MASS LOADING AND FATE OF VOLATILE METHYL SILOXANES IN TWO DIFFERENT TYPES OF SEWAGE TREATMENT PLANTS FROM JAPAN

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Introduction

The determination of siloxanes includes cyclic and linear volatile methylsiloxanes (VMS) in environment is important for the evaluation of human and environmental risks. VMS have been widely used in consumer products [1] because VMS have low surface tension, high thermal and chemical stabilities, and believed to be inert. However, a part of VMS is recently identified as priority chemicals for environmental risk assessment due to their persistence in the environment and bioaccumulative potency [2]. Analysis of VMS in environment is very challenging due to their high volatility and potential sources of background contamination. Limited information is available on the concentration, distribution, and fate of VMS in water environment. Sewage treatment plants (STPs) are a potential of point source of VMS in the water environment, because personal care products and cosmetics are the important market for VMS directly used in the products. In this study, concentrations of cyclic and linear VMS in aqueous, gaseous, and solid matrices at various stages of treatment in two STPs from Saitama, Japan. We calculated mass flows and removal efficiencies of VMS in the two different treatment types of STPs. A developed purge and trap (PT) -solvent elution method was used for water extraction and clean-up of extracts from sludge samples. To our best knowledge, this is the first study to report individual concentrations of VMS in STPs from Japan.

Materials and methods

Samples. Grab samples were collected during July to October, 2013. STP1 serves a population of 322,703 and receives 133,710 m^3 of sewage per day. STP2 serves a population of 15,334 and revieves 3,985 m^3 of sewage per day. These two STPs treat primarily domestic and commercial wastewaters, and STP1 and 2 employ a conventional activated sludge treatment process and oxidation ditch treatment process, respectively. In STP1, influent, primary effluent, mixed liquor, secondary settling tank water, final effluent, dewatered sludge, and aeration gas were collected. In STP2, influent, mixed liquor, secondary settling tank water, final effluent, dewatered sludge, and aeration gas were collected. Because STP1 aeration gas is treated with activated carbon by deodorization facility, aeration gas collected both before and after deodorization was analyzed for this STP. Thirty litters of aeration gas was collected using a low-volume air sampler attached with SPE cartridge (Sep-Pak plus PS-2, Waters), at the flow rate of 0.5 L/min. Wastewater samples were collected in clean 600-mL screw top glass bottles without headspace to prevent evaporation of the target chemicals. All samples were stored in cooler boxes immediately after the sampling and transported to the laboratory, then kept at 4°C for wastewater samples and -20°C for solid samples. For water analysis, samples were extracted within 4 days after the collection.

Chemical analysis. Analytical procedure for the extraction of wastewater samples was similar to a previous report [3]. Firstly, 600 mL of water was gently transferred into a 1-L glass gas washing bottle and 100 ng of ^{13}C-labeled octamethylcyclotetrasiloxane (D4), decamethylcyclohexasiloxane (D5), dodecamethylcyclohexasiloxane (D6) in acetone was added into the sample as an internal standard. The wastewater sample was purged for 120 min at the flow rate of 1 L/min using a vacuum pump with assistance of ultrasonic vibration at 50°C. A SPE cartridge (Sep-Pak plus PS-2) as a gas trap was mounted on the outlet of the gas washing bottle. After purging the samples, the SPE cartridge was dried by purging pure nitrogen gas for 20 min, then target chemicals were eluted with 1.5 mL of dichloromethane directly into a GC vial. Aliquots of sludge samples (0.2 g wet weight) were taken in polypropylene tubes, then 200 ng of the internal standard was added. The samples were shaken with 4 mL of *n*-hexane/acetonitrile mixture (1:1) for 30 min and treated in ultrasonic water bath for 10 min, then centrifuged at 3000 rpm for 10 min. The *n*-hexane layer was transferred into a glass test tube. Another 2 mL of *n*-hexane was added into the polypropylene tube and the samples were reextracted two times as above (6 mL in total). To remove non-volatile fraction such as colored comportment and mineral oil in the extract, a PT extraction technique used for water extraction was applied for cleaning-up of the extracts of solid samples.

Conditions of PT clean-up were slightly changed from those of water. About 300 mL of ultrapure water and 30 g of sodium chloride were added into a 1-L glass gas washing bottle and the whole *n*-hexane extract was transferred into it. Purge time was set to be 60 min at the flow rate of 1 L/min. Seven individual VMS were measured in this study; they included hexamethylcyclotrisiloxane (D3), D4, D5, D6 for cyclic VMS and octamethylsiloxane (L3), decamethyltetrasiloxane (L4), dodecamethylpentasiloxane (L5) for linear VMS. Quantification of VMS was performed on a GC/MS (Thermoscientific, Trace GC ultra, ISQ). The GC/MS conditions were slightly modified from previous study [1].

QA/QC. Because methylsiloxanes are present in many consumer products, the analyst took care not use hand lotions or other possible sources of contamination before or during the analysis. The presence of VMS in laboratory products and reagents, GC parts, and also ambient air, are the major difficulty in the analysis of VMS. To reduce contamination, blank levels of VMS for all products and reagents used were tested. We selected silicone free or low bleed materials to achieve high precision analysis of VMS in water samples. Procedural blanks were analyzed with the samples to check for contamination arising from reagents and lab materials. Travel blanks were prepared for each sampling day. A standard mixture of VMS (100 ng each) was added into water samples was passed through the above described analytical procedure for water and solid samples. The mean recoveries of VMS were 83±7.6% for water (n=6), 89±12% for solid samples (n=3). Recoveries of internal standards in the samples were 90±3.2% for water, 96±7% for sediment, and 90±7.2% for fish. Method detection limit (MDL) and method quantification limit (MQL) values for VMS were calculated from variance associated with replicate analysis (n=5). MDL and MQL were set to be 3 times and 10 times of the standard deviation (SD), respectively, from replicate analysis in trace level of VMS, divided by sample volume (or weight) and multiplied the injection volume. MDL for individual VMS ranged from 0.6 ng/L (L3, L4) to 3.4 ng/L (D6) for water and 2 ng/g ww (L3-L5) to 43 ng/g ww (D3) for sludge. For statistical analysis, below MDL values were assigned to be a half of the MDL.

Results and discussion

STPs employ a variety of treatment processes, the concentrations and fate of VMS will vary. Concentrations of total VMS in two different types of STPs were shown in Table 1. The concentration in the water samples widely varied from 420 ng/L to 49,000 ng/L in STP1 and 200 ng/L to 61,000 ng/L in STP2. The highest concentration was found in the mixed liquor taken from reaction tank both in STP1 and 2, because VMS have strong adsorption to organic carbon and low water solubility. Concentrations of VMS in influent from both STPs were 15-40 times higher than those in effluent. Distribution of VMS was similar in both STPs. D5 account for >80% in total was the predominant compound in all samples analyzed, followed by D6 or D4. D4 compositions in aeration gas (11-13%) were two times higher than those in effluent (5-6%) and sludge (2-4%), whereas D6 distribution in aeration gas (3-4%) was found to be lower than effluent and sludge, depending on their physical-chemical property. Compositions of linear VMS were observed at <1% in total VMS. VMS compositions found in influent were quite similar to those in personal care products such as shampoo, hair conditioner, and cosmetics, reported by Horii et al. 2008[1]. The concentrations of D5 in effluent determined in this study were in the range of previous reports from Canada[4] and Nordic countries[5], but were slightly lower than those from Greece [6], with the concentration of 1,790 ng/L.

Table 1. Concentrations of VMS in wastewater, sludge, and aeration gas samples from two different types of STPs

Compound	Influent (ng/L)		Mixed liquor (ng/L)		Final effluent (ng/L)		Aeration gas (ng/m^3)		Dewatered sludge (ng/g ww)	
	STP1	STP2	STP1	STP2	STP1	STP2	STP1	STP2	STP1	STP2
D3	<24	25	<24	<24	14	17	380	2300	69	<43
D4	420	420	1900	1500	18	17	28000	67000	560	220
D5	8100	12000	44000	55000	360	280	170000	540000	15000	16000
D6	620	1300	2600	3500	21	14	8400	17000	1200	1100
L3	<7	<7	10	13	<0.6	<0.6	170	530	2.6	1.6
L4	55	20	66	42	<0.6	<0.6	240	420	34	21
L5	100	86	290	280	2.5	1.3	610	2100	120	100
Total	9300	14000	49000	61000	420	330	210000	630000	17000	18000

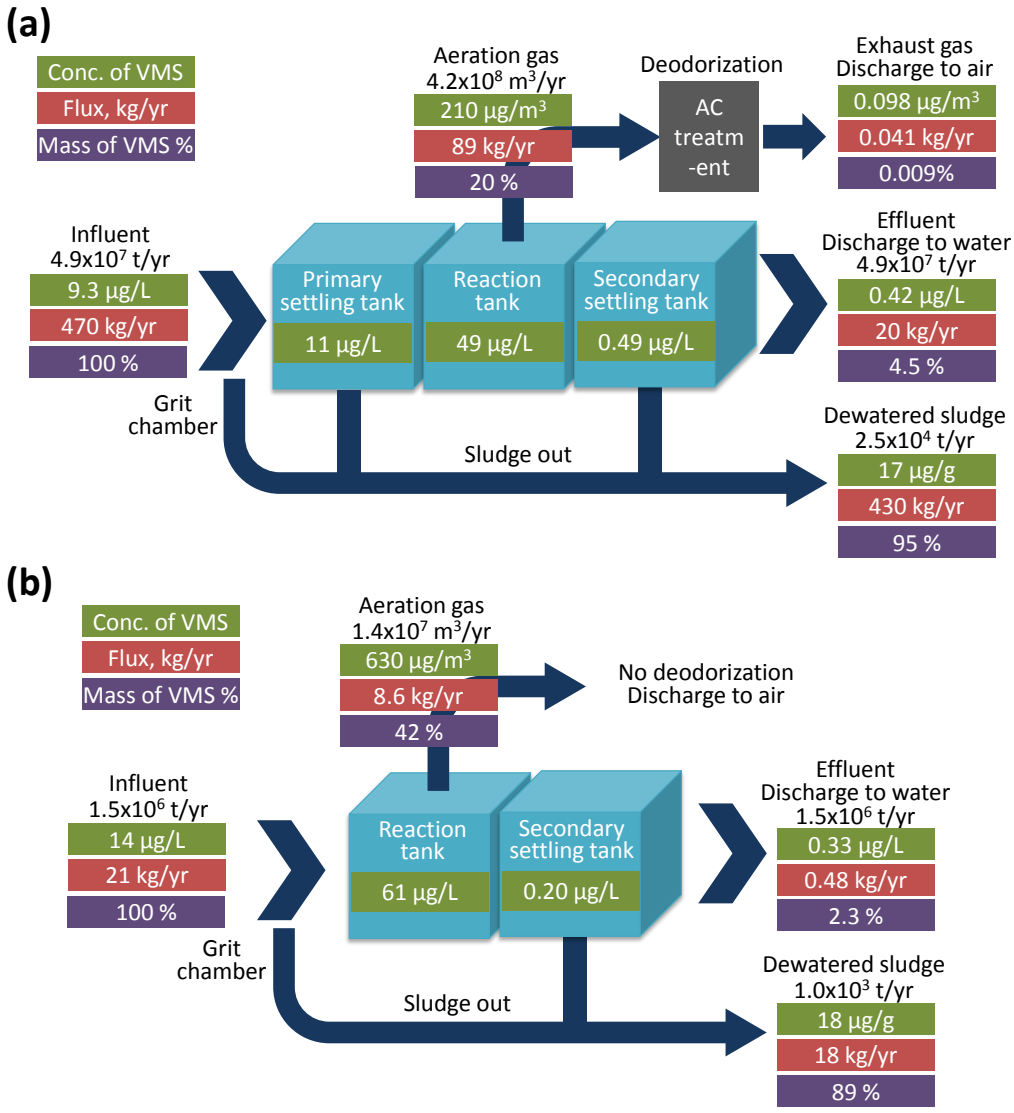

Fig. 1. Concentrations, fluxes, and mass% of VMS in two different types of STPs. (a) STP1; conventional activated aludge treatment process, (b) STP2; oxidation ditch treatment process.

Mass loadings were calculated based on the concentrations of VMS with the annual flow of sewage and solid waste produced at the STPs (Fig. 1). The annual inflow of VMS calculated for D4, D5, D6, and total VMS was 27 kg, 526 kg, 38 kg, and 598 kg for STP1, and it was 0.6 kg, 18 kg, 1.8 kg, and 21 kg for STP2. The outflow through effluent discharge into rivers for D4, D5, D6, and total VMS was 1.4 kg, 32 kg, 3.1 kg, and 39 kg for STP1, and it was 0.025 kg, 0.41 kg, 0.020 kg, and 0.48 kg for STP2. Based on the estimated mass loading, the removal efficiencies of total VMS in STP1 and 2 can be calculated to 96% and 98%, respectively. The removal efficiencies of VMS were similar to those reported in other STPs which employ activated sludge treatment process[4,5]. The removal efficiencies in our study includes partitioning and removal through settling to sludge and aeration gas at reaction tank. Adsorption to sludge and volatilization were main mechanisms of reduction of VMS in STPs, because of the high vapor pressures and partitioning coefficient to organic carbon (Koc) of VMS [7]. Reduction amount of total VMS in sludge for STP1 and 2 was 430 kg/yr (95% in inflow) and 18 kg/yr (89%), respectively (Fig.1). Volatilization of total VMS was calculated to be 89 kg/yr (20%) and 8.6 kg/yr (42%).

Outflow through aeration gas discharge into atmosphere for total VMS was 0.041 kg/yr (0.009%) in STP1 and 8.6 kg/yr (42%) in STP2 because of aeration gas was passed through deodorization facility in STP1 which employ activated carbon treatment process; this can remove almost 100% of VMS from aeration gas. The discharge amount of VMS in STP2 was about 200 times greater than that in STP1, although receiving sewage volume in STP1 is 30 times higher than that in STP2. It indicates that deodorization facility in STP can be the key of reduction for VMS discharge into atmosphere.

We found a mass gain of 139 kg/yr (31%) for total VMS in STP1 and 2.9 kg/yr (14%) in STP2. Previous study reported that a distinct diurnal variation of VMS flux in raw sewage, probably linked with the use of personal care products[8]. In additional investigation, we also found diurnal variation in VMS flux; the VMS fluxes during day time were found to be two times higher than those in night time. Mass balance calculation obtained here is based on the concentration from one time grab sampling carried out in day time. Diurnal variation in VMS flux can be the reason for mass gain of VMS observed in the STPs. Specific sampling method (grab or composite) and sampling time can influence the concentrations of VMS in STPs. The result presented here are for grab samples collected at snapshots from each stage.

Mass loading of D5 in STP1 and 2 was calculated to be 3.4 and 3.2 mg/capita/day, respectively. The UK Environment Agency risk assessment reported mass loading to waste water was predicted at 11.6 mg/capita/day for D5[7]. The emissions to the environment through the use of personal care products by the general public were taken to be 90% to air and 10% to sewage system. Measured mass loadings of D5 found in this study are similar to those in large scale UK STP (2.7 mg/capita/day) [8], but are slightly lower than the predicted value. The concentrations of VMS in sludge were on the order of several tens parts per million, and settling of VMS to sludge was the major removal mechanism in the STPs. It is recognized that incineration of sludge to the atmosphere or disposal of sludge to the terrestrial environment through landfill and/or agricultural application can contribute to environmental release of VMS. STP effluent can reflect to concentration profiles of VMS in the water environment.

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