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Distribution, source, fate and bioaccumulation of methyl siloxanes in marine environment

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ABSTRACT

Studies have shown that some cyclic methyl siloxanes were identified as characterized of persistent, bioaccumulated, toxic, and potential to ecological harm. In this study, we determined methyl siloxanes in seawater, sediment and bottom fish samples collected from marine environment in Northeast China. The mean concentrations of total methyl siloxanes were 46.1 ± 27.2 ng/L, 12.4 ± 5.39 ng/g dry weight (dw) and 5.10 ± 1.34 wet weight (ww) in seawater, sediment and fish, respectively. Very strong and significant correlations ($r = 0.94$, $p < 0.0001$) were found in compositions of methyl siloxanes between seawater and sewage, indicating that sewage was the main source of methyl siloxanes in the marine area studied. It was found that the mean value of biota-sediment accumulation factor (BSAF) was.0.716 ± 0.456 for D_4, 0.103 ± 0.0771 for D_5, 1.06 ± 0.528 for D_6 and 0.877 ± 0.530 for D_7.

1. Introduction

Methyl siloxanes, which consist of a backbone of alternating silicon–oxygen (Si–O) units with methyl side attached to each silicon atom, are widely used in various products in our daily life over the last three decades, such as personal care products, cookware, medical devices and so on. There are two basic structures for methyl siloxanes, one is linear structure, and the other is cyclic structure (Fig. S1). Linear methyl siloxanes are also called polydimethylsiloxane (PDMS), usually expressed as L_n (L means linear structure and n is the numbers of silicon atom). Cyclic methyl siloxanes are usually expressed as D_n (D means cyclic structure and n is the numbers of silicon atom) (Hamelink, 1992; Hobson et al., 1997). According to the information from the USEPA, the annual production of D_4 in the United States was in the range of 22 500–45 000 tonnes between 1986 and 2002 (USEPA, 2007). Due to extensive usage, D_4, D_5 and D_6 have been cataloged as high production volume (HPV) chemicals by the US Environmental Production Agency (USEPA, 2007) and the Organization for Economic Co-operation and Development (OECD, 2007).

Reports suggested methyl siloxanes have the estrogen effect to biota (Hayden and Barlow, 1972; Quinn et al., 2007). Methyl siloxanes can cause immune system disorders or connective tissue disease (Granchi et al., 1995; Hea et al., 2003), and even lead to liver and lung injury (Lieberman et al., 1999). Meeks et al. (2007) indicated that, six hours before mating, inhaling a certain amount of D_4 would lead to a decline in fertility to female mice. Environmental risk assessment on cycle siloxanes has been carried out in North America and Europe. In 2008, the Environment Canada and Health Canada published risk assessment reports of D_4, D_5 and D_6 (Environment Canada and Health Canada, 2008a, 2008b; 2008c). In their reports, D_4 and D_5 were identified as characterized of persistent, bioaccumulated, toxic, and potential to ecological harm, but D_6 had none of the above characteristic (Environment Canada and Health Canada, 2008a, 2008b; 2008c). Compared to the above reports, the risk assessment report published by the UK Environment Agency in 2009 gained the same results for D_4 and D_6, but not for D_5 (Brooke et al., 2009a, 2009b; 2009c). Due to the lack of relevant experiment data, the above reports mainly used the model to assess, which led to greatly uncertainty in the evaluation results. For this reason, further investigations on siloxanes are needed to assess the risks posed by these chemicals.

The investigation of bioaccumulation has yielded apparently contradictory results, with high laboratory fish bioconcentration

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factors on the one hand and low field trophic magnification factors on the other. For D_4 and D_5, the available bioconcentration factors (BCFs) for fish were 12400 and 7060, respectively, in laboratory condition (Brooke et al., 2009a, 2009b). Kierkegaard et al. (2011) reported that D_4 and D_5 presented relative high bioaccumulation factors (BAFs) in ragworm and flounder. A survey of trophic magnification factors (TMFs) study for cyclic methyl siloxanes in Norwegian lakes showed that D_5 and D_6 biomagnified with TMFs of 2.9 and 2.3, respectively, and D_4 had substantially lower biomagnification than D_5 and D_6 (Borgå et al., 2012, 2013). TMF studies in a benthic fresh water food web of Lake Pepin, on the upper Mississippi, USA (Powell et al., 2009) and in the marine food web of the Oslofjord, Norway (Powell et al., 2010) both indicated that D_5 was not biomagnified (TMF below 1).

Methyl siloxanes are manufactured products and are not found in nature, nonetheless, these compounds have been detected in various environmental matrices including water, sediment, sewage sludge, landfill gas, personal care products, indoor dust, fish tissues and mammal (Brooke et al., 2009a, 2009b; 2009c; Watanabe et al., 1984; Zhang et al., 2011b; Lu et al., 2010, 2011; Qin and Weng, 2006; Powell et al., 1999; Fendinger et al., 1997; Kaj et al., 2005a,b; Horii and Kannan, 2008). Global air concentrations of volatile methyl siloxanes were ranged from 1.62 to 413 ng/m^3 (Genualdi et al., 2013). McLachlan et al. (2010) reported the D_5 concentration ranged from 0.3 to 9 ng/m^3 in ambient air at a rural site in Sweden. Krogseth et al. (2012) reported that concentrations of D_5 and D_6 were respectively 0.73 ± 0.31 and 0.23 ± 0.17 ng/m^3 in late summer and 2.94 ± 0.46 and 0.45 ± 0.18 ng/m^3 in early winter. In fresh water, an earlier report indicated that the concentrations of methyl siloxanes were ranged from 2000 to 52400 ng/L from the Nagara River, Japan (Watanabe et al., 1984), which was much higher than concentrations from Sweden (total of D_4, D_5 and $D_6 < 270$ ng/L (Kaj et al., 2005a)), Northern Europe (total of D_4, D_5 and $D_6 < 190$ ng/L (Kaj et al., 2005b)) and UK ($D_5 < 29$ ng/L (Sparham et al., 2008)). There are a few studies on sediment concentration of methyl siloxanes. The study area was including Europe (Brooke et al., 2009a, 2009b), Canada (Environment Canada and Health Canada, 2008a, 2008b; 2008c; Kellershohn and Tsanis, 1999), UK (Sparham et al., 2011; Kierkegaard et al., 2011), North America (Fendinger et al., 1997), Japan (Watanabe et al., 1984), and Spain (Sanchís et al., 2013). Among the above studies, the highest concentrations were found in Hamilton Harbor, Ontario Canada (<200–309000 ng/g dw for linear methyl siloxanes) (Kellershohn and Tsanis, 1999). For the other area, methyl concentrations were from several to several thousand ng/g dw.

The production capacity of siloxanes in China has expanded to 1 million tons every year (Bai, 2010). Farther more, many new silicone projects have been carried out in recent years (Bai, 2010). It was reported that the concentrations of total methyl siloxanes were from 10 to 2050 ng/g dry weight (dw) in sediments from the Songhua River and 1410–3920 ng/g dw in sewage sludge from wastewater treatment plants in northeastern China (Zhang et al., 2011b). The concentrations of methyl siloxanes ranged from 21.5 to 21000 ng/g were reported in indoor dust (Lu et al., 2010). Lu et al. (2011) found the concentrations of methyl siloxanes as high as 52.6 mg/g after determining158 personal care products. However, there is little information available for the distribution of methyl siloxanes in the marine environment, especially in China.

The current study investigates siloxanes concentration in surface seawater, sediment, and fish in the marine environment of the northern Chinese sea. The objectives of this study are (i) to determine the pollution levels and potential sources of siloxanes, (ii) to study differences in abundances and compositions of siloxane among different media in marine environment, and (iii) to assess the bioaccumulation of these siloxanes.

2. Materials and methods

2.1. Sampling

Surface seawater samples were collected at 29 sites from marine area around Dalian, northeast China, in July, 2011 (Fig. 1). Among the 29 sample sites, we divided them into three groups: the sites in Group I (Sites W01–W11) were close to the urban place, those in Group III (Sites W22–W29) were far away from the urban place, and those in Group II (Sites W12–W21) were in the midway between Groups I and III. Six bottom fish (*Hexagrammos otakii*) samples were collected at site W02. Sediment samples were collected from 20 sampling sites from coastal area around Dalian, in September, 2010 (Fig. S2). Each seawater and sediment sample was composed of well mixed five sub-samples collected from different locations at each site. Besides, domestic sewage samples (effluent) were collected from five municipal sewage treatment plants in the city of Dalian during November 2011 to January 2012. The locations of the five municipal sewage treatment plants were given in Fig. S3.

All samples (water, sediment, fish and sewage) were packed in solvent-rinsed glass bottles with Teflon-lined caps. Surface sediment (0–5 cm) was collected using a bucket grab. After collection, all samples were sent to the laboratory of the International Joint Research Center for Persistent Toxic Pollutants (IJRC-PTS), Dalian Maritime University, Dalian, China, for processing and analysis. For fish samples, an acetone rinsed bistoury was used to harvest the different organs, including gills, muscles, intestines, eyes, brains, sexual glands. For muscles, we collected a small part from the back of fish, for other organs, we collected all. The rest of the fish were also collected after removing bones, and coded fish-body. Gills, muscles, intestines and fish-bodies were treated as independent samples depending on fishes; eyes, brains and sexual glands were mixed depending organs. Thus as results, we have six samples for gills, muscles, intestines and fish-body, but only one samples for eyes, brains and sexual glands. Sediment and fish samples were stored at −20 C and 1 L seawater samples were mixed with 100 mL dichloromethane (DCM) for storage at 4 C until extraction.

2.2. Chemical and reagents

Standard samples of D4, D5 and D6 were obtained from Tokyo Chemical Industry (Wellesley Hills, MA, USA). PDMS 200 fluid (Viscosity of 5 cSt) including D7 and linear siloxanes (L4–L17) was obtained from Sigma–Aldrich (St.Louis, MO, USA). A surrogate standard containing Tetrakis (trimethylsiloxy)-silane (M4Q; PURITY 97%) was from Aldrich. PCB-30 was purchased from AccuStandard (New Haven, CT, USA), and was used as an internal standard. Organic solvents and reagents used in this study were of pesticide grade purity (J.T. Baker, Phillipsburg, NJ).

2.3. Extraction and analyses

One liter seawater and sewage samples were spiked with 100 ng of surrogate standard (M4Q) and extracted with 100 mL DCM in a separatory funnel with agitation followed by a 1 h settling time. The extracts were filtered through a funnel filled with anhydrous sodium sulfate. Extraction was thrice repeated, followed by DCM collection and rotary-evaporation to 1 mL. Two gram sediment (previously freeze dried and homogenized) and 0.5 g fish (previously homogenized, wet sample) was taken separately in a 10-mL polypropylene tube, and mixed 100 ng of M4Q for 30 min. Then, samples were shaken with 5 mL of n-hexane/ethyl acetate mixture (1:1 v/v) for 30 min and then centrifuged for 5 min at a centrifugal force of 1000 *g*. The solvent layer was then transferred into a flat-bottom flask. The process of extraction was repeated three times. The extract was rotary evaporates to 1 mL, then solvent-exchanged into isooctane and reduced to 1 mL under nitrogen (purity 99.999%) prior to GC–MS analysis. The internal standard PCB-30 was added to correct volume difference prior to GC–MS analysis.

All extracts were identified and quantified using a Thermo Trace gas chromatograph (Thermo TRACE 2000) coupled with a Polaris Q mass spectrometer. Splitless injection was used (2 μL), along with a DB-5 column, (HP 30 m × 0.25 mm i.d. × 0.25 μm film thickness). The GC column oven temperature was programmed at a rate of 20 °C/min from an initial temperature of 40 °C–220 °C, at a rate of 10 °C/min to 280 C (held for 10 min), at a rate of 10 °C/min to 300 °C (held for 5 min). The temperatures of injector, transfer line and ion source were held at 200, 280 and 250 °C, respectively. Electronic impact (EI) ionization with selective ion mode (SIM) was used for quantification.

2.4. Total organic mater and lipid determination

Ten grams of sediment samples (previously freeze dried and homogenized) were used for total organic mater (TOM) measurement. The sediment samples were placed in a muffle furnace and total organic mater determined by measuring their loss after baked at 550 °C for five hours. The details of determination of total organic mater can also be found elsewhere (Jia et al., 2011; Liu et al., 2013). Two grams of fish samples were Soxhlet extracted for 24 h with 100 mL mixed solvent (hexane/acetone, 1:1 v/v). After extraction, the extract was water removing with anhydrous sodium and rotary-evaporation to 1 mL. And then, lipid determine gravimetrically. The details of determination of lipid can also be found elsewhere (Jia et al., 2010, 2011).