Flame Retardants in the South African Indoor Environment

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2020

Summary

Flame retardants (FRs), such as brominated flame retardants (BFRs), organophosphorus flame retardants (OPFRs), and chlorinated paraffins (CPs) are a diverse group of compounds used in a wide range of materials to delay ignition. Although these compounds are useful for the intended purpose, most of them have a clear disadvantage. Many of them end up in the environment due to their persistence, through leaching from products or discharge when deteriorating materials reach their end of useful life. Several of these compounds are also toxic and bioaccumulate in organisms. Globally, the prevalence of these compounds is well documented. However, there is limited information on the distribution of these compounds in the South African outdoor and indoor environment. This thesis aims to provide new information on the occurrence of FRs in the South African environment, and to improve the capacity for the analysis of BFRs, OPFRs, and CPs, to evaluate their levels in the South African indoor environment.

The literature review showed that FR analyses in Africa were mainly targeted at BFRs, and mostly performed in South Africa or through outsourced analyses in non-African countries. Developing countries in Africa have limited facilities that specialise in FR analysis and analytical approaches are mainly based on ease of operation, low cost, and availability of technologies and instrumentation in most laboratories. The review further confirmed the ubiquitous occurrence of polybrominated diphenyl ethers (PBDEs) in various environmental compartments in Africa. Due to a scarcity of data for FRs proposed as alternatives, it is unclear to what extend banned formulations were replaced in Africa. There is inadequate data on the levels and occurrence of CPs and OPFRs.

Using cat hair as matrix, comprehensive two-dimensional gas chromatography with high-resolution time-of-flight mass spectrometry (GC×GC–HR-TOF-MS) was positively tested as a screening method to identify BFRs and other organohalogenated compounds (OHCs). More than seventy OHCs were identified in the samples, and included known FRs such as PBDEs, and legacy contaminants such as polychlorinated biphenyls (PCBs) and organochlorine, organophosphorous and pyrethroid pesticides, of which some are categorised as persistent organic pollutants (POPs) listed in the United Nations Stockholm Convention. In addition, a first report on the detection of the alternative BFRs decabromodiphenyl ethane (DBDPE), trisbromoneopentyl alcohol (TBNPA), hexabromocyclododecane (HBCD), pentabromoethylbenzene (PBEB), and the two chloroalkyl-OPFRs (Cl-OPFR) tris(2-chloroethyl) phosphate (TCEP) and tris(2-chloroisopropyl) phosphate (TCIPP) in the South African indoor environment was provided.

The accurate quantification of BFRs, OPFRs, and CPs revealed higher levels of CPs in indoor dust and cat hair followed by OPFRs and BFRs. These first data in South African indoor samples showed that medium-chain CPs (MCCPs, C_{14-17}) were the dominant CP group, and that concentrations of short-chain CP concentrations (SCCPs, $\leq C_{13}$) were higher than those of long-chain CPs (LCCPs, $\geq C_{18}$). Nontraditional Kendrick mass defect (MD) analysis showed that carbon chain lengths for the CP congeners in cat hair ranged from C_9 to C_{36} and the profile for indoor dust samples went as high as C_{37}. Evidence of LCCPs with an average carbon chain length of C_{25} confirm the use of wax grade LCCP formulations in the South African indoor environment. The MD plots provided additional evidence on possible interferences, emphasising the use of very strict identification criteria for CP analysis. To support the quality of the data the sources of uncertainty were identified during method validation for BFRs and OPFRs. The major contributions to the combined uncertainties were associated with recovery and repeatability. The relative expanded uncertainties for all compounds in dust and hair were acceptable (<34%).

In general, the indoor dust and cat hair show comparable FR profiles. Although dust is widely used as a measure for indoor exposure, the use of cat hair provides specific information on indoor exposure and could be seen as a non-invasive passive sampling method to continued exposure of FRs in the indoor environment. Shorter chain CPs with lower chlorine substitution, alkyl-OPFRs and alt-BFRs were prominent in cat hair samples, whereas the Cl-OPFR contribution was higher in dust. This indicate that indoor dust partly contributes to the pattern observed in cat hair, and that some FRs could favourably be adsorbed to the hair due to contribution from indoor dust or direct migration from sources in the indoor environment. BFRs, dominated by BDE209, were present at low concentrations with no significant contribution to the total FR congener profile for the two matrices.

An estimation of the human exposure to OPFRs and BFRs via dust ingestion showed that a high ingestion exposure estimate for TCIPP (the major FR in the dust) was 8-fold lower than the reference dose. The estimated exposures for cats were up to three times higher than estimated for toddlers, and considering that the dust ingestion rate for cats is unknown and could be vastly underestimated. The high levels of CPs and the carcinogenic chlorinated-OPFRs are a cautionary warning that warrants more attention to these compounds when the reduction of indoor contamination is considered.