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Distribution characteristics of volatile methylsiloxanes in Tokyo Bay watershed in Japan: Analysis of surface waters by purge and trap method

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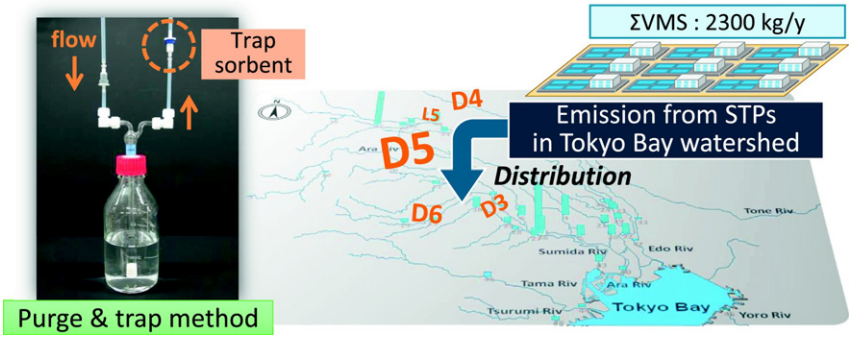
HIGHLIGHTS

- A sensitive purge and trap method was developed to determine cyclic and linear VMSs in water.
- Distribution of VMSs in Tokyo Bay watershed was studied for the first time.
- Annual emission of total VMSs through sewage treatment plants into Tokyo Bay watershed was 2300 kg.
- Distribution of cyclic VMS in river water was significantly correlated with TOC.

GRAPHICAL ABSTRACT



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ABSTRACT

Surface waters including river water and effluent from sewage treatment plants (STPs) were collected from Tokyo Bay watershed, Japan, and analyzed for seven cyclic and linear volatile methylsiloxanes (VMSs), i.e., D3, D4, D5, D6, L3, L4, and L5 by an optimized purge and trap extraction method. The total concentrations of seven VMSs (ΣVMS) in river water ranged from <4.9 to 1700 ng/L (mean: 220 ng/L). The individual mean concentrations of cyclic VMSs in surface waters were; 10 ng/L for D3, 13 ng/L for D4, 180 ng/L for D5, and 18 ng/L for D6. The concentrations of ΣVMS determined in STP effluents varied widely from 99 to 2500 ng/L and the individual mean concentrations were 21 ng/L for D3, 27 ng/L for D4, 540 ng/L for D5, and 45 ng/L for D6. D5, which is widely used in personal-care products, was found to be the most abundant compound in both river water and STP effluent. Linear VMSs were detected at much lower frequency and concentrations than those of cyclic VMSs. The measured concentrations of D4 were below the no-observed effect concentration (NOEC). The annual emission of ΣVMS through STPs into Tokyo Bay watershed was estimated at 2300 kg. Our results indicate widespread distribution of VMSs in Tokyo Bay watershed and the influence of domestic wastewater discharges as a source of VMSs in the aquatic environment.

1. Introduction

Volatile methylsiloxanes (VMSs) have been widely used in personal-care and household products (Horii and Kannan, 2008), in the

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production of silicone polymer, and in a range of industrial applications, owing to their low surface tension, high thermal and chemical stabilities. In 2009, the value of global sale of silicones (e.g. oligomers and polymers) was US$ 11.5 billion (Wang et al., 2013b). China was the largest manufacturer and consumer of silicones in the world in 2009, with a production and consumption volume of 270,000 and 430,000 tons, respectively (Wang et al., 2013b). Japan is also a major consumer of silicones, with an annual silicone consumption at 117000 tons in 2009; approximately 15% of the production was used in personal-care and life style products (Silicone Industry Association of Japan, 2009). Some cyclic VMSs were reported to meet regulatory criteria for large production volume, persistence in the environment, and bioaccumulation by environmental programs in the United Kingdom (Brooke et al., 2009a; Brooke et al., 2009b; Brooke et al., 2009c), Canada (Environment Canada, 2008a, 2008b, 2008c), and the United States (US-EPA, 2014). Three cyclic VMSs identified as priority pollutants by the aforementioned international agencies for regulation were; octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6). Cyclic VMSs possess unique physico-chemical properties, including high volatility (4.6–132 Pa at 25 °C) (Flaningam, 1986), hydrophobicity (e.g. low water solubilities: 5.3–56 μg/L) and high octanol-water partition coefficient (log K_{ow}: 6.98–8.87) (Varaprath et al., 1996; Xu and Kropscott, 2012). In 2012, Environment Canada proposed measures to prevent or minimize the releases of D4 into the aquatic environment during production and usage (Environment Canada, 2012). In 2015, the UK proposed restriction on D4 and D5 in wash-off use personal care products that contain >0.1% (by weight) of these two cyclic VMSs (ECHA, 2015). The US Environment Protection Agency has entered into an Enforceable Consent Agreement for D4 in 2014 (US-EPA, 2014).

VMSs have been reported to occur in a wide range of environmental samples including atmosphere (Genualdi et al., 2011; Krogseth et al., 2013b; Yucuis et al., 2013), indoor air (Lu et al., 2010), sediment (Sparham et al., 2011; Zhang et al., 2011), fish (Kierkegaard et al., 2010; Warner et al., 2014), surface water (Companioni-Damas et al., 2012; Sparham et al., 2008), coastal environment (Hong et al., 2014; Jia et al., 2015), and polar regions (Krogseth et al., 2013a; Warner et al., 2010). Surveys of VMSs in Nordic countries (Kaj et al., 2005) including Norway (Schlabach et al., 2007) reported that these compounds were found in every environmental and biological matrix analyzed including air, surface water, sediment, and fish with the exception of sea water. High concentrations of VMSs were found in sediment collected near sewage treatment plants (STPs) (Kaj et al., 2005).

Because of their high volatility, VMSs in personal-care and household products are expected to be emitted into air, but a fraction can be released into the aquatic environment through wastewater discharges. Recent studies have focused on the biomagnification of cyclic VMS in the aquatic food webs (Borga et al., 2012; Borga et al., 2013); trophic magnification factor (TMF) in freshwater foodwebs leading to brown trout was estimated at 2.9 for D5 and 2.3 for D6 (Borga et al., 2013). Nevertheless, other studies reported a TMF of <1 for D4 and D5 (McGoldrick et al., 2014; Powell et al., 2017; Powell et al., 2010; Powell et al., 2009).

Analysis of VMSs in environmental water samples is still challenging due to their unusual physico-chemical properties and potential background contamination (in laboratories). VMSs have been measured in water using headspace gas chromatography/mass spectrometry (HS-GC/MS) (Sparham et al., 2008), headspace-solid phase microextraction (HS-SPME) coupled with GC/MS (Companioni-Damas et al., 2012), membrane-assisted solvent extraction (MASE) with a large-volume injection (Wang et al., 2013a), and purge and trap (PT) extraction followed by GC/MS analysis (Kaj et al., 2005). Monitoring studies have shown that the concentrations of cyclic VMSs in surface waters were generally below few tens of ng/L, which are often close to the detection limits of the methods. Because certain VMSs are ubiquitous in the laboratory environment and instrumentation including the components of gas chromatography (GC), we developed an analytical method for accurate and precise analysis of 7 VMSs (4 cyclic and 3 linear VMSs including hexamethylcyclotrisiloxane (D3), D4, D5, D6, octamethyltrisiloxane (L3), decamethyltetrasiloxane (L4), and dodecamethylpentasiloxane (L5)) at concentrations below 3 ng/L, by reducing background levels of contamination. We examined the extraction efficiency of the target chemicals in various types of water samples. As VMSs have high volatility and low water solubility, stability and storage studies were performed to provide appropriate information required for collection and storage of samples.

The optimized purge and trap (PT) method was applied for the analysis of waters from the Tokyo Bay watershed. We investigated the concentration profiles of the 7 VMSs in 48 river water samples. Because down-the-drain discharge is considered to be the major route by which VMSs reach the aquatic environment (Horii and Kannan, 2008; Horii et al., 2007), effluents from 25 STPs around the Tokyo Bay watershed were analyzed for the 7 VMSs and the discharge amount (i.e., emission) of VMSs into the aquatic environment was estimated. VMSs have been reported to occur in STP effluents from the UK (van Egmond et al., 2013), Canada (Wang et al., 2013c), China (Xu et al., 2013), Greece (Bletsou et al., 2013), and the Nordic countries (Kaj et al., 2005) at concentrations on the order of few to hundreds of μg/L for D5. The determination of VMSs in the aquatic environment including STP effluents is the first step towards evaluation and characterization of their sources and environmental exposures. To date, this is the first study to report spatial distribution of VMSs in the aquatic environment of Japan.

2. Materials and methods

2.1. Samples

Tokyo Bay watershed covers an area of 9200 km^2 and is the home for over 29 million people. Seven rivers including the Ara River, Naka River, Sumida River, Edo River, Yoro River, Tama River, and Tsurumi River are the major inflowing rivers to Tokyo Bay. Annually, over 4 km^3 of sewage effluents drain into the inner part of the bay directly or via the rivers. The river mouths of Ara River, Naka River, and Sumida River are located near the North-western inner bay (Fig. 2), which is the most highly urbanized region (receiving domestic and industrial wastewater discharge) (Managaki et al., 2006). A water sampling campaign was conducted during October 2012 to April 2013, in the major inflowing rivers of Tokyo Bay. For the investigation of spatial distribution of VMSs in river water, sites (also known as environmental standard sites) at mid- and down-streams (near the river mouths) of six major inflowing rivers into Tokyo Bay (Ara River, Sumida River, Edo River, Yoro River, Tama River, and Tsurumi River) were selected for sampling (R-40–R-48, Table A1 in the Supporting information). Moreover, a detailed monitoring survey was conducted at environmental standard sites of the Ara River, Sumida River, and Naka Rivers (R-01–R-39, Table A1). In total, forty eight river water samples (grab) were collected using a clean stainless steel bucket and stored in 600-mL screw-top glass bottles without any headspace to prevent evaporation of the target chemicals. Grab samples of effluents from STPs ($n = 25$) that serve populations ranging from 707 to 1,730,000 were taken from around Tokyo Bay (Japan Sewage Works Association, 2013; Saitama Sewage systems Agency, 2013). The STPs studied were categorized as small- and large-scale plants based on the population served (small scale: <1000 people; large scale: ≧1000 people). Further details of the samples such as location and sampling date are given in Tables A1 and A2 (Supporting information). The water samples were kept in ice-filled cooler boxes immediately after collection and transported to the laboratory, and stored at 4 °C until analysis. The samples were analyzed within 4 days after collection. Water quality parameters such as suspended solids (SS) and total organic carbon (TOC) were obtained. TOC was measured using Shimadzu TOC-L equipped with ASI-L auto sampler (Shimadzu