CONCENTRATIONS AND ORAL BIOACCESSIBILITY OF PHOSPHORUS FLAME RETARDANTS IN INDOOR DUST OF A POLYURETHANE INDUSTRY

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Introduction

Phosphorus flame retardants (PFRs) have been in use for over 150 years and are considered as suitable alternatives for brominated flame retardants (BFRs) (1). Before 1977, the most widely used additive flame retardant for children's sleepwear in the United States was tris(2,3-dibromopropyl) phosphate (tris-BP), a known mutagen and carcinogen in rats and mice (1). Federal regulations, such as the California Technical Bulletin (TB 117) for furniture, and the Underwriters'Laboratories 94 (UL 94), the standard for safety flammability of plastic materials for parts in devices and appliances (1) requiring children's sleepwear, mattresses, mattress pads and carpets meet flammability standards, have resulted in a decrease in the number of burn injuries and death (1). PFRs have been detected in various environmental media including air; surface and drinking waters and sediments; biota and indoor dust of various microenvironments in several locations worldwide (1).

Total contaminant concentrations are frequently used in risk assessment of contaminated sites to human health (2). Such assessment, though advantageous for precautionary measures, may lead to overestimation of the amount of contaminant absorbed by humans (2). These overestimations have significant implications for cost and sustainability of brownfield remediation; hence, the uses of bioaccessible and bioavailaible fractions of contaminants for site specific risk assessment are very important parameters.

The idea of bioaccessibility and oral bioavailability are essential for quantifying the risks that are associated with oral exposure to environmental contaminants (2). The use of gastrointestinal tract (GIT) extraction systems, such as the Universal Bioaccessibility Method (UBM), is a valuable tool in assessing the human health risk of persistent organic pollutants. These extraction processes tend to imitate the process of the human digestive system to determine the bioacessibility of accidentally or intentionally ingested contaminants (2). Though, a close association between dust concentrations of PFRs and household items such as foams and furniture, the sources of PFRs in the indoor environment, are still unclear. No direct regulations are currently in place in South Africa with regards to production and use of flame retardant chemicals; hence the use and applications of flame retardants in various industrial sectors are unknown. The paucity of data on phosphorus flame retardants in the African continent motivated the present study which was aimed to investigate the levels of PFRs in indoor dust of industries with a history of flame retardant use by their international counterparts. Specifically, we investigated the indoor dust collected from a polyurethane industry in South Africa. As a second objective, we studied for the first time, the oral bioaccessibility of PFRs following the UBM *in vitro* gastrointestinal test for accurate risk assessment.

Materials and Method

Sample Collection

A total of three dust samples were collected from the indoor environments of a polyurethane factory. Because, the authors and research team were not allowed access to the polyurethane plants, samples from this industry were collected from the vacuum cleaners of the industry after instructions regarding study and sampling protocol were given to the management of the industry. Samples were transported in an ice chest to the laboratory and stored at -10 ºC in a cold room. The polyurethane industry sample 2 was employed for oral bioaccessibility studies. Extraction, clean-up and GC-MS analysis of total PFRs in dust samples followed a previously reported method (Abafe and Martincigh, 2014)[1]

Preparation of gastrointestinal fluids

The physiologically based extraction tests in the present study were based on the Unified BARGE method (UBM) of Europe. All GIT fluids were prepared in advance and stored at <4 ºC. The major modifications of our methods compared to those of Lorenzi *et al*.[3] are basically prolonged extraction time, increased bile fluid for extraction (i.e. 9 mL) and optimum gastric pH. The analytical protocols involved GIT extractions followed by liquid-liquid extractions employed for the recovery of PFRs from the supernatants of the GIT fluid extracts;

whereas ultrasonic-assisted extraction was employed for the determination of residual PFRs in the matrix and for the total PFR determination in dust samples. Silica gel column chromatography was applied for the purification of sample extracts prior to gas chromatographic mass-spectrometric determination of PFRs. Factors, such as pH, incubation time and dust-to-solution chemistry, responsible for the oral bioaccessiblities of PFRs were optimized in this study. A mass-balance exercise was carried out to determine the percentage recovery of PFRs in a standard reference material (SRM 2585) and in contaminated dust samples following the *in vitro* GIT method. Equation 1 depicts the equation used to determine the recovery of each of the PBDE congeners following *in vitro GIT* extractions.

$$\%\ recovery = \frac{Average\ mass\ of\ each\ PFR\ \ in\ supernatants\ of\ modified\ \ UBM + average\ mass\ of\ the\ PFR\ in\ solute\ after\ GIT\ \ extraction}{Average\ mass\ of\ \ PFR\ \ in\ the\ extracted\ dust}$$

The % bioaccessibility was calculated as:

$$\text{Bioaccessibility (\%)} = \frac{Average\ amount\ of\ each\ PFR\ in\ the\ supernatant\ of\ GIT\ medium}{Average\ amount\ \square f\ each\ PFR\ \ originally\ present\ in\ extracted\ dust} \times 100$$

Results

Levels of PFRs in dust samples

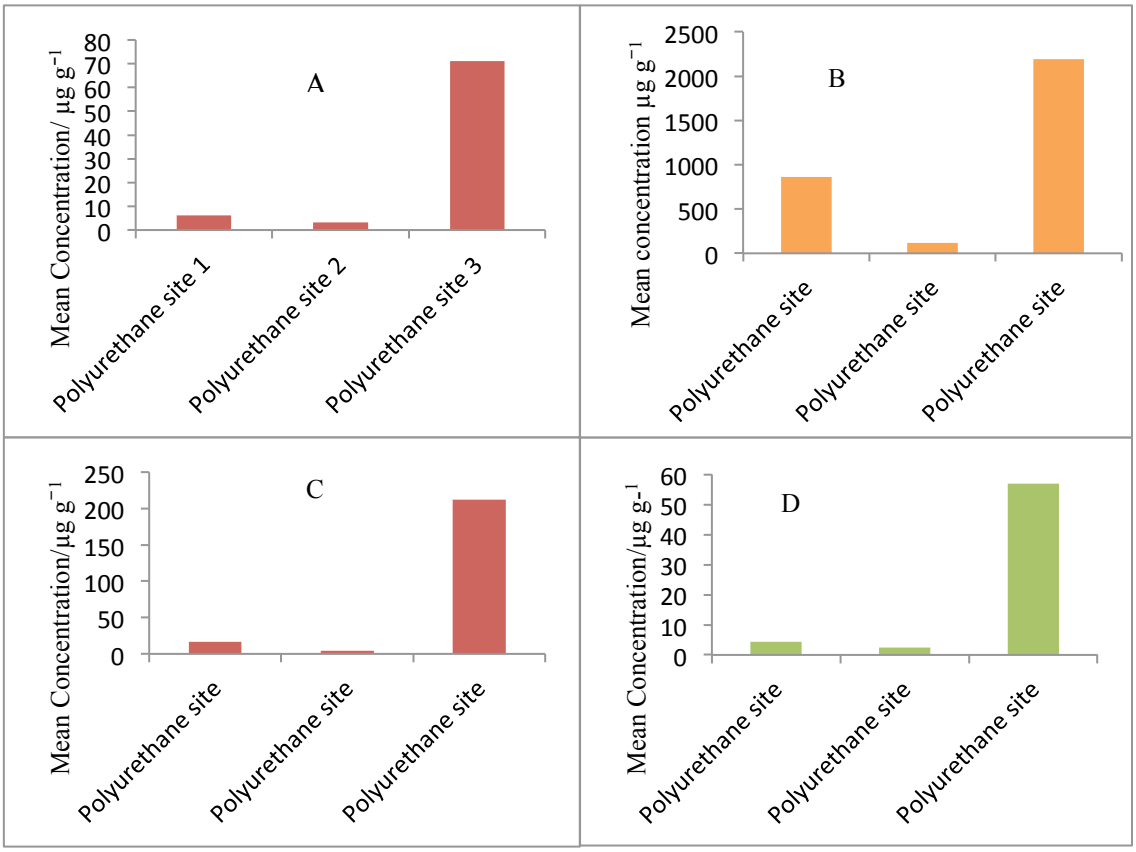

Figure 1 Distribution of PFRs in dust (A) TCEP (B) TCPP (C) TDCPP and (D) TPP in the dust from the two industries.

Oral Bioaccessibility of Organophosphate Flame Retardants

The analytical performance of the UBM method was evaluated by performing a mass balance exercise by using the polyurethane dust sample. The recovery of the analytes after GIT extraction was calculated by using Equation 2. Good recoveries ranging from 59 – 110 % were obtained for all target compounds (Table 1). Following the UBM method, the percentage bioaccessible fractions (% BAF) ranged from 0.9 – 40.0 %. The known human carcinogen, TCEP, had the highest observed bioaccessible fraction (40.0 %) whilst TDCPP exhibited the least oral bioaccessibility (0.9 %) of the studied PFRs. A % BAF of 26.3 % and 19.6 % were observed for TCPP and TPP respectively. The bioacessibility of PFRs was independent of the log K_{ow}. The % BAF showed a negative correlation (p value of 0.2000) with the log K_{ow} of the respective PFR. However, a strong dependent relationship was observed for the % BAF of PFRs and their water solubility. The % BAF exhibited a strong positive correlation (r = 0.834, p value of 0.1657) with the water solubility of the PFRs.

Table 1 Concentrations ($\mu g\ g^{-1}$) of PFRs in supernatant and solute of GIT fluids (n = 3 for supernatants, and n = 2 for solute).

GIT Media	TCEP	TCPP	TDCPP	TPP
Mean concentration in supernatant	1.27 ± 0.31	30.1 ± 1.12	0.04 ± 0.01	0.47 ± 0.08
Mean concentration in solute	1.70 ± 0.23	41.4 ± 2.00	4.58 ± 0.49	0.96 ± 0.13
% Recovery[a]	93.0	63.0	110	59.3
%BAF[b]	40.0	26.3	0.87	19.6
log Ko_w[c]	1.44	2.59	3.80	4.59
[d]Water solubility/$mg\ L^{-1}$	7000	1600	1.5	1.9

[a] % recovery of PFRs following the balance equation; [c,d] van der Veen and de Boer (4)
[b] %bioaccessible fractions of PFRs

Conclusions

The present study has indicated high volume application of PFRs in the polyurethane industry in South Africa. The implication is that, contrary to widespread belief and reports that sources of PFRs in the indoor environment are primarily from household products such as electronics, carpets, foams and furniture; textile materials and other clothing materials may contain a greater amount of PFRs and they can be released during the products' useful life, hence contaminating the indoor environment. There would be a greater risk of exposure to PFRs from clothing, since PFRs are known to rapidly absorb through the skin. We have also shown that PFRs particularly the carcinogenic tris(2-chloroethyl) phosphate is bioaccessible to as high as 40.0 % whilst the most abundant PFR found in South African homes and other indoor environments, namely TDCPP is weakly bioaccessible (0.87%). Generally, less than 40% of PFRs ingested from contaminated dust samples would potentially be available for absorption in the human gastrointestinal tracts. Contrary to the abundance of TDCPP and TCEP in South African homes, offices, automobiles and computer laboratories, TCPP was the most abundant PFR found in the South African industry.

Acknowledgement

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