Volatile methyl siloxanes in WWTPs: where do they come from?

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Introduction

Being synthetic compounds, volatile methylsiloxanes (VMSs) belong to the class of organosilicons. Based on the structure, VMSs can be divided into two major groups, linear volatile methylsiloxanes (lVMSs) and cyclic volatile methylsiloxanes (cVMSs) (Horii et al., 2019). Due to their interesting properties (low water solubility and surface tension, thermal stability, etc.), they are widely used in the manufacture of innumerable types of products such as cosmetics, medical devices and electronics (Varaprath et al., 1996).

After consumption, up to 10% may be released to the drain and will eventually reach at wastewater treatment plants (WWTPs) (Montemayor et al., 2013). These compounds are drawing more and more attention from environmental scientists and regulatory authorities. Their dispersion in the environment may be augmented by partitioning between air and water/soil/biota, leading to a ubiquitous presence (Kim et al., 2018). Furthermore, they may also jeopardize biota living in the discharge media, due to a potential bioaccumulation and biomagnification, that still requires further indagating (Bernardo et al., 2022a).

In this study, seven VMSs (L3, L4, L5, D3, D4, D5, D6) were investigated in wastewater collected from four different sources that were forwarded to a WWTP in Portugal. Most literature revolved around the analysis of influent and/or final effluent of the WWTPs, rather than contrasting the different wastewater sources that reach at the WWTP entrance, to identify the main routes of contamination. Not only did the stipulated approach allow the evaluation of similitude of VMSs levels, relatively to wastewaters from other countries, but also fathom possible sources of contamination. To analyse different scenarios, a long monitoring period was selected, to include the four seasons (autumn, winter, spring and summer). Several consecutive days were contemplated, to try to pin down trends in the concentrations. Finally, a risk assessment was conducted to gauge the potential risk related to the emission in the aquatic media.

Materials and Methods

The studied influents were forwarded to a WWTP established in the north of Portugal. The WWTP treats wastewater originated from four different inputs. It comprises: a) Entrance 1: Influent that covers urban, rural and industrial areas around the WWTP; b) Entrance 2: Influent from an outfall encompassing the areas near the beaches; c) Entrance 3: Influent forwarded from an industrial area close to the WWTP; d) Entrance 4: It consists in urban influent (including a hospital, the University Campus and the port). Altogether, 110 composite samples (24 h) (analyzed in duplicate) were collected in December 2020 and also February, June and August 2021, namely: 28 at Entrance 1, 28 at Entrance 2, 26 at Entrance 3 and 28 at Entrance 4. The sampling equipment was programed for time-paced composite sampling with sampling bottles (500 mL) of HDPE. To ensure safe transport, cooler boxes were utilized, and the samples were stored at -20 °C.

The extraction procedure relied on a small-scale liquid-liquid extraction method, while the analysis was done by gas chromatography-mass spectrometry analysis (Bernardo et al., 2022b). In short, the extractions were carried out using 50 mL conical polypropylene centrifuge tubes. It only required 30 mL of wastewater sample and 10 mL of n-hexane as extraction solvent, alongside 125 ng of internal standard. The samples were vortexed (5 min), sonicated (10 min) and centrifuged (5 min) and reduced to 500 µL, before injecting in the Varian Ion Trap GC–MS system. Retention times and the relative abundance of the monitored ions allowed the identification of each VMS (details in Bernardo et al., 2022b).

Results and Discussion

VMSs in wastewater: All seven VMSs were detected at least once in each entrance sample. D5 was the one that presented higher detection frequency, ranging from 75% (Entrance 1) to 100% (Entrance 2 and 4). After it were D6, L5, D4 and L4, with D3 and L3 being the least detected. When analysing the sampled year, that is, including all four seasons, Entrance 1 presented a mean value of 2.1 µg L^{-1} (range: <MDL – 7.4 µg L^{-1}), Entrance 2 of 20.2 µg L^{-1} (range: 1.4 – 68.1 µg L^{-1}), Entrance 3 of 4.5 µg L^{-1} (range: <MDL – 15.1 µg L^{-1}) and Entrance 4 of 6.4 µg

L^{-1} (range: 0.9 – 19.6 μg L^{-1}). Significant differences ($p < 0.05$) among entrances were detected mostly during spring season, followed by winter. Autumn presented significant differences between Entrance 1 and Entrance 2 ($p = 0.021$) and Entrance 1 and Entrance 4 ($p = 0.009$), while in summer only between Entrance 2 and Entrance 3 ($p = 0.031$). In general, these results demonstrate that different influents may present distinct concentrations of VMSs, even if the samples are collected in the same season, demonstrating the variability by the type of influent. Analysing the whole sampled year, the mass flows mean values were 18.8 g day^{-1} (Entrance 1), 23.7 g day^{-1} (Entrance 2), 0.7 g day^{-1} (Entrance 3) and 101.8 g day^{-1} (Entrance 4).

Risk asssessment: Considering the combination of the 4 Entrances in a single input and considering a direct discharge without any treatment (Figure 1), 4 samples (14%) exhibited high risk, mainly due to the presence of D5, while the other 24 samples (86%) demonstrated medium risk.

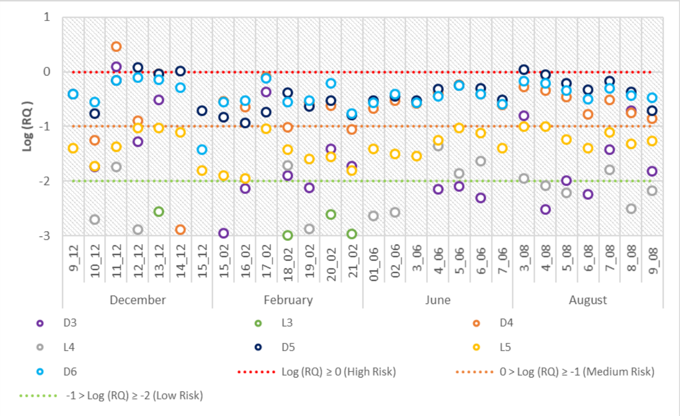

Figure 1. Environmental risk assessment for the 4 entrances combined.

Conclusions

The VMS concentrations varied randomly between each day, suggesting a variable usage by the consumers or industry instead of a constant discharge. But this does not preclude that in other situations/case studies, depending on the type of influent, the results may present more consistent values of concentration or even an identifiable pattern. In cases with direct discharge without any treatment, a risk to the environment may occur. However, it is still important to check their behaviour in the WWTP treatment steps to verify if the risk levels decrease or not, before being discharged in the receptor media. Not only that, but after discharge, VMSs may still come into contact with biota and other phenomena may occur, such as biomagnification, spreading these compounds across food webs or produce chronic risks after long-term exposure.

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