Gridded atmospheric emission inventories of organophosphate flame retardants in China

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Introduction

Organophosphate flame retardants (PFRs) are widely used to reduce the inflammability of products and delay the spread of fire after ignition.[1] Most PFRs are applied as additive flame retardants (FRs), which can release into the environment through leaching, volatilization and abrasion.[1] PFRs are found toxic to aquatic organisms, carcinogenic for animals, and could accumulate in human livers and kidneys, which have been caused increasing concern.[1-4] Besides, they have potential to undergo long-range transport in the atmosphere.[5] In China, the consumption of PFRs increased from 11,000 tons in 1995 to 70,000 tons in 2007. [6, 7]The emissions of PFRs into the environment are expected to increase due to the rapid rise of their production and usage. The establishment of PFR emission inventory is essential for the risk assessment and regulation of PFRs in China.[8, 9] This study has investigated the national, provincial and gridded emission inventory of nine PFRs in China from 2010 to 2021. This study improves the knowledge of spatial emission of PFRs in the atmosphere.

Materials and methods

PFRs can be released into the atmosphere during their production, as well as during the formulation of systems for products such as foams.[10] Besides, the PFRs can also be emitted into the air during the manufacture and usage of the products that containing PFRs. According to the market report from Shanghai Shuoxun Chemical Technology Company (SSCTC), in China, PFRs are mainly used in the industries of plastic, textile, paint and others. Six emission sectors are set in this study, including (1) production of PFRs, (2) formulation of systems, (3) plastic sector, (4) textile sector, (5) paint sector, (6) others sector.

The annual national emissions were obtained through multiplying the consumption in different sectors by the corresponding emission factors. The national emissions was then distributed into provincial scale by using the industrial activity rate. At last, the province emissions are scattered into a grid map, which adopted the gross domestic product (GDP) from secondary industry as the surrogate data.

In China, there is very few PFR consumption data available. In order to overcome this problem, a market report on PFRs in China was purchased for this study from SSCTC. The PFR report provided the annual production and usage data of PFR, import/export of PFR products, consumption pattern from 2010 to 2021 and the locations of main PFR industries. [11] The total production of these nine PFRs has been increased from 63,000 tons in 2010 to 103,000 tons in 2016 and expected to 140,000 tons in 2021.

The emission factors in this study are originated from A-tables of the Technical Guidance Document (TGD),[12] the Emission Scenario Document (ESD) for Additives Used in the Plastics Industry,[13] the European Union (EU) risk assessment reports[10, 14, 15] and reference Document on Best Available Techniques for the Textiles Industry.[16]

The investigated nine PFRs are Tris-(2-chloroethyl) phosphate (TCEP), Tris-(1-chloro-2-propyl) phosphate (TCPP), Tris-(1,3-dichloro-2-propyl) phosphate (TDCP), Tri-iso-butyl phosphate (TiBP), Tri-n-butyl phosphate (TnBP), of Triphenyl phosphate (TPhP), Tripentyl phosphate (TPeP), TEHP and Tricresyl phosphate (TCP).

Results and discussion:

The annual emission of total nine PFRs is 170 ± 38 t (Table 1). From 2010 to 2021, a total amount of 2050 t of PFRs is estimated that is released into the air. The plastic sector emits the most PFRs with an average discharge of 100 ± 23 t/y among all emission sectors, which followed by textile sector (mean: 29 ± 6.3 t/y). The emissions from formulation (14 t/y), paint (12 t/y) and others (13 t/y) sectors are similar. The production emits the least PFRs (1 ± 0.2 t/y), which contribute to the low emission factor value that estimated for production process.

Jiangsu province emitted the highest level of PFRs into air with the average emission of 35 ± 7.8 t/y, followed by Zhejiang (34 ± 11 t/y), Guangdong (16 ± 2 t/y) and Shandong (12 ± 2 t/y). The gridded emissions of PFRs in China from 2010 to 2021 has been established with a resolution of 1 km (Figure 1). The result show that PFRs are mainly emitted in coastal region like the Yangzi River Delta (YRD) in eastern China, the Bohai Economic Rim (BER) in northern China and the Pearl River Delta (PRD) in southern China (Figure 1). For production sector, YRD region emitted the highest levels of PFRs into air. This result from over 50% of the nine PFR industries are located in Jiangsu and Zhejiang provinces. There are also PFR factories distributed in BER region (~17%, mainly in Hebei, Shandong and Tianjin provinces) and Henan province (8%) in central China.[11] Higher PFR emissions from plastic sector can be identified as the largest PFR emission source in these areas, especially in Shanghai, Tianjin, Beijing and Guangdong. The production of primary plastic in these four provinces accounts for 24% of annual national production. For the textile sector, higher PFR emissions are primarily found in Jiangsu, Zhejiang and Fujian, which contribute to their higher production of chemical fiber. Guangdong, Jiangsu, Shanghai and Chongqing emitted the highest levels of PFRs into air from paint sector, where the PFRs were used extensively in industries and household products.

In order to validate the emission inventories that estimated in this study, the grid emissions were converted to the air concentration by using the simplified Gaussian model[17], and compared with monitored data. The comparison results show that the modeled PFR levels of Beijing were quite close to the measurements, with the average ratio of measured to modeled concentrations is increased from 0.3 ± 0.2 for TPhP to 2.8 ± 2.4 for TCPP. Nevertheless, the modeled data for Shanghai are 1-2 orders of magnitude higher than measurements.

A Monte Carlo technique was used to quantify the uncertainties. The results show that the total emission of nine PFRs reached a normal distribution with a wide variation from 100 to 360 t. The mean annual emission estimated in this study (mean: 170 ± 38 t) was in the range of this frequency plot.

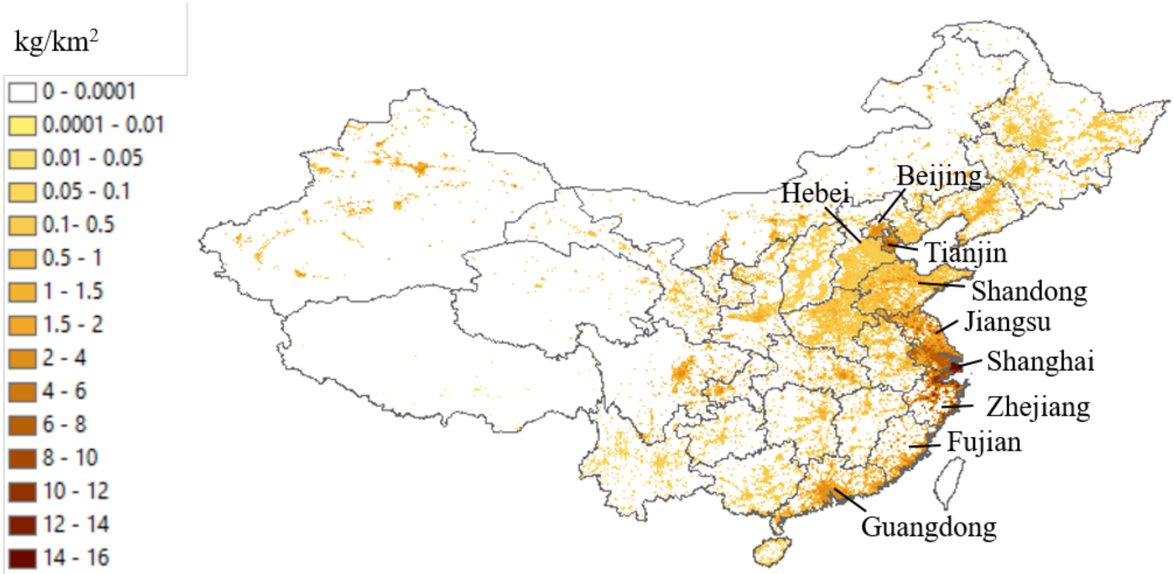

Figure 1. Gridded emission inventories of PFRs in China during the period of 2010 to 2021

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