formulation	0.0477	0.0676	0.0528	0.0512	0.0745	0.07	0.0468
- processing	NA	0.0416	NA	NA	NA	NA	NA
Aviation	0.0417	0.0588	0.0468	0.0452	0.0685	0.064	0.0408
Fire fighting foams -formulation	31	31	31	31	31	NA	NA
- use A	0.0434	0.0634	0.0485	0.047	0.0702	0.0657	NA
- use B	0.0653	0.0852	0.0703	0.0688	0.0921	0.0875	NA
Photolithography	NA	0.386	NA	NA	NA	NA	NA
Fabrics - application	NA	0.151	NA	NA	NA	NA	NA
Paper treatment	NA	19.6	NA	NA	NA	NA	NA
Coatings	NA	0.528	NA	NA	NA	NA	NA
Regional	0.021	0.041	0.026	0.025	0.048	0.043	0.020

Table 3.26 Predicted concentrations in marine predators (mg/kg wwt)

Use area	Scenario number						
	1	2	3	4	5	6	7
Chromium plating	0.0432	0.0838	0.0533	0.0502	0.0968	0.0878	0.0414
Photography - formulation	0.0536	0.0935	0.0638	0.0607	0.107	0.0982	0.0518
- processing	NA	0.0831	NA	NA	NA	NA	NA
Aviation	0.0513	0.090	0.0614	0.0583	0.105	0.0958	0.0495
Fire fighting foams -formulation	12.5	12.5	12.5	12.5	12.5	NA	NA
- use A	0.0519	0.0918	0.0621	0.059	0.106	0.0965	NA
- use B	0.0607	0.101	0.0708	0.0677	0.114	0.105	NA
Photolithography	NA	0.221	NA	NA	NA	NA	NA
Fabrics - application	NA	0.127	NA	NA	NA	NA	NA
Paper treatment	NA	7.9	NA	NA	NA	NA	NA
Coatings	NA	0.277	NA	NA	NA	NA	NA
Regional	0.043	0.082	0.052	0.050	0.096	0.086	0.041

Table 3.27 Predicted concentrations in terrestrial biota (worms) (mg/kg wwt)

Use area	Scenario number						
	1	2	3	4	5	6	7
Chromium plating	$1.94x10^{-3}$	$2.8x10^{-3}$	$3.8x10^{-3}$	$3.4x10^{-3}$	$9.99x10^{-3}$	$8.22x10^{-3}$	$1.99x10^{-3}$
Photography - formulation	0.0136	0.0144	0.0155	0.0151	0.0216	0.0199	0.0136
- processing	NA	$1.84x10^{-3}$	NA	NA	NA	NA	NA
Aviation	$9.3x10^{-3}$	0.0102	0.112	0.0108	0.0173	0.0156	$9.35x10^{-3}$
Fire fighting foams -formulation	15.1	15.1	15.1	15.1	15.1	NA	NA
- use A	$9.38x10^{-4}$	$1.79x10^{-3}$	$2.8x10^{-3}$	$2.4x10^{-3}$	$8.99x10^{-3}$	$7.21x10^{-3}$	NA
- use B	6.36	6.36	6.36	6.36	6.36	6.36	NA
Photolithography	NA	0.141	NA	NA	NA	NA	NA
Fabrics - application	NA	0.0726	NA	NA	NA	NA	NA
Paper treatment	NA	9.48	NA	NA	NA	NA	NA
Coatings	NA	0.238	NA	NA	NA	NA	NA
Regional[a]	$1.86x10^{-3}$	$3.56x10^{-3}$	$4.25x10^{-3}$	$3.36x10^{-3}$	0.0166	0.0141	$1.93x10^{-3}$

Note: the calculation of local soil PECs (from which the local contributions to levels in biota are estimated) use the concentration in natural soil (arising from deposition only) as the regional background. The regional contribution to the biota concentrations is estimated from the concentrations in agricultural soil, which are generally higher than the natural soil levels through sludge application. Hence where the local input is small. The regional contribution to the biota concentration dominates and the purely regional biota concentration can be higher than the local concentrations.

In addition to the above concentrations, EUSES also calculates concentrations in plants (leaf and root), in meat (cattle) and in milk. Rather than present the complete results here, the ranges of values calculated for each use area and for the regional background are presented in Table 3.28. It should be noted that the calculations for these concentrations all involve the use of the log Kow value. A surrogate value has been estimated for PFOS as the actual value cannot be determined for this substance. In this situation the suitability of the methods used is uncertain, and hence the results should be treated as having a high degree of uncertainty.

3.3.5.2 Measured environmental concentrations in biota

PFOS and related fluorochemicals have been traced in animals in a number of studies. These studies (a selection of which are outlined in Table 3.29) have taken place in a variety of locations around the globe and have shown concentrations exceeding 2 ppm in birds and 4 ppm in minks.

Some of the following studies relate to studies already included in part in the OECD hazard assessment (OECD, 2002).

Kannan and Giesy (2002) summarised the results of the analyses on archived samples referred to in the first item in Table 3.29 The tissues analysed came from marine mammals, birds, fish, reptiles and amphibians from around the world, including the Arctic and Antarctic Oceans. Samples collected in the 1990s were used. Around 1,700 samples were analysed, with concentrations in liver, egg yolk, muscle or blood plasma determined. The detection limit varied from 1 to 35 ppb wet weight. A summary of the results is in Table 3.30.

PFOS was detectable in most of the samples, including those from remote marine locations, at concentrations >1 ng/g. The authors compared the results from remote areas with those from more industrial locations. They comment that PFOS is distributed in remote regions, including the polar regions, but that the levels found in more urban and industrial areas (e.g. the Baltic, Great Lakes) are several times higher. The tissues of fish-eating birds in Canada, Italy, Japan and Korea all contained detectable levels of PFOS, suggesting that they are exposed through the fish they consume. The sulphonamide compound, FOSA, was only detected in ~10-15% of samples.

Table 3.28 Calculated concentrations in plants, meat and milk (mg/kg)

	Regional	Use area										
		Chromium plating	Photography – formulation	Photography – processing	Aviation	Fire-fighting foams			Photo-lithography	Fabrics – application	Paper treatment	Coatings
						Formulation	Use A	Use B				
Plant root	0.02-0.18	0.022-0.038	0.28-0.29	$1.3x10^{-3}$	0.18-0.20	328	$1.3x10^{-4}$ – 0.016	139	3.04	1.54	207	5.1
Plant leaf	$(2.5\text{-}24)x10^{-5}$	$(2.8\text{-}54)x10^{-5}$	$(5.6\text{-}6)x10^{-4}$	$1.8x10^{-6}$	$(2.3\text{-}2.6)x10^{-4}$	0.67	$(0.26\text{-}31)x10^{-6}$	0.17	$3.8x10^{-3}$	$1.9x10^{-3}$	0.26	$6.4x10^{-3}$
Meat	$(7.4\text{-}67)x10^{-6}$	$(5.3\text{-}12)x10^{-6}$	$(0.95\text{-}1.0)x10^{-4}$	$4.1x10^{-6}$	$(4.4\text{-}5.1)x10^{-5}$	0.11	$(0.62\text{-}1.3)x10^{-5}$	0.033	$7.3x10^{-4}$	$3.7x10^{-4}$	0.05	$1.2x10^{-3}$
Milk	$(2.3\text{-}21)x10^{-6}$	$(1.7\text{-}3.9)x10^{-6}$	$(3\text{-}3.2)x10^{-5}$	$1.3x10^{-6}$	$(1.4\text{-}1.6)x10^{-5}$	0.034-0.036	$(2.0\text{-}4.1)x10^{-6}$	0.011	$2.3x10^{-4}$	$1.2x10^{-4}$	0.011	$3.9x10^{-4}$

Table 3.29 Monitored Levels of PFOS in Animals (data from selected studies, based on OECD, 2002)

Description	Ref	Highest Reported Concentration	Location of Highest Concentration
Global monitoring survey of marine mammals (Florida, California, Alaska, northern Baltic Sea, Mediterranean Sea, Arctic, Sable Island (Canada))	OECD, 2002	Bottlenose dolphin: 1,520 ng/g wet wt (liver)	Florida
		Ringed seal: 475 ng/mL (blood)	Northern Baltic Sea
US Fish & Wildlife Service survey of piscivorous fish	A	Bald eagle: 1,047 ppb (plasma)	US
		Six bird species: 2,055 ppb (liver)	US
Survey of fish-eating water birds (US, Europe, North Pacific Ocean, Antarctic)	B	Fish: 923 ng/g wet wt. (muscle)	Belgian estuary
		Carp: 296 ng/g wet wt. (muscle)	US Great Lakes
Survey of fish-eating birds (US, Baltic Sea, Mediterranean Sea, Japanese coast, Korean coast)	C	Bald eagle: 2,200 ng/mL (plasma)	Midwest US
		Brandts cormorant: 1,780 ng/g wet wt. (liver)	US
Survey of mink and river otter in the US	D	Mink: 4,800 ng/g wet wt. (liver)	US
		River otter: 994 ng/g wet wt. (liver)	US
Survey of oysters in the US (Chesapeake Bay & Gulf of Mexico)	E	Oysters: 1,225 ng/g dry wt.	US
Clam and fish samples upstream and downstream of 3M facility in Decatur, Alabama, US	F	Fish: 59.1 µg/kg wet wt. (whole body - upstream) Fish: 1,332 µg/kg wet wt. (whole body - downstream)	Decatur, US
		Clam: 15.6 µg/kg wet wt. (upstream) Fish: 14.1 µg/kg wet wt. (downstream)	Decatur, US
First Environmental Survey of PFOS in Japan	G	Fish: 345 ng/mL (average blood levels)	Lake Biwa, Japan
Swedish urban and background fish samples	H	Perch: 3 - 8 ng/g (urban sites in the vicinity of municipal STPs); 20-44 ng/g in Lake Malaren and near Stockholm	Sweden (Lake Malaren)

Sources: A: 3M (2000); B: Giesy and Kannan (2001a); C: Giesy and Kannan (2001b); D: Giesy and Kannan (2001c); E: Giesy and Kannan (2001d); F: Giesy and Kannan (2001e); G: Taniyasu et al (2002); H: Jarnberg and Holmstrom (2003)

Table 3.30 Summary of global archive sample analysis

Species	Maximum concentration ng/g wwt	Frequency of detection
Marine mammals	1520	77%
Mink and otter	4900	100%
Birds	2570	60%
Fish	1000	38%

Martin et al (2004) measured the levels of PFOS in liver samples from biota in the Canadian Arctic. PFOS was found in the vast majority of the samples (all except the black guillemot). The highest levels were found in polar bear, with a mean level of 3,100 ng/g from seven animals (maximum value >4,000 ng/g). Generally, higher levels were found in animals higher up the food chain. The sulphonamide FOSA was also found in most of the samples. It was associated with PFOS to some extent. The concentration of FOSA was higher than that of PFOS in fish, but not in mammals. The pattern may be the result of both exposure and metabolism.

A recent conference presentation (personal communication, KEMI, Sweden) reported that the concentration of PFOS in guillemot (*Uria aalge*) eggs collected from the Baltic Sea has increased by more than 30-fold since 1968, with annual average increases of 7-11%.

Van de Vijver et al (2003) measured the concentrations of PFOS in aquatic invertebrates from the Western Scheldt estuary, in starfish (*Asterias rubens*), crab (*Carcinus mainas*) and

shrimp (*Crangon crangon*). Eight locations were sampled. Mean whole body concentrations were 16±3 - 93±34 ng/g in starfish, 40±13 - 319±70 for shrimp and 93±38 - 292±45 ng/g for crab. There were indications of a concentration gradient, with possible sources of PFOS including a fluorochemical manufacturing site and industrial regions drained by a canal entering the estuary.

Hoff et al (2003) sampled fish (bib, *Trisopterus luscus*, and plaice, *Pleuronectes platessa*) from the Western Scheldt and the Belgian North Sea, with four separate locations for each fish. Some of the locations were similar to those in the Van de Vijver et al (2003) study above. PFOS was found in the livers of all of the plaice collected (detection limit 10 ng/g wwt); levels up to 7,760 ng/g were found at estuarine sites, the values at marine sites were lower. In plaice muscle, PFOS was detected in 20-30% of the marine samples and 75% of the estuarine samples (maximum concentration 87 ng/g). For bib, again all liver samples had concentration above the detection limit, though the highest concentration were lower than those found in plaice, at ~200 ng/g. In bib muscle, marine sites had 50% of samples above 10 ng/g, while the two innermost estuarine sites had all samples above the detection limit. The maximum concentration measured was 111 ng/g.

The first environmental survey of PFOS and related substances in Japan (which followed a Japanese study that showed measurable levels of PFOS in human blood) suggests that PFOS is present in the blood and livers of all fish in surface waters in Japan (Taniyasu *et al*, 2002).

In the 3M Multi City study (see Section 3.3.3.2), measurable quantities of PFOS (up to 0.852 ng/g) were found in four milk samples and one ground beef sample. One of the four milk samples was from a control city, although cities with fluorochemical substances production or use tended to give measurable PFOS levels. The testing included produce such as green beans, apples, pork muscle, cow's milk, chicken muscle, chicken eggs, bread, hot dogs, catfish and ground beef.

3.3.5.3 Comparison of predicted and measured environmental concentrations

The information on measured levels in biota has been largely presented as summaries and ranges, and so the predicted concentrations are also considered as ranges. These are:

Freshwater fish	200 – 800 µg/kg (ng/g)
Salt water fish	20 – 100 µg/kg (ng/g)
Marine predators	40 – 120 µg/kg (ng/g)
Soil organisms	1 – 20 µg/kg (ng/g)

The concentrations predicted in fish appear to agree reasonably well with the summarised measured values in Tables 3.27 and 3.28. If anything the calculated values are generally lower than the upper ends of the ranges, particularly if the predicted concentrations related to the formulation and use of foams are excluded. However, the measured values relate in many cases to specific tissues, whereas the calculated values are whole body concentrations and so would be expected to be lower than tissue concentrations in most cases. Many of the measurements on levels in biota from the environment have been performed on samples taken from relatively remote areas. As such these cannot easily be compared to the calculated levels, which relate to locations closer to sources.

The majority of the calculated concentrations in milk are of the same order or are below the highest reported concentration of 0.852 ng/g ($8.5x10^{-4}$ mg/kg), but data for comparison are limited. The concentrations calculated for three of the use areas are very much higher.

Concentrations in vegetation and fruits were measured as part of the plant toxicity study discussed in Sections 4.2.1 and 3.2.6.2. The actual concentrations are not appropriate for comparison with the calculated levels, as the measurements are not from environmental samples. It is of interest to compare the plant:soil concentration ratios for the measured and calculated concentrations. As described in Section 3.2.6.2, the measured levels in vegetative tissues were 1-2 times those in the soil; for the calculated concentrations, the calculated levels in plant leaf are 0.01-0.05 tmes those calculated for the soil. The plant root calculated concentrations are not really comparable with the fruit measurements, as most of the fruits were above ground, but the calculated values are 26 times those in soil, while the measured fruit values were less than 10% of those in soil. It thus appears that using the model and values selected, the model may under-estimate the levels in plant leaves but over-estimate those in root crops.

4 EFFECTS ASSESSMENT: HAZARD IDENTIFICATION AND DOSE (CONCENTRATION) - RESPONSE (EFFECT ASSESSMENT)

The ecotoxicity data relating to PFOS were reviewed for the OECD Hazard Assessment (OECD, 2002). The studies reviewed in the OECD report have not been re-examined for this evaluation. A comparison has been made against the updated 3M report (3M, 2003) to check for any corrections or for new tests. A literature search for studies from 2002 onwards has also been conducted.

4.1 AQUATIC COMPARTMENT (INCLUDING SEDIMENT)

4.1.1 Aquatic studies

4.1.1.1 Fish

The results from the studies on fish toxicity reviewed by the OECD and considered to be of a good or acceptable standard are presented in Tables 4.1 and 4.2. Results are expressed in terms of the potassium salt of PFOS. Where a different salt was used in the study, the result has been converted for this evaluation (and noted in the tables). For further details of the studies see the OECD assessment (OECD, 2002).

Table 4.1 Acute toxicity data for fish (after OECD, 2002)

Species	Protocol	Result (mg/l)	Study standard
Freshwater			
Fathead minnow (*Pimephales promelas*)	OECD 203 & OPPTS 850.1075 (static)	96-h LC_{60} = 9.5	Good
	Not noted (static)	96-h LC_{50} = 5.0	Acceptable[a]
	OECD 203 (static)	96-h LL_{50} = 133	Acceptable[b]
Bluegill sunfish (*Lepomis macrochirus*)	OECD 203 & OPPTS 850.1075 (static)	96-h LC_{50} = 6.9	Acceptable[c]
Rainbow trout (*Oncorhynchus mykiss*)	Standard procedures for testing acute lethality of liquid effluents (Environment Canada)	96-h LC_{50} = 7.8	Acceptable
	OECD 203 & OPPTS 850.1075 (static)	96-h LC_{50} = 22	Acceptable
Seawater			
Sheepshead minnow (*Cyprinodon variegatus*)	OECD 203 & OPPTS 850.1075 (semi-static, 24 h renewal))	96-h LC_{50} > 15	Acceptable
Rainbow trout (*Oncorhynchus mykiss*)	Standard procedures for testing acute lethality of liquid effluents (Environment Canada)	96-h LC_{50} = 13.7	Acceptable

Notes: a – original value 4.7 mg/l, for lithium salt
b – original value 200 mg/l, for didecyldimethylammonium salt
c – original value 7.8 mg/l, for DEA salt

Table 4.2 Long-term toxicity data for fish (after OECD 2002)

Species	Protocol	Result (mg/l)	Study standard
Freshwater			
Fathead minnow (*Pimephales promelas*)	OECD 210 & OPPTS 850.1400 (flow-through)	42-d $NOEC_{surv}$ = 0.30 42-d $NOEC_{growth}$ = 0.30 5-d $NOEC_{hatch}$ = ≥ 4.6	Good
	Non-standard (flow-through)	30-d $NOEC_{els}$ = 1	Acceptable
Bluegill sunfish (*Lepomis macrochirus*)	OECD 305 & OPPTS 850.1731	62-d $NOEC_{mortality}$ = >0.086, <0.87	Good

The long-term study with bluegill sunfish was a bioconcentration study (discussed as such in Section 3.2.6.1). All fish exposed to 0.87 mg/l died by the 35th day of the exposure. At

0.086 mg/l, two fish of the ninety exposed died (2.2%). There were no deaths in the controls. As there were no repeat exposures it is not considered suitable for the determination of a NOEC value. However, the observations in this study are not in contradiction to those in the other long term studies.

Hoff et al (2003) administered a single intraperitoneal injection of PFOS into carp (six concentrations over two experiments) and monitored selected biochemical endpoints. Levels of PFOS in fish liver were measured after one and five days. No mortality was seen, nor inflammation of the liver, peroxisome proliferation, or any effect on serum anti-oxidant levels. The levels of liver enzymes in serum were elevated, indicating a disruption of the liver membrane. In terms of the concentration in the fish, the EC_{10} values for this effect were determined as 164 ng/g in wet tissue or 258 ng/g in wet liver respectively (concentrations after five days).

4.1.1.2 Invertebrates

The results from the studies on fish toxicity reviewed by the OECD and considered to be of a good or acceptable standard are presented in Tables 4.3 and 4.4. Results are expressed in terms of the potassium salt of PFOS. Where a different salt was used in the study, the result has been converted for this evaluation (and noted in the tables). For further details of the studies see the OECD assessment (OECD, 2002). Results from a more recent publication (Boudreau et al, 2003a) are also included in the tables. These used ASTM methods, and are considered valid for use in the evaluation. As specific details of the tests have not been seen, they have been graded as acceptable in the tables.

Table 4.3 Acute toxicity for invertebrates

Species	Protocol	Result (mg/l)	Study standard
Freshwater			
Water flea (*Daphnia magna*)	OECD 202 & OPPTS 850.1010 (static)	48-h EC_{50} = 61	Good
	ASTM 1981 & OECD 1981 (static)	48-h EC_{50} = 27	Acceptable
	Not noted (static)	48-h EC_{50} = 223	Acceptable[b]
	OECD 202 (static)	48-h EL_{50} = 2.66	Acceptable[c]
	ISO, 1982	48-h EC_{50} = 58	Acceptable
	ASTM	48-h EC_{50} = 67.2	Acceptable[a]
W\ater flea (*Daphnia pulicaria*)	ASTM	48-h EC_{50} = 134	Acceptable[a]
Freshwater mussel (*Unio complamatus*)	OECD 203, OPPTS 850.1075 & ASTM-E-729-88a (semi-static)	96-h LC_{50} = 59	Good
Saltwater			
Mysid shrimp (*Mysidopsis bahia*)	OPPTS 850.1035 (static)	96-h LC_{50} = 3.6	Good
Eastern oyster (*Crassostrea virginica*)	OPPTS 850.1025 (static)	96-h EC_{50} = >3.0	Good
Brine shrimp (*Artemia sp.*)	Draft ISO, 1981	48-h LC_{50} = 8.9	Acceptable

Note: information taken from OECD (2000) except for those marked “a” which are from Boudreau et al (2003a).
b – original value 210 mg/l, for lithium salt
c – original value 4.0 mg/l, for didecyldimethylammonium salt

Table 4.4 Chronic toxicity to invertebrates

Species	Protocol	Result (mg/l)	Study standard
Freshwater			
Water flea (*Daphnia magna*)	OECD 211, OPPTS 850.1300 & ASTM 1193-87E (semi-static)	21-d $NOEC_{repro}$ = 12 21-d $NOEC_{surv}$ = 12 21-d $NOEC_{growth}$ = 12	Good
	ASTM 1981 & OECD 1981 (semi-static)	28-d $NOEC_{repro}$ = 7	Acceptable
	ASTM	21-d $NOEC_{surv}$ = 5.3	Acceptable[a]
Seawater			
Mysid shrimp (*Mysidopsis bahia*)	OPPTS 850.1350 (flow-through)	35-d $NOEC_{repro}$ = 0.25 35-d $NOEC_{surv}$ = 0.55 35-d $NOEC_{growth}$ = 0.25	Good

Note: information taken from OECD (2000) except for those marked "a" which are from Boudreau et al (2003a)

4.1.1.3 Aquatic plants

Toxicity data for aquatic plants are presented in Table 4.5. As for invertebrates, these are largely from OECD (2002), with some additional results from Boudreau et al (2003a).

Table 4.5 Toxicity to aquatic plants

Species	Protocol	Result (mg/l)	Study standard
Freshwater			
Selenastrum capricornutum (algae)	OECD 201, OPPTS 850.5400 & ASTM 1218-90E (static)	96-h EC_{50} = 71 (cell density) 96-h EC_{50} = 126 (growth rate) 96-h NOEC = 44 (cell density, growth rate)	Good
	OECD 201, US EAP 600/9-78-018 & ASTM-E-35.23 (static)	96-h EC_{50} = 82 (cell density) 96-h EC_{10} = 10 (cell density)	Acceptable
	ASTM	96-h IC_{50} = 48.2 (cell density)	Acceptable[a]
Anabaena flos-aquae (algae)	OPPTS 850.5400	96-h EC_{50} = 176 (growth rate) 96-h NOEC = 94 (growth rate)	Good
Navicula pelliculosa (algae)	OPPTS 850.5400	96-h EC_{50} = 305 (growth rate) 96-h NOEC = 206 (growth rate)	Good
Chlorella vulgaris (algae)	ASTM	96-h IC_{50} = 81.6 (cell density)	Acceptable[a]
Lemna gibba (duckweed)	ASTM	7-d IC_{50} = 31.1	Acceptable[a]
Seawater			
Skeletonema costatum (algae)	OPPTS 850.5400	96-h EC_{50} >3.2 (growth rate) 96-h NOEC >3.2 (growth rate)	Good

Note: information taken from OECD (2000) except for those marked "a" which are from Boudreau et al (2003a)

4.1.1.4 Microcosms

Two microcosm studies have been conducted with PFOS. In the first, indoor microcosms containing zooplankton were exposed to PFOS (potassium salt) for 35 days at three concentrations - 1, 10 and 30 mg/l. The endpoints used were zooplankton species and abundance. Phytoplankton were added as a supplementary food supply at intervals (Sanderson et al, 2002).

Concentrations in the microcosms were measured on days 1, 8 and 35 of the study. Little change in the concentrations was observed, the greatest percentage change being found at the lowest concentration with a 19% reduction over the 35 days. The exposures showed a significant influence of PFOS on the zooplankton community at 10 mg/l after 14 days, with several species markedly reduced or eliminated. The relative susceptibility, assuming all effects due to PFOS exposure, was Copepoda > Cladocera > Roifera. The statistical power of the study was insufficient to allow a conclusion of no effect at 1 mg/l to be reached.

In the second microcosm study, the effects of PFOS were studied on the zooplankton community and on the floating macrophyte *Lemna gibba* in outdoor microcosms (Boudreau et al, 2003b). The studies were run in triplicate, with PFOS concentrations of 0.3, 3, 10 and 30 mg/l. The potassium salt was used. Concentrations were monitored through the study, and no significant decrease in concentration was noted. The results were based on the nominal concentrations. The zooplankton community was significantly altered from that in the controls at 10 mg/l and 30 mg/l. The NOEC for community effects was 3 mg/l for days 4-28, and 0.3 mg/l for day 35. For *Lemna*, growth was only significantly reduced at 30 mg/l.

4.1.2 Sediment toxicity

No test results on sediment-dwelling organisms have been located.

4.1.3 Wastewater treatment plant (WWTP) micro-organisms

Only one study on activated sludge micro-organisms was considered valid in the OECD assessment. In a 3 hour respiration inhibition test (OECD 209), the highest exposure concentration of 905 mg/l (nominal) resulted in 39% inhibition. The IC_{50} is therefore >905 mg/l.

4.1.4 Predicted No Effect Concentrations (PNECs) for the aquatic compartment

4.1.4.1 Calculation of a PNEC for surface water

The lowest acute and chronic aquatic toxicity studies from the discussion above are summarised briefly in Table 4.6 The table includes freshwater and marine species.

Table 4.6 Summary of aquatic toxicity data

Acute	Fish	Fathead minnow (*Pimephales promelas*) (96-h): LC_{50} = 4.7 mg/L Rainbow trout (*Oncorhynchus mykiss* - saltwater) (96-h): LC_{50}=13.7 mg/l
	Invertebrates	*Daphnia magna* (48-h): EC_{50} = 27 mg/L Mysid shrimp (*Mysidopsis bahia* - saltwater) (96-h): LC_{50} = 3.6 mg/L
	Algae	*Selenastrum capricornutum* (96-h): EC_{50}=126 mg/l *Skeletonema costatum* (saltwater) (96-h): EC_{50} > 3.2 mg/L
Long-term	Fish	Fathead minnow (*Pimephales promelas*) (42-day): $NOEC_{survival}$ = 0.3 mg/L
	Invertebrates	*Daphnia magna* (28-day): $NOEC_{reproduction}$ = 7 mg/L Mysid shrimp (*Mysidopsis bahia* - saltwater) (35-day): $NOEC_{reproduction}$ = 0.25 mg/L
	Algae	*Selenastrum capricornutum* (96-h): NOEC=44 mg/l. *Skeletonema costatum* (saltwater) (96-h): NOEC>3.2 mg/l Duckweed (*Lemna gibba*) (7-day): NOEC = 15.1 mg/L

Acute toxicity data are available for fish, invertebrates and algae in freshwater and in seawater. The values for freshwater and saltwater fish are close together, those from invertebrates have a greater difference with the salt water value lower. The algal values cannot be compared as the lower, marine, value is a limit value with no effect at the highest concentration achievable in the test medium.

Results from long term tests with species in three taxonomic groups (fish, invertebrates, algae) are available for the freshwater environment. There are also long term results with a salt water invertebrate and a salt water algae (again a limit value). The results of the microcosm tests are similar to the lowest NOEC values obtained in single species tests.

The lowest NOEC from the whole data set is 0.25 mg/l, for Mysid shrimp This will be used for the PNEC derivation. The next lowest value is 0.3 mg/l, for fathead minnow (and for part of a microcosm test) so a PNEC based on freshwater data alone would be similar. As three taxonomic groups are represented a factor of 10 is used, giving a PNEC for freshwater of 25 µg/l.

For the marine environment, there are three taxonomic groups represented. Although there are saltwater species for two of these, there are no additional marine taxonomic groups in the data set. The TGD indicates a factor of 100 in this situation, giving a PNEC of 2.5 µg/l.

There are some intermittent release scenarios. For these, the PNEC is based on the acute data. The lowest acute value is 3.6 mg/l, again for Mysid shrimp (the saltwater algal value is lower, at 3.2 mg/l, but this is a limit value and no effects were seen at this level). A factor of 100 is used, giving a PNEC of 36 µg/l.

4.1.4.2 Sediment PNEC

In the absence of any toxicity data for sediment organisms, the usual approach would be to use the equilibrium partitioning method. The use of this method may be questioned for substances with the properties of PFOS. However, the log Kow value does not have to be used as a measured value for Kd with sediment is available (8.7 l/kg, see Section 3.2.5.1). Using this gives a freshwater sediment PNEC of 67 µg/kg wwt and a marine sediment PNEC of 6.7 µg/kg wwt.

4.1.4.3 Calculation of PNEC for WWTP micro-organisms

The IC_{50} for activated sludge respiration inhibition was determined as >905 mg/l (Section 4.1.3) The appropriate assessment factor for this test is 100, giving a PNEC of >9.05 mg/l.

4.2 TERRESTRIAL COMPARTMENT

4.2.1 Terrestrial toxicity data

No terrestrial toxicity data were available at the time the OECD assessment was produced. A study on earthworms was referred to in the assessment as being planned; this is included in the 3M revised assessment (3M, 2003). The OECD assessment also mentions a planned study on plant toxicity, but this has not been seen.

A 14-day earthworm toxicity test is reported by 3M (2003). A robust study summary for this test is included in the 3M assessment, and only the main points relating to the test are included here. The test protocol was based on OECD Guideline 207. The test was conducted in an artificial soil substrate, at five exposure concentrations (ranging from 78 - 1250 mg/kg nominal) plus control. Concentrations of PFOS in the soil were measured on days 0 and 14, and were found to be within 80% of the nominal concentrations. The results are based on the concentrations at day 0. The contents of the test chambers were removed at 7 days for observations and returned to the chambers without the addition of further substance. The endpoints observed were mortality, burrowing behaviour, body weight and clinical signs of toxicity. The results of the test are in Table 4.7.

Table 4.7 Toxicity results for earthworms (3M, 2003)

Endpoint	Time	Value (mg/kg dwt)	95% CI
LC_{50}	7 days	398	289 - 488
	14 days	373	316 - 440
NOEC	7 days	289	
	14 days	77	

The toxicity of PFOS to plants through soil exposure has been investigated using a method based on the OECD 21-day test guideline (3M, 2004). The endpoints examined were emergence, survival, shoot height and shoot weight. These endpoints were measured after 21 days of exposure. Where possible, the plants were allowed to continue growing after this time until they produced fruit or sufficient leaf for analysis. The results of these later analyses are included in Section 3.2.6.2.

The seven plant species included in the study were: lettuce (*Lactuca sativa*); ryegrass (*Lolium perenne*); tomato (*Lycopersicon esculentum*); onion (*Allium cepa*); alfalfa (*Medicago sativa*); flax (*Linum usitatissimum*); and soybean (*Glycine max*). The nominal concentrations used in the tests were 3.91, 15.6, 62.5, 250 and 1000 mg/kg. Concentrations measured in the soil at the beginning of the exposures were all within 70% of the nominal values. Concentrations were also measured at the final termination of the study after 205 days, when the concentrations ranged from 22.8% to 62.8% of nominal. Samples were taken at 21 days, but the results were considered to be artefacts due to the irrigation and sampling methods used. The results presented are based on the nominal concentrations. The lowest no effect concentrations for each endpoint were as follows:

Emergence	62.5 mg/kg	onion, ryegrass
Survival	15.6 mg/kg	onion, tomato
Shoot height	<3.91 mg/kg	lettuce (23% reduced compared to control)
Shoot weight	<3.91 mg/kg	lettuce (35% reduced compared to control)

4.2.2 Calculation of PNEC for the soil compartment

One short term test result is available for earthworms. A factor of 1000 is applied to the LC_{50} from this test, 373 mg/kg dwt, giving a PNEC of 373 µg/kg dwt.

The plant test available can be considered to be a chronic study. As there is only one such study, an assessment factor of 100 is indicated according to the TGD. Effects were seen on lettuce at the lowest exposure concentration, so that the PNEC is <39 µg/kg wwt.

When terrestrial toxicity data are limited, the Technical Guidance document recommends that a PNEC be calculated from the aquatic PNEC using the equilibrium partitioning method. This method may not be appropriate for a substance with the properties of PFOS, but a measured Kd value is available for soil. A value of 26.9 is used in this evaluation (see Section 3.2.5.1), which corresponds to a $K_{soil\text{-}wter}$ of 40.6. Using this method gives a PNEC of 597 µg/kg wwt, or 680 µg/kg dwt.

The values obtained from the worm toxicity test and the partitioning method are similar, but the value from the plant test is much lower.. The value derived from the toxicity test for plants, <39 µg/kg wwt (or 46 µg/kg dwt based on 15% moisture in the soil) will be used in the evaluation, recognising that a PNEC derived from the actual effect level is expected to be below this.

4.3 ATMOSPHERIC COMPARTMENT

No data on effects of PFOS through exposure via the atmosphere were located, either for biotic or abiotic effects. The low volatility of the substance suggests that significant exposure through the vapour phase would not be expected.

4.4 NON-COMPARTMENT SPECIFIC EFFECTS RELEVANT TO THE FOOD CHAIN (SECONDARY POISONING)

4.4.1 Mammalian toxicity data

Mammalian toxicity data were reviewed for the OECD assessment (OECD, 2002). Results from acute, sub-chronic and chronic exposures to rats, sub-chronic exposures to monkeys, and a two-generation study on rats are available. Details of these studies are not included here, they can be found in the OECD assessment.

In a two year carcinogenicity assay using rats, effects on the liver were monitored. From this study the NOAEL for PFOS was considered to be 0.5 ppm in food in male rats and 2 ppm in food in female rats. The corresponding LOAELs were 2 ppm for males and 5 ppm for females. These values are taken from the main text of the OECD assessment. In the summary of the OECD assessment the LOAEL for male rats is said to be 0.5 ppm, with no NOAEL established. The main text indicates that the effects seen on male rats at 0.5 ppm were considered to be due to old age and were not treatment related. For comparison, a level in food of 0.5 ppm is equivalent to a dose of 0.025 mg/kg bw/day using the conversion factors in the Technical Guidance document. The range of doses estimated from the study was 0.015 to 0.057 mg/kg bw/day, so this fits into the observed range. The value required for the risk evaluation is the concentration in food.

Doses of 4.5 mg/kg bw/day were lethal to Rhesus monkeys over a seven week exposure.

In the two generation study on rats, the NOAEL for reductions in pup weights in the second generation was 0.1 mg/kg bw/day, with a LOAEL of 0.4 mg/kg bw/day.

Adult female Sprague-Dawley rats were injected intraperitonealy daily for 14 days (Austin et al, 2003). The doses were 1 and 10 mg/kg bw/day. Food intake and body weight were monitored daily. The oestrus cycle of the rats was also monitored. At the end of the exposures, the levels of leptin and corticosterone in the serum were measured, as were monoamines in the hypothalamus. PFOS levels were measured in a range of tissues at the end of the exposures.

PFOS was found in all of the tissues sampled after exposure, including blood, liver, serum, kidneys, heart, ovaries, adrenal, brain and spleen. Levels in liver were 26,627 ng/g at the low dose and 97,358 ng/g at the high dose. There were marked changes in body weight and food uptake at the higher dose. There was a significant decrease in serum leptin levels by the end of two weeks exposure at the higher dose, and also a significant increase in serum corticosterone levels. All of the animals in the control groups had regular oestrus cycles, compared to 66% in the lower dose group and 42% in the higher dose group.

4.4.2 Avian toxicity

Two studies on the acute toxicity of PFOS to birds are included in the OECD assessment (2002) and the 3M (2003) assessment. Both were 5-day studies, followed by 3 or 17 days observation. The concentration of the PFOS potassium salt was measured in the food. The LC_{50} values derived from the studies were 628 mg/kg food for mallard duck (*Anas platyrhynchos*) and 220 mg/kg food for northern bobtail quail (*Colinus virginianus*).

The effects of PFOS administered in the diet on mallard ducks (*Anas platyrhynchos*) and northern bobwhite quail (*Colinus virginianus*) have been investigated in 21-week dietary reproduction studies (3M, 2004). Adult birds were brought into the reproductive phase at week 11 (mallard) or week 7 (quail). After hatching, the chicks were fed an untreated diet for 14 days. The exposure levels for both species were 0, 10, 50 and 150 ppm in food. In both cases, overt toxicity at the two highest dose levels led to early termination of these exposures.

For mallard, a NOAEC of 10 ppm was established for mortality, body weight, liver weight, and reproduction in adults, and for survivability, bodyweight and liver weight in offspring. Gross pathology in females also had a NOAEL of 10 ppm. In males, there was an increase in the incidence of small testis size and decreased spermatogenesis at 10 ppm. Although these effects are normal in the early post-reproductive phase, PFOS may have accelerated the process compared to untreated birds. Based on these effects the LOAEC was determined to be 10 ppm.

The results for northern bobwhite were similar. The NOAEC was 10 ppm for mortality, body weight, food consumption, liver weight (males) and gross pathology (females). Effects were seen on liver weight in females at 10 ppm, and similar effects on the testes and sperm in males as for mallard. Again, the exposure to PFOS appeared to accelerate the post-reproductive phase regression, and a LOAEC of 10 ppm was determined for this endpoint. A statistically significant reduction in offspring survival was seen at 10 ppm, together with slight, not statistically significant, reductions in fertility and hatchability. A LOAEC of 10 ppm was determined for offspring survival.

4.4.3 Derivation of $PNEC_{oral}$

The lowest no effect level is 0.5 ppm, for liver effects in male rats. This is from a chronic study, so an assessment factor of 30 is appropriate. This gives a PNEC of 0.0167 mg/kg in food.

In comments from the consultation on the draft evaluation report, it was suggested that the above may be an over-conservative choice of endpoint for the assessment of secondary poisoning. Alternatives proposed were the 2 ppm LOAEC from the same study, or the NOEAL of 0.1 mg/kg bw/day from the reproduction study. The 2 ppm level from the carcinogenicity study gies a PNEC of 0.067 mg/kg using the same assessment factor of 30 as above. For the NOEAL of 0.1 mg/kg bw/day, the conversion factor from dose to concentration in food is 20 from the Technical Guidance Document, so that the NOEC from this study is 2 mg/kg. With an assessment factor of 30 for a chronic study this also gives a PNEC of 0.067 mg/kg. This value will also be considered in the risk evaluation.

The chronic studies on birds show an NOAEC of 10 ppm for most of the endpoints, but a LOAEC for effects on males and on survival of offspring. A PNEC derived from this figure

would be 0.33 mg/kg using an assessment factor of 30. Although the no effect level is not fully defined, this result suggests that the PNECs derived from the mammalian data can be considered to cover the risk to birds as well.

4.5 CLASSIFICATION FOR ENVIRONMENTAL HAZARD

PFOS is not listed as a substance on EINECS and has no classification. The acid form of PFOS is not classified on Annex I of Directive 67/548/EEC, and neither are any of the usual salts (potassium, ammonium, lithium).

From Section 4.1.1, there are a number of species for which the $L(E)C_{50}$ values are in the range 1 – 10 mg/l for the potassium salt. This substance is not readily biodegradable. On the basis of this information the substance should be classified as dangerous to the environment, N R51-53 (toxic to aquatic organisms, may cause long term adverse effects in the aquatic environment

There are also invertebrate test results for the lithium salt, DEA salt and didecyldiemthylammonium salt below 10 mg/l. Although these substances have not been specifically tested for biodegradation, on the basis of the evidence it is unlikely that the PFOS moiety will be degraded. Hence these should also be classified as N R51-53.

5 RISK EVALUATION

The exposure estimates in Section 3.3 considered seven possible scenarios for combinations of releases from different uses and with different degradation rates for PFOS-substances. The scenarios were:

1 - PFOS-salt releases only (all relevant uses in Table 3.8)
2 - PFOS-salt plus PFOS-substances, assuming instant degradation to PFOS (all relevant uses in Table 3.8).
3 - PFOS-salt plus PFOS-substances, assuming a 20 day half life for degradation to PFOS (all relevant uses in Table 3.8).
4 - PFOS-salt plus PFOS-substances, assuming a 1 year half life for degradation to PFOS (all relevant uses in Table 3.8).
5 - PFOS-salt, PFOS-substances with 20 day half life, PFOS-polymer with 30 year half life degradation to PFOS (all uses in Table 3.8).
6 - PFOS-salt, PFOS-substances with 20 day half life, PFOS-polymer with 30 year half life degradation to PFOS (uses in Table 3.8 excluding foam formulation, fabric treatment, paper treatment and coatings).
7 - PFOS-salt, PFOS-substances with 20 day half life degradation to PFOS (chromium plating, photographic, aviation, photolithography only)

As well as calculating the risk characterisation ratios, back-calculations have been performed to estimate the amount of PFOS which if released into waste water would result in a concentration equal to the PNEC value. The standard assumptions for water flows, dilutions, sludge applications etc have been used in the calculations. For the aquatic and terrestrial compartments, these calculations assume that there is no regional background contribution, this seems a reasonable assumption as the background concentrations calculated in this evaluation are low compared to the PNECs for these end points (see below). The same is not true for the secondary poisoning endpoints, where the regional background concentrations are significant and the exposure concentrations depend on both the local and the regional contributions. For these, a range of concentrations is presented. The upper value is the release which would lead to a risk with no regional contribution, the lower value would give a risk if the regional contribution were the same as the local contribution.

5.1 AQUATIC COMPARTMENT

5.1.1 Surface water and sediment

The risk characterisation is based on the predicted environmental concentrations from Section 3.3.2.1. The predicted no effect concentration (PNEC) is 25 µg/l, from Section 4.1.4.1.

Table 5.1 shows the risk characterisation ratios for freshwater for the seven scenarios and the various uses. As both the exposure and effect concentrations for sediment are derived by the equilibrium partition method, and the sorption coefficient is below the threshold for the extra factor of 10, the ratios for sediment are the same as for water, and are not presented separately.

Table 5.1 Risk characterisation ratios for freshwater

Use area	Scenario number						
	1	2	3	4	5	6	7
Chromium plating	0.002	0.003	0.002	0.002	0.004	0.003	0.002
Photography - formulation	0.005	0.006	0.005	0.005	0.007	0.006	0.005
- processing	NA	0.003	NA	NA	NA	NA	NA
Aviation	0.004	0.005	0.004	0.004	0.006	0.005	0.004
Fire fighting foams - formulation	3.89	3.89	3.89	3.89	3.9	NA	NA
- use A	0.793	0.794	0.793	0.793	0.794	0.794	NA
- use B	1.14	1.14	1.14	1.14	1.14	1.14	NA
Photolithography	NA	0.039	NA	NA	NA	NA	NA
Fabrics - application	NA	0.021	NA	NA	NA	NA	NA
Paper treatment	NA	2.45	NA	NA	NA	NA	NA
Coatings	NA	0.084	NA	NA	NA	NA	NA
Regional	0.002	0.003	0.002	0.002	0.004	0.003	0.001

NA – local concentration not calculated for this use pattern in the particular scenario

Two of the use patterns have ratios above one for all scenarios. The calculation of emissions from the formulation of fire fighting foams uses a large site and default emission factors, and so could be refined. (The site in fact no longer uses PFOS-based chemicals in the production of foams.) Foam use B is the situation where spent foam is collected and discharged to a waste water treatment plant. This is probably only likely in an industrial setting. The other release pattern for foams, use A, is where the release is split 50:50 between surface water (no treatment) and soil, and this does not give a risk. The emission scenario for foam use in both cases considers an arbitrary release of 1% of the annual use in one fire, and the actual distribution of foam emissions between the different compartment will be different for every fire location. Hence the ratios for these two scenarios are only indicative. They do suggest that the release of foams from fires may have effects on aquatic organisms. The revised calculation for foam use based on different assumptions (in Appendix 4) shows no risks for direct effects on aquatic organisms.

One other use pattern gives a ratio above one – this is for paper treatment, and assumes the complete conversion of PFOS-substance to PFOS before release. As such it is likely that the PFOS concentration is over-estimated. Against this, there are no data on the toxicity of the PFOS-substances themselves.

The ratios for the regional aquatic environment are all well below one, the highest being 0.004. Hence the risk ratios for the use patterns are governed by the local emissions. The regional concentration in water does not vary greatly between the scenarios, a factor of three covering all of the results. The variation in degradation rate for the PFOS substances between the scenarios has little effect on the water concentration, and so it may not be necessary to have precise information about this rate. The yield of PFOS from the breakdown of the substances (and polymers) may have more influence on the concentrations – this is considered in Appendix 3.

The measured levels in surface water are below the PNEC value.

The PNEC for the aquatic compartment is derived from three long-term NOEC values, and so is not likely to be increased by further testing. The calculations of emissions, and hence the exposure estimates, could be revised.

The release to waste water calculated to give a risk for this endpoint is 0.69 kg/day.

5.1.2 Wastewater treatment plant (WWTP) micro-organisms

The estimated effluent concentrations are included in Section 3.3.2.1, with the highest value being 0.97 mg/l. The PNEC for micro-organisms is >9.05 mg/l (Section 4.1.4.3). Hence all ratios are below one, and no risks are indicated.

5.2 TERRESTRIAL COMPARTMENT

The risk characterisation is based on the predicted environmental concentrations from Section 3.3.3.1. The predicted no effect concentration (PNEC) is 25 µg/l, from Section 4.2.2.

Table 5.2 shows the risk characterisation ratios for the terrestrial compartment for the seven scenarios and the various uses.

Table 5.2 Risk characterisation ratios for terrestrial compartment

Use area	Scenario number						
	1	2	3	4	5	6	7
Chromium plating	0.022	0.022	0.035	0.037	0.036	0.025	0.022
Photography - formulation	0.274	0.274	.0287	0.290	.0287	0.277	0.274
- processing	NA	0.001	NA	NA	NA	NA	NA
Aviation	0.181	0.181	0.195	0.196	0.195	0.184	0.182
Fire fighting foams - formulation	326	326	326	326	326	326	326
- use A	<0.001	<0.001	0.013	0.015	0.014	0.003	NA
- use B	137	137	138	138	138	137	NA
Photolithography	NA	3.03	NA	NA	NA	NA	NA
Fabrics - application	NA	1.53	NA	NA	NA	NA	NA
Paper treatment	NA	205	NA	NA	NA	NA	NA
Coatings	NA	5.1	NA	NA	NA	NA	NA
Regional	0.017	0.042	0.05	0.033	0.17	0.15	0.017

NA – local concentration not calculated for this use pattern in the particular scenario

The risk characterisation ratios for soil follow a similar pattern to those for the aquatic compartment. The formulation of fire-fighting foams gives ratios above one for all scenarios. As noted above, the emissions estimates use default emission factors and are based on a large site which no longer uses PFOS-based substances. The foam use pattern B also indicates a risk. This use pattern has release via a waste water treatment plant, and sludge from the plant after treatment of the foam is applied to soil. The calculation assumes that sludge is applied once a year, containing the same level of PFOS from the release. As the release is considered to be intermittent, it is unlikely that the same waste water treatment plant will receive the same foam release each year and the sludge be applied to the same soil. Hence this is not considered to be a realistic scenario. However, the soil concentration following a single application of sludge for this scenario would be enough to give a risk characterisation ratio of 36.

Risks are also indicated for the use areas of photolithography, fabrics, paper treatment and coatings in Scenario 2. In this scenario, instant transformation of PFOS-substance to PFOS is assumed. In addition, default emission factors are used for some of these areas (mainly paper treatment), so the emission estimates for these use patterns could be revised.

The highest ratio for the regional environment is 0.17, so there are no risks at this scale. Note that the concentrations used for this risk characterisation are the regional concentrations in agricultural soil, not the natural soil values included in Section 3.3.3.1. The regional soil concentrations are affected much more by the differences between the scenarios, the natural soil concentrations varying over two orders of magnitude. The risk characterisation ratios

show the influence of the release from polymers, with the two highest ratios being those for Scenarios 5 and 6 which include the polymer emissions.

The PNEC for the terrestrial compartment is derived from one long-term toxicity test result and so could be refined. As noted above the emission estimates could also be revised.

The calculated emission to waste water which would give rise to a risk for the terrestrial compartment is 7.4 g/day. This is for applications of sludge over 10 years, the emission which would give rise to a risk following a single application is 0.67 kg/day.

5.3 ATMOSPHERIC COMPARTMENT

No data on effects on organisms from exposure through the air were located. The estimated concentrations are very low, so PFOS is not expected to contribute significantly to abiotic effects in the atmosphere. No assessment is carried out.

5.4 NON-COMPARTMENT SPECIFIC EFFECTS RELEVANT TO THE FOOD CHAIN (SECONDARY POISONING)

5.4.1 Freshwater food chain

The concentrations for exposure through the freshwater food chain are in Section 3.3.5.1. The PNEC for secondary poisoning is 0.0167 mg/kg wwt in food, from Section 4.4.3.

The risk characterisation ratios for the aquatic food chain are presented in Table 5.3.

Table 5.3 Risk characterisation ratios for freshwater food chain exposure

Use area	Scenario number						
	1	2	3	4	5	6	7
Chromium plating	13	25.7	16.1	15.1	29.6	26.8	12.5
Photography - formulation	24.3	36.3	27.4	26.4	40.8	38.1	23.7
- processing	NA	25	NA	NA	NA	NA	NA
Aviation	21.7	32.4	24.8	23.8	38.3	35.5	21.2
Fire fighting foams - formulation	13400	13400	13400	13400	13400	NA	NA
- use A	26.1	38.1	29.2	28.2	42.7	39.9	NA
- use B	31.9	43.9	35	34	48.4	45.7	NA
Photolithography	NA	174	NA	NA	NA	NA	NA
Fabrics - application	NA	72.3	NA	NA	NA	NA	NA
Paper treatment	NA	8470	NA	NA	NA	NA	NA
Coatings	NA	235	NA	NA	NA	NA	NA
Regional	12.8	24.6	15.9	14.9	29.1	26.3	12.2

NA – local concentration not calculated for this use pattern in the particular scenario

For the freshwater food chain all of the use areas indicate a risk for all of the scenarios for which they are relevant. Consumption of prey exposed only to the regional background concentrations is also indicated as a risk for all scenarios. As noted above the regional water concentrations are only affected a little by the different release patterns in the scenarios. However, in most cases the specific uses also make a significant contribution to the exposure through this route, similar to or greater than that from the regional concentration. The exceptions to this are chromium plating and the processing life stage for photography.

None of the emission estimates are based on specific information about the releases of PFOS from the specific industry area. Hence they could all be refined. Considering only the

possible continuing uses (those included in Scenario 7), for chrome plating the local calculation is based on a scenario for the industry, but the overall emissions assume complete release of the amount used each year in the absence of information on its fate. Assumptions have been made on the nature of the substances released in the production of film and its developing. Data on the releases from photolithography come from the industry, but there may be more specific treatment of waste waters than assumed here. The aviation emissions are based on an emission scenario for hydraulic fluids, but do not relate specifically to the aviation industry.

The PNEC value is based on the results of a 2-year study with rats, so it is unlikely that the PNEC would be changed significantly in the light of further tests. An alternative PNEC of 0.067 mg/kg was also derived in Section 4.4.3. If this PNEC were used, all of the ratios would still be above one.

A comparison of the PNEC value with measured concentrations for freshwater fish shows that the highest measured concentrations reported exceed the PNEC of 0.0167 mg/kg. A number of values also exceed the alternative PNEC value of 0.067 mg/kg. It should be noted that this comparison is based on the highest values. In some cases these relate to specific tissues rather than whole body levels. Also, from the global archive sample analysis, PFOS was only detected in 38% of the samples. Nevertheless, measurements such as those in the Scheldt Estuary may indicate the presence of PFOS in aquatic biota at levels expected to have effects.

The emissions to waste water giving rise to a risk for this food chain are estimated to be 83 – 166 mg/day. Assuming a similar pattern of releases to air, water and soil, the regional emissions would need to be reduced by a factor of over twelve times (for the alternative PNEC, by three times) to remove the risk at the regional level.

5.4.2 Terrestrial food chain

The concentrations for exposure through the terrestrial food chain are in Section 3.3.5.1. The PNEC for secondary poisoning is 0.0167 mg/kg wwt in food, from Section 4.4.3.

The risk characterisation ratios for the terrestrial food chain are presented in Table 5.4.

Table 5.4 Risk characterisation ratios for exposure through the terrestrial food chain

Use area	Scenario number						
	1	2	3	4	5	6	7
Chromium plating	0.117	0.168	0.228	0.204	0.599	0.493	0.119
Photography - formulation	0.816	0.867	0.927	0.903	1.3	1.19	0.818
- processing	NA	0.11	NA	NA	NA	NA	NA
Aviation	0.558	0.609	0.67	0.646	1.04	0.934	0.561
Fire fighting foams - formulation	9.03	9.03	9.03	9.03	9.04	NA	NA
- use A	0.056	0.108	0.168	0.144	0.539	0.433	NA
- use B	381	381	382	381	382	382	NA
Photolithography	NA	8.47	NA	NA	NA	NA	NA
Fabrics - application	NA	4.36	NA	NA	NA	NA	NA
Paper treatment	NA	569	NA	NA	NA	NA	NA
Coatings	NA	14.3	NA	NA	NA	NA	NA
Regional	0.11	0.21	0.26	0.20	0.99	0.84	0.12

NA – local concentration not calculated for this use pattern in the particular scenario

Most use patterns indicate a risk in one or more of the scenarios for the terrestrial food chain. Exceptions are chromium plating, and the fire fighting foams use pattern Use A. No risks

through regional exposure are indicated, although one scenario has a ratio just below one. This is the scenario involving the greatest uncertainty, as it includes releases from the breakdown of polymeric material, about which there is no specific information. The scenario assumes eventual breakdown of polymer to PFOS in the environment, which is a worst case assumption; it is therefore considered unlikely that this scenario will actually lead to a risk. The comments on these uses in the section above on the freshwater food chain are relevant here, as the route to the terrestrial environment is through sludge application and hence depends on the emissions to water treatment. As above, the PNEC is unlikely to be changed by new tests. Using the alternative PNEC value of 0.067 mg/kg, photography and aviation would not show a risk.

The emissions to waste water giving rise to a risk for the terrestrial food chain are estimated to be 1.65 – 3.30 g/day. These are for 10 years of application; the emissions giving a risk from a single application of sludge are estimated to be 15 – 30 g/day.

5.5 MARINE ENVIRONMENT

5.5.1 PBT assessment

The PBT assessment included here relates to PFOS itself, and uses data from tests on PFOS salts. It does not apply directly to PFOS-substances. However, the potential for the substances to degrade to PFOS in the environment makes this assessment relevant to the general consideration of the group of substances.

5.5.1.1 Persistence

PFOS (as the potassium salt) has been tested for biodegradability in a series of tests commissioned by 3M and reported in the risk assessment of PFOS (3M, 2003). The following tests were conducted:

- activated sludge;
- acclimated activated sludge (including added soil and sediment materials) in both aerobic and closed vial exposures;
- aerobic soil and sediment cultures;
- anaerobic sludge from sludge digester; and
- pure microbial cultures.

None of these studies showed any evidence for the biodegradation of PFOS. 3M also reported the results of standard studies on hydrolysis (at 50°C and a range of pHs) and photolysis. Neither study showed any evidence for degradation of PFOS. The OECD hazard assessment (OECD, 2002) includes the results of a MITI-I study (ready biodegradability) which showed no evidence for ultimate or primary degradation (removal of the parent compound). The conclusion is that PFOS meets the screening criteria for P (Persistent) or vP[9] (very Persistent) criteria.

5.5.1.2 Bioaccumulation

There are a limited number of studies available on bioaccumulation of PFOS. A flow-through study on bluegill sunfish (*Lepomis macrochirus*) is cited in both 3M and the OECD

[9] Classification as a vP is on the basis that no degradation has been observed in any study to date, which makes it likely that the substance would meet this criterion.

assessment. The bioconcentration factors for edible tissues, non-edible tissues and whole fish were calculated from the rates of uptake and depuration because steady state had not been reached after 56 days of exposure.[10] The values obtained were 1124 (edible), 4103 (non-edible) and 2796 (whole fish). The exposure concentration was 0.086 mg/l.

A flow-through study on carp (*Cyprinus carpio*) resulted in lower values of 720 at 20 µg/l exposure and 200-1500 at 2 µg/l exposure. Higher values of 6,300 - 125,000 have been reported (for bioaccumulation factors) for in situ measurements at the scene of a spill of fire fighting foam, but these were considered to be due to the uptake of derivatives which were then metabolised to PFOS, hence the values were over-estimated.

In summary, BCF values up to 2800 have been measured in laboratory studies, and this meets the B or 'Bioacumulative' criterion.

The occurrence in a range of biota supports this; PFOS has been found in a wide range of higher organisms in Europe, including seals, dolphins, whales, cormorants, eagles, swordfish, tuna and salmon. The Global Biophase Monitoring Programme found PFOS in livers, blood and other tissues of animals, especially in fish-eating animals.

5.5.1.3 Toxicity

According to the assessment criteria laid out in the EU TGD, toxicity criteria is based on either aquatic toxicity or on classification.

The lowest aquatic NOEC value (from the OECD and 3M reports) is 0.25 mg/l, which is above the criterion level of 0.01 mg/l for the T criterion. On this basis, PFOS does not meet the T criterion. The NOAEC from chronic bird studies is 10 ppm for most endpoints, which is below the criterion value of <30 mg/kg in food. The level of 10 ppm was also considered a LOAEC for some effects in the same studies. Hence PFOS meets the T criterion on this basis.

PFOS is not listed as a substance on EINECS and has no classification. The acid form of PFOS is not classified on Annex I of Directive 67/548/EEC, and neither are any of the usual salts (potassium, ammonium, lithium). The mammalian toxicity data included in the OECD and 3M assessments has thus been used to consider what classification would be appropriate for PFOS.

Various toxicity studies have been conducted (as highlighted in earlier sections) to determine the toxicity of PFOS related substances, with the tests conducted in:

- a 90-day repeat dose toxicity study on rats showing that all rats died when fed on diets containing 300ppm PFOS and above (equivalent to 18 mg/kg bw/day and above). Some deaths (5 out of 10 animals) were also noted in rats fed diets containing 100 ppm PFOS (6 mg/kg bw/day)[11]. All rats receiving diets containing 30 ppm PFOS

[10] 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.

[11] The criteria for the classification of a substance as 'Toxic' with a risk phrase R48 are based on observations of serious damage to health at concentrations ≤5.0 mg/kg bw/day in a 90-day study, while the

(2.0 mg/kg/day) survived until the end of the study, but small changes in body and organ weights were reported. The effects seen in rats receiving 6.0 mg/kg/day suggest that PFOS fulfils the criteria for classification as Toxic, with the risk phrase R48, and hence meets the PBT criteria for T;

- a two year carcinogenicity study showing significant increases in hepatocellular adenomas observed in both male and female rats at 1 mg/kg bw/day. In view of the lack of effects in a number of genotoxicity test systems, the 3M report concluded that the carcinogenic effect was due to a threshold mediated non-genotoxic mechanism. This test could result in a Category 3 classification for carcinogenicity or could even provide insufficient evidence to warrant classification as a carcinogen, and thus may not fulfill the PBT criteria for T;

- a two generation rat study with PFOS showing significant reductions in the viability of pups in the F1 generation at exposure levels of 1.6 and 3.2 mg/kg bw/day. A subsequent study determined a NOAEL for pup mortality and growth of 1.2 mg/kg bw/day. No effects on mortality were observed over the whole study at 0.4 mg/kg bw/day. This may not fulfill the criteria for classification as "Toxic for Reproduction", and hence not meet the T criterion for PBT. The view of Sweden in their comments on the draft RER is that the data fulfill the criteria for reproductive toxicity as category 3, and possibly also for category 2. Comments from the Norwegian Institute of Public Health also support classification as a reproductive toxicant category 3;

- developmental and reproductive toxicity studies on rabbits showing effects on the development of the foetus at doses of *5* and 10 mg/kg bw/day. These are largely maturational delays and reduced foetal body weight. A NOAEL of 1 mg/kg bw/day has been determined for most of these effects in rats. Signs of maternal toxicity are also observed at similar levels, and in some cases the NOAEL for maternal effects is lower than that for developmental effects. The 3M RAR concluded that there was no indication of specific teratogenic effects. These may not meet the requirements for classification as "Toxic for Reproduction" and hence not meet the T criterion for PBT; and

- tests on rhesus monkeys showing that all animals died at 10 mg/kg bw/day, the lowest dose tested, with a follow up study showing deaths at 4.5 mg/kg bw/day. There were no deaths at 1.5 mg/kg bw/day, but there were signs of gastrointestinal toxicity. The results of this test show that PFOS fulfils the criteria for classification as Toxic, with the risk phrase R48, and hence meets the T criterion for PBT.

PFOS has been shown to cause death in both rats and monkeys at doses of 6.0 and 4.5 mg/kg/day respectively in repeat-dose 90-day toxicity studies, although significant signs of toxicity were not seen in groups of rats or monkeys receiving lower doses of PFOS. Despite this apparent steep dose-response relationship in its toxicity, the severity of the effects seen at doses around 5.0 mg/kg/day warrant classification as "Toxic" and assigned the Risk Phrase R48.

It is therefore concluded that PFOS should be classified as 'Toxic' and carry the Risk Phrase R48. There is also support for classification as toxic for reproduction, category 3. It therefore

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classification of a substance as 'Harmful' with a risk phrase R48 is based on observations of serious damage to health at concentrations of the order of ≤50 mg/kg bw/day in a 90-day study.

meets the T or 'Toxicity' criterion on this basis , as well as on the basis of the bird feeding studies.

5.5.1.4 PBT conclusion

PFOS meets the vP, B and T criteria and hence is considered as a PBT substance. It should be noted that this conclusion does not apply directly to PFOS-substances, but the potential for the substances to be degraded to PFOS means that it is of relevance in the consideration of the substances.

5.5.2 Marine risk evaluation

As PFOS meets the PBT criteria, there is strictly no requirement for a risk evaluation. However the relevant results are generated as part of the modelling and so are included here.

5.5.2.1 Marine water

The concentrations of PFOS in marine waters have been calculated as part of the modelling described in Section 3. The values are presented in Table 5.5.

The risk characterisation ratios for the marine aquatic compartment are presented in Table 5.6. The PNEC is 2.5µg/l. As for freshwater, the exposure and effect concentrations are derived from the aquatic values by equilibrium partitioning, and so the ratios are the same as those for the aquatic compartment.

Table 5.5 Predicted environmental concentrations in marine water

Use area	Scenario number						
	1	2	3	4	5	6	7
Chromium plating	$4.76x10^{-6}$	$8.33x10^{-6}$	$5.67x10^{-6}$	$5.39x10^{-6}$	$9.56x10^{-6}$	$8.75x10^{-6}$	$4.6x10^{-6}$
Photography - formulation	$1.52x10^{-5}$	$1.88x10^{-5}$	$1.61x10^{-5}$	$1.58x10^{-5}$	$2.0x10^{-5}$	$1.92x10^{-5}$	$1.51x10^{-5}$
- processing	NA	$7.47x10^{-6}$	NA	NA	NA	NA	NA
Aviation	$1.14x10^{-5}$	$1.49x10^{-5}$	$1.23x10^{-5}$	$1.2x10^{-5}$	$1.62x10^{-5}$	$1.53x10^{-5}$	$1.12x10^{-5}$
Fire fighting foams - formulation	0.0135	0.0135	0.0135	0.135	0.135	NA	NA
- Use A	$2.85x10^{-3}$	$2.86x10^{-3}$	$2.85x10^{-3}$	$2.85x10^{-3}$	$2.86x10^{-3}$	$2.86x10^{-3}$	NA
- Use B	$5.7x10^{-3}$	$5.71x10^{-3}$	$5.7x10^{-3}$	$5.7x10^{-3}$	$5.71x10^{-3}$	$5.71x10^{-3}$	NA
Photolithography	NA	$1.32x10^{-4}$	NA	NA	NA	NA	NA
Fabrics - application	NA	$7.09x10^{-5}$	NA	NA	NA	NA	NA
Paper treatment	NA	$8.51x10^{-3}$	NA	NA	NA	NA	NA
Coatings	NA	$2.19x10^{-4}$	NA	NA	NA	NA	NA
Regional	$3.86x10^{-6}$	$7.43x10^{-6}$	$4.77x10^{-6}$	$4.51x10^{-6}$	$8.68x10^{-6}$	$7.87x10^{-6}$	$3.71x10^{-6}$

NA – local concentration not calculated for this use pattern in the particular scenario

The pattern of the risk characterisation ratios for the marine aquatic compartment is similar to that for freshwater (Section 5.1.1) and the same comments and conclusions apply. In addition to the freshwater areas indicting risks, the other use of foam (Use A) also shows a risk for the marine compartment. This use is also discussed in Section 5.1.1. The scenarios for the use of foams could be considered to be relevant for the offshore use of foams in the first instance.

The emission to waste water calculated to give rise to a risk for the marine aquatic compartment is 0.5 kg/day.

Table 5.6 Risk characterisation ratios for the marine aquatic compartment

Use area	Scenario number						
	1	2	3	4	5	6	7
Chromium plating	0.002	0.003	0.002	0.002	0.004	0.004	0.002
Photography - formulation	0.006	0.008	0.006	0.006	0.008	0.008	0.006
- processing	NA	0.003	NA	NA	NA	NA	NA
Aviation	0.005	0.006	0.005	0.005	0.006	0.006	0.004
Fire fighting foams - formulation	5.4	5.4	5.4	5.4	5.4	NA	NA
- Use A	1.14	1.14	1.14	1.14	1.14	1.14	NA
- Use B	2.28	2.28	2.28	2.28	2.28	2.28	NA
Photolithography	NA	0.053	NA	NA	NA	NA	NA
Fabrics - application	NA	0.028	NA	NA	NA	NA	NA
Paper treatment	NA	3.4	NA	NA	NA	NA	NA
Coatings	NA	0.088	NA	NA	NA	NA	NA
Regional	0.002	0.003	0.002	0.002	0.004	0.003	0.002

NA – local concentration not calculated for this use pattern in the particular scenario

5.5.2.2 Secondary poisoning in the marine environment

There are two calculations for secondary poisoning in the marine environment, to include two levels of predator. These are a fish-eating bird or mammal, similar to that in the freshwater environment, and a top predator. The concentrations in the food organisms for these endpoints were included in Section 3.3.5.1. The risk characterisation ratios for these two are presented in Tables 5.7 and 5.8.

Table 5.7 Risk characterisation ratios for fish-eating bird or mammal (marine)

Use area	Scenario number						
	1	2	3	4	5	6	7
Chromium plating	1.3	2.59	1.6	1.51	2.91	2.63	1.24
Photography - formulation	2.86	4.06	3.17	3.07	4.47	4.2	2.81
- processing	NA	2.5	NA	NA	NA	NA	NA
Aviation	2.5	3.53	2.81	2.71	4.11	3.84	2.45
Fire fighting foams - formulation	1860	1860	1860	1860	1860	NA	NA
- Use A	2.61	3.8	2.91	2.82	4.21	3.94	NA
- Use B	3.92	5.11	4.22	4.13	5.52	5.25	NA
Photolithography	NA	23.2	NA	NA	NA	NA	NA
Fabrics - application	NA	9.08	NA	NA	NA	NA	NA
Paper treatment	NA	1170	NA	NA	NA	NA	NA
Coatings	NA	31.7	NA	NA	NA	NA	NA
Regional	1.26	2.46	1.56	1.50	2.87	2.57	1.20

NA – local concentration not calculated for this use pattern in the particular scenario

Table 5.8 Risk characterisation ratios for marine top predator

Use area	Scenario number						
	1	2	3	4	5	6	7
Chromium plating	2.59	5.03	3.2	3.01	5.81	5.27	2.48
Photography - formulation	3.22	5.61	3.83	3.64	6.44	5.89	3.11
- processing	NA	4.99	NA	NA	NA	NA	NA
Aviation	3.08	5.4	3.68	3.5	6.29	5.75	2.97
Fire fighting foams - formulation	747	749	748	747	750	NA	NA
- Use A	3.12	5.51	3.72	3.54	6.33	5.79	NA
- Use B	3.64	6.03	4.25	4.06	6.86	6.31	NA
Photolithography	NA	13.3	NA	NA	NA	NA	NA
Fabrics - application	NA	7.61	NA	NA	NA	NA	NA
Paper treatment	NA	474	NA	NA	NA	NA	NA
Coatings	NA	16.6	NA	NA	NA	NA	NA
Regional	2.57	4.91	3.11	2.99	5.75	5.15	2.46

NA – local concentration not calculated for this use pattern in the particular scenario

The ratios for the marine food chain exposures are lower than those from the freshwater food chain, but are all above one. Risks are also indicated at the regional level for all scenarios. The same comments as for the freshwater food chain (Section 5.4) are relevant here. Using the alternative PNEC, most of the use areas would have a ratio above one for at least one of the scenarios, although there would be no ratios above one for the marine food chains for Scenario 7.

The emissions to waste water estimated to give rise to a risk for these endpoints are 0.6 – 1.2 g/d for the fish-eating predator, and 0.3 – 3.0 g/day for the marine predator.

5.6 UNCERTAINTIES

It is to be expected in a risk evaluation that there will be some areas of uncertainty due to a lack of sufficiently detailed information in some areas. In the case of PFOS, the nature of the substance and the use of a large number of derivatives or related substances add further to the usual types of uncertainty. These areas have been indicated in the evaluation as they have arisen, but are discussed again here, with in some cases additional consideration of the effect of the uncertainty on the outcome of the evaluation.

5.6.1 PFOS-salt properties

The unusual properties of PFOS mean that the usual approach of estimating a number of properties from the log Kow value cannot be taken here. To circumvent this, the values for properties such as soil-water partition have been taken as far as possible from direct measurements. It is recognised that these properties are likely to depend to some extent on the characteristics of the environment. There is no information on this dependence, and therefore no calculations have been carried out to examine this variation. As the values used come from measurements on particular soils, sediment or sludge then they can be considered to relate at least to these materials. The standard approach assumes a fixed composition for these materials, and so in that sense the current approach is not very different.

The effect of considering the range of solubility values determined for PFOS salts, and the uncertainty in the air-water partition coefficient, have been considered in Appendix 8. These changes have no impact on the levels or distribution calculated in the model.

For one specific use area, hydraulic fluids in aircraft, the substance used is not PFOS but a related substance. This evaluation has assumed that the properties of this substance are similar to those of PFOS, which is a further area of uncertainty with regard to this use.

5.6.2 PFOS releases

These comments relate to the releases of PFOS-substance as well as PFOS-salt. The emission estimates made in the risk evaluation are based on the most specific information available. There are no specific measurements of the releases of PFOS at specific locations and relating to particular processes. Information on the amounts used in each area is available, and in some cases there are estimates of the total amounts released on an EU basis. Where possible, information has been taken from emission scenarios related to the particular use area, although it is not possible in all cases to find information related to the specific use of the PFOS-related substance. There is only one area in which the Technical Guidance Document default values have been used, and that is for fire-fighting foams. Here the formulation step is based on defaults. The nature of the use of such foams means that complete release to the environment is possible. Alternative estimates for the amount used at a single incident have been made in Appendix 4. For other areas, it is recognised that better information could allow the assessment of emission (and hence the calculation of environmental concentrations) to be refined. No extra calculations have been performed in the absence of more specific information, with the exception of photolithography, where the cessation of use for a specific purpose has been considered (Appendix 3).

5.6.3 PFOS-substance properties

The property values used in the evaluation are those for N-EtFOSE. There are a large number of substances which come under this grouping, and clearly some will have properties which differ from those of the chosen substance. However, it is felt that having selected one substance to represent the group it is better to use data only for this substance rather than vary the values to try to cover the possible range within the group. There is one exception to this, which is the degradation of the substances, and this is considered below.

5.6.4 PFOS-substance degradation

This is one of the key areas of uncertainty in the evaluation. Information on the breakdown of PFOS-substances was discussed in Sections 3.2.2.2.1 and 3.3.1.1.2. The data available are limited, but they do appear to show that N-EtFOSE can be broken down by aerobic biodegradation in a series of steps, the eventual products from which appear to be PFOS and PFOA. At least one estimate of the yield of PFOS from this process has been presented in the literature, but both the yields and the rates of the steps are uncertain.

The main calculations in the evaluation include scenarios in which the PFOS-substances are degraded to PFOS on or before release, and scenarios where the half life for degradation to PFOS is 20.5 days or 1 year. Comments from the consultation argued that the overall rate may be much longer than this. Appendix 5 considers a longer half life of 10 years as well as the two shorter half lives. These calculations show a reduction in the amount degraded in the region at steady state as the half lives in water and soil increase. It should be noted that most of the PFOS-substance released in the model is removed from the regional model and the continental mode by water flow and air movement before it can be degraded. This has the potential to degrade in more remote areas, and so contribute to the overall global burden. The longer the half lives used for the regional model, the greater the proportion of releases which are moved to more remote areas. It should also be borne in mind that the biodegradation half

lives used here are for the overall process, from PFOS-substance to PFOS. There will be intermediate products along this process, some of which may have significant lifetimes in the environment. As such they may behave differently to the example PFOS-substance used in the calculations. There is at present no way to address this aspect.

The second aspect is the degree to which the degradation of PFOS-substances leads to PFOS itself. The effect of a lower yield of PFOS from this degradation is investigated in Appendix 3, using the scenario for photolithography in isolation. Where the assumptions relate to the fraction of PFOS-substance released as PFOS from waste water treatment, the effect on concentration is essentially linear. Hence the assumption of a 20% yield leads to local concentrations which are 20% of those when complete conversion to PFOS is assumed.

The calculations on the behaviour of PFOS-substance show that degradation in air is also important in terms of the production of PFOS from PFOS-substance. The value for the half life of this process is calculated from the structure of the PFOS-substance, and strictly relates to the initial reaction of the substance with hydroxyl radicals, rather than the formation of PFOS. There is no real information on the products of the reactions of PFOS-substances in air. Appendix 5 considers the effect of a longer overall lifetime for degradation in air, but with the process leading to PFOS. The calculations are performed on the emissions estimated for Scenario 7. The appendix also includes the situation where the degradation does not lead to PFOS.

The effect of a longer half life is a reduced contribution to the overall production of PFOS from the air compartment. The concentration of PFOS calculated for a scenario will also be reduced where the degradation in air made a significant contribution to the inputs of PFOS. For the Scenario 7 emissions (considering the PFOS-substance emissions only), the regional concentration in surface water is reduced by ~4 times when the half life in air is increased by two orders of magnitude. The same effect would be seen if only a proportion of the degradation of PFOS-substance in air lead to PFOS.

The key areas which affect the predicted concentrations appear to be: the degree to which PFOS-salt is produced from PFOS-substances in waste water treatment, and to a lesser extent the degree to which this occurs in the environment; and the production of PFOS-salts from PFOS-substances through degradation in air, and the rate of this process. Nevertheless, even when a number of less conservative assumptions are made, risks are still indicated from the releases of very low concentrations of PFOS-substances.

5.7 SUMMARY OF CONCLUSIONS

The major area of concern is for secondary poisoning, in particular for water. All of the use patterns considered in the evaluation lead to a risk for secondary poisoning in the relevant scenarios, for the freshwater, marine predator and marine top predator endpoints. This is true of the uses releasing only small amounts overall, such as photography and aviation, as well as for the uses with larger emissions. Calculations for each of the uses considered to be continuing, carried out individually and not shown in this evaluation, indicate that four (chromium plating, photography (formulation), aviation and photolithography) could lead to a risk based on the assumptions made in this evaluation (and assuming instant conversion of PFOS-substance to PFOS where relevant). The only use pattern not leading to a risk is the use in photography (developing). Risks are indicated at the regional level for secondary poisoning through the freshwater and marine food chains for all scenarios considered. Some measured values in aquatic biota are above the PNEC for secondary poisoning. For

freshwater, the regional emissions would need to be reduced to less than one twelfth of the estimated values in order to remove the risk at the regional level (assuming a similar distribution of emissions). In the case of the alternative PNEC, the reduction would need to be by over two-thirds.

The PNEC value for secondary is derived from a two-year feeding study, and is not likely to be changed by further tests. The alternative PNEC also comes from long term testing. The bioconcentration factor for fish comes from valid measurements, and PFOS has been measured in fish. The biomagnification factor used in the calculations, a value of two, is the default value from the Technical Guidance Document, and so could be revised through measurement, but reducing this to a factor of one would not remove the concerns in most cases. The main scope for revising the evaluation would appear to be through better estimates of emissions.

There are also indications of risk for the aquatic and terrestrial compartments for direct effects on organisms. These relate mostly to the fire-fighting foams, where releases on use may be sufficient to cause concern. These calculations are very dependent on the assumptions about how much foam is used at an individual fire. The calculation for the formulation of the foams also shows a risk, but the exposure estimate is based on defaults and on a site which no longer uses PFOS-related substances.

N.B. No assessment of risk to humans has been carried out.

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ABBREVIATIONS

ASTM	American Society for Testing and Materials
B	Bioaccumulative, within the meaning of the PBT criteria
BCF	Bioconcentration Factor
bw	body weight / *Bw*, *b.w.*
CAS	Chemical Abstract Services
EC	European Communities
EC10	Effect Concentration measured as 10% effect
EC50	median Effect Concentration
ECB	European Chemicals Bureau
EINECS	European Inventory of Existing Commercial Chemical Substances
EPA	Environmental Protection Agency (USA)
EPCI	European Photographic Chemicals Industry
ESD	Emission Scenario Document
ESIA	European Semi-Conductor Industry Association
ESR	Existing Substances Regulation
EU	European Union
EUSES	European Union System for the Evaluation of Substances [software tool in support of the Technical Guidance Document on risk assessment]
FOSA	Perfluorooctanesulphonamide
IC50	median Immobilisation Concentration or median Inhibitory Concentration
ISO	International Organisation for Standardisation
Kow	octanol/water partition coefficient
Kd	solids-water partition coefficient
L(E)C50	median Lethal (Effect) Concentration
LC50	median Lethal Concentration
LOAEL	Lowest Observed Adverse Effect Level
MITI	Ministry of International Trade and Industry, Japan
N	Dangerous for the environment (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC
N-EtFOSE	N-ethylperfluorooctanesulphonamidoethanol (structure in Section 1.1)
N-MeFOSE	N-methylperfluorooctanesulphonamidoethanol
NOAEL	No Observed Adverse Effect Level
NOEC	No Observed Effect Concentration
nt.	Normal, Temperature and Pressure
OECD	Organisation for Economic Cooperation and Development
OSPAR	Oslo and Paris Convention for the protection of the marine environment of the Northeast Atlantic
P	Persistent, within the meaning of the PBT criteria
PBT	Persistent, Bioaccumulative and Toxic
PEC	Predicted Environmental Concentration
PFOA	Perfluorooctane carboxylic acid
PFOS	Perfluorooctane sulphonate (used to refer to the anion, or the moiety in other substances) (structure in Section 1.1)
PNEC	Predicted No Effect Concentration
QSAR	(Quantitative) Structure-Activity Relationship
RAR	Risk Assessment Report
SEMI	Semiconductors Equipment and Materials International
SIDS	Screening Information Data Set, OECD
SNUR	Significant New Use Rule (US EPA)

STP	Sewage Treatment Plant
T	Toxic, within the meaning of the PBT criteria
TG	Test Guideline
TGD	Technical Guidance Document
US EPA	Environmental Protection Agency, USA
vP	very Persistent, within the meaning of the PBT criteria
w/w	weight per weight ratio
WWTP	Waste Water Treatment Plant

Appendix 1 - Draft List of Compounds Potentially Degrading to PFOS in the Environment

Table A1.1: Draft List of Compounds Potentially Degrading to PFOS in the Environment		
Ref No.	**CAS Number**	**PFOS related substance**
1	307-35-7	1-Octanesulphonyl fluoride, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-
2	376-14-7	2-Propenoic acid, 2-methyl-, 2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl ester
3	383-07-3	2-Propenoic acid, 2-[butyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl ester
4	423-82-5	2-Propenoic acid, 2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl ester
5	423-86-9	1-Octanesulphonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-2-propenyl-
6	754-91-6	1-Octanesulphonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-
7	1652-63-7	1-Propanaminium, 3-[[(heptadecafluorooctyl)sulphonyl]amino]-*N*,*N*,*N*-trimethyl-, iodide
8	1691-99-2	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(2-hydroxyethyl)-
9	1763-23-1	1-Octanesulphonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-
10	1869-77-8	Glycine, *N*-ethyl-*N*-[(heptadecafluorooctyl)sulphonyl]-, ethyl ester
11	2250-98-8	1-Octanesulphonamide, *N*,*N*',*N*''- [phosphinylidynetris(oxy-2,1-ethanediyl)]tris[*N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-
12	2263-09-4	1-Octanesulphonamide, *N*-butyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(2-hydroxyethyl)-
13	2795-39-3	1-Octanesulphonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, potassium salt
14	2991-50-6	Glycine, *N*-ethyl-*N*-[(heptadecafluorooctyl)sulphonyl]-
15	2991-51-7	Glycine, *N*-ethyl-*N*-[(heptadecafluorooctyl)sulphonyl]-, potassium salt
16	3820-83-5	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-[2-(phosphonooxy)ethyl]-
17	3871-50-9	Glycine, *N*-ethyl-*N*-[(heptadecafluorooctyl)sulphonyl]-, sodium salt
18	4151-50-2	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-
19	13417-01-1	1-Octanesulphonamide, *N*-[3-(dimethylamino)propyl]-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-
20	14650-24-9	2-Propenoic acid, 2-methyl-, 2- [[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl ester
21	24448-09-7	1-Octanesulphonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(2-hydroxyethyl)-*N*-methyl-
22	24924-36-5	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-2-propenyl-
23	25268-77-3	2-Propenoic acid, 2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl ester
24	29081-56-9	1-Octanesulphonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, ammonium salt
25	29117-08-6	Poly(oxy-1,2-ethanediyl), .alpha.-[2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl]-.omega.-hydroxy-

Table A1.1: Draft List of Compounds Potentially Degrading to PFOS in the Environment		
Ref No.	**CAS Number**	**PFOS related substance**
26	29457-72-5	1-Octanesulphonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, lithium salt
27	30295-51-3	1-Octanesulphonamide, N-[3-(dimethyloxidoamino)propyl]-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-
28	30381-98-7	1-Octanesulphonamide, *N*,*N*'-[phosphinicobis(oxy-2,1-ethanediyl)]bis[*N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, ammonium salt
29	31506-32-8	1-Octanesulphonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-methyl-
30	38006-74-5	1-Propanaminium, 3-[[(heptadecafluorooctyl)sulphonyl]amino]-*N*,*N*',*N*''-trimethyl-, chloride
31	50598-29-3	1-Octanesulphonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(phenylmethyl)-
32	52550-45-5	Poly(oxy-1,2-ethanediyl), α-[2-[[(heptadecafluorooctyl)sulphonyl]propylamino]ethyl]-ω -hydroxy-
33	56773-42-3	Ethanaminium, *N*,*N*',*N*''-triethyl-, salt with 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulphonic acid (1:1)
34	57589-85-2	Benzoic acid, 2,3,4,5-tetrachloro-6-[[[3- [[(heptadecafluorooctyl)sulphonyl]oxy]phenyl]amino]carbonyl]-, monopotassium salt
35	58920-31-3	2-Propenoic acid, 4-[[(heptadecafluorooctyl)sulphonyl]methylamino]butyl ester
36	61577-14-8	2-Propenoic acid, 2-methyl-, 4-[[(heptadecafluorooctyl)sulphonyl]methylamino]butyl ester
37	61660-12-6	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-[3-(trimethoxysilyl)propyl]-
38	67939-42-8	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-[3-(trichlorosilyl)propyl]-
39	67969-69-1	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-[2-(phosphonooxy)ethyl]-, diammonium salt
40	67939-88-2	1-Octanesulphonamide, *N*-[3-(dimethylamino)propyl]- 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, monohydrochloride
41	68081-83-4	Carbamic acid, (4-methyl-1,3-phenylene)bis-, bis[2-[ethyl[(perfluoro-C4-8-alkyl)sulphonyl]amino]ethyl] ester
42	68298-11-3	1-Propanaminium, 3-[[(heptadecafluorooctyl)sulphonyl](3-sulphopropyl)amino]-*N*-(2-hydroxyethyl)-*N*,*N*-dimethyl-, hydroxide, inner salt
43	68329-56-6	2-Propenoic acid, eicosyl ester, polymer with 2-[[(heptadecafluorooctyl)sulphonyl] methylamino]ethyl 2-propenoate, hexadecyl 2-propenoate, 2-[methyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-propenoate and octadecyl 2-propenoate
44	68239-73-6	1-Octanesulphonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(4-hydroxybutyl)-*N*-methyl-
45	68310-75-8	1-Propanaminium, 3-[[(heptadecafluorooctyl)sulphonyl]amino]-*N*,*N'*,*N''*-trimethyl-, iodide, ammonium salt
46	68541-80-0	2-Propenoic acid, polymer with 2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate and octadecyl 2-propenoate
47	68555-90-8	2-Propenoic acid, butyl ester,polymer with 2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl 2-propenoate, 2-[methyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-propenoate and 2-[methyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-propenoate

Table A1.1: Draft List of Compounds Potentially Degrading to PFOS in the Environment		
Ref No.	**CAS Number**	**PFOS related substance**
48	68555-91-9	2-Propenoic acid, 2-methyl-, 2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl ester, polymer with 2-[ethyl[(nonafluorobutyl)sulphonyl]amino] ethyl 2-methyl-2-propenoate, 2-[ethyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2-[ethyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2- [ethyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate and octadecyl 2-methyl-2-propenoate
49	68555-92-0	2-Propenoic acid, 2-methyl-, 2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl ester, polymer with 2- [methyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2- [methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2- [methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2- [methyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate and octadecyl 2-methyl-2-propenoate
50	68608-14-0	Sulphonamides, C4-8-alkane, perfluoro, *N*-ethyl-*N*-(hydroxyethyl), reaction products with 1,1'-methylenebis[4-isocyanatobenzene]
51	68649-26-3	1-Octanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(2-hydroxyethyl)-, reaction products with *N*-ethyl-1,1,2,2,3,3,4,4,4-nonafluoro-*N*-(2-hydroxyethyl)-1-butanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-*N*-(2-hydroxyethyl)- 1-heptanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-*N*-(2-hydroxyethyl)-1-hexanesulphonamide, *N*-ethyl-1,1,2,2,3,3,4,4,5,5,5-undecafluoro-*N*-(2-hydroxyethyl)-1-pentanesulphonamide, polymethylenepolyphenyleneisocyanate and stearyl alc.
52	68867-60-7	2-Propenoic acid, 2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl ester, polymer with 2-[methyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-propenoate, 2- [methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-propenoate and.alpha.-(1-oxo-2-propenyl)-.omega.-methoxypoly(oxy-1,2-ethanediyl)
53	68877-32-7	2-Propenoic acid, 2-methyl-, 2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl ester, polymer with 2-[ethyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2-[ethyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2-[ethyl[(tridecafluoro-hexyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2-[ethyl[(undecafluoro-pentyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate and 2-methyl-1,3-butadiene
54	68891-96-3	Chromium, diaquatetrachloro[.mu.-[*N*-ethyl-*N*- [(heptadecafluorooctyl)sulphonyl] glycinato-.kappa.O:.kappa.O']]-.mu.-hydroxybis(2-methylpropanol)di-
55	68909-15-9	2-Propenoic acid, eicosyl ester, polymers with branched octylacrylate, 2- [[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl acrylate, 2-[methyl [(nonafluorobutyl)sulphonyl]amino]ethyl acrylate, 2- [methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl acrylate, 2-[methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl acrylate, 2- [methyl[(undecafluoropentyl)sulphonyl]amino]ethyl acrylate, polyethylene glycol acrylate Me ether and stearyl acrylate
56	68958-61-2	Poly(oxy-1,2-ethanediyl), .alpha.-[2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl]-.omega.-methoxy-
57	70225-14-8	1-Octanesulphonic 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)
58	70776-36-2	2-Propenoic acid, 2-methyl-, octadecyl ester, polymer with 1,1-dichloroethene, 2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl 2-propenoate, *N*-(hydroxymethyl)-2-propenamide, 2-[methyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-propenoate and 2-[methyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-propenoate
59	71463-78-0	Phosphonic acid, [3-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]propyl]-
60	71463-80-4	Phosphonic acid, [3-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]propyl]-, diethyl ester
61	71487-20-2	2-Propenoic acid, 2-methyl-, methyl ester, polymer with ethenylbenzene, 2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl 2-propenoate, 2-[methyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-propenoate, 2- [methyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-propenoate, 2-[methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-propenoate, 2- [methyl[(undecafluoropentyl)sulphonyl]amino]ethyl 2-propenoate and 2-propenoic acid

Table A1.1: Draft List of Compounds Potentially Degrading to PFOS in the Environment		
Ref No.	**CAS Number**	**PFOS related substance**
62	91081-99-1	Sulphonamides, C_{4-8}-alkane, perfluoro, *N*-(hydroxyethyl)-*N*-methyl, reaction products with epichlorohydrin, adipates (esters)
63	92265-81-1	Ethanaminium, *N*,*N*,*N*-trimethyl-2-[(2-methyl-1-oxo-2-propenyl)oxy]-, chloride, polymer with 2-ethoxyethyl 2-propenoate, 2-[[(heptadecafluorooctyl)sulphonyl] methylamino]ethyl 2-propenoate and oxiranylmethyl 2-methyl-2-propenoate
64	94133-90-1	1-Propanesulphonic acid, 3-[[3-(dimethylamino)propyl][(heptadecafluorooctyl) sulphonyl]amino]-2-hydroxy-, monosodium salt
65	94313-84-5	Carbamic acid, [5-[[[2-[[(heptadecafluorooctyl)sulphonyl]methylamino]ethoxy]carbonyl]amino]-2-methylphenyl]-, 9-octadecenyl ester, (Z)-
66	98999-57-6	Sulphonamides, C_{7-8}-alkane, perfluoro, *N*-methyl-*N*-[2-[(1-oxo-2-propenyl)oxy]ethyl], polymers with 2-ethoxyethyl acrylate, glycidyl methacrylate and *N*,*N*,*N*-trimethyl-2-[(2-methyl-1-oxo-2-propenyl)oxy]ethanaminium chloride
67	127133-66-8	2-Propenoic acid, 2-methyl-, polymers with Bu methacrylate, lauryl methacrylate and 2-[methyl[(perfluoro-C_{4-8}-alkyl)sulphonyl]amino]ethyl methacrylate
68	129813-71-4	Sulphonamides, C_{4-8}-alkane, perfluoro, *N*-methyl-*N*-(oxiranylmethyl)
69	148240-78-2	Fatty acids, C_{18}-unsatd., trimers, 2-[[heptadecafluorooctyl)sulphonyl]methylamino]ethyl esters
70	148684-79-1	Sulphonamides, C_{4-8}-alkane, perfluoro, *N*-(hydroxyethyl)-*N*-methyl, reaction products with 1,6-diisocyanatohexane homopolymer and ethylene glycol
71	160901-25-7	Sulphonamides, C_{4-8}-alkane, perfluoro, *N*-ethyl-*N*-(hydroxyethyl), reaction products with 2-ethyl-1-hexanol and polymethylenepolyphenylene isocyanate
72	178094-69-4	1-Octanesulphonamide, *N*-[3-(dimethyloxidoamino)propyl]-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-,potassium salt
73	178535-22-3	Sulphonamides, C_{4-8}-alkane, perfluoro, *N*-ethyl-*N*-(hydroxyethyl)-, polymers with 1,1'-methylenebis[4-isocyanatobenzene] and polymethylenepolyphenylene isocyanate, 2-ethylhexyl esters, Me Et ketone oxime-blocked
74	182700-90-9	1-Octanesulphonamide, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-methyl-, reaction products with benzene-chlorine-sulphur chloride (S_2Cl_2) reaction products chlorides
75	L-92-0151 (US Pre-manufacture notice)	2-Propenoic acid, 2-methyl-, butyl ester, polymer with 2-[ethyl[(heptadecafluorooctyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2-[ethyl[(nonafluorobutyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2- [ethyl[(pentadecafluoroheptyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate, 2-[ethyl[(tridecafluorohexyl)sulphonyl]amino]ethyl 2-methyl-2-propenoate and 2-propenoic acid
76	P-94-2205 (US Pre-manufacture notice)	Polymethylenepolyphenylene isocyanate and bis(4-NCO-phenyl)methane reaction products with 2-ethyl-1-hexanol, 2-butanone, oxime, *N*-ethyl-*N*-(2-hydroxyethyl)-1-C_4-C_8 perfluoroalkanesulphonamide
77	192662-29-6	Sulphonamides, C_{4-8}-alkane, perfluoro, *N*-[3-(dimethylamino)propyl], reaction products with acrylic acid
78	251099-16-8	1-Decanaminium, *N*-decyl-*N*,*N*-dimethyl-, salt with 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulphonic acid (1:1)
79	306973-46-6	Fatty acids, linseed-oil, dimers, 2- [[(heptadecafluorooctyl)sulphonyl]methylamino]ethyl esters
80	306973-47-7	Sulphonamides, C_{4-8}-alkane, perfluoro, *N*-(hydroxyethyl)-*N*-methyl, reaction products with 12-hydroxystearic acid and 2,4-TDI, ammonium salts

Table A1.1: Draft List of Compounds Potentially Degrading to PFOS in the Environment		
Ref No.	**CAS Number**	**PFOS related substance**
81	306974-19-6	Sulphonamides, C_{4-8}-alkane, perfluoro, *N*-methyl-*N*-[(3-octadecyl-2-oxo-5-oxazolidinyl)methyl]
82	306974-28-7	Siloxanes and Silicones, di-Me, mono[3-[(2-methyl-1-oxo-2-propenyl)oxy]propylgroup] -terminated, polymers with 2-[methyl[(perfluoro-C4-8-alkyl)sulphonyl]amino]ethyl acrylate and stearyl methacrylate
83	306974-45-8	Sulphonic acids, C_{6-8}-alkane, perfluoro, compounds with polyethylene-polypropylene glycol bis(2-aminopropyl) ether
84	306974-63-0	Fatty acids, C_{18}-unsatd.,dimers, 2-[methyl[(perfluoro-C_{4-8}-alkyl)sulphonyl]amino] ethyl esters
85	306975-56-4	Propanoic acid, 3-hydroxy-2- (hydroxymethyl)-2-methyl-, polymer with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol and *N*,*N*',2-tris(6-isocyanatohexyl)imidodicarbonic diamide, reaction products with *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(2-hydroxyethyl)-1-octanesulphonamide and *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-*N*-(2-hydroxyethyl)-1-heptanesulphonamide, compounds with triethylamine
86	306975-57-5	Propanoic acid, 3-hydroxy-2-(hydroxymethyl)-2-methyl-, polymer with 1,1'-methylenebis[4- isocyanatobenzene] and 1,2,3-propanetriol, reaction products with *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-*N*-(2-hydroxyethyl)-1-octanesulphonamide and *N*-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoro-*N*-(2-hydroxyethyl)-1-heptanesulphonamide, compounds with morpholine
87	306975-62-2	2-Propenoic acid, 2-methyl-, dodecyl ester, polymers with 2- [methyl[(perfluoro-C_{4-8}-alkyl)sulphonyl]amino]ethyl acrylate and vinylidene chloride
88	306975-84-8	Poly(oxy-1,2-ethanediyl), .alpha.-hydro-.omega.-hydroxy-, polymer with 1,6-diisocyanatohexane, *N*-(hydroxyethyl)-*N*-methyl perfluoro C_{4-8}-alkane sulphonamides-blocked
89	306975-85-9	2-Propenoic acid, 2-methyl-, dodecyl ester, polymers with *N*-(hydroxymethyl)-2-propenamide, 2-[methyl[(perfluoro-C_{4-8}-alkyl)sulphonyl]amino]ethyl methacrylate, stearyl methacrylate and vinylidene chloride
90	306976-25-0	1-Hexadecanaminium, *N*,*N*-dimethyl-*N*-[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]-, bromide, polymers with Bu acrylate, Bu methacrylate and 2-[methyl[(perfluoro-C_{4-8}-alkyl)sulphonyl]amino]ethyl acrylate
91	306976-55-6	2-Propenoic acid, 2-methyl-, 2-methylpropyl ester, polymer with 2,4-diisocyanato-1-methylbenzene, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol and 2-propenoic acid, *N*-ethyl-*N*-(hydroxyethyl)perfluoro-C_{4-8}-alkanesulphonamides-blocked
92	306977-58-2	2-Propenoic acid, 2-methyl-, 3-(trimethoxysilyl)propyl ester, polymers with acrylic acid, 2-[methyl[(perfluoro-C_{4-8}-alkyl)sulphonyl]amino]ethyl acrylate and propylene glycol monoacrylate, hydrolysed, compounds with 2,2'-(methylimino)bis[ethanol]
93	306978-04-1	2-Propenoic acid, butyl ester, polymers with acrylamide, 2-[methyl[(perfluoro-C_{4-8}-alkyl)sulphonyl]amino]ethyl acrylate and vinylidene chloride
94	306978-65-4	Hexane, 1,6-diisocyanato-, homopolymer, *N*-(hydroxyethyl)-*N*-methyl perfluoro-C_{4-8}-alkane sulphonamides- and stearyl alc.-blocked
95	306979-40-8	Poly(oxy-1,2-ethanediyl), .alpha.-[2-(methylamino)ethyl]-.omega.-[(1,1,3,3-tetramethylbutyl)phenoxy]-, *N*-[(perfluoro-C_{4-8}-alkyl)sulphonyl]
96	306980-27-8	Sulphonamides, C_{4-8}-alkane, perfluoro, *N*,*N*'-[1,6-hexanediylbis[(2-oxo-3,5-oxazolidinediyl)methylene]]bis[*N*-methyl-

Sources: US EPA (2002a); US EPA (2002b); Environment Agency (2001); Consultation with Environment Canada (note that RPA reviewed a confidential draft list of PFOS precursors that was provided by Environment Canada. This was developed from the 182 PFAS that were listed in a June 2000 survey to Canadian industry (Environment Canada, 2000). The draft list will be available as an appendix in the draft screening assessment report on PFOS and its Precursors that the Departments of Environment and Health Canada will release for public comment in early 2004 (Windle, 2003)).

Appendix 2 – Indirect emissions of PFOS from PFOS-substances and PFOS-polymers

The emissions in the tables below are used in Scenarios 3 to 7 to allow for the production of PFOS in the environment through the degradation of PFOS-substances or PFOS-polymers. For each scenario the EUSES model was run with the properties of PFOS-substance or PFOS-polymer from Section 3.3.1.1 of the evaluation and the relevant emissions of the substance or polymer for that scenario (emissions in Table 3.8). From the results of this modelling for the regional scale, the rate of degradation of PFOS-substance or polymer in each compartment was determined - these values are in the columns labelled "Degradation rate" in the tables. These rates were then converted into formation rates for PFOS (as 94% in the case of PFOS-substance, 30% for polymers). These values are in the columns labelled "PFOS formation". These rates were added to the direct emissions of PFOS-salt for the scenario to give the total emissions.

Scenario 2 is not included, because in this case the PFOS-substance emissions were converted directly to PFOS before release to the environment, and added directly to the PFOS-salt releases.

Scenario 3 - PFOS-substance, half life 20.5 days.

PFOS-substance

Compartment	Degradation rate (kg/year)	PFOS formation (kg/year)	Direct release of PFOS (kg/year)	Total (kg/year)
Air	353	332	0.034	332
Waste water	-	-	1000	1000
Surface water	15.9	14.9	28.5	43.4
Agricultural soil	200	188	-	188
Industrial soil	32	30	29.5	59.5

Scenario 4 - PFOS-substance, half life 1 year.

PFOS-substance

Compartment	Degradation rate (kg/year)	PFOS formation (kg/year)	Direct release of PFOS (kg/year)	Total (kg/year)
Air	406	382	0.034	383
Waste water	-	-	1000	1000
Surface water	1.16	1.09	28.5	29.6
Agricultural soil	11.8	11.1	-	11.1
Industrial soil	11.8	11.1	29.5	40.6

Scenario 5 - PFOS-substance, half life 20.5 days plus PFOS-polymer, half life 30 years.

Polymer

Compartment	Degradation rate (kg/year)	PFOS formation (kg/year)	Combined release of PFOS from Scenario 3 (kg/year)	Total (kg/year)
Air	-	-	332	332
Waste water	-	-	1000	1000
Surface water	4.66	1.4	43.4	44.8
Agricultural soil	6130	1840	188	2028
Industrial soil	2020	606	59.5	665.5

Scenario 6 - PFOS-substance, half life 20.5 days, PFOS-polymer, half life 30 years, from selected use areas.

PFOS-substance

Compartment	Degradation rate (kg/year)	PFOS formation (kg/year)	Direct release of PFOS (kg/year)	Total (kg/year)
Air	63.2	59.4	0.034	59.4
Waste water	-	-	1000	1000
Surface water	6.08	5.72	28.5	34.2
Agricultural soil	25	23.5	-	23.5
Industrial soil	32	30.1	29.5	59.6

Polymer

Compartment	Degradation rate (kg/year)	PFOS formation (kg/year)	Combined releases of PFOS from above (kg/year)	Total (kg/year)
Air	-	-	59.4	59.4
Waste water	-	-	1000	1000
Surface water	4.59	1.38	34.2	35.6
Agricultural soil	5920	1776	23.5	1800
Industrial soil	2020	606	59.6	666

Scenario 7 - PFOS-substance, half life 20.5 days, from selected use areas.

PFOS-substance

Compartment	Degradation rate (kg/year)	PFOS formation (kg/year)	Direct release of PFOS (kg/year)	Total (kg/year)
Air	8.84	8.31	0.034	8.34
Waste water	-	-	1000	1000
Surface water	0.302	0.284	-	0.28
Agricultural soil	5.35	5.03	-	5.03
Industrial soil	-	-	1.02	1.02

Appendix 3 - Alternative calculation for releases from photolithography

The calculation of releases from photolithography in the main evaluation report includes the use of PFOS-related substances in developers in this industry. SEMI and ESIA have commented that this is not a critical use, and that such use could b phased out within the next five years. The calculations below reflect the emissions expected if this use were phased out, with no concomitant increase in the use in resists. These revised emission estimates are also used to explore the possible effect of different assumptions about the degree to which PFOS-substances degrade to PFOS-salts in the environment.

Emissions

ESIA-SEMI provided a mass balance for the use of PFOS-related substances in this area in October 2003. The key steps in this for this alternative calculation are as follows. All quantities relate to annual use in the EU.

Resist materials – 7% of substance used (46 kg) remains on wafer = 3.2 kg.
TARC materials – 40% of substance used (136 kg) remains on wafer = 54.4 kg.
BARC materials – 7% of substance used (8 kg) remains on wafer = 0.56 kg.

The wafers are then treated with developer, which for this calculation is assumed to no longer contain any PFOS-related substance. Removal of PFOS-related substance by the developer is as follows:

100% of TARC material is removed, hence 54.4 kg.
50% of resist material is removed, hence 1.6 kg.
No removal of BARC material by developer.

The revised estimate of releases to waste water is therefore 56 kg per year.

The calculation in Section 3.1.3 of the main report assumes the use of 13 kg of PFOS-related substance per year at a representative site; this amount is 4.7% of the total EU usage of 276 kg in this area (this total excludes developer). Taking the same percentage the annual release for a site would be 2.63 kg, and for 360 days operation the release would be 7.3 g/day. The regional emissions would be 10% of the total, or 5.6 kg/year, and the continental emission 50.4 kg/year. These are in terms of PFOS-substance.

Predicted environmental concentrations

The worst case assumption for the local situation is that the PFOS-substances are converted to PFOS-salt before release. The above emissions of PFOS-substances correspond to emissions of PFOS-salt as follows: local, 6.9 g/day; regional 5.3 kg/year; continental, 47.4 kg/year.

These revised emission figures have been used to examine the effect of different assumptions about the extent to which PFOS-substances break down to give PFOS. (The effects of considering different rates for the breakdown process are considered elsewhere).

Two different assumptions have been made. The first is as in the main evaluation report, so that the PFOS-substance breaks down to PFOS-salt on release. This is recognised as likely to

be an over-estimation, but provides a worst case estimate. For the second case, it is assumed that 20% of the PFOS-substance is degraded to PFOS under aerobic biodegradation treatment. The remaining 80% is released as PFOS-substance and is distributed in the environment according to the properties in Section 3.3.1.1.2. The half life in water, sediments and soil is assumed to be one year. At steady state, it is assumed that 50% of the PFOS-substance is converted to PFOS. This production of PFOS is added to the 20% emitted directly.

The results of these calculations are presented in Table A3.1. As the main area of potential concern from the main assessment is for secondary poisoning, only the concentrations relevant to this endpoint have been included here. Also included in the table are the equivalent concentrations calculated using the full releases estimated for this use area in Scenario 7 of the main report, assuming instant conversion to PFOS, but without any input from other uses.

Table A3.1 Calculated concentrations for secondary poisoning from photolithography (mg/kg)

	Main report releases, instant conversion	Reduced releases, instant conversion	Reduced releases, 20% instant, 80% indirect
Local			
Freshwater fish	2.53	0.687	0.14
Marine fish	0.35	0.095	0.019
Marine predator	0.14	0.038	7.8×10^{-3}
Earthworms	0.14	0.039	7.8×10^{-3}
Regional			
Freshwater fish	4.9×10^{-3}	1.1×10^{-3}	3.1×10^{-4}
Marine fish	4.8×10^{-4}	1.1×10^{-4}	3.1×10^{-5}
Marine predator	9.6×10^{-4}	2.2×10^{-4}	6.2×10^{-5}
Earthworms	4.4×10^{-5}	9.7×10^{-6}	6.3×10^{-6}

The assumption of reduced emissions reduces the predicted concentrations as expected. The alternative assumptions regarding the degradation of PFOS-substance to PFOS-salt also result in reduced concentrations. The calculated concentrations in freshwater and marine fish are above the PNEC of 0.0167 mg/kg in all three cases. Those for marine predators and earthworms are below the PNEC for the less conservative assumptions. All of the regional concentrations are below the PNEC.

If the less conservative PNEC of 0.067 mg/kg is used, the concentration in freshwater fish is above the PNEC for the local scenario.

Appendix 4 – Alternative calculations for fire fighting foam use

The estimation of emissions to the environment from the use of PFOS-containing fire fighting foams in the main evaluation assumes that 15% of the amount stockpiled is used in one year. This is in line with the overall level of use of foams in the UK for 2002. However, the level of use of PFOS-containing foams for this period was only 0.5%. The higher value was used for a number of reasons. It was felt that the low use may be due to holders trying to minimise the use of this type of foam, or due to a limited occurrence of the type of fire requiring their use. If the level of use was only 0.5%, then for a 20-year shelf life around 90% of the foam would be disposed of at the end of its life without being used, which seemed high. However, a calculation has been performed assuming the lower rate of use to apply.

For the UK stockpile of 76,000 litres of PFOS-containing foam concentrates, use of 0.5% per year is 380 litres of foam, or 380 kg assuming a density of 1 kg/l. At a content of 1% in the concentrate, this contains 3.8 kg of PFOS-salt. The main report considers the use of 1% of the annual total at a single fire. In this calculation that would be only 3.8 litres of foam, which seems too small. Therefore in this case use of 10% at one (worst case) fire is assumed, giving a release of 0.38 kg. As in the main report, this is assumed to go either to drain and to soil (50% each, so 0.19 kg each), or to waste water treatment (100%, so 0.38 kg) for calculation of local concentrations.

Assuming the UK emissions to be 20% of those in the EU, the total EU emissions are 19 kg. The regional emission is 0.95 kg/year, with half to surface water and half to soil. The continental emissions are 8.55 kg/year, again split equally between surface water and soil.

These revised emissions have been used to replace those from fire fighting foams in Scenario 1 and the calculations of concentration repeated. The resulting concentrations are included in Table A4.1 Only the local and regional concentrations in surface water and freshwater fish for secondary poisoning have been included as the most significant for the evaluation. The relevant PEC/PNEC ratios are also included.

Table A4.1 Revised concentrations for fire fighting foam use

Use area	Freshwater (mg/l)	PEC/PNEC	Fish (mg/kg)	PEC/PNEC
Use A	9.54×10^{-3}	0.38	0.279	16.8
Use B	0.0137	0.55	0.312	18.7
Regional	3.7×10^{-5}	0.001	0.207	12.4

The revised scenario has no risks to the freshwater environment from direct effects for either use pattern. However, both use patterns and the regional concentration indicate a possible risk through secondary poisoning. The regional concentration in water is reduced by less than 1% from that in the main report.

Appendix 5 - Effects of the half life for PFOS-substance degradation

Scenarios 3 and 4 in the main report explore the effect of differing degradation rates for PFOS-substances. The degradation rates used in these scenarios are 20.5 days and 1 year respectively. The effect of the change is masked to some degree in the main report as there are also direct releases of PFOS-salts in these scenarios, although Appendix 2 shows the contribution from PFOS-substance degradation for the two scenarios. To make the effect clearer and to consider other aspects of degradation, calculations have been performed on the emission estimates for Scenario 7 with different values for the degradation rates in the various compartments.

For water, sediment and soil, half lives of 20.5 days and 1 year, as in the main assessment, and 10 years have been used. As in the main report, the model has been run using the properties for PFOS-substances in Section 3.3.1.1.2, and the PFOS-substance emissions relevant for Scenario 7 from Table 3.8. From the results of the modelling, the degradation rates for PFOS-substance (as kg/year) have been calculated. In this case they have not been converted to the equivalent production rate of PFOS. The results are in Table A5.1 .

Table A5.1 Degradation rates for PFOS-substances assuming different half lives in water, sediment and soil.

	Half life		
Compartment	20.5 days	1 year	10 years
Air	8.84	9.92	10.7
Surface water	0.3	0.02	0.002
Soil	5.35	3.14	1.4
Total	16.5	13.1	12.1

As the half life in the three compartments increases, the amount degraded in the air compartment increases, that in water decreases significantly, and that ion soil decreases more slowly. The overall total input is reduced, but only by ~25% over the range of half lives.

From the above, degradation in the air compartment is a significant route for PFOS-substance in the model, and if conversion to PFOS is assumed then it is a significant source of PFOS in terms of indirect production. The half-life used above is 16 hours, calculated using the AOP program. This half-life is strictly for the initial reaction of the substance with OH radicals rather than for the production of PFOS or other species. To investigate the effect of variation in this half-life, calculations were performed with values of 160 and 1600 hours in addition to the original 16 hour value. These were performed with the half-life of 1 year for water, sediment and soil and the other values the same as above. The results are in Table A5.2 .

Table A5.2 Degradation rates for PFOS-substances assuming different half lives in air (kg/year)

	Half life		
Compartment	16 hours	160 hours	1600 hours
Air	9.92	2.08	0.30
Surface water	0.02	0.02	0.02
Soil	3.14	3.14	3.14
Total	13.08	5.24	3.46

In this case, the increasing half-life in air results in a lower amount being degraded in air but no change in the amounts in other compartments. Overall the amount degraded in the system (and potentially producing PFOS) decreases.

The amounts degraded were assumed to be converted into PFOS on a 1:1 basis. Taking these as the only emissions the resulting regional concentrations in freshwater were 0.21, 0.085 and

0.057 ng/l for 16, 160 and 1600 hours respectively. Hence a change of two orders of magnitude in the half life results in a decrease of ~4 times in the concentration.

Appendix 6 - Effect of choice of log Kow value for polymer

Calculations were performed with EUSES using the releases of polymer for Scenario 6 from the main report. The data from the main report (Table 3.16) were used, but the value for the log Kow was 6, 8 or 10. The concentrations in the compartments for the regional scale are presented in Table A6.1.

Table A6.1 Concentrations of PFOS-polymer in regional model

Compartment (units)	Log Kow = 6	Log Kow = 8	Log Kow = 10
Surface water (mg/l)	$5.4x10^{-5}$	$2.45x10^{-5}$	$2.26x10^{-5}$
Sea water (mg/l)	$5.4x10^{-6}$	$2.22x10^{-6}$	$1.89x10^{-6}$
Air (mg/m^3)	$4.5x10^{-7}$	$1.24x10^{-7}$	$4.33x10^{-9}$
Agricultural soil (mg/kg)	0.0314	0.0421	0.044
Natural soil (mg/kg)	0.0112	$7.29x10^{-3}$	$3.55x10^{-4}$
Industrial soil (mg/kg)	0.257	0.59	0.815
Freshwater sediment (mg/kg)	0.187	0.603	0.649
Marine sediment (mg/kg)	0.0199	0.125	0.161

The calculated rates of PFOS-salt formation from the degradation of the polymer are in Table A6.2.

Table A6.2 Production of PFOS-salt from PFOS-polymer (in kg/year):

Compartment	Log Kow = 6	Log Kow = 8	Log Kow = 10
Surface water	1.38	0.62	0.58
Agricultural soil	1776	2382	2490
Industrial soil	606	1389	1920

The regional concentrations of PFOS-salt resulting from the polymer emissions for Scenario 6 and log Kow values of 6 or 10 are shown in Table A6.3.

Table A6.3 Regional PFOS-salt concentrations from polymer emissions

Compartment (units)	Log Kow = 6	Log Kow = 10
Surface water (mg/l)	$7.98x10^{-5}$	$1.13x10^{-4}$
Sea water (mg/l)	$7.87x10^{-6}$	$1.11x10^{-5}$
Air (mg/m^3)	$2.74x10^{-10}$	$3.74x10^{-10}$
Natural soil (mg/kg)	$1.32x10^{-4}$	$1.61x10^{-4}$
Soil pore water (mg/l)	$2.49x10^{-4}$	$3.33x10^{-4}$

The change in concentration in all compartments is less than a factor of two for the four order of magnitude change in the log Kow value.

Appendix 7 – Contribution of use areas to overall emissions

Table A7.1 presents the estimated emissions to the regional model from each of the use areas according to the various scenarios. All emissions in the table are total emissions, i.e. the combined value for all compartments. For PFOS-salts these are the direct emissions. For PFOS-substances, these are the emissions estimated based on the various assumptions about the rate of degradation to PFOS-salt. The same is true for the PFOS-polymer contributions where relevant. The percentage which each source contributes to the total emission is also given.

Table A7.1 Summary of Emissions based on Scenarios

Use	Regional release (kg/year)	Percentage
Scenario 1 – PFOS-salt		
Chrome plating	1000	94.4
Photography (film production)	0.71	0.07
Aviation	1.46	0.14
Fire fighting foams	57	5.4
Scenario 2 – PFOS-salt plus instant release of PFOS-substance		
Chrome plating	1000	48.8
Photography (film production)	0.71	0.03
Aviation	1.46	0.05
Fire fighting foams	57	2.8
PFOS-substances (total) of which:	991	48.3
Photolithography	23.5	1.2
Photography (developing)	0.71	0.03
Textiles (treatment)	3.2	0.16
Textiles (service life)	169.5	8.3
Paper treatment	753	36.7
Coatings	42.5	2.1
Scenario 3 – PFOS-salt plus PFOS-substance with 20.5 day half life		
Chrome plating	1000	61.5
Photography (film production)	0.71	0.04
Aviation	1.46	0.09
Fire fighting foams	57	3.5
PFOS-substances (total) of which:	568	34.9
Photolithography	13.6	0.84
Photography (developing)	0.4	0.02
Textiles (treatment)	1.8	0.11
Textiles (service life)	97.1	6.0
Paper treatment	431	26.5
Coatings	24.4	1.5
Scenario 4 – PFOS-salt plus PFOS-substance with 1 yr half life		
Chrome plating	1000	67.1
Photography (film production)	0.71	0.05
Aviation	1.46	0.10
Fire fighting foams	57	3.8
PFOS-substances (total) of which:	431	28.9
Photolithography	10.3	0.7
Photography (developing)	0.3	0.02
Textiles (treatment)	1.38	0.09
Textiles (service life)	73.7	5.0
Paper treatment	327	21.9
Coatings	18.5	1.2

Scenario 5 - PFOS-salt plus PFOS-substance with 20.5 day half life plus PFOS-polymer		
Chrome plating	1000	24.1
Photography (film production)	0.71	0.02
Aviation	1.46	0.04
Fire fighting foams	57	1.4
PFOS-substances (total) of which:	568	13.7
Photolithography	13.6	0.33
Photography (developing)	0.4	0.01
Textiles (treatment)	1.8	0.04
Textiles (service life)	97.1	2.3
Paper treatment	431	10.4
Coatings	24.4	0.6
PFOS-polymer (total) of which:	2517	60.7
Textile (treatment)	46	1.1
Textiles (service life)	2471	59.6
Scenario 6 – PFOS-salt plus PFOS-substances with 20.5 day half life plus PFOS-polymers for current uses		
Chrome plating	1000	27.5
Photography (film production)	0.71	0.02
Aviation	1.46	0.04
Fire fighting foams	57	1.6
PFOS-substances (total) of which:	119	3.3
Photolithography	14.5	0.4
Photography (developing)	0.43	0.01
Textiles (treatment)	104	2.9
PFOS-polymer (textile service life)	2454	67.6
Scenario 7 – PFOS-salts plus PFOS-substances with 20.5 day half life for continuing uses		
Chrome plating	1000	98.4
Photography (film production)	0.71	0.07
Aviation	1.46	0.14
PFOS-substances (total) of which:	14.5	1.4
Photolithography	14.1	1.4
Photography (developing)	0.4	0.04

Appendix 8 - Effect of varying solubility and air-water partitioning values for PFOS-salt

The following calculations were performed using the emissions from Scenario 1, i.e. emissions of PFOS-salt only. The property values from Table 3.14 were used for all properties except solubility, where the two values of 519 mg/l (as in Table 3.14) and 680 mg/l were used. For these two calculations the air-water partition coefficient was 3.19×10^{-4} Pa m^3 $mole^{-1}$ (1.35×10^{-7} dimensionless). A further calculation using a Henry's law constant of 2×10^{-6} (dimensionless) and the solubility of 680 mg/l was carried out. The resulting concentrations in water are presented in the table.

	Concentration in water (mg/l)		
Use area	**sol = 519 mg/l**	**sol = 680 mg/l**	**Ka-w = 2×10^{-6}**
Chromium plating	4.52×10^{-5}	4.52×10^{-5}	4.52×10^{-5}
Photography - formulation	1.21×10^{-4}	1.21×10^{-4}	1.21×10^{-4}
Aviation	9.28×10^{-5}	9.28×10^{-5}	9.28×10^{-5}
Fire fighting foams - formulation	0.0973	0.0973	0.0973
- use A	0.0285	0.0285	0.0285
- use B	0.0411	0.0411	0.0411
Regional	3.87×10^{-5}	3.87×10^{-5}	3.87×10^{-5}

Variation in the values of these properties over these ranges has no impact on the predicted concentrations.