Regional Characteristics and Temporal Trends of Methylsiloxanes in the Atmospheric Environment, Saitama, Japan −Simultaneous Analysis for 20 Compounds−

Horii Y[1*], Minomo K[1], Ohtsuka N[1], Motegi M[1], Nojiri K[1], Takemine S[1], Yamashita N[2]

[1]Center for Environmental Science in Saitama (CESS), 914 Kamitanadare, Kazo, Saitama 347-0115, Japan
[2]National Institute of Advanced Industrial Science and Technology, 16-1 Onoagwa, Tsukuba 305-8569, Japan

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 (cVMS) 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. cVMS 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 cVMS ends up in the atmosphere because cVMS 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 proposed restriction on octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) not only in wash-off use personal care products, but also in leave-on products [3]. However, information concerning the concentration and distribution of cVMS 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 (CMS and LMS) in air samples collected from Saitama Prefecture, Japan. Regional characteristics and seasonal trends were analyzed for the atmospheric environment. Moreover, continuous monitoring (7-days sampling) was conducted in Center for Environmental Science in Saitama (CESS) during June, 2016 to February, 2017, to examine temporal trends of siloxanes. The influence of meteorological conditions on air concentrations of siloxanes were evaluated.

Materials and methods

Samples. Air samples were collected at 9 air monitoring stations located in Saitama Prefecture in July, October 2016, and January 2017 (Fig.1). Continuous sampling was conducted in our center (CESS, Kazo city, N36˚5'5", E139˚33'39") from June 2017. 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). 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 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}-phenanthlene 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=21), ranging from 0.08 ± 0.01 ng/m^3 (D4) to 0.22 ± 0.06 ng/m^3 (D5). Mean recoveries of surrogate standards spiked in the samples were 89% for $^{13}C_6$-D3, 95% for $^{13}C_8$-D4, 107% for $^{13}C_5$-D5, and 106% 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
Concentration profiles in Saitama. 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 July, October, 2016, and January, 2017 were 340 ng/m^3 (240–430 ng/m^3), 460 ng/m^3 (110–670 ng/m^3), and 350 ng/m^3 (33–510 ng/m^3), respectively (Table 1). For sum of 13 LMS (ΣLMS), the mean and range concentrations were 15 ng/m^3 (7.3–21 ng/m^3), 20 ng/m^3 (5.4–32 ng/m^3), and 13 ng/m^3 (1.6–21 ng/m^3), respectively. Concentrations of CMS and LMS in mountainous area (remote site, St.9) were found to be the lowest. CMS were the predominant compounds in all samples; the proportion of D5 at

Table 1. Mean and range of concentrations for cyclic and linear methylsiloxanes (CMS and LMS) in seasonal air samples.

Sample		Concentration (ng/m^3)		
		ΣCMS [a]	ΣLMS [b]	Total [c]
Summer	Mean	340	15	360
(July, 2016)	Range	240-430	7.3-21	250-450
Autumn	Mean	460	20	480
(October, 2016)	Range	110-670	5.4-32	110-710
Winter	Mean	350	13	360
(January, 2017)	Range	33-510	1.6-21	35-530

[a] Sum of D3-D9, [b] Sum of L3-L15, [c] Sum of CMS and LMS

55% (based on the mean concentration) was the highest, followed by D4 (25%), D3 (10%), and D6 (3.6%). Interestingly, we found regional differences for CMS profiles between in south (St.1–5) and north area (St.6–8) in Saitama Prefecture (Fig. 1). The south area which is highly populated area showed higher concentrations of D5 than those in the south area, however, D4 concentrations in the north area (rural or suburban sites) were 2-3 times higher than those in south area. Release from personal care and household products is a major pathway for CMS in the atmosphere. The majority of D5 used in personal care applications (>90% of the total mass) is volatilized to air during or after use[5]. In fact, the concentration distributions of D5 obtained in this study were explained by the distributions of population density. On the other hand, as for D4, the distributions showed higher concentrations in the rural and suburban area (North area), suggesting that D4 distributions can be influenced by other emission sources and/or meteorological conditions. Due to the differences in atmospheric half-life for D4 (10.6 days) and D5 (6.9 days), D4/D5 ratios in air samples increased according to the migration distance [6]. In this study D4/D5 ratios in north area (0.94) were higher than those in south area (0.29), however D4 distributions was also found to be high in the south. Taken together, it is assumed that D4 distributions cannot be explained only by advection from the urban area. Air concentrations for LMS were very low and near MDL, especially for long LMS. The profiles found in this study were different from those of indoor air (residential house) which has relatively high proportion of LMS (L3–

L11); the composition of L8 occupied 22% of the total concentration [7], probably due to lower volatility and shorter atmospheric half-life (For L8; 2.98 days, calculated by EPI suite) for long LMS.
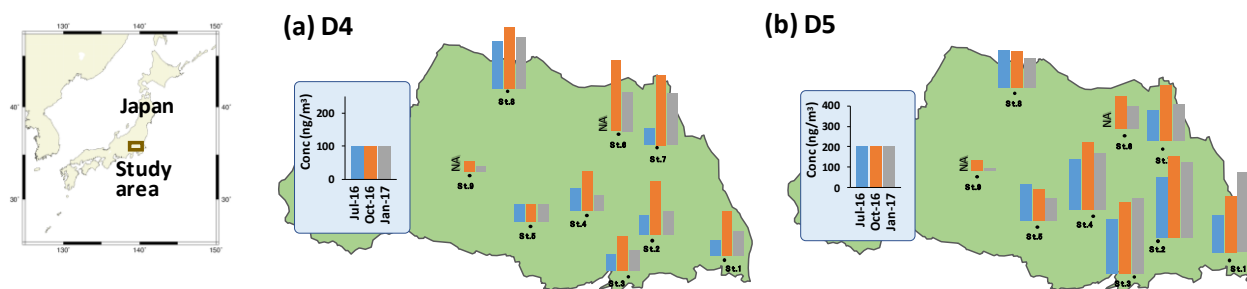

Fig 1. Distributions and seasonal profiles (ng/m^3) of D4 (a) and D5 (b) in Saitama air

Temporal trends. Air samples collected in CESS during 22 June, 2016 to 28 February, 2017 were analyzed for CMS and LMS. Concentrations of ΣCMS ranged from 100 to 960 ng/m^3, with the mean concentration at 420 ng/m^3 (Fig. 2). D7, D8, D9, and L3–L10 were detectable but the concentrations were very low (a few ng/m^3 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, 550 ng/m^3), followed by in winter (December-February, 460 ng/m^3) and in summer (June−August, 240 ng/m^3). The seasonal trends in this study were similar to that found in Toronto [8]. 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: 130±48 ng/m^3, range: 64−260 ng/m^3), whereas D4 concentrations widely varied from 15 to 440 ng/m^3, with the seasonal trends which showed higher concentrations in the autumn and winter (Fig. 2). The concentration ratios of D4/D5 increased from the summer (0.5) to the autumn (1.6) and the winter (1.8). The seasonal trends, the increase in the concentration of CMS observed in this study were mainly influenced by the concentration variability of D4. The D4 compositions in the total increased from 13% in the summer (20−26 July, 2017) to the maximum of 53% in the autumn (11−15 November, 2016), whereas D5 compositions were high in the summer at 50±10%. D3 also showed similar profiles with D4. D4 is mainly used for intermediate of silicone polymers. Volatilization of siloxanes from silicone polymers can be another source of D4 in the air samples because D4 is more volatile than D5. Further study is needed to investigate other sources and emission routes for D4 to elucidate the factors on the temporal changes for D4.

We also examined the relationships of air concentrations for CMS and meteorological conditions such as temperature (°C), precipitation (mm), cumulative net radiation (MJ/m^2), and photochemical oxidants (ppb) using Pearson correlation analysis: weekly averages were used for meteorological conditions. Significant correlations were found between individual CMS and temperatures, photochemical oxidants, or net radiation, but not for precipitation. Especially, strong negative correlations were found between D4 concentrations and net radiation. It is known that atmospheric boundary layer altitude becomes high with increasing net radiation. Previous study [6] reported that D5

concentrations in nighttime were higher than in daytime, which is due to the fluctuations of the atmospheric boundary layer. Seasonal variability, lower concentrations in the summer was also explained by the seasonality in OH radical concentrations [9]. The seasonal trends found in this study can be also explained, in part by fluctuations of atmospheric boundary layer and by photochemical degradation.
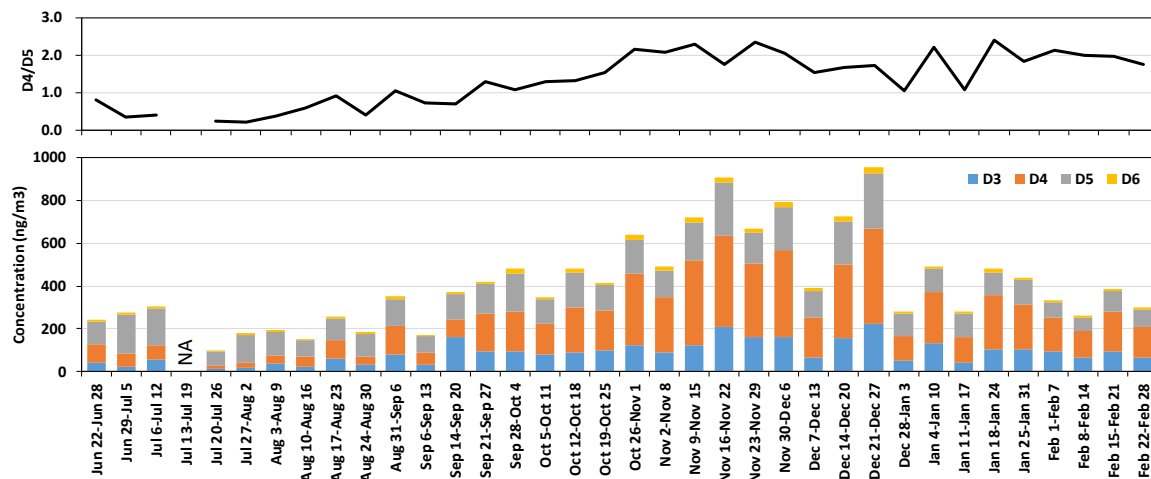

Fig 2. Concentration profiles of cyclic methylsiloxanes and D4/D5 ratios in air samples during June, 2016 to February, 2017, along with daily average temperatures and precipitation.

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