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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.

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 [1]. 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 [2]. 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 [3]. Studies also suggest that postnatal exposure to polybrominated diphenyl ethers (PBDEs) is

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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 [4]. Household dust was shown to be a major source of human exposure to OHCs [5]. 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 [6]. Pets, especially cats, share similar environments with toddlers and have been presented as a potential bio-sentinel for indoor pollution exposure [7]. 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 [7,8] and detected in hair samples taken from pet cats and dogs from Pakistan [8]. Hair, as a non-destructive monitoring system, has been used as a bio-indicator for human exposure to organic pollutants [9]. 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 [10]. 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-TOFMS) [11,12]. 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-TOFMS and ultra-high resolution Fourier transform type mass spectrometers using electron impact ionization (EI) and electron capture negative ionization (ECNI) techniques [13–17]. New approaches used direct probe and GC as sample introduction systems to HR-TOFMS with atmospheric pressure chemical ionization (APCI) [18]. 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) [19], 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 [20–23].

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-TOFMS) in EI mode and GC × GC coupled to HR-TOFMS in APCI and ECNI modes to be successfully used in environmental forensic investigations and in targeted and non-targeted analysis of OHCs [16,18,19,24].

Advances in commercially available HR-TOFMS allows for reproducible collection of HR-EI mass spectra at unmatched scan speeds to resolve more discrete chemical compounds [25]. By combining GC × GC with HR-TOFMS, the peak capacity of the chromatographic separation process is complemented with the advantage of recording HR-EI mass spectra over a large mass range [16,26,27]. As opposed to Fourier transform type mass spectrometers where resolution and mass accuracy are negatively correlated with the mass spectral acquisition frequency, the HR-TOFMS does not suffer from this phenomenon and mass resolving power increases with *m/z* [25]. 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 [17].

Although screening using GC × GC-HR-TOFMS has not previously been applied to the analysis of cat hair samples, this technique was successfully applied to the identification of OHCs in dust [26], flame retardants and plasticisers in electronic waste and car interiors [18], organic pollutants in water [28], and chlorinated and brominated polycyclic aromatic hydrocarbons in soil [27]. In the present study, hair samples taken from six longhair Persian cats were analysed using GC × GC-HR-TOFMS. 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. [29], unwashed cat hair was extracted; the extracts fractionated and screening analysis was performed to identify BFRs and other OHCs using GC × GC-HR-TOFMS.

2. Experimental

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 60–200 Mesh was obtained from Merck (Darmstadt, Germany). Cleaned Florisil® and silica gel was heated for 48 h 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

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 [30].

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

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