Occurrence and behaviour of volatile methyl siloxanes (VMSs) in biogas from wastewater treatment plants

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Introduction: Biogas is one of the most promising sources of renewable energy. It can be obtained from residues, such as wastewater treatment plant (WWTP) sludge, through anaerobic digestion. However, its use can be limited by the presence of impurities, which can reduce the calorific power of biogas and even present toxic properties (Gao et al., 2018). Among these impurities, volatile methyl siloxanes (VMSs) are becoming one of the most problematic. These silicon-based compounds are extensively used in industrial and personal care products (PCPs) and find their way into WWTPs via residual waters. Due to their high volatility and low solubility in water, VMSs end up in the anaerobic digester's sludge, where they vaporize and become part of biogas. Once this biogas is combusted, VMSs form SiO_2 deposits along the combustion system, corroding valves and turbines and reducing the efficiency of the process (Shen et al., 2018).

In order to evaluate the potential of WWTP biogas to be used as fuel it is important to know its VMSs concentrations. However, nowadays in Portugal siloxanes are not monitored in WWTP biogas, despite it is already used for in-facility energy generation, and corrosion problems have been reported in some plants. Therefore, the main objective of this study is to assess the occurrence, levels and composition of VMSs in WWTPs treating diverse kinds of wastewaters. Thus, it will be possible to evaluate different VMSs removal strategies and improve the energetic potential of biogas in a country still extremely dependent on fossil fuels.

Materials and Methods: A sampling campaign was launched in the summer of 2019, as some previous studies indicate that the load of siloxanes in WWTPs may be peaked in the warmer months due to the heavy affluence of tourists to the beaches and subsequent use of VMS-containing PCPs (Ratola et al., 2016). A total of 18 WWTPs were sampled along Portugal. Biogas was collected at the exit of the anaerobic digester, by means of Tedlar® bags and analyzed by GC-IMS-SILOX®. Four linear (L2-L5) and three cyclic (D3-D5) VMSs were quantified.

Results and discussion: Average values of total Si were 2382 ± 522 $\mu g/m^3$, which is superior to the recommended E.U. limits to be suitable for diluted injection into the natural gas grid (1000 $\mu gSi/m^3$) (CEN, 2016). This value was exceeded in every WWTP, with only six plants showing values below 2000 $\mu g/m^3$. These results can be explained by the lack of siloxane-specific biogas purification system in any sewage plant.

Concentration ranges and overall average values of linear VMSs were lower than cyclic siloxanes (**Figure *1***). This is because cyclic VMSs are more used than linear siloxanes in the formulations of PCPs (Horii and Kannan, 2008). Regarding compound-specific data, occurrence and mean values of linear VMSs showed a direct correlation with the chain length, except for L5 which was not detected at all. Thus, L2 was only present in one WWTP, L3 occurred only in three WWTPs, and L4 was detected in eight plants. The mean concentrations were 17 ± 9 (L2), 23 ± 15 (L3), and 26 ± 15 (L4) $\mu g/m^3$. This trend is explained by the inherent chemical characteristics of VMSs: their solubility and volatility decrease when increasing the chain length, which reduce their chances to be removed from sewage during early stages of water treatment process (Kuhn et al., 2017). The lower presence of L5 if compared with shorter linear VMSs has been reported in previous studies, and may be explained by its minor use in PCPs (Paolini et al., 2018).

Concerning cyclic VMSs, the same chain-length driven pattern was described regarding their occurrence and levels. Thus, D3 was present in thirteen WWTPs, while D4 and D5 were detected in all of them. The average levels of D3 were 62 ± 6 $\mu g/m^3$, while D4 displayed 491 ± 275 $\mu g/m^3$. However, the prevalent siloxane was D5, with average values of 5683 ± 1410 $\mu g/m^3$. In every WWTP, D5 apportioned for more than 90% of the total mass of VMSs, being above upper quantification limit of the measuring equipment (7200 $\mu g/m^3$) in seven facilities. A similar outcome has been observed in the literature, since this compound is the more extensively used VMSs in PCPs formulations (European Chemicals Agency, 2016).

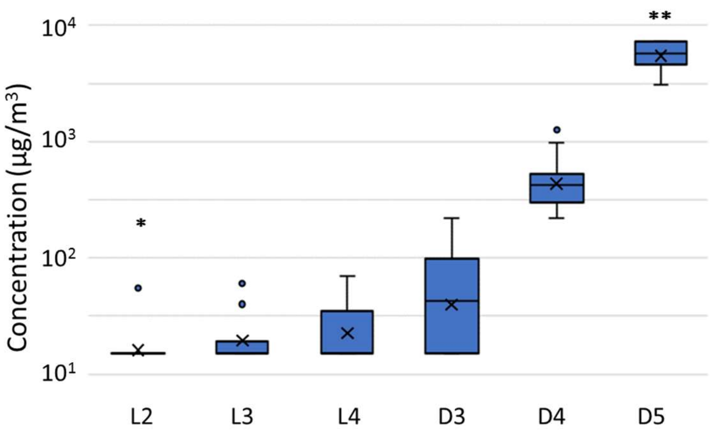

Figure 1: Distribution of VMSs among the sampled WWTPs (n=18). L5 was not detected in any sample. Black horizontal lines represent median values; crosses represent average values; bottom and upper limits of the boxes represent first and third quartile, respectively; lower and upper whiskers represent the minimum and maximum values, respectively; colored dots represent outliers.*: Only one sample above limit of detection (30 µg/m^3); **: Seven samples were above upper limit of quantification (7200 µg/m^3).

Conclusions and ongoing research: Levels of total Si in every WWTP biogas were higher than European standards of 1000 µgSi/m^3. D5 was the most prevalent VMS, representing more than 90% of total Si content in every WWTP. This study reveals the need to implement siloxane removal strategies in Portugal. Mass balances of VMSs within biogas-producing digestors in WWTPs are being performed to understand the fate of every compound and help the facility managers in the design of optimal approaches to optimize the energetic valorization of the biogas produced.

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