CONCENTRATION PROFILES OF VOLATILE METHYLSILOXANES IN RIVER WATER, SEDIMENT AND FISH SAMPLES FROM TOKYO BAY WATERSHED

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Introduction

The determination of siloxanes include 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 potencies [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 real water environment. In this study, we investigated the concentration profiles of cyclic and linear VMS in surface water, sediment, and fish samples collected from selected Tokyo Bay inflow rivers. A developed purge and trap (PT)-solvent elution method was used for water extraction and clean-up of extracts from sediment and fish samples. To our best knowledge, this is the first study to report VMS in water, sediment, and fish samples collected from same locations in Japan.

Materials and methods

Samples. A sampling campaign was conducted during October to November 2012 in major Tokyo Bay inflow rivers, including Ara River, Sumida River, Edo River, Yoro River, Tama River, Tsurumi River (Fig. 1). Nine river water samples were collected using a clean stainless steel grab sampler and stored in 600-mL screw top glass containers without headspace to prevent evaporation of the target chemicals. Nine sediment samples were collected from same locations as river water using a clean stainless steel grab sampler. Fish samples (n=85 in 9 species) were collected from three locations in Ara River (St.2), Tama River (St.6), and Yoro River (St.8). All samples were stored in cooler boxes immediately after the sampling and transported to the laboratory, then kept at 4°C for water samples and -20°C for sediment and fish samples. For water analysis, samples were extracted within 4 days after the collection.

Fig. 1 Sampling locations of VMS monitoring

Chemical analysis. Analytical procedure for the extraction of water samples was similar to a previous report [3]. Firstly, 600 mL of water was gently transferred into an 1-L glass gas washing bottle and 50 ng of ^{13}C-labeled octamethylcyclotetrasiloxane (D4), decamethylcyclohexasiloxane (D5), dodecamethylcyclohexasiloxane (D6) in acetone was added into the sample as an internal standard. The water 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, Waters) as a gas trap was mounted on the outlet of the gas washing bottle. The extraction efficiency in different extraction times and water bath temperatures was examined in a previous report [3]. After purging the samples, the SPE cartridge was dried by purging pure nitrogen gas for 20 min, then target chemicals were eluted with 3 mL of dichloromethane. The eluant was gently concentrated to 1 mL. Fish samples collected were separated in species and in locations, then whole fish was homogenized using a stainless steel mixer. Aliquots of solid samples (1 g of sediment or 2 g of fish) were taken in polypropylene tubes, then 50 or 100 ng of the internal standard was added into it. 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, mineral oil, and lipid in the extract, we applied a PT extraction technique used for water extraction to cleaning-up of the extracts of solid samples. Conditions of PT clean-up were slightly changed from those of water. About 300 mL of *n*-hexane washed water and 30 g of sodium chloride were added into an 1-L glass gas washing bottle and the whole *n*-hexane extract was transferred into it. Purge time was set to be 60 min for sediment and 120 min for fish 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 environmental 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 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, from 0.6 ng/g ww (L3, L5) to 17 ng/g ww (D3, D4) for sediment, and from 0.1 ng/g ww (L3) to 4.3 ng/g ww (D3) for fish. For statistical analysis, below MDL values were assigned to be a half of the MDL. Triplicate analyses of individual nine river water were performed and the precision (RSD) was 18% for D3, 12% for D4, 4.2% for D5, 8.9% for D6, and 4.3% for L5. Concentrations of L3 and L4 were below MDL in most of the water samples.

Results and discussion

River water. Nine river water samples (n=3 each) were analyzed for cyclic and linear VMS (Fig. 2). The total concentrations of VMS in river water ranged from 32 ng/L to 470 ng/L at the mean concentration of 130 ng/L. The mean and ranges of concentrations for cyclic VMS were 8.6 ng/L (4.3-13 ng/L) for D3, 6.4 ng/L (2.9-16 ng/L) for D4, 110 ng/L (16-410 ng/L) for D5, 9.7 ng/L (4.1-30 ng/L) for D6. D5 (73% in total VMS) was the predominant VMS in the river water, followed by D3 (11%) and D6 (8%). Trace levels of linear L5 were

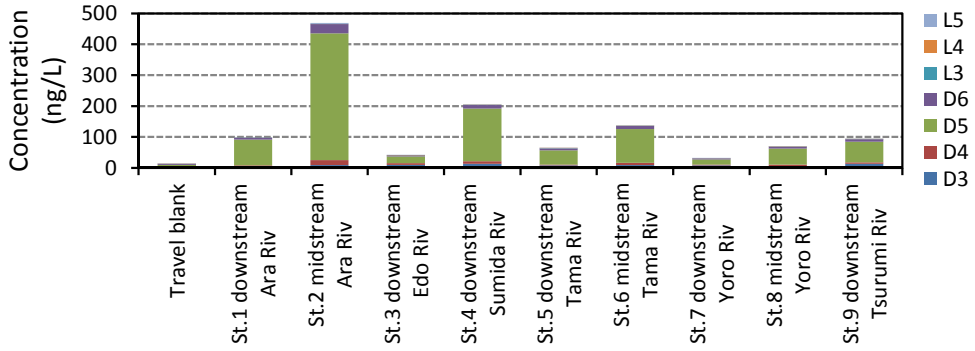

Fig. 2 Concentrations of VMS in river water samples, along with travel blank

observed, and L3 and L4 were found to be below the MDL in most of the samples. The highest concentration of VMS was detected from midstream of Ara River where the sampling station is located near the downstream of two large scale waste water treatment plants (WWTPs), indicating WWTP effluent can be a major source of VMS in river water. VMS are widely used in personal care products such as hair care products, skin lotion, and cosmetics as ingredient. In previous study [1], daily usage rate to cyclic and linear methylsiloxanes from use of personal care products was estimated at 307 mg/day/capita. The highest usage rate was found for D5 at 233 mg/day/capita. Environmental exposures are expected to arise from down-the drain rinsing of methylsiloxanes and transport through the sewer system to WWTP. This might reflect to concentration profiles found in the river water. In previous studies, D5 concentrations in water from the Nene and Great Ouse Rivers in Eastern England ranged <10-29 ng/L and 13-27 ng/L, respectively [4]. Nationwide surveies in Nordic countries found no detectable or trace level of cyclic VMS in water samples collected from background, urban site, and point sources [5].

River sediment. Nine river sediments taken from exactly same location with the river water were analyzed (Fig. 3). The concentrations were reported in dry weight basis. The total concentrations of VMS in river sediment ranged from 46 ng/g dw to 2000 ng/g dw at the average concentration of 810 ng/g dw. The mean and range of concentrations of cyclic VMS were 690 ng/g dw (<7.3-1700 ng/g dw) for D5 and 71 ng/g dw (<4.3-150 ng/g dw) for D6. D3, D4, and linear VMS were found to be below MDL or trace level. D5 (81% in total VMS) was the predominant VMS in the river sediment, followed by D6 (9%). Mean concentration of cyclic VMS was about 100 times higher than those of linear VMS. The highest concentration of VMS was detected from Sumida River.

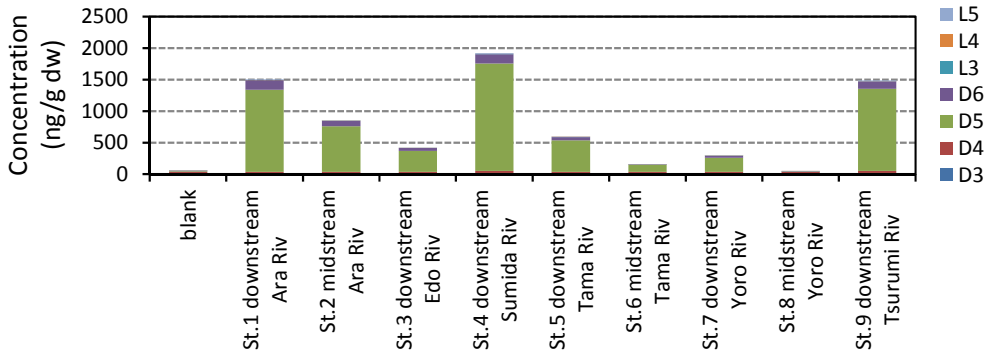

Fig. 3 Concentrations of VMS in river sediment samples, along with procedural blank

We also measured grain size distribution and total organic carbon (TOC) in the sediment using element analyzer (2400II, PerkinElmer). A significant positive correlation (r^2=0.57) was found between total VMS and TOC (Fig. 4). Widely varied concentrations found in the river sediment can be influenced by amount of TOC and/or grain size distribution of sediment. Concentration profiles of VMS found in our results were comparable to those from the Great Ouse River (12-24 ng/g dw of D4 and 82-1450 ng/g dw of D5) [6] and Nordic countries (~ 2300 ng/g dw of cyclic VMS at Roskilde, Denmark) [5], however the compositions were different with those from Songhua River, northeastern China which has higher proportion of D6 [7].

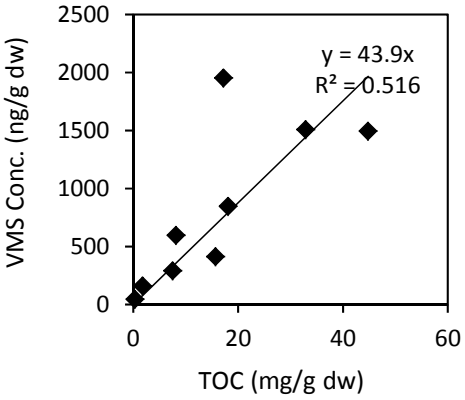

Fig. 4 Correlation between concentrations of total VMS and TOC in the sediment samples

Fish. Fourteen fish samples collected from midstream of Ara River (St.2), Tama River (St.6), and Yoro River (St.8) were measured for VMS (Fig. 5). The concentrations were reported in wet weight basis. Concentrations of total VMS widely ranged from 74 ng/g ww (*Tridentiger obscursu*, Yoro River) to 2200 ng/g ww (*Plecoglossus altivelis*, Tama River). Among cyclic VMS, mean concentration of D5 was the highest at 550 ng/g ww, followed by D4 at 35 ng/g ww and D6 at 7.2 ng/g ww. Linear VMS measured were found to be trace level or below MDL. Although limited number of samples were analyzed, the profiles of fish concentrations among the rivers were compared. The highest mean concentrations of total VMS was observed in Tama River's fish at 1000 ng/g ww, this is 8 times higher than those in Yoro River's fish, probably because several WWTPs were located around St. 6. Our results are in agreement with previous findings within Nordic countries [5], where higher fish concentrations of cyclic VMS were found near urban area.

Under field conditions, biota sediment accumulation factors (BSAFs, g-lipid/g-TOC) were estimated for detectable VMS in fish samples. BSAFs were found to be 1.2 for D4, 0.5 for D5, and 0.08 for D6 in Ara River and 0.1 for D4, 0.3 for D5, and 0.06 for D6 in Tama River. In this study, D4 concentrations in the sediment were below MDL in both sampling stations, so a half of MDL values were used for the estimation of D4. BSAFs greater than one were found only for D4 from Ara River's fish. It should be noted that this is a preliminary results of VMS monitoring on river environment and limited number of samples were analyzed at this stage.

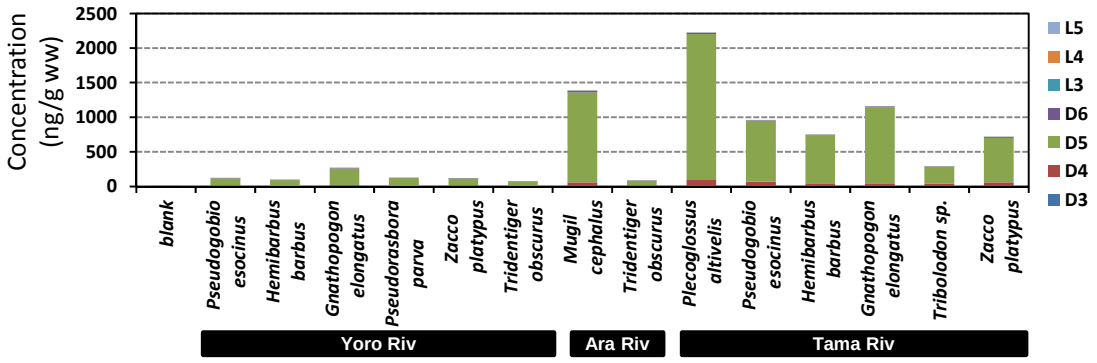

Fig. 5 Concentrations of VMS in fresh water fish from three rivers, along with procedural blank

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