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DIOXIN-LIKE ACTIVITIES, HALOGENATED FLAME RETARDANTS, ORGANOPHOSPHATE ESTERS AND CHLORINATED PARAFFINS IN DUST FROM AUSTRALIA, UNITED KINGDOM, CANADA, SWEDEN, AND CHINA

F. Wong[1], G. Suzuki[2], C. Michinaka[2], B. Yuan[3], H. Takigami[2], C.A. De Wit[3]

[1]Air Quality Processes Research Section, Environment and Climate Change Canada, 4905 Dufferin Street, Toronto, Ontario, M3H 5T4, Canada

[2]Center for Material Cycles and Waste Management Research, National Institute for Environmental Studies (NIES), 16-2 Onogawa, Tsukuba 305-8506, Japan

[3]Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University, SE-106 91 Stockholm, Sweden

Introduction

Dust is a sink for many organic pollutants in the indoor environments, and particularly high concentrations of flame retardants (FRs) in dusts have been reported[1, 2,3,4]. The abundance of FRs in dusts is influenced by the national fire regulations which differ among countries. For example, deca-bromodiphenyl ethers (BDEs) are phased-out in Europe and North America, but are still produced in China. North America used more penta-BDE relative to Europe. Short-chain chlorinated paraffins are restricted in Europe but not in China. As penta- and octa-BDE mixtures are banned under the Stockholm Convention, many alternative FRs have been introduced worldwide. However, information about the environmental levels, production volumes, human exposure and toxicity of the alternative FRs is limited.

Ingestion of dust is an important human exposure pathway for FRs and may pose a risk to human health[5]. Suzuki et al. [6,7] demonstrated that dioxin-like (DL) activity in Japanese indoor dust was higher than in contaminated sediments, and the DL activity was partly linked to polybrominated dioxins/furans, which are impurities and degradation products of PBDEs. Tue et al. [8] reported that compounds with known potencies (i.e. polychlorinated and polybrominated dioxins/furans (PCDD/F, PBDD/F), and co-planar polychlorinated biphenyls) only explain up to 50% of the DL activities measured in house dust from Vietnam. There is hence still a substantial portion of unknown contaminants in dust that contribute to the overall in vitro dioxin- like activity.

The aim of this study was a) to characterize level of FRs (PBDEs, halogenated flame retardants (HFRs), organophosphate esters (OPEs), chlorinated paraffins (CPs)) in dust collected from different countries and b) to characterize the DL activity and determine if there were correlations between DL activity and concentrations of different FRs.

Materials and methods

Dust samples were kind gifts donated from collaborators. Dust samples were collected during 2008 to 2014 in offices, homes and building lobbies using the method described in Harrad et al.[9] Samples were extracted by using a rapid solvent extractor with acetone/hexane mixture (1:1 v/v, 80 mL), followed by toluene. Extracts underwent cleanup using silica column adapted from methods described elsewhere[10, 11.] Target analytes included 17 HFRs, 17 PBDEs, 13 OPEs and CPs from C_{10} to C_{30}. Instrumental analyses for PBDEs and HFRs were performed using GC-MS in ECNI mode[4,10] and OPEs in EI mode[11]. Analysis of CPs was done by APCI quadrupole time-of-flight MS, with quantification according to Bogdal et al.[12] An aliquot of each extract representing 0.1 g of dust was used for the Dioxin Related Chemical-Activated LUciferase gene eXpression (DR-CALUX) assay. The CALUX-TEQ (2,3,7,8-TCDD equivalent) experiment for each dust sample was carried out three times independently. Details of the assay are given elsewhere[13-15].

Results and discussion

Figure 1 presents the sum of HFRs, PBDEs, OPEs and CPs in all the dust samples collected from Australia (AU, n = 4), United Kingdom (UK, n = 4), Canada (CA, n = 6), Sweden (SE, n = 5), China (CH, n = 5), and NIST standard reference material 2585 (SRM, n = 2).

HFRs and PBDEs The detection frequencies of HFRs in all samples ranged from 42 to 100% and for PBDEs, from 29 to 100%. Hexabromocyclododecane (HBCDDs) (sum of a-, b-, g-HBCDD), decabromodiphenyl ethane (DBDPE) and bis(2-ethylhexyl)tetrabromophthalate (BEH-TEBP) had the highest concentrations with medians of 1.0, 0.63, and 0.33 μg/g, respectively. BDE209 had the highest concentration of the PBDEs (median of 1.3 μg/g). The more volatile chemicals such as allyl 2,4,6-tribromophenyl ether (TBP-AE), tetrabromoethylcyclohexane (DBE-DBCH), pentabromotoluene (PBT), 2,3-dibromopropyl-2,4,6-tribromophenyl ether (TBP-DBPE), hexabromobenzene (HBB), BDE17 and BDE28 had the lowest concentrations. The HFR concentrations were in the same range as for the PBDEs. There was no significant difference in HFRs and PBDEs between the countries.

BDE209 predominated in dust from Australia, UK, Sweden and China, (50 to 70% of total PBDEs). The lowest percentage of BDE209 was in the dust from Canada (20% of the total PBDEs), and the penta-BDE mixture predominated (sum of BDE47, -99 and -100 = 51% of total PBDE). This is probably due to the high use of the penta-BDE mixture in North America.

OPEs The detection frequencies for most OPEs ranged from 79 to100% in all samples. The OPE concentrations were up to 3 orders of magnitude higher than the PBDEs and HFRs. Tris(2-butoxyethyl)phosphate (TBOEP), tris(2R)-1-chloro-2-propyl)phosphate (TCIPP) and 2-ethylhexyl diphenyl phosphate (EHDPP) were the three OPEs measured at highest concentrations, with medians of 26, 8.8 and 2.0 μg/g, respectively. There was no significant difference in OPEs between the countries, which may reflect the diverse application of OPEs in consumer products and building materials.

CPs The concentrations of total CPs were significantly higher than all the other measured contaminants. The highest concentrations were measured in dust from China, with median of 3410 μg/g. CPs in dust from other countries ranged from 280 to 1330 μg/g. Long-chain CPs (C_{18} to C_{30}) were the predominant congeners in dust from Sweden, with median of 84% of total CPs. Medium-chain CPs (C_{14} to C_{17}) were the major congener in dust from other countries, ranging from 41 - 65% of total CPs. Short-chain congeners (SCCPs, C_{10} to C_{13}) were 6.3 to 18% of total CPs in dust from all countries except Sweden; SCCPs in dust from the latter were only 0.7% (median) of total CPs. This reflects the ban of SCCPs in Sweden.

Dioxin-like (DL) activities and correlation with HFRs, PBDEs and CPs The dioxin-like activity levels (pg CALUX-TEQ/g) for each country and SRM are shown in Figure 2. The highest DL level was found in a sample from Canada (CA5) with 590 pg CALUX-TEQ/g. There was no significant difference in DL activities between the countries.

Total concentrations of HFRs, PBDEs, and CPs were plotted against DL activity levels for individual dust sample (Figure 3). Correlation analysis between OPEs and DL activity was not performed because the extract was treated with acid prior to the DR-CALUX assay. There were no significant correlations between DL activity level and HFRs, PBDEs and CPs for all samples. However, when CA5, the outlier, was excluded, PBDEs and CPs were positively significantly correlated with DL activity. The DL activity may due to the presence of PCDD/F in the dust or other DL chemicals. One possibility is PBDD/Fs as PBDEs were positively correlated with DL activity, and it is known that PBDD/Fs are present as impurities of technical PBDE mixture[16].

Although this study does not account for the DL activity contributed by the OPEs, Suzuki et al.[17] reported that TDCIPP and triphenyl phosphate (TPhP) exhibited similar endocrine effects as the penta-BDEs. We found that median concentrations of tris(1,3-dichloroisopropyl)
phosphate (TDCIPP) and TPhP were 2.0 and 1.0 μg/g respectively. The potential endocrine or dioxin-like activities caused by the OPEs thus cannot be neglected and merit for further investigation.

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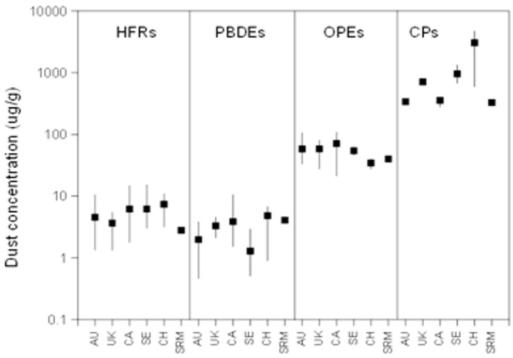

Figure 1. Total concentrations of HFRs, PBDEs, OPEs and CPs in dust from different countries and SRM. The square indicates the mean and the lines indicate the range (i.e. minimum and maximum concentration). AU = Australia, UK = United Kingdom, CA = Canada, SE = Sweden, CH = China, SRM = Standard reference material

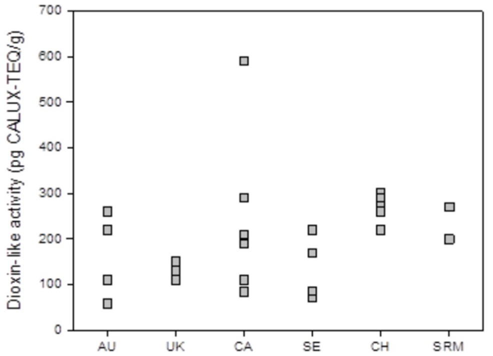

Figure 2. Dioxin-like activity level (pg CALUX-TEQ/g) obtained in indoor dust from different countries and SRM.

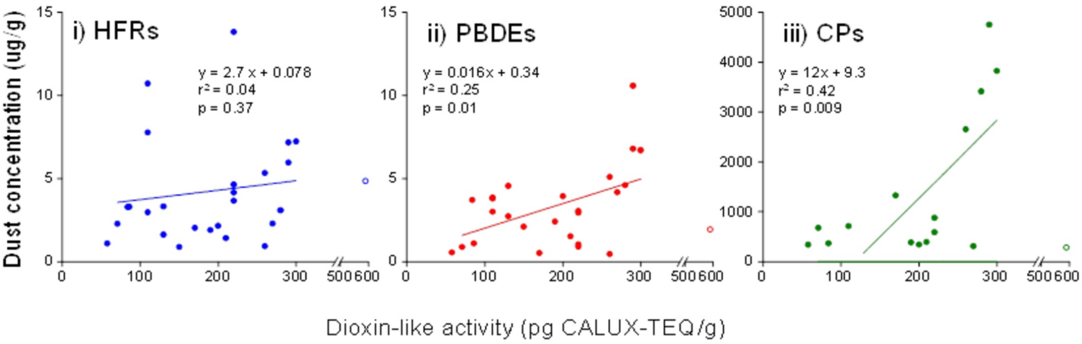

Figure 3. Correlation between dioxin-like activity levels (pg CALUX-TEQ/g) and concentrations of i) HFRs, ii) PBDEs and iii) CPs in dust. Open circle represents the outlier, i.e. CA5 and it is excluded from the regression analysis.