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ORGANOPHOSPHOROUS FLAME RETARDANTS IN HOUSE DUST FROM THE PHILIPPINES: IMPLICATIONS ON HUMAN EXPOSURE

Maricar Prudente[1], Joon Woo Kim[2], Tomohiko Isobe[2], Shinsuke Tanabe[2] and Socorro Aguja[3]

[1]Science Education Department, De La Salle University, Taft Avenue, Manila 1004 Philippines
[2]Center for Marine and Environmental Studies, Ehime University, Matsuyama 790-8577, Japan
[3]Biology Department, Institute of Arts and Sciences, Far Eastern University, Manila, Philippines

Abstract

Levels and patterns of seven PFRs were analyzed in house dust samples collected from houses in two areas in the Philippines. The objectives of this study were: (1) to provide background information on indoor contamination by PFRs in the Philippines, (2) to estimate the non-dietary exposure to PFRs via dust ingestion for children and adults, and (3) to compare the relative significance of nondietary exposures to that of literature estimates of PFR exposure from dietary sources. House dust samples (n=37) were collected from Malate (residential area) and Payatas (municipal dumping area) in the Philippines and analyzed using ultrahigh-performance liquid chromatography coupled with tandem mass spectrometry. Present results clearly indicate that PFRs are ubiquitously found in the home environments at these two study sites. High rate of occurrences and concentrations of PFRs, particularly TPP, were found, but their levels were still lower than those in developed countries. The contamination by PFRs in house dust from Malate (550 ng/g) was two times higher ($p<0.05$) than in Payatas (240 ng/g), suggestive of the specific applications of these compounds in Malate. The estimates of the Philippines resident's exposure to PFRs via dust ingestion were found to be below guideline values. However, intake of total PFRs by toddlers was estimated as five times higher than that for adults, suggesting potential risk for toddlers if PFRs are continuously used in household products because of toddler's frequent hand-to-mouth contact and tendency to play on floors. Fish consumption, as estimated from literature, was generally the primary source of exposure to PFRs in the Philippines, but, in worst-case exposure, TPP exposure of human was higher through ingestion of dust. Thus, more efforts are needed to understand the behavior of PFRs in house and other microenvironments and overall exposure pathways for the country's populace. To our knowledge, this is a first report on PFR contamination in house dust from a developing country.

Introduction

In recent years, the use of organophosphorus compounds (OPCs) as flame retardants and plasticizers has increased extensively due to the ban of common mixtures (i.e., penta- and octa-BDE mixtures). Among the OPCs, chlorinated alkyl phosphates (tris-2-chloroethyl phosphate: TCEP) is mostly used as flame retardants in both flexible and rigid polyurethane foams (EFRA, 2006a). The presence of both chlorine and phosphorus is advantageous for the optimum upon flammability, working in both the solid and gaseous phase. TCEP is also included in the European Commission second priority list (EEC, 1995). On the other hand, non-chlorinated aryl phosphates (triphenyl phosphate: TPhP and tricresylphosphate: TCP) are widely used as flame retardants in PVC, artificial leather, tents, tarpaulins, electrical cables and conveyor belts. They are also found in cellulosic polymers (cellulose acetate), engineering thermoplastics and synthetic rubber (EFRA, 2006b). The current production of TCP mainly includes a mixture of the meta- and para-isomers, and the content of the ortho-isomer is usually minor (WHO, 1990). However, it has been suggested that several congeners of TCP (*m*-, *p*-, *o*-tricresyl phosphate) have adverse biologic effect. TPhP can cause contact dermatitis in humans and is a potent inhibitor of human carboxyl esterase (WHO, 1991a). Tri-n-butyl phosphate (TnBP) and tris(2-ethylhexyl) phosphate (TEHP) were recognized as neurotoxic and skin irritation (WHO, 1991b; 2000). TCEP has been found to be teratogenic and haemolytic effects and has carcinogenic potential in rats and mice (Beth-Hubner, 1999; Sato et al., 1997).

After their use, large amounts of OPCs are discharged into environment, and they have already been detected ubiquitously from various environments including drinking water, river, wastewater, sediment, air and indoor dust (Andresen et al., 2004; Meyer and Bester, 2004; Bacaloni et al., 2007; Martínez-Carballo et al., 2007; Regnery and Puttmann, 2009). Furthermore, OPCs have also been detected in wildlife and human breast milk (Sundkvist et al., 2010; Kim et al., 2011a). However, the majority of these studies have been conducted in Europe and United States, and the information on the distribution of OPCs in the environments and potential effects to human health in developing countries is still very limited.

House dust is a repository for various contaminants that are transported into the home from outside or originate from sources within the home itself, and is the subject of growing concern in recent years. In the present study, the levels and pattern of seven OPCs were analyzed using house dust samples collected from the residential homes in two sites in the Philippines. In addition, we evaluated the role of house dust as a human non-dietary exposure route by comparing their daily intake with guideline standards for adults and toddlers, to determine the potential risk of OPCs to humans. Thus, it is necessary to evaluate indoor contaminants concentrations and distributions for assessment of total human exposure. However, there is no information available on their presence in house dust and risks of human exposure in the Philippines.

Methodology

Sampling

House dust samples (n = 37) were collected in August, 2008 from randomly from two different characteristic locations in the Philippines, namely Malate (residential area; n = 17) and Payatas (municipal dumping area; n = 20). Samples were collected using nylon sample socks mounted in the furniture attachment tube of the vacuum cleaner. After sampling, socks were closed with a twist tie, sealed in a plastic bag and shipped to the laboratory in Japan under frozen condition and stored at -25 ºC in the Environmental Specimen Bank (*es*-BANK) of Ehime University until chemicals analysis (Tanabe, 2006). Plastic materials were avoided throughout the collection procedures. Informed consent was obtained from all the participants, and this study was approved by the Ethical Committee of Ehime University, Japan.

Chemical Analysis

Analysis of OPCs was performed following the procedure by Kim et al. (2011b) and Stapleton et al. (2009), with slight modification. Seven OPCs were identified and quantified using an UHPLC (UFLC-XR, Shimadzu Corporation, Japan) coupled with a Applied Biosystems API 5500 electrospray triple-quadrupole mass spectrometer (ESI-MS/MS) (Applied Biosystems/MDS Sciex, Foster City, CA, USA). Calibration curves, ranging from 0.01 to 10 ng mL^{-1}, were established from compound. We used internal standards-response factor to establish our calibration and use it for quantification.

Data Analysis

Statistical analysis was performed using the SPSS software (SPSS 12.0 for Windows: SPSS Inc., 2001). Mann-Whitney U test was used to compare the concentration values between the two locations. Spearman's rank correlation was used to measure the relationship between concentrations of OPCs in house dust samples.

Results and Discussion

OPCs levels in house dust

Among the seven targeted OPCs, TPhP was the predominant compound in house dust from both locations, Malate and Payatas at average concentration of 362 and 126 ng g^{-1}, respectively, whereas other compounds were lower. TPhP is used as both a plasticizer and flame retardant in a variety of applications (plastics, resins, rubber); thus the high levels detected here could be resulted from its use in either application (Stapleton et al., 2009). Furthermore, the higher concentration of TPhP might be due to their high affinity of absorption particle, large past usage and continuous release into the indoor environment. The OPCs profiles in the house dust from the Malate and Payatas are illustrated in Fig. 1. Generally, the composition of OPCs was dominated by TPhP accounting for 37.9 % in Malate and 34.9 % in Payatas. However, the contributions of the other OPCs were slightly different between the two study areas. The difference in OPCs profiles between locations in the Philippines could be attributed to different in sources in the domestic environment. However, it is difficult to identify the specific source of pollutants in house that is furnished and equipped with various products due to the existence of numerous unknown sources.

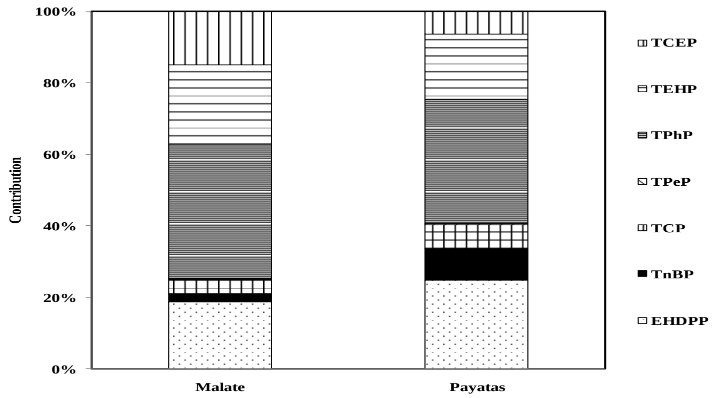

Fig. 1. Contribution of OPCs in house dust from Malate and Payatas.

There is a significant difference in concentrations of OPCs between residential area and dumping area ($p < 0.05$). The average concentrations of ΣOPCs in dust from Malate (950 ng g^{-1}) was 2 times higher than in Payatas (360 ng g^{-1}). Furthermore, the average concentration of TCEP in Malate (143 ng g^{-1} dust) was an order of magnitude higher than in Payatas (23.3 ng/g). On the other hand, levels of TnBP and TPeP were higher in Payatas than in Malate (Fig. 2), though the differences were not statistically significant. Higher concentrations of most OPCs in Malate than in Payatas may suggest that the specific applications of these compounds in Malate. Based on Spearman's rank correlation, significant positive correlations ($p < 0.05$) were found among the concentrations of OPCs. Statistically significant correlations were found among the concentrations of EHDPP and other compounds including TCP, TPhP and TCEP in Malate ($p < 0.05$). Significant positive correlations were also observed for most of the OPCs. The strong correlations between concentrations of individual OPCs in house dust indicate that they may share similar environmental behavior or contamination source. Takigami et al. (2009) also found positive correlations between TPhP and TCEP, and TCP and TPhP in indoor dust from Japan.

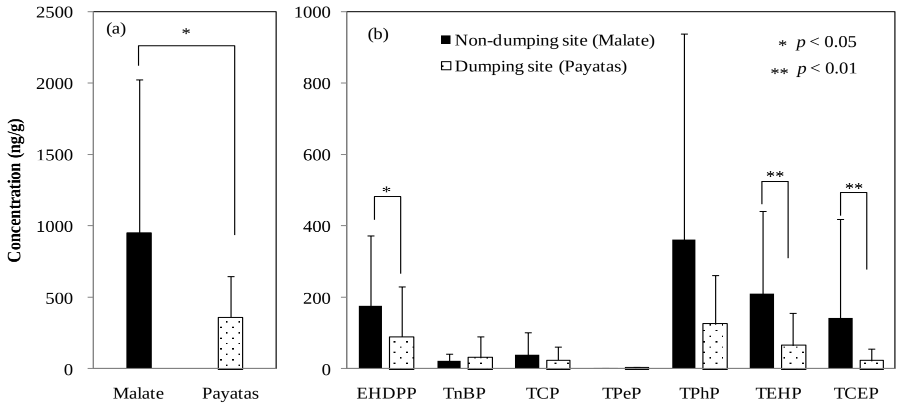

Fig. 2. Concentrations of (a) ΣOPCs and (b) individual OPC in house dust from Malate and Payatas

Exposure to OPCs via dust ingestion

Ingestion of house dust could be an important pathway of exposure for the residents. For instance, the SVOCs with ester bonds, such as OPCs, can be hydrolyzed by lipase in the lung or in the digestive track, allowing the compounds to be absorbed into the human body (Kanazawa et al., 2010). However, information on the human exposure to OPCs in the Philippines is not available. Therefore, we estimated the exposure of adults and toddlers to OPCs via house dust ingestion. Our calculated EDIs of TnBP for adults and toddlers through dust ingestion were 4-5 orders of magnitude lower than guideline values. EDI of TnBP for toddlers under the worst-case exposure in Malate (9.82 ng day^{-1} divided by 15 kg body weight of toddler = 0.66 ng kg^{-1} day^{-1}) was 10 times lower than those reported in Belgium (6.4 ng kg^{-1} day^{-1}) by Van den Eede et al. (2011). Using mean dust ingestion and P50 concentrations, normal EDIs of TPhP through house dust for toddler was 4.27 ng/day (0.29 ng kg^{-1} day^{-1}) in Malate and 3.04 ng day^{-1} (0.20 ng kg^{-1} day^{-1}) in Payatas, which was almost five orders of magnitude lower than the guideline value of 105,000 ng day^{-1}. The EDIs of total OPCs were 570 ng day^{-1} for toddlers in Malate and 106 ng day^{-1} for adults, respectively, when high dust ingestion and P95 concentrations are applied. This result implies that toddlers may be at higher risk of exposure to OPCs compared to adults, considering their sensitivity to potential human health effect during the developmental stage.

The relative importance of the specific exposure routes can be considered as the dust ingestion and intake of food. Thus, we derived estimates for two exposure scenarios: (1) fish consumption, and mean dust ingestion (20 mg day^{-1}) and normal exposure (P50 dust concentrations), (2) fish consumption, and high dust ingestion (50 mg day^{-1}) and worst-case exposure (P95 dust concentrations) (data from Kim et al., 2011a). The results demonstrated the significance of house dust ingestion exposure pathways in the daily TPhP exposure of the Philippines population. And total human exposure to TnBP, TCP, TPhP and TEHP though fish consumption and house dust ingestion were well below the guideline values. However, due to lack of detailed information on OPCs in other exposure pathways such as milk, various food stuffs and inhalation of air, and dermal absorption parameters which may also influence body burden, the actual daily intake could not be accurately determined. The exposure to OPCs through house dust should be supplemented with other exposure pathway in further research. To our knowledge, there is no estimate of dietary exposure to OPCs in the Philippines so far.

Conclusions

The present study investigated for the first time in the Philippines, the concentrations of OPCs in house dust samples. The results clearly showed that OPCs are ubiquitously found in home environment of the Philippines. Remarkably high rate of occurrences and concentrations of OPCs, particularly TPhP were found, but their levels were still lower than those in developed countries. The higher contamination by OPCs in house dust from Malate compared with Payatas is suggestive of the specific applications of these compounds in Malate. The estimates of the Philippines resident's exposure to OPCs via dust ingestion were the below guideline values. However, intake of total OPCs by toddler was 5 times higher than adults, suggesting potential risk for toddlers if those OPCs are continuously used in household products. Overall, fish was the primary source of exposure to OPCs in the Philippines, but in worst-case exposure, human to TPhP exposure was higher through ingestion of dust. Thus, more efforts are needed to understand the behavior of OPCs indoors in house and other microenvironments and overall exposure pathways for inhabitants in these areas..

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