Master's Thesis

DISTRIBUTION OF SILOXANES IN COASTAL SEDIMENTS COLLECTED FROM INDUSTRIAL BAYS IN SOUTH KOREA

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Department of Urban and Environmental Engineering

(Environmental Science and Engineering)

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Sung-Duek Choi

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Abstract

Siloxanes have been used as chemical additives in various consumer and industrial products since the 1940s. Based on their extensive usage, cyclic siloxanes are categorized as high production volume chemicals. However, siloxanes are known to cause potential toxic effects and result in environmental persistence and bioaccumulation. Furthermore, previous studies have detected the high levels of siloxanes in various environmental matrices, which can lead to negative effects on the ecosystem. Therefore, siloxanes are an emerging concern as contaminants in the environment.

In this study, 6 cyclic siloxanes (D4–D9) and 13 linear siloxanes (L3–L15) were analyzed in coastal sediment collected from southeastern industrial bays in Ulsan, Busan, Jinhae, and Gwangyang, South Korea (March–April 2016). The four bays are heavily industrialized and designated as special management sea areas by the Korean government, because of severe coastal pollution originating from industrial complexes and commercial ports. A total of 69 surface sediment samples were collected using grab samplers and were extracted by shaking with organic solvents and then analyzed using gas chromatography mass spectrometry (GC/MS). From the results, contamination levels, spatial distribution, and correlationship of siloxanes in coastal sediment was investigated. Additionally, the hazard quotients (HQs) for siloxanes were evaluated using Monte Carlo simulation.

The total concentrations of siloxanes were in the range of 10.1 to 3,877.2 (mean: 304.2) ng/g dry weight (dw) for all studied samples. The relative composition of D5 (28%) and D6 (33%) were the highest, followed by L11 (5.9%) and L10 (5.2%). The highest concentration of total siloxanes was found in Busan (579.4 ng/g dw), followed by Ulsan (315.8 ng/g dw), Jinhae (266.2 ng/g dw), and Gwangyang (31.1 ng/g dw). The total concentration levels of siloxanes in South Korea are similar to other countries. Significant correlations exist among the concentrations of siloxanes, the concentrations of persistent organic pollutants (POPs), and TOC content in sediment. The hazard quotients (HQs) for siloxanes in coastal sediment were less than 1, indicating that there is no risk to organisms of the exposure of siloxanes in coastal sediment.

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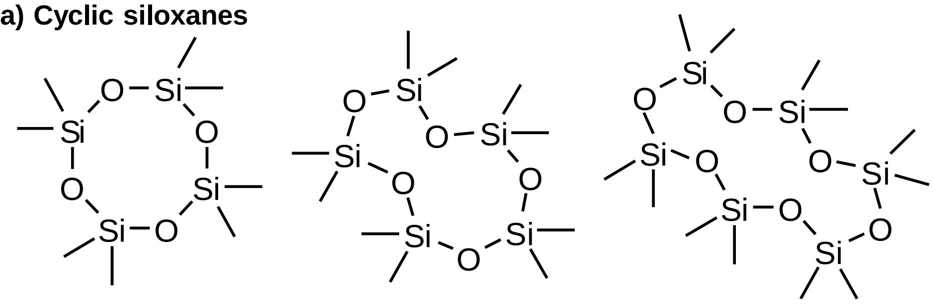
Ⅰ. INTRODUCTION

Siloxanes are polymeric organosilicon molecules with a backbone of repeating silicon-oxygen units. Each silicon atom is connected with organic side chains. Siloxanes have two basic structures, cyclic and linear. They are usually expressed as abbreviations Ln or PDMS (polydimethylsiloxane) for linear siloxanes, and Dn for cyclic siloxanes (n is the number of silicone atoms).

(a) Cyclic siloxanes



(b) Linear siloxanes

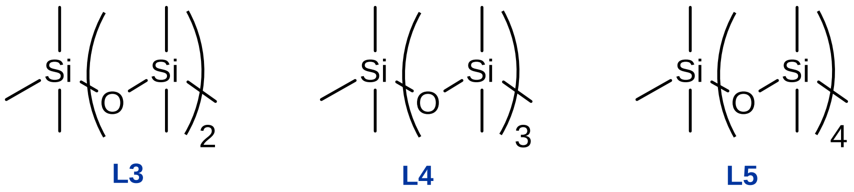


Figure 1. Chemical structures of cyclic and linear siloxanes.

Because of their attractive characteristics like low surface tension, smooth texture, thermal stability, and chemical inertness (Lee et al., 2018; Zhang et al., 2011), siloxanes have been widely used as chemical additives in industrial (e.g., lubricant, waterproof, and antifoamer products) and consumer products (e.g., personal care, cosmetic, and healthcare products) since the 1940s (Dudzina et al., 2015).

In 2006, the United States produced large amounts of octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) in the range of 45,000–225,000, 22,500–45,000, and 450–4,500 tons, respectively (Wang et al., 2013b). Based on their extensive usage, the three cyclic siloxanes have been categorized as high production volume chemicals by the US Environmental Production Agency (Hong et al., 2014). There is no information about the production amounts of siloxanes in South Korea. However, amounts of silicone resin in South Korea has been recorded since 2000, and the amounts have increased, reaching an annual silicone resin production of 180,000 tons in 2017 (Statistics Korea, 2017).

The cyclic siloxanes possess typical physicochemical properties including high volatility (vapor pressure: 2.26–124.5 Pa at 25 ℃) (Lei et al., 2010), hydrophobicity (water solubility: 5.3–56 μg/L), and high octanol-water partition coefficients (log K_{OW}: 6.49–9.06) (Woodburn et al., 2018). Therefore, the main emission routes of siloxanes are volatilization into the atmosphere or down the drain removal from wastewater treatment plants (WWTPs). During the wastewater treatment processes, most siloxanes are removed through volatilization and sorption by organic matter. A proportion of siloxanes adsorbed on suspended organic matter are released as effluent into the aquatic environment. Finally, they are deposited into sediments constantly (Homem et al., 2017).

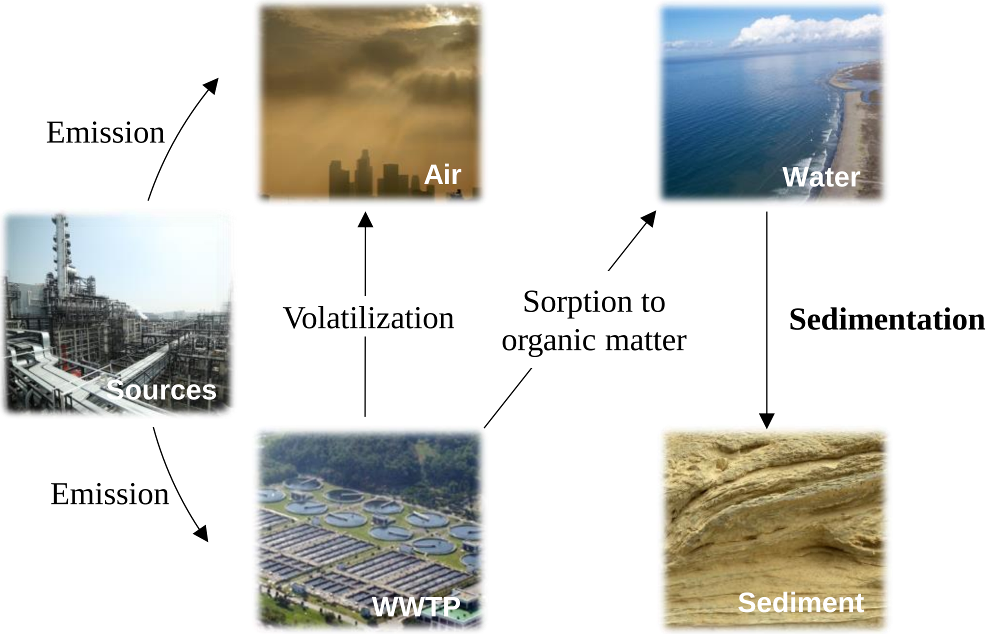


Figure 2. Main emission routes of siloxanes.

Based on their volatility and suspected persistence in the atmosphere (Homem et al., 2017), they can be transported to remote regions. Therefore, dispersal of siloxanes in the environment is expected and many studies have detected these compounds in various environmental matrices including sediment (Lee et al., 2018; Zhang et al., 2011; Zhi et al., 2018), air (Genualdi et al., 2011; Krogseth et al., 2013), soil (Sanchez-Brunete et al., 2010; Wang et al., 2013c), biota (Wang et al., 2017; Warner et al., 2014; Xu et al., 2015), surface water (Horii et al., 2017; Sparham et al., 2008; Zhi et al., 2018), coastal environment (Hong et al., 2014), and polar areas (Warner et al., 2010).

Previous studies have found toxic effects caused by siloxanes, especially estrogen mimicry, reproductive problems, and liver damage. Inhalation of D4 reduced the number of pups born and live litter size, and inhalation of D5 increased the liver weight in female rats (McKim et al., 1999; Siddiqui et al., 2007). The European Commission defined D4 as a reproductively toxic compound and the Danish EPA listed D4 as a impairing fertility compound (European Commission, 2005; Lassen et al., 2005). Therefore, siloxanes are regulated in many countries. For example, Canada made a proposal to minimize or prevent the emission of D4 into the environment (Environment Canada, 2012), and the UK proposed a limitation on the content of D4 and D5 in wash-off products (ECHA, 2016). To date, no legislation about the restricted concentration levels of siloxanes in the environmental matrices and in products exists in South Korea.

Among various environmental matrices, coastal sediments are important sinks of pollutants. Therefore, there should pay special attention to investigate the contamination distribution of siloxanes. The lipophilic nature of siloxanes ($\log K_{OW} > 6.49$, $\log K_{OC} > 4.22$) (Woodburn et al., 2018), make the sediment sorption a principle removal mechanism of siloxanes. Therefore, the major exposure route of siloxanes in aquatic systems is likely to be via sediment (Mackay et al., 2015). However, only a few studies have been done to assess their occurrence in sediment, because analytical determination of siloxanes is difficult due to their ubiquitous nature, which hampers their accurate measurement (Wang et al., 2013a). As can be seen in Figure 3, research on siloxane contamination levels in sediment have been carried out since 2010. All the studies analyzed cyclic siloxanes, whereas only half analyzed both cyclic and linear siloxanes.

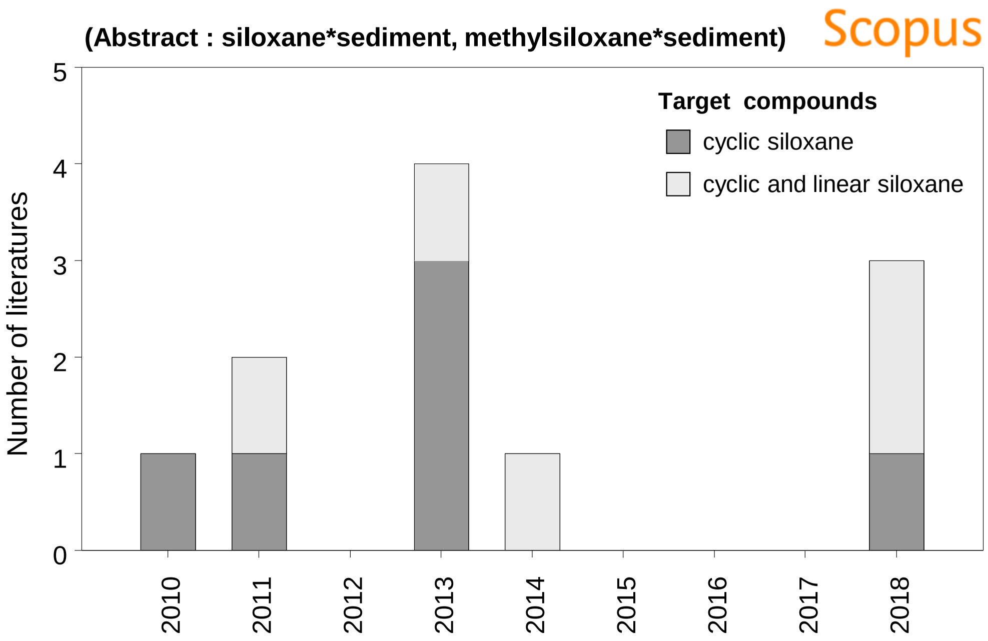


Figure 3. Number of literatures about the analysis of siloxanes in sediments. (Literatures, which contained concentration levels of siloxanes in sediment were selected)

Therefore, this study aimed to investigate concentration levels and spatial distribution of siloxanes in coastal sediment collected from southeastern industrial bays in South Korea with a suitable analytical method. Finally, the ecological risk of siloxanes in the coastal sediment to organisms was assessed based on probabilistic distributions of hazard quotients.

Ⅱ. MATERIALS AND METHODS

2.1 Sampling of sediments

Coastal sediment samples were obtained during March–April 2016 from the southeastern maritime industrial regions: Ulsan bay (US1–US15), Busan bay (BS1–BS18), Jinhae bay (JH1–JH20), and Gwangyang bay (GY1–GY16), which are the most heavily industrialized bays in South Korea. The four bays are designated as special management sea areas by the Korean government (MOF, 2016), because of severe coastal pollution originating from industrial complexes and commercial ports.

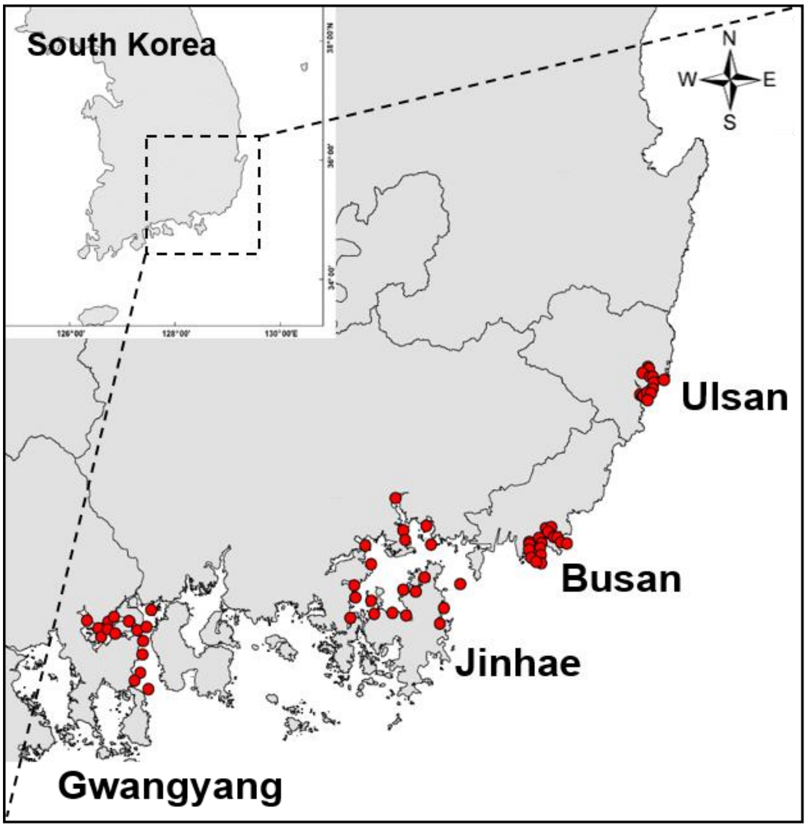


Figure 4. Sampling map for coastal sediments in South Korea: Ulsan, Busan, Jinhae, and Gwangyang.

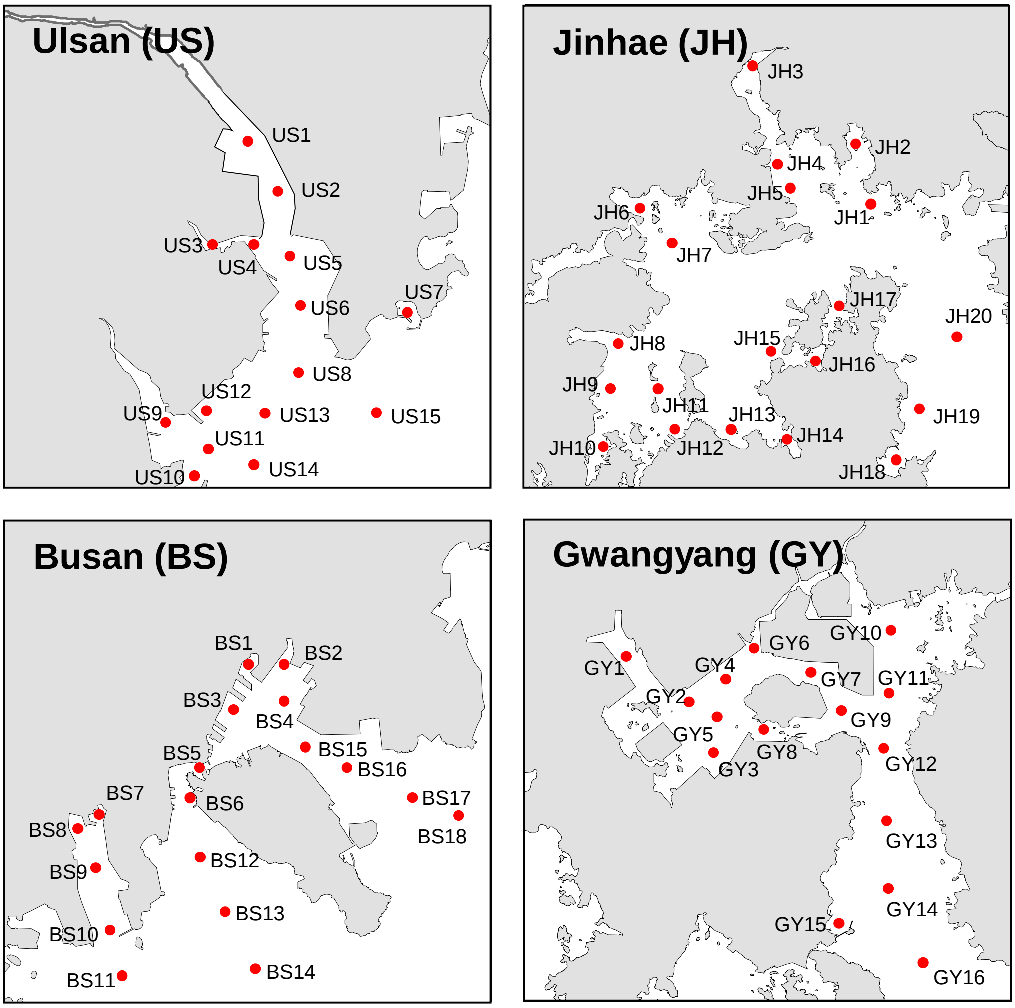


Figure 5. Locations of coastal sediment sampling sites in each bay.

Ulsan bay, which is heavily industrialized bays, is located on the southeastern part of Korea. The dominant industrial productions of the bay are petrochemical products, non-ferrous metals, automobiles, and ships (Choi et al., 2012). The major river in Ulsan, the Taehwa River flows through the center of Ulsan city and ends in Ulsan bay. Busan is the largest commercial port area in Korea and includes North, South, and Gamchen port. The coastline of the bay has shipyard, electronics, chemical fertilizer, and steel production facilities (Moon et al., 2008). The Dong Stream, which flows through residential areas with a total length of 4.9 km, ends in Busan port. Severe contamination of the stream has emerged as a serious environmental problem in Busan. Jinhae is a typical semi-enclosed bay, comprising of the seriously polluted eastern zone (Masan bay) and a less polluted western zone. Masan bay, which is located northeast of Jinhae bay is surrounded by various industrial complexes and a wastewater treatment plant. The WWTP accelerate the pollution of the coastal environment in Masan bay (Kannan et al., 2010). Commercial and fishing harbors, shipyards, and shellfish farming are located along Jinhae bay (Kim et al., 2014). Gwangyang bay, located on the southern coast of Korea, is also semi-enclosed. There have been land reclamations for industrial and port facilities on the western parts of Gwangyang bay. The Bay is utilized for steel manufacturing and petrochemical facilities on the inner shores (Kim et al., 2008).

A total of 69 coastal sediment samples (0 to 5 cm) were obtained using Van Veen grab samplers and stored in glass bottles at -20 ℃. The samples were freeze-dried for about 72 h, and sieved through a 2-mm a stainless-steel sieve. Total organic carbon (TOC) of the coastal sediment was measured using TOC analyzer (TOC-5000, Shimadzu, Japan).

2.2 Chemical and reagents

Total 6 cyclic siloxanes and 2 linear siloxanes including, octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), dodecamethylcyclohexasiloxane (D6), tetradecamethylcycloheptasiloxane (D7), hexadecamethylcyclooctasiloxane (D8), octadecamethylcyclononasiloxane (D9), octamethyltrisiloxane (L3), and decamethyltetrasiloxane (L4) (all >95% purity) were purchased from Tokyo Chemical Industries (Tokyo, Japan). One linear siloxane, dodecamethylpentasiloxane (L5) (>97% purity) and PDMS (viscosity of 5 cSt), which contains target linear siloxanes (L6–L15) were acquired from Sigma Aldrich (Oakville, ON, Canada). The PDMS mixture used as a standard for the identification and quantification of the linear siloxanes. $^{13}C_4$-D4, $^{13}C_5$-D5, and $^{13}C_6$-D6 were purchased from Moravek (Brea, CA, USA). They are used as the internal standards of native siloxanes to calculate their concentrations by adding them to the samples before the extraction. Phenanthrene-d_{10} was obtained from Sigma Aldrich and used as the internal standard for the three labeled siloxanes to calculate recoveries and to compensate for differences in injection volumes by adding them to the samples before the instrumental analysis.

2.3 Extraction methods for sediment

2.5 g of freeze-dried sediment was taken in a 15 mL polypropylene tube and a mixture of $^{13}C_4$-D4, $^{13}C_5$-D5, and $^{13}C_6$-D6 was added to the sample. Then, a 5 mL mixture of hexane and ethyl acetate (1:1) was added to the sediment sample and shaken for 30 min using a shaker (NB-101MT, N-Biotek, Korea) at 250 rpm. The extract was centrifuged at 3,500 rpm for 10 min (Combi-514R, Hanil, Korea), and the supernatant was transferred to a glass tube. The extraction process was done two more times. The extract was concentrated to 0.5 mL under a gentle stream of nitrogen with a nitrogen evaporator (Eyela MG-2200, Tokyo Rikakikai, Japan). Prior to GC/MS analysis, Phenanthrene-d_{10} was spiked into each extract.

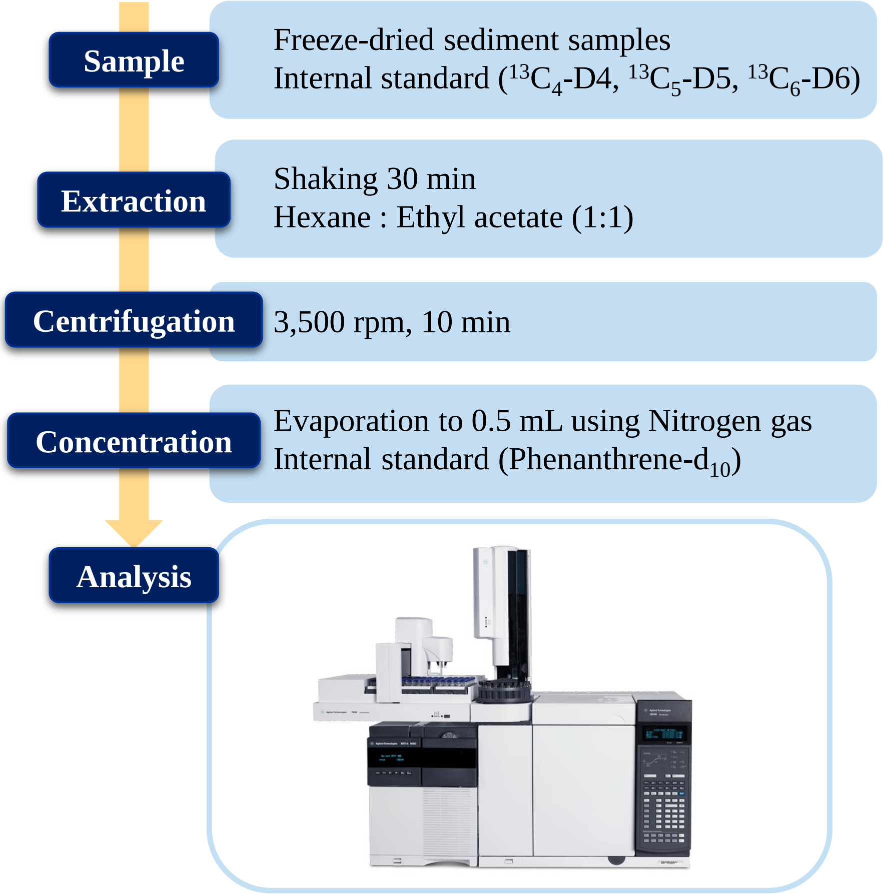


Figure 6. Analysis procedural for siloxanes in coastal sediment samples.

2.4 Instrumental analysis

Nineteen siloxanes were analyzed using an Agilent 7890A gas chromatograph interfaced with an Agilent 5975C mass spectrometer (GC/MS; Agilent Technologies, Palo Alto, CA) in an electron impact selected ion monitoring (SIM). Separations of target materials were achieved using a DB-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). One microliter of extract was injected to GC in splitless mode at inlet temperature of 200˚C. The carrier gas was helium at a flow rate of 1.0 mL/min. The temperature program of the GC oven was started at 40˚C for 2 min, then increased to 220˚C at 20˚C /min, then to 270˚C at 5˚C /min. Finally, a postrun time at 300˚C for 5 min was run to remove impurities from the column. The temperature of transfer line was 300˚C. The retention time and monitored ions of target siloxanes are presented in Table 1. PDMS mixture was analyzed by an Agilent 7890A gas chromatograph with a flame ionization detector (GC/FID; Agilent Technologies, Palo Alto, CA).

Table 1. Molecular formula, purity, retention time and monitored ions of target compounds.

Target compounds		Purity (%)	Retention time (min)	Ion monitored (m/z)
Analyte	Molecular Formula			
Octamethylcyclotetrasiloxane (D4)	$C_8H_{24}O_4Si_4$	>98	5.445	281, 282
Decamethylcyclopentasiloxane (D5)	$C_{10}H_{30}O_5Si_5$	>97	6.789	267, 355
Dodecamethylcyclohexasiloxane (D6)	$C_{12}H_{36}O_6Si_6$	>95	8.071	341, 429
Tetradecamethylcycloheptasiloxane (D7)	$C_{14}H_{42}O_7Si_7$	>95	9.207	147, 281
Hexadecamethylcyclooctasiloxane (D8)	$C_{16}H_{48}O_8Si_8$	>96	10.217	147, 355
Octadecamethylcyclononasiloxane (D9)	$C_{18}H_{54}O_9Si_9$	>98	11.087	147, 429
Octamethyltrisiloxane (L3)	$C_8H_{24}O_2Si_3$	>98	4.348	221, 222
Decamethyltetrasiloxane (L4)	$C_{10}H_{30}O_3Si_4$	>97	6.098	207, 208
Dodecamethylpentasiloxane (L5)	$C_{12}H_{36}O_4Si_5$	>97	7.480	147, 281
Tetradecamethylhexasiloxane (L6)	$C_{14}H_{42}O_5Si_6$		8.648	147, 221
Hexadecamethylheptasiloxane (L7)	$C_{16}H_{48}O_6Si_7$		9.671	147, 221
Octadecamethyloctasiloxane (L8)	$C_{18}H_{54}O_7Si_8$		10.585	147, 221
Icosamethylnonasiloxane (L9)	$C_{20}H_{60}O_8Si_9$		11.430	147, 221
Docosamethyldecasiloxane (L10)	$C_{22}H_{66}O_9Si_{10}$		12.371	147, 221
Tetracosamethylundecasiloxane (L11)	$C_{24}H_{72}O_{10}Si_{11}$		13.498	147, 221
Hexacosamethyldodecasiloxane (L12)	$C_{26}H_{78}O_{11}Si_{12}$		14.840	147, 221
Octacosamethyltridecasiloxane (L13)	$C_{28}H_{84}O_{12}Si_{13}$		16.374	147, 221
Triacontamethyltetradecasiloxane (L14)	$C_{30}H_{90}O_{13}Si_{14}$		18.027	147, 221
Dotriacontamethylpentadecasiloxane (L15)	$C_{32}H_{96}O_{14}Si_{15}$		19.737	147, 221
2,4,6,8-$^{13}C_4$-octamethyl cyclotetrasiloxane ($^{13}C_4$-D4)	$^{13}C_4C_4H_{24}O_4Si_4$	>98	5.445	284, 285
2,4,6,8,10-$^{13}C_5$-decamethyl cyclopentasiloxane ($^{13}C_5$-D5)	$^{13}C_5C_5H_{30}O_5Si_5$	>98	6.789	359, 360
2,4,6,8,10,12-$^{13}C_6$-dodecamethyl cyclohexa-siloxane ($^{13}C_6$-D6)	$^{13}C_6C_6H_{36}O_6Si_6$	>98	8.071	345, 435
Phenanthrene-d_{10}	$C_{14}D_{10}$		11.309	188, 189

2.5 Quality assurance and quality control

The wide uses of siloxanes can significantly affect accurate measurement in various ways. Therefore, the analyst should avoid the use of personal care products (PCPs). To minimize the background contamination of siloxanes, where possible, equipment materials including silicone were substituted with other materials. For examples, GC vials were capped with viton septa, nitrogen blowing equipment was used with a metal tube, and GC inlet septa were replaced with fluorocarbon material. Before the GC/MS analysis, hexane was injected to minimize the instrumental background levels, and analyzed after every sediment sample to assess the background level. To identify the siloxane contamination that occurred during the pretreatment process, procedural blanks (n=7) were also analyzed using 2.5 g of free-siloxane sand. The procedural blanks contained detectable levels of cyclic siloxanes, D4 (4.83 ± 0.39 ng/g; average ± standard deviation), D5 (1.84 ± 0.12 ng/g), D6 (1.43 ± 0.12 ng/g), D7 (1.47 ± 0.28 ng/g), D8 (2.69 ± 0.57 ng/g), and D9 (8.70 ± 1.04 ng/g), and some linear siloxanes were also found in low levels in the procedural blanks. However, the other target siloxanes were below the detection limits or not detected in the procedural blanks. The detectable blank levels were subtracted from the measured concentration values in all sediment samples. Other studies also found contaminations of cyclic siloxanes in procedural blanks, which ranged from 1.45 to 5.67 ng/g for D5–D7 (Lee et al., 2018), 1.07 to 2.32 ng/g for D4–D6 (Zhi et al., 2018), and 1.0 to 1.7 ng/g for D4–D6 (Liu et al., 2014). To calculate limits of detections (LODs) and limits of quantifications (LOQs), signal to noise ratio (Lee et al., 2014; Tran et al., 2015) and procedural blank concentration (Hong et al., 2014) were generally used. In this study, due to the relatively high concentrations of cyclic siloxanes in procedural blanks, LODs for cyclic siloxanes were calculated by average blank concentrations plus three times the standard deviation of procedural blanks, which ranged from 0.40 to 3.13 ng/g. For linear siloxanes, LODs were defined as three times the signal to noise ratio, which ranged from 0.06 to 0.91 ng/g. Recoveries of the surrogate standard, $^{13}C_4$-D4, $^{13}C_5$-D5, and $^{13}C_6$-D6 from all sediment samples had values of 54 ± 13%, 69 ± 16%, and 67 ± 16%, respectively. Recoveries of the three labeled siloxanes showed similar values in previous studies, in that the recoveries of $^{13}C_4$-D4, $^{13}C_5$-D5, and $^{13}C_6$-D6 are 69%, 71%, and 74% for sediment samples (Wang et al., 2013a) and 57%, 66%, and 70% for air samples (Ahrens et al., 2014).

2.6 Risk assessment

The ecological risk of siloxanes was assessed by the hazard quotient (HQ) (Homem et al., 2017; Zhi et al., 2018). The HQs were calculated using the below equation:

$$\text{Hazard Quotient (HQ)} = \frac{\text{MEC}}{\text{PNEC}}$$

where MEC is defined as the measured environmental concentrations of siloxanes in sediment, and PNEC is defined as the predicted no effect concentration of siloxanes. The PNEC was calculated using the below equation:

$$\text{Predicted No Effect Concentration (PNEC)} = \frac{\text{L(E)C50 or NOEC}}{\text{Assessment factor}}$$

PNEC was calculated with toxicity data, LC50 (the median lethal dose), EC50 (the half maximal effective concentration) or NOEC (the no observed effect concentration) of the sediment dwelling organisms. The assessment factors, which bridge the gap of toxicity values of different experimental animals and conditions, were adapted from the previous study (Assessment factor: 10 (D4 and D5), 100 (D6); Homem et al. (2017)). For the worst-case scenario, concentrations of siloxanes below detection limits were substituted by half of the detection limits, and the lowest NOEC values (D4: 13 mg/kg dw (blackworms), D5: 69 mg/kg dw (midge), and D6: > 484 mg/kg dw (blackworms)) were acquired from the previous study (Redman et al., 2012). As a result, if the value of HQ is over 1, the chemicals are assumed to be a potential hazard to the aquatic environment. However, a risk assessment using single point values may lead to high uncertainty, whereas the Monte Carlo simulation, which results in a probabilistic approximation, can decrease the uncertainty of estimations (Fakhri et al., 2018). Therefore, in this study, HQs were calculated using a Monte Carlo simulation with probabilistic distributions of siloxane concentrations in coastal sediment. The concentrations of siloxanes were assumed to follow the log normal distribution to generate the distributions of hazard quotients by the 5,000 repetitions of the simulation. D4, D5, and D6 were chosen as the representative targets. This probabilistic distribution of hazard quotient approach was also applied in other studies to evaluate the risk assessment of polycyclic aromatic hydrocarbons (PAHs) in water in China (Guo et al., 2012), of heavy metals from the ingestion of instant noodles in Iran (Tajdar-Oranj et al., 2018), and of onions in Iran (Fakhri et al., 2018).

2.7 Statistical analysis

Statistical analyses were carried out to interpret and discuss the collected data. Spearman correlation analysis was done to identify the relationships among the concentrations of siloxanes in sediment, total organic carbon (TOC) contents, and the concentrations of POPs with IBM SPSS Statistics 20 (Chicago, IL, USA). Using the program, Principal component analysis was performed to investigate the relationships between each compound and sampling sites. Mann-Whitney rank sum test was done to compare the statistically significant differences among the four sampling sites using SigmaPlot software 12.0 (San Jose, CA, USA). Monte Carlo simulations were performed with Crystal Ball (Redwood city, CA, USA). To avoid detection limit artifacts, concentration of congeners below detection limits was set to half of the detection limits for statistical analyses.

Table 2. Detection frequency (%), mean, median, range, and LOD (ng/g dw) of siloxane concentrateons at 69 sites in Korea

Compounds		Detection frequency	Mean ± SD[a]	Median	Range	LOD[b]
Cyclic siloxanes	D4	87%	5.70 ± 11.3	3.34	n.d.[c]–86.0	1.17
	D5	100%	83.7 ± 227	20.7	1.77–1,733	0.40
	D6	100%	101 ± 148	35.9	5.56–724	0.46
	D7	97%	10.7 ± 17.3	5.10	<LOD–110	0.90
	D8	67%	6.55 ± 9.39	4.73	n.d.–55.1	1.72
	D9	77%	11.2 ± 10.1	9.43	n.d.–44.1	3.13
Linear siloxanes	L3	39%	0.41 ± 1.31	n.d.	n.d.–6.92	0.06
	L4	88%	0.96 ± 2.01	0.44	n.d.–10.7	0.17
	L5	77%	0.33 ± 0.40	0.26	n.d.–2.49	0.11
	L6	78%	0.51 ± 0.74	0.37	n.d.–5.29	0.17
	L7	70%	4.01 ± 3.75	4.39	n.d.–18.7	0.24
	L8	94%	4.92 ± 7.56	3.10	<LOD–52.5	0.32
	L9	100%	9.73 ± 16.9	5.02	0.48–113	0.31
	L10	96%	15.8 ± 27.8	8.24	n.d.–181	0.50
	L11	96%	17.9 ± 33.6	7.79	n.d.–222	0.44
	L12	65%	14.2 ± 29.6	7.75	n.d.–198	0.57
	L13	57%	11.5 ± 25.4	3.61	n.d.–166	0.90
	L14	4%	4.10 ± 20.7	n.d.	n.d.–140	0.43
	L15	3%	1.18 ± 7.78	n.d.	n.d.–61.9	0.63
ΣCyclic			219 ± 393	88	8.23–2,716	
ΣLinear			85.5 ± 168	42	1.69–1,162	
ΣTotal			304 ± 547	133	10.1–3,877	

[a] SD; standard deviation
[b] LOD; limit of detection
[c] n.d.; not detected

Ⅲ. RESULTS AND DISCUSSION

3.1 Levels of siloxanes in coastal sediment

Detection frequency, mean, median, range, and LOD of siloxane concentrations from the four regions are summarized in Table 2. Siloxanes were found in all 69 coastal sediment samples from the four regions. The total concentrations of siloxanes in sediments were in the range of 10.1 to 3,877.2 (mean: 304.2) ng/g dw for all collected samples. Among cyclic siloxanes, the detection frequency of D5 and D6 was the highest (detection rate: 100%), followed by D7 (97%), D4 (87%), D9 (77%), and D8 (67%). The ranges of each compound were D4 (n.d.–86.0 ng/g dw), D5 (1.77–1,733 ng/g dw), D6 (5.56–724 ng/g dw), D7 (<LOD–110 ng/g dw), D8 (n.d.–55.1 ng/g dw), and D9 (n.d.–44.1 ng/g dw), respectively. The sum of cyclic siloxane concentrations ranged from 8.23 to 2,715.6 (mean: 219) ng/g dw. Linear siloxanes (L3–L15) were also frequently detected in the sediment samples. Among the linear siloxanes, L8, L9, L10, and L11 were analyzed at high rates. L3, L4, L5, L6, L7, L12, and L13 were analyzed in over 39% of the samples and L14 (4%) and L15 (3%) were rarely detected in sediments. The sum of linear siloxane concentrations ranged from 1.69 to 1,161.7 (mean: 85.5) ng/g dw.

The previous studies, which measured levels of siloxanes in sediment from other countries are compared with this study in Table 3. Only a few studies have investigated the distribution of both cyclic and linear siloxanes in sediment. The sum of D4, D5 and D6 was 751.7 ng/g dw in sediment from Denmark, 42.8 ng/g dw from Finland, 19.3 ng/g dw from Iceland, 15.4 ng/g dw from Norway (Kaj et al., 2005), 187.2 ng/g dw from China (Zhang et al., 2018), 172.7 ng/g dw from China (Zhi et al., 2018), and 136.0 ng/g dw from China (Zhang et al., 2011). The concentrations of cyclic and linear siloxanes in the four bays are shown in Figures 7 and 8. The total concentration of three compounds (D4–D6) found in Jinhae (mean: 131.7 ng/g dw) is generally similar to concentration levels reported from the other studies. Whereas the total concentrations of the siloxanes in Busan (mean: 392.6 ng/g dw) and Ulsan (mean: 206.8 ng/g dw) showed relatively higher, and Gwangyang (mean: 20.1 ng/g dw) showed lower concentrations than the other countries. Lee et al. (2018) also reported the distribution of 19 siloxanes (D4–D7, L3–L17) in Ulsan. Total mean concentration levels of cyclic siloxanes and the composition profile of linear siloxanes are similar to those found in our study, except Gosa Stream, which had a significantly high concentration. The two studies of Ulsan indicate that concentration levels in the site are generally higher than the other countries. Therefore, we can suggest that pollution levels of siloxanes in Ulsan is a critical issue. Tran et al. (2015) also found that indoor dust in Korea (Ansan and Anyang) showed a relatively high median concentration of siloxanes among 12 specific countries.

Table 3. Global comparison of cyclic siloxanes concentrations (ng/g dw) in sediment samples between this study and previous study.

Country	Cyclic siloxanes					Linear siloxanes	Reference
	D4	D5	D6	D7	ΣCyclic	ΣLinear (Target compounds)	
Norway	0.00	15.4	0.00	-	15.4	0.25 (L2–L5)	Kaj et al., 2005
Iceland	0.00	18.3	1.00	-	19.3	<LOQ[a] (L2–L5)	Kaj et al., 2005
Sweden	0.00	29.8	5.13	-	34.9	0.66 (L2–L5)	Kaj et al., 2005
Finland	0.00	38.5	4.30	-	42.8	<LOQ (L2–L5)	Kaj et al., 2005
Denmark	28.0	667	56.7	-	752	28.7 (L2–L5)	Kaj et al., 2005
China	7.23	52.7	76.1	124	260	12.7 (L4–L16)	Zhang et al., 2011
Spain	125	221	-	-	346	15.1 (L3–L5)	Sanchís et al., 2013
China	0.67	9.72	1.45	0.60	12.4	n.d. (L8–L12)	Hong et al., 2014
Korea	-	138	76.4	14.4	245	467 (L3–L17)	Lee et al., 2018
China	54.4	65.8	67.0	-	187	-	Zhang et al., 2018
China	18.3	59.9	94.6	-	173	985 (L5–L16)	Zhi et al., 2018
Ulsan, Korea	5.12	76.8	125	10.6	207	81.5 (L3–L15)	This study
Jinhae, Korea	5.72	53.9	72.0	7.19	132	106 (L3–L15)	
Busan, Korea	9.84	192	191	22.3	393	135 (L3–L15)	
Gwangyang, Korea	1.59	5.62	12.9	1.92	20.1	7.36 (L3–L15)	

[a] LOQ; limit of quantification

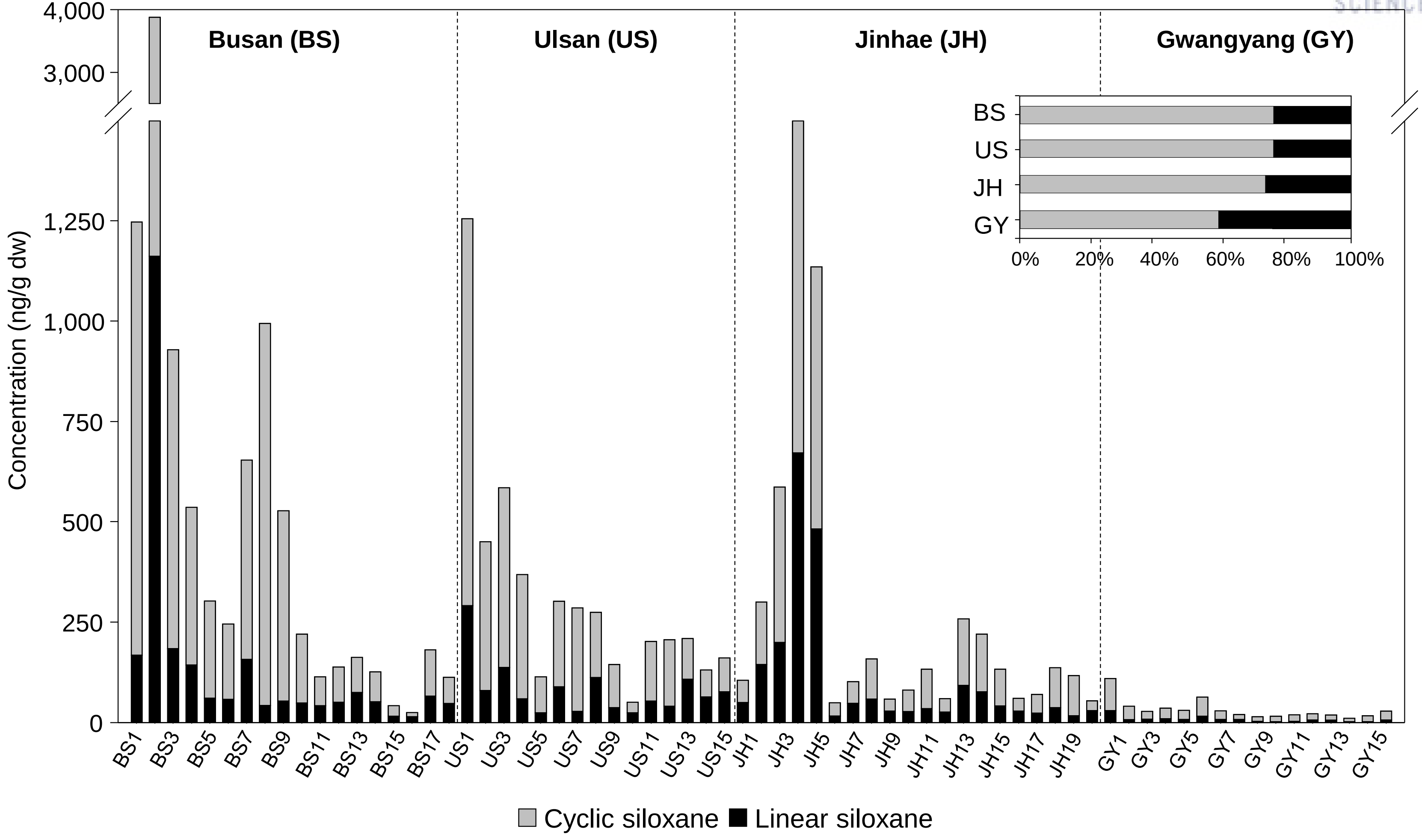


Figure 7. Total concentrations of cyclic and linear siloxanes at 69 sites in Korea.

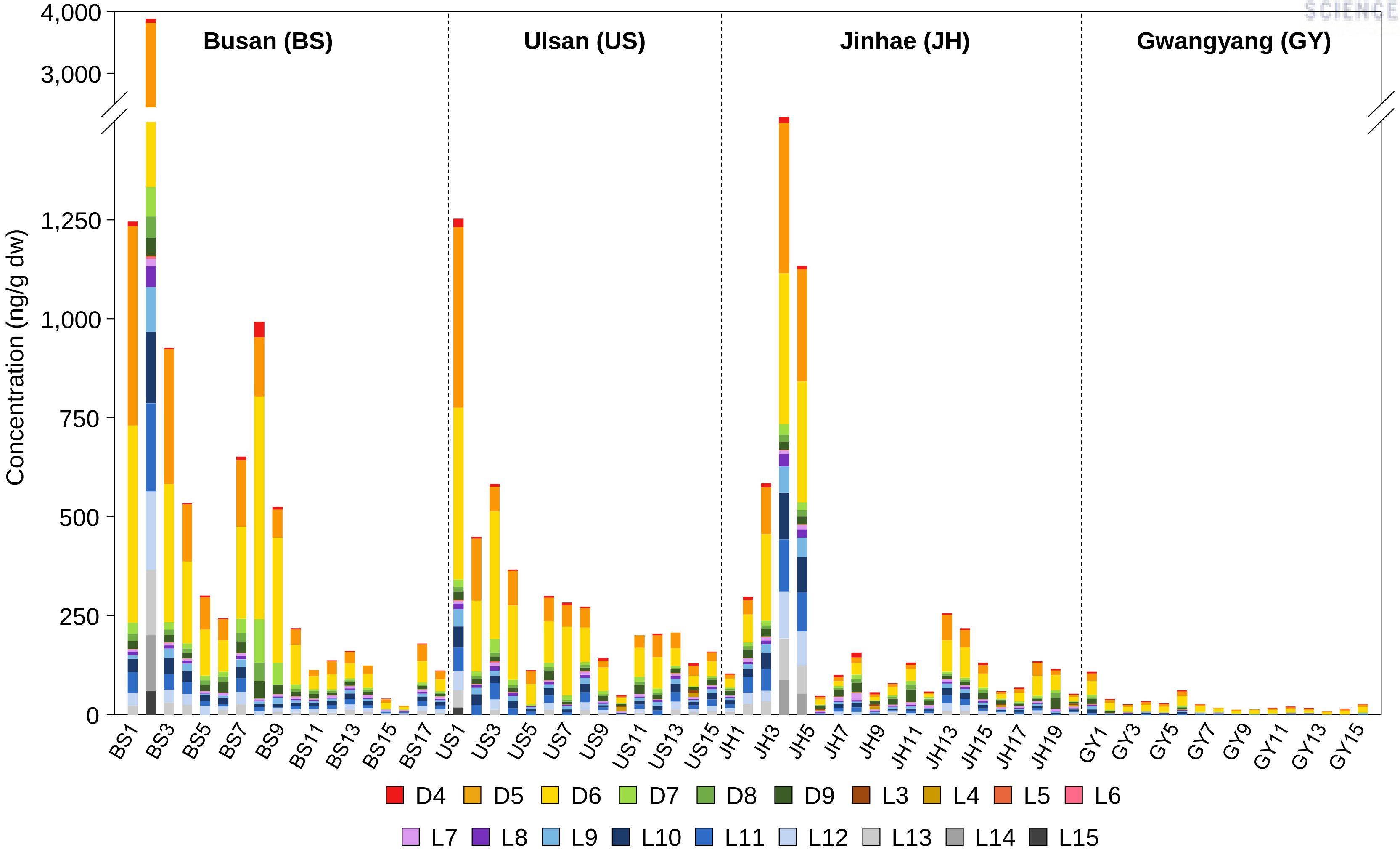


Figure 8. Concentrations of each siloxanes at 69 sampling sites in Korea.

3.2 Profile of siloxanes in coastal sediment

The proportions of measured siloxanes in sediment to the total concentrations are shown in Figure 9. Among the six cyclic siloxanes, the relative composition of D5 and D6 was higher than that of the other cyclic siloxane congeners in almost all sampling sites. This distribution of cyclic siloxanes in sediment is similar to previous studies in Dongting lake, China (D4: 29.1%, D5: 35.2%, and D6: 35.8%; Zhang et al. (2018)) and Dalian, China (D4: 5.4%, D5: 78.1%, D6: 11.7%, and D7: 4.8%; Hong et al. (2014)), which concluded that D5 and D6 were the predominant compounds, followed by D4 and D7. Earlier studies on other environmental matrices, including sludge, wastewater, and seawater also found similar distribution patterns (Hong et al., 2014; Lee et al., 2014; Zhi et al., 2018). The composition of siloxane was similar to those detected in PCPs, which are regarded as the major pollution source of siloxanes in the environment (Wang et al., 2013b). Other studies also showed that the two cyclic siloxanes are the dominant compounds in PCPs (Dudzina et al., 2014; Horii and Kannan, 2008; Lu et al., 2011). Therefore, the extensive usage of the compounds in the commercial products can explain the composition profiles.

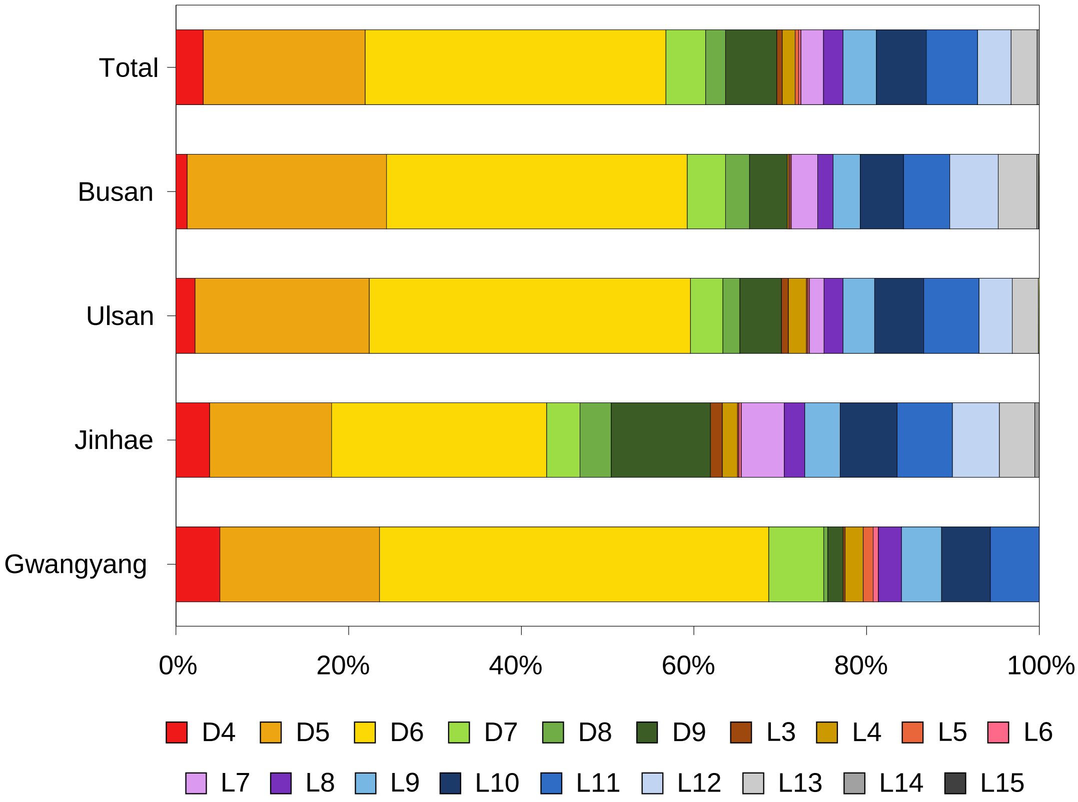


Figure 9. Relative contribution of siloxanes in coastal sediment samples.

The composition fraction of linear siloxanes in the four sampling areas increased from L6 to L11 and decreased from L12 to L15. This distribution is consistent with the other studies not only in sediment (Lee et al., 2018), but also in various matrices like sludge, seawater, and wastewater (Bletsou et al., 2013; Hong et al., 2014; Lee et al., 2014; Zhang et al., 2011). A previous study estimated solid-liquid distribution coefficients, which are the indexes for the sorption capacities of siloxanes (Bletsou et al., 2013). They compared siloxane concentrations in particulate phase and those in dissolved phase during the wastewater treatment process. In the results, the coefficients of linear siloxanes generally increased from L5 to L9 and decreased from L10 to L14, which showed a similar pattern to the concentration distributions of siloxane in the present study. Detailed mechanisms of these trends were not discussed in other studies. However, these increasing and decreasing trends are shown in the binding affinities of perfluoroalkyl substances (PFCAs) to serum protein (Zhang et al., 2013), suggesting that binding affinities increase to increasing specific number of chain length, and then diminish due to changes of the physical properties of compounds.

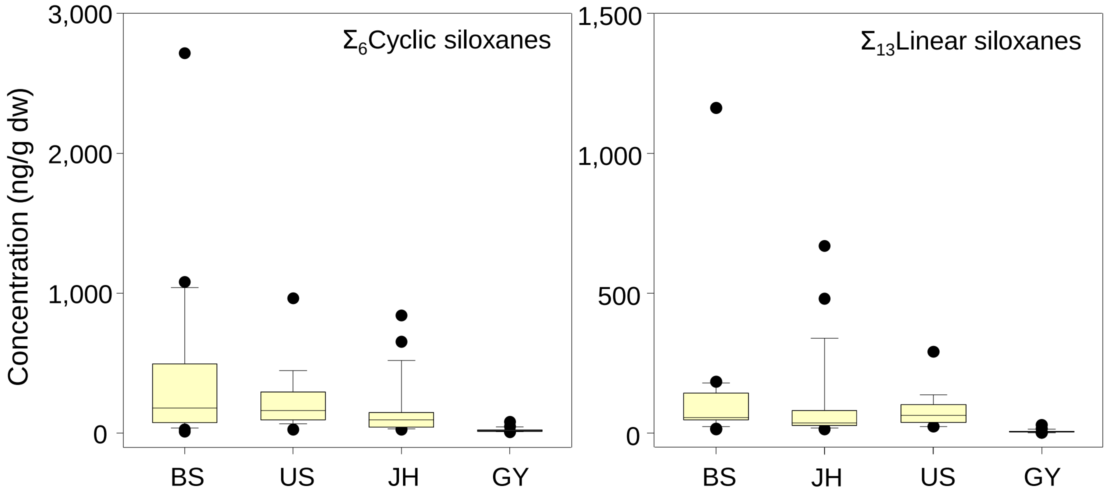


Figure 10. Concentrations of cyclic and linear siloxanes in the four regions. The error bars represent standard deviations.

Cyclic and linear concentrations of four sites are shown in Figure 10. In the four areas, cyclic siloxanes (D4–D9) accounted for 70% of the total siloxane concentrations, whereas linear siloxanes (L3–L15) made up only 30%. This implies that cyclic siloxanes were the most prevalent chemicals in the sampling sites. This abundant distribution pattern of cyclic siloxanes can be explained by the cyclic siloxanes having a higher consumption tendency than linear siloxanes (Lee et al., 2018; Lee et al., 2014). However, the compositions of siloxanes were different depending on the sampling area. In Busan samples, cyclic siloxanes, D5 and D6 accounted for 23% and 35% of the total siloxane concentrations, and the linear siloxanes (L3–L15) made up 29%. In contrast, Jinhae samples contained a much higher fraction of linear siloxanes, at 38%. In general, industrial products have a higher fraction of linear siloxanes than PCPs (Horii and Kannan, 2008; Xu et al., 2015). Therefore, the high fraction of linear siloxanes in Jinhae can be explained by the effects of specific industrial activities in this site.

3.3 Spatial distribution and pollution sources of siloxanes in coastal sediment

There was no statistically significant difference in the total mean concentrations of siloxanes among three bays (Mann-Whitney rank sum test: $p > 0.05$), except for Gwangyang bay (Mann-Whitney rank sum test: < 0.01).

The concentrations of siloxanes in the sediments from Busan bay ranged from 24.2 to 3,877.2 ng/g dw (mean 579.4 ng/g dw), and the total mean value in Busan was the highest among the four bays studied. According to Statistics Korea, the sampling areas in Busan had the highest number of rubber related manufacturers (0.3 companies/km^2) compared to the other bays (Statistics Korea, 2015). Spatial distribution and profiles of cyclic and linear siloxanes in Busan are shown in Figure 11. The inner part of Busan bay (BS1–BS9) had siloxane concentrations that were approximately eight times higher than the outer part of the bay (BS10–BS18). The inner bay is comprised of three different commercial ports: Busan North, Busan South, and Gamcheon port. Among them, the largest container port, Busan North port, which is connected to the Dong Stream, showed the highest siloxane concentration. The Busan Institute of Health and Environment reported that the water quality of the stream has deteriorated as a result of the serious pollution from domestic wastewater and river sediment (IHE, 2016). Therefore, sites with the highest contamination in Busan North port were significantly affected by the contaminated river and port related activities. Gamcheon and Busan South port, located near shipyards, also showed high concentrations. A previous study in China also found that one sampling site near a shipyard had the highest concentration of cyclic siloxanes (D4–D6) in sediment (Zhang et al., 2018). Our finding suggests that the commercial ports and domestic activities were the major contamination sources of Busan bay.

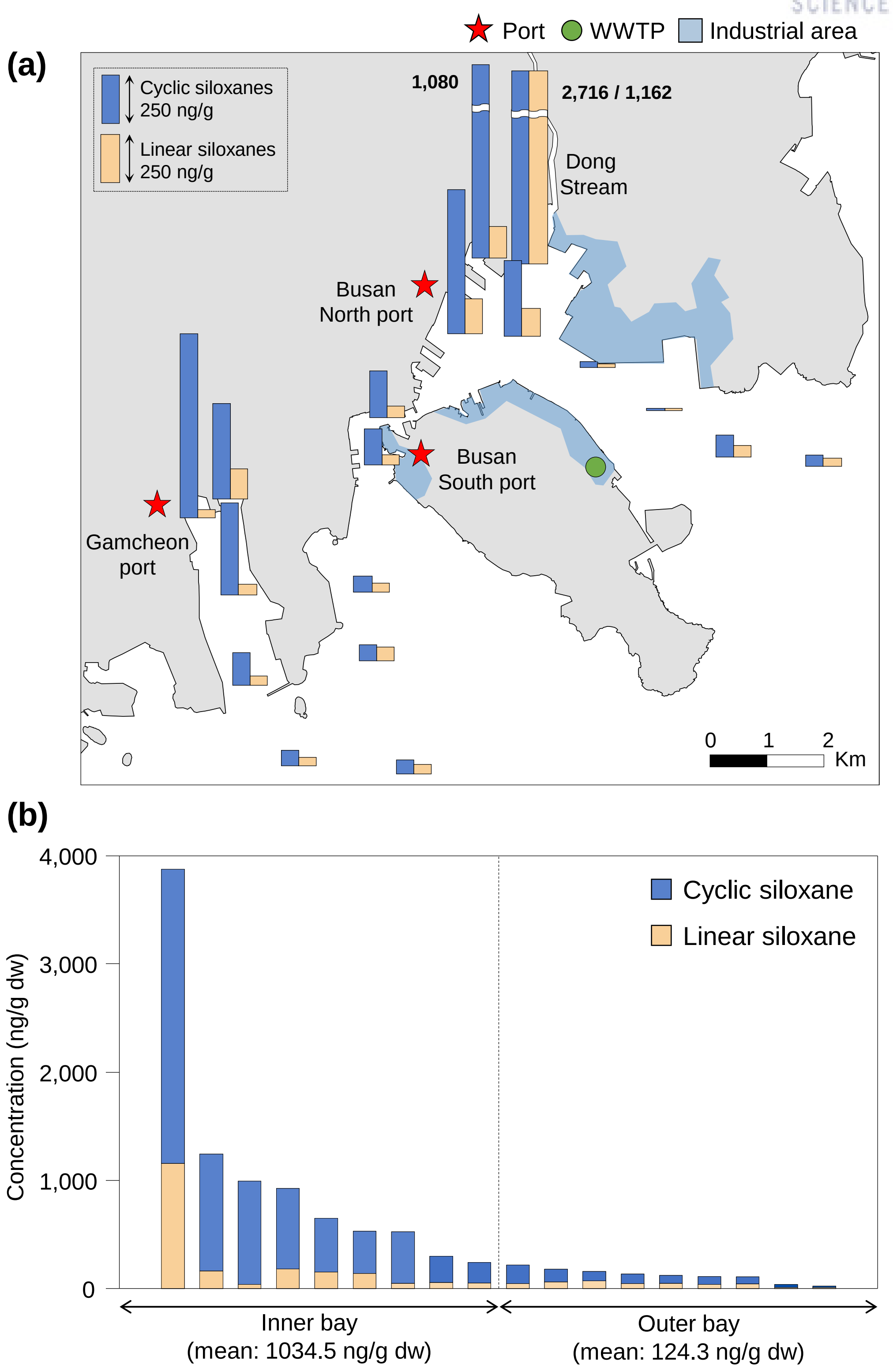


Figure 11. (a) Spatial distribution of $\Sigma_6$cyclic siloxanes and Σ_{13}linear siloxanes in coastal sediment collected from Busan, Korea. (b) Profiles of $\Sigma_6$cyclic siloxanes and Σ_{13}linear siloxanes from industrial and rural area in Busan.

Ulsan had the second highest siloxanes concentration among the four bays, which ranged from 50.5 to 1,254.4 ng/g dw (mean: 315.8 ng/g dw). Spatial distribution and profiles of cyclic and linear siloxanes in Ulsan are shown in Figure 12. In general, the concentrations of siloxanes in Ulsan tended to decline from the estuary to the sea, which is consistent with the siloxanes distribution pattern of previous study (Hong et al., 2014). This result indicates that emissions of siloxanes are associated with the industrial complexes along the estuary. The highest concentration of siloxanes was detected downstream of the Taehwa River, which is affected by both industrial and domestic activities, and near to Ulsan port surrounded by petrochemical and automobile facilities. The second highest concentration was found downstream of Gosa Stream, which is surrounded by a commercial port and chemical facilities. We compared the spatial distribution of Ulsan found in our study with that of a previous study (Lee et al., 2014). This study also reported that siloxane levels increase in line with increasing proximity to the inner bays. In addition, they also found that except for the extremely high concentration sites upstream of Gosa Stream, which are not included in our sampling area, the highest concentration was detected near the Taehwa River and Ulsan port, followed by downstream of Gosa Stream. Their results about the spatial distribution trends in Ulsan are consistent with our study, indicating that industrial activities along the estuary and Taehwa River can significantly contribute to siloxane contamination.

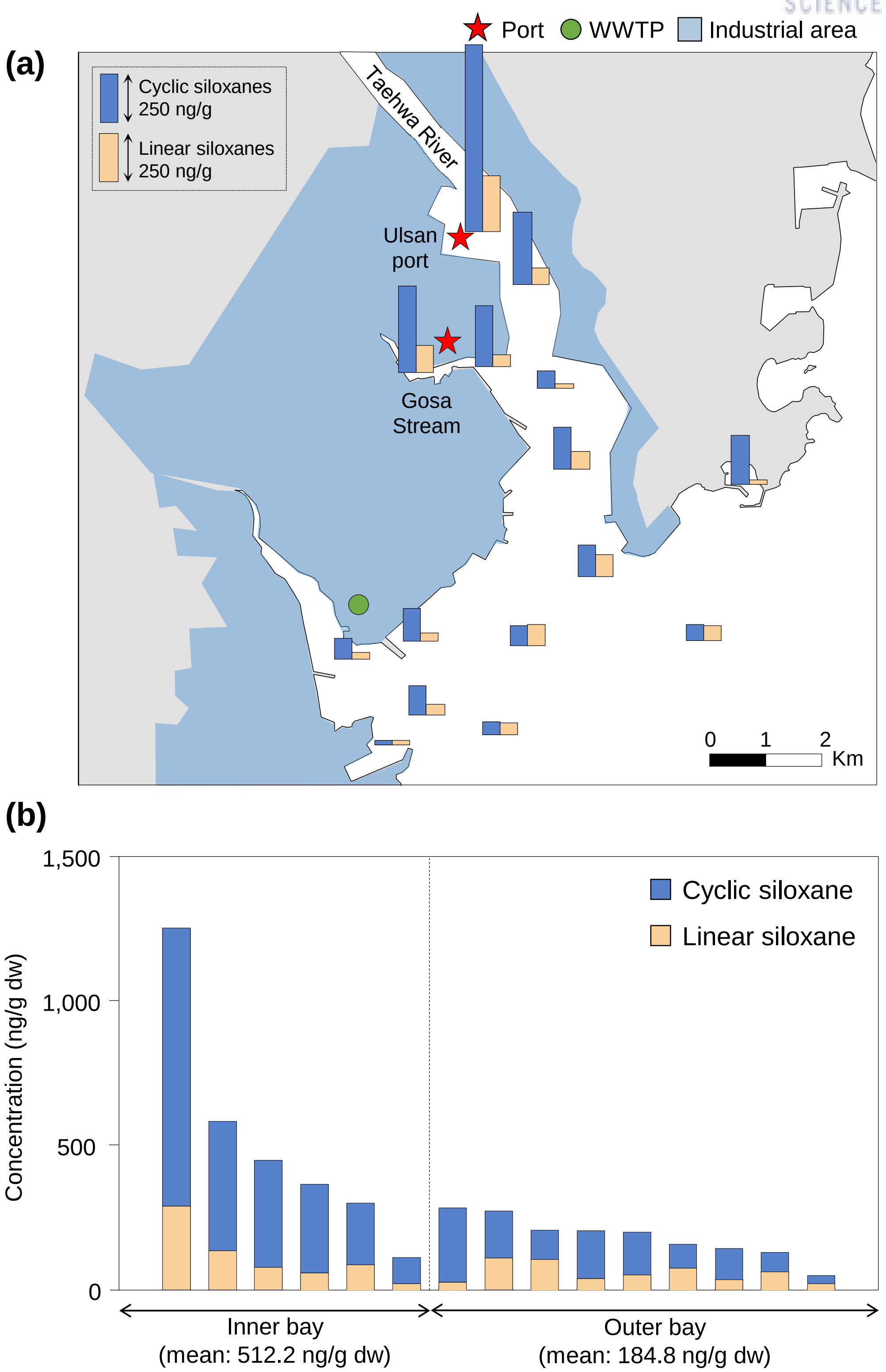


Figure 12. (a) Spatial distribution of $\Sigma_6$cyclic siloxanes and Σ_{13}linear siloxanes in coastal sediment collected from Ulsan, Korea. (b) Profiles of $\Sigma_6$cyclic siloxanes and Σ_{13}linear siloxanes from industrial and rural area in Ulsan.

In Jinhae, the concentrations of siloxane in coastal sediment ranged from 48.6 to 1,511.3 ng/g dw (mean: 266.2 ng/g dw). Spatial distribution and profiles of cyclic and linear siloxanes in Jinhae are shown in Figure 13. Linear siloxanes in this bay had a high fraction and the second highest levels next to Busan bay. The highest concentration of siloxanes was detected near Masan bay (JH3, JH4, and JH5). JH4 and JH5 were close to a Duck-dong WWTP, which manages industrial and domestic wastewater. It is known to play an important role in the pollution distribution of Masan bay (Kannan et al., 2010), indicating that the WWTP directly contributed to high levels of siloxanes in Masan bay. JH3 was located near the commercial port and the downstream of a river which passes through the large scale industrial complexes. As a result, the siloxane concentrations in Masan bay was approximately six times higher than that in the less polluted western zone. However, sediments collected from industrial complexes in western zone also showed relatively high concentrations. The mean concentration of siloxanes near industrial areas was higher than those near rural and coastal areas. Therefore, urban areas rather than rural areas are considered to be the important source of siloxane contamination in coastal sediment (Hong et al., 2014; Zhang et al., 2018). These findings suggest that the major contamination sources in Jinhae were the activities of WWTP and industrial areas. As mentioned before, Jinhae bay had a higher fraction of linear siloxanes than the other bays, indicating that Jinhae sites were more influenced by industrial activities. Indeed, sampling sites near WWTPs (JH2, JH4, and JH5) showed high fractions of linear siloxanes (45%), suggesting that the activities of WWTPs act as a major factor in increasing linear siloxane concentrations.

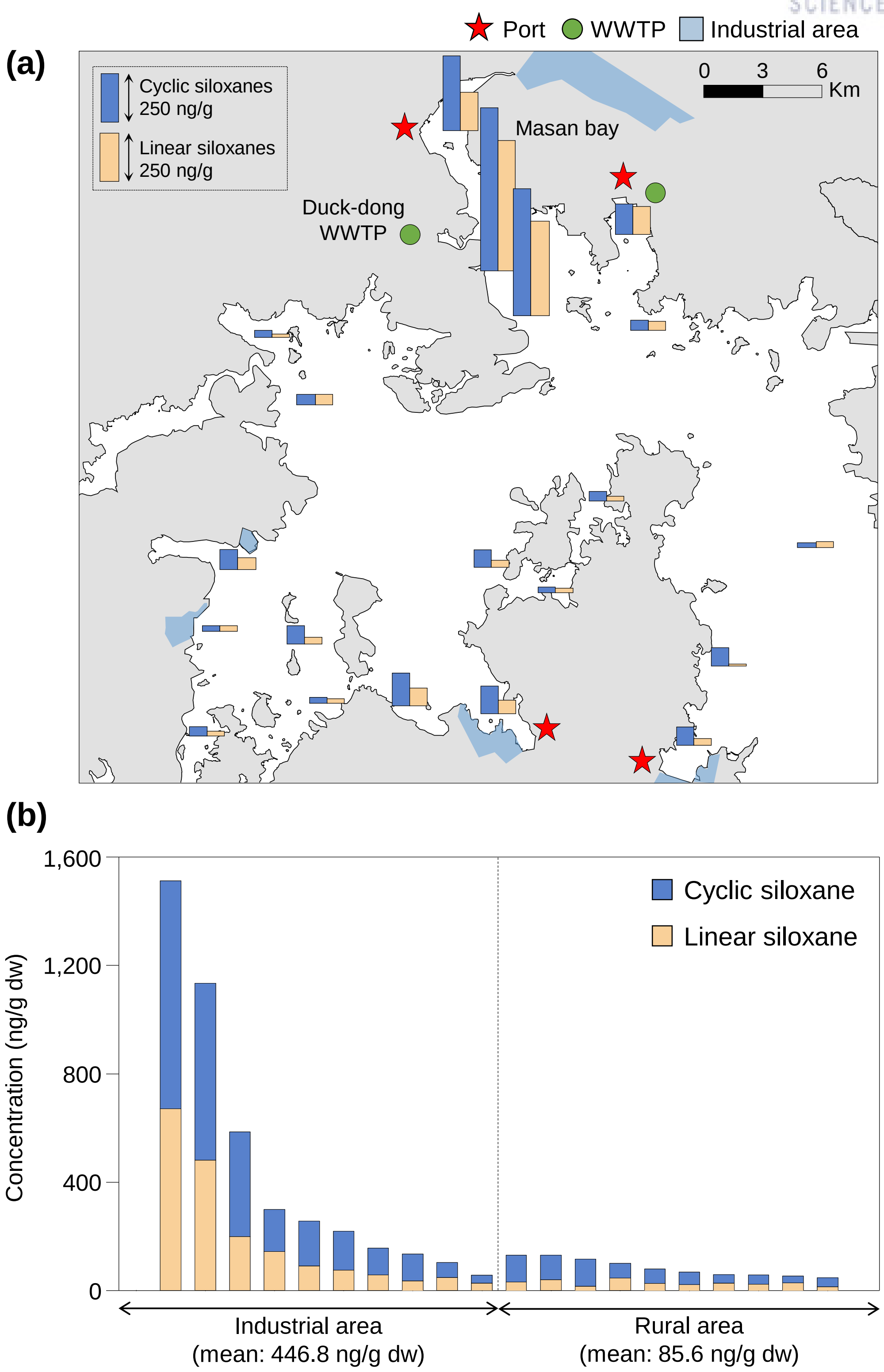


Figure 13. (a) Spatial distribution of $\Sigma_6$cyclic siloxanes and Σ_{13}linear siloxanes in coastal sediment collected from Jinhae, Korea. (b) Profiles of $\Sigma_6$cyclic siloxanes and Σ_{13}linear siloxanes siloxanes from inner and outer bay in Jinhae.

Sediments collected from Gwangyang bay had the lowest concentrations compared to the other bays, ranging from 10.1 to 109.8 ng/g dw (mean: 31.1 ng/g dw). The total mean concentration of siloxanes in Gwangyang bay is about 20 times lower than that in Busan bay. The low concentration trend of Gwangyang bay can be explained by dredging for land reclamation in this area or by a lower number of rubber related manufacturers (0.01 companies/km^2) than the other bays (Statistics Korea, 2015). Spatial distribution and profiles of cyclic and linear siloxanes in Gwangyang are shown in Figure 14. The sediments sampled near WWTPs (GY1 and GY6) contained the highest levels of siloxanes. Also, the average concentration in the inner part of the bay (GY1–9), which was surrounded by industrial complexes, was about two times higher than that in the outer bay near residential areas (GY10–16). Therefore, WWTPs and industrial complexes were the major pollution sources in coastal sediment in Gwangyang.

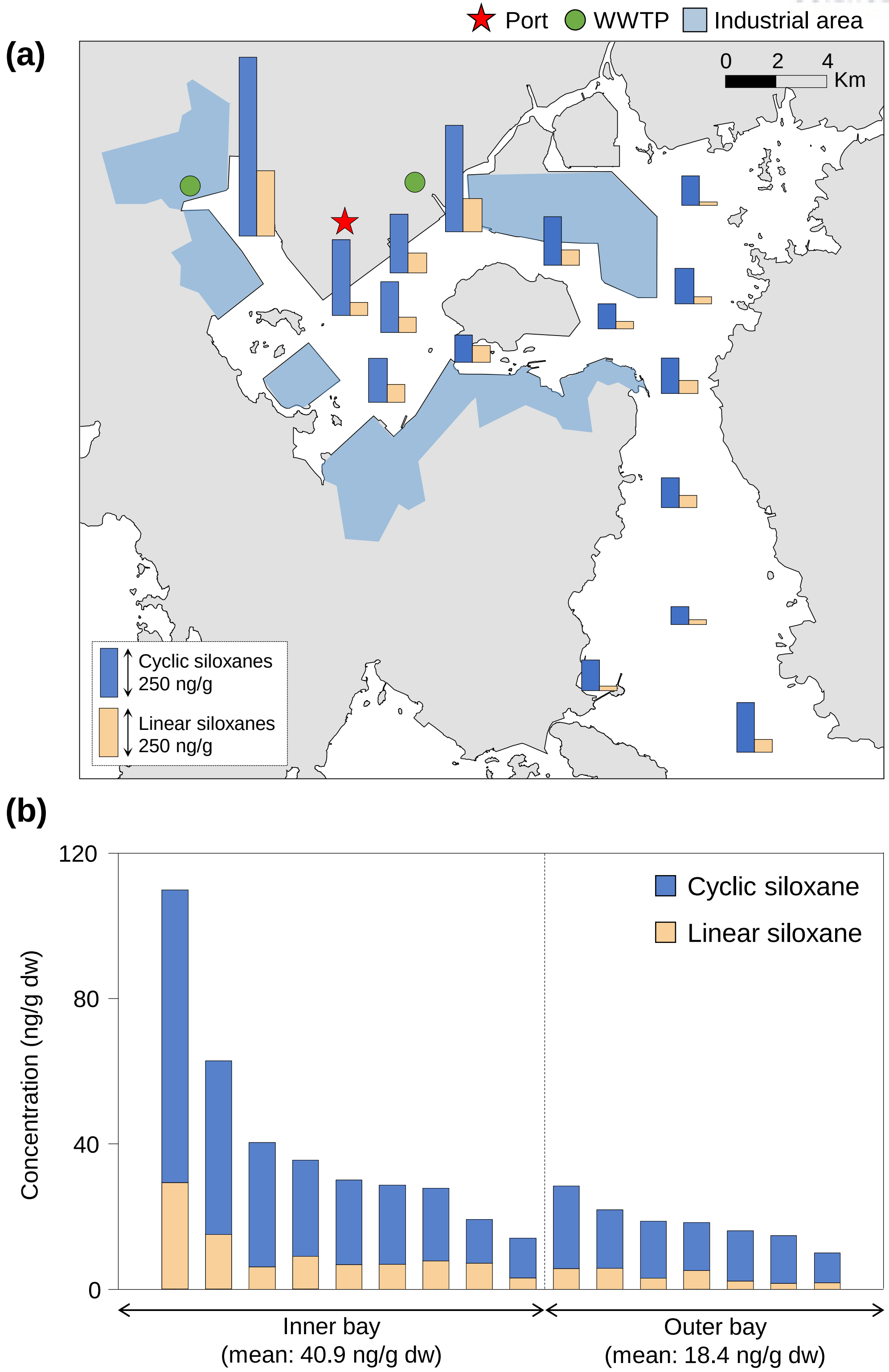


Figure 14. (a) Spatial distribution of $\Sigma_6$cyclic siloxanes and Σ_{13}linear siloxanes in coastal sediment collected from Gwangyang, Korea. (b) Profiles of $\Sigma_6$cyclic siloxanes and Σ_{13}linear siloxanes siloxanes from inner and outer bay in Gwangyang.

3.4 Correlations of siloxanes in coastal sediment

The relationships among cyclic siloxanes, linear siloxanes, and total organic carbon (TOC) were identified by Spearman correlation analysis (Table 4). Siloxanes, except two linear siloxanes (L3 and L4), were correlated with the sum of cyclic and linear siloxane concentrations as well as each other, suggesting the common pollution sources of siloxanes. Since 1940, silicone blends, which contain a mixture of siloxanes have been applied as major additives in various products (Chandra, 1997; Horii and Kannan, 2008). Therefore, the usage of the silicone blends in industrial complexes near the sampling sites is likely to be a reason for the correlation results.

The relationship between siloxane concentrations and TOC content in sediment was also examined. Positive correlations are shown between the concentrations of almost all siloxanes, except low molecular weight linear siloxanes (L3, L4, and L5), and TOC content in sediment. This indicates that cyclic siloxanes and high molecular weight linear siloxanes have a strong binding affinity to organic carbon. The TOC content significantly affects concentrations of siloxanes in sediment due to inherent properties of siloxanes, such as high $\log K_{OC}$ and $\log K_{OW}$ (Woodburn et al., 2018; Xu and Kropscott, 2012). A previous study also reported that increasing TOC content reduces degradation of siloxanes in sediment (Shi et al., 2015). Therefore, organic carbon is the primary contributor in determining the contamination levels of siloxanes in the coastal environment. Other studies also found positive correlations between concentrations of siloxanes and TOC content in sediment (Lee et al., 2018; Lee et al., 2014; Zhang et al., 2011).

Table 4. Spearman correlations among cyclic siloxanes, linear siloxanes, and total organic carbon contents in coastal sediments.

	D4	**D5**	**D6**	**D7**	**D8**	**D9**	**L6**	**L7**	**L8**	**L9**	**L10**	**L11**	**L12**	**L13**	**L14**	**L15**	**ΣCyclic**	**ΣLinear**	**ΣTotal**	**TOC**
D4	1	.621**	.623**	.669**	.593**	.648**	.518**	.479**	.580**	.581**	.564**	.524**	.465**	.297*	.329**	.287*	.696**	.570**	.682**	.631**
D5		1	.972**	.902**	.797**	.679**	.675**	.540**	.867**	.911**	.915**	.885**	.735**	.637**	.336**	.286*	.970**	.886**	.971**	.545**
D6			1	.937**	.806**	.693**	.672**	.511**	.829**	.877**	.861**	.844**	.707**	.615**	.322**	.282*	.979**	.838**	.967**	.520**
D7				1	.880**	.827**	.757**	.599**	.834**	.860**	.836**	.814**	.697**	.565**	.315**	.252*	.960**	.821**	.944**	.584**
D8					1	.865**	.686**	.634**	.792**	.769**	.812**	.809**	.713**	.555**	.339**	.261*	.853**	.789**	.850**	.545**
D9						1	.618**	.670**	.671**	.704**	.708**	.640**	.669**	.521**	.270*	.249*	.786**	.725**	.776**	.612**
L6							1	.502**	.797**	.773**	.737**	.761**	.540**	.484**	.341**	.279*	.707**	.710**	.709**	.439**
L7								1	.627**	.637**	.654**	.644**	.822**	.719**	.348**	.225	.597**	.744**	.639**	.575**
L8									1	.955**	.939**	.913**	.724**	.678**	.353**	.282*	.860**	.921**	.892**	.579**
L9										1	.941**	.899**	.761**	.718**	.353**	.282*	.900**	.928**	.926**	.561**
L10											1	.947**	.813**	.740**	.353**	.282*	.887**	.973**	.925**	.595**
L11												1	.821**	.728**	.353**	.282*	.860**	.940**	.901**	.516**
L12													1	.883**	.361**	.288*	.731**	.890**	.792**	.517**
L13														1	.369**	.294*	.620**	.819**	.684**	.387**
L14															1	.405**	.620**	.819**	.684**	.387**
L15																1	.620**	.819**	.684**	.387**
ΣCyclic																	1	.872**	.987**	.606**
ΣLinear																		1	.925**	.600**
ΣTotal																			1	.611**

**Correlation is significant at the 0.01 level (2-tailed) and *Correlation is significant at the 0.05 level (1-tailed)

The Stockholm Convention regulates PCDD/F, PCB, and PCN as persistent organic pollutants (POPs), because of their environmental persistence, biological accumulation, toxicity, and long range transport (Rodan et al., 1999). The three POPs were analyzed in the same sediment samples that we used in our study (Son et al., unpublished data). From the data, we investigated the correlation between concentrations of siloxanes and POPs in Table 5. TOC normalized concentrations were applied as the input data for the Spearman correlation analysis.

Table 5. Spearman correlation analysis between siloxanes and POPs.

	Cyclic siloxanes	**Linear siloxanes**	**Total siloxanes**
PCDD/Fs	.486**	.490**	.511**
PCBs	.807**	.677**	.802**
PCNs	.707**	.637**	.730**

**Correlation is significant at the 0.01 level (2-tailed)

As a result, cyclic and linear siloxanes had positive correlations with the POPs. The POPs have similar physicochemical properties to siloxanes, in that they have hydrophobicity and lipophilic characteristics (Herbert et al., 2004; Nguyen et al., 2016). In addition, the main pollution sources of POPs are paint and chemical facilities, as is the case with siloxanes (Lee et al., 2018; Nguyen et al., 2016; Xu et al., 2015). Therefore, their similar properties and common pollution sources may have led to the positive correlation. In addition, both siloxanes and POPs showed high concentration levels near commercial ports, WWTPs, and downstream of industrial complexes, indicating that the mixture of industrial activities rather than a specific industry is the major contamination sources of the contaminants.

3.5 Principal component analysis (PCA)

PCA was done to identify the relationships between distribution patterns of siloxane congeners and sampling sites. The siloxane profiles of sediment in the four bays were used for the analysis. The 8 compounds (D4–D7, L8–L11) which had a detection frequency of over 80% were selected, and any value below the detection limits was substituted by half of the detection limits. For the normalization, concentrations of the selected siloxanes were divided by the total siloxane concentrations of all 8 compounds at each site. These normalized siloxane concentrations were used as input data for PCA.

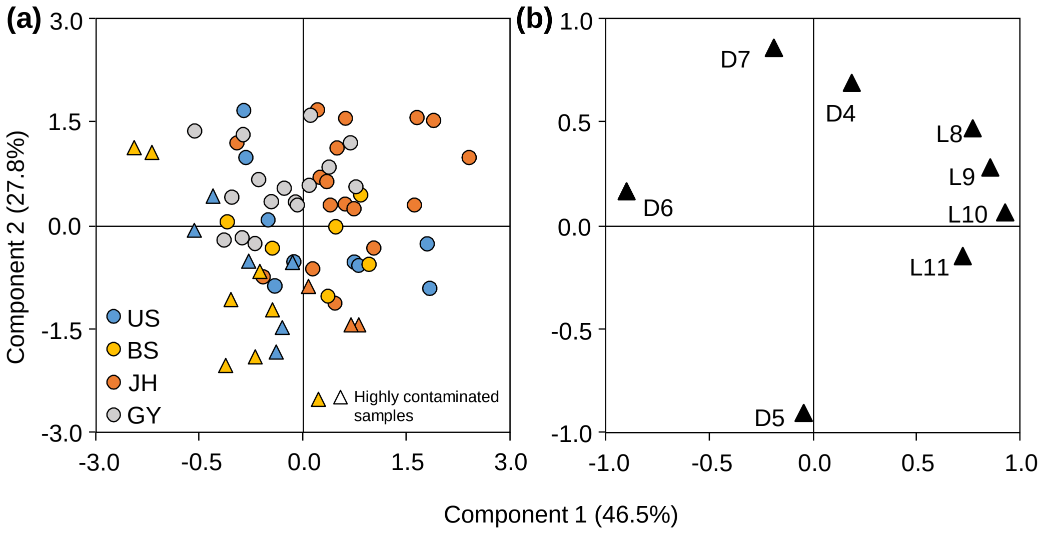


Figure 15. Results of principal component analysis: (a) score and (b) loading plots.

The results of PCA are shown in Figure 15. In the loading plot, the principal component 1 (PC 1), explaining 46.5% of the total variance, have positive PC loading values for the linear siloxane group and negative values for the cyclic siloxane group, except for D4. In the score plot, most of the sediment samples collected from Jinhae bay (orange dots) have positive PC 1 scores, indicating that Jinhae sites were much more correlated with linear compounds than cyclic compounds. As we mentioned earlier, Jinhae bay had a higher proportion of linear siloxanes to total concentration (38%) than the other three bays (27%). Meanwhile, negative PC 1 loading values were related to the three cyclic siloxanes (D5–D7). Among them, D5 and D6 are mainly associated with the samples represented by triangles, which have the top 25% concentration levels, in the score plot. This suggests that the cyclic compounds contributed more to the highly contaminated sediment samples. Indeed, the two cyclic siloxanes had higher fractions in the top 25% concentration sites (67%) than the other sites (49%).

3.6 Probabilistic distributions of hazard quotients

Cyclic siloxanes were detected in all 69 coastal sediments from the four regions with high concentrations and are known to cause potential toxic effects on marine organisms (Rücker and Kümmerer, 2015). Therefore, it is required to evaluate the possible risks to organisms of siloxanes in coastal sediment. The results of the Monte Carlo simulations of hazard quotient for the three cyclic siloxanes (D4–D6) are shown in Table 6 and Figure 17.

The results show that all the HQs are lower than the threshold levels (HQ < 1), suggesting that the three compounds do not seem to cause ecological risk to sediment dwelling organisms. According to the 95th percentile values of the hazard quotient, the highest HQ value was found in Busan, followed by Ulsan, Jinhae, and Gwangyang. In addition, D6 had the highest value among the three target compounds. The result of the Monte Carlo simulations in our study was similar to previously reported data, which also concluded that the risk of siloxanes to organisms is low (Fairbrother and Woodburn, 2016; Liu et al., 2014; Woodburn et al., 2018; Zhi et al., 2018). However, risk assessment in our study was done for only one environmental compartment (sediment) with a limited amount of toxicity data. Due to the scarcity of information and potential cocktail effects of siloxanes, it is necessary to investigate the ecological risk of siloxanes in various environmental compartments in further studies.

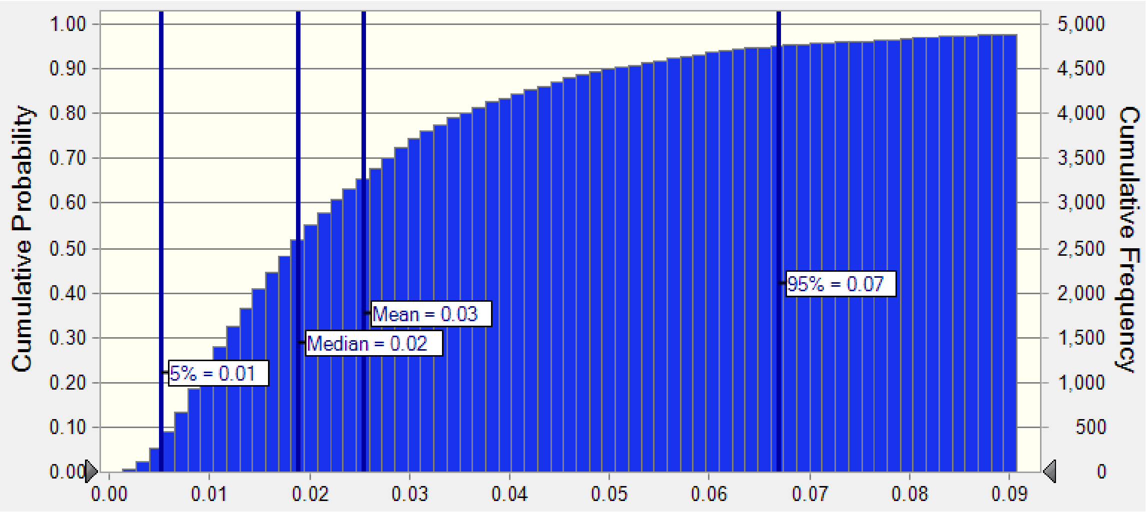


Figure 16. Example of the Monte Carlo simulation for D6 in Ulsan.

Table 6. Hazard quotients of three cyclic siloxanes in sediment of the four regions.

Compounds	Site	Mean	Percentile			PNEC (ng/g dw)
			5th	50th	95th	
D4	Busan	7.6E-03	4.0E-04	3.2E-03	2.8E-02	1,300
	Ulsan	4.1E-03	7.7E-04	2.9E-03	1.1E-02	
	Jinhae	4.4E-03	1.4E-03	3.7E-03	9.6E-03	
	Gwangyang	1.3E-03	4.6E-04	1.1E-03	2.9E-03	
D5	Busan	2.8E-02	1.4E-03	1.2E-02	1.0E-01	6,900
	Ulsan	1.1E-02	1.1E-03	6.2E-03	3.6E-02	
	Jinhae	7.7E-03	5.1E-04	3.8E-03	2.7E-02	
	Gwangyang	8.2E-04	2.2E-04	6.6E-04	2.0E-03	
D6	Busan	3.9E-02	6.0E-03	2.6E-02	1.1E-01	4,840
	Ulsan	2.5E-02	5.1E-03	1.9E-02	6.7E-02	
	Jinhae	1.5E-02	1.5E-03	8.6E-03	4.9E-02	
	Gwangyang	2.7E-03	9.3E-04	2.3E-03	5.7E-03	

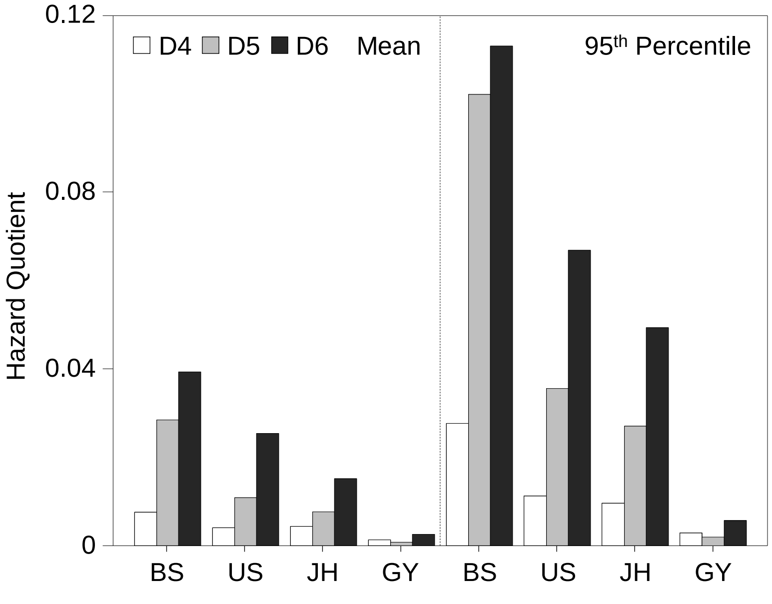


Figure 17. Mean and 95th percentile of HQs of three cyclic siloxanes in sediment of the four regions.

Ⅳ. CONCLUSIONS

This study identified the widespread distribution of siloxanes in coastal environments in South Korea because siloxanes were detected with high concentration levels in all surface sediment samples. Generally, D5 and D6 were the predominant compounds among cyclic siloxanes in coastal sediment, and L10 and L11 were the predominant compounds among the linear siloxanes. In addition, cyclic siloxanes accounted for much more of the total siloxanes than linear siloxanes, implying the higher consumption tendency of cyclic siloxanes in the sampling areas.

From the spatial distribution analysis for the four studied sites, the highest concentration of siloxanes was found in Busan, followed by Ulsan, Jinhae, and Gwangyang. Additionally, the concentration levels in Busan and Ulsan are among the highest in the world. Relatively high concentrations of siloxanes were found in the coastal sediment collected from rivers near cities, commercial ports, WWTPs, and industrial complexes, reflecting the significant influences of industrial and domestic activities on siloxane contaminations. Therefore, the concentrations of siloxanes generally decline from the estuary to the sea.

According to the Spearman correlation analysis, each siloxane, except low molecular weight linear siloxanes, had a positive correlation with the other congeners, suggesting common pollution sources such as silicone blends. Furthermore, siloxanes had positive correlations with TOC content in sediment and concentrations of POPs, due to the hydrophobic and lipophilic nature of siloxanes. The results of PCA confirmed that the highly contaminated sites were significantly influenced by cyclic siloxanes, and the sites in Jinhae were strongly contaminated by linear siloxanes.

Eventually, the Monte Carlo simulations of hazard quotient for the cyclic siloxanes indicated that the risk of cyclic siloxanes to aquatic organisms is negligible. However, due to a limited amount of data at present, and potential cocktail effects of siloxanes in coastal environments, it is necessary to further evaluate other potential ecological risks of siloxanes in various environmental compartments.

REFERENCES

Ahrens, L., Harner, T., Shoeib, M., 2014. Temporal variations of cyclic and linear volatile methylsiloxanes in the atmosphere using passive samplers and high-volume air samplers. Environmental Science and Technology 48.

Bletsou, A.A., Asimakopoulos, A.G., Stasinakis, A.S., Thomaidis, N.S., Kannan, K., 2013. Mass loading and fate of linear and cyclic siloxanes in a wastewater treatment plant in Greece. Environmental Science and Technology 47, 1824-1832.

Environment Canada, 2012. Notice requiring the preparation and implementation of pollution prevention plans in respect of cyclotetrasiloxane, octamethyl-(siloxane D4) in industrial effluents. http://www.gazette.gc.ca/rp-pr/p1/2012/2012-06-02/html/sup2-eng.html.

Chandra, G., 1997. Organosilicon materials. The handbook of environmental chemistry. Berlin, Germany.

Choi, S.-D., Kwon, H.-O., Lee, Y.-S., Park, E.-J., Oh, J.-Y., 2012. Improving the spatial resolution of atmospheric polycyclic aromatic hydrocarbons using passive air samplers in a multi-industrial city. Journal of Hazardous Materials 241-242, 252-258.

Dudzina, T., Delmaar, C.J.E., Biesterbos, J.W.H., Bakker, M.I., Bokkers, B.G.H., Scheepers, P.T.J., van Engelen, J.G.M., Hungerbuehler, K., von Goetz, N., 2015. The probabilistic aggregate consumer exposure model (PACEM): Validation and comparison to a lower-tier assessment for the cyclic siloxane D5. Environment International 79, 8-16.

Dudzina, T., von Goetz, N., Bogdal, C., Biesterbos, J.W.H., Hungerbühler, K., 2014. Concentrations of cyclic volatile methylsiloxanes in European cosmetics and personal care products: Prerequisite for human and environmental exposure assessment. Environment International 62, 86-94.

European Chemicals Agency (ECHA), 2016. UK proposes restriction on octamethylcyclotetr asiloxane(D4) and decamethylcyclopentasiloxane (D5) in personal care products that are washed off in normal use. https://www.echa.europa.eu/-/committee-for-socio-economic-analysis-concludes-on-restricting-d4-and-d5.

European Commission, 2005. Scientific committee on consumer products. opinion on octa methylcyclotetrasiloxane (D4) cyclomethicone. https://ec.europa.eu/health/ph_risk/committeees/04_sccp/docs/sccp_o_035.pdf.

Fairbrother, A., Woodburn, K.B., 2016. Assessing the aquatic risks of the cyclic volatile methyl siloxane D4. Environmental Science & Technology Letters 3, 359-363.

Fakhri, Y., Mousavi Khaneghah, A., Conti, G.O., Ferrante, M., Khezri, A., Darvishi, A., Ahmadi, M., Hasanzadeh, V., Rahimizadeh, A., Keramati, H., Moradi, B., Amanidaz, N., 2018. Probabilistic risk assessment (Monte Carlo simulation method) of Pb and Cd in the onion bulb (Allium cepa) and soil of Iran. Environmental Science and Pollution Research 25, 30894-30906.

Genualdi, S., Harner, T., Cheng, Y., MacLeod, M., Hansen, K.M., van Egmond, R., Shoeib, M., Lee, S.C., 2011. Global distribution of linear and cyclic volatile methyl siloxanes in air. Environmental Science and Technology 45, 3349-3354.

Guo, G., Wu, F., He, H., Zhang, R., Feng, C., Li, H., Chang, M., 2012. Characterizing ecological risk for polycyclic aromatic hydrocarbons in water from Lake Taihu, China. Environmental Monitoring and Assessment 184, 6815-6825.

Herbert, B.M.J., Halsall, C.J., Fitzpatrick, L., Villa, S., Jones, K.C., Thomas, G.O., 2004. Use and validation of novel snow samplers for hydrophobic, semi-volatile organic compounds (SVOCs). Chemosphere 56, 227-235.

Homem, V., Capela, D., Silva, J.A., Cincinelli, A., Santos, L., Alves, A., Ratola, N., 2017. An approach to the environmental prioritisation of volatile methylsiloxanes in several matrices. Science of The Total Environment 579, 506-513.

Hong, W.-J., Jia, H., Liu, C., Zhang, Z., Sun, Y., Li, Y.-F., 2014. Distribution, source, fate and bioaccumulation of methyl siloxanes in marine environment. Environmental Pollution 191, 175-181.

Horii, Y., Kannan, K., 2008. Survey of organosilicone compounds, including cyclic and linear siloxanes, in personal-care and household products. Archives of Environmental Contamination and Toxicology 55, 701.

Horii, Y., Minomo, K., Ohtsuka, N., Motegi, M., Nojiri, K., Kannan, K., 2017. Distribution characteristics of volatile methylsiloxanes in Tokyo Bay watershed in Japan: Analysis of surface waters by purge and trap method. Science of The Total Environment 586, 56-65.

The Busan Institute of Health and Environment (IHE), 2016. http://heis.busan.go.kr/data/data007.aspx. in Korean

Kaj, L., Schlabach, M., Andersson, J., Palm Cousins, A., Schmidbauer, N., Brorström-Lundén, E., 2005. Siloxanes in the Nordic Environment. Nordic Council of Ministers Research. Nordic Council of Ministers. Copenhagen, Denmark.

Kannan, N., Hong, S.H., Yim, U.H., Kim, N.S., Ha, S.Y., Li, D., Shim, W.J., 2010. Dispersion of organic contaminants from wastewater treatment outfall in Masan Bay, Korea. Toxicology and Environmental Health Sciences 2, 200-206.

Kim, N.S., Hong, S.H., Yim, U.H., Shin, K.-H., Shim, W.J., 2014. Temporal changes in TBT pollution in water, sediment, and oyster from Jinhae Bay after the total ban in South Korea. Marine Pollution Bulletin 86, 547-554.

Kim, Y.-S., Eun, H., Cho, H.-S., Kim, K.-S., Sakamoto, T., Watanabe, E., Baba, K., Katase, T., 2008. Organochlorine pesticides in the sediment core of Gwangyang Bay, South Korea. Archives of Environmental Contamination and Toxicology 54, 386-394.

Krogseth, I.S., Zhang, X., Lei, Y.D., Wania, F., Breivik, K., 2013. Calibration and Application of a passive air sampler (XAD-PAS) for volatile methyl siloxanes. Environmental Science & Technology 47, 4463-4470.

Lassen, C., Libak Hansen, C., Hagen Mikkelsen, S., J., M., 2005. Siloxanes - consumption, toxicity and alternatives. The Danish Environmental Protection AgencyResearch. The Danish Environmental Protection Agency. Denmark.

Lee, S.-Y., Lee, S., Choi, M., Kannan, K., Moon, H.-B., 2018. An optimized method for the analysis of cyclic and linear siloxanes and their distribution in surface and core sediments from industrialized bays in Korea. Environmental Pollution 236, 111-118.

Lee, S., Moon, H.-B., Song, G.-J., Ra, K., Lee, W.-C., Kannan, K., 2014. A nationwide survey and emission estimates of cyclic and linear siloxanes through sludge from wastewater treatment plants in Korea. Science of The Total Environment 497-498, 106-112.

Lei, Y.D., Wania, F., Mathers, D., 2010. Temperature-dependent vapor pressure of selected cyclic and linear polydimethylsiloxane oligomers. Journal of Chemical & Engineering Data 55, 5868-5873.

Liu, N., Shi, Y., Li, W., Xu, L., Cai, Y., 2014. Concentrations and distribution of synthetic musks and siloxanes in sewage sludge of wastewater treatment plants in China. Science of The Total Environment 476-477, 65-72.

Lu, Y., Yuan, T., Wang, W., Kannan, K., 2011. Concentrations and assessment of exposure to siloxanes and synthetic musks in personal care products from China. Environmental Pollution 159, 3522-3528.

Mackay, D., Cowan-Ellsberry, C.E., Powell, D.E., Woodburn, K.B., Xu, S., Kozerski, G.E., Kim, J., 2015. Decamethylcyclopentasiloxane (D5) environmental sources, fate, transport, and routes of exposure. Environmental Toxicology and Chemistry 34, 2689-2702.

McKim, J.J.M., Choudhuri, S., Wilga, P.C., Madan, A., Burns-Naas, L.A., Gallavan, R.H., Mast, R.W., Naas, D.J., Parkinson, A., Meeks, R.G., 1999. Induction of hepatic xenobiotic metabolizing enzymes in female Fischer-344 rats following repeated inhalation exposure to decamethylcyclopentasiloxane (D5). Toxicological Sciences 50, 10-19.

Ministry of Maritime Affairs and Fisheries (MOF), 2016. http://www.mof.go.kr/article/view.do?artic leKey=338&boardKey=2&currentPageNo=1.in Korean

Moon, H.-B., Choi, H.-G., Lee, P.-Y., Ok, G., 2008. Congener-specific characterization and sources of polychlorinated dibenzo-p-dioxins, dibenzofurans and dioxin-like polychlorinated biphenyls in marine sediments from industrialized bays of Korea. Environmental Toxicology and Chemistry 27, 323-333.

Nguyen, T.N.T., Kwon, H.-O., Lee, Y.-S., Kim, L., Lee, S.-E., Choi, S.-D., 2016. Spatial distribution and source identification of indicator polychlorinated biphenyls in soil collected from the coastal multi-industrial city of Ulsan, South Korea for three consecutive years. Chemosphere 163, 184-191.

Rücker, C., Kümmerer, K., 2015. Environmental Chemistry of Organosiloxanes. Chemical Reviews 115, 466-524.

Redman, A.D., Mihaich, E., Woodburn, K., Paquin, P., Powell, D., McGrath, J.A., Di Toro, D.M., 2012. Tissue-based risk assessment of cyclic volatile methyl siloxanes. Environmental Toxicology and Chemistry 31, 1911-1919.

Rodan, B.D., Pennington, D.W., Eckley, N., Boethling, R.S., 1999. Screening for persistent organic pollutants: techniques to provide a scientific basis for POPs criteria in international negotiations. Environmental Science & Technology 33, 3482-3488.

Sanchís, J., Martínez, E., Ginebreda, A., Farré, M., Barceló, D., 2013. Occurrence of linear and cyclic volatile methylsiloxanes in wastewater, surface water and sediments from Catalonia. Science of The Total Environment 443, 530-538.

Sanchez-Brunete, C., Miguel, E., Albero, B., Tadeo, J.L., 2010. Determination of cyclic and linear siloxanes in soil samples by ultrasonic-assisted extraction and gas chromatography-mass spectrometry. Journal of Chromatography A 1217, 7024-7030.

Shi, Y., Xu, S., Xu, L., Cai, Y., 2015. Distribution, elimination, and rearrangement of cyclic volatile methylsiloxanes in oil-contaminated soil of the Shengli oilfield, China. Environmental Science & Technology 49, 11527-11535.

Siddiqui, W.H., Stump, D.G., Plotzke, K.P., Holson, J.F., Meeks, R.G., 2007. A two-generation reproductive toxicity study of octamethylcyclotetrasiloxane (D4) in rats exposed by whole-body vapor inhalation. Reproductive Toxicology 23, 202-215.

Sparham, C., Van Egmond, R., O'Connor, S., Hastie, C., Whelan, M., Kanda, R., Franklin, O., 2008. Determination of decamethylcyclopentasiloxane in river water and final effluent by headspace gas chromatography/mass spectrometry. Journal of Chromatography A 1212, 124-129.

Statistics Korea, 2015. http://kosis.kr/statHtml/statHtml.do?orgId=101&tblId=DT_1KI1510&vw_cd=MT_ZTITLE&list_id=K2_KI_Y_2&seqNo=&lang_mode=ko&language=kor&obj_var_id=&itm_id=&conn_path=MT_ZTITLE. in Korean

Statistics Korea, 2017. http://kosis.kr/statisticsList/statisticsListIndex.do?menuId=M_01_01&vwcd=MT_ZTITLE&parmTabId=M_01_01#SelectStatsBoxDiv. in Korean

Tajdar-Oranj, B., Shariatifar, N., Alimohammadi, M., Peivasteh-Roudsari, L., Khaniki, G.J., Fakhri, Y., Mousavi Khaneghah, A., 2018. The concentration of heavy metals in noodle samples from Iran's market: probabilistic health risk assessment. Environmental Science and Pollution Research 25, 30928-30937.

Tran, T.M., Abualnaja, K.O., Asimakopoulos, A.G., Covaci, A., Gevao, B., Johnson-Restrepo, B., Kumosani, T.A., Malarvannan, G., Minh, T.B., Moon, H.-B., Nakata, H., Sinha, R.K., Kannan, K., 2015. A survey of cyclic and linear siloxanes in indoor dust and their implications for human exposures in twelve countries. Environment International 78, 39-44.

Wang, D.-G., Alaee, M., Steer, H., Tait, T., Williams, Z., Brimble, S., Svoboda, L., Barresi, E., DeJong, M., Schachtschneider, J., Kaminski, E., Norwood, W., Sverko, E., 2013a. Determination of cyclic volatile methylsiloxanes in water, sediment, soil, biota, and biosolid using large-volume injection–gas chromatography–mass spectrometry. Chemosphere 93, 741-748.

Wang, D.-G., de Solla, S.R., Lebeuf, M., Bisbicos, T., Barrett, G.C., Alaee, M., 2017. Determination of linear and cyclic volatile methylsiloxanes in blood of turtles, cormorants, and seals from Canada. Science of The Total Environment 574, 1254-1260.

Wang, D.-G., Norwood, W., Alaee, M., Byer, J.D., Brimble, S., 2013b. Review of recent advances in research on the toxicity, detection, occurrence and fate of cyclic volatile methyl siloxanes in the environment. Chemosphere 93, 711-725.

Wang, D.-G., Steer, H., Tait, T., Williams, Z., Pacepavicius, G., Young, T., Ng, T., Smyth, S.A., Kinsman, L., Alaee, M., 2013c. Concentrations of cyclic volatile methylsiloxanes in biosolid amended soil, influent, effluent, receiving water, and sediment of wastewater treatment plants in Canada. Chemosphere 93, 766-773.

Warner, N.A., Evenset, A., Christensen, G., Gabrielsen, G.W., Borgå, K., Leknes, H., 2010. Volatile siloxanes in the European arctic: Assessment of sources and spatial distribution. Environmental Science & Technology 44, 7705-7710.

Warner, N.A., Nøst, T.H., Andrade, H., Christensen, G., 2014. Allometric relationships to liver tissue concentrations of cyclic volatile methyl siloxanes in Atlantic cod. Environmental Pollution 190, 109-114.

Woodburn, K.B., Seston, R.M., Kim, J., Powell, D.E., 2018. Benthic invertebrate exposure and chronic toxicity risk analysis for cyclic volatile methylsiloxanes: Comparison of hazard quotient and probabilistic risk assessment approaches. Chemosphere 192, 337-347.

Xu, L., Shi, Y., Liu, N., Cai, Y., 2015. Methyl siloxanes in environmental matrices and human plasma/fat from both general industries and residential areas in China. Science of The Total Environment 505, 454-463.

Xu, S., Kropscott, B., 2012. Method for simultaneous determination of partition coefficients for cyclic volatile methylsiloxanes and dimethylsilanediol. Analytical Chemistry 84, 1948-1955.

Zhang, T., Sun, H., Lin, Y., Qin, X., Zhang, Y., Geng, X., Kannan, K., 2013. Distribution of poly- and perfluoroalkyl substances in matched samples from pregnant women and carbon chain length related maternal transfer. Environmental Science & Technology 47, 7974-7981.

Zhang, Y., Shen, M., Tian, Y., Zeng, G., 2018. Cyclic volatile methylsiloxanes in sediment, soil, and surface water from Dongting Lake, China. Journal of Soils and Sediments 18, 2063-2071.

Zhang, Z., Qi, H., Ren, N., Li, Y., Gao, D., Kannan, K., 2011. Survey of cyclic and linear siloxanes in sediment from the songhua river and in sewage sludge from wastewater treatment plants, northeastern China. Archives of Environmental Contamination and Toxicology 60, 204-211.

Zhi, L., Xu, L., He, X., Zhang, C., Cai, Y., 2018. Occurrence and profiles of methylsiloxanes and their hydrolysis product in aqueous matrices from the Daqing oilfield in China. Science of The Total Environment 631-632, 879-886.

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학위논문 심사위원으로 참여해주신 조경화 교수님과 이인석 박사님께도 감사드립니다. 조언해주신 내용을 반영하여 더 좋은 졸업 논문을 작성할 수 있었습니다.

2 년 동안 함께했던 EACL 연구실 분들께 감사드립니다. 논문 작성과 영어에 많은 조언해주신 김이선 박사님과 Thang 박사님. 아무것도 모르던 신입생 때부터 졸업할 때까지 많은 도움 주신 사수, 민규 오빠. 실험·과제에서 전체적인 방향과 방법을 알려주신 성준, 진우 오빠. 어려움이 있을 때마다 해결해주시는 손지민 선생님. 사소한 질문 하나하나 열심히 알려준 상진 오빠. 졸업하고 나서도 계속 도움 주는 현진이, 지영이. 언제나 친절하고 믿음직한 든든한 동기, 호영이, 대학원 생활 동안 행복한 추억 만들어준 혜경 언니. 졸업 논문 작성할 때 많은 도움을 준 인규. 고민도 들어주고 의지할 수 있었던 나라. 실험하면서 많이 도와준 혜지, 근우. 실험과 논문 작성에 도움 준 Nam, Quang. 자기 맡은 일 열심히 하는 Renato, Tien. 모든 분의 도움 덕분에 소중한 경험과 즐거운 추억을 얻을 수 있었습니다.

그리고 UCRF 환경분석센터 선생님께 감사드립니다. 실록산 실험에서 모든 부분을 조언해주신 이윤세 선생님, 실험 과정에서 도움 주신 김철수 선생님, 실록산 분석에 조언해주신 예진 선생님, 중금속 실험에 도움 주신 손희식 선생님 덕분에 실험을 잘 마칠 수 있었습니다.

마지막으로, 사랑하는 가족에게도 감사드립니다. 아낌없는 사랑과 응원 덕분에 석사 과정을 잘 마칠 수 있었습니다. 저를 항상 믿고 응원해주셔서 감사합니다.