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Occurrence and fate of chlorinated methylsiloxanes in surrounding aqueous systems of Shengli oilfield, China

Nannan Liu[1,2,*], Jie Zhang[1], Xudan He[3], Lin Xu[4,*], Yaqi Cai[2,4,5]

[1] School of Environmental and Municipal Engineering, Tianjin Chengjian University, Tianjin 300384, China
[2] State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Science, Chinese Academy of Sciences, Beijing 100085, China
[3] Institute of Resources and Environment, Beijing Academy of Science and Technology, Beijing 100089, China
[4] School of Environment, Hangzhou Institute for Advanced Study, UCAS, Hangzhou 330106, China
[5] University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

Mono-chlorinated products of cyclic volatile methylsiloxanes (cVMS), i.e., Monochlormethylheptamethylcyclotetrasiloxane [D3D(CH_2Cl)], monochlormethylnonamethylcyclopentasiloxane [D4D(CH_2Cl)], and monochlormethylundemethylcyclohexasiloxane [D5D(CH_2Cl)], were detected in water [<LOQ (Limit of quantitation) -86.3 ng/L, df (detection frequency) = 23%-38%, n=112] and sediment samples [<LOQ-504 ng/g dw (dry weight), df = 33%-38%, n=112] from 16 lakes located in Shengli oilfield of China, and had apparent increasing trends (31%-34% per annum) in sediments during Year 2014-2020. Simulated experiments showed that chloro-cVMS in sediment-water system had approximately 1.7-2.0 times slower elimination rates than parent cVMS. More specifically, compared with those of parent cVMS, volatilization (86-2558 days) and hydrolysis (135-549 days) half-lives of chloro-cVMS were respectively 1.3-2.0 and 1.8-2.1 times longer. In two species of freshwater mussels (n=1050) collected from six lakes, concentrations of chloro-cVMS ranged from 9.8-998 ng/g dw in *Anodonta woodiana* and 8.4-970 ng/g dw in *Corbicula fluminea*. Compared with parent cVMS, chloro-cVMS had 1.1-1.5 times larger biota-sediment accumulation factors (2.1-3.0) and 1.1-1.7 times longer half-lives (13-42 days). Their stronger persistence in sediment and bioaccumulation in freshwater mussels suggested that environmental emission, distribution and risks of chloro-cVMS deserve further attention.

Introduction

For decades, methylsiloxanes, made of -Si(CH_3)$_2$-O- units, have been widely used in both industrial processes and consumer products (Guo et al., 2019; Horii and Kannan, 2008; Lu et al, 2011; SEHSC, 2011), with annual global production reaching seven million tones in Year 2019 (Garside, 2020). Following the vast usage, some oligomers of these compounds, especially cyclic volatile methylsiloxanes [cVMS, such as D4 (octamethylcyclotetrasiloxane), D5 (decamethylcyclopentasiloxane) and D6 (dodecamethylcyclohexasiloxane)], may be released to the surrounding environment. In view of their

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[*] Corresponding authors.
E-mails: lnn979@126.com (N. Liu), linxu@rcees.ac.cn (L. Xu).

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potential ecological effects (Granchi et al., 1995; He et al., 2003; Liebierman et al., 1999; Quinn et al., 2007; Zhi et al., 2019), many studies have been focusing on occurrence and fate of cVMS in both environmental compartments and biota (Bletsou et al., 2013; Dewil et al., 2007; Kierkegaard et al., 2011; Lee et al., 2014; Mclachlan et al., 2010; Mclachlan et al., 2014; Sanchez-Brunete et al., 2010; Wang et al., 2013; Wang et al., 2015).

Recently, methylsiloxanes have been used as de-emulsifier and de-foamer agents for crude oil production in Shengli Oilfield - the second largest oilfield in China (Shi et al., 2015), and hence cyclic methylsiloxanes (D4-D6) were found in pretreatment oil-production wastewater samples from this area, with concentrations ranging from 12.5-34.3 µg/L (Xu et al., 2019). Furthermore, since Year 2007, electro-oxidation technology has been applied in two oil-wastewater treatment stations (Shinan and Guangli) of this oilfield, and might lead oxidation of halogen ions (from formation water of oil reservoirs) to free halogen compounds. This information suggested the potential generation of halogenated products of methylsiloxanes during oil-wastewater treatment, because H atoms of methylsiloxanes could be substituted by free halogen atoms (Atkinson et al., 1995). In fact, one previous study reported that in electro-oxidation units of Shinan and Guangli stations, following the generation of free chlorine compounds in oil-wastewater, about 4.7% - 28% of cVMS were found to undergo chlorination (Xu et al., 2019). As chlorinated products of cVMS were generated, these compounds may be released to surrounding aqueous systems following effluent discharge and sludge disposal, and hence it was necessary to investigate behaviors of these compounds in aqueous matrices (water and sediment), especially their potential stronger persistence than parent cVMS due to higher lipophilicity of -CH_2Cl than -CH_3. In addition, bio-concentrations of chlorinated methylsiloxanes may be greater than those of their parent methylsiloxanes because of higher lipophilicity of chloromethyl. However, until now, there was no literature focusing on fates of chloro-cVMS in environmental aquatic systems around oilfield and their distribution in benthic organisms.

Based on analysis of environmental/biota samples and simulated elimination experiments, the main objectives of this study were: (1) to determine the profiles and elimination of chlorinated cVMS in aquatic environment of Shengli oilfeild; (2) to assess the presence and bioaccumulation in benthic animal (freshwater mussels).

1. MATERIALS AND METHODS

1.1. *Standards and chemicals*

Monochlormethylheptamethylcyclotetrasiloxane [D3D(CH_2Cl)], monochlormethylnonamethylcyclopentasiloxane [D4D(CH_2Cl)], and monochlormethylundemethylcyclohexasiloxane [D5D(CH_2Cl)] were custom-synthesized (purity > 95%) in Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. Cyclic methylsiloxanes (D4, D5, D6, purity>98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA), while ^{13}C-labeled D4, D5, and D6 were purchased from both Moravek Biochemicals (Brea, CA, USA) and Cambridge Isotope Laboratories (Andover, MA, USA).

Ethyl acetate, acetone and *n*-hexane were purchased from Fisher Scientific (Fair Lawn, New Jersey, USA).

1.2. *Sampling*

Shengli Oilfield, mainly located in Dongying City of Shandong Province (Appendix A **Fig. S1**), is the second largest oilfield in China. At Year 2018, the annual oil production capacity of this oilfield was about 23.8 million tons. The Guangli and Shinan stations, respectively having oil-production wastewater treatment capacity of 11000 and 7000 m^3/day, have been equipped with electro-oxidation units (working voltage = 3.4-3.7 v, current density = 55-65 mA/cm^2) as the first treatment process since Year 2007. Both stations included electro-oxidation unit, primary setting tank, coagulation reactor, secondary setting tank, and filtration tank.

During Year 2014-2020, 28 de-watered sludges, 112 paired water/sediment samples, and 1050 freshwater mussels were collected from Shengli Oilfield (Fig. 1). More specifically, in each year, (1) four de-watered sludges were grabbed from Guangli, Shinan, and two reference stations (Kenxi and Tuoliu) without electro-oxidation units; (2) 16 paired water and sediment samples were collected, respectively using 1 L glass bottles and one stainless-steel shovel, from 16 lakes (pH = 7.3-7.8, mean = 7.6) closed to these four oil-wastewater treatment stations (Appendix A **Fig. S1**). Total organic carbon (TOC) of sediment was determined with a TOC analyzer (TOC-VCPH, Shimadzu); (3) *Anodonta woodiana* (n = 5) and *Corbicula fluminea* (n = 20) were collected from each of the six lakes (L8-L13) closed (50-250 m away) to Guangli and Shinan stations. The average length of *Anodonta woodiana* and *Corbicula fluminea* was 6.4 ± 0.7 cm and 2.2 ± 0.3 cm, respectively. After cleaning with ultrapure water, tissue of mussels was collected by excision with a stainless steel scalpel.

Aqueous, solid and oil samples as well as tissues were separately stored at 4°C in sealed glass tubes without headspace, and then analyzed within 48 hr of the sample collection.

1.3. *Sample analysis*

When pre-treating all kinds of samples, $^{13}C8$-D4, $^{13}C10$-D5 and $^{13}C12$-D6 were applied as internal standards for both cVMS and chloro-cVMS with the same number of Si moieties per molecule.

1.3.1. *Aqueous samples*

100 mL of sample and 40 µL of acetone solution of internal standards (500 µg/L) were mixed in a separatory funnel, and then extracted with 20 mL of *n*-hexane followed by 20 mL of *n*-hexane/ethyl acetate (1:1 by volume). Subsequently, the organic layer was concentrated to approximately 10 mL at 30°C in a rotary evaporator and then dewatered by a 1.0 g anhydrous sodium sulfate cartridge (Bond Elut, Agilent Technology, USA). At last, the eluent was concentrated to 0.5 mL under a gentle stream of nitrogen until gas chromatography-mass spectrometry (GC-MS) analysis.

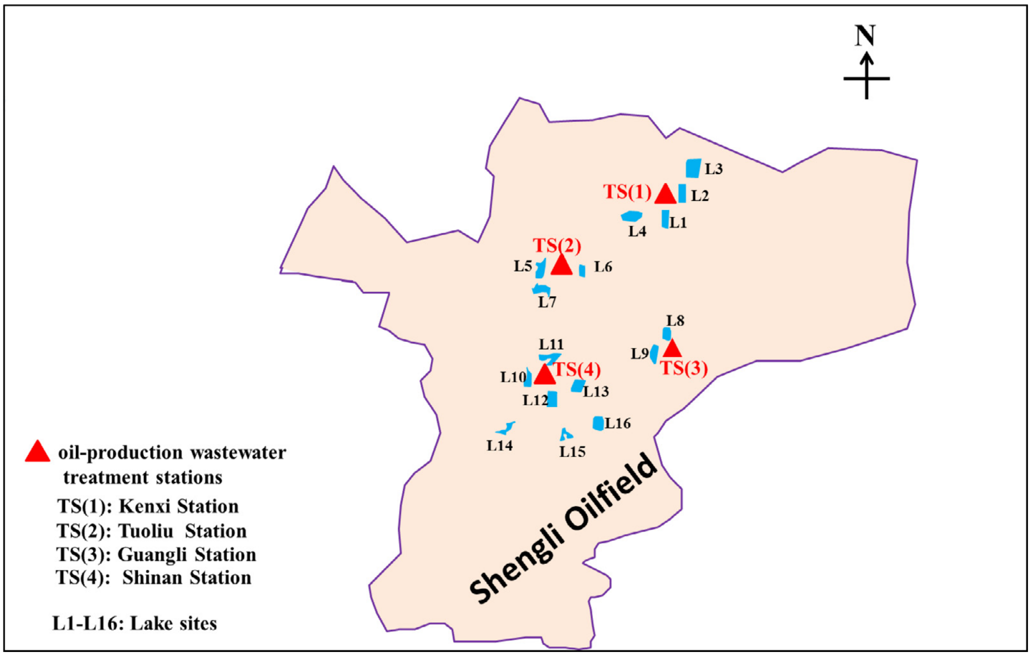

Fig. 1 – Sampling sites in Shengli oilfiled. *paired water/sediment was collected from geometrical center of each lake.

1.3.2. *Sludge and sediment samples*

Before extraction, visible debris such as sticks or gravel in sludge/sediment samples was picked out with the tweezers. Then, sludge (1.0 g) and sediment (1.0 g) were separately spiked with 50 μL of acetone solution of internal standards (1 mg/L). After vortex for 20 min with 5 mL of *n*-hexane/ethyl acetate (1:1 by volume), the mixture was centrifugated at 12000 rpm for 10 min, and then the supernatant was transferred to a glass vial. The samples were re-extracted for two times, and the total extract was dewatered by a 1.0 g anhydrous sodium sulfate cartridge (Bond Elut, Agilent Technology, USA). The eluent was concentrated to 1 mL under a gentle stream of nitrogen. Notably, although solid samples were not dried before extraction avoiding lost, the siloxane concentrations were calculated by dry weight with the following method: another aliquot (1.0 g) of each sludge/sediment sample was separated, and its water content was measured based on the weights taken before and after drying in oven at 105°C for 4 hr.

1.3.3. *Freshwater mussels*

For each lake, all *Anodonta woodiana* (or *Corbicula fluminea*) individuals were freeze-dried, smashed, and then homogenized by electric disperser. After being freeze-dried and homogenized by electric disperser, 0.5 g (dry weight) of sample was extracted with the same procedures as those for soil samples, except that the duration of the third extraction was 6 hr.

Both cVMS and chloro-cVMS were measured by selected ion monitoring (SIM) of Agilent 7890A gas chromatograph - 5975C mass spectrometric detector equipped with HP-5MS column (30 m × 0.25 mm × 0.25 μm). The MS was operated in electron ionization mode (EI) at 70 eV, ion source temperature of 230°C and quadrupole temperature of 150°C. MS parameters for compounds were summarized in Appendix A **Table S1**.

1.4. *Quality Assurance/Quality Control (QA/QC)*

Similar to the previous literatures (Huang et al., 2020; Zhi et al., 2018), in order to avoid/reduce the contamination of siloxanes during sample collection and analysis: (1) the analyst refrained from using hand lotions or other cosmetics containing siloxanes; (2) prior to use, each glass tubes/funnel was cleaned with 20-50 mL of *n*-hexane; (3) not silicone pipes but steel pipes were used for nitrogen concentration process; (4) both seven field blanks and procedural blanks were prepared. Field blanks of water samples were prepared with ultrapure water, solid samples were collected from the non-surface sediment (depth>50 cm) of marshy area far away from human activities. Target siloxanes-free mussels were from the raised mice in the laboratory for toxicology.

As D3D(CH_2Cl), D4D(CH_2Cl) and D5D(CH_2Cl) were not found in any field or procedural blank, LODs and LOQs of these chloro-cVMS were respectively determined as 3 and 10 times the standard deviation of signals of field blanks ($n = 7$) spiked with target compounds at low concentrations (10.0 ng/L for water and 10.0 ng/g dw for sludge/sediment/tissue). Mean field blanks of D4-D6 were 1.9-4.7 ng/L in aqueous samples, 4.3-4.9 ng/g dw in solid sludge, 2.5-3.8 ng/g dw in sediment, and 3.4-4.9 ng/g dw in mussel tissues, while their mean procedural blanks were 1.5-2.3 ng/L in aqueous samples, 2.1-3.1 ng/g dw in solid sludge, 1.8-2.7 ng/g dw in sediment, and 2.3-2.7 ng/g dw in mussel tissues, respectively. For these cVMS, limits of detection (LODs) and quantitation (LOQs) were determined as 3 and 10 times the standard deviation of the field blank signals ($n = 7$), respectively. Overall, LOQs of chloro-cVMS and cVMS were 0.9-3.0 ng/L in aqueous samples, 2.6-4.8 ng/g dw in sludges, 1.7-3.8 ng/g dw in sediments and 2.3-4.2 ng/g dw in mussel tissues, while their recoveries were 89%-95% in aqueous samples, 90%-95% in sludges, 88%-95% in sediments, and 83%-92% in mussel tissues, respectively (Appendix A **Table S2**). Recoveries of chlorinated cVMS were tested by spiking their standards into three types of samples (water, sediment and biota samples) without target chlorinated cVMS at three concentration gradients (Appendix A **Table S2**). In this study, the chloro-cVMS concentrations measured in the samples were all corrected by the recoveries of internal standards, and the recoveries of $^{13}C_8$- D4, $^{13}C_{10}$-D5 and $^{13}C_{12}$-D6 were in the range of 82%-94%.

1.5. *Biota-sediment accumulation factors (BSAFs)*

BSAFs of cVMS and chloro-cVMS were calculated with the following equation:

$$\mathrm{BSAF} = \frac{C_m/f_{lipid}}{C_s/f_{oc}} \quad (1)$$

where C_m (ng/g dw) and C_s (ng/g dw) are the concentrations of target siloxanes in freshwater mussels and sediments, respectively; f_{lipid} is the mean lipid content of freshwater mussels (3.8% for *Anodonta woodiana* and 4.4% for *Corbicula fluminea*), and f_{oc} is the organic carbon content of the sediment (Appendix A **Table S3**).

1.6. *Elimination experiments for chloro-methylsiloxanes and methylsiloxanes*

1.6.1. *Water-sediment system*

For each target compound, the experiment system was prepared by the following method: 50 µL of its actone solution (40 mg/L), 5 g of sediment (TOC = 2.2 %) and 50 mL of ultrapure water (pH = 7.6, adjusted by hydrochloric acid-tris(hydroxymethyl)aminomethane buffer) were mixed in one glass vial (52 mL), immediately capped and incubated at room temperature (25°C). For each compound of cVMS and chloro-cVMS, 18 capped vials were prepared, and then at each of the pre-determined time intervals (0, 20, 50, 80, 120 and 150 days), three vials were sacrificed for the determination of the remaining total concentrations of target compound in both aqueous and solid phases. Meanwhile, another open set of 18 glass vials were also incubated under the same conditions. Furthermore, for evaluating hydrolysis of target compound in aqueous phase, one capped set of 18 glass vials, were prepared by mixing its actone solution (50 µL, 4 mg/L) with 50 mL of water (pH = 7.6), and then at each of the pre-determined time intervals (0, 0.5, 1, 2, 5 and 10 days), three vials were sacrificed for determination of the remaining concentrations of target compounds. For maintaining water content in opened system, ultrapure water was daily added based on measuring mass loss.

1.6.2. *Freshwater mussels*

18 *Anodonta woodiana* (6.4 ± 0.7 cm) and 72 *Corbicula fluminea* (2.2 ± 0.3 cm) individuals, collected from one lake (L10) in Shengli Oilfield, were respectively incubated in 10 L of freshwater where target cVMS and chloro-cVMS were not detected. At each of time intervals (0, 4, 8, 15, 20 and 30 days), 3 *Anodonta woodiana* individuals and 12 *Corbicula fluminea* individuals (four individuals were homogenized for each composite sample) were sacrificed for the determination of the remaining concentrations of target compounds.

2. RESULTS AND DISCUSSION

2.1. *Profiles of chlorinated methylsiloxanes in sediments from surrounding lakes in Shengli oilfield*

2.1.1. *Spatial trends*

Target chlorinated cVMS were not found in those dewatered-sludges collected from two reference treatment stations without electro-oxidation units during Year 2014 to 2020, while they were detected in sludges from two oil-production wastewater treatment stations (Shinan and Gguangli) equipped with electro-oxidation units, with concentration ranging from 8.1-13.7 µg/g dw for D3D(CH2Cl), 24.2-45.7 µg/g dw for D4D(CH2Cl), and 45.4-91.8 µg/g dw for D5D(CH2Cl), respectively (Appendix A**Table S4**). In view of the comparative study (Xu et al., 2016), concentraitons of chloro-cVMS in sludges from these two oil-production wastewater treatment stations were 1-2 orders of magnitude higher than those from paper-making wastewater treatment [882 - 8.55 µg/g dw for D3D(CH_2Cl) - D5D(CH_2Cl)]. In general, final wastewater steams from oil-production wastewater treatment stations of Shengli Oilfield were re-injected to wellbores, while sludges were treated via incineration or landfill, indicating that both cVMS and chloro-cVMS may be difficult to be released from oil-wastewater treatment stations to surrounding surface water systems. However, during Year 2014 to 2020, cVMS were detected in all 16 surrounding lakes in Shengli Oilfield (Appendix A **Table S5**), with concentrations in the range of <LOQ-242 ng/mL [detection frequency (df) = 13%-81%] in water samples and <LOQ-717 ng/g dw (df = 88%-99%) in sediment samples. Meanwhile, chloro-cVMS were detected in some lakes, with concentrations in the range of <LOQ-86.3 ng/L (df = 38%) for D3D(CH_2Cl) and <LOQ-18.7 ng/L (df = 23%) for D4D(CH_2Cl) in water samples, while <LOQ-287 ng/g dw (df = 38%) for D3D(CH_2Cl), <LOQ-504 ng/g dw (df = 38%) for D4D(CH_2Cl), and <LOQ-399 ng/g dw (df = 33%) for D5D(CH_2Cl) in sediments, respectively. More specifically, these chlorinated compounds were merely found in the six lakes L8-L13 close (50-250 m away) to Guangli or Shinan stations. These data indicated that emission of cVMS in Shengli Oilfield were ubiquitous due to their vast usage, while chloro-cVMS in aqueous compartments were mainly attributed to chlorination of cVMS during electro-oxidation process of oil-production wastewater treatments. One previous literature might also support the above speculation, chloro-cVMS concentrations (<LOD-586 ng/g dw) in soil samples nearby Guangli or Shinan stations decreased roughly exponentially with respect to the distance away from these two stations (Xu et al., 2019). cVMS and chloro-cVMS may migration to surrounding lakes via various pathways, such as volatilization during wastewater treatment processes followed by deposition, leakage of oil/sludge during transferring, and leakage of sludge-landfill leachates, *etc*. However, at this juncture, the dominant migration pathways were not clear, and should be further clarified.

Overall, proportions of D3D(CH_2Cl), D4D(CH_2Cl) and D5D(CH_2Cl) to total chloro-cVMS were 37%, 42% and 19% at mean in sediments, which were different from those in de-watered sludges from Shinan and Guangli stations- 9%

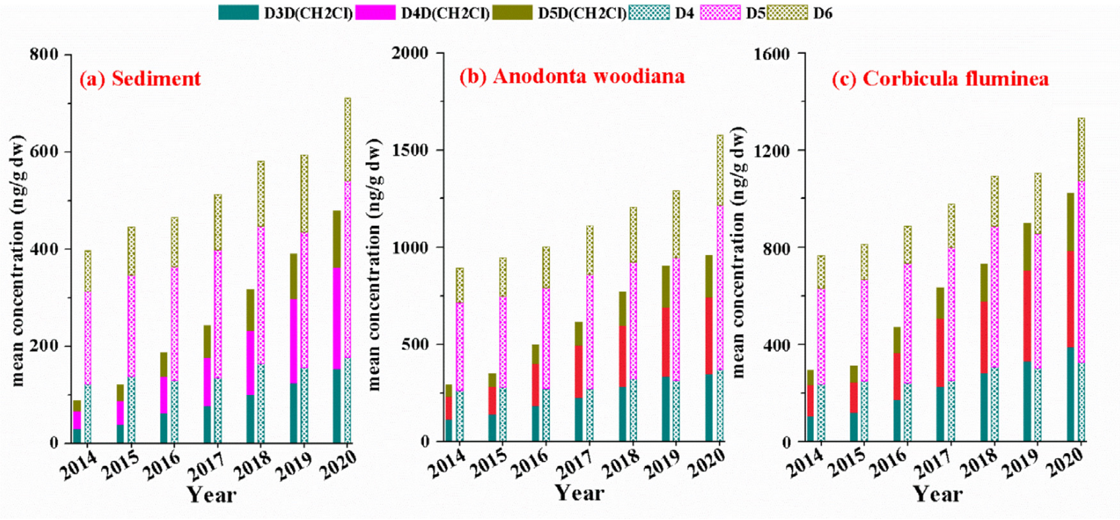

Fig. 2 – Temporal trends of average concentrations of target siloxanes in sediments (a) and freshwater mussels (b and c) from L8-L13 lakes.

for D3D(CH_2Cl), 33% for D4D(CH_2Cl) and 58% for D5D(CH_2Cl). Obviously, as the molecular weights of analogs increased, their migration ability to surrounding aqueous compartment had decreasing trend, which should be caused by many reasons. For example, chloro-cVMS analogs with higher molecular weights should have lower volatilization from wastewater/sludge/oil and stronger sorption to sludge/oil, which would weaken their migration to surrounding lakes by volatilization-deposition and subsurface/surface runoff.

2.1.2. *Temporal trends*

During Year 2014 to 2020, concentrations of total chloro-cVMS (Σchloro-cVMS) in excess sludges ranged from 77.7 to 115 µg/g dw in Shinan Station and from 110 to 145 µg/g dw in Guangli Station, respectively (Appendix A **Table S4**). According to the earlier study on these two oil-production wastewater treatment stations during Year 2008-2014, the concentration of Σchloro-cVMS in dewatered sludges from Shinan Station increased from 81.8 to 97.6 µg/g dw, and from 61.1 to 74.2 µg/g dw in Guangli Station, respectively (Xu et al., 2019). Continuous increase of Σchloro-cVMS concentration in sludge during Year 2008-2020 indicated the continual generation of these compounds in oil-production wastewater treatment stations equipped with electro-oxidation units. Correspondingly, continual emission of chloro-cVMS to surrounding aqueous compartments was also found: in the six lakes close to Guangli or Shinan stations, mean sediment concentrations of Σchloro-cVMS were gradually elevated from 87.2 to 478 ng/g dw in this period (Fig. 2a). Notably, although sediment concentrations of chloro-cVMS were approximately one order of magnitude lower than those of their parent cVMS in these six lakes (Appendix A **Table S5**), mean annual growing rates of chloro-cVMS in sediments - 31% for D3D(CH_2Cl), 34% for D4D(CH_2Cl), and 31% for D5D(CH_2Cl) - were much higher than those of their parent methylsiloxanes - 6.9% for D4, 12% for D5, and 11% for D6. The above data indicated stronger sediment-accumulation of chloro-cVMS than their parent cVMS. Overall, the accumulation of cVMS and chloro-cVMS in sediments should be related with both input and removal of these compounds. At this juncture, it was difficult to calculate their input rates into sediment in this area. Without considering effects of input, the stronger sediment accumulation of chloro-cVMS than parent cVMS may be attributed to their lower removal rates. Therefore, in the following section, based on simulated experiments, the removal (volatilization and degradation) mechanisms of chloro-cVMS and cVMS in water-sediment system were roughly compared.

2.2. *Removal of chloro-cVMS in simulated water-sediment system*

2.2.1. *Volatilization*

Overall, in the opened water-sediment systems, the half-lives of D3D(CH_2Cl), D4D(CH_2Cl) and D5D(CH_2Cl) were 53, 258 and 452 days, respectively, which were 1.7-2.0 times longer than those of parent cVMS - 26 days for D4, 136 days for D5 and 260 days for D6, indicating the strengthened accumulation of chloro-cVMS. By subtracting the slopes of semi-log plots in the capped system (Fig. 3) from the values in paired opened system, the calculated volatilization half-lives in water-sediment systems were 86 days for D3D(CH_2Cl), 904 days for D4D(CH_2Cl) and 2558 days for D5D(CH_2Cl), respectively, which were 1.3-2.0 times longer than those of parent cVMS - 43 days for D4, 580 days for D5 and 1938 days for D6. In the L8-L13 lakes, apparent mean sediment-water partition coefficients of chloro-cVMS [5486 L/g for D3D(CH_2Cl) and 29466 L/g for D4D(CH_2Cl)] were 1.8-2.0 times higher those of parent cVMS [2741 L/g for D4 and 16653 L/g for D5], indicating the higher lipophilicity of -CH_2Cl than -CH_3. Hence, it could be also speculated that in water-sediment system, sorption of chlorinated methylsiloxanes in sediment would be stronger than those of parent methylsiloxanes, and hence their volatilization to air would be weakened more strongly.

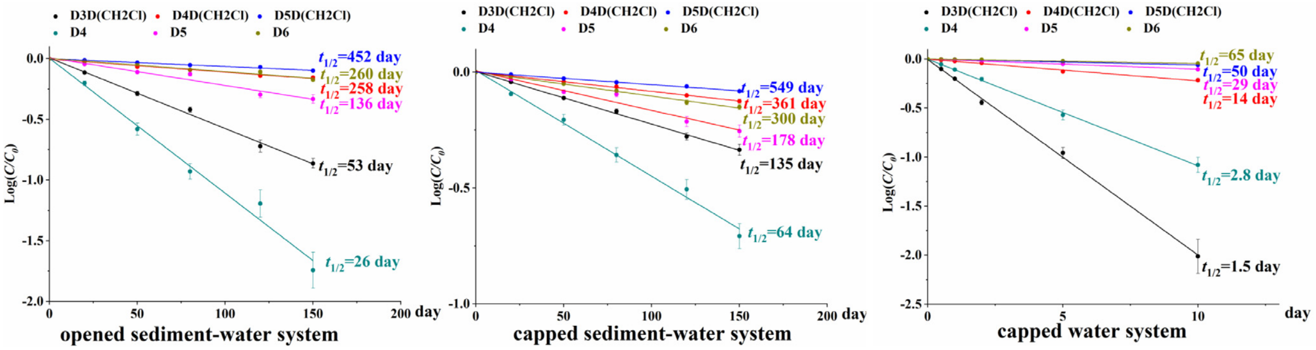

Fig. 3 – Average ratios of target compound concentrations (C) in different incubation times compared to its original spiked concentrations (C_0).

2.2.2. *Degradation*

In capped water-sediment systems, half-lives of chloro-cVMS and cVMS in unsterile samples were approximately equal to those sterile samples, indicating that similar to parent methylsiloxanes (Brooke et al., 2009a, 2009b, 2009c), not biodegradation but abiotic degradation (such as hydrolysis and photo-degradation) should be the dominant degradation mechanism in water-sediment system. In detail, in capped water-sediment system, half-lives of target compounds were 135 days for D3D(CH_2Cl), 361 d ays for D4D(CH_2Cl) and 549 days for D5D(CH_2Cl), respectively, which were 1.8-2.1 times longer than those of their parent cVMS, i.e., 64 days for D4, 178 days for D5 and 300 days for D6 (Fig. 3). However, different from those in water-sediment systems, half-lives of chloro-cVMS [1.5 days for D3D(CH_2Cl), 14 days for D4D(CH_2Cl) and 50 days for D5D(CH_2Cl)] in closed water systems (pH = 7.6) under non-illumination were 1.3-2.1 times shorter than those of parent cVMS (2.8 days for D4, 29 days for D5 and 65 days for D6), which should be caused by stronger electrophilicity of -CH_2Cl than -CH_3. In other words, Si-O bonds with one branch of -CH_2Cl would be more easily to be broken than Si-O bonds linked with two -CH_3 groups. Hence, based on the above data, it could be speculated that in water-sediment system, the slower hydrolysis rates of chloro-cVMS than parent cVMS should be caused by their stronger adsorption to solid phase (especially organic matter) of sediment. Overall, sediment could influence the hydrolysis of siloxanes with the following mechanisms: (1) water adsorbed by clay of sediment would reduce the adsorption sites on clay with siloxanes and hence weaken clay catalysis effect for Si-O-Si cleavage; (2) organic carbon (2.2 %) of sediment would strongly adsorb siloxanes and reduce their sorption by clay. The second mechanism could explain the slower hydrolysis of chloro-cVMS (with stronger sediment-adsorption) than parent cVMS. However, due to lack of standard, levels of $(CH_2Cl)MeSi(OH)_2$, as the hydrolysis product of chloro-cVMS, were not measured in the present study, and hence the effects of -CH_2Cl to siloxane hydrolysis in sediment-water system were not further investigated.

2.3. *Accumulation and elimination of chloro-cVMS in freshwater mussels*

The detection of chloro-cVMS and cVMS in sediments suggested their potential uptake by some deposit feeders, such as freshwater mussels. In the studied area, similar to those in sediments, chloro-cVMS were merely found in freshwater mussels (*Anodonta woodiana* and *Corbicula fluminea*) collected from six lakes close (50-250 m away) to Guangli or Shinan stations. Overall, concentrations of D3D(CH_2Cl), D4D(CH_2Cl) and D5D(CH_2Cl) respectively ranged from 28.0-796 ng/g dw (df = 100%), 30.4-998 ng/g dw (df = 100%) and 9.8-728 ng/g dw (df = 100%) in *Anodonta woodiana,* while 32.3-970 ng/g dw (df = 100%), 22.8-944 ng/g dw (df = 100%) and 8.4-837 ng/g dw (df = 88%) in *Corbicula fluminea*, and were up to two orders of magnitude lower than those (38.6 ng/g dw - 1.9 µg/g dw, df = 100%, Appendix A **Table S6**) of parent cVMS in the same samples. During Year 2014 to 2020, mean annual increasing rates of Σchloro-cVMS (Fig. 2b and 2c) in *Anodonta woodiana* (22.4%) and *Corbicula fluminea* (24.1%) were 2.2-2.6 times larger than those of ΣcVMS (10.2% for *Anodonta woodiana* and 9.9% for *Corbicula fluminea*), which may be caused by various reasons, e.g., 1) compared with parent cVMS, the faster increase of chloro-cVMS in sediments (discussed in Section 2.2) suggested that the uptake of these compounds by freshwater mussels would have larger growing rates; (2) chloro-cVMS may have stronger bio-accumulation than parent cVMS, as discussed in the following paragraphs.

Based on their concentrations in both mussels and pair sediments (Eq. (1)), the calculated mean BSAFs of D3D(CH_2Cl), D4D(CH_2Cl) and D5D(CH_2Cl), were 3.0, 2.7 and 2.5 in *Anodonta woodiana*, while 2.6, 2.3 and 2.1 in *Corbicula fluminea*, which were 1.1 - 1.5 times larger than those of parent cVMS: 2.2 for D4, 2.4 for D5 and 2.2 for D6 in *Anodonta woodiana*, while 1.7 for D4, 1.9 for D5 and 1.4 for D6 in *Corbicula fluminea*. These data suggested faster uptake and (or) lower elimination of chloro-cVMS than parent cVMS. In the present study, elimination rates of these compounds were roughly calculated by incubating these collected freshwater mussels in freshwater free of target compounds. As shown in Fig. 4, elimination half-lives of chloro-cVMS were 13 days for D3D(CH_2Cl), 30 days for D4D(CH_2Cl) and 39 days for D5D(CH_2Cl) in *Anodonta woodiana,* while 15 days for D3D(CH_2Cl), 29 days for D4D(CH_2Cl) and 42 days for D5D(CH_2Cl) in *Corbicula fluminea*. Overall, half-lives of chloro-cVMS in these two kinds of freshwater mussels were 1.1-1.7 times longer than those of parent cVMS - 7.6 days for D4, 22 days for D5 and 32 days for D6 in *Anodonta woodiana*, while 10 d ays for D4, 24 days for D5 and 37 days for D6 in *Corbicula fluminea*. The weaker elimination of chloro-

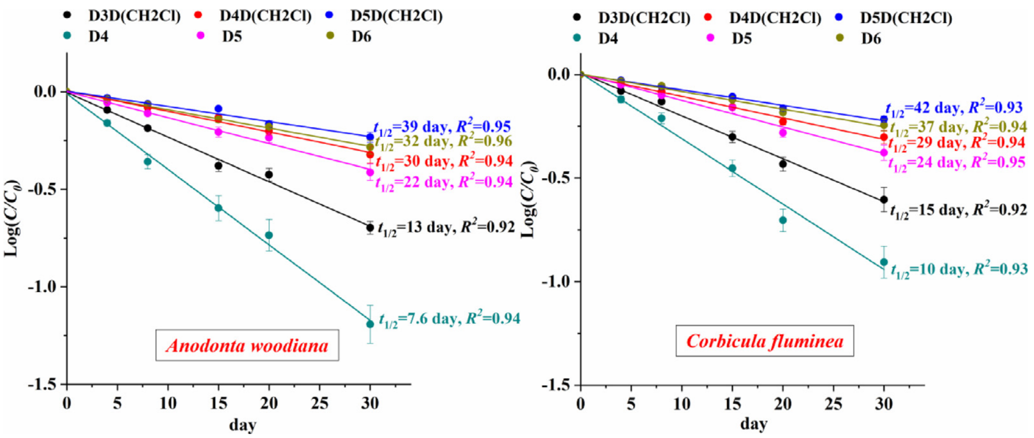

Fig. 4 – Elimination trends of target siloxanes in *Anodonta woodiana* and *Corbicula fluminea*.

cVMS than parent cVMS may be attributed to the several reasons. First, due to their higher lipophilicity, more proportions of chloro-cVMS than parent cVMS would be more prone to accumulating in fat (Więckowski et al., 2007). Second, as weaker volatilities (as mentioned in Section 2.2), exhalation of chloro-cVMS in freshwater mussels would be lower than those of parent cVMS. In addition, metabolization should be also another elimination mechanism of siloxanes. At this juncture, it was difficult to measure concentrations of all metabolites in these freshwater mussels, and hence metabolization rates of chloro-cVMS could not be calculated. However, as oxidation of branched group should be the first and important step for siloxane metabolization (Varaprath et al., 2003), it could be speculated that chloro-cVMS may have slower metabolization rates than parent cVMS due to stronger electrophilicity of -CH_2Cl than -CH_3 (Xiang et al., 2021; Xu et al., 2016).

3. CONCLUSIONS

This is one systematical study to clarify environmental distribution and bioaccumulation of chlorinated methylsiloxanes in oilfield. First, the present study confirmed the generation of chloro-methylsiloxanes in oil-wastewater treatment plants equipped with electro-oxidation processes. Second, the detection of chloro-methylsiloxanes in lake sediments and freshwater mussels closed to oil-wastewater treatment stations indicated actual emission of these compounds during crude oil production. Third, compared with the corresponding parent methylsiloxanes, chloro-methylsiloxanes showed stronger environmental persistence (in sediments) and bioaccumulation (in freshwater mussels), suggesting that environment fates and potential ecological effects of these compounds in both oil-production and other industrial areas deserve further attention.

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