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The inventory of sources, environmental releases and risk assessment for perfluorooctane sulfonate in China

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ABSTRACT

With about 100 t/y of the production volume, perfluorootane sulfonates (PFOS) are mainly used for metal plating, aqueous fire-fighting foams (AFFFs) and sulfluramidin China, and the use amount is about 30–40 t/y, 25–35 t/y and 4–8 t/y respectively. Based on the inventory of PFOS production and uses with geographic distribution educed from statistics, environmental risk assessment of PFOS was taken by using EUSES model, as well as its environmental releases were estimated both in local and regional levels in China. While the environmental release from manufacture is significant in Central China region, metal plating was identified as the major PFOS release source in regional level. The East China region shows the most strong emission strength of PFOS. Though the predicted environmental concentrations (PECs) were not exceed current relevant predicted no effect concentrations (PNECs) of the risk characterization for PFOS, higher PECs was estimated around major PFOS release sources showing undesirable environmental risk at local level.

1. Introduction

With the unique properties of high surface activity, chemical stability and acid resistance, perfluorooctane sulfonate (PFOS) and related substances have been used in a wide range of products and industrial processes, such as fire-fighting foams, carpets, leather/apparel, textiles/upholstery, coatings and coating additives, industrial and domestic/household cleaning products, pesticides and insecticides, photolithography, semi-conductor, hydraulic fluids and metal plating (UNEP, 2006). Due to the properties of persistence, bioaccumulation and toxicity, Perfluorooctane sulfonate and related compounds were listed into the Annex B by Stockholm Convention on Persistent Organic Pollutants (POPs) in May 2009 (UNEP, 2009) to restrict or eliminate their production and uses. Currently, because of lacking of cost-effective alternative technologies in certain applications, PFOS and related substances are still manufactured and used in China. The production volume of PFOS is about 100 tons per year, which is mainly used in metal plating as chrome mist inhibitor, in fire-fighting foams as surfactant, in sulfluramid as a raw material and in other industries.

Recently a decade, PFOS and related substances have been monitored in water, sediment, soil mediums from some areas as the upper reaches and delta of Yangtze River (Pan and You, 2010; Yamashita et al., 2007), Pearl River Delta (Jin et al., 2010; Yamashita et al., 2007), the Haihe River (Sun et al., 2011) and coastal areas of Bohai Sea (Lu et al., 2011a) and so on. Simultaneously, concentrations of PFOS from general population in some areas of China were about the same levels as that in America and Japan (Li et al., 2009; Yamashita et al., 2008). The trend of health risk assessment for PFOS is found gradually upward in China (Jiang et al., 2006; Jin et al., 2004; Li et al., 2009). Nevertheless, separated monitoring data of PFOS at scattered local areas could not reveal a systematic environmental risk status of PFOS in large territory of China due to lacking of detailed information on sources, releases and associate risk assessment of PFOS.

In this paper, an inventory of the production and use of PFOS was developed based on surveys. The distribution of PFOS sources and environmental releases were estimated based on the inventory, relevant statistics and specific natural and environmental management situation of China, and an overall environmental risk assessment of PFOS was taken by using state-modified EUSES model.

2. Production and uses of PFOS

2.1. Production of PFOS

Since 3M Company, the largest manufacturer of PFOS, announced to phase out production of PFOS in 2000 (3M, 2000), global production volume of PFOS had declined significantly (Sweetman et al., 2009). However, the number of PFOS producers increased from 2002 to 2006 in China (Huang et al., 2010), which

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reached 13–15 at the peak. Also the trend of production volumes of PFOS was an upward in China as the almost only production country. In 2002, production volume of PFOS was about 30 t in China, and then it increased to 246.88 t in 2006. Since then, under the impact of the international policy to restrict or eliminate PFOS production, production volume of PFOS was declined to about 100 t/y in 2008 (Huang et al., 2010). Fig. 1 shows that the trend for production volumes of PFOS from 2002 to 2008 in China.

According to surveys for PFOS manufacture enterprises, Yangtze River chemical plant first began to carry out research and development for PFOS manufacture in late 1970s. Due to increasing market demand of PFOS and related substances, the PFOS production volume continued to expand in China. About 10 producers were located in Hubei Province, including the largest company in China, whose annual output was about 60 t. Production volume of PFOS in Hubei Province accounted for 80%–90% of that in China. The other 3 PFOS producers were located in Fujian province, where occupied lower share of production in China.

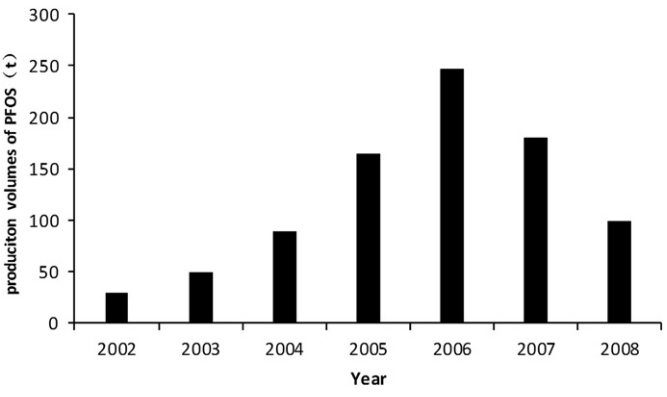

Fig. 1. Production volumes of PFOS from 2002 to 2008 in China.

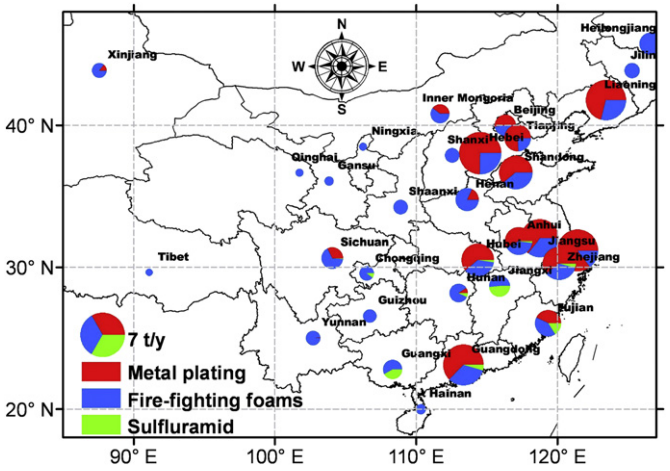

Fig. 2. The distribution of PFOS use amounts used in metal plating, fire-fighting foams and sulfluramid applications in 31 provinces of China.

2.2. Uses of PFOS

PFOS and related substances had ever been extensively used in textiles, carpets, leathers about five years ago, while now it is not be used in these applications due to the international restriction of such applications. The use amount of PFOS is very limited in semi-conductors and aviation (Mei, 2008). Currently, PFOS and related substances are mainly used in metal plating, aqueous fire-fighting foams (AFFFs) synthesis and sulfluramid formulation.

2.3. PFOS use in metal plating (chromium)

In metal plating process, PFOS are mainly used assurfactant/wetting agent and mist suppressants in hard and decorative chromeplating, which can reduce the emission of chromium and improve the work environment in this sector. The amount of PFOS used in China was been estimated as 30–40 t/y from metal plating industry survey in 2008. Such a using level maintained stable in the last years. More than thousands of metal plating processing enterprises are densely located in Jiangsu, Zhejiang, Shanghai, Liaoning and Guangzhou Provinces where steel and mechanical treatment industry are relatively developed in China. Based on the statistics of production volumes of clad sheet in different provinces of China (CISA, 2010), the distributions of the PFOS using amount in metal plating across China are derived as Fig. 2, reflecting large using amount in metal plating are concentrated around coastal areas of China.

2.4. PFOS use in fire-fighting foams

PFOS has been widely used to synthesize aqueous fire-fighting foams (AFFFs) for its high efficiency, low-cost, easy-to-use (Moody and Field, 2000). Fluorinated surfactants mainly contribute to the performance of AFFFs to prevent re-ignition of fuel and oils. A survey conducted by Fire Department of Ministry of Public Security of China indicated that, 28% of fire-fighting foams producers were using PFOS as a raw material to synthesize AFFFs. The percentage of AFFFs in all types foams were keeping increasing from 24.8% to 32.4% (Yu et al., 2010). Assuming that the percentage of PFOS among AFFFs product is 0.5%–1.5% (Moody and Field, 2000), the use of PFOS in this application was 25–35 t per year as fluorinated surfactants. AFFFs containing PFOS are especially applied for fire protection in petrochemical, fire brigade and military facilities and similar areas. By contrast, it is a minimal amount used in residential and commercial buildings fire services. The use tonnage of AFFFs containing PFOS accounted for 24.6 percent of production volumes per year, averaged from 2001 to 2008 (Yu et al., 2010). In 2008, the amount of PFOS released to environment was 6.15–8.61 t/y due to extensive use of AFFFs in the course of fire. The remaining AFFFs usually were stored in the fixed fire-extinguishing systems or mobile fire-fighting equipment (fire foam engines) of different provinces in China. According to the sizes of the projected provincial fire services equipment (FDMPS, 2009), a distribution of using amount of PFOS in fire-fighting foams, including use for fire services and stock, is estimated as shown in Fig. 2. It shows that higher use amounts of PFOS were in Guangdong, Jiangsu, Heilongjiang Provinces for fire-fighting foams use and stock, where having intensive petroleum and chemical industry.

2.5. PFOS use in sulfluramid

Sulfluramid, an important intermediate as fluorinated surfactants to formulate organic fluorine pesticide, has been mainly used to control termites and other crawling insects due to its insecticidal effect in cities (Harrad and Goosey, 2011). It also becomes an alternative for mirex which was prohibited by Stockholm Convention as a POPs (Gao et al., 2001). Actually, sulfluramid is a salt formulated using PFOS as raw materials. In China, there was only one sulfluramid manufacturer, which is located in Jiangsu Province. About 4–8 t/y of PFOS was used to formulate in