Risk assessments of polybrominated diphenyl ethers (PBDEs) during sludge application in China

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Abstract. Due to increasingly less space in municipal environment, waste management has become an urgent issue worldwide. As one of common municipal waste, sewage sludge from wastewater treatment plants (WWTPs) contains abundant nutrients, some of which can be quite essential for plant growth. In consideration of nutrient recycling and energy saving, sludge application has been frequently promoted in many countries across the world. However, even after several sludge stabilization procedures, sewage sludge may still contain a large variety of toxic pollutants, especially some emerging organic contaminants (EOCs). Applied in various household products and plastic industries as additives, polybrominated diphenyl ethers (PBDEs) have been constantly detected in sewage sludge samples from several cities in China since 2005, as well as some biosolid samples after sludge stabilization processes, suggesting their strong persistence and wide occurrence. During sludge application onto farmland soils, PBDEs may desorb from sludge particles and get attached by soil organic matter (SOM), followed by plant root uptake and translocation to aboveground tissues. In this study, data about current pollution of PBDEs in sewage sludge samples from China was reviewed, and the potential risks during sludge application was comprehensively assessed.

1. Introduction

As a by-product of municipal wastewater treatment processes, sewage sludge is mainly from primary and secondary settling tanks. The water content of sewage sludge can reach up to 90-99%, therefore gravity thickening, flotation and mechanical thickening followed by chemical thickening are often to separate solids from liquids. In China, of all the 30 million tons of sewage sludge generated every year, 10 to 15% is used as agricultural fertilizers, and most of them was disposed at landfill sites along with municipal waste[1]. Considering that space for landfill sites becoming more and more limited, sludge application after proper digestion technologies has been promoted nationwide in China. During sludge digestion and other stabilization processes, pollutants like heavy metals often receive much concern, due to their high levels and usually strong acute toxicities[2]. In contrary, organic pollutants have been paid enough attention to, despite their strong persistence and bioaccumulation potentials.

Applied as flame retardants, polybrominated diphenyl ethers (PBDEs) have been widely added in many textile products and electronic device. With the wide occurrence of PBDEs in different environment compartments, the strong persistence and large biomagnification potential with food chain have been realized, and two of three major PBDE products, penta-BDEs and octa-BDEs, have been included in the list of persistent organic pollutants (POPs) under the Stockholm Convention[3]. In domestic environment, PBDEs released from household products may accumulate in wastewater and finally reach to WWTPs. Due to their strong hydrophobicity and large molecule size, PBDEs can hardly degrade during wastewater treatment processes, and transport to sludge processing system during sedimentation technologies[4]. With mass balance analysis, over 90% of total PBDEs in WWTP influents will be detected in sewage sludge, which should be considered as a major sink for PBDEs in municipal environment[5].

Agricultural application can be viewed as a promising technology for sludge management in developing countries like China. However, POPs like PBDEs in sewage sludge may be introduced in soil-plant system during sludge application[6]. In consideration of the strong persistence and transport potential of PBDEs, they are likely to be adsorbed by plant root and further move to aboveground tissues, which can pose an urgent risk to human health via food intake. In this study, major targets include :1) reviewing current pollution status of PBDEs in sewage sludge samples from China and predicting further situations; 2) assessing potential risks of PBDEs during sludge application by calculating their accumulation levels in sludge-amended soils.

2. Materials and Methods

In this study, data reporting the occurrence of PBDEs in sewage sludge samples across the world were firstly summarized, and they were further categorized into three groups, including North America, European countries, and China. According to their origin in consumer products, PBDE congeners were divided into penta-BDEs, octa-BDEs and deca-BDEs. The temporal trends of PBDE levels in sewage sludge samples were examined, followed by prediction of their future pollution situations. The concentrations of PBDEs in sludge-amended soils were estimated based on their average concentrations reported in related studies, and potential risks posed by PBDEs in agricultural soils were assessed based on their half-lives in soils.

3. Results and discussions

3.1. Current pollution situation of PBDEs in sewage sludge samples from China

The concentrations of PBDEs detected in sewage sludge samples from China are shown in Figure 1. In 2007, PBDEs were detected in 31 sewage sludge samples from 26 cities across China, and the average concentrations of penta-BDEs and BDE209 were determined to be 25.5 ng/g dry weight (dw) and 68.5 ng/g dw[7]. In comparison to European countries and the United States, the primary PBDE congener was found to be BDE209 in sewage sludge samples from China. The concentration of penta-BDEs appeared to decrease after 2005, and remained to be around 100 ng/g dw after 2010. In 2007, the production and application of penta-BDEs was completely prohibited in China, but since there were still a large number of consumer products containing penta-BDEs in the market, the concentrations of penta-BDEs in sewage sludge would remain to be around 100 ng/g dw in the next decade. Currently, China had become the largest consumer market of deca-BDE products, and the concentrations of BDE209 and total PBDEs had increased significantly since 2006. In sewage sludge samples from 17 WWTPs in Guangdong province, the average concentration of PBDEs exceeded 1 mg/g dw, suggesting the extensive occurrence of PBDEs in sewage sludge samples from China[8].

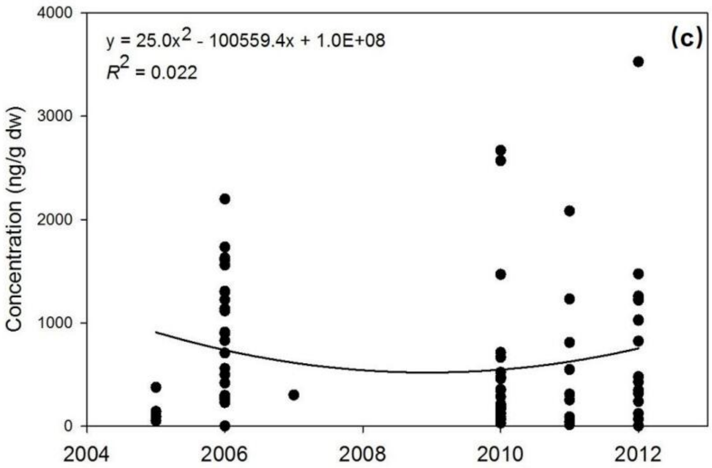

Figure 1. Concentrations of PBDEs in sewage sludge samples from China

The release of PBDEs from consumer products tended to be quite slow, especially for BDE209, due to their strong hydrophobicity and large molecule size[9]. Therefore, the trend of PBDE concentrations in sewage sludge would be slower than that in indoor dust and air samples. Although the usage of deca-BDE products increased heavily in the last decade, the concentrations of BDEs in sewage sludge samples from China did not increase correspondingly. During the end section of the life cycle of consumer products, the release rates of PBDEs would accelerate, resulting in the sudden rise of PBDE levels in sewage sludge. Moreover, along with electronic device and decoration textiles, plastic components of electronic bikes became another major application of PBDEs. Besides the increasing production and consumption of electronic bikes in China, the addition of PBDEs in plastic components was also increasing, to meet the strict flame retardant requirements. The application of deca-BDEs would continue to increase in next decades, which would bring more stringent pollution situation of PBDEs in sewage sludge.

3.2. Risk assessments of PBDEs during sludge application

In order to estimate the accumulation levels of PBDEs in sludge-amended soils, the following assumptions were made: 1) no background pollution was present in soils; 2) sewage sludge was applied yearly from 2000 to 2014; 3) application rate, soil depth, and soil density were set to be 4540 kg/ha, 20 cm, and 1.3 g/cm^3, respectively; 4) the dissipation processes of PBDEs in sludge-amended soils, including biodegradation, photodegradation, and plant uptake, were described with their half-life values. The accumulation levels of PBDEs in sludge-amended soils were shown in Figure 2.

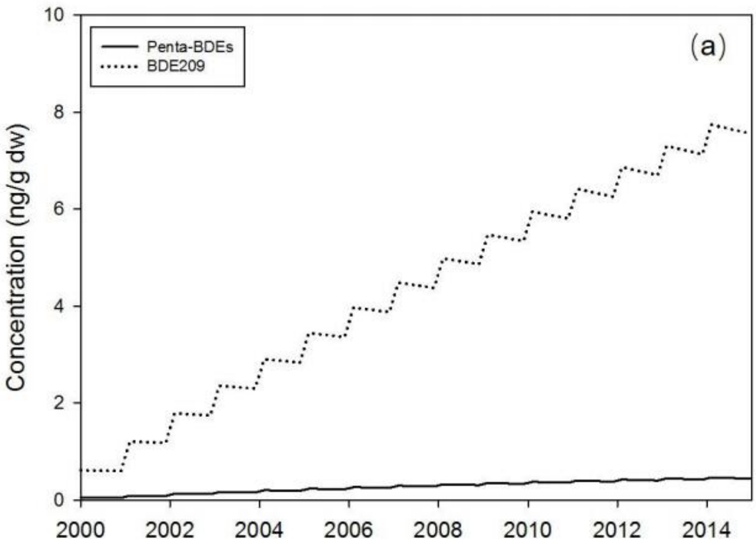

Figure 2. Accumulation levels of PBDEs in sludge-amended soils in China

The median values of BDE209 in sewage sludge samples from North America, China, and European countries were found to be 1553 ng/g dw, 350 ng/g dw, and 312 ng/g dw, respectively. Due to strong binding force between BDE209 and SOM, BDE209 can hardly metabolized by soil organisms or transport in surrounding atmosphere[10]. After sludge application for 15 years, the concentrations of BDE209 in soils would reach 66.8 ng/g dw, 7.5 ng/g dw, and 27.2 ng/g dw in North America, China, and European countries, respectively, which were quite comparable to that detected in actual sludge-amend soil samples. In comparison to background soils, PBDE concentrations in farmland soils with sludge application could be over 5,000 times higher, suggesting the significant accumulation effect of PBDEs during sludge application[10]. The accumulation levels of penta-BDEs in sludge-amended soils appeared to be much lower than BDE209, which was all observed in three regions. In China and European countries, the concentrations of penta-BDEs in sludge-amended soils after 15 years' sludge application were calculated to be 0.44 ng/g dw and 4.5 ng/g dw, one order of magnitude lower than that of BDE209. Besides their low consumption, the strong transport potential of penta-BDEs also contributed to their low accumulation levels in sludge-amended soils[11]. The vapor pressures of penta-BDEs were quite low, and their octanol-air partition coefficient were quite high, resulting in a high tendency to evaporate from soils and transport to remote areas via atmospheric particles. Meanwhile, the bioavailability of penta-BDEs was much stronger than BDE209, so they can be easily adsorbed by plant roots, and pose a greater risk to human health via food intake[12].

After 2015, PBDE concentrations in sludge-amended soils would continue to decrease. In China and European countries, the accumulation levels of penta-BDEs in sludge-amended soils were lower than 10 ng/g dw, and these levels decreased by 99% from 2016 to 2100. In China, the concentrations of BDE209 in sludge-amended soils would decreased to 0.9 ng/g dw in 2100, closed to that estimated in European countries. However, in North America, even 50 years after sludge application the concentrations of penta-BDEs and BDE209 in sludge-amended soils were estimated to be 4.1 ng/g dw and 21.7 ng/g dw, respectively, higher than the original accumulation levels in China and European countries. In this study, only dissipation processes like degradation and evaporation were considered, and PBDEs can also transport to deep soil layers or absorbed by plant roots[13]. Therefore, the decreasing in concentrations of PBDEs in sludge-amended soils does not necessarily suggest the lower environmental risks.

4. Conclusions

The concentrations of PBDEs in sewage sludge samples from China was lower than that in North America and European countries, and the major congener was found to be BDE209. The concentrations of penta-BDEs in sewage sludge samples from China were one order of magnitude lower than that of BDE209. Since 2005, the concentrations of BDE209 continued to increase, which was consistent with their application situation in China. After 15 years' sludge application, the concentrations of BDE209 in sludge-amended sols would reach 66.8 ng/g dw, 7.5 ng/g dw, and 27.2 ng/g dw, respectively. Even 100 years after sludge application, PBDEs can still be detected in sludge-amended soils, suggesting the potential risks of PBDEs during sludge application. Therefore, organic pollutants like PBDEs should be considered during the establishment of sludge application regulation.

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