Occurrence and Distribution of Organophosphate Flame Retardants (OPFRs) in Soil and Outdoor Settled Dust from A Multi-waste Recycling Area in China

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Introduction

Organophosphate flame retardants (OPFRs) are prevalently utilized as the alternatives of brominated flame retardants (BFRs) in a variety of commercial products such as polyvinyl chloride (PVC) plastic, polyurethane foams (PUFs), furniture, textile coatings, paints, electronics and building materials etc [1]. However, they are easily released into the environment during production, use, and disposal of these products [2,3]. OPFRs have been detected in various environmental matrices [4-8] and some of them, especially the halogenated ones, have been reported to have carcinogenicity and neurotoxicity [9].

Electronic waste (E-waste) recycling sites are one of the high risk area of flame retardants, including OPFRs. China accepts 70% E-waste from the world [10]. Hence high levels of OPFRs were reported in indoor dust (2180-70000 ng/g) and sediment samples (48-470 ng/g) from e-waste area in south China [11-13]. Furthermore, the open storage of electronic and plastic waste and primitive recycling operations would cause OPFRs contamination in surrounding soil, even contaminate the nearby farmlands [8,14].

Recent researches on OPFRs in waste recycling area often focused on the e-waste recycling sites. Actually, the OPFRs are also released from many other household materials and car seats [15,16]. The recycling of these materials may also lead the emission of OPFRs. Besides, data about OPFRs occurrence in soil and outdoor settled dust is quite limited. Therefore, in the present study, surface soil and outdoor settled dust from a recycling area (located in Tianjin, China) including the open recycling sites (ORS) and semi-closed recycling sites (SCRS), which was composed by well-planed workshop, of multiple wastes (E-waste, plastic waste, rubber, household appliances and abandoned vehicles) was analysed to investigate OPFRs distribution and assess the ecological risk.

Materials and methods

Samples

A multi-waste recycling area (116˚45'43.55"E ~ 116˚47'54.40"E; 38˚49'49.36"N ~ 38˚53'9.08"N), which is composed of ORS and SCRS, was studied in present research. Surface soil samples (0–2 cm) were collected using iron shovels near the ORS and SCRS (n=24, ZY-1 to ZY-24) and from the farmlands around this area (n = 12, F-1 to F-12). The outdoor settled dust samples were collected by woolen brushes from the outer surface of buildings' windowsills or other objects in sampling sites ZY1-ZY17 and ZY20-ZY24 (n=22).

Chemicals and standards

Tris(1,3-dichloro-2-propyl) phosphate (TDCPP) was purchased from Accustandard (USA), tri-isobutyl phosphate (TIBP) was purchased from Toronto Research Chemicals (Canada), triethyl phosphate (TEP), tripropyl phosphate (TPP), tri-n-butyl phosphate (TNBP), tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), tris(butoxyethyl) phosphate (TBOEP), triphenyl phosphate (TPHP), ethylhexyl diphenyl phosphate (EHDPP), tris(2-ethylhexyl) phosphate (TEHP) and tricresyl phosphate (TCRP) were purchased from

Ehrenstorfer GmbH (Germany). The isotope internal standards, tri-n-butyl phosphate-d27 (TNBP-d27) were purchased from Cambridge Isotope Laboratories (USA) and triphenyl phosphate-d15 (TPHP-d15) were purchased from Toronto Research Chemicals (Canada).

Sample preparation

For soil samples, an accurately weighed sample (2.0 g) was spiked with internal standard TNBP-d27 (10 ng) and TPHP-d15 (20 ng), and then were extracted by 10 mL n-hexane (Hex)–acetone (1:1, v/v) using vortexing (1 min) and ultrasonic extraction (10 min), which was repeated 3 times. The extracts were combined together, and then centrifuged for 3 min (4200 rpm) and evaporated to near dryness under a gentle N_2 stream and re-dissolved in 2.5 mL of Hex. The re-dissolved extract was purified by Florisil cartridge (CNW Florisil, 3 mL, 500 mg), which was pre-cleaned with 2.5 mL MeOH, 5 mL ethyl acetate (EA), and 5 mL Hex sequentially and was eluted with 10 mL EA. Finally, the EA effluents were evaporated to near dryness under a gentle N_2 stream and re-dissolved in 200 µL isooctane for GC-MS analysis. For dust samples, all preparation process was the same as soil but the sample weight (75 mg) and extraction solvent volume (5 mL Hex–Ac (1:1, v/v)) were different.

Instrumental analysis

An Agilent 7890A gas chromatograph (GC) equipped with 5975C mass spectrometer (MS) (electron impact ion source (EI)) was used for analysis. Three micro-liter sample was injected into GC and the target compounds were separated by DB-5MS (30 m×0.25 mm×0.25 µm) column with the temperature program (70 ˚C, hold 1.0 min, ramp to 250 ˚C at 12 ˚C/min, ramp to 270 ˚C at 2 ˚C/min, ramp to 300 ˚C at 15 ˚C/min; kept at 300 ˚C for 2 min (post run)) and the helium flow of 1.0 mL/min. Temperature of injection, ion source and interface were set at 280 ˚C, 230 ˚C and 280 ˚C, respectively and the electron multiplier voltage was 2.2 kV.

Results and discussion

All of the investigated OPFRs were detectable except TPP, which didn't appear in any soil and dust samples (Figure 1.). The median level of ΣOPFRs in soil samples from the studied area was 171 ng/g, which was comparable with those reported from waste treatment areas (196 ng/g-398 ng/g) [8,14]. For dust samples, the median value of ΣOPFRs was 6084 ng/g, which was significantly lower than indoor dust from e-waste area in south China (33100 ng/g) [13].TCIPP was the most dominating OPFR (54.7/<MDL-1374 ng/g; median/range) in soil samples from all sites and followed by TPHP (12.8/0.53-303 ng/g) and TBOEP (35.8/21.1-306 ng/g). Similar trend of OPFRs was found in dust samples but individual OPFRs concentration in outdoor dust was 1-2 order of magnitude higher than those in soil. In general, the levels of OPFRs indicate the extensive usage of chlorinated OPFRs (especially TCIPP), TBOEP and TPHP in multiple materials from north China.

The ΣOPFRs concentration was the highest in soil sample at ZY14 (2104 ng/g). The ΣOPFRs level (696/122-2104 ng/g) in soil samples from ORS were significantly higher than those from SCRS(116/58.5-316 ng/g) and farmlands (56.3/37-156 ng/g) (Figure 2.). This suggested that the primitive open recycling operation would bring more OPFRs releasing to nearby soil than the semi-closed workshop operation. Similar phenomena were observed in dust samples. The concentration of ΣOPFRs in dust decreased significantly from ORS (6589/1391-42740 ng/g) to SCRS (2688/914-7940 ng/g) and the highest ΣOPFRs was detected at ZY14, which was the same site with soil. The open recycling operation made the waste expose directly into the air, which might aggravate the emitting processes of OPFRs compounds into air and the settling down on dust in turns. ΣOPFRs in outdoor dust were much lower than in indoor dust from e-waste recycling area (25000/3300-70000 ng/g; 33100/4660–350000 ng/g) [11,13], which meant recycling waste in a semi-closed workshop was a very efficient way for reducing OPFRs diffusing to outside environment.
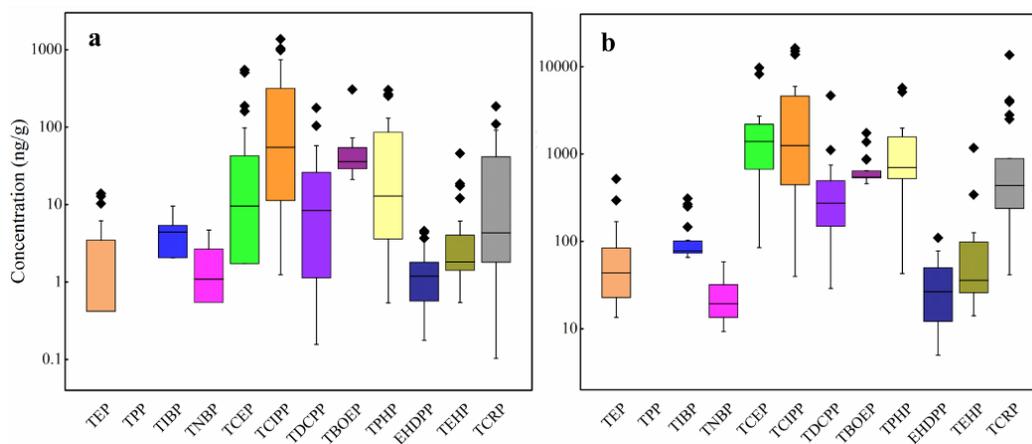
Figure 1. Concentrations (ng/g dw) of OPFRs in the surface soil (a) and outdoor settled dust (b) from multi-waste recycling sites, Tianjin China. (The black horizontal line inside each box represents the median, the boxes represent the 25th and 75th percentiles of concentrations, whiskers represent value of 3*SD and the dots represent outliers.)
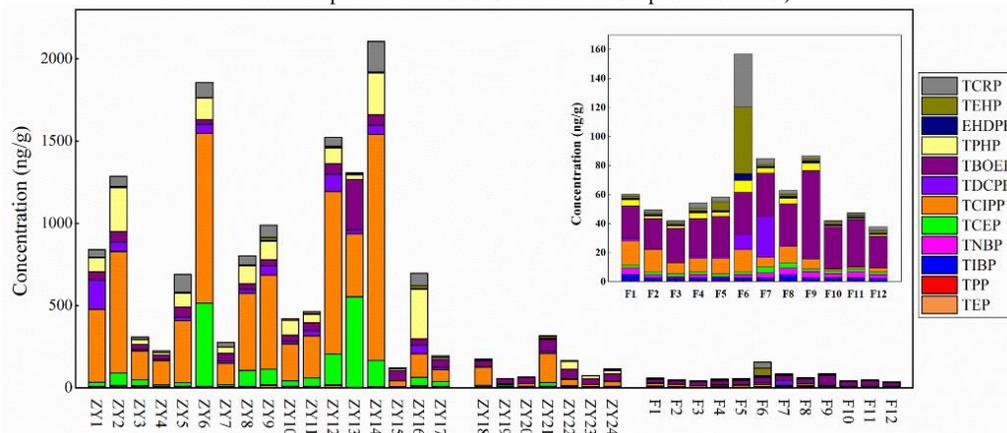
Figure 2. Spatial distribution of OPFRs in soil samples from multi-waste recycling sites, Tianjin China (soil samples ZY1-ZY17 were from ORS; ZY18-ZY24 from SCRS and F1-F12 from farmlands).

Spearman rank correlation coefficients for TCEP, TCIPP and TPHP between soil and dust samples were 0.677, 0.607 and 0.553, respectively, with the significant level P<0.01. Correlation coefficient of TCRP was 0.481 with significant level P<0.05. These results indicated the concentrations of major detected OPFRs between soil and outdoor dust were significantly correlated and OPFRs occurrence in soil and dust might be caused by the same sources at least with some extent. Furthermore, it had been proved that OPFRs had the abilities of atmospheric transport [6] and atmospheric deposition was the major source for their occurrence in soil [17]. Therefore, the diffusive air-dust exchange might be an important process determining OPFRs appearing in outdoor dust, and both the air-soil exchange and dust deposition contribute to their occurrence in soil.

The risk quotient values (RQs) (RQs=measured environmental concentration (MEC)/predicted no effect concentration (PNEC)) were calculated for 6 OPFRs (TCIPP, TCEP, TDCIPP, TPHP, EHDPP and TCRP). When MEC were set as maximum measured values, in soil from ORS, high eco-toxicological risk (RQs>1) was obtained for TCRP (RQs=68.5), TPHP (RQs=2.33) and TCEP (RQs=1.42) with other OPFRs being assessed as medium (0.1>RQs>1) risk, which illustrated that these compounds with a high potential harmful effects on ecological environment. The soil from the SCRS showed a less adverse influence on environment. This suggested that recycling wastes in a semi-closed workshop would reduce the environmental risks of OPFRs significantly. TCRP showed much higher risk in soil than other compounds for its RQs>1 in all soil samples, implying its great potential harmful effects for the environment.

Primitive open recycling operation were an important factor contributing to the occurrence of OPFRs in nearby soil and dust. TCIPP, TBOEP and TPHP were the dominating compounds in both matrices and TCRP showed high ecological risk for the soil from recycling area. These OPFRs compounds should be paid more attention at multi-waste recycling area.

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