

# Distribution, Elimination, and Rearrangement of Cyclic Volatile Methylsiloxanes in Oil-Contaminated Soil of the Shengli Oilfield, China

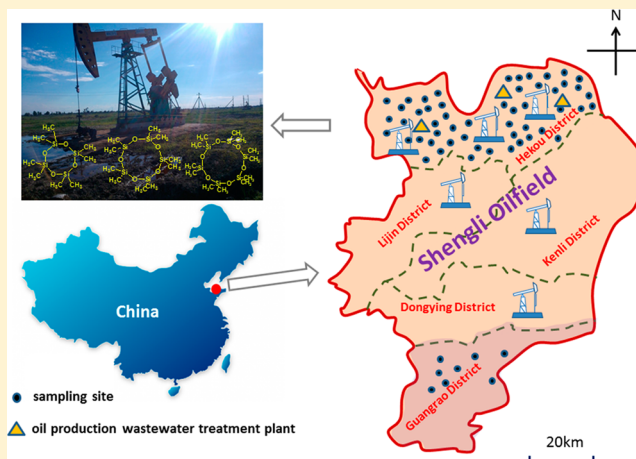
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## S Supporting Information

**ABSTRACT:** Cyclic methylsiloxane standards (D4, D5, and D6) and linear methylsiloxanes (L3 through L16) were detected with high total concentrations (from  $5.20 \times 10^4$  to  $1.07 \times 10^6$  ng/g dw) in 18 oil sludge samples collected from the Shengli oilfield during 2008–2013. In 306 soil samples from this oilfield, the mean concentrations (43.4–125 ng/g dw) and the detection frequencies (65–76%) of D4–D6 were 10.9–11.9 and 2.05–2.24 times higher than those in reference soil samples, respectively. The concentrations of total cyclic siloxanes ( $\Sigma$ Cyclic) had positive correlations ( $R^2 = 0.79$ ,  $p < 0.05$ ) with the total petroleum hydrocarbons concentration (TPH) in soil, indicating that oil production could release cyclic siloxanes to the environment. During 2008–2013, an increasing tendency (mean of 13.4% per annum) of  $\Sigma$ Cyclic was found in soil with high TPH ( $>5000$  mg/kg) but was not found in soil with lower TPH. Elimination experiments showed that petroleum hydrocarbons could reduce the degradation and volatilization rates of D4, D5, and D6 in impacted oilfield soil. The half-lives of D4, D5, and D6 in the opened and capped soil systems with TPH = 400–40 000 mg/kg were 1.19–22.2 and 1.03–7.43 times larger than those in common soil (TPH = 80 mg/kg), respectively. Furthermore, the petroleum hydrocarbons could affect the rearrangement-reaction rates of D5 and D6 in soil.



## 1. INTRODUCTION

In recent years, environmental occurrence of cyclic volatile methylsiloxanes (cVMS), including octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6), have become a concern because of their large emission rates, relatively long persistence, and potentially toxic effects animals.<sup>1–3</sup> These compounds have low surface tension, high thermal stability, and lubricating properties and have been widely used in consumer products and industrial processes for decades.<sup>4–6</sup> The annual import volumes of these compounds into Canada in 2006 were about 1.0–10 million kilograms for D4 or D5 and 0.1–1.0 million kilograms for D6.<sup>7–9</sup> In the United States, D4, D5, and D6 have been categorized as high production volume (HPV) chemicals (greater than 0.45 million kilograms produced or imported annually).<sup>7–9</sup> As a result of their widespread use and persistence, cyclic siloxanes have been found to be in water, air, indoor dust, soil, sediment, sludge, and biota.<sup>10–20</sup>

At present, oil is one of the most important energy sources and industrial raw materials in the world. Crude oil production

includes three distinct phases: primary, secondary, and tertiary (or enhanced) recovery. In primary and second recovery, 20–50% of the crude oil in the oil reservoir is recovered by the natural pressure of the oil reservoirs and injection of pressurized water or gas, respectively. With much of the easy-to-produce oil already recovered, tertiary recovery is operated for ultimately recovering the rest of the oil in reservoirs by chemical techniques.<sup>21</sup> In tertiary recovery, due to the injection of oil-displacing chemical agents such as polymers and surfactants, the crude oil out of the wellbore is in a form of an oil-in-water emulsion. For oil refining, the emulsion needs to be broken by physical and chemical techniques such as the addition of de-emulsifiers.<sup>22</sup> In addition, during crude oil production, with the pressure of the reservoir reduced, dissolved gas in oil is liberated and forms gas–oil foam,

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which must be eliminated using defoamers because the foam could reduce the production efficiency of crude oil and hinder the separation of oil and gas.<sup>23</sup> In recent years, polydimethylsiloxanes (PDMS) and other silicone polymers have been widely utilized as both de-emulsifiers and defoamers in crude oil production.<sup>22,23</sup> cVMS, especially D3 and D4, are important monomers in the manufacture of silicone polymers. As a result, these compounds and their rearrangement products such as D5 and D6 often exist as impurities in silicone fluids. In addition, some reports also suggest the cVMS may be formed during silicone polymer degradation under some conditions.<sup>1,24,25</sup> Therefore, application of silicone de-emulsifiers and defoamers in oil production could result in release of cVMS to environmental matrices (such as soil) in oilfields. For example, in the Shengli oilfield, the second largest oilfield in China, 10% of the crude oil was produced via the tertiary recovery process. In this process, methylsiloxanes are widely used as defoamers and de-emulsifiers. In an oilfield, wastewater and waste gas from oil production were recycled or treated in a capped system, and little of the siloxanes could be released to the surrounding environment. However, oil production brought great amounts of oil sludge containing cVMS (about 10 000 tons per annum). That oil sludge was transferred from wastewater treatment plants to storage pools at regular intervals (about twice per year). Methyl siloxanes in oil sludge may enter the surrounding air compartment via volatilization from open storage pools, and the leakage of oil sludge during transfer also could release siloxanes to the surrounding soil environment.

In nonoilfield soils, cVMS do not tend to accumulate due to two competing removal mechanisms. Under dry conditions, cVMS undergo clay-catalyzed hydrolysis to form silanols rapidly.<sup>26,27</sup> Under the wet conditions, cVMS become volatilized, with volatilization half-lives of days.<sup>27</sup> As a result, the measured cVMS concentrations in agricultural soils amended with biosolids can only account for a fraction of the total cVMS carried over from the biosolid application.<sup>28</sup> However, in an oilfield, soil always contains high levels of petroleum hydrocarbon, which could affect the fate, distribution, and accumulation of cVMS.

To the best of our knowledge, there are no systematic studies on the occurrence and fate of cVMS in oil-contaminated soil in oilfields. In the present study, we investigated the change of cVMS profiles in oil sludge and soil samples collected from the Shengli oilfield from the year 2008 to the year 2013. Furthermore, we studied the influence of petroleum hydrocarbon, a common soil contaminant around oilfields, on the degradation, volatilization, and rearrangement of cVMS in soil.

## 2. MATERIALS AND METHODS

**2.1. Sampling.** The annual oil production volume of the Shengli oilfield is about 27 million tons, 80% of which is produced in Hekou, Lijin, Kenli, and the Dongying district, Shandong Province, China.

In the present study, the Hekou district was selected as the sampling area for the following reasons: on the one hand, this district has the biggest annual oil-production volume (about 13 million tons), accounting for 50% of the total oil-production volume in the Shengli oilfield. On the other hand, compared with the latter three districts, the Hekou district had much fewer industrial (except for oil production) and residential facilities. Each year from 2008 to 2013, 63 samples were collected: three sludge samples from three oil production wastewater treatment plants and 52 soil samples in the crude-

oil-production areas of the Hekou district. Meanwhile, eight field soil samples were collected from the reference area, the Guangrao district, where the soil was not oil-contaminated. Before pretreatment, the collected soil and sludge samples were stored in sealed glass tubes without headspace at  $-18^{\circ}\text{C}$ . The total organic carbon (TOC) of soil samples was determined by TOC analyzer (TOC-VCPH, Shimadzu). The total petroleum hydrocarbons (TPH) in soil were extracted according to the procedure recommended in the U.S. EPA test method 8015B<sup>29</sup> and then analyzed via gas chromatography with a flame ionization detector (GC-FID, 7890A, Agilent).

**2.2. Standards and Chemicals.** Cyclic methylsiloxane standards (D4, D5, D6, purity >98%), linear methylsiloxanes [L3, L4, polydimethylsiloxane mixture (PDMS)], and tetrakis(trimethylsiloxy)silane (M4Q) were purchased from Sigma-Aldrich (St. Louis, MO, USA). The compositions of linear siloxanes (L5 to L16) in the PDMS mixture were measured (Table S1) by gas chromatography coupled with atomic emission detection (GC-AED) as reported previously.<sup>30</sup> Methanol, ethyl acetate, and *n*-hexane were purchased from Fisher Scientific (Fairlawn, New Jersey, USA).

**2.3. Sample Pretreatment: Methyl Siloxanes.** The pretreatment of soil and sludge was similar to the methods described in previous studies,<sup>12–14</sup> with some modifications. Sludge samples were freeze-dried first. Before they were sieved through a 500  $\mu\text{m}$  mesh sieve in a clean room, sludge and the majority of soil samples were not ground, but the hardened soil samples were ground slightly to loosen them. A sample of 0.2 g of the sieved soil or sludge sample was spiked with 100  $\mu\text{L}$  of M4Q solution (1 mg/L, internal standard). The spiked sample was vortexed for 5 min at 2500 rpm with 10 mL of ethyl acetate/*n*-hexane mixture (1:1 by volume) and then centrifuged at 3500 rpm for 10 min (2100g), and the supernatant was transferred to a glass vial. The samples were re-extracted three times. The total extract was concentrated to 5 mL with a gentle stream of nitrogen, and then centrifuged at 12000 rpm for 5 min. The supernatant was purified by passing it through a drying cartridge filled with 1.0 g of anhydrous sodium sulfate. The eluent was collected in a glass vial and concentrated to 1 mL under a gentle stream of nitrogen before GC-MS analysis. Mass-to-charge ratios of ions used to monitor the signals of compounds are summarized in Table S2.

**2.4. Quality Assurance and Quality Control.** We made efforts to avoid siloxane contamination during sample collection and analysis: (1) the analyst did not use hand lotions or other consumer products containing siloxanes; (2) prior to use, all glass tubes were cleaned with hexane and then combusted at  $300^{\circ}\text{C}$ ; (3) prior to use, anhydrous sodium sulfate cartridges were immersed in hexane for 4 h and subsequently rinsed with 10 mL of hexane, and then after being rinsed, the cartridges were dried using purified nitrogen and stored in capped glass tubes; (4) in the nitrogen blow process, only steel pipes (but not instruments containing silicone pipes) were used; and (5) during sampling events, field blanks were collected to assess potential ambient contamination.

Laboratory blanks of cVMS (D4, D5, and D6) in soil with TPH = 80, 1000, or 10 000 mg/kg had concentrations of 0.2–0.5, 0.3–0.7, and 0.6–1.0 ng/g, respectively. Field blanks of D4, D5, and D6 in soil with TPH = 80, 1000, and 10 000 mg/kg had concentrations of 0.7–1.9, 1.5–2.7, and 0.8–1.8 ng/g, respectively. For these three compounds, limits of quantitation (LOQs) were determined as 10 times the standard deviation of the field blank signals ( $n = 7$ ). Concentrations of D4, D5, and

D6 were reported in the present study with the field blank subtracted. L3 through L16 were not detected in laboratory or field blanks, and their LOQs were determined as 10 times the standard deviation of signals of field blank samples ( $n = 7$ ) spiked with these compounds at a known concentration (5 ng/g). LOQs of 17 target compounds in soil with TPH = 80, 1000, or 10 000 mg/kg were 0.5–1.0, 0.5–1.5, and 0.9–2.5 ng/g, respectively. Recoveries of 17 compounds in soil with TPH = 80, 1000, and 10 000 mg/kg were 81–94%, 79–92%, and 76–88%, respectively. Detailed information on recoveries and LOQs was described in Table S3.

The siloxane concentrations in both the sludge samples and the soil samples were reported on a dry weight (dw) basis throughout the study. Oil-sludge samples with siloxane concentrations exceeding the linear range of standard curves in GC–MS were further diluted (10–50 times) and reanalyzed.

## 2.5. Experiments for Elimination Characteristics of cVMS (D4, D5, and D6) in Crude-Oil-Contaminated Soil.

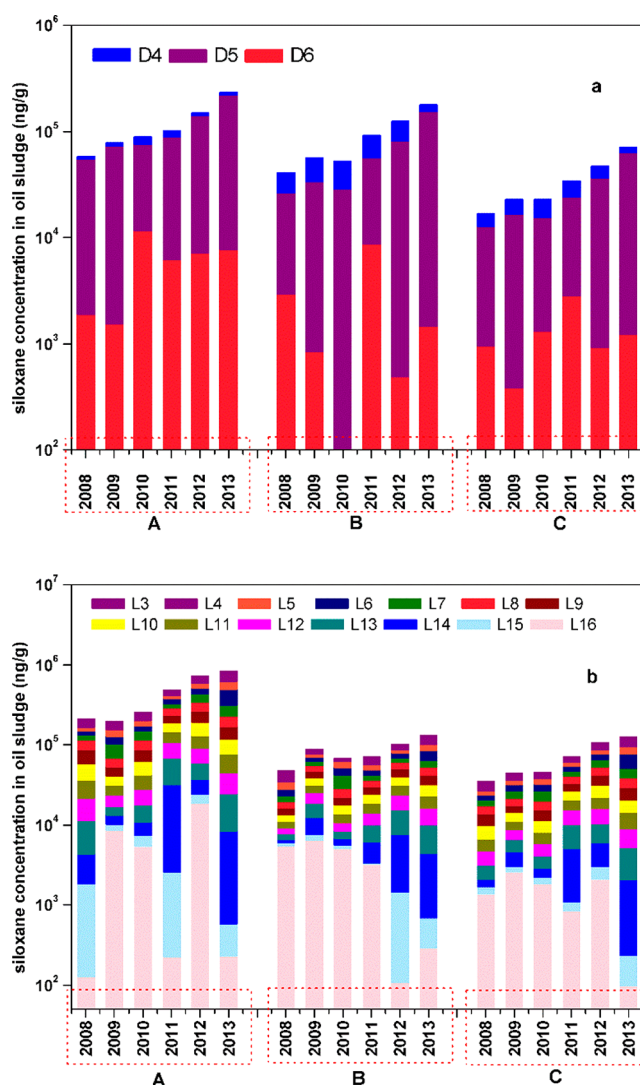
**Preparation for Crude-Oil-Contaminated Soil.** The crude oil from the Shengli oilfield was mixed with petroleum ether. The mixture was centrifuged at 3500 rpm for 20 min, and then the supernatant was collected as a petroleum ether solution of crude oil. The soil sample, collected from the reference area (Guangrao district) and used in this experiment, had a pH of 7.1 and consisted of 1.48 g/kg TOC and 20.7% clay. The major clay mineral in this soil was illite. The original TPH concentration of this soil sample was 80 mg/kg. Spiked with a petroleum ether solution of crude oil, soil samples with TPH concentrations of 400, 2000, 10 000, and 40 000 mg/kg were prepared. For mixing petroleum hydrocarbons with soil uniformly, additional petroleum was added and mixed with soil in a mass ratio of 1:1. Subsequently, the petroleum ether in the soil sample was evaporated for 24 h by a gentle stream of nitrogen. It should be noted that TPH concentrations were detected after the 24 h evaporation procedure.

**Elimination Experiments.** Eliminations of D4, D5, and D6 in soil were studied in separated incubated systems. For each cVMS, 1 mL of its pentane solution (400  $\mu\text{g/L}$ ) and 2 g of soil (19.6–19.7% water content) were mixed in one glass vial. The vial was flushed with nitrogen for 2 min to evaporate pentane, immediately capped, and then incubated at room temperature (25 °C). For each spiked concentration level of TPH, 30 capped vials were prepared for determining the effects of THP concentrations on cVMS hydrolysis kinetics. At each of the predetermined time intervals (0, 1, 2, 4, 6, 18, 48, 92, 192, and 384 h), three vials were sacrificed for the determination of the remaining cVMS concentrations in soil. In addition, another set of 30 vials were prepared the same way as those described above except that those vials were incubated without capping (open systems) to determine the effects of the THP concentrations on the volatilization of cVMS from the tested soil.

## 3. RESULTS AND DISCUSSION

**3.1. Methyl Siloxanes in Oil Sludge and Soil of Oilfields.** *Oil Sludge.* In the oil sludge samples ( $n = 18$ ) from three oil production wastewater treatment plants during 2008 to 2013, the detection frequencies of cVMS (D4, D5, and D6) and linear (L3 through L16) siloxanes were 100%, and the total concentrations of cVMS ( $\Sigma\text{Cyclic}$ ) and linear siloxanes ( $\Sigma\text{Linear}$ ) were from  $1.67 \times 10^4$  to  $2.33 \times 10^5$  ng/g dw (mean =  $8.12 \times 10^4$  ng/g, median =  $6.41 \times 10^4$  ng/g) and from  $3.53 \times 10^4$  to  $8.36 \times 10^5$  ng/g dw (mean =  $2.04 \times 10^5$  ng/g, median =

$1.05 \times 10^5$  ng/g), respectively (Figure 1). These values were greater than the  $\Sigma\text{Cyclic}$  and  $\Sigma\text{Linear}$  values reported for sludge



**Figure 1.** Methylsiloxane concentrations (dw) in oil sludge samples from three oil production wastewater treatment plants (A, B, and C).

from seven municipal wastewater treatment plants (WWTP) in China by 1–3 orders of magnitude.<sup>14</sup> In addition, they were also several times higher than the reported concentrations of siloxanes in sewage sludge from some developed countries.<sup>15,16</sup> For example,  $\Sigma\text{Cyclic}$  and  $\Sigma\text{Linear}$  values in sewage sludge from a municipal WWTP in Greece were  $2.11 \times 10^4$  and  $5.39 \times 10^4$  ng/g, respectively.<sup>15</sup>  $\Sigma\text{Cyclic}$  and  $\Sigma\text{Linear}$  values in sludge from 40 WWTPs in Korea were  $2.05 \times 10^4$  and  $2.23 \times 10^4$  ng/g dw (mean), respectively.<sup>16</sup>

**Soils.** In soil samples ( $n = 48$ ) collected from reference area during 2008–2013, cVMS were detected with concentrations ranging from <LOQ to 28.0 ng/g dw (mean = 3.91 ng/g, median < LOQ, df = 29%) for D4, <LOQ to 45.0 ng/g dw (mean = 8.95 ng/g, median <LOQ, df = 37%) for D5, and <LOQ to 93.5 ng/g dw (mean = 11.4 ng/g, median <LOQ, df = 33%) for D6, respectively, while linear siloxanes were not detected. The mean concentrations of  $\Sigma\text{Cyclic}$  in reference soil samples were 23.5 ng/g dw in 2008, 18.0 ng/g dw in 2009, 30.0

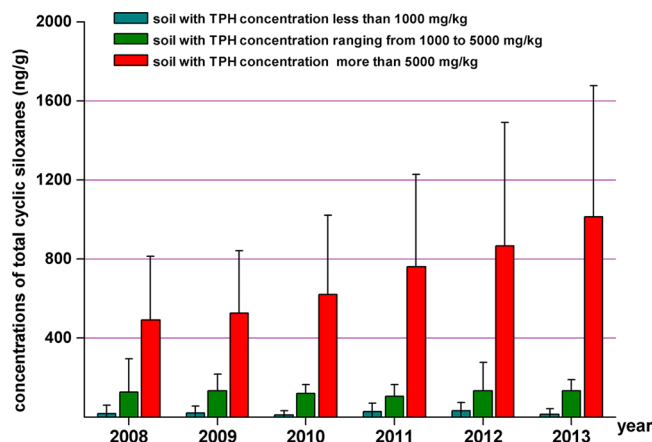


ng/g dw in 2010, 17.1 ng/g dw in 2011, 16.9 ng/g dw in 2012, and 25.0 ng/g in 2013, respectively.

In soil samples ( $n = 306$ ) collected from the studied oilfield during 2008–2013, the concentrations of cVMS were in the range of <LOQ to 505 ng/g dw (mean = 43.4 ng/g, median = 12.6 ng/g,  $df = 65\%$ ) for D4, <LOQ to 917 ng/g dw (mean = 107 ng/g, median = 39.3 ng/g,  $df = 76\%$ ) for D5, and <LOQ to  $1.14 \times 10^3$  ng/g dw (mean = 125 ng/g, median = 31.7 ng/g,  $df = 74\%$ ) for D6, respectively. In other words, the mean concentrations and detection frequencies of cVMS in soils from Shengli Oilfield were 10.9–11.9 times and 2.05–2.24 times higher than those in soil samples from reference area, respectively.

In the present study, L3, L4, and L5 had low concentrations in oil sludge samples; their total concentrations ( $1.05 \times 10^3$  to  $3.66 \times 10^4$  ng/g dw) were about 3.1–36 (mean = 16.9) times lower than those of cVMS ( $1.67 \times 10^4$  to  $2.33 \times 10^5$  ng/g dw), indicating their poor application in the oil field. The poor application also resulted in their low concentrations and detection frequencies in soil of oil field: only L5 was detected (3.40 and 26.5 ng/g dw) in two soil samples collected in 2011, indicating that their application in the oilfield might be poor. Although linear siloxanes with high molecular weights, such as L6 through L16, had comparable concentrations ( $3.33 \times 10^4$  to  $8.28 \times 10^5$  ng/g dw at total) in oil sludge samples to cyclic compounds, they were hardly detected in soil from oilfields; L6, L8, and L9 were detected in two samples collected in 2011, with total concentrations of 4.65 and 37.3 ng/g dw, respectively, which should be due to their low vapor pressures.<sup>31</sup>

During 2008–2013, the  $\Sigma$ Cyclic in soil samples from the Shengli oilfield had statistically positive correlations ( $R^2 = 0.79$ ,  $p < 0.05$ ,  $n = 306$ , Figure S1) with TPH concentrations in soil, an important indicator of oil contamination. According to the TPH concentrations, we divided the soil samples from the Shengli oilfields into three categories: TPH < 1000 mg/kg, TPH = 1000–5000 mg/kg, and TPH > 5000 mg/kg. Although the TPH concentrations in soil samples varied among different sampling times, all the soil samples from the same sampling sites taken between 2008 and 2013 were in the same categories. Figure 2 showed that the mean  $\Sigma$ Cyclic values in soil samples with TPH > 5000 mg/kg were 22.4–63.1 times and 3.82–7.58 times higher than those in soil samples with TPH < 1000 mg/kg and soil samples with TPH of 1000–5000 mg/kg, respectively.

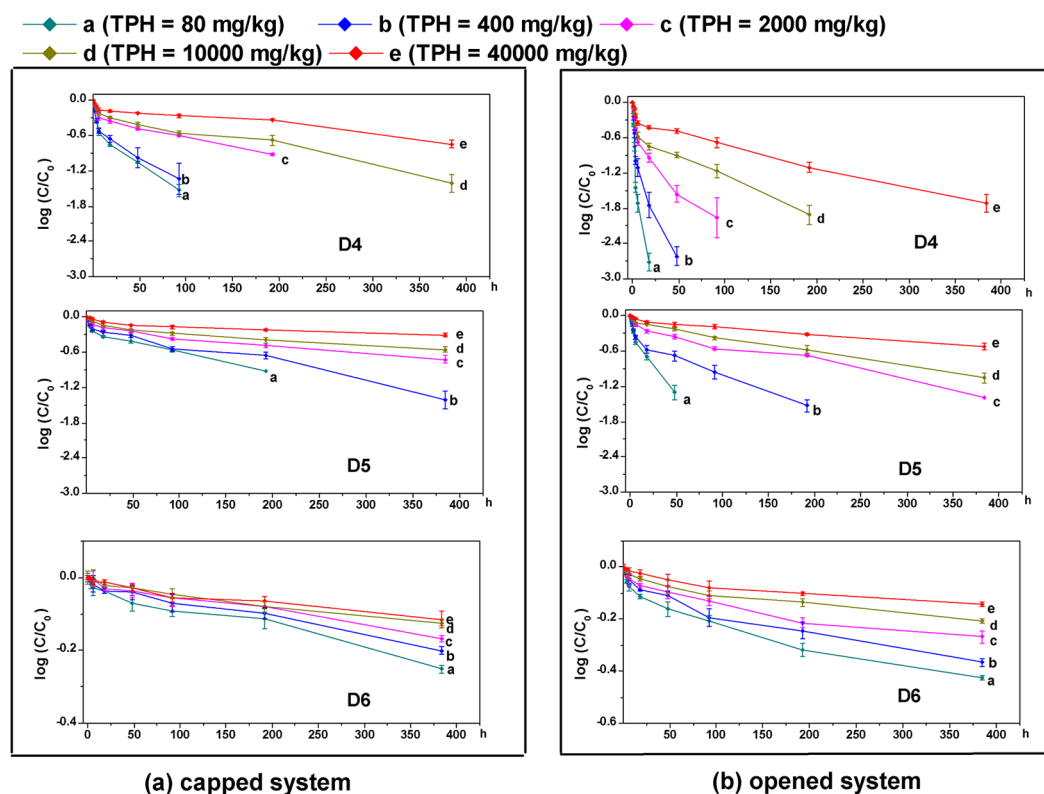


**Figure 2.** Average concentrations (dw) of total cVMS in soil with different TPH concentrations. Error bars represent standard deviation.

These results indicated that the oil contamination had dominant influence on the siloxane distributions in the Shengli oilfield.

The mean concentrations of  $\Sigma$ Cyclic in soil samples from this oilfield were 204 ng/g dw in 2008, 218 ng/g dw in 2009, 240 ng/g dw in 2010, 284 ng/g dw in 2011, 327 ng/g dw in 2012, and 369 ng/g dw in 2013, respectively, indicating that  $\Sigma$ Cyclic had an increasing tendency in soil during six years, perhaps due to the increasing application of siloxanes. In the recent years, to maintain the constant production volume of crude oil in the Shengli oilfield, the volume of oil produced via tertiary recovery has been being elevated, and the average annual growing rates of oil-displacing agent usage were about 11%,<sup>32</sup> indicating that the usage volume of siloxanes as defoamer and de-emulsifier perhaps has been increased in this oilfield. Currently, although there were no accurate data about the annual usage volume of siloxanes, the phenomenon that  $\Sigma$ Cyclic in oil sludge samples increased year by year during 2008 to 2013 (Figure 1) may support our speculation to some extent. For oil-contaminated soil samples over the entire sampling period, there was no apparent change of  $\Sigma$ Cyclic in soil samples with TPH content < 1000 mg/kg or in the range of 1000 to 5000 mg/kg, while a substantial increase in  $\Sigma$ Cyclic was observed in soil with TPH content > 5000 mg/kg (Figure 2), with the annual growth rates in the range of 6.9–22.5%. In the present study, soil samples with higher TPH concentrations were closer to the oil production wastewater treatment plants than those with lower TPH concentrations (Figure S2), suggesting that the import rates of siloxanes in soil samples with higher TPH concentrations would be larger than those in samples with lower TPH concentrations. It should be noted that these results were different with those in previous study, which reported that even in soil with repeated large mass loading of siloxanes, siloxanes were not prone to accumulating in soil due to their fast volatilization and degradation (hydrolysis).<sup>33</sup> This difference may be because that the soil in the oil field had different physical or chemical properties with common soil, and these differences would change (reduce) the elimination rates of siloxanes in soil: petroleum hydrocarbons elevated the content of organic matter in soil, and in the present study, TOC concentrations in soil had a significant correlation ( $R^2 = 0.85$ ,  $p < 0.05$ ,  $n = 306$ ) with TPH concentration. The mean TOC concentration (35.5 g/kg) in soil with TPH > 5000 mg/kg was 19 and 4.2 times higher than those in soil samples with TPH < 1000 mg/kg (1.85 g/kg) and TPH of 1000–5000 mg/kg (8.44 g/kg), respectively. Organic matter in soil could adsorb siloxanes with high lipophilicities and reduce their elimination rates. In the following section, through elimination experiments, we discussed the influence of petroleum ether on siloxane elimination in soil.

**3.2. Effects of Petroleum Hydrocarbon on the Kinetics of cVMS Elimination in Soil. In the Closed Systems.** The degradation of D4, D5, and D6 in capped soil were illustrated as semilog plots in Figure 3. The kinetics of D4 degradation had two phases (a rapid phase at 0–6 h and a slow phase thereafter) regardless of the TPH contents. In soil with five TPH levels (80, 400, 2000, 10 000, and 40 000 mg/kg), the half-lives of D4 in the rapid phase varied from 3.34 to 11.6 h, which were 8.0–17.2 times faster than those (26.9–200 h) in the slow phase (Table 1). Previous studies reported that the hydrolysis was the dominant degradation pathway for methyl siloxanes under this condition.<sup>26,27</sup> Methyl siloxanes in soil formed oligomeric diols via ring-opening hydrolysis, such as a



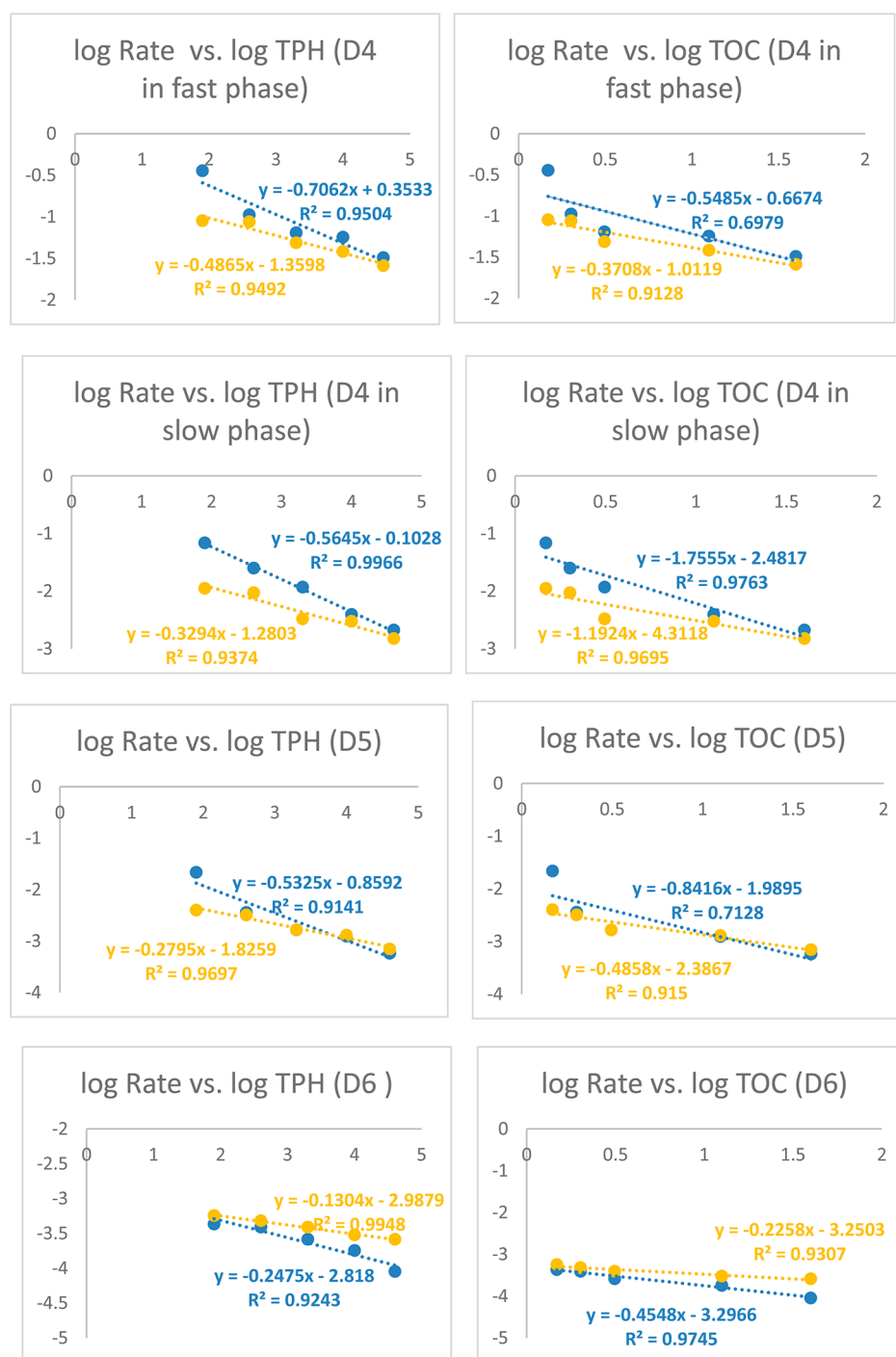
**Figure 3.** Average ratios of cyclic siloxane mass ( $M$ ) in different incubation times compared to its original spiked mass ( $M_0$ ). Error bars represent standard deviation.

**Table 1.** Apparent Elimination Constants (Slopes) and Half-Lives of cVMS in Opened and Capped Soils

		TPH (mg/kg)	slope	opened system				capped system		
				$R^2$	$p$	$T_{1/2}$ (h)	slope	$R^2$	$p$	$T_{1/2}$ (h)
D4	rapid phase	80	0.4492	0.98	< 0.05	0.67	0.089883	0.97	< 0.05	3.34
		400	0.192834	0.99	< 0.05	1.56	0.08739	0.99	< 0.05	3.44
		2000	0.113421	0.99	< 0.05	2.65	0.048803	0.99	< 0.05	6.17
		10000	0.095323	0.98	< 0.05	3.15	0.038287	0.97	< 0.05	7.86
		40000	0.058235	0.98	< 0.05	5.16	0.025858	0.99	< 0.05	11.6
	slow phase	80	0.080023	0.95	< 0.05	3.76	0.011195	0.99	< 0.05	26.9
		400	0.034589	0.99	< 0.05	8.70	0.009403	0.99	< 0.05	32.0
		2000	0.01496	0.97	< 0.05	20.1	0.0033	0.99	< 0.05	91.2
		10000	0.006923	0.97	< 0.05	43.4	0.003	0.97	< 0.05	100
		40000	0.003609	0.99	< 0.05	83.4	0.0015	0.94	< 0.05	200
D5		80	0.025670	0.94	< 0.05	11.7	0.00404	0.91	< 0.05	74.5
		400	0.006825	0.91	< 0.05	44.1	0.003214	0.96	< 0.05	93.6
		2000	0.003258	0.96	< 0.05	92.4	0.001654	0.91	< 0.05	182
		10000	0.002536	0.98	< 0.05	118	0.001303	0.88	< 0.05	231
		40000	0.001283	0.94	< 0.05	235	0.00074	0.86	< 0.05	407
D6		80	0.001045	0.91	< 0.05	288	0.000565	0.96	< 0.05	533
		400	0.00087	0.91	< 0.05	346	0.000478	0.98	< 0.05	630
		2000	0.000652	0.92	< 0.05	462	0.000391	0.97	< 0.05	770
		10000	0.000478	0.92	< 0.05	630	0.000304	0.96	< 0.05	990
		40000	0.000348	0.96	< 0.05	866	0.000261	0.94	< 0.05	1155

pentamer diol (for D5), tetramer diol, trimer diol, etc., all of which would ultimately be transformed to dimethylsilanediol.<sup>27</sup> In air-dried soil, hydrophobic chemicals like D4 can be sorbed on both mineral surfaces and organic carbon, and the fraction of D4 on a mineral surface undergoes fast hydrolysis due to the clay catalysis effect for Si–O–Si cleavage.<sup>26,27,34</sup> Due to a lack of clay catalysis, the hydrolysis rate of D4 partitioned into organic carbon is reduced significantly. At TPH = 80 mg/kg,

the hydrolysis of D4 in the rapid phase accounted for 98% of D4 hydrolyzed. As the soil TPH content increased from 80 to 40 000 mg/kg, the organic carbon content in the soil increased from 1.48 to 39.8 g/kg, and the hydrolysis fraction of D4 in the rapid phase decreased to 54%. More precisely, the fraction of D4 hydrolyzed in the rapid phase is inversely related to the logarithm of the TOC content (mg/kg) of soil (Figure S3):



**Figure 4.** Correlations between logarithms of the degradation rate constants (unit of 1/h, yellow points) of cVMS and logarithms of TPH (TOC) in soil and correlations between logarithms of the volatilization rate constants (unit of 1/h, blue points) of cVMS and logarithms of TPH (TOC) in soil.

$$\text{fraction of D4 degraded in the rapid phase} = 0.996 - 0.278 \log(\text{TOC})$$

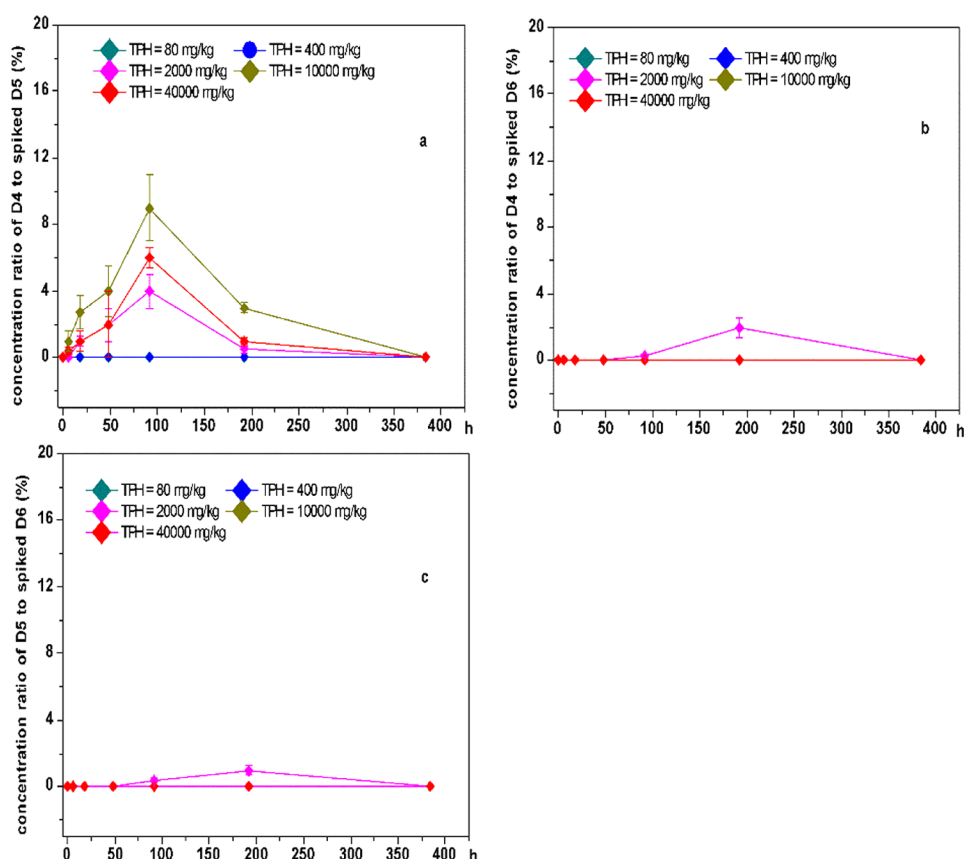
$$R^2 = 0.938 \quad (p < 0.05)$$

The intercept of 0.996 with a corresponding TOC of 1 mg/kg can be interpreted as the lowest OC for 100% D4 degradation in rapid hydrolysis.

Different from D4, D5 and D6 in soil appeared to have one, not two, degradation phases, with the rapid phase not significant (Figure 3). This difference among various cVMS compounds may be due to their different partition properties. Logarithms of organic carbon-water partitioning coefficient

(Log K<sub>oc</sub>) values of D5 (5.17<sup>35</sup>) and D6 (6.16<sup>36</sup>) are much higher than that of D4 (4.23<sup>35</sup>). More fractions of D5 and D6 will be expected to be sorbed in organic matter of soil than that of D4, and hence, their hydrolysis kinetics by clay mineral would be reduced.

The effect of petroleum hydrocarbon on the degradation of cVMS also manifested in the dependence of the degradation rates in soil as affected by TPH addition. As shown in Figure 4, the logarithms of the apparent degradation rate constants (the slopes in Figure 3) for D4, D5, and D6 is inversely related to



**Figure 5.** (a) Average concentration ratios of D4 to originally spiked D5 in a capped system for D5; (b) average concentration ratios of D4 to originally spiked D6 in a capped system for D6; (c) average concentration ratios of D5 to originally spiked D6 in capped system for D6. Error bars represent standard deviation.

the logarithms of TPH (and TOC) contents for both rapid and slow phases. The rapid and slow half-lives of D4 and overall half-lives of D5 and D6 in soil with higher petroleum ether (TPH = 400, 2000, 10 000, and 40 000 mg/kg) were 1.03–3.47, 1.19–7.43, 1.25–5.46, and 1.18–2.17 times larger than those in common soil with low TPH content (80 mg/kg), respectively. These results indicated that petroleum hydrocarbon contamination may significantly reduce the hydrolysis rates of D4, D5, and D6 in soil.

It needs to be pointed out that petroleum hydrocarbon in soil also could be adsorbed by clay and compete for the adsorption sites on clay with cVMS. Meanwhile, petroleum hydrocarbon could increase the organic carbon content in soil. Because cVMS were lipophilic, organic carbon would reduce the sorption of cVMS by clay in soil. Therefore, the catalysis efficiency of clay minerals for siloxanes hydrolysis would be reduced by petroleum hydrocarbon in soil, and the hydrolysis rates of siloxanes would decrease.

**In the Open Systems.** Table 1 showed that in open systems, the half-lives of D4 in both rapid and slow phases and the half-lives of D5 and D6 in soil with TPH = 80 mg/kg were 4.98, 7.15, 6.37, and 1.85 times shorter than those in the capped systems, respectively. This result indicated that besides degradation, volatilization would be another important pathway for siloxane elimination in soil, as demonstrated elsewhere.<sup>28</sup> Similar to those in the capped system, elimination rates of cVMS in open systems decreased with the increased TPH concentrations (Figure 3 and Table 1). We calculated the apparent volatilization rate constants of cVMS by subtracting

the slopes of the semilog plots of cVMS in the capped soil from the values in paired open soil and found that the logarithms of volatilization rate constants for D4, D5, and D6 were negatively correlated with the logarithms of TPH concentrations (Figure 4).

In addition, Figure 4 showed that the volatilization rate constants of D4 in soil with each quantity of TPH content was higher (1.3–4.0 times in rapid phase and 1.3–6.1 times in slow phase) than its degradation rate constants, indicating that volatilization is the predominate removal process for D4 in soil. This is due to its high vapor pressure (124 Pa)<sup>31</sup> and low octanol/air partition coefficient (4.34, logarithm value at 25 °C).<sup>37</sup> D5 also had a relatively lower vapor pressure (20.4 Pa)<sup>31</sup> and a relatively higher octanol/air partition coefficient (5.06, logarithm value at 25 °C),<sup>37</sup> and hence, volatilization had a dominant contribution for its elimination in soil with lower TPH content (volatilization rate constants of D5 in soil with TPH = 80 and 400 mg/kg were 5.35 and 1.12 times higher than its degradation rate constants, respectively). However, with the increased TPH, the volatilization rate of D5 was reduced significantly, and degradation became the dominant pathway for D5 elimination. In fact, the volatilization rate constants of D5 in soil with TPH = 2000, 10 000, and 40 000 mg/kg were 1.03, 1.05, and 1.36 times lower than its degradation rate constants, respectively. Compared with D4 and D5, D6 had a much lower vapor pressure (2.26 Pa)<sup>31</sup> and a higher octanol/air partition coefficient (5.81, logarithm value at 25 °C),<sup>37</sup> and volatilization had less contribution than did degradation for its elimination in soil with each TPH content (the volatilization



rate constants of D6 were 1.17–1.74 times lower than its degradation rate constants).

**3.3. Effects of Petroleum Hydrocarbon on Rearrangement of cVMS in Soil.** In the oil-sludge samples, the proportions of D4, D5, and D6 to the total cVMS were 0.04 at mean (median = 0.03), 0.73 at mean (median = 0.72), and 0.22 at mean (median = 0.24), respectively, while in soil samples from the oilfield, the proportions of D4, D5, and D6 to the total cVMS were 0.17 at mean (median = 0.13), 0.42 at mean (median = 0.40), and 0.40 at mean (median = 0.40), respectively. The above data clearly showed an enrichment of D4 in the soil relative to that in oil sludge. More precisely, the mean and median ratios of D4 to the total cVMS in soil were higher than those in oil sludge by factors of 4.25 and 4.33, respectively.

One of the explanations for the enrichment of D4 in soil is the possible rearrangement of other cVMS in oil-contaminated soil. During the hydrolysis of methyl siloxanes in soil, their degradation intermediates (oligomeric diols) can condense to reform linear and cyclic siloxanes, i.e., the rearrangement reaction, under certain conditions.<sup>1,24–26</sup> In the present study, we did not detect other target siloxanes (D5, D6, L3 through L16) in capped systems for D4. In capped systems spiked with D5, D4 was not detected in soil with low TPH content (80 or 400 mg/kg) but were detected in soil with TPH content  $\geq 2000$  mg/kg. In these samples, with the increased incubation time, concentrations of oligomeric diols increased, and the concentration ratios of D4 to that of spiked D5 increased from 0 to 92 h as a transient intermediate (Figure 5). As shown in the earlier studies,<sup>26</sup> those intermediates are not stable, and the final degradation product is dimethylsilanediol. Therefore, as the incubation time increased (from 92 to 384 h), the ratios of D4 decreased, which should be due to the further hydrolysis of D4, residual D5, and oligomeric diols to the final products. The highest concentration ratios of D4 to spiked D5 in capped soil with TPH values of 2000, 10 000, and 40 000 mg/kg were 4% (92 h), 9% (92 h), and 6% (92 h), respectively (Figure 5). Overall, in the capped soil systems with a TPH content of 10 000 mg/kg, the concentration ratios of D4 to the spiked D5 were 1.4–2.5 times higher than those in soil with a TPH content of 2000 mg/kg at the same time points. The higher D4 concentrations in soil with higher TPH content suggested that the D4 formed from hydrolysis of D5 is probably partitioned to and protected by the TPH carbon phase. It should also be clear that the formation of D4 was a temporary event, only occurring when D5 hydrolysis was fast enough, and hence, there was an accumulation of diols as the transient intermediates. Therefore, the TPH content should not be too high, or otherwise the oligomeric diols may not be accumulated enough to promote the formation of D4; the rearrangement of D5 to D4 would be weakened. This could explain that in the capped soil system with a TPH content of 40 000 mg/kg, the concentration ratios of D4 to that of the spiked D5 were 1.1–1.9 times lower than those in soil with a TPH of 10 000 mg/kg (Figure 5).

The hydrolysis rate of D6 in the capped soil systems (TPH = 80, 400, 2000, 10 000, and 40 000 mg/kg) were 2.8–7.0 times lower than that of D5 (Table 1), suggesting that concentrations of oligomeric diols from D6 hydrolysis should be much lower than those from D5 hydrolysis. Therefore, the rearrangement reaction rate of D6 would be much less significant than that of D5. Actually, D4 and D5 were detected as the rearrangement products of D6 only in soil with a TPH content of 2000 mg/kg

(Figure 5). The highest concentration ratios of D4 and D5 to spiked D6 were 2% and 1% (192 h), respectively.

According to the highest proportions of D5 and D6 transferring to D4 (2–9%) in soil with TPH content from 2000 to 40 000 mg/kg obtained through experiments, the mean and median concentrations of D4 from the rearrangement of D5 and D6 in soil samples ( $n = 160$ ) from the Shengli oilfield with TPH content of 2000–40000 mg/kg were about 3.66–16.5 and 1.56–7.02 ng/g dw, respectively (accounting for 4.7–21.4% and 4.0–18.0% of mean and median concentrations of D4 in these samples, also respectively). These results indicated that although the proportions of D5 and D6 transferring to D4 were limited in soil, their rearrangement reactions in the field soil of the Shengli oilfield could not be neglected.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b03197.

Tables showing the mass profiles of L5–L16 in the PDMS standard, MS parameters of target compounds, and the LQQ recovery of the method for soil samples. Figures showing the linear relationship between  $\Sigma$ Cyclic concentrations and TPH concentrations in soil samples, a LOEES curve of the TPH concentrations in soil samples, and a fraction degraded of D4 in rapid phase versus log TOC. (PDF)

## ■ AUTHOR INFORMATION

### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Brook, D. N.; Crookes, M. J.; Gray, D.; Robertson, S. *Environmental risk assessment report: Octamethylcyclotetrasiloxane*; Environment Agency of England and Wales: Bristol, U.K., 2009.
- (2) He, B.; Rhodes-Brower, S.; Miller, M. R. Octamethylcyclotetrasiloxane exhibits estrogenic activity in mice via ER alpha. *Toxicol. Appl. Pharmacol.* **2003**, *192*, 254–261.
- (3) OEHA. Toxicity data review: Decamethylcyclopentasiloxane (D5). <http://www.arb.ca.gov/toxics/dryclean/oehhad5review.pdf> (accessed 2007).
- (4) Silicones Environmental, Health, and Safety Center (SEHSC). Available from: <http://sehsc.americanchemistry.com> (accessed 2015).
- (5) Horii, Y.; Kannan, K. Survey of organosilicon compounds, including cyclic and linear siloxanes, in personal-care and household products. *Arch. Environ. Contam. Toxicol.* **2008**, *55*, 701–710.
- (6) Lu, Y.; Yuan, T.; Wang, W. H.; Kannan, K. Concentrations and assessment of exposure to siloxanes and synthetic musks in personal care products from China. *Environ. Pollut.* **2011**, *159*, 3522–3528.
- (7) Environment Canada. Screening assessment for the challenge Octamethylcyclotetrasiloxane (D4). [http://www.ec.gc.ca/substances/ese/eng/challenge/batch2/batch2\\_556-67-2\\_en.pdf](http://www.ec.gc.ca/substances/ese/eng/challenge/batch2/batch2_556-67-2_en.pdf) (accessed 2008).
- (8) Environment Canada. Screening assessment for the challenge Decamethylcyclopentasiloxane (D5). [http://www.ec.gc.ca/substances/ese/eng/challenge/batch2/batch2\\_541-02-6\\_en.pdf](http://www.ec.gc.ca/substances/ese/eng/challenge/batch2/batch2_541-02-6_en.pdf) (accessed 2008).



- (9) Environment Canada. Screening assessment for the challenge Dodecamethylcyclohexasiloxane (D6). [http://www.ec.gc.ca/ese-ees/FC0D11E7-DB34-41AA-.../batch2\\_540-97-6\\_en.pdf](http://www.ec.gc.ca/ese-ees/FC0D11E7-DB34-41AA-.../batch2_540-97-6_en.pdf) (accessed 2008).
- (10) Warner, N. A.; Evenset, A.; Christensen, G.; Gabrielsen, G. W.; Borgå, K.; Leknes, H. Volatile siloxanes in the European arctic: assessment of sources and spatial distribution. *Environ. Sci. Technol.* **2010**, *44* (19), 7705–7710.
- (11) Kierkegaard, A.; Mclachlan, M. S. Determination of decamethylcyclopentasiloxane in air using commercial solid phase extraction cartridges. *J. Chromatogr. A* **2010**, *1217*, 3557–3560.
- (12) Sanchez-Brunete, C.; Miguel, E.; Alberro, B.; Tadeo, A. J. Determination of cyclic and linear siloxanes in soil samples by ultrasonic-assisted extraction and gas chromatography-mass spectrometry. *J. Chromatogr. A* **2010**, *1217* (45), 7024–7030.
- (13) Dewil, R.; Appels, L.; Baeyens, J.; Buczynska, A.; Van Vaeck, L. The analysis of volatile siloxanes in waste activated sludge. *Talanta* **2007**, *74* (1), 14–19.
- (14) Zhang, Z. F.; Qi, H.; Ren, N. Q.; Li, Y. F.; Gao, D. W.; Kannan, K. Survey of Cyclic and Linear Siloxanes in Sediment from the Songhua River and in Sewage Sludge from Wastewater Treatment Plants, Northeastern China. *Arch. Environ. Contam. Toxicol.* **2011**, *60*, 204–211.
- (15) Bletsou, A. A.; Asimakopoulou, A. G.; Stasinakis, A. S.; Thomaidis, N. S.; Kannan, K. Mass loading and fate of linear and cyclic siloxanes in a wastewater treatment plant in Greece. *Environ. Sci. Technol.* **2013**, *47* (4), 1824–1832.
- (16) Lee, S.; Moon, H. B.; Song, G. J.; Ra, K.; Kannan, K.; Lee, W.-C. A nationwide survey and emission estimates of cyclic and linear siloxanes through sludge from wastewater treatment plants in Korea. *Sci. Total Environ.* **2014**, 497–498, 106–112.
- (17) Mclachlan, M. S.; Kierkegaard, A.; Hansen, K. M.; van Egmond, R.; Christensen, J. H.; Skjøth, C. A. Concentrations and Fate of Decamethylcyclopentasiloxane (D5) in the Atmosphere. *Environ. Technol.* **2010**, *44* (14), 5365–5370.
- (18) Kaj, L.; Andersson, J.; Palm Cousins, A.; Schmidbauer, N.; Brorström-Lundén, E. *Results from the Swedish National Screening Programme 2004, Subreport 4: Siloxanes; IVL*; Technical Report for the Swedish Environmental Research Institute: Stockholm, Sweden, October 2005.
- (19) Lu, Y.; Yuan, T.; Yun, S. H.; Wang, W. H.; Wu, Q.; Kannan, K. Occurrence of Cyclic and Linear Siloxanes in Indoor Dust from China, and Implications for Human Exposures. *Environ. Sci. Technol.* **2010**, *44*, 6081–6087.
- (20) Kierkegaard, A.; van Egmond, R.; Mclachlan, M. S. Cyclic volatile methylsiloxane bioaccumulation in flounder and ragworm in the Humber Estuary. *Environ. Sci. Technol.* **2011**, *45*, 5936–5942.
- (21) Envirofluid. Oil Recovery Techniques - The Need for Enhanced Oil Recovery. <https://envirofluid.com/info-library/eor-oil-recovery-techniques> (accessed 2014).
- (22) Daniel-David, D.; Pezron, I.; Dalmazzone, C.; Noik, C.; Clause, D.; Komunjer, L. Elastic Properties of Crude Oil/Water Interface in Presence of Polymeric Emulsion Breakers, Colloid. *Colloids Surf., A* **2005**, *270–271*, 257–262.
- (23) Shaban, H. I. A study of foaming and carry-over problems in oil and gas separators. *Gas Sep. Purif.* **1995**, *9* (2), 81–86.
- (24) Brooke, D. N.; Crookes, M. J.; Gray, D.; Robertson, S. Environmental Risk Assessment Report: Decamethylcyclopentasiloxane; Environment Agency of England and Wales: Bristol, U.K., 2009.
- (25) Brooke, D. N.; Crookes, M. J.; Gray, D.; Robertson, S. Environmental Risk Assessment Report: Dodecamethylcyclohexasiloxane; Environment Agency of England and Wales: Bristol, U.K., 2009.
- (26) Xu, S. Fate of cyclic methylsiloxanes in soils. 1. The degradation pathway. *Environ. Sci. Technol.* **1999**, *33*, 603–608.
- (27) Xu, S.; Chandra, G. Fate of cyclic methylsiloxanes in soils. 2. Rates of degradation and volatilization. *Environ. Sci. Technol.* **1999**, *33*, 4034–4039.
- (28) Wang, D.; Steer, H.; Tait, T.; Williams, Z.; Pacepavicius, G.; Young, T.; Ng, T.; Smyth, S. A.; Kinsman, L.; Alaei, M. Concentrations of cyclic volatile methylsiloxanes in biosolid amended soil, influent, effluent, receiving water, and sediment of wastewater treatment plants in Canada. *Chemosphere* **2013**, *93* (5), 766–773.
- (29) U.S. EPA, Test methods for evaluating solid waste physical/chemical methods. Washington, DC, USA, 1996.
- (30) Kala, S. V.; Lykissa, E. D.; Lebovitz, R. M. Detection and characterization of poly(dimethylsiloxane)s in biological tissues by GC/AED and GC/MS. *Anal. Chem.* **1997**, *69*, 1267–1272.
- (31) Lei, Y. D.; Wania, F.; Mathers, D. Temperature-dependent vapor pressure of selected cyclic and linear polydimethylsiloxane oligomers. *J. Chem. Eng. Data* **2010**, *55*, 5868–5873.
- (32) Fan, F. The growing demand for injecting agent in downstream oil production. Available at: <http://stock.hexun.com/2012-09-28/146373581.html>. 2012.
- (33) Griessbach, E. F.; Lehmann, R. G. Degradation of polydimethylsiloxane fluids in the environment - A review. *Chemosphere* **1999**, *38*, 1461–1468.
- (34) Xu, S. Hydrolysis of poly(dimethylsiloxanes) on clay minerals as influenced by exchangeable cations and moisture. *Environ. Sci. Technol.* **1998**, *32*, 3162–3168.
- (35) Kozerski, G. E.; Xu, S.; Miller, J.; Durham, J. Determination of soil–water sorption coefficients of volatile methylsiloxanes. *Environ. Toxicol. Chem.* **2014**, *33* (9), 1937–1945.
- (36) Xu, S.; Kozerski, G.; Mackay, D. Critical Review and Interpretation of Environmental Data for Volatile Methylsiloxanes: Partition Properties. *Environ. Sci. Technol.* **2014**, *48* (20), 11748–11759.
- (37) Xu, S.; Kropscott, B. Octanol/air partition coefficients of volatile methylsiloxanes and their temperature dependence. *J. Chem. Eng. Data* **2013**, *58*, 136–142.