



Helping WWTP managers to address the volatile methylsiloxanes issue—Behaviour and complete mass balance in a conventional plant

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ABSTRACT

Volatile methylsiloxanes (VMSs) are a group of additives employed in different consumer products that can affect the quality of the biogas produced in wastewater treatment plants (WWTPs). The main objective of this study is to understand the fate of different VMSs along the treatment process of a WWTP located in Aveiro (Portugal). Thus, wastewater, sludge, biogas, and air were sampled in different units for two weeks. Subsequently, these samples were extracted and analyzed by different environment-friendly protocols to obtain their VMS (L3-L5, D3-D6) concentrations and profiles. Finally, considering the different matrix flows at every sampling moment, the mass distribution of VMSs within the plant was estimated. The levels of \sum VMSs were similar to those showed in the literature (0.1–50 $\mu\text{g/L}$ in entry wastewater and 1–100 $\mu\text{g/g dw}$ in primary sludge). However, the entry wastewater profile showed higher variability in D3 concentrations (from non detected to 49 $\mu\text{g/L}$) than found in previous studies (0.10–1.00 $\mu\text{g/L}$), likely caused by isolated releases of this compound that could be related to industrial sources. Outdoor air samples showed a prevalence of D5, while indoor air locations were characterized by a predominance of D3 and D4. Differences in sources and the presence of an indoor air filtration system may explain this divergence. Biogas was characterized by \sum VMSs concentrations ($8.00 \pm 0.22 \text{ mg/m}^3$) above the limits recommended by some engine manufacturers and mainly composed of D5 (89%). Overall, 81% of the total incoming mass of VMSs is reduced along the WWTP, being the primary decanter and the secondary treatment responsible for the highest decrease (30.6% and 29.4% of the initial mass, respectively). This reduction, however, is congener dependant. The present study demonstrates the importance of extending sampling periods and matrices (i.e., sludge and air) to improve sample representativity, time-sensitivity, and the accuracy of mass balance exercises.

Abbreviations: AR, addition ratio; D3, hexamethylcyclotrisiloxane; D4, octomethylcyclotetrasiloxane; D5, decamethylcyclopentasiloxane; D6, dodecamethylcyclohexasiloxane; DCM, dichloromethane; EA, ethyl acetate; EI, electron ionization; GC-IMS-SILOX, gas chromatography coupled with ion mobility spectrometry; GC-MS, gas chromatography-mass spectrometry; HEX, n-hexane; L3, octamethyltrisiloxane; L4, decamethyltetrasiloxane; L5, dodecamethylpentasiloxane; LLE, liquid-liquid extraction; LMC, lowest measurable concentration; LOD, limit of detection; M4Q, tetrakis(trimethylsilyloxy) silane; PP, polypropylene; PTFE, polytetrafluoroethylene; QuEChERS, quick, easy, cheap, effective, rugged and safe; PCP, personal care product; SIS, selected ion storage; SPE, solid-phase extraction; VMS, volatile methylsiloxanes; WWTP, wastewater treatment plant.

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1. Introduction

Volatile methylsiloxanes (VMSs) are silicon-based compounds formed by Si–O bonds with aliphatic chains attached to silicon atoms (Appels et al., 2008). They have small or medium molecular weights (<500 g/mol), and present structures that can be either linear (L-n) or cyclic (D-n), where “n” indicates the number of silicon atoms in the molecules of each congener (de Arespacochaga et al., 2015). They have low surface tension, high thermal stability, low chemical reactivity, are poorly soluble in water and easily soluble in non-polar solvents (Gaj and Pakuluk, 2015). Due to their properties, VMSs are widely used in industrial processes and added in the formulation of numerous consumer products (Rücker and Kümmerer, 2015) such as detergents, adhesives, paints, lacquers, cosmetics, and with a great extent in personal care products, which include a myriad of contaminants hardly removed from aqueous matrices without advanced treatment (Priya et al., 2022).

Since VMSs are semi-volatile, they are predominantly released to the atmosphere after their application, either in gas form or embedded in the particulate/dust phase (Anh et al., 2021; Zhu et al., 2023). However, after washing off, a significant part arrives to wastewater treatment plants (WWTPs) via grey waters (Bletsou et al., 2013; Capela et al., 2017). In these facilities, VMSs partition differently among the different matrices present (i.e., water, sludge, air) depending on their physical-chemical properties. The most volatile congeners are released to the air in the initial steps of the wastewater treatment. Due to their stability, they can remain unaltered in the air for several days, being able to reach remote locations (Katsoyiannis et al., 2014; Krogseth et al., 2013a). Since there is not a specific treatment for VMSs in WWTPs, a fraction of the most water-soluble compounds can leave via the effluent, where some congeners, considered as ecotoxic for aquatic organisms, are a cause of concern (ECHA, 2019). About 60% of the entering VMSs partition into the sludge, and from there, they can end up in biogas (Bletsou et al., 2013; Cabrera-Codony et al., 2014), when this renewable fuel is produced, by anaerobic digestion, to reduce the energy dependency of the plants (Alengebawy et al., 2022; Chozhavendhan et al., 2023). Once there, VMSs can generate different technical problems in cogeneration or other energy-producing engines when biogas is combusted, from blockage to corrosion (Bragança et al., 2020; Gaj and Pakuluk, 2015). Consequently, the thorough monitoring of VMSs in WWTPs is the first step to take in order to reduce the environmental impacts of siloxanes and ensure the most cost-effective use of biogas as a renewable energy source.

Several strategies have been reported in the literature to cope with this situation. Some studies focused their efforts on analyzing VMSs in wastewater and sludge in WWTPs and undertake, following different kind of approaches, a mass balance for VMSs in these installations (Bletsou et al., 2013; van Egmond et al., 2013; Wang et al., 2015a, 2015b). Also, more recent studies have developed monitoring strategies to elucidate the content of VMSs in WWTPs air (Horii et al., 2019; Li et al., 2016). However, in order to improve the knowledge regarding the fate of VMSs in WWTPs, some issues must be addressed. To begin with, the sampling period in all the aforementioned studies was never above one week, which could be not representative enough depending on the characteristics (e.g. hydraulic retention times, influent sources) of the different WWTPs. Moreover, biogas was never considered, and information regarding VMSs migration to this resource and its subsequent use is lacking. Finally, to the best of our knowledge, apart from a just published first effort of our group (Sánchez-Soberón and Ratola, 2022), there are no studies measuring VMSs inside indoor WWTPs buildings, which could be useful in order to understand the dispersion of these compounds once released to the air.

The main objective of this pilot study is to develop a comprehensive monitoring of four cyclic (hexamethylcyclotrisiloxane (D3), octomethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D6), and dodecamethylcyclohexasiloxane (D6)) and three linear (octamethyltrisiloxane (L3), decamethyltetrasiloxane (L4), and

dodecamethylpentasiloxane (L5)) VMSs in order to understand their dynamics within a conventional WWTP. To do so, an unprecedented combination of samples of wastewater, sludge, indoor and outdoor air, and biogas were collected during a 14-day sampling campaign and VMSs analyzed using different low solvent analytical protocols. Finally, a complete mass balance of VMSs was performed to elucidate the fate of the different target VMSs. With this exercise, we aim to give WWTP managers new insights to develop better VMS removal strategies and improve the energetic efficiency of the plants with the production of a higher quality biogas.

2. Materials and methods

2.1. Sampling location and strategy

Wastewater, sludge, air and biogas samples were collected during 14 consecutive days in August 2020 in the municipal WWTP of Ílhavo (Portugal), managed by Águas do Centro Litoral, S.A. This sampling period was chosen to cover in the best way not only the domestic discharges (more likely to follow a weekly seasonal-dependent pattern) but also industrial effluents (highly variable, and dependent on the industrial activity), thus improving the representativity of the sampling. The plant is prepared to receive effluents of 159,000 population equivalent and treat about 40,000 m³/day of wastewater. The WWTP is based on a secondary treatment system, using biological treatment by an activated sludge system in a prolonged aeration regime, with removal of organic matter. According to the flowchart in Fig. 1, the effluent treatment process comprises two lines: water and the sludge. In the water line, the WWTP has a pre-treatment to remove large solids and grease, primary decantation, biological treatment with air bubbling, and secondary decantation. In the sludge line, the sludge resulting from previous treatments is subjected to thickening or flocculation, FeCl₃ addition to reduce the production of H₂S in biogas, and then forwarded to an anaerobic digester, which results in the production of biogas, further employed as a renewable fuel for energy cogeneration. Finally, the digested sludge is dewatered in a centrifuge. Further details on processing conditions of the WWTP can be consulted in S.I.

For wastewater, daily composite samples were collected at four different stages of the treatment process (Fig. 1): influent (W1), preliminary treatment effluent (W2), primary treatment effluent (W3) and secondary treatment effluent (W4). Also, during the first week of sampling, 6-h composite samples were collected at 0 h, 6 h, 12 h and 18 h. 250 mL PTFE bottles were used and samples were stored at –20 °C immediately after collection until analysis.

Daily composite samples of sludge were taken at six points (Fig. 1): primary sludge (S1), thickened sludge (S2), chlorinated sludge (S3), digested sludge (S4), dewatered (dry) sludge (S5) and secondary sludge (S6). As in the case of wastewater, 250 mL polytetrafluoroethylene (PTFE) bottles were used to collect samples S1-4 and S6. Since dewatered sludge (S5) is solid, approximately 200 g of this matrix were wrapped in pre-baked aluminum foil and stored at –20 °C until analysis into a plastic zip-lock bag.

Biogas point samples were collected in five different days using Tedlar bags prerinsed with biogas, which were then stored below 20 °C, protected from light, and analyzed within 24 h of collection.

Finally, passive air samples were collected at nine points of the WWTP (Fig. 1). Whereas four of them were taken from above treatment stages (preliminary treatment (A1), secondary treatment (A3), sludge thickening (A2), sludge dehydration (A4)), another four were taken inside the office buildings (individual office (A6), laboratory (A7), canteen (A8), workshop (A5)), and one outside the facility to assess background levels (A9). The sampling of indoor and outdoor air in this work was done using two aluminum mesh cylinders (10 cm long, 2 cm diameter) filled with approximately 10 g of XAD-2 resin, both protected with a stainless-steel cover case in each location. Custom-made cylinders and metal cases based on the study by Krogseth et al. (2013b) were

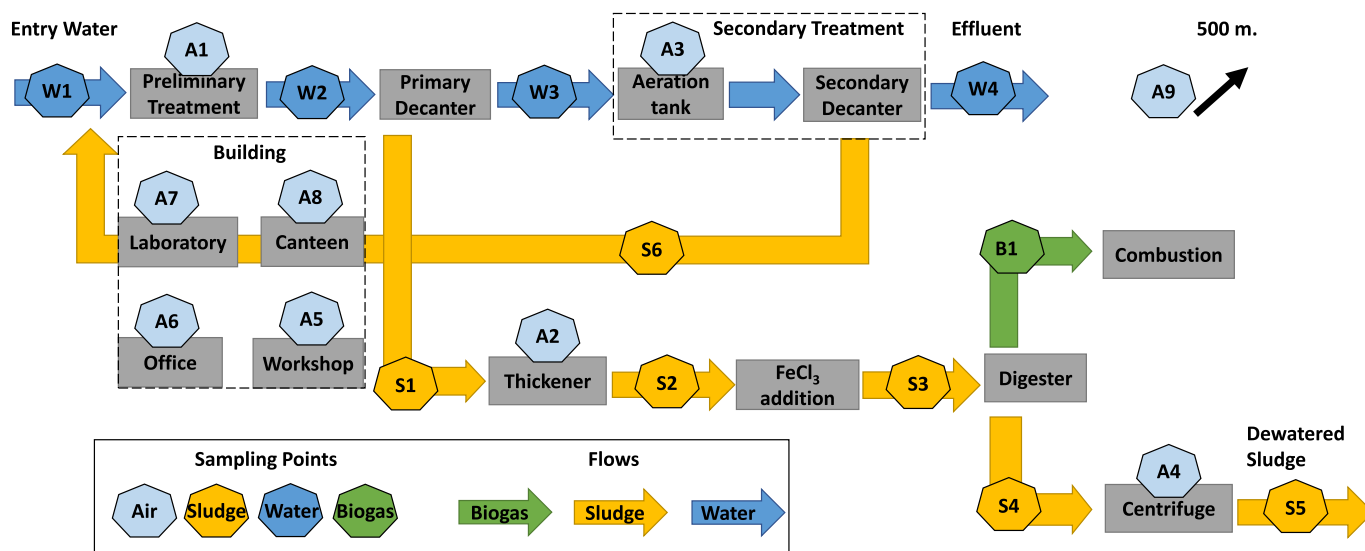


Fig. 1. Flowchart describing the treatment scheme and the sampling points within the WWTP. Point A9 was used as air background and was located 500 m NE of the plant. Details on processing conditions are described in S.I.

deployed at the beginning of the sampling campaign and collected at the end, totaling 14 days of exposure. After collection, the mesh cylinders were wrapped in aluminum foil and stored in the freezer at $-20\text{ }^{\circ}\text{C}$ until analysis.

According to the meteorological data collected at the closest weather station to the WWTP (data from www.ipma.pt), the mean temperature during the period of analysis was $18.6\text{ }^{\circ}\text{C}$, with no occurrence of precipitation.

2.2. Extraction and quantification analysis

The protocols used to analyze the four matrices were, as much as possible, developed under the principles of green analytical chemistry and green sample preparation (Gałuszka et al., 2013; López-Lorente et al., 2022). Recoveries, limits of detection (LODs), and the lowest measurable concentrations (LMCs) for the different compounds and matrices can be found in Tables S1–2. Detailed information on chemicals and materials can be found in S.I.

2.2.1. Wastewater samples

A liquid-liquid extraction (LLE) procedure was used, in which 30.0 mL of wastewater were transferred to 50 mL Falcon-type PP tubes, together with 100 μL of M4Q (tetrakis (trimethylsilyloxy) silane, surrogate standard) at 5 mg/L. The polypropylene (PP) tubes were then shaken manually and left to stand for stabilization for 30 min. Afterwards, 10 mL of *n*-hexane (HEX) were added and vortexed for 5 min, followed by 10 min in a sonication bath with 50/60 Hz (JP Selecta, Barcelona, Spain). The organic phase was transferred to 12 mL amber vials and evaporated to a final volume of about 0.5 mL under a gentle nitrogen stream. The reduced extracts were then transferred to 1.5 mL GC-MS vials, rinsing three times with HEX that was also transferred to the injection vials. The final volume of the extracts was adjusted to 1 mL, and the vials stored at $-20\text{ }^{\circ}\text{C}$ until analysis.

2.2.2. Sludge samples

For the liquid sludge extraction, 100 μL of M4Q (5 mg/L in HEX) were mixed to 20 mL of sludge into a 50 mL PP tube and homogenized for 1 min by vortex. Then, 10 mL of acetone and 10 mL of HEX were added, and the tube was vortexed for 5 min. The samples were then shaken for 2 h at 500 rpm in a KS 130 Basic orbital shaker from IKA (Staufen, Germany) and centrifuged at 2760 g for 5 min. The upper organic phase (about 10 mL) was collected and transferred to a 12 mL

vial, where it was reduced to a volume of about 0.5 mL under nitrogen. The protocol for solid sludge extraction was based on QuEChERS, a solvent-saving dispersive solid-phase extraction (SPE) method (Prestrelo et al., 2019) and on the extraction sequence described in Bletsou et al. (2013) and subsequently applied by Silva et al. (2021) in the LEPABE research group. In the first step, 2.5 g of sludge was added to 2.5 g of MgSO_4 and 100 μL of M4Q (5 mg/L in HEX) in 50 mL PP tubes and homogenized by vortex for 1 min. After that, 5 mL of HEX were added. The sample was vortexed for 1 min, sonicated for 10 min and finally centrifuged at 2760 g for 5 min, to separate the organic phase. This process was repeated twice, the first time using 5 mL of a mixture of HEX:DCM (*n*-hexane:dichloromethane, 1:1) and the second time using 5 mL of a mixture of HEX:EA (*n*-hexane:ethyl acetate, 1:1). The three extracts were combined, and 300 mg of MgSO_4 , 300 mg of PSA and 50 mg of C_{18} were added, before vortexing for 1 min and centrifugation at 2760g for 5 min. The supernatant was transferred into 15 mL amber vials and then reduced to about 0.5 mL under a nitrogen stream. In the end, both solid and liquid sludge extracts were transferred to 1.5 mL GC-MS (gas chromatography-mass spectrometry) vials, rinsing three times with HEX. The final volume was adjusted to 1 mL under nitrogen and the vials were stored at $-20\text{ }^{\circ}\text{C}$ until analysis.

2.2.3. Passive air samples

For the passive air samples, an SPE procedure was employed using glass separation funnels. A small quantity of pre-baked glass fiber was placed in the bottom of 100 mL funnels to prevent XAD runoff and the system was cleaned with 3 rinses of HEX. The 10 g of XAD were placed in the funnel and spiked with 50 μL of M4Q (5 mg/L in HEX). After 15 min, 30 mL of HEX were initially added to the funnel. Then, the slurry was hand shaken for 5 min, and the solvent was collected in a 60 mL amber glass vial. The previous step was repeated twice but adding only 10 mL HEX each time and combining the extracts. Their volume was then reduced to 1 mL under nitrogen and transferred to 1.5 mL GC-MS vials, which were stored at $-20\text{ }^{\circ}\text{C}$ until analysis.

2.2.4. Quantification analysis

The quantification of wastewater, sludge, and air extracts was performed by a Varian 240 Ion Trap GC-MS system (Walnut Creek, CA, USA), coupled with a 4000-GC gas chromatograph, a 240-MS electronic ionization mass spectrometer, and an injector mounted with a Merlin Microseal system instead of a septum. 1 μL of the extracts was injected and the target analytes were separated using helium as carrier gas at 1

mL/min on an ultra-inert low bleed DB-5MS column (30 m, 0.25 mm inner diameter, 0.25 μm film thickness; J&W Agilent, Palo Alto CA, USA) and quantified using the Internal Standard method. M4Q was used as the internal standard, with the same concentrations as described in sections 2.2.1-2.2.3. The oven temperature program started at 35 $^{\circ}\text{C}$, held for 5 min, ramped at 10 $^{\circ}\text{C}/\text{min}$ to 95 $^{\circ}\text{C}$, to 140 $^{\circ}\text{C}$ at 5 $^{\circ}\text{C}/\text{min}$ and to 300 $^{\circ}\text{C}$ at 35 $^{\circ}\text{C}/\text{min}$ (held for 5.5 min) - runtime of 30 min. The injection was done in splitless mode in the first minute, then a split ratio of 100 from 1 to 5 min and a split ratio of 5 until the end of the run. The temperatures of the injector, ion trap, transfer line and the ion manifold were 200, 220, 250 and 50 $^{\circ}\text{C}$, respectively. The emission current of the filament was. Finally, the mass spectrometer was operated in the electron ionization (EI) mode (70 eV) with an emission current of the filament of 50 μA . The mass spectrometer was operated in the EI mode and for the quantitative analysis of the target compounds, the selected ion storage mode (SIS) was applied.

The VMSs present in the biogas samples were quantified by gas chromatography coupled with ion mobility spectrometry (GC-IMS-SILOX) from G.A.S. (Dortmund, Germany). The separation takes place in a 30 m capillary column by retention time and by ionization with β radiation. This equipment allows the direct aspiration of biogas from Tedlar bags (approximately 250 mL) and determines the concentration of VMSs (L3-L5, D3-D5), silica and total silicon. The carrier gas used was nitrogen with a flow rate of 15 mL/min, completing a run time of 40 min. At least two repetitions were performed per sample.

2.3. Mass balance of VMSs

To calculate the mass flows of VMSs for wastewater, sludge, and biogas, Equation (1) was applied:

$$MF_{i,j,k} = \frac{\sum_{l=1}^{14} C_{i,j,k,l} \times Q_{i,j,l} \times 10^{-6}}{14} \quad (1)$$

where $MF_{i,j,k}$ (g/d) represents the 14-day average mass flow of compound "i" in sampling point "j", for matrix "k", $C_{i,j,k,l}$ is the concentration of compound "i" in matrix "k" in the sampling point "j" on day "l" ($\mu\text{g}/\text{L}$) and $Q_{i,j,l}$ is the flow of matrix "k", in sampling point "j" and day "l" (L/d; values in Table S3). While $C_{i,j,k,l}$ values were obtained from the collected samples, $Q_{i,j,l}$ values (as well as the water content of sludge) were facilitated by the WWTP management. The mass flows for a given compound, sampling point, and matrix were divided by their corresponding mass flow entering the WWTP (considered as 100%), in order to obtain the percent mass distributions along the plant. Since the sampled air volumes are unknown, so are the mass flows for this matrix. Therefore, for each treatment unit, the air mass flow was estimated as the difference between the input mass flows and the output mass flows. As stated in previous studies, it was considered that almost all this burden is attributed to volatilization, although some small fraction can be due to VMS degradation (Xu et al., 2013).

2.4. Quality assurance/quality control (QA/QC) and statistical analysis

Details regarding QA/QC and the statistical analysis performed in this study can be found in S.I.

3. Results and discussion

3.1. Presence of VMS in the WWTP

3.1.1. Wastewater

A composite sample consists of a mixture of several individual samples collected at regular and specified time periods. The mean concentration of VMSs given by the composite samples along the water line is presented in Fig. 2 (detailed results can be found in Table S4). The

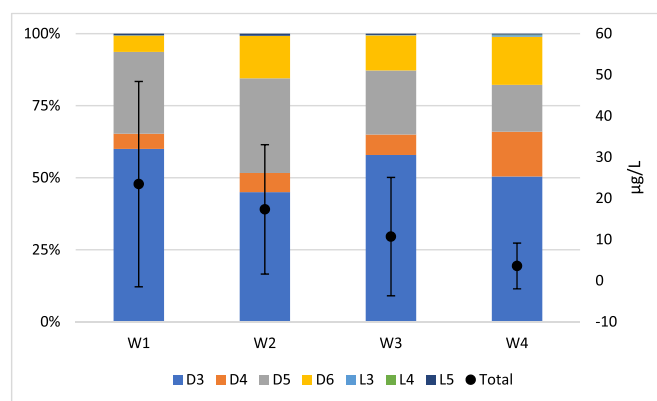


Fig. 2. VMS profiles (color bars, left Y-axis) and concentrations of ΣVMSs (black line, right Y-axis) in the different steps of the wastewater treatment. Error bars represent standard deviations. W1: Entry water; W2: Post-preliminary treatment; W3: Post-primary treatment; W4: Effluent.

mean concentrations of ΣVMSs were $23.45 \pm 24.94 \mu\text{g}/\text{L}$, $17.32 \pm 15.70 \mu\text{g}/\text{L}$, $10.70 \pm 14.37 \mu\text{g}/\text{L}$ and $3.57 \pm 5.56 \mu\text{g}/\text{L}$ in influent (W1), after preliminary treatment (W2), after primary treatment (W3) and after secondary treatment (effluent) (W4) sampling points, respectively. Consequently, the concentration in ΣVMSs is reduced along the water line in $91.59\% \pm 8.29\%$. Similar removal rates have been reported in literature (Hori et al., 2019; Nu Nguyen et al., 2021; Wang et al., 2015a). The secondary and primary treatments are, respectively, the steps where the concentrations of ΣVMSs are most reduced. This is explained since the preliminary treatment refers to the removal of large solids, oils, grease and other materials to protect wastewater treatment facilities, with no other specific treatment being performed. Moreover, literature has shown that in those final two stages of the wastewater treatment, most VMSs either partition to sludge or volatilize (Hori et al., 2019; Li et al., 2016). However, it is possible to perceive different trends between cyclic and linear VMSs: while the former migrates to the sludge, the latter are mostly volatilized. The reduction in VMSs content observed along the treatment process is not related to an effective removal by the treatments applied, but rather due to a physico-chemical partition to air (mainly the most volatile) and sludge, where a large amount (particularly of the larger molecules) tends to aggregate to the extracellular polymeric substances of the organic matter in the sludge due to their high octanol-water partition coefficients (K_{ow}) (van Egmond et al., 2013).

Among the target VMSs, the cyclic ones represented about 99.3% of the total influent mean load. The prevalent congener in our study was D3, contributing to almost 60% of the total mass of VMSs in the entry water, followed by D5, which represented close to 30% of this mass. This result is expectable, taking into consideration that these are the two VMSs mostly added in the PCPs (personal care products) and cosmetics sold in Portugal (Capela et al., 2016a, 2016b). However, it is important to note that there are two different trends in the VMSs profile depending on the week of sampling. While in the first week D5 and D3 represented, respectively, 61% and 19% of the total concentration of VMSs entering the WWTP ($7.38 \pm 2.56 \mu\text{g}/\text{L}$), in the second week these numbers changed to 23 and 67% respectively (concentration of ΣVMSs was $36.92 \pm 27.57 \mu\text{g}/\text{L}$; Table S4). As can be seen from the high standard deviations, the entry water presents a strong inter-day variability in the VMSs content, but also from week to week. These kind of fluctuations are also reported in literature, but at lower levels (Bletsou et al., 2013; Hori et al., 2019; Li et al., 2016), which can be explained by two facts. First, the Ílhavo WWTP treats entry water from different sources, from domestic to industrial. Compared to the aforementioned studies, the contributions from industrial sources are higher. Unlike domestic, these wastewaters may be characterized by highly polluted point discharges, which can cause sudden changes in the VMSs profile depending on the

industrial activity (An et al., 2023). Moreover, our sampling period is longer than usually described in literature, increasing the probability of registering some of these sudden discharges. As observed for the \sum VMSs concentrations, the levels of D3 (from $14.08 \pm 18.23 \mu\text{g/L}$ in entry water to $1.84 \pm 4.01 \mu\text{g/L}$ in effluent), D4 (from $1.24 \pm 1.54 \mu\text{g/L}$ in entry water to $0.57 \pm 1.04 \mu\text{g/L}$ in effluent), and D5 (from $6.68 \pm 6.05 \mu\text{g/L}$ in entry water to $0.60 \pm 1.11 \mu\text{g/L}$ in effluent) decreased in every treatment step along the water line. This trend, however, is not followed by D6. The mean concentrations of this compound experienced an increase from $1.33 \pm 1.10 \mu\text{g/L}$ in entry water to $2.56 \pm 1.84 \mu\text{g/L}$ in post-preliminary treatment water. This increase in water concentrations after preliminary treatment is observed for D6 in every single day of sampling (except on August 15th). Interestingly, this phenomenon is extensible to most compounds from August 3rd to 7th. Similar increases in VMS concentrations were reported in the same WWTP by Bernardo et al., (submitted for publication), attributing them to the intrusion of runoff waters from recirculation of secondary sludge to preliminary treatment (more details are discussed in Section 3.2.1) and could also be caused by the addition of lubricants and cleaning products which could include D6 into their formulations, during the frequent maintenance in the pretreatment steps (ECHA, 2019). The linear VMSs represent a minor fraction of the \sum VMSs concentrations and among them L5 was predominant in entry water ($0.13 \pm 2.56 \mu\text{g/L}$), one order of magnitude higher than L4 ($0.01 \pm 0.01 \mu\text{g/L}$). This outcome could be due to the higher use of L5 in some PCPs and cosmetics, such as sunscreen lotions, aftershaves, and shower (Bragança et al., 2020; Capela et al., 2016a). Close to 2/3 of the entry samples reported L3 concentrations below its limits of detection (7.81 ng/L).

When comparing the mean levels of VMSs in entry water with literature, the ranges are the same for most compounds, except for D3, which is higher in this study (values in literature are usually in the range

of $1.00\text{--}0.10 \mu\text{g/L}$) (Capela et al., 2017; Horii et al., 2019). This may be due to the characteristics of the influent that are related to the activities performed in the region of the WWTP (domestic, industrial, agricultural), meteorologic conditions (temperature, precipitation, etc.) and even the design of the treatment process. However, in general, studies demonstrate a higher presence of cyclic VMSs.

To study the intra-day variation of VMSs in entry water, four 6-h composite samples were taken during the first week of sampling (Table 1 and Tables S5–8). Unlike in previous studies (Bernardo et al., submitted for publication), no specific hourly pattern was observed in 6-h samples. The mean levels of the 6-h composite samples were 9.23 ± 5.94 , 8.08 ± 3.90 , 3.90 ± 1.56 , and $0.83 \pm 1.11 \mu\text{g/L}$ for W1 to W4, respectively. These results do not differ significantly from the mean of daily composite samples during the first week. The VMSs profile remained very similar in the two types of samples, with a couple of exceptions. A non-significant 10% increase in D3 and an equal decrease in D5 in mean 6-h samples with respect to the mean of composite samples was found in entry water (W1). This divergence is likely influenced by a sudden increase in D3 ($18.50 \pm 0.41 \mu\text{g/L}$) on August 6th at 0 h (Table S5). As mentioned above, this event could be a consequence of an isolated industrial discharge (An et al., 2023). Also, a non-significant 18% increase in D6 and a 10% decrease in the individual levels of D3 and D4 was observed in effluent (W4) when comparing the mean of 6-h composite with the mean of daily samples. This result is caused by an increase in D6 ($1.46 \pm 0.03 \mu\text{g/L}$) on August 5th at 18 h (Table S8). Tracking back the origin of this increase is complicated, since no samples were taken from W3 and W4 at 12 h on August 5th. However, a peak of D6 ($3.08 \pm 0.51 \mu\text{g/L}$) was observed at 12 h on August 5th in W2 (Table S6), which might have influenced the result obtained at 18 h in W4.

Table 1

Average VMSs content ($\mu\text{g/L}$) quantified in wastewater samples collected 4 times a day for 7 days in four sampling points: entry water (W1), post-preliminary treatment (W2), post-primary treatment (W3) and effluent (W4).

| | | 0 h | | 6 h | | 12 h | | 18 h | |
|----|-------|---------|---------|---------|---------|---------|----------|---------|---------|
| | | Mean | S.D. | Mean | S.D. | Mean | S.D. | Mean | S.D. |
| W1 | D3 | 5.09 | 6.97 | 2.20 | 3.61 | 1.53 | 1.60 | 1.69 | 2.46 |
| | D4 | 0.712 | 0.399 | 0.674 | 0.362 | 0.556 | 0.352 | 0.465 | 0.322 |
| | D5 | 5.81 | 2.62 | 4.55 | 1.18 | 5.13 | 2.27 | 4.05 | 2.14 |
| | D6 | 0.927 | 0.426 | 1.190 | 0.971 | 0.832 | 0.380 | 0.899 | 0.861 |
| | L3 | 0.0137 | 0.0217 | 0.0133 | 0.0157 | 0.00491 | 0.0023 | 0.0139 | 0.0242 |
| | L4 | 0.0103 | 0.00692 | 0.0149 | 0.0130 | 0.0106 | 0.00439 | 0.00891 | 0.00816 |
| | L5 | 0.0994 | 0.0441 | 0.0813 | 0.0260 | 0.0833 | 0.0278 | 0.0796 | 0.0362 |
| | Total | 12.70 | 9.20 | 8.73 | 4.53 | 8.15 | 3.76 | 7.20 | 4.26 |
| W2 | D3 | 1.21 | 1.22 | 0.309 | 0.452 | 1.16 | 1.98 | 0.347 | 0.367 |
| | D4 | 0.652 | 0.217 | 0.350 | 0.254 | 0.599 | 0.463 | 0.584 | 0.338 |
| | D5 | 5.44 | 2.85 | 3.46 | 1.28 | 5.28 | 3.36 | 6.18 | 2.93 |
| | D6 | 1.82 | 0.493 | 1.47 | 0.609 | 2.24 | 0.706 | 2.10 | 0.695 |
| | L3 | 0.00963 | 0.0131 | 0.0118 | 0.0172 | 0.00711 | 0.00575 | 0.00835 | 0.00867 |
| | L4 | 0.0142 | 0.0109 | 0.0188 | 0.0322 | 0.0110 | 0.00701 | 0.01100 | 0.00573 |
| | L5 | 0.108 | 0.0647 | 0.0798 | 0.0669 | 0.124 | 0.0648 | 0.124 | 0.0554 |
| | Total | 9.25 | 3.37 | 5.71 | 1.86 | 8.07 | 5.34 | 9.30 | 3.91 |
| W3 | D3 | 0.379 | 0.482 | 0.263 | 0.381 | 0.329 | 0.426 | 0.266 | 0.263 |
| | D4 | 0.425 | 0.566 | 0.341 | 0.447 | 0.410 | 0.500 | 0.296 | 0.263 |
| | D5 | 1.59 | 0.304 | 1.67 | 0.781 | 1.63 | 0.532 | 1.80 | 0.341 |
| | D6 | 0.883 | 0.237 | 0.834 | 0.385 | 0.860 | 0.280 | 0.987 | 0.162 |
| | L3 | 0.0181 | 0.0355 | 0.0464 | 0.110 | 0.0233 | 0.0450 | 0.0188 | 0.0389 |
| | L4 | 0.00579 | 0.00829 | 0.0119 | 0.0230 | 0.00831 | 0.0131 | 0.00673 | 0.00876 |
| | L5 | 0.0440 | 0.0189 | 0.0316 | 0.0136 | 0.0348 | 0.0131 | 0.0449 | 0.00802 |
| | Total | 3.34 | 1.60 | 3.19 | 2.08 | 2.83 | 1.86 | 3.42 | 0.64 |
| W4 | D3 | 0.177 | 0.426 | 0.146 | 0.351 | 0.0819 | 0.176 | 0.0939 | 0.222 |
| | D4 | 0.226 | 0.518 | 0.226 | 0.520 | 0.088 | 0.141 | 0.105 | 0.214 |
| | D5 | 0.186 | 0.182 | 0.146 | 0.227 | 0.120 | 0.109 | 0.124 | 0.0611 |
| | D6 | 0.272 | 0.292 | 0.302 | 0.464 | 0.553 | 0.555 | 0.473 | 0.512 |
| | L3 | 0.0182 | 0.0349 | 0.0256 | 0.0552 | 0.0086 | 0.0105 | 0.0300 | 0.0640 |
| | L4 | 0.00354 | 0.00259 | 0.00521 | 0.00941 | 0.00201 | 0.000477 | 0.00812 | 0.0141 |
| | L5 | 0.00653 | 0.00150 | 0.00534 | 0.00300 | 0.00838 | 0.00277 | 0.00653 | 0.00150 |
| | Total | 0.889 | 1.35 | 0.857 | 1.61 | 0.861 | 0.924 | 0.840 | 0.619 |

3.1.2. Sludge

The mean concentrations of each target VMS in sludge compound studied, in the six sampling points, are shown in Fig. 3 (detailed results in Table S9). Unlike wastewater, the mean sludge concentrations present lower standard deviation values, which is indicative of a lower inter-day variability in siloxane concentrations. This result, also observed in the literature, is caused by the fact that the retention times in sludge are higher than in water (Bletsou et al., 2013; Li et al., 2016). Consequently, the samples collected daily are representative of a blend of more than one day.

The mean levels of \sum VMSs in this study (8.24 ± 3.65 and 7.67 ± 3.05 $\mu\text{g/g dw}$ respectively for primary (S1) and secondary (S6) sludge) are within the ranges reported in literature (Capela et al., 2017; Horii et al., 2019). However, it is noteworthy to see how, in this case, no significant differences were detected in the content of total VMSs between primary and secondary sludges, while in other studies, secondary sludge presents usually notably higher levels of \sum VMSs (Surita and Tansel, 2015; Wang et al., 2015a). This result likely reflects the fact that in Ílhavo WWTP the secondary sludge is completely recirculated to the preliminary treatment, influencing thus the load of VMSs in the primary sludge (Fig. 1). The total content of VMSs is reduced along the sludge line in $75.82\% \pm 8.90\%$. As in the case of the water line, the levels of VMSs in sludge fluctuate depending on the treatment applied to this matrix. Thus, a slight increase in \sum VMSs concentrations is experienced after the thickener (S2), from 8.24 ± 3.65 in the input to 8.40 ± 3.22 $\mu\text{g/g dw}$ in the output sludge, as a consequence of the dehydration of sludge in this treatment step. Afterwards, a reduction in \sum VMSs concentrations is reported after the addition of FeCl_3 (S3; from 8.40 ± 3.22 in input to 5.94 ± 2.99 $\mu\text{g/g dw}$ in output sludge), an action primarily intended for the reduction of H_2S in biogas (Bragança et al., 2020), and in the anaerobic digester (S4; from 5.94 ± 2.99 in input to 3.25 ± 1.35 $\mu\text{g/g dw}$ in output sludge). The latter step is where the content of total VMSs is most reduced (68% reduction of total VMSs between the input and output of the digester), probably due to volatilization into the biogas, favored by the technical characteristics of this facility (37°C and 21 days of retention time) (Arhoun et al., 2021).

Following the centrifugation process, the \sum VMSs concentration in the final dewatered sludge (S5) increases with respect to the post-digester sludge from 3.25 ± 1.35 to 5.48 ± 1.10 $\mu\text{g/g dw}$. These levels are one order of magnitude lower than those reported in literature (Bletsou et al., 2013; Horii et al., 2019; Lee et al., 2014). This outcome could be explained by several reasons. To begin with, those studies were developed in different countries, with a diverse pattern of use of cosmetics and PCPs, and/or different contributions from industrial or domestic sources. Also, all of them were focused on WWTPs treating a

higher number of population equivalent (i.e., in the range of 1×10^6 – 4×10^6). And finally, in none of them detailed the production of biogas from sludge in digesters, which, as discussed previously, has a critical impact in the presence of VMSs in sludge.

Focusing on the VMSs profile in sludge, the mean values for the sampling period are highly enriched (85–90% of total VMSs depending on the treatment step) in D5, followed by D6 (8–10% of total VMSs). These variations in the profile of VMSs between water and sludge are explained by the differences in the physical-chemical properties between the target VMSs. Thus, despite D3 is the prevalent VMSs in the entry wastewater (W1), it has higher volatility, higher water solubility, and lower lipophilicity than D5 and D6 (de Arespacochaga et al., 2015). This favors the migration of this compound to air, and/or its permanence in water unlike the larger molecules D5 and D6, which have a higher affinity towards sludge. A similar trend is observed with the linear VMSs: while their total load in water represents less than 1% regardless of treatment step, this number increases 1.44–1.74% on sludge samples. Among them, L5 is the predominant, representing 1.25–1.52% of the total VMSs. As in the case of D5 and D6, L5 has a higher affinity for the lipidic substances present in the sludge, comparing to the other linear congeners targeted (Kim et al., 2018). The VMS profile described here is constant among the different sludge treatments, except in the case of dewatered sludge (S5), in which slight changes in the content of D5 and D6 are noticed (ranges of 80–83% and 12–15%, respectively). Despite some variations in the concentrations mentioned above, similar VMSs profiles have been reported previously (Horii et al., 2019; Wang et al., 2015a).

3.1.3. Air

To estimate the air concentrations of VMSs from the levels found in XAD-2, passive sampling rates (PSRs) previously reported were used (Sánchez-Soberón and Ratola, 2022). As expected, the analysis of air samples revealed variations in concentrations among the sampling points, and different profiles between indoor (A5-8; laboratory, canteen, office, and workshop) and outdoor (A1-4,9; pretreatment, aeration tank, centrifuge, thickener, and background) locations (Fig. 4 and Table S10). Although not statistically significant, higher overall concentrations of \sum VMSs were reached indoors than outdoors (2037 ± 1908 and 633 ± 695 ng/m^3 , respectively). This outcome is opposed to the result observed in the same WWTP in a subsequent summer sampling campaign (Sánchez-Soberón and Ratola, 2022) and can be explained by the pandemic conditions. The Ílhavo WWTP is located next to a popular beach destination, receiving its peak of VMSs in summer as a consequence of the population increase due to tourism, and the subsequent more intense use of PCPs such as sunscreen lotions during this season

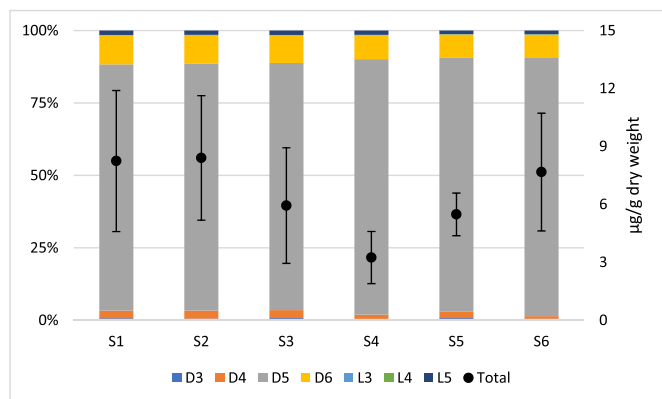


Fig. 3. VMS profiles (color bars, left Y-axis) and concentrations of \sum VMSs (black line, right Y-axis) in the different steps of the sludge treatment. Error bars represent standard deviations. S1: Primary sludge; S2: Thickened sludge; S3: Chlorinated sludge; S4: Digested sludge; S5: Dewatered sludge; S6: Secondary sludge.

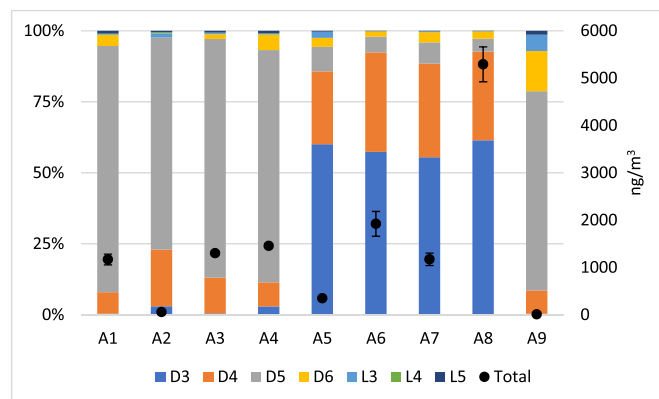


Fig. 4. VMS profiles (color bars, left Y-axis) and mean concentrations of \sum VMSs (black line, right Y-axis) in the different air sampling locations. Error bars represent standard deviations. A1: Preliminary treatment; A2: Sludge thickener; A3: Aeration tank; A4: Sludge centrifuge building; A5: Workshop; A6: Office; A7: Laboratory; A8: Canteen; A9: Background.

(Dudzina et al., 2014). However, due to the pandemic restrictions, the affluence of people to the area in the summer of 2020 was lower than usual and more random, decreasing the outdoor concentrations in air and contributing for the high standard deviations. Since the indoor concentrations are more influenced by the use of PCPs and cosmetics by workers, stabler values along the year are expectable. However, the pandemic work arrangements also contributed to a wider standard deviation of the concentrations, as the access to the facilities was limited and rotating people and work in-person and from home.

With the exception of the sludge centrifuge building, the indoor samples present a profile of VMSs (see Fig. 4) in which D3 is the prevalent compound (55–62% of \sum VMSs), followed by D4 (25–35% of \sum VMSs), in line with another recent study in the same WWTP (Sánchez-Soberón and Ratola, 2022). This trend is different from the usually found in indoor environments, where D5 is the prevalent VMSs (Tran et al., 2019). However, some studies have reported other VMSs, such as D4 or D6, as predominant in laboratories and offices, likely emitted from the existing consumables (Anh et al., 2021; Sha et al., 2018; Tran et al., 2017). Moreover, the presence of a filtering system to purify the entry air in the main office buildings might be also influencing the levels of indoor air VMSs, by retaining with more efficiency the higher molecular weight VMSs (such as D5 and D6) than the smaller structures (like D3 and D4). Consequently, and as highlighted before, the indoor presence of VMSs is more influenced by “indoor sources”, such as PCPs, cosmetics, and consumables, which can display a VMSs profile enriched in D3 and/or D4 (Anh et al., 2021; Capela et al., 2016a). In the case of the sludge centrifuge building (A4), the profile is characterized by a prevalence of D5, as for the outdoor air samples. During the centrifugation, the sludge is concentrated inside a building with low human occupancy and one open gate to the exterior for ventilation. Therefore, the main contributor to VMSs levels here is likely the sludge, which, as seen in the previous section, is enriched in D5. In terms of concentrations, the canteen registered the maximum \sum VMSs levels ($5291 \pm 91.18 \text{ ng/m}^3$), followed by the office ($1921 \pm 64.97 \text{ ng/m}^3$), the centrifuge building ($1454 \pm 20.64 \text{ ng/m}^3$), the laboratory ($1171 \pm 32.65 \text{ ng/m}^3$), and the workshop ($347.7 \pm 2.19 \text{ ng/m}^3$). The concentrations obtained in the canteen can be related to a higher occupancy of the space, lower ventilation rates, or higher consumption of foods rich in VMSs-based additives (Younes et al., 2020). The VMS load in the centrifuge falls within the annual range described in the literature for the same plant (Sánchez-Soberón and Ratola, 2022), and the levels obtained in the office and laboratory are in the same range of those reported in the literature for similar indoor spaces (Pieri et al., 2013; Sha et al., 2018; Tran et al., 2017; Tran and Kannan, 2015). The lowest levels registered in the workshop could be a consequence of the characteristics of this location. Although it is an indoor location, two gates are permanently open, increasing its ventilation rate.

Unlike indoors, samples collected outdoors above key treatment steps are characterized by a prevalent D5 profile (70–87% of \sum VMSs), followed by D4 (7–20% of \sum VMSs) and D6 (0–14% of \sum VMSs). This trend is typical from other WWTPs described in the literature, and it is explained by the high use of D5 in cosmetics/PCPs formulations (Cheng et al., 2011; Li et al., 2016; Okan et al., 2021). With respect to the concentrations, the aeration tank registered the maximum \sum VMSs levels ($1299 \pm 33.75 \text{ ng/m}^3$) as expected, followed by the pretreatment ($1167 \pm 113.5 \text{ ng/m}^3$), the sludge thickener ($57.37 \pm 5.39 \text{ ng/m}^3$), and finally the background location outside the WWTP ($8.13 \pm 1.62 \text{ ng/m}^3$). These levels fall within the range of concentrations described in the literature for \sum L3-L5, D3-D6 in WWTPs for all locations except the background, that showed concentrations typical of rural or remote areas ($1\text{--}100 \text{ ng/m}^3$) (Cheng et al., 2011; Gallego et al., 2018; Okan et al., 2021; Shoeib et al., 2016).

3.1.4. Biogas

The levels of \sum VMSs in the biogas reached a mean value of $8.00 \pm 0.22 \text{ mg/m}^3$ (Fig. 5 and Table S11). This concentration is above the

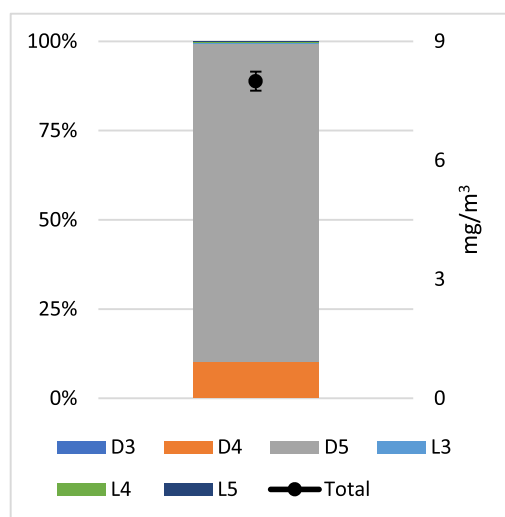


Fig. 5. VMS profile (color bars, left Y-axis) and concentrations of \sum VMSs (black line, right Y-axis) in biogas. Error bars represent standard deviations.

levels considered as safe by some manufacturers of internal combustion engines (*i.e.*, 5.00 mg/m^3), and biogas purification strategies should be put in place in order to ensure a good biogas quality and the highest energy throughput (de Arespacochaga et al., 2015). Nevertheless, from the VMS congeners analyzed by the GC-IMS-SILOX instrument (L3-L5 and D3-D5), only D4 and D5 were present above the limits of detection, with mean concentrations of 0.08 ± 0.07 and $7.11 \pm 0.16 \text{ mg/m}^3$, respectively. This profile is in line with the reported in the literature (Bragança et al., 2020), and is very similar to the VMSs profile in sludge, taking into consideration that D6 was not analyzed in biogas. However, a significant increase in the D4/D5 ratio in biogas (0.11 ± 0.01) with respect to digester's input sludge (0.03 ± 0.01) suggest a close to four-fold enrichment in D4 in the former matrix, as a consequence of the higher volatility of this compound (Gaj, 2018).

3.2. Mass balance of VMSs

3.2.1. Global mass balance

A percent mass flow diagram for the different VMSs in wastewater (considering only the composite samples), sludge, biogas, and air (estimated as the difference between total VMS inputs and outputs) can be seen in Fig. 6. The mass flows for the dewatered sludge (S5) were not included in the balance, as the sludge from this treatment is removed non-continuously and its mass is representative for a period longer than the sampled interval. As seen in Fig. 6, the total mass of VMSs is reduced along the WWTP treatment sequence. The entry water had a mean flow of $508 \pm 530 \text{ g/d}$ of \sum VMSs, while the sum of the outputs (effluent, digested sludge, and biogas) decreases to $95.5 \pm 115 \text{ g/d}$ (Tables S12–14). The reduction in \sum VMSs flow in the different steps of the WWTP ranged from 30.6% (primary decanter) to 0.8% (sludge thickener). For a given chemical structure (linear or cyclic) it is possible to observe a correlation between the mean mass flows in entry waters and the mean percent removal in the WWTP. This dynamic is typical of an exponential degradation processes, previously reported for VMSs in other aqueous environments (Krogseth et al., 2017). For cyclic VMSs this correlation showed a significant R^2 equal to 0.9098, corresponding to removals of 87.7%, 86.2%, 54.4%, and 50.3% of D3, D5, D6, and D4 inputs respectively. In the case of linear VMSs this trend is followed by L5 (removal of 86.2% of inputs) and L4 (49.8%), but not for L3, which showed negative removals (−20.4%). This last result is likely a mathematical artifact, caused by the fact that most of the L3 concentrations in entry water were below the LOD, and half of this value was used instead.

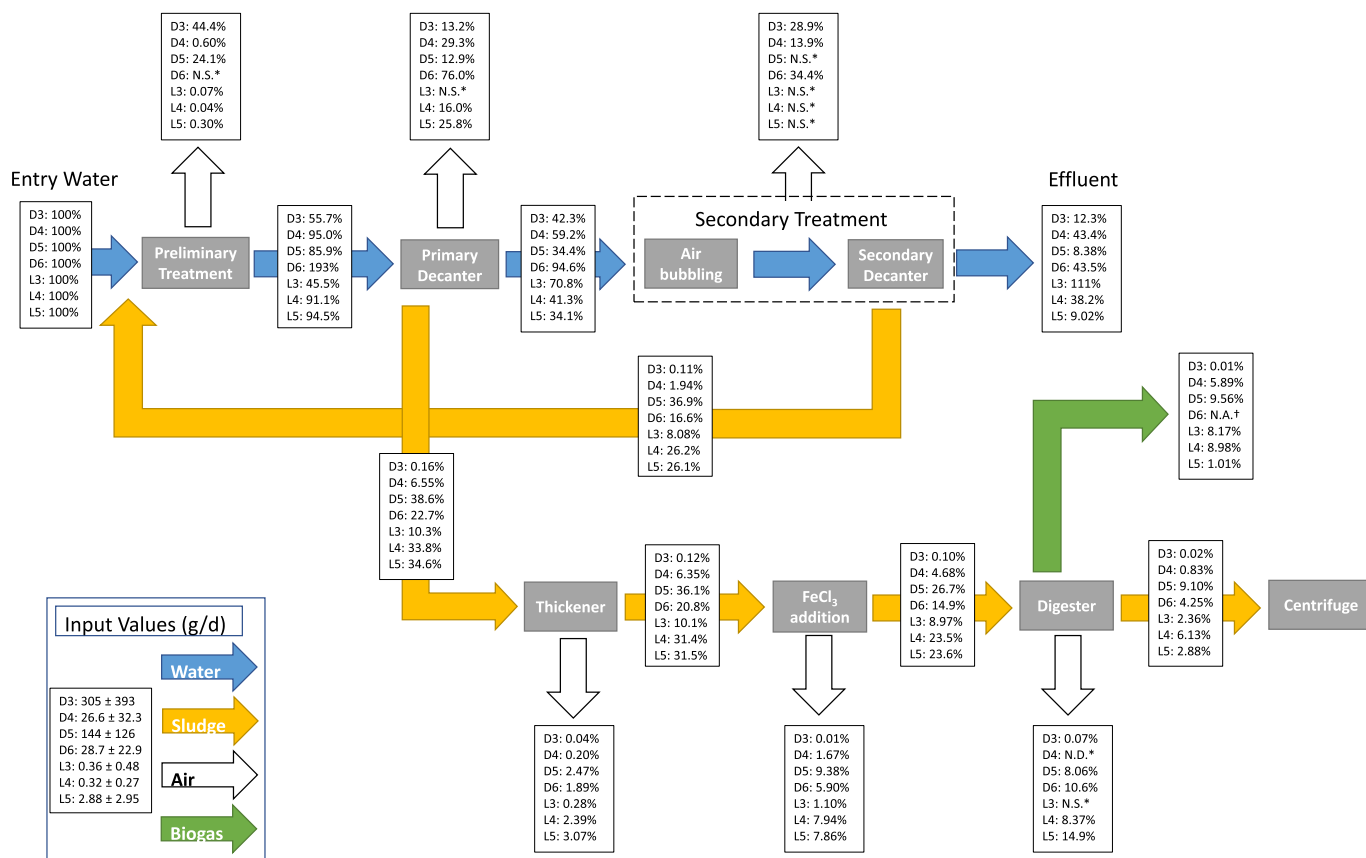


Fig. 6. D3-D6 and L3-L5 percent mass distribution in the different treatment units of the WWTP. Values are referred to input values, described in the bottom left square. *N.S.: not shown (negative values); †N.A.: not acquired.

3.2.2. Mass balance by treatment units

Apart from the global overview, it is important to have a detailed idea on the behavior of VMSs in the main treatment units of the WWTP as depicted in Fig. 6.

Although not statistically significant, the preliminary treatment exerts a reduction in mean \sum VMSs flow of 25.7% (\sum VMSs in S1 is equal to 508 ± 530 g/d, reduced in S2 to 377 ± 343 g/d). In general terms, all VMSs but D6 experienced different degrees of flow reduction percentages in the pretreatment. However, as explained in Section 3.1.1, there are some exceptions to this rule, especially in the period from August 3rd to 7th, caused by the recirculation of secondary sludge. By calculating the Addition Ratio (AR) of \sum VMS for day "i" as expressed in Equation (2):

$$AR_{\sum VMS,i} = \frac{MF_{\sum VMS,S6,sludge,i}}{MF_{\sum VMS,W1,water,i}} \quad (2)$$

It is possible to estimate the contribution of \sum VMS from recirculated sludge to the preliminary treatment input water. Despite not significant, the mean values of AR in the period from August 3rd to 7th showed higher values (0.24 ± 0.11) than for the rest of sampling period (0.16 ± 0.07). Therefore, this higher contribution during the first sampling days could be the main cause of the flow percentages increase in the preliminary treatment. Considering the results obtained in this unit, the estimated D3 contributions in the air sampled (as depicted in Fig. 6) should be higher, due to its volatilization, than its contributions actually observed from air samples (as shown in Fig. 4, sampling point A1). Several causes could explain this situation. First, air is an open compartment, and the air from the pre-treatment is more or less influenced by the other treatment units. Moreover, the mechanical removal of foams is performed in the preliminary treatment. These foams are produced by the presence of surfactants in sewage (Collivignarelli et al., 2020), that could favor the

entrapment D3 within the foam structure. Finally, the D3 concentrations measured in outdoor air could be underestimated. As observed by Krogseth et al. (2013b), 95% of the D3 uptake in XAD-2 takes place during the first 13 days of sampling. Considering that our sampling period is 14 days, and that outdoor average temperature in our case is higher than the one experienced by Krogseth et al. (2013b), D3 losses could be expected.

As mentioned previously, the primary decanter registers the higher decrease in the content of VMSs as a whole (30.6%). However, focusing on every congener, this result varies. According to our results, it is possible to see a trend in the reduction of compounds under the following two premises: for the same number of Si atoms in the molecular structure, the reduction is higher for linear VMSS, and the higher the molecular weight, the higher the reduction in water. Thus, it is possible to see how the contents in D3 are only reduced 13.4%, while in the case of D6 this number rises to 98.7%. This result seems to be related with the lipophilicity and water solubility of the compounds (de Arespacochaga et al., 2015). In fact, it is noteworthy how D5 and L5 partition almost equally to water and primary sludge (S1), while D3, D4 and L4 remain mostly in water (W3). An exception is D6, which remains mostly in water (43.5% of the initial content in W4 vs 22.7% in S1). It is important to remark again that, unlike in other WWTPs, secondary sludge (S6) is recirculated to the preliminary treatment, and hence the contents of VMSs in primary sludge are highly influenced by this sludge. In fact, the mass of \sum VMSs in the secondary sludge represents 91.2% of the same mass in primary sludge, indicating that it is likely more influenced in terms of VMS load by the recirculated secondary sludge than by the wastewater entering the plant.

In the secondary treatment the reduction in the aqueous VMS mass is similar to the obtained in the primary treatment (29.4% of the entry \sum VMSs). This reduction, however, is congener-dependent, being higher in the case of the cyclic compounds, and those with higher molecular

weight. Thus, in this treatment step, D6 shows the maximum relative mass reduction, while L4 displays the minimum value (W4 mass flow values represent 51.1% and 3.1% of their W3 counterpart, respectively). D3 is the only exception to this rule, being its mass reduced 30.0% with respect to the previous step. However, this result may not be very representative of the period studied, since D3 concentrations in the secondary treatment present a high variability ($1.84 \pm 4.01 \mu\text{g/L}$). Only L5 and D5 present a higher partition to sludge in this unit, likely due to their higher lipophilicity. Unlike other studies, D4 and D6 exit the WWTP mostly in the effluent (43.8 and 43.5% of the entry levels, respectively), migrating to sludge in lower quantities (1.94 and 16.6%, respectively) (Horii et al., 2019; Wang et al., 2015b). Attending to the results obtained in this unit, D3 and D6 should have a higher presence in air than actually observed in A3 samples (Fig. 4). As in the case of pretreatment, the intrusion of air from other treatment units may be influencing the results of A3. Moreover, the degradation of D6 could be taking place before or after volatilization, as referred by Bletsou et al. (2013).

The reduction in the VMS mass in the sludge thickener is the lowest along the WWTP, representing only 0.8% of the initial $\sum\text{VMSs}$ mass. D5 and D6 were the compounds with the highest decreases (2.5 and 1.9% of their initial masses, respectively). In Ílhavo WWTP this treatment step consists of two gravity thickening units, that reduce the water content in sludge by sedimentation but lacking any thermal process, which explains the low reduction in VMS mass experienced (Ferreira, 2015). Here, the estimated air profile depicts higher contributions of D6 and L5 and lower presence of D3 and L3 than observed in A2 samples (Fig. 4). Again, a plausible degradation of these high molecular weight VMSs into linear low molecular weight VMSs (Rücker and Kümmerer, 2015), and the influence of the surrounding air could explain these divergences. Higher reductions were reached after the addition of FeCl_3 to the sludge (3.4% of the initial $\sum\text{VMSs}$), which was notably higher for D5, D6, L4, and L5 (reductions ranging from 5.9 to 9.4% of their entry masses). Garcia et al. (2016) reported a reduction of D5 in biogas when sludge was treated with FeCl_3 . The authors claim that this compound could degrade cyclic VMSs to form soluble substances via polymerization, which would explain that decrease.

The anaerobic digester is the unit that showed the highest reduction in the VMSs mass within the sludge line (5.9% of the initial $\sum\text{VMSs}$ mass). As in the case of the thickener, D5, D6, L4, and L5 presented the highest flow decreases, with values ranging from 9.10 to 7.69% of the entry water levels. This outcome is the result of the higher retention time and temperatures in the digester (21 days and 37°C), which favors the migration of VMSs to biogas. However, when adding the $\sum\text{VMSs}$ flows present in biogas and in the sludge exiting the digester, the value represents 67% of the digester entry mass (30.17 and 44.59 g/day, respectively). This mismatch can be explained by several factors. First, biogas is collected after being conducted through an adsorbent tower designed to remove H_2S , which is likely to retain VMSs at some degree. Then, the degradation of VMSs to other compounds is likely to happen in the digester, since the hydrolysis of Si–O and Si–C bonds in these units has already been reported (Huang et al., 2020). Finally, D6 was not measured in biogas due to analytical limitations of the GC-IMS-SILOX.

All these estimations of the mass balances are obviously influenced by the high variability (daily and sometimes even hourly) of the VMS load entering the WWTP. Nevertheless, these results shed a light on the levels and ranges that WWTP managers can expect in facilities of this size and purpose. In the future, it would be important to study thoroughly the contributions to the entry wastewater, aiming to assess the most important sources of VMSs and try to come up with some preventive measures that could reduce (or at least maintain less variable) the VMS content.

4. Conclusions

The concentrations of $\sum\text{VMSs}$ ($23.45 \pm 24.94 \mu\text{g/L}$) and the profile of VMSs in entry water for the sampling period as a whole were similar

to the literature, except for D3, for which the influent levels ($14.08 \pm 18.23 \mu\text{g/L}$) were one order of magnitude higher than reported previously. This phenomenon could result from isolated releases of this compound rather than from baseline levels. The primary and secondary sludge $\sum\text{VMSs}$ concentrations (8.24 ± 3.65 and $7.67 \pm 3.05 \mu\text{g/g dw}$, respectively) and the congener profiles (predominance of D5 followed by D6) were in line with literature. The VMSs profiles in air are highly influenced by the sampling location: while outdoor samples showed a prevalence of D5, indoor samples were characterized by a predominance of D3 and D4. Different sources of VMSs between these two environments, in addition to an indoor air filtering system in the office buildings are the main factors explaining this outcome. The mean concentrations of $\sum\text{VMSs}$ in biogas ($8.00 \pm 0.22 \text{ mg/m}^3$) were above the limits recommended by some manufacturers for internal combustion engines for cogeneration and consisted only of D5 (89%) and D4 (11%), but D6 was not analyzed. A reduction of 81% in the total incoming mass of VMSs is observed along the WWTP ($\sum\text{VMSs}$ mass flows of 508 ± 530 and $95.5 \pm 115 \text{ g/d}$ for inputs and outputs, respectively). Most of this mass (61%) was reduced in the water line, as a consequence to partition to sludge and air. Increasing sampling periods, as well as including biogas and indoor air as sampling matrices, has proven useful in order to improve the representativity, time-sensitivity, and accuracy on mass balance exercises. Future studies should be undertaken to fill the knowledge gaps still existing in the seasonal effect of VMSs influents (and their respective sources) and emissions on WWTPs.

Credit author statement

Francisco Sánchez-Soberón: Writing – original draft, Visualization, Validation, Formal analysis, Investigation, Data curation; **Gabriel F. Pantuzza** Writing – original draft, Investigation; **Madalena Fernandes:** Validation, Investigation; **Vera Homem:** Methodology, Conceptualization; **Arminda Alves:** Funding acquisition, Project administration; **Milton Fontes:** Resources, Conceptualization, Technical Supervision; **Magda André:** Resources, Technical Supervision; **Joana Cunha:** Resources, Technical support; **Nuno Ratola:** Writing – review & editing, Conceptualization, Supervision, Investigation, Funding acquisition, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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