



# An optimized method for the analysis of cyclic and linear siloxanes and their distribution in surface and core sediments from industrialized bays in Korea<sup>☆</sup>

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## ABSTRACT

Environmental contamination by siloxanes is a matter of concern due to their widespread consumption in personal care as well as industrial products and potential toxicity. Nevertheless, methods for simultaneous determination of cyclic and linear siloxanes in sediment are lacking. In this study, we developed an optimized analytical method to determine cyclic and linear siloxanes based on gas chromatography coupled to tandem mass spectrometry (GC-MS/MS). This method was applied to determine concentrations of 19 siloxane compounds in surface and core sediments from industrialized bays in Korea to assess contamination status, spatial distribution, and historical trends. Total concentrations of siloxanes ranged from 15.0 to 11730 (mean: 712) ng/g dry weight, which were similar to or higher than those reported in other countries. The highest concentrations of siloxanes were found in rivers/streams that discharge into coastal waters and bays close to industrial complexes, indicating that industrial activities are major sources of siloxane contamination. Cyclic siloxanes such as D5 and D6 were predominant in surface and core sediments. A significant correlation existed between the concentrations of cyclic and linear siloxanes, suggesting similar sources in the marine coastal environment. The historical record of cyclic siloxanes in core sediments revealed a clear increasing trend since the 1970s. This finding is consistent with the history of local industrialization and global production of siloxanes. This is the first study of historical trends in siloxanes in the coastal environment.

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## 1. Introduction

Siloxanes are polymeric organosilicon molecules composed of silicon linked to oxygen [Si-O], and form a cyclic or linear backbone structures. Siloxanes are widely used as intermediates in chemical production (silicone polymers) and personal care products (e.g., cosmetics, fragrances, deodorants, hair- and skin-care products, and nail polishes) because of their low surface tension, high thermal stability, smooth texture, and chemical inertness (Horii and

Kannan, 2008; Zhang et al., 2011; Wang et al., 2013a; Lee et al., 2014). Siloxanes have been commercially produced since the late 1940s, and consumption of products containing siloxanes has increased rapidly since the 1970s (Dudzina et al., 2014). In 2002, the total production of silicone was 2 million tons worldwide, of which 33% was consumed in western Europe, 34% in North America, and 28% in Asia (Brooke et al., 2009). Some cyclic siloxanes, such as octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6), are designated as high production volume chemicals by the United States Environmental Protection Agency (US EPA, 2002) and the Organization for Economic Cooperation and Development (OECD, 2009).

Previous studies have reported a long half-life in sediment for D4 (588 days at 25 °C) and D5 (3100 days at 25 °C) and a high

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bioconcentration factor for these two cyclic siloxanes (BCF >10,000) in fathead minnow (*Pimephales promelas*) (Fackler et al., 1995; Wang et al., 2013a). Relatively high vapor pressure and low water solubility of siloxanes cause high value of air/water partition coefficients (Wang et al., 2013a). Studies have shown reproductive effects of siloxanes in laboratory animals (Meeks et al., 2007; Siddiqui et al., 2007; Quinn et al., 2007; Lu et al., 2011; Zhang et al., 2011). Considering their environmental persistence, potential for bioaccumulation and toxicity, siloxanes are contaminants of emerging concern (Horii and Kannan, 2008; Zhang et al., 2011).

Although studies have documented the occurrence of siloxanes in various environmental compartments including air, water, sludge and sediment (Genualdi et al., 2011; Sparham et al., 2011; Zhang et al., 2011; Hong et al., 2014; Lee et al., 2014), analytical methods to accurately determine the concentrations of cyclic and linear siloxanes at low levels in environmental matrices have not been well established. Previous studies have shown that certain siloxanes are contaminants in laboratory air, solvents and components of instruments used in the analysis (Horii and Kannan, 2008; Kierkegaard et al., 2010; Sparham et al., 2011). Therefore, it is important to establish appropriate analytical methods with rigorous quality assurance and control (QA/QC) for accurate determination of cyclic and linear siloxanes in complex environmental matrices such as sediment.

Considering the persistence and hydrophobicity of siloxanes (Wang et al., 2013a), sediment is thought to be a major reservoir of these contaminants in coastal waters. Sediment cores can be used to evaluate the history of organic contaminants in aquatic environments (Moon et al., 2009). Few studies have examined the distribution of siloxanes in coastal sediments in China (Zhang et al., 2011; Hong et al., 2014). No earlier studies have reported historical records of siloxanes in the aquatic environment. In this study, we optimized an analytical method for simultaneous determination of cyclic and linear siloxanes in sediments based on four different methods. The optimized method was applied in the analysis of siloxanes in surface and core sediment samples from industrialized bays to assess the distribution, potential sources, and historical trends of siloxanes. This is the first historical record of cyclic and linear siloxanes in the aquatic environment.

## 2. Materials and methods

### 2.1. Standards and reagents

D4, D5, D6, octamethyltrisiloxane (L3), and L4 (all >97% purity) were purchased from Tokyo Chemical Industries America (Portland, OR, USA). PDMS (200 fluid, viscosity of 5cSt), which contains tetradecamethylcycloheptasiloxane (D7), and linear siloxanes (L6–L17) were purchased from Sigma-Aldrich. <sup>13</sup>C-labeled D4, D5, and D6, purchased from Moravek Biochemicals and Radiochemicals (Brea, CA, USA), were used as internal standards. Analytical-grade hexane (95% *n*-hexane), ethyl acetate, and dichloromethane (DCM) were obtained from J.T. Baker (Center Valley, PA, USA). Anhydrous sodium sulfate was purchased from GL Sciences (Tokyo, Japan). The composition of the PDMS mixture used in this study was identified and quantified by an Agilent 6890 gas chromatograph interfaced with a flame ionization detector (GC/FID; Agilent Technologies, Wilmington, DE, USA) (Horii and Kannan, 2008) and was used as a standard for the identification of D7 and other linear siloxanes.

### 2.2. Sample collection

Ulsan and Onsan Bays, located in southeastern coast of Korea, are the most heavily industrialized regions with the largest

commercial harbors (Fig. 1). Industries in those regions produce petrochemical products, automobiles, machines, non-ferrous metals, and ships (Moon et al., 2008). Earlier studies have shown that these coastal regions are highly contaminated by persistent organic pollutants (POPs) such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) (Moon et al., 2007, 2008).

Surface sediment samples (0–4 cm depth) were systematically collected at 42 locations in November 2014 from the inner to the outer parts of the bays: Ulsan Bay (U1–U18), Onsan Bay (O1–O8), Taehwa River (T1–T7), Woihwang River (W1–W4), and Gosa Stream (G1–G5). Surface sediments were sampled using a box-corer deployed from a research vessel. The collected samples were individually wrapped in an aluminum foil and then transported to the laboratory and frozen at –20 °C until further analysis. Sediment core was collected by SCUBA divers using acryl tubing (length 80 cm, internal diameter 11 cm) in July 2015. The collected sediment core was immediately sliced at 2–5 cm intervals using stainless steel plates, and the sectioned core samples were wrapped in aluminum foil and transported to the laboratory. Samples were stored in a –20 °C freezer until further processing.

### 2.3. Sample preparation

Sediment samples were freeze-dried and homogenized. Sediment (~5 g) was placed into 50-mL polypropylene (PP) tubes and spiked with 1 µg of <sup>13</sup>C-labeled D4, D5, and D6 as internal standards. Samples were extracted by shaking in an orbital shaker at 250 rpm for 60 min with 10 mL hexane, followed by 10 mL of hexane:DCM (1:1) and hexane:ethyl acetate (1:1). The extract was centrifuged at 4000 rpm for 20 min, and the supernatant was transferred into a 15 mL PP tube. All extracts were combined and concentrated to 1 mL under a gentle nitrogen stream for instrumental analysis.

Sep-Pak<sup>®</sup> PS2 solid phase extraction (SPE) cartridges (3 mL/300 mg, 80 µm; Milford, MA, USA) were conditioned with 25 mL of hexane, and then the sediment extract (1 mL) was eluted with 9 mL hexane and concentrated to 1 mL for instrumental analysis.

### 2.4. Instrumental analyses

Concentrations of 4 cyclic (D4–D7) and 15 linear (L4–L17) siloxanes in sediment were determined with two instruments: a gas chromatograph/mass spectrometer (GC/MS; Agilent 7890/5975C, Wilmington, DE, USA) and a gas chromatograph/tandem mass spectrometer (GC-MS/MS; Agilent 7890/7000C). For GC/MS and GC/MS/MS, the same GC operating conditions were used with a DB-5MS capillary column (30 m length, 0.25 mm inner diameter, 0.25 µm film thickness; J&W Scientific, Palo Alto, CA, USA) (Lee et al., 2014). The carrier gas was helium at a constant flow rate of 1 mL/min. Oven temperature was programmed to increase from 40 °C (2 min) to 220 °C at a rate of 20 °C/min and to 280 °C at a rate of 5 °C/min. This latter temperature was held for 10 min followed by 5 min at 300 °C. The MS was operated in electron impact ionization (EI) mode at 70 eV. D4, D5, and D6 were quantified using the internal standard method, while D7 and linear siloxanes (L4–L17) were quantified using an external standard method.

### 2.5. Sediment characteristics and dating

Specific activities of <sup>210</sup>Pb and <sup>226</sup>Ra in sediment core were measured to determine the sedimentation rate (Kim and Burnett, 1983). Sectioned sediments were dried and sieved through a 2-mm mesh. Three grams of sediment were transferred into a

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