Occurrence and fate of volatile methylsiloxanes in an urban WWTP

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Introduction

Volatile methyl siloxanes (VMSs) are a group of organosilicon additives used in cosmetics and personal care products (PCPs). Despite an extensive body of knowledge describing their pernicious effects on aquatic ecosystems and biogas generation, there is still very few papers describing their behavior in wastewater treatment plants (WWTPs) [1]. The **objective** of the present study is to determine the levels and fate of VMSs in a municipal WWTP by performing a mass balance in the different treatment steps of the facility.

Materials and Methods

- 250 mL silicone-free plastic jars were used to collect daily 24-hour composite samples of water and sludge in different points of a WWTP (Figure 1) for 15 days in August 2020.
- During the same period, 5 samples of biogas were taken from the anaerobic digester using 1 L Tedlar® bags.
- Passive air samples consisting of two mesh cylinders containing 10 g of XAD® resin were deployed for the duration of the sampling campaign to estimate the levels of VMSs in air.
- Water and sludge samples were extracted by subsequent steps of LLE in presence of organic solvents (i.e., hexane and acetone) by sonication and separation by centrifugation. Air samples were extracted by hand shaking XAD® resin in a separation funnel containing hexane. The extracts obtained were reduced to 1 mL in GC/MS injection vials under a gentle N_2 stream.
- Vials were injected into a GC/MS, and contents of three linear (L3-L5) and four cyclic (D3-D6) were analyzed.
- Tedlar® bags containing biogas were directly injected into a GC-IMS-SILOX to obtain L3-L5 and D3-D5

Results and Discussion

- Cyclic VMSs are predominant in the entry water. D3 is the prevalent compound in this matrix, since this is the VMSs most extensively used in the PCPs consumed in Portugal [2].
- The secondary treatment is the step where most of the content VMSs is reduced in the water line. This is due to the migration of the most lipophilic congeners (L5, D5-D6) to sludge and the most volatile (L3-L4, D4) to air favored by the activity of the aeration tank in this unit [3].
- 85% of the VMSs load is reduced in the effluent with respect to the entry water.

- The profile of siloxanes in sludge is more consistent than in water, with D5 representing 85-90 % of total VMSs regardless of the treatment step.
- The anaerobic digester is the step where most of the content VMSs is reduced in the sludge line (about 65%). This result is due to the specific characteristics of this process (37 °C and 21 days of retention time) which lead to volatilization to biogas and air.
- Although the final sludge is solid, the profile of siloxanes is similar to the one described for liquid sludge, confirming the consistency of this matrix.

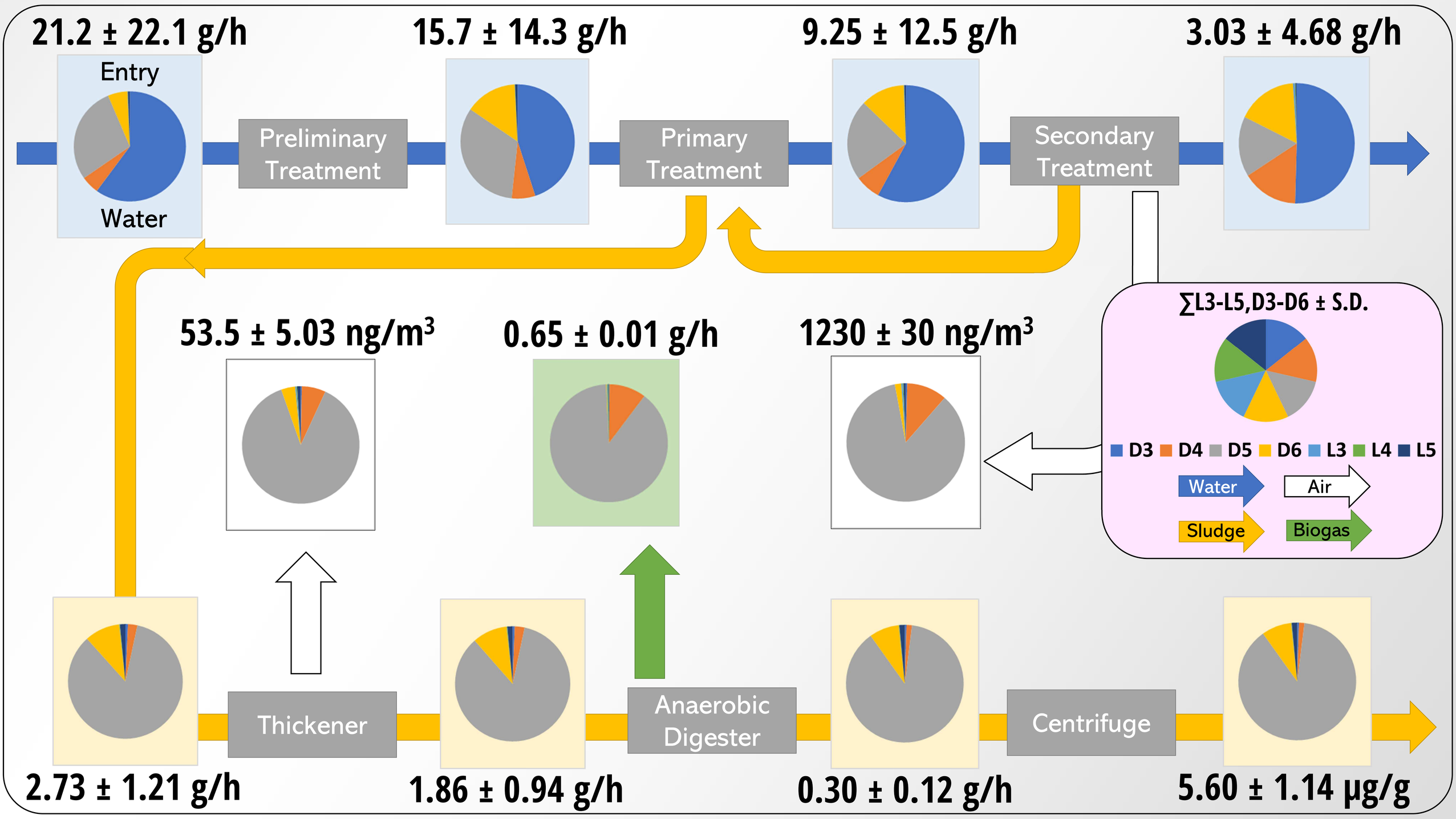

Figure 1: Congener profiles, flows (for water, sludge and biogas), and concentrations (air, final sludge) of total VMSs in the different treatment steps of the WWTP.

- The profile of VMSs in biogas is characterized by the prevalence of D5 (>85%) and significative contents of D4.
- The mean total VMSs concentrations in biogas reached values of 7.97 ± 16.5 mg/m^3. This result is concerning, since some internal combustion engine manufacturers recommend concentrations below 5 mg/m^3 [1] for a safe operation.

- The profile of VMSs in air shows a predominance of D5 both nearby the sludge line (thickener) or the water line (secondary treatment).
- However, concentrations in the secondary treatment are about 20 times higher than in the sludge line, as aeration favors the partition to air.
- The concentrations found were similar to previous studies in literature [4].

Conclusions

A reduction in the content of VMSs is patent along the WWTP. Although in the entry water D3 is the main congener, the rest of matrices are enriched in D5, which suggest that possible transformations of D3 could be taking place in the plant. Measures to reduce the content of siloxanes in sludge or biogas should be taken in order to improve the quality of this renewable fuel and the energy yield of the cogeneration systems.

References

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