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Flame retardants in the South African indoor environment

by

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Philosophiae Doctor

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Declaration

I, Marthinus Brits, declare that the dissertation, which I hereby submit for the joint degree Philosophiae Doctor (Chemistry) at the University of Pretoria and Vrije Universiteit Amsterdam, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.

Contributions by co-workers are acknowledged in the separate chapters.

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Signature

_23/03/2020__
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Summary

Flame retardants (FRs), such as brominated flame retardants (BFRs), organophosphorus flame retardants (OPFRs), and chlorinated paraffins (CPs) are commonly used in consumer products such as electrical and electronic equipment, furniture, carpets, insulation materials and other commercial products. Due to their unique physiochemical properties, these compounds are useful for the intended purpose to reduce product flammability, and to meet fire safety requirements. The disadvantage is that a number of these FRs end up in the environment and several are also toxic and bioaccumulate in organisms.

Developing countries in Africa have limited facilities that specialise in FR analysis. The literature review showed that the analyses in Africa were mainly targeting BFRs. BFR levels were reported for various environmental compartments, whereas there is insufficient data on the levels and occurrence of CPs and OPFRs. In this study, analytical methods for the various FR classes were developed and/ or implemented to provide reliable data for BFR, OPFRs, and CPs in South African environmental matrices. Screening analysis using cat hair as matrix, allowed us to identify FRs and other organohalogenated compounds (OHCs). More than seventy OHCs were identified, and included known FRs, and legacy contaminants such as polychlorinated biphenyls (PCBs) and pesticides. Concentrations for BFRs, OPFRs, and CPs were further determined in indoor dust and hair samples obtained for some of the indoor pet cats. 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 South African indoor environment shows high levels of CPs followed by OPFRs and BFRs. This first report on CPs in South Africa shows that medium-chain CPs (MCCPs) are the dominant CP group while concentrations of short-chain CPs (SCCPs) are higher than for long-chain CPs (LCCPs). This study also shows for the first time that, of the three main OPFR groups, chloroalkyl-OPFRs (Cl-OPFRs) dominate the indoor dust profile with high contributions from tris(2-chloroisopropyl) phosphate (TCIPP). BFR concentrations are relatively low, compared to those of OPFRs and CPs and dominated by BDE209. Although hair and indoor dust samples showed comparable FR profiles, shorter chain CPs with lower chlorine substitution, alkyl-OPFRs and alternative BFRs were prominent in cat hair samples, whereas the Cl-OPFR contribution was higher in dust. As dust is widely used as a measure for indoor exposure, the use of cat hair provides specific information on indoor exposure and can be seen as a non-invasive passive sampling method to continued exposure of FRs in the indoor environment. An estimation of the human exposure to OPFRs and BFRs via dust ingestion showed a high ingestion exposure estimate for TCIPP, and exposures for cats could be up to three times higher than estimated for toddlers. 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. Toddlers share the same environment as cats and exposure could result in health risks for children.

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Content

Abbreviations

alkyl-OPFR	Alkyl-organophosphorus flame retardant
alt-BFR	Alternative brominated flame retardant
aryl-OPFR	Aryl-organophosphorus flame retardant
APCI	Atmospheric pressure chemical ionization
BEH-TEBP	Bis(2-ethylhexyl)-3,4,5,6- tetrabromo-phthalate
BFR	Brominated flame retardant
BTBPE	1,2-Bis(2,4,6-tribromophenoxy) ethane
bw	Body weight
Cl-OPFR	Chloroalkyl organophosphorus flame retardant
CP	Chlorinated paraffin
CRM	Certified reference material
^{1}D	First dimension
^{2}D	Second dimension
Da	Dalton
DBDPE	Decabromodiphenyl ethane
DCM	Dichloromethane
DIR	Dust ingestion rate
DP	Dechlorane plus®
DPTE	(2,3-Dibromopropyl) (2,4,6-tribromophenyl) ether
dw	Dry weight
ECD	Electron capture detector
ECNI	Electron capture negative ionisation
EHDPP	2-Ethylhexyl diphenyl phosphate
EH-TBB	2-Ethylhexyl-2,3,4,5- tetrabromobenzoate
EI	Electron impact
EPA	Environmental Protection Agency
EU	European Union
FR	Flame retardant
FWHM	Full width at half maximum
GC	Gas chromatography
GC×GC	Comprehensive two-dimensional gas chromatography
HBB	Hexabromobenzene
HBCD	Hexabromocyclododecane
HCDBCO	Hexachlorocyclopentadienyldibromocyclooctane
HR-TOF-MS	High-resolution time-of-flight mass spectrometry
IDL	Instrumental detection limit
IS	Internal standard
LC	Liquid chromatography
LCCP	Long-chain chlorinated paraffin
LLE	Liquid-liquid extraction
LOD	Limit of detection
LOQ	Limit of quantitation

LR-MS	Low-resolution mass spectrometry
LSE	Liquid-solid extraction
Log K_{ow}	Log octanol/water partition coefficient
lw	Lipid weight
MCCP	Medium-chain chlorinated paraffin
MD	Mass defect
MDL	Method detection limit
MS	Mass spectrometry
MS/MS	Tandem mass spectrometry
m/z	Mass-to-charge ratio
NIST	National Institute of Standards and Technology
NMISA	National Metrology Institute of South Africa
NRF	National Research Foundation
OCP	Organochlorine pesticide
OHC	Organohalogenated compound
OPFR	Organophosphorus flame retardant
OPP	Organophosphorus pesticide
PBB	Polybrominated biphenyl
PBDE	Polybrominated diphenyl ether
PBEB	Pentabromoethylbenzene
PBT	Pentabromotoluene
PCB	Polychlorinated biphenyl
PFTBA	Perfluorotributylamine
POP	Persistent organic pollutant
PUF	Polyurethane foam
PVC	Polyvinyl chloride
QA	Quality assurance
QC	Quality control
QTOF-MS	Quadrupole time-of-flight mass spectrometer
RfD	Reference dose
RSD	Relative standard deviation
Rt	Retention time
SC	Stockholm Convention
SCCP	Short-chain chlorinated paraffin
SIM	Selective ion monitoring
SPE	Solid phase extraction
SRM	Selected reaction monitoring
SS	Syringe standard
TBBPA	Tetrabromobisphenol-A
TBBPA-DBPE	Tetrabromobisphenol A-bis(2,3-dibromopropylether)
TBCO	1,2,5,6 Tetrabromocyclooctane
TBECH	Tetrabromoethylcyclohexane

TBNPA	Trisbromoneopentyl alcohol
TBOEP	Tris(2-butoxyethyl)phosphate
TIC	Total ion chromatogram
TIPPP	Tris(2-isopropylphenyl) phosphate
TCP	Triscresyl phosphate
TCEP	Tris(2-chloroethyl)phosphate
TCIPP	Tris(2-chloroisopropyl)phosphate
TDCIPP	Tris(1,3-dichloroisopropyl)
TEHP	Tris(2-ethylhexyl) phosphate
TMPP	Tris(methylphenyl) phosphate
TNBP	Tributyl phosphate
TOC	Total organic carbon
TOF-MS	Time-of-flight mass spectrometry
TPHP	Triphenyl phosphate
UAE	Ultrasound-assisted extraction
UK	United Kingdom
UNEP	United Nations Environment Programme
USA	United States of America
v/v	Volume per volume
WC	Wattled Crane
WHO	World Health Organization
w/w	Weight per weight
ww	Wet weight
WWTP	Wastewater treatment plant
XIC	Extracted ion chromatogram

Chapter 1

General introduction and outline

1.1 General introduction

1.1.1. Flame retardants

Flame retardants (FRs) are chemicals that exhibit a diversity of beneficial physicochemical properties to be favourably applied to combustible materials to reduce their flammability, to delay ignition and to meet fire safety requirements. The diverse group of FR chemicals includes brominated flame retardants (BFRs), halogenated and non-halogenated organophosphorus flame retardants (OPFRs), polychlorinated *n*-alkanes or chlorinated paraffins (CPs), other chlorinated FRs, metal-based FRs, and a suite of non-halogenated organic FRs. These FRs are commonly used in consumer products intended for indoor use, such as electrical and electronic equipment, furniture foams, upholstery textiles, carpets, building construction and insulation materials and other commercial products. They are also heavily applied in cars and airplanes (Alaee *et al.*, 2003; van der Veen and de Boer, 2012). Some of these chemicals are also used as plasticizers, and in hydraulic fluid and lubricating oils (van der Veen and de Boer, 2012; van Mourik *et al.*, 2016). The principle of incorporating FRs in combustible materials are to exploit their properties to impede on some steps of the ignition/combustion process which involve preheating, volatilization/decomposition, combustion and propagation. The mode of actions are typically instigated by the thermal heating of the FR incorporated material and involves gas/fuel dilution; thermal quenching; formation of protective coating/charring; chemical interaction; or a combination of these mechanisms (EHC-192, 1997). FRs have also been associated with fire toxicity due to increased formation of carbon monoxide and hydrogen cyanide (McKenna *et al.*, 2018). Burning of BFR containing polymeric materials also result in the emission of toxic polybrominated dibenzodioxins and dibenzofurans (Dumler *et al.*, 1989).

1.1.2. Restriction and use

For many years polybrominated diphenyl ether (PBDE) formulations were the most widely used BFRs (Alaee *et al.*, 2003). In 2003, penta-BDEs were banned by the European Union (EU) and soon after other PBDE formulations were either banned (in the EU) or voluntarily phased out (in the USA) (European Commission, 2003). Since 2009, two commercial mixtures (penta-BDE and octa-BDE) have also been restricted under the United Nations Stockholm Convention (SC), while the deca-BDE formulation was added in 2017. International restrictions on the use of BFRs have resulted in the introduction of alternative-BFRs (alt-BFRs) as replacements for banned formulations. For example, 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE) and decabromodiphenyl ethane (DBDPE) were introduced as a replacement for octa-BDE and deca-BDE formulations, and bis(2-ethylhexyl)-3,4,5,6- tetrabromo-phthalate (BEH-TEBP) and 2-ethylhexyl-2,3,4,5- tetrabromobenzoate (EH-TBB) were introduced as replacement for penta-BDE (Covaci *et al.*, 2011; Stapleton *et al.*, 2008). In addition to the alt-BFRs, OPFRs are considered as replacement FRs for banned or restricted BFRs (van der Veen and de Boer, 2012). Halogenated and non-halogenated

OPFRs are used in different applications as FRs and non-flammable plasticizers. OPFRs are mostly used as additives in plastics, rubber, paints, floor polish, polyurethane foam (PUF), textiles, electronic equipment, isolation materials, and food packaging (Marklund *et al.*, 2003; van der Veen and de Boer, 2012; Wei *et al.*, 2015). CPs, which consist of complex formulation mixtures with various carbon chain lengths and degrees of chlorination are mainly used as FRs and plasticizer additives in polyvinyl chloride (PVC), plastics, rubber, sealants, adhesives, paints and varnishes (Glüge *et al.*, 2016). Additionally, CPs are also used as FRs in textiles and polymer materials, extreme pressure additives and lubricants in metal work applications, and fat-liquoring agents in leather treatments (Glüge *et al.*, 2016). Based on the carbon chain length, CPs are classified as short-chain (SCCPs, ≤ C_{13}), medium-chain (MCCPs, C_{14} to C_{17}), or long-chain (LCCPs, ≥ C_{18}). In China, mixtures with specified degree of chlorination and undefined carbon chain lengths occur (Li *et al.*, 2018). As environmentally hazardous substances, the production and use of SCCPs have been restricted by international conventions and regulatory agencies and in some cases, MCCPs and LCCPs are produced as alternatives (Glüge *et al.*, 2016; UNEP, 2012; van Mourik *et al.*, 2016). Many alternatives or replacement FRs are chemical-by-chemical substitution of phase-out substances to produce structurally similar chemicals which often show similar hazardous profiles, e.g. brominated aromatic FRs in the case of PBDEs and longer-chain CPs in the case of SCCPs. This process temporarily exploits scientific uncertainty as less information on exposure pathways and potential environmental and health effects of the replacement FRs are available.

1.1.3. Toxicity

Many of the aforementioned FRs are present in the environment and may accumulate in animals and humans resulting in adverse health effects. The metal-based FRs and non-halogenated FRs show a much lower bioaccumulation potential. PBDEs have been shown to affect reproductive endpoints, neurodevelopment and thyroid hormone regulation in humans (Dishaw *et al.*, 2014). There is limited information on the potential toxicity of the alt-BFRs, BEH-TEBP and EH-TBB, and evidence suggests that the reproductive and thyroid systems might be affected (Dishaw *et al.*, 2014). Toxicity studies of OPFRs are still inadequate, and indications show that several OPFRs are toxic, carcinogenic, and may affect hormone levels (van der Veen and de Boer, 2012). Tris(2-butoxyethyl)phosphate (TBOEP), tributyl phosphate (TNBP) and tris(methylphenyl) phosphate (TMPP, also known as triscresyl phosphate (TCP)) have shown neurotoxic effects in animal studies (Bruchajzer *et al.*, 2015). Human exposure to TMPP exhibits neurotoxic effects (Bruchajzer *et al.*, 2015). The chlorinated-OPFRs, tris(1,3-dichloroisopropyl)phosphate (TDCIPP) and tris(2-chloroethyl)phosphate (TCEP) have been proven to be carcinogenic and tris(2-chloroisopropyl)phosphate (TCIPP) is a suspected carcinogen (World Health Organization, 1998). Concentrations of TDCIPP and triphenyl phosphate (TPHP) in house dust may also be associated with altered hormone levels and reduced sperm concentration (Meeker and Stapleton, 2010). The acute toxicity of CPs is generally low, and chronic toxicity and sub-lethal effects have been reported to affect the liver, kidneys, and the thyroid and parathyroid glands (Ali *et al*., 2010). Evidence shows toxicity to some aquatic species and developmental toxicity seems to be most sensitive in mammals (Ali *et al*., 2010). The toxicological effects of SCCPs are generally more prominent than those of MCCPs and LCCPs. The most relevant metabolic pathways influenced by SCCP exposure were shown to be the glycerophospholipid and linoleic acid metabolisms, and the tricarboxylic acid cycle (Wang *et al.*, 2018). The SCCPs have also shown to exhibit potential endocrine-disrupting effects (Zhang *et al.*, 2016). Despite human health and environmental concerns, halogenated FRs are still in use (de Boer and Stapleton, 2019). The European research project ENFIRO (www.enfiro.eu) investigated halogen-free FRs and proposed alternatives that are less toxic, and not persistent and bioaccumulative.

1.1.4. Environmental relevance

Some of the FR classes are developed to be highly resistant toward acids, bases, heat, light, and reducing and oxidizing compounds, to provide specific functions as ingredients in consumer products. Conversely, these high resistance additive type FRs, are discharged into the environment throughout their entire lifetime where they persist for long periods of time. Initial concerns regarding the occurrence of PBDEs in the marine environment were reported by de Boer *et al.*, (1998) and thereafter several reviews on the global levels and trends of BFRs in abiotic and biotic environmental samples have been published (Alaee *et al.*, 2003; Covaci *et al.*, 2011; de Wit, 2002; Law *et al.*, 2014; Toms *et al.*, 2012; Wu *et al.*, 2012). Following the ban and restrictions on the use of PBDEs, the industry needed other FRs as replacements. OPFRs and CPs may be considered as alternative or replacements for certain PBDE formulations, but should rather be seen as “re-emerging” rather than emerging FRs. First reports on OPFRs and CPs in the environment date back to the late 1970s (Campbell and Mcconnell, 1980; Saeger *et al.*, 1979; Sheldon and Hites, 1978). Muir *et al.* (1983) was the first to report on the bioaccumulation and biodegradation of OPFRs, while much later the ubiquitous contamination of indoor dust, air, water, sediment and soil and biota was globally well-documented (van der Veen and de Boer, 2012; Wei *et al.*, 2015). Reviews on the environmental manifestation of CPs were mainly focussed on SCCP and MCCPs (Bayen *et al.*, 2006; Coelhan and Hilger, 2014; de Boer, 2010; Feo *et al.*, 2009; Glüge *et al.*, 2018; Mukherjee, 1990; van Mourik *et al.*, 2016; Wei *et al.*, 2016). Although information continues to be reported in the scientific literature on SCCPs and MCCPs, limited information is available for LCCPs. Recent studies provided evidence on the prevalence of LCCPs in indoor dust, sewage sludge, sediment, human plasma and terrestrial animals (Brandsma *et al.*, 2017; Li *et al.*, 2017; Wong *et al.*, 2017; Yuan *et al.*, 2017, 2019b).

1.1.5. Indoor exposure

The indoor environment can be seen as a substantial reservoir of FRs. Depending on their properties these chemicals may be transported from possible sources to dust by means of volatilization, leaching and abrasion, and/or direct transfer to dust (Coelhan and Hilger, 2014; Marklund *et al.*, 2003; Olofsson *et al.*, 2013; van der Veen and de Boer, 2012). Humans are ubiquitously exposed to various FRs, via diet, through direct contact with consumer products and through household dust, which is used to measure indoor chemical contamination, and can serve as an important exposure pathway to assess human exposure risks (Jones-Otazo *et al.*, 2005; Whitehead *et al.*, 2011). Indoor pet cats and toddlers share similar areas in the indoor environment and dust exposure actions (e.g. hand-to-mouth for toddlers, meticulous grooming for cats) could result in greater exposures to FRs through dust ingestion than adults (Norrgran Engdahl *et al.*, 2017; Wei *et al.*, 2015). FRs have also been reported in cat blood (Ali *et al*., 2013; Henríquez-Hernández *et al*., 2017; Norrgran Engdahl *et al.*, 2017) and detected in hair samples taken from pet cats (Ali *et al*., 2013). Pet cats have previously been presented as a potential bio-sentinel for indoor pollution exposure (Dye *et al*., 2007; Dirtu *et al.*, 2013b; Norrgran Engdahl *et al.*, 2017). Indoor cats might therefore have relevance as indoor exposure models for children. Human hair has been used as a bioindicator for human exposure to organic pollutants as a non-destructive monitoring system (Appenzeller and Tsatsakis, 2012). Cat hair is also directly exposed to the environment and constantly accumulates contaminants from indoor air and dust. Being a non-invasive matrix, hair samples allow for sample stability, information on compound exposure and the high lipid content allows for the analysis of a wide range of FRs. Contamination levels in cat hair may therefore be seen as an early warning system for the assessment of human exposure (especially of toddlers). Similarly, exposures via indoor dust ingestion, dermal contact or inhalation could also be significant exposure routes for pet cats, since they share activity areas (e.g. floors, rugs, carpets, sofas, etc.) and activities (crawling, grooming and licking) similar to toddlers.

1.1.6. Analytical methods

Information on the environmental behaviour of BFRs, OPFRs, and CPs hinges on the availability and the development of adequate analytical methods. Accurate and precise measurements of FRs concentrations are critical for risk assessment and decision making. The challenge in accurate quantification of these large FR groups is due to variation in physicochemical properties concerning polarity, solubility, volatility and persistence. The main criteria for specific analytical methods in the analysis of FRs in environmental samples are low detection limits and high selectivity. In addition, these toxic compounds are sometimes present at relatively low concentrations as complex mixtures, in the presence of structurally related matrix interferences. Sample preparation is, therefore, an important aspect of the analytical process. Although sample preparation may vary depending on the nature of the matrix, the major steps would include one or a combination of the following requirements: to release the analytes of interest from the sample matrix through exhaustive extraction, removal of the sample matrix through selective clean-up (which may involve purification and fractionation) and pre-concentration of the analyte. BFRs and CPs are typically stable when destructive clean-up approaches (e.g. treated with sulphuric acid or sulphuric acid impregnated silica gel) are used (Dirtu *et al.*, 2013a; Yuan *et al.*, 2019a). For OPFRs, non-destructive clean-up methods are required as some of these compounds are prone to degradation under strong acidic or basic conditions (Kucharska *et al.*, 2014). Gas chromatography (GC) coupled to mass spectrometer (MS) operating in the electron capture negative ionisation (ECNI) mode is mostly used for BFR analysis (Covaci *et al.*, 2011). Both liquid chromatography (LC) and GC coupled to tandem mass spectrometry (MS/MS) are employed for OPFR analysis. Due to ion suppression of observed in LC–MS/MS, GC–MS methods were recommended for the analysis of OPFRs in dust samples (Brandsma *et al.*, 2014). The analysis of CPs is a challenging task due to the extreme complexity of CP mixtures, which can comprise thousands of congeners with similar physicochemical properties. (Tomy *et al.*, 1997; van Mourik *et al.*, 2015) Organochlorine contaminants, e.g. polychlorinated biphenyls (PCBs), chlorinated pesticides and chlorinated olefins or di-olefins, further interfere with the instrumental analysis (Yuan *et al.*, 2019a). Due to analytical limitations of electron capture detectors (ECD), GC-ECNI-MS is most often applied for measuring CPs. Low resolution MS results in self-interference of CPs, which could be resolved with high resolution MS instrumentation, such as quadrupole time-of-flight MS (QTOF-MS) (van Mourik *et al.*, 2015; Yuan *et al.*, 2019a). Recent advances in CP analysis introduced chlorine adduct formation using negative ion atmospheric pressure chemical ionization (APCI) LC hyphenated with QTOF-MS (Bogdal *et al.*, 2015; Zencak and Oehme, 2004). Currently, there is a lack of higher order analytical measurement capabilities in South Africa.

The research and monitoring of these environmental toxicants and emerging organic pollutants in developing countries is essential, not only due to the adverse effects these chemicals can impose on environmental and human health, but also because of their potential impact on international trade and consequently on the economy. The lack of research with regard to emerging pollutants in South Africa offers a potential problem for the export of goods, especially food, due to stringent legislations and an ever increasing list of potentially hazardous chemicals. As there is virtually no substantial information for BFRs, OPFRs, and CPs to provide a comprehensive status on FRs in South Africa, there was a need to investigate the occurrence of these chemicals in the indoor environment in correlation with the rest of the world.

1.2. Scope and outline of the thesis

The scope of this thesis is to study the occurrence of BFRs, OPFRs and CPs in the South African indoor environment. The following aims/objectives have been set for this project; (1) provide an overview of existing information on BFRs in environmental compartments from different African countries; and to summarise the analytical method performance in Africa to analyse these compounds (*Chapter* 2), (2) evaluate the use of comprehensive two-dimensional gas chromatography coupled to high-resolution time-of-flight mass spectrometry (GC×GC-HR-TOF-MS) as a screening method to tentatively identify FRs and other organohalogenated compounds (OHCs) in cat hair, as a model for indoor exposure (*Chapter 3*), (3) to perform accurate quantitative analysis of BFRs, OPFRs, and CPs in indoor dust and cat hair and provide a preliminary estimation of the human exposure to OPFRs and BFRs via dust ingestion (*Chapter 4 and 5*).

Chapter 2 presents a review on BFR levels in the African environment and the various analytical methodologies applied in Africa or (often) at a different continent when capacity in Africa was lacking. The first part summarises the analytical methods used for the determination of BFRs, including sample preparation, detection techniques, and general comments from an analytical quality assurance perspective. The second part of the chapter discusses the current status of BFR levels in Africa compiled for environmental compartments from different countries. The matrices discussed include indoor dust, soil, aquatic environment (water, sediment, and aquatic organisms), eggs, wastewater treatment plant compartments, landfills (leachate and sediment), and human breast milk. In *Chapter 3*, a GC×GC-TOF-MS screening method was developed and hair from South African pet cats was studied to investigate the occurrence of OHCs in the domestic environment. Tentative identification of these compounds was supported by mass spectral database searches and elemental formula prediction from the experimentally determined accurate mass data. In *Chapter 4*, we focussed on the accurate quantification of eight PBDE congeners, two alt-BFRs, ten OPFRs in indoor dust and pet cat hair from South Africa. The measurement uncertainty associated with each compound for each matrix was estimated during the method validation procedure using a bottom-up approach. The contributing uncertainties were combined in a mathematical model that best represents their interactions in the measurement process to support the quality of the data and to identify uncertainty sources in the analytical method. In *Chapter 5* we report concentrations of ΣSCCPs, ΣMCCPs, and ΣLCCPs in the same indoor dust and pet cat hair from South Africa. Samples were analysed using flow injection mass spectrometry with negative ion APCI coupled to QTOF-MS under chlorine-induced adduct formation conditions. The accurate mass information was used to construct non-traditional Kendrick mass defect plots to obtain information on the magnitude of CPs and provide evidence of possible interfering compounds. Discussion, conclusions and implications are presented in *Chapter 6*.

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Chapter 2

Critical review of the analysis of brominated flame retardants and their environmental levels in Africa

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Abstract

World-wide, the prevalence of brominated flame retardants (BFRs) is well documented for routine analysis of environmental and biological matrices. There is, however, limited information on these compounds in the African environment and insufficient information on the analytical approaches used to obtain data. This paper presents a review on BFR levels in the African environment and the various analytical methodologies specifically applied in Africa for polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls and alternative-BFRs. The analyses include liquid sample preparation using liquid-liquid and solid phase extraction and solid sample preparation involving Soxhlet extraction, with ultrasound-assisted extraction increasingly being applied. Instrumental detection techniques were limited to gas chromatography coupled with electron capture detector and electron impact ionisation with single quadrupole mass spectrometers. Information on congener profile prevalence in indoor dust, soil, aquatic environment (water, sediment, and aquatic organisms), eggs, wastewater treatment plant compartments, landfills (leachate and sediment) and breast milk are presented. Although PBDEs were inconsistently detected, contamination was reported for all investigated matrices in the African environment. The manifestation in remote regions indicates the ubiquitous prevalence and long-range transport of these compounds. Levels in sediment, and breast milk from some African countries were higher than reported for Asia and Europe. Due to limited data or non-detection of alternative-BFRs, it is unclear whether banned formulations were replaced in Africa. Most of the data reported for BFR levels in Africa were obtained in non-African laboratories or in South Africa and formed the basis for our discussion of reported contamination levels and related methodologies.

2.1. Introduction

Flame retardants (FRs) are frequently applied to combustible materials to reduce their flammability, to delay ignition and to meet fire safety requirements. Brominated flame retardants (BFRs) exhibit a variety of beneficial physicochemical properties that can be favourably applied to combustible materials (e.g., polymers, plastics, wood, paper and textiles) and have been widely used in electronic and electric equipment, furniture, construction materials and other commercial products (Alaee *et al.*, 2003). Depending on the FR characteristics, the physical and chemical combustion processes which involve preheating, volatilization/decomposition, combustion and propagation, can be either delayed or some steps can be prevented in the solid, liquid or gas phase (EHC-192, 1997). The physical actions involve fuel dilution (where large non-combustible gas volumes are released), cooling (where endothermic processes cool the process to below temperatures required to sustain propagation), and charring (where combustible layers are isolated from the fuel source and/or insulated to reduce heat transfer) (EHC-192, 1997). The chemical modes of action involve reactions in the solid phase, through the formation of low thermal conductive surface films (where heat transfer rates are reduced and the formation of char barriers are promoted), and in the gaseous phase through the free radical mechanism where the FR dissociates into radical species that interfere with the flame propagating step (EHC-192, 1997). Halogens have the ability to capture free radicals produced during the combustion process to remove the flames' capability to spread. The capturing efficiency increases with the size of the halogen atom (F<Cl<Br<I) (Alaee *et al.*, 2003). Organobromine, organochlorine and organofluorine compounds are commonly used as FRs since iodinated compounds are unstable and decompose to some extent at elevated temperatures (Alaee *et al.*, 2003). Higher trapping efficiency and the ability to deliver halogen radicals at lower temperatures, make organobromines ideal FR candidates (Alaee *et al.*, 2003). Because of their toxic effects and their persistence, the pervasive environmental distribution of BFRs have been a subject of concern over the past decades. The most commonly used BFRs are polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), tetrabromobisphenol-A (TBBPA) and polybrominated biphenyls (PBBs) (Alaee *et al.*, 2003). However, PBB production stopped shortly after the 1973 disaster, where it was accidentally substituted for a non-toxic supplement in cattle feed and distributed to farms in the lower peninsula of Michigan (Carter, 1976).

Conventions and international governmental departments have introduced projects and guidelines to study the production, use and release of BFRs to provide information concerning environmental contamination, to evaluate the significance of the contamination and to assist with regulatory actions (Kemmlein *et al.*, 2003, 2009). Despite these prohibitions, BFR levels continue to be reported in the environment. The stringent regulations on worldwide use of BFRs have resulted in the introduction of alternative-BFRs (alt-BFRs) as replacements for banned formulations. For example, decabromodiphenyl ethane (DBDPE) was introduced as a replacement for deca-BDE, 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE) as a replacement for octa-BDE, bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) as replacement for penta-BDE. Alternative FRs include tetrabromobisphenol A-bis(2,3-dibromopropylether) (TBBPA-DBPE) and hexachlorocyclopentadienyldibromocyclooctane (HCDBCO) (Alaee *et al.*, 2003; Shaw *et al.*, 2014). The HBCD and commercial penta- and octa-PBDE mixtures are restricted under the Stockholm Convention (SC), whereas deca-BDE is on the list of proposed chemicals to be added (http://chm.pops.int/).

Numerous overviews on the global levels and trends of BFRs in environmental samples have been published (Alaee *et al.*, 2003; Covaci *et al.*, 2003, 2011; Cruz *et al.*, 2015; de Wit, 2002; de Wit *et al.*, 2010; Law *et al.*, 2014; Toms *et al.*, 2012; Wu *et al.*, 2012). Polder *et al.* (2008) presented one of the first reports on BFR levels in the African environment, in particular on PBDEs and HBCD in bird eggs from South Africa. Following this report, levels of BFRs were identified in abiotic and biotic environmental samples, collected from South Africa, Nigeria, Tanzania, Ghana, Congo, Egypt, Guinea-Bissau, Senegal, Tunisia, Uganda, Kenya and Ile Cocos, an island in the Indian Ocean (Table S2-1, Supporting material). Of the fifty papers reviewed here, twenty six of the papers describing BFR analysis were performed in non-African laboratories in Europe, North America and Asia. As stringent global regulations pose potential threats to international trade and industry in developing economies, African laboratories should ensure that the capability to accurately quantify persistent organic pollutants such as BFR's is committedly developed, established and maintained.

Due to the differences in the physicochemical properties of BFRs and their prevalence in various matrices, a wide variety of analytical approaches for sample preparation have been developed. Recent reviews on analysis methods for BFRs applied worldwide are available in the literature (Covaci *et al.*, 2003, 2007, 2011; Dirtu *et al.*, 2013; Fulara and Czaplicka, 2012; Król *et al.*, 2012; Papachlimitzou *et al.*, 2012; Stapleton, 2006; Xu *et al.*, 2013) and is not the scope of this paper.

The aim of this paper was to summarise published studies on BFR occurrence in environmental compartments from different African countries to present the current status on BFR levels; and to critically review the chemical analysis performance in Africa to analyse these compounds. In order to provide an overview of the current analytical status for the analysis of BFRs in Africa, twenty-four papers were selected where the procedure for BFR analysis was described and analysis performed in an African laboratory. The following sections summarise the analytical methods used for the determination of BFRs, including sample preparation, instrument detection techniques, general comments from an analytical quality assurance perspective and BFR levels in the African environment.

2.2. Analytical methods utilised in Africa

2.2.1. Sample preparation

Sample preparation is an important aspect of the analytical process. The analysis of target BFRs at low concentrations in complex environmental matrices often requires the inclusion of multi-step sample preparation. Depending on the nature of the matrix, sample preparation may vary, but the major steps would include one or a combination of the following requirements: to release and isolate the analytes of interest from the sample matrix through exhaustive extraction, removal of part of the sample matrix through selective clean-up (which may involve purification and fractionation) and pre-concentration of the analyte.

2.2.1.1. Extraction methods

In line with recommendations from previous international inter-laboratory comparisons (de Boer and Cofino, 2002; de Boer and Wells, 2006), most of the selected publications as summarised in Table 2-1 indicated that samples were collected in pre-cleaned amber or aluminium foil covered glass containers and stored at low temperatures (4 to -20 °C). Solid sample pre-treatment involved air drying (evaporation), sieving and grinding with a chemical drying agent, e.g. sodium sulphate (Na_2SO_4). Final extracts have also been treated with additional Na_2SO_4 to remove any residual moisture before analysis. Liquid sample pre-treatment involved filtration, to remove solid particles and acidification of the water samples (preservation). Extraction techniques employed included liquid-liquid extraction (LLE) and solid phase extraction (SPE) for liquid samples and Soxhlet extraction, ultrasound-assisted extraction (UAE) and liquid-solid extraction (LSE) for solid samples (Table 2-1). During extraction efficiency evaluation through recovery experiments, the terms recovery should be defined as recovery or apparent recovery to avoid confusion. Recovery refer to the yield from sample preparation steps of an analytical process compared to the amount of analyte in the original sample reported (Burns *et al.*, 2002). Apparent recovery is reported, when the calculated value obtained using an analytical procedure that involves a calibration graph is compared to a reference value (Burns *et al.*, 2002).

Liquid-liquid extraction is a simple and cost effective method for the extraction of BFRs from aqueous matrices. The choice of solvents to achieve exhaustive extraction of the analytes of interest is important. Other parameters include sample-solvent ratio, extraction time and the evaporation procedure (Moldoveanu and David, 2015). Because of the hydrophobicity of PBDEs and their relatively low concentrations in water, large sample volumes of up to 1 L are required for LLE (Fulara and Czaplicka, 2012). Odusanya *et al.* (2009) employed LLE and determined the extraction efficiencies of nine solvent systems using hexane, dichloromethane (DCM), petroleum ether, acetone and combinations of these solvents by spiking landfill leachates with PBDEs. Liquid-liquid extraction of 100 mL sample using petroleum ether (60 – 80 °C), gave better apparent recoveries. Olukunle *et al.* (2014) similarly investigated the extraction efficiency of nine solvent systems using hexane, DCM, toluene and combinations of these solvents for the extraction of fourteen BDE congeners from ultrapure water. Even though this matrix is not representative of the matrix under investigation, they concluded that DCM provided adequate recoveries (75 to 101%). Dichloromethane was previously used for the extraction of selected PBDEs and PBB153 from river water (Daso *et al.*, 2013a). In this study, spiked river water gave higher recoveries (106 to 131%) compared to ultrapure water (69 to 97%) (Daso *et al.*, 2013a). Due to the low water solubility and high log octanol/water partition coefficient (Log K_{ow}) it is expected that PBDEs tend to bind to the organic fraction of particulate matter. This extraction technique also provided sufficient recoveries for the extraction of PBDEs and BB153 from matrix spiked sewage sludge (Daso *et al.*, 2012) and alt-BFRs from landfill leachates (Olukunle and Okonkwo, 2015).

Solid phase extraction was also used for the extraction of PBDEs, PBBs, HBCD and TBBPA. Chokwe *et al.* (2012) evaluated the extraction efficiency of four different SPE cartridges using spiked wastewater samples. The recommended Strata™-X SPE product showed apparent recoveries from 53% (HBCD) to 110% (BB10). It was reported that recoveries improved when samples were spiked after filtration, this can be attributed to target analytes retained by particulate matter.

Table 2-1 *Summary of the sample preparation procedures used for the analysis for BFR analysis in Africa.*

Analytes	Sample type and size	Sample pre-treatment	Extraction technique	Clean-up technique	Recovery (%)	Ref.
Tri- to hepta-BDE	Landfill leachate (100 mL)	Not provided	LLE: 3 × 15 mL petroleum ether	0.5 cm^3 Na_2SO_4 + 6 g Silica column Elute with petroleum ether	Spiked matrix 102.9 - 108.0%	(Odusanya *et al.*, 2009)
Deca-BDE	Dust wipes (not provided)	Sieved (250 µm), homogenised	Soxhlet: hexane/acetone (2:1, v/v) for 8 h	Multi-layer silica column: 0.25 g Na_2SO_4, 0.25 g acid silica, 0.25 g basic silica, 0.25 g neutral silica, elute with hexane/acetone mixture	CRM: 84% Spiked matrix: 67 - 102%	(Kefeni *et al.*, 2011)
Tri- to hepta-BDE BB153	Sediment (10 g)	Dried and sieved (1 mm)	2 g Cu powder added to sample LSE: 120 mL hexane/acetone (2:1, v/v) for 12 h	Multi-layer silica column: 0.1 g Na_2SO_4, 0.1 g activated silica, 0.4 g acid silica, (44% w/w, conc. H_2SO_4) 0.1 g activated silica, 0.2 g (30% w/w, 1 N NaOH) basic silica, 0.1 g activated silica, elute with hexane	Spiked matrix: 84.4 - 110%	(Daso *et al.*, 2011)
Tri- to Hepta-, Deca-BDE BB153	Effluent (800 mL), Sewage sludge (10 g)	Effluent – No pre-treatment Sewage sludge dried at 50 °C, ground and sieved (500 µm)	Effluent - LLE: 3 × 40 mL DCM Sewage sludge - Soxhlet: hexane/acetone (3:1, v/v) for 16 h, concentrated at 45 °C	Effluent - Multi-layer silica column: 0.1 g Na_2SO_4, 0.1 g activated silica, 0.4 g 44% acid silica, 0.1 g activated silica, 0.2 g basic silica, 0.1 g activated silica, elute with hexane Sludge - Multi-layer silica column: 4 g Na_2SO_4, 2 g activated silica, 8 g 44% acid silica (44% H_2SO_4, w/w), 1 g activated silica, 4 g basic silica (30% NaOH, w/w), 1 g activated silica, elute with hexane	Surrogates: 58 – 102% Spiked matrix: 65 – 112%	(Daso *et al.*, 2012)
Tri- to hepta-, deca-BDE	Sediment (10 g)	Dried and sieved (150 µm)	Soxhlet: hexane/acetone (2:1, v/v) for 10 h	Extracts treated with 2 g Cu powder Multi-layer silica column: 0.2 g Na_2SO_4, 0.2 g neutral silica, 0.4 g acid silica, 0.2 g neutral silica, 0.2 g basic silica, 0.2 g neutral silica, elute with hexane/DCM (3:1, v/v)	Spiked matrix: 41.7% - 130%	(Olukunle *et al.*, 2012)
Tetra- to hexa-, deca-BDE Mono- to Tri-, hexa-, deca-BB	Dust (0.89 - 2.4 g)	Sieved (250 µm), homogenised with Cu powder	Soxhlet: hexane/acetone (2:1, v/v) for 8 h	Multi-layer silica column: 0.2 g Na_2SO_4, 0.2 g acid silica, 0.2 g neutral silica, 0.2 g basic silica, 0.2 g neutral silica, elute with hexane/DCM (5:1, v/v)	CRM: 84 ± 5.7 – 137 ± 7.9%	(Kefeni and Okonkwo, 2012)
Penta-, octa-BDE Mono-BB	Landfill leachates (not provided)	Filtered	SPE: C18 Elute with 5 mL hexane	-	Not provided	(Nomngongo *et al.*, 2012)
Mono- to tetra-BB HBCD TBBPA	Water (250 mL)	Acidified to pH 3, filtered using 0.47 µm pore size	SPE: Strata™-X Elute with 3 × 2 mL DCM/hexane (4:1, v/v) **Derivatization** HFBA heated to 55 °C for 2 h	-	Spiked matrix: 52.50 ± 6.23 – 117.50 ± 9.19%	(Chokwe *et al.*, 2012)
Di- to hexa-, deca-BDE	Dust (1 g)	Sieved (250 µm), homogenised with Cu powder	Soxhlet: hexane/acetone (2:1, v/v) for 8 h	Multi-layer silica column: 0.2 g Na_2SO_4, 0.2 g acid silica, 0.2 g neutral silica, 0.2 g basic silica, 0.2 g neutral silica, elute with hexane/DCM (5:1, v/v)	CRM: 78 ± 5 – 112 ± 6% Surrogate: 72 – 112%	(Kefeni and Okonkwo, 2013)
Tri- to hepta-, deca-BDE Hexa-BB	Water (800 mL)	No pre-treatment	LLE: 3 × 40 mL DCM Concentrated at 45 °C	Multi-layer silica column: 1 g Na_2SO_4, 0.1 g activated silica, 0.4 g acid silica (44% conc. H_2SO_4, w/w), 0.1 g activated silica, 0.2 g basic silica (30% NaOH, w/w), 0.1 g activated silica, elute with hexane	Milli-Q water QC: 69 – 97% Spiked matrix: 106 – 131%	(Daso *et al.*, 2013a)
Tri- to hepta-, deca-BDE BB153	Landfill leachate (800 mL)	No pre-treatment	LLE: 3 × 40 mL DCM Concentrated at 45 °C	Multi-layer silica column: 1 g Na_2SO_4, 0.1 g activated silica, 0.4 g 44% acid silica, 0.1 g activated silica, 0.2 g basic silica, 0.1 g activated silica, elute with hexane	Spiked matrix: 50.1 - 136% Surrogate: 54 - 92%	(Daso *et al.*, 2013b)
Mono- to hexa-, deca-BDE Di-, deca-BB	Dust (2.3 - 3.5 g)	Sieved (250 µm) and homogenised	Add 0.3 g Cu powder Soxhlet: hexane/acetone (2:1, v/v) for 8 h	Multi-layer silica column: 0.2 g Na_2SO_4, 0.2 g acid silica, 0.2 g neutral silica, 0.2 g basic silica, 0.2 g neutral silica, elute with hexane/DCM (5:1, v/v)	CRM: 78 ± 5 – 112 ± 6% Surrogate: 72 - 112%	(Kefeni *et al.*, 2014)
Mono- to hexa-, deca-BDE	Dust (2.3 - 3.5 g) Polymers (0.5 g)	Sieved (<45 µm to >150 µm)	Add 0.3 g Cu powder Soxhlet: hexane/acetone (2:1, v/v) for 8 h	Multi-layer silica column: 0.2 g Na_2SO_4, 0.2 g acid silica, 0.2 g neutral silica, 0.2 g basic silica, 0.2 g neutral silica, elute with hexane/DCM (5:1, v/v)	CRM: 78 ± 5 – 112 ± 6% Surrogate: 72 - 112%	(Kefeni and Okonkwo, 2014)

Analytes	Sample type and size	Sample pre-treatment	Extraction technique	Clean-up technique	Recovery (%)	Ref.
Tri- to hepta-, deca-BDE	leachates (500 mL) sediment (10 g)	Not provided	Leachates - LLE: 3 × 40 mL DCM, concentrated at 45 °C Sediment - Add 2 g Cu powder Soxhlet: hexane/acetone (2:1, v/v) for 16 h	Extracts treated with 2 g Cu powder. Multi-layer silica column: 0.2 g Na_2SO_4, 0.2 g neutral silica, 0.4 g acid silica, 0.2 g neutral silica, 0.2 g basic silica, 0.2 g neutral silica, elute with hexane/DCM (3:1, v/v)	Spiked matrix: 75 – 101% Surrogate: 81 – 90%	(Olukunle *et al.*, 2014)
Tri- to hepta-, deca-BDE	Dust (0.8 g)	Sieved (212 µm) and homogenised	Sonication: 2 × 10 mL hexane/MeOH (1:3, v/v) for 30 min at a 40 °C	0.8 g Na_2SO_4, 3 g Silica, fraction 1 elute with 25 mL hexane, fraction 2 elute with diethyl ether/hexane (1:1 v/v)	CRM: 95.7 – 111.8%	(Abafe and Martincigh, 2014, 2015)
Tri- to hepta-, deca-BDE	Eggshells and egg membranes and albumen (1 - 2 g)	Dried, separated membranes and grounded	Sonication: 2 × 5 mL hexane/DCM (1:1, v/v) for 60 and 30 min at a 65 °C followed by 2 mL hexane/DCM (1:1, v/v) for 30 min at a 65 °C Concentrated at 45 °C	Florisil: 2 g, elute with hexane	Surrogate: 40.00 - 135.94%	(Daso *et al.*, 2015)
Tri- to hepta-, deca-BDE	Dust (0.1 g)	Sieved	Add 2 g Cu powder Soxhlet: hexane/acetone (2:1, v/v) for 8 h	Multi-layer silica column: 0.5 g Na_2SO_4, 0.1 g silica, 0.16 g acid silica, 0.16 g silica, 0.16 g basic silica, 0.16 g silica, elute with hexane/DCM (5:1, v/v)	Surrogate: 65 - 90% CRM: 70 – 111%	(Olukunle *et al.*, 2015a)
Tetra- to hepta-, deca-BDE	Dust (100 mg)	Dried and sieved (150 µm)	Sonication: 3 cycles toluene/DCM (1:1, v/v) at 55 °C for 15 min, centrifuged and reduced under a gentle flow of N2 to about 1 mL	Multi-layer silica column: 0.5 g Na_2SO_4, 0.16 g silica, 0.06 g Pesticarb, 0.16 g silica, elute with toluene/DCM (1:1, v/v)	Surrogate: 104 - 126% CRM: 70 – 111%	(Olukunle *et al.*, 2015b)
Tri- to hepta-BDE PBB101 HBCD	Fish (5 g)	Grounded with 20 g Na_2SO_4	Sonication: 2 cycles, 20 mL hexane/acetone (4:1, v/v) at 55 °C for 45 min, treated with conc. H_2SO_4 and evaporated to dryness	Re-constituted in 2.5mL MeOH, diluted to 250 mL, and acidified with acetic acid SPE (Strata-X Polymeric Reverse Phase), elute with DCM/hexane (4:1, v/v) elutes were collected and reduced to dryness under gentle stream of nitrogen **Derivatization** TEA and HFBA heated to 50 °C for 30 min	Spiked matrix: 50.02 [a] - 90.88%	(Chokwe *et al.*, 2015a)
Tetra- to hepta-BDE PBB101 HBCD	Water (250 mL) Sediment (5 g) Fish (5 g)	Water (acidified) Sediment (grinded with 20 g Na_2SO_4) Fish (Grinded with 20 g Na_2SO_4)	Water – SPE: Strata™-X Sediment –Sonication: 2 cycles, hexane/acetone (4:1, v/v) at 55 °C for 45 min, 2 g Cu added, evaporated to dryness Fish - Sonication: 2 cycles, 20 mL hexane/acetone (4:1, v/v) at 55 °C for 45 min, treated with conc. H_2SO_4 and evaporated to dryness	Re-constituted in 2.5mL MeOH, diluted to 250 mL, and acidified with acetic acid SPE (Strata-X Polymeric Reverse Phase), elute with DCM/hexane (4:1, v/v) elutes were collected and reduced to dryness under gentle stream of nitrogen **Derivatization** TEA and HFBA heated to 55 °C for 2 h	Spiked matrix: 63 – 99%	(Chokwe *et al.*, 2015b)
Tri- to hepta-BDE Tri- to penta-BB TBBPA HBCD	Sewage sludge (5 g)	Centrifuged, precipitate mixed with 20 g Na_2SO_4	Sonication: 2 cycles, 30 mL hexane/acetone (4:1, v/v) at 55 °C for 45 min 3 g acid silica, elute with 40 mL DCM Add 2 g Cu concentrate	Re-constituted in 2.5mL MeOH, diluted to 250 mL, and acidified with acetic acid SPE (Strata-X Polymeric Reverse Phase), elute with DCM/hexane (4:1, v/v) elutes were collected and reduced to dryness under gentle stream of nitrogen **Derivatization** TEA and HFBA heated to 50 °C for 30 min	Spiked matrix: 38.65 - 78.63%	(Chokwe *et al.*, 2015c)
EH-TBB, BTBPE, DBDPE, BEH-TEBP, HBCD	Sediment (10 g) Leachates (500 mL)	Sediment – Dried, ground sieved (150 µm) Leachates - filtered	Sediment – Soxhlet: 180 mL hexane/DCM (1:1, v/v) for 16 h Leachates - LLE: 3 × 40 mL DCM Concentrated at 45 °C	Multi-layer silica column: 0.5 g Na_2SO_4, 0.16 g silica, 0.06 g Pesticarb, 0.16 g silica, elute with hexane	Surrogate: 65% and 110%	(Olukunle and Okonkwo, 2015)
Tri- to hepta-, deca-BDE BB153	Sediment (10 g)	Dried and sieved (500 µm)	2 g Cu powder added to sample LSE: 120 mL hexane/acetone (2:1, v/v) for 12 h	Multi-layer silica column: 0.1 g Na_2SO_4, 0.1 g activated silica, 0.4 g acid silica, (44% w/w, conc. H_2SO_4) 0.1 g activated silica, 0.2 g (30% w/w, 1 N NaOH) basic silica, 0.1 g activated silica, elute with hexane	Spiked matrix: 90.3 - 130%	(Daso *et al.*, 2016)

[a] Recovery include nonylphenol penta ethoxylates isomer (NPPE2)

Soxhlet extraction is the well-established extraction technique for persistent organic pollutants (POPs). This continuous extraction process, often applied to solid or semi-solid samples, is used to extract organic analytes into a solvent. Samples are usually dried (e.g. with Na_2SO_4) and ground to increase the surface area of the particles prior to extraction. The number of extraction cycles used depends on the analyte solubility and the capacity of the solvent to penetrate the matrix (Moldoveanu and David, 2015). It is a cost-effective technique that allows for high process efficiency, but requires long extraction times and large volumes of solvent. As shown in Table 2-1, Soxhlet extraction was used for the extraction of BFRs from dust, sewage sludge and sediment. PBDEs and PBBs were extracted from dust using a mixture of hexane/acetone (2:1, v/v) for 8 h. This method was used to analyse a dust certified reference material (CRM) and apparent recoveries of between 78 ± 5 ng/g for BDE209 and 112 ± 6 ng/g for BDE17 were reported (Kefeni and Okonkwo, 2013, 2014; Kefeni *et al.*, 2014). This solvent system was also used for the extraction of sediment, applying different extraction times (Olukunle *et al.*, 2012, 2014). The 16 h extraction time gave sufficient recoveries (81 to 90%), while shorter extraction times had lower recoveries for BDE209. Alt-BFRs were extracted from sediment for 16 h using Soxhlet with hexane/DCM (1:1, v/v) and recoveries ranged from 65 to 110% (Olukunle and Okonkwo, 2015).

Ultrasound-assisted extraction (UAE), where high frequency electrical energy is converted into ultrasound waves, was used in a number of studies for the extraction of PBDEs, PBBs, HBCD and TBBPA. Four solvent system combinations comprising of hexane, DCM, acetone and toluene were evaluated by spiking Na_2SO_4 (Olukunle *et al.*, 2015b). It was concluded that toluene/DCM (1:1, v/v) using three 15 min cycles at 55 °C gave optimal recovery. Abafe and Martincigh (2015, 2014) used hexane/methanol (MeOH) (1:3, v/v) as solvent and extracted a dust CRM at 40 ^{0}C for 30 min and reported recoveries between 96 and 112%. Ultrasound-assisted extraction was also used for the extraction of PBDEs from eggshells, eggshell membranes and residual albumen using hexane/DCM (1:1, v/v) for 60 min and two further cycles of 30 min at 65 °C and a wider recovery range was reported (Daso *et al.*, 2015). When comparing apparent recoveries obtained from the extraction of a dust CRM with Soxhlet extraction (hexane/acetone 2:1, v/v for 8 hours) and UAE (three 15 min cycles with toluene/DCM 1:1, v/v at 55 °C), identical apparent recoveries were reported for the tri- to hepta- and deca-BDEs ranging from 70% for BDE153 to 111% for BDE183 (Olukunle *et al.*, 2015a, 2015b). Liquid-solid extraction was employed in a single study for the extraction of tri- to hepta-BDEs and BB153 from sediment by mechanical shaking with a mixture of hexane/acetone (2:1, v/v) for 12 h (Daso *et al.*, 2011, 2016).

2.2.1.2. Clean-up methods

Sulphur removal from abiotic and lipid removal from biotic matrices should be included in the clean-up step to improve chromatographic separation of BFRs. For the removal of sulphur from dust and sediment, metallic copper powder was either added to the sample during the homogenisation step before extraction (Daso *et al.*, 2016; Kefeni and Okonkwo, 2012, 2013), mixed during extraction (Kefeni and Okonkwo, 2014; Kefeni *et al.*, 2014; Olukunle *et al.*, 2014, 2015a) or added after extraction (Chokwe *et al.*, 2015b). Non-destructive lipid removal was applied to eggshells, eggshell membranes and remaining albumin using Florisil® as fat retainer (Daso *et al.*, 2015). Destructive methods using concentrated sulphuric acid were used for the remove of fat from fish (Chokwe *et al.*, 2015a, 2015b; Daso *et al.*, 2015).

Clean-up and fractionation of BFRs are summarised in Table 2-1. The process mainly involved the use of multi-layer silica columns containing Na_2SO_4 (0.1 to 1 g), neutral activated silica (0.25 to 4 g), sulphuric acid impregnated silica (0.16 to 8 g), potassium hydroxide impregnated silica (0.16 to 4 g) or combinations thereof. The multi-layer silica columns were modified by replacing the acid- and basic silica combinations with Pesticarb (0.06 g) for the clean-up of PBDEs from dust extracts (Olukunle *et al.*, 2015b) and alt-BFRs from landfill sediment and leachates (Olukunle and Okonkwo, 2015). A column system consisting of Na_2SO_4 and activated silica was used for PBDEs cleaned-up from landfill leachate extracts (Odusanya *et al.*, 2009). Abafe and Martincigh (2014, 2015) used Na_2SO_4, activated silica and Florisil® for clean-up and fractionation of dust extracts. The first fraction was eluted with hexane, containing BDE 209 and the second fraction eluted using diethyl ether/hexane (1:1, v/v) to collect the remaining PBDEs.

2.2.2. Instrumental analysis

Injection and detection techniques and column characteristics are imperative for the analysis of BFRs. Where gas chromatography (GC) analysis is used as a separation technique, identification and quantitation of BFRs is often performed using electron capture detector (ECD), a sensitive detection technique for organohalogenated compounds. Although, compound co-elution is an important consideration for complex samples (Stapleton, 2006). The disadvantage of GC-ECD is poor selectivity; all halogen containing compounds produce a signal and the presence of PCBs at high concentrations may influence the accurate quantitation of PBDEs (Alaee *et al.*, 2001). The ECD is not isotope selective. Therefore, the use of $^{13}C_{12}$-labelled internal standards is impractical due to co-elution with the native compounds. Alaee *et al.* (2001) used GC-ECD configured with a 30 m 5-MS (diphenyl dimethylpolysiloxane) type column to investigate the co-elution of thirty-four di- to hepta-BDE congeners with commonly occurring PCBs and other organochlorine (OC) compounds. Potential co-elutions for ten PBDE congeners with PCBs and OCs were reported, and of particular concern is the interference of CB180 with BDE47. While these considerations have to be taken into account when using GC-ECD, co-elutions may be resolved by using mass spectrometry (MS). The determination of PBDEs using low-resolution mass spectrometry (LR-MS) is typically performed with either electron capture negative ionisation (ECNI) or electron impact ionisation (EI), either in full scan, selective ion monitoring (SIM) or selective reaction monitoring modes in MS/MS instruments. As shown in Table 2-2, a number of studies have reported BFR analysis using GC-ECD and electron impact ionisation with single quadrupole mass spectrometers (GC-EI-

MS) in full scan and SIM modes. In some studies GC-ECD was solely used for the analysis of BDE209 (Kefeni and Okonkwo, 2012; Olukunle *et al.*, 2012). GC-time-of-flight mass spectrometry (GC-TOF-MS) was also used but limited to structural confirmation of target compounds (Daso *et al.*, 2013a, 2016). For the analysis of BFRs using GC-EI-MS in full-scan and SIM mode, the molecular ions $[M]^{+\bullet}$ were used for quantitation and identification was confirmed by retention time comparison and the presence of two qualifier ions (Kefeni and Okonkwo, 2012, 2013, 2014; Kefeni *et al.*, 2014; Olukunle *et al.*, 2012, 2014, 2015a). Ions formed during EI ionisation depend on the degree of bromination and the intensity of the molecular ion $[M]^{+\bullet}$ decrease with an increase in the number of bromine atoms. The mass spectra of higher brominated BDEs are mostly dominated by fragment ions e.g. $[M\text{-}Br_2]^{+\bullet}$. Only three studies specified the use of fragment ions $[M\text{-}Br_2]^{+\bullet}$ and/or molecular ions $[M]^{+\bullet}$ as quantitation ions for SIM analysis of PBDEs (Abafe and Martincigh, 2014, 2015; Daso *et al.*, 2015).

2.2.2.1. Injection technique

The injection technique applied to introduce analytes into a GC column needs to be carefully selected and optimised to ensure sample integrity. The most frequently used injection techniques for the analysis of PBDEs include splitless or pulsed splitless injection, on-column injection and programmed temperature vaporizing (PTV) injection (Król *et al.*, 2012; Stapleton, 2006). Splitless injection mode allows for the introduction of low analyte concentrations, but this method may be limited by smaller injection volumes and high inlet temperatures (Björklund *et al.*, 2004; Król *et al.*, 2012; Stapleton, 2006). The temperature and the injection time prior to column transfer are important factors contributing to the response (Björklund *et al.*, 2004). Pressure-pulsed splitless injection is recommended to reduce injector residence times at high temperatures for BDE209 and other higher brominated BDEs (de Boer and Wells, 2006; Stapleton, 2006). As shown in Table 2-2, splitless injection with volumes of 1 µl is the most frequently used injection technique. For the analysis of PBDEs, PBBs and HBCD the injector temperatures ranged from 250 to 300 °C, whereas 225 °C was used for the analysis of alt-BFRs (Olukunle and Okonkwo, 2015). Abafe and Martincigh (2014, 2015) used pulsed splitless injection with the injector temperature at 285 °C. Kefeni *et al.* (2011) optimised various chromatographic parameters for the analysis of BDE209, and demonstrated an increase in response with increased inlet temperatures from 250 to 300 °C.

Table 2-2 *Summary of the analytical procedures used for the analysis for BFR analysis in Africa.*

Analyte groups	**Injection volume (µL), mode, temp (°C)**	**Carrier gas, flow rate (mL/min)**	**Column (m × mm × µm)**	**GC oven conditions**	**Separation and detection**	**LOD**	**Ref.**
Tri- to hepta-BDE	1, Splitless, 250	He, 3	ZB-5 (30 × 0.25 × 0.25)	90 °C (1 min), 210 °C at 30 °C/min, 290 °C at 10 °C/min	GC-ECD	10 - 500 pg/L^a	(Odusanya *et al.*, 2009)
Deca-BDE	1, Splitless, 290	N$_2$/He, 1.5 (for 30 m column), 2.5 (for 15 m column)	ZB-5 (15 × 0.25 × 0.25) ZB-5 (30 × 0.25 × 0.25)	90 °C (1 min), 300 °C at 30 °C/min (5 min), 310 °C at 10 °C/min (4.5 min for 15 m) (32 min for 30 m)	GC-ECD	0.5 ng/g^b	(Kefeni *et al.*, 2011)
Tri- to hepta-BDE BB153	1, Splitless, 280	He, 1.5	DB-5 MS (60 × 0.25 × 0.1)	100 °C (2 min), 220 °C at 20 °C/min, 300 °C at 4 °C/min (7 min)	GC-ECD	0.03 - 0.13 ng/g^b	(Daso *et al.*, 2011)
Tri- to Hepta-, Deca-BDE BB153	1, Splitless, 280 (BDE209 – 250)	He, 1.5 (BDE209: He, 3.0)	DB-5 MS (60 × 0.25 × 0.1) BDE209 - DB-5 MS (15 × 0.25 × 0.1)	100 °C (2 min), 220 °C at 20 °C/min, 300 °C at 4 °C/min (7 min) BDE209: 100 °C (1 min), 150 °C at 50 °C/min, 310 °C at 12.5 °C/min	GC-ECD	Not provided	(Daso *et al.*, 2012)
Tri- to hepta-, deca-BDE	1, Splitless, 290	He, 1.5 (BDE209: N$_2$, 2.5)	DB-5 (30 × 0.25 × 0.10). BDE209 - ZB-5 (15 × 0.25 × 0.25)	90 °C (1 min), 300 °C at 30 °C/min (5 min), 310 °C at 10 °C/min (1 min), for BDE209 (3 min) Transfer line: 300 °C	GC-EI-MS (full scan) and ECD	0.03 - 0.32 ng/g BDE209: 4.66 ng/g	(Olukunle *et al.*, 2012)
Tetra- to hexa-, deca-BDE Mono- to Tri-, hexa-, deca-BB	1, Splitless, 290	He, 1.5 (BDE209: N$_2$, 2.5)	DB-5 (30 × 0.25 × 0.10). BDE209 - ZB-5 (15 × 0.25 × 0.25)	90 °C (1 min), 300 °C at 30 °C/min (5 min), 310 °C at 10 °C/min (1 min), for BDE209 (3 min) Transfer line: 300 °C	GC-EI-MS (full scan) and ECD	0.3 - 0.5 ng/g^b BB209: 0.8 ng/g^b BDE209: 1.2 ng/g^b	(Kefeni and Okonkwo, 2012)
Penta-, octa-BDE Mono-BB	Not provided	He, 1	BPX5 (30 × 0.25 × 0.25)	80 °C (2 min), 140 °C at 50 °C/min (1.5 min), 220 °C at 20 °C/min (1 min), 280 °C at 2 °C/min, 300 °C at 30 °C/min (10 min) Transfer line: 280 °C	GC-EI-MS (full scan)	Not provided	(Nomngongo *et al.*, 2012)
Mono- to tetra-BB HBCD TBBPA	1, Splitless, 275	He, 40 cm/s	DB-5 (15 and 30 × 0.25 × 0.25) Rtx-1614 (15 × 0.25 × 0.10)	50 °C to 120 °C at 7.5 °C/min , 275 °C at 15 °C/min , 300 °C at 25 C/min (2 min) Transfer line: 300 °C	GC-EI-MS^c	0.01 - 0.1 µg/L^b	(Chokwe *et al.*, 2012)
Di- to hexa-, deca-BDE	1, Splitless, 290	He, 1.5	HP-5MS (30 × 0.25 × 0.25) BDE209 - ZB-5 (15 × 0.25 × 0.1)	90 °C (1 min), 300 °C at 30 °C/min (5 min), 310 °C at 10 °C/min (1 min) Transfer line: 300 °C	GC-EI-MS (SIM)	0.04 - 0.7 ng/g BDE209: 1.3 ng/g	(Kefeni and Okonkwo, 2013)
Tri- to hepta-, deca-BDE Hexa-BB	1, Splitless, 280 (BDE209 – 250)	He, 1.5 (BDE209: He, 3.0)	DB-5 MS (60 × 0.25 × 0.1) BDE209 - DB-5 MS (15 × 0.25 × 0.1)	100 °C (2 min), 220 °C at 20 °C/min, 300 °C at 4 °C/min (7 min) BDE209: 100 °C (1 min), 150 °C at 50 °C/min, 310 °C at 12.5 °C/min	GC-EI-TOF-MS (Identification) GC-ECD (Quantification)	0.16 - 1.54 ng/L^b	(Daso *et al.*, 2013a)
Tri- to hepta-, deca-BDE BB153	1, Splitless, 280 (BDE209 – 250)	He, 1.5 (BDE209: He, 3.0)	DB-5 MS (60 × 0.25 × 0.1) BDE209 - DB-5 MS: (15 × 0.25 × 0.1)	100 °C (2 min), 220 °C at 20 °C/min, 300 °C at 4 °C/min (7 min) BDE209: 100 °C (1 min), 150 °C at 50 °C/min, 310 °C at 12.5 °C/min	GC-ECD	0.1 - 1 ng/mL^a BDE209: 5 ng/mL^a	(Daso *et al.*, 2013b)
Mono- to hexa-, deca-BDE Di-, deca-BB	1, Splitless, 290	He, 1.5	HP-5MS (30 × 0.25 × 0.25) BDE209 - ZB-5 (15 × 0.25 × 0.1)	90 °C (1 min), 300 °C at 30 °C/min (5 min), 310 °C at 10 °C/min (1 min) Transfer line: 300 °C	GC-EI-MS (SIM)	0.13 – 1.8 ng/g	(Kefeni *et al.*, 2014)

Analyte groups	Injection volume (µL), mode, temp (°C)	Carrier gas, flow rate (mL/min)	Column (m × mm × µm)	GC oven conditions	Separation and detection	LOD	Ref.
Mono- to hexa-, deca-BDE	1, splitless, 290	He, 1.5	HP-5MS (30 × 0.25 × 0.25). BDE209 - ZB-5 (15 × 0.25 × 0.1)	90 °C (1 min), 300 °C at 30 °C/min (5 min), 310 °C at 10 °C/min (1 min) Transfer line: 300 °C	GC-EI-MS (SIM)	0.04 to 0.7 ng/g BDE209: 1.8 ng/g	(Kefeni and Okonkwo, 2014)
Tri- to hepta-, deca-BDE	1, Splitless, 290	He, 1.5	ZB-5 (15 × 0.25 × 0.25)	90 °C (1 min), 300 °C at 30 °C/min (5 min), 310 °C at 10 °C/min (10 min) Transfer line: 300 °C	GC-EI-MS (SIM)	0.02 - 0.3 ng/µL BDE209: 0.9 ng/µL	(Olukunle *et al.*, 2014)
Tri- to hepta-, deca-BDE	1, Pulsed Splitless, 285	He – 1.2	Rtx-1614 (15 × 0.25 × 0.10)	90 °C (2 min), 270 °C at 20 °C/min, 325 °C at 10 °C/min (5 min) Transfer line: 350 °C	GC-EI-MS (SIM)	0.03 – 0.16 ng/g	(Abafe and Martincigh, 2014, 2015)
Tri- to hepta-, deca-BDE	1, Splitless, 270	He, 2.33	ZB-5 (15 × 0.25 × 0.25)	90 °C (1 min), 200 °C at 40 °C/min, 250 °C at 25 °C/min, 310 °C at 7.5 °C/min (5 min) Transfer line: 280 °C	GC-EI-MS (SIM)	0.03 – 8.88 ng/g[b]	(Daso *et al.*, 2015)
Tri- to hepta-, deca-BDE	1, Splitless, 290	He, 1.5	ZB-5 (15 × 0.25 × 0.25)	90 °C (1 min), 300 °C at 30 °C/min (5 min), 310 °C at 10 °C/min (10 min) Transfer line: 300 °C	GC-EI-MS (SIM)	0.01 - 0.024 ng/µL[a]	(Olukunle *et al.*, 2015a)
Tetra- to hepta-, deca-BDE	1, Splitless, 290	He, 1.5	DB 5 (15 × 0.25 × 0.1)	90 °C (1 min), 300 °C at 30 °C/min (5 min), 310 °C at 10 °C/min (10 min) Transfer line: 300 °C	GC-EI-MS (SIM)	0.009 - 0.025 ng/µL[a]	(Olukunle *et al.*, 2015b)
Tri- to hepta-BDE PBB101 HBCD	1, Splitless, 275	He - linear velocity 40 cm/s	Rtx-1614 (15 × 0.25 × 0.10)	50 °C to 120 °C at 7.5 °C/min, 275 °C at 15 °C/min, 280 °C at 25 °C/min (1 min) Transfer line: 280 °C	GC-EI-MS[c]	Not provided	(Chokwe *et al.*, 2015a)
Tetra- to hepta-BDE PBB101 HBCD	Not provided, 280	He - linear velocity 40 cm/s	Rtx-1614 (15 × 0.25 × 0.10)	50 °C to 120 °C at 7.5 °C/min, 275 °C at 15 °C/min, 300 °C at 25 °C/min (2 min) Transfer line: 300 °C	GC-EI-MS[c]	0.01 – 0.2 µg/L 0.12 – 0.48 ng/g	(Chokwe *et al.*, 2015b)
Tri- to hepta-BDE Tri- to penta-BB TBBPA HBCD	1, Splitless, 300	He - linear velocity 40 cm/s	Rtx-1614 (15 × 0.25 × 0.10)	50 °C to120 °C at 7.5 °C/min, 275 °C at 15 °C/min, 300 °C at 25 °C/min (2min) Transfer line: 275 C	GC-EI-MS[c]	0.30 - 4.50 ng/g[b]	(Chokwe *et al.*, 2015c)
EH-TBB, BTBPE, DBDPE, BEH-TEBP, HBCD	1, Splitless, 225	He, 2	DB 5 (15 × 0.25 × 0.1)	100 °C (2 min), 160 °C at 10 °C/min (2 min), 300 °C at 40 °C/min (10 min) Transfer line: 280 °C	GC-EI-MS (SIM)	0.005 - 0.025 ng/µL[a]	(Olukunle and Okonkwo, 2015)
Tri- to hepta-, deca-BDE BB153	1, Splitless, 280 (BDE209 – 250)	He, 1.5 (BDE209: He, 3.0)	DB-5 MS (60 × 0.25 × 0.1) BDE209 - DB-5 MS (15 × 0.25 × 0.1)	100 °C (2 min), 220 °C at 20 °C/min, 300 °C at 4 °C/min (7 min) BDE209: 100 °C (1 min), 150 °C at 50 °C/min, 310 °C at 12.5 °C/min	GC-EI-TOF-MS (Identification) GC-ECD (Quantification)	0.03 - 0.13 ng/g[b]	(Daso *et al.*, 2016)

[a] Instrument detection limit
[b] Method detection limit
[c] Instrument scan mode not provided

2.2.2.2. GC column system

The GC capillary column stationary phase, length, film thickness, inner diameter and carrier gas flow rate are considerations influencing the separation characteristics and response of PBDEs. Although a range of different columns have been used for the determination of PBDEs in environmental samples, the most widely used GC columns for the analysis of BFRs are non-polar to mid-polarity stationary phases (Björklund *et al.*, 2004; Korytár *et al.*, 2005). Thicker stationary phase columns (> 0.25 μm) require increased elution temperatures and long GC columns (> 30 m) results in extended exposure time at elevated temperatures and may contribute to thermal degradation of the higher brominated congeners (Björklund *et al.*, 2004). De Boer *et al.* (2001) reported that good separation for the majority of PBDEs can be obtained by using a 50 m column, and a shorter (15 m) column for deca-BDE. Shorter GC columns produce narrower chromatographic peaks and more compressed chromatograms and depending on the detector used, sufficient data points should be recorded over the peak detected (Van Leeuwen and de Boer, 2008). The GC analysis times can be reduced by using higher carrier gas flow rate, increased temperature program heating rates and by using shorter column lengths, thinner column diameters and thinner stationary phases (Klee and Blumberg, 2002). Narrow bore columns (< 0.15 mm) provide more theoretical plates per length of column resulting in improved chromatographic resolution, but restrict the amount of sample to be loaded on the column.

Björklund *et al.* (2004) proposed that due to the high boiling point of BDE209, a final oven temperature of 300 °C should be used to compromise between PBDE degradation and peak broadening since the GC oven temperature program affects the chromatographic resolving power, peak shape and response. Kefeni *et al.* (2011) investigated different final GC oven temperatures and concluded that temperatures between 300 and 310 °C, using a 5% phenyl-methylpolysiloxane stationary phase column (15 m × 0.25 mm × 0.25 μm), provide good chromatographic resolution and improved response for BDE209. As shown in Table 2-2, final GC oven temperatures employed for the analysis of PBDEs range from 290 to 310 °C. Typical column diameters employed included 0.25 mm diameter with film thickness ranging from 0.1 to 0.25 μm with non-polar stationary phases. Limited information on the behaviour and degradation of congeners with higher degree of bromination and BDE209 was provided; some studies discussed the problems associated with BDE209 analysis and the reasons for not analysing the congener (Chokwe *et al.*, 2015a, 2015b; Daso *et al.*, 2011; Odusanya *et al.*, 2009). BDE209 response was evaluated using two columns with different lengths (15 and 30 m) with identical stationary phase and dimensions and a threefold increase in response was reported when using the shorter column (Kefeni *et al.*, 2011). Improved chromatographic resolution was achieved for columns with thin film thickness (0.1 μm) compared to identical columns with film thickness of 0.25 μm (Kefeni and Okonkwo, 2012). BDE209 breakdown during analysis was also observed when using a 60 meter thin film (0.1 μm) column (Daso *et al.*, 2012).

Korytár *et al.* (2005) compiled an extensive retention-time database for PBDE congeners using different capillary GC columns and reported on elution patterns for the hundred twenty-six PBDE congeners analysed. Sixty-three co-elutions were reported for the DB-5 (30 m × 0.25 mm × 0.25 µm) column including the co-elution of BDE154 with BB153 and dimethylated tetrabromobisphenol-A (Me-TBBP-A). Covaci *et al.* (2003) provided a detailed summary of several potential chromatographic interferences and showed that BDE153 co-elutes with TBBP-A on a DB-5-type column and also suggested that BDE47 and BDE99 may have interferences with breakdown products of HBCD. Daso *et al.* (2011) reported on the co-elution of BDE154 and BB153 using a 30 m (0.25 mm × 0.25 µm) column, this co-elution was resolved by using a longer thin film column (60 m × 0.25 mm × 0.1 µm). Olukunle *et al.* (2012) analysed 16 PBDE congeners using a 30 m DB-5 column and found that BDE85 co-elutes with BDE126.

2.2.3. Quality assurance/quality control

Accurate analysis of BFRs is important to facilitate scientists in providing reliable data for environmental policy makers. In order to minimize errors and ensure sufficient quality of data obtained, a number of quality assurance (QA) procedures, that include quality control (QC) measures, should be applied prior and during analysis. This includes the use of high quality calibrants such as certified reference materials (CRM), blank analysis (procedural and method blanks), recovery experiments, analysis of matrix matched CRMs and the participation in inter-laboratory studies (Covaci *et al.*, 2003).

In the reviewed papers, where analysis was performed in Africa, special reference was made to ensure that glassware used during the analysis was sufficiently cleaned to eliminate any contamination (de Boer and Cofino, 2002; de Boer and Wells, 2006). Solvent and method blanks were regularly analysed and authors typically reported on the absence of any BFRs, with one exception where detectable levels were found in the method blanks and blank correction was applied (Daso *et al.*, 2015). Blank correction procedure is not recommended as the background should preferably be clean enough to provide minimal blank values. Depending on the sample clean-up procedure and the detection method employed, column selection should also include the evaluation of possible co-elution of target analytes and structurally related analytes present in the sample. Limited information on chromatographic interferences with BFR target analytes were reported in the reviewed papers.

The reliability of the obtained result significantly increases with the use of $^{13}C_{12}$-labelled standards as internal standards (IS) and/or syringe standards (SS) (de Boer and Cofino, 2002), but these standards do have additional financial implications on the analysis. Only one study described the use of $^{13}C_{12}$-labelled BDE analogues added prior to extraction where recoveries were used to assess method accuracy (Daso *et al.*, 2015). Matrix matched CRMs are commercially available from different suppliers and used to assess precision and trueness of measurement methods, calibration, establishing traceability, and generally to assist in method validation (ISO GUIDE 33, 2015). Due to limited availability of CRMs for some of the investigated matrices, matrix matched QC samples were used (Chokwe *et al.*, 2012, 2015a, 2015b; Daso *et al.*, 2013a, 2016; Odusanya *et al.*, 2009; Olukunle and Okonkwo, 2015; Olukunle *et al.*, 2012, 2014). For the analysis of dust, a dust CRM was regularly used to assess apparent recoveries (Kefeni and Okonkwo, 2013, 2014; Kefeni *et al.*, 2014; Olukunle *et al.*, 2015a, 2015b). Abafe and Martincigh (2014, 2015) used this CRM to assess the method accuracy and it is not clear if this was included in the result uncertainties. Although matrix matched CRMs were included for PBDE analysis, the results were mainly used for recovery studies. The obtained values often did not overlap within the uncertainty of the reference value, indicating that the methods might not be fully mastered and more routine analyses are needed. Data reliability has to be seriously addressed. In one case it was found that identical CRM recovery data were presented for two different extraction techniques giving a false indication of the method performance (Olukunle *et al.*, 2015a, 2015b). Results from the second round (2012/2013) of the biennial global inter-laboratory assessment on persistent organic pollutants showed very low participation from Africa and only one laboratory submitted results for PBDEs (http://www.unep.org/chemicalsandwaste/Science/tabid/268/Default.aspx). This study concluded that training and capacity building for POP analysis are still needed in developing regions, including Africa.

As shown in Table 2-2, various detection limits were reported and included instrumental detection limit (IDL), method detection limit (MDL) and limit of detection (LOD). These detection limits are dependent on the instrument detection technique, sample amount used and blank interferences. Limit of quantitation (LOQ) was only reported in four studies (Abafe and Martincigh, 2014; Chokwe *et al.*, 2012, 2015c; Kefeni *et al.*, 2011).

Considerable efforts were undertaken to address general aspects of QA/QC which include precautionary measures with sample treatment, glassware cleaning and regular analysis of instrumental (solvent) and procedural blanks. More emphasis needs to be placed on information required to achieve acceptable accuracy and precision for the qualitative analysis and analysis performance relating to laboratory participation in international proficiency tests. Limited or incomplete information was often provided for QA/QC related to instrumentation. This needs to be critically evaluated and reported to reach adequate chromatographic resolution of complex mixtures, reproducible mass spectra, reasonable detection limits and acceptable stability of target analyte response. Criteria should be set for analyte retention time deviation and identification based on definite abundance of analyte specific ion ratios.

2.3. BFR levels reported in environmental samples

Table 2-3 provides an overview of PBDE levels in various matrices sampled in Africa. The BFR levels reported in each matrix is discussed and include indoor dust, soil, aquatic environment (water, sediment, and aquatic organisms), eggs, wastewater treatment plant compartments, landfills (leachate and sediment), and human breast milk.

Table 2-3 *Summary of PBDE occurrence in Africa.*

Matrix	Country	Samples	Congeners	Dominant congeners	ΣPBDE concentration range	ΣPBDE concentration	Ref.
Dust	South Africa	Offices	BDE209	-	-	103 ng/g (mean)	(Kefeni *et al.*, 2011)
Dust	South Africa	Hotel rooms	BDE209	-	-	118 ng/g (mean)	(Kefeni *et al.*, 2011)
Dust	South Africa	Computer room	BDE209	-	-	26 ng/g (mean)	(Kefeni *et al.*, 2011)
Dust	South Africa	Offices	BDE47, 66, 85, 99, 153, 209	BDE99 > 47	21.4 - 578.6 ng/g	169.1 ng/g (mean)	(Kefeni and Okonkwo, 2012)
Dust	South Africa	Offices	BDE15, 47, 66, 85, 99, 100, 153, 154, 209	BDE99 > 47	5.8 – 86.3 ng/g (mean)	-	(Kefeni and Okonkwo, 2013)
Dust	South Africa	Homes	BDE15, 47, 66, 85, 99, 100, 153, 154, 209	BDE99 > 47	1.5 – 20.6 ng/g (mean)	-	(Kefeni and Okonkwo, 2013)
Dust	South Africa	Homes	BDE3, 15, 47, 66, 85, 99, 100, 153, 154, 209	BDE209 > 99	<0.3 – 234 ng/g	18.3 ng/g (median)	(Kefeni *et al.*, 2014)
Dust	South Africa	Homes	BDE3, 15, 47, 66, 85, 99, 100, 153, 154, 209	BDE209 > 99	30.9 - 205 ng/g	-	(Kefeni and Okonkwo, 2014)
Dust	South Africa	Offices	BDE3, 15, 47, 66, 85, 99, 100, 153, 154, 209	BDE209 > 99	73.8–625 ng/g	-	(Kefeni and Okonkwo, 2014)
Dust	South Africa	Homes	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE209	689 – 3,290 ng/g (mean)	1,710 ng/g (mean)	(Abafe and Martincigh, 2014)
Dust	South Africa	Computer rooms	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE153	319 – 2,720 ng/g (mean)	818 ng/g (mean)	(Abafe and Martincigh, 2014)
Dust	South Africa	Offices	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE209	226 – 5,020 ng/g (mean)	1,520 ng/g (mean)	(Abafe and Martincigh, 2014)
Dust	South Africa	W/EEE facilities	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE209 > 99	2,632 – 44,203 ng/g	20,094 ng/g (mean)	(Abafe and Martincigh, 2015)
Dust	Nigeria	Homes	BDE47, 99, 100, 153, 154, 183, 209	BDE209 > 47	-	57 ng/g (mean)	(Olukunle *et al.*, 2015a)
Dust	Nigeria	Offices	BDE47, 99, 100, 153, 154, 183, 209	BDE209 > 153	-	79.8 ng/g (mean)	(Olukunle *et al.*, 2015a)
Dust	Nigeria	Cars	BDE47, 99, 100, 153, 154, 183, 209	BDE209	159 – 736 ng/g (mean)	-	(Olukunle *et al.*, 2015b)
Dust	Egypt	Homes	BDE17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 209	BDE209	5.04 – 1,918 ng/g	248 ng/g (mean)	(Hassan and Shoeib, 2015)
Dust	Egypt	Workplaces	BDE17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 209	BDE209	38.1 – 72,279 ng/g	14,993 ng/g (mean)	(Hassan and Shoeib, 2015)
Dust	Egypt	Cars	BDE17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 209	BDE209	171 – 37,440 ng/g	6,943 ng/g (mean)	(Hassan and Shoeib, 2015)
Soil	Tanzania	Mount Meru	BDE17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190	BDE47 > 99	136 – 952 pg/g dw	386 pg/g dw (mean)	(Parolini *et al.*, 2013)
Soil	Kenya	Rural areas	BDE28, 47, 99, 100, 153, 154, 183	BDE99/47	2.54 – 13.65 ng/g dw (mean)	-	(Sun *et al.*, 2016)
Soil	Kenya	Suburban area	BDE28, 47, 99, 100, 153, 154, 183	BDE47	1.12 – 4.20 ng/g dw	2.19 ng/g dw (mean)	(Sun *et al.*, 2016)
Soil	Kenya	Conservancy	BDE28, 47, 99, 100, 153, 154, 183	BDE28	0.19 – 3.13 ng/g dw	1.03 ng/g dw (mean)	(Sun *et al.*, 2016)
Water	South Africa	River	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE47	2.60 – 4.83 ng/L (mean)	-	(Daso *et al.*, 2013a)
Water	South Africa	River	BDE99, 100, 153, 154, 183	-	0.09–0.26 µg/L	-	(Chokwe *et al.*, 2015b)
Sediment	South Africa	River	BDE28, 47, 99, 100, 153, 154, 183	BDE99 > 153	-	4.63 ng/g dw (mean)	(Daso *et al.*, 2011)
Sediment	South Africa	Rivers	BDE28, 47, 99, 100, 153, 154, 183	BDE183 > 99	0.00 - 4.43 ng/g dw (mean)		(Daso *et al.*, 2011)
Sediment	South Africa	River	BDE17, 28, 47, 66, 77, 99, 85, 153, 138, 183, 209	BDE209 > 99	0.92 - 6.76 ng/g dw	23.85 ng/g dw (sum)	(Olukunle *et al.*, 2012)
Sediment	South Africa	Rivers	BDE28, 47, 66, 85, 99, 100, 153, 154, 183,206, 209	BDE209 > 99	ND – 46,300 ng/g TOC	3,750 ng/g TOC (mean)	(La Guardia *et al.*, 2013)
Sediment	South Africa	Rivers	BDE17, 47, 99, 100, 153, 154, 183, 209	BDE100	0.8 - 44 ng/g (mean)	2.4 ng/g (mean)	(Olukunle *et al.*, 2014)

Matrix	Country	Samples	Congeners	Dominant congeners	ΣPBDE concentration range	ΣPBDE concentration	Ref.
Sediment	South Africa	River	BDE99, 100, 153, 154, 183	Not discussed	10.5 – 24.5 ng/g ww	-	(Chokwe *et al.*, 2015b)
Sediment	South Africa	River	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE209	0.06 – 2.47 ng/g (mean)	-	(Daso *et al.*, 2016)
Sediment	South Africa	River	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE47	0.22 – 9.95 ng/g (mean)	-	(Daso *et al.*, 2016)
Sediment	Senegal	Estuaries	BDE47, 99, 119, 153	BDE47/99	<LOQ – 1.2 ng/g dw (mean)	-	(Bodin *et al.*, 2011)
Sediment	Tanzania	Rivers	BDE47, 99, 100, 153, 154, 183	BDE99> 47	38 – 2,175 pg/g dw	-	(Hellar-Kihampa *et al.*, 2013)
Sediment	DRC	River Basin	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE209 > 47	<LOQ – 0.49 ng/g dw (median)	-	(Verhaert *et al.*, 2013)
Sediment	Uganda	Lake	BDE17, 28, 47, 66, 85, 99, 100, 138, 153, 154, 183	BDE47 > 99	60.8 – 179 pg/g dw (mean)	-	(Ssebugere *et al.*, 2014)
Muscle	South Africa	Fish	BDE28, 47, 99, 100, 153, 154, 183	BDE99	11.58 - 18.68 ng/g (l.w)	-	(Chokwe *et al.*, 2015a)
Muscle	South Africa	Fish	BDE47, 99, 100, 153, 154, 183	BDE99	4.63 –33 ng/g lw	-	(Chokwe *et al.*, 2015b)
Muscle	Ghana	Fish	BDE15, 28, 47, 66, 99, 100, 154, 155, 197/204, 206, 207, 208, 209	BDE47 > 209	0.89 to 19 ng/g lw (mean)	7.3 ng/g lw (mean)	(Asante *et al.*, 2013)
Muscle	DRC	Fish	BDE47, 99, 100, 153, 154	BDE99> 47	<LOQ - 188 ng/g lw	-	(Verhaert *et al.*, 2013)
Muscle	Tanzania	Fish	BDE28, 47, 99, 100, 153, 154, 207, 208, 209	BDE209 > 47	1.5 – 34.3 ng/g lw (mean)	-	(Polder *et al.*, 2014)
Muscle	Uganda	Fish	BDE17, 28, 47, 66, 85, 99, 100, 138, 153, 154, 183	BDE47 > 99	48.2 – 177 pg/g lw (mean)	-	(Ssebugere *et al.*, 2014)
Eggs	South Africa	Birds	BDE28, 47, 99, 100, 153, 154, 183, 209	-	2.3 – 396 ng/g lw (mean)		(Polder *et al.*, 2008)
Eggs	Rodrigues	Birds	BDE47, 99, 100, 153, 154, 183, 206, 207, 208	BDE47 > 100	0.7 – 0.8 ng/g lw (mean)		(Bouwman *et al.*, 2012)
Eggs	South Africa	Birds	BDE28, 47, 99, 100, 153, 154, 183, 207, 208, 209	-	<LOQ – 61 ng/g lw (mean)	-	(Bouwman *et al.*, 2013)
Eggs	South Africa	Birds	BDE47, 99, 100, 153, 154, 183, 206 207, 208, 209	-	0.33 – 2.3 ng/g ww (median)	-	(Bouwman *et al.*, 2015)
Eggs	South Africa	Penguins	BDE47, 99, 100, 153, 154, 183, 206 207, 208, 209	-	0.14 – 2.3 ng/g ww (median)	-	(Bouwman *et al.*, 2015)
Eggs	South Africa	Crocodiles	BDE28, 47, 99, 100, 154, 183	-	1.6 – 3.3 ng/g lw (mean)	-	(Bouwman *et al.*, 2014)
Eggshells	South Africa	Birds	BDE17, 47, 99, 100, 153, 154, 183, 209	BDE47/100	46.63 – 80.77 µg/g lw (mean)	-	(Daso *et al.*, 2015)
Eggs	Tanzania	Chickens	BDE28, 47, 99, 100, 153, 154, 183, 206, 207, 208, 209	BDE209 > 183	19 – 81 ng/g lw (mean)	40 ng/g lw (median)	(Polder *et al.*, 2016)
Leachate	South Africa	Landfills	BDE28, 47, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 183	BDE47 > 71	8,392 – 54,761 pg/L (mean)	-	(Odusanya *et al.*, 2009)
Leachate	South Africa	Landfills	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE209	0.28 – 2,240 ng/L (mean)	-	(Daso *et al.*, 2013b)
Leachate	South Africa	Landfills	BDE47, 99, 100, 153, 154, 183, 209	-	127 – 3,703 pg/L	-	(Olukunle *et al.*, 2014)
Sediment	South Africa	Landfills	BDE47, 99, 100, 153, 154, 183, 209	BDE209 > 99	0.8 – 8.4 ng/g dw	-	(Olukunle *et al.*, 2014)
Effluent	South Africa	WWTP	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE209 > 99	2.48 – 1,240 ng/L (mean)	-	(Daso *et al.*, 2012)
Sludge	South Africa	WWTP	BDE28, 47, 99, 100, 153, 154, 183, 209	BDE209 > 47	2.09 – 48.4 ng/g (mean)	-	(Daso *et al.*, 2012)
Breast milk	Ghana	Humans	BDE15 28, 47, 99, 100, 153, 154, 183, 196, 197, 206, 207, 209	BDE47	0.86 – 18 ng/g lw	4.5 ng/g lw (mean)	(Asante *et al.*, 2011)
Breast milk	South Africa	Humans	BDE28, 47, 66, 99, 100, 153, 154, 183	BDE183	0.7 – 6.3 ng/g lw	1.7 ng/g lw (mean)	(Darnerud *et al.*, 2011)
Breast milk	Tunisia	Humans	BDE28, 47, 66, 99, 100, 138, 153, 154, 183	BDE183 > 47	2.49 – 22.62 ng/g lw (mean)	10.74 ng/g lw (mean)	(Hassine *et al.*, 2012)
Breast milk	Tanzania	Humans	BDE28, 47, 99, 100, 153, 154, 183	BDE99 > 47	<LOD – 785.8 ng/g lw (median)	19.8 ng/g lw (median)	(Müller *et al.*, 2016)

2.3.1. Indoor dust

Indoor dust is a complex heterogeneous mixture of organic compounds and particle-bound matter present in homes, schools, offices, hotels and cars. Indoor dust is always in close proximity to human activity. Dust in the indoor environment can therefore be a major source of human exposure to environmental contaminants and may even be the largest route of PBDE exposure to toddlers (Jones-Otazo *et al.*, 2005).

BFR levels were reported for dust samples from South Africa, Nigeria and Egypt. Kefeni *et al.* (2011) reported on the presence of BDE209 in dust from a computer classroom, offices and hotel rooms in South Africa. Average concentrations obtained from office dust (103 ng/g) and hotel rooms (118 ng/g) were higher than reported for surface wipes from the computer classroom (26 ng/g). Subsequently, a comprehensive study was undertaken to determine the concentrations of sixteen PBDE and PBB congeners in pooled dust samples taken from offices at the same university (Kefeni and Okonkwo, 2012). Although BDE99 and 47 were the only congeners found with median concentrations above the LOD with detection frequencies of 81 and 63%, respectively. The mean concentration for the Σ_6PBDE was 169 ng/g, with BDE209 concentrations ranging from <LOD to 571 ng/g. BB209 was the dominant PBB congener and mean concentration for the Σ_5PBB was 38 ng/g. Abafe and Martincigh (2014) analysed PBDEs in dust from homes, computer laboratories and offices and reported mean Σ_8PBDE levels ranging from 818 to 1,710 ng/g. BDE209 was the dominant congener in the house and office samples, with BDE153 dominant in the samples collected from the computer rooms. Indoor dust was also collected from two e-waste dismantling and recycling facilities and an electronic repair workshop (Abafe and Martincigh, 2015). Mean Σ_8PBDE levels were 20,094 ng/g and varied from 2,632 to 44,203 ng/g, with BDE209 and 99 as the dominant congeners with BDE209 levels ranging from 1,862 to 34,010 ng/g. The PBDE levels in dust from the electronic workshop were lower than reported for recycling facilities (Abafe and Martincigh, 2015).

Dust samples from cars in four states in Nigeria presented Σ_7PBDE concentrations from 159 to 736 ng/g (Olukunle *et al.*, 2015b). BDE209 was the main congener contributing up to 47% with a detection frequency of 92%. BDE47 was detected in all samples. Pooled dust samples collected from ten houses and eleven offices in Nigeria showed PBDE detection frequencies between 70 and 100% (Olukunle *et al.*, 2015a). BDE209 had mean concentrations of 141 ng/g in house dust and 180 ng/g in office dust.

Hassan and Shoeib (2015) investigated PBDE and alt-BFR levels in house, workplace and car dust samples from Egypt. The mean Σ_{14}PBDE concentrations ranged from 248 to 14,993 ng/g for the investigated areas. BDE209 was reported as the dominant congener with concentrations ranging from 2.20 to 591 ng/g in the houses, 26 to 72,096 ng/g in the workplaces and 159 to 36,927 ng/g in the cars (manufactured between 1999 and 2012) (Hassan and Shoeib, 2015). Eleven alt-BFRs including; ally-2,4,6- tribromophenyl ether (ATE), beta-tetrabromoethylcyclohexane (*β*-TBECH), 2-

bromoallyl-2,4,6-tribromophenyl ether (BATE), beta-1,2,5,6 tetrabromocyclooctane (*β*-TBCO), bis(2-ethylhexyl)-3,4,5,6- tetrabromo-phthalate (BEH-TEBP), hexabromobenzene (HBB), hexabromocyclododecane (HBCD), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), 1,2-bis (2,4,6-tribromophenoxy) ethane (BTBPE) and Dechlorane plus (syn-DP, anti-DP) were also analysed in the respective matrices. ΣHBCD was shown to be the most abundant alt-BFR detected in all three matrices, with mean concentrations ranging from 20.7 to 47.7 ng/g. EH-TBB levels were reported to be 2 to 5-fold lower than the penta-BDE concentrations. The concentrations for ATE, *β*-TBECH, BATE, *β*-TBCO and BEH-TEBP were present at higher concentrations in car samples with maximum concentrations ranging from 1.34 to 18.9 ng/g (Hassan and Shoeib, 2015).

2.3.2. Soil

Parolini *et al.* (2013) reported background levels for PBDEs in soil from the Mount Meru area in the Arusha district, Tanzania. Surface soil samples were collected at different altitudes at the end of the dry season. The Σ_{13}PBDE ranged from 136.35 to 952.15 pg/g dry weight (dw) with a mean concentration of 386 pg/g dw; BDE47 was reported as the main congener followed by BDEs 99, 190 and 100 (Parolini *et al.*, 2013). PBDE concentrations initially decreased with altitude, followed by a consistent increase with altitude. This effect was previously observed and discussed by Wang *et al.*, (2009a). The initial decrease in concentration could be due to a dilution effect as the distance from the anthropogenic influence, or possible source of emission, increases; the subsequent increase in concentration might be due to a condensation or distillation effect as a result of the decreased temperature with altitude. Sun *et al.* (2016) investigated organohalogenated contaminant concentrations in soils from Kenya. Soil samples were collected from three rural areas, a suburban area and at Mount Suswa conservancy surrounding Nairobi. The mean Σ_7PBDE concentrations in the soil samples from the rural areas ranged from 2.54 to 13.65 ng/g dw, with concentrations in the suburban and conservancy area of 2.19 and 1.03 ng/g, respectively (Sun *et al.*, 2016).

The PBDE concentrations in soil from Tanzania and Kenya were higher than reported for north-eastern China (Wang *et al.*, 2009b) and Sweden (Sellström *et al.*, 2005). Although the levels for Tanzania were comparable with results reported for background levels in UK (Hassanin *et al.*, 2004), levels reported for Kenya were much higher. PBDEs found in soil from pristine mountain areas showed an increase in concentration associated with increased altitude and levels were higher than those reported for the east edge of the Tibetan Plateau (Zheng *et al.*, 2012).

2.3.3. Aquatic environment

Information on PBDE levels in dissolved and suspended phases of water samples is scarce due to the compounds' hydrophobicity, which will cause preferred adsorption to particulate matter and deposition in sediments (Wurl *et al.*, 2006). The entire aquatic environment including water, suspended particulate matter, sediments and aquatic organisms analysed in samples from Southern, Central and Western Africa are discussed in this section.

Daso *et al.* (2013a) reported on eight PBDE and BB153 concentrations in river water. Sampling was done at three locations: upstream, at the point where effluent from a wastewater treatment plant (WWTP) enters the river and downstream from the outlet point. Mean Σ_8PBDEs concentrations of 2.60, 4.83 and 4.29 ng/L were reported for the respective sampling points. The concentration of BB153 was highest at the discharge point (Daso *et al.*, 2013a). The Σ_8PBDE levels for sediment taken from two rivers in South Africa ranged from 5.32 to 239 ng/g dw with BDE209 as the major congener in the first river and BDE47 as the major congener in the second river (Daso *et al.*, 2016). River sediment samples from six rivers were also analysed and Σ_8PBDE concentrations ranged from 0.8 to 44 ng/g (Olukunle *et al.*, 2014). The Σ_8PBDE concentrations (44 ng/g) reported for one of the rivers was significantly higher than previously reported for the same region (Olukunle *et al.*, 2012). La Guardia *et al.* (2013) determined concentrations of eleven PBDEs, EH-TBB, BEH-TEBP, BTBPE, DBDPE and *α*-, *β*-, *γ*-HBCD in inland and coastal sediment in South Africa and found higher alt-BFR than PBDE levels, with BDE209 and EH-TBB as the most frequently detected compounds. Levels of up to 46 300 ng/g total organic carbon (TOC) for Σ_{11}PBDE were reported for inland sediment and the median concentration at the Durban Bay area was 3,240 ng/g TOC, varying from 1,850 to 25,400 ng/g TOC (La Guardia *et al.*, 2013). These levels were higher than previously reported for San Francisco Bay (Klosterhaus *et al.*, 2012) and comparable with the studies from the Pearly River Estuary in China (Mai *et al.*, 2005). Wepener *et al.* (2011) assessed the influence of multiple stressors on a river in South Africa by collecting fish at various points and reported a mean concentration for the ΣPBDE that ranged from 5.9 to 43.4 ng/g lipid weight (lw).

Hellar-Kihampa *et al.* (2013) studied sediments collected during different seasons from the Pangani river basin (PRB) in Tanzania. The most frequently detected PBDEs were BDE99, with concentrations ranging from 38 to 1,097 pg/g, and BDE47 ranging from 50 to 734 pg/g. The Σ_6PBDE concentrations ranged from 38 to 920 pg/g during the dry season, 295 to 2,175 pg/g before the rainy season and 50 to 940 pg/g during the rainy season (Hellar-Kihampa *et al.*, 2013). PBDE concentrations were determined in sediments and fish from the Murchison Bay of Lake Victoria (Uganda) (Ssebugere *et al.*, 2014). The mean Σ_{11}PBDE concentrations for sediment ranged from 60.8 to 179 pg/g dw and from 48.2 to 177 pg/g lw for fish samples (Ssebugere *et al.*, 2014). Similarly, as with to the sediment samples, BDE47 was the dominant congener followed by BDE99 (BDE209 was not analysed due to analytical limitations). Verhaert *et al.* (2013) reported on PBDE levels in sediments and biota from the Congo River Basin (CRB). The ΣPBDE concentrations ranging from < LOQ to 1.9 ng/g dw for sediment, < LOQ to 7.9 ng/g lw for invertebrate and < LOQ to 188 ng/g lw for fish samples. BDE209 was the major congener in the sediment, with BDE47 and 99 dominant in the biotic samples (Verhaert *et al.*, 2013). The presence of halogenated contaminants was also analysed in inland and coastal fish from Ghana and mean

Σ_{14}PBDE concentrations for three fish species ranged from 0.89 to 19 ng/g lw with BDE47 and 99 as the dominant congeners (Asante *et al.*, 2013). Polder *et al.* (2014) investigated the levels and patterns of POPs in fish from four different lakes in Tanzania. BDE209 had the highest concentrations and mean Σ_9PBDE concentrations ranged from 1.5 to 34.3 ng/g lw for the different lakes. HBCD was found in 78% of the samples from one lake with mean ΣHBCD concentrations of 2.4 ng/g lw (Polder *et al.*, 2014). PBDEs, with BDEs 47 and 99, were irregularly detected at low concentrations in sediment and mollusc samples collected from a delta and a stretch of coast in Senegal (Bodin *et al.*, 2011).

2.3.4. Eggs

Polder *et al.* (2008) reported on levels of PBDEs and HBCD in eggs of different bird species in South Africa. The mean Σ_8PBDE concentrations for eight species ranged from 2.3 to 396 ng/g lw. The PBDE congener pattern displayed inconsistencies, imitating diverse trophic levels, migratory behaviour, and exposure distance to different PBDE mixtures (Polder *et al.*, 2008). Low BFR levels were reported for eggs collected from terrestrial and aquatic birds in the most northern part of South Africa, with mean Σ_{10}PBDE concentration ranges from < LOQ to 61 ng/g lw (Bouwman *et al.*, 2013). PBDE levels were investigated in eggshells of the population declining Southern Ground-Hornbill (SGH) and Wattled Crane (WC) (Daso *et al.*, 2015). The Σ_8PBDE concentrations were 46.63 and 80.77 µg/g lw for the SGH and WC eggshells. The WC eggs' outer membranes containing possible traces of albumin were separately analysed for the content of PBDEs. The mean Σ_8PBDE concentrations were found to be greater than the concentrations reported for the eggshells (Daso *et al.*, 2015). Exposure to environmental PBDE levels was reported to be a possible contributor to the poor breeding success and therefore the decline in population of the WC, but more data is needed to support these findings. The halogenated organic pollutants were also studied in African Penguin and Nile crocodile eggs (Bouwman *et al.*, 2015, 2014). The mean Σ_{10}PBDE concentration reported for penguin eggs ranged from 0.14 to 2.3 ng/g wet weight (ww) and bird species included in the study, reported similar concentrations (Bouwman *et al.*, 2015). Nile crocodile eggs collected after an unexpected incident of deaths in June 2008 showed mean Σ_6PBDE concentrations ranging from 0.02 to 0.44 ng/g ww (Bouwman *et al.*, 2014). Although BFR concentrations were irregularly reported at low concentrations, this study presented the first data on BFRs in crocodile eggs.

Bouwman *et al.* (2012) reported on POP levels in marine bird eggs from an oceanic island in the Indian Ocean. The eggs from two species had mean Σ_9PBDE concentrations of 0.7 ng/g lw with both BDE47 and 100 at quantifiable levels (Bouwman *et al.*, 2012). As part of a project to monitor and assess contaminant risk in Southern Africa, Polder *et al.* (2016) studied the occurrence of POPs (including BFRs) in native free-range chicken eggs from urban transition in Tanzania. Collective egg samples from four villages showed the prevalent occurrence of BFRs, specifically BDE209, HBCD and BTBPE. The mean concentrations of the Σ_{11}PBDE was 40 ng/g lw ranging from 19 to 81 ng/g lw with mean HBCD concentrations of 8.4 ng/g lw (Polder *et al.*, 2016). This study reported the occurrence of BTBPE in the African environment for the first time, with mean concentrations of 2.3 ng/g lw varying from 0.79 to 4 ng/g lw.

2.3.5. Landfills

Leachates and sediment from landfills are complex environmental matrices containing organic and inorganic compounds mainly determined by the composition and solubility of the waste constituents. BFRs were only analysed in leachate samples from South Africa. Odusanya *et al.* (2009) found PBDEs in leachate samples collected from five landfills. The mean Σ_{13}PBDEs (excluding BDE209) concentrations ranged from 8,392 to 54,761 pg/L with BDE47 as the major congener at three of the sites (Odusanya *et al.*, 2009). Olukunle *et al.* (2014) analysed PBDEs in landfill leachate and sediment samples from six operational landfills and high detection frequency for BDE47, 99, 100, 153, 154, 183 and 209 was reported. The concentrations for the Σ_7PBDEs for the leachates range from 127 to 3,703 pg/L, with BDE209 concentrations up to 1,930 pg/L (Olukunle *et al.*, 2014). The levels for two of the landfills were lower than reported by Odusanya *et al.* (2009), collected from the same sites. Landfill sediment samples reportedly contained Σ_7PBDE concentrations ranging from 0.8 to 8.4 ng/g dw (Olukunle *et al.*, 2014). Leachate samples, collected from three landfills over a one year period showed increased BDE concentrations for the period with a high frequency of rainfall (Daso *et al.*, 2013b). The mean concentration for Σ_8PBDEs ranged from 0.28 to 2 240 ng/L and BDE209 was reported as the major congener followed by BDE153 and 183. BB153 concentrations ranged from 7.14 to 70.4 ng/L (Daso *et al.*, 2013b). In the only study targeting alt-BFRs in leachate and sediment samples from six landfill sites, EH-TBB, BEH-TEBP, BTBPE, DBDPE and ΣHBCD were analysed (Olukunle and Okonkwo, 2015). Concentrations in the leachate samples ranged from 8.7 to 142 pg/L for EH-TBB, 4.8 to 40 pg/L for ΣHBCD and 4.4 to 15 pg/L for BTBPE. The sediment samples showed a detection frequency from < 20% to 50% for the alt-BFRs and DBDPE was not detected in any of the samples (Olukunle and Okonkwo, 2015).

2.3.6. Wastewater treatment plants

Daso *et al.* (2012) collected effluent and sludge samples over a one year period at different purification process stages of a WWTP in South Africa. For effluent samples, BDE28, 47, 99 and 209 were reported as the dominant congeners. The mean Σ_8PBDEs concentrations range from 369 to 4,370 ng/L for the raw water, 19.2 to 2,640 ng/L for the secondary effluent and 90.4 to 15,100 ng/L for the final effluent (Daso *et al.*, 2012). The authors concluded that WWTPs might be seen as a source for PBDE exposure to aquatic environments. Sludge collected from the dewatering unit had mean Σ_8PBDE concentrations from 2.09 to 48.4 ng/g dw with BDE47, 153, 183 and 209 as the dominant congeners (Daso *et al.*, 2012). Alt-BFRs were also analysed in sludge samples collected prior to the digestion process from three different WWTPs in South Africa and showed irregular detection of TBBPA and ΣHBCD (Chokwe *et al.*, 2015c). One of the investigated sites reported concentrations of 19.24 ng/g for TBBPA and 133.16 ng/g for ΣHBCD. (Chokwe *et al.*, 2015c).

2.3.7. Breast milk and serum

Human breast milk and blood/serum are used as markers to assess human exposure to POPs and BFRs and provide information on contaminant transfer to infants. Four studies reported on BFR levels in breast milk collected from South Africa, Tunisia, Ghana and Tanzania. Darnerud *et al.* (2011) investigated non-occupational exposure to BFRs by collecting breast milk samples from mothers residing in a rural district in South Africa. Mean Σ_8PBDE concentrations were reported as 1.7 ng/g lw ranging from 0.7 to 6.3 ng/g lw. BDE47, 99, 153 and 183 were the dominant congeners, and one of the analysed samples reported a BDE183 level of 4.5 ng/g lw. Hassine *et al.* (2012) determined PBDE concentrations in breast milk collected in Tunisia; the Σ_8PBDE ranged from 2.49 to 22.62 ng/g lw with a mean concentration of 10.74 ng/g lw. BDE183 was the dominant congener with a concentration of 2.49 ng/g lw followed by BDE47 and 153 (Hassine *et al.*, 2012). Asante *et al.* (2011) analysed breast milk samples collected in Ghana during 2004 and 2009 to evaluate human exposure to BFRs. The mean Σ_{16}PBDE concentrations (excluding BDE209) for the samples collected in 2004 were reported as 2.2 ng/g lw and the Σ_{17}PBDE (including BDE209) in 2009 were reported as 4.5 ng/g lw. BDE47, 209, 99, 100, and 153 were reported as the dominant congeners. Higher PBDE levels were reported for milk collected from urban areas as compared to rural areas. The ΣHBCD concentrations ranged between 0.01 and 3.2 ng/g lw with a mean concentration of 0.54 ng/g lw (Asante *et al.*, 2011). This is in good agreement with the concentration for ΣHBCD (0.55 ng/g lw) reported for South Africa (Darnerud *et al.*, 2011). Linderholm *et al.* (2010) investigated serum collected from adult men between 1990 and 2007 in Guinea-Bissau. Low PBDE levels were reported with BDE209 and 153 as the major congeners. No temporal trend was observed for BDE209 while BDE153 levels increased over time. Müller *et al.* (2016) assessed BFR levels in breast milk from mothers in the northern part of Tanzania. The median concentrations for the Σ_7PBDE were 19.8 ng/g lw and ranged from <LOD to 785.8 ng/g lw with BDE47, 99, 100 and 153 detected in more than 80% of the samples. BDE28, 154, 183 and HBCD reported detection frequencies of > 40% and HBB, 2,3,4,5,6-pentabromoethylbenzene (PBEB), 2,3,4,5,6-pentabromotoluene (PBT), BTBPE and (2,3-dibromopropyl) (2,4,6-tribromophenyl) ether (DPTE) were not detected. Higher levels for BDE47 were reported for samples collected from mothers living in urban areas compared to rural areas (Müller *et al.*, 2016). In this study, mothers consuming a clay product, used as a mineral supplement and anti-emetic for pregnancy related nausea, had higher BDE47, 99, 100 and 153 levels than individuals who did not take the product during pregnancy (Müller *et al.*, 2016). The PBDE levels reported for Tanzanian breast milk samples were higher than previously reported for Europe and Asia (Frederiksen *et al.*, 2009). The BDE congener profiles were dominated by BDE99 and 47 in samples collected from Tanzania and Ghana (Asante *et al.*, 2011; Müller *et* *al.*, 2016), and BDE183 in South Africa and Tunisia (Darnerud *et al.*, 2011; Hassine *et al.*, 2012).

The Secretariat of the SC, the United Nations Environment Programme (UNEP) and the World Health Organization (WHO) implemented a global monitoring plan to provide a consistent framework to present global differences for POPs listed in the Stockholm Convention in human breast milk (UNEP, 2013). Results from the survey showed large variations in global POP contamination; contamination associated with dioxin-like compounds was among the highest for certain African countries (UNEP, 2013). Results pertaining to PBDEs showed their ubiquitous presence with high levels reported for pooled samples from industrialised countries, such as USA and Australia, the Pacific Islands and countries in Latin American and the Caribbean (UNEP, 2013).

Since 2008, an increased number of reports on the presence of BFRs in the African environment is being produced. Most of the reports contain valuable information on the manifestation of these compounds in all environmental compartments and differences in concentrations may reflect differences in exposure routes. Recent publications provide information indicating an increase in BFR concentrations reported for dust, sediment and breast. Indoor dust samples also showed that work environments contain HBCD and levels reported for banned penta-BDE formulations were higher than for BFR replacements. The redistribution of BFRs to aquatic environments was mostly associated with more industrialised cities with high PBDE concentrations reported for sediment. Although data on landfills and WWTPs were only available for South Africa, this was seen as a major source. Limited information is however available on the usage of BFRs in Africa and it is likely that these compounds enter the African environment through the use and disposal of manufactured and imported BFR-containing products, and from non-point sources such as atmospheric fallout and urban runoff. The redistribution of these compounds to landfills, WWTPs, sediment and eventually to food (fish and chicken eggs) and humans (breast milk) underlines the need for ongoing investigation in support of continuous environmental and human monitoring to understand the origin, fate and impact of these chemicals. Despite the scarcity of systematic monitoring studies on BFR levels in the African environment, exposure to the general population seems to be highly variable between different geographical areas and even within countries.

2.4. Conclusion

Until recently, BFR analyses in Africa were effectively only carried out in South Africa. Although information on BFR contamination in other parts of Africa was available, this was often acquired through outsourced analyses in non-African countries or South Africa. Clearly, further development of analytical methodology, including sufficient QA/QC in the entire continent is needed.

Brominated flame retardant levels pertaining to indoor dust were limited to PBDEs and PBBs in South Africa and Nigeria, with information on the prevalence of PBDEs and alt-BFRs in Egypt. Recent publications from South Africa indicated that PBDE levels are comparable with the rest of the world. Dust PBDE levels from South Africa are higher than reported for Nigeria and Egypt. Limited information on the occurrence of alt-BFRs in indoor dust are available, with only one study for Egypt where ΣHBCD was shown to be the major alt-BFR. PBDEs found in soil from pristine mountain areas show an increase in concentration associated with increased altitude and levels are higher than reported for similar environments in central Asia. South Africa had higher PBDE levels in river sediment than reported for the rest of Africa. These were shown to be affected by seasonal rainfall. Sediment PBDE levels reported for Durban Bay are comparable and higher than reported for renowned contaminated areas in the USA and China. PBDE levels in fish from South Africa are comparable with levels reported for fish from different lakes in Tanzania. The prevalence and occurrence for BFRs in wild bird, and penguin eggs in South Africa is dependent on the geographic area and dietary habits. Brominated flame retardants were commonly detected at low concentrations, with the highest levels reported for the African sacred ibis. Although at low levels, PBDEs were also reported in bird eggs collected from a remote island in the Indian Ocean. Chicken eggs from Tanzania reported high BFR levels indicating that the environment is exposed to commercial BDE mixtures and banned BFR replacements. BFRs in landfills were only analysed in South Africa and showed irregular detection of PBDEs, with BDE209 as the major congener and regular presence of the tetra-, penta- and tri-BDE congeners. PBDE levels analysed in WWTP compartments in South Africa are lower than reported for river sediment. BFR levels were reported in human breast milk for South Africa, Tunisia, Ghana and Tanzania. The highest levels are reported for Tanzania, compared to South Africa, Tunisia and Ghana and countries in Europe and Asia.

The majority of countries in Africa, as signatories of the Stockholm Convention (SC), have the responsibility to undertake appropriate research, development, monitoring and cooperation pertaining to persistent organic pollutants including PBDEs. Due to lack of established monitoring programmes, Africa exclusively depended on global surveys such as programs implemented by the UNEP and WHO. Developing countries in Africa have limited facilities that specialise in BFR analysis and this has required the development of alternative approaches influenced by ease of operation, low cost and availability in most laboratories. In cases where BFR analyses were performed in Africa, liquid sample preparation was generally limited to LLE. Solid sample preparation included Soxhlet extraction which remains the default method for exhaustive extraction, with ultrasound-assisted extraction (UAE) increasingly being used. Clean-up and fractionation of BFRs mainly involved the use of miniaturised multi-layer silica columns. These sample preparation approaches were generally implemented from conventional methods developed for POPs and/or BFR analysis. Considering instrumental techniques, analyses were limited to GC-ECD and GC-LR-EI-MS for the qualitative analysis of BFRs at low concentration levels with GC-TOF-MS employed for structural confirmation. The inclusion of alt-BFRs and emerging contaminants in monitoring protocols highlights the need for commercially available reference standards (labelled and un-labelled) and appropriate matrix matched CRMs.

This study has shown that low BFR levels were mostly found in the studies reported for African environmental matrices. This raises the question whether the standard deviation related to repeated measurements, in several cases at or near the LOD, can realistically be used for the determination of uncertainty values. The calculation of uncertainty, for the analysis of organic contaminants in environmental matrices is a complex process. Practical uncertainty contributions may include measurement reproducibility, the error associated with the concentration estimate (specifically if a concentration near or at the LOQ is reported) and the contribution as a result of bias (where matrix matched CRMs were analysed). To perform a realistic estimation of the measurement uncertainty for an analytical method, the parameters influencing the measurement result, as well as the magnitude of their effect, needs to be determined as fit for the intended purpose of the data being generated.

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Supplementary material S2

Table S2-1 *Summary of publications on BFRs in Africa.*

Sampling Year	Sample Origin (Country)	Analysed (Country)	Summary	Ref.
2004-2005	South Africa	Norway	PBDEs and HBCD in bird eggs (first report on the presence of BFRs in biota from South Africa) • BFR contamination not only around industrialised areas, but entered the food chain along the western coastline • BFRs should be recognised as a potential chemical risk to bio-diversity, ecology and human health	(Polder *et al.*, 2008)
Not Provided	South Africa	South Africa	Occurrence of PBDEs in leachates from selected landfill sites • High concentrations of PBDEs with BDE209 not detected • Due to inadequate lining of landfill sites, leachates may migrate into the underlying soil and ground water	(Odusanya *et al.*, 2009)
2000-2002	Tanzania	Norway	Composition of organohalogen compounds in blubber of dolphins from the coastal waters of Zanzibar • Methoxylated PBDEs found at higher concentrations than anthropogenic organochlorine pesticides	(Mwevura *et al.*, 2010)
1990-2007	Guinea-Bissau	Sweden	Levels and temporal trend of human exposure to legacy and emerging POPs • Presence of emerging POPs with decrease in temporal trends for legacy POPs • PBDEs found at low concentrations, with increasing temporal trend for BDE153	(Linderholm *et al.*, 2010)
Not Provided	South Africa	South Africa	Influences of gas chromatographic parameters on the analysis of BDE209 in indoor dust (first report on BDE209 in South African indoor dust) • Indoor dust in South Africa contain BDE209, lower than global concentrations	(Kefeni *et al.*, 2011)
2004 & 2009	Ghana	Japan	Human exposure to PCBs and BFRs, including PBDEs and HBCDs (first report on BFRs in human breast milk from Africa) • Human breast milk contains PCB, PBDE and HBCD with elevated levels reported for densely populated cities • Increased temporal trend in concentrations for PCBs and PBDEs	(Asante *et al.*, 2011)
2007 & 2008	Senegal	France	PCB, OCP and PBDE contamination status in sediments and molluscs (first report on POPs contamination in the Senegalese marine environment) • Exploited molluscs exposed to the same POPs as reported for sediment • Low concentrations pose no health risk to humans through shellfish consumption	(Bodin *et al.*, 2011)
2004	South Africa	Sweden	PBDEs and HBCD in breast milk and unique BDE congener profiles (first report on PBDEs and HBCD in South African breast milk) • Breast milk contains BFRs at levels comparable to European countries • Congener patterns differ from European countries with dominance of BDE183	(Darnerud *et al.*, 2011)
2010	South Africa	South Africa	Analytical procedure for the analysis of PBDEs and BB153 in sediment (first report on PBDEs in South African sediment) • Municipal and industrial effluents might contain penta- and octa-BDE formulations, BDE209 not analysed • WWTP effluent proposed as possible source of contamination in the investigated river	(Daso *et al.*, 2011)
Not Provided	South Africa	Belgium	Multivariate procedures to determine relationship between water and sediment quality, bio accumulative pollutant exposure and the related responses of fish • Decreased fish health demonstrated by increased oxidative stress due to exposure to metals and organic pollutants	(Wepener *et al.*, 2011)

Sampling Year	Sample Origin (Country)	Analysed (Country)	Summary	Ref.
2010-2011	South Africa	South Africa	Assess levels of selected PBDEs and BB153 in wastewater effluent and sewage sludge samples from a WWTP • Inadequate removal of PBDEs from treated effluent • WWTPs could be an important source of PBDEs to the aquatic environment	(Daso *et al.*, 2012)
2010	South Africa	South Africa	Occurrence of PBDEs in river sediment • Sediment contain PBDEs with BDE209 as the major congener • PBDE levels were lower than reported from developed countries and may be affected by seasonal rainfall	(Olukunle *et al.*, 2012)
Not Provided	South Africa	South Africa	PBB and PBDE concentrations and congener profiles in indoor dust (first report on levels and congener profiles in South African indoor dust) • Low PBDE concentrations compare to developed countries • No correlation between PBB and PBDE concentrations and amount of electronic equipment	(Kefeni and Okonkwo, 2012)
2009-2010	Nigeria	China	Comparative assessment of heavy metal, PAH, PCB and PBDE contamination in soil and plants; evaluate the genotoxicity of e-waste leachates using human peripheral blood lymphocyte comet assay • PBDEs were detected in the soil and plant samples from Nigeria with BDE209 as the major congener	(Alabi *et al.*, 2012)
2008	Ile Cocos	Norway	POPs, in marine bird eggs from an Indian oceanic island (first report on BFRs in marine bird eggs from a remote island in the Indian Ocean) • Provide concentrations for PCBs, DDTs, Mirex, chlordanes, toxaphenes and BFRs • Low levels of BFRs detected in marine bird eggs distant from notable sources	(Bouwman *et al.*, 2012)
2010	Tunisia	Spain	OCP, PCB, and PBDE residues in breast milk of Tunisian mothers (first report on PBDEs in Tunisian human milk) • DDTs, HCB and PCBs were dominant compounds identified in all breast milk samples • Higher PBDEs concentrations than reported for European and Asiatic countries	(Hassine *et al.*, 2012)
Not Provided	South Africa	South Africa	Amperometric horseradish peroxidase biosensor for the determination of selected POPs in landfill leachates, compare results with GC–MS data • Inhibition mechanism is competitive for PBDEs and non-competitive for biphenyls (PCBs and PBBs) • Biosensor as a screening method for different halogenated aromatic hydrocarbons; comparable with GC-MS data	(Nomngongo *et al.*, 2012)
Not Provided	South Africa	South Africa	Development of a GC-MS method for APEs and BFRs analysis, using SPE and derivatization with HFBA • Method showed acceptable relative recoveries for the determination of APEs and BFRs in wastewater samples • Levels for TBBPA and HBCD were reported and lower substituted PBBs were not detected	(Chokwe *et al.*, 2012)
Not Provided	South Africa	South Africa	PBDEs in indoor dust; examine the correlation between congener and trace metal concentrations • Settled indoor dusts are contaminated with organic and inorganic chemicals • Significant correlation between PBDE and trace metal concentrations from home dust	(Kefeni and Okonkwo, 2013)
2009-2011	Tanzania	Belgium	Concentrations and profiles of organohalogenated compounds in environmental samples from the Pangani river basin (PRB) • Low levels for POPS were reported for the PRB • PCB and PBDE concentrations were linked to urbanisation and atmospheric deposition	(Hellar-Kihampa *et al.*, 2013)

Sampling Year	Sample Origin (Country)	Analysed (Country)	Summary	Ref.
2010-2011	South Africa	South Africa	PBDEs and BB153 in river water and source identification • Low PBDE concentrations with BDE47 as dominant congener • Potential PBDE contamination sources include WWTP, grey water intrusion, seepages from landfill sites, urban and agricultural runoff	(Daso *et al.*, 2013a)
2010-2011	South Africa	South Africa	PBDE and BB153 concentrations in landfill leachates • High PBDE concentrations with BDE209 as major congener • Landfill leachates could be a possible source of PBDE contamination in ground and surface water	(Daso *et al.*, 2013b)
2011	Tanzania	Italy	PBDE congeners in an altitudinal soil transect in Tanzania • PBDE concentrations might be higher than similar semi-remote environment • PBDE contamination pattern characterised by the prevalence of intermediate brominated congeners	(Parolini *et al.*, 2013)
2010	Ghana	Japan	BFR and PCB contamination in fish from water bodies in Ghana (first report on PBDEs and HBCDs in fish from Ghana) • Freshwater environments in Ghana are exposed to PBDEs and HBCDs • PBDE and HBCD concentrations pose no health risk to humans through fish consumption	(Asante *et al.*, 2013)
Not Provided	South Africa	Norway	Investigate the presence, levels, relationships, impacts, and risks of pesticides, PCBs, and BFRs in terrestrial and aquatic bird eggs in South Africa • Highest ΣDDT levels in wild bird eggs • BFR concentrations were lower compare to similar studies	(Bouwman *et al.*, 2013)
2010	Congo	Belgium	POPs in sediment and biota (first report on POPs in sediment, invertebrates and fish from Congo) • Low PBDE levels in sediment and biota compared to similar studies • Increase in BDE47 and 99 concentrations in river basins with increased trophic levels	(Verhaert *et al.*, 2013)
2011	South Africa	USA	PBDEs and alt-BFRs in inland and coastal sediment (first data reported for alt-BFRs in South African sediment) • High PBDE and alt-BFR concentrations in sediment with BDE209 and EH-TBB as most frequent detected BFRs • PBDE levels were higher than previously reported for the San Francisco Bay	(La Guardia *et al.*, 2013)
2008-2010	Uganda	Canada	Measured temporal variation of PBDEs and alt-BFRs in air samples and estimated the fluxes of the BFRs in precipitation samples (first study to report FRs in high volume air samples and precipitation in Equatorial Africa) • PBDEs and Alt-BFRs levels in air generally increased from 2008 to 2010 • PBDE levels in air samples have been associated with slow moving low altitude air masses with BTBPE as the most frequent detected alt-BFR	(Arinaitwe *et al.*, 2014)
2010-2011	South Africa	South Africa	PBDE and PBB concentrations and congener profiles in indoor dust; examine the correlation with socioeconomic status • Low concentrations of PBDEs • No correlation between the PBDE concentration and the three socioeconomic categories considered	(Kefeni *et al.*, 2014)
2011	South Africa	South Africa	Correlation between PBDE congener distribution and indoor dust particle size • PBDE concentrations increase with particle size factions • Imported electronic products identified as a major contamination source	(Kefeni and Okonkwo, 2014)

Sampling Year	**Sample Origin (Country)**	**Analysed (Country)**	**Summary**	**Ref.**
2009	South Africa	Norway	Selected halogenated organic pollutants in crocodile eggs to assess the possible role in mortalities (first report on BFRs in crocodile eggs) • Low BFR concentrations and unlikely that targeted pollutants have contributed to the mortalities	(Bouwman *et al.*, 2014)
2011	Tanzania	Norway	Occurrence of POPs in fish from four different Lakes in Tanzania, assess the implications on human health • BDE47 and BDE209 were only PBDEs detected, with BDE209 prevalent at highest levels in all lakes • Industrial area close to the shoreline identified as a possible contamination source	(Polder *et al.*, 2014)
Not Provided	Uganda	China	PBDEs in sediments and fish from Lake Victoria (first report on PBDEs in sediments and fish from Murchison Bay, Lake Victoria) • Concentrations in sediment and fish were low to moderate compared to similar studies • Fish consumption from the study area does not pose any risk to human health regarding PCDD/Fs and PBDEs	(Ssebugere *et al.*, 2014)
2013	South Africa	South Africa	PBDE concentration in landfill leachate and sediment and river sediment; investigate the relationship between trace metals, anions and water quality parameters • High PBDE concentrations with BDE209 as major congener • Highest PBDE concentrations for leachates from landfill sites equipped with geomembranes	(Olukunle *et al.*, 2014)
2011	Nigeria	Germany	Assess the presence of the PBDE (listed as POPs) and other BFRs in plastic of cathode ray tubes (CRT) from TV and computer monitors • CRT casings from TVs and computers imported to Nigeria contain high levels of BFRs • PBDEs present in TV CRT casings from the 1980s; BDE209 predominantly in all the CRT casings, EEE and e-waste from the last 30 years	(Sindiku *et al.*, 2014)
2011-2012	South Africa	Norway	Present the prevalence and levels of organic pollutants in the African Penguin eggs; compare results to previous studies • ΣDDT concentrations remained mostly unchanged, while ΣPCBs levels decreased • PBDEs detected at low concentrations	(Bouwman *et al.*, 2015)
2012	South Africa	South Africa	Provide data on PCBs and PBDEs in indoor dust • PCB levels were lower than PBDE levels • PBDE concentrations were lower than reported for developing countries	(Abafe and Martincigh, 2014)
2012 & 2013	South Africa	South Africa	Examine the presence of PBDEs and PCBs in the indoor dust from e-waste recycling sites and electronic equipment repair workshop • PBDEs were detected at high concentrations • Outdated recycling technology may cause exposure to high levels for tetra- to hexa-BDEs and BDE 209	(Abafe and Martincigh, 2015)
2012-2013	South Africa	South Africa	PBDE congeners in eggshells from two bird species • PBDE levels indicate an accumulation of the lower PBDE congeners • Estimated hazard quotients indicate Wattled Crane was subjected to high risk due to PBDE exposure	(Daso *et al.*, 2015)
Not Provided	South Africa	South Africa	GC-MS method for the analysis of APEs, PBDEs, PBB101 and HBCD in fish, using ultrasonic extraction, SPE clean-up and derivatization • APEs and BFRs could simultaneously be analysed using the derivatization method • Moderate contamination of APEs and BFRs in fish, with inconsistent BFR levels	(Chokwe *et al.*, 2015a)

Sampling Year	Sample Origin (Country)	Analysed (Country)	Summary	Ref.
2013	South Africa	South Africa	APE, PBDE, PBB101 and HBCD concentrations in water, fish, and sediment • Higher ΣHBCD concentrations reported for all matrices • WWTPs proposed as a possible source of contamination	(Chokwe *et al.*, 2015b)
Not Provided	South Africa	South Africa	GC-MS method for simultaneous analysis of APEs and BFRs in sewage sludge from WWTPs, using ultrasonic extraction and HFBA derivatization • Industrial activities could be a potential source for contamination for one of the sampling sites	(Chokwe *et al.*, 2015c)
2012	Nigeria	South Africa	PBDE concentrations in indoor dust in Nigeria • Positive correlation between PBDE concentrations and amount of electronic equipment • Higher dust exposure estimate compared to South Africa	(Olukunle *et al.*, 2015a)
2014	Nigeria	South Africa	PBDE levels in car dust in Nigeria (first report on BDEs in car dust and ingestion rate estimations for Nigeria) • Car dust does contain PBDEs with BDE209 as dominant congener • Low daily ingestion rates show no health risk associated with PBDE exposure	(Olukunle *et al.*, 2015b)
2013	Egypt	England	PBDE and alt-BFRs concentrations in indoor dust from the Greater Cairo region • PBDE congeners and alt-BFRs were detected, with BDE209 and HBCD as major congeners • PBDE and alt-BFRs concentrations in Egyptian dust are among the lowest levels reported	(Hassan and Shoeib, 2015)
2013	South Africa	South Africa	Alt-BFR and HBCD concentrations for landfill leachates and sediments (first report on alt-BFRs and HBCD in South African landfills) • The Alt-BFR detection frequency was higher in leachates than in sediment • Higher ΣHBCD concentrations compare to river sediment from The Netherlands and Ireland	(Olukunle and Okonkwo, 2015)
2010-2011	South Africa	South Africa	Provide baseline information on selected PBDE congeners and BB153 in sediment from two major rivers • The BFR contamination patterns vary for both rivers • Grey water from informal settlements and atmospheric deposition from landfills are possible contamination sources	(Daso *et al.*, 2016)
2015	Kenya	China	Investigate the occurrence of OCPs, PCBs and PBDEs in soils from southern Kenya • The soils were less contaminated by PBDEs compared to OCP and PCBs • The dominant PBDE congeners were penta-, tri- or tetra-BDEs, varying among different sampling sites	(Sun *et al.*, 2016)
2012	Tanzania	Norway	Reported POPs in native free-range chicken eggs and relate levels to human health (first report on BTBPE levels in African chicken eggs) • PBDE levels vary in collective egg samples with BDE209 as dominant congener • HCBD found in moderate to high levels with BPBPE at lower concentrations	(Polder *et al.*, 2016)
2012	Tanzania	Norway	BFRs in breast milk from the Northern parts of Tanzania (first study reporting on BFRs in human breast milk from Tanzania) • PBDE levels an order of magnitude higher that reported for Europe, Asia and other Sub-Saharan African countries • Mothers taking a clay product, used as mineral supplement and anti-emetic for pregnancy related nausea had higher PBDE levels	(Müller *et al.*, 2016)

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Chapter 3

Comprehensive two-dimensional gas chromatography coupled to high resolution time-of-flight mass spectrometry for screening of organohalogenated compounds in cat hair

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Abstract

The coupling of comprehensive two-dimensional gas chromatography with high-resolution time-of-flight mass spectrometry offers the best separation efficiency combined with accurate mass measurements over a wide mass range. The tremendous power of this screening tool is illustrated by trace qualitative screening analysis of organohalogenated compounds (OHCs) in pet cat hair. Tentative identification was supported by mass spectral database searches and elemental formula prediction from the experimentally determined accurate mass data. This screening approach resulted in the first tentative identification of pentabromoethylbenzene, decabromodiphenyl ethane, hexabromocyclododecane, trisbromoneopentyl alcohol, tris(2-chloroethyl) phosphate and tris(2-chloroisopropyl)phosphate in the South African indoor environment. A total of seventy-two OHCs were identified in the samples and include known flame retardants, such as polybrominated diphenyl ethers, and legacy contaminants such as polychlorinated biphenyls and organochlorine, organophosphorous and pyrethroid pesticides. The results obtained from cat hair indicate that these pets are exposed to complex mixtures of OHCs and the detection of these compounds suggests that non-invasive cat hair samples can be used to model indoor exposure with reference to external deposition of OHCs present in the air and dust surrounding people. Toddlers share the same environment as pet cats and therefore also the same health risks.

3.1. Introduction

Organohalogenated compounds (OHCs) constitute one of the largest and most diverse groups of chemicals characterised by the presence of one or more halogens. Among this group of chemicals polychlorinated biphenyls (PCBs), organohalogen pesticides and brominated flame retardants (BFRs) have been widely used in industry and society. The pesticides were intentionally introduced into the environment while the PCBs and BFRs unintentionally leached from electronic and electric equipment, textiles and other materials. Recently, a review on dust related contaminants reported that 485 compounds have been identified in literature (Zhang *et al.*, 2015). Many of these OHCs are toxic, persistent, and resistant to environmental degradation and are included or listed for inclusion in the Stockholm Convention on persistent organic pollutants (POPs) (http://chm.pops.int/). In addition to these priority pollutants, several potentially persistent and bio-accumulative chemicals currently in use are regularly detected in a variety of environmental matrices (Howard and Muir, 2010). Because of their ubiquitous prevalence and use in household items and consumer products, indoor contamination may be a significant source of human exposure to OHCs, especially for toddlers.

Many OHCs are known to have adverse neurotoxic effects, such as the development of the brain (Kodavanti and Curras-Collazo, 2010). Studies also suggest that postnatal exposure to polybrominated diphenyl ethers (PBDEs) is associated with a higher risk of certain Attention Deficit Hyperactivity Disorder (ADHD) symptoms and poor social competence of children at the age of 4 years (Gascon *et al.*, 2011). Household dust was shown to be a major source of human exposure to OHCs (Lankova *et al.*, 2015). The exposure to BFRs in indoor environments can overshadow that of the outdoor environment due to strong indoor sources, poor ventilation, deposition and organic film build-up on indoor surfaces, resuspension of indoor dust caused by human activities and slower chemical degradation (Liagkouridis *et al.*, 2014). Pets, especially cats, share similar environments with toddlers and have been presented as a potential bio-sentinel for indoor pollution exposure (Dirtu *et al.*, 2013). Apart from inhalation, their meticulous grooming make cats particularly susceptible to exposure to house dust and in turn, to the chemicals accumulated on dust particles. OHCs have been reported in cat blood (Ali *et al.*, 2013; Dirtu *et al.*, 2013) and detected in hair samples taken from pet cats and dogs from Pakistan (Ali *et al.*, 2013). Hair, as a non-destructive monitoring system, has been used as a bio-indicator for human exposure to organic pollutants (Appenzeller and Tsatsakis, 2012). Being a non-invasive matrix, hair samples allow for sample stability, information on short to long term exposure (depending on the length of the hair) and the high lipid content allows for the analysis of a wide variety of lipophilic OHCs. Hair is also directly exposed to the environment allowing for continuous accumulation of environmental contaminants from air or dust particles.

Several OHCs are complex mixtures, consisting of several theoretically possible congeners (Korytár *et al.*, 2006). Mass spectrometry (MS) is the detection technique most extensively used for non-targeted analysis of OHCs. Recent screening studies employed liquid chromatography (LC) and comprehensive two-dimensional liquid chromatography (LC×LC), hyphenated to an Orbitrap analyzer and high resolution time-of-flight mass spectrometer (HR-TOF-MS) (Cariou *et al.*, 2016; Ouyang *et al.*, 2017). Gas chromatography was predominately used as separation technique for OHC screening analysis coupled to different MS systems. These include low resolution quadrupole MS systems, HR-TOF-MS and ultra-high resolution Fourier transform type mass spectrometers using electron impact ionization (EI) and electron capture negative ionization (ECNI) techniques (Byer *et al.*, 2014; Fernando *et al.*, 2014; Hauler and Vetter, 2015; Jobst *et al.*, 2013; Rosenfelder *et al.*, 2010). New approaches used direct probe and GC as sample introduction systems to HR-TOF-MS with atmospheric pressure chemical ionization (APCI) (Ballesteros-Gómez *et al.*, 2013). The large number of possible compounds that can be detected, along with their degradation products present an analytical challenge for a reliable identification and interpretation of an unprecedented quantity of data generated by modern mass spectrometers. Since the advent of comprehensive two-dimensional gas chromatography (GC×GC) (Liu and Phillips, 1991), this unique separation technique has been frequently applied for the analysis of complex samples. Numerous detailed overviews on the principle, development and application of multidimensional chromatography have been published (Adahchour *et al.*, 2006; Dallüge *et al.*, 2003; Marriott *et al.*, 2012; Meinert and Meierhenrich, 2012).

The distribution of the analytes over a two-dimensional retention plane created by two independent columns, allows GC×GC to provide improved separation of complex compound mixtures, resulting in higher peak capacity. The retention structure of different compound classes provides additional information to assist with the identification of structurally related compounds. These advantages allow GC×GC coupled with time-of-flight mass spectrometry (GC×GC-TOF-MS) in EI mode and GC×GC coupled to HR-TOF-MS in APCI and ECNI modes to be successfully used in environmental forensic investigations and in targeted and non-targeted analysis of OHCs (Ballesteros-Gómez *et al.*, 2013; Fernando *et al.*, 2014; Liu and Phillips, 1991; Megson *et al.*, 2016).

Advances in commercially available HR-TOF-MS allows for reproducible collection of HR-EI mass spectra at unmatched scan speeds to resolve more discrete chemical compounds (Klitzke *et al.*, 2012). By combining GC×GC with HR-TOF-MS, the peak capacity of the chromatographic separation process is complemented with the advantage of recording HR-EI mass spectra over a large mass range (Fernando *et al.*, 2014; Ieda *et al.*, 2011; Ubukata *et al.*, 2015). As opposed to Fourier transform type mass spectrometers where resolution and mass accuracy are negatively correlated with the mass spectral acquisition frequency, the HR-TOF-MS does not suffer from this phenomenon and mass resolving power increases with *m/z* (Klitzke *et al.*, 2012). With appropriate mass spectral information and accurate mass measurements, elemental composition of compounds can be calculated, which allows rapid identification of molecular ions (and fragments) belonging to a homologous series (Jobst *et al.*, 2013).

Although screening using GC×GC-HR-TOF-MS has not previously been applied to the analysis of cat hair samples, this technique was successfully applied to the identification of OHCs in dust (Ubukata *et al.*, 2015), flame retardants and plasticisers in electronic waste and car interiors (Ballesteros-Gómez *et al.*, 2013), organic pollutants in water (Hernández *et al.*, 2007), and chlorinated and brominated polycyclic aromatic hydrocarbons in soil (Ieda *et al.*, 2011). In the present study, hair samples taken from six longhair Persian cats were analysed using GC×GC-HR-TOF-MS. These cats are typically closely associated with indoor environments, thus sharing a common environment with toddlers. Cat hair was specifically selected as sample matrix since the lipid content allows for the analysis of a wide variety of OHCs. Since indoor cats shed hair all year round, the exposure time frame includes both short and long term exposure; the samples reflect a real-time snapshot of the current exposure to their surroundings. Due to difficulties in distinguishing between external and internal exposure as previously reported by Kucharska *et al.* (2015b), unwashed cat hair was extracted; the extracts fractionated and screening analysis was performed to identify BFRs and other OHCs using GC×GC-HR-TOF-MS.

3.2. Experimental

3.2.1 Chemicals and reagents

High purity grade acetone, hexane, dichloromethane (DCM) and toluene were purchased from Burdick and Jackson (Honeywell International Inc., USA). Florisil®, concentrated sulphuric acid (H_2SO_4) and sodium sulphate (Na_2SO_4) were from Sigma–Aldrich (Chemie GmbH, Germany). Silica gel 60 to 200 Mesh was obtained from Merck (Darmstadt, Germany). Cleaned Florisil® and silica gel was heated for 48 hours in an oven at 160 °C. The PBDE mixture (BFR-PAR) containing 41 PBDE congeners, pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) and decabromodiphenyl ethane (DBDPE) was purchased from Wellington Laboratories Inc. (Guelph, ON, Canada). Individual BDE209 was purchased from Sigma-Aldrich (Johannesburg, South Africa). Aldrin, cis and trans-Chlordane, 4,4'-DDT, 2,4'-DDT, 4,4'-DDE, 4,4'-DDD, Dieldrin, Endosulfan I and II, Endosulfan sulphate, Endrin, Heptachlor, Heptachlor epoxide and Hexachlorocyclohexane (alpha, beta, delta and gamma isomers) were purchased from Restek, Bellefonte, USA. All GC capillary columns were purchased from Restek, Bellefonte, USA.

3.2.2. Sample preparation

Cat hair samples were collected from a local pet grooming service in Pretoria, South Africa, during September 2016. The cats originated from six family homes in the Pretoria area. The hair samples were placed in resealable plastic bags and stored in the dark at room temperature until chemical analysis. Compound losses because of the storage conditions and absorption to labware were not taken into account. To avoid possible compound losses due to hair swelling, as previously reported for forensic hair analysis, samples were not frozen (Cooper *et al.*, 2012).

During the development of the extraction method, the identification of OHCs from internal incorporation or absorption through the outer layer of the hair shafts was considered. After extraction (as discussed below), the hair was subjected to digestion using a weak acid as previously described for human hair (Kucharska *et al.*, 2015a). The results (not discussed in this paper) were ambiguous and no OHCs could be identified. The procedure for the extraction and clean-up was subsequently modified from previously described methods for the analysis of brominated and organophosphate flame retardants in dust and human hair (Ali *et al.*, 2011; Kucharska *et al.*, 2015a; Van den Eede *et al.*, 2012). Two grams of unwashed/untreated hair was cut into small pieces (<5 mm) using pre-cleaned stainless steel scissors, added to clean amber glass vials, 30 mL of hexane/acetone (3:1, v/v) added, extracted by sonication in an ultrasonic bath (Brandson 8800, USA) for 10 min at 25 °C, followed by vortexing and centrifugation at 3500 rpm for 5 min. The solvent fraction was transferred to a clean glass test tube. This step was repeated twice and the combined solvent extracts were evaporated to near dryness at 35 °C under a gentle steam of nitrogen and reconstituted in 1 mL of hexane. The extracts were fractionated on Florisil® prior to clean-up on acidified silica. Pre-cleaned empty glass columns fitted with ceramic frits were filled from the bottom with 4 g of Florisil® and 0.5 g anhydrous Na_2SO_4 and conditioned with 10 mL DCM followed by 20 mL hexane. The extracts were quantitatively transferred to the column and the first fraction (F1) eluted with 10 mL hexane, the second fraction (F2) with 20 ml DCM/hexane (1:4, v/v) and the third fraction (F3) with 10 mL DCM. All fractions were evaporated to near dryness at 35 °C under a gentle steam of nitrogen. Fractions 1 and 3 were reconstituted in 25 µL toluene for instrumental analysis, and the DCM/hexane fraction was reconstituted in 1 mL of hexane for clean-up on acidified silica. Glass columns were filled from the bottom with 0.5 g Na_2SO_4, 4 g acidified silica gel (44:56, *w/w*) and 0.5 g Na_2SO_4. The column was conditioned with 20 mL hexane and the F2 extract quantitatively transferred and eluted with 20 mL hexane, evaporated to near dryness at 35 °C under a gentle steam of nitrogen and reconstituted in 25 µL toluene. No OHC contamination was detected in either the method blanks subjected to the same analytical procedure as used on the actual samples, or solvent blanks included in the analysis sequence. A schematic representation of the sample extraction procedure is shown in Figure 3-1.

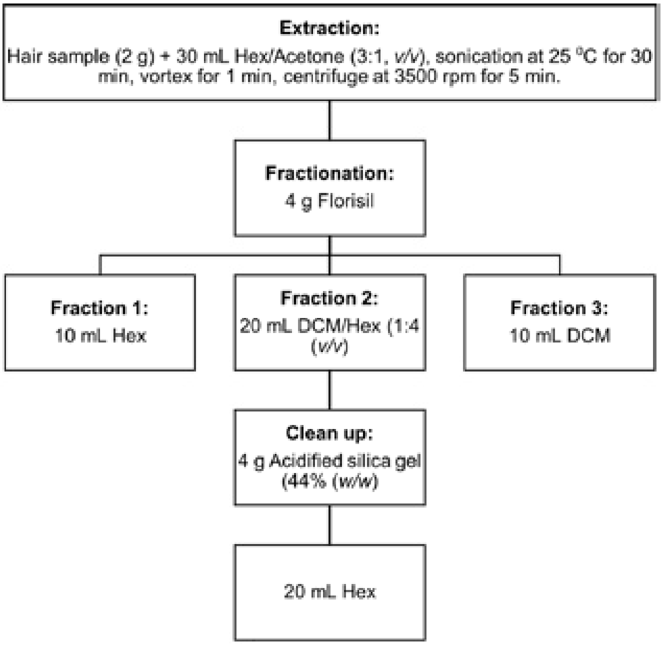

Figure 3-1. *Schematic representation of the sample extraction procedure.*

3.2.3. Instrumental conditions and data analysis

The GC×GC–HR-TOF-MS system used was a Pegasus® GC-HRT equipped with an electron ionisation source operated in high resolution mode (>25,000 FWHM at *m/z* 218.98) (LECO Corporation, St Joseph, MI, USA). The GC×GC system comprised both primary and secondary column ovens and fitted with a non-moving quadjet dual stage thermal modulator. A 15 m Rxi-5HT (0.25 mm I.D. × 0.1 µm df) was used as the first dimension (^{1}D) column and a 1 m Rxi-PAH (0.25 mm I.D. × 0.1 µm df) as the second dimension (^{2}D) column. Detailed instrument parameters are provided in the

Supplementary Material. A distinguishing feature of this instrument is the multi-reflecting TOF mass analyser based on the Folded Flight Path® concept providing a long ion path, thereby achieving HR measurements without significant loss in sensitivity (Verentchikov *et al.*, 2005).

3.2.4. GC×GC–HR-TOF-MS mass calibration

To collect accurate mass data, correct mass calibration is an important instrumental process to be performed. The mass calibration generates coefficients that allow for the conversion of time-of-flight data to mass-to-charge (*m/z*) data, by fitting a set of user definable exact masses to the TOF data that is collected. Perfluorotributylamine (PFTBA) was used as mass calibration compound. Eight masses were used for the pre-analysis calibration corresponding to CF_3 (*m/z* 68.9947), C_2F_4 (*m/z* 99.9931), C_3F_5 (*m/z* 130.9915) C_4F_9 (*m/z* 218.9851), $C_5F_{10}N$ (*m/z* 263.9866), $C_8F_{16}N$ (*m/z* 413.9770), $C_9F_{18}N$ (*m/z* 463.9738) and $C_9F_{20}N$ (*m/z* 501.9706). The mass accuracy root mean square (RMS) was better than 0.3 ppm. Data was acquired with constant infusion of the reference compound PFTBA during the entire analysis. The mass of the electron (0.000549 Da) was taken into account for the calculation of the ionic masses.

3.2.5. Data processing and compound identification

The GC×GC–HR-TOF-MS data processing was performed using the LECO ChromaTOF-HRT® software (version 1.90.). Data processing for screening analysis included automatic peak finding using mass spectral deconvolution (embedded within software). Peak identification was performed through spectral searching against three low (nominal) resolution mass spectral libraries, NIST 2014 (NIST/EPA/NIH Mass Spectral Library, NIST 2014) and two user libraries previously created at NMISA using authentic standards and built to assist in the correct identification of POPs and pesticides. Elemental composition was obtained by comparing the experimentally determined accurate mass of a molecular and/or fragment isotope ion with the software calculated exact mass. The formula calculator parameters were set to limit the elements used for formula prediction to the formula derived from the library search result. Identification through these database queries must therefore be regarded as tentative and not as conclusive identification. Retention times for PBDEs and organochlorine pesticides (OCPs) were compared to authentic standards.

3.3. Results and discussion

3.3.1. Analyte elucidation - Chromatographic considerations and peak detection

The sample extraction and clean-up processes are crucial considerations when compounds with different physical and chemical properties are targeted. Although the hexane/acetone (3:1, v/v) solvent mixture has shown to sufficiently extract OHCs from the surface of the hair samples, it is not possible to assess how much was extracted from the inner cortex and medulla of the hair. One of the major challenges in the screening analysis of the cat hair samples, was the lipid rich matrix and the large number of detected compounds over a wide concentration range. To remove most of the matrix interference while extracting as wide a selection of OHCs as possible, partial fractionation using Florisil® was performed to elute most of the PBDEs and alt-BFRs in a single fraction. Although column chromatography using alumina, and gel permeation chromatography has frequently been used for lipid separation (de Boer *et al.*, 2001), these options were not explored. Figure 3-2 shows the ^{2}D total ion chromatogram (TIC) plots of the three hair extract fractions. The fractionation improved the performance of the acid silica step on F2 by reducing the number of polar compounds thereby limiting the conversion of higher molecular mass compounds to lower molecular mass interferences. The extraction method allowed for OHCs with different polarities to be extracted. The fractionation steps reduced the sample complexity and the PBDEs and alternative BFRs (alt-BFRs) could be separated into a single fraction to be subjected to additional acid silica clean-up.

The GC×GC separation was optimised using a PBDE mixture, to limit the well-known degradation of higher molecular weight PBDEs (de Boer *et al.*, 2001), and to obtain good separation between the target compounds and matrix components. An individual BDE209 standard was injected to evaluate the possible formation of breakdown products in the system and no thermal degradation was observed. A short thin film low-polarity phase column was used in the ^{1}D in combination with a 1 m mid-polarity column in the ^{2}D. The ^{1}D column provided good chromatographic separation with good response for BDE209 and DBDPE. The ^{2}D column with the same column diameter and film thickness was used to separate components by polarity, moving the analytes further away from the matrix interferences. The two columns successfully separated the components due to different physical properties, providing more comprehensive separation than could be achieved by using a single column. Different oven temperature programs and modulation times were evaluated to limit the target analytes wrapping around into the region of the interference. Lower temperature ramp rates resulted in more modulation slices because of the broadening of ^{1}D peak widths. This resulted in more ^{2}D peak slices with low intensities, which had a negative impact on the mass spectrum deconvolution process. A modulation time of 6 s was selected to provide one large and two smaller symmetrical peak slices to maximise detection sensitivity for BDE209, and reduce wrap-around. The disadvantage in using long modulation times to increase sensitivity for PBDEs is that ^{1}D separations can be compromised resulting in co-elution of the closely eluting congeners in the same homologue group. This method allowed sufficient ^{2}D separation of the analytes, although the chromatographic space was not fully utilised.

As part of the screening approach, a series of steps were taken to attempt identification of the various OHCs. The contour plot layout is very useful to locate compound classes diagonally on the two-dimensional plane. In addition to the chromatographic structure, the full scan accurate mass spectra acquired over a large mass range (*m/z* 60, to 980) allows for comparison with mass spectral libraries. The predicted identity from the library search results with reverse match factors of more than 650 were used as a guide and mass spectra from isolated chromatographic peaks were examined for the presence of characteristic identifiable fragment ions (often halogenated isotopic clusters). The accurate mass measurement of ions recorded was then used to generate a list of recommended elemental formulae and provides values for the *m/z* error between the measured *m/z* and predicted theoretical *m/z*. The OHCs were then tentatively identified when the difference for molecular ions was lower than 2 ppm. In cases where the reverse match factors were less than 650 and/or in the absence of molecular ions, the mass error had to remain below 2 ppm for the postulated fragment ions. Retention times for PBDEs and OCPs were compared to authentic standards to support the identification, as many of these compounds produce similar mass spectra. Due to the peak slicing, the largest GC×GC modulation slice was used to determine the reported retention times.

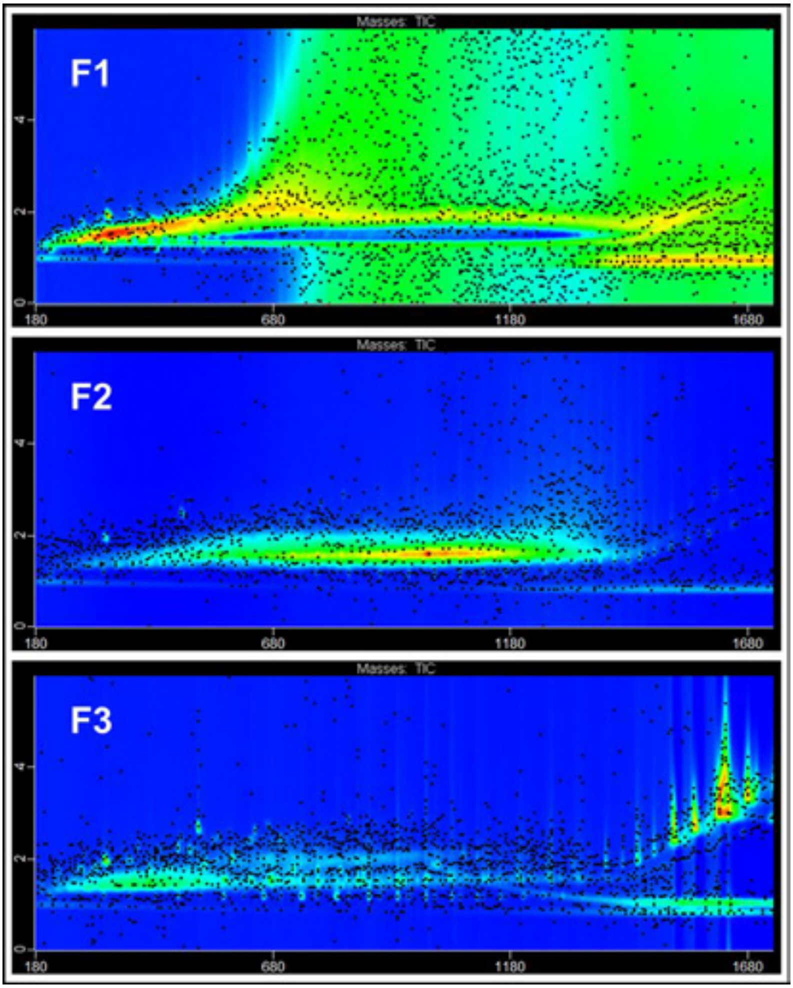

Figure 3-2. *Two-dimensional total ion chromatogram (TIC) of the cat hair extract fractions eluted with hexane (F1), DCM/hexane (1:4,* v/v*) (F2) and DCM (F3).*

The matrix contained a broad range of low *m/z* masses, which could saturate the dual microchannel plate detector, and suppress the detection of analytes present at low concentrations. This can be observed by monitoring an accurate mass of the constantly infused reference compound, which should ideally result in constant intensity. When detector saturation occurs, a decrease in the abundance of the reference mass is typically observed, indicating that the signal for other ions may also be reduced. It has also been suggested that shielding of the electron beam might occur at high matrix concentrations resulting in more electron-matrix collisions and fewer electron-reference gas collisions. As shown in Figure 3-3, the high abundance of the matrix compounds does have an effect on the intensity of the reference mass. The intensity of the reference compound *m/z* 68.9947 (± 0.0005), as shown in the extracted ion chromatogram (XIC), follows an inverse chromatographic pattern to the total ion chromatogram (TIC) extracted for the samples. This decrease in abundance of reference masses shows possible signal suppression of *m/z* ions of the unknown compounds. This can be seen in cases where poor library match factors were obtained from mass spectra lacking low intensity peaks (Supplementary Information). All results obtained from the samples were therefore manually inspected. In some cases, where peaks were miss-assigned or not found, the peaks were manually added, which is permitted by the data processing software. This peak assignment was done by using two background subtraction regions (each the width of the peak) at the start and end of the peak and selecting the average scans over the entire peak.

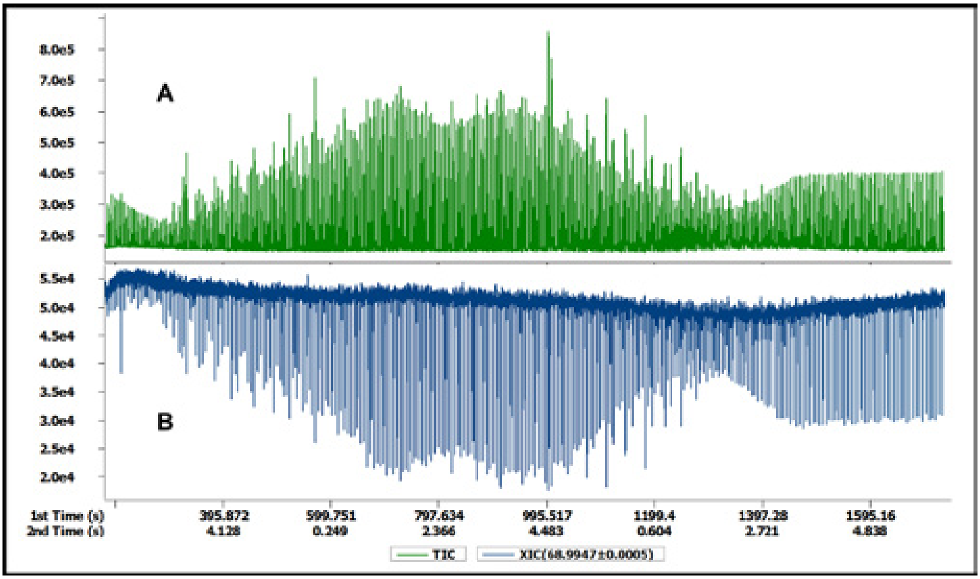

Figure 3-3. *(A) The total ion chromatogram (TIC) constructed from m/z 60–980 for the cat hair extract (F2). (B) The extracted ion chromatogram (XIC) of the reference compound m/z 68.9947 (± 0.0005).*

Table 3-1. *Non-target screening results for organohalogenated chemicals tentatively identified in the cat hair samples*

				Commercial (low res) library search result		Isotope molecular/ fragment ions					
Compound name	**^{1}D RT[a] (s)**	**^{2}D RT[b] (s)**	**Elemental composition**	**S match factor[c]**	**R match factor[d]**	**Elemental composition**	**Measured *m/z***	**Theoretical *m/z***	**Mass error (ppm)**	**Detection frequency**	**Fraction**
Trichloroaniline	341.904	2.196	$C_6H_4Cl_3N$	685	790	$C_6H_4Cl_3N$	194.9403	194.9404	-0.65	6/6	F3
						C_6H_3ClN	123.9947	123.9949	-1.13		
Trisbromoneopentyl alcohol (TBNPA)	365.89	2.366	$C_5H_9Br_3O$	861	870	$C_4H_6Br_2$	211.8834	211.8831	1.37	4/6	F3>F2
						C_4H_6Br	132.9648	132.9647	0.78		
Alpha-hexachlorocyclohexane	431.851	2.298	$C_6H_6Cl_6$	714	714	$C_6H_5Cl_4$	216.9137	216.9140	-1.18	4/6	F2
						$C_6H_4Cl_3$	180.9375	180.9373	0.94		
Hexachlorobenzene (HCB)	443.844	2.077	C_6Cl_6	703	783	C_6Cl_6	281.8126	281.8131	-1.73	1/6	F2
						C_6Cl_5	246.8439	246.8443	-1.65		
Beta-hexachlorocyclohexane	467.829	2.842	$C_6H_6Cl_6$	890	893	$C_6H_5Cl_4$	216.9141	216.9140	0.34	6/6	F2
						$C_6H_4Cl_3$	180.9375	180.9373	1.03		
Gamma-hexachlorocyclohexane	473.826	2.366	$C_6H_6Cl_6$	926	927	$C_6H_5Cl_4$	216.9140	216.9140	0.10	6/6	F2
						$C_6H_4Cl_3$	180.9375	180.9373	1.25		
Dichlorobiphenyl (Di-CB)	479.822	2.136	$C_{12}H_8Cl_2$	959	959	$C_{12}H_8Cl_2$	221.9999	221.9998	0.74	6/6	F2>F1
						$C_{12}H_8$	152.0622	152.0621	1.27		
Tris(2-chloroethyl) phosphate (TCEP)	479.822	2.459	$C_6H_{12}Cl_3O_4P$	511	564	$C_6H_{12}Cl_2O_4P$	248.9855	248.9850	1.91	2/6	F3
						$C_4H_8Cl_2O_3P$	204.9585	204.9588	-1.69		
Tris(2-chloroisopropyl) phosphate (TCIPP)	503.808	1.976	$C_9H_{18}Cl_3O_4P$	662	772	$C_9H_{18}Cl_2O_4P$	291.0316	291.0314	0.23	3/6	F3>F2
						$C_8H_{16}Cl_2O_4P$	277.0156	277.0158	-0.59		
Delta-hexachlorocyclohexane	503.808	2.776	$C_6H_6Cl_6$	865	865	$C_6H_5Cl_4$	216.9137	216.9140	-1.25	4/6	F2
						$C_6H_4Cl_3$	180.9375	180.9373	1.05		
Tris(2-chloroisopropyl)phosphate (TCIPP)	509.805	2.169	$C_9H_{18}Cl_3O_4P$	744	775	$C_9H_{18}Cl_2O_4P$	291.0315	291.0314	0.22	3/6	F3>F2
						$C_9H_{16}Cl_3O_3$	277.0161	277.0160	0.39		
Diazinone	509.805	1.873	$C_{12}H_{21}N_2O_3PS$	792	792	$C_{12}H_{21}N_2O_3PS$	304.1002	304.1005	-0.93	1/6	F3
						$C_{11}H_{18}N_2O_3PS$	289.0766	289.0770	-1.57		
Trichlorobiphenyls (Tri-CB)	539.787	2.192	$C_{12}H_7Cl_3$	797	844	$C_{12}H_7Cl_3$	255.9612	255.9608	1.58	6/6	F2
						$C_{12}H_7Cl$	186.0233	186.0231	1.03		
Dichloroanthracene	605.748	2.550	$C_{14}H_9Cl$	486	760	$C_{14}H_9Cl$	212.0390	212.0393	-1.10	6/6	F2
						$C_{14}H_6$	174.0468	174.0470	-0.63		
Chlorpyrifos	611.744	2.086	$C_9H_{11}Cl_3NO_3PS$	687	688	$C_9H_{11}Cl_2NO_3PS$	313.9568	313.9569	-0.37	6/6	F3
						$C_5H_2Cl_3NO$	196.9200	196.9196	1.57		
Tetrachlorobiphenyls (Tetra-CB)	647.723	2.210	$C_{12}H_6Cl^4$	713	843	$C_{12}H_6Cl_4$	289.9214	289.9218	-1.26	6/6	F2
						$C_{12}H_6Cl_2$	221.9811	221.9812	-0.22		
trans-Chlordane	665.712	2.310	$C_{10}H_6Cl_8$	809	822	$C_{10}H_6Cl_8$	405.7976	405.7972	0.91	6/6	F2
						$C_{10}H_6Cl_7$	370.8286	370.8284	0.71		

				Commercial (low res) library search result		Isotope molecular/ fragment ions					
Compound name	¹D RT[a] (s)	²D RT[b] (s)	Elemental composition	S match factor[c]	R match factor[d]	Elemental composition	Measured *m/z*	Theoretical *m/z*	Mass error (ppm)	Detection frequency	Fraction
cis-Chlordane	677.705	2.257	$C_{10}H_6Cl_8$	838	854	$C_{10}H_6Cl_8$	405.7970	405.7972	-0.60	6/6	F2
						$C_{10}H_6Cl_7$	370.8280	370.8284	-0.88		
Endosulfan I	683.702	2.214	$C_9H_6Cl_6O_3S$	806	821	$C_9H_4Cl_5O_3S$	370.8258	370.8265	-1.92	3/6	F2
						$C_9H_6Cl_5O_3$	336.8763	336.8760	0.94		
trans-Nonachlor	689.698	1.980	$C_{10}H_5Cl_9$	700	711	$C_{10}H_5Cl_9$	441.7555	441.7553	0.56	6/6	F2
						$C_{10}H_5Cl_8$	404.7890	404.7894	-0.93		
2,3,3',4,4',5,5'-Heptachloro-1'-methyl-1,2'-bipyrrole	695.695	1.973	$C_9H_3Cl_7N_2$	674	865	$C_9H_3Cl_7N_2$	383.8115	383.8116	-0.34	4/6	F2
						$C_9H_3Cl_6N_2$	348.8421	348.8422	-0.27		
Dichlorophenylaniline	695.695	2.645	$C_{12}H_9Cl_2N$	625	805	$C_{12}H_9Cl_2N$	237.0110	237.0107	1.46	4/6	F3
						$C_{12}H_8ClN$	201.0341	201.0340	0.68		
4,4'-DDE	707.687	2.201	$C_{14}H_8Cl_4$	852	895	$C_{14}H_8Cl_4$	315.9374	315.9375	-0.30	6/6	F2
						$C_{14}H_8Cl_2$	245.9998	245.9998	0.05		
Dieldrin	707.687	2.287	$C_{12}H_8Cl_6O$	657	657	$C_{12}H_8Cl_6O$	377.8700	377.8706	-1.79	1/6	F2
						$C_7H_2Cl_5$	260.8598	260.8599	-0.33		
Endrin	725.677	2.448	$C_{12}H_8Cl_6O$	765	766	$C_{12}H_8Cl_5O$	342.9020	342.9018	0.65	1/6	F2
						$C_7H_2Cl_5$	260.8598	260.8599	-0.35		
Endosulfan II	737.67	2.627	$C_9H_6Cl_6O_3S$	854	855	$C_9H_6Cl_5O_3$	338.8735	338.8730	1.40	3/6	F2
						$C_9H_6Cl_5O$	306.8826	306.8832	-1.95		
Pentachlorobiphenyls (Penta-CB)	743.666	2.281	$C_{12}H_5Cl_5$	749	820	$C_{12}H_5Cl_5$	325.8799	325.8799	0.09	6/6	F2
						$C_{12}H_5Cl_3$	255.9423	255.9422	0.29		
cis-Nonachlor	755.659	2.262	$C_{10}H_5Cl_9$	667	674	$C_{10}H_5Cl_8$	404.7891	404.7894	-0.72	2/6	F2
						C_5Cl_6	269.8127	269.8126	0.55		
4,4'-DDD/ 2,4'-DDT	755.659	2.359	$C_{14}H_{10}Cl_4$	777	833	$C_{14}H_9Cl_4$	318.9421	318.9423	-0.85	6/6	F2
						$C_{13}H_9Cl_2$	235.0075	235.0076	-0.34		
Pentabromoethylbenzene (PBEB)	773.648	2.525	$C_8H_5Br_5$	591	616	$C_8H_5Br_5$	497.6276	497.6282	-1.22	2/6	F2
						$C_7H_2Br_5$	482.6039	482.6047	-1.81		
Endosulfan sulfate	779.645	2.785	$C_9H_6Cl_6O_4S$	849	856	$C_9H_6Cl_6O_4S$	419.8112	419.8112	-0.09	6/6	F2
						C_5Cl_6	271.8098	271.8096	0.79		
4,4'-DDT	791.638	2.375	$C_{14}H_9Cl_5$	790	795	$C_{14}H_9Cl_5$	351.9140	351.9141	-0.30	6/6	F2
						$C_{13}H_9Cl_2$	235.0076	235.0076	-0.04		
Hexachlorobiphenyls (Hexa-CB)	797.634	2.251	$C_{12}H_4Cl_6$	681	784	$C_{12}H_4Cl_6$	357.8435	357.8439	-1.04	6/6	F2
						$C_{12}H_4Cl_4$	287.9060	287.9062	-0.39		
Endrin ketone	827.616	2.908	$C_{12}H_8Cl_6O$	819	819	$C_{12}H_8Cl_5O$	342.9017	342.9018	-0.29	6/6	F2
						$C_{11}H_8Cl_5$	316.9035	316.9039	-1.26		

Compound name	^{1}D RT^a (s)	^{2}D RT^b (s)	Elemental composition	Commercial (low res) library search result		Isotope molecular/ fragment ions				Detection frequency	Fraction
				S match factor^c	R match factor^d	Elemental composition	Measured *m/z*	Theoretical *m/z*	Mass error (ppm)		
Heptachlorobiphenyls (Hepta-CB)	869.591	2.119	$C_{12}H_3Cl_7$	495	528	$C_{12}H_3Cl_7$	391.8051	391.8049	0.49	3/6	F2
						$C_{12}H_3Cl_5$	321.8673	321.8672	0.45		
Tetrabromodiphenyl ether (Tetra-BDE)	869.591	2.557	$C_{12}H_6Br_4O$	689	733	$C_{12}H_6Br_4O$	481.7145	481.7147	-0.32	6/6	F2
						$C_{12}H_6Br_2O$	325.8760	325.8759	0.04		
Biphenthrin	881.584	1.712	$C_{23}H_{22}ClF_3O_2$	846	856	$C_{23}H_{22}ClF_3O_2$	422.1254	422.1255	-0.16	5/6	F3
						$C_{14}H_{13}$	181.1010	181.1012	-1.16		
Pentabromodiphenyl ether (Penta-BDE)	983.524	2.597	$C_{12}H_5Br_5O$	651	713	$C_{12}H_5Br_5O$	559.6260	559.6252	1.54	5/6	F2
						$C_{12}H_5Br_3O$	401.7879	401.7885	-1.58		
Permethrin	1013.51	2.021	$C_{21}H_{20}Cl_2O_3$	883	891	$C_{21}H_{20}Cl_2O_3$	390.0786	390.0784	0.41	6/6	F3
						$C_{13}H_{11}O$	183.0802	183.0804	-1.23		
Cypermethrin	1013.51	2.218	$C_{22}H_{19}Cl_2NO_3$	788	790	$C_{14}H_{10}NO$	208.0755	208.0757	-0.71	6/6	F3
						$C_7H_9Cl_2$	163.0074	163.0076	-1.41		
Hexabromodiphenyl ether (Hexa-BDE)	1085.46	2.643	$C_{12}H_4Br_6O$	749	749	$C_{12}H_4Br_6O$	643.5292	643.5295	-0.50	2/6	F2
						$C_{12}H_4Br_4O$	483.6945	483.6949	-0.83		
Hexabromocyclododecane isomers (HBCD)	1109.45	2.903	$C_{12}H_{18}Br_6$	656	674	$C_{12}H_{15}Br_2$	316.9539	316.9540	-0.37	1/6	F2
						$C_{12}H_{14}Br$	237.0274	237.0279	-1.87		
Heptabromodiphenyl ether (Hepta-BDE)	1181.41	2.848	$C_{12}H_3Br_7O$	509	523	$C_{12}H_3Br_7O$	719.4424	719.4427	-0.39	6/6	F2
						$C_{12}H3Br_5O$	563.6044	563.6039	0.86		
Octabromodiphenyl ether (Octa-BDE)	1289.34	3.101	$C_{12}H_2Br_8O$	493	516	$C_{12}H_2Br_8O$	799.3504	799.3511	-0.91	6/6	F2
						$C_{12}H_2Br_6O$	641.5143	641.5144	-0.17		
Nonabromodiphenyl ether (Nona-BDE)	1409.27	3.383	$C_{12}HBr_9O$	645	652	$C_{12}HBr_9O$	879.2590	879.2596	-0.70	6/6	F2
						$C_{12}HBr_7O$	719.4241	719.4250	-1.15		
Decabromodiphenyl ether (Deca-BDE)	1541.19	5.131	$C_{12}Br_{10}O$	646	685	$C_{12}Br_{10}O$	959.1674	959.1681	-0.64	6/6	F2
						$C_{12}Br_8O$	799.3328	799.3334	-0.76		
Decabromodiphenyl ethane (DBDPE)	1637.14	1.004	$C_{14}H_4Br_{10}$	676	676	$C_{14}H_4Br_{10}$	971.2061	971.2044	1.69	6/6	F2
						$C_7H_2Br_5$	484.6032	484.6027	1.10		

[a] First dimension retention time.
[b] Second dimension retention time.
[c] Software similarity match factor.
[d] Software reverse match factor.

3.3.2. Identification of OHCs

The structured chromatographic separation, full scan mass spectra and the exact mass measurement generated by the GC×GC-HR-TOF-MS, in combination with the elemental formula prediction, can yield tentative identification of the compounds and compound classes. An overview of OHCs found on the six cat hair samples is presented in Table 3-1. As observed from the accurate mass measurement results, all ions gave good mass accuracy; less than 2 ppm mass error using PFTBA as internal mass calibration compound. Commercial (low resolution) mass spectral libraries were used to identify the compounds (mass spectra are provided in the Supplementary Information). The OHCs tentatively identified in this study were limited to compounds listed in libraries and it must be noted that ultimately, comparison of retention times with authentic analytical standards is still necessary to confirm identity.

This screening analysis also resulted in the identification of chloro-phosphorous flame retardants. Tris(2-chloroethyl) phosphate (TCEP) and two tris(2-chloroisopropyl)phosphate (TCIPP) isomers have been reported to be mainly used as flame retardants in polyurethane products (Salthammer *et al.*, 2003). As shown in Table 3-1, these chlorinated organophosphate esters were detected in all samples. No molecular ion was observed in the mass spectra. The elemental composition could be proposed based on the accurate mass of the fragment resulting from a loss of chlorine ([M-Cl]) and supported by the full scan mass spectra. As shown in Figure 3-4, the elution order for these esters using a 5% phenyl-methylpolysiloxane stationary phase column was similar to previous studies (Haglund, 2005; Möller *et al.*, 2012).

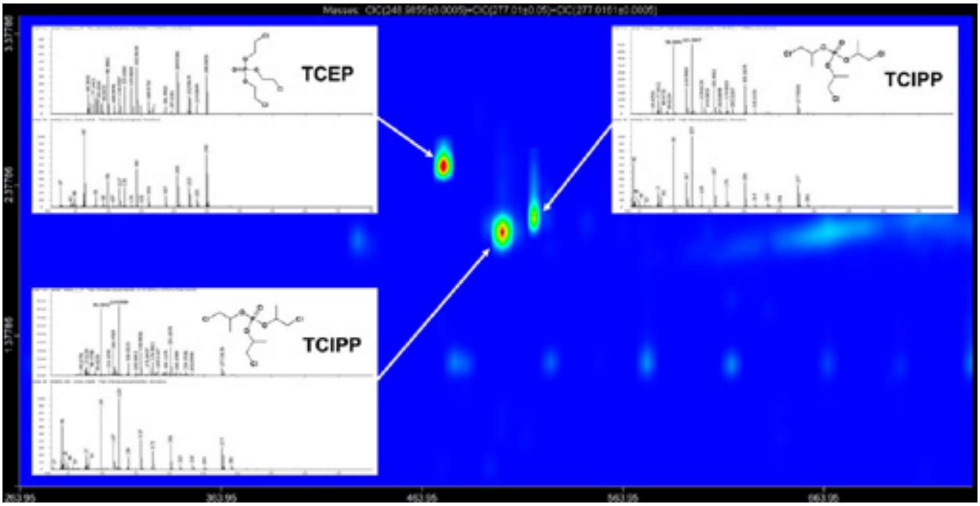

Figure 3-4. *The extracted mass two-dimensional contour plot and mass spectra tentatively identified as tris(2-chloroethyl) phosphate (TCEP) and the two tris(2-chloroisopropyl)phosphate (TCIPP) isomers in a cat hair extract.*

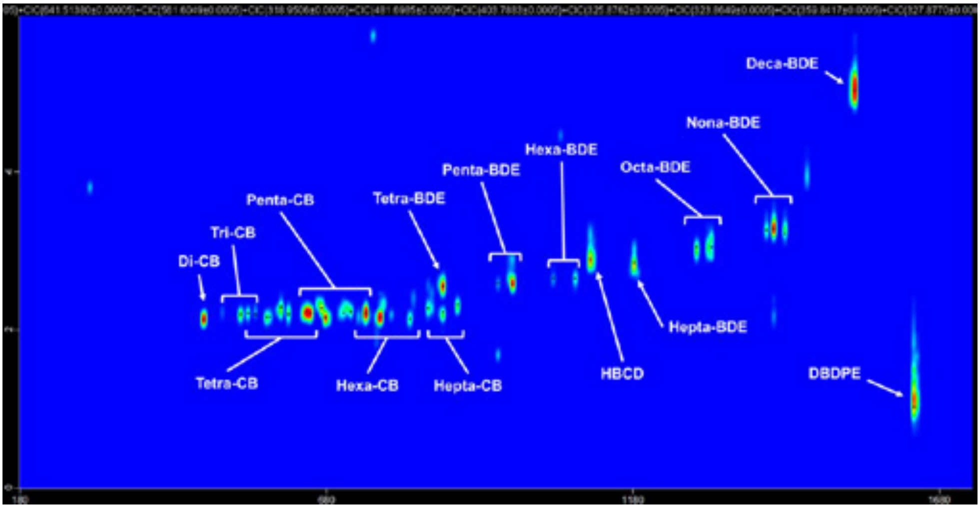

Figure 3-5. *Extracted mass two-dimensional contour plot of brominated flame retardants and di- to hepta chlorinated biphenyl congeners tentatively identified in a cat hair extract.*

Seven PBDE homologue groups and four alt-BFRs were also identified in the samples (Figure 3-5). To support the identification of these compounds, retention times were compared to the standard mixture (BFR-PAR). Based on the full scan mass spectra and the retention time comparison, BDE47 was identified as the only tetrabromodiphenyl ether (tetra-BDE), BDE99 and 100 as the pentabromodiphenyl ethers (penta-BDE) and BDEs 153 and 154 as the hexabromodiphenyl ethers (hexa-BDE). Three nonabromodiphenyl ethers (nona-BDE) were identified as BDE206, 207 and 208. Although library matching results for heptabromodiphenyl ether (hepta-BDE) and octabromodiphenyl ether (octa-BDE) were low, the retention time comparison showed that the hepta-BDE could be identified as BDE183. Due to a co-elution on this specific column set, the octa-BDEs were tentatively identified as either BDE204 or 197 and BDE196. The tetra, penta-, octa-, nona and decabromodiphenyl ethers were present in all six hair samples and hexa- and hepta-BDE congeners only in two of the samples. Of the four alt-BFRs suggested, the retention times for PBEB and DBDPE could be confirmed through the standard mixture. Based on the mass spectral match factor and the accurate mass measured for specific fragments, hexabromocyclododecane (HBCD) and trisbromoneopentyl alcohol (TBNPA) could be identified. In addition to PBDEs, the occurrence of HBCD has been reported in indoor environments (dust) and on children’s handwipes (Stapleton *et al.*, 2014). This compound consists of three diastereomers, primarily analysed using liquid chromatography coupled to mass spectrometry (LC-MS); and GC methods are not able to separate the diastereomers resulting in a broader peak compared to the PBDEs (de Boer and Law, 2003). The peak identified as HBCD elutes in the region where the hexa-BDEs elute, similar to the elution order previously reported by Korytár *et al.*, (2006). Tribromoneopentyl alcohol is a reactive BFR used in the synthesis of high molecular-weight flame retardants and as an additive in the manufacturing of polymers (Segev *et al.*, 2009).

As shown in Table 3-1, PCBs were detected in all six cat hair samples. The prevalence of tri- through hepta-CB congeners in indoor dust has been reported with regular detection of the low and high molecular weight congeners (Harrad *et al.*, 2009). In a recent study from South Africa, three PCB congeners representing the tri-, hexa- and hepta-CB groups were analysed in indoor dust samples (Abafe and Martincigh, 2015). The higher molecular mass congeners were found at higher intensities. As shown in Figure 3-5, di- through hepta-CB congeners could be detected in the cat hair samples. The di- through hexa-CBs were present in all six samples and the hepta-CB congeners were only detected in three of the samples. Interestingly, a single di-CB congener was present in all samples at very high intensities. Recent publications reported on the detection of the dichloro congener 3,3′dichlorobiphenyl (PCB 11) in air, water, biota, and sediment (Rodenburg *et al.*, 2010). This compound is produced during the production of diarylide yellow pigments used in printing and other applications. As no authentic PCB standards were used in this study, the congeners could not be verified.

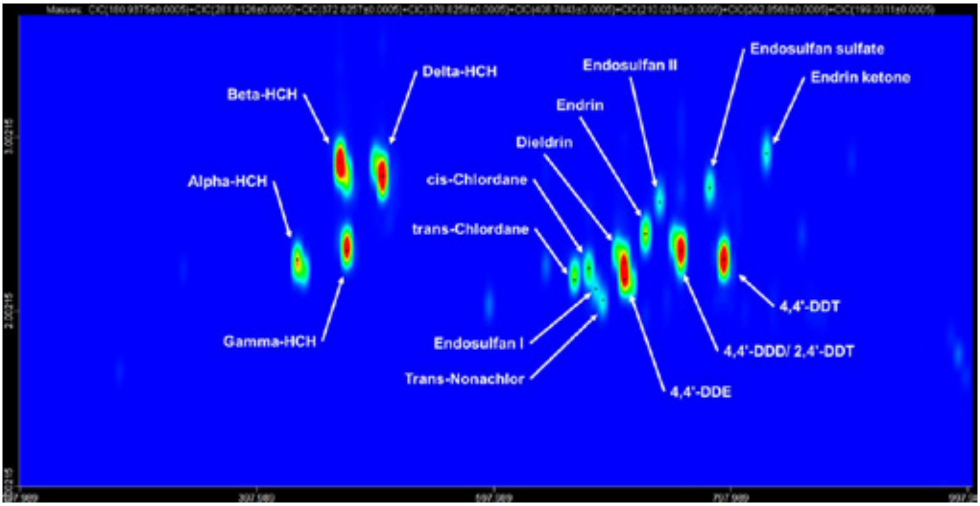

Figure 3-6. *Extracted mass two-dimensional contour plot of pesticides tentatively identified in a cat hair extract.*

The screening approach employed also resulted in the detection and identification of numerous organochlorine pesticides (OCPs), organophosphorous pesticides (OPPs) and pyrethroids (Figure 3-6). Because many of the OCPs produce similar mass spectra, retention time comparison with authentic standards aided the identification. As one of the major importers of pesticides on the African continent, South-Africa has a highly organised agricultural sector with vast rural areas. A wide range of toxic chemicals are used for crop protection; DDT and other chemicals are also used to control the vector mosquitoes (Quinn *et al.*, 2011). Of the POPS listed in the Stockholm Convention, the four hexachlorocyclohexane (HCH) isomers (alpha, beta, gamma and delta-HCH), hexachlorobenzene, chlordanes (cis and trans), dieldrin, endrin, DDT, DDD, DDE could be identified. Although OCPs were not previously reported for South African indoor dust, their occurrence is well documented for ambient air in industrial and residential areas (Batterman *et al.*, 2008). It must be emphasised that the sampling site is more than 400 km from the nearest known site where DDT is legally used for indoor spraying.

This approach also enables detection and tentatively identification of 2,3,3',4,4',5,5'-Heptachloro-1'-methyl-1,2'-bipyrrole (MBP-Cl_7); a compound with similar physical properties to PBDEs (Tittlemier *et al.*, 2004). Vetter was the first to identify this compound as a natural heptachloro compound associated with the marine environment and found in fish, seabirds and marine mammals (Vetter *et al.*, 2009). Fujii *et al.* (2012) reported on MBP-Cl_7 levels in Japanese breast milk and suggested that the possible source may be through biota or the food chain. As this compound was detected in four of the six samples, the only plausible source might be from cat food containing fish products, but this would have to be confirmed by analysing the food.

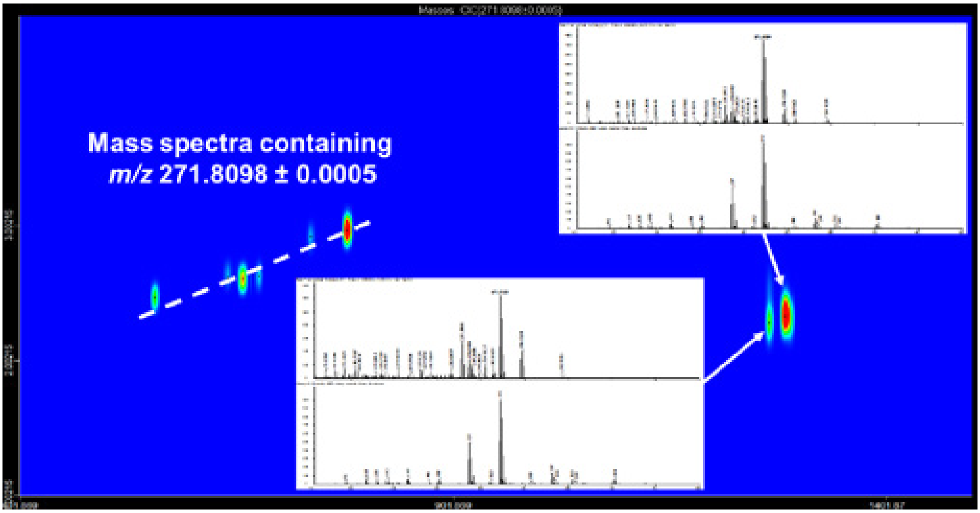

Figure 3-7. *Contour plot of a cat hair extract showing the elution of compounds containing m/z 271.8098 (± 0.0005 Da) in their mass spectra and the accurate full scan mass spectrum extracted for the two compounds identified by the library search as Mirex.*

This screening analysis using GC×GC-HR-TOF-MS in electron impact (EI) ionisation mode also presents some limitations. As shown in Figure 3-7, two compounds eluting at 1265.36 s (^{1}D Rt), 2.287 s (^{2}D Rt) and 1283.35 s (^{1}D Rt), 2.341 s (^{2}D Rt) were identified by the library as Mirex. Mirex, an OCP, is also used as the flame retardant Dechlorane (Gandhi *et al.*, 2015). Analogues of Dechlorane have been studied in environmental samples under EI conditions. Due to the extreme fragmentation and the low intensity of the molecular ion as a result of the retro Diels-Alder fragmentation, the most intense fragment isotope ion produced is $C_5Cl_6^+$ with theoretical *m/z* of 271.8096 (Sverko *et al.*, 2011). The retention time of these two compounds was comparable to those from previous studies where BFRs and Dechlorane Plus (DP) were analysed on a similar low-polarity phase column. It is thus proposed that these compounds might be syn-DP and anti-DP (Zhang *et al.*, 2011). As seen in Figure 3-7, the characteristic ion is also present in the mass spectra of other early eluting OHCs and the information is therefore not sufficient to positively identify DP.

3.4. Conclusion

This paper presents a first report using hair from South African pet cats to investigate the occurrence of OHCs in the domestic environment. The screening method utilises GC×GC coupled to a HR-TOF-MS system to detect as many GC-amenable compounds as possible. This technique can successfully screen samples as it provides structured separation of compound classes and library searchable full scan EI mass spectra with accurate mass measurements (mass accuracy of better than 2 ppm) to predict chemical formulae for molecular and corresponding fragment ions. The matrix effects in quantitative TOF-MS analysis was confirmed, but posed no limitation to the screening procedure proposed. The method allows for the detection and tentative identification of various OHC classes including pesticides (OCPs, OPPs, pyrethroids), PCBs and halogenated flame retardants. Although OHCs were previously reported in the South African environment, the majority of the studies applied a targeted analysis approach. While the solvent mixture allows for the adequate extraction of OHCs from the hair samples, further studies will be conducted to distinguish between external deposition and internal incorporation. The PBDEs and PCBs detected in cat hair samples were comparable to those found in house dust, demonstrating that cat hair might be a possible indicator for environmental exposure with reference to external deposition of OHCs present in the air and dust surrounding people. This study is also the first to report detection of DBDPE, TBNPA, HBCD, PBEB, TCEP and TCIPP in the South African indoor environment and confirms the ubiquitous occurrence of halogenated flame retardants in the indoor environment.

The results obtained from the hair samples indicates that cats are exposed to complex mixtures of industrial chemicals and the detection of these compounds suggests the use of cat hair as a non-invasive sample for modelling indoor exposure. Toddlers share the same environment as cats and exposure would result in similar health risks. The presence of these persistent chemicals in cat hair may sound a cautionary warning for the immediate and long term health of children.

Acknowledgement

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Supplementary material S3

S3.1. GC×GC–HR-TOF-MS instrumental parameters

The instrument control, data acquisition (100 Hz) and processing was carried out using Chroma-TOF software (LECO Corporation, St Joseph, MI, USA). The GC×GC separation was achieved using a 15 m Rxi-5HT (0.25 mm I.D. × 0.1 µm df; Restek, Bellefonte, USA) as the first dimension (^{1}D) column and 1 m Rxi-PAH (0.25 mm I.D. × 0.1 µm df; Restek, Bellefonte, USA) as the second dimension column. The injector and transfer line temperatures were maintained at 280 °C and 320 °C, respectively. The ion source temperatures was set at 250 °C and operated at 70 eV. Helium (99.999%; Air Products, Kempton Park, South Africa) was used as the carrier gas at 1.0 mL/min. Injections of 1 µL aliquots were made in the splitless mode with a 60 s purge delay and the primary GC oven temperature was kept constant at 90 °C for 1 min, raised at 10 °C per minute to 320 °C, and held for 5 min. The secondary oven temperature was programmed as the primary oven with a +20 °C offset. The modulation period was set to 6 s with a 1.8 s hot pulse and the modulator temperature was programmed as the primary oven with a +15 °C offset relative to the secondary oven temperature. During modulation, cold pulses were generated using dry nitrogen gas cooled by liquid nitrogen (Air Products, Kempton Park, South Africa), and hot pulses through dry nitrogen heated by a modulator heating block. Modulation gasses were supplied from a nitrogen generator (Genius 1052, Peak Scientific, Scotland). Full scan data was collected at an acquisition rate of 60 spectra/s and extraction frequency of 1.4 kHz in the high resolution mode (>25,000 FWHM at *m/z* 218.98).

Figure S3-1 to S3-47. Mass spectra comparison with commercial mass spectral database results

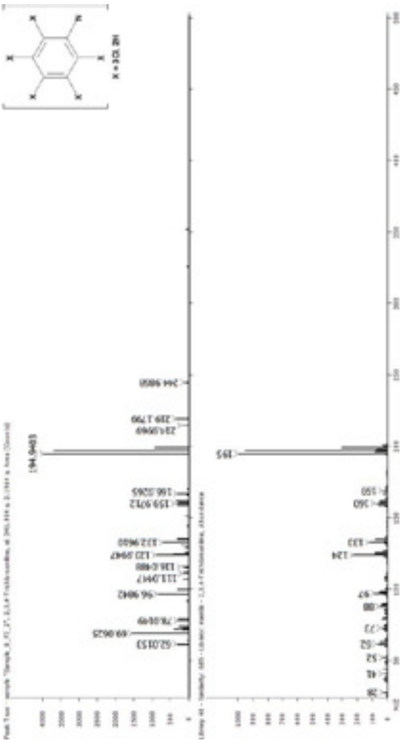

Figure S3-1. Trichloroaniline

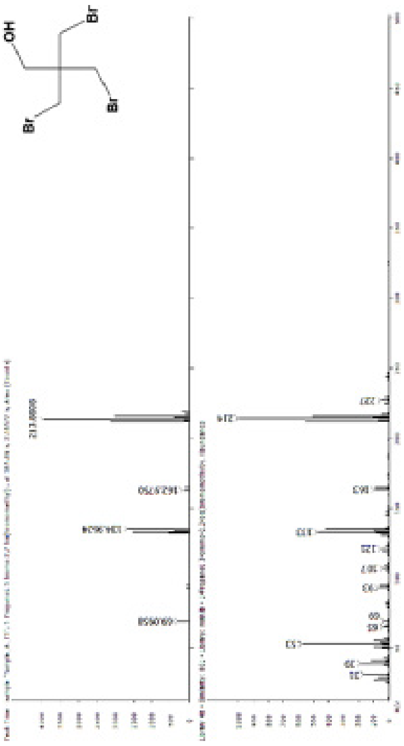

Figure S3-2. Trisbromoneopentyl alcohol (TBNPA)

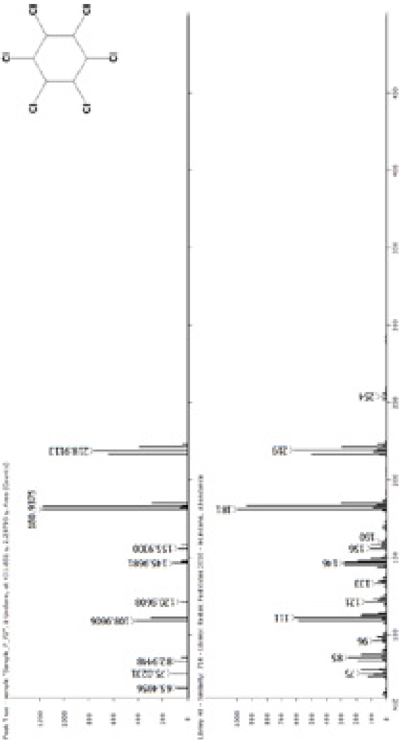

Figure S3-3. Alpha-hexachlorocyclohexane

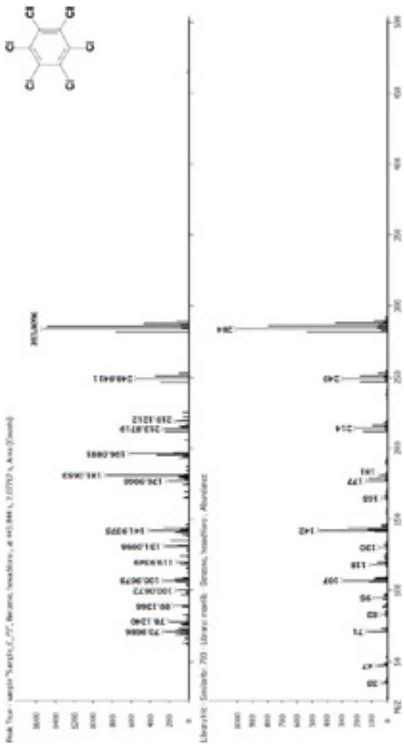

Figure S3-4. Hexachlorobenzene (HCB)

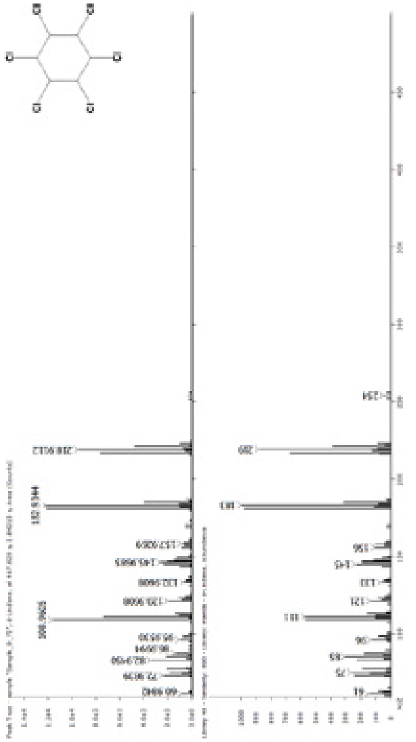

Figure S3-5. Beta-hexachlorocyclohexane

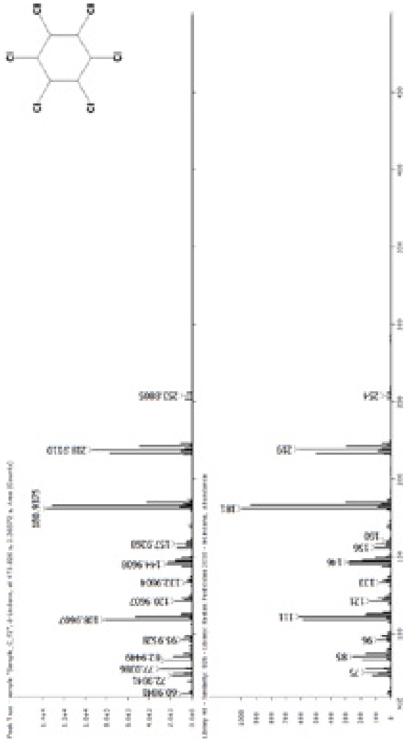

Figure S3-6. Gamma-hexachlorocyclohexane

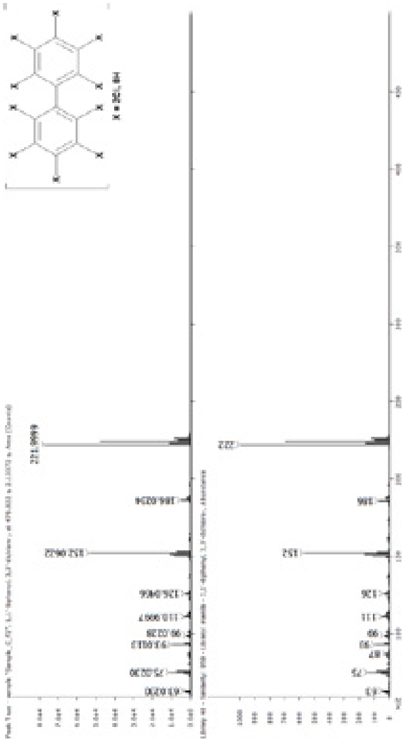

Figure S3-7. Dichlorobiphenyl (Di-CB)

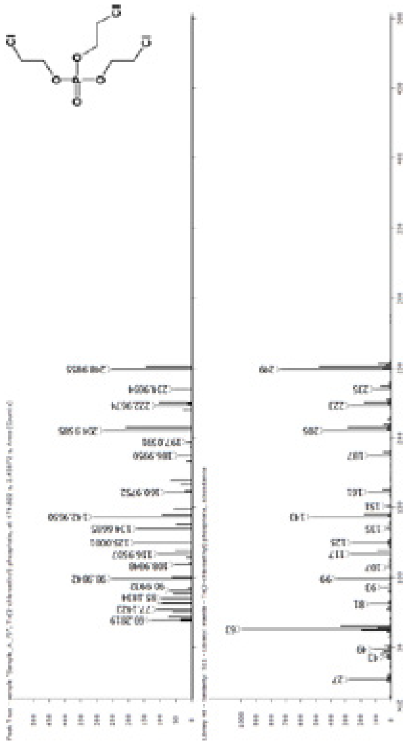

Figure S3-8. Tri(2-chloroethyl) phosphate (TCEP)

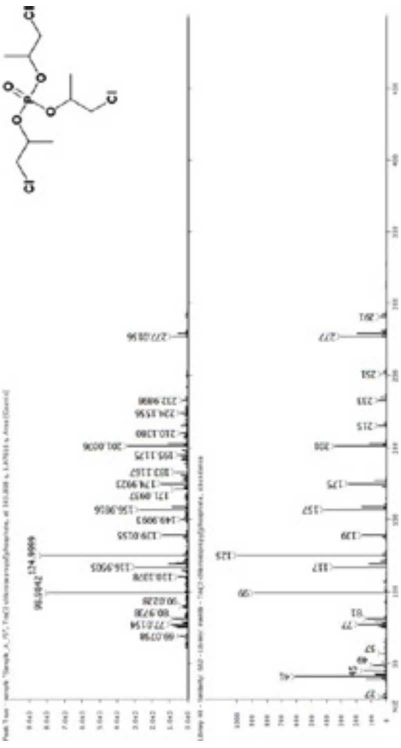

Figure S3-9. *Tris(2-chloroisopropyl)phosphate (TCIPP)*

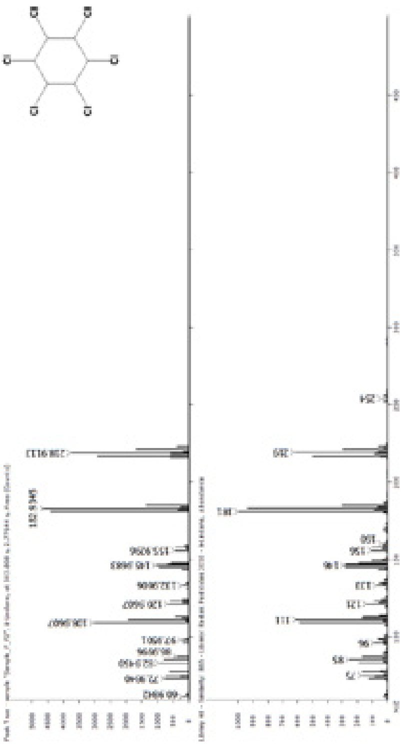

Figure S3-10. *Delta-hexachlorocyclohexane*

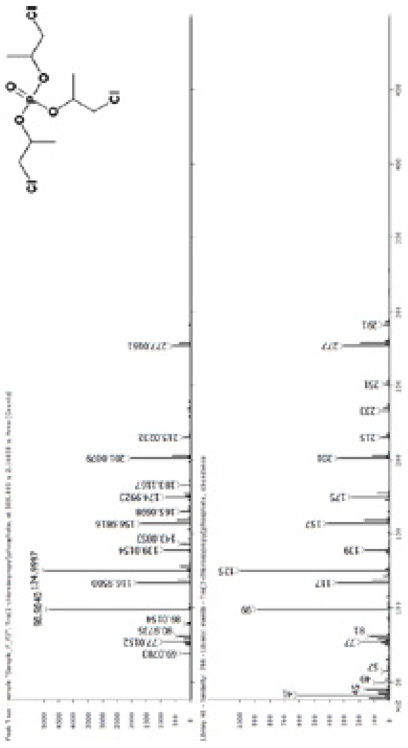

Figure S3-11. *Tris(2-chloroisopropyl)phosphate (TCIPP)*

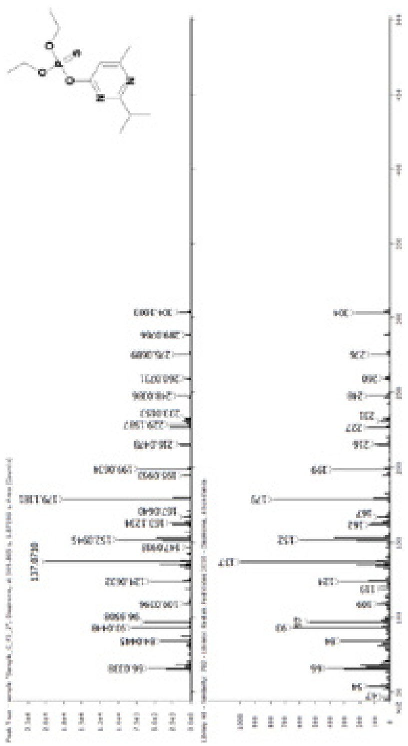

Figure S3-12. *Diazinone*

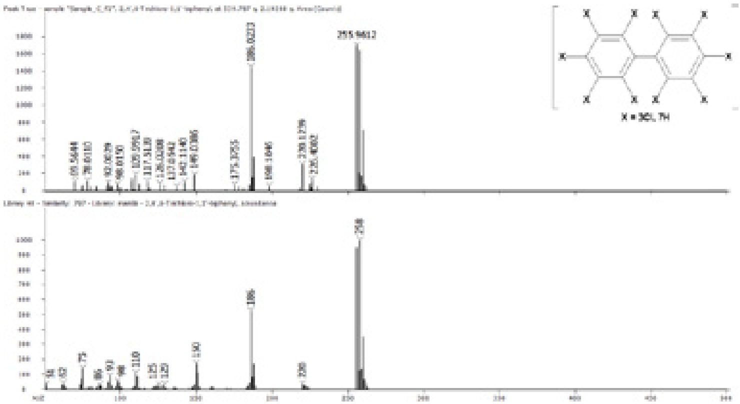

Figure S3-13. Trichlorobiphenyls (Tri-CB)

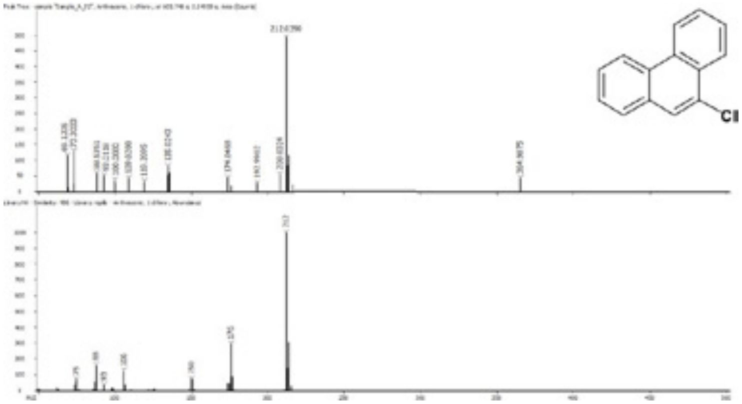

Figure S3-14. Dichloroanthracene

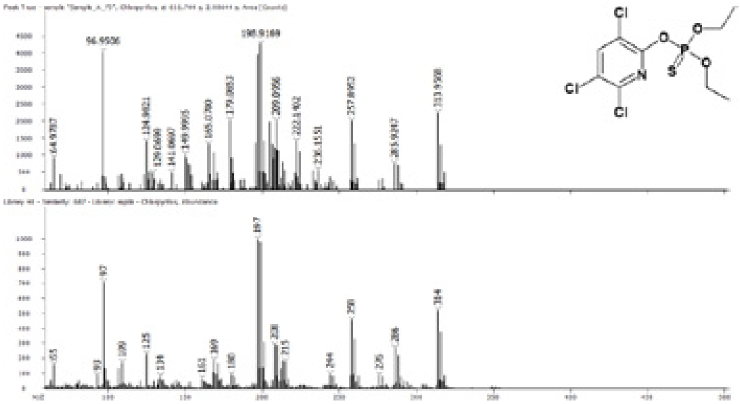

Figure S3-15. Chlorpyrifos

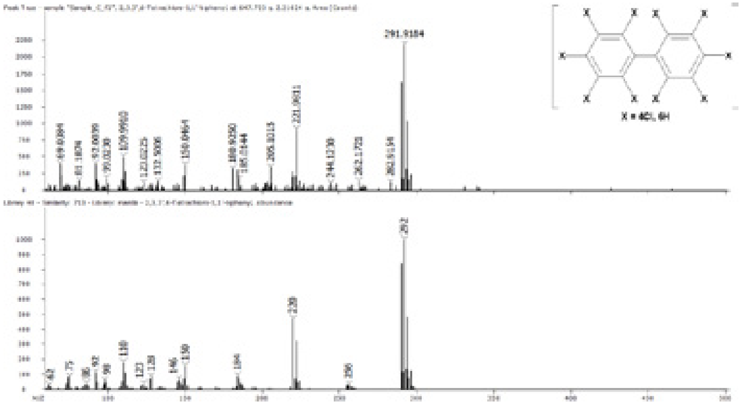

Figure S3-16. Tetrachlorobiphenyls (Tetra-CB)

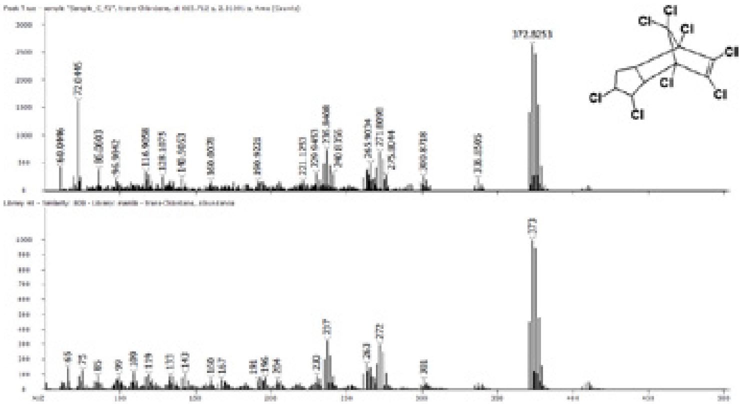

Figure S3-17. *trans-Chlordane*

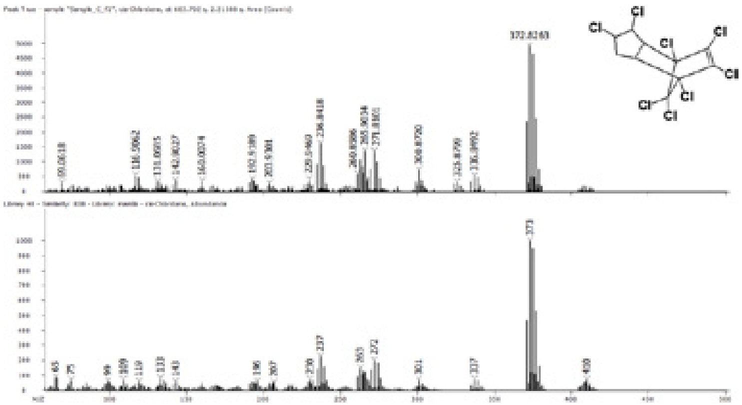

Figure S3-18. *cis-Chlordane*

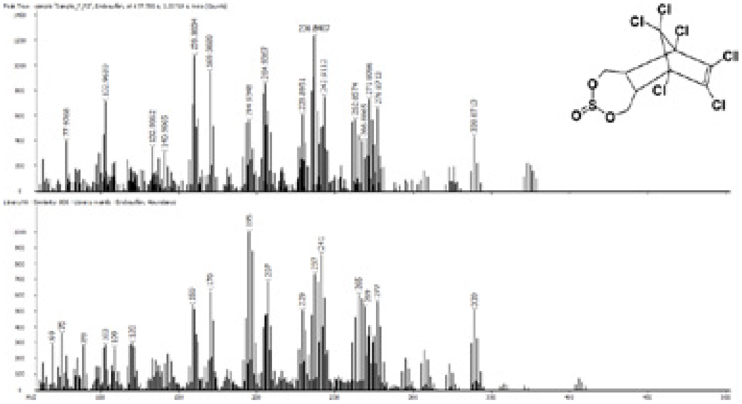

Figure S3-19. Endosulfan I

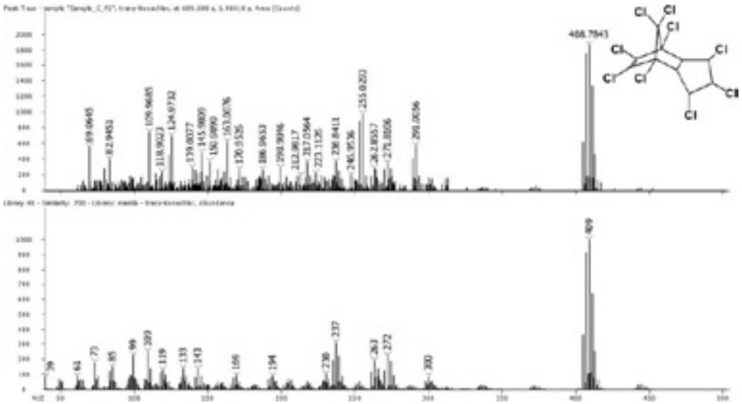

Figure S3-20. *trans-Nonachlor*

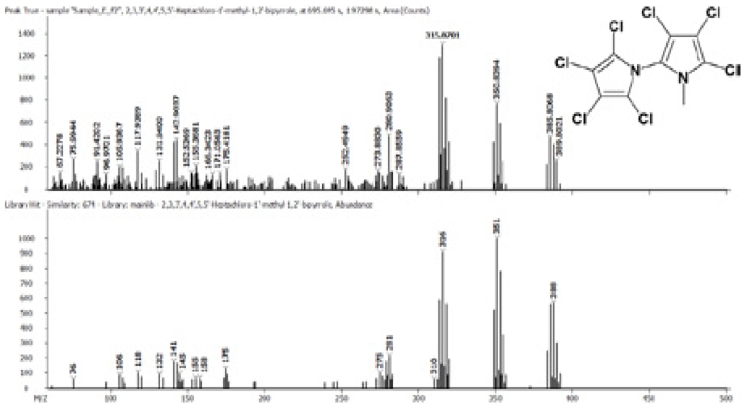

Figure S3-21. *2,3,3',4,4',5,5'-Heptachloro-1'-methyl-1,2'-bipyrrole*

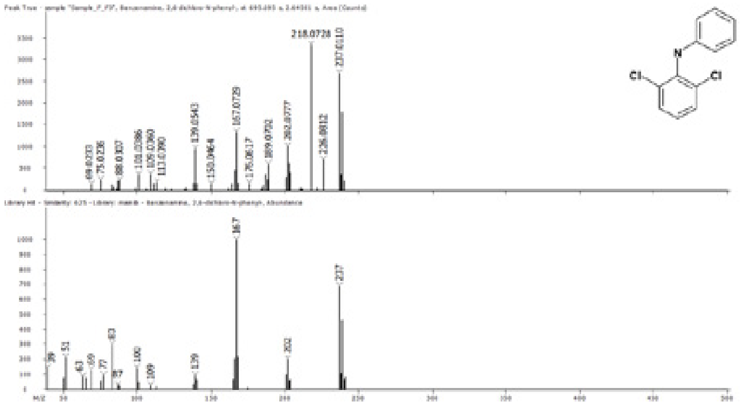

Figure S3-22. *Dichlorophenylaniline*

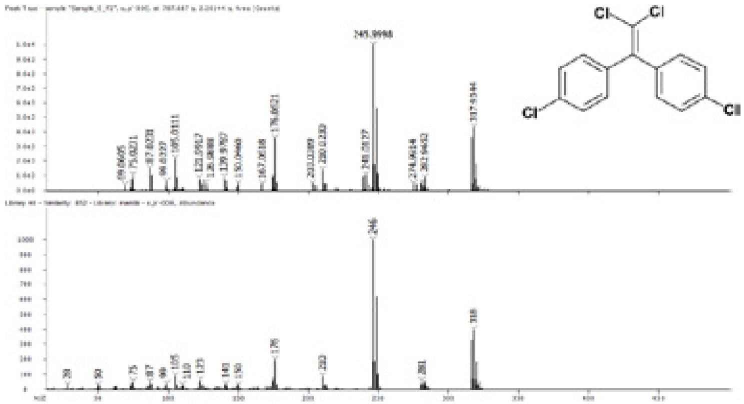

Figure S3-23. *4,4'-DDE*

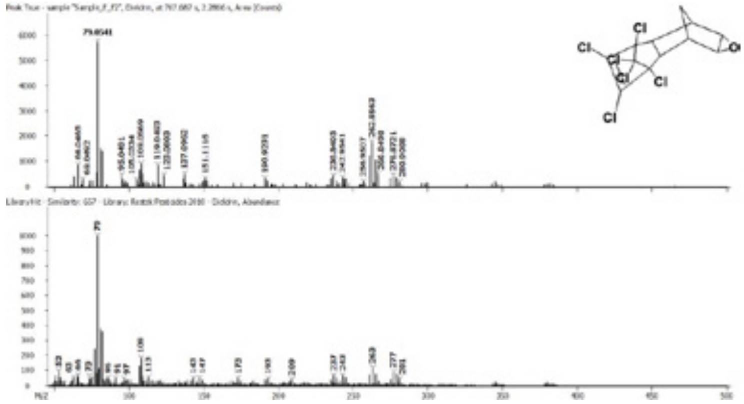

Figure S3-24. *Dieldrin*

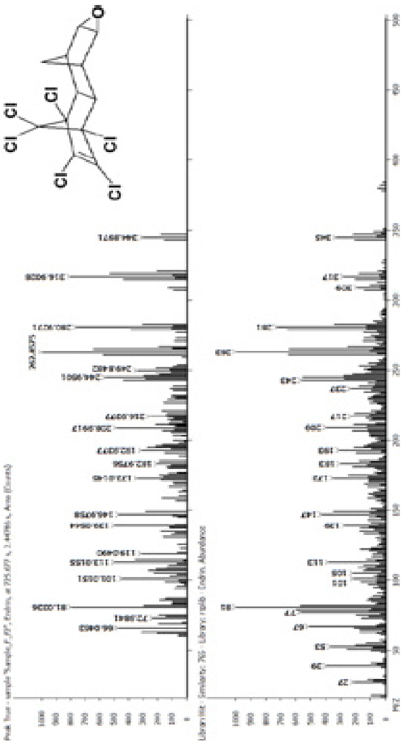

Figure S3-25. Endrin

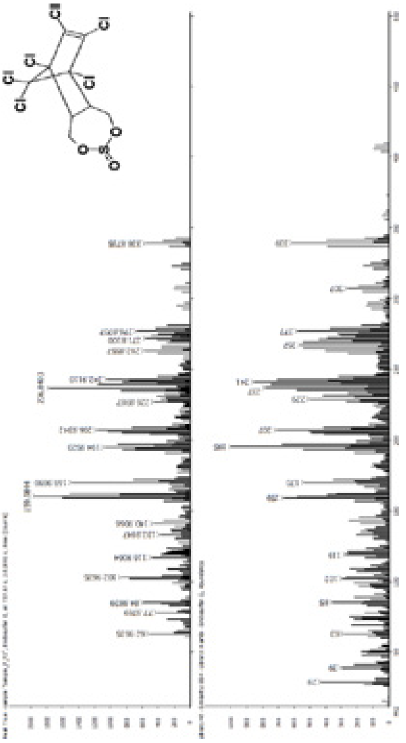

Figure S3-26. Endosulfan II

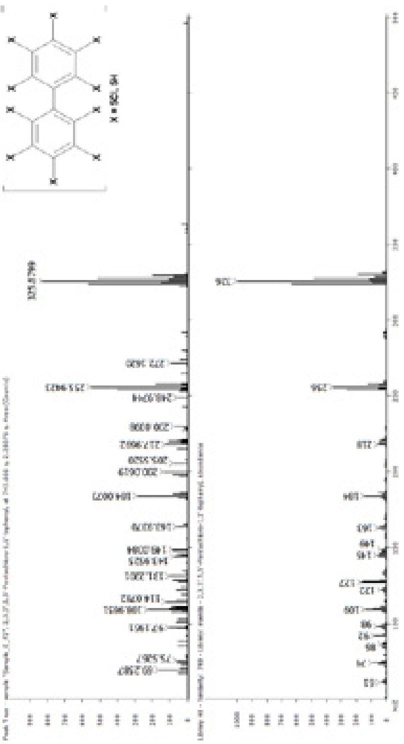

Figure S3-27. Pentachlorobiphenyls (Penta-CB)

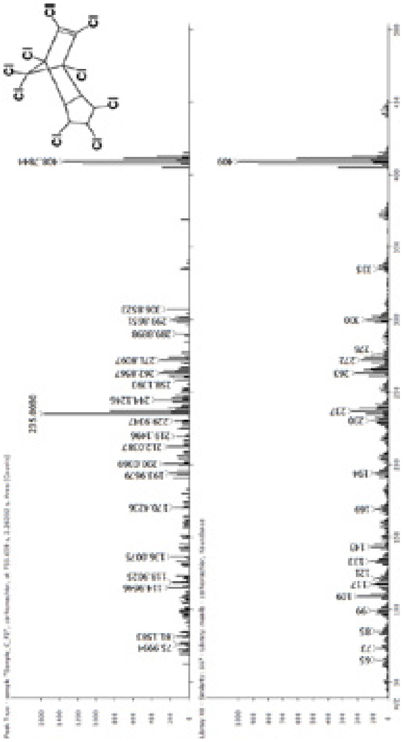

Figure S3-28. cis-Nonachlor

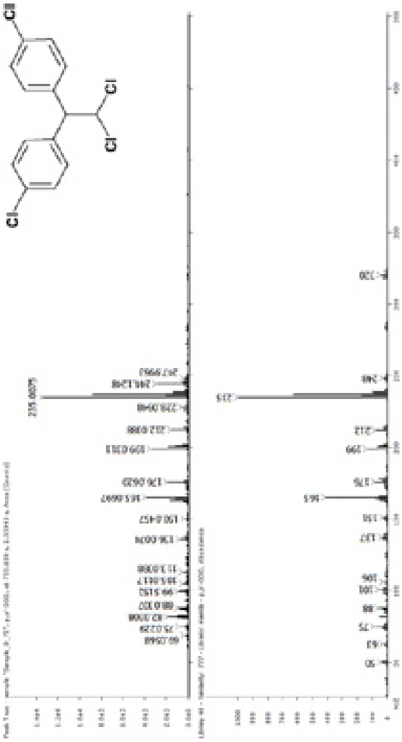

Figure S3-29a. 4,4'-DDD

Figure S3-29b. 2,4'-DDT

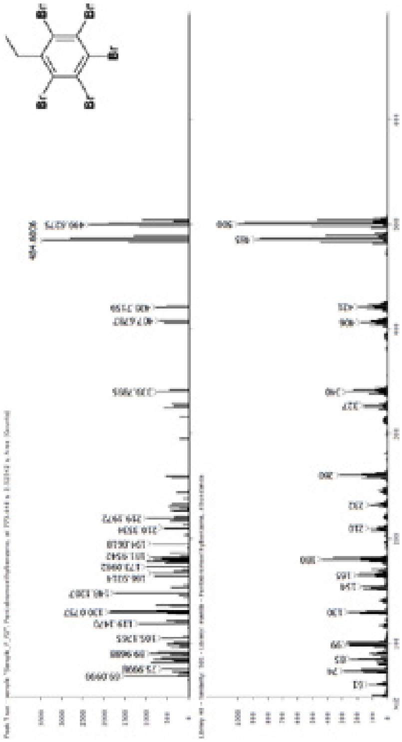

Figure S3-30. Pentabromoethylbenzene (PBEB)

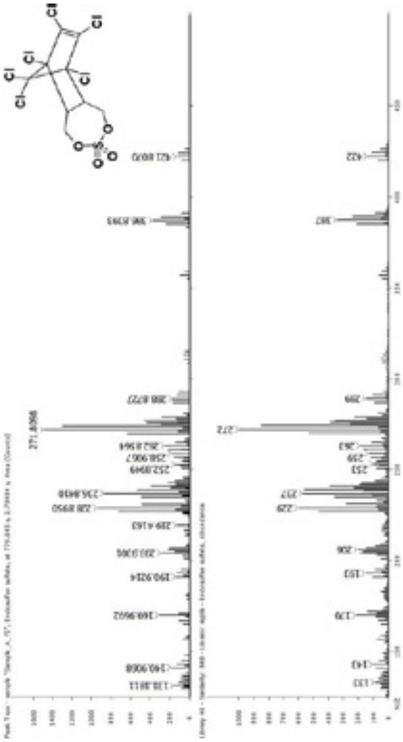

Figure S3-31. Endosulfan sulfate

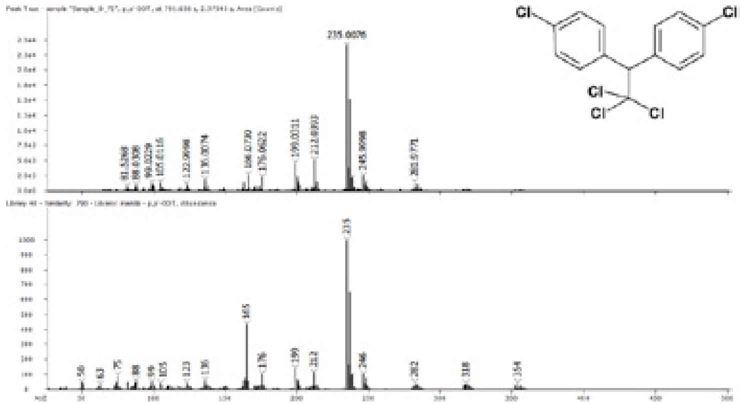

Figure S3-32. *4,4'-DDT*

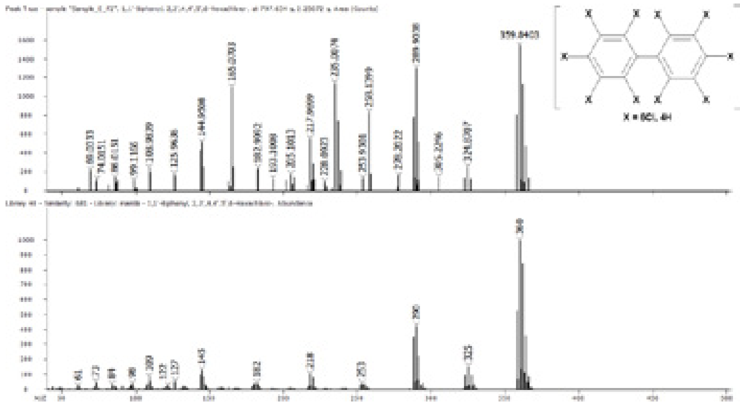

Figure S3-33. *Hexachlorobiphenyls (Hexa-CB)*

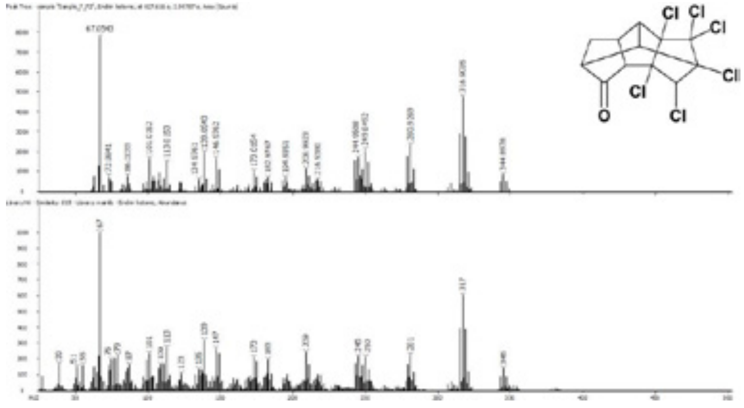

Figure S3-34. *Endrin ketone*

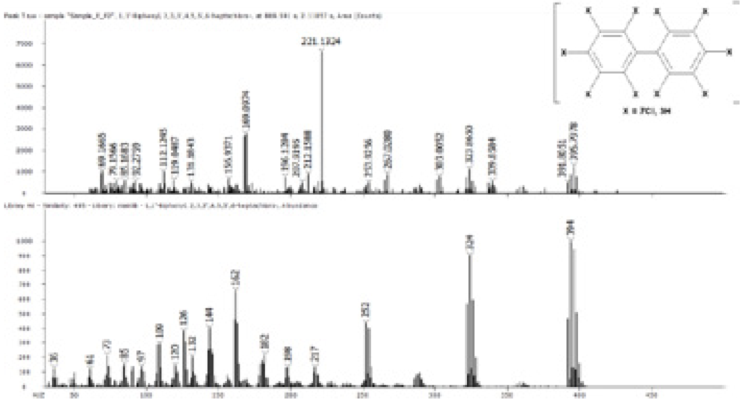

Figure S3-35. *Heptachlorobiphenyls (Hepta-CB)*

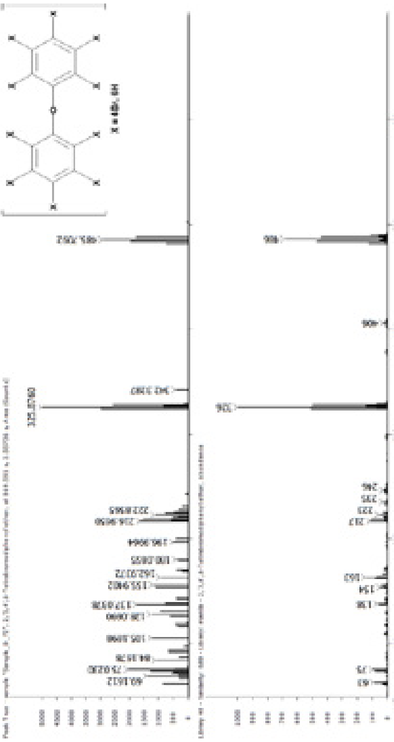

Figure S3-36. *Tetrabromodiphenyl ether (Tetra-BDE)*

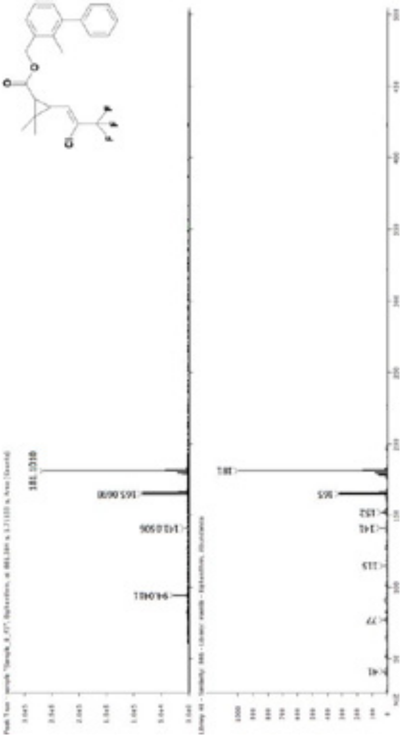

Figure S3-37. *Biphenthrin*

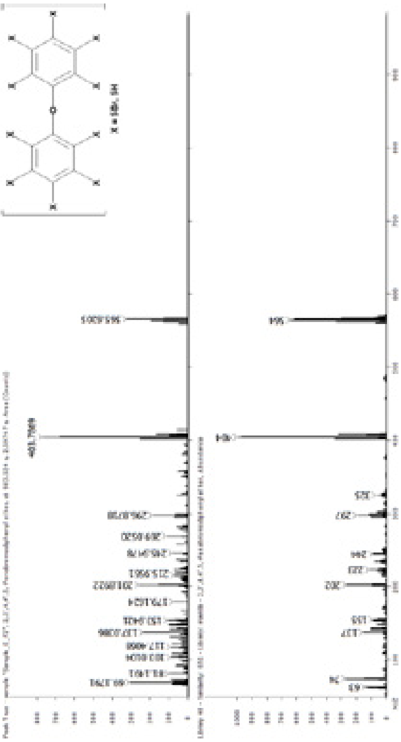

Figure S3-38. *Pentabromodiphenyl ether (Penta-BDE)*

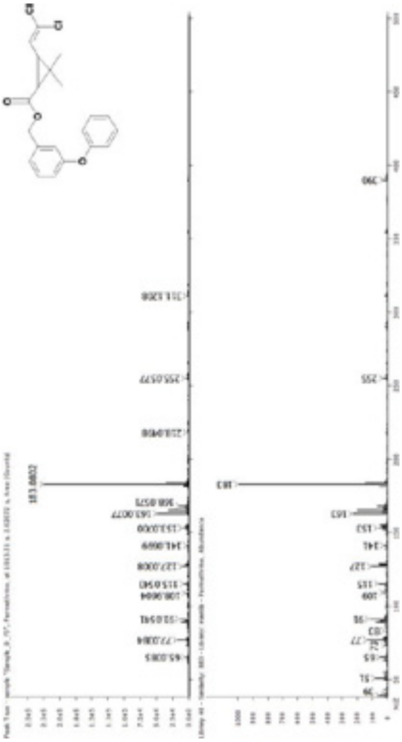

Figure S3-39. *Permethrin*

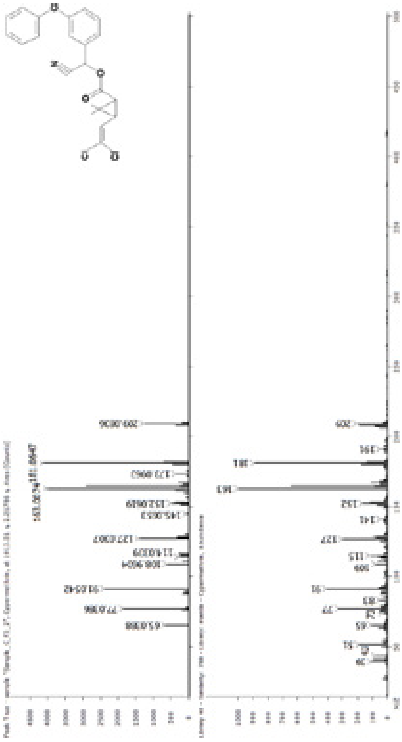

Figure S3-40. Cypermethrin

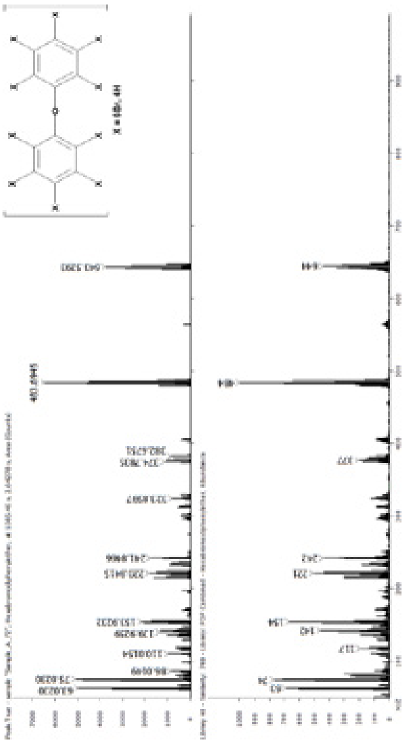

Figure S3-41. Hexabromodiphenyl ether (Hexa-BDE)

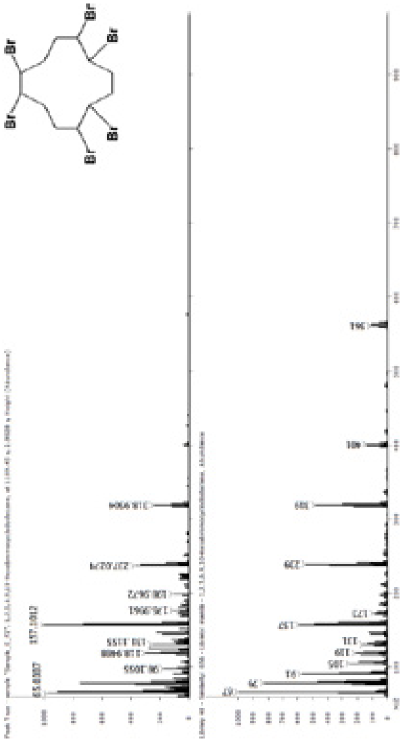

Figure S3-42. Hexabromocyclododecane isomers (HBCD)

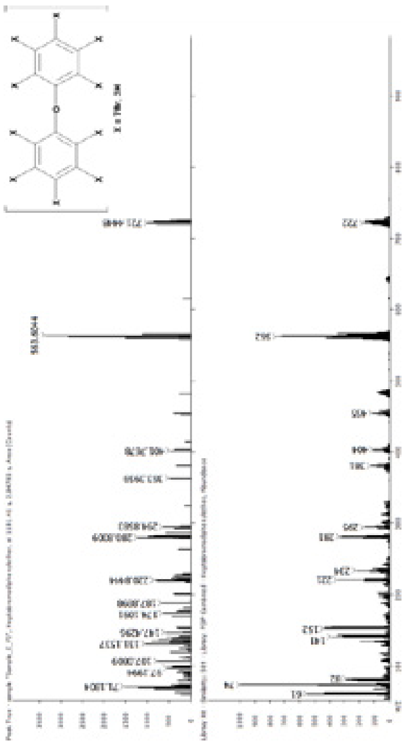

Figure S3-43. Heptabromodiphenyl ether (Hepta-BDE)

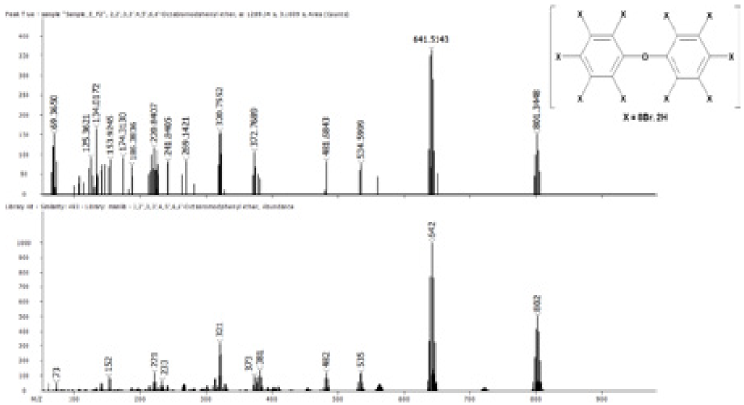

Figure S3-44. Octabromodiphenyl ether (Octa-BDE)

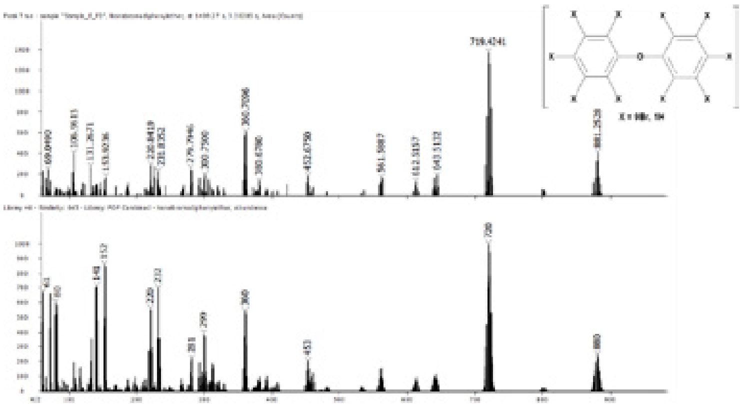

Figure S3-45. Nonabromodiphenyl ether (Nona-BDE)

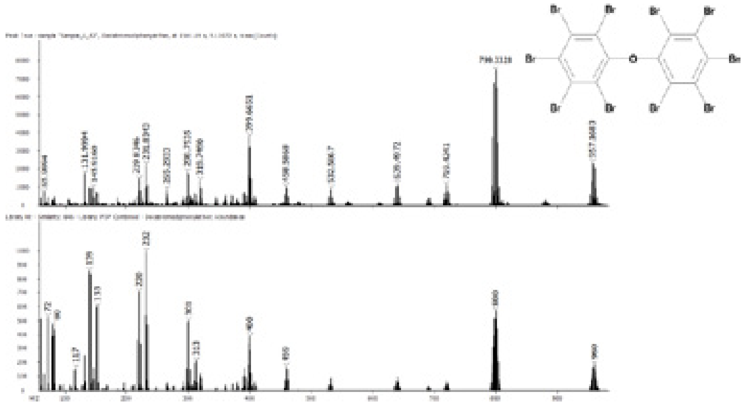

Figure S3-46. Decabromodiphenyl ether (Deca-BDE)

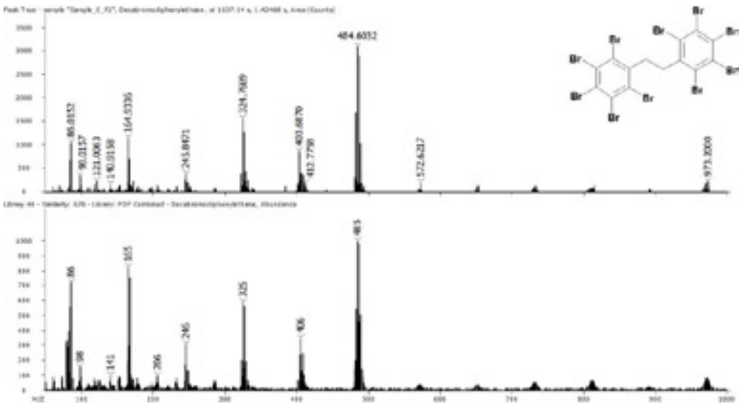

Figure S3-47. Decabromodiphenyl ethane (DBDPE)

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Chapter 4

Brominated and organophosphorus flame retardants in South African indoor dust and cat hair

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Abstract

Flame retardants (FRs), such as brominated flame retardants (BFRs) and organophosphorus flame retardants (OPFRs), are diverse groups of compounds used in various products related to the indoor environment. In this study concentrations of eight polybrominated diphenyl ethers (PBDEs), two alternative BFRs and ten OPFRs were determined in indoor dust (n=20) and pet cat hair (n=11) from South Africa. The OPFRs were the major FRs, contributing to more than 97% of the total FR concentration. The median Σ_{10}OPFRs concentrations were 44,800 ng/g in freshly collected dust (F-dust), 19,800 ng/g in the dust collected from vacuum cleaner bags (V-dust), and 865 ng/g in cat hair (C-hair). Tris(1-chloro-2-propyl) phosphate (TCIPP) was the dominant OPFR in the dust samples with median concentrations of 7,010 ng/g in F-dust and 3,590 ng/g in V-dust. Tris(2-butoxyethyl) phosphate (TBOEP) was the dominant OPFR in C-hair, with a median concentration of 387 ng/g. The concentrations of Σ_8PBDEs were higher in F-dust than in V-dust. BDE209 was the dominant BFR in all three matrices. Bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP) and 2-ethylhexyl-2,3,4,5- tetrabromobenzoate (EH-TBB) showed notable contributions to the BFR profile in cat hair. A worst-case dust exposure estimation was performed for all analytes. The estimated TCIPP daily intake through dust ingestion was up to 1,240 ng/kg bw for toddlers. The results indicate that OPFRs are ubiquitous in South African indoor environment. Indoor dust is a major source of human exposure to environmental contaminants. This can for example occur through hand-to-mouth contact of toddlers, and is an important route of exposure to currently used FRs accumulated on dust particles. The presence of FRs, in particular high concentrations of OPFRs, suggests that children and indoor pet cats may have greater exposure to FRs than adults.

4.1. Introduction

Indoor exposure of humans to flame retardants (FRs) is of concern from a human health perspective. Because of the specific physicochemical properties, FRs such as brominated FRs (BFRs) and organophosphorus FRs (OPFRs) are applied in relatively high concentrations (percentages) to combustible materials, to reduce their flammability and to meet fire safety requirements (Alaee *et al.*, 2003; van der Veen and de Boer, 2012). These materials are used in indoor environments, such as in textiles, building materials, and electrical and electronic equipment (Alaee *et al.*, 2003). For many years polybrominated diphenyl ether (PBDE) formulations were the most widely used BFRs e.g. in polyurethane foam and textile, in acrylonitrile-butadiene-styrene (ABS) resins and in different polymeric materials including high-impact polystyrene (HIPS), ABS, polypropylene, and in cotton and polyester containing textiles (Alaee *et al.*, 2003; Covaci *et al.*, 2011; Shaw *et al.*, 2014). The commercial penta-BDE and octa-BDE mixtures have been restricted under the Stockholm Convention (SC) since 2009, and deca-BDE formulation was added to that Convention in 2017 (http://chm.pops.int/). In 2003 penta-BDEs were banned in the European

Union (EU) and not much later other PBDEs were either banned (in the EU) or voluntarily phased out (in the USA) (European Commission, 2003).

The restrictions on the production and use of PBDEs has led to an increase in the production and use of OPFRs and alternative-BFRs (alt-BFRs) in products (van der Veen and de Boer, 2012). Whereas PBDE concentrations have been reported for the South African indoor environment, limited information is available for the two alt-BFRs, bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) (Brits *et al.*, 2016). BEH-TEBP and EH-TBB have been found in indoor dust, and air at various concentrations (Al-Omran and Harrad, 2017; Cristale *et al.*, 2018; McGrath *et al.*, 2018; Newton *et al.*, 2015; Stapleton *et al.*, 2009, 2008), and levels were also reported in hair from pet cats and dogs (Ali *et al.*, 2013). In addition to BFRs, OPFRs are considered as effective FRs but are also used as plasticizers and anti-foaming agents in various materials and consumer products associated with the indoor environment (Marklund *et al.*, 2003; van der Veen and de Boer, 2012). OPFRs are an additive type of FR, i.e. they are mixed into the polymer and can, therefore, migrate from products into the indoor environment by means of volatilization, leaching and abrasion, and/or direct transfer to dust (Marklund *et al.*, 2003; van der Veen and de Boer, 2012). OPFR concentrations have been reported in indoor air, dust and wipe test samples from electronic equipment and window protection film (Brandsma *et al.*, 2014; Cao *et al.*, 2019; Stapleton *et al.*, 2011, 2009; Van den Eede *et al.*, 2012; Vykoukalová *et al.*, 2017). OPFR levels have also recently been reported in dog hair (González-Gómez *et al.*, 2018). Generally, OPFRs in dust from homes and other indoor environments are dominated by tris(2-butoxyethyl) phosphate (TBOEP), followed by the chlorinated OPFRs (Wei *et al.*, 2015). Recent studies from Europe, China, and South Africa, have shown that chlorinated OPFRs dominate indoor dust profiles (Abafe and Martincigh, 2019; Peng *et al.*, 2017; Wei *et al.*, 2015). Some OPFRs are suspected carcinogens and others exhibit neurotoxic effects, adverse effects on fertility and hormone levels and decreased semen quality in males (Wei *et al.*, 2015). Humans and pets are ubiquitously exposed to various FR's, *via* diet, through direct contact with consumer products, and through household dust, which is used to measure indoor chemical contamination and to assess human exposure risks (Jones-Otazo *et al.*, 2005; Whitehead *et al.*, 2011). Children and indoor pet cats may, therefore, have greater exposures to FRs through dust ingestion than adults (Norrgran Engdahl *et al.*, 2017). Since pet cats have previously been presented as a potential bio-sentinel for indoor pollution exposure, cats might therefore, have relevance as indoor exposure models for children (Dirtu *et al.*, 2013). Cat hair is also directly exposed to the environment and constantly accumulates contaminants from indoor air and dust. Being a non-invasive matrix, hair samples allow for sample stability, information on compound exposure and the high lipid content allows for the analysis of a wide variety of FRs. Evidence suggests that FR exposure through dust ingestion is orders of magnitude higher for toddlers than adults due to potential higher dust ingestion rates (Wei *et al.*, 2015). Accurate and precise measurements of FRs concentrations are critical for risk assessment and decision making.

In previous work, we employed qualitative screening analysis to identify organohalogenated compounds, including BFRs and halogenated OPFRs in the South African indoor environment by using cat hair as matrix (Brits *et al.*, 2017). This study aims to accurately quantify BFRs and OPFRs in indoor dust and cat hair, to estimate the measurement uncertainty associated with each compound, and to preliminary evaluate exposure to toddlers and adults via dust ingestion. Hair samples from six longhair Persian cats and indoor dust were collected. The measurement uncertainty during the method validation procedure was performed, to support the quality of the data and to identify uncertainty sources in the analytical method.

4.2. Materials and methods

4.2.1. Chemicals

Standards of tributyl phosphate (TNBP), tris(2-ethylhexyl) phosphate (TEHP), triphenyl phosphate (TPHP), 2-ethylhexyl diphenyl phosphate (EHDPP), tris(2-isopropylphenyl) phosphate (TIPPP), tris(methylphenyl) phosphate (mixture of 3 isomers) (TMPP), TBOEP, TCEP, TCIPP, and TDCIPP were purchased from AccuStandard Inc., New Heaven, USA. The PBDE mixture (BDE-MXE), BEH-TEBP, EH-TBB, and the internal standards, $^{13}C_{12}$-BDE209, BDE58, TPHP-d15, TNBP-d27, TCEP-d12, TDCIPP-d15, were purchased from Wellington Laboratories Inc., Guelph, ON, Canada. The purity of analytical standards for OPFRs was >98%, except for TBOEP (>94%). Dust standard reference material (SRM 2585) was purchased from The National Institute of Standards and Technology (NIST) (Gaithersburg, MD, USA). The solvents and chemicals used were all analytical or HPLC grade, unless otherwise stated. Dichloromethane (DCM), methanol acetone, iso-octane, toluene, and n-hexane were purchased from J.T Baker, Deventer, The Netherlands. Whatman® grade 541 filter paper, silica gel, and Florisil® were purchased from Sigma-Aldrich (now Merck), Amsterdam, The Netherlands.

4.2.2. Sample collection

Dust samples (n=20) were collected in January 2018, from homes in Pretoria, South Africa. F-dust was collected from living rooms where cats spend more than 50% of their time to investigate contamination in a single room over a short time-span. The participants were asked not to vacuum this area for at least one week prior to sampling to ensure sufficient dust accumulated for collection. The F-dust samples (n=9) were collected as a mixture of floor dust and elevated surface dust using a 2000 W household vacuum cleaner, similar to previous studies (Cristale *et al.*, 2018). Dust particles were retained on a cone-shaped folded filter paper placed between the hose and a pre-cleaned (stainless steel) nozzle. The sampling protocol involves approximate vacuuming time of 2 min for carpeted floors and 4 min for hard surface floors, 2 min for surfaces (tables, TV stands, and shelves) and 1 min for sofas and armchairs. The filter paper was wrapped in aluminium foil, placed in a resealable plastic bag and transported to the laboratory for processing. V-dust samples (n=11) were also collected from the existing vacuum cleaner bags to examine wide indoor contamination over periods of months (average 3 months). The V-dust was collected by emptying the total content of the vacuum cleaner bag or by emptying the contents of canisters from bag-less vacuums on aluminium foil. The aluminium foil was folded, sealed in a plastic re-sealable bag and transported to the laboratory for processing. After sampling, the F-dust was removed from the filters. The dust samples were sieved through a pre-cleaned stainless steel sieve (500 μm) and stored in a pre-cleaned amber vial with Teflon lined lids until chemical analysis. During sample collection Na_2SO_4, spread on aluminium foil was collected as field blank (n=3 for F-dust, and n=3 for V-dust) using the same method employed to collect the dust samples and treated as samples. Cat hair samples (n=11) were collected from Persian cats at a pet grooming service in Pretoria, representing 6 homes. These cats are typically closely associated with indoor environments, thus sharing a common environment with toddlers. Pre-cleaned glass wool was exposed to the air and used to simulate blanks during the hair collection (n=3). All animal owners provided full consent after being informed of the study's objectives. The hair samples were rinsed with distilled water (3 times), dried at room temperature, and wrapped in aluminium foil, placed in resealable plastic bags. The dust and hair samples were stored at room temperature until chemical analysis. To avoid possible compound losses due to hair swelling, as previously reported for forensic hair analysis, samples were not frozen (Cooper *et al.*, 2012). Details on the samples associated with the homes are provided in the Supplementary Material (Table S4-1).

4.2.3. Sample pre-treatment

An accurately weighed aliquot of dust (between 20 and 50 mg) and cat hair (between 200 and 500 mg) was spiked with a mixture of internal standards containing 50 ng $^{13}C_{12}$-BDE209, and BDE58 and 80 ng of TPHP-d15, TNBP-d27, TCEP-d12, and TDCIPP-d15. The hair samples were cut into small pieces (<5 mm) using pre-cleaned stainless steel scissors prior to the addition of internal standards. Three blanks and three SRM 2585 samples were analysed together with each batch of samples. Sample extraction was carried out using accelerated solvent extraction (ASE) with hexane/acetone (3:1, v/v) as previously described by Brandsma *et al.* (2015). The extracts were concentrated to near dryness, at 30 °C under gentle nitrogen flow. The dust extracts were reconstituted in 0.5 mL hexane to follow fractionation. A major challenge in the analysis of OPFRs in the cat hair samples was the presence of a lipid-based waxy substance (sebum), which resulted in substantial chromatographic interferences. Basic or acidic treatment like saponification could not successfully be applied since OPFRs are prone to degradation under extremely acidic or basic conditions (Kucharska *et al.*, 2014). The cat hair extracts were reconstituted in 2 mL methanol and subjected to a freezing-lipid precipitation step, prior to fractionation, as previously employed for complex lipid-rich samples (Liu *et al.*, 2018). After the addition of methanol, the tube was vortexed for 2 minutes and stored in the freezer for 2 hours at -20 °C. Since most of the wax-like compounds were precipitated as a white condensed precipitate at the bottom of the tube, the cold supernatant was transferred to a pre-cleaned tube. The procedure was repeated with two aliquots of methanol and the combined supernatant was evaporated at 30 °C to near dryness and reconstituted in 0.5 mL hexane. This method efficiently removed the chromatographic interferences. The dust and hair extracts were fractionated on silica-florisil columns. Pre-cleaned empty glass columns (inner diameter 10 mm) were fitted with a glass wool plug and filled from the bottom with 0.5 g Silica gel, 0.5 g Florisil and 0.5 g anhydrous Na_2SO_4. The column was conditioned with 40 mL hexane. The extracts (in hexane) were quantitatively transferred to the column and the first fraction was eluted with 15 mL hexane and 15 mL DCM/hexane (1:1, v/v), the second fraction with 15 mL ethyl acetate. All fractions were evaporated to near dryness at 30 °C under a gentle stream of nitrogen. The first fraction was reconstituted in 500 µL iso-octane for analysis of PBDEs and the two alt-BFRs. The second fraction was reconstituted in 1000 µL iso-octane for the analysis of OPFRs.

4.2.4. Instrumental analysis

The quantification of PBDEs was performed using two analytical columns, on an Agilent 6890 gas chromatograph (GC) coupled to a 5975 mass spectrometer (MS) in electron capture negative ionisation (ECNI) as previously described by Brandsma *et al.* (2015). The two alt-BFRs were included in the analysis method for BDE209 and quantified by monitoring *m/z* 356.7 and 358.7 for EH-TBB and *m/z* 463.6 and 461.6 for BEH-TEBP. OPFR analysis was performed using an Agilent 7890B GC coupled to a 7010A triple quadrupole MS in electron impact (EI) mode. The GC method conditions were used as previously described by Brandsma *et al.* (2014) and quantitation was done in selected reaction monitoring (SRM) mode. The optimised quantitation and qualifier ion transitions, and collision energies are listed in Table S4-2.

4.2.5. Quality assurance and quality control

Positive identification of the analytes was made when ion ratios of 2 product ions (for SIM and SRM analysis) were within ±30% (relative) and retention times do not differ by more than 0.1 second from the average of calibration standards. The limits of quantification (LOQ) were calculated as the mean values plus three times standard deviation of analytes in blanks. For compounds not detected in the blanks, the LOQs were estimated by a signal-to-noise ratio of 10. Based on maximum sample intake of 50 mg dust and 500 mg hair the LOQs ranged from 0.9 ng/g to 187 ng/g and 0.09 ng/g to 18.7 ng/g respectively (Table S4-3). The correlation coefficient (R^2) for all the analytes was greater than 0.999 (Table S4-3). If the measurement uncertainty associated with the result overlapped with the LOQ, the concentration was reported to be below LOQ. The validation of the analytical method was accessed by analysis (n=9) of the dust standard reference material (SRM 2585), and triplicate spiking experiments on both matrices at two concentrations. As shown in Table S4-4, relative recoveries between 84 and 105% were obtained for the dust samples, with relative standard deviations (RSDs) ranging from 1.9 to 17%. Recoveries for the cat hair samples ranged from 81 to 104%, with RSDs between 0.7 and 20%. Recovery uncertainties were included in the uncertainty budget. As shown in Table S4-5, results obtained for the SRM 2585 samples agree with the certified values for the PBDE congeners and the reference values for the four OPFRs. There are currently no reference values assigned to for the two alt-BFRs and additional OPFRs included in this study. The results obtained for these compounds (Table S4-6) compared well with data previously reported for SRM 2585. TCIPP (RSD = 7%), TBOEP (RSD = 11%) and EHDPP (RSD = 11%) were detected in field blanks at average concentrations of 9.2 ng/g, 5.2 ng/g, and 3.2 ng/g, respectively. The blank contamination was present at levels of ≤10% of the lowest detected concentrations in the samples and therefore blank corrections were not applied. TNBP was detected at levels between 7 and 21% of the samples (average 4.4 ng/g), and therefore TNBP concentrations were blank corrected. The uncertainty of measurement for the compounds in the two matrices was estimated using validation data.

4.2.6. Estimation of the measurement uncertainty

The measurement uncertainties for PBDEs, alt-BFRs, and OPFRs in dust and hair were estimated as described by Ellison and Williams (2012). The uncertainty sources were identified as sample weighing, gravimetric preparation of the purity-corrected native and labelled standard stock solutions used to prepare the calibration range, uncertainty in the calibration graph, recovery and repeatability. The uncertainty associated with the recovery was estimated as described by Barwick and Ellison (1999). The calculations used to quantify the uncertainty components and finally calculate combined uncertainty are described in the Supplementary Material. The combined standard measurement uncertainty of the analyte in the matrixes was calculated by Eq. (1).

$$\frac{u_c(A)}{C_A} = \sqrt{\left(\frac{u(C_{Std})}{C_{Std}}\right)^2 + \left(\frac{u(C_{Istd})}{C_{Istd}}\right)^2 + \left(\frac{u(c_0)}{c_0}\right)^2 + \left(\frac{u(R_m)}{R_m}\right)^2 + u(r)^2} \tag{1}$$

where,

$u_c(A)$	Combined standard measurement uncertainty of the analyte
C_A	Concentration of the analyte
$u(C_{Std})$	Combined standard measurement uncertainty of standard solution
C_{Std}	Concentration of standard solution
$u(C_{Istd})$	Combined standard measurement uncertainty of internal standard solution
C_{Istd}	Concentration of internal standard solution
$u(c_0)$	Combined standard measurement uncertainty of calibration curve
c_0	Calculated concentration of the analyte in the sample using calibration curve
$u(R_m)$	Combined standard measurement uncertainty of recovery
R_m	Calculated recovery
$u(r)$	Combined standard measurement uncertainty of repeatability

The expanded uncertainty was obtained from the combined standard measurement uncertainty, calculated with the use of coverage factor k=2, corresponding to a confidence level of 95%. The relative expanded uncertainties (%) for all compounds in the two matrices ranged from 13 to 30% in dust and 11 to 34% for hair (Table S4-7). The major contributions to the combined uncertainty were due to the uncertainties associated with recovery and repeatability (Figure. S4-1 and S4-2).

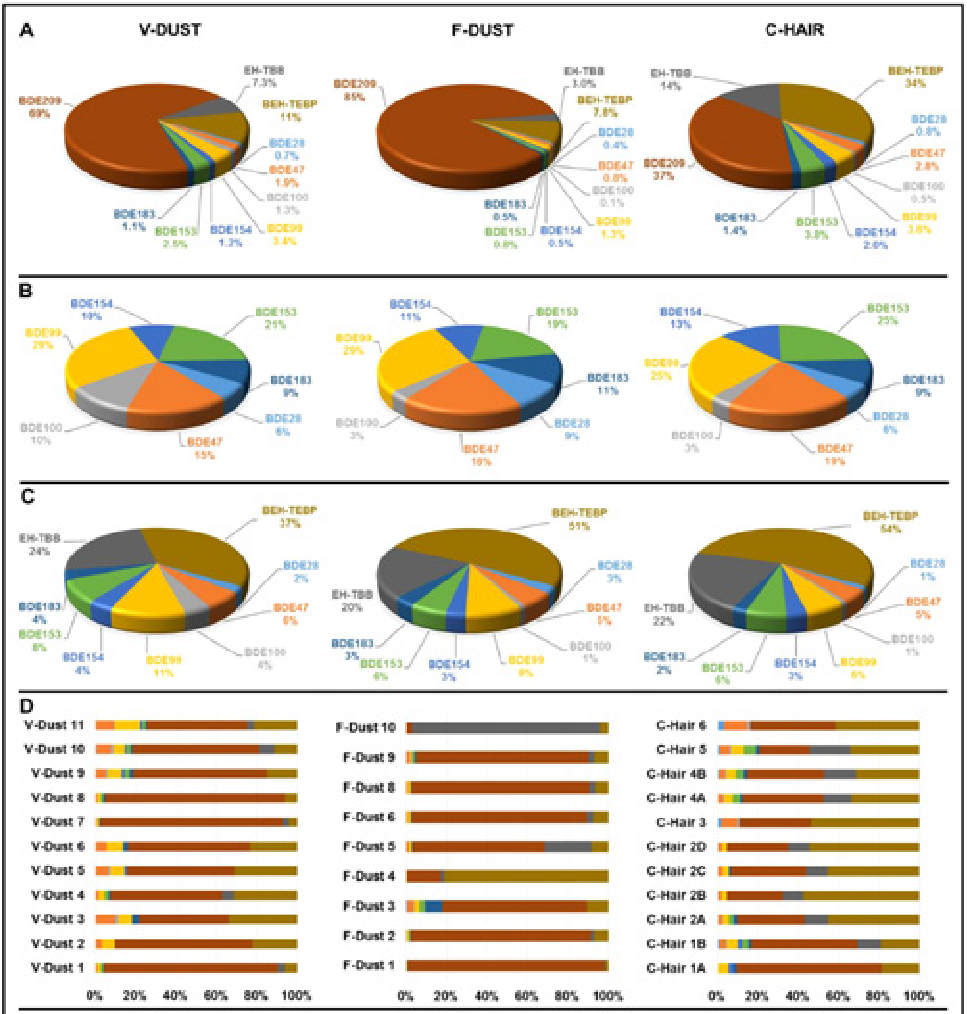
4.2.7. Statistical analysis

Basic and descriptive statistics were calculated using Microsoft Excel software. Normality of the data was checked by Shapiro–Wilk test. One-way ANOVA was employed to determine if analyte concentrations were significantly different in dust collected using the two sampling methods.

4.3. Results and discussion

4.3.1. Brominated flame retardants

The BFR congener profiles for the different matrices with detection frequencies, mean, median, concentration ranges, and standard deviation are shown in Figure 4-1. BDEs 47, 99, 209 and BEH-TEBP were detected in all dust and hair samples. BDE209 was the dominant congener contributing 85% of the total BFR concentrations in F-dust, 69% in the V-dust samples and 37% in the cat hair samples. The presence of PBDEs in the samples suggests release from legacy sources and products. Concentrations of Σ_8PBDEs ranged from 97 to 878 ng/g (median 307 ng/g) and 647 to 4,620 ng/g (median 903 ng/g) in the V-dust and F-dust respectively, and were significantly different ($p<0.05$). The concentration ranges for F-dust were comparable to ranges previously reported (689 to 3,290 ng/g) for freshly collected indoor dust in South Africa (Abafe and Martincigh, 2014). Higher median concentration of the Σ_8PBDEs (2,000 ng/g) was reported for Australian house dust (McGrath *et al.*, 2018). The median concentration of the Σ_8PBDEs in cat hair samples was 11.1 ng/g and ranged from 7.7 to 18.1 ng/g. Significantly ($p<0.05$) higher concentrations of BDE209 were detected in F-dust samples, ranging from 570 to 4,590 ng/g (median of 887 ng/g), compared to V-dust which ranged from 77 to 857 ng/g (median of 272 ng/g). Abafe and Martincigh (2014) previously reported BDE209 concentrations ranging from 59.2 to 2,190 ng/g, with a median concentration of 656 ng/g in South African indoor dust. The median BDE209 concentration in the cat hair samples was 9.1 ng/g with concentrations ranging from 4.3 to 14.1 ng/g. When BDE209 is excluded from the PBDE profile (Figure 4-1B), comparable congener profiles of the Σ_7PBDE were observed for the matrices, with BDE99 as the dominant congener. The median Σ_7PBDE concentrations were 33 ng/g (ranging from 26 to 139 ng/g) and 35 ng/g (ranging from 19 to 290 ng/g) for F-dust and V-dust respectively ($p>0.05$). The BDE209 concentrations influenced the correlation observed between PBDE levels found using the two dust collection methods, indicating that BDE209 might have room-specific sources.



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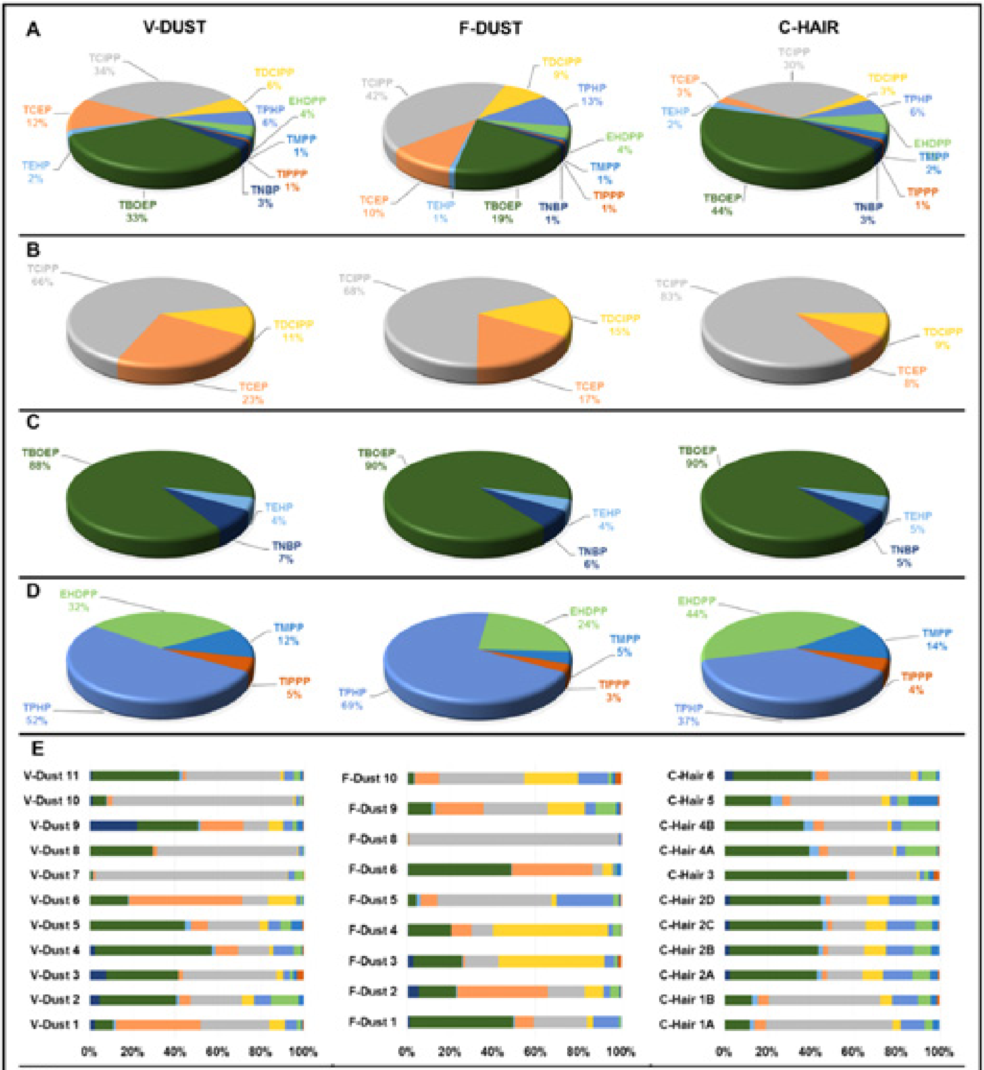
(ng/g)		Mean	Median	Min	Max	SD	DF	Mean	Median	Min	Max	SD	DF	Mean	Median	Min	Max	SD	DF
BDE28	🟦	2.7	2.7	<LOQ	2.9	0.2	18	4.0	4.0	<LOQ	5.0	1.4	22	0.27	0.20	<LOQ	0.50	0.15	45
BDE47	🟧	22.8	7.3	6.0	99.5	28.7	100	13.6	8.3	6.5	36.9	10.0	100	0.85	0.70	<LOQ	1.78	0.35	100
BDE100	⬜	4.8	5.0	<LOQ	7.9	2.8	55	2.6	1.4	<LOQ	7.8	2.3	89	0.14	0.12	<LOQ	0.26	0.05	64
BDE99	🟨	28.3	13.5	10.4	142	38.4	100	16.0	13.1	11.2	32.2	6.5	100	0.97	0.94	0.63	1.46	0.24	100
BDE154	🟦	6.7	4.5	<LOQ	13.4	4.5	36	4.6	4.7	<LOQ	4.8	0.3	44	0.48	0.48	<LOQ	0.53	0.07	18
BDE153	🟩	10.7	9.9	<LOQ	18.4	3.9	55	11.0	8.7	<LOQ	23.5	7.0	56	0.91	0.92	<LOQ	1.03	0.13	45
BDE183	🟦	5.5	4.2	<LOQ	15.5	3.9	82	13.3	5.1	3.20	67.1	20.7	100	0.36	0.34	<LOQ	0.54	0.09	64
BDE209	🟫	364	272	76.6	857	252	100	1,440	877	570	4,590	1,326	100	9.2	9.1	4.3	14.1	3.0	100
Penta-BDE		62.5	31.2	16.5	283	77.2	-	41.0	29.7	19.9	93.4	25	-	2.5	2.4	1.3	4.0	0.9	-
Σ_7PBDE		67.0	34.8	19.0	290	78.8	-	54.3	33.3	25.7	139	39	-	2.8	2.9	1.3	4.4	0.9	-
Σ_8PBDE		431	307	96.9	878	276	-	1,500	903	647	4,620	1,315	-	12.0	11.1	7.7	18.1	3.2	-
EH-TBB	⬛	32.1	28.6	<LOQ	39.3	5.4	45	3,180	30.6	<LOQ	24,800	8,723	89	3.3	3.3	<LOQ	3.6	0.2	73
BEH-TEBP	🟫	86.3	44.3	29.9	246	69.9	100	1,560	80.2	64.7	12,400	4,092	100	9.7	8.3	3.7	19.0	4.9	100

Figure. 4-1. *Comparison of congener profiles of (A) eight PBDEs with EH-TBB and BEH-TEBP in V-dust (n=11), F-dust (n=9) and cat hair (n=11) samples, (B) seven PBDEs (excluding BDE209) and (C) seven PBDEs (excluding BDE209) with EH-TBB and BEH-TEBP. (D) Relative abundances (%) of the eight PBDEs, EH-TBB and BEH-TEBP in the individual V-dust, F-dust and cat hair samples. (E) Summary of the mean, median, concentration range (ng/g), standard deviation (SD) and detection frequency (DF %) for the eight PBDEs, EH-TBB and BEH-TEBP.*

Estimates of exposure for BDE209 through dust ingestion using household vacuum cleaner dust might therefore underestimate exposure. The Σ_7PBDE concentrations in cat hair samples ranged from 1.3 to 4.3 ng/g with a median concentration of 2.9 ng/g. Ali *et al.* (2013b) reported median concentration on 2.15 ng/g for Σ_4PBDE (excluding BDE209) for cat hair collected in Pakistan.

EH-TBB and BEH-TEBP, the two alt- BFRs used in FM 550, contributed to 19% of the BFR profile in V-dust, 11% in F-dust and 48% in the cat hair (Figure 4-1A). BEH-TEBP was detected in all samples and EH-TBB had a lower detection frequency in the V-dust compared to the F-dust and the hair samples. The median concentrations for BEH-TEBP in the F-dust samples were 80 ng/g, ranging from 65 to 12,400 ng/g and 44 ng/g in V-dust samples, ranging from 30 to 246 ng/g. The median concentration of EH-TBB was 31 ng/g in F-dust and 29 ng/g in V-dust; the concentration ranged from <LOQ to 24,800 ng/g in F-dust and <LOQ to 39 ng/g in V-dust. It should be noted that the F-dust samples 4 and 10 had an exceptionally high concentration of BEH-TEBP and EH-TBB respectively, which resulted in the wider concentration ranges. This could be due to the dust sample containing small particles from products which contain these compounds. The analysis of household products could provide more information on the BFR formulations present in these products. McGrath *et al.* (2018) reported EH-TBB concentration ranges up to 370 ng/g (median of 19 ng/g) for Australian house dust, and BEH-TEBP concentrations up to 130 ng/g, although levels were indicative only. EH-TBB and BEH-TEBP contributed to almost 50% of the total BFR concentration profile in the cat hair, with median concentrations of 3.3 ng/g for EH-TBB and 8.3 ng/g for BEH-TEBP. The greater relative abundance of the two alt-BFRs indicates that cats may be in close contact with sources where these contaminants may migrate from the products to the hair. EH-TBB and BEH-TEBP are for example used in PUF and mattresses (Knudsen *et al.*, 2016). The BFR profile, excluding BDE209 (Figure 4-1C), show comparable profiles for cat hair and F-dust. The ratio of EH-TBB/BEH-TEBP was similar in all sample matrices (0.4 to 0.7) which is much lower than the ratio previously reported in FM 550 (Stapleton *et al.*, 2014). This suggests that other sources in the home may also be contributing to levels of BEH-TEBP found in dust because degradation of EH-TBB is unlikely. BEH-TEBP is the primary ingredient in a flame retardant mixture known as Uniplex FRP-45, which is used in cable and wires, adhesives, coatings, films and coated fabrics (Silva *et al.*, 2016). Animal studies have shown that EH-TBB and BEH-TEBP absorb to skin and EH-TBB was more permeable (Knudsen *et al.*, 2016). Skin and hair may act as a lipophilic “trap” and given the highly lipophilic nature of EH-TBB and BEH-TEBP, diffusion into the skin may be significant. For absorption, chemicals would have to partition from the dust to the skin if dust is in contact with skin. Dermal absorption rates for cats and toddlers is of particular importance because of the increased surface area to volume ratio compared to adults.



F

(ng/g)		Mean	Median	Min	Max	SD	DF	Mean	Median	Min	Max	SD	DF	Mean	Median	Min	Max	SD	DF
TNBP	🟦	900	294	245	4,610	1,446	82	558	212	194	1,730	587	78	23.9	22.5	<LOQ	31.0	4.1	45
TBOEP	🟩	7,260	3,510	960	36,000	10,064	100	7,900	3,140	485	21,600	8,838	100	321	387	56.2	488	155.7	100
TEHP	🟦	232	175	<LOQ	695	194	91	186	142	109	319	78	100	25.4	20.9	10.0	54.2	16.1	100
TCEP	🟧	2,270	1,270	310	8,630	2,550	100	5,040	1,730	402	16,900	5,585	100	31.7	25.3	20.6	53.9	13.2	100
TCIPP	⬜	25,100	3,590	1,470	139,000	44,385	100	26,200	7,010	2090	178,000	57,246	100	251	264	149	372	84.5	100
TDCiPP	🟨	729	610	208	2,140	574	100	11,500	1,530	322	57,700	19,625	100	47.4	26.9	13.2	99.3	36.2	100
TPHP	🟦	1,250	619	277	4,970	1,383	100	2,330	2,140	391	6,500	1,914	100	70.2	53.2	12.0	130	44.8	100
EHDPP	🟩	987	379	187	6,580	1,865	100	945	733	162	4,380	1,318	100	74.8	63.3	16.2	188	59.4	100
TMPP	🟦	235	140	75.5	635	197	100	303	141	52.2	1,130	361	100	29.5	19.9	7.6	113	29.7	100
TIPPP	🟧	136	60.9	<LOQ	636	202	73	395	91.3	<LOQ	1,440	559	78	8.8	6.3	<LOQ	24.6	7.0	64
Σ_{10}OPFR		38,900	19,800	6,070	156,000	50,845	-	55,200	44,800	7,740	183,000	57,104	-	868	865	483	1,230	227	-

Figure 4-2. *Comparison of congener profiles of (A) the OPFRs in V-dust (n=11), F-dust (n=9) and cat hair (n=11) samples, (B) the Cl-OPFRs, (C) the alkyl-OPFRs and (D) the aryl-OPFRs. (E) Relative abundances (%) of the OPFRs in the individual V-dust, F-dust and cat hair samples. (F) Summary of the mean, median, concentration range (ng/g), standard deviation (SD) and detection frequency (DF %) for the ten OPFRs.*

4.3.2. Organophosphorus flame retardants

The OPFR profiles for the different matrices with detection frequencies, mean, median, concentration ranges, and standard deviation for the individual OPFRs are shown in Figure 4-2. The OPFRs analysed in this study were detected in more than 90% of the samples, except for TNBP and TIPPP. These results are the first to report on the occurrence of chloroalkyl (Cl-OPFR), alkyl (alkyl-OPFRs), and aryl (aryl-OPFRs) OPFRs in the South African indoor environment. As shown in Figure 4-2A, TCIPP was the dominant OPFR congener in F-dust, contributing to 42% to the OPFR congener profile. The V-dust shows approximately equal contributions of TCIPP and TBOEP, contributing with 34% and 33%, respectively to the OPFR congener pattern. The cat hair samples present a different profile, with TBOEP (44%) as the dominant congener followed by TCIPP (30%). The median concentrations of Σ_{10}OPFRs were 44,800 ng/g in F-dust (ranging from 7,740 to 183,000 ng/g) compared to 19,800 ng/g in the V-dust (ranging from 6,070 to 156,000 ng/g), and were not significantly different ($p>0.05$). Similar to previous studies, comparable results were obtained from the two dust sampling methods (Fan *et al.*, 2014). Dust from household vacuum cleaners may be an economical alternative to sophisticated dust sampling for OPFR analysis. The median Σ_{10}OPFRs in cat hair was 865 ng/g and levels ranged from 483 to 1,230 ng/g. To our knowledge, no studies have been published on the analysis of OPFRs in pet cat hair. Recent results on the analysis of organic pollutants in dog hair reported that TPHP, TCIPP, and TBOEP were the most abundant compounds (González-Gómez *et al.*, 2018). Henríquez-Hernández *et al.* (2017) reported high detection frequencies for TCIPP, TBOEP, TCEP, EHDPP, and TPHP in cat blood. TCIPP was also found to be one of the major OPFRs found in human hair from China (Li *et al.*, 2016)(M.-J. He *et al.*, 2018). When comparing the three main OPFR groups, Cl-OPFR, alkyl-OPFRs, and aryl-OPFRs, the Cl-OPFRs dominate the profile in dust samples and the alkyl-OPFRs in cat hair. Previous studies have shown that there is a stronger correlation for alkyl-OPFRs between human hair and air than for dust (Kucharska *et al.*, 2015). The dominance of alkyl-OPFRs in the hair might support the finding that indoor dust partly contributes to the pattern observed in the hair.

The Cl-OPFR profiles, comprising TCEP, TCIPP, and TDCIPP, were dominated by TCIPP for the dust and hair matrices (Figure 4-2B). The median concentrations of TCIPP, TCEP and TDCIPP in V-dust were 3,590 ng/g, 1,270 ng/g and 610 ng/g and in F-dust 7,010 ng/g, 1,730 ng/g and 1,530 ng/g. The dust matrices show similar patterns for TCIPP, TCEP, and TDCIPP with 66%, 23% and 11% for V-dust and 68%, 17% and 15% in F-dust. A recent study by Shoeib *et al.* (2019) reported twice as high median Cl-OPFR concentrations (TCIPP = 8,800 ng/g, TCEP = 2,600 ng/g and TDCIPP = 2,000 ng/g) in dust samples from Vancouver, Canada, collected from vacuum cleaner bags, the pattern (66%, 19% and 15%) was similar to that found in this study. Contradictory to our study, TDCIPP was reported as the dominant Cl-OPFR in indoor dust from South Africa (Abafe and Martincigh, 2019). The median TCIPP concentration in the cat hair samples was 264 ng/g hair and ranged from 149 to 372 ng/g. TCEP and TDCIPP contributed only 17% to the Cl-OPFR profile in the cat hair samples. Cl-OPFRs are mainly used as FRs in flexible and rigid PUFs used in furniture, upholstery, plastic foams, resins, latex, adhesives, and coatings (van der Veen and de Boer, 2012; Wei *et al.*, 2015). In our study, the concentrations of TCEP were lower than TCIPP in both matrices and the ratio TCEP:TCIPP was approximately 1:3 in dust and 1:10 in cat hair, which could most likely be due to increasing use of TCIPP and TDCIPP as a replacement of TCEP (World Health Organization, 1998).

As shown in Figure 4-2C, the alkyl-OPFR congener profile consisting of TNBP, TBOEP, and TEHP was dominated by TBOEP in all matrices (~90%). TBOEP was detected in 100% of the samples and median concentrations in V-dust were 3,510 ng/g and 3,140 ng/g in F-dust. The TBOEP concentrations in our study was approximately 5-fold lower than recently reported values for freshly collected dust from Australia (15,000 ng/g) (C. He *et al.*, 2018), and Brazil (15,900 ng/g) (Cristale *et al.*, 2018), and vacuum cleaner dust from Canada (23,000 ng/g), and Egypt (13,000 ng/g) (Shoeib *et al.*, 2019). TBOEP was the dominant OPFR in dust, which is in contrast with our study. Regnery and Püttmann (2010) previously showed rapid photochemical degradation of TBOEP when exposed to direct sunlight. However, in the cat hair samples of our study, TBOEP was the dominant OPFR with concentrations ranging from 56.2 to 488 ng/g (median 387 ng/g). A possible explanation for this could be that cats may be in direct contact with a possible source, as TBOEP is used in floor polishing products, as plasticizer in rubber and plastics (van der Veen and de Boer, 2012). The TBOEP concentration in the cat hair was comparable to levels previously reported in hair from children (Kucharska *et al.*, 2015). TNBP and TEHP, which are mainly used as plasticizers but also as FRs (Dodson *et al.*, 2012), had median concentrations of 294 and 175 ng/g in V-dust, 212 and 142 ng/g in F-dust and 22.5 and 20.9 ng/g in cat hair, respectively.

The aryl-OPFR congeners constitute ~10% of the total OPFRs in dust and 22% in the cat hair samples. As shown in Figure 4-2D, the aryl-OPFR profile was dominated by TPHP (69% in F-dust and 52% in V-dust) in the dust samples and by EHDPP in the cat hair samples. TPHP is an effective additive FR in many polymers and is used in combination with halogenated and non-halogenated FR mixtures in FM 550 (Stapleton *et al.*, 2009; van der Veen and de Boer, 2012). The median TPHP concentrations were 619 ng/g and 2,140 ng/g in V-dust and F-dust, respectively. The median concentration found in our study was lower than the levels reported for freshly collected dust from the UK (3,300 ng/g) (Brommer and Harrad, 2015) and Brazil (3,900 ng/g) (Cristale *et al.*, 2018). The median EHDPP concentration in cat hair was 53.2 ng/g.

A comparison of median OPFR concentrations from this study with those previously reported for house dust is presented in Figure S4-3. The variations in OPFR concentrations between the different studies and countries might be influenced by fire safety regulations, restrictions on the use of specific chemicals as FRs and the import and export of consumer products. The irregular OPFR profiles observed between the dust studies suggest that not only regional differences in the use of OPFRs or mixtures for these compounds but also (seasonal) temperature changes affect the congener patterns and concentrations (Cao *et al.*, 2014). The climate in South Africa is classified as semi-arid. It has a considerable variation which ranges from Mediterranean in the South West, subtropical in the North East, and semi-arid in the central and North West of the country. Pretoria has a subtropical climate with short cool to cold, dry winters and long humid and hot rainy summers. FRs have different partition characteristics between air, dust, and hair and compounds with higher vapor pressures are more sensitive to temperature changes and photochemical degradation. Temperature could influence the emission of FRs from the products and the partitioning of FRs between air and dust and hair, and the residence of FRs in the indoor environment could also be influenced by ventilation especially in warmer seasons.

4.3.3 Implications

No information could be sourced on local production of FRs, and we can therefore not provide a full description of the use of FRs, specifically on OPFRs. Recent studies in indoor dust, leachate, and sediment from landfill sites in South Africa also reported high concentrations of Cl-OPFRs, TBOEP was not included in the analysis (Abafe and Martincigh, 2019; Sibiya *et al.*, 2019). The high concentrations of Cl-OPFRs in indoor dust and landfill sites could indicate that imported consumer products could be an important source for these compounds. The Department of Environmental Affairs is involved in implementing measures to restrict the production and use of listed pesticides in order to fulfill its SC commitments. Based on the information provided in the national implementation plan (accessed through http://chm.pops.int/) there are no immediate actions taken for FRs. Although many of the OPFRs are used in textile, foams and insulation materials, a recent study suggested that handheld electronic devices may also be sources of OPFRs (Yang *et al.*, 2019). This also raises questions about these compounds when they are being re-introduced into recycled products. Given the high levels of OPFRs found, substantially higher than the BFR levels, it may be wise for South Africa authorities not only to follow the SC but also pay attention to the OPFRs when reduction of indoor contamination is considered. The inclusion of samples from townships and informal settlements should provide a more comprehensive demographic representation of the exposure to FRs in South Africa to provide concrete evidence to enforce regulations.

4.3.4. Human exposure to house dust

The preliminary estimations of the exposure to BFRs and OPFRs through dust ingestion (assuming 100% absorption from the ingested dust) were calculated for adults and toddlers using the median and 95th percentile concentrations (Table 4-1). The assumption may introduce exposure estimate uncertainties, and more research is required to fully explain the toxicological effects of such exposure in both adults and toddlers. We calculated the expected daily intake based on mean body weights of 11.4 kg for children between the ages of 1 and 2 years and 80 kg for adults, and average dust ingestion rates (DIR) of 50 mg/day for toddlers and 20 mg/day for adults and high DIR of 100 mg/day and 60 mg/day for the respective groups as recommended in the Environmental Protection Agency (EPA) exposure factor handbook (EPA, 2011).

Table 4-1. *Exposure estimation of the median and high (95th percentile) dust content (ng/kg bw/day) of flame retardants via South African indoor dust ingestion (mean and high dust intake) for adults and toddlers, and reference doses (RfD) (ng/kg bw/day).*

Compound	Toddlers				Adults				RfD
	Mean ingestion 50 mg/day		High ingestion 100 mg/day		Mean ingestion 20 mg/day		High ingestion 60 mg/day		
	Median estimate	High estimate	Median estimate	High estimate	Median estimate	High estimate	Median estimate	High estimate	
BDE209	2.6	11.4	5.2	23	0.2	0.7	0.5	2.0	7,000[a]
Σ_8PBDE	3.0	12	6.0	23	0.2	0.7	0.5	2.0	
EH-TBB	0.1	44	0.3	89	0.008	2.5	0.02	7.6	20,000[b]
BEH-TEBP	0.3	7.2	0.7	14	0.02	0.4	0.06	1.2	20,000[b]
ΣBFR	3.8	70	7.6	139	0.2	4.0	0.7	12	
TNBP	1.3	10.8	2.5	22	0.07	0.6	0.2	1.8	10,000[a]
TCEP	7.2	46	14	91	0.4	2.6	1.2	7.8	7,000[a]
TCIPP	25	618	50	1,240	1.4	35	4.3	106	10,000[a]
TDCIPP	3.2	131	6.4	261	0.2	7.4	0.6	22	20,000[a]
TBOEP	15	98	29	196	0.8	5.6	2.5	17	15,000[b]
TPHP	4.5	22	9.0	44	0.3	1.3	0.8	3.8	70,000[b]
EHDPP	1.8	20	3.5	39	0.1	1.1	0.3	3.4	600,000[c]
TEHP	0.8	2.1	1.5	4.1	0.04	0.1	0.1	0.4	100,000[a]
TMPP	0.6	2.9	1.2	5.9	0.04	0.2	0.1	0.5	20,000[a]
TIPPP	0.3	4.8	0.7	9.5	0.02	0.3	0.06	0.8	
Σ_3Alkyl- OPFR	17	101	35	201	1.0	5.7	3.0	17	
Σ_3Cl-OPFR	55	629	110	1,260	3.1	36	9.4	108	
Σ_4Aryl-OPFR	8.6	42	17	84	0.5	2.4	1.5	7.2	
Σ_{10}OPFR	89	689	178	1,380	5.1	39	15	118	

[a] Data from USEPA (2017).
[b] Data from Ali *et al.* (2012).
[c] Data from C. He *et al.* (2018).

Due to the relative small sample size, the results should be seen as indicative only, showing average and worst-case scenario exposure estimations from dust ingestion. The exposure estimate of most of the FRs included in this study was lower than their respective reference doses (RfDs). The human exposure (adults and toddlers) through mean dust ingestion ranged from 0.2 to 11.4 ng/kg bw/day for BDE209, from 0.008 to 44 ng/kg bw/day for EH-TBB and 0.02 to 7.2 ng/kg bw/day for BEH-TEBP. The mean dust ingestion scenarios for the OPFRs show exposures ranging from 2.6 to 46 ng/kg bw/day for TCEP, 5.6 to 98 ng/kg bw/day for TBOEP, 7.4 to 131 ng/kg bw/day for TDCIPP and 35 to 618 ng/kg bw/day for TCIPP. The high ingestion exposure estimate for TCIPP (the major FR in the dust) ranged up to 1,240 ng/kg bw/day for toddlers, which were only 8 times lower than the RfD. The high ingestion exposure estimate for TCEP, TDCIPP, and TBOEP were approximately 80-fold lower than their respective RfDs for toddlers. TCIPP, TDCPP, and TBOEP have been suspected to be carcinogenic and neurotoxic effects have been observed for TCEP, TNBP, and TPHP (Wei *et al.*, 2015). The ubiquitous occurrence of these OPFRs in the indoor environment may pose a threat to human health. In addition, several studies also reported adverse effects in lab animals (Van den Eede *et al.*, 2011). To estimate the ingestion exposure for cats, an average body weight of 4.3 kg was used, with similar ingestion rate as toddlers. The ingestion exposure estimate for TCIPP ranged from

1,640 to 3,270 ng/kg bw/day for cats. Although there is undoubtedly a high level of uncertainty associated with the exposure estimate for cats, this provides an indication of the probable exposure range. The estimated exposures via dust ingestion for cats could be up to three times higher than estimated for toddlers, considering that the dust ingestion rate for cats is unknown and could be vastly underestimated. The grooming behaviour of cats might increase their ingestion as well. Cat hair is exposed to the environment and constantly accumulate contaminants from indoor air and dust. The toxicity of most FRs is not completely understood and exposure to FR mixtures may result in dose-additive effects. The results obtained from the hair samples indicate that cats are directly exposed to mixtures of FRs. In addition to inhalation and dermal contact, the hand-to-mouth activity of toddlers is an important route of exposure to FRs accumulated on dust particles. This activity is most often observed in toddlers, and cat’s meticulous grooming behavior.

4.4. Conclusion

This study presents concentrations of BFRs and OPFRs in indoor dust and cat hair from South Africa. In both matrices the OPFR concentrations were considerably higher than those of the BFRs. Compared to previous studies, low levels for PBDEs were found in indoor dust, with BDE209 as the dominant congener. The two alt-BFRs, BEH-TEBP and EH-TBB showed notable contributions to the BFR profile in cat hair. OPFR profiles in the indoor dust were dominated by the Cl-OPFRs, with TCIPP as the major congener. Although the Cl-OPFRs were regularly detected in the cat hair samples, the alkyl-OPFRs dominated the profile with higher contributions from TBOEP. For the first time, we show that Cl-OPFRs, alkyl-OPFRs, and aryl-OPFRs are ubiquitous in the South African indoor environment. The hand-to-mouth contact of toddlers is an important route of exposure to currently used FRs accumulated on dust particles. The presence of BFRs and OPFRs in indoor dust and cat hair suggests that children may have greater exposure to FRs than adults. To date, there is limited data on OPFRs, especially the Cl-OPFRs, in the South African indoor environment and more research is needed to identify sources in order to understand indoor exposures and fate of FRs.

Although the small number of samples analysed in the current study may limit conclusions, the quantitative results can represent an important baseline study for developing larger studies to assess exposure estimates for the volatile FRs, such as TCIPP. The differences in FR congener profiles between dust and cat hair may be of particular importance considering that dust and soil-ingestion rates are commonly used for risk assessments. Cat hair provides specific information on continuous indoor exposure and might be seen as a non-invasive passive sampler to chronic exposure of FRs in the indoor environment. Although international restrictions are set for the production and use of some BFRs, more attention should be paid to OPFRs when measures to reduce indoor contamination is considered.

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Supplementary material S4

Table S4-1. *Details on samples associated with vacuum cleaner bags (V-dust), freshly collected dust (F-dust) and cat hair (C-hair).*

	V-dust	F-dust	C-hair
House 1	V-dust 1	F-dust 1	C-Hair 1A C-Hair 1B
House 2	V-dust 2	F-dust 2	C-Hair 2A C-Hair 2B C-Hair 2C C-Hair 2D
House 3	V-dust 3	F-dust 3	C-Hair 3
House 4	V-dust 4	F-dust 4	C-Hair 4A C-Hair 4B
House 5	V-dust 5	F-dust 5	C-Hair 5
House 6	V-dust 6	F-dust 6	C-Hair 6
House 7	V-dust 7		
House 8	V-dust 8	F-dust 8	
House 9	V-dust 9	F-dust 9	
House 10	V-dust 10	F-dust 10	
House 11	V-dust 11		

Table S4-2. *List of BFRs and OPFR target analytes with quantitation and qualification transition with associated collision energies and internal standards used.*

Compound	Abbreviation	CAS Number	Quantitation transition	Collision Energy	Qualification transition	Collision Energy	Internal standard
2,4,4'-Tribromodiphenyl ether	**BDE28[a]**	**41318-75-6**	**79**		**81**		**BDE58**
2,2',4,4'-Tetrabromodiphenyl ether	**BDE47[a]**	**5436-43-1**	**79**		**81**		**BDE58**
2,2',4,4',5-Pentabromodiphenyl ether	**BDE99[a]**	**60348-60-9**	**79**		**81**		**BDE58**
2,2',4,4',6-Pentabromodiphenyl ether	**BDE100 [a]**	**189084-64-8**	**79**		**81**		**BDE58**
2,2',4,4',5,5'-Hexabromodiphenyl ether	**BDE153[a]**	**68531-49-2**	**79**		**81**		**BDE58**
2,2',4,4',5,6'-Hexabromodiphenyl ether	**BDE154[a]**	**207122-15-4**	**79**		**81**		**BDE58**
2,2',3,4,4',5',6-Heptabromodiphenyl ether	**BDE183[a]**	**207122-16-5**	**79**		**81**		**BDE58**
2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether	**BDE209[a]**	**1163-19-5**	**486.4**		**484.4**		**^{13}C-BDE209**
Bis(2-ethylhexyl) tetrabromophthalate	**BEH-TEBP[a]**	**26040-51-7**	**463.6**		**461.6**		**^{13}C-BDE209**
2-Ethylhexyl-2,3,4,5-tetrabromobenzoate	**EH-TBB[a]**	**183658-27-7**	**356.7**		**358.7**		**^{13}C-BDE209**
2,3,3',5'-Tetrabromodiphenyl ether	**BDE58[a]**		**79**		**81**		
$^{13}C_{12}$-decabromodiphenyl ether	**^{13}C-BDE209[a]**		**494.4**		**496.4**		
Tri-n-butyl phosphate	**TNBP[b]**	**126-73-8**	**155.0 > 99.0**	**4**	**211.0 > 99.0**	**13**	**TNBP-d27**
Tris (2-chloroethyl) phosphate	**TCEP[b]**	**115-96-8**	**204.9 > 142.9**	**3**	**248.9 > 125.0**	**12**	**TCEP-d12**
Tris (1-chloro-2-propyl) phosphate (multiple isomers)	**TCIPP[b]**	**13674-84-5**	**200.9 > 99.1**	**30**	**276.9 > 125.1**	**10**	**TCEP-d12**
Tris (1,3-dichloro-2-propyl) phosphate	**TDCIPP[b]**	**13674-87-8**	**209.0 > 99.0**	**7**	**190.9 > 155.0**	**5**	**TDCIPP-d15**
Tris (2-butoxyethyl) phosphate	**TBOEP[b]**	**78-51-3**	**125.0 > 99.0**	**15**	**153.0 > 125.0**	**7**	**TPHP-d15**
Triphenyl phosphate	**TPHP[b]**	**115-86-6**	**215.0 > 168.0**	**25**	**169.0 > 115.0**	**35**	**TPHP-d15**
2-Ethylhexyl diphenyl phosphate	**EHDPP[b]**	**1241-94-7**	**251.1 > 77.0**	**35**	**251.1 > 152.0**	**32**	**TPHP-d15**
Tris (2-ethylhexyl) phosphate	**TEHP[b]**	**78-42-2**	**112.0 > 81.9**	**10**	**113.0 > 57.0**	**5**	**TPHP-d15**
Tricresyl phosphate (mixture of 3 isomers)	**TMPP[b]**	**1330-78-5**	**368.0 > 165.0**	**35**	**277.0 > 179.0**	**15**	**TPHP-d15**
Tris (2-isopropylphenyl) phosphate	**TIPPP[b]**	**64532-95-2**	**335.1 > 251.0**	**15**	**452.2 > 118.1**	**15**	**TPHP-d15**
Tri-n-butyl phosphate-d27	**d27-TNBP[b]**		**167.0 > 103.0**	**5**	**231.0 > 103.0**	**12**	
Tris(2-chloroethyl) phosphate-d12	**d12-TCEP[b]**		**261.0 > 131.0**	**13**	**213.0 > 148.0**	**4**	
Tris(1,3-dichloro-2-propyl) phosphate-d15	**d15-TDCIPP[b]**		**217.0 > 103.0**	**8**	**197.0 > 160.0**	**7**	
Triphenylphosphate-d15	**d15-TPHP[b]**		**243.0 > 176.0**	**22**	**223.0 > 176.0**	**35**	

[a] Analysed using GC-ECNI-MS.
[b] Analysed using GC-EI-MS/MS.

Table S4-3. *Calibration parameters (using an eight-point calibration curve) listing the correlation coefficients (R^2), response factor (RF), response factor relative standard deviation (RSD) and limit of quantitation (LOQ).*

Compound	Correlation coefficient (R^2)	Response factor (RF)	Response factor RSD (%)	LOQ dust (ng/g)[a]	LOQ hair (ng/g)[b]
BDE28	0.9999	1.49	2.6	1.3	0.13
BDE47	0.9996	0.97	11.1	5.2	0.52
BDE100	0.9999	1.56	2.2	0.9	0.09
BDE99	0.9998	1.52	3.8	4.6	0.46
BDE154	0.9999	1.60	3.7	4.0	0.40
BDE153	0.9999	1.48	3.2	5.5	0.55
BDE183	0.9997	1.11	5.1	1.9	0.19
BDE209	0.9998	0.64	8.4	12	1.2
EH-TBB	0.9998	0.14	9.6	23	2.3
BEH-TEBP	0.9995	0.22	5.7	24	2.4
TNBP	0.9998	1.10	2.4	**157**	**15.7**
TCEP	0.9998	1.16	4.1	58	5.8
TCIPP	0.9999	1.51	4.4	**187**	**18.7**
TDCIPP	0.9999	1.22	6.0	78	7.8
TBOEP	0.9987	0.18	14.2	**131**	**13.1**
TPHP	0.9999	1.11	6.8	16	1.6
EHDPP	0.9997	1.77	10.5	**80**	**8.0**
TEHP	0.9998	0.31	14.8	43	4.3
TMPP	0.9997	0.33	4.9	36	3.6
TIPPP	0.9994	0.48	11.5	49	4.9

[a]Based on maximum dust sample intake of 50 mg.
[b]Based on maximum hair sample intake of 500 mg.
Bold LOQ value represent analytes which were present in blanks.

Table S4-4. *Results of triplicate spiking experiments for dust and cat hair samples, listing spiking concentration (ng), average percentage recoveries (%) and relative standard deviation (RSD).*

Compound	Dust						Cat hair					
	Low spike (ng)	Low spike recovery (%)	RSD (%)	High spike (ng)	High spike recovery (%)	RSD (%)	Low spike (ng)	Low spike recovery (%)	RSD (%)	High spike (ng)	High spike recovery (%)	RSD (%)
BDE28	1.7	96	8.0	19	98	4.6	1.7	99	7.5	19	99	6.6
BDE47	1.7	92	5.7	19	99	4.1	1.7	94	8.4	19	97	4.4
BDE100	1.7	102	8.4	19	99	5.8	1.7	97	6.7	19	99	4.2
BDE99	1.7	93	5.4	19	101	4.7	1.7	97	11.5	19	103	5.0
BDE154	3.4	93	8.9	39	100	4.4	3.4	95	8.7	39	96	5.8
BDE153	3.4	94	6.7	39	98	5.6	3.4	95	11.5	39	99	6.3
BDE183	3.4	94	10.8	39	98	5.8	3.4	95	9.4	39	97	4.5
BDE209	8.5	95	1.9	97	96	7.5	8.6	99	9.9	97	99	5.8
EH-TBB	49	92	10.2	100	96	5.7	49	90	9.0	100	93	3.0
BEH-TEBP	48	94	4.5	97	96	5.0	48	95	3.5	97	97	3.7
TNBP	50	95	5.2	101	98	3.6	50	88	6.7	101	97	3.4
TCEP	48	102	2.5	98	105	2.7	48	102	4.2	101	99	3.6
TCIPP	50	97	6.3	101	94	15.2	50	95	19.6	101	99	19.3
TDCIPP	48	100	2.0	98	99	6.3	48	98	9.9	98	100	8.5
TBOEP	48	84	12.1	98	99	9.3	48	91	7.9	98	96	11.5
TPHP	50	97	9.3	100	103	8.0	50	96	12.3	100	99	9.1
EHDPP	50	100	7.5	101	102	3.1	50	99	11.5	100	105	7.6
TEHP	49	90	5.7	99	101	3.1	49	86	7.5	99	102	1.9
TMPP	49	94	17.2	99	105	10.9	49	94	14.7	99	105	12.7
TIPPP	48	87	4.7	98	99	3.0	48	85	1.7	98	101	0.7

Table S4-5. *Results (mean concentration and standard deviation) of FR analysis of SRM 2585 dust samples, compared to certified and reference values, and with expanded relative uncertainty (U) values.*

Compound	**Assigned value (ng/g)**	**Batch 1 (V-dust) (n=3)** Mean (ng/g)	**Batch 2 (F-dust) (n=3)** Mean (ng/g)	**Batch 3 (C-hair) (n=3)** Mean (ng/g)	**U%**
BDE28	46.9 ± 4.4[a]	44.2 ± 5.3	46.2 ± 5.5	47.3 ± 5.7	12
BDE47	497 ± 46[a]	488 ± 64	502 ± 66	507 ± 67	13
BDE99	892 ± 53[a]	878 ± 124	857 ± 121	868 ± 123	14
BDE100	145 ± 11[a]	143 ± 19	144 ± 19	152 ± 20	13
BDE153	119 ± 1[a]	117 ± 18	118 ± 18	122 ± 18	15
BDE154	83.5 ± 2.0[a]	82.4 ± 11.6	83.8 ± 11.8	82.4 ± 11.6	14
BDE183	43.0 ± 3.5[a]	44.4 ± 7.0	45.0 ± 7.0	42.6 ± 6.7	16
BDE209	2510 ± 190[a]	2410 ± 376	2362 ± 368	2417 ± 377	16
TNBP	276 ± 14[b]	276 ± 30	265 ± 29	280 ± 31	11
TCEP	925 ± 149[b]	927 ± 100	948 ± 103	947 ± 103	11
TCIPP	1220 ± 350[b]	1502 ± 258	1298 ± 223	1395 ± 240	17
TPHP	1190 ± 130[b]	1199 ± 195	1274 ± 208	1183 ± 193	16

[a] Certified value.
[b] Reference value.

Table S4-6. *Comparison of concentrations (ng/g) and standard deviation (SD) of OPFRs in dust reference material (NIST SRM 2585) between different studies.*

Compound	**This study (n=9)**		**Brandsma *et al.* (2013)***		**Cristale *et al.* (2018) (n=3)**		**Persson *et al.* (2018) (n=13)**		**Bergh *et al.* (2012) (n=7)**		**Van den Eede *et al.* (2012) (n=6)**	
	Mean (ng/g)	**SD**	**Mean (ng/g)**	**SD**	**Mean (ng/g)**	**SD**	**Mean (ng/g)**	**SD**	**Mean (ng/g)**	**SD**	**Mean (ng/g)**	**SD**
EH-TBB	71	15			49	8					26	2
BEH-TEBP	950	170			1,018	14					574	49
TNBP	270	29	269	19	234	2	185	22	190	20	190	10
TCEP	940	102	792	127	714	8	550	99	840	60	680	60
TCIPP	1,204	360	944	264	778	6	603	110	880	140	860	70
TDCIPP	1840	276	1,556	529	1,808	2	1,230	240	2,300	280	3,180	70
TBOEP	76,800	15,900	73,464	32,324	54,848	2	60,000	7,010	82,000	6,500	63,000	2,000
TPHP	1,220	199	1,104	99	1,139	9	700	130	1,100	100	1160	140
EHDPP	1,430	230	963	202	978	2	741	100	1,300	120		
TEHP	334	38	265	111	331	2			370	40		
TMPP	1,030	225							740	110	1,140	30

* calculated from RSD/CV%.

S4.1. Estimation of uncertainty

Identification of uncertainty sources. The main parameters estimated to affect the measurand concentration were estimated from preparation of the standard and internal standard solutions, calibration curve, recovery and repeatability.

Estimation of the uncertainty derived from standard and internal solution preparation. The combined standard uncertainty associated with the gravimetric preparation of the native and labelled standard stock solutions was calculated using Eq. (1),

$$u(C_{Std}) = C_{Std}\sqrt{\left(\frac{u(P)}{P}\right)^2 + (u_{dil})^2 + \left(\frac{u(W)}{W}\right)^2} \tag{1}$$

were,

$U(C_{Std})$	Combined standard measurement uncertainty of standard stock solution.
C_{Std}	Concentration of the standard stock solution.
$u(P)$	Standard measurement uncertainty from purity of standard solution.
P	Purity of standard stock solution (obtained from manufacturers certificate).
u_{dil}	Combined standard measurement uncertainty for the dilution of standard stock solution
(W)	Weight of the standard stock solution.
$u(W)$	Combined measurement uncertainty for weighing, obtained through Eq. (2),

$$u(W) = \sqrt{(u_{Std})^2 + (u_{solvent})^2 + \left(u_{Sample}\right)^2} \tag{2}$$

where,

u_{Std}	Standard measurement uncertainty of balance from weighing standard stock solution.
$u_{Solvent}$	Standard measurement uncertainty from weighing solvent.
u_{Sample}	Standard measurement uncertainty from weighing sample.

Estimation of the uncertainty from linear calibration graph. The combined uncertainty associated with the linear calibration was calculated using Eq. (3),

$$u(c_0) = \frac{s_{y/x}}{b}\sqrt{\frac{1}{m} + \frac{1}{n} + \frac{(x_0 - \bar{x})^2}{S_{xx}}} \qquad S_{xx} = \sum_{i-1}^{n}(x_i - \bar{x})^2 \tag{3}$$

where,

$u(c_0)$	Calibration uncertainty.
$s_{y/x}$	Residual standard deviation of the data points from the regression line.
b	slope of linear calibration graph.
m	Number of repeat measurements of sample to obtain the value for x_0.
n	Number of calibration points.
x_0	Calculated analyte concentration of sample using calibration curve.
$\bar{x}$	Mean value for x in the calibration summated over n number of calibration points.
x_i	Individual calibration concentrations obtained from the calibration curve.

Estimation of uncertainties associated with recovery. The combined uncertainty for selected analytes associated with the recovery from the CRM for dust was obtained from E.q (4),

$$u(R_m) = R_m \times \sqrt{\frac{s_{obs}^2}{n \times C_{obs}^2} + \left(\frac{u(C_{CRM})}{C_{CRM}}\right)^2} \tag{4}$$

where,

R_m	Mean recovery, calculated from E.q (5),

$$R_m = \frac{C_{obs}}{C_{CRM}} \tag{5}$$

C_{obs}	Mean concentration of the results from the replicate analysis of the CRM.
C_{CRM}	The certified value for the CRM, obtained from the certificate.
s_{obs}	Standard deviation of the results from the replicate analyses of the CRM.
n	Number of replicate analysis of the CRM.
$u(C_{CRM})$	Standard uncertainty in the certified value for the CRM, obtained from the certificate.

Spiking experiments at a low (n=3) and high (n=3) concentration were performed to assess for recovery. A Student's t-test was used to determine whether the mean recovery was significantly different from 1.0.

The combined uncertainty associated with each spiking experiment was calculated using E.q (6) and included in the uncertainty estimation.

$$u(R_m) = R_m \times \sqrt{\frac{s_{obs}^2/n + s_{native}^2}{(C_{obs} - C_{native})^2} + \left(\frac{u(C_{spike})}{C_{spike}}\right)^2} \tag{6}$$

where,

R_m	Mean recovery, calculated from E.q (7).

$$R_m = \frac{C_{obs} - C_{native}}{C_{spike}} \tag{7}$$

s_{obs}	Standard deviation of the results from the replicate analyses of the spiked sample.
n	Number of replicate analysis of spiked sample.
s_{native}	Standard deviation of the mean of the results of repeat analyses of the unspiked matrix.
C_{obs}	Mean concentration of the results from the replicate analysis of the spiked sample.
C_{native}	Mean concentration of the analyte in the unspiked sample.
$u(C_{spike})$	Standard uncertainty in the concentration of the spiked sample.
C_{spike}	Prepared concentration of the analyte in the spiked sample.

Estimation of uncertainty of repeatability. The standard uncertainty associated with the repeatability of the method was obtained from E.q (8),

$$u(r) = \frac{RSD}{\sqrt{n}} \tag{8}$$

where,

$u(r)$	Standard uncertainty of repeatability.
RSD	Relevant standard deviation of the repeat measurements.
n	Number of repeat measurements.

The combined standard measurement uncertainty for the analytes in the matrices was calculated using Eq. (9) and multiplied by 2 (coverage factor) at 95% confidence level. The expanded relative uncertainty for the analytes in the two matrices are listed in Table S1,

$$\frac{u_c(A)}{C_A} = \sqrt{\left(\frac{u(C_{Std})}{C_{Std}}\right)^2 + \left(\frac{u(C_{Istd})}{C_{Istd}}\right)^2 + \left(\frac{u(c_0)}{c_0}\right)^2 + \left(\frac{u(R_m)}{R_m}\right)^2 + u(r)^2} \tag{9}$$

where,

$u_c(A)$	Combined standard measurement uncertainty of the analyte.
C_A	Concentration of the analyte.
$u(C_{Std})$	Combined standard measurement uncertainty of standard solution.
C_{Std}	Concentration of standard solution.
$u(C_{Istd})$	Combined standard measurement uncertainty of internal standard solution.
C_{Istd}	Concentration of internal standard solution.
$u(c_0)$	Combined standard measurement uncertainty of calibration curve.
c_0	Calculated concentration of the analyte in the sample using calibration curve.
$u(R_m)$	Combined standard measurement uncertainty of recovery.
R_m	Calculated recovery.
$u(r)$	Combined standard measurement uncertainty of repeatability.

Table S4-7. *Expanded relative uncertainty (U) values for all target compounds in dust and cat hair matrix.*

Compound	Dust	Cat hair
	U (%)	U (%)
BDE28	15	20
BDE47	17	22
BDE100	17	17
BDE99	19	22
BDE154	19	21
BDE153	20	22
BDE183	21	24
BDE209	21	22
EH-TBB	14	15
BEH-TEBP	14	13
TNBP	14	15
TCEP	14	13
TCIPP	23	34
TDCIPP	20	23
TBOEP	28	27
TPHP	22	23
EHDPP	22	22
TEHP	14	16
TMPP	30	29
TIPPP	13	11

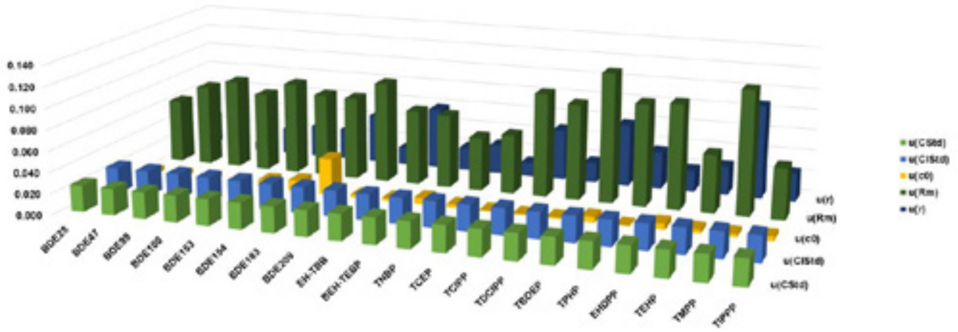

Figure S4-1. *The uncertainty contribution of the uncertainty sources for FRs in dust.*

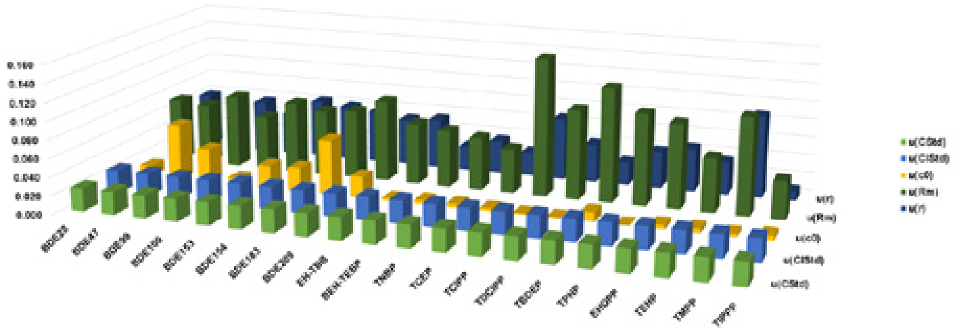

Figure S4-2. *The uncertainty contribution of the uncertainty sources for FRs in hair.*

Table S4-8. *The concentration of BFRs in dust and cat hair samples (ng/g).*

Sample	BDE28	BDE47	BDE100	BDE99	BDE154	BDE153	BDE183	BDE209	EH-TBB	BEH-TEBP
V-Dust 1	<LOQ	6.12	1.11	11.1	<LOQ	9.42	2.34	635	28.6	44.3
V-Dust 2	<LOQ	6.04	<LOQ	13	<LOQ	<LOQ	<LOQ	135	<LOQ	43.8
V-Dust 3	<LOQ	44.8	6.92	29.6	<LOQ	<LOQ	15.5	204	<LOQ	156
V-Dust 4	<LOQ	7.31	<LOQ	13.5	<LOQ	10.4	3.63	272	27.9	154
V-Dust 5	<LOQ	18.6	3.13	21.2	4.24	<LOQ	<LOQ	161	<LOQ	95.4
V-Dust 6	<LOQ	6.94	<LOQ	10.5	<LOQ	<LOQ	2.92	76.6	<LOQ	29.9
V-Dust 7	<LOQ	6.06	<LOQ	10.4	<LOQ	<LOQ	4.52	857	28.1	38.6
V-Dust 8	<LOQ	6.17	<LOQ	10.4	<LOQ	7.69	5.29	567	<LOQ	38.1
V-Dust 9	<LOQ	14.3	2.93	20.6	4.15	7.9	4.15	198	<LOQ	44.1
V-Dust 10	2.85	35.3	7.87	29	4.81	10.4	4.07	329	39.3	58.7
V-Dust 11	2.58	99.5	6.83	142	13.4	18.4	6.91	565	36.4	246
F-Dust 1	<LOQ	6.8	1.14	17	4.81	<LOQ	3.61	4590	30	68.1
F-Dust 2	<LOQ	6.46	1.45	12.7	<LOQ	6.67	5.1	1430	28.3	117
F-Dust 3	5.01	21.4	4.04	18.3	<LOQ	23.5	67.1	570	<LOQ	85.4
F-Dust 4	<LOQ	8.24	1.08	14	4.09	8.79	18.9	2510	298	12400
F-Dust 5	<LOQ	11.5	1.43	12.7	<LOQ	<LOQ	3.2	618	221	80.2
F-Dust 6	<LOQ	8.32	<LOQ	13.1	<LOQ	<LOQ	4.73	877	31.2	76.9
F-Dust 8	<LOQ	7.5	1.25	11.2	<LOQ	<LOQ	5.81	868	28.7	64.7
F-Dust 9	<LOQ	15	2.87	12.7	4.6	7.53	6.53	882	30	74.5
F-Dust 10	3	36.9	7.8	32.2	4.83	8.68	4.75	653	24800	1080
C-Hair 1A	<LOQ	0.608	<LOQ	1.06	0.429	<LOQ	0.336	14.1	<LOQ	3.73
C-Hair 1B	0.204	0.824	0.124	1.46	0.525	0.877	0.336	13.8	3.09	5.04
C-Hair 2A	<LOQ	0.687	0.096	0.892	<LOQ	0.713	0.541	10.1	3.55	13.7
C-Hair 2B	<LOQ	0.677	<LOQ	0.797	<LOQ	<LOQ	<LOQ	9.13	3.38	19
C-Hair 2C	<LOQ	0.695	<LOQ	0.868	<LOQ	<LOQ	0.342	10.6	3	13
C-Hair 2D	<LOQ	0.666	<LOQ	0.634	<LOQ	<LOQ	<LOQ	8.8	3.05	15.9
C-Hair 3	0.31	1.19	0.149	0.636	<LOQ	<LOQ	<LOQ	5.45	<LOQ	8.27
C-Hair 4A	<LOQ	0.736	0.116	1.07	<LOQ	1	0.39	10.6	3.6	8.98
C-Hair 4B	0.149	0.65	0.121	0.937	<LOQ	0.916	0.314	8.01	3.29	6.66
C-Hair 5	0.163	0.87	0.143	1.1	<LOQ	1.03	0.251	4.33	3.54	5.96
C-Hair 6	0.502	1.78	0.261	1.18	<LOQ	<LOQ	<LOQ	6.64	<LOQ	6.54

Table S4-9. *The concentration of OPFRs in dust and cat hair samples (ng/g).*

Sample	TNBP	TBOEP	TEHP	TCEP	TCIPP	TDCIPP	TPHP	EHDPP	TMPP	TIPPP
V-Dust 1	275	960	130	4350	3590	790	617	212	93.1	58.7
V-Dust 2	284	2170	91.3	310	1470	338	484	783	147	<LOQ
V-Dust 3	1490	6700	<LOQ	458	8610	668	619	313	334	636
V-Dust 4	274	6430	179	1270	1700	208	1130	422	75.5	57.4
V-Dust 5	<LOQ	3510	210	628	1880	343	448	371	418	59.9
V-Dust 6	<LOQ	2910	90.6	8630	1990	2140	277	187	92.8	<LOQ
V-Dust 7	245	1640	695	1780	139000	610	4970	6580	92.9	75.4
V-Dust 8	324	36000	221	2210	81100	790	2470	480	76.7	<LOQ
V-Dust 9	4610	5910	172	4180	2490	1390	911	379	635	55.6
V-Dust 10	307	1680	83.4	647	21900	289	415	329	140	61.9
V-Dust 11	294	11900	446	553	12800	458	1390	802	474	82.2
F-Dust 1	203	8670	142	1550	4410	558	2140	162	77.2	<LOQ
F-Dust 2	958	3140	109	7610	3160	1530	565	763	127	74.6
F-Dust 3	1730	13000	319	402	8970	28300	2600	748	314	933
F-Dust 4	396	21600	225	10000	10700	57700	2130	4380	141	116
F-Dust 5	<LOQ	586	234	1040	7010	322	3480	354	88.2	91.3
F-Dust 6	194	21500	125	16900	2090	2050	470	334	1130	<LOQ
F-Dust 8	212	485	110	919	178000	372	2660	165	52.2	55.6
F-Dust 9	<LOQ	885	141	1730	2310	1340	391	733	147	57.3
F-Dust 10	210	1240	272	5220	18700	11700	6500	862	647	1440
C-Hair 1A	<LOQ	56.2	10.3	26.3	285	19.2	53.2	18	15.6	<LOQ
C-Hair 1B	<LOQ	65.6	12.8	25.3	264	26.9	62.1	29.9	14.3	6.58
C-Hair 2A	23.1	387	22.6	22.8	159	91.1	130	78	35.5	7.64
C-Hair 2B	22.2	396	21.2	22.5	160	99.3	123	77.4	37.5	<LOQ
C-Hair 2C	22.5	414	20.9	21.6	152	93.2	128	74.3	29	5.55
C-Hair 2D	20.6	364	20.3	20.6	149	85.9	111	63.3	30.7	<LOQ
C-Hair 3	<LOQ	488	10	23.1	245	13.2	18	16.2	19.9	24.6
C-Hair 4A	<LOQ	485	54.2	53.9	372	16.5	51.6	184	8.81	5.81
C-Hair 4B	<LOQ	418	50.6	53.3	338	19.1	51.9	188	7.64	5.49
C-Hair 5	<LOQ	177	42.9	32.6	344	32.5	31	39.5	113	6.26
C-Hair 6	31	283	13.8	47.3	297	24.4	12	53.7	12.2	<LOQ

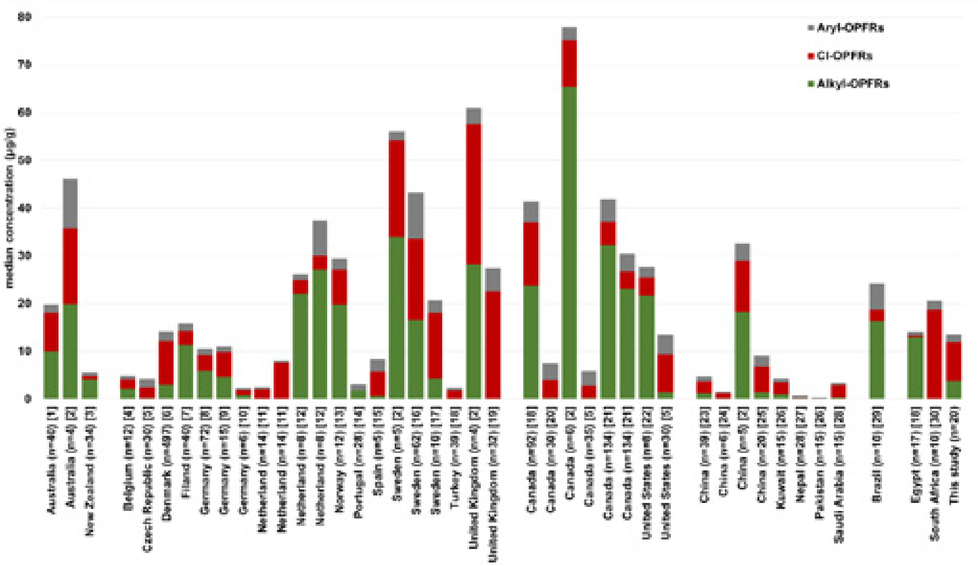

Figure S4-3. *Comparison of median concentrations of alkyl-OPFRs (sum of TNBP, TBOEP, TEHP), Cl-OPFRs (sum of TCEP, TCIPP, TDCPP) and aryl-OPFRs (sum of TPHP, EHDPP, TMPP, TIPPP) in indoor house dust (µg/g) from different studies.* ***[1]*** *(C. He* et al., *2018),* ***[2]*** *(Wong* et al., *2017),* ***[3]*** *(Ali* et al., *2012),* ***[4]*** *(Van den Eede* et al., *2011),* ***[5]*** *(Vykoukalová* et al., *2017),* ***[6]*** *(Langer* et al., *2016),* ***[7]*** *(Rantakokko* et al., *2019),* ***[8]*** *(Zhou and Püttmann, 2019),* ***[9]*** *(Zhou* et al., *2017),* ***[10]*** *(Brommer* et al., *2012),* ***[11]*** *(Sugeng* et al., *2017),* ***[12]*** *(Brandsma* et al., *2014),* ***[13]*** *(Cequier* et al., *2014),* ***[14]*** *(Coelho* et al., *2016),* ***[15]*** *(Cristale* et al., *2016),* ***[16]*** *(Luongo and Östman, 2016),* ***[17]*** *(Bergh* et al., *2011),* ***[18]*** *(Shoeib* et al., *2019),* ***[19]*** *(Brommer and Harrad, 2015)(mean values),* ***[20]*** *(Liu and Mabury, 2018),* ***[21]*** *(Fan* et al., *2014),* ***[22]*** *(Kim* et al., *2019),* ***[23]*** *(Cao* et al., *2019),* ***[24]*** *(M.-J. He* et al., *2018),* ***[25]*** *(Tan* et al., *2017),* ***[26]*** *(Ali* et al., *2013),* ***[27]*** *(Yadav* et al., *2017),* ***[28]*** *(Ali* et al., *2016),* ***[29]*** *(Cristale* et al., *2018),* ***[30]*** *Abafe and Martincigh, (2019).*

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Chapter 5

Short-, medium-, and long-chain chlorinated paraffins in South African indoor dust and cat hair

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Abstract

Polychlorinated n-alkanes or chlorinated paraffins (CPs) contain a magnitude of structural isomers and are categorised as short-chain (SCCPs), medium-chain (MCCPs), and long-chain (LCCPs) CPs, according to the carbon chain lengths. In this study the ΣSCCPs, ΣMCCPs, and ΣLCCP concentrations are reported for South African indoor dust and pet cat hair. The median concentrations of the ΣCPs (C_9-C_{37}) ranged from 33 to 663 µg/g for freshly collected dust (FD), 36 to 488 µg/g for dust collected from household vacuum cleaner bags (VD), and 1.2 to 15 µg/g for cat hair (CH) samples. MCCPs were the dominant CP group, followed by SCCPs and LCCPs. The ΣMCCP concentration ranged from 13 to 498 µg/g in dust and 0.6 to 6.5 µg/g in cat hair. SCCPs with shorter carbon chains and lower chlorine substitution were observed in cat hair. LCCPs with carbon chains >C_{20} were detected in dust and hair samples, possibly indicating the use of wax grade LCCP formulations. Non-traditional Kendrick mass defect plots were used to obtain information on the magnitude of CPs and provide evidence of possible interfering compounds. This is the first report on the occurrence of SCCPs, MCCPs, and LCCPs in the South African indoor environment.

5.1. Introduction

Chlorinated paraffins (CPs) are complex mixtures of synthetic polychlorinated n-alkanes with various degrees of chlorination. Based on the carbon chain length, CPs are classified as short-chain (SCCPs, ≤ C_{13}), medium-chain (MCCPs, C_{14} to C_{17}), and long-chain (LCCPs, ≥ C_{18}). The LCCPs with chain lengths longer than C_{20} are also referred to as wax grade or very long-chain CPs (Mukherjee, 1990; Schinkel *et al*., 2018). International conventions and regulatory agencies have classified SCCPs as environmentally hazardous substances and restricted their production and use, and in some cases, MCCPs and LCCPs are produced as alternatives (Glüge *et al*., 2016; UNEP, 2012; van Mourik *et al*., 2016). There are currently no immediate actions on the production and use of SCCPs in South Africa. According to a report published in 2015, South Africa produced approximately 10,000 tonnes of CPs per year of which 50% is exported (ICIS, 1995). In South Africa, four MCCP formulations are produced with chlorine contents from 45% to 55% (http://www.ncp.co.za/chlorinated-parrafin-plasticlor). Concerns regarding the potential toxicity of MCCPs exist for aquatic environments, due to their possible persistence and the temporal concentration increase in soil, biota, and most sediment cores (Glüge *et al*., 2018). Chlorinated paraffins are mainly used as flame retardants and plasticizer additives in polyvinyl chloride (PVC), lubricating oils, paints, coatings, sealants, and adhesives. They are thus closely associated with the indoor use of these products in vinyl flooring, carpet backing, textiles and fabrics, floor polishes, furniture, wallpaper, and kitchen equipment and appliances (Coelhan and Hilger, 2014; Fiedler, 2010; Gallistl *et al*., 2018; Mukherjee, 1990; van Mourik *et al*., 2016; Wang *et al*., 2018; Yuan *et al*., 2017b). There is currently no evidence of natural sources of CPs in the environment and the anthropogenic releases of CPs into the environment are mainly through volatilization, wash-off, and abrasion (Muir, 2010). As a result of their widespread use, levels for CPs have been reported for different environmental compartments including dust, air, water, sewage sludge, soil, sediment, and biota (Coelhan and Hilger, 2014; Tomy *et al*., 1997; van Mourik *et al*., 2016). It is proposed that SCCPs are more likely to migrate through the vapour phase due to the dominance of C_{10} and C_{11} carbon chain SCCPs in air, while longer chain CPs and/or higher chlorine contents are likely adsorbed to particles, like dust (Coelhan and Hilger, 2014; Zhou *et al*., 2018). It was also suggested that CPs might evaporate (at a low evaporation rate) from plastic materials and partition to dust. (Olofsson *et al*., 2013). There is, however, limited information on LCCPs in indoor dust: recent results showed that LCCPs were the dominant congeners in dust from Sweden (Wong *et al*., 2017). CP levels are considerably higher than those of other flame retardants in outdoor and indoor environments (de Boer *et al*., 2016). Dust is one of the most frequently studied matrices in the indoor environment and inhalation (by adults) and dust ingestion (by toddlers) are suggested to be significant routes for human exposure to CPs (Fridén *et al*., 2011). Hair has been presented as an indicator for the detection of atmospheric exposure, and possible estimation of corresponding air concentrations (Schramm, 2008). Pet cats share a common environment with toddlers and cat hair is also directly exposed to the environment and may accumulate contaminants from indoor air and dust. Cats have been selected as good sentinels for human indoor exposure to flame retardants (Dye *et al*., 2007; Norrgran Engdahl *et al*., 2017). Being a non-invasive matrix, hair might, therefore, have relevance as indoor exposure model for children.

Aspects of the analysis of CPs in environmental matrices are discussed in the review from van Mourik *et al*. (2015). One of the major advances in CP analysis by Zencak and Oehme (2004) introduced chlorine adduct formation using negative ion atmospheric pressure chemical ionization (APCI) hyphenated with liquid chromatography. Bogdal *et al*. (2015) employed a direct flow injection method using this unique ionization technique coupled to a high-resolution time-of-flight mass spectrometer (HR-TOF-MS). CPs were quantified by reconstructing the CP patterns in the samples into a linear combination of CP patterns from technical formulations using a mathematical deconvolution algorithm. In addition to the improved selectivity and sensitivity, the accurate mass information obtained from the HR-TOF-MS analysis can also be used to comprehensively explore data from complex samples by constructing mass defect (MD) plots. Kendrick (1963) introduced a smart approach to identify organic ions belonging to a homologous series. The use of non-traditional Kendrick MD plots corresponding to the substitution of chlorine for hydrogen (H/Cl) was previously used to facilitate the identification of halogenated contaminants in environmental samples (Cariou *et al*., 2016; Jobst *et al*., 2013; Taguchi *et al*., 2010).

In this study, concentrations for the ΣSCCP, ΣMCCP, and ΣLCCP in South African indoor dust and cat hair (CH) were determined using APCI coupled to a high-resolution quadrupole time-of-flight mass spectrometry (qTOF-MS) with chlorine-induced adduct formation and the accurate mass full scan data were evaluated using non-traditional Kendrick MD plots. Two indoor dust types were collected from houses as fresh or "active" dust (FD) and dust taken from household vacuum cleaner bags (VD). The FD represents samples from a single room over a short time-span and VD contamination over periods of months from multiple rooms. In addition to the dust, hair samples were obtained for some of the indoor pet cats, which share a common environment with toddlers.

5.2. Materials and methods

Information about the standards, chemicals, and suppliers is provided in the Supporting Information (S5-1) of this manuscript.

5.2.1. Sample collection

Dust samples (n=20) were collected from homes in Pretoria, South Africa. Details on the sample collection are provided in Brits *et al*. (2019) and samples associated with each home are provided in the supporting information (Table S5-1). Briefly, FD (n=9) was collected from the living room, as a mixture of floor dust and elevated surface dust, and VD (n=11) was collected from household vacuum cleaner bags or canisters (for vacuum cleaners without bags). During sample collection, sodium sulphate (Na_2SO_4) spread on aluminium foil, was collected using the same method employed to collect dust samples as field blanks (n=6). The samples were wrapped in aluminium foil, placed in plastic resealable bags and transported to the laboratory for processing. Dust and field blank samples were sieved (stainless steel sieve, 500 µm) and stored in amber vials at room temperature until chemical analysis. The CH samples (n=10) were collected from Persian cats at a pet grooming service, representing six homes. Glass wool was exposed to the air during hair sampling to simulate field blanks (n=3). The samples were wrapped in aluminium foil, placed in resealable plastic bags, and stored at room temperature until chemical analysis.

5.2.2. Sample pre-treatment

Dust (~50 mg) and cat hair (~500 mg) was extracted using accelerated solvent extraction (ASE) with hexane/acetone (3:1, v/v) as previously described by Brits *et al*. (2019) Three blanks and three SRM 2585 samples were analysed together with each batch of nine to eleven samples. The cat hair samples were subjected to a freezing-lipid precipitation step with methanol to reduce the presence of polar wax-like compounds prior to fractionation as previously employed for complex lipid-rich samples (Liu *et al*., 2018). The extracts were fractionated on pre-cleaned glass columns fitted with a glass wool plug and filled from the bottom with 0.5 g silica gel, 0.5 g florisil and 0.5 g anhydrous Na_2SO_4. The column was conditioned with 40 mL hexane. The extracts, solvent exchanged to hexane, were quantitatively transferred to the glass column. The CPs were eluted from the column with 15 mL hexane and 15 mL dichloromethane/hexane (1:1, v/v). The combined eluents were evaporated to near dryness at 30 °C under low nitrogen flow and reconstituted to 0.5 mL with acetonitrile, followed by the addition of $^{13}C_{10}$-anti-Dechlorane Plus® as injection standard.

5.2.3. Instrumental analysis

The CP analysis was based on the analytical method previously described by Brandsma *et al*. (2019). Flow injection mass spectrometry was performed into an APCI source coupled to a qTOF-MS (Compact, Bruker, Bremen, Germany). The sample extracts (10 µL) were injected using an Agilent 1290 infinity HPLC system (Agilent Technologies, Amstelveen, The Netherlands) with a mixture of acetonitrile/ dichloromethane (10:1, v/v) as mobile phase at a flow rate of 250 µL/min. Detailed settings of the qTOF-MS are given in the Supporting Information (S5-2). An average full scan mass spectrum of the peak in the chromatogram was background subtracted and accurate masses, with a signal-to-noise of more than 3 at an absolute intensity threshold of 100 counts, were extracted using Bruker Compass DataAnalysis software. The accurate mass list was exported to Microsoft Excel software for quantitation.

5.2.4. Quantitation and deconvolution

Strict criteria were set to assign peak areas to each CP congener group to confirm positive identification and accurate quantitation of the CP congeners. The two most abundant $[M+Cl]^-$ ion pairs were used as quantitation and qualifier ions (Table S5-2). Peak areas of the congeners were only included when, (1) the unique $[M+Cl]^-$ ions were present at a signal-to-noise higher than 10 with a mass accuracy of ≤ 5 ppm from the theoretical mass, (2) the ion pair intensity ratio was within 10% of the theoretical ratios. In total 1,278 target ions for CPs ranging from $C_9H_{17}Cl_3$ to $C_{40}H_{56}Cl_{26}$ were considered. The quantitation of the CPs was performed using the deconvolution algorithm previously applied by Bogdal *et al*. (2015) Detailed information on the deconvolution procedure for SCCPs, MCCPs, and LCCPs can be found in the supporting information of Brandsma *et al*. (2017). The goodness-of-fit was calculated between measured patterns and deconvoluted patterns and expressed as the coefficient of determination (R^2). CP concentrations for samples with an R^2 <0.5 should be taken as indicative values (Bogdal *et al*., 2015; Brandsma *et al*.,2017). The degree of chlorination calculated for the seven standard technical CP formulations compared well with the stated chlorination degree of the manufacturer (Table S5-3).

5.2.5. Quality assurance and quality control

Field blanks for dust and hair samples were included in the analysis of each batch of nine to eleven samples. No LCCPs were detected in the eight field blanks. The ΣSCCP and ΣMCCPs in the blanks were 10 ng and 43 ng absolute, which amount to 4% of the lowest concentration found in the samples, and hence no background subtraction was performed. The limits of quantification (LOQ) were calculated as the mean values plus ten times the standard deviation of the congeners in the blanks. Based on an average sample intake of 0.05 g dust and 0.5 g hair, the LOQs for ΣSCCPs were 60 ng/g and 6.0 ng/g and the LOQs for ΣMCCPs were 387 ng/g and 39 ng/g for the respective matrices. As no LCCPs were detected in the blanks, the LOQ was set at the concentration of the lowest calibration standard, which was 198 ng/g for dust and 20 ng/g for the hair samples. Linearity was assessed using five-point (10 to 200 ng) calibration curves for each CP formulation and the correlation coefficients (R^2) for the formulations were better than 0.998. The CP recoveries for both matrices were assessed through triplicate spiking experiments. Dust and hair samples were spiked with a mixture containing 500 ng of SCCP (SCCP 55.5% Cl), MCCP (MCCP 42% Cl), and LCCP (LCCP 36% Cl) standards and underwent the same sample pre-treatment and analysis procedures as the samples. The relative recoveries in the dust were 99 ± 11% for ΣSCCPs, 107 ± 12% for ΣMCCPs, and 107 ± 14% for ΣLCCPs. The recoveries from the cat hair were 90 ± 13% for ΣSCCPs, 94 ± 10% for ΣMCCPs and 92 ± 11% for ΣLCCPs. The R^2 for the ΣSCCPs and ΣMCCPs were higher than 0.51 for all samples (Table S5-5). The deconvolution method applied in this study resulted in low R^2 values for the ΣLCCPs, due to the lack of standard technical mixtures containing carbon chain lengths $>C_{20}$. Limitations regarding analytical standards were previously discussed by Schinkel *et al*. (2018).

5.3. Results and discussion

5.3.1. CP concentrations in house dust SRM 2585

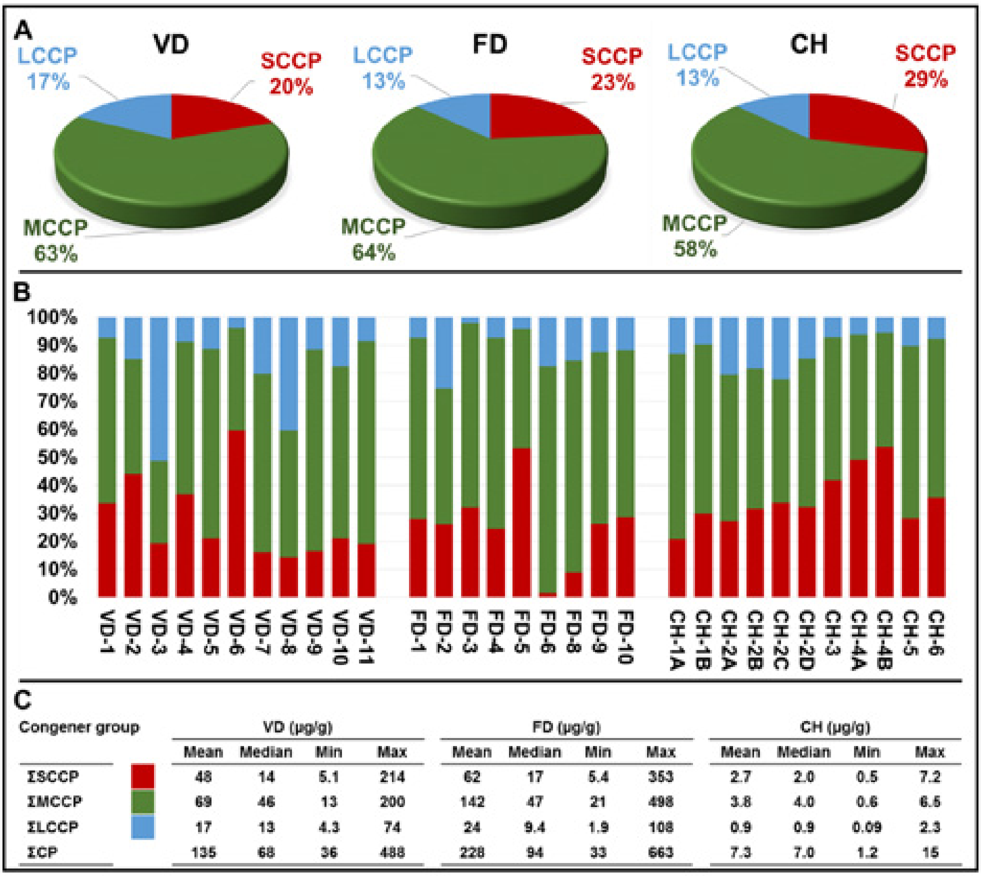
There is currently no reference material for CPs in dust or hair. The concentrations of ΣSCCPs, ΣMCCPs, and ΣLCCPs for the NIST SRM 2585 material in this study were 8.65 ± 0.16 µg/g (R^2=0.82), 11.98 ± 0.24 µg/g (R^2=0.73), and 19.26 ± 0.56 µg/g (R^2=0.02), respectively (additional information on the method validation and CP composition in the NIST SRM 2585 material are provided in Table S5-4 and Figure S5-1). The results obtained from our study were lower than the first report on concentrations of CPs in the NIST SRM 2585 (n=2), which were 102 and 119 µg/g for ΣSCCPs, 116 and 121 µg/g for ΣMCCPs, and 87 and 112 µg/g for ΣLCCPs (Wong *et al*., 2017). Shang *et al*. (2019) reported concentrations of 7.58 ± 0.43 µg/g for ΣSCCPs and 16.4 ± 2.1 µg/g for ΣMCCPs for the SRM 2585. Brandsma *et al*. (2019) recently reported average levels of 7.1 ± 0.2 µg/g for the ΣSCCPs, 10 ± 0.2 µg/g for ΣMCCPs and 16 ± 0.4 µg/g for ΣLCCP. The concentrations reported in our study compare well with these two studies, taking into account that the between-laboratory coefficient of variation reported for the same sample in a recent inter-laboratory comparison was 68% (van Mourik *et al*., 2018). The congener profile of the ΣSCCP was dominated by carbon chain lengths of C_{12} (followed by C_{11} and C_{13}) and chlorine substitution of Cl_6 and Cl_7 (followed by approximately equal contributions of Cl_5 and Cl_8) similar to the profile previously reported by Wong *et al*. (2017). The ΣMCCPs were dominated by equal contributions of C_{14} and C_{15} and chlorine substitution of Cl_6 followed by Cl_7 and Cl_5. The ΣLCCP profile showed a higher prevalence of C_{22} to C_{25} carbon chain lengths and chlorine substitution of Cl_6 and Cl_7. The mean chlorine contents in ΣSCCPs, ΣMCCPs, and ΣLCCPs were 59%, 52%, and 40% respectively. This was similar to the degree of chlorination previously reported (59% for ΣSCCPs, 52% for ΣMCCPs, and 43% for ΣLCCPs) (Brandsma *et al*., 2019).

5.3.2. CP concentrations in indoor dust and cat hair

SCCPs, MCCPs, and LCCPs were detected in all samples analysed and large variations were observed for CP congener profiles between matrices and for the individual samples (see Table S5-5 and Figure S5-13 to S5-43). The ΣCP concentration in the FD ranged from 33 to 663 µg/g, with a median concentration of 94 µg/g and the concentration in the VD ranged from 36 to 488 µg/g, with a median concentration of 68 µg/g (Figure 5-1). The ΣMCCPs were the dominant CP group contributing between 58% and 64% to the CP concentration, followed by ΣSCCPs (20 to 29%) and ΣLCCPs (13 to 17%). The median concentrations of the ΣSCCPs were 17 µg/g in the FD and 14 µg/g in the VD, with concentration ranging from 5.4 to 353 µg/g and 5.1 to 214 µg/g for the respective dust matrices (Figure 5-1). The ΣSCCP concentrations in the dust samples were higher than previously reported in house dust from Australia (13 µg/g) (He *et al*., 2019), Canada (6.2 µg/g) (Shang *et al*., 2019), Germany (5 µg/g) (Hilger *et al*., 2013) and Sweden (5 to 9 µg/g) (Wong *et al*., 2017) and lower than reported for Australia (Wong *et al*., 2017), China (Chen *et al*., 2018; Liu *et al*., 2017; Shi *et al*., 2017; Wong *et al*., 2017), and the UK (Wong *et al*., 2017) (Table S5-6). The median concentrations of the ΣMCCPs were 47 µg/g in the FD and 46 µg/g in the VD with concentrations ranging from 21 to 498 µg/g and 13 to 200 µg/g respectively (Figure 5-1). The ΣMCCP concentration in the South African dust was higher than reported for Canada (19 µg/g) (Shang *et al*., 2019) but lower than reported for China (Chen *et al*., 2018; Shi *et al*., 2017; Wong *et al*., 2017) and Germany (Hilger *et al*., 2013) (Table S5-6). The median ΣMCCP concentration was similar to results reported for indoor dust from Australia (He *et al*., 2019).

The median concentration of the ΣLCCPs in the VD was 13 µg/g, which ranged from 4.3 to 74 µg/g, and 9.4 µg/g in the FD, ranging from 1.9 to 108 µg/g (Figure 5-1). The ΣLCCP concentrations from indoor dust samples were previously reported in house dust from five countries (Wong *et al*., 2017). The concentrations of the ΣLCCP ranged from 92 to 1,995 µg/g, which were higher than the levels found in this study (Table S5-6). The ΣLCCPs were higher than recently reported for house dust from Australia (He *et al*., 2019).

The median concentrations of the ΣCPs in the cat hair were 7.0 µg/g, with concentrations ranging from 1.2 to 15 µg/g. There is, however, no other literature on the occurrence of CPs in human or pet cat hair. The median concentration of ΣSCCPs, ΣMCCPs, and ΣLCCPs in the CH samples were 2.0 µg/g, 4.0 µg/g, and 0.9 µg/g, respectively. So, SCCPs, MCCPs and LCCPs were found in house dust and cat hair from an indoor environment contaminated with CPs. Considering that the samples sizes limit meaningful statistical analysis, the levels in cat hair were found to be roughly 10-fold lower than in dust for all three CP classes.



Congener group		VD (µg/g)				FD (µg/g)				CH (µg/g)			
		Mean	Median	Min	Max	Mean	Median	Min	Max	Mean	Median	Min	Max
ΣSCCP	🟥	48	14	5.1	214	62	17	5.4	353	2.7	2.0	0.5	7.2
ΣMCCP	🟩	69	46	13	200	142	47	21	498	3.8	4.0	0.6	6.5
ΣLCCP	🟦	17	13	4.3	74	24	9.4	1.9	108	0.9	0.9	0.09	2.3
ΣCP		135	68	36	488	228	94	33	663	7.3	7.0	1.2	15

Figure 5-1. *CP congener profiles of (A) the median ΣSCCPs, ΣMCCPs and ΣLCCPs in VD, FD and CH, (B) the relative abundances (%) in the individual VD, FD and CH samples. (C) Summary of the mean, median, and concentration range (µg/g).*

5.3.3. CP congener group profiles

Non-traditional Kendrick MD plots were used to assess the carbon chain lengths and degree of substitution of SCCPs, MCCPs, and LCCPs in the dust and hair samples. As shown in Figure 5-2, the chlorine adduct formation using negative ion APCI improved the selectivity and sensitivity for halogen-containing compounds. The non-traditional Kendrick MD plots could constructively be used to provide an informative picture of the CP contamination present in the dust and hair samples. A detailed discussion on the construction of these plots is provided in the supporting information (S5-3). As shown in Figure 5-2A, the carbon chain lengths for the CP congeners in the dust samples went up to C_{37}. The CP congeners in the CH samples (Figure 5-2D), ranged from C_9 to C_{36}. Screening studies have previously reported the identification of LCCPs up to C_{35} in European eel samples (Cariou *et al*., 2016). In addition to obtaining information on the magnitude of CPs, which aids in the selection of the target list for quantitation, the MD plots also provide evidence on possible interferences. As shown in Figure 5-2C (and Figure S5-2), the pattern observed for VD-6 shows abundant C_{19} and prominent congeners $\geq C_{30}$. The difference between measured and theoretical masses for the C_{19} homologue group were within 10 ppm of the theoretical masses. The ratios of the quantitation and qualifier ions do however vary by more than 40% from the theoretical ion pair intensity ratios (examples of mass scale-expanded segments for mass spectra are provided in Figure S5-3). This emphasises the use of very strict mass accuracy criteria and the use of ion ratios to distinguish between positive identified CPs and the presence of possible interferences. This pattern was also observed for the cat hair (CH-6) taken from the same household.

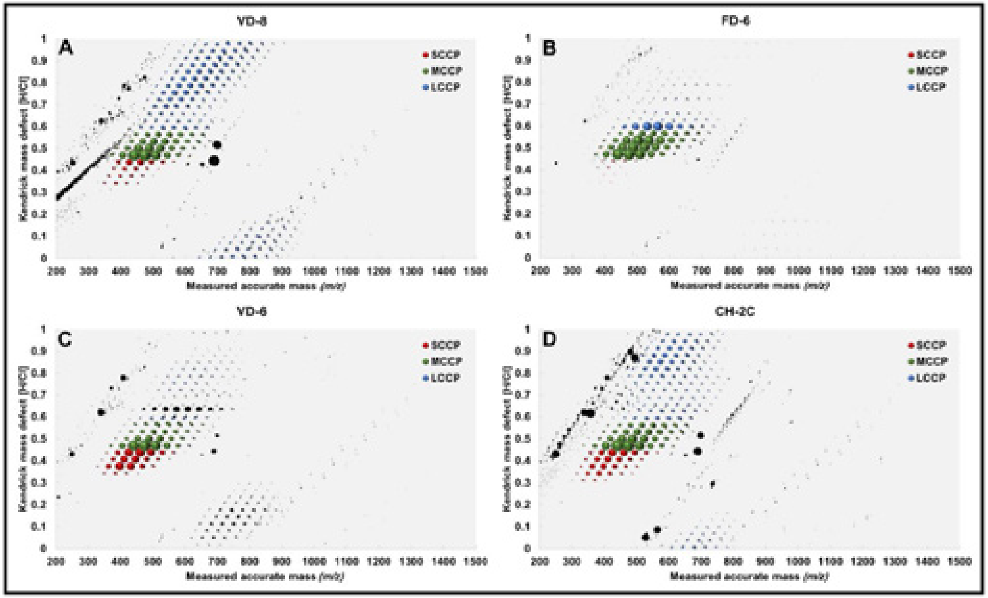


Figure 5-2. *Non-traditional Kendrick MD plots constructed for (A) sample VD-8, (B) sample FD-6, (C) sample VD-6, (D) sample CH-2C. The red spheres represent the quantifier and qualifier $[M+Cl]^-$ ions for SCCPs, the green for MCCPs and the blue for LCCPs, the sphere sizes represent the instrument response (See Supplementary Material for details).*

As shown in Figure 5-3, comparable patterns were observed for the dust, with carbon chain lengths of C_{13} dominating the ΣSCCP profile. The chlorine substitution for the ΣSCCPs ranged from Cl_4 to Cl_{10} and was dominated by Cl_6 and Cl_7 followed by approximately equal contributions of Cl_5 and Cl_8. Although C_{13} carbon chain lengths were also dominant in cat hair, C_9 to C_{11} congeners with lower chlorine substitution (Cl_4 and Cl_5) were observed. Zhou *et al*., (2018) previously showed that longer-chain and higher chlorinated SCCP congeners adsorb to small particles and shorter-chain and lower chlorinated CP congeners can migrate from small particles to larger particles. This could imply that these shorter-chain and lower chlorinated CP congeners could accumulate through volatilization and condensation processes on the large surface area of hair from the small dust particles. In addition, lower molecular weight SCCP congeners are more prone to volatilization (Wang *et al*.,2013; Wang *et al*., 2015). The volatile shorter chain SCCPs with fewer chlorine atoms were previously reported to be dominant in indoor air (Fridén *et al*., 2011; Wang *et al*., 2013) and it was reported that these congener groups can be taken up by the protective epicuticular wax layer of pine needles through kinetically limited gaseous deposition (Wang *et al*., 2015). Although gaseous exchange and atmospheric particle deposition play a role in CP transport, generally, higher levels are found in dust compared to air. This might suggest that SCCPs with shorter carbon chains and lower chlorine substitution could be adsorbed to the waxy sebum layer on cat hair over time, possibly due to contributions from indoor dust or direct migration from possible source in the indoor environment. Toxicokinetic studies further showed that distributions of SCCPs congener groups in blood, urine, and faeces from Sprague Dawley rats depended on octanol/water partition coefficients (K_{ow}) (Geng *et al*., 2016). Lower chlorinated Cl_5-SCCPs were associated with blood and urine, and Cl_{8-10}-SCCPs were eliminated via the faeces. Although no data are available for the unmetabolised CPs partitioning between blood and hair we cannot exclude that internal exposure may have a substantial contribution. The current analytical method did not allow to distinguish between internal/absorbed levels and external/adsorbed levels on the cat hair. Theoretically, internal blood levels of CPs could be transported to the hair follicles and further stored in the hair structure. The influences of atmospheric deposition, direct migration from sources, or endogenous mechanisms on the hair concentrations are not fully understood, and factors may vary for different CP congeners. Further research is needed to investigate the migration and leaching behaviour of CPs from products to evaluate the potential human exposure to CPs. The carbon chain length profiles for dust were similar to previously reported for SCCPs in dust samples from Canada (Shang *et al*., 2019; Wong *et al*., 2017), China (Chen *et al*., 2018; Wong *et al*., 2017), and Australia (He *et al*., 2019; Wong *et al*., 2017). The chlorine distribution calculated in this study does, however, differ from studies in house dust from Canada (Shang *et al*., 2019), China (Chen *et al*., 2018; Liu *et al*., 2017; Shi *et al*., 2017), and Germany, (Hilger *et al*., 2013) where Cl_7 and Cl_8 dominated the ΣSCCP profile. This is probably an indication that different commercial CP mixtures are used in these countries. The degree of chlorination of the ΣSCCPs ranged from 56% to 59% in all samples analysed, similar to results reported for house dust from Canada (ranging from 53.8% to 57.2%) (Shang *et al*., 2019) and lower than results for Germany (60% and 62.5%) (Hilger *et al*., 2013).

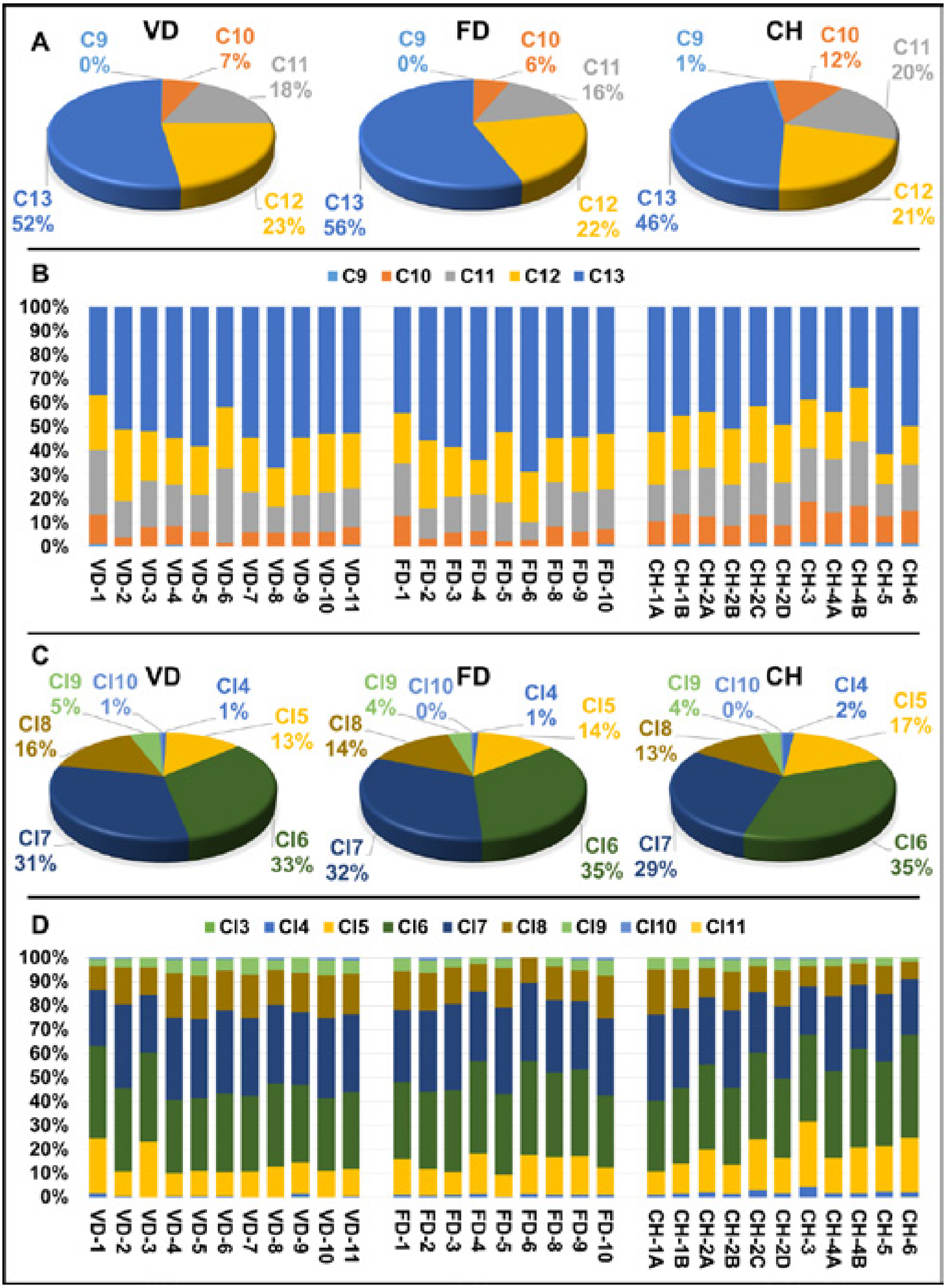


Figure 5-3. *Congener profiles of the median ΣSCCPs in the dust and hair samples where (A), is the composition based on carbon chain length, (B) is the carbon chain length in the individual samples, (C) is the composition based on chlorine substitution, (D) is the chlorine substitution in the individual samples.*

As shown in Figure 5-4**,** similar patterns for the ΣMCCPs carbon chain length profiles were observed for all samples, with C_{14} dominating the congener profile followed by C_{15}, C_{16}, and C_{17}. The MCCP chlorine homologue groups ranged from Cl_4 to Cl_{11} and were dominated by Cl_7 followed by nearly equal contributions for Cl_6 and Cl_8. Similar carbon chain length profiles were previously reported for dust samples from Canada, (Shang *et al*., 2019; Wong *et al*., 2017) China, (Chen *et al*., 2018; Shi *et al*., 2017; Wong *et al*., 2017) and Australia (He *et al*., 2019; Wong *et al*., 2017). The profile from Sweden was dominated by C_{17} carbon chain lengths (Wong *et al*., 2017). The chlorine distribution calculated in this study differs from studies from Canada where Cl_8 was the dominant group, (Shang *et al*., 2019) Cl_7 and Cl_8 were the dominant contributors in China, (Chen *et al*., 2018; Shi *et al*., 2017) and Cl_6 was dominant for Germany (Hilger *et al*., 2013). The degree of chlorination for the ΣMCCPs ranged from 54 to 56% in all the samples analysed, similar to results reported for house dust samples from Canada (ranging from 53.8 to 57.2%) (Shang *et al*., 2019) and higher than results for Germany (44.5 and 49.5%) (Hilger *et al*., 2013).

The ΣLCCP congener profiles differ between the sample types and large variation could be observed for the individual samples (see Figure 5-5). The C_{18} congeners dominate the profiles followed by C_{19} and C_{20}. The chlorine homologue groups for LCCPs in the dust samples were dominated by Cl_8 and Cl_7 followed Cl_9. The profile in CH was dominated by equal contributions from Cl_7 and Cl_8, followed by Cl_6 and Cl_9. As shown in the Kendrick MD plot (Figure 5-2B), and Figure 5-1, the CP profile for FD-6 consists mostly of MCCPs and C_{18}-LCCPs. The ΣLCCP congener profile for this sample (Figure S5-29) shows a unique profile which was dominated by C_{18} carbon chain lengths; no C_{21} was observed and from C_{26} to C_{36}, only even carbon chain lengths were observed. This CP profile in this dust sample could be influenced by the presence of small particles from products which contain a CP formulation of which the LCCPs could be possible impurities. The analysis of household consumer products could provide more information on the type of CP formulations present in these products. The LCCP congener profile in sample FD-2 and the cat hair samples (CH-2A to 2D) taken from the same house were dominated by C_{25} carbon chain lengths which might confirm the use of wax grade LCCP formulations. This profile was also observed for two of the VD samples (VD-3 and VD-8). We also observed low and high chlorination for the LCCP carbon chain lengths C_{24} to C_{27} in sample VD-2 and to a lesser extent in FD-4 (Figure S5-14 and S5-27), this “double” chlorination pattern could indicate that combinations of CP formulations, present in products, might contribute to this congener profile. The ΣLCCPs with carbon chain lengths longer than C_{21} contributed more to the ΣLCCP concentration in VD as compared with the FD and CH samples. This variation between the dust types might be due to various factors that influence the partitioning of CPs from products to suspended particles and deposition on dust. As the VD samples represent dust from multiple rooms, it might include particles from products which contain CPs such as flexible PVC or polyurethane insulation foams.

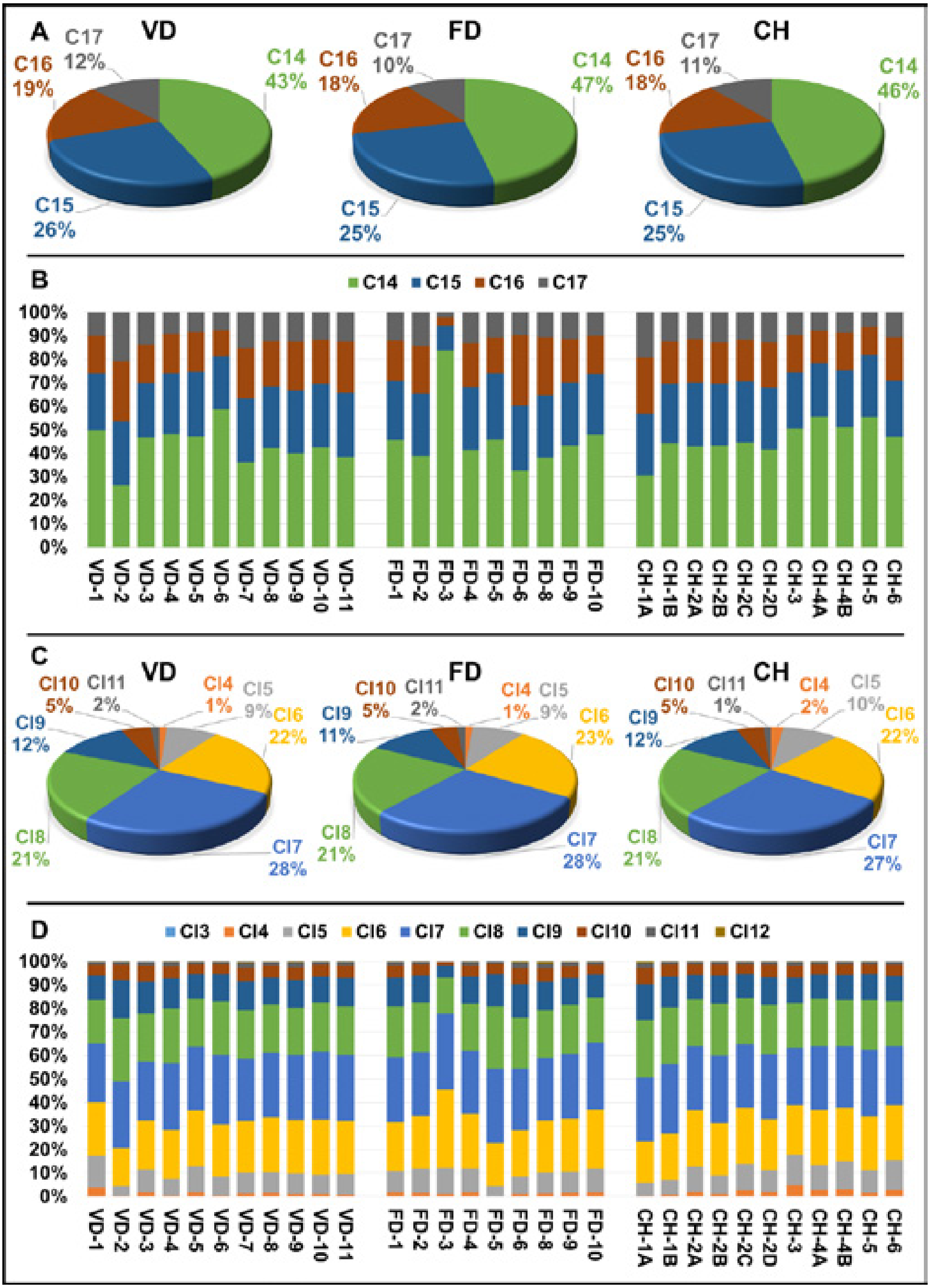


Figure 5-4. *Congener profiles of the median ΣMCCPs in the dust and hair samples where (A), is the composition based on carbon chain length, (B) is the carbon chain length in the individual samples, (C) is the composition based on chlorine substitution, (D) is the chlorine substitution in the individual samples.*

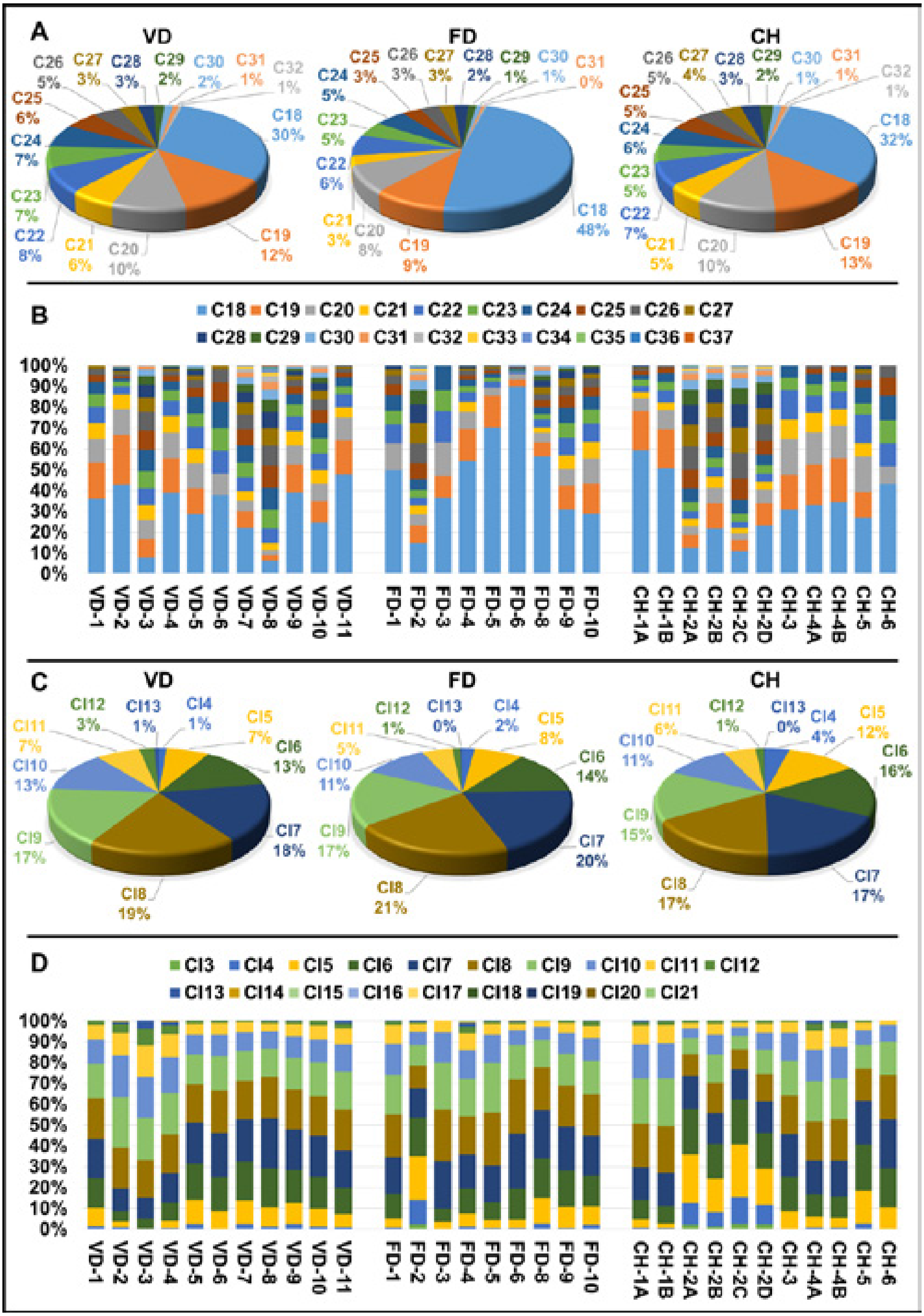


Figure 5-5. *Congener profiles of the median ΣLCCPs in the dust and hair samples where (A), is the composition based on carbon chain length, (B) is the carbon chain length in the individual samples, (C) is the composition based on chlorine substitution, (D) is the chlorine substitution in the individual samples.*

5.3.4. Implications

The occurrence of CPs in the South African indoor environments indicates that humans and pets are exposed to these compounds. To date, there is limited data on CPs, especially LCCPs in the indoor environment, and more research is needed to understand indoor exposures in order to estimate the risk and fate of CPs. Dust ingestion was suggested to be a significant CP exposure route for toddlers (Fridén *et al*., 2011; Gao *et al*., 2018; Shi *et al*., 2017). Toddlers spend more time indoors and are usually in close proximity to indoor dust; their crawling activity and frequent hand-mouth contact enhances the direct contact and exposure to dust and subsequently contaminants found in dust. While this pilot study may somewhat limit conclusions, the results represent an important baseline for developing larger studies to assess CP exposure estimates. Health-based reference values for CP congeners are lacking and it is unclear if the positions of chlorine substitution and the degree of chlorination would have a substantial impact on health effects. Indoor environments such as child care centers and schools have to be taken into consideration when exposure to CPs are characterised for children.

SCCPs have been listed as persistent organic pollutants (POPs) under the Stockholm Convention of the United Nations. However, for this class of chemicals an unusual long list of exemptions was made. They may still be used as adhesives in the rubber industry; rubber products in industries related to mining and forestry, waterproofing paints, adhesives, lubricant additives, secondary plasticizers in flexible PVC products and flame retardant in paints and plastics (UNEP, 2012). The effectiveness of the ‘POP label’ for SCCPs can therefore be questioned. Given the very high global production volumes of CPs and the recently published UN Global Chemicals Outlook II,(ICIS, 1995) which predicts a doubling of the total amount of chemicals used worldwide within the coming decade, it seems imperative for the UN to reduce the current restrictions on the SCCPs in the Stockholm Convention and in addition consider MCCPs for a POP label. ΣSCCP, ΣMCCP, and ΣLCCP levels have recently been reported in sewage sludge, (Brandsma *et al*., 2017) sediment, (Du *et* al., 2018; Yuan *et al*., 2017a) human plasma, (Li *et al*., 2017) and terrestrial animals (Yuan *et al*., 2019). These studies indicate that not only SCCPs but also MCCPs and LCCPs have a bioaccumulative potential. With the current regulatory situation in South Africa, adequate environmental monitoring data are available for some of the POP pesticides. CPs have, however, not received attention and only limited data is available. It was previously reported that background soil concentrations for ΣMCCPs in South Africa, (Quinn *et al*., 2009) were as high as soil collected from sites close to a CP production plant in China (Glüge *et al*., 2018). The congener profiles reported in this study show that the ΣMCCPs are the major CP group in the indoor environment. Congener profiles of local commercial formulations are needed to confirm if the MCCPs found, could be from a locally produced technical MCCP mixture. However, the contribution from the ΣSCCPs and ΣLCCPs may be due to formulations used in imported products. International restrictions of SCCPs may result in an increased use of MCCPs and

LCCPs, which underlines the importance of including and monitoring of these two groups to support the enforcement of regulations.

5.4. Conclusion

We have reported for the first time the occurrence of SCCPs, MCCPs, and LCCPs in the South African indoor environment. The results of the study emphasise the need for strict identification criteria to distinguish between positively identified CPs and possible interferences. The ΣMCCPs were the major CP group in the samples followed by ΣSCCPs and ΣLCCPs. The congener profiles for the ΣLCCP confirms the presence of wax grade LCCP formulations. C_9 to C_{11} SCCPs with lower chlorine substitution (Cl_4 and Cl_5) were observed in the cat hair samples, suggesting that SCCPs with shorter carbon chains and lower chlorine substitution could be favourably adsorbed to the hair. This might indicate that indoor dust partly contributes to the pattern observed in the hair. The differences in congener profiles between cat hair and dust may be of importance considering that dust ingestion rates are regularly used for risk assessments. Cat hair provides specific information on indoor exposure and could be seen as a non-invasive passive sampler to continued exposure of CPs in the indoor environment. This study further supports the analytical capability to provide reliable data on present and future levels of chlorinated paraffins in South African environmental matrices.

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Supplementary material S5

S5.1. Materials

Seven commercially available CP standard mixtures C_{10}-C_{13} (SCCP 51.5%Cl), C_{10}-C_{13} (SCCP 55.5%Cl), C_{14}-C_{17} (MCCP 42%Cl), C_{14}-C_{17} (MCCP 52%Cl), C_{14}-C_{17} (MCCP 57%Cl), C_{18}-C_{20} (LCCP 36%Cl), C_{18}-C_{20} (LCCP 49%Cl), and $^{13}C_{10}$-anti-Dechlorane Plus® ($^{13}C_{10}$-anti-DP) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Dust standard reference material (SRM 2585) was purchased from The National Institute of Standards and Technology (NIST) (Gaithersburg, MD, USA). The solvents and chemicals used were all analytical or HLPC grade, unless otherwise stated. Dichloromethane (DCM), methanol, acetone, and n-hexane were purchased from J.T Baker, Deventer, The Netherlands. Whatman® grade 541 filter paper, silica gel, and Florisil® were purchased from Sigma-Aldrich (now Merck), Amsterdam, The Netherlands.

Table S5-1. *Details on samples associated with vacuum cleaner bags (VD), freshly collected dust (FD) and cat hair (CH).*

	VD	FD	C-hair
House 1	VD-1	FD-1	CH-1A, CH-1B
House 2	VD-2	FD-2	CH-2A, CH-2B, CH-2C, CH-2D
House 3	VD-3	FD-3	CH-3
House 4	VD-4	FD-4	CH-4A, CH-4B
House 5	VD-5	FD-5	CH-5
House 6	VD-6	FD-6	CH-6
House 7	VD-7		
House 8	VD-8	FD-8	
House 9	VD-9	FD-9	
House 10	VD-10	FD-10	
House 11	VD-11		

S5.2. Quadrupole time-of-flight mass spectrometry (QTOF-MS) settings

The atmospheric pressure chemical ionization (APCI) source parameters included: vaporizer and drying gas temperatures of 300 °C and 200 °C respectively, and nitrogen gas flow rates of 2.0 L/min for the nebulizer and drying gas. The capillary voltage was set at 2.0 eV and the corona current at 6000 nA. The QTOF-MS was operated in negative ion mode and full scan data was collected from *m/z* 200 to 1500 at a resolution of 25,000 FWHM (full width at half maximum). Internal mass calibration was performed by introducing the Agilent APCI-L low concentration tuning mix (part No: G1969-85010). The standard deviation for the mass calibration was better than 0.3 ppm. The total analysis run time was 4 minutes.

Table S5-2. *Theoretical m/z ratios and isotopic abundances ratios of quantitation and qualifier [M+Cl]$^-$ ions for CPs.*

Formula [M+Cl]$^-$	Quan ion	Qual ion	Ratio (%)	Formula [M+Cl]$^-$	Quan ion	Qual ion	Ratio (%)	Formula [M+Cl]$^-$	Quan ion	Qual ion	Ratio (%)
C9H17Cl3	267.0061	265.0090	77.9	C24H43Cl7	615.0822	613.0850	87.8	C32H47Cl19	1140.7312	1138.7340	96.3
C9H16Cl4	300.9671	302.9642	64.3	C24H42Cl8	649.0432	647.0460	77.0	C32H46Cl20	1174.6922	1172.6950	90.7
C9H15Cl5	334.9281	336.9252	80.2	C24H41Cl9	683.0042	685.0014	86.7	C32H45Cl21	1208.6532	1210.6504	91.9
C9H14Cl6	368.8891	370.8862	96.2	C24H40Cl10	716.9652	718.9624	97.3	C32H44Cl22	1242.6142	1244.6113	97.2
C9H13Cl7	404.8472	402.8502	89.1	C24H39Cl11	752.9234	750.9262	92.6	C32H43Cl23	1278.5723	1276.5752	97.5
C9H12Cl8	438.8083	436.8112	78.0	C24H38Cl12	786.8844	784.8873	84.3	C32H42Cl24	1312.5333	1310.5362	92.7
C9H11Cl9	472.7693	474.7664	85.5	C24H37Cl13	820.8454	822.8426	89.0	C32H41Cl25	1346.4943	1348.4915	92.5
C10H19Cl3	281.0217	279.0246	77.8	C24H36Cl14	854.8064	856.8036	97.0	C32H40Cl26	1380.4554	1382.4525	97.0
C10H18Cl4	314.9828	316.9799	64.3	C24H35Cl15	890.7646	888.7674	95.3	C32H39Cl27	1416.4135	1414.4164	98.4
C10H17Cl5	348.9438	350.9409	80.3	C24H34Cl16	924.7256	922.7284	88.5	C32H38Cl28	1450.3745	1448.3774	94.2
C10H16Cl6	382.9048	384.9019	96.3	C24H33Cl17	958.6866	960.6837	90.4	C32H37Cl29	1484.3355	1486.3327	92.9
C10H15Cl7	418.8629	416.8658	89.1	C24H32Cl18	992.6476	994.6447	96.8	C33H65Cl3	603.3821	601.3846	74.4
C10H14Cl8	452.8239	450.8268	78.0	C24H31Cl19	1028.6057	1026.6086	96.9	C33H64Cl4	637.3430	639.3406	67.7
C10H13Cl9	486.7849	488.7820	85.5	C24H30Cl20	1062.5668	1060.5696	91.3	C33H63Cl5	671.3040	673.3015	83.7
C10H12Cl10	520.7460	522.7430	96.2	C24H29Cl21	1096.5278	1098.5249	91.3	C33H62Cl6	705.2650	707.2624	99.6
C11H21Cl3	295.0374	293.0403	77.7	C24H28Cl22	1130.4888	1132.4859	96.7	C33H61Cl7	741.2233	739.2260	86.6
C11H20Cl4	328.9984	330.9955	64.4	C24H27Cl23	1166.4469	1164.4498	98.0	C33H60Cl8	775.1843	777.1817	77.2
C11H19Cl5	362.9594	364.9565	80.4	C24H26Cl24	1200.4079	1198.4108	93.2	C33H59Cl9	809.1453	811.1426	87.9
C11H18Cl6	396.9205	398.9175	96.4	C25H49Cl3	491.2567	489.2594	76.0	C33H58Cl10	843.1063	845.1036	98.5
C11H17Cl7	432.8786	430.8815	89.0	C25H48Cl4	525.2177	527.2151	66.1	C33H57Cl11	879.0645	877.0673	91.6
C11H16Cl8	466.8396	464.8425	77.9	C25H47Cl5	559.1787	561.1760	82.1	C33H56Cl12	913.0255	911.0283	83.5
C11H15Cl9	500.8006	502.7977	85.6	C25H46Cl6	593.1397	595.1369	98.0	C33H55Cl13	946.9865	948.9837	89.9
C11H14Cl10	534.7616	536.7587	96.3	C25H45Cl7	629.0979	627.1007	87.7	C33H54Cl14	980.9475	982.9447	97.9
C11H13Cl11	570.7197	568.7226	93.5	C25H44Cl8	663.0589	661.0617	76.9	C33H53Cl15	1016.9057	1014.9085	94.5
C12H23Cl3	309.0531	307.0559	77.6	C25H43Cl9	697.0199	699.0171	86.8	C33H52Cl16	1050.8667	1048.8695	87.8
C12H22Cl4	343.0141	345.0112	64.5	C25H42Cl10	730.9809	732.9781	97.4	C33H51Cl17	1084.8277	1086.8249	91.1
C12H21Cl5	376.9751	378.9722	80.5	C25H41Cl11	766.9391	764.9419	92.5	C33H50Cl18	1118.7887	1120.7859	97.5
C12H20Cl6	410.9361	412.9332	96.4	C25H40Cl12	800.9001	798.9029	84.2	C33H49Cl19	1154.7469	1152.7497	96.2
C12H19Cl7	446.8942	444.8971	88.9	C25H39Cl13	834.8611	836.8583	89.1	C33H48Cl20	1188.7079	1186.7107	90.7
C12H18Cl8	480.8552	478.8582	77.9	C25H38Cl14	868.8221	870.8193	97.1	C33H47Cl21	1222.6689	1224.6660	92.0
C12H17Cl9	514.8163	516.8133	85.6	C25H37Cl15	904.7803	902.7831	95.2	C33H46Cl22	1256.6299	1258.6270	97.3
C12H16Cl10	548.7773	550.7744	96.3	C25H36Cl16	938.7413	936.7441	88.5	C33H45Cl23	1292.5880	1290.5909	97.5
C12H15Cl11	584.7354	582.7383	93.5	C25H35Cl17	972.7023	974.6994	90.5	C33H44Cl24	1326.5490	1324.5519	92.7
C12H14Cl12	618.6964	616.6993	85.0	C25H34Cl18	1006.6633	1008.6604	96.9	C33H43Cl25	1360.5100	1362.5072	92.5
C13H25Cl3	323.0687	321.0716	77.6	C25H33Cl19	1042.6214	1040.6243	96.8	C33H42Cl26	1394.4710	1396.4682	97.1
C13H24Cl4	357.0297	359.0269	64.6	C25H32Cl20	1076.5824	1074.5853	91.2	C33H41Cl27	1430.4292	1428.4320	98.4
C13H23Cl5	390.9907	392.9879	80.5	C25H31Cl21	1110.5434	1112.5406	91.4	C33H40Cl28	1464.3902	1462.3930	94.1
C13H22Cl6	424.9518	426.9489	96.5	C25H30Cl22	1144.5044	1146.5016	96.7	C34H67Cl3	617.3978	615.4002	74.2
C13H21Cl7	460.9099	458.9128	88.9	C25H29Cl23	1180.4626	1178.4655	98.0	C34H66Cl4	651.3587	653.3563	68.0
C13H20Cl8	494.8709	492.8738	77.8	C25H28Cl24	1214.4236	1212.4265	93.1	C34H65Cl5	685.3197	687.3172	83.9
C13H19Cl9	528.8319	530.8290	85.7	C25H27Cl25	1248.3846	1250.3817	92.1	C34H64Cl6	719.2807	721.2781	99.8
C13H18Cl10	562.7929	564.7900	96.4	C26H51Cl3	505.2724	503.2750	75.8	C34H63Cl7	755.2390	753.2417	86.4
C13H17Cl11	598.7510	596.7540	93.4	C26H50Cl4	539.2334	541.2307	66.3	C34H62Cl8	789.2000	791.1974	77.4
C13H16Cl12	632.7121	630.7150	85.0	C26H49Cl5	573.1943	575.1917	82.3	C34H61Cl9	823.1610	825.1583	88.0
C13H15Cl13	666.6731	668.6702	88.3	C26H48Cl6	607.1553	609.1526	98.2	C34H60Cl10	857.1219	859.1192	98.6
C14H27Cl3	337.0844	335.0872	77.5	C26H47Cl7	643.1136	641.1164	87.6	C34H59Cl11	893.0802	891.0829	91.5
C14H26Cl4	371.0454	373.0425	64.7	C26H46Cl8	677.0746	675.0774	76.8	C34H58Cl12	927.0412	925.0439	83.4
C14H25Cl5	405.0064	407.0035	80.6	C26H45Cl9	711.0356	713.0328	86.9	C34H57Cl13	961.0022	962.9994	90.0
C14H24Cl6	438.9674	440.9645	96.6	C26H44Cl10	744.9966	746.9938	97.5	C34H56Cl14	994.9632	996.9604	98.0
C14H23Cl7	474.9255	472.9284	88.8	C26H43Cl11	780.9548	778.9576	92.4	C34H55Cl15	1030.9214	1028.9242	94.4
C14H22Cl8	508.8866	506.8895	77.8	C26H42Cl12	814.9158	812.9186	84.2	C34H54Cl16	1064.8824	1062.8852	87.7
C14H21Cl9	542.8476	544.8447	85.8	C26H41Cl13	848.8768	850.8739	89.2	C34H53Cl17	1098.8434	1100.8406	91.2
C14H20Cl10	576.8086	578.8057	96.4	C26H40Cl14	882.8378	884.8349	97.2	C34H52Cl18	1132.8044	1134.8016	97.6
C14H19Cl11	612.7667	610.7696	93.4	C26H39Cl15	918.7959	916.7988	95.1	C34H51Cl19	1168.7625	1166.7654	96.2
C14H18Cl12	646.7277	644.7306	84.9	C26H38Cl16	952.7569	950.7598	88.4	C34H50Cl20	1202.7235	1200.7264	90.6
C14H17Cl13	680.6887	682.6858	88.3	C26H37Cl17	986.7179	988.7151	90.6	C34H49Cl21	1236.6845	1238.6817	92.0
C14H16Cl14	714.6498	716.6469	96.3	C26H36Cl18	1020.6789	1022.6761	96.9	C34H48Cl22	1270.6455	1272.6427	97.4
C15H29Cl3	351.1000	349.1029	77.4	C26H35Cl19	1056.6371	1054.6400	96.8	C34H47Cl23	1306.6037	1304.6065	97.4
C15H28Cl4	385.0610	387.0582	64.8	C26H34Cl20	1090.5981	1088.6010	91.1	C34H46Cl24	1340.5647	1338.5675	92.6
C15H27Cl5	419.0221	421.0192	80.7	C26H33Cl21	1124.5591	1126.5562	91.5	C34H45Cl25	1374.5257	1376.5229	92.6
C15H26Cl6	452.9831	454.9802	96.7	C26H32Cl22	1158.5201	1160.5172	96.8	C34H44Cl26	1408.4867	1410.4839	97.2
C15H25Cl7	488.9412	486.9441	88.7	C26H31Cl23	1194.4783	1192.4811	97.9	C34H43Cl27	1444.4449	1442.4477	98.3
C15H24Cl8	522.9022	520.9051	77.7	C26H30Cl24	1228.4393	1226.4421	93.1	C34H42Cl28	1478.4059	1476.4087	94.1

Formula $[M+Cl]^-$	**Quan ion**	**Qual ion**	**Ratio (%)**	**Formula $[M+Cl]^-$**	**Quan ion**	**Qual ion**	**Ratio (%)**	**Formula $[M+Cl]^-$**	**Quan ion**	**Qual ion**	**Ratio (%)**
C15H23Cl9	556.8632	558.8603	85.8	C26H29Cl25	1262.4003	1264.3974	92.1	C35H69Cl3	631.4135	629.4159	73.9
C15H22Cl10	590.8243	592.8214	96.5	C26H28Cl26	1296.3613	1298.3584	96.7	C35H68Cl4	665.3744	667.3720	68.2
C15H21Cl11	626.7824	624.7853	93.3	C27H53Cl3	519.2881	517.2907	75.6	C35H67Cl5	699.3353	701.3329	84.1
C15H20Cl12	660.7434	658.7463	84.9	C27H52Cl4	553.2490	555.2464	66.5	C35H66Cl6	735.2938	733.2963	100.0
C15H19Cl13	694.7044	696.7015	88.4	C27H51Cl5	587.2100	589.2073	82.4	C35H65Cl7	769.2547	767.2573	86.2
C15H18Cl14	728.6654	730.6625	96.4	C27H50Cl6	621.1710	623.1683	98.4	C35H64Cl8	803.2157	805.2131	77.6
C15H17Cl15	764.6235	762.6265	95.8	C27H49Cl7	657.1293	655.1320	87.4	C35H63Cl9	837.1766	839.1740	88.2
C16H31Cl3	365.1157	363.1185	77.3	C27H48Cl8	691.0902	689.0930	76.7	C35H62Cl10	871.1376	873.1349	98.8
C16H30Cl4	399.0767	401.0739	64.9	C27H47Cl9	725.0512	727.0485	87.0	C35H61Cl11	907.0959	905.0986	91.4
C16H29Cl5	433.0377	435.0349	80.8	C27H46Cl10	759.0122	761.0095	97.7	C35H60Cl12	941.0569	939.0596	83.3
C16H28Cl6	466.9987	468.9959	96.8	C27H45Cl11	794.9704	792.9732	92.3	C35H59Cl13	975.0178	977.0151	90.2
C16H27Cl7	502.9569	500.9598	88.7	C27H44Cl12	828.9314	826.9343	84.1	C35H58Cl14	1008.9788	1010.9761	98.1
C16H26Cl8	536.9179	534.9208	77.6	C27H43Cl13	862.8924	864.8896	89.3	C35H57Cl15	1044.9371	1042.9398	94.3
C16H25Cl9	570.8789	572.8760	85.9	C27H42Cl14	896.8534	898.8506	97.3	C35H56Cl16	1078.8980	1076.9008	87.7
C16H24Cl10	604.8399	606.8370	96.6	C27H41Cl15	932.8116	930.8144	95.0	C35H55Cl17	1112.8590	1114.8563	91.3
C16H23Cl11	640.7980	638.8009	93.3	C27H40Cl16	966.7726	964.7755	88.3	C35H54Cl18	1146.8200	1148.8172	97.7
C16H22Cl12	674.7591	672.7620	84.8	C27H39Cl17	1000.7336	1002.7308	90.6	C35H53Cl19	1182.7782	1180.7810	96.1
C16H21Cl13	708.7201	710.7172	88.4	C27H38Cl18	1034.6946	1036.6918	97.0	C35H52Cl20	1216.7392	1214.7420	90.5
C16H20Cl14	742.6811	744.6782	96.4	C27H37Cl19	1070.6528	1068.6556	96.7	C35H51Cl21	1250.7002	1252.6974	92.1
C16H19Cl15	778.6392	776.6421	95.8	C27H36Cl20	1104.6138	1102.6166	91.1	C35H50Cl22	1284.6612	1286.6584	97.4
C16H18Cl16	812.6002	810.6031	89.0	C27H35Cl21	1138.5748	1140.5719	91.5	C35H49Cl23	1320.6194	1318.6222	97.3
C17H33Cl3	379.1314	377.1342	77.1	C27H34Cl22	1172.5358	1174.5329	96.9	C35H48Cl24	1354.5804	1352.5832	92.5
C17H32Cl4	413.0924	415.0896	65.0	C27H33Cl23	1208.4939	1206.4968	97.9	C35H47Cl25	1388.5414	1390.5386	92.7
C17H31Cl5	447.0534	449.0505	80.9	C27H32Cl24	1242.4549	1240.4578	93.0	C35H46Cl26	1422.5024	1424.4996	97.2
C17H30Cl6	481.0144	483.0115	96.9	C27H31Cl25	1276.4160	1278.4131	92.2	C35H45Cl27	1458.4606	1456.4634	98.2
C17H29Cl7	516.9725	514.9754	88.6	C27H30Cl26	1310.3770	1312.3741	96.7	C35H44Cl28	1492.4216	1490.4244	94.0
C17H28Cl8	550.9336	548.9364	77.6	C27H29Cl27	1346.3351	1344.3380	98.7	C36H71Cl3	645.4291	643.4315	73.7
C17H27Cl9	584.8946	586.8917	86.0	C28H55Cl3	533.3037	531.3063	75.4	C36H70Cl4	679.3901	681.3877	68.4
C17H26Cl10	618.8556	620.8527	96.6	C28H54Cl4	567.2647	569.2621	66.7	C36H69Cl5	713.3510	715.3486	84.3
C17H25Cl11	654.8137	652.8166	93.2	C28H53Cl5	601.2257	603.2230	82.6	C36H68Cl6	749.3095	747.3120	99.7
C17H24Cl12	688.7747	686.7776	84.8	C28H52Cl6	635.1867	637.1840	98.6	C36H67Cl7	783.2704	781.2730	86.1
C17H23Cl13	722.7357	724.7328	88.5	C28H51Cl7	671.1449	669.1477	87.3	C36H66Cl8	817.2313	819.2288	77.7
C17H22Cl14	756.6968	758.6939	96.5	C28H50Cl8	705.1059	703.1087	76.6	C36H65Cl9	851.1923	853.1897	88.3
C17H21Cl15	792.6549	790.6578	95.7	C28H49Cl9	739.0669	741.0642	87.2	C36H64Cl10	885.1533	887.1506	98.9
C17H20Cl16	826.6159	824.6188	88.9	C28H48Cl10	773.0279	775.0251	97.8	C36H63Cl11	921.1116	919.1143	91.3
C17H19Cl17	860.5769	862.5740	90.0	C28H47Cl11	808.9861	806.9889	92.2	C36H62Cl12	955.0725	953.0753	83.2
C18H35Cl3	393.1470	391.1498	77.0	C28H46Cl12	842.9471	840.9499	84.0	C36H61Cl13	989.0335	991.0308	90.3
C18H34Cl4	427.1080	429.1052	65.1	C28H45Cl13	876.9081	878.9053	89.4	C36H60Cl14	1022.9945	1024.9918	98.2
C18H33Cl5	461.0690	463.0662	81.1	C28H44Cl14	910.8691	912.8663	97.4	C36H59Cl15	1058.9527	1056.9555	94.1
C18H32Cl6	495.0301	497.0272	97.0	C28H43Cl15	946.8273	944.8301	94.9	C36H58Cl16	1092.9137	1090.9165	87.6
C18H31Cl7	530.9882	528.9911	88.5	C28H42Cl16	980.7883	978.7911	88.2	C36H57Cl17	1126.8747	1128.8720	91.4
C18H30Cl8	564.9492	562.9521	77.5	C28H41Cl17	1014.7493	1016.7465	90.7	C36H56Cl18	1160.8357	1162.8329	97.8
C18H29Cl9	598.9102	600.9074	86.1	C28H40Cl18	1048.7103	1050.7075	97.1	C36H55Cl19	1196.7939	1194.7967	96.0
C18H28Cl10	632.8712	634.8684	96.7	C28H39Cl19	1084.6685	1082.6713	96.6	C36H54Cl20	1230.7549	1228.7577	90.4
C18H27Cl11	668.8294	666.8323	93.1	C28H38Cl20	1118.6295	1116.6323	91.0	C36H53Cl21	1264.7159	1266.7131	92.2
C18H26Cl12	702.7904	700.7933	84.7	C28H37Cl21	1152.5905	1154.5876	91.6	C36H52Cl22	1298.6769	1300.6741	97.5
C18H25Cl13	736.7514	738.7485	88.6	C28H36Cl22	1186.5515	1188.5486	96.9	C36H51Cl23	1334.6351	1332.6379	97.2
C18H24Cl14	770.7124	772.7095	96.5	C28H35Cl23	1222.5096	1220.5125	97.8	C36H50Cl24	1368.5961	1366.5989	92.5
C18H23Cl15	806.6705	804.6734	95.7	C28H34Cl24	1256.4706	1254.4735	93.0	C36H49Cl25	1402.5571	1404.5543	92.7
C18H22Cl16	840.6316	838.6345	88.9	C28H33Cl25	1290.4316	1292.4288	92.2	C36H48Cl26	1436.5181	1438.5152	97.3
C18H21Cl17	874.5926	876.5897	90.0	C28H32Cl26	1324.3926	1326.3898	96.8	C36H47Cl27	1472.4762	1470.4791	98.2
C18H20Cl18	908.5536	910.5507	96.4	C28H31Cl27	1360.3508	1358.3537	98.7	C37H73Cl3	659.4448	657.4472	73.5
C19H37Cl3	407.1627	405.1655	76.9	C28H30Cl28	1394.3118	1392.3147	94.4	C37H72Cl4	693.4057	695.4034	68.7
C19H36Cl4	441.1237	443.1209	65.2	C29H57Cl3	547.3194	545.3220	75.2	C37H71Cl5	727.3667	729.3643	84.6
C19H35Cl5	475.0847	477.0819	81.2	C29H56Cl4	581.2804	583.2778	66.9	C37H70Cl6	763.3251	761.3277	99.5
C19H34Cl6	509.0457	511.0429	97.2	C29H55Cl5	615.2413	617.2387	82.8	C37H69Cl7	797.2861	795.2886	85.9
C19H33Cl7	545.0039	543.0067	88.4	C29H54Cl6	649.2023	651.1997	98.8	C37H68Cl8	831.2470	833.2444	77.9
C19H32Cl8	578.9649	576.9677	77.4	C29H53Cl7	685.1606	683.1633	87.2	C37H67Cl9	865.2080	867.2054	88.5
C19H31Cl9	612.9259	614.9230	86.2	C29H52Cl8	719.1216	721.1189	76.7	C37H66Cl10	899.1690	901.1663	99.1
C19H30Cl10	646.8869	648.8840	96.8	C29H51Cl9	753.0826	755.0798	87.3	C37H65Cl11	935.1273	933.1299	91.1
C19H29Cl11	682.8450	680.8479	93.1	C29H50Cl10	787.0436	789.0408	97.9	C37H64Cl12	969.0882	967.0909	83.1
C19H28Cl12	716.8061	714.8089	84.7	C29H49Cl11	823.0018	821.0046	92.1	C37H63Cl13	1003.0492	1005.0465	90.4
C19H27Cl13	750.7671	752.7642	88.6	C29H48Cl12	856.9628	854.9656	83.9	C37H62Cl14	1037.0102	1039.0075	98.4
C19H26Cl14	784.7281	786.7252	96.6	C29H47Cl13	890.9238	892.9210	89.5	C37H61Cl15	1072.9684	1070.9712	94.0
C19H25Cl15	820.6862	818.6891	95.6	C29H46Cl14	924.8848	926.8820	97.5	C37H60Cl16	1106.9294	1104.9322	87.5
C19H24Cl16	854.6472	852.6501	88.8	C29H45Cl15	960. 8430	958.8458	94.8	C37H59Cl17	1140.8904	1142.8876	91.5

Formula $[M+Cl]^-$	Quan ion	Qual ion	Ratio (%)	Formula $[M+Cl]^-$	Quan ion	Qual ion	Ratio (%)	Formula $[M+Cl]^-$	Quan ion	Qual ion	Ratio (%)
C19H23Cl17	888.6082	890.6053	90.1	C29H44Cl16	994.8040	992.8068	88.2	C37H58Cl18	1174.8514	1176.8486	97.9
C19H22Cl18	922.5693	924.5664	96.5	C29H43Cl17	1028.7650	1030.7621	90.8	C37H57Cl19	1210.8096	1208.8124	95.9
C19H21Cl19	958.5274	956.5303	97.2	C29H42Cl18	1062.7260	1064.7231	97.2	C37H56Cl20	1244.7706	1242.7734	90.4
C20H39Cl3	421.1784	419.1811	76.7	C29H41Cl19	1098.6841	1096.6870	96.6	C37H55Cl21	1278.7316	1280.7288	92.3
C20H38Cl4	455.1394	457.1366	65.4	C29H40Cl20	1132.6451	1130.6480	90.9	C37H54Cl22	1312.6926	1314.6898	97.6
C20H37Cl5	489.1004	491.0976	81.3	C29H39Cl21	1166.6061	1168.6033	91.7	C37H53Cl23	1348.6508	1346.6536	97.2
C20H36Cl6	523.0614	525.0586	97.3	C29H38Cl22	1200.5671	1202.5643	97.0	C37H52Cl24	1382.6118	1380.6146	92.4
C20H35Cl7	559.0195	557.0224	88.3	C29H37Cl23	1236.5253	1234.5282	97.7	C37H51Cl25	1416.5728	1418.5699	92.8
C20H34Cl8	592.9806	590.9834	77.4	C29H36Cl24	1270.4863	1268.4892	92.9	C37H50Cl26	1450.5338	1452.5309	97.4
C20H33Cl9	626.9416	628.9387	86.2	C29H35Cl25	1304.4473	1306.4444	92.3	C37H49Cl27	1486.4919	1484.4948	98.1
C20H32Cl10	660.9026	662.8997	96.9	C29H34Cl26	1338.4083	1340.4055	96.8	C38H75Cl3	673.4605	671.4628	73.2
C20H31Cl11	696.8607	694.8636	93.0	C29H33Cl27	1374.3665	1372.3693	98.6	C38H74Cl4	707.4214	709.4191	68.9
C20H30Cl12	730.8217	728.8246	84.6	C29H32Cl28	1408.3275	1406.3303	94.4	C38H73Cl5	741.3824	743.3800	84.8
C20H29Cl13	764.7827	766.7799	88.7	C29H31Cl29	1442.2885	1444.2856	92.7	C38H72Cl6	777.3408	775.3433	99.3
C20H28Cl14	798.7438	800.7409	96.7	C30H59Cl3	561.3351	559.3376	75.0	C38H71Cl7	811.3017	809.3043	85.7
C20H27Cl15	834.7019	832.7048	95.5	C30H58Cl4	595.2960	597.2935	67.1	C38H70Cl8	845.2627	847.2601	78.1
C20H26Cl16	868.6629	866.6658	88.8	C30H57Cl5	629.2570	631.2544	83.0	C38H69Cl9	879.2237	881.2211	88.7
C20H25Cl17	902.6239	904.6210	90.2	C30H56Cl6	663.2180	665.2153	99.0	C38H68Cl10	913.1846	915.1820	99.3
C20H24Cl18	936.5849	938.5820	96.5	C30H55Cl7	699.1763	697.1790	87.0	C38H67Cl11	949.1429	947.1456	91.0
C20H23Cl19	972.5430	970.5459	97.1	C30H54Cl8	733.1373	735.1346	76.8	C38H66Cl12	983.1039	981.1066	83.0
C20H22Cl20	1006.5041	1004.5070	91.5	C30H53Cl9	767.0983	769.0955	87.4	C38H65Cl13	1017.0649	1019.0622	90.5
C21H41Cl3	435.1940	433.1968	76.6	C30H52Cl10	801.0592	803.0565	98.1	C38H64Cl14	1051.0259	1053.0232	98.5
C21H40Cl4	469.1550	471.1523	65.5	C30H51Cl11	837.0175	835.0202	92.0	C38H63Cl15	1086.9841	1084.9869	93.9
C21H39Cl5	503.1160	505.1132	81.5	C30H50Cl12	870.9785	868.9813	83.8	C38H62Cl16	1120.9451	1118.9478	87.4
C21H38Cl6	537.0770	539.0742	97.4	C30H49Cl13	904.9395	906.9367	89.6	C38H61Cl17	1154.9061	1156.9033	91.6
C21H37Cl7	573.0352	571.0380	88.2	C30H48Cl14	938.9005	940.8977	97.6	C38H60Cl18	1188.8671	1190.8643	98.0
C21H36Cl8	606.9962	604.9991	77.3	C30H47Cl15	974.8586	972.8615	94.7	C38H59Cl19	1224.8253	1222.8281	95.8
C21H35Cl9	640.9572	642.9544	86.3	C30H46Cl16	1008.8196	1006.8225	88.1	C38H58Cl20	1258.7863	1256.7891	90.3
C21H34Cl10	674.9182	676.9154	97	C30H45Cl17	1042.7806	1044.7778	90.9	C38H57Cl21	1292.7473	1294.7445	92.4
C21H33Cl11	710.8764	708.8793	92.9	C30H44Cl18	1076.7416	1078.7388	97.3	C38H56Cl22	1326.7083	1328.7055	97.7
C21H32Cl12	744.8374	742.8403	84.5	C30H43Cl19	1112.6998	1110.7026	96.5	C38H55Cl23	1362.6665	1360.6693	97.1
C21H31Cl13	778.7984	780.7955	88.8	C30H42Cl20	1146.6608	1144.6637	90.9	C38H54Cl24	1396.6274	1394.6303	92.3
C21H30Cl14	812.7594	814.7565	96.8	C30H41Cl21	1180.6218	1182.6190	91.7	C38H53Cl25	1430.5884	1432.5856	92.9
C21H29Cl15	848.7176	846.7204	95.5	C30H40Cl22	1214.5828	1216.5800	97.1	C38H52Cl26	1464.5494	1466.5466	97.5
C21H28Cl16	882.6786	880.6815	88.7	C30H39Cl23	1250.5410	1248.5438	97.7	C39H77Cl3	687.4762	685.4785	73.0
C21H27Cl17	916.6396	918.6367	90.2	C30H38Cl24	1284.5020	1282.5048	92.8	C39H76Cl4	721.4371	723.4348	69.2
C21H26Cl18	950.6006	952.5977	96.6	C30H37Cl25	1318.4630	1320.4601	92.3	C39H75Cl5	755.3980	757.3956	85.1
C21H25Cl19	986.5587	984.5616	97.1	C30H36Cl26	1352.4240	1354.4211	96.9	C39H74Cl6	791.3565	789.3590	99.0
C21H24Cl20	1020.5197	1018.5226	91.4	C30H35Cl27	1388.3821	1386.3850	98.6	C39H73Cl7	825.3174	823.3200	85.5
C21H23Cl21	1054.4807	1056.4779	91.2	C30H34Cl28	1422.3431	1420.3460	94.3	C39H72Cl8	859.2784	861.2758	78.2
C22H43Cl3	449.2097	447.2124	76.5	C30H33Cl29	1456.3042	1458.3013	92.8	C39H71Cl9	893.2393	895.2368	88.8
C22H42Cl4	483.1707	485.1680	65.7	C30H32Cl30	1490.2652	1492.2623	96.8	C39H70Cl10	927.2003	929.1977	99.5
C22H41Cl5	517.1317	519.1289	81.6	C31H61Cl3	575.3508	573.3533	74.8	C39H69Cl11	963.1586	961.1613	90.8
C22H40Cl6	551.0927	553.0899	97.6	C31H60Cl4	609.3117	611.3092	67.3	C39H68Cl12	997.1196	995.1223	82.8
C22H39Cl7	587.0509	585.0537	88.1	C31H59Cl5	643.2727	645.2701	83.2	C39H67Cl13	1031.0806	1033.0779	90.7
C22H38Cl8	621.0119	619.0147	77.2	C31H58Cl6	677.2337	679.2310	99.2	C39H66Cl14	1065.0415	1067.0388	98.6
C22H37Cl9	654.9729	656.9701	86.4	C31H57Cl7	713.1920	711.1947	86.9	C39H65Cl15	1100.9998	1099.0025	93.8
C22H36Cl10	688.9339	690.9311	97.1	C31H56Cl8	747.1529	749.1503	76.9	C39H64Cl16	1134.9608	1132.9635	87.3
C22H35Cl11	724.8921	722.8949	92.8	C31H55Cl9	781.1139	783.1112	87.6	C39H63Cl17	1168.9218	1170.9190	91.7
C22H34Cl12	758.8531	756.8559	84.5	C31H54Cl10	815.0749	817.0722	98.2	C39H62Cl18	1202.8827	1204.8800	98.1
C22H33Cl13	792.8141	794.8112	88.8	C31H53Cl11	851.0332	849.0359	91.9	C39H61Cl19	1238.8410	1236.8437	95.7
C22H32Cl14	826.7751	828.7722	96.8	C31H52Cl12	884.9941	882.9969	83.7	C39H60Cl20	1272.8020	1270.8047	90.2
C22H31Cl15	862.7332	860.7361	95.4	C31H51Cl13	918.9551	920.9524	89.7	C39H59Cl21	1306.7629	1308.7602	92.5
C22H30Cl16	896.6942	894.6971	88.6	C31H50Cl14	952.9161	954.9133	97.7	C39H58Cl22	1340.7239	1342.7212	97.8
C22H29Cl17	930.6552	932.6524	90.3	C31H49Cl15	988.8743	986.8771	94.7	C39H57Cl23	1376.6821	1374.6849	97.0
C22H28Cl18	964.6163	966.6134	96.7	C31H48Cl16	1022.8353	1020.8381	88.0	C39H56Cl24	1410.6431	1408.6459	92.2
C22H27Cl19	1000.5744	998.5773	97	C31H47Cl17	1056.7963	1058.7935	91.0	C39H55Cl25	1444.6041	1446.6013	93.0
C22H26Cl20	1034.5354	1032.5383	91.4	C31H46Cl18	1090.7573	1092.7545	97.3	C39H54Cl26	1478.5651	1480.5623	97.5
C22H25Cl21	1068.4964	1070.4935	91.2	C31H45Cl19	1126.7155	1124.7183	96.4	C40H79Cl3	701.4919	699.4941	72.7
C22H24Cl22	1102.4574	1104.4545	96.6	C31H44Cl20	1160.6765	1158.6793	90.8	C40H78Cl4	735.4528	737.4506	69.5
C23H45Cl3	463.2254	461.2281	76.3	C31H43Cl21	1194.6375	1196.6347	91.8	C40H77Cl5	769.4137	771.4113	85.3
C23H44Cl4	497.1864	499.1837	65.8	C31H42Cl22	1228.5985	1230.5957	97.1	C40H76Cl6	805.3722	803.3747	98.8
C23H43Cl5	531.1474	533.1446	81.8	C31H41Cl23	1264.5567	1262.5595	97.6	C40H75Cl7	839.3331	837.3356	85.3
C23H42Cl6	565.1084	567.1056	97.7	C31H40Cl24	1298.5177	1296.5205	92.8	C40H74Cl8	873.2941	875.2916	78.4
C23H41Cl7	601.0666	599.0694	88	C31H39Cl25	1332.4787	1334.4758	92.4	C40H73Cl9	907.2550	909.2524	89.0
C23H40Cl8	635.0276	633.0304	77.1	C31H38Cl26	1366.4397	1368.4368	97.0	C40H72Cl10	941.2160	943.2134	99.6

Formula $[M+Cl]^-$	Quan ion	Qual ion	Ratio (%)	Formula $[M+Cl]^-$	Quan ion	Qual ion	Ratio (%)	Formula $[M+Cl]^-$	Quan ion	Qual ion	Ratio (%)
C23H39Cl9	668.9886	670.9857	86.5	C31H37Cl27	1402.3978	1400.4007	98.5	C40H71Cl11	977.1743	975.1770	90.7
C23H38Cl10	702.9496	704.9467	97.2	C31H36Cl28	1436.3588	1434.3617	94.3	C40H70Cl12	1011.1353	1013.1326	82.8
C23H37Cl11	738.9077	736.9106	92.7	C31H35Cl29	1470.3198	1472.3170	92.9	C40H69Cl13	1045.0962	1047.0936	90.8
C23H36Cl12	772.8687	770.8716	84.4	C32H63Cl3	589.3664	587.3689	74.6	C40H68Cl14	1079.0572	1081.0545	98.8
C23H35Cl13	806.8297	808.8269	88.9	C32H62Cl4	623.3274	625.3249	67.5	C40H67Cl15	1115.0155	1113.0182	93.7
C23H34Cl14	840.7908	842.7879	96.9	C32H61Cl5	657.2883	659.2858	83.4	C40H66Cl16	1148.9765	1146.9792	87.2
C23H33Cl15	876.7489	874.7518	95.3	C32H60Cl6	691.2493	693.2467	99.4	C40H65Cl17	1182.9374	1184.9347	91.9
C23H32Cl16	910.7099	908.7128	88.6	C32H59Cl7	727.2077	725.2103	86.7	C40H64Cl18	1216.8984	1218.8957	98.2
C23H31Cl17	944.6709	946.6680	90.3	C32H58Cl8	761.1686	763.1660	77.1	C40H63Cl19	1252.8567	1250.8594	95.6
C23H30Cl18	978.6319	980.6291	96.7	C32H57Cl9	795.1296	797.1269	87.7	C40H62Cl20	1286.8177	1284.8204	90.1
C23H29Cl19	1014.5901	1012.5929	97	C32H56Cl10	829.0906	831.0879	98.3	C40H61Cl21	1320.7786	1322.7759	92.6
C23H28Cl20	1048.5511	1046.5540	91.3	C32H55Cl11	865.0488	863.0516	91.8	C40H60Cl22	1354.7396	1356.7369	97.9
C23H27Cl21	1082.5121	1084.5092	91.3	C32H54Cl12	899.0098	897.0126	83.6	C40H59Cl23	1390.6978	1388.7006	96.9
C23H26Cl22	1116.4731	1118.4702	96.6	C32H53Cl13	932.9708	934.9681	89.8	C40H58Cl24	1424.6588	1422.6616	92.2
C23H25Cl23	1152.4312	1150.4341	98.1	C32H52Cl14	966.9318	968.9290	97.8	C40H57Cl25	1458.6198	1460.6170	93.0
C24H47Cl3	477.2410	475.2437	76.1	C32H51Cl15	1002.8900	1000.8928	94.6	C40H56Cl26	1492.5808	1494.5780	97.6
C24H46Cl4	511.2020	513.1994	66	C32H50Cl16	1036.8510	1034.8538	87.9				
C24H45Cl5	545.1630	547.1603	81.9	C32H49Cl17	1070.8120	1072.8092	91.1				
C24H44Cl6	579.1240	581.1213	97.9	C32H48Cl18	1104.7730	1106.7702	97.4				

Table S5-3. *Calculated degree of chlorination for the ΣSCCP, ΣMCCP and ΣLCCP technical mixtures.*

Technical mixture	Calculated Cl-degree
SCCP (51.5%)	55.5%
SCCP (55.5%)	57.8%
MCCP (42%)	49.3%
MCCP (52%)	54.1%
MCCP (57%)	57.4%
LCCP (36%)	38.2%
LCCP (49%)	49.3%

Table S5-4. *Total ΣSCCPs, ΣMCCPs and ΣLCCPs concentration in µg/g measured in the dust reference material (SRM 2585) with the degree of chlorination. The goodness of fit (R^2) below 0.5 are given in Italic and highlighted red with indicated that the reported values are tentative.*

Sample	SCCP (µg/g)	R^2	Cl %	MCCP (µg/g)	R^2	Cl %	LCCP (µg/g)	R^2
NIST 2585(1)	8.5	0.8	59%	11.9	0.7	52%	19.1	*<0.1*
NIST 2585(2)	8.6	0.8	59%	11.6	0.7	52%	18.1	*<0.1*
NIST 2585(3)	8.9	0.8	59%	12.4	0.7	52%	19.6	*<0.1*
NIST 2585(4)	8.8	0.8	59%	11.9	0.7	52%	19.0	*<0.1*
NIST 2585(5)	8.5	0.8	59%	11.7	0.7	52%	19.0	*<0.1*
NIST 2585(6)	8.9	0.8	59%	12.0	0.7	52%	19.6	*<0.1*
NIST 2585(7)	8.6	0.8	59%	12.2	0.7	52%	20.1	*<0.1*
NIST 2585(8)	8.5	0.8	59%	12.1	0.7	52%	19.6	*<0.1*
NIST 2585(9)	8.5	0.8	59%	12.1	0.7	52%	19.2	*<0.1*

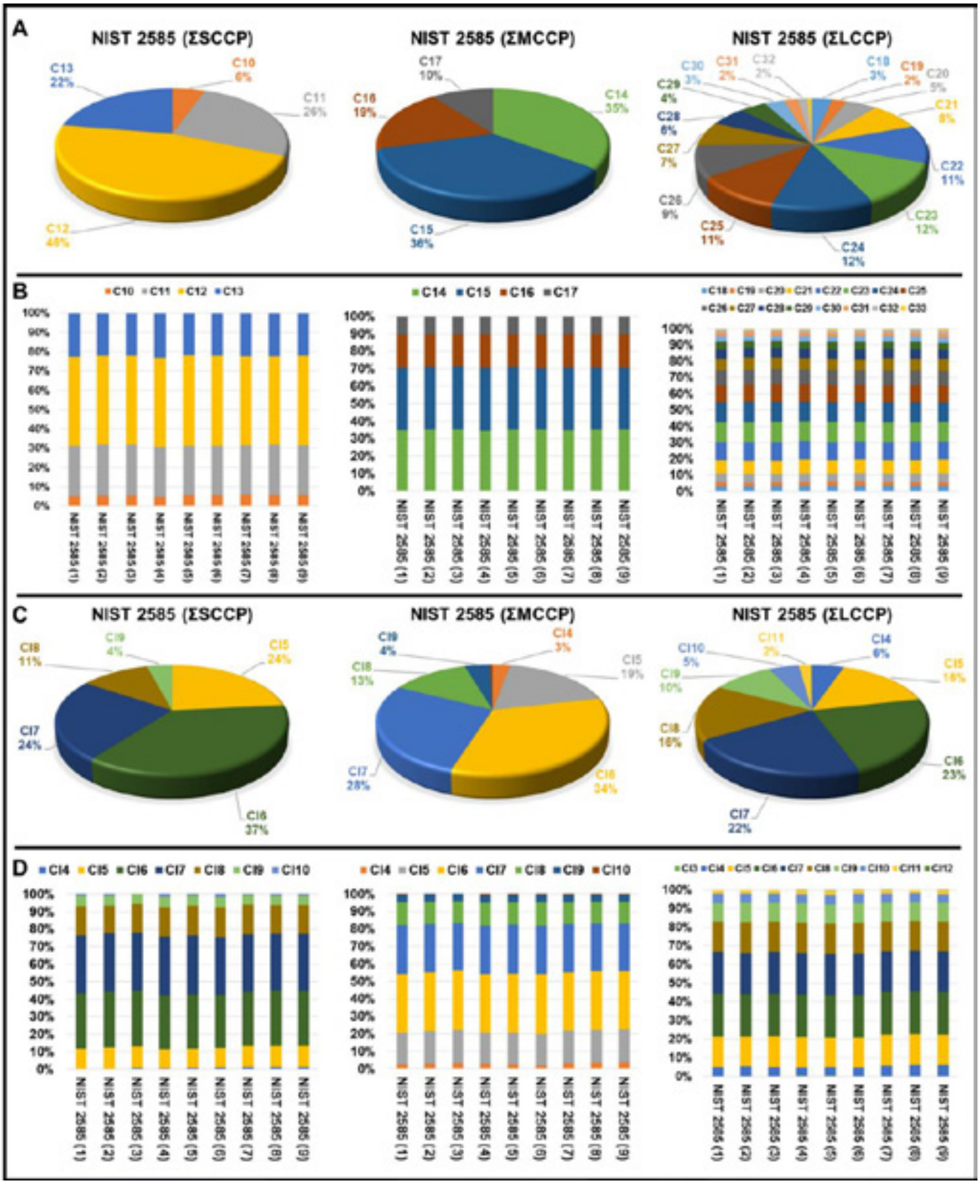

Figure S5-1. *Composition of CPs in the dust reference material (SRM 2585) (A), ΣSCCP, ΣMCCP, and ΣLCCP composition based on carbon chain length, (B) ΣSCCP, ΣMCCP, and ΣLCCP carbon chain length in the repeat measurements, (C) ΣSCCP, ΣMCCP, and ΣLCCP composition based on chlorine substitution, (D) ΣSCCP, ΣMCCP, and ΣLCCP chlorine substitution in the repeat measurements.*

S5.3. The use of non-traditional Kendrick MD plots for the identification of CP congeners

An average full scan mass spectrum of the chromatographic peaks was extracted using Bruker Compass DataAnalysis software and the accurate mass list was exported to Microsoft Excel. The non-traditional Kendrick MD plots were constructed by converting the measured IUPAC *m/z* to [−H/+Cl] mass scales corresponding to the mass of a chlorine atom minus the mass of a hydrogen atom.

$$Accurate\ H/Cl\ scaled\ mass = Accurate\ mass\ (IUPAC\ mass)\ \times \left(\frac{34}{33.961028}\right)$$

$$H/Cl\ \ scaled\ mass\ detect = nominal\ mass\ (rounded) -\ accurate\ H/Cl\ scaled\ mass$$

As shown in Figure S5-2, the Kendrick MD plots are graphically constructed as bubble plots by positioning the accurate masses on the x-axis and the corresponding H/Cl scaled mass defects on the y-axis with peak intensity as the bubble size. The CP congeners with the same carbon chain length (C_9 to C_{40}) and increased degree of substitution (Cl_3 <) are positioned on horizontal lines separated by H/Cl substitution. The congeners with the same degree of substitution and increased carbon chain length are positioned on diagonal lines. The coloured spheres in the Kendrick MD plots represent the quantifier and qualifier $[M+Cl]^-$ ions for SCCPs (red), MCCPs (green) and LCCPs (blue) which were positively identified based on the criteria discussed in the quantitation and deconvolution section. To briefly explain the outlay of the plot using C_{19}-congeners as an example, the $[M+Cl]^-$ IUPAC masses for $C_{19}H_{34}Cl_6$, $C_{19}H_{33}Cl_7$, and $C_{19}H_{32}Cl_8$ are 507.0486, 541.0096, and 574.9706 respectively. These masses are then converted to the H/Cl scaled masses, resulting in 507.6304, 541.6304, and 575.6304. By subtracting the new accurate H/Cl scaled masse from the rounded nominal mass, the H/Cl scaled mass defect for all three C_{19}-congeners is 0.6304. As shown in the enlarged region in Figure S5-2B, these C_{19}-congeners are positioned on a horizontal line separated by H/Cl substitution. The CP congeners with carbon chains C_{31} to C_{40} appear at the bottom of the plot resulting in “wrap-around” due to the increase in mass defect as a result of the high proportion of hydrogen atoms. For example, when the IUPAC masses for $C_{30}H_{59}Cl_3$ (559.3376) and $C_{31}H_{61}Cl_3$ (573.3533) are converted to the respective H/Cl scaled masses, the new accurate H/Cl scaled masses are 559.9795 and 574.0112. The H/Cl scaled mass defect for $C_{30}H_{59}Cl_3$ is 0.9795, which are positioned at the top of the plot, and $C_{31}H_{61}Cl_3$ is 0.0112 which “wrap-around” to be positioned at the bottom of the plot.

As shown in Figure S5-2B and S2C, the pattern observed for the VD-6 differs from the pattern observed for VD 2, where more abundant C_{19} and congeners >C_{29} were observed. The enlarged section shows the difference between measured and theoretical masses for the C_{19} homologue group ($C_{19}H_{35}Cl_5$ to $C_{19}H_{28}Cl_{12}$) depicted as black circles. The accurate masses for these congeners were within 10 ppm of the theoretical masses, but the ion ratios varied by more than 40% from the theoretical ion ratios (Figure S3). This was also observed for the CP congeners with carbon lengths of C_{30} and longer. This emphasises the use of strict mass accuracy criteria and the use of ion pair intensity ratios to distinguish between positive identified CPs and the presence of possible interferences. This pattern was also observed for the cat hair (CH-6) taken from the same household.

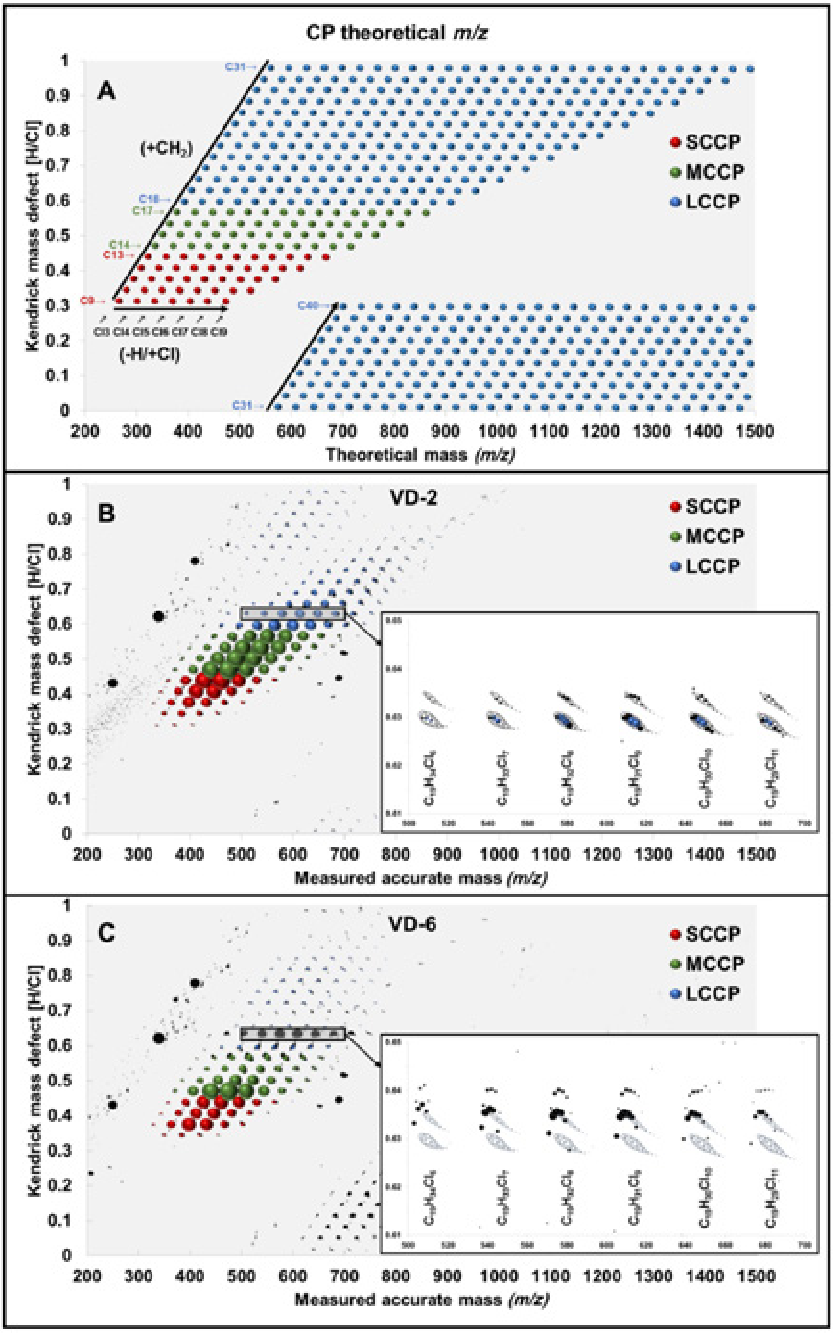

Figure S5-2. *Non-traditional Kendrick MD plots, (A) constructed from the theoretical m/z quantitation and qualifier [M+Cl]- ions for CPs listed in Table S5-1 (see text below for detailed explanation), (B) constructed for VD-2, (C) and VD-6. The red spheres represent the quantifier and qualifier [M+Cl]$^-$ ions for SCCPs, the green for MCCPs and the blue for LCCPs the sphere size represent the instrument response. The enlarged region shows the theoretical m/z and ion intensity ratios for* $C_{19}H_{34}Cl_6$ *to* $C_{19}H_{29}Cl_{11}$ *depicted as black circles.*

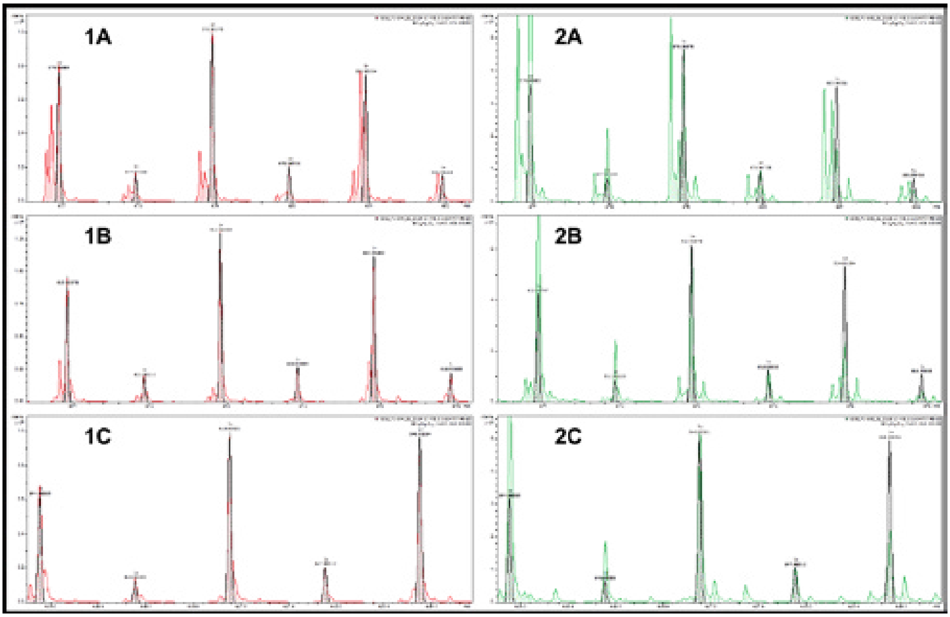

Figure S5-3. *Negative ion APCI-qTOF-MS mass scale-expanded segments of the mass spectra extracted for (A) $C_{19}H_{32}Cl_8$, (B) $C_{19}H_{31}Cl_9$, and (C) $C_{19}H_{30}Cl_{10}$ from (1) VD-2 in red and (2) VD-6 in green. The black profile represents the mass spectra for the theoretical $[M+Cl]^-$ ions of the respective congeners. This figure emphasises the ion ratio deviation observed for VD-6.*

Table S5-5. *Total ΣSCCPs, ΣMCCPs, and ΣLCCPs concentration in µg/g for VD, FD and CH with the degree of chlorination. The goodness of fit (R^2) below 0.5 are given in Italic and highlighted red with indicated that the reported values are tentative.*

Sample	SCCP (µg/g)	R^2	Cl %	MCCP (µg/g)	R^2	Cl %	LCCP (µg/g)	R^2	Cl %
VD-1	19	0.8	58%	34	0.9	54%	4.3	0.7	50%
VD-2	214	0.8	58%	200	0.5	56%	74	*0.4*	54%
VD-3	8.6	0.7	57%	13	0.9	55%	23	*0.1*	50%
VD-4	58	0.6	59%	86	0.9	56%	14	0.5	52%
VD-5	14	0.6	59%	46	0.9	55%	7.7	0.6	48%
VD-6	136	0.8	59%	84	1.0	56%	8.6	0.5	48%
VD-7	10	0.6	59%	40	0.8	55%	13	*0.4*	43%
VD-8	5.1	0.5	58%	16	0.9	55%	14	*<0.1*	38%
VD-9	12	0.7	58%	54	0.8	55%	8.8	0.7	48%
VD-10	7.5	0.7	59%	22	0.9	55%	6.2	0.6	46%
VD-11	44	0.7	59%	165	0.8	55%	19	0.7	51%
FD-1	9.3	0.7	59%	21	0.9	55%	2.5	0.5	51%
FD-2	25	0.7	58%	47	0.8	55%	24	*0.2*	39%
FD-3	30	0.6	58%	62	0.9	55%	1.9	0.5	51%
FD-4	93	0.6	57%	259	0.9	55%	28	0.7	52%
FD-5	353	0.8	58%	283	0.9	56%	27	0.5	53%
FD-6	10	0.6	56%	498	0.6	56%	108	0.8	52%
FD-8	5.4	0.7	58%	46	0.8	55%	9.4	0.8	47%
FD-9	12	0.7	58%	29	0.9	55%	5.9	0.6	48%
FD-10	17	0.6	59%	36	0.9	55%	7.2	0.7	49%
CH-1A	1.5	0.6	59%	4.6	0.7	56%	0.9	0.6	53%
CH-1B	2.0	0.7	59%	4.0	0.9	56%	0.7	0.5	53%
CH-2A	3.0	0.8	58%	5.8	0.9	55%	2.3	*0.1*	38%
CH-2B	1.7	0.7	59%	2.6	0.9	55%	1.0	*0.4*	43%
CH-2C	2.4	0.8	58%	3.2	0.9	54%	1.6	*0.1*	37%
CH-2D	2.0	0.7	58%	3.2	0.9	55%	0.9	*0.4*	42%
CH-3	0.5	0.7	57%	0.6	0.9	54%	0.1	0.5	50%
CH-4A	7.2	0.7	58%	6.5	1.0	55%	0.9	0.5	52%
CH-4B	6.2	0.8	58%	4.7	1.0	55%	0.6	0.6	52%
CH-5	2.2	0.5	57%	4.8	1.0	55%	0.8	0.5	47%
CH-6	0.8	0.7	57%	1.4	0.9	54%	0.2	0.6	48%

Table S5-6. *Comparisons of ΣSCCP, ΣMCCP and ΣLCCP concentrations (µg/g) in indoor dust.*

Country	Dust type	ΣSCCP (µg/g) Median (Range)	ΣMCCP (µg/g) Median (Range)	ΣLCCP (µg/g) Median (Range)	Reference
Sweden	Apartment	7.5 (3.2 - 18.0)			(Fridén *et al.*, 2011)
Germany (n=11)	House	5 (4 - 27)	176 (9 - 892)		(Hilger *et al.*, 2013)
Taiwan (n=5)	House/office	(1.2 - 31.2)			(Chen *et al.*, 2016)
China (n=14)	Building[a]	76.7 (6.0 - 361.4)	101.7 (5.0 - 285.9)		(Shi et al., 2017)
Australia (n=1)	Office	61	180	99	(Wong *et al.*, 2017)
Canada (n=4)	Office	55 (22 - 65)	185 (140 - 192)	134 (92 - 161)	(Wong *et al.*, 2017)
China (n=5)	Office	580 (106 - 808)	1398 (330 - 1948)	1432 (153 - 1995)	(Wong *et al.*, 2017)
Sweden (n=3)	Office	7 (5 - 9)	101 (67 - 158)	710 (567 - 1264)	(Wong *et al.*, 2017)
UK (n=1)	House	93	463	157	(Wong *et al.*, 2017)
China (n=30)	Apartment	44.1 (10.1 - 158.2)			(Liu *et al.*, 2017)
China (n=5)	Office	50.9 (40.5 - 80.6)			(Liu *et al.*, 2017)
China (n=22)	Commercial store	53.8 (13.3 - 173)			(Liu *et al.*, 2017)
China (n=15)	House	46.5 (27.8 - 173)	166 (74 - 539)		(Chen *et al.*, 2018)
China (n=30)	Houses[b]	412 (34.5 - 2030)	1250 (79.2 - 6510)		(Chen *et al.*, 2018)
China (n=20)	Apartment/office	(0 - 171)			(Huang *et al.*, 2018)
China (n=115)	House	98.7 (5.35 – 1022)	89.8 (2.10 – 725)		(Gao *et al.*, 2018)
Canada (n=48)	House	6.2 (4 - 57)	19 (5.9 - 901.0)		(Shang *et al.*, 2019)
Australia (n=27)	House	13* (1.0 – 42)	46 (8.8 – 380)	3.0* (<0.0014 – 15)	(He et al., 2019)
South Africa (n=20)	House	16 (5.1 - 353)	46 (13 - 498)	11 (1.9 - 108)	This study

*Average
[a] Building material mall
[b] Near E-waste site

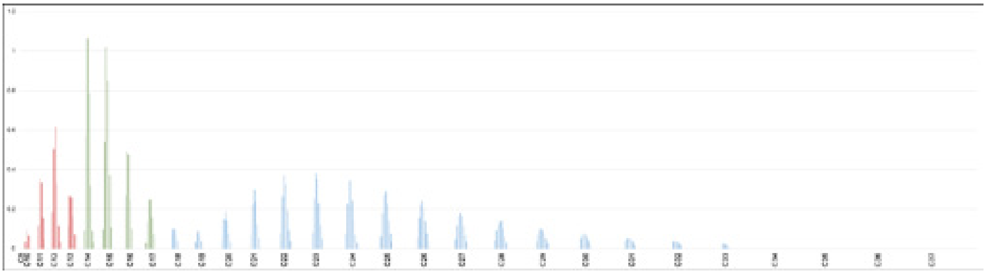

Figure S5-4. *Congener group patterns of CPs for NIST 2585 (1).*

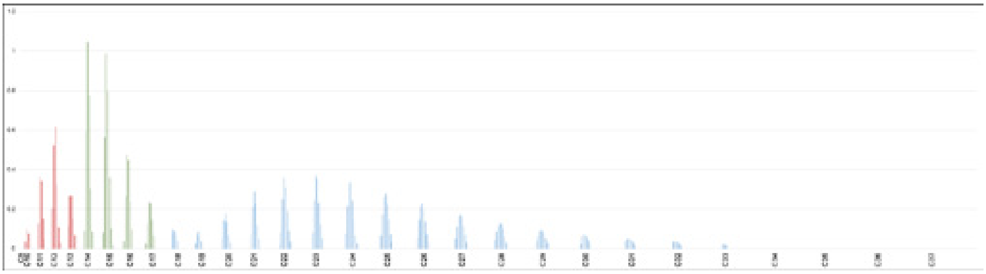

Figure S5-5. *Congener group patterns of CPs for NIST 2585 (2).*

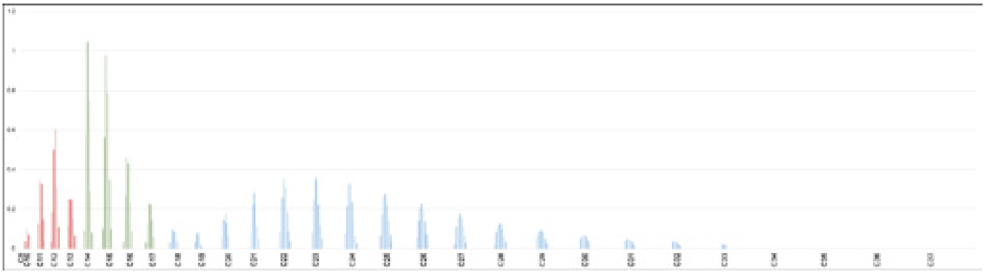

Figure S5-6. *Congener group patterns of CPs for NIST 2585 (3).*

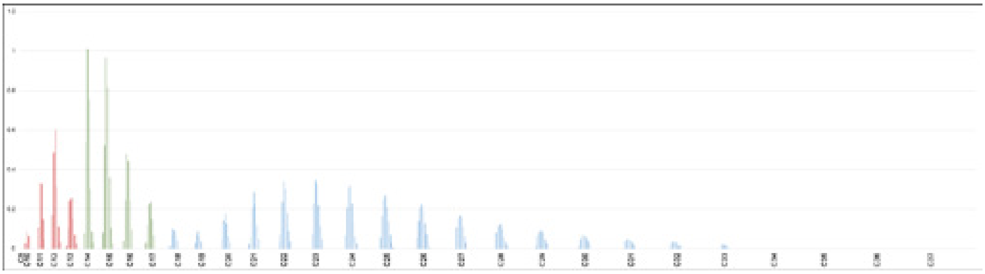

Figure S5-7. *Congener group patterns of CPs for NIST 2585 (4).*

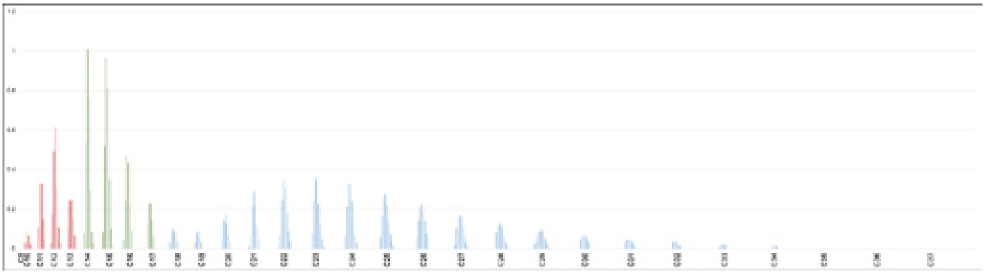

Figure S5-8. *Congener group patterns of CPs for NIST 2585 (5).*

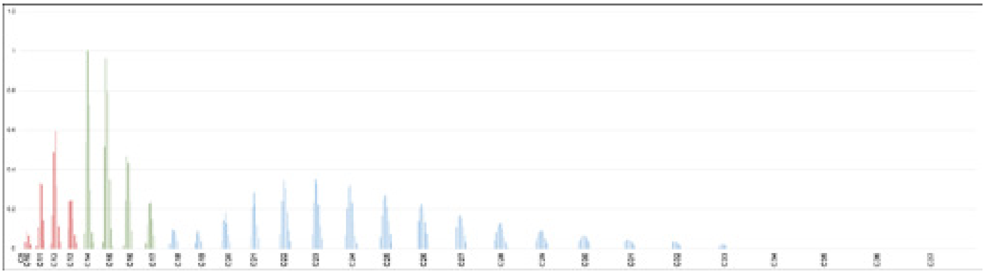

Figure S5-9. *Congener group patterns of CPs for NIST 2585 (6).*

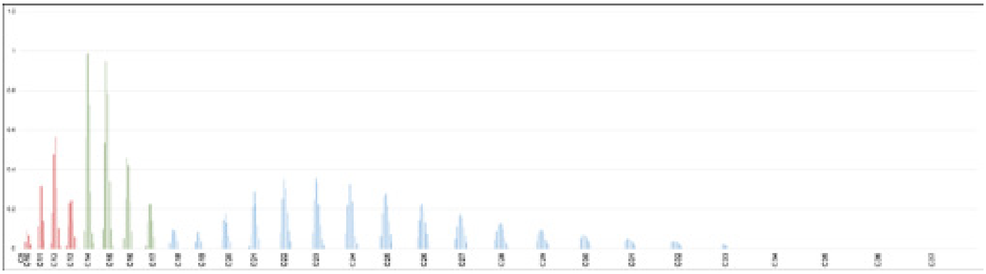

Figure S5-10. *Congener group patterns of CPs for NIST 2585 (7).*

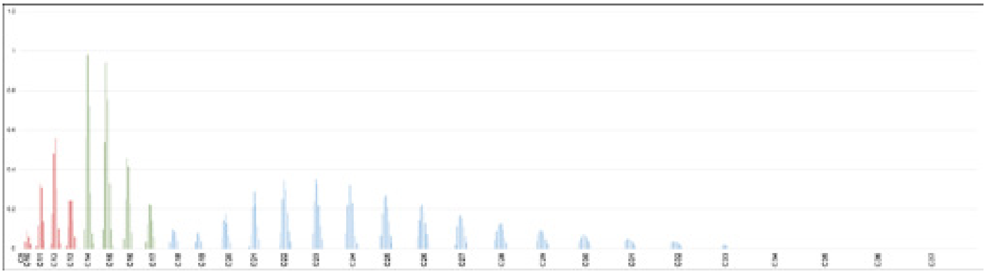

Figure S5-11. *Congener group patterns of CPs for NIST 2585 (8).*

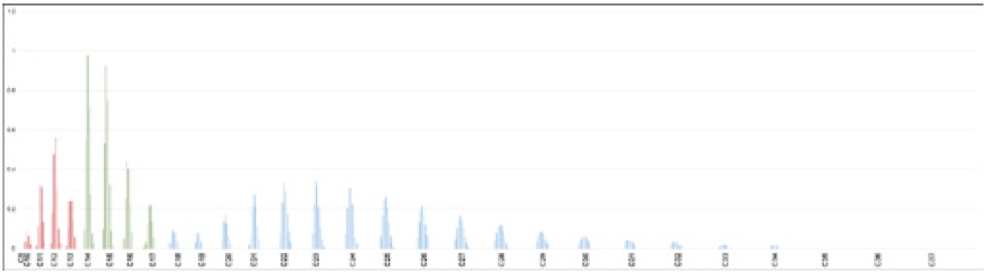

Figure S5-12. *Congener group patterns of CPs for NIST 2585 (9).*

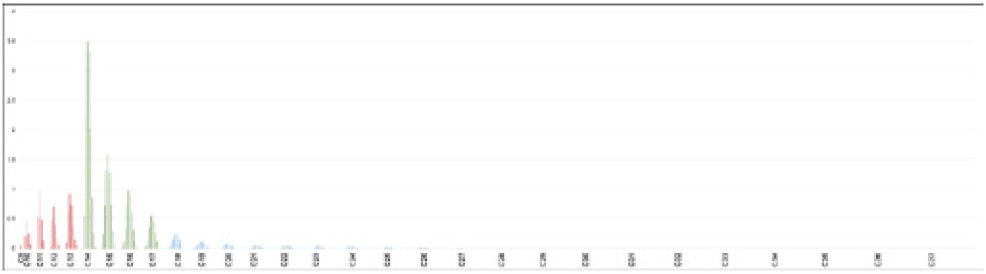

Figure S5-13. *Congener group patterns of CPs for VD-1.*

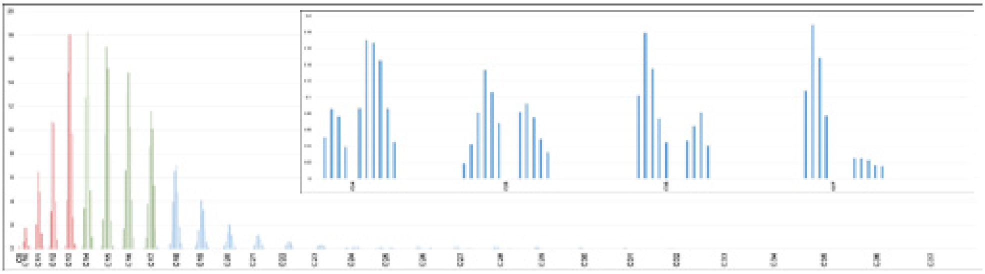

Figure S5-14. Congener group patterns of CPs for VD-2, the enlarged region show the double chlorination peak observed for C_{24} to C_{27}.

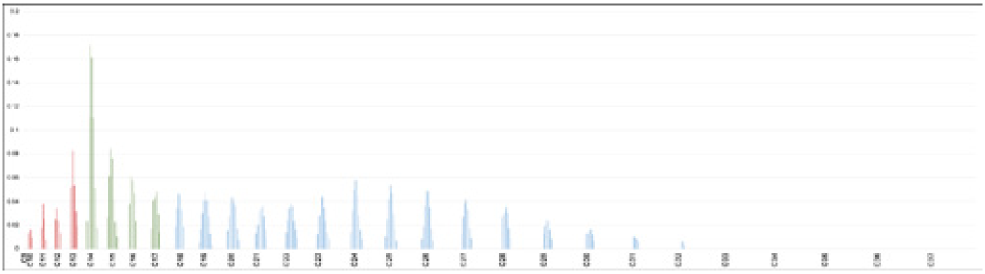

Figure S5-15. Congener group patterns of CPs for VD-3.

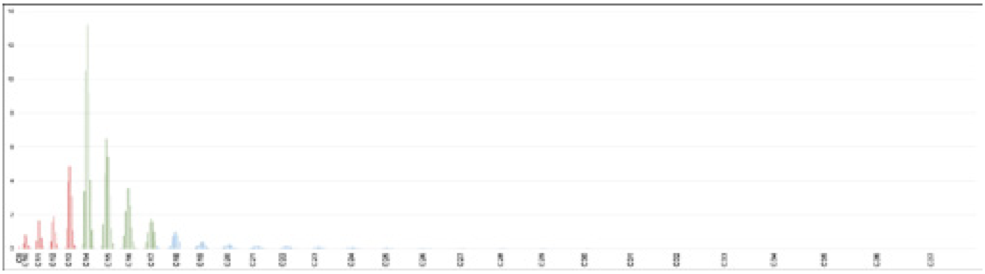

Figure S5-16. Congener group patterns of CPs for VD-4.

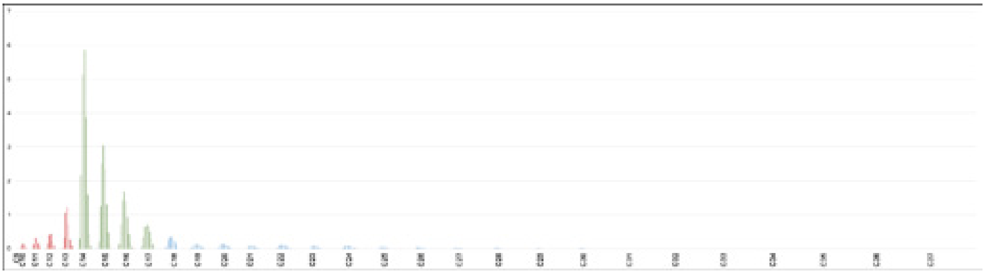

Figure S5-17. Congener group patterns of CPs for VD-5.

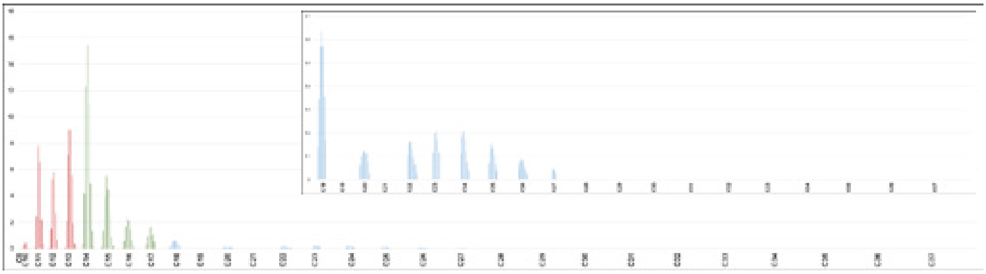

Figure S5-18. *Congener group patterns of CPs for VD-6, the enlarged region show the pattern for* C_{18} *to* C_{37}*.*

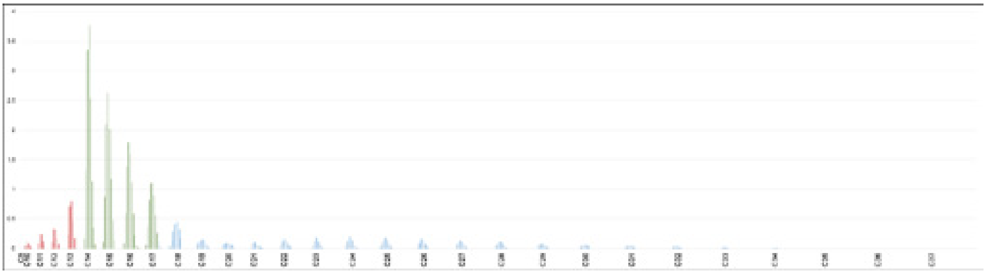

Figure S5-19. *Congener group patterns of CPs for VD-7.*

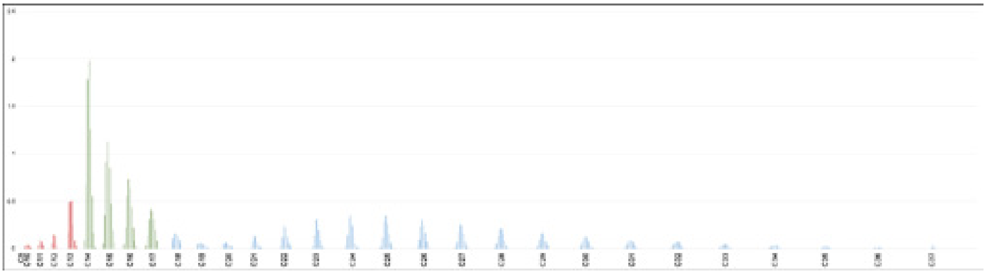

Figure S5-20. *Congener group patterns of CPs for VD-8.*

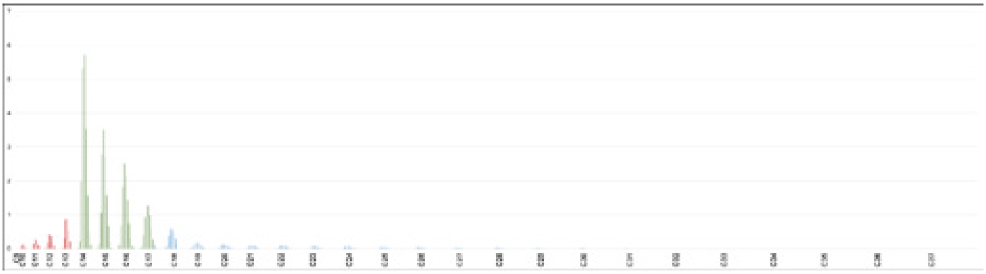

Figure S5-21. *Congener group patterns of CPs for VD-9.*

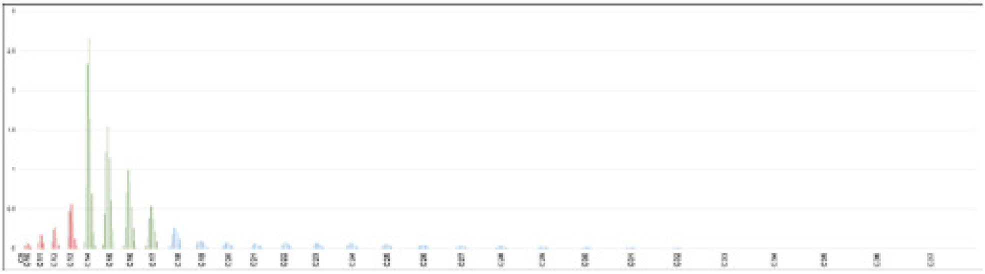

Figure S5-22. *Congener group patterns of CPs for VD-10.*

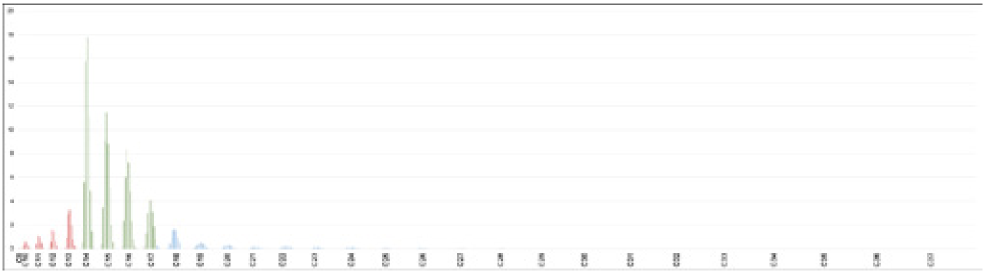

Figure S5-23. *Congener group patterns of CPs for VD-11.*

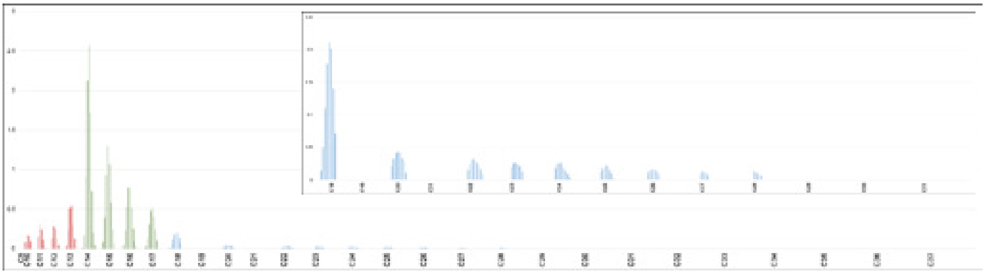

Figure S5-24. *Congener group patterns of CPs for FD-1, the enlarged region show the pattern for C_{18} to C_{31}.*

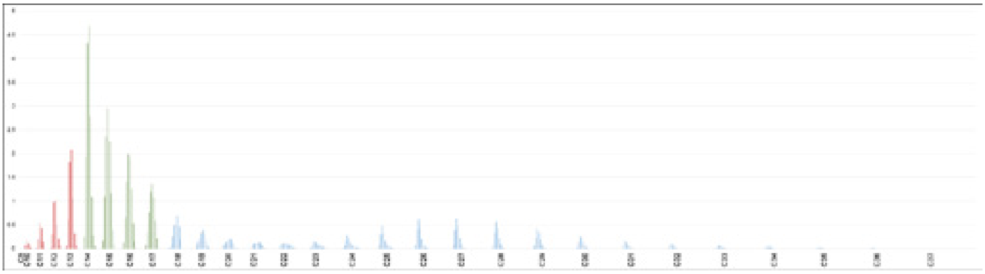

Figure S5-25. *Congener group patterns of CPs for FD-2.*

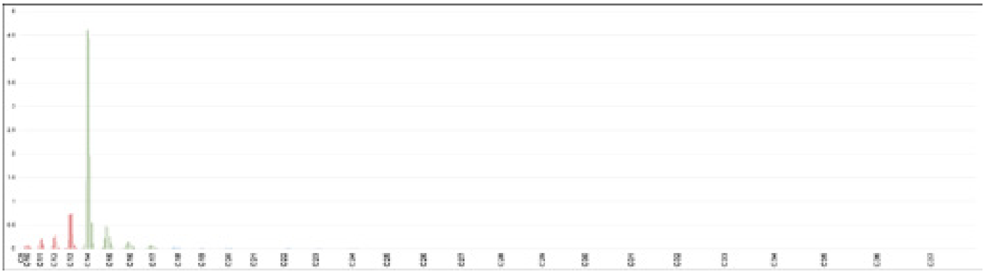

Figure S5-26. *Congener group patterns of CPs for FD-3.*

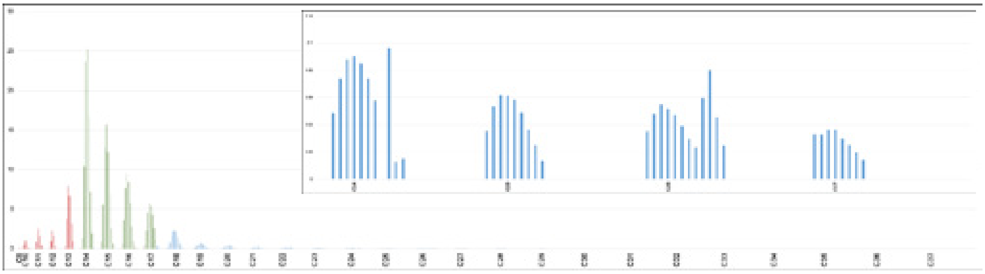

Figure S5-27. *Congener group patterns of CPs for FD-4, the enlarged region show the double chlorination peak observed for C_{24} to C_{27}.*

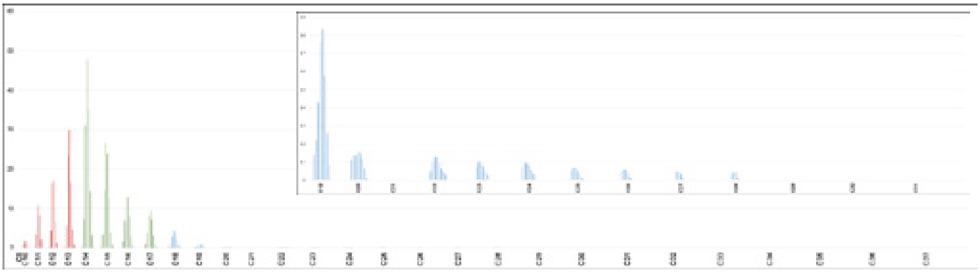

Figure S5-28. *Congener group patterns of CPs for FD-5, the enlarged region show the pattern for C_{19} to C_{37}.*

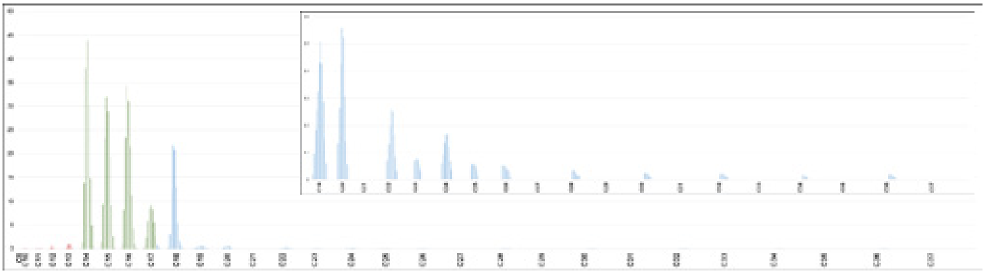

Figure S5-29. *Congener group patterns of CPs for FD-6, the enlarged region show the CP pattern from C_{19} to C_{31}, no C_{21} was observed and from C_{26} only even carbon chain lengths were observed.*

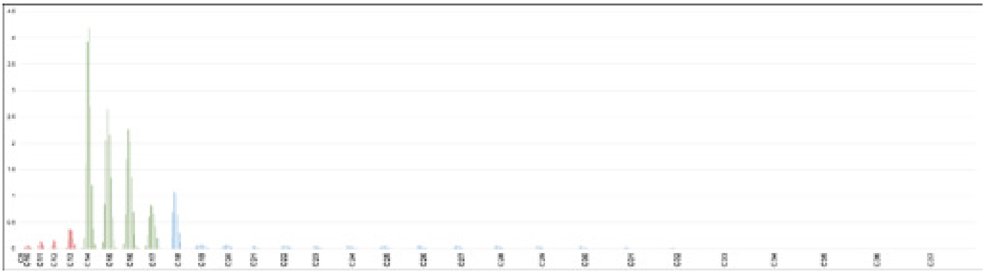

Figure S5-30. Congener group patterns of CPs for FD-8.

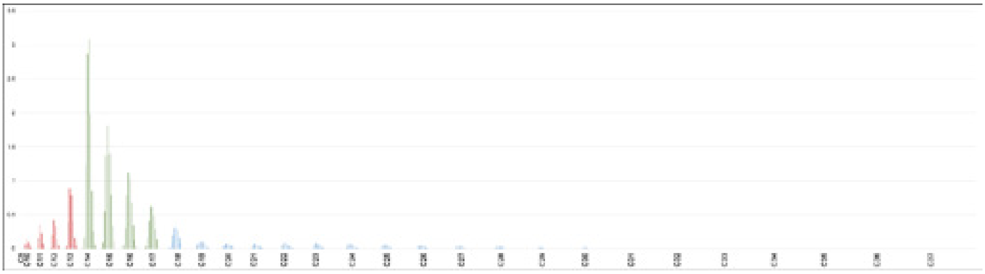

Figure S5-31. Congener group patterns of CPs for FD-9.

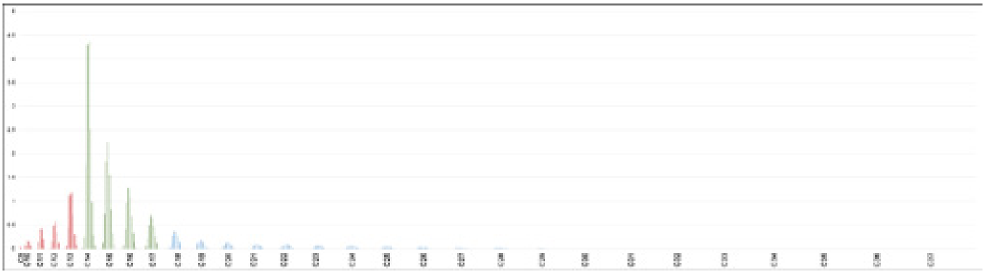

Figure S5-32. Congener group patterns of CPs for FD-10.

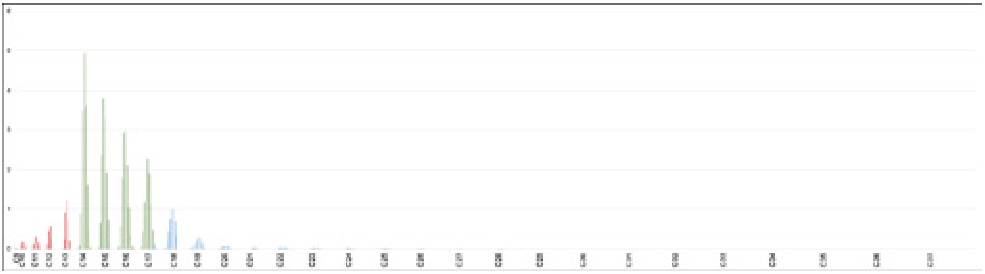

Figure S5-33. Congener group patterns of CPs for CH-1A.

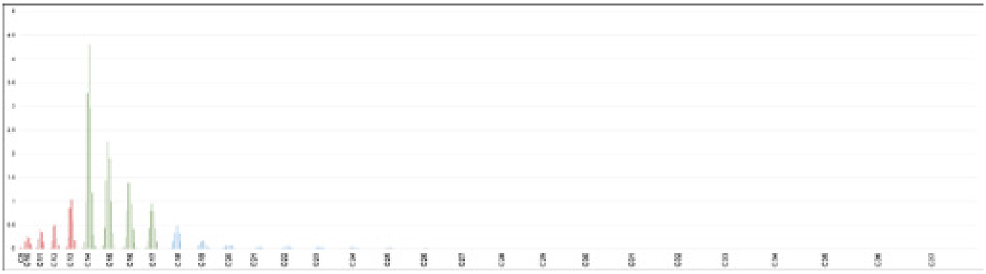

Figure S5-34. *Congener group patterns of CPs for CH-1B.*

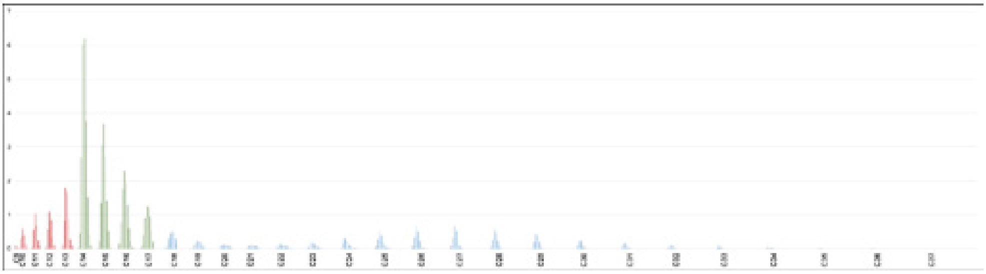

Figure S5-35*. Congener group patterns of CPs for CH-2A.*

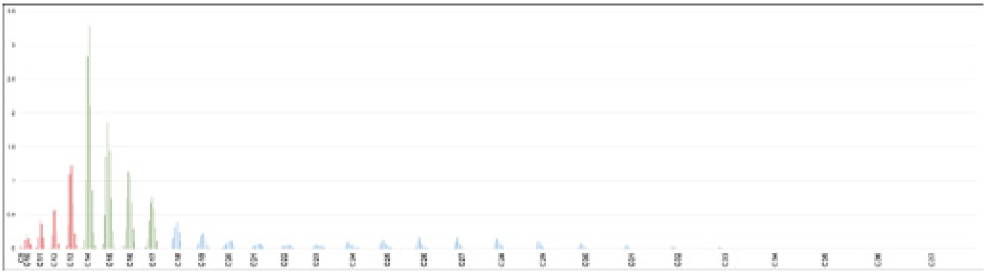

Figure S5-36*. Congener group patterns of CPs for CH-2B.*

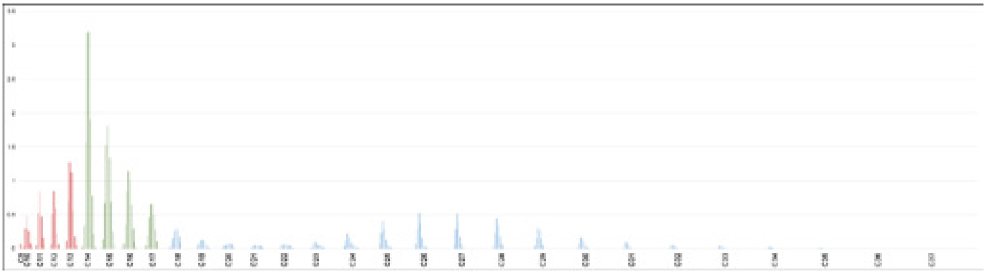

Figure S5-37. *Congener group patterns of CPs for CH-2C.*

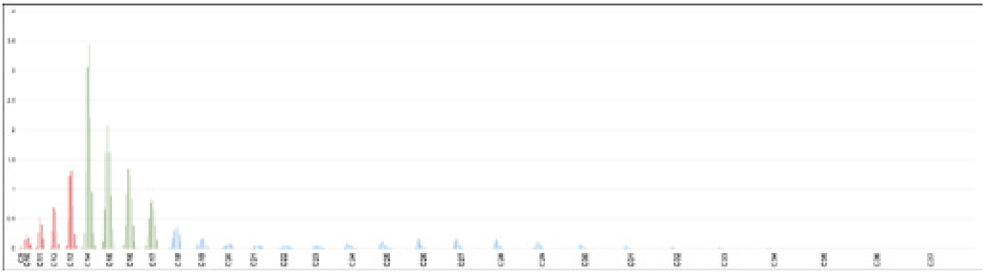

Figure S5-38. *Congener group patterns of CPs for CH-2D.*

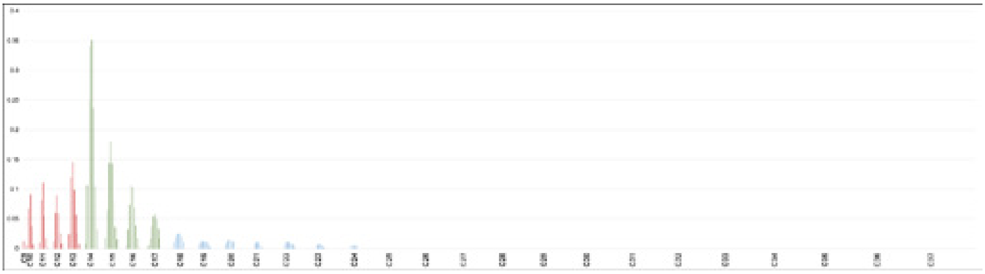

Figure S5-39*. Congener group patterns of CPs for CH-3.*

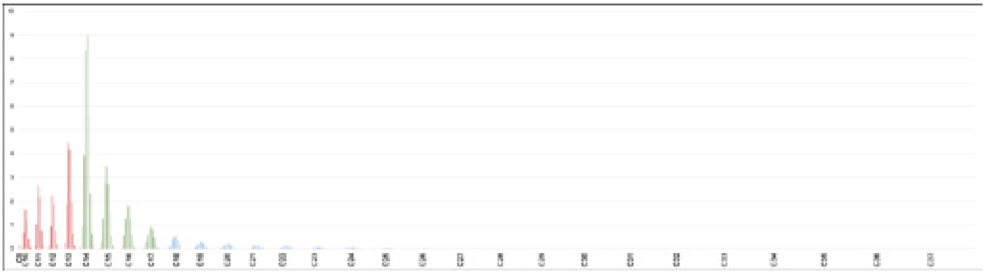

Figure S5-40. *Congener group patterns of CPs for CH-4A.*

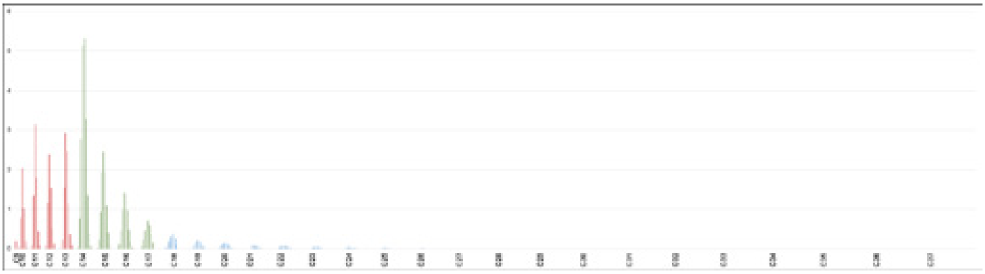

Figure S5-41*. Congener group patterns of CPs for CH-4B.*

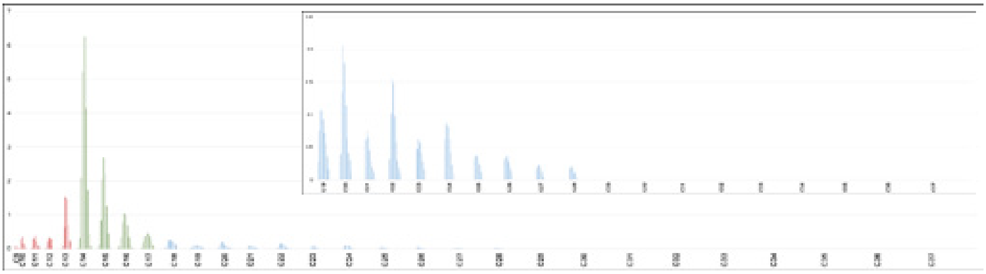

Figure S5-42. *Congener group patterns of CPs for CH-5, the enlarged region show the pattern for* C_{19} *to* C_{37}.

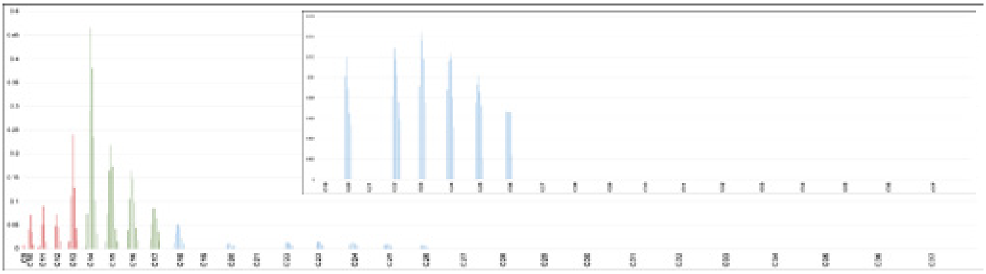

Figure S5-43. *Congener group patterns of CPs for CH-6, the enlarged region show the pattern for* C_{19} *to* C_{37}.

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Chapter 6

General discussion, conclusion and implications

6.1 General discussion

The global distribution of flame retardants (FRs) including brominated FRs (BFRs), organophosphorus FRs (OPFRs), and chlorinated paraffins (CPs) is well documented for environmental and biological matrices (Covaci *et al*., 2011; de Boer, 2010; de Wit, 2002; Law *et al*., 2014; van der Veen and de Boer, 2012; van Mourik *et al*., 2016; Wei *et al*., 2016, 2015). There is, however, inadequate information on the presence of these compounds in the African environment, including South Africa.

A literature review was conducted in *Chapter 2* to provide information on the occurrence of BFRs in the South African and African environment and to provide information on analytical capacity. The analytical part of this review showed that developing countries in Africa have limited facilities that specialise in FR analysis. Analytical approaches are often compromised by lack of training, shortage of funding and unavailability of high-quality instrumentation. BFR analyses in Africa are mostly carried out in South Africa or outsourced to non-African countries. The BFR analyses performed in South Africa are mainly based on Soxhlet extraction as the default method for exhaustive extraction of solid samples, with ultrasound-assisted extraction (UAE) increasingly being used. Clean-up and fractionation methods of BFRs are generally implemented from conventional methods developed for persistent organic pollutants (POPs) and/or BFR analysis elsewhere. Considering instrumental techniques, qualitative analyses are limited to gas chromatography (GC) coupled to electron capture detector (ECD) and low-resolution single quadrupole mass spectrometers operated in the electron impact ionisation mode (GC-LR-EI-MS). GC-time-of-flight mass spectrometry (GC-TOF-MS) was, however, also used for structural confirmation of target compounds (Daso *et al*., 2016). Although general aspects of QA/QC were considered, which include precautionary measures to reduce UV-radiation during sample treatment, glassware cleaning and regular analysis of instrumental (solvent) and procedural blanks, similar issues were identified as previously reported by Van Leeuwen *et al*. (2013), which includes blank problems, analytical challenges related to the decabrominated diphenylether (BDE209), co-elution of other BFRs and interfering compounds. Mass-labeled internal standards are being used whenever possible. While matrix matched certified reference materials (CRMs) were included, the obtained values often did not overlap with the uncertainty of the reference value. It is clear that investment and further development of analytical methodology are needed to fulfil the requirements for appropriate research, development, and monitoring of the Stockholm Convention (SC). The South African Department of Environmental Affairs is involved in implementing measures to restrict the production and use of listed organochlorine pesticides in order to fulfil its SC commitments and adequate environmental monitoring data are meanwhile available for some of the POP pesticides (Bouwman, 2004). With the current regulatory situation in South Africa, there are no immediate actions taken for FRs, and CPs have not received any attention. The situation is even worse in other parts of Africa and the implementation of National Implementation Plans (NIPs) regarding POPs greatly depends on continued international support. The National Metrology Institute of South Africa (NMISA) has embarked on establishing a unit to provide analytical measurement capabilities for challenging analyses of POPs and other organic pollutants to maintain international equivalence.

The last section of the review in *Chapter 2* provides information on the environmental distribution of BFRs in indoor dust, air, soil, aquatic environment (water, sediment, and aquatic organisms), eggs, wastewater treatment plant compartments, landfills (leachate and sediment) and breast milk from Africa. The data confirm the ubiquitous occurrence of polybrominated diphenyl ethers (PBDEs) in various environmental compartments in Africa and, due to the scarcity of data for FRs proposed as alternatives, it is unclear but likely that banned formulations were replaced in Africa. There is limited data on the levels and occurrence of CPs and OPFRs and these groups were consequently not included in the review. The PBDE levels in dust from South Africa are higher than reported for Nigeria and Egypt, the most populated countries in Africa, and comparable with the rest of the world (Abafe and Martincigh, 2014). The growing population asks for more consumer products and as a result increased volumes of waste are generated. The BFR concentrations associated with landfills in South Africa are higher than previously reported for Japan and the USA (Odusanya *et al*., 2009). Studies also report on the occurrence of polybrominated biphenyls (PBBs), specifically PBB153, which represents technical PBB formulations that were discontinued in the 1970s (Daso *et al*., 2013). The absence of recycling infrastructure unfortunately means that these products end up in landfill sites and waste disposal, therefore becoming important sources of BFR release into the environment. The occurrence of BFRs in indoor dust and landfills indicates that BFRs could originate from unregulated importation of older, deteriorating or poorly-manufactured BFR treated furniture, electrical appliances, and other consumer products. BFR levels in wastewater treatment plants (WWTP) indicate that discharged wastewater might be a significant source of BFRs in river water. Alt-BFRs are higher than PBDE levels for inland and coastal sediment, with BDE209 and 2-ethylhexyl-2,3,4,5- tetrabromobenzoate (EH-TBB) as the most frequently detected BFRs (La Guardia *et al*., 2013). The BFR concentrations are comparable and in some cases even higher than those reported for renowned contaminated areas in the USA and China. A major concern for PBDEs is the long-range atmospheric transport leading to global distribution, even in locations remote from sources. PBDE concentrations in soil from pristine mountain areas in Tanzania were higher than reported for similar environments in central Asia (Parolini *et al*., 2013). Although at low levels, PBDEs were also reported in bird eggs collected from Ile Cocos off the coast of Rodrigues, a remote island in the Indian Ocean (Bouwman *et al*., 2012). Uncontrolled e-waste disposal was suggested to be a significant source of PBDEs in breast milk. PBDE levels in breast milk samples from Tanzania and South Africa were higher than previously reported for Europe and Asia (Müller *et al*., 2016). The growth rate of information technology and related electronics (e.g. mobile phones, tablets, computers, televisions, etc.) in developing countries has been fuelled by the importation of affordable and/or used equipment from developed countries. Due to the significant growth and the rapid product obsolescence, discarded electronic equipment or e-waste is now regarded as the fastest growing waste stream. As FRs are not commonly produced in African countries, the regulation on imported products requires improved analysis capabilities to control and subsequently reduce potential sources. These analytical capabilities further support environmental monitoring standards to sufficiently regulate waste management and recycling practices. Recycling of polymers also raises questions about chemical FRs when they are being re-introduced into recycled products.

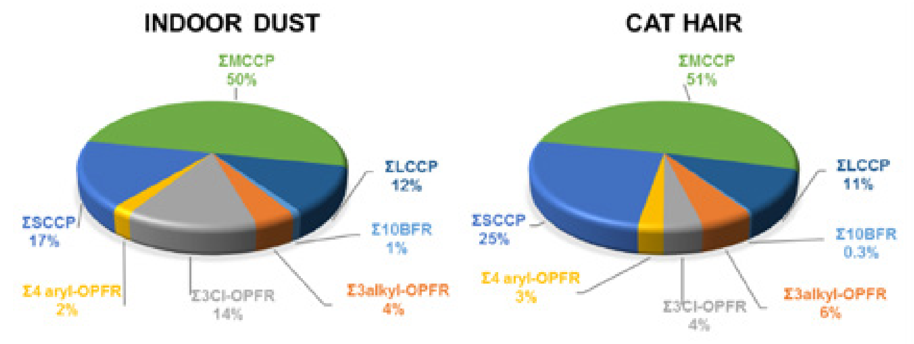
Chapter 3 discusses the use of comprehensive two-dimensional gas chromatography with high-resolution TOF-MS (GC×GC–HR-TOF-MS) to identify BFRs and other organohalogenated compounds (OHCs). The study presents a comprehensive analysis of chromatographic considerations, peak detection, and modulation and oven temperature ramp changes, which affect chromatographic separation and the mass spectrum deconvolution process. The instrumental analysis approach provides structured separation of compound classes and library searchable full scan EI mass spectra with accurate mass measurements (mass accuracy of better than 2 ppm) to predict chemical formulae for molecular and corresponding fragment ions. The screening method was applied to hair from South African pet cats as a proxy for indoor exposure of toddlers. The resulting list of seventy-two tentatively identified compounds contained various OHC classes including pesticides (organochlorine and organophosphorous pesticides, and pyrethroids), polychlorinated biphenyls (PCBs) and confirms the ubiquitous occurrence of halogenated FRs. Of the POPs listed in the Stockholm Convention, the four hexachlorocyclohexane (HCH) isomers (alpha-, beta-, gamma-, and delta-HCH), alpha- and beta-endosulfan, hexachlorobenzene (HCB), cis- and trans-chlordanes, dieldrin, endrin, dichloro-diphenyl-trichloroethane (DDT), hexabromocyclododecane (HBCD) and PBDE could be identified. This study is also the first to report detection of decabromodiphenyl ethane (DBDPE), trisbromoneopentyl alcohol (TBNPA), 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.

When the chemicals of interest present adverse environmental and health effects, accurate and precise measurements become crucial for risk assessment and decision making. Modern analytical science (and service) laboratories are encouraged to provide analytical results together with their uncertainties. In a risk assessment of potentially harmful chemicals, it is crucial that data are precise and accurate, including a specified uncertainty. *Chapter 4* presents the estimated measurement uncertainty associated with the determination of BFRs and OPFRs for each matrix. The measurement uncertainty during the method validation procedure was calculated using a bottom-up approach. The major contributions to the combined uncertainty were associated with recovery and repeatability, and the relative expanded uncertainties for all compounds in dust ranged from 13 to 30% and 11 to 34% for hair. The uncertainties were acceptable, when for example compared to criteria of 50%

expanded uncertainty, which is required for pesticide residue analysis in food and feed (European Commission, 2017). The relative expanded uncertainties for PBDEs varied between 15 – 21%, similar to uncertainties previously reported (16 – 21%) for house dust (Korcz *et al*., 2014). The relative expanded uncertainties of PBDEs were in general higher for cat hair than for dust. Due to low PBDE concentrations in the cat hair the uncertainty associated with the calibration curve showed significant contributions to the combined uncertainty, alluding to the importance of this estimation. Measurement uncertainties have not previously been estimated for OPFRs. The highest uncertainties were associated with compounds that do not have analyte specific mass-labelled internal standards. The relative expanded uncertainties of TCIPP were higher for cat hair than for dust due to the uncertainty associated with precision. OPFRs have different physicochemical properties and subsequently behave differently in the analysis procedure. The measurement uncertainties could be further improved by analysing appropriate certified reference materials that include certified values for the analytes of interest and the use of analyte-specific mass-labelled internal standards to reduce the uncertainty contributions from recovery and repeatability. When regulatory limits for FRs will be introduced, uncertainty evaluation will gain more importance. CPs present additional challenges as at present well-characterised calibrant solutions, isotopically labelled internal standards covering the full range of CP carbon chain lengths, and certified matrix reference materials are not commercially available (Schinkel *et al*., 2018).

A major challenge in the analysis of cat hair samples was the presence of a lipid-based waxy substance (sebum), which resulted in substantial chromatographic interferences. Although the sample preparation was sufficient for the screening analysis, basic or acidic treatment like saponification could not successfully be applied for the quantitation of OPFRs (*Chapter 4*) as these compounds are prone to degradation under strong acidic or basic conditions (Kucharska *et al*., 2014). The fractionation steps were therefore, further optimised and a freezing-lipid precipitation method previously applied for biological samples containing high levels of lipids was included (Liu *et al*., 2018). This method efficiently removed the chromatographic interferences. The fractionation using silica-florisil columns allows for the partitioning of BFRs, CPs, and OPFRs in two fractions. Although the three classes could be separated in three fractions, the first two fractions were combined as BEH-TEBP did not elute completely in the first fraction (Dirtu *et al*., 2012; Van den Eede *et al*., 2012). This did not affect the analysis but future improvements should be made to optimally fractionate the three FR classes.

Indoor dust and cat hair were used to investigate FR contamination in the South African indoor environment. The accurate quantification of eight PBDE congeners, two alt-BFRs, ten OPFRs and SCCPs, MCCPs and LCCPs in the South African indoor environment is described in *Chapter 4 and 5*. The dust samples were collected using two sampling techniques, from vacuum cleaner bags (V-dust) to investigate wide indoor contamination over periods of months and fresh or "active" dust (F-dust) was sampled to investigate contamination in a single room over a short time-span. In addition to the dust, hair samples (C-hair) were obtained from indoor pet cats associated with some of the houses. These Persian cats typically remain indoors, so they are closely related to their environment, and thus sharing a common environment with toddlers. Figure 6-1 provides a summary for the FR congener profiles for indoor dust and cat hair from *Chapter 4 and 5*. The ΣCPs shows the largest contribution to the FR congener profile followed by OPFRs and BFRs.



		INDOOR DUST (µg/g)				CAT HAIR (µg/g)			
		Mean	Median	Min	Max	Mean	Median	Min	Max
Σ_{10}BFRs	🟦	2.9	0.87	0.13	27	0.024	0.026	0.016	0.033
$\Sigma_3$alkyl-OPFRs	🟧	8.3	4.0	0.81	37	0.36	0.43	0.07	0.54
Σ_3Cl-OPFRs	⬜	35	13	2.1	179	0.33	0.32	0.26	0.44
$\Sigma_4$aryl-OPFRs	🟨	3.2	2.0	0.56	12	0.18	0.21	0.08	0.25
Σ_{10}OPFR		46	20	6.1	183	0.87	0.87	0.48	1.2
ΣSCCP	🟦	54	16	5.1	353	2.7	2.0	0.51	7.2
ΣMCCP	🟩	102	46	13	498	3.8	4.0	0.63	6.5
ΣLCCP	🟦	20	11	1.9	108	0.90	0.88	0.09	2.3
ΣCPs		177	72	33	663	7.3	7.0	1.2	15

Figure 6-1. *Summary of FR congener profiles for the median concentrations of the ΣSCCPs, ΣMCCPs, ΣLCCPs, the Σ_{10}BFRs (PBDEs, EH-TBB, and BEH-TEBP), Σ_3Cl-OPFR (TCEP, TCIPP, and TDCIPP), $\Sigma_3$alkyl-OPFR (TNBP, TBOEP, and TEHP), and $\Sigma_4$aryl-OPFR (TPHP EHDPP, TMPP and TIPPP) in indoor dust and cat hair. The table provides a summary of the mean, median, and minimum and maximum concentration ranges (µg/g).*

The SCCPs, MCCPs, and LCCPs were detected in all samples analysed and variations were observed for CP congener profiles between individual samples. The MCCPs were the dominant CP group and levels for ΣSCCPs were higher than for ΣLCCPs. The concentrations of the ΣSCCP, ΣMCCP, and ΣLCCP were approximately 10-fold higher in the indoor dust than in the C-hair on a weight basis. Important contributions for SCCPs including the shorter chain lengths (C_{10} and C_{11}) with lower chlorine substitution (Cl_4 and Cl_5) were observed in the C-hair samples. The influences of atmospheric deposition, direct migration from sources, or endogenous mechanisms on the hair concentrations are not fully understood, and factors may vary for different CP congeners. SCCPs with shorter carbon chains and lower chlorine substitution could be favourably adsorbed to the waxy sebum layer on cat hair over time, possibly due to contributions from indoor dust or direct migration from possible source in the indoor environment. The current analytical method did not allow to distinguish between internal/absorbed levels and external/adsorbed levels on the cat hair, internal exposure cannot be excluded and may have a substantial contribution.

The median concentrations for the sum of SCCPs and MCCPs in the dust were approximately ten times higher than previously reported for dust samples from Canada (Shang *et al*., 2019) and Sweden (Fridén *et al*., 2011) but lower than levels reported for China (Shi *et al*., 2017) and Germany (Hilger *et al*., 2013). Information on LCCP levels in the indoor environment is scarce and only one study previously reported ΣLCCP concentrations from indoor dust samples from five countries (Wong *et al*., 2017). They reported concentrations that were considerably higher than the levels found in this study. There is no literature information on the occurrence of CPs in human or pet cat hair.

The negative ion atmospheric pressure chemical ionization (APCI) coupled to a high-resolution quadrupole time-of-flight mass spectrometry (QTOF-MS) with chlorine-induced adduct formation provides improved selectivity and sensitivity for halogen-containing compounds, and specifically for CPs. These analytical advantages allow for the construction of non-traditional Kendrick mass defect (MD) plots from the accurate mass full scan data to constructively assess the carbon chain lengths and degree of substitution of SCCPs, MCCPs, and LCCPs in the samples. The carbon chain lengths for the CP congeners in the C-hair ranged from C_9 to C_{36}, and up to C_{37} in the indoor dust. Evidence of LCCPs with average carbon chain lengths of C_{25}, confirm the use of wax grade LCCP formulations in the indoor environment. According to a report published in 2015, South Africa produces approximately 10,000 tonnes of MCCP formulations (C_{14} to C_{17}) with a chlorine content from 45% to 55% under the name Plasticlor® (ICIS, 1995). The congener profiles reported in this study show that the ΣMCCPs are the major CP group in the indoor environment. Congener profiles of local commercial formulations are needed to confirm if the MCCPs found, could be from a locally produced technical MCCP mixture. In addition to obtaining information on the magnitude of CPs, which aids in the selection of the target list for quantitation, the MD plots also provide evidence on possible interferences. This emphasises the use of very strict identification criteria to distinguish between positively identified CPs and the presence of interferences.

Data on the concentrations of OPFRs in the South African indoor environment are still scarce. When comparing the three main OPFR groups, Cl-OPFR, alkyl-OPFRs, and aryl-OPFRs analysed in this study, the Cl-OPFRs dominate the profile in dust samples with major contributions from TCIPP. The Cl-OPFRs in the indoor dust were 40-fold higher than the C-hair. The Cl-OPFR congener profiles for dust could most likely be due to increasing use of TCIPP and TDCIPP as a replacement of TCEP (World Health Organization, 1998). The F-dust was also collected from upholstered furniture, which could also have been sampled by the study participants as part of their regular house cleaning routine, present in the V-dust. Cl-OPFRs have previously been reported for furniture containing polyurethane foam (Stapleton *et al*., 2009). The alkyl-OPFRs were more prominent in the in cat hair due to the contribution from tris(2-butoxyethyl) phosphate (TBOEP). Previous studies have shown that there is a stronger correlation for alkyl-OPFRs between human hair and air than for indoor dust (Kucharska *et al*., 2015). The dominance of alkyl-OPFRs in C-hair might support the finding that indoor dust partly contributes to the pattern observed in the hair. As shown in Figure 6-1, the contribution of the Σ_3Cl-OPFRs in indoor dust was comparable with those of ΣSCCPs and ΣLCCPs.

The BFRs show very low contributions to the FR congener profile for indoor dust and C-hair with BDE209 dominating the BFR profile. In general low PBDE concentration were detected in the indoor dust samples, and this compares with previous studies summarised in *Chapter 2*. The concentrations of Σ_8PBDEs were higher in F-dust than in V-dust. Bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (BEH-TEBP) and 2-ethylhexyl-2,3,4,5- tetrabromobenzoate (EH-TBB) showed notable contributions to the BFR profile in cat hair. Animal studies have shown that EH-TBB and BEH-TEBP absorb to the skin and EH-TBB was more permeable (Knudsen *et al*., 2016). Skin and hair may act as a lipophilic “trap” and given the highly lipophilic nature of EH-TBB and BEH-TEBP, diffusion into the skin may be significant.

A preliminary estimation of human exposure to OPFRs and BFRs via dust ingestion was performed based on two possible intake scenarios (*Chapter 4*). The high ingestion exposure estimate for TCIPP (the major FR in the dust) ranged up to 1,240 ng/kg bw/day for toddlers, which were 8-fold lower than the reference dose (10,000 ng/kg bw/day). To provide ingestion exposure estimates for cats, an average body weight of 4.3 kg was used, with similar ingestion rate as toddlers. The high ingestion exposure estimate for TCIPP ranged from 1,640 to 3,270 ng/kg bw/day for cats. 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. Although there is undoubtedly a high level of uncertainty associated with the exposure estimate for cats, this provides a first indication of the probable exposure range.

6.2. Conclusion and implications

The comprehensive dataset of both previously and currently used FRs presented in this study can be used to establish a baseline against which future measurements in the South African indoor environment may be compared. Currently, the South African indoor environment shows high levels of CPs followed by OPFRs and BFRs. This first report on CPs in South Africa shows that MCCPs are the dominant CP group while concentrations of ΣSCCPs are higher than for ΣLCCPs. While CP congener profiles of locally produced formulations are needed to confirm if the MCCP contamination is from local produced formulations; the contributions of SCCPs and LCCPs may be from imported technical mixtures and/or formulations used in imported products. This study also shows for the first time that, of the three main OPFR groups, Cl-OPFRs dominate the indoor dust profile with high contributions from TCIPP. BFRs concentrations are relatively low, compared to OPFRs and CPs. BDE209 dominates the BFR profile.

In this study, analytical methods for various FR classes were improved to provide reliable data for BFR, OPFRs, and CPs in South African environmental matrices. The screening method employing GC×GC coupled to an HR-TOF-MS system allows structured separation of compound classes and library searchable full scan EI mass spectra with sufficiently accurate mass measurements to predict chemical formulae of GC-amenable compounds. For the quantitative analysis, GC-MS in the electron capture negative ionisation (ECNI) was used for the analysis of PBDEs and alt-BFRs and a method employing GC coupled with triple quadrupole MS (GC-MS/MS) in electron impact (EI) mode was developed for OPFR analysis. The parameters affecting isolation and fragmentation of precursor ions were optimised for OPFRs in order to improve selectivity and sensitivity. Low detection limits were achieved and spiking experiments and the analysis of a certified reference material for house dust showed that both methods were sufficiently accurate, precise and sensitive for BFR and OPFR analysis. Acceptable measurement uncertainties were achieved for both matrices. APCI coupled to a high-resolution QTOF-MS with chlorine-induced adduct formation was implemented for CP analysis. This analytical technique achieved a good mass accuracy (≤ 5 ppm) and allowed for the analysis of SCCPs, MCCPs, and LCCPs. Non-traditional Kendrick MD plots were constructed from the full scan accurate mass information to comprehensively explore data obtained from the dust and cat hair samples.

The indoor dust and cat hair show comparable FR profiles. Although dust is widely used as a measure for indoor exposure, cat hair does provide more specific information on indoor exposure and could be seen as a non-invasive passive sampler, and as an indicator of exposure to FRs from the indoor environment. SCCPs with lower chlorine substitution, alkyl-OPFRs and alt-BFRs were prominent in the cat hair samples. The Cl-OPFRs contribution was, however higher in the dust. The higher Cl-OPFR levels in the dust could be a result of the sampling, where dust was also collected from sofas. This might suggest that indoor dust partly contributes to the pattern observed in the cat hair and some FRs could be adsorbed to the hair due to a contribution from indoor air or direct transfer from sources. The analysis of household consumer products could provide more information on the FR formulations present in upholstered furniture, floor polish, carpet padding, and isolation materials to confirm the contributions to the two matrices. The minor differences in congener profiles between cat hair and dust may be of importance considering that dust ingestion rates are regularly used for risk assessments. Profiles and levels in hair could be relevant for external exposure, as the partitioning of FRs between sources and dust and/or hair differs and not all compounds present in dust can be transferred into/onto the human body. An exposure assessment based on levels in dust alone might therefore, result in misinterpretations. Screening analyses performed on cat hair samples tentatively identified various pesticides (organochlorine pesticides, organophosphorous pesticides, and pyrethroids), polychlorinated biphenyls (PCBs), halogenated FRs and confirmed the ubiquitous occurrence in South Africa of numerous POPs listed in the Stockholm Convention. The presence of these chemicals in cat hair may be a cautionary warning for the immediate and long term health risk for children. Toddlers share the same environment as cats and exposure may result in similar health risks. More specific studies are warranted here.

Developing countries in Africa have a shortage of facilities that specialise in FR analysis and analytical approaches are influenced by ease of operation, low cost, and available instrumentation. According to the review, in Africa, FR analyses were limited to BFRs and mostly performed in South Africa or through outsourced analyses in non-African countries. BFR levels were reported for various environmental compartments, whereas there is insufficient data on the levels and occurrence of CPs and OPFRs. SCCPs have been listed as POPs under the Stockholm Convention of the United Nations. Conversely, there is an unusually long list of exemptions made for this class of chemicals in this Convention, which makes the basis for restrictions on CP use and production rather weak. This is of concern because it has been shown that not only SCCPs but also MCCPs and LCCPs have a bioaccumulative potential. Monitoring of all CP groups to support the enforcement of regulations is therefore important, not only in Africa but globally. The high levels of CPs and the carcinogenic chlorinated-OPFRs are a cautionary warning and more attention should be paid to these compounds when the reduction of indoor contamination is considered. Continued monitoring of previously and currently used FRs, including CPs, OPFR, and BFRs is required to determine whether there may be an increase or decrease in use of these FRs due to changes in flammability standards. As many of these FRs originate from imported products, efforts should also be made to analyse these compounds in consumer products to correlate possible sources with human exposure. There is also a scarcity of information on the fate of these compounds when they are being re-introduced into recycled products. Future work on CPs should focus on obtaining more data on the production and use of these chemicals in South Africa. The inclusion of samples from townships and informal settlements in further research should provide a more comprehensive demographic representation of human exposure to FRs in South Africa and would assist in enforcing regulations.

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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, $\geq C_{18}$). Non-

traditional 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.

Samenvatting

Brandvertragende stoffen (FRs) zoals broomhoudende brandvertragers (BFRs), organofosfor-brandvertragers (OPFRs) en gechloreerde paraffines (CPs) zijn groepen verbindingen met een grote diversiteit die worden gebruikt in een breed scala van materialen om ontbranding te tegen te gaan. Hoewel deze verbindingen nuttig zijn voor het beoogde doel, hebben de meeste een duidelijk nadeel: ze zijn persistent en door uitloging, of lozingen/dumpingen van gebruikte materialen die het einde van hun nuttige levensduur hebben bereikt, komen ze in het milieu terecht. Velen zijn toxisch en kunnen bioaccumuleren. Wereldwijd is het voorkomen van deze verbindingen goed gedocumenteerd. Er is echter maar weinig informatie over de verspreiding van deze verbindingen in de Zuid-Afrikaanse buiten- en binnenomgeving. Dit proefschrift had tot doel nieuwe informatie te verschaffen over het voorkomen van FRs in het Zuid-Afrikaanse milieu en de capaciteit van laboratoria voor de analyse van BFRs, OPFRs en CPs te verbeteren, om daarmee een voorlopige evaluatie van hun gehalten in de Zuid-Afrikaanse binnenomgeving mogelijk te maken.

De resultaten van een literatuurstudie tonen aan dat FR analyses in Afrika tot nu toe vooral gericht waren op BFRs en voornamelijk werden uitgevoerd in Zuid-Afrika of via uitbestede analyses in niet-Afrikaanse landen. Ontwikkelingslanden in Afrika hebben beperkte faciliteiten voor de analyse van FRs en analytische methoden zijn voornamelijk gebaseerd op bedieningsgemak, lage kosten en beschikbaarheid van technologieën en instrumentatie in de meeste laboratoria. De literatuurstudie bevestigde het alomtegenwoordige voorkomen van polybroomdifenylethers (PBDEs) in verschillende milieucompartimenten in Afrika. Vanwege een gebrek aan gegevens over alternatieve FRs, is het onduidelijk in hoeverre verboden FR formuleringen inmiddels zijn vervangen in Afrika. Er zijn ook onvoldoende gegevens over de gehalten en het voorkomen van CPs en OPFRs.

Gebruikmakend van kattenhaar als matrix, werd twee-dimensionale gaschromatografie met hoge-resolutie time-of-flight massaspectrometrie (GC×GC-HR-TOF-MS) positief getest als screeningsmethode om BFRs en andere organohalogeenverbindingen (OHCs) te identificeren. Meer dan zeventig OHCs werden in de monsters geïdentificeerd en omvatten bekende FRs, zoals PBDEs en ‘verouderde’ contaminanten zoals polychloorbifenylen (PCBs), organochloor-en organofosfor pesticiden en pyrethroïden, waarvan sommige onder de Stockholm Conventie van de Verenigde Naties zijn gecategoriseerd als persistente organische verontreinigende stoffen (POPs). Daarnaast werden de brandvertragers decabroomdifenylethaan (DBDPE), trisbroomneopentylalcohol (TBNPA), hexabroomcyclododecaan (HBCD), pentabroomethylbenzeen (PBEB) en de twee chlooralkyl-OPFRs (Cl-OPFRs) tris (2-chloorethyl) fosfaat (TCEP) en tris (2-chloorisopropyl) fosfaat (TCIPP) voor het eerst gemeten en gedetecteerd in het Zuid-Afrikaanse binnenmilieu.

De nauwkeurige kwantificering van BFRs, OPFRs en CPs liet zien dat gehalten van CPs in huisstof en kattenhaar hoger waren dan die van OPFRs en BFRs. Deze eerste

gegevens laten zien dat CPs met een gemiddelde ketenlengte (MCCPs, C_{14-17}) de dominante CP groep vormen en tevens dat concentraties van CPs met een korte keten (SCCPs, ≤ C_{13}) hoger zijn dan die van CPs met lange keten (LCCPs, ≥ C_{18}). Niet-traditionele Kendrick-massadefect (MD) analyse toonde aan dat de koolstofketenlengtes van de CP congeneren in kattenhaar varieerden van C_9 tot C_{36} en dat het profiel in huisstof doorliep tot C_{37}. De aanwezigheid van LCCPs met gemiddelde koolstofketenlengtes van C_{25} bevestigde het gebruik van zogenaamde 'wax'- LCCP formuleringen in het binnenmilieu. De MD plots lieten ook zien dat mogelijke interferenties aanwezig kunnen zijn. Daaruit blijkt dat voor een juiste CP-analyse zeer strikte identificatiecriteria nodig zijn. Om de kwaliteit van de gegevens te ondersteunen en om de onzekerheid in de analysemethode tijdens de validatie vast te stellen, werd een meetonzekerheidsanalyse uitgevoerd voor BFRs en OPFRs. Over het algemeen zijn de profielen in huisstof en kattenhaar vergelijkbaar. Hoewel huisstof op grote schaal wordt gebruikt als een matrix om blootstelling aan FRs binnenshuis vast te stellen, biedt het gebruik van kattenhaar specifieke informatie over blootstelling binnenshuis en kan het worden gezien als een niet-invasieve bemonsteringsmethode om de voortdurende blootstelling van organismen aan FRs in het binnenmilieu te meten. Korte keten SCCPs met een lagere chloorsubstitutie, alkyl-OPFRs en alt-BFRs waren prominent aanwezig in kattenhaar en de Cl-OPFR-bijdrage was hoger in huisstof. Dit geeft aan dat huisstof voor een deel bijdraagt aan het patroon dat wordt waargenomen in kattenhaar maar ook dat sommige FRs beter aan het haar worden geadsorbeerd vanwege een bijdrage van de binnenhuis atmosfeer of directe overdracht van bronnen. BFRs, gedomineerd door BDE209, waren alleen aanwezig in zeer lage concentraties en droegen niet significant bij aan het FR-congeneerprofiel in de twee matrices.

Een voorlopige inschatting van de menselijke blootstelling aan OPFRs en BFRs via stofinname laat zien dat een maximale opname van TCIPP (de belangrijkste FR in huisstof) acht keer lager uitkomt dan de referentiedosis. Hoewel de precieze hoeveelheid stof die katten inslikken onbekend is, kan de geschatte blootstelling van huiskatten driemaal hoger zijn dan voor peuters. De hoge gehalten van CPs en de kankerverwekkende gechloreerde OPFRs geven aan dat deze stoffen als eerste aandacht moeten krijgen als men de verontreiniging van de binnenhuisomgeving wil aanpakken.

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