Presence and fate of volatile methylsiloxanes in anaerobic digesters from WWTPs

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Introduction

Formed by a Si-O backbone saturated with methyl groups, volatile methyl siloxanes (VMSs) are a family of anthropogenic compounds, extensively used in the formulation of numerous industrial and consumer products, such as cosmetics and personal care products (PCPs) (Gaj and Pakuluk, 2015). After their use, a significant part of VMS release to the environment is through wastewaters, ending up in wastewater treatment plants (WWTPs) (Capela *et al*., 2016). Inside these facilities, VMSs congeners are distributed among the different matrices present in the treatment steps, depending on their chemical properties. Being lipophilic, a high percentage of VMSs tend to partition to the sludge, and their semi-volatile character also favours volatilization into the atmosphere (de Arespacochaga *et al*, 2015). The combination of these two properties is crucial when WWTPs have anaerobic digesters for the sludge, in which they produce biogas that can be used as a renewable fuel to produce calorific and electric energy, mainly via cogeneration systems (Paolini *et al*, 2018). In fact, when sludge is digested, a portion of the VMSs is to biogas, potentiating a severe problem in the operation of cogenerators (and other energy-producing approaches). When biogas is combusted, VMSs form microcrystalline SiO_2 particles that deposit and corrode different parts of the engines, lowering the energetic yield and causing costly part replacements and days without work (Bragança *et al*, 2020). Therefore, monitoring these compounds within WWTPs is crucial to design strategies for their removal and treatment.

In current literature it is possible to find only a few studies focused on monitoring VMSs in the water and sludge lines of different WWTPs (*e.g.*, Bletsou *et al*, 2013), but there are no studies focusing on the presence and dynamics of VMSs in biogas digesters (Horii *et al*, 2019). To overcome this gap, this study aims to assess the partition and fate of VMSs in anaerobic digesters by collecting and analyzing samples of sludge (both pre and post digested) and biogas in several WWTPs in Portugal.

Materials and Methods

Several sampling campaigns were conducted in September 2021 in five Portuguese WWTPs (4 near the coast and 1 inland) with similar technical characteristics between them, although serving different population equivalents. 250 mL of input and output sludge to the anaerobic digesters were collected using pre-washed polypropylene flasks and biogas was collected in the same days at the exit of the anaerobic digester using 1 L Tedlar® bags.

The analytical protocol for sludge samples consisted of a LLE with a 1:1 mixture of n-hexane and acetone as extraction solvent. The extracts were vortexed for 5 min, placed in an orbital shaker for 2 h, centrifuged for 5 min at 4000 rpm ad the supernatant was collected and blown down to 1 mL with a gentle N_2 stream before quantification by GC-MS. For biogas, the samples in the bags were analysed directly using a gas chromatograph (GC-IMS-SILOX) especially designed to quantify VMSs. Three linear (L3-L5) and three cyclic (D3-D5) VMSs were chosen to perform the mass balance, as D6 could only be analyzed in sludge and L2 only in biogas.

Results and Discussion

Sludge concentrations: Regardless of plant and compound assessed, the input concentrations of total VMSs were higher (from 80 up to 400 µg/L) than the output concentrations (from 30 up to 120 µg/L), as expected. The inland plant showed the highest entry levels, which could be related to the proximity to industrial and agricultural sources that can have a stronger impact in a less densely populated area. Cyclic VMSs were predominant in the profile of both input and output sludge of every WWTP, with D5 representing more than 85% of the total concentrations of VMSs regardless of the plant. This VMS is typically the most used in the formulations of numerous products and also the most found in almost all environmental matrices (Jiménez-Guerrero and Ratola, 2021). D6 was the second most prevalent, probably due to its use in waxes and polishes (ECHA, 2019). With regard to linear VMSs, L5 was the only detected compound and is the most frequently found in sludge due to its major use and higher lipophilicity comparing to the others (Capela *et al*, 2017).

Biogas concentrations: As seen in Figure 1, cyclic VMSs were also predominant in the profile of every WWTP, again with the prevalence of D5, which is not surprising given its percentage in sludge and volatile properties. The presence of D4 is also noticeable in most WWTPs. Since some plants showed a high difference in the content of this compound between input and output sludge, this could suggest an almost complete volatilization into biogas. Linear VMSs were almost absent, except for L2 in plant 5. Plants 3, 4, and 5 showed levels of total

VMSs above 5 mg/m^3, the limit recommended as safe by some internal combustion engine manufacturers (de Arespacochaga *et al*, 2015), which highlights the causes for concern.

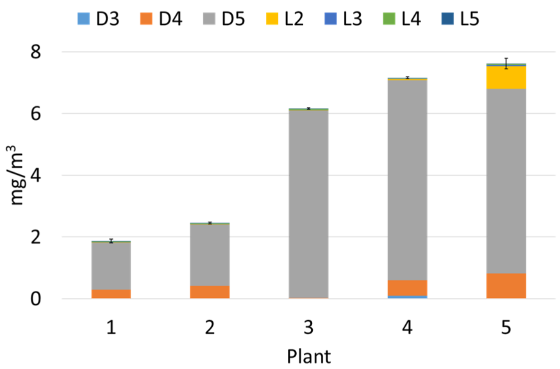

Figure 1. Levels of VMSs in biogas collected from five WWTPs in Portugal.

Mass balance: The mass balance of all the WWTPs as a whole suggest that high molecular weight VMSs present a better consistency between input and output values in anaerobic digesters than low molecular weight compounds. D3 and L3 showed average recovery values above 100%. This is explained by the fact that compounds were mostly not detected in the in the biogas analyzer (GC-IMS-SILOX). Consequently, the limits of detection (LODs) of the equipment divided by two were used instead to allow an estimate, being in some cases higher than the concentrations found in input sludge by GC-MS, which has a lower sensitivity. D4 presented a total recovery of 73 ± 49%. Most of this mass partitioned to the biogas (47 ± 33%) while a smaller portion (26 ± 19%) remained in the sludge. An opposite trend was shown by D5, which yielded total recoveries of 71 ± 19%, but most of its mass remained in the sludge (45 ± 24%) while approximately one quarter was transferred into biogas (26 ± 8.4%). This different behavior could be explained by the differences in their boiling points (176 and 211 °C for D4 and D5 respectively). Although D6 was not displayed by GC-IMS-SILOX, the output sludge incidence suggests its presence mostly in this matrix. Despite their low concentrations in sludge and biogas and poor recovery results, these point towards a higher migration of L4 to biogas, and a higher affinity of L5 for the output sludge.

Conclusions

Cyclic VMS, and more specifically, D5 were predominant in both biogas and sludge, while linear VMSs showed contributions lower than 5% in every matrix and WWTP. Total VMSs were higher in input than in output sludge regardless of WWTP, suggesting a migration of VMSs from sludge to biogas. Good overall mass balances were obtained for D4 and D5, suggesting no transformation to lower molecular weight VMSs in the digesters. The levels of total VMSs in biogas of three WWTPs were above the threshold proposed by some internal combustion engine manufacturers. Therefore, VMSs removal technologies should be considered for those facilities.

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