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Methyl siloxanes in environmental matrices and human plasma/fat from both general industries and residential areas in China

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HIGHLIGHTS

- Siloxanes are detected in additives/products from general industries in China.
- Their plasma concentrations in industrial workers were higher than reference group.
- Siloxanes are more likely to distribute in human fat than plasma.
- Linear but not cyclic compounds had an apparent accumulation in human fat.
- Population's half-lives of L8–L10 in human fat were about 1.49–1.80 years.

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ABSTRACT

We investigated human exposure to methyl siloxanes in three general industries (building, automobile, and textile industries) and residential areas in China. Usage volumes of methyl siloxanes *per capita* in these industries were 2–5 orders of magnitudes higher than those in residential areas. Methyl siloxane concentrations in indoor air and dust samples from industrial facilities were 1–3 orders of magnitudes higher than those in residential houses. Both cyclic (D4–D6) and linear (L5–L16) siloxanes were detected in plasma of industrial workers (1.00–252 ng/mL, detection frequencies = 3.7–71%, n = 528), while only cyclic compounds (D4–D6) were detected in plasma of general population (n = 519) with much lower concentrations (1.10–7.50 ng/mL) and detection frequencies (1.7–3.7%). During the occupational exposure, anti-dust mask can reduce 30% of intake of cyclic siloxanes and 74% of intake of linear siloxanes, respectively. In addition, PM-10 could elevate intake of linear siloxanes. Calculated fat-plasma partition ratios of methyl siloxanes (D4–D6, L6–L11) in the present study were 5.3–241 mL/g. Linear rather than cyclic siloxanes had an apparent accumulation in abdominal fat. Population's half-lives of L8–L10 in abdominal fat of general population were approximately 1.49–1.80 years.

1. Introduction

Because of their low surface tension, high thermal stability and smooth texture, methyl siloxanes have been widely used for several decades in personal care products (PCPs) and industrial additives/products, such as lubricants, polishes, paints, lacquers, and textile products (Horii and Kannan, 2008; Wang et al., 2009; SEHSC, 2011). The total annual production volumes of cyclic methyl siloxanes in USA and China, including octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6), were approximately 470 and 800 million kg, respectively (CNKI, 2009; EPA, 2002). Recently, methyl siloxanes have been detected in aquatic, terrestrial, and atmospheric compartments (Dewil et al., 2007; Lu et al., 2010; Mclachlan et al., 2010; Zhang et al., 2011; Bletsou et al., 2013; Pieri et al., 2013; Lee et al., 2014).

In view of their toxic effects on human reproductive, immune, and nervous systems (Liebierman et al., 1999; He et al., 2003; OEHHA, 2007), human exposure to siloxanes has become a public health concern (Horii and Kannan, 2008; Lu et al., 2010). One previous study demonstrated that plasma concentrations of methyl siloxanes in workers from one siloxane production facility in China were much higher than those in general population (Xu et al., 2012). However, besides the workers involved in siloxane production, people in some general industries, such as building, textile, and automobile industries, also have potential exposure to methyl siloxanes due to the large usage of siloxane products (Kaj et al., 2005; Lassen et al., 2005; SEHSC, 2011), which should attract our attention because these three industries have a

Abbreviations: E, intake rate; PCPs, personal care products; PEL, pseudo-exposure level; ∑CMS, total concentrations of cyclic methyl siloxanes; ∑LMS, total concentrations of linear methyl siloxanes; TVOC, total volatile organic compounds; V_c, usage volume of methyl siloxane *per capita*; V_d, volume of distribution.

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large amount of employed population — approximately 100 million in China (Zhang, 2002). However, to the best of our knowledge, there is no study on occupational exposure to methyl siloxanes in these three industries based on biological matrices of workers.

Non-occupational exposure to many typical organic pollutants, such as polyfluorinated compounds and polybrominated diphenyl ethers, can be investigated efficiently based on plasma/blood samples (Liu et al., 2009; Qin et al., 2011). However, despite the wide use in general public, methyl siloxanes were scarcely detected in plasma of general population (Flassbeck et al., 2001; Xu et al., 2012). It was difficult to efficiently evaluate non-occupational exposure to siloxanes basing on plasma samples. Because siloxanes have high log *Kow* values, such as 6.49 for D4, 8.03 for D5, 9.06 for D6, and 6.0 for L5 (Brooke et al., 2009a,b,c; Kaj et al., 2005), they are prone to transferring from plasma to fat (Flassbeck et al., 2003; Kala et al., 1998), indicating that human fat may be a sensitive indicator for human exposure to methyl siloxanes. As far as we know, there is lack of studies on distribution, accumulation, and elimination of methyl siloxanes in human fat during non-occupational or occupational exposure.

In the present study, we collected industrial additives/products (n = 33), environmental matrices (n = 42), human plasma (n = 528), and abdominal fat (n = 41) samples from seven industrial facilities – involved in building, automobile, and textile industries – in northern China. Meanwhile, environmental matrices (n = 140), human plasma (n = 519), and abdominal fat (n = 249) samples from residential areas were collected. We systematically assessed the sources and distribution of cyclic (D4–D6) and linear (L3–L16) siloxanes in these samples. Subsequently, we estimated the influence of human and environmental factors on human intake of methyl siloxanes during occupational exposure. Finally, we investigated the accumulation and elimination potential of methyl siloxanes in abdominal fat of both occupational participants and non-occupational participants.

2. Materials and methods

2.1. Sampling

2.1.1. Plasma and abdominal fat samples

In total, 1047 participants were enrolled in the present study: 528 participants, as the occupational group, were from seven industrial facilities — including 2 construction sites, 2 paint production plants, 1 automobile plant, 1 engine plant, and 1 textile plant. Meanwhile, 519 participants from seven cities in northern China, without industrial work experiences, served as the control group. It should be noted that although some control participants in the present study were from the same city with the participants in our previous study (Xu et al., 2012), the participants had no overlap between these two studies. During January to March 2012, each of 487 occupational participants and 270 control participants provided one plasma sample (5 mL) voluntarily. Subsequently, during June 2012 to March 2014, 7 participants from one paint production plant, 26 participants from the engine plant, 8 participants from the textile plant, and 249 control participants, as the patients receiving abdominal operations, provided paired plasma/abdominal fat samples. The sampling was conducted in two hospitals in Shandong Province, and written consent was provided by their institutional review boards. Each participant completed a questionnaire with auxiliary information such as age, gender, body mass index (BMI), number of daily-used PCPs, occupational history, and use of exposure protection equipment (Supplementary data, Table S1).

2.1.2. Industrial products/additives

During January to March 2012, 33 samples were collected, including 8 home paint product samples from two construction sites, 16 home paint products from two paint production plants, 3 car shell paint and 1 car shell polish – a cream mixture that can remove grime and scrapes from car shell – from the automobile plant, 2 machine lubricant samples from the engine plant, 2 fabric softening agent samples and 1 spot remover – a mixture of solvents plus ultrafine multiholed powder that can dissolve and remove oil stains on fabric – from the textile plant.

2.1.3. Air and dust/soil samples

During January to March 2012, air and dust/soil samples were collected. Each of the construction sites, paint production plants, and textile plant had two workshops, while the automobile plant and engine plant had six and nine workshops, respectively. It was difficult to obtain samples from all workshops in the latter two facilities. Therefore, in each of the seven industrial facilities, we collected indoor air (8 h) and floor dust samples from two workshops (named as A and B). Meanwhile, one outdoor air (8 h) and one soil sample were also collected from each industrial facility. At each sampling site, we collected duplicate air samples using solid phase extraction cartridges as previously reported with minor modifications (Kierkegaard and Mclachlan, 2010). In brief, for collecting each air sample, two 250 mg ENV + cartridges, rinsed with 10 mL of n-hexane prior to sampling, were assembled in series and mounted under a precipitation shield with the down-facing inlets. The assembled cartridges were connected to a diaphragm pump with Teflon tubing. The pump was used to pull air through the cartridges at a flow rate of 1.0 L/min. After sampling, cartridges were sealed and stored at −18 °C. The breakthrough of methyl siloxanes during air sampling was determined by mounting a backup cartridge in series with the primary cartridge. The concentrations of methyl siloxanes in backup cartridges were approximately 145–569 times lower than those in primary cartridges, indicating that breakthrough could be neglected. Dust samples were collected using vacuum cleaners and brushes, and then sealed in glass tubes and stored at −18 °C.

The environmental factors of the studied workshops were measured (Table S2), including floor area, number of workers, vent wind speed, temperature, indoor concentrations of particulate matter (PM-10), and indoor concentrations of total volatile organic compounds (TVOC). TVOC was measured by PhoCheck 5000 portable TVOC monitor with photoionization detector (Ion Science, UK). The range of TVOC measurement is 0.01–10,000 mg/m^3.

In addition, 60 paired indoor air (24 h)/floor dust samples and 10 paired outdoor air/soil samples were collected in residential areas.

2.2. Standards and chemicals

Cyclic siloxanes (D4, D5, D6), linear siloxanes [L3, L4, polydimethylsiloxane mixture (PDMS)], and tetrakis (trimethylsilyoxy) silane (M4Q) were purchased from Sigma-Aldrich (St. Louis, MO, USA). The compositions of linear siloxanes (L5–L16) in the PDMS mixture were measured (Table S3) by gas chromatography coupled with atomic emission detection (GC/AED) as reported previously (Kala et al., 1997). Methanol, ethyl acetate, and n-hexane were HPLC grade and obtained from Fisher Scientific (Fair Lawn, New Jersey, USA).

2.3. Sample pretreatment and analysis

2.3.1. Additives/products

The pretreatment referred to methods for extracting siloxanes from personal care products (Horii and Kannan, 2008; Wang et al., 2009), with some modifications. 1 mL of the sample, spiked with 100 μL of M4Q solution (10 mg/L, internal standard), was vortexed for 5 min at 2500 rpm with 3 mL n-hexane, and then extracted by ultrasonic for 40 min. Subsequently, the mixture was centrifuged at 3000 rpm for 10 min, and the solvent layer was transferred into a glass tube. Each sample was extracted three times. The third extraction was carried out after soaking the sample with 3 mL of n-hexane for 12 h.