Regional Characteristics and Annual and Diurnal Variations of Methylsiloxanes in the Atmospheric Environment, Saitama, Japan

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Introduction

The determination of cyclic and linear methylsiloxanes (Siloxanes) in environment is important for the evaluation of human and environmental risks. Siloxanes have been widely used in consumer products [1] because siloxanes have low surface tension, high thermal and chemical stabilities, and believed to be inert. However, a part of volatile cyclic methylsiloxanes (CMS) has recently been identified as priority chemicals for environmental risk assessment due to their persistence in the environment and bioaccumulative potency [2]. 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. CMS 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 CMS ends up in the atmosphere because CMS possess high volatility (4.6–132 Pa at 25°C) and hydrophobicity (e.g. low water solubilities: 5.3–56 μg/L)[2]. Recently, the European commission decided restriction on octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) in wash-off use personal care products [3]. Moreover, D4 and dodecamethylcyclohexasiloxane (D6) was registered on the list of monitoring chemicals in Act on the Evaluation of Chemical Substances and Regulation of Their Manufacture, etc., Japan. However, information concerning the concentration and distribution of CMS in the environment in Japan is still very limited [4].

In view of the urgent need for environmental risk assessment of cVMS, in this study, we investigated concentration profiles of 20 individual cyclic and linear methylsiloxanes in air samples collected from Saitama Prefecture, Japan. Regional characteristics were analyzed for the atmospheric environment. To examine annual and diurnal trends of siloxanes, moreover, over one-year monitoring and high-resolution time monitoring were conducted in Center for Environmental Science in Saitama (CESS).

Materials and methods

Samples. Air samples were collected at 9 air monitoring stations located in Saitama Prefecture in four seasons during June, 2016 to October, 2017 (in total 6 times). Continuous sampling was conducted in our center (CESS, Kazo city, N36°5'5", E139°33'39") during the same period. The air samples were collected for 168 h (7 days) at a flow rate of 0.2 L/min using diaphragm pumps with mass flow controller (MP-Σ30N, Shibata Scientific Technology). High-resolution time sampling was conducted during 3-9 August, 2017 with 0.8 L/min flow rate for 4 h. Pre-washed SPE cartridges (Sep-Pak plus PS-2, Waters) were used as trap sorbent for the target compounds.

Chemical analysis. Siloxanes determined in this study were D3–D9 for CMS and L3–L15 for linear methylsiloxanes (LMS); the numbers represent siloxane unit. Firstly, the SPE cartridge was dried using pure nitrogen gas for 10 min, and then 100 ng of $^{13}C_6$-D3, $^{13}C_8$-D4, $^{13}C_5$-D5, $^{13}C_6$-D6 in hexane was added onto the top of SPE cartridge as surrogate standards. The target compounds were subsequently eluted with 1.5 mL of hexane using a glass syringe. The eluate (about 1 mL volume) was collected directly into a GC vial. One hundred ng of d_8-naphthalene and d_{10}-phenanthrene was added as a recovery standard and an internal standard for L7–L15, respectively. Quantification of siloxanes was performed on a GC/MS (Thermoscientific, Trace GC ultra, ISQ). The GC/MS conditions were slightly modified from previous study [1]. PDMS fluid (Sigma-Aldrich, 5 cSt) was used as quantification standard for L7–L15. The compositions of individual LMS were determined in advance using GC/FID; the values were corrected based on carbon content.

QA/QC. Because siloxanes are present in many consumer products, the analyst took care not use hand lotions or other possible sources of contamination during sampling and analysis. Procedural blanks were analyzed with the samples to check for contamination arising from reagents and lab materials. Trace levels of CMS (D3-D6) were detected in the procedural blanks (n=35), ranging from 0.11±0.09 ng/m^3 (D4) to 0.30±0.25 ng/m^3 (D5). The lowest concentration of D5 found in air samples analyzed was enough high comparing with the procedural blank level. Mean recoveries of surrogate standards spiked in the samples were 93% for $^{13}C_6$-D3, 93% for $^{13}C_8$-D4, 104% for $^{13}C_5$-D5, and 101% for $^{13}C_6$-D6. Method detection limit (MDL) and method quantification limit (MQL) values for siloxanes were calculated from variance associated with replicate analysis (n=7). 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 siloxanes, divided by sample volume (2.016 m^3). MDL for individual targets ranged from 0.06 ng/m^3 for D4 and D6 to 0.6 ng/m^3 for L14.

Results and discussion

Reginal concentration profiles. The target chemicals except L11-L15 were detected in most of air samples collected in Saitama Prefecture. The mean and range concentrations of 7 CMSs (ΣCMS) in the seasonal investigation were 358 ng/m^3 (33.2–699 ng/m^3). For sum of 13 LMS (ΣLMS), the mean and range concentrations were 13.4 ng/m^3 (ND–31.8 ng/m^3). Concentrations of CMS and LMS in mountainous area were found to be the lowest. CMS were the predominant compounds in all samples; the proportion of D5 at 56% (based on the mean concentration) was the highest, followed by D4 (25%), D3 (10%), and D6 (3.6%). Interestingly, we found regional differences in CMS profiles between in south and in north regions of Saitama Prefecture, which has high proportions of D4 in the north region (agricultural and sub-urban area); the ratios of D4/D5 were found to be 0.9 for the north and 0.3 for the south.

Annual variation. Air samples collected in CESS during 22 June, 2016 to 17 October, 2017 were analyzed for CMS and LMS. Concentrations of ΣCMS ranged from 103 to 960 ng/m^3, with the mean concentration at 364 ng/m^3 (Fig. 1). D7, D8, D9, and L3–L10 were detectable but the concentrations were very low (a few ng/m^3

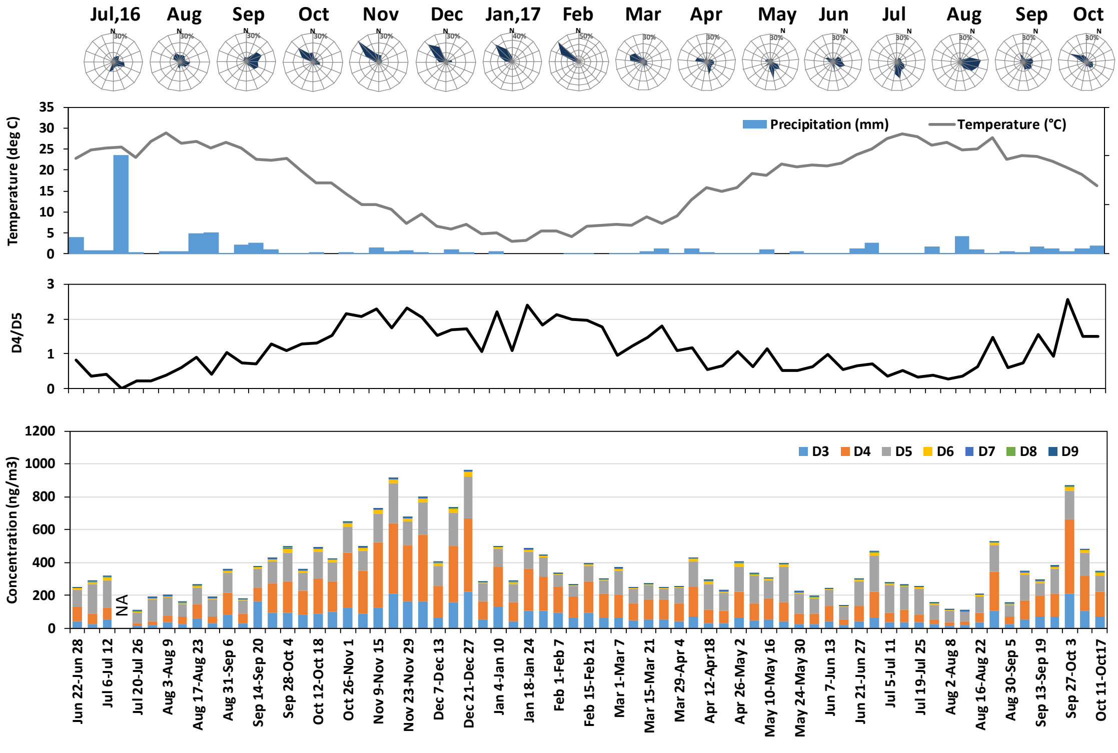

Fig. 1: Concentration profiles of cyclic methylsiloxanes and D4/D5 ratios in air samples collected over one year, along with meteorological information.

levels). Concentrations of longer LMS (L11–L15) were below MDL. The mean concentrations of ΣCMS were compared during distinct seasons: generally, the ΣCMS concentrations were higher in autumn (September-November), followed by in winter (December-February), which had the predominant window direction in the northwestward. We examined relationships of among the concentrations of CMS (D3–D6) in all air samples for continuous monitoring using Pearson correlation analysis. Significant positive correlations ($p < 0.001$) were found for most of pairs among CMS, indicating that common emission sources and transport mechanisms. However, interestingly, we found different seasonal trends of individual CMS. For example, D5 concentrations were relatively constant during the sampling period (mean±SD: 128±45 ng/m^3, range: 58–258 ng/m^3), whereas D4 concentrations widely varied from 15 to 452 ng/m^3, with the seasonal trends which showed higher concentrations in the autumn and winter (Fig. 1). The concentrations of ΣCMS tended to be high with increasing the ratios of D4/D5, indicating the concentrations of D4 can cause the seasonal variations of ΣCMS found in the samples.

Diurnal variation. Concentrations of CMS were determined in the samples collected every 4 h. We found diurnal variation of D5 concentrations, which increased in nighttime up to 185 ng/m^3 and decreased in daytime down to 28 ng/m^3. It is known that atmospheric boundary layer altitude becomes high with increasing net radiation. Previous study [5] reported that D5 concentrations in nighttime were higher than in daytime, which is due to the fluctuations of the atmospheric boundary layer. Lower concentrations in the daytime was also explained by OH radical degradation of methylsiloxanes [6]. Interestingly, we found different specific profiles for D3 and D4. In general, concentrations of D3 and D4 showed similar profile to those of D5, however, the concentrations of D3 and D4 drastically increased on 9 August, 2017 when the predominant wind direction was changed to the northwestward. Backward trajectory analysis performed by using NOAA HYSPLIT showed the different trajectories between the beginning of sampling on 4 August and the end of sampling on 9 August, suggesting the air samples collected on 9 August might be influenced by other specific sources having predominant D3 and/or D4.

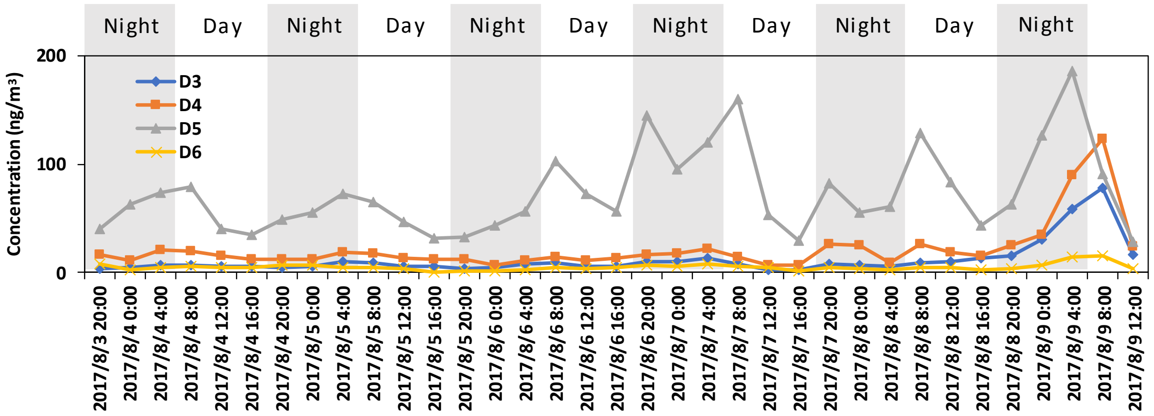

Fig. 2: Concentration profiles of cyclic methylsiloxanes in the air samples collected in every 4 h (high-resolution air sampling) during 3-9 August, 2017.

Source analysis. Non-negative matrix factorization (NMF) is the approximation of $n \times m$ non-negative matrix V by a product of $n \times r$ non-negative factor matrix W and $r \times m$ non-negative load matrix H[7]. Applying NMF to concentration data of multiple compounds in environmental samples is expected to obtain the profiles and contributions from chemical sources [8]. We applied NMF to the data of CMS concentrations for the all air samples (n=154). Firstly, we examined the relationship between number of factors, r (e.g. number of emission sources) and the objective function value by NMF. The objective function value drastically decreased between giving one-factor to two-factors and then monotonously decreased with increasing the r. This profile indicates that mainly two kinds of emission sources influenced on the atmospheric CMS in Saitama.

The matrix W obtained by NMF corresponds to the concentration compositions of emission. The CMS profiles resulting from two emission sources were shown in Fig. 3. The obtained matrix H corresponds to the contribution rates for the emission sources in each air samples. The predominant CMS in the Factor #2 was D5, followed by D4 and D6. The profile was very similar to those found in indoor air [9], suggesting that Factor #2 might represent common emission source caused by personal care and household products. For Factor #1, D4 was the predominant, followed by D3 and D5. The contributions of the two emission sources in the annual and diurnal air monitoring showed that the proportions of Factor #1 increased with increasing the ΣCMS concentrations when the predominant wind direction in the northwestward was shown. This suggests that Factor #1 might represent the CMS proportion in specific emission source transported from northwestward to Saitama. Further information regarding type of emission sources and its amount for CMS is needed to elucidate distribution of CMS in the atmospheric environment, Japan.

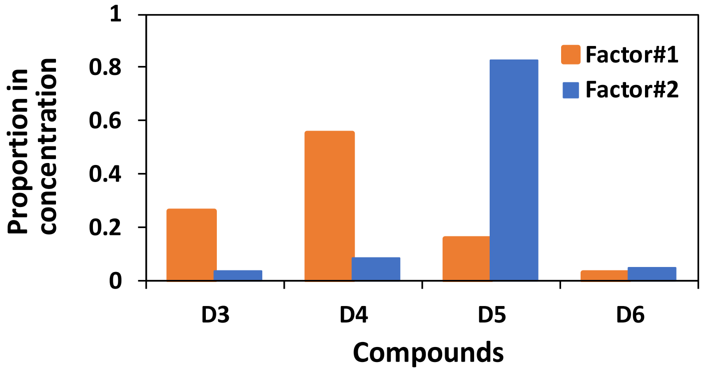

Fig. 3: Profiles of cyclic methylsiloxanes in the two emission sources estimated by non-negative matrix factorization (NMF).

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