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ANNUAL PROFILES OF VOLATILE METHYLSILOXANES IN ATMOSPHERIC ENVIRONMENT IN SAITAMA, JAPAN

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Introduction

The determination of methylsiloxanes includes cyclic and linear volatile methylsiloxanes (VMSs) in environment is important for the evaluation of human and environmental risks. VMS have been widely used in consumer products ¹ because VMSs have low surface tension, high thermal and chemical stabilities, and believed to be inert. However, a part of VMSs have recently been identified as priority chemicals for environmental risk assessment due to their persistence in the environment and bioaccumulative potency ². Based on the available scientific information, ECHA has reported that D4 meets the criteria of REACH for “persistent, bioaccumulative and toxic (PBT)” and D4 is a substance with worldwide dispersive uses and is detected in the environment. The European Commission therefore is seeking to submit a proposal for the listing of D4 to the Stockholm Convention on Persistent Organic Pollutants (POPs) ³. Japan is a major consumer of siloxanes, with an annual silicone consumption at 117000 tons in 2009; approximately 15% of the production was used in personal-care and life style products. VMSs are high production volume chemicals and have been reported to occur in a wide range of environmental samples including atmosphere, sediment, fish, surface water, and polar region. A major proportion of existing VMSs ends up in the atmosphere because VMSs possess high volatility (4.6–132 Pa at 25°C) and hydrophobicity (e.g. low water solubilities: 5.3–56 µg/L) ², and information about VMSs in the atmospheric environment is essential to reveal the environmental processes and environmental fate of VMSs and to evaluate their potential risk. However, information concerning the concentration and distribution of VMSs in the atmospheric environment in Japan is still very limited. In view of the urgent need for environmental risk assessment of VMSs, the objectives of the present study include the development of a high-precision analysis of VMSs in air samples from Japan and a study of occurrence of VMSs in the atmospheric environment.

First, air sampling conditions using a low-volume, mass-flow pump in combination with solid-phase extraction (SPE) cartridges were optimized for the sampling of VMSs, including cyclic and linear VMSs. This sampling method then was applied to annual monitoring of VMSs in 2014–2015 at Center for Environmental Science in Saitama (CESS) to examine annual trend of VMSs in the atmospheric environment. The results were analyzed together with meteorological information. To our best knowledge, this is the first study to report individual concentrations of VMSs in the atmospheric environment (outdoor air) from Japan.

Materials and methods

Samples. Air samples were collected at CESS (Kazo city, N36°5'5", E139°33'39") which located in a rural site 60 km northwest of Tokyo, Japan. One day sampling was conducted every week over a period of one year, from February, 2014 to February, 2015. A diaphragm pump with mass flow controller (MP- Σ 300N, Shibata Scientific Technology) was used to pull air through an SPE cartridge (Sep-Pak plus PS-2, Waters) at flow rate of 0.5 mL/min for 24 h. The SPE cartridge was rinsed with 3 mL dichloromethane (DCM), and then was dried using pure nitrogen immediately before the sample collection.

Chemical analysis. Prior to the sample collection, 100 ng of ¹³C-labeled octamethylcyclotetrasiloxane (D4), decamethylcyclohexasiloxane (D5), dodecamethylcyclohexasiloxane (D6) in hexane was added onto the top of SPE cartridge as an internal standard. Air samples were extracted within a day after the collection. Firstly, the SPE cartridge was dried using pure nitrogen for 10 min, and was subsequently eluted with 1 mL of DCM using a glass syringe. The eluate (about 0.5 mL) was collected directly into a GC vial. One hundred ng of d₈-naphthalene was added as a recovery standard. Seven individual VMSs were measured in this study; they included hexamethylcyclotrisiloxane (D3), D4, D5, D6 for cyclic VMSs and octamethylsiloxane (L3), decamethyltetrasiloxane (L4), dodecamethylpentasiloxane (L5) for linear VMSs. Quantification of VMSs 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 VMSs in laboratory products and reagents, GC parts, and also ambient air, are the major difficulty in the analysis of VMSs. To reduce contamination, blank levels of VMSs for all products and reagents used were tested. We selected silicone free or low bleed materials to achieve high precision analysis of VMSs in water samples. Procedural blanks were analyzed with the samples to check for contamination arising from reagents and lab materials. Mean recoveries of internal standards spiked in the samples were 101% for 13C-D4, 104% for 13C-D5, and 108% for 13C-D6. Method detection limit (MDL) and method quantification limit (MQL) values for VMSs 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 VMSs, divided by sample volume. MDL for individual VMSs ranged from 0.3 ng/m³ for L5 to 3 ng/m³ for D6. For statistical analysis, below MDL values were assigned to be a half of the MDL.

Results and discussion

Method performance.

Elution test: The elution profile of the targets was studied using the SPE cartridges. 200 ng each of VMSs was added onto the top of the SPE cartridges, and the cartridges were subsequently dried using pure nitrogen. DCM or n-hexane was applied in 4 portions (1.0 mL, 0.5 mL, 0.5 mL, and 0.5 mL) and 4 fractions were directly collected into GC vials and analyzed separately. The elution profiles showed that >99% of the targets eluted in the first fraction of DCM, indicates 1.0 mL of DCM was a suitable solvent for the elution. In case of n-hexane, 94% of D3 was eluted in the first fraction, this found to be slightly low comparing with those of DCM. The results were similar to found in previous study 4.

Breakthrough test: Although recovery rates of internal standards spiked before the sampling were assessed, the breakthrough of 7 VMSs through the SPE cartridge was assessed by analysis of a second cartridge mounted behind the primary SPE cartridge for 7-days sampling. No of the targets was detected exceed 1% of primary SPE cartridge and the breakthrough of VMSs was negligible. The results indicated that this sampling conditions can be applied for 7-days monitoring using the same SPE cartridge at flow of 0.5 L/min.

Sample storage test: To check any leakage or contamination of VMSs from SPE cartridge, storage of the SPE cartridge spiked with the internal standards in a freezer was studied for 7 days. The recoveries of ¹³C-D4, D5, and D6 spiked were more than 93%, this includes loss in analytical procedure, and the loss of the targets were found to be very low when the cartridges were stored below -20°C. Moreover, the targets were found be below detection limit in the storage experiments. Although, in general, the SPE cartridge was eluted within a day after sampling, SPE cartridge can be stored over 7 days without any leakage and contamination.

Concentrations.

Most of the targets were detected from air samples collected in CESS. The total concentrations of 7 VMSs (Σ VMS) in air sample widely ranged from 63 ng/m³ to 1146 ng/m³ (median: 242 ng/m³). The mean and ranges of concentrations for cyclic VMSs were 70 ng/m³ (5.5–359 ng/m³) for D3, 123 ng/m³ (11–567 ng/m³) for D4, 118 ng/m³ (34–327 ng/m³) for D5, and 12 ng/m³ (3.6–34 ng/m³) for D6. Concentrations of linear VMSs including L3, L4, and L5 were one to two orders of magnitude lower than those of cyclic VMSs.

Several studies have reported the occurrence of VMSs in atmospheric environment including indoor, outdoor, and near point sources such as wastewater treatment plants. The reported concentrations of D4, D5, and D6 in outdoor air ranged from ND to 320 ng/m³, 2.9 to 190 ng/m³, and 0.45 to 77 ng/m³, respectively. The mean concentrations found in this study were comparable to those reported for urban and sub-urban air in Chicago, USA, Rao, Sweden, and Jagtvejen, Denmark, whereas Σ VMS concentrations of up to 1150 ng/m³ were found in our study. The concentrations of D4 from this study can be compared with earlier reports of 3.5 and 300 ng/m³ in air at a background station in Sweden ^{4,5}, 16 ng/m³ for urban site in Toronto ⁶, and 280 ng/m³ in Chicago ⁷ (Fig 2).

Characteristics of VMSs in the atmospheric environment.

Cyclic VMSs were the predominant compounds in all samples; the proportion of D4 at 37% (based on the mean concentration) was the highest, followed by D5 (36%), D3 (21%), and D6 (3.8%). We examined relationships of among the concentrations of VMSs in all air samples analyzed using Pearson correlation analysis. A significant positive correlation ($p < 0.01$) was found between D3 and D4 ($r = 0.98$), but it was weak between D4 and D5 ($r = 0.43$), among pair of cyclic VMSs (Fig 3). Indoor air and aeration gas from sewage treatment plant can be major sources of VMSs in the atmospheric environment because methylsiloxanes are used in a wide range of personal-care products. In our previous study, we determined the concentrations of cyclic and linear siloxanes in a variety of consumer products. D5 was the predominant compound in most of personal care products including hair-care products, skin lotions, and cosmetics. On the other hand, relatively high proportions of D4 were found in sealants and sanitation products. Although high proportions of linear siloxanes were observed in body washes, skin lotions, and sanitation products, majority of linear siloxanes comprise compounds higher than L6. We also analyzed indoor air of laboratory and office at the CESS. The concentrations of Σ VMS were 372 ng/m³ (n=7, range: 121–730 ng/m³) and 1400 ng/m³ (n=1) in the laboratory and office, respectively, with the predominant proportions of D5 (34%). The concentrations of D5 in the laboratory air were one to two orders of magnitude lower than those from previous study⁷ and the composition of D5 found in this study was not as high as that found in previous study (97% in average). Those results may suggest different consumption patterns of VMSs in personal-care and laboratory materials between countries. D4 is mainly used for intermediate of silicone polymers. Volatilization of VMSs from silicone polymers (e.g. PDMS) can be another source of D4 in the air samples because D4 is more volatile than D5 and high molecular siloxanes contained in silicone polymers. We also examined the relationships of concentrations of VMSs in air samples and meteorological data such as temperature (°C), precipitation (mm), solar radiation (MJ/m²), and SPM ($\mu\text{g}/\text{m}^3$). No correlation between VMS concentrations and meteorological data was found in this study.

Ratio of D5 to D4.

Previous study⁷ has reported unique profiles of D5/D4 ratios in indoor and outdoor air; D5/D4 ratios in outdoor air (4.5, 3.1, and 2.1 for Chicago, Cedar Rapids, and West Branch, respectively) decreased with increasing distance from emission sources of two chemicals. Half-lives of D4 and D5 with respect to atmospheric oxidation are 11 and 7 d, respectively. Because of this, D5/D4 ratios can be highest at the points of common emission of the two chemicals, and can decrease as air masses move away from the emission source and undergo oxidative aging⁷. In this study, D5/D4 ratios (mean and range) in outdoor and indoor air samples were 2.0 (range: 0.3–5.0) and 1.9 (range: 0.5–5.0), respectively (Fig 1). Interestingly the trends of ratios found both in outdoor and indoor were very similar and the high concentrations of VMSs in outdoor air were found with low D5/D4 ratios (e.g. samples collected in 26 Feb, 28 May, and 5 Nov in 2014), suggesting considerable amount of D4 can be discharged into the atmospheric environment whereas D5 is the largest contributor to mass of siloxane in common personal-care products.

As described above, D4 is considered as the listing of additional chemicals to the Stockholm Convention on POPs. Further study is necessary to reveal significant emission sources of D4 to the atmospheric environment.

Acknowledgements

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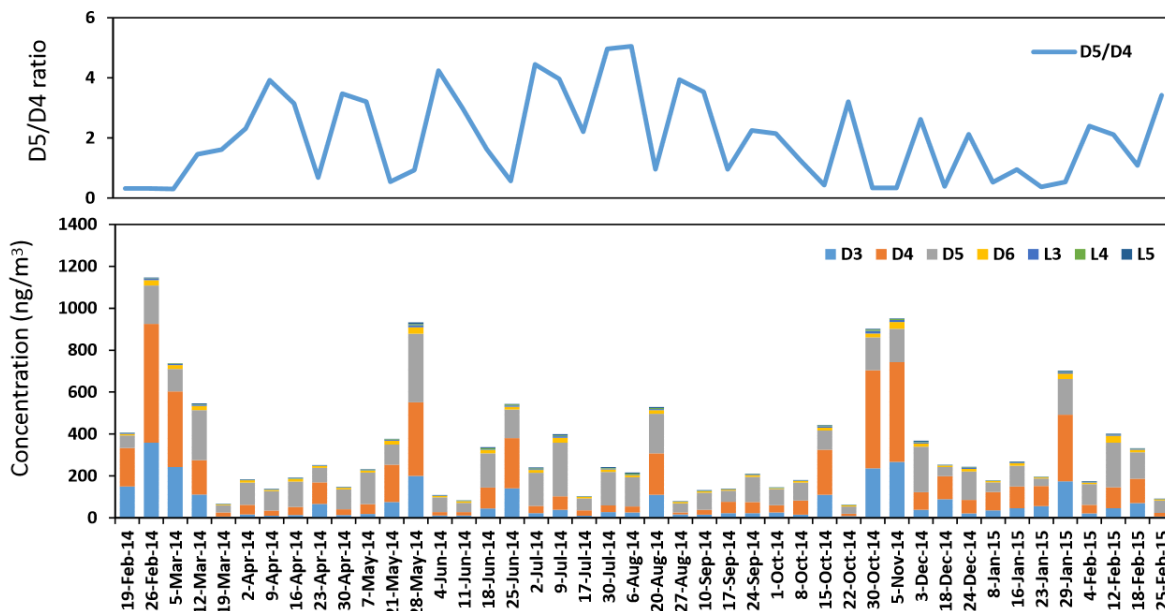


Fig 1. Annual profiles of VMS concentrations and D5/D4 ratios in air samples collected from a rural site in Kazo, Japan

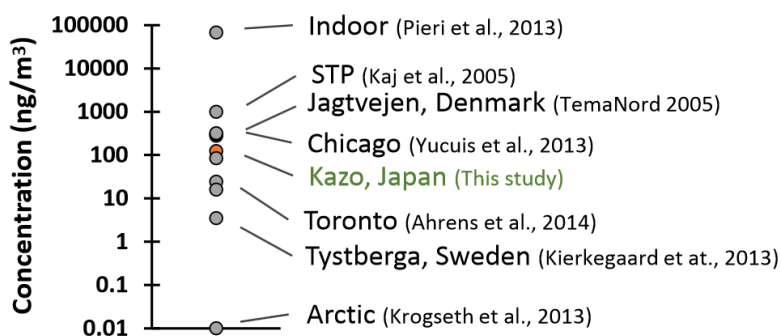


Fig 2. Comparison of D4 concentrations in air samples between this study and previous studies

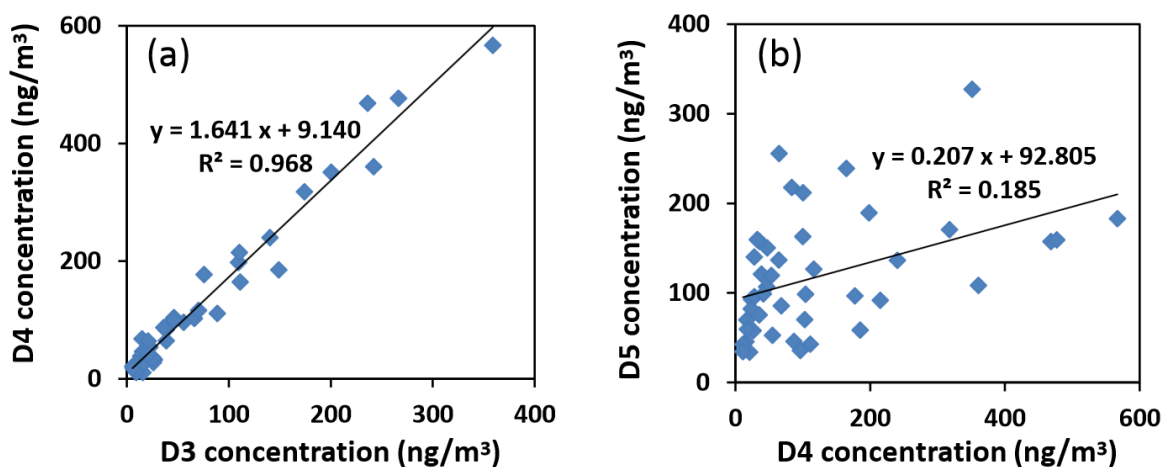


Fig 3. Relationships among concentrations of cyclic VMSs in outdoor air samples; (a) D3 versus D4 and (b) D4 versus D5