Distribution of methylsiloxanes in benthic mollusks from the Chinese Bohai Sea

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ABSTRACT

Methylsiloxanes are a class of silicone compounds that have been widely used in various industrial processes and personal care products for several decades. This study investigated the spatial distribution of three cyclic methylsiloxanes (D4–D6) and twelve linear methylsiloxanes (L5–L16) in mollusks collected from seven cities along the Bohai Sea. D4–D6 (df = 71%–81%) and L8–L16 (df = 32%–40%) were frequently detectable in the mollusk samples, while L5–L7 were not found in any mollusk samples. Cyclic methylsiloxanes (D4–D6) were found in mollusks with the mean concentrations of 15.7 ± 12.3 ng/g ww for D4, 24.6 ± 15.8 ng/g ww for D5 and 34.0 ± 23.0 ng/g ww for D6. Among the seven sampling cities, the cyclic methylsiloxanes were predominant in mollusks, with the total cyclic methylsiloxanes (sum of D4–D6, ∑CMS) accounting for 74.2%–80.7% of the total methylsiloxanes. ∑CMS along the coastline demonstrated a clear gradient, with the highest concentrations in mollusks at the sampling sites located in the western part of the Bohai Sea and the lowest concentrations in mollusks from cities located in the eastern part of the Bohai Sea. The biota-sediment accumulation factors for cyclic methylsiloxanes (D4–D6) and linear methylsiloxanes (L8–L16) were estimated as 0.42 ± 0.06–0.53 ± 0.06 and 0.13 ± 0.03–0.19 ± 0.05, respectively.

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Introduction

Methylsiloxanes are a class of silicone compounds containing Si–O bonds with methyl side groups attached to each silicon atom, which can be classified into cyclic and linear analogs according to their structures. In the past several decades, due to their low surface tension, high thermal stability, and smooth texture (Horii and Kannan, 2008; Wang et al., 2009; Rücker and Kümmerer, 2015; Xu et al., 2017), methylsiloxanes have been widely used in various industrial process and personal care products, as antifoaming agents, sealants, and coatings (Kaj et al., 2005). In China, the annual production of cyclic methylsiloxanes was about 800,000 tons in 2008. In 2009, China became the largest producer and consumer of silicones in the world, with the output and consumption of polysiloxanes at 270,000 and 430,000 tons, respectively (Wang

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et al., 2013; Rücker and Kümmerer, 2015; Arespacochaga et al., 2015; Mojsiewicz-Pienkowska and Krenczkowska, 2018). The production of silicone fluids, elastomers and resins all over the word was 4.7 million tons in 2012 (Rücker and Kümmerer, 2015). Due to increasing end-use markets, the worldwide demand for silicones is expected to experience a yearly increase of 6% until 2022 (Arespacochaga et al., 2015). D4, D5 and D6 have been recognized as high production volume (HPV) chemicals by the Organization for Economic Cooperation and Development and the US Environmental Production Agency (Dudzina et al., 2014; Xu et al., 2017).

The widespread use of methylsiloxanes has led a growing concern about their environmental occurrence. These chemicals were recently detected in various environmental matrices, including water (Horii et al., 2017; Xu et al., 2016; Hong et al., 2014; Sanchís et al., 2013; Zhang et al., 2011; Sparham et al., 2008), sediment (Zhi et al., 2018; Hong et al., 2014; Wang et al., 2013; Sanchís et al., 2013; Zhang et al., 2011), air (Tran and Kannan, 2015; Buser et al., 2013; Xu et al., 2012; Genualdi et al., 2011; McLachlan et al., 2010), soil (Shi et al., 2015; Sanchís et al., 2015) and biotas (Powell et al., 2018; Wang et al., 2017; Jia et al., 2015; Kierkegaard et al., 2013; Kaj et al., 2005). Additionally, it has been reported that cyclic methylsiloxanes are involved in adverse immunologic responses, disorders in connective tissues, liver and lung damage and endocrine disruption in laboratory animal studies (Capela et al., 2017; Rücker and Kümmerer, 2015; Wang et al., 2013). Environmental risk assessments for D4, D5, and D6 have been conducted in Canada, Sweden and the UK (Kaj et al., 2005; Environment Canada and Health Canada, 2008; Brooke et al., 2009a, 2009b, 2009), indicating that methylsiloxanes have the potential to cause ecological harm and other damaging effects on the environment. Recently, concerns have been raised about the persistence and bioaccumulation of methylsiloxanes in the aquatic environment. The European Chemical Agency Member State Committee suggested that D4 should be classified as a persistent, bioaccumulative, and toxic (PBT) substance and D5 as a very persistent and very bioaccumulative (vPvB) substance (ECHA, 2015). Methylsiloxanes have been reported to have the potential to accumulate in aquatic biota based on several sets of field-monitoring data in aquatic organisms. For example, Jia et al. (2015) investigated the trophic transfer of four cyclic methylsiloxanes and found that these chemicals undergo trophic magnification in the marine food web. Conversely, Powell et al. (2018) pointed that trophic dilution of cyclic methylsiloxanes, not trophic magnification, occurred across the sampled food webs in Oslofjord. Controversies of the bioaccumulation of methylsiloxanes still remain due to the lack of relevant experimental data.

Mollusks are present in marine ecosystems with a wide geographical distribution and have good tolerance to a broad range of pollutants. Mollusks usually exist together with polluted water and sediment and are easy to identify and collect. Thus, mollusks are commonly used as potential biomonitors in the aquatic environment (Tanabe, 1994; Tanabe et al., 2000). The Bohai Sea watershed is one of the most populated and industrialized regions in China, which has been heavily contaminated by the inputs and discharge of toxic chemicals along with rapid economic development and urbanization over the past decades. The Bohai Sea, a unique semi-enclosed inner sea located in the northeast of China, is one of the sampling regions of the Asia-Pacific Mussel Watch Program, and mollusks collected from this region have previously been used as potential bioindicators/biomonitors of various POPs (Zhao et al., 2005; Pan et al., 2010; Yang et al., 2004).

However, to the best of our knowledge, there is a lack of information with regard to the distribution and bioaccumulation of methylsiloxanes in mollusks. This study was carried out to investigate the levels and the spatial distribution patterns of cyclic methylsiloxanes (D4–D6) and linear methylsiloxanes (L5–L16) in mollusks collected from coastal areas along the Bohai Sea. Additionally, the biota-sediment accumulation factor for methylsiloxanes was also discussed in our study.

1. Materials and methods

1.1. Reagents and chemicals

Octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), dodecamethylcyclohexasiloxane (D6) and linear siloxanes [polydimethylsiloxane mixture (PDMS)] as well as tetrakis(trimethylsiloxy)silane (M4Q) were supplied by Sigma-Aldrich (St. Louis, MO, USA). The compositions of linear siloxanes (L5 to L16) in the PDMS mixture have been reported previously and are described in the supporting materials (Appendix A Table S1). ^{13}C-D4, ^{13}C-D5, and ^{13}C-D6 were obtained from Cambridge Isotope Laboratories (Andover, MA, USA). HPLC-grade ethyl acetate and n-hexane were supplied by Fisher Scientific (Fair Lawn, New Jersey, USA).

1.2. Sampling collection

Bohai Sea is surrounded by Liaodong Peninsula, the North China Plain and Shandong Peninsula with a total area of 77,300 km^2, and is known to be abundant in coastal and marine resources, such as fisheries, oil and gas. In the present study, a total of 205 mollusks including mussel (*Mytilus galloprovincialis*), venus clam (*Cyclina sinensis*) and oyster (*Crassostrea talienwhanensis*) were collected from culturing rafts in seven coastal cities along the Bohai Sea in September 2015. The sampling sites (Appendix A Fig. S1) were located in Dongying ($n = 25$), Penglai ($n = 30$), Qinhuangdao ($n = 30$, Shouguang ($n = 25$), Tianjin ($n = 25$), Weihai ($n = 35$) and Yantai ($n = 35$), respectively. When sampling, the mollusks were depurated in filtered water for about 12 hr. After being transported to the laboratory, the mollusks were cleaned by water. The soft tissues of mollusks were excised using an acetone-rinsed stainless-steel scalpel blade and then thoroughly rinsed with Milli-Q water to remove extraneous impurities (Liu et al., 2016; Zhu et al., 2012). For each sample and sampling site, three individuals were composited into one sample and packed in solvent-rinsed glass bottles with Teflon liners. In addition, a total of 35 sediment samples (0–5 cm) were obtained in the seven cities. In each sampling city, we collected five sediment samples respectively. Each sediment sample consisted of five well-mixed sub-samples collected from different locations at each site using a bucket grab sampler. After collection, all the samples were frozen immediately and stored at −20°C until analysis.

1.3. Sample preparation

1.3.1. Mollusk samples

The pretreatment procedures for mollusk samples were consistent with the methods of Jia et al. (2015) and Hong et al. (2014), with some modifications. Briefly, 1 g (wet weight) homogenized samples were placed separately in 10 mL glassware tubes and spiked with 100 ng of internal standard (a mixture of ^{13}C-D4, ^{13}C-D5, ^{13}C-D6 and M4Q). The samples were then mixed using an automatic vortexer for 5 min and kept undisturbed for 30 min. The samples were then extracted with 5 mL n-hexane/ethyl acetate (1:1, V/V) for 30 min and centrifuged at 5000 r/min for 10 min. The process of extraction was performed three times. After that, the extracts were combined and concentrated to 1 mL under a gentle stream of nitrogen. The remaining extract was passed through a drying cartridge filled with 1.0 g of anhydrous sodium sulfate, and then concentrated to 0.5 mL and diluted to 1 mL using n-hexane/ethyl acetate (1:1, V/V) prior to gas chromatography mass spectrometry (GC/MS) analysis.

1.3.2. Sediment samples

The pretreatment method of sediment was performed according to the method of Krogseth et al. (2017) with a few modifications. 1.2 g of sediment was transferred to a 15 mL glass centrifuge tube with a screw cap and centrifuged at 2500 r/min for 10 min. The supernatant water was discarded, and the mass of the sediment was recorded. Then, the samples were spiked with a mixture of internal standards (100 μL, 500 μg/L of M4Q, ^{13}C-D4, ^{13}C-D5 and ^{13}C-D6) in an acetone solution. After that, the samples were vortexed for 5 min at 2500 r/min with 10 mL ethyl acetate/n–hexane (1:1, V/V) and then sonicated for 15 min. The samples were extracted three times and the extracts were combined. After extraction, the total extract was concentrated to 5 mL under a gentle nitrogen stream. The remaining extract was purified by passing through a drying cartridge filled with 1.0 g of anhydrous sodium sulfate. The eluents were concentrated to 1 mL under a gentle nitrogen flow before analysis.

1.4. Instrumental analysis

Analysis of methylsiloxanes (D4–D6, L5–L16) was implemented on an Agilent 7890 gas chromatograph coupled with an Agilent 5975C mass selective detector (GC–MS). The separation of the compounds was achieved by a 5% phenyl methylsiloxane capillary column (HP-5 ms; 30 m × 0.25 mm i.d. × 0.25 μm). The MS was operated under selective ion monitoring (SIM) mode. Ultra-high purity helium was selected as the carrier gas, and a constant flow rate of 1.0 mL/min was used. For D4–D6, the temperatures of the injector port (splitless mode), ionization source, mass analyzer, and transfer line were maintained at 200, 230, 150 and 280°C, respectively; for L5–L16, the temperatures were maintained at 300, 280, 150 and 280°C, respectively. The MS parameters of all the analyzed compounds are provided in Appendix A Table S2.

1.5. Total organic carbon (TOC) and lipid determination

The TOC of sediment samples was determined by a TOC analyzer (TOC-VCPH, Shimadzu). The lipid content was determined gravimetrically. 2 g mollusk samples were mixed with sodium sulfate and extracted with n-hexane/dichloromethane (1:1, V/V) using ASE according to the method of Kierkegaard et al. (2013). After extraction, the solvent was evaporated to dryness and the residue was weighed.

1.6. Quality assurance/quality control

Similar to our previous study, a series of precautions were taken to reduce contamination in sampling and treatment. First, any personal care products containing silicone were prohibited and nitrile gloves were worn during sample collection, packaging and preparation processes. Second, all the glass containers were incubated at 300°C for 4 hr prior to use, and pre-cleaned steel pipes (not silicone tubing) were also utilized when a nitrogen-blowing concentrator was used. During GC/MS analysis, silicone-based septa in GC vials were replaced with aluminum foil. In addition, each sample was analyzed in duplicate and procedural blanks were prepared and analyzed along with the real samples to monitor background contamination in the extraction and analysis procedures. The limits of quantification (LOQ) were calculated as 10 times the standard deviation (SD) of signals based on seven mollusk samples spiked with target compounds (10 ng/g). The LOQs of methylsiloxanes ranged from 1.7–3.5 ng/g ww in mollusk samples (Appendix A Table S3) and 1.4–3.1 ng/g in sediment samples (Appendix A Table S4). The matrix spike recoveries of methylsiloxanes ranged from 77% to 92% for mollusk samples (Appendix A Table S3) and 89%–96% for sediment samples (Appendix A Table S4). The relative standard deviation (RSD, %) of the concentrations of methylsiloxanes in duplicate samples was less than 15%.

2. Results and discussion

2.1. Methylsiloxane levels in mollusks in the Bohai Sea

A summary of the wet-weight-based concentrations and detection frequencies of three cyclic (D4–D6) and 12 linear siloxanes (L5–L16) in all the mollusk samples ($n = 205$) from the Bohai sea listed in Table 1. Among all the methylsiloxanes analyzed, D4–D6 (df = 71%–81%) and L8–L16 (df = 32%–40%) were frequently detectable in the mollusk samples, while L5–L7 were not found in any mollusk samples. As shown in Table 1, the mean concentrations of methylsiloxanes (D4–D6, L8–L16) in all the mollusk samples ranged from 2.17 ± 3.36 to 34.0 ± 23.0 ng/g wet weight (ww), with the median values ranging from <LOQ to 34.3 ng/g ww.

Of three cyclic methylsiloxanes, D6 (df = 79%; mean = 34.0 ± 23.0 ng/g ww; median = 34.3 ng/g ww) was the most prominent in the mollusk samples, with the concentrations ranging from <LOQ to 30.1 ng/g ww. The concentrations of D4 (df = 71%; mean = 15.7 ± 12.3 ng/g ww; median = 16.6 ng/g ww) and D5 (df = 81%; mean = 24.6 ± 15.8 ng/g ww; median = 25.1 ng/g ww) were in the range of <LOQ–47.6 ng/g ww and <LOQ–77.3 ng/g ww, respectively. These results were approximately two to three times the concentrations of cyclic methylsiloxanes in invertebrate animals (6.51 ± 2.90 ng/g ww for D4, 8.92 ± 6.03 ng/g ww for D5 and 14.0 ± 8.48 ng/g ww for

Table 1 – The concentrations of methylsiloxanes in mollusks (ng/g ww) from seven sampling cities along the Bohai Sea.

		D4	D5	D6	L8	L9	L10	L11	L12	L13	L14	L15	L16	∑CMS	∑LMS	∑Siloxane
Dongying (n = 25)	Mean	24.9	40.7	56.9	3.86	3.54	4.10	4.67	4.35	4.56	3.95	3.05	3.61	123	35.7	158
	SD	141	15.0	23.3	5.59	4.97	4.94	5.45	5.19	5.04	4.71	4.42	4.89	40.0	15.1	39.9
	Min	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	41.3	12.1	64.8
	Median	29.3	42.2	65.5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	140	35.7	157
	Max	46.0	64.5	88.5	14.5	15.7	12.6	15.8	17.3	12.7	12.4	12.7	14.7	190	64.9	226
	df (%)	80	96	92	36	40	44	48	48	48	44	36	40			
Penglai (n = 30)	Mean	13.2	19.8	27.0	2.38	1.88	2.11	2.34	1.97	2.81	2.21	2.44	2.67	59.9	20.8	80.7
	SD	8.46	9.70	14.0	3.30	2.73	3.13	3.26	2.98	3.45	3.45	3.59	3.99	15.0	7.51	16.7
	Min	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	24.4	9.03	35.4
	Median	16.1	22.3	32.5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	56.3	20.0	80.8
	Max	22.6	30.5	39.1	9.03	6.57	9.03	9.63	10.3	9.48	13.0	13.4	11.3	85.9	35.4	109
	df (%)	73	83	80	37	33	33	37	33	43	33	37	33			
Qinhuangdao (n = 30)	Mean	13.8	22.2	27.2	1.66	2.16	2.82	2.51	1.82	2.68	2.45	2.59	2.49	63.1	21.2	84.3
	SD	8.76	9.35	14.23	2.92	2.72	3.41	3.01	2.65	3.20	2.94	3.57	3.88	16.2	9.87	20.9
	Min	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	19.0	4.77	33.4
	Median	17.5	25.2	33.0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	59.1	19.8	80.6
	Max	7.47	11.1	14.1	3.25	2.18	3.28	2.89	2.29	2.67	2.78	3.17	3.66	28.9	14.5	42.7
	df (%)	73	87	80	27	40	43	43	33	43	43	37	33			
Shouguang (n = 25)	Mean	13.0	21.0	30.1	2.43	1.78	2.77	2.48	2.66	2.59	2.96	1.99	2.58	64.2	22.2	86.3
	SD	8.52	11.0	17.7	3.09	2.69	3.00	3.21	3.11	3.11	3.88	2.76	3.58	19.4	8.63	20.3
	Min	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	23.1	5.25	42.2
	Median	17.1	24.7	37.2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	64.3	24.1	90.6
	Max	23.1	31.8	47.0	7.13	6.99	7.02	9.09	7.26	8.94	9.78	7.17	9.06	96.2	35.0	115
	df (%)	72	80	76	40	32	48	40	44	44	40	36	36			
Tianjin (n = 25)	Mean	29.1	41.2	64.0	4.76	4.23	4.14	4.29	4.57	4.71	4.15	3.67	3.10	134	37.6	172
	SD	16.0	19.8	19.9	5.58	5.76	4.62	5.24	5.58	5.21	5.23	4.09	3.82	41.3	13.3	44.0
	Min	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	46.7	7.59	69.4
	Median	34.6	44.4	66.6	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	150	41.9	191
	Max	47.6	77.3	90.4	16.3	17.5	12.2	14.1	15.0	13.6	15.4	10.9	10.6	194	54.5	235
	df (%)	80	88	96	48	40	48	44	44	48	44	48	44			
Weihai (n = 35)	Mean	9.28	15.4	19.12	1.19	1.23	1.35	1.40	0.89	1.28	1.05	0.90	1.22	43.8	10.5	54.3
	SD	8.42	11.5	15.50	2.23	2.32	2.56	2.47	2.01	2.49	2.15	2.02	2.52	14.7	5.72	15.4
	Min	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	19.0	<LOQ	26.1
	Median	13.6	21.1	28.0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	42.8	10.3	53.3
	Max	22.9	30.7	38.5	5.76	6.63	8.28	7.26	6.03	8.91	6.57	6.33	8.23	79.2	21.8	93.1
	df (%)	57	66	63	23	23	23	26	17	23	20	17	20			
Yantai (n = 35)	Mean	11.5	19.3	25.9	1.76	1.62	1.75	1.50	1.38	1.88	1.42	1.29	1.18	56.6	13.8	70.4
	SD	8.30	11.8	16.0	2.66	2.65	2.47	2.43	2.40	2.68	2.48	2.47	2.22	20.1	5.66	21.4
	Min	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	14.7	4.68	25. 7
	Median	14.7	24.0	33.3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	58.3	11.2	70.0
	Max	21.7	32.1	41.1	7.02	8.13	6.09	6.57	6.00	7.35	7.29	8.28	6.21	88.5	26.4	105
	df (%)	69	74	74	31	29	34	29	26	34	26	23	23			
All the samples (n = 205)	Mean	15.7	24.6	34.0	2.44	2.24	2.59	2.60	2.36	2.79	2.45	2.17	2.30	74.0	21.9	96.0
	SD	12.3	15.8	23.0	3.82	3.58	3.55	3.75	3.68	3.75	3.67	3.36	3.61	39.9	13.3	48.1
	Min	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	14.72	<LOQ	25. 7
	Median	16.6	25.1	34.3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	63.1	19.0	81.8
	Max	47.6	77.3	90.4	16.3	17.5	12.6	15.8	17.3	13.6	15.4	13.4	14.7	194	64.9	235
	df (%)	71	81	79	34	33	38	37	34	40	35	32	32			

L5–L7 were not found in any samples.
∑CMS: the total cyclic methylsiloxanes (sum of D4–D6); ∑LMS: the total linear methylsiloxanes (sum of L8–L16); ∑siloxane: total methylsiloxanes (sum of D4–D6 and L8–L16); <LOQ: less than the limit of quantification.

D6) reported by Jia et al. (2015) in the study of the marine food web in Dalian Bay. Additionally, there are also other studies concerning the concentrations of cyclic methylsiloxanes (D4–D6) in biotas. For example, Powell et al. (2018) reported that the concentrations of cyclic methylsiloxanes (D4–D6) in mussels ranged from 2.66–3.77 ng/g ww for D4, 27.8–252 ng/g ww for D5 and 1.35–8.69 ng/g ww for D6 in one study about the aquatic marine food webs of the Oslofjord. The concentration of D5 in mollusks collected from the Bohai Sea in the present study is approximately one order of magnitude lower than the value Powell et al. (2018) reported, while the concentration of D4 in our study is several times higher than those Powell et al. (2018) reported, demonstrating that the composition profiles of methylsiloxanes are different in the two areas. In addition, previous studies have reported the concentrations of D4–D6 in other aquatic organisms, such as ragworm (<1.6–20 ng/g ww for D4, 5–760 ng/g ww for D5, 2.5–27 ng/g ww for D6) and flounder (<0.8–10.4 ng/g ww for D4, 12–300 ng/g ww for D5,

<0.2–4.7 ng/g ww for D6) from Humber Estuary and herring (12 ± 10 ng/g ww for D4, 137 ± 148 ng/g ww for D5 and 35 ± 31 ng/g ww for D6) from the Baltic sea (Kierkegaard et al., 2013). The concentrations of D4 and D6 in our study are comparable to those observed in previous studies, but the concentration of D5 was one order of magnitude lower than in the previous studies.

Trace levels of linear methylsiloxanes (L8–L16) were found in the mollusks (Table 1). The concentrations of L8–L16 (from 2.17 ± 3.36 to 2.79 ± 3.75 ng/g ww) in mollusks were approximately one order of magnitude lower than those of D4–D6 (from 15.7 ± 12.3 to 34.0 ± 23.0 ng/g ww). In terms of mean values, the concentrations of L8–L16 in mollusks were present in the following decreasing order: L13 (2.79 ± 3.75 ng/g ww) > L11 (2.60 ± 3.75 ng/g ww) > L10 (2.59 ± 3.55 ng/g ww) > L14 (2.45 ± 3.67 ng/g ww) > L8 (2.44 ± 3.82 ng/g ww) > L12 (2.36 ± 3.68 ng/g ww) > L16 (2.30 ± 3.61 ng/g ww) > L9 (2.24 ± 3.58 ng/g ww) > L15 (2.17 ± 3.36 ng/g ww). Lower concentrations of linear methylsiloxanes in mollusks might be due to relatively lower concentrations of these chemicals in the aqueous environment. The concentrations of methylsiloxanes in sediments will be discussed in Section 2.3. Currently, data on the linear methylsiloxanes in mollusks are relatively limited all over the world, and only a few studies have provided the levels of linear methylsiloxanes in aquatic organisms. Our results are comparable to the concentrations in fish muscles (<LOQ– 3.93 ng/g ww for L11) reported by Hong et al. (2014). In the study of Jia et al. (2015), linear methylsiloxanes (L12–L16) were not detectable in any sample, and only L9–L11 were detectable in less than 30% of the total samples, with the concentrations similar to those in our results.

2.2. Spatial distribution and composition profiles in different cities

Table 1 shows the methylsiloxane levels, total methylsiloxanes (sum of three cyclic methylsiloxanes and nine linear methylsiloxanes, ∑siloxanes), total cyclic methylsiloxanes (sum of D4–D6, ∑CMS) and total linear methylsiloxanes (sum of L8–L16, ∑LMS) in mollusk samples from different cities along the Bohai Sea. The concentrations of methylsiloxanes in mollusks varied between different sampling cities. D4–D6 in mollusks were more frequently detected in Dongying (df = 80% for D4; 96% for D5; 92% for D6) and Tianjin (df = 80% for D4; 88% for D5; 96% for D6), which were slightly higher than those of the other five cities — the detection frequencies of D4–D6 in mollusks were 73%–83% for Penglai, 73%–87% for Qinhuangdao, 72%–80% for Shouguang, 57%–66% for Weihai, 69%–74% for Yantai, respectively. The highest levels of ∑CMS in mollusks were found in Tianjin (mean = 134 ± 41.3 ng/g ww; median = 150 ng/g ww, followed by Dongying (mean = 123 ± 40.0 ng/g ww; median = 140 ng/g ww). ∑CMS in mollusks from Weihai were generally the lowest among the seven cities, with the mean concentration of 43.8 ± 14.7 ng/g ww and the median value of 42.8 ng/g ww. The mean concentrations of ∑CMS in mollusks from the other four cities (Table 1) varied from 56.6 ± 20.1 ng/g ww to 64.1 ± 19.4 ng/g ww, with the median value ranging from 58.3 ng/g ww to 64.3 ng/g ww.

For linear methylsiloxanes (L8–L16) in mollusks for the seven cities, the detection frequencies (range from 17%–26% to 44%–48%) were relatively lower than those of cyclic methylsiloxanes (range from 57%–66% to 80%–96%). The distribution pattern of linear methylsiloxanes among the seven cities was similar to that of cyclic methylsiloxanes (D4–D6). As shown in Table 1, higher concentrations in mollusks were also found in Tianjin and Dongying, and the lowest concentrations in mollusks were observed in Weihai. Meanwhile, the concentrations of L8–L16 in mollusks from the seven cities were substantially lower (approximately 1–2 orders of magnitude) than those of cyclic methylsiloxanes.

Overall, ∑siloxane in mollusks among the seven cities ranged from 54.3 ± 15.4 ng/g ww to 172 ± 44.0 ng/g ww. The composition profiles of ∑CMS and ∑LMS in the total methylsiloxane concentrations (∑siloxane) for mollusks from the seven cities are shown in Fig. 1. ∑CMS accounted for 77.4%, 74.2%, 74.9%, 74.2%, 78.1%, 80.7% and 80.4% of the total methylsiloxane content in mollusks collected from Dongying, Penglai, Qinhuangdao, Shouguang, Tianjin, Weihai and Yantai, respectively. Although the concentrations of ∑CMS and ∑LMS in mollusks varied among cities, the composition profiles of ∑CMS and ∑LMS were similar among the different sampling cities, demonstrating that ∑CMS was predominant in mollusks from all the sampling cities. Additionally, a clear spatial gradient along the coastline was observed (Fig. 2), with the highest concentrations in mollusks at the sampling sites located in the western part of the Bohai Sea and the lowest concentrations in mollusks from cities located in the eastern part of the Bohai Sea. The results are probably due to the focus of industries related to petrochemicals in Tianjin and Dongying, which contributed to large inputs of methylsiloxanes to the marine environment. In particular, Tianjin is the largest city in the Bohai Sea region and an important chemical base in China. Liu et al. (2014) have reported that the highest ∑siloxane in sewage sludge of wastewater treatment plants (WWTPs) among 42 WWTPs from 23 representative cities in China was found in Dongying. Besides, model calculation indicated that water inputs are the dominant source of cyclic methylsiloxane contamination in aquatic ecosystems (Brooke et al., 2009a; Kierkegaard et al., 2013) and Hong et al. (2014) pointed out that sewage was the main source of methylsiloxanes in marine areas.
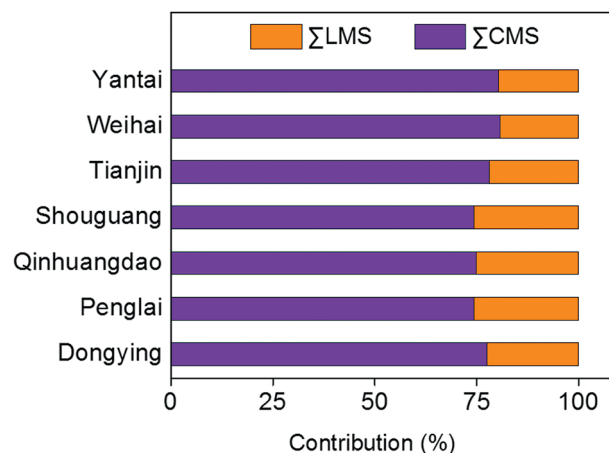

Fig. 1 – Composition profiles of total cyclic methylsiloxanes (∑CMS) and total linear methylsiloxanes (∑LMS) in mollusks from seven cities along the Bohai Sea.
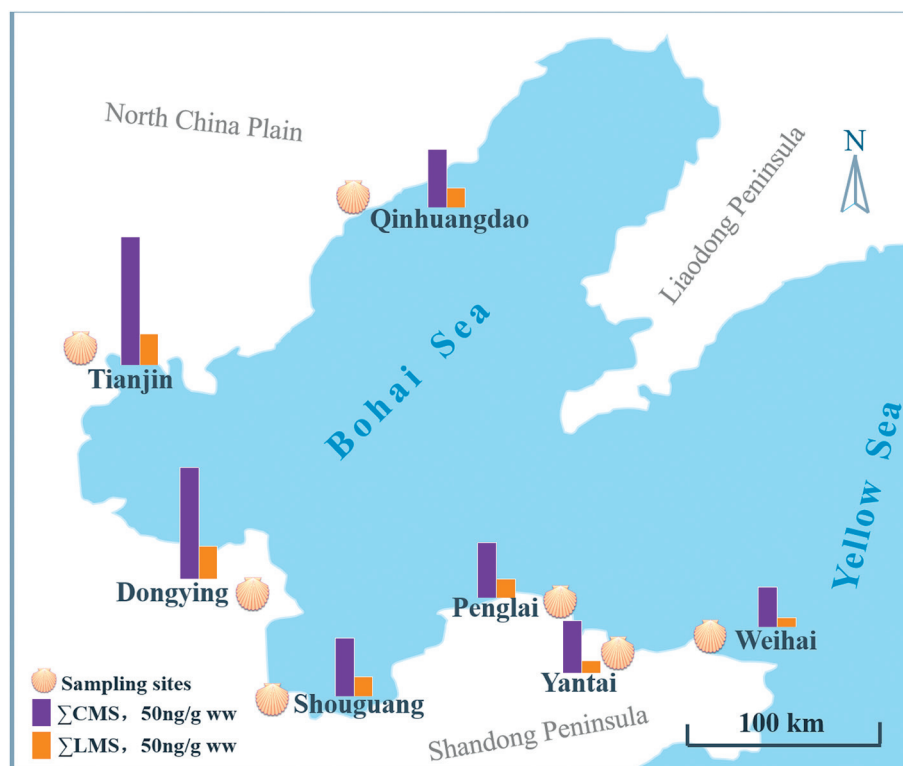
Fig. 2 – Spatial distributions of total cyclic methylsiloxanes (∑CMS) and total linear methylsiloxanes (∑LMS) in mollusks from seven cities along the Bohai Sea.

2.3. Biota-sediment accumulation factor for methylsiloxanes

When released into the aquatic environment, methylsiloxanes have a tendency to adsorb to particles that deposit to sediments (Powell et al., 2018), indicating that sediment might be a direct source for the aquatic organisms. Therefore, the concentration levels of methylsiloxanes in sediments were also investigated in the present study. Briefly, D4–D6 were detected in the sediment (Table 2) collected from the seven cities, with concentrations ranging from 37.3–75.5 ng/g dry weight for Dongying, 23.2–33.2 ng/g dw for Penglai, 21.4–38.6 ng/g dw for Qinghuangdao, 20.4–36.4 ng/g dw for Shouguang, 39.8–80.6 ng/g dw for Tianjin, 14.9–28.3 ng/g dw for Weihai and 21.7–32.9 ng/g dw for Yantai, respectively. For linear methylsiloxanes, L5–L7 were not found in any of the sediment samples. L8–16 were in the range of <LOQ–20.3 ng/g dw for Dongying, <LOQ–12.4 ng/g dw for Penglai, <LOQ–13.0 ng/g dw

for Qinghuangdao, <LOQ–11.3 ng/g dw for Shouguang, 14.6–19.9 ng/g dw for Tianjin, <LOQ–11.8 ng/g dw for Weihai and <LOQ–10.7 ng/g dw for Yantai, respectively. The spatial distribution of methylsiloxanes in sediment among the seven cities was similar to those of mollusk samples discussed above, indicating that sediment should be one of the important sources of methylsiloxanes for mollusks in the study area. In addition, the concentrations of methylsiloxanes in sediment have been widely reported from different locations around the world, with values ranging from several to several hundreds of ng/g dw. For example, the concentrations of D4, D5 and D6 in sediment in Canada (Wang et al., 2013) ranged from <3 to 49 ng/g dw, from 11 to 5840 ng/g dw, and from 4 to 371 ng/g dw, respectively. The highest concentration for D5 in the sediment collected from Llobregat River in Catalonia (Sanchís et al., 2013) was 1270 ng/g dw. Additionally, the mean concentrations for D4–D6 were 5.92–161 ng/g dw in sediment from Tokyo Bay (Powell et al.,

Table 2 – The concentrations (ng/g dw) of methylsiloxanes in sediments from seven sampling cities along the Bohai Sea.												
	D4	D5	D6	L8	L9	L10	L11	L12	L13	L14	L15	L16
Dongying	37.3	46.5	75.5	14.3	15.4	11.9	12.2	12.6	20.3	<LOQ	12.9	19.9
Penglai	23.2	26.0	33.2	8.28	9.72	<LOQ	12.4	10.3	10.3	10.8	<LOQ	11.8
Qinhuangdao	21.4	34.9	38.6	9.81	10.4	10.6	11.3	<LOQ	13.0	9.63	12.0	<LOQ
Shouguang	20.4	29.5	36.4	10.5	11.0	<LOQ	9.81	10.7	11.3	10.3	<LOQ	9.87
Tianjin	39.8	49.2	80.6	15.4	15.8	14.6	16.1	18.3	19.9	16.5	15.1	14.7
Weihai	14.9	18.4	28.3	6.54	8.61	<LOQ	8.28	<LOQ	11.8	<LOQ	<LOQ	8.55
Yantai	22.6	21.7	32.9	10.3	9.18	8.37	9.24	8.97	10.7	<LOQ	9.66	10.6

L5–L7 were not found in any samples. <LOQ: less than the limit of quantification.

2017) and 0.671–9.72 ng/g dw in sediment from marine environment of the northern Chinese sea (Hong et al., 2014), respectively.

In aquatic systems, the biota-sediment accumulation factor (BSAF) is an important parameter which is employed to describe bioaccumulation in sediment-dwelling organisms and fish relative to chemical concentrations in sediment. In previous studies, BSAF have been used to assess the bioaccumulation of methylsiloxanes in biotas (Hong et al., 2014; Warner et al., 2010). Bioaccumulation is implied when a BSAF is (significantly) greater than one. A theoretical value of 1.7 has been estimated based on partitioning of non-ionic organic compounds between tissue lipids and sediment carbon. Previous studies pointed out that a value of BSAF less than 1.7 indicates less partitioning of an organic compound into lipids than predicted. On the contrary, a value of BSAF greater than 1.7 indicates more uptake of the compound. (Hong et al., 2014; Ozkoc et al., 2007; Brunson et al., 1998). BSAFs of methylsiloxanes were estimated according to Eq. (1):

$$BSAF = (C_M/C_S) \cdot (TOC/L) \tag{1}$$

where C_M (g/kg ww) is the concentration of methylsiloxanes in mollusks; C_S (g/kg dw) is the concentration of methylsiloxanes in sediment; TOC (g organic carbon/g dw) is the total organic carbon content in sediment; L (g lipid/g mollusks) is the lipid content in mollusks.

During calculation, mean values of C_M and L for mollusks collected in each site paired with C_S in the corresponding sampling site were used. The value of TOC and L are listed in Appendix A Table S5. For cyclic methylsiloxanes, the values of BSAF based on mollusks were calculated to be 0.42 ± 0.06 for D4, 0.53 ± 0.06 for D5 and 0.51 ± 0.03 for D6, respectively. For L8–L16, the values of BSAF were estimated to range from 0.13 ± 0.03 to 0.19 ± 0.05. All of the calculated values of BSAF in our study were less than 1.7, which indicated less potential bioaccumulation for cyclic methylsiloxanes. Several studies have reported the BSAF values of methylsiloxanes. According to the concentration of D5 in fish (Atlantic cod and shorthorn sculpin) and sediment in the European Arctic environment, the BSAF for D5 has been calculated by Warner et al. (2010), with a median value of 2.1 and 1.5 for cod and sculpin. Powell et al. (2009) reported that the BSAF values of D4, D5, and D6 were greater than 1 in many species (especially for some benthic invertebrate species) in a freshwater lake. The BSAF in fish reported by Hong et al. (2014) ranged from 0.445–1.61 for D4, 0.0403–0.251 for D5, 0.632–2.06 for D6. In a sediment toxicity test with midges, the average BSAF for D5 was calculated to be 1.2, 1.1, 0.83, and 0.46 at treatment concentrations of 13, 30, 73, and 180 mg/kg, respectively (Environment Canada and Health Canada, 2008). Our results are comparable with some of these reports. Based on the wide range of BSAF values for methylsiloxanes reported in previous studies, further investigation of BSAF for methylsiloxanes is still necessary in the future.

3. Conclusions

This study focused on the concentrations and spatial distributions of methylsiloxanes in mollusk samples collected from the Bohai Sea. Cyclic methylsiloxanes (D4–D6) were more frequently detected than linear methylsiloxanes (L8–L16) in the mollusks from the seven sampling cities. L5-L7 were not found in any mollusks. Among the seven sampling cities, the spatial distribution of ∑CMS and ∑LMS demonstrated a clear gradient along the coastline, with the highest concentrations in mollusks at the sampling sites located in the western part of the Bohai Sea and the lowest concentrations in mollusks from cities located in the eastern part of the Bohai Sea. In all the sampling cities, ∑CMS was predominant in mollusks. Additionally, the concentrations in the sediment in the seven sampling areas were also investigated, and the biota-sediment accumulation factors for methylsiloxanes were also calculated. Our results are comparable with some of the previous studies. However, due to the wide range of BSAF values for methylsiloxanes reported in previous studies, it is necessary to further investigate BSAF in the future.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2018.04.026.

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