PRELIMINARY STUDY ON THE ENVIRONMENTAL FRIENDLINESS OF PFOS SUBSTITUTES FOR KEY APPLICATIONS IN CHINA

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Introduction

China is the latecomer of PFOS/PFOSF production, which began the R&D activity in 1970s and the commercial production in the middle of 1980s. Just like the saying "East heats up as west cools down", the actual annual production of PFOSF in China grows rapidly after the voluntary phase-out of 3M, from 30 tons in 2001 to about 250 tons in 2008[1]. According to recent reviews, PFOS and related substances had ever been extensively used in textiles, carpets, leathers about ten years ago, while now it is not be used in these applications due to the international restriction of such applications[2]. The use amount of PFOS is very limited in semi-conductors and aviation. Currently, PFOS and related substances are mainly used in metal plating, aqueous fire-fighting foams (AFFFs) synthesis and sulfluramid formulation[1].

China just announced the entry-into-force of two amendments about newly listed POPs on March 26, 2014. It's urgent to get a clear understanding about the availability of PFOS substitutes for key applications in China. Also the environment related properties (e.g. PBT profiles) should be examined to ensure the safety of forthcoming replacement of PFOS. The present study is aiming at such purpose.

Materials and methods

A survey on available PFOS substitutes was firstly conducted with the coordination of China Association of Fluorine and Silicone Industry (CAFSI). The participants include experts from the industrial associations and companies as end users.

Some 'non-PFOS' alternatives were sampled from both producers and the market and tested in laboratory for the concentrations of C4~C8 perfluoroalkyl sulfonates (PFOS, PFHxS, PFBS) and carboxylates (PFOA, PFHxA, PFBA).As PFHxS and PFOA have been considered to be of high environmental risks, they have been included in some regulations, e.g. the long-chain perfluorinated chemicals (PFCs) action plan issued by U.S. EPA. The determination results can confirm whether some alternatives are based on these long-chain PFCs of environmental concerns. A modified method of GB/T 24169-2009 based on UHPLC-MS/MS was adopted for the quantitative analysis.

Two approaches were used for a preliminary evaluation of the environmental friendliness of found PFOS substitutes: one is to test the biodegradation and fish toxicity by experiments[3], the other is to predict using the PBT profiler (www.pbtprofiler.net) - the online software by U.S. EPA[4].

Results and discussion:

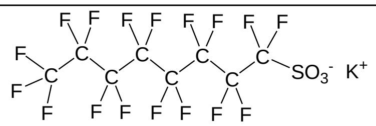
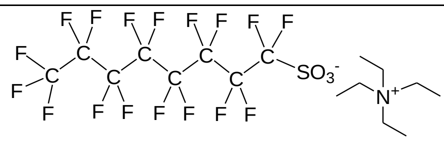
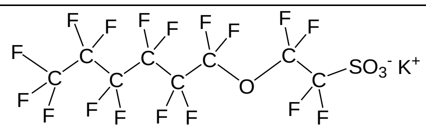
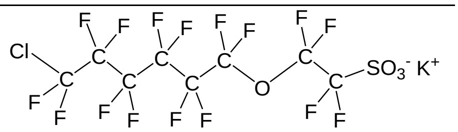
Available PFOS substitutes in Chinese market

Main PFOS substitutes can be divided into two categories: imported product and domestic product. For the former one, both PFBS and C6-telomer based products are available because the product upgrdae strategy of main organofluorine companies (e.g. 3M, DuPont, Daikin). Besides, there are some China-specific PFOS substitutes found during the survey, including:

(1) Chrome mist surpressant

Perfluoroalkyl ether potassium sulfonate (F-53, $C_8F_{17}O_4SK$) was first developed as a mist suppressant for the hard chrome plating industry, by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences in 1975. After successful demonstrations in four local electroplating plants in Shanghai, F-53 was found to be excellent in performance but high in synthesis cost. F-53B is the modified version of F-53, with the replacement of one fluorine atom by a chlorine. This modification was made to simplify the production process and reduce the cost where chlorination is used in the last step, and prevent the use of toxic and expensive chemicals (e.g. $SbCl_5$ and SbF_3). Therefore the commercialized product was F-53B instead of F-53. For several years, this compound had remained as the only available mist suppressant in the Chinese electroplating industry, until the emergence of FC-80 in 1982, and FC-248 later , which are actually both PFOS with different counter ions.

Table 1 Main mist suppressants on the Chinese market

Product Name	CAS Number	Chemical Formula	Structure
FC-80	2795-39-3	$C_8F_{17}O_3SK$	
FC-248	56773-42-3	$C_{16}H_{20}F_{17}O_3NS$	
F-53	Not available	$C_8F_{17}O_4SK$	
F-53B	73606-19-6	$C_8ClF_{16}O_4SK$	

(2) Surfactant for AFFF
Due to the historical reasons, China self-developed some fluorosurfactants for AFFF which are not based on telomer. For example, FC-4 is a fluorosurfactant for AFFF provided by Shanghai Synica Co., Ltd. Its color is creamy yellow or white. The surface tension can be less than 16.8mN/m when the concentration is 0.01-0.05%. The chemical structure of FC series fluorosurfactants of Synica can be expressed as "$C_3F_7O(CF(CF_3)CF_2O)_nCF(CF_3)CONH(CH_2)_3N^+ (CH_3)(C_2H_5)_2I^-$", the exact number of n has not been disclosed. There's no data about the environment-related properties of FC-4 in literatures. Therefore their environmental soundness needs further evaluation; in particular PBT profiles should be experimentally tested.

(3) Active ingredient (A.I.) in baits
According to the registered pesticides database maintained by the Institute for Control of Agrichemicals at the Ministry of Agriculture, currently there are three termite bait products using non-PFOS A.I. registered in China, including two imported products and a local one

Table 2 Bait products for termite control registered in China

Producer	**Name**	**A.I.**	**Content**	**Certificate No.**	**Period of Validity**	**Toxicity**
Ensystex, Inc. USA	Chlorfluazuron bait	Chlorfluazuron	0.10%	WP20100125	2010-10-27 ~2015-10-27	Low toxic
Dow AgroSciences LLC	Termite bait	Hexaflumuron	0.50%	WP20070015	2012-07-18 ~2017-07-18	Low toxic
Suzhou Jiangfeng Termite Prevention and Cure Co., Ltd	Termite bait	Hexaflumuron	0.50%	WP20090384	2009-12-24 ~2014-12-24	Slightly toxic

During the period of 2006 to 2011, a GEF project titled “Demonstration of Alternatives to Chlordane and Mirex in Termite Control” was implemented in China. Baits with hexaflumuron and chlorfluazuron as A.I. illustrated good performance of termite control during the demonstration process. Actually all three currently registered products have been involved in this project. Proven cost-effectiveness and environmentally friendliness mean such bait products are suitable in termite control. Based on the experiences from this demonstration project, the national replication is ready for implementation.

Besides, bait is also the dominant formulation of insecticide products for cockroach control. According to the registered pesticides database maintained by the Institute for Control of Agrichemicals at the Ministry of Agriculture, there are more than 100 products using non-PFOS A.I. registered in China. Some A.I. substances appeared in the table have been recommended by WHO: boric acid, chlorpyrifos, fenitrothion, fipronil, hydramethylnon, propoxur, imidacloprid. Also all products are non-POPs based and classified as slightly toxic or low toxic.

Table 3 Bait products for cockroach control registered in China

A.I.	Frequency	CAS No.	Formula
Chemical source A.I.			
Acephate	26	30560-19-1	$C_4H_{10}NO_3PS$
Imidacloprid	23	138261-41-3	$C_9H_{10}ClN_5O_2$
Propoxur	19	114-26-1	$C_{11}H_{15}NO_3$
Fipronil	14	120068-37-3	$C_{12}H_4C_{l2}F_6N_4OS$
Chlorpyrifos	12	2921-88-2	$C_9H_{11}Cl_3NO_3PS$
Boric acid	10	10043-35-3	H_3BO_3
Hydramethylnon	7	67485-29-4	$C_{25}H_{24}F_6N_4$
Fenitrothion	5	122-14-5	$C_9H_{12}NO_5PS$
Chlorbenzuron	2	35409-97-3	$C_{14}H_{10}Cl_2N_2O_2$
Tetramethrin	2	7696-12-0	$C_{19}H_{25}NO_4$
Permethrin	2	52645-53-1	$C_{21}H_{20}Cl_2O_3$
Cypermethrin	2	52315-07-8	$C_{22}H_{19}Cl_2NO_3$
Deltamethrin	1	52918-63-5	$C_{22}H_{19}Br_2NO_3$
Azamethiphos	1	35575-96-3	$C_9H_{10}ClN_2O_5PS$
Flufiprole	1	704886-18-0	$C_{16}H_{10}Cl_2F_6N_4OS$
Biological source A.I.			
Emamectin benzoate	3	/	/
Metarhizium anisopliae	2	/	/
Periplaneta fuliginosa desovirus (PfDNV)	1	/	/

Contents of long chain PFCs

High concentrations of PFHxS have been detected in several samples of domestic PFOS substitutes products. These products are mainly used in surfactants for AFFF, e.g. VF-230 (5,082 mg/L), VF-9126 (1771 mg/L), and VF-9128 (583 mg/L). Actually the producer of above products purchased the “non-PFOS” fluorocarbon surfactants from other vendors with the guarantee of non-PFOS. However, PFHxS has not been noticed by both sides and no such information was provided.

PBT concerns of F-53B

There is ample evidence that PFOS is environmentally persistent, bioaccumulative, and toxic to human and animals. The similarity in chemical structures between F-53B and PFOS makes it reasonable to assume that they possess similar physicochemical properties and environmental behaviour. However, data are lacking, with rare information available on the environmental presence and potential impact of F-53B.

As the results of our preliminary assessment, there seems to be no significant difference between F-53B and PFOS. Whilst current usage is limited to the chrome plating industry, the ban of PFOS may result in expanded usage. Future assessments on the effects of this overlooked contaminant and its presence and fate in the environment should be conducted.

(1) F-53B was found in high concentrations (43-78 μg/L and 65-112 μg/L for the effluent and influent, respectively) in wastewater from the chrome plating industry in the city of Wenzhou, China.

(2) F-53B was not successfully removed by the wastewater treatments in place. Consequently, it was detected in surface water which receives the treated wastewater at similar levels to PFOS (ca. 10-50 ng/L); and the concentration decreased with the increasing distance from the wastewater discharge point along the river.

(3) Initial data presented here suggest that F-53B is moderately toxic (Zebrafish LC50-96 h 15.5 mg/L) and is as resistant to degradation as PFOS.

PBT concerns of non-PFOS A.I. in baits

Main A.I. chemicals in the bait products as mentioned in Table 2 and 3 were evaluated using the PBT Profiler. Judged by the resulting data, all A.I. chemicals in existing bait products are not persistent organic pollutants.

Table 4 Estimated PBT prfoiles of non-PFOS A.I. in baits

No.	Name of A.I.	CAS No.	$t_{1/2}$ (d)				Percentage (%)				BCF	ChV (fish), mg/L
			Air	Soil	Sediment	Air	Air	Soil	Sediment	Air		
1	Acephate	30560-19-1	38	75	340	1.4	46	54	0	0	3.2	5,800
2	Imidacloprid	138261-41-3	60	120	540	0.1	47	53	0	0	3.2	440
3	Propoxur	114-26-1	38	75	340	0.5	33	67	0	0	3	15
4	Fipronil	120068-37-3	180	360	1,600	0.17	5	93	2	0	240	0.00094
5	Chlorpyrifos	2921-88-2	180	360	1,600	0.18	4	76	20	0	1,300	NA
6	Hydramethylnon	67485-29-4	180	360	1,600	0.096	1	49	50	0	550	NA
7	Fenitrothion	122-14-5	38	75	340	0.27	18	81	1	0	69	NA
8	Chlorbenzuron	35409-97-3	60	120	540	1.1	8	85	7	0	560	NA
9	Tetramethrin	7696-12-0	38	75	340	0.019	14	69	17	0	20	0.023
10	Permethrin	52645-53-1	60	120	540	0.71	2	40	58	0	450	0.00073
11	Cypermethrin	52315-07-8	180	360	1,600	0.75	3	74	23	0	970	0.000057
12	Deltamethrin	52918-63-5	60	120	540	0.67	2	40	57	0	270	0.01
13	Azamethiphos	35575-96-3	60	120	540	0.11	43	57	0	0	1.3	130
14	Flufiprole	704886-18-0	180	360	1,600	0.092	4	95	1	0	2,200	NA
15	Hexaflumuron	86479-06-3	180	360	1,600	0.75	2	66	32	0	4,700	NA
16	Chlorfluazuron	71422-67-8	180	360	1,600	0.83	2	58	40	0	5,800	NA

Acknowledgements

This research was financially supported by the National High-Tech Research and Development Program (No. 2013AA06A305) and the Chinese National Environmental Protection Public Welfare Industry Targeted Research Fund (No. 201009026; 201309001).

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