CHLORINATED PARAFFINS IN INDOOR DUST FROM AUSTRALIA

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Introduction

Chlorinated paraffins (CPs) are a complex mixture of polychlorinated n-alkanes (PCAs) with different carbon chain lengths and number of chlorine atoms [1]. CPs can be divided according to their carbon chain length into three groups: short-chain chlorinated paraffins (SCCPs) with a carbon chain length shorter than C_{13}, medium-chain chlorinated paraffins (MCCPs) with a carbon chain length between C_{14} and C_{17}, and long-chain chlorinated paraffins (LCCPs) with a carbon chain length longer than C_{17} [2]. SCCPs was listed in the Stockholm Convention on POPs in 2017, while the global production of MCCPs and LCCPs has increased recently[3]. Data on the levels of CPs in the indoor environment is limited. The key reason is that analysis of CPs remains a major challenge. Commercial mixtures of CPs typically consist of several thousands of individual CP congeners [4,5], this, as well as the lack of separation for chromatography based analysis [6] contributes to difficulty of analysis.
Indoor dust has been found to be the major source of exposure for several organic pollutants such as polybrominated diphenyl ethers (PBDEs) and organophosphate esters (OPEs) [7-9]. So far, the concentrations of CPs in indoor dust are poorly characterized although recent studies suggest that dust ingestion and dermal contact with dust might be a relevant pathway for exposure to CPs. In Australia, MCCPs are still being manufactured [10], and there is no restrictions on the use of CPs [11]. Furthermore, there is limited data on the occurrence and exposure to CPs in the Australian population [12, 13].
The aims of this study are therefore to: 1) measure the concentrations of CPs in Australian indoor dust samples collected from different microenvironments including private houses, offices and vehicles, and 2) estimate the daily intake of CPs through indoor dust by the Australian general population.

Materials and methods

Sampling area and sample collection

Indoor dust samples (n = 44) were collected in Brisbane, Sydney and Canberra, Australia, in January to March 2015. Samples were from 27 private houses, ten offices, and seven public transport vehicles (buses, trains, and planes). The dust was collected into a clean nylon sampling sock inserted into the entry hose of a vacuum cleaner. Vacuuming was typically conducted along the edges of walls where dust usually gathers, and the dust from living areas and bedrooms was combined into a single sample to gain an overall dust profile of the sampled home. Sampling socks were sealed in a zip lock bag, and stored at -20 °C once they arrived at laboratory. All samples and related information were collected in accordance with an ethics approval obtained from The University of Queensland (approval number: 2015000153).

Sample pre-treatment

The dust samples were sieved using a pre-cleaned 1-mm mesh sieve to remove larger particles and to ensure the homogeneity of the sample. Approximately 0.05 g of each sieved dust samples was weighed and transferred into glass tubes pre-cleaned with acetone, and spiked with 100 µL of ^{13}C-BDE 209 (0.1 ng/µL in ACN, used as internal standard). Samples were vortexed for 1 min with 4 mL of acetone/hexane (1:1, v/v), sonicated for 30 min and then centrifuged at 2000 g for 10 min. The supernatant was transferred into a new glass tube. Residual dust was re-extracted as above. Both the original extract supernatant and the re-extract supernatant were combined to a single extract. The extracts were then blown down using a gentle stream of nitrogen at 40 °C to near dryness and reconstituted with 1 mL of n-hexane. A sample cleanup column was prepared by packing a glass pasteur pipette (230 mm × id 6 mm) with Kimwipes and 0.85 g of acid silica gel (40 % of sulphuric acid, w/w). Each cleanup column was cleaned and conditioned with 8 mL of *n*-hexane:DCM (1:1 v/v). The reconstituted sample was loaded onto the column and the target chemicals were eluted with 5 mL of *n*-hexane:DCM (1:1, v/v). The purified sample extracts were concentrated under a gentle stream of nitrogen at 40 °C to near dryness and reconstituted with 100 µL of ACN. The samples were stored at 4 °C until instrumental analysis.

Instrumental analysis

The instrumental method used for CPs and ^{13}C-BDE 209 analysis was adopted from our previous study [13]. Briefly, 10 µL of the dust extract was directly injected, without using an analytical column, into a quadrupole time-of-flight high resolution mass spectrometer (QToF-HRMS, Triple TOF 5600+ Sciex, Concord, Ontario, Canada) using the negative Atmospheric Pressure Chemical Ionization (APCI) mode. ACN was used as eluent with an isocratic flow of 250 µL/min. To improve the response of CPs in APCI mode, DCM at a flow rate of 40 µL/min was used as a dopant and mixed with the eluent just prior to entering the ion source.

QA/QC

Field blank (n=6) samples were prepared by adding pre-baked sodium sulphate into sampling socks for several hours. Field blanks were treated the same as dust samples, and extracted and analysed with each batch of samples. The levels detected in field blanks were, on average, 0.29, 1.1 and 0.094 ng abs for SCCPs, MCCPs, and LCCPs, respectively. Blank correction was applied to all samples.

QC spiked samples were prepared by spiking known amounts of binary mixtures of CP standards (1.0-10 µg), which covered all eight commercial CP standards, into an aliquot of a previously pooled dust sample. QC spiked samples were analysed together with real dust samples and the calculated concentrations were then compared with expected concentrations. The recovery of ^{13}C-BDE 209 in dust samples ranged from 72 – 120. Limits of quantification (LOQs) were defined as the average concentrations plus 10 times the standard deviation in field blanks. The LOQ for SCCPs, MCCPs, and LCCPs were 0.0080, 0.053, and 0.0014 µg/g, respectively. The value of LOQ/2 was used for statistical analysis when the analyte was not detected.

Quantification

Quantification of the CPs was based on a mathematical algorithm developed by Bogdal et al. [14] Briefly, the method linearly combined the patterns (C_nCl_m) of the CP standards to fit the patterns in analyzed samples. Contribution from each CP standard was then calculated separately. Calibration curves were then used to calculate the amount attributed from each standard. The sum of attributions from all commercial standards represents the concentration of a given CP in the sample.

Statistics

Because data on the concentrations of CP subgroups in dust were right skewed, data were log10 transformed prior to any statistical analysis. One-way ANOVA was used to assess the differences of CP concentrations in different microenvironments, and bivariate correlations (Pearson correlation coefficients) were used to investigate the correlations between different groups of CPs. Human exposure to CPs via dust was estimated using models developed previously [15, 16], and more details were shown in Supplementary Material.

Results and discussion:

Concentrations of CPs in Australian indoor dust

Concentrations of ∑CPs (C_{10}-C_{21}) in Australian indoor dust ranged from 5.4 to 590 µg/g, with a median value of 110 µg/g. MCCPs were the dominant CPs in Australian indoor dust and were detected in all samples. The concentration of MCCPs across all the microenvironments ranged from 5.1 to 530 µg/g with a median concentration of 95 µg/g. CPs with a carbon chain length of C_{14} were dominating the congener profile of the MCCPs, accounting for approximately 50% of ∑MCCPs. SCCPs were also detected in all the dust samples with concentrations ranging from 0.29 to 58 µg/g. CPs with a carbon chain length of C_{13} dominated the congener profile of the SCCP, accounting for 57 % of ∑SCCPs. LCCPs were detected in 86% of the dust samples with concentrations ranging from <0.0014 to 27 µg/g.

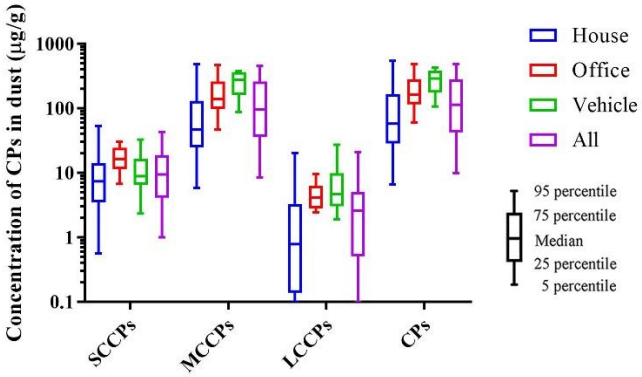

Figure 1 Box-whisker plot comparing concentrations of different CP groups and sum CPs in dust samples collected from different environment

The SCCP (9.4 µg/g) and MCCP (95 µg/g) concentrations in the indoor dust found in this study were comparable to the concentrations of SCCPs (6 µg/g) and MCCPs (176 µg/g) in indoor dust in Germany [38], but higher than the concentrations in Sweden (∑CPs, 3.2-18 µg/g) [17]. However, the concentration of CPs in Australia was more than 10 times lower than that in China (MCCPs, 1200 µg/g; SCCPs, 510 µg/g), which may not be unexpected because China is the largest CP producer and consumer in the world [12]. The contribution of LCCPs in our study (2.5 %) was lower than the contribution in Australian dust (n=2) that reported by Wong et al. (29 %) [12], one possible reason was only C_{18}-C_{21} were measured in our study while C_{18}-C_{31} were measured by Wong et al.[12]. Concentrations of SCCPs, MCCPs, and LCCPs were correlated with each other significantly across all the

types of microenvironment (SCCPs vs. MCCPs: r=0.793, P<0.001; SCCPs vs. LCCPs: r=0.696, P<0.001; MCCPs vs. LCCPs: r=0.792, P<0.001). This suggested these three subgroups of CPs might share similar sources. The carbon and chlorine homologue groups for SCCPs, MCCPs and LCCPs in Australian indoor dust were shown in Figure 2. CPs with chlorine atoms between 6 to 8 ($Cl_{6\text{-}8}$) had the highest contribution to SCCPs, MCCPs, and LCCPs. This finding consisted with the predominance of Cl6-8 that found in sludge and air [6, 13]. However, it was slightly different to the pattern found in marine sediments from China (dominated by $Cl_{5\text{-}7}$) [18]. The calculated chlorination degree for dust samples ranged from 56% to 62% for SCCPs, from 59% to 62% for MCCPs, and from 45% to 56% for LCCPs. These were again consistent with the study of Wong et al. [12], who found similar chlorination degree of SCCPs (57%), MCCPs (52%), and LCCPs (50%) in indoor dust that collected from Australia, Canada, China, Sweden, and UK. In addition, C^{13} and C^{14} were the predominant of SCCPs and MCCPs for all dust samples, except for one collected from office, while C^{18} had the highest contribution to LCCPs for most samples. The pattern was consistent with other studies on dust [12, 19], but in contrast with the pattern in air [20, 21]. This was caused by longer half-lives of C10-12 CPs in air [22].

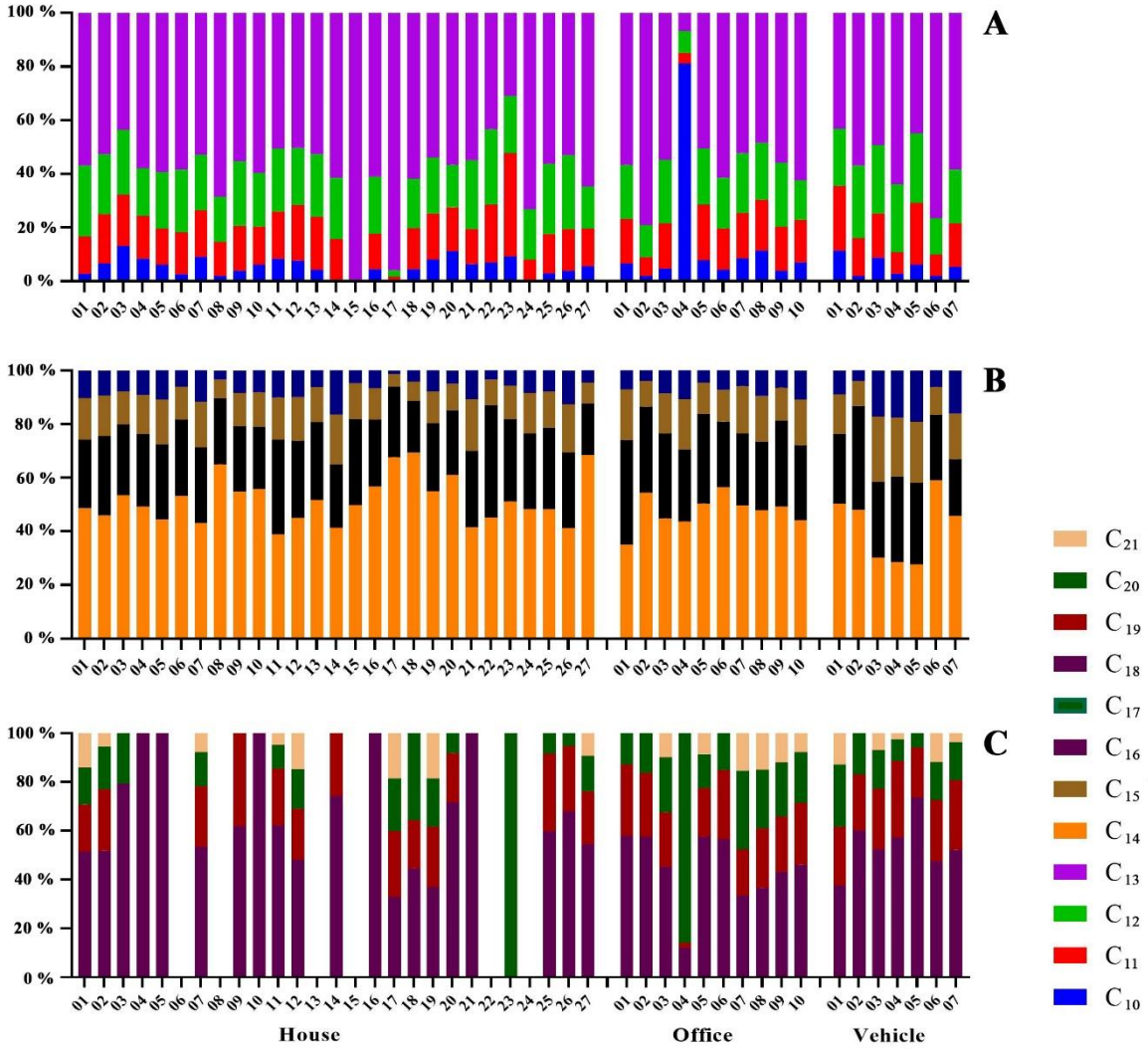

Figure 2 Carbon chain length based profile of SCCP (A), MCCP (B), and LCCP (C) congeners in individual indoor dust

CPs in different microenvironments

Concentrations of CPs in different microenvironments, including private houses (n=27), offices (n=10), and vehicles (n=7), are presented separately in Figure 1. Higher median concentration of ∑CPs (C_{10}-C_{21}) was found in vehicles (290 µg/g), while the median concentrations in offices and houses were 160 µg/g and 57 µg/g, respectively. This difference was mostly caused by the higher concentrations of MCCPs in vehicles (median, 280 µg/g) compared with houses (median, 46 µg/g) and offices (median, 140 µg/g). Higher concentrations of SCCPs and LCCPs were also found in vehicles. The higher concentrations in the vehicles might be caused by more polymer and plastic products in vehicle cabins.

Congener group profiles of the dust samples were also assessed in the different microenvironments based on the carbon chain length and chlorine atom substitution (Fig. 2).The abundance of C_{14} and C_{15} groups in the different microenvironments were very stable with no significant differences among different types of rooms. For example, the median contributions of C_{14} group were 43%, 42%, and 41% of ∑CPs in houses, offices and vehicles, respectively. The chlorine content in different microenvironments were also similar, with medians of 52 %, 50 % and 52 % in houses, offices, and vehicles, respectively. However, we found a significant (P=0.036) difference between the carbon chain length based profile of LCCPs, where C_{18} group contributed 64% of the total LCCPs in dust that collected from houses, while C_{18} group only contributed 44 % for dust collected from offices. These findings suggested that LCCPs might have different sources in different microenvironments, while the sources of SCCPs and MCCPs might be similar.

Human exposure assessment to CPs

Using the median concentrations of CPs in the dust samples, human exposure to CPs via dust, both via ingestion and dermal exposure, was estimated. The medians of estimated daily intake of ∑CPs for Australian adults and toddlers were 80 and 620 ng/kg/day, respectively. These results were lower than intakes in China (150 ng/kg/day for adults) [23], but higher than intakes in Sweden (∑CPs, 2.5 ng/kg/day for adults and 240 ng/kg/day for toddlers) [17]. The ∑CPs intake through dust was comparable to the dietary intake (100-370 ng/kg/day) estimated in Japan [24], suggesting that dust ingestion and dermal contact with dust from indoor environment may be an important exposure pathway for CPs in Australia. The reference doses (RfDs) for SCCPs, MCCPs, and LCCPs, based on neoplastic effects, are 10, 100 and 100 µg/kg/day, respectively as recommended by the International Programme on Chemical Safety [25]. The daily intake of CPs for Australian residents were, in the worst-case scenario (95th percentile concentrations of CPs were used), 2-3 orders of magnitudes lower than the RfDs. However, further research is required to improve the understanding on the safety based reference doses to human.

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