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THE WORKING PARTY ON CHEMICALS, PESTICIDES AND BIOTECHNOLOGY**

**ENV/JM/MONO(2006)36**  
**Unclassified**

**RESULTS OF THE 2006 SURVEY ON PRODUCTION AND USE OF PFOS, PFAS, PFOA, PFCA,  
THEIR RELATED SUBSTANCES AND PRODUCTS/MIXTURES CONTAINING THESE  
SUBSTANCES**

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AND USE OF PFOS, PFAS, PFOA, PFCA, THEIR  
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INTER-ORGANIZATION PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS

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Paris 2006**

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## FOREWORD

The 36<sup>th</sup> Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology (4-6 February 2004) endorsed the collection of data on production, importation and use of PFOS, PFAS, PFOA, their related substances and products/mixtures containing these substances. The data were collected for the year 2003 via an OECD questionnaire in 2004. The questionnaire was also forwarded via UNEP to all Designated National Authorities (DNA) for the implementation of the Rotterdam Convention and to the Focal Points of the Stockholm Convention.

At the 37<sup>th</sup> Joint Meeting (17-19 November 2004), responses to the survey from 25 OECD and non-OECD countries and the European Commission were discussed. The Joint Meeting agreed that a further survey of these chemicals would be undertaken in 2006 (and every two years thereafter), and that a list of relevant chemicals with CAS numbers be developed to assist countries reporting at the next round of data collection.

Australia compiled preliminary lists of fluorinated chemicals in 4 groups, to support the 2006 survey on the production and use of fluorinated compounds. The 38<sup>th</sup> Joint Meeting (8-10 June 2005) accepted the draft preliminary lists. The 39<sup>th</sup> Joint Meeting (15-17 February 2006) declassified the "Preliminary Lists of PFOS, PFAS, PFOA and Related Compounds and Chemicals that may degrade to PFCA" [ENV/JM/MONO(2006)15], and reviewed the draft questionnaire for the 2006 OECD survey.

This document presents the results of the 2006 survey of production and use information on PFOS, PFAS, PFOA, PFCA, their related substances and products/mixtures containing these substances, concerning the 2005 situation (or 2004 if 2005 data did not exist). The 40<sup>th</sup> Joint Meeting (15-17 November 2006) reviewed the results of the 2006 survey and agreed to their declassification.

This document was prepared by Australia on the basis of the responses received mainly by 8 September 2006. Responses received after that date from three countries are also included in this document.

This document is published on the responsibility of the Joint Meeting of the Chemicals Committee and Working Party on Chemicals, Pesticides and Biotechnology.

## INTRODUCTION

The questionnaire for the 2006 survey was sent to OECD member countries on 25 April 2006 and responses were requested by 31 July 2006. The questionnaire was also sent at the end of May 2006 via UNEP to all Designated National Authorities (DNA) for the implementation of the Rotterdam Convention and to the Focal Points of the Stockholm Convention.

This paper summarises the responses to the 2006 questionnaire. Responses received from OECD member countries, non-OECD countries, European Commission and some companies manufacturing these chemicals have been included in this paper. Definitions of the substances included in the survey are reproduced below.

Perfluorooctane sulfonate (PFOS) refers to fully fluorinated (eight-carbon chain length) sulfonate-containing substances. The acid form of PFOS is 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonic acid (CAS No. 1763-23-1). PFOS related substances may be salts of PFOS, e.g. potassium, lithium, ammonium or diethanolamine, or polymers that contain the PFOS as a portion of the entire structure.

Perfluoroalkyl sulfonate (PFAS) is a generic term used to describe any fully fluorinated carbon chain length sulfonate, including higher and lower homologues as well as PFOS. PFAS related substances may be salts of PFAS, or polymers that contain the PFAS as only a portion of the entire polymer. For the purposes of the questionnaire, this group included PFAS and PFAS related substances (with a fully fluorinated four and more carbon chain length) other than PFOS and PFOS related substances mentioned above.

Perfluorooctanoic acid (PFOA), or pentadecafluorooctanoic acid, is a fully fluorinated eight-carbon chain carboxylic acid (CAS No. 335-67-1). PFOA related substances may be salts of PFOA or polymers that contain PFOA as only a portion of the entire polymer. PFOA is primarily a reactive intermediate, while its salts, such as ammonium perfluorooctanoate, are used as processing aids in the production of fluoropolymers and fluoroelastomers and in other surfactant uses.

Perfluorocarboxylic acid (PFCA) is a generic term used to describe any fully fluorinated carbon chain length carboxylic acid, including PFOA. For the purposes of the questionnaire, this group included PFCA and PFCA related substances (with a fully fluorinated four and more carbon chain length) other than PFOA and PFOA related substances mentioned above.

PFCA related substances may be salts of PFCA or polymers that contain PFCA as a portion of the entire polymer. PFCA related substances also include PFCA precursors, which are chemicals that can break down to form PFCA.

## DATA COLLECTION AND METHODOLOGY OF ANALYSIS

Responses were received from 17 OECD countries, 6 non-OECD countries and 2 companies. The European Chemicals Bureau (ECB) provided information on these chemicals from the IUCLID database.

Australia	Belgium	Brazil	Canada
Cyprus	Finland	Denmark	Gambia
Germany	Ireland	Italy	Jamaica
Japan	Korea	New Zealand	Norway
Oman	Romania	Slovak Republic	Sweden
Switzerland	Turkey	United States	

Data were collected on production, import and use of the above substances for the year 2005 (or 2004 if 2005 did not exist). Most countries provided the manufacture and importation data for 2005; however, data for 2005 was not available to some countries. Two countries provided data for 2004 and 1 country for 2003. It was assumed that the information provided for 2003 or 2004 were indicative for 2005 and all these data were combined for estimating total volumes.

One country provided information on a perfluorocarbon substance. Since this chemical is not within the scope of the survey it was not included in the analysis. Five countries provided negative responses (Cyprus, Jamaica, Oman, Slovak Republic and Turkey).

Most countries provided information on volumes manufactured and imported as ranges due to confidentiality of business information or regulatory restrictions. Some of the responses provided included all the data requested, such as chemical name, CAS numbers, volumes, use information, and concentrations when present in a mixture/product. These responses are indicated as complete responses. Responses where data such as name or volumes were not provided are designated as incomplete responses.

Importation could not be easily distinguished from manufacture for several responses. In these cases, data could only be compiled on the total trade of chemicals or products. Therefore, the total volumes could exceed the actual amount in trade if a substance is counted twice, i.e. for both manufacture and importation in two different countries.

The total volume for an individual chemical group is expressed in this paper in volume ranges, because as mentioned earlier, a number of countries provided the volumes (manufactured/imported) in ranges. In estimating total quantities, for data such as <1000 kg, a range that includes one tenth volume of the full volume (e.g. 100-1000 kg) is used.

A comparison of the 2006 survey results with the 2004 survey is difficult, the main reason being deficiencies in both sets of data. Altogether 17 OECD member countries responded in 2004 and 17 in 2006. Among them, only 13 countries provided responses to both surveys. Other factors include wide volume ranges of chemicals, wide ranges of volumes and/or concentrations of products/mixtures, and insufficient details on use.

A brief discussion is included in this paper evaluating the usefulness of the Preliminary OECD Lists of PFOS, PFAS, PFOA and related compounds, and chemicals that may degrade to PFCA.

### Perfluorooctane sulfonate (PFOS) related Substances

For the 2006 survey, four countries reported manufacture and 7 countries importation of PFOS related substances while 4 countries reported manufacture and 9 countries importation of products/mixtures containing PFOS related substances.

#### *Manufacture/Importation of PFOS related Substances*

Data from the complete responses to the 2006 survey indicate that a total volume of 73-162 tonnes of PFOS related compounds were *manufactured* in 2005. The chemicals manufactured in high volumes were:

- heptadecafluorooctane sulphonyl fluoride (CAS No. 307-35-7) - up to 70 tonnes
- tetraethylammonium heptadecafluorooctanesulphonate (CAS No. 56773-42-3) - up to 30 tonnes
- potassium heptadecafluorooctane-1-sulphonate (CAS No. 2795-39-3) - up to 20 tonnes
- N-ethyl-heptadecafluorooctane sulphonamide (CAS No. 4151-50-2) - 17 tonnes

The manufactured volumes for other 7 PFOS related substances were less than 10 tonnes per annum:

- 1-Octanesulfonamide, N-[3-(dimethylamino)propyl]-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro- (CAS No. 13417-01-1) - less than 1 tonne
- 1-Propanaminium, 3-[[heptadecafluorooctyl)sulfonyl] amino]-N,N,N-trimethyl-, iodide (CAS No. 1652-63-7) - less than tonne
- 1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, ammonium salt (CAS No. 29081-56-9) - less than 1 tonne
- Poly(oxy-1,2-ethanediyl),  $\alpha$ -[2-[[heptadecafluorooctyl) sulfonyl] propylamino] ethyl]- $\omega$ -hydroxy- (CAS No. 52550-45-5) - less than 1 tonne
- 1-Octanesulfonamide, N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6, 7,7,8,8,8-heptadecafluoro-N-[3-(trimethoxysilyl)propyl]- (CAS No. 61660-12-6) - less than 1 tonne
- 1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro- (CAS No. 1763-23-1) - 1-10 tonnes
- 1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-, lithium salt (CAS No. 29457-72-5) - 1-10 tonnes

One country reported an *importation* volume of 10-30 tonnes of heptadecafluorooctane sulphonyl fluoride in 2005.

Four countries reported a total of 1.5-12 tonnes of importation of PFOS related substances, but exact identities of the chemicals were not provided. In addition, import of 4 PFOS related substances by one country was reported, but the quantities were not provided.

One country indicated importation but the volume units were not clear, and the response has not been included here.

#### *Manufacture/Importation of Products/Mixtures*

Based on the complete responses to the 2006 survey, 3 countries manufactured/imported 7 products containing 3 PFOS related chemicals. Concentrations of PFOS related substances in these products/mixtures were low (<10%) except one product that contained 25% heptadecafluoro-octanesulphonic acid, compound with 2,2'-iminodiethanol (1:1) (CAS No. 70225-14-8). Tetraethyl-ammonium heptadecafluorooctanesulphonate was the main compound found in products/mixtures, and appeared in 4 products.

From the incomplete responses to the 2006 survey, 14-24 tonnes of products/mixtures containing PFOS related substances were manufactured/imported, but the exact identities are not known. Fourteen PFOS related substances were reported in the products/mixtures, but the quantities are unknown.

	Countries that manufacture/import	Number of chemicals	Concentration	PFOS volume (tonnes)
<b>Complete data</b>				
Chemical	5	11	Technical grade	73-162
Product/Mixture	3	3	0.0005-25%	<0.01
<b>Incomplete data</b>				
Chemical	4	4	Technical grade	1.5-12
Product/Mixture	9	14	0-100%	(14-24)
Total	-	-	-	74-175

The volume in brackets is not included in the total volume as it indicates volume of products.

### *Use Information*

The 2006 survey results showed that up to 90 tonnes of PFOS related substances, mainly heptadecafluorooctanesulphonyl fluoride (CAS No. 307-35-7), were used as intermediates in industrial applications. The use patterns of end-use products containing these intermediates were unknown, but it is likely that the intermediates were used to produce some of the products for the uses described below.

Both tetraethylammonium heptadecafluorooctanesulphonate (CAS No. 56773-42-3) and potassium heptadecafluorooctane-1-sulphonate (CAS No. 2795-39-3) were used in the mining industry as a mist suppressing agent at an annual volume of up to 50 tonnes.

Approximately 20 tonnes of lithium heptadecafluorooctanesulphonate (CAS No. 29457-72-5) and heptadecafluorooctane-1-sulphonic acid (CAS No. 1763-23-1) were used as an antireflective agent in photographic industry.

Other industrial uses of PFOS related substances at less than 10-tonne include as a component in photo-resist formulations/anti-reflective coatings in the photo-microlithography processes to produce semiconductors or other electronic or miniaturized devices; as an anti-erosion additive of hydraulic fluids in aviation industry; as surfactants in metal plating industry including galvanisation; and as anti-foam agents in fire-fighting industry. Low volume of PFOS related substances were also used in sealant and adhesive products.

PFOS related products used as Class B fire fighting foam continue to be held in stock, at many end-user sites with flammable material such as petrol, oil and paper.

Three new uses of PFOS related substances were identified in this 2006 survey. Seventeen tonnes of N-ethyl heptadecafluorooctane sulphonamide (CAS No. 4151-50-2) was used as an ingredient in insecticide products at a concentration of 0.01-1%. The insecticides were for industrial uses in areas such as highways, railroads, pipelines and high-voltage lines, as well as for consumer uses like granulated bait for amateur gardening. In addition, less than 1 tonne of N-ethylheptadecafluoro-N-[3-(trimethoxysilyl)propyl] octanesulphonamide (CAS No. 61660-12-6) was reported to be used as an additive in toner or printing inks.

### *Trend*

Based on the 2004 OECD survey, PFOS related substances were manufactured in 4 countries and altogether 10 countries had manufacturing/importation activities with 13 PFOS related substances in 2003.

In this 2006 survey, neither manufacturing nor importation of PFOS related substances was reported in 12 countries. Two countries reported that use of PFOS compounds had been phased out by 2001-2002; one country indicated 2003 and a few countries also reported that use had been phased out in 2005.

For the 2006 survey, 14 countries reported manufacture/importation activities of 20 PFOS related substances or products/mixtures containing these compounds. Four countries manufactured PFOS related substances and 4 countries formulated PFOS containing products/mixtures in 2005. And 9 countries showed importation of products/mixtures containing PFOS compounds occurred in 2005.

In the 2004 survey, more than 3 000 tonnes of PFOS compounds were reported to be manufactured/imported in 2003. The EU estimated a volume of up to 10 000 tonnes (10 chemicals with up to 1000 tonnes each). While the combined volume of PFOS related substances, from both complete and incomplete responses in the 2006 survey, is 74-175 tonnes.

The use patterns of PFOS related substances are similar in both the 2004 and 2006 survey responses. It is not clear if the uses in insecticides, toners and printing inks are new or have been in existence, since the countries that reported these uses for the 2006 survey had not responded to the 2004 survey.

This 2006 survey included a question on PFOS alternatives. The specific identities of replacements or substitutes for PFOS related substances have been claimed as confidential business information. In general, these substances include lower homologue perfluoroalkyl sulfonates (PFAS) and various fluorinated telomers. 3M has commercialised some substitutes for the protective treatment of carpet, textiles and leather products. Perfluorobutane sulfonate (PFBS) has been introduced as an alternative for PFOS related substances as a surfactant in coating products, and as a mist suppression agent in mining industry.

### **Perfluoroalkyl sulfonate (PFAS) related Substances**

For the 2006 survey, 5 countries reported manufacture and 6 countries importation of PFAS related substances while 7 countries manufactured and 10 imported products/mixtures containing PFAS related substances.

#### ***Manufacture/Importation of PFAS related Substances***

Analysis of the complete responses to the 2006 survey indicated that 3 countries manufactured/imported 3 PFAS related substances in 2005, all 3 chemicals were perfluorobutane sulfonate (PFBS) based substances. The chemicals were:

- 1-butanefulfonic acid, 1,1,2,2,3,3,4,4,4-nonafluoro-, potassium salt (CAS No. 29420-49-3) – 50 to 160 tonnes
- 1-butanefulfonyl fluoride, 1,1,2,2,3,3,4,4,4-nonafluoro- (CAS No. 375-72-4) – 40 to 60 tonnes
- bis-[2-(N-methylperfluorobutane sulfonamido)ethoxy] phosphoric acid (CAS No. 120945-47-3) – 20 to 50 kg.

In addition, 7 countries provided incomplete responses to the 2006 survey on PFAS related substances. Only 1 compound, PFBS potassium salt, was identified with probably another 4 PFBS based substances. The total volume was 1 to 2.4 tonnes in 2005.

#### ***Manufacture/Importation of Products/Mixtures***

Four PFAS related substances from 3 countries were identified in the complete responses to the 2006 survey. The total amount of PFAS compounds in the product was approximately 10 kg. Two PFAS related substances, one C9 and another C10 compound, appeared in one product at less than 25% concentration. The other two C6 PFAS related substances were at low concentrations of <0.05% in products.

The incomplete responses to the 2006 survey indicated that 8 countries imported/manufactured products containing 29 PFAS related substances. Among these PFAS related substances, the compounds with perfluorinated carbon chains of C4, C5, C6 and C7 were in 6, 5, 6 and 6 products respectively, with a few mixtures of C4-8, C7-8 and cyclohexane-sulfonic acid derivatives. The concentrations of PFAS related substances in the products varied from 0-100%. Volume of the products/mixture was 12 tonnes that may contain less than 1 tonne PFAS related substances.

	Countries that manufacture/import	Number of chemicals	Concentration	PFAS volume (tonnes)
<b>Complete responses</b>				
Chemical	3	3	Technical grade	90-220
Product/Mixture	3	4	0.0005-25%	0.01
<b>Incomplete responses</b>				
Chemical	7	1	Technical grade	1.0-2.4
Product/Mixture	8	29	0-100%	(11.6)
Total				91-222

### *Use Information*

Up to 160 tonnes of PFBS based substances were used in 2005 as manufacturing intermediates for the production of catalysts, and for other PFAS related substances. About 30-50 tonnes PFBS based compounds were used as flame retardants and another 10 tonnes as an additive in plastics. Other uses with low concentrations of PFBS chemicals include additive in industrial coating products (less than 500 kg), in acid mist suppression formulations (about 50 kg), in rubber moulding and as defoamer in electroplating industry. Minimal amount of PFBS based substances were used as analytical reagents in laboratories.

Smaller amounts of PFAS related substances (approximately 1 kg) with longer perfluorinated carbon chains (C4-C10) were used in wax, varnish and paint products, floor sealers, alcohol resistant fire-fighting foams and in the semiconductor industry.

### *Trend*

#### **2003**

Number of countries	Number of chemicals	Total quantity
7 (5 manufacture)	55	130-207 tonnes
ECB	6	Up to 6 000 tonnes

#### **2005**

Number of countries	Number of chemicals	Total quantity
8 (5 manufacture)	4	90-220 tonnes

The new uses identified in 2005 were as catalysts, fire-retardants, and additives in plastic and rubber products.

PFAS related substances in this 2006 survey refer to the sulfonate compounds with a C<sub>≥</sub>4 perfluorinated carbon chain. However, most countries in this survey indicated that PFBS based substances (C4) were the main PFAS compounds used.

### **Perfluorooctanoic acid (PFOA) and related Substances**

For the 2006 survey, three countries reported manufacture and 8 countries importation of PFOA related substances while 6 countries manufactured and 8 countries imported products/mixtures containing PFOA related substances.

***Manufacture/Importation of PFOA related Substances***

Complete responses to the 2006 survey indicate that 4 countries manufacture/import 4 PFOA related substances. These were PFOA, PFOA ammonium salt (CAS No. 3825-26-1) and PFOA sodium salt (CAS No. 335-95-5). The PFOA was either in the linear form as pentadecafluorooctanoic acid (CAS No. 335-67-1) or as a mixture of the linear and branched forms (branched pentadecafluorooctanoic acid, CAS No. 90480-55-0). The volumes of PFOA, PFOA ammonium salt and PFOA sodium salt in 2005 were up to 10 tonnes, 260 tonnes and 10 tonnes, respectively.

Three countries provided incomplete responses to the 2006 survey on PFOA related substances. One country imported 100-1 000 kg of a PFOA related substance, but the chemical identify was not reported while another country reported that pentadecafluorooctanoic acid (CAS No. 335-67-1) was imported in 2005 without providing details of volume.

***Manufacture/Importation of Products/Mixtures***

The complete responses to the 2006 survey indicate that 3 countries manufacture/import PFOA-containing products/mixtures. Two PFOA related substances, ammonium pentadecafluoro-octanoate (CAS No. 3825-26-1) and sodium pentadecafluorooctanoate (CAS No. 335-95-5), were identified in the products with volumes ranging between 2-18 tonnes and 6-7.5 kg, respectively. The concentrations of PFOA ammonium salt in products varied from 1 ppm to 30%, and the concentration of PFOA sodium salt in products was reported as 3 ppm.

Eight countries provided incomplete responses to the 2006 survey with one compound (PFOA ammonium salt) identified in products/mixtures with no volume data and a volume of approximately 45 tonnes of PFOA related substances reported without chemical names.

In addition, one country reported that a total of 15-80 g PFOA existed as an impurity in more than 15 tonnes of imported products/mixtures in 2005.

	<b>Countries that manufacture/import</b>	<b>Number of chemicals</b>	<b>Concentration</b>	<b>PFOA volume (tonnes)</b>
<b>Complete responses</b>				
Chemical	4	4	Technical grade	66-302
Product/Mixture	3	2	0.0001-30%	2-18
<b>Incomplete responses</b>				
Chemical	3	1	Technical grade	0.1-1
Product/Mixture	8	1	0.004-10%	(45-46)
Total	-	-	-	69-320

The volume in brackets is not included in the total volume as it indicates volume of products.

***Use Information***

Almost all of the PFOA related substances, mainly ammonium pentadecafluoro-octanoate, (CAS No. 3825-26-1) and pentadecafluorooctanoic acid (CAS No. 335-67-1), were used in 2005 as polymerisation aids in the manufacture of fluoropolymers and as a constituent in aqueous fluoropolymer dispersions. Small volumes of PFOA related substances were used as industrial dedusting products and as a laboratory chemical. The fluoropolymer dispersions were formulated into paints, photographic film additives and in the textile finishing industry. Products/mixtures containing PFOA related substances were for industrial uses only, however, some paintings could be for consumer use as well. The fluoropolymer resin was used for glass fibre impregnation in tubes, cables and tapes for industrial use.

One of the countries indicated that coated products are thermally treated (sintered) during the industrial coating processing. Consequently, the PFOA substance was removed and destroyed during the process. Industries also have implemented technologies to remove the ammonium salt of PFOA from aqueous dispersion products of fluoropolymers to a low level, such as less than 100 ppm. Some companies committed to transfer all their products to that standard by 2005. The PFOA ammonium salt removed from dispersions were recovered and recycled in the processes.

### *Trend*

#### **2003**

Number of countries	Number of chemicals	Total quantity
10 (5 manufacture)	11	291-1 000 tonnes
ECB	2	Up to 2 000 tonnes

#### **2005**

Number of countries	Number of chemicals	Total quantity
8 (3 manufacture)	4	66-303 tonnes

For the 2006 survey, one country indicated that manufacture of PFOA related substance had been phased out in 2002 and some other countries indicated the reduction or phasing out of PFOA related substances in the future.

Use information in this 2006 survey was similar to that collected in the 2004 survey.

### **Perfluorocarboxylic acid (PFCA), related Substances and PFCA Precursors**

For the 2006 survey, 4 countries reported manufacture and 7 countries importation of PFCA related substances while 7 countries manufactured and 10 countries imported products/mixtures containing PFCA related substances.

#### *PFCA related Substances*

For the 2006 survey, one country indicated import of a product in powder form containing 100 ppm of ammonium perfluorocarboxylate (C7-13) (CAS No. 72968-38-8). The imported volume was 50 tonnes. The content of PFCA related substance was 5 kg. The product was used for coil coating for industrial use only.

#### *Manufacture/Importation of PFCA Precursors*

Complete responses to the 2006 survey showed that 4 countries manufactured/imported 22 PFCA precursors. The volumes for the perfluoro PFCA precursors and fluoro PFCA precursors were 384-2 580 tonnes and 344-3 440 tonnes, respectively. The 22 PFCA precursors manufactured/imported in 2005 included:

- 1 perfluoro-amine compound 10-100 tonnes;
- 2 perfluoro-ether compounds 240-1 140 tonnes;
- 4 perfluoro-iodide compounds 112-1 120 tonnes;
- 4 partial perfluoro compounds 22-220 tonnes;
- 3 fluoro-alcohol compounds 21-210 tonnes;
- 5 fluoro-ester compounds 212-2 120 tonnes;
- 1 fluoro phosphate compound 10-100 tonnes; and
- 2 partial fluoro compounds 101-1 010 tonnes.

An annual volume of up to 1 000 tonnes included 5 chemicals (see the use information section below). Based on the length of perfluorinated carbon chains, the number of chemicals with C4, C6, C8 and C10 were 2, 9, 9 and 2 respectively while an additional 16 chemicals had mixed perfluorinated carbon chain lengths.

The incomplete responses to the 2006 survey included 5 countries with 12 PFCA precursors. These were:

- 1 perfluoro-amine compound;
- 2 perfluoro-iodide compounds;
- 2 partial perfluoro compounds;
- 1 fluoro-ester compound;
- 2 fluoro-ether compounds;
- 1 fluoro-iodide compound;
- 2 fluoro-phosphate compounds; and
- 1 partial fluoro compound.

The total volume of these compounds is not known. Volume in the table below is from 2 countries. According to the estimation of one country, the volume in that country was 14.4-1 224 tonnes in 2005. The real volume is likely to be higher as only 2 countries provided information on quantity.

#### ***Manufacture/Importation of Products/Mixtures containing PFCA Precursors***

Complete responses to the 2006 survey provided by 2 countries indicated manufacture and importation of products containing 16 PFCA precursors. The concentrations of PFCA precursors in products ranged from very low to 50%. The volume of products was > 115 tonnes and the content of PFCA precursors were approximately 28 tonnes. The chemicals were:

- 2 perfluoro phosphonic/phosphinic compounds;
- 4 fluoro-esters;
- 1 fluoro-ether;
- 6 fluoro-phosphates;
- 1 fluoro sulfonate; and
- 2 partial fluoro compounds.

Two chemicals had a perfluorinated C6 carbon chain and the rest had mixtures of various perfluorinated carbon chains. Of the 28 tonnes of PFCA precursors, 2 fluoro-esters – 2-propenoic acid, 2-methyl-, 2-(dimethylamino) ethyl ester, polymers with  $\gamma$ - $\omega$ -perfluoro-C<sub>10-16</sub>-alkyl acrylate and vinyl acetate, acetates (CAS No. 196316-34-4) in coating products at about 25% contributed about 26 tonnes and  $\alpha$ -fluoro- $\omega$ -[2-[(1-oxo-2-propenyl)oxy]ethyl] poly(difluoromethylene) (CAS No. 65605-70-1) in paper packaging products at 18% another 1.6 tonnes.

Incomplete responses to the 2006 survey received from 8 countries, indicated that a total of 64 PFCA precursors, 8 perfluoro chemicals and 56 fluoro chemicals were used in formulated products/mixtures. Among them, there were 1 perfluoro-amine, 2 perfluoro-ethers, 1 perfluoro-iodides, 2 perfluoro phosphonic/phosphinic compounds, 2 partial perfluoro compounds, 8 fluoro-alcohols, 1 fluoro-amine, 18 fluoro-esters, 1 fluoro-ether, 2 fluoro-iodides, 9 fluoro-phosphates, 2 fluoro-sulfonates, 2 fluoro-siloxanes, 10 fluoro-thioethers, and 3 fluoro-urethanes. Based on the length of perfluorinated carbon chains the number of chemicals with C4, C6, C8, C10, C12, C14 and C16 were 3, 6, 5, 2, 2, 2 and 1, respectively. The rest had perfluorinated carbon chains of mixed lengths. The individual volume of these compounds was not reported and a total volume of 123-152 tonnes was estimated on the basis of responses from 3 countries. The actual volume is likely to be higher.

	Countries that manufacture/import	Number of chemicals	Concentration	PFCA precursor volume (tonnes)
<b>Complete Responses</b>				
Chemical	4	22	Technical grade	728-6 020
Product/Mixture	2	16	0.00004-50%	28
<b>Incomplete Responses</b>				
Chemical	5	12	Technical grade	15-1 224
Product/Mixture	8	64	0-100%	(123-152)
Total	-	-	-	771-7 273

The volume in brackets is not included in the total volume as it indicates volume of products.

### Use Information

Large volumes (443-4 440 tonnes) of PFCA precursors were used in 2005 as intermediates in various industry sectors. Four chemicals had an annual use volume between 100-1 000 tonnes. These chemicals include:

- octane, 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptafluoro-8-iodo- (CAS No. 507-63-1);
- 2-propenoic acid, 2-methyl-, 3-chloro-2-hydroxypropyl ester, polymer with 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafluorododecyl 2-propenoate, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyl 2-propenoate, N-(hydroxymethyl)-2-propenamide, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,13,14,14,15,15,16,16,16-nonacosafluorohexadecyl 2-propenoate, octadecyl 2-propenoate and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-pentacosafluorotetradecyl 2-propenoate (CAS No. 119973-85-2);
- poly (difluoromethylene),  $\alpha$ -fluoro- $\omega$ -[2-[(1-oxo-2-propenyl)oxy]ethyl]- (CAS No. 65605-70-1); and
- 1-pentanol, 2,2,3,3,4,4,5,5-octafluoro- (CAS No. 355-80-6).

Approximately 252 to 1 111 tonnes were used in 2005 as solvents for industrial uses. Chemicals used at high volumes as solvents were:

- furan, 2,2,3,3,4,4,5-heptafluorotetrahydro-5-(nonafluorobutyl)- (CAS No. 335-36-4) – 100 to 1000 tonnes;
- heptafluorotetrahydro(nonafluorobutyl)furan (CAS No. 40464-54-8) - up to 140 tonnes; and
- 1-butanamine, 1,1,2,2,3,3,4,4,4-nonafluoro-N,N-bis(nonafluorobutyl)- (CAS No. 311-89-7) - 10-100 tonnes.

Other chemicals reported were:

- 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-hexadecafluorononan-1-oic acid (CAS No. 76-21-1) – 10 to 100 tonnes used as additives in resins;
- phosphoric acid,  $\gamma$ - $\omega$ -perfluoro-C<sub>8-16</sub>-alkyl esters, compounds with diethanolamine (CAS No. 74499-44-8) and perfluoro compounds, C<sub>5-18</sub> (CAS No. 86508-42-1) - up to 100 tonnes used for paper packaging coating and other wax/polishing treatment; and
- 2-propenoic acid, 2-methyl-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptafluorodecyl ester, polymer with methyl 2-methyl propenoate (CAS No. 93705-98-7) – up to 10 tonnes in electronic industry.

PFCA precursors were also reported in coating formulations or cleaning/washing products for textile, leather, paper, glass, masonry and concrete surfaces, in anti-foam formulations, in silicone rubber products, in ink cartridges of printers and analytical laboratory uses. All these uses were at low volumes.

## **REVIEW OF THE PRELIMINARY OECD LISTS OF PERFLUORINATED CHEMICALS**

The quality of responses to this 2006 survey, particularly regarding chemical names and CAS numbers, has improved as compared to the 2004 survey. It is likely that this improvement was due to the OECD preliminary perfluorinated chemical lists as responses from several countries were in the same order as in the OECD lists.

The ECB utilised the CAS numbers of the Lists to search for PFOS, PFAS and PFOA related substances in the IUCLID. The EINECS included 640 substances and 23 substances were in the IUCLID. The ECB provided a list of 23 substances with information on companies that manufactured them.

Three perfluorinated chemicals were identified from the responses that were not included in the OECD Lists indicating that the Lists need to be updated.

## CONCLUSIONS

The 2006 OECD survey is a follow up of the 2004 survey. Due to limited responses, the current survey results do not provide a complete picture of the global production and use of perfluorinated chemicals. However, this survey has shown a phase out of several types of perfluorinated chemicals and a reduction in production volumes.

The survey of PFAS related substances shows that more PFBS based chemicals are replacing PFOS/PFOA related substances. The production volume of PFBS based compounds has increased markedly since the 2004 survey.

There is a decrease in the numbers and quantities of PFOS and PFOA related substances.

Only one PFCA related substance was reported to this 2006 survey. However, the quantities and types of PFCA precursors were much greater than that reported in the other chemical groups surveyed. In future, greater focus will be on chemicals in this group specifically relating to the degradation mechanisms, toxicity, definition of PFCA precursors and the subclasses of precursors.