CYCLIC AND LINEAR SILOXANES IN SLUDGE FROM WASTEWATER TREATMENT PLANTS (WWTPs) IN KOREA

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Introduction

Cyclic and linear siloxanes (polydimethylsiloxane; PDMS) are polymeric organosilicon molecules that consist of a backbone of altering silicon-oxygen [Si-O] bonds, with organic side chains attached to each silicon atom. These compounds have been widely used in consumer products such as electronics, furniture, cookware, healthcare products and cosmetics, because silicones have low surface tension, high thermal stability, smooth texture and chemically inert[1]. Among cyclic siloxanes, octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) have received considerable attention in recent years. D4 is listed for safety assessment by the US Environmental Protection Agency (EPA) in 2013-2014 and D4 and D5 are considered to be persistent and bioaccumulative[2,3]. Cyclic siloxanes have been implicated in endocrine disruption, connective tissue disorders, adverse immunologic responses and live and lung damage in laboratory animal studies[4,5]. Due to their low water solubility (0.002 to 0.056 mg/L at 25ºC)[6] and high sorption coefficients, once discharged down a drain, siloxanes adsorb to particulate matter and settle down as sludge during the wastewater treatment processes[7]. High concentrations of siloxanes are expected in sludge and some studies are reported high concentrations of siloxanes in sludge samples from Greece[7] and China[8]. Nevertheless, occurrence of siloxanes in sludge from wastewater treatment plants (WWTPs) in Korea has not been studied. The objectives of this study were to investigate the occurrence of cyclic and linear siloxanes in sludge samples collected from three different types of Korean WWTPs (domestic, mixed and industrial) and to estimate emission fluxes of siloxanes and their usage pattern in Korean environment. This study is useful for further evaluation of potential risks and management of siloxanes usage in industry in Korea.

Materials and methods

Forty sludge samples were collected from representative WWTPs between July to October in 2011. Considering regions (4 cities and 7 provinces), watershed (4 rivers and 3 seas) and wastewater capacity, the WWTPs were selected for this study. To obtain a representative sludge sample for each facility, the sample was homogenized after the collection during 3 days in each facility. The WWTPs were divided into three types, dependent on inflow rates of industrial wastewater to each plant: from 0% to 3% for domestic, from 20% to 60% for mixed and over 70% for industrial. Table 1 presents the detailed information on the WWTPs including the influents sources, wastewater capacity, equivalent habitants and sludge production rate. All samples were poured into pre-cleaned polypropylene (PP) bottles and stored in a freezer at -20ºC until extraction. Preparation and instrumental analyses of cyclic and linear siloxanes in sludge samples have reported from previous studies[1,7,8].

Results and discussion

Occurrence of cyclic and linear siloxanes

Concentrations of cyclic and linear siloxanes in sludge samples collected from three types of WWTPs in Korea are summarized in Table 1. The concentrations of total cyclic siloxanes (sum of D3, D4, D5, D6 and D7) ranged from 0.05 to 48.0 μg/g dry weight (dw) with a mean value of 20.2 μg/g dw. Among three types of WWTPs, the highest concentrations of total siloxanes were found in sludge from domestic-WWTPs (D-WWTPs; mean: 34.2 μg/g dw), followed by mixed-WWTPs (M-WWTPs; 22.0 μg/g dw) and industrial-WWTPs (I-WWTPs; 4.19 μg/g dw). The concentrations of total linear siloxanes (sum of L3 to L17) ranged from <LOQ to 128 μg/g dw with a mean value of 25.5 μg/g dw. D- WWTPs (mean: 31.87 μg/g dw) and M-WWTPs (35.6 μg/g dw) were similar concentrations and around 3 times higher than I-WWTPs (12.6 μg/g dw). This pattern was similar with

the concentrations of cyclic siloxanes, suggesting that the major source of siloxanes is derived from domestic area.

Table 1. Concentrations of cyclic and linear siloxanes (µg/g dry weight) in WWTP sludge samples collected from Korea

	Cyclic siloxanes					Linear siloxanes
	D3	D4	D5	D6	D7	∑L3-L17
Domestic-WWTPs (n = 16)						
Mean	0.25	0.34	26.4	6.53	0.73	31.9
Median	-	-	27.7	6.08	0.73	28.2
Range	nd-2.52	nd-2.91	15.0-38.4	3.50-11.1	0.41-1.28	13.0-61.9
DR (%)	18.8	12.5	100	100	100	100
Mixed-WWTPs (n = 9)						
Mean	-	2.25	15.2	3.66	0.82	35.6
Median	-	-	12.8	4.05	0.97	27.6
Range	nd	nd-19.4	5.97-23.4	1.41-5.92	0.29-1.18	9.27-128
DR (%)	0	22.2	100	100	100	100
Industrial-WWTPs (n = 15)						
Mean	0.03	0.33	1.73	1.28	0.81	12.6
Median	-	-	0.78	0.29	0.11	0.02
Range	nd-0.29	nd-4.37	0.05-9.15	nd-5.42	nd-3.93	nd-100
DR (%)	13.3	13.3	100	73.3	80.0	53.3
Total (n = 40)						
Mean	0.11	0.77	14.6	3.92	0.78	25.5
Median	-	-	13.9	4.02	0.72	22.3
Range	nd-2.52	nd-19.4	0.05-38.4	nd-11.1	nd-3.93	nd-128
DR (%)	12.5	15.0	100	90.0	92.5	82.5

Limited studies have reported on the occurrence of siloxanes in sludge samples worldwide. The cyclic, linear and total siloxanes concentrations in sludge measured in Korea were similar with those reported for other countries (Table 2). The concentrations of cyclic siloxanes in our study were lower than those reported from Denmark[9] and Finland[9], and were higher than those reported from Faroe Islands[9], Iceland[9], Sweden[9] and China[8]. The concentrations of linear siloxanes in our study were higher than those reported from China[8], but were lower than those reported from Greece[7].

Table 2. Comparison of cyclic and linear siloxanes (µg/g dry weight) in sludge measured in this study with those reported from other countries

	Sampling year	n	D4	D5	D6	Cyclic siloxanes	Linear siloxanes	Total siloxanes	Reference
Denmark	2004	2	0.61	38.5	1.95	41.1	-	-	Kaj et al. (2005)
Faroe Islands	2004	1	0.19	4.30	1.00	5.49	-	-	Kaj et al. (2005)
Finland	2005	5	0.62	39.2	4.44	44.3	-	-	Kaj et al. (2005)
Iceland	2004	2	0.11	1.35	0.23	1.69	-	-	Kaj et al. (2005)
Sweden	2004	4	0.27	10.6	1.44	12.3	-	-	Kaj et al. (2005)
China	2009	8	0.06	0.28	0.18	1.00	1.74	2.74	Zhang et al. (2011)
Greece	2012	7	0.11	15.1	5.03	21.1	53.9	75.0	Bletsou et al. (2013)
Korea	2011	40	0.77	14.6	3.92	20.2	25.5	45.7	This study

Profiles of individual cyclic and linear siloxanes

The relative contribution of individual siloxanes to the total siloxanes was presented in Figure 1. D5 was the most abundant siloxanes, accounting for 39.7% to the total siloxanes. D7 in sludge from I-WWTPs (15.7%) has higher contribution to the total siloxanes than those measured from D-WWTPs (1.14%) and M-WWTPs (1.66%), suggesting that some industries have specific sources for D7. Three types of WWTPs showed similar patterns of linear siloxanes. The relative contributions increased with increasing chain length from L4 to L10, but they decreased from L11 to L17. L10 was the most abundant linear siloxanes, accounting for 12.4% to the total siloxanes. The profile of linear siloxanes in sludge samples was similar to that reported for sludge in China[8].

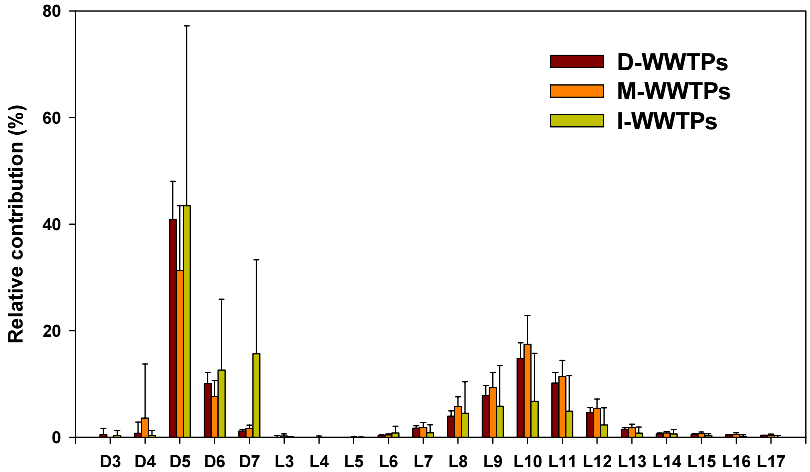

Figure 1. Relative contributions of individual siloxanes to the total siloxanes in sludge from WWTPs. Whiskers on the bars represent standard deviations for each siloxanes.

A significant positive correlation observed between the concentrations of cyclic and linear siloxanes in sludge samples except for 3 samples (Figure 2). This correlation suggests that cyclic and linear siloxanes derived from similar sources. Zhang et al. (2011)[8] also reported the correlation between concentrations of total cyclic and linear siloxanes in sediment samples collected from China, but no correlation was observed in sludge samples. Three sludge samples were excluded the correlation, which collected from mixed and industrial source nearby manufactures of textile, chemical, metal and machinery industries. This result suggests that those industries use different ratios of cyclic and linear siloxanes compared with other locations in Korea.

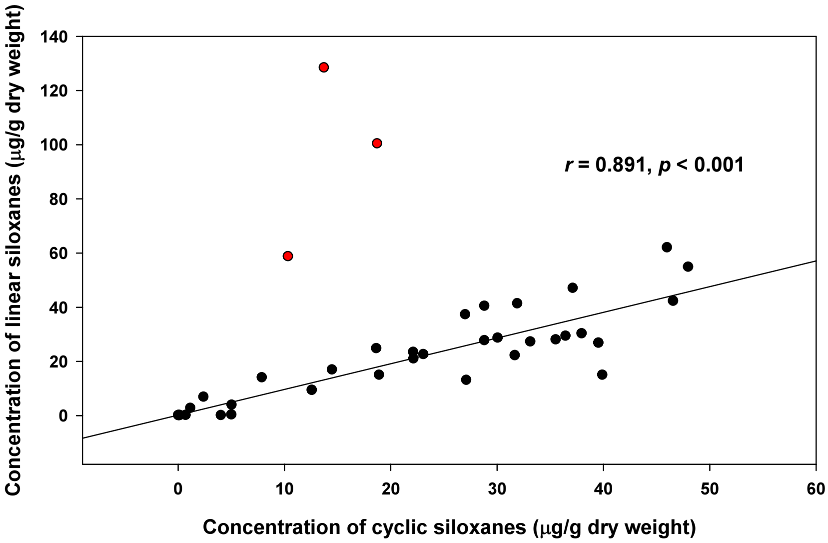

Figure 2. Correlation between concentrations of total cyclic and linear siloxanes in sludge samples from the WWTPs, Korea. Red circles were excluded the correlation.

Emission fluxes of cyclic and linear siloxanes through sludge from WWTPs

To evaluate the environmental impact of cyclic and linear siloxanes in Korea, the nationwide annual emission fluxes of cyclic and linear siloxanes were calculated using total sludge production estimated in 2011. According to the report of Ministry of Environment of Korea, sludge produced from WWTPs in Korea was estimated to be approximately 3.0 million tonnes[10]. The estimated emission fluxes were 50 and 60 kg/year for cyclic and linear siloxanes, respectively. Considering the high levels of cyclic and linear siloxanes in sludge from the present study, sludge could be acted as secondary source of cyclic and linear siloxanes in the environment. Therefore, systematic monitoring and risk assessment programs for these contaminants should be instituted to protect the health of wildlife and humans in Korea.

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