



Methylsiloxanes in children silicone-containing products from China: Profiles, leaching, and children exposure



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ABSTRACT

Methylsiloxanes (D4–D6, L5–L16) were detected in children silicone-containing products ($n = 190$, detected frequencies = 46–89%) marketed in China. For the 15 target compounds, the average concentrations ranged from $<LOQ - 0.005 \pm 0.007 \mu\text{g/g}$ in hard toys, $0.084 \pm 0.281 - 22.2 \pm 29.6 \mu\text{g/g}$ in pacifiers, $0.020 \pm 0.023 - 20.6 \pm 16.0 \mu\text{g/g}$ in teethers, and $0.005 \pm 0.009 - 2.81 \pm 3.22 \mu\text{g/g}$ in soft rubber toys. Linear methylsiloxanes were predominant in these four types of children products. In the leaching test, except for L6, the other 14 methylsiloxanes were detected (mean = $0.001 \pm 0.008 - 0.770 \pm 2.60 \text{ ng/mL}$) in saliva leachates for children products, with the detection frequencies ranging from 4 to 46%. The conservative mouthing exposure for children were 6.87–18.05 ng/kg bw-day via pacifiers and 0.44–2.29 ng/kg bw-day via teether/soft rubber toys for \sum cyclic methylsiloxanes, and 7.89–20.74 ng/kg bw-day via pacifiers and 0.41–2.12 ng/kg bw-day via teether/soft rubber toys for \sum linear methylsiloxanes. Methylsiloxanes conservative mouthing exposure associated with children products were 1–2 order of magnitudes lower than the sum of children's daily inhalation exposure and dust ingestion exposure in the indoor environment. The above results indicated that although methylsiloxanes, as the impurities of polydimethylsiloxane, distributed in children silicone-containing products, exposure arising from directly mouthing these products may not be the dominated pathway for children exposure of methylsiloxanes.

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1. Introduction

Methylsiloxanes, one of the most important oligomeric species in organosilicon compounds, are predominantly comprised of a backbone of repeating $-\text{Si}(\text{CH}_3)_2-\text{O}-$ units, which can be divided into two major groups, cyclic methylsiloxanes (D) and linear methylsiloxanes (L). Because of the distinct physicochemical characteristics of these compounds, such as high stability, surface activity, biocompatibility, and lubrication performance, methylsiloxanes have been widely used in many industrial processes and consumer products since the 1940s (Hunter et al., 1946; Horii and Kannan, 2008). Due to its substantial production and extremely wide range of applications, octamethylcyclotetrasiloxane (D4), dodecamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) have been categorized as “high production volume (HPV) chemicals” by the US Environmental Protection Agency and the Organization for Economic Cooperation and Development (Dudzina et al., 2014).

Abbreviations: \sum siloxane, sum of three cyclic and 12 linear methylsiloxanes analyzed; \sum CMS, total concentrations of cyclic methyl siloxanes; \sum LMS, total concentrations of linear methyl siloxanes; PCPs, personal care products.

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Recently, methylsiloxanes have been found in a variety of environmental sources, including surface water (Sparham et al., 2008; Zhang et al., 2011), ambient air (Xu et al., 2015; Buser et al., 2013; Xu et al., 2012; McLachlan et al., 2010; Warner et al., 2010), indoor air and dust (Tran et al., 2015; Tran and Kannan, 2015; Pieri et al., 2013; Lu et al., 2010), sediment (Wang et al., 2013; Zhang et al., 2011), sewage sludge (Lee et al., 2014; Bletsou et al., 2013), biota (Jia et al., 2015; McGoldrick et al., 2014) and human plasma (Xu et al., 2015), and even in remote regions (Sanchis et al., 2015). For adults, dermal and inhalation were the main exposure pathways of methylsiloxanes, with exposure rates three orders of magnitudes higher than those through dust ingestion (Xu et al., 2012; Lu et al., 2010; Lu et al., 2011; Tran and Kannan, 2015). However, besides inhalation, dust ingestion, and dermal contact, children/infants may have unique exposure pathways of chemicals because their behavioral characteristics are different from those of adults. For example, Zhang et al. (2012) and Horii and Kannan (2008) detected cyclic (D4–D6) and linear (L4–L14) methylsiloxanes in some children products (pacifier/nipples and bakewares) from USA, with concentrations ranging from 0.2–7030 $\mu\text{g/g}$, indicating that children silicone-containing products (such as non-nutritive sucking/chewing pacifier/nipples, teethers and toys, etc.) may be potential exposure sources of methylsiloxanes. Furthermore, children might be different from adults in their vulnerability and susceptibility due to the immaturity of

metabolic systems and clearance mechanisms, which may lead to longer half-lives of environmental contaminants (Clewett et al., 2004; Ginsberg et al., 2002). Therefore, exposure to chemicals in the pediatric population deserves specially dedicated attention and study. Owing to their thermal stabilities and physiochemical inertness, silicone polymers, especially polydimethylsiloxane (PDMS) can be used to manufacture siliconized rubber products for children, such as pacifiers, teethingers, cookware, and rubber toys. As impurities of PDMS, methylsiloxanes might be released from these products into the ambient environment during use. More importantly, with respect to young children, especially those between 3 and 36 months old, direct ingestion of methylsiloxanes in children products would be a potentially significant exposure pathway. To the best of our knowledge, there have been no systematic studies on the exposure to methyl siloxanes in the pediatric population as associated with children silicone-containing products.

In the present study, we investigated the distribution of methylsiloxanes in various children silicone-containing products (pacifiers, teethingers, hard toys, and soft rubber toys) made in China, and explored their leaching from children silicone-containing products in artificial saliva. Additionally, the exposure levels of children to methylsiloxanes via children silicone-containing products were also calculated.

2. Materials and methods

2.1. Sample collection

A total of 190 children products, which contained silicone components reported by their commercial specifications, were collected from 30 supermarkets in fifteen cities in China. They were divided into four groups: hard toys ($n = 40$), pacifiers ($n = 74$), teethingers ($n = 32$), and soft rubber toys ($n = 44$).

2.2. Materials

Individual standard cyclic siloxanes (D4, D5, D6) and linear siloxanes [polydimethylsiloxane mixture (PDMS)], as well as an internal standard, tetrakis(trimethylsiloxy)silane (M4Q) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Details of the composition of the PDMS mixture are described in the supporting materials (Table S1). *n*-Hexane was obtained from Fisher Scientific (Fair Lawn, New Jersey, USA). The chemicals used in the preparation of artificial saliva came from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Ultrapure water was prepared by using a Milli-Q water purification system (Millipore, Bedford, MA, USA).

2.3. Sample preparation

In order to eliminate external contamination, the samples were pre-cleaned with ultrapure water and air-dried at room temperature. Several pieces of matrix were broken off from the main body of each sample. They were then cut into small fragments with a size of 2 mm or less by *n*-hexane cleaned scissors.

2.3.1. Extraction experiment

For the analysis of D4–D6 and L5–L16, 1 g of sample was immersed in 5 mL of *n*-hexane in a glass container. The sample was spiked with 100 ng of M4Q and shaken (250 rpm) for 24 h. After sonicating for 10 min, the solvent layer was transferred into a glass tube. Each sample was extracted three times. The second and the third extractions were performed using 3 mL of *n*-hexane, shaken for 30 min, and sonicated for 10 min. The extracts were combined and concentrated to 1 mL under a gentle nitrogen flow before instrumental analysis. Necessary dilutions were performed if the concentrations exceed the linear range of calibration.

2.3.2. Artificial saliva leaching experiment

The time-dependent (5–600 min) immersion test in our study was conducted to systematically investigate the migration behaviors (migration capacities and equilibrium time) of methylsiloxanes between silicone-contained children products and saliva. Each sample (about 1 g) was immersed in 5 mL of artificial saliva in a glass container. The artificial saliva was prepared according to a previous literature (Kusu et al., 1998; Niessner and Klampfl, 2000) and the details are provided in supporting information. The containers were filled without headspace and sealed hermetically. Then, they were shaken (120 rpm) for different durations (5, 20, 40, 60, 120, 240, 600 min) at 37 °C (Allami et al., 2010). The target compounds in artificial saliva were extracted by a liquid–liquid extraction (LLE) method as reported in a previous study (Bletsou et al., 2013) with some modifications. In brief, the artificial saliva leachates were transferred into a separatory funnel and spiked with 100 ng of M4Q. Then, the leachates were extracted with 5 mL *n*-hexane three times. Subsequently, the mixture was centrifuged at 3000 rpm for 10 min and concentrated to 1 mL as described above for analysis.

2.4. Chemical analysis

To analyze cyclic and linear methylsiloxanes, an Agilent 7890A gas chromatograph (GC) equipped with a 5% phenyl methylsiloxane capillary column (HP-5 ms; 30 m \times 0.25 mm i.d. \times 0.25 μ m) was used for separation. An Agilent 5975C mass spectrometer with an electron impact (EI) ion source in the selected ion monitoring (SIM) mode was used for detection. Helium was used as the carrier gas at a flow rate of 1 mL/min. For D4–D6, the injector port (splitless mode), ionization source, mass analyzer, and transfer line temperatures were maintained at 200, 230, 150 and 280 °C, respectively. Likewise, for L5–L16, the temperatures were maintained at 300, 280, 150, 280 °C, respectively. Table S2 lists the mass-to-charge ratios of the ions used to monitor the signal of each compound.

2.5. Quality assurance and quality control

Due to the ubiquitous use of methylsiloxanes in many consumer products and laboratory products, the analyst should take particular care in preventing contamination during sample treatment procedures. Any personal care products containing siloxanes were prohibited in time of sample collection and analysis. To minimize background contamination, all of the glass containers were heated to 300 °C for 4 h and pre-cleaned with *n*-hexane before use (Hori and Kannan, 2008; Lu et al., 2010; Bletsou et al., 2013). No silicon-based materials were used. For GC–MS analysis, silicone-based septa in GC vials were replaced with aluminum foil. Instrument blanks and procedural blanks were analyzed in parallel with every set of 5 samples to monitor interferences and cross-contaminations. The concentration found in the procedural blank was subtracted from the concentrations for the samples. When the analyte concentrations exceeded the linear dynamic range of the calibration curve, they were diluted to a proper concentration and re-quantified. D4, D5, and D6 were detected in procedural blanks at trace levels in children product samples (0.9–1.7 ng/g) and artificial saliva leachates (0.01–0.03 ng/mL), whereas linear methylsiloxanes were not observed in procedural blanks. Hence, for D4–D6, the LOQs were defined as 10 times the standard deviation of the procedural blank concentrations ($n = 7$). For L3–L16, as they were not detected in procedural blanks, LOQs were determined as 10 times the standard deviation of signals of laboratory blank samples ($n = 7$) spiked with known concentrations of the target compounds. LOQs for methylsiloxanes (D4–D6 and L5–L16) were in the range of 0.4–1.4 ng/g for children products and 0.01–0.06 ng/mL for artificial saliva leachates. Recoveries for children silicone-containing products and artificial saliva leachates were 88–96% and 81–94%, respectively. The relative standard deviations (RSD, %) of methyl siloxanes concentrations in duplicate children silicone-containing product samples were <15%.

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