Chemosphere 93 (2013) 1804–1810

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Occupational exposure to synthetic musks in barbershops, compared with the common exposure in the dormitories and households

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HIGHLIGHTS

- The SMs in barbershop dusts were much higher than those from non-occupational sites.
- The SMs increase with the number of barbers and the time of cleanup intervals.
- The calculated daily exposure doses were high for hairdressers.
- There was no significant difference between the hairdressers and normal adults.

ARTICLE INFO

Article history:
Received 4 February 2013
Received in revised form 23 May 2013
Accepted 2 June 2013
Available online 9 July 2013

Keywords:
Synthetic musks
Barbershops
Indoor dust
Occupational exposures
Blood

ABSTRACT

Synthetic musks (SMs) have been widely used as fragrance ingredients in personal care and sanitary commodities. Due to their high volatility and particle-binding affinity, the indoor dust is a major reservoir of SMs, and dust ingestion could be an important exposure way to special populations, such as hairdressers. In spite of the known toxicity of SMs, there is no information regarding the occurrence of SMs in barbershop dusts and the exposure of hairdressers through indoor dust ingestion. In the present study, the levels of two nitro musks and five polycyclic musks were measured from indoor dust samples collected from barbershops, and some other indoor dust samples were also collected from dormitories, bathhouses and households for comparison. The concentrations of ∑SMs in barbershop dusts were 10–100 times higher than those from the other three indoor microenvironments. Polycyclic musks accounted for 89.4% of ∑SMs on average in all samples, of which two compounds, HHCB and AHTN jointly dominated 97.9% of polycyclic musks. The levels of HHCB and AHTN varied from 12.2 to 8.39×10^5 and from 13.2 to 3.49×10^5 ng g^{-1}, respectively. The daily intakes (DIs) of ∑SMs through house dust ingestion were estimated using the model of high dust ingestion and worst-case exposure (P95), and the corresponding exposure rates were 2791, 135 and 727 ng d^{-1} for the hairdressers, general population and toddlers. SMs were also detected in blood samples collected from the hairdressers and normal adults ($n = 50$ and 10, respectively). There was no significant difference between these two groups. Despite the absence of higher SM concentrations in hairdresser's blood, we should not overlook the potential occupational health risks due to their high SMs ingestion rate.

1. Introduction

Synthetic musks (SMs), as economical substitutes for natural musks, have been widely used as fragrance ingredients in personal care and sanitary commodities (e.g., perfumes, shampoos, air fresheners, fabric softeners and cigarettes) since 1950s (Roosens et al., 2007). Sanchez-Prado et al. (2011) found that only two samples were completely free of musk fragrance in 70 commercial brands of perfumes. Reiner and Kannan (2006) reported that the concentrations of HHCB (Galaxolide®) and AHTN (Tonalide®) ranged from <5 ng g^{-1} to over 4000 μg g^{-1}, and from <5 μg g^{-1} to 451 μg g^{-1} in consumer products. Currently, two typical groups of SMs, nitro musks and polycyclic musks, are mainly used in SMs market, of course have specifically been the focus of the attention (Moon et al., 2012). Due to their identified toxic properties , nitro musks have been replaced by the polycyclic musks (Villa et al., 2012). Until now, polycyclic musks are still dominant, of which two compounds HHCB and AHTN represented 95% of the global polycyclic musk production in 1996 (Lignell et al., 2008).

The hydrophobic properties of SMs ($\log K_{OW} \geqslant 4$) are similar to those of the persistent organic pollutants (POPs), consequently, which have led to their wide distribution in both the physical environment and biota (Brausch and Rand, 2011). SMs in the environment mainly originate from the release of production and usage of products containing SMs. In Europe, about 77% of the total SMs

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http://dx.doi.org/10.1016/j.chemosphere.2013.06.027

ended up in wastewater treatment plants after the consumption of fragrance products, and subsequently found their way to the ecosystem due to insufficient treatment of the discharged effluents and exhausted sludge (Horii et al., 2007; Reiner et al., 2007). Furthermore, release of SMs to atmospheric environment, due to their semi-volatility, should not to be ignored (Kubwabo et al., 2012), moreover, their high particle-binding affinities made most of the released SMs adsorb onto the dust and make the indoor dust the major reservoir of SMs (Lu et al., 2011). The accumulation of SMs has posed various health risks. For example, toxicities of SMs and their harmful effects to the endocrine system have been recognized through *in vitro* and *in vivo* experiments on laboratory animals; MK (Musk ketone, belonging to nitro musks) may amplify the genotoxicity of benzo[a]pyrene on humans (Schmeiser et al., 2001); and polycyclic musks have estrogenic effects in fish and weak estrogenic effects in laboratory rats (Seinen et al., 1999).

Indoor dust is the major medium and human exposure route of volatile and semi-volatile organic compounds (VOCs and SVOCs), and it has attracted growing concerns in recent years (Mercier et al., 2011; Little et al., 2012). Unfortunately there are only few studies on the SMs occurrence in indoor dust, comparing with many studies on POPs such as polycyclic aromatic hydrocarbons (PAHs) and polybrominated diphenyl ethers (PBDEs) (Harrad et al., 2008a,b; Kim et al., 2012). It was reported that high levels of SMs could be detected in dust samples from ordinary locations (Fromme et al., 2004). However, there is no relevant report about the levels of SMs in the dust from occupational exposure sites, such as barbershops, where various hair conditioners including hair gel creams and shampoos are widely consumed each day. When Kallenborn et al. studied SMs in ambient and indoor air, they found the highest concentrations of HHCB and AHTN in a barbershop (Kallenborn et al., 1999), suggesting that the dust in such microenvironment may contain relatively high concentrations of SMs. Moreover, poor ventilation conditions, high stability of SMs, and long service hours may expose hairdressers to much higher SMs concentration via dust ingestion than the general public. Therefore, it is necessary to investigate the SMs residue levels in the barbershop dusts and to evaluate their exposure to hairdressers.

The purpose of this study is to: (a) determine and compare the levels and compositions of SMs in barbershop dusts with those from non-occupational dusts; (b) estimate the corresponding exposure levels to human, especially the hairdressers, through indoor dust ingestion; and (c) detect the concentrations of SMs in blood of hairdressers to evaluate the risk of dust ingestion to their occupation health. To the best of our knowledge, this is the first study to document the presence of SMs in high-exposure indoor dust samples and assess the exposure risks for hairdressers as one occupational group.

2. Materials and methods

2.1. Sampling and preparation

During April and July of 2012, a total of 144 indoor dust samples were collected from barbershops ($n = 55$), urban households ($n = 36$, from bedrooms, parlors and bathrooms), university dormitories ($n = 28$ and 23 for female and male, respectively) and bathhouses ($n = 2$) in Tianjin, China. Sampling was performed through active sampling (wiping and brushing from no-floor surfaces of furniture). All samples were sieved using 60-μm stainless steel sieves to remove large debris, packed in solvent-washed aluminum foil, and then stored at −20 °C until analysis.

Blood samples from fifty hairdressers, and ten non-hairdresser adults as reference were collected. Participation of the study was voluntary for all individuals with 300 RMB as compensation. After collection, the blood samples were immediately transferred to a −20 °C refrigerator until later analysis.

Different questionnaires were handed to the participants. For barbershops, the questionnaires covered information about the frequencies of spraying air freshener, the number of immobile workers, daily working hours, types and amount of hair-personal care products used each day. For households, the questionnaires contain information about the number of occupants in the household and the time since their last clean up (sweeping or mopping).

2.2. Reagents, assay standards and other materials

The two nitro musks (MK and MX), five polycyclic musks (AHTN, HHCB, ADBI (Celestolide®), AHMI (Phantolide®) and ATII (Traseolide®)), and the internal standard HCB-$^{13}C_6$ were all obtained from Dr. Ehrestorfer (Augsburg, Germany). The surrogate standard d_{10}-fluoranthen was purchased from Supelco Inc. (Bellefonte, PA, USA). All solvents, including dichloromethane (DCM), *n*-hexane (HEX) and acetone, were of high-performance liquid chromatography (HPLC) grade. Anhydrous sodium sulfate and silica gel (100–200 mesh) were baked at 450 °C for 4 h prior to use.

2.3. Sample extraction and clean-up

2.3.1. Dust sample

To extract and purify the analytes in dust, an accelerated solvent extraction system (ASE) (ASE 350, Dionex Corporation) was employed. The ASE cell (34 mL) was first filled with approximately 4 g of activated silica followed by the addition of a mixture containing 28 g anhydrous Na_2SO_4 and 0.1 g dust. The surrogate standard (20 μL of a 100 μg L^{-1} solution of d_{10}-fluoranthen in *n*-hexane) was then added. The samples were extracted with HEX/DCM (1:1 v/v) at 60 °C, 1500 psi and a static period of 15 min, and this process was repeated twice. The eluant was collected and rotary-evaporated to approximately 1 mL. Subsequently, the solvent was dried with high-purity N_2 stream, and exchanged with HEX to 0.5–1 mL. The extracts were then passed through a 8 mL *n*-hexane pre-cleaned glass chromatography column (1 cm i.d.×15 cm) which was packed consecutively with glass wool, 3 g activated silica gel and 0.5 g anhydrous Na_2SO_4. The elution was performed with 5 mL *n*-hexane, 15 mL of HEX/DCM (2:1), 15 mL of HEX/DCM (1:2) and 20 mL of HEX/DCM (1:3). In the end, the four eluants were combined, concentrated to 1 mL, and added 100 ng internal standard (HCB-$^{13}C_6$) before instrumental analysis.

2.3.2. Blood sample

The samples (2 mL) were defrosted and well resuspended before 15 μL of a 100 μg L^{-1} solution of d_{10}-fluoranthen in hexane was added as the surrogate standard. Prior to liquid–liquid extraction, ethanol (1 mL) was added and vigorously mixed with each blood sample, followed by addition of 2 mL *n*-hexane. The mixture was again mixed on the vortexer (for 1 min), and then sonicated for 5 min. Finally, after a 5 min centrifugation at 3000 rpm, the supernatant *n*-hexane was transferred into a new glass tube, while the precipitate was subjected to a second time extraction. The combined n-hexane phases were concentrated to 1 mL and further purified by a silica gel (0.7 g) packed glass cartridge which was conditioned with 5 mL *n*-hexane, 5 mL DCM, and 5 mL *n*-hexane successively prior to use. Purified products were eluted with 8 mL HEX, 12 mL HEX/DCM (1:3) and 8 mL HEX/DCM (1:4) subsequently. The eluants were combined, concentrated to 1 mL, and added 1 ng HCB-$^{13}C_6$ as the internal standard prior to instrumental analysis.

2.4. Instrument analysis

The target compounds were analyzed by a gas chromatograph coupled with a mass spectrometer system (Agilent 7890A GC/5975C MSD), and separation of target analytes was achieved with