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A nationwide survey and emission estimates of cyclic and linear siloxanes through sludge from wastewater treatment plants in Korea

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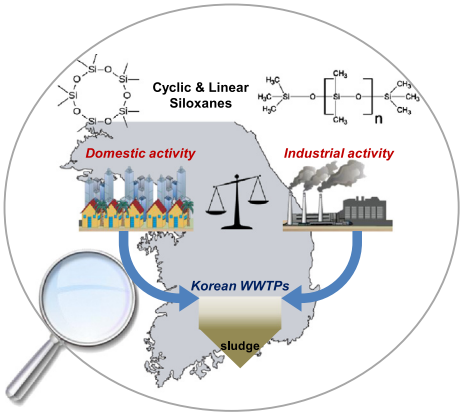
HIGHLIGHTS

- Highest levels of siloxanes were found in domestic WWTP sludge from Korea.
- Compositional profiles of siloxanes varied domestic and industrial WWTP sludge.
- The nationwide emission flux of siloxanes via sludge discharge was estimated.
- Population-served is a determinant of siloxanes in sludge from WWTPs.

GRAPHICAL ABSTRACT



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ABSTRACT

Siloxanes are widely used in various industrial applications as well as in personal care products. Despite their widespread use and potential toxic effects, few studies have reported on the occurrence of siloxanes in the environment. In this study, we determined the concentrations of 5 cyclic and 15 linear siloxanes in sludge collected from 40 representative wastewater treatment plants (WWTPs) in Korea. Total concentrations of 20 siloxanes (Σsiloxane) in sludge ranged from 0.05 to 142 (mean: 45.7) μg/g dry weight, similar to the concentrations reported in European countries but higher than those reported in China. The concentrations of siloxanes in sludge from domestic WWTPs were significantly ($p < 0.01$) higher than those from industrial WWTPs, indicating higher consumption of siloxanes in various personal care products (e.g. shampoos and conditioners). The major siloxane compounds found in sludge were decamethylcyclopentasilane (D5), docosamethyldecasiloxane (L10) and dodecamethylcyclohexasilane (D6), which collectively accounted for, on average, 62% of the Σsiloxane concentrations. Non-parametric multidimensional scaling ordination of the profiles of siloxanes indicated the existence of different usage patterns of siloxanes between industrial and household activities. Multiple linear regression analysis of siloxane concentrations and WWTP characteristics suggested that D5, D6 and linear siloxane

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concentrations in sludge were positively correlated with population served by a WWTP. Environmental emission fluxes of cyclic and linear siloxanes through sludge disposal in Korea were 14,800 and 18,500 kg/year, respectively. This is the first report describing occurrence and environmental emission of siloxanes through sludge in Korea.

1. Introduction

Siloxanes are polymeric organosilicon molecules that have alternating silicon–oxygen [Si–O] backbones with each silicon atom attached to one or more organic groups. Organosiloxanes, comprising both cyclic and linear siloxanes (such as polydimethylsiloxane, or PDMS), are widely used in consumer products such as electronics, furniture, cookware, healthcare products and cosmetics, for their unique characteristics such as low surface tension, high thermal stability, smooth texture and chemical inertness (Horii and Kannan, 2008; Wang et al., 2009; Lu et al., 2011). The total worldwide production of silicones was two million tons in 2002, of which 33% was used in Western Europe, 34% in North America, and 28% in Asia (Brooke et al., 2009). China was the largest manufacturer and occupied 40% of the global production for organosiloxanes in the world in 2009 (CRCSI, 2010). Three widely used cyclic siloxanes are octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasilane (D6) (Wang et al., 2013).

Some cyclic siloxanes have been reported to elicit endocrine disruption potentials, adverse immunologic responses, and liver and lung damage in laboratory animals (Lassen et al., 2005). Oral exposure of mice to D4 was associated with estrogenic activity mediated through estrogen receptor-α (He et al., 2003). LC_{50} value in *Hyalella azteca* exposed for 28 days (chronic) through D5-spiked sediment (0.5% organic carbon) was 191 μg/g dry weight (Norwood et al., 2013). Based on toxicological evidences and its persistence in the environment, D4 was regulated in the United States (US), Canada, and European countries (Brooke et al., 2009; CEPA, 2012; US EPA, 2013). However, limited studies on the occurrence of cyclic and linear siloxanes are available in environmental compartments such as air (Genualdi et al., 2011; Kierkegaard and McLachlan, 2013), water (Wang et al., 2013), sediment (Zhang et al., 2011), sludge (Zhang et al., 2011; Bletsou et al., 2013; Xu et al., 2013; Liu et al., 2014) and biota (Kierkegaard et al., 2013).

Sewage sludge is an excellent medium for monitoring usage patterns of hydrophobic chemicals in domestic and industrial settings (Lee et al., 2014). On the basis of a mass balance study in wastewater treatment plants (WWTPs), 68% of siloxanes were shown absorbed onto sludge (Bletsou et al., 2013). High levels (on the order of μg/g) of siloxanes were reported in sludge from WWTPs in Greece (Bletsou et al., 2013) and China (Zhang et al., 2011). There are approximately 500 WWTPs in Korea, which treat over 25 million tons of wastes on a daily basis (MoE, 2012). In 2001, 3.0 million tons of sludge were produced by WWTPs in Korea, which were discharged or treated via ocean dumping (33%), recycling (26%), incineration (22%), landfilling (8.4%) and fuelization (7.2%) (MoE, 2012). There have been no reports regarding the occurrence and environmental emission of siloxanes in sludge from WWTPs in Korea.

In this study, we described the occurrence, concentrations, and compositional profiles of 5 cyclic and 15 linear siloxanes in sludge from three types of Korean WWTPs (domestic, mixed, and industrial). Environmental emission fluxes of siloxanes were calculated based on measured concentrations of siloxanes and the production rate of sludge. In addition, the factors that affect concentrations of siloxanes in sludge were investigated using multiple linear regression analyses of WWTP characteristics, such as treatment capacity and population-served.

2. Materials and methods

2.1. Standards and reagents

Hexamethylcyclotrisiloxane (D3), D4, D5, and D6 (all > 95% purity) were purchased from Tokyo Chemical Industries America (Portland, OR, USA). Octamethyltrisiloxane (L3) (98%), decamethyltetrasiloxane (L4) (97%) and dodecamethylpentasiloxane (L5) (97%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). PDMS (200 fluid, viscosity of 5cSt), which contains tetradecamethylcycloheptasilane (D7), and linear siloxanes (L6–L17) was purchased from Sigma-Aldrich. $^{13}C_5$-D5, purchased from Moravek Biochemicals and Radiochemicals (Brea, CA, USA) was used as a surrogate standard. Analytical grade hexane (95% *n*-hexane), ethyl acetate, dichloromethane (DCM), and sodium sulfate anhydrous were obtained from J.T. Baker (Center Valley, PA, USA). The composition of the PDMS mixture used in this study was identified and quantified by an Agilent 6890 gas chromatograph with a flame ionization detector (GC/FID; Agilent Technologies, Wilmington, DE, USA) and was used as a standard for the identification of linear siloxanes (L6–L17) and D7. Details of the composition of this PDMS mixture were described in our previous study (Horii and Kannan, 2008).

2.2. Sample collection

Detailed information regarding sample collection is available elsewhere (Lee et al., 2014). In brief, on the basis of locations (four cities and seven provinces), watershed (four rivers and three seas), wastewater treatment capacity (WTC: 1048–957,782 m^3/day), and population-served (IE: 128–3,622,800), a representative sample of 40 WWTPs were selected. Forty sludge samples were collected from WWTPs during July–October 2011. To obtain a representative sample from each WWTP, the grab dewatered sludge samples were taken in three consecutive days for each sampling campaign and were then homogenized by shaking. All samples were collected in pre-cleaned polypropylene (PP) bottles, transported to the laboratory, and stored in a freezer at −20 °C until extraction. Based on the proportion of industrial wastewater received, the WWTPs were categorized as domestic (D-WWTPs; 0–3% industrial), mixed (M-WWTPs; 20–60% industrial), and industrial (I-WWTPs; >70% industrial). The WWTP characteristics such as influent sources, WTC, IE, annual sludge production (ASP), and hydraulic retention time (HRT) are provided in Table S1 (Supporting information).

2.3. Sample preparation

Sludge samples were freeze-dried and mixed thoroughly. Analyses of siloxanes in sludge were performed by the methods described elsewhere (Horii and Kannan, 2008; Bletsou et al., 2013), with minor modifications. Briefly, approximately 0.5 g of sludge was weighed and transferred into 50 mL PP tubes. Then, 1 μg of $^{13}C_5$-D5 was spiked and allowed to equilibrate for 30 min at −4 °C. Sludge was extracted by shaking in an orbital shaker (Eberbach, Ann Arbor, MI) at 250 oscillations/min, for 60 min with 10 mL hexane followed by 10 mL hexane: DCM (1:1) and then with 10 mL hexane:ethyl acetate (1:1). After each extraction, the mixture was centrifuged at 5000 *g* for 5 min (Eppendorf Centrifuge 5804, Hamburg, Germany), and the supernatant was transferred into a glass tube. All extracts were combined and concentrated to 1 mL under a gentle nitrogen stream for instrumental analyses.

The moisture content in each sludge sample was determined based on their weights taken before and after freeze-drying. Total organic carbon (TOC) was also measured in sludge using an Elemental Analyzer (Flash 2000 series, Thermo Scientific Co., MA, USA) after removal of inorganic carbon with 1 N HCl.

2.4. Instrumental analysis

The concentrations of 5 cyclic (D3–D7) and 15 linear (L3–L17) siloxanes in sample extracts were determined by an Agilent 7890 gas