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Development of matrix solid-phase dispersion method for the extraction of short-chain chlorinated paraffins in human placenta

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ABSTRACT

Chlorinated paraffins (SCCPs) are widely used worldwide, and they can be released into the environment during their production, transport, usage and disposal, which pose potential risks for human health. In this work, an efficient, reliable and rapid pretreatment method based on matrix solid-phase dispersion (MSPD) was developed for the analysis of short-chain CPs (SCCPs) in human placenta by gas chromatograph-electron capture negative ion low-resolution mass spectrometry (GC-ECNI-LRMS) and gas chromatography–quadrupole time-of-flight mass spectrometry (GC–QTOF-HRMS). The MSPD-relevant parameters including dispersing sorbent, sample-to-sorbent mass ratio, and elution solvent were optimized using the orthogonal test. Silica gel was found to be the optimal dispersing sorbent among the selected matrices. Under the optimal conditions, 44% acidic silica gel can be used as the co-sorbent to remove lipid and eluted by the mixture of hexane and dichloromethane (v:v, 7:3). The spiked recoveries of the optimized method were 77.4% and 91.4% for analyzing SCCPs in human placenta by GC-ECNI-LRMS and GC–QTOF-HRMS, and the corresponding relative standard deviations were 10.2% and 5.6%, respectively. The method detection limit for the total SCCPs was 36.8 ng/g (dry weight, dw) and 19.2 ng/g (dw) as measured by GC-ECNI-LRMS and GC–QTOF-HRMS, respectively. The concentrations of SCCPs in four human placentas were in the range of <method detection limit (MDL) to 782 ng/g (dw), which is also the first description of SCCPs detected in placentas.

Introduction

Short-chain chlorinated paraffins (SCCPs) are highly complex technical mixtures of polychlorinated n-alkanes. SCCPs can be released into the environment during production, storage, transportation and product use as fire retardants and plasticizers in PVC, rubber, other plastics, varnishes, sealants, metal-cutting oils, *etc.* (Campbell and McConnell, 1980). SCCPs

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have been found in a variety of environmental matrices, such as water (Coelhan, 2010), soil and sediment (Chen et al., 2011; Gao et al., 2012; Zeng et al., 2013), air (Barber et al., 2005; Wang et al., 2013), dust (Fridén et al., 2011), food (Harada et al., 2011; Iino et al., 2005), aquatic biota (Bennie et al., 2000; Jansson et al., 1993; Tomy et al., 2000), and breast milk (Thomas et al., 2006). Due to their persistence, toxicological properties, capability to bioaccumulate and potential long-range air transport, SCCPs have aroused wide attention. In 2006, the European Union submitted a proposal to list SCCPs under the Stockholm Convention (SC) as Persistent Organic Pollutants (POPs). After ten years, the eighth Conference of Parties finally decided to list SCCPs in Annex A in 2017 of the SC.

At different stages of human development, toxic chemicals can enter the human body *via* different pathways which embody placenta transport such as fetuses, breast milk to infants, and food as children and adults (Cheng et al., 2015). Like other POPs (*e.g.*, dioxins, polychlorinated biphenyls (PCBs) and organochlorine pesticides), SCCPs can cause toxicological effects in mammals and may affect the liver, thyroid hormone system, and kidneys, *e.g.*, by causing hepatic enzyme induction and thyroid hyperactivity, further leading to carcinogenicity in these organs (UNEP/POPRC.11/10/Add.2, 2015). SCCPs may lead to adverse effects for human health, especially for fetuses that have weak defense mechanisms to toxicant. The pre- and neo-natal periods are the most crucial periods of individual growth. During these periods the organs are developing gradually, and the defense mechanisms against toxic substance are poorly developed. Thus, the effect of such intake of toxic substances can be especially detrimental and permanent, which have been proved about the adverse effects of prenatal exposure to various POPs (*e.g.*, polycyclic aromatic hydrocarbons (PAHs), PCBs, polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polybrominated diphenyl ethers (PBDEs), and dechlorane plus (DP)) on fetal development (Ben et al., 2014; Dewailly et al., 1993; Huel et al., 1992; Main et al., 2007).

The placenta is an ephemeral organ that grows with the developing fetus. Although the placenta acts as a barrier and transports nutrients and oxygen to the fetus, many toxic compounds can be transported across the placenta to some degree and therefore influence the unborn child (Myren et al., 2007). Therefore, the chemical concentration at the time of child delivery may indicate the burden for both the mother and neonate and reflect the levels of exposure during the entire pregnancy. However, to our knowledge, no investigation on prenatal exposure to SCCPs has been performed due to the lack of methods for analyzing SCCPs in the placenta.

Matrix solid-phase dispersion (MSPD) is a simple, rapid and efficient method of sample preparation for complex matrices, and it has been applied to pretreat solid, semi-solid and highly viscous and toughened samples. The method does not require special instruments and it allows simultaneous sample dispersion, extraction and cleanup in one single step. The MSPD procedure consists of blending the matrix onto a solid sorbent, allowing matrix cell disruption and subsequently extracting the target analytes by means of a suitable elution solvent (Barker, 2000; Capriotti et al., 2010). The MSPD extraction technique has been successfully applied to the trace analysis of POPs from biological matrixes such as PCBs from animal fatty samples (Criado et al., 2004), pesticides, PCBs, PBDEs and polybrominated biphenyl (PBBs) from several marine species (Carro et al., 2005), and PAHs from fish tissue (Pensado et al., 2005).

In this work, we aimed to develop a simple, rapid, efficient, and economic method based on MSPD to analyze SCCPs in human placenta by gas chromatograph-electron capture negative ion low-resolution mass spectrometry (GC-ECNI-LRMS) and gas chromatography–quadrupole time-of-flight high-resolution mass spectrometry (GC–QTOF-HRMS). Three factors (dispersing sorbent, sample-to-sorbent mass ratio and elution solvent) are critical to the MSPD extraction performance for SCCPs, and they were optimized by using a three-factor, four-level orthogonal test. The final proposed method was applied to real human placenta samples. To our knowledge, this is the first study on the analytical method of placenta samples, which can help us to investigate the potential internal exposure of SCCPs of pregnant woman, further to assess the potential risk to the fetus by CPs.

1. Materials and methods

1.1. Chemicals and reagents

The SCCP mixture standards (C_{10}–C_{13}, chlorine contents of 51.5%, 55.5%, 63.0%, 100% purity, 100 ng/μL) and ε-hexachlorocyclohexane (ε-HCH, 99.9% purity, 10 ng/μL) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). 1,5,5,6,6,10-Hexachlorodecane ($^{13}C_{10}$, 100 ng/μL solution in cyclohexane) was obtained from Cambridge Isotope Laboratories (USA). Cyclohexane, dichloromethane (DCM), hexane, and acetone for the pesticide residue analysis were obtained from J.T. Baker (USA). Sulfuric acid and anhydrous sodium sulfate were all guaranteed reagents purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. (China). Bondesil-C_8 (40 μm), and Bondesil-C_{18} (40 μm) were purchased from Agilent Technologies (USA). Silica gel (0.063–0.100 mm) was obtained from Merck KGaA (Darmstadt, Germany). Florisil (60–100 mesh) was obtained from Supelco (Bellefonte, PA). Before use, anhydrous sodium sulfate and silica gel were heated to 650 and 550°C, respectively, in a muffle furnace for 10 hr. Florisil was heated to 140°C in a muffle furnace for 7 hr.

1.2. Sample preparation

Four placenta samples were collected from a hospital and then stored in a freezer at −20°C. The procedures were approved by the Ethic Committee of Research Center for Eco-Environmental Sciences and were in compliance with research requirements regarding human subjects. Before extraction, the excess blood from the placenta was washed away with Milli-Q pure water, and the connective tissues were also removed. Then, the placenta was cut into small pieces, freeze-dried, homogenized in a pulverizer, and packed tightly with aluminum foil and a valve bag.

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