SEASONAL VARIATION AND TEMPERATURE-DEPENDENT REMOVAL EFFICIENCIES OF CYCLIC VOLATILE METHYLSILOXANES IN FIFTEEN WASTEWATER TREATMENT PLANTS

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Introduction

The cyclic volatile methylsiloxanes (cVMS) -octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) - are used in many commercial applications. They are used as intermediates for the polymerization of polyorganosiloxanes in cosmetic and personal care products, defoamers, sealants, adhesives and coatings [1-3]. cVMS have $\log K_{OW} > 6$ and $\log K_{AW} > 2$ indicating they have high long-range atmospheric transport (LRAT) potential; however they remain in the atmosphere even under low Arctic temperature conditions. Consequently, atmospheric deposition processes represent negligible inputs to the aquatic environment. Direct inputs from wastewater treatment activities influence cVMS concentrations in water and are therefore important point sources to the surrounding aquatic environment. The removal efficiencies of cVMS in WWTPs play a key role in the discharge of cVMS to the aquatic environment. Only a few studies have been completed to survey the concentrations in both influent and effluent of WWTPs to evaluate the removal efficiency of wastewater treatment. All the studies have demonstrated that cVMS can be well removed by WWTPs using secondary activated sludge processes. In our previous studies, greater than 80% removal efficiencies (>80%) were observed in summer (high temperature) sampling from 11 Canadian WWTPs using chemically assisted primary, secondary activated sludge, and lagoon [4] processes.

These studies have provided necessary fundamental data to show that cVMS can be effectively removed through WWTPs. However, none of the studies has explored the occurrence and concentrations of cVMS in various WWTPs based on long monitoring periods, which made it difficult to describe the seasonal variations of cVMS in the influent and effluent, and the temperature dependence of removal efficiency. Previous studies have provided proof that pharmaceuticals and personal care products (PPCPs) varied seasonally in wastewater influent and effluent [5]. The removal efficiencies of some PPCPs were temperature-dependent [5]. Hence, the objective of this study is to determine the seasonal variations of concentrations in influent and effluent, and removal efficiencies in various types of municipal WWTPs. These treatment types include secondary activated sludge (SAS), aerated lagoon (ALA), facultative lagoon (FLA), and chemically-assisted primary (CAP). We also focused on the special emphasis about the comparison of temperature dependence for the four treatment processes in a 3-year continuous investigation of 15 WWTPs.

Materials and methods

Fifteen WWTPs in Southern Ontario and Southern Quebec were sampled in low- and high-temperature periods during 2010-2012. These WWTPs include seven activated sludge plants, one facultative lagoon, two aerate lagoons, and two chemically-assisted primary plants. At least two sets of samples were collected in low- and high-temperature months under normal weather conditions with no precipitation. Influent and effluent samples were collected without headspace in 100-mL glass bottles and quickly crimp sealed with Teflon coated butyl septa and aluminum seals. Duplicate trip and field blanks consisting of 100 mL of Milli-Q water sealed in the bottles were included in each sampling event. Trip blank samples (used to evaluate bottle contamination) were sealed for the entire sampling trip and procedure. Field blanks samples (used to subtract possible diffusive contamination) were uncapped and exposed to the air for one sampling cycle in the sampling location and recapped after finishing the sampling procedure. The pretreatment and analysis of samples is described in our previous studies [4, 6].

Results and discussion

Concentrations of cVMS in all influent samples from the sampling campaigns in warm and cold seasons are listed in Figure 1. cVMS show seasonal variations (paired *t*-test), which can be explained by the specific usage of cVMS. cVMS are mainly used in cosmetic and personal-care products such as antiperspirant, body lotion and cream [7], which occurred more frequently during warmer months; cVMS exhibited correspondingly higher concentrations in the warm season and lower concentrations in the cold season for most of the WWTPs.

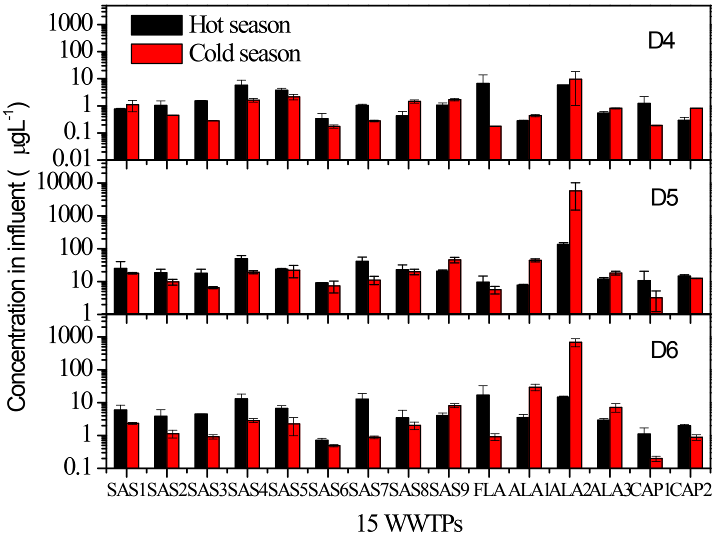

Figure 1. Influent concentration variations for D4, D5, and D6 in warm and cold seasons collected from 15 WWTPs with four types: secondary activated sludge (SAS), aerated lagoon (ALA), facultative lagoon (FLA), and chemically-assisted primary (CAP).

The proportion of residential wastewater versus industrial inputs might have an influence on influent concentrations. The Site LA had much higher concentrations of D5 in winter (5000 µg L-1) compared to summer (135 µg L-1). This WWTP received about 80% municipal wastewater coming from >10 000 residences and 20% industrial wastewater including a facility manufacturing cosmetic and personal care products incorporating cVMS. The flow rate of municipal wastewater decreased in winter due to lower consumption of water, which makes the cVMS higher concentrations with lower dilution from industrial effluent. In addition, the fluctuation of influent flows would affect the influent concentrations due to the use of personal care products. The distinct diurnal variability of cVMS was observed with cVMS concentrations reach maximums with the morning and evening high influent flows and reach minimums with overnight and afternoon influent flows. Morning and evening high mass flows contributed approximately equally to 40% of the total daily cVMS mass. However, the sampling times were kept consistent in various seasons in this study at morning high flow, and thus, the effects of influent flow variability were excluded as a main influencing factor.

Concentrations of cVMS in all effluent samples from the sampling campaigns in warm and cold seasons are listed in Figure 1B. In comparison with the influents, cVMS show opposite seasonal variation patterns in the WWTP effluents: lower concentrations in the warm season and higher concentrations in the cold season. The concentrations in the WWTP effluents could be affected by several factors such as temperature and rainfall. Temperature is likely the most important factor for biodegradation efficiency in removal for many PPCPs, resulting in lower effluent concentrations. Many studies suggested that a higher rate of biodegradation during summer led to higher effective elimination and lower concentration of PPCPs in the effluent [8]. Temperatures in the aeration tanks of two WWTPs ranged between 10-14 °C in cold season, which is unfavorable for activated sludge, whereas when temperatures rose to 25-27 °C in summer, biodegradation efficiency increased. For cVMS, biodegradation plays a very small role in the removal because their low water solubilities are thought to limit their biological availability [9].

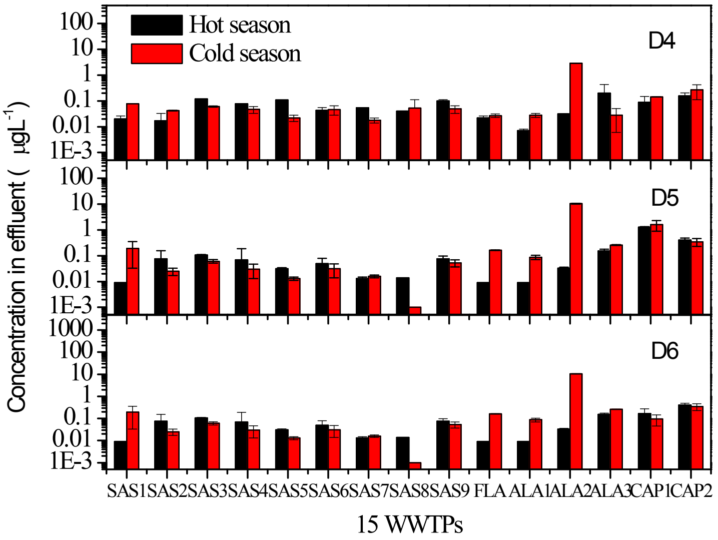

Figure 2. Effluent concentration variations for D4, D5, and D6 in warm and cold seasons collected from 15 WWTPs with four types: secondary activated sludge (SAS), aerated lagoon (ALA), facultative lagoon (FLA), and chemically-assisted primary (CAP).

Temperature would also affect the partitioning processes in the air-water-biomass system. Therefore the removal mechanisms of cVMS during municipal wastewater treatment which is controlled by volatilization into the air and adsorption onto sewage sludge in WWTPs is also affected [10]. cVMS concentrations notably increase in effluent due to lower partition coefficients of air/water and biomass/water resulting in lower sludge adsorption and volatilization.

WWTPs removed cVMS via volatilization and partitioning to solids during their normal operation. The removal efficiencies of cVMS by various treatment types are compared in Figure 3. cVMS can be highly removed in four types of WWTPs in summer, with mean removal efficiencies >70%. Therefore, there is no apparent difference in removal efficiency from WWTPs with different treatment types. Particularly, the removal efficiencies are >80% in SAS, ALA, and FLA. The CAP has relatively lower removal efficiency compared to the other WWTPs. This process uses chemically-assisted settling to remove suspended solids, with a shorter retention time and no aeration of the wastewater, giving fewer opportunities for adsorption or volatilization removal mechanisms. In contrast to the CAP, the other mechanical treatment plants have primary treatment followed by secondary activated sludge treatment, with aeration and longer hydraulic retention times.

Temperature has more influence on the FLA and CAP than SAS and ALA. There is no apparent difference in removal efficiency (>80%) from WWTPs with the SAS and ALA treatment types in winter. However, the removal efficiencies of the FLA and CAP show a downward trend, decreasing rapidly from almost 100% to 66% and from 78% to 59% for FLA and CAP.

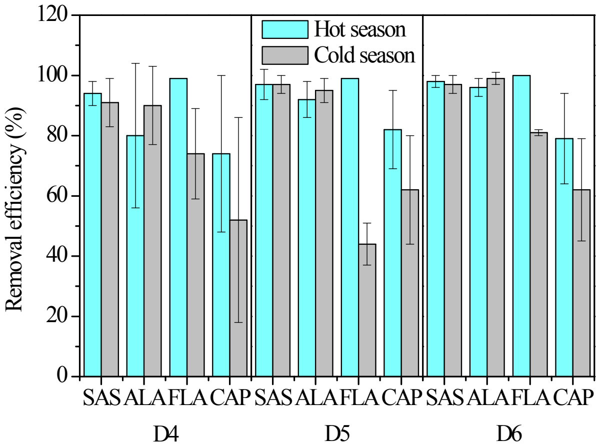

Figure 3. Comparison of removal efficiencies in warm and cold seasons in four types of WWTPs: secondary activated sludge (SAS), aerated lagoon (ALA), facultative lagoon (FLA), and chemically-assisted primary (CAP).

The removal efficiencies of cVMS in SAS and ALA are higher than FLA and CAP in winter due to SAS and ALA both having aeration processes. Our previous studies found that the aeration tank played a key role in removing cVMS in a SAS plant, in which cVMS can be removed >30% by the aeration process. In winter, cVMS preferred stay in the water phase compared to the air or sludge phases because the K_{AW} and K_{OC} values decrease with decreasing temperature (Figure S1 and S2). Therefore, the WWTPs using the FLA and CAP processes without aeration have lower removal efficiencies than those using the SAS and ALA in winter. In Canadian winters, the lagoons can be completely or partially frozen. Volatilization of cVMS can be decreased or halted, resulting in lower removal efficiency. In addition, temperature has an influence on the biomass in the lagoon: the biomass would decline and the fraction of organic carbon in the particle phase and lagoon sediment decreased. The corresponding adsorption to particles and the sediment phase will decrease.

Temperature affects many parameters in the WWTP such as mass transfer coefficients, viscosity-dependent particle settling, sludge bulking and sedimentation [11]. Consequently, the evaluation of temperature-dependent partition coefficients for air/water (K_{AW}) and organic carbon/water (K_{OC}) was performed in this study. K_{AW} and K_{OC} values play very important roles in controlling the two removal pathways of volatilization and adsorption to sludge. Although biodegradation rate is temperature dependent [11], it was not considered in our study because cVMS resist biodegradation . The selected temperature range (0–40°C) is only for illustrative purpose, since the water temperature in the WWTPs should fluctuate less than this range. The values of K_{AW} and K_{OC} are a strong function of temperature, with increases of 66–179 and 6–10 times for K_{AW} and K_{OC} respectively for a temperature increase from 0–40°C. These results suggest that cVMS preferred to enter into air or the organic phase when the temperature increased, and preferred to stay in the water phase in cold seasons, resulting in lower removal efficiency in winter than in summer.

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