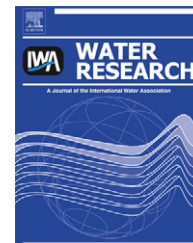


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# Occurrence and fate of volatile siloxanes in a municipal Wastewater Treatment Plant of Beijing, China

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## ABSTRACT

The occurrence and fate of four cyclic and two linear volatile siloxanes were studied in a municipal Wastewater Treatment Plant (WWTP), Beijing City, China. Aqueous and sludge samples were analyzed by solid-phase microextraction (SPME) coupled with gas chromatography–mass spectrometry (GC–MS). In the studied WWTP, four cyclic analogs (D3–D6) had significantly higher concentrations and frequencies than the two linear analogs [Octamethyltrisiloxane (L3) and Decamethyltetrasiloxane (L4)], with inputs into the WWTP ranging from 78.2 to 387.7 kg/year. Removal efficiencies of volatile cyclic siloxanes in two parallel secondary treatment processes ranged from 59.3 to 92.7%. For volatile cyclic siloxanes, relative fractions of mass loss by adsorption to sludge ranged from 8.3 to 53.0%, and their adsorption capacities were significantly affected by the dissolved organic matter. Besides adsorption, they were eliminated mainly in anaerobic units (44.4–84.3%). Through *in vitro* biodegradation experiments, we concluded that in the anaerobic compartments, Hexamethylcyclotrisiloxane (D3) and Dodecamethylcyclohexasiloxane (D6) were eliminated mostly by volatilization, while Octamethylcyclotetrasiloxane (D4) and Decamethylcyclopentasiloxane (D5) may be eliminated by both volatilization and degradation. Furthermore, microbe catalysis hydrolysis was identified as one of the main degradation pathways for D4 and D5 in anaerobic compartments.

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## 1. Introduction

Siloxanes, a subgroup of silicones, consist of Si–O bonds with aliphatic chains (mostly methyl groups) attached to Si atoms. Due to their low surface tension, high thermal stability and lubricating properties, siloxanes have been widely used for decades in industrial processes and consumer products such as cosmetics and health care products (SEHSC, 2011; Kannan, 2008). It was reported that the annual import/production volumes in the USA were 45–226 million kilograms for Octamethylcyclotetrasiloxane (D4) or Decamethylcyclopentasiloxane (D5) and 4.5–22.6 million kilograms for Dodecamethyl-

cyclohexasiloxane (D6) (EPA, 2002). China is leading the world in cyclic siloxane production capacity, with an annual production of about 800 million kilograms (CNKI, 2009). Because the siloxane are produced in large quantities and used ubiquitously in consumer products, it is likely that they will enter into the environment. Because of their stability, siloxane residues may be persistent in the environment, and have the potential to bioaccumulate in organisms (Flassbeck et al., 2001; Kala et al., 1997). There have been studies reporting direct or indirect toxic effects of volatile siloxanes on both aquatic and terrestrial life. In an *in vitro* study, exposure to D4 via injection in mice caused fatal liver and lung damage

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(Liebierman et al., 1999). Other reports indicated that oral exposure to D4 caused estrogenic effects on rats, and inhalation of D5 caused adverse effects on the nervous system of rats (He et al., 2003; OEHHA, 2007). Also, the European Union suggested that D4 interfered with human hormone function and might impair human fertility (EC, 2009).

One of the most significant pollution sources of volatile siloxanes is the emission from cosmetics, personal care and household products used by the general public. Approximately, 10% of them enter into domestic wastewater (EA, 2009a,b,c). The first step of removing volatile siloxane residues from domestic wastewater takes place at the WWTPs. It is therefore important to characterize the occurrence and fate of volatile siloxanes during the wastewater treatment processes. However, systematic investigations of their migration and removal mechanism are scarce. In one study, the removal behavior of D4 and D5 was analyzed by continuously dosing the influent with exaggerated amounts of these two compounds in a pilot-scale plant (Parker et al., 1999). However, because dosed compounds in the influent were inhomogeneous and did not reach equilibrium between the aqueous and solid phases, the mass balances of D4 and D5 were poor. In another study, the mass flow and removal efficiency of D5 in a sewage plant were reported, but the mass balance was neglected (Kazuyuki et al., 2007). In both studies, investigations of the volatile siloxane behavior were performed in a conventional activated sludge process. To the best of our knowledge, there is no report of the volatile siloxane behavior in the anaerobic–anoxic–oxic (traditional A<sup>2</sup>/O) process or anoxic–anaerobic–oxic (reversed A<sup>2</sup>/O) process, both of which were extensively utilized in municipal WWTPs.

In terms of sample matrices, residual levels of volatile cyclic and linear siloxanes have been analyzed in environmental matrices including air, soil, sludge, sediment, and biota. The analytical methods involved include solid phase extraction and organic solvent extraction/gas chromatography–mass spectrometry (GC–MS) and gas chromatography–atomic emission detection (GC–AED) (Warner et al., 2010; Sanchez-Brunete et al., 2010; Boehmer and Gerhards, 2003). Currently, there are only a few analytical methods of volatile siloxanes in aqueous samples, including gas stripping process (Huppmann et al., 1996), purge and trap GC–MS procedure (Kaj et al., 2005), and headspace gas chromatography with mass spectrometry (Sparham et al., 2008). Solid-phase microextraction (SPME) is a simple, economical, solvent-free, and reliable method for the simultaneous determination of volatile organic compounds from aqueous samples (Stiles et al., 2008; Pazarro et al., 2010; Negreira et al., 2010; Dong et al., 2005). In this paper, SPME coupled with GC–MS is used to determine four cyclic and two linear volatile siloxanes in aqueous and sludge samples from a WWTP. Using the developed method, we report the determination of volatile siloxane concentrations in aqueous and sludge samples from different treatment units, and study their degradation characteristics *in vitro*. Finally, we carry out systematic analysis of the occurrence and migration of volatile siloxanes in secondary treatment processes of one WWTP in Beijing City of China.

## 2. Materials and methods

### 2.1. Sampling collection

The studied WWTP locates in the north of Beijing City, China, and has a capacity of 400,000 m<sup>3</sup>/d domestic wastewater. The catchment area of the WWTP covers about 159.42 km<sup>2</sup>, with a population of 810,000. In the WWTP, primary treatments, including bar screens and grit chamber, are followed by two parallel secondary treatment processes including traditional A<sup>2</sup>/O and reversed A<sup>2</sup>/O, each having a capacity of 200,000 m<sup>3</sup>/d domestic wastewater.

In the traditional A<sup>2</sup>/O process, the hydraulic retention times in the anaerobic, anoxic and oxic tanks were 1.5, 3 and 10.8 h, respectively. After settling in the secondary clarifier, part of the activated sludge was returned to the anaerobic tank, and the rest was conveyed to be dehydrated. The total solid retention time was 20–25 d. While in the reversed A<sup>2</sup>/O process, the hydraulic retention times in anoxic, anaerobic and oxic tank were 1.5, 2.5 and 10.0 h, respectively. The total solid retention time was 6–7 d.

Two sampling events were carried out at the primary effluent (W1), secondary effluent (W5a and W5b), and outflows of different treatment processes in January and April, 2011 (Fig. 1). Using the methods described in a previous study (Guedez and Püttmann, 2011), 24 h composite samples were collected in a flow proportional mode. At equal time increments (2 h), samples were collected and composited with volume proportionally to the flow rate at the time of each sampling. Both composite aqueous and sludge–liquid samples were collected into 4 L glass bottles. Sludge–liquid samples from two secondary treatment processes were centrifuged at 3500 rpm for 10 min. The solid layer was collected as the sludge sample, and the liquid layer as the aqueous sample. Due to the ubiquity of siloxanes in the environment and in many consumer products, precautions were taken during sample collection. First, laboratory personnel participating in this study were forbidden to use any cosmetic products including hair mousses, styling gels, nail polishes, moisturizers, creams, lotions, etc. Second, no sampling or storage device during field collection was made of silica gel, and all devices were cleaned by chromatography-grade methanol. Third, field blank samples (*n* = 8) were prepared to assess ambient contamination during two samples events. Samples were stored at 4 °C using sealed containers with no headspace until sample pretreatment, which occurred within 48 h of the sample collection.

### 2.2. Sampling preparation

Reagents and materials used in our study were shown in the [Supplementary material](#). M4Q has been widely used as an internal standard for analyzing both cyclic and linear siloxanes in various environmental matrices (Kannan, 2008; Sanchez-Brunete et al., 2010) because it is similar in chemical composition with siloxanes, hardly detectable in environment matrices and not interfering with siloxanes in the analysis.

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