

Occurrence and fate of volatile methylsiloxanes in an urban WWTP

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Introduction

Volatile methylsiloxanes are non-organic silicon compounds formed by Si-O bonds with aliphatic chains attached to silicon atoms. Due to their properties, VMSs are widely used in industrial processes and added in the formulation of numerous consumer products such as detergents, adhesives, paints, cosmetics, and personal care products (Rücker and Kümmerer, 2014). Since VMSs are semi-volatile, they are predominantly released to the atmosphere after their application. However, many end up in landfills and wastewater from the washing-off of many products (Capela *et al.*, 2017). Although reported as potentially toxic, with carcinogenicity and bioaccumulation capability, their impact on living organisms is still poorly known (Gaj and Pakuluk, 2015).

In wastewater treatment plants (WWTPs), VMSs arrive via grey waters, where the different compounds partition to the different environmental matrices depending on their chemical properties. However, according to some authors, about 60% of the entering VMSs partition into the sludge due to low water solubility and high molecular weight (Capela *et al.*, 2017). Once there, they can migrate to biogas under anaerobic digestion, and with the biogas combustion, are partially oxidized into SiO₂ particles that deposit on the inner surface of equipment and get to the engine oil (Gaj and Pakuluk, 2015).

In order to design strategies to reduce the load of VMSs in biogas due to the aforementioned consequences, it is important to study the occurrence and fate of VMSs in WWTPs first. In this context, this work aims to investigate the occurrence of four cyclic (D3-D6) and four linear (L2-L5) VMSs in a municipal WWTP, including wastewater, sludge, air, and biogas samples analysis, covering the full study of presence and fate of VMSs in the process. To do so, we designed a sampling campaign that consisted in 14 days collecting water, sludge, biogas, and passive air samples. All the matrices were analyzed following a low-solvent approach, as recommended by the green analytical sample preparation principles (López-Lorente *et al.*, 2022).

Materials and Methods

Wastewater, sludge, air and biogas samples were collected during 14 consecutive days in August 2020 in a municipal WWTP located in Portugal. A total of 250 mL of wastewater were collected every six hours at four different stages of the treatment process in inert polypropylene (PP) bottles. Sludge samples (also 250 mL in PP bottles) were taken at six points. Wastewater and sludge samples were frozen at -20 °C until analysis. Passive air samples were deployed and collected after 14 days at four points of the WWTP, using two aluminum mesh cylinders (10 cm long, 2 cm diameter) filled with 10 g of XAD-2 resin protected with a stainless-steel cover case in each location. After collection, the mesh cylinders were wrapped in aluminum foil and stored in the freezer at -20 °C until analysis. Finally, biogas samples were collected in five different days using 1-L Tedlar bags and analyzed within 24 hours of collection.

The analytical protocol for wastewater samples is a liquid-liquid extraction (LLE) procedure in which 30 mL of wastewater were added in 50 mL PP tubes to 10 mL of hexane and vortexed for 5 min, followed by 10 min in an ultrasonic bath. The extract was evaporated to a final volume of 1 mL, under a gentle N₂ stream. For liquid sludge samples it consisted of an 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 and the supernatant was collected and blown down to 1 mL under N₂. For the dry sludge, the protocol was based on QuEChERS, a solvent-saving dispersive solid-phase extraction (SPE) method. In the first step, 2.5 g of sludge was added to 2.5 g of MgSO₄ and 5 mL of hexane, vortexed for 1 min, placed for 10 minutes in an ultrasonic bath and finally centrifuged at 2760 g for 5 minutes, so the organic phase was separated. This process was repeated twice, the first time using 5 mL of a mixture of hexane and dichloromethane (1:1) and the second time using 5 mL of a mixture of hexane and ethyl acetate (1:1). The three extracts were combined in another 50 mL polypropylene tubes, and 300 ng of MgSO₄, 300 ng of PSA and 50 ng of C18 were added. After the three extractions were completed, the sample was vortexed for 1 minute and centrifuged for 5 minutes at 2760 g. The supernatant was transferred into 15 mL vials, blown down to 1 mL under N₂ before quantification. For the passive air samples, an SPE procedure was employed using separation funnels. The 10 g of XAD was placed in the funnel and 30 mL of hexane were initially added. Then, 5 min hand agitation was performed, and the excess solvent was collected in an amber glass jar. The previous step was repeated twice but adding only 10 mL hexane each time. The volume of

the extract was then reduced to 1 mL under N₂. The quantification of all these samples was performed by gas chromatography with detection by mass spectrometry (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

For composite wastewater samples, the mean concentrations of Σ VMSs were 23.49±23.75, 17.35±15.08, 10.76±13.82 and 3.66±5.34 µg/L in influent (WS1), after preliminary treatment (WS2), after primary treatment (WS3) and after secondary treatment (effluent) (WS4), respectively. Cyclic siloxanes consisted in about 99.3% of the total influent mean concentration, with D3 consisting 59.9% of the total. The average concentration of VMSs along the water line is presented in Table 2. In the hourly samples, those collected at 0h have higher VMSs levels.

Table 1. Mean VMSs content in composite wastewater samples collected for 14 days in four sampling points

VMS	Influent (WS1) (µg/L)	Preliminary treatment (WS2) (µg/L)	Secondary treatment (WS3) (µg/L)	Effluent (WS4) (µg/L)
D3	14.08 ± 17.38	7.76 ± 12.84	6.20 ± 13.72	1.84 ± 3.85
D4	1.24 ± 1.47	1.17 ± 1.41	0.77 ± 0.98	0.57 ± 1.00
D5	6.68 ± 5.77	5.71 ± 3.01	2.41 ± 1.51	0.60 ± 1.06
D6	1.33 ± 1.05	2.56 ± 1.77	1.32 ± 0.96	0.61 ± 0.79
L3	0.02 ± 0.02	0.01 ± 0.01	0.01 ± 0.03	0.02 ± 0.05
L4	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
L5	0.13 ± 0.13	0.13 ± 0.07	0.05 ± 0.03	0.01 ± 0.02
Mean Total	23.49 ± 23.75	17.35 ± 15.08	10.76 ± 13.82	3.66 ± 5.34

The mean values in sludge samples present a VMSs profile in which D5 is predominant, followed by D6. The total content of VMSs is reduced along the sludge line in 75.82±8.90%. The anaerobic digestion is where the content of total VMSs is most reduced, probably due volatilization into the biogas, decreasing its quality and energy yield. In air samples, VMSs concentrations showed mostly D5 and D4 in its composition, although significant concentrations of D3, D6 and L3 were also found. In the biogas quantification analysis, only D4 and D5 were detected, with mean concentrations of 0.084 ± 0.07 mg/m³ and 7.20 ± 0.15 mg/m³, respectively.

Conclusions

Among the VMSs evaluated, all cyclic and linear were detected in wastewater, sludge, and air samples. On the other hand, only D4 and D5 were detected in biogas. Analysing the concentration profiles, D5 was the siloxane in the highest concentration in most studies, except for the water line where it is surpassed by D3, and indoor passive air, with higher amounts of D3 and D4. Different profiles of composition were observed in the different matrices. In general, during the wastewater treatments, the siloxanes do not tend to degrade, but to transfer to other matrices.

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