Understanding the effects of the origin, occurrence, monitoring, control, fate and removal of siloxanes on the energetic valorization of sewage biogas – A review

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Abstract

This paper reviews the effects of the origin, occurrence, monitoring, control, fate and removal of siloxanes on the energetic valorization of sewage biogas, which can be severely compromised by its volatile organic silicon compound (VOSiC) content. Almost 25 years after identifying silicon dioxide in the exhaust gases from engines powered using sewage and landfill gas, a wide range of studies have been conducted addressing the different stages of the siloxane life cycle. The cycle starts with the production and use of polydimethylsiloxane polymers in a wide range of industrial and domestic applications and its further dispersal into environmental compartments. Siloxanes are subsequently introduced into wastewater treatment plants, where as a result of their low biodegradability and high affinity to dissolved and particulate matter, they are first transferred from wastewater into sludge and later volatilized in biogas in anaerobic digesters. Biogas treatment technologies can reduce siloxane concentrations to less than 0.1 mg/m^3; adsorbent materials with micro- and mesoporous structures appear to be the most relevant technology in technical and economic terms. The state-of-the-art on siloxanes is vast and extensive, but there are still some knowledge gaps to be addressed in the future, such as the standardization of the methodology for off-line analysis, the development of on-line monitoring equipment, better understanding the fates of siloxanes in wastewater treatment processes to operate at specific conditions to avoid siloxanes-related problems, the development of more selective and regenerative removal technologies from biogas to reduce operating costs and even to recover silicon, and better understand the detrimental effects on energy recovery technologies to determine the inlet concentration limits. This work compiles the most relevant results available in the literature for each stage of the siloxane life cycle.

Keywords: biogas, volatile methyl siloxane, PDMS, analysis, removal, fate, energy recovery

1. Introduction

Biogas produced in landfills and wastewater treatment plants (WWTPs) by microorganisms during the anaerobic degradation process of organic compounds is commonly used in energy production. Moreover, in several countries, methane-rich gas from landfills must be collected and burned or used for energy production to prevent the methane from being released into the atmosphere. For this reason and increasing interest in renewable fuels, biogas has become a notable alternative to conventional fuels in the production of electricity and heat. Indeed, biomethane, upgraded from biogas, has also become an interesting alternative for vehicle fuel.

Biogas contains mainly methane (from 40 to 60%) and carbon dioxide (40 to 55%); however, in the case of landfills, it may also contain nitrogen and oxygen [1]. Along with the main compounds, biogas may also contain trace compounds, such as hydrogen sulphide, halogenated compounds, and organic silicon compounds.

The energetic utilization of biogas is severely compromised by its volatile organic silicon compound (VOSiC) content. The scientific community has determined that VOSiCs in biogas are produced by the degradation and/or volatilization of organosilicon materials [1,2]. Organosilicons are a broad family of synthetic polymers with a wide variety of forms and uses. All of these polymers are manmade; the organosilicon linkage (the linkage between a silicon atom and a methyl group or any other organic group) is not found in nature. The organosilicon compounds present in biogas are oxidized during biogas combustion into microcrystalline silicon dioxide, a residue with chemical and physical properties similar to glass. Silicon dioxide deposits on valves, cylinder walls, and liners, cause abrasion and blockage of pistons, cylinder heads, and valves. In gas turbines, siloxane deposits usually form on the nozzles and blades, causing erosion of the turbine blades and subsequently decreasing the operating efficiency [3]. Moreover, the glassy residues can deactivate the surface of the emission control system catalyst [1,3-5]. The use of spark ignition engines has increased the number of engine failures caused by siloxanes, as previous dual fuel engines were less vulnerable to silica deposits [6]. A correlation between increasing CO emissions and the build-up of silicates in engine oil after the combustion process was reported by Tower (2003) [3]. In this case, the oil in the engine needs to be changed more frequently, which resulted in the introduction of a 1 mg/L limit for silicon in the oil of gas engines by some gas engine manufacturers [7]. Furthermore, the deposited layers can break off and clog lines. Other undesired effects include the poisoning of the catalysts used in steam reforming [8] or fuel cells [9]. The catalysts used for both pre-combustion [10] and post-combustion gas purification (i.e., to reduce formaldehyde concentrations in exhaust gas) are also prone to deactivation by siloxanes. All of these negative effects are associated with increases in operating costs. Therefore, plant operators are facing a choice between either installing gas purification equipment or controlling the problems with more frequent maintenance (i.e., more frequent oil changes, engine inspections, downtime and associated loss of financial reimbursement [11]).

Reviews addressing the topic of “siloxanes” [4,6,12,13] are mainly focused on siloxane removal technologies, with minor references to quantification and occurrence issues. Within this context, no thorough study has been conducted compiling all of the information available in the literature at all stages of the siloxane life cycle. In this work, section 2 presents the production and use of polydimethylsiloxane polymers in a wide range of domestic and industrial applications and its dispersal into various environmental compartments. Section 3 assesses the environmental and health risk concerns of siloxanes. Section 4 collects the available siloxane quantification methods in different environmental matrices, including air, water, soil, sediment, sludge and biogas. Section 5 reviews the fates of siloxanes through the different urban/industrial wastewater treatment processes (both the sewage and sludge treatment trains) and its final transference into biogas. Section 6 compiles the different siloxane removal technologies from biogas. Finally, section 7 presents the detrimental effects of siloxanes on the performance of energy conversion technologies.

2. Anthropogenic cycle of siloxanes: production, uses and release into the environment

2.1 Classifications and definitions

Organosilicon compounds are organic compounds that contain carbon–silicon [Si-C] bonds, which are longer and weaker than carbon–carbon [C-C] bonds [14]. Commercially available organosilicon materials can be classified into the following structural classes: organosilanes and organosiloxanes [15]. While organic silanes are polymeric compounds containing silicon–silicon [Si-Si] bonds with organic side-chains. Siloxanes consist of a backbone of alternating silicon−oxygen [Si-O] units with organic side-chains attached to each silicon atom [16]. They are chemically and physically inert, resistant to oxidation and to high temperatures, have low surface tensions, relatively small changes in viscosity with temperature or rate of shear, good low-temperature performance, water repellence and high compressibility. Polydimethylsiloxane (PDMS, $CH_3[Si(CH_3)_2O]_nSi(CH_3)_3$) is the most widely used silicon-based organic polymer and commonly referred to as silicone or dimethicone. The basic silicone molecule can be altered to obtain a wide range of properties by partially replacing the methyl groups with other organic groups [17].

Volatile Methyl Siloxanes (VMSs) are low molecular weight organosilicon fluids with high vapour pressures at ambient conditions and can be produced due to PDMS hydrolysis. The structure of VMS can be linear (l-VMS) or cyclic (c-VMS) as shown in Figure 1. Table 1 shows the most commonly identified organic silicon compounds in digester and landfill gas.

Figure 1.

Table 1.

2.2 Industrial and domestic uses of silicones and siloxanes

Silicones (PDMS) and siloxanes are divided into three classes depending on the number of cross-links between chains: fluids (without cross-links), elastomers (rubbers) and resins (with high numbers of cross-links). They are used in several industrial and domestic applications, including as antifoaming agents, in automotive care products as coatings, in construction as sealants, and in cosmetics and personal care products (shampoos, lotions, cosmetics, hair care products, deodorants, antiperspirants, nail polishes, skin cleaners and sanitizers) [18-21]. Several studies [22-28] assessed the siloxane concentrations in different household products, showing values ranging from 5 to 700 mg/g (wet weight).

According to the Centre Européen des Silicones (CES), the global market for silicones was approximately 2000 ktonnes in 2002 and increased to approximately 2600 ktonnes in 2009 [29,30]. The market has experienced an important geographical shift in the recent years, as China became the largest producer and consumer of silicones in the world in 2009 [31], overtaking both Western Europe and the USA. Due to increasing end-use markets, the worldwide demand is anticipated to increase by 6% per year until 2022 [32-34].

2.3 Releases of siloxanes into the environment

Table 2 depicts some industrial and domestic applications of silicones, its consumption in Western Europe in 2002 and the main routes for introduction into the environment from fluid, elastomer and resin applications.

Table 2.

The vast majority of siloxanes from fluid applications are lost into the atmosphere from ‘‘leave-on’’ personal care products [35,36] as a result of their volatility, where they are expected to be broken down via reactions with hydroxyl radicals. Alternatively, they are lost from "rinse-off" products resulting in emission into wastewater [37]. It is estimated that 10% of VMS enter domestic sewage systems; therefore, WWTP are one of the most important routes for siloxane introduction into the environment [30]. Strangely enough, siloxanes have also been used to suppress foaming episodes caused by detergents in the aeration basins of WWTPs due to their antifoaming properties. This explains their presence in the biogas energy recovery line. Furthermore, the majority of siloxanes used in elastomers and resins are disposed of via incineration or in landfills with building materials.

3. Environmental and health risk concerns of siloxanes

c-VMS are a group of chemicals with environmental and health risk concerns because of their physical properties [35-37]. Nevertheless, few siloxanes (L2, D4, D5 and D6) are described in the literature with regard to environmental and health effects; therefore, it is not possible to draw broad conclusions and comparisons of the VMS toxicity from the compiled information.

Although siloxanes are generally not toxic to aquatic organisms at their low values of solubility in aqueous media, they have relatively high bioconcentration factors, implying some potential for bioaccumulation [38,40]. Cyclic siloxanes are involved in adverse immunologic responses, disorders in connective tissues, liver and lung damage and endocrine disruption in laboratory animal studies [30]. *In vivo* metabolisms in fish have been studied on the laboratory scale [41]. Significant gaseous exchange via the lungs is predicted in air breathing organisms [42], suggesting that c-VMS may not bioaccumulate in birds, cetaceans and pinnipeds. Moreover, *in vitro* exposure to D4 via injection in mice caused fatal liver and lung damage [43], oral exposure to D4 caused oestrogenic effects [44-46] and inhalation of D5 affected the nervous system [47]. In the case of human beings, although in short-term and controlled studies no immunologic or pro-inflammatory effects of D4 were observed, the European Union suggested some damaging effects on hormone function that may result in infertility [48].

Environmental risk assessments have been conducted for D4, D5, and D6 in Canada [49-51], the UK [35,39], Sweden [52] and a consortium of Nordic countries [19,29]. The study in Canada concluded that D4 and D5 have the potential to cause ecological harm and other damaging effects on the environment and its biological diversity [22,53-55]. Moreover, the risk assessment in the UK concluded with the recommendation of classifying D4 as persistent, bioaccumulative and toxic (PBT) and D5 as very persistent and very bioaccumulative (vPvB) under REACH [34,35,39].

4. Quantification of siloxanes in environmental matrices: air, water, soils, sediments, sludge and biogas

Quantification of siloxanes in wastewater is still limited because of the lack of regulations on their requirement levels and potential influence on the process performance. Additionally, the complex nature of the samples (water, soils, sediments, sludge, and biogas), the low concentration levels and the large amount of compounds present in the samples have limited the development of robust analytical methodologies for the analysis and monitoring of siloxanes.

4.1 Quantification of siloxanes in gaseous matrices

Most of the efforts into quantification have been focused on gaseous samples because of the possible risks to human health (air matrices) and impacts on energy recovery technologies (biogas matrices). Although several studies regarding off-line analysis of both biogas and air matrices have already been published [12,56-58], it should be noted that there is not a standard method for the analysis of VMS in a gaseous matrix. Tables 3 and 4 summarize the analytical methodology used for biogas and air matrices. Gas Chromatography coupled with Mass Spectrometry (GC-MS) is the most commonly used technique [6,7,12,58-61], but other detection equipment such as photoionization detectors (PIDs) [57,62], flame ionization detectors (FIDs) [63] and even direct analysis by atmospheric pressure ionization and mass spectrometry (APCI-MS/MS) [64] have also been employed.

Moreover, reliable sampling techniques are also required for adequate quantification. Different sampling techniques both for biogas and air samples have been assessed: metallic canisters [1], Tedlar® bags [12,58], adsorbent tubes [7,40,57-59,61] impingers [58] and passive air samplers [65]. The different sampling techniques have advantages and disadvantages; for example, Tedlar® bags, despite not having the ability to concentrate the sample compared to other sampling methods, are easy and quick to use and are well accepted by WWTP operators. Within this context, [66] showed that biogas samples stored in commercial Tedlar® bags with polypropylene fittings were more stable than those stored in bags with stainless steel fittings. On the other hand, if really low concentrations are expected (e.g., downstream a biogas treatment system), adsorbent tubes or impingers are recommended [58].

Table 3.

Table 4.

In parallel to off-line analysis, new developments in the on-line monitoring of siloxanes are appearing as a result of concentration fluctuations over time [57,68] and the requirement of determining the performance of biogas treatment systems for the biogas-to-energy market. Arnold and Kajolinna [57] developed an on-line and portable analyser based on FT-IR and GC-PID techniques. The system simultaneously provided information about the main biogas components (CH_4 and CO_2) and siloxanes as well as the other trace components that hinder the utilization of biogas (e.g., ammonia, sulphur compounds, aromatic hydrocarbons and halogenated compounds). The siloxanes were determined using the GC-PID system. Monitoring results from six field cases in Finland (three landfill sites and three WWTP) were reported, but no economic comparison between on-line monitoring and high frequency off-line analysis was included. More recently, an on-line FT-IR was directly used to measure the siloxanes concentration at the inlets and outlets of biogas adsorption beds [69], thus giving real-time protection to the downstream energy conversion equipment (an internal combustion engine in that case). Cyclic and linear siloxanes were analysed at 798 – 817 and 837 – 867 cm^{-1}, respectively. The Antaris Industrial Gas System (Thermo Fisher Scientific Inc., Waltham, MA, USA), which had a detection limit of 7 mg/m^3 and an accuracy of 10%, was capable of measuring siloxane concentrations six times per hour and gave results within two minutes of sampling.

4.2 Quantification of siloxanes in aqueous samples

The main limitations in the quantification of aqueous samples are blank contamination (leading to an increase in the limit of detection) and the high vapour pressures of the siloxanes (responsible for siloxane losses from samples). Some analytical methods have been reported to quantify the residual levels of c-VMS and l-VMS in water and wastewater samples, including purge and trap using helium followed by adsorption on a macroporous polymeric sorbent (i.e., XAD resins) [70], purge and trap followed by GC-MS [19], thermostatic bath and mechanical shaking before injection by headspace

GC-MS [71], headspace-solid phase micro-extraction (HS-SPME) into the GC [60] or an ultrasound-assisted dispersive liquid-liquid micro-extraction (USA-DLLME) into the GC [72]. As shown, GC–MS using single quadrupole is the most common quantification technique [73-75]. However, a reduced number of cases with GC coupled to other detectors, such as flame ionization detectors (FIDs) [63,70], atomic emission spectroscopy (AES) or triple quadrupole MS instruments, have been used [64,67].

In addition, a small but growing number of studies assessing their occurrence in WWTP effluents and river samples have been published. For example, the methodology described by Sparham et al. [71] was used to observe the disposal of D5 at trace levels through WWTP discharge. Sanchis et al. [76] first applied GC–MS/MS to analyse methylsiloxane in surface water and river sediments from two rivers in Spain and the influents and effluents of 17 WWTPs. Methylsiloxanes were present in all of the analysed samples, with c-VMS being found at higher concentrations and D5 was the predominant compound with a maximum concentration of 8915 ng/L in the influent and treated effluents and an average concentration of 273 ng/L.

A newly developed large volume injection (septum less head adapter and cooled injection system) GC-MS method was used to avoid contamination originating from instrumental analysis, to determine the occurrence of three c-VMS (D4, D5 and D6) in environmental compartments impacted by wastewater effluent discharges [32]. More recently, Xu et al. [77] used SPME coupled with GC-MS to determine four c-VMS in aqueous and sludge samples from a WWTP.

4.3 Quantification of siloxanes in solid samples (soils, sediments, sludge)

Quantification in soil and sediment matrices has been explored through solid–liquid extraction (SLE) [74,78,79] and accelerated solvent liquid extraction (ASE) through mechanical vibration or sonication together with an organic solvent, such as n-hexane [26,63,75]. In addition, quantification in sludge matrices has also been studied through the purge and trap method [70] and by solid-liquid extraction [26,76]. Table 5 shows the analytical methodology used for water, wastewater, soil, sludge and biota matrices.

Table 5.

5. The fate of siloxanes in the urban/industrial wastewater cycle

As previously mentioned in Table 4, the sinks for most non-volatile siloxanes and a non-negligible portion of the volatile siloxanes are WWTPs. For instance, the total feed of siloxanes into wastewater was estimated at 17 ktonnes/y in the USA [6,80]. This section assesses the fate of siloxanes in the sewage and sludge trains of a WWTP.

5.1 The physico-chemical properties of siloxanes affecting their fates in WWTPs

Siloxanes are relatively long lived in water because they are not biodegradable, giving rise to concerns about their persistence [81]. However, they can undergo acid- and base-catalysed hydrolysis with estimated half-lives ranging from a few hours to 100 days, depending on the compound, pH and temperature [35,39]. At pH 7 and 12°C, the hydrolysis half-lives for D4 and D5 were estimated to be 17 and 315 days in freshwater, while at higher and lower pH values, they were significantly shorter [82,83]. On the other hand, the hydrolysis half-lives of D4 and D5 at pH 8 and 9°C in sea water were estimated to be 3 and 64 days, respectively, indicating c-VMS have shorter half-lives in sea water than surface water. Biodegradation is expected to play a small role in the removal of c-VMS because the very low water solubility is thought to limit their biological availability [18,84-86].

Furthermore, biodegradation of c-VMS has been demonstrated in dry soils [85,86] through a multistep process, initiated by ring-opening hydrolysis of the cyclic compounds to form linear oligomeric siloxane diols, followed by further hydrolysis of these intermediates to the ultimate degradation product of monomer dimethylsilanediol [85]. Half-lives for D4, D5, and D6 were estimated to be approximately 4 – 5, 10 – 13 and 158 – 202 days, respectively, for dry temperate soils in equilibrium with air with relative humidity of 50 – 90% [87]. A slow degradation rate was observed for ^{14}C-labeled D5 in aquatic sediment under both aerobic and anaerobic conditions [88]. The half-lives at 24°C were estimated to be of 1200 days under the biotic aerobic conditions, 2700 days under sterile aerobic conditions, 3100 days under biotic, anaerobic conditions, and 800 days under sterile anaerobic conditions, respectively [26].

Finally, due to siloxanes high saturated vapour pressures and low aqueous solubilities, they tend to be distributed into the atmosphere (where they can potentially be transported over long distances) [26,36,40,47] and to dissolved and particulate matter [89]. In fact, siloxanes have both high Henry constants (K_H) and log octanol-water partition coefficients (log K_{ow}) (17 and 5, respectively, for D4, [90]), indicating a propensity to distribute from water to air (K_H) and an affinity for dissolved and particulate organic carbon (K_{ow}).

Overall, given these physico-chemical properties and the relatively slow hydrolysis rates, volatilization and adsorption onto extracellular polymeric substances (EPS) in sludge flocks are expected to be the most significant mechanisms contributing to siloxanes removal from sewage lines [26,90,91]. Figure 2 illustrates siloxane partitioning in wastewater/sludge streams into three phases: free dissolved chemical, adsorbed to Particulate Organic Carbon (POC) present as suspended solids, and adsorbed to Dissolved Organic Carbon (DOC).

Figure 2.

5.2 Sewage treatment line

WWTPs are designed to remove solids, nutrients and biodegradable organic matter. These plants also remove many types of compounds via volatilization, biological degradation and partitioning to bio-solids during their normal operation. In general, the most common sequence of treatment processes is pre-treatment (for the removal of screens, fats and grit), primary settling followed by biological treatment, secondary clarification and disinfection.

The first studies assessing the fates of siloxanes in sewage treatment date back to 1990s. Mueller [90] reported D4 concentrations in influent and effluent from WWTPs ranging from 2.1 – 7.1 µg/L and 0.06 – 0.4 µg/L, respectively. The removal efficiencies of D4 ranged from 91% to 99% [90] with the following distribution: 42% as primary sludge, 33 – 38% volatized into the atmosphere and 15 – 18% as secondary sludge. Parker [59] also reported high removal efficiencies at an activated sludge plant: 87% for D4 and 96% for D5. The mass balances for D4 and D5 could not be closed as removal by volatilization accounted for 36 ± 12% and 22 ± 14% and removal by sorption on the sludge accounted for 9 ± 3% and 8 ± 6%, respectively. Kaj [19] reported lower D4, D5 and D6 concentrations in influent and effluent samples at Swedish WWTPs. For the influent samples, D4 was not detected in any sample, while the D5 concentration ranged from 0.1 – 1 µg/L (detected in three out of four samples), and D6 ranged from 0.06 – 0.3 µg/L. For the effluent samples, D5 was only observed in one out of twelve samples (0.05 µg/L), and D6 was measured five times (0.05 – 0.23 µg/L). Moreover, the D5 and D6 concentrations in the effluent from a pulp and paper WWTP were 0.06 and 0.15 µg/L, respectively [19].

Wang et al. [26] assessed the concentrations of D4, D5 and D6 at eleven WWTPs in Canada with different treatment configurations (one with chemically assisted primary treatment, three with primary treatment followed by activated sludge and the rest with primary treatment followed by lagoon). The obtained concentrations were in the range of 0.3 – 6.7 µg/L, 8 – 135 µg/L, and 1.5 – 27 µg/L in the influent and <0.01 – 0.045 µg/L, <0.03 – 1.6 µg/L, and <0.02 – 0.09 µg/L in the effluent. The average removal efficiencies at the eleven plants were 98%, 98% and 99% for D4, D5 and D6, respectively. There were no apparent differences in the removal efficiencies from the WWTPs with different biological treatment configurations, confirming that biodegradation plays a minor role in the removal of siloxanes. Nevertheless, the chemically assisted WWTP showed lower removal efficiencies, probably as a result of the lower retention time and the lack of aeration, resulting in fewer opportunities for adsorption or volatilization removal mechanisms. On the other hand, the WWTPs with larger overall hydraulic retention times showed greater siloxane removal efficiencies.

Van Egmond [37] obtained removal efficiencies greater than 99% for c-VMS in a WWTP in Ditchford Lane (UK). The D5 and D6 concentrations in the influent ranged from 6 – 36 and 2 – 24 μg/L, respectively, while the effluent concentrations were less than 0.4 μg/L and 0.2 μg/L for D5 and D6, respectively. D4 was observed in neither the influent nor the effluent samples. The calculated siloxane loads in urban WWTPs were estimated at 2.7 and 1.3 mg/day/capita for D5 and D6, respectively, which is smaller than the previous estimates from the UK Environmental Agency [35,39]. Moreover, c-VMS partitioning was also studied on the effluent samples, showing that the freely dissolved phase accounted for 73±4% for D5 and 26±6% for D6. Although a correlation of the freely dissolved c-VMS content with DOC and POC could not be realized due to instrument failure, the organic matter removal efficiency was envisaged to have a major influence on the c-VMS removal efficiency.

Bletsou et al. [16] studied the occurrence and fate of 5 cyclic (D3 to D7) and 12 linear (L3 to L14) siloxanes in raw and treated wastewater (both particulate and dissolved phases) as well as in sludge from a WWTP in Athens (Greece). c-VMS and l-VMS (except for L3) were detected in all influent samples at mean concentrations of 20 μg/L (the sum of 17 siloxanes). The predominant siloxane compounds were L11 (24% of the total siloxanes content), L10 (16%) and D5 (13%). For 10 of the 16 compounds detected in influents, the removal efficiency was higher than 80%. The siloxane mass flow was estimated as 15 kg/day at the influent and 3 kg/day at the outlet. On the other hand, the mean sludge concentration was 75 mg/kg, and D5 (20%) and L10 (15%) were the predominant siloxanes in the sludge. The linear siloxanes showed higher solid−liquid distribution coefficients (K_d) than the cyclic compounds.

Finally, Xu [77] studied the occurrence and fate of four c-VMS (D3, D4, D5 and D6) and two l-VMS (L3 and L4, concentrations below detection limit) in a municipal WWTP in Beijing (China) in the water and sludge streams. In the WWTP, as shown in Figure 3, the primary treatment (bar screens and grit chamber) was followed by two parallel secondary treatment lines, A2O (bottom) and reversed A2O (top), each having a capacity of 200,000 m^3/d. In the A2O line, the hydraulic retention times were 1.5, 3 and 11 hours, respectively, and the total solid retention time was 20 – 25 days. In contrast, in the reversed A2O line, the hydraulic retention times were 1.5, 2.5 and 10 hours, respectively, and the total solid retention time was 6 – 7 days. The c-VMS removal efficiencies were higher in the A2O process (75 – 88%) than in the reversed A2O (56 – 81%). The contributions of the different stages were assessed, showing that c-VMS were mostly (e.g., 44 – 84%) removed in the anaerobic tanks rather than in oxic and anoxic zones in both configurations of the A2O process. The measurements of the siloxanes in the sludge showed that adsorption to sludge accounted for 8 – 9%, 19 – 29%, 32 – 38% and 40 – 53% for D3, D4, D5 and D6, respectively.

Figure 3.

Overall, these studies confirm that volatilization into air and adsorption onto sewage sludge are the main removal mechanisms of c-VMS from the sewage line in municipal wastewater treatment. While adsorption and volatilization are expected to be competitive in the aeration tank, the former can be ignored in the primary clarification due to the lack of aeration; therefore, removal is expected to occur via adsorption. Biodegradation is expected to play a minor role in the removal of siloxanes. However, the mass balances carried out cannot yet conclusively determine the contribution of each mechanism on siloxanes removal from wastewater.

5.3 Sludge treatment lines and the final disposal sludge

During anaerobic sludge digestion, where the temperature of the sludge can reach 35 to 60°C depending on the operating conditions (mesophilic digestion for the former and thermophilic digestion for the latter), siloxanes can significantly volatilize and end up in the formed biogas [6,7] because this process is temperature dependent [29,58]. Along with the most common silicon compounds, biogases may also contain organic silicon compounds other than siloxanes; for example, methoxytrimethylsilane, tetramethylsilane, trimethylfluorosilane and trimethylpropoxysilane [7].

However, compared to sewage lines, fewer researchers have systematically studied the fates of siloxanes and their removal from sludge lines. For example, sludge thickening and dewatering processes, which are typically installed both in small and big WWTPs, have not been studied. Xu et al. [77] used *in vitro* biodegradation anaerobic experiments to assess siloxanes removal in anaerobic digestion (the temperature was not given). Experiments showed that D4 and D5 were eliminated by both volatilization and degradation. In particular, after 60 hours, approximately 25 – 40% was transferred to the biogas phase and approximately 44 – 63% was degraded into dimethylsilanediol [$Me_2Si(OH)_2$] and other analogues [$HO(Me_2SiO)_nH$]. Microbe catalysis hydrolysis was envisaged as the main degradation mechanism for D4 and D5 under anaerobic conditions. On the other hand, D3 was eliminated mostly by volatilization (81% present after 60 hours in the biogas) and D6 was hardly removed in the process due to its low volatility and poor bioavailability.

Finally, Wang et al. [26] studied c-VMS in biosolid-amended soil at eleven Canadian farms. The observed D4, D5 and D6 concentrations were <0.01 – 0.02 µg/g dw (dry weight), <0.01 – 0.2 µg/g dw, and <0.01 – 0.7 µg/g dw, respectively. Other sludge final disposal routes, such as incineration or landfills, were not studied. The fates of siloxanes in sludge drying processes and other sludge final disposal routes such as incineration or landfilling have not been assessed.

6. Removal of siloxanes in the energetic valorization of biogas

Various siloxane removal technologies from biogas based on adsorption, absorption, refrigeration/condensation, membrane separation and biological degradation have been reported and some of them have been commercialized at the industrial level [4,8,12,13,92-98]. Some previous studies conducted a thorough review of siloxanes removal technologies from biogas [12,13]. A summary of the most relevant findings, operating performance, energy consumption and costs for each technology is summarized in Table 6.

Table 6.

6.1 Adsorption processes

Adsorption on porous solids represents the most common practice today to abate siloxane compounds. The most common adsorbents used to remove siloxanes are activated carbons (AC), which have been widely implemented to treat synthetic gas and real landfill/sewage gas due to their excellent adsorption capacities [2,4,6,8,11,69,94-96,99-104]. Inorganic adsorbents, such as silica gel, zeolites and alumina, and other polymeric adsorbents, such as polyurethane foams, have also been widely employed [4,8,70,94-96,106].

The accessibility of siloxane molecules to the internal adsorption surface depends on the adsorbent properties. A positive correlation between the siloxane adsorption capacity and the specific surface area (BET area (m^2/g)) and the meso- (2 – 50 nm) and micro- (0.7 – 2 nm) pore volumes was observed [94,96,103], indicating that larger variables indicate higher siloxane removals. In contrast, no correlation with the narrow micropores (< 0.7 nm) was observed [103], which is consistent with the siloxane size (1.08 - 1.03 nm in the case of D4). Apart from the properties of the adsorbent material, the most relevant variables influencing the siloxane adsorption capacity are the biogas composition and siloxane concentration. Most of the lab-scale experiments (both with AC and inorganic materials) are conducted in N_2 dry matrices and at very high siloxanes concentrations (not representing sewage biogas conditions), leading to higher adsorption capacities, which are not later observed in real operation [4,94,100-102]. For example, a relative humidity of 50 – 70% can reduce the siloxanes adsorption capacity a factor of 10 or greater [4,106], probably as a result of water adsorption and formation of hydrogen bonds with oxygen functional groups on the adsorbent material surface, which block the adsorption sites. Moreover, Hepburn et al. [69] showed that bed dimensioning (height-diameter ratio) also plays an important role in the siloxane adsorption capacity, concluding that operation at high Reynolds number favoured siloxane adsorption.

A well-reported problem related to adsorption technologies is concentration roll-up, which consists of the desorption of compounds previously adsorbed in downstream zones of the filter bed being replaced by more strongly adsorbed compounds. In the context of siloxanes and sewage biogas, it is assumed that D5 can displace previously adsorbed D4 and eventually result in outlet concentrations greater than the inlet ones [94,101]. Due to its smaller size, the early breakthrough of D4 may be prevented or delayed using materials with higher percentages of micropores.

Finally, according to both landfill gas treatment practices and laboratory experiments, adsorbent materials can only be partially regenerated from siloxanes after use [4,8,93] even with advanced oxidation processes (O_3, H_2O_2) [107]. Detection of D5, D6 and D7 on exhausted AC only exposed to D4 as the silicon source revealed a polymerization mechanism on the surfaces of the carbons [103], which can explain the low regeneration efficiencies. Although several patents have been issued claiming the development of regenerable adsorbents for siloxanes (see the review [12]), it seems to still be an unsolved problem in practice.

6.2 Absorption processes

Due to the chemical nature of siloxanes, the most suitable absorbents are polar organic solvents, such as Selexol™ (polyethylene glycol or dimethyl ethers) [12]. Reactive absorption methods with concentrated solutions of acids, which cleave Si-O bonds, achieved moderate siloxane removal efficiencies, but their utilization complicated plant design due to safety concerns, resulting in higher capital and operational costs. The application of alkaline solutions is unpractical, as the presence of carbon dioxide results in high caustic consumption and precipitation of carbonates in the absorption column [13]. Finally, because many organic silicon compounds are at least partially water soluble, water could also be a physical absorbent, but it has not been a very effective medium for siloxane removal [108]; thus, more comprehensive study of this field is required [12,109].

In practice, gas scrubbing systems often combine other pre- and post-treatment methods. Because the absorption process operates better at lower temperatures, gas is often cooled prior to the absorption stage. AC adsorption can also be used as a polishing step after gas scrubbing [97].

6.3 Refrigeration/Condensation and Deep Chilling processes

The application of refrigeration/condensation techniques is carried out to remove water from gases. In parallel to water removal, other substances, such as aromatics and siloxanes, can also be partially removed. Performance of a refrigeration/condensation system can vary from low to moderate (15 – 50% siloxane removal) depending on the refrigeration temperature employed and the initial siloxane concentration [100]. Therefore, the refrigeration/condensation process is used as a gas pre-treatment prior to the use of AC, significantly increasing the AC lifetime, but it cannot achieve the overall siloxane removal requirements as a stand-alone system [97].

In deep chilling conditions, the theoretical removal efficiency depends on each siloxane saturation partial pressure ($P_{sat}(T)$) [12]. Although the theory predicts removal efficiencies of 26% at – 25ºC [6,12], experimentation with deep chilling processes clearly exceed theoretical performance [99]. In any case, the energetic requirements for the application of deep chilling systems are so high that such a process is not profitable unless there are very high biogas flows and/or siloxane concentrations [10,12].

6.4 Membrane separation processes

This technology consists of selective siloxane permeation by dissolution and diffusion through dense polymeric or inorganic membrane material [12,110], while methane is ideally retained on the other side of the membrane. Membranes are characterized by large surface areas available for separation while occupying small volumes, which makes the technology very compact [111-113]. A selection of elastomeric membranes was assessed to determine the permeability and selectivity of the siloxanes (L2, L3, L4, D3, D4 and D5) towards methane in a real landfill gas matrix at 40°C and ambient pressure [12,13]. A higher siloxane/methane selectivity will result in lower methane losses over the membrane. Membrane processes seem especially suitable when biogas upgrading is required, as CO_2 can also be removed from the biogas matrix.

6.5 Biological degradation processes

The biological removal of pollutants from gaseous phases presents certain advantages, such as high treatment capacities and reduced operating costs [12,13]. The removal efficiency of gas contaminants in biological systems depends on either the gas–liquid or the subsequent liquid-biofilm transfer rate [114-116]. However, Popat and Deshusses [98] estimated that the maximum D4 elimination capacity in a Biotrickling Filter (BTF) is 30 – 100 $mg \cdot m^{-3} \cdot h^{-1}$, which is 1000 times smaller than biological H_2S removal [117], introducing remarkable doubts about the industrial implementation of biological processes for siloxane removal.

The prospects for biological biogas treatment must also take into consideration the presence of hydrogen sulphide in biogas. BTF have already been demonstrated for the removal of hydrogen sulphide from biogas under anoxic conditions [117]. Simultaneous removal of both hydrogen sulphide and siloxane could represent an attractive cost-effective alternative to more expensive conventional biogas treatment technologies [97].

7. Effect of the presence of siloxanes on biogas-powered Energy Conversion Technologies: siloxane limits and operating concerns for energetic valorization

Several Energy Conversion Systems (ECS) for biogas energy valorization are installed today in WWTPs, including boilers, internal combustion engines, combustion turbines, micro-turbines, fuel cells and Stirling engines [118-121]. Together with the other biogas contaminants, siloxanes pose a risk to the short- and long-term performance of ECS [6,7]. Comparisons are sometimes difficult to make as different manufacturers use different units, such as mg/m^3, mg/Nm^3, mgSi/m^3, mgSi/Nm^3 and ppm$_v$.

During combustion (Equations 1 and 2), siloxanes are oxidized to silicon dioxide (silica, $SiO_2(s)$) [6,122].

D4 combustion: $[(CH_3)_2SiO]_4(g) + 16\ O_2(g) \rightarrow 4\ SiO_2(s) + 8\ CO_2(g) + 12\ H_2O(g)$ Eq. 1

D5 combustion: $[(CH_3)_2SiO]_5(g) + 20\ O_2(g) \rightarrow 5\ SiO_2(s) + 10\ CO_2(g) + 15\ H_2O(g)$ Eq. 2

$SiO_2(s)$ condensation progressively forms nanoparticles and nanoclusters, which will continue to grow into larger aggregates or agglomerates by taking up free $SiO_2(g)$ molecules [123]. Temperature plays an important role on the morphology and size of these particles, which will eventually deposit as microcrystalline quartz in the combustion chamber, turbine blades, heat exchangers, spark plugs, valves, cylinder heads, etc. Different field tests with biogas-powered ECS [4,6] observed silica films (with a thickness of several millimetres) on the surfaces of the equipment, which was difficult to remove both chemically and mechanically. On the other hand, siloxanes can also affect the efficiency of the exhaust gas catalytic treatment [64,124], poisoning Pt and Pd supported catalysts by blocking the surface of the metal with silicon atoms [102,125].

On the other hand, $SiO_2(s)$ particles ranging from 5 to 10 nm that are not deposited inside the combustion chamber are emitted into the atmosphere. Silica nanoparticles are described as fibrous dusts and as carcinogenic, mutagenic, asthmogenic or reproductive toxic (CMAR) [126]. Considering 10% deposition, an emission of approximately 55 and 73 kg/year of $SiO_2(s)$ was estimated for a 1 MW_e installation during combustion of biogas containing D4 at 14 mg/m^3 and D5 at 15 mg/m^3.

7.1 Internal Combustion Engines (ICE)

Reciprocating internal combustion engines are a well-established, proven power generation technology, and they have a long track record of use in biogas applications [118]. These reciprocating engines are somewhat less sensitive to contaminant levels in the biogas than some of the other engine technologies; however, some treatment is still required. There have been a number of cases where gas contamination was ignored, resulting in damage to internal parts that are exposed to the gas and resulting in early system failure. The sharp edges of the engine parts are prone to super heating and, hence, accumulation of deposits [127].

Few systematic scientific studies on the effect of siloxanes in internal combustion engines are available. Nair et al. [128] compared the performance of two pilot ICEs (250 and 150 W_e each) operated with natural gas; one was spiked with D4 and L2 (equimolar composition; 10 ppm_v total) and the other had no impurities. The exhaust gas composition (CO, CO_2, CH_4, NO, NO_2, and NO_x) before and after catalytic treatment was monitored over 500 hours, showing a reduction in the efficiency of CO conversion from 90% to 50% for the engine using the gas containing siloxanes. This performance reduction was confirmed by a decrease in both the total volume and the BET area of the catalyst. Silica particles ranging from 10 – 180 nm (average 73 nm) were observed at a concentration of approximately 10 $\mu g/m^3$ after the exhaust gas treatment. On the other hand, silica deposits on piston heads, oxygen sensors and spark plugs were observed in the siloxane engine after 96 hours and were confirmed through SEM-EDX analysis. The silica deposit basically consisted of two layers: a bottom one that appeared to be strongly adhered to the metal surfaces and a top one that was more porous and less dense, which easily flaked from the surface. Finally, silicon was also observed in the engine oil.

Engine manufacturers claim higher siloxane limits in biogas than other ECS, but there is a wide range of limits depending on the manufacturer, ranging from 12 mg/m^3 (Jenbacher) to 28 mg/m^3 (Caterpillar) or 30 mg/m^3 (Waukesha) [6,69,129].

7.2 Micro-turbines

Combustion gas turbines generate power through a compressor, combustor and turbine using the Brayton power cycle. However, the very smallest of these units is approximately 3 MW$_e$ (most product families start at 5 MW$_e$ and go up to hundreds of megawatts); hence, the use of these systems powered by biogas, especially sewage digester biogas, is rare because only the very largest biogas applications would produce sufficient biogas fuel for combustion turbines.

A micro-turbine is a smaller version of a combustion turbine, developed to be economical at low output ranges. The available capacity ranging from 30 to 250 kW$_e$ is well-suited to many biogas applications, and they have been installed at municipal WWTPs, landfills, and some dairy farms. The greatest technical challenge for micro-turbines in these applications has been assuring proper fuel treatment. Some early installations were shut down prematurely due to inadequate fuel moisture removal, gas compressor corrosion problems and the lack of siloxane filtering [130,131]. Although inadequate moisture and hydrogen sulphide removal can cause component corrosion issues, siloxanes have been identified as the most important contaminant for micro-turbines, as silica causes significant erosion of the turbine nozzles, blades and bearings, which results in turbine failure. In this context, the siloxane limits are much more stringent that in ICEs.

No systematic scientific study on the effects of siloxane on micro-turbines has been identified. Capstone Microturbines, the leading manufacturer of this ECS, claim a very stringent limit of 0.03 mg/m^3 and can include the biogas treatment system in the battery limits.

7.3 Fuel Cells

Fuel cells convert chemical energy directly into electrical energy through electrochemical reactions. There are five major types of fuel cells characterized by the electrolyte and electrode materials used: Alkaline (AFC), Phosphoric Acid (PAFC), Proton Exchange Membrane (PEMFC), Molten Carbonate (MCFC), and Solid Oxide (SOFC). Theoretically, all types of fuel cells could be fuelled by biogas by extracting the hydrogen from it and removing all poisoning compounds. However, practically, only a few types of fuel cells can be considered for biogas use. At present, there are a number of industrial-scale PAFC and MCFC successfully operating using anaerobic digester gas at municipal WWTP as well as some pilot-scale PEMFC and SOFC projects.

Fuel cells employ catalytic surfaces at the anode and cathode, which are deactivated by sulphur, siloxanes and chlorine contaminants in the gas. In addition, the electrolyte in the MCFC fuel cell reacts with chlorine to form volatile compounds that deplete the fuel cell of electrolyte. Therefore, the biogas fuelling these generators must be deeply cleaned. Sasaki et al. [132] showed the progressive reduction in cell voltage of a SOFC by 10 ppm_v siloxane (D5) in 3%-humidified H_2 at 800ºC, 900ºC and 1000ºC. The Open Circuit Voltage (OCV) dropped from 1 V to below 0.5 V in less than 30 hours and degradation was faster at lower operating temperatures. After 30 – 50 hours, siloxane poisoning, a fatal degradation of cell performance, was observed. This degradation was confirmed to be associated with the formation of $SiO_2(s)$ in the porous cermet anodes according to Equations 3 and 4 [9].

$$[(CH_3)_2SiO]_5(g) + 25\ H_2O \rightarrow 5\ Si(OH)_4(g) + 10\ CO(g) + 30\ H_2(g) \qquad \text{Eq. 3}$$

$$Si(OH)_4(g) \rightarrow SiO_2(s) + 2\ H_2O \qquad \text{Eq. 4}$$

Consequently, based on these studies, fuel cell manufacturers claim inlet siloxane limits in the range of 0.05 – 0.1 mg/m^3.

7.4 Stirling Engines

The Stirling engine is an external combustion engine, in which the combustion occurs continuously in a combustion chamber that is separate from the working gas (usually Helium) and engine moving parts. Therefore, the Stirling engine may offer the advantage of being more tolerant to contaminants in the fuel gas [133]. At the time this paper was written, no full-scale Stirling engine references were available for power generation [133,134]. However, because of its potential for applications using alternative fuels, such as biogas and waste heat, there have been significant developments in Stirling engine technologies in recent years. Stirling engine manufacturers (Stirling Biopower in the US and Stirling Denmark and CleanEnergy in Europe) claim that these engines can be powered without biogas treatment; therefore, no siloxane removal is required, and only regular cleaning of the heat exchanger and other engine parts is necessary.

7.5 Domestic gas boiler

Previously described ECS are used in WWTP for on-site energy generation (both electrical and thermal). In recent years, biogas upgraded to biomethane and its further injection in the natural gas grid has become an interesting alternative for off-site biogas valorization [135-137]. Several biomethane injection standards are available in different European countries, and a major concern for gas grid operators is the potential malfunctioning of downstream equipment (e.g., domestic gas boilers) as a result of the presence of siloxane and other biogas contaminants. However, there is not yet a common European injection standard for siloxanes in the gas grid. For example, Spain [138] and Austria [139] apply a maximum of 10 mg/m^3 siloxanes, while the specification in the Netherlands [140] is 5 ppm$_v$ siloxanes.

Some studies have recently been undertaken to assess the effects of siloxanes on natural gas powered equipment. Van Essen et al. [141] studied the effects of siloxanes in five domestic condensing boilers with air/gas ratio control and one flow-through hot water heater with a conventional heat exchanger design and burner control. After exposure to 5 ppm$_v$ of D5 for 600 hours, the thermal output of the boilers fell by 35%, probably as a result of the deposition of an insulating layer on the heat exchanger. On the other hand, as a result of the air-gas ratio control, the CO concentration in the flue gas in boilers was not affected by the siloxane concentration. However, when the boiler was operated without air-gas ratio control, an increase in the CO level was observed. Finally, silica was also detected on the ionization probes typically employed as Flame Failure Devices (FFD), which corresponded to an eventual shut-down of the boiler after only 50 hours.

Nair et al. [142] also observed a detrimental effect of siloxanes on the flame sensors in a domestic pulse-combustion furnace exposed to L2 and D4 (equimolar composition; 2, 10 and 20 ppm_v total). No clear trend in the shut-down time was observed, as the furnace exposed to 20 ppm_v stopped later than that exposed to 10 ppm_v but earlier than that exposed to 2 ppm_v. SEM-EDX analysis confirmed the presence of silica on the tip of the sensor and in the condensate water collected from the furnace. Similar to the experimentation with ICEs, silica particles with a mean diameter of 75 nm were detected in the flue gas.

7.6 Siloxane limits in Energy Conversion Systems

Unless the siloxane concentrations are very low, upstream removal is recommended because either the degradation in the performance of the energy conversion system or the control of the problem with more frequent maintenance may exceed the investment and operating costs of the installed gas purification system. Table 7 summarizes the siloxane concentration limits for the previously described ECS, indicating the suggested corresponding biogas treatment train.

Table 7.

8. Conclusions, knowledge gaps and outlook

Volatile methyl siloxanes are considered one of the most adverse components for efficient biogas energy recovery in Waste Water Treatment Plants. As a result of the fact that they are produced in large quantities and are used in a wide range of consumer products, VMS are introduced into the wastewater environment.

Although there is not a standardized methodology for VMS analysis in different matrices, siloxanes can be properly analysed in biogas, air, water, wastewater, sludge, soils and sediment samples. However, off-line analysis methods are time-consuming and costly; therefore, the future should deliver advanced on-line siloxane monitoring equipment, using FT-IR or GC-MS, for example, as some authors have suggested; which will improve the control and reliability of biogas treatment trains, guaranteeing more stable and safer operation of energy conversion units.

Removal efficiencies greater than 95% can be obtained for all VMS in the sewage treatment line. Volatilization/stripping to the atmosphere and adsorption into sewage sludge (and its further volatilization into biogas in anaerobic digesters) are the main removal mechanisms in WWTPs, while biodegradation is expected to play a minor role. However, the mass balances still do not accurately match. Therefore, better understanding of the mechanisms involved and their contribution should be addressed in the future both on the sewage and sludge lines, allowing for smarter operation of the treatment processes at specific conditions to avoid siloxane-related problems.

Satisfactory siloxane removal from biogas can be accomplished using a preliminary refrigeration/condensation stage followed by adsorption, showing removal efficiencies greater than 99% and achieving outlet concentrations below 0.1 mg/m^3. Adsorbent materials with high surface areas and high micro- and mesopore volumes should be selected to achieve the most efficient technical-economic performance. Alternatives methods to avoid concentration increases of the lighter siloxane compounds, which may result in outlet concentrations that are greater than those at the inlets, should be further understood and studied. Future trends will focus on developing more selective and regenerative removal systems from biogas to reduce the associated operating costs and even the silicon recovery and valorization.

Finally, current studies assessing the effects of siloxanes on energy conversion systems on the short- and long-term cannot yet conclusively determine the involved degradation mechanisms and establish scientifically sound inlet concentration limits. Standardization of the units used by the different manufacturers should also be fostered. The results reported in this work confirm that, unless the concentrations are low, either a degradation in the performance of the ECS or controlling the problem with more frequent maintenance may exceed the investment and operating costs of the installed gas purification system; therefore, upstream siloxanes removal is recommended. Collaborative research between biogas producers, suppliers of biogas treatment systems and manufacturers of ECS are warranted to address this issue further.

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Symbols and Acronyms

A2/O: anaerobic, anoxic, oxic
A2/O reversed: anoxic, anaerobic, oxic
AC: activated carbon
AFC: Alkaline Fuel Cell
ASE: accelerated solvent liquid extraction
ATD-GC-MS: Automated Thermal Desorption Gas Chromatography – Mass Spectrometry
BTF: Biotrickling Filter
CES: Centre Européen des Silicones
CMAR: Carcinogenic, Mutagenic, Asthmogenic or Reproductive toxic
c-VMS: Cyclic volatile metil siloxane
DOC = Dissolved Organic Carbon

EPS = Extracellular Polymeric Substance
FFD: Flame Failure Device
GC: Gas Chromatography
GC-AES: Gas Chromatography coupled to atomic emission spectroscopy
GC-APCI-MS/MS: Gas Chromatography coupled to flame ionization detector atmospheric pressure ionization and mass spectrometry
GC–FID: Gas Chromatography coupled to flame ionization detector
GC-MS: Gas Chromatography coupled to Mass Spectrometry
GC-PID: Gas Chromatography coupled to photoionization detector
HS-GC-MS: Head Space Gas Chromatography – Mass Spectroscopy
HS-SPME: headspace-solid phase micro-extraction
LFG: Landfill Gas
LVI-GC-MS: Large Volume Injection Gas Chromatography – Mass Spectroscopy
ICE: Internal Combustion Engine
l-VMS: linear volatile metil siloxane
MCFC: Molten Carbonate Fuel Cell
MSW: Municipal Solid Waste
PAFC: Phosphoric Acid Fuel Cell
PBT: persistent, bioaccumulative and toxic
PDMS: polydimethylsiloxanes
PEMFC: Proton Exchange Membrane Fuel Cell
POC = Particulate Organic Carbon
REACH: Registry, Evaluation and Authorisation of Chemical Substances
SE-GC-MS: Solvent Extraction Gas Chromatography – Mass Spectroscopy
SEM-EDX: Scanning Election Microscopy-Energy Dispersive X-Ray
SLE: solid–liquid extraction
SOFC: Solid Oxide Fuel Cell
USA-DLLME: ultrasound-assisted dispersive liquid-liquid micro-extraction solid–liquid extraction
VOC: Volatile organic compound
VOSiC: Volatile organic silicon compounds
vPvB: very persistent and very bioaccumulative
WWTP: Waste Water Treatment Plant

9. References

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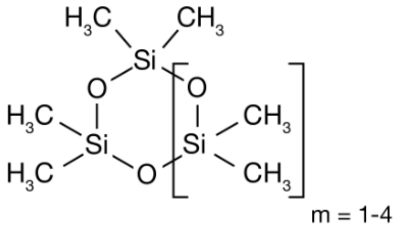
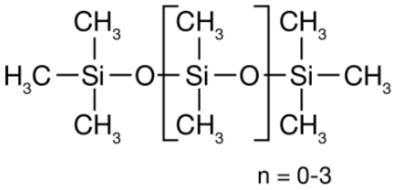
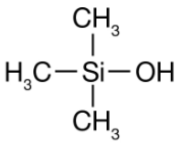
Figure 1 reviewed in word format



m = 1 Hexamethylcyclotrisiloxane (D3)
m = 2 Octamethylcyclotetrasiloxane (D4)
m = 3 Decamethylcyclopentasiloxane (D5)
m = 4 Dodecamethylcyclohexasiloxane (D6)



n = 0 Hexamethyldisiloxane (L2)
n = 1 Octamethyltrisiloxane (L3)
n = 2 Decamethyltetrasiloxane (L4)
n = 3 Dodecamethylpentasiloxane (L5)



Trimethylsilanol

Figure 2 reviewed in word format

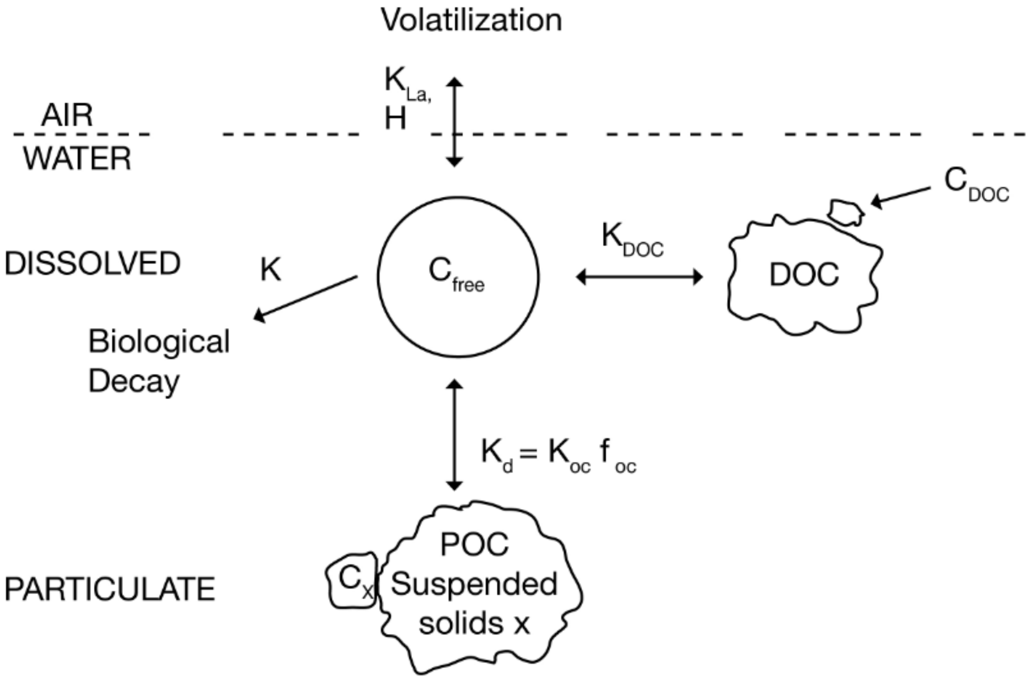


Figure 3 reviewed in word format

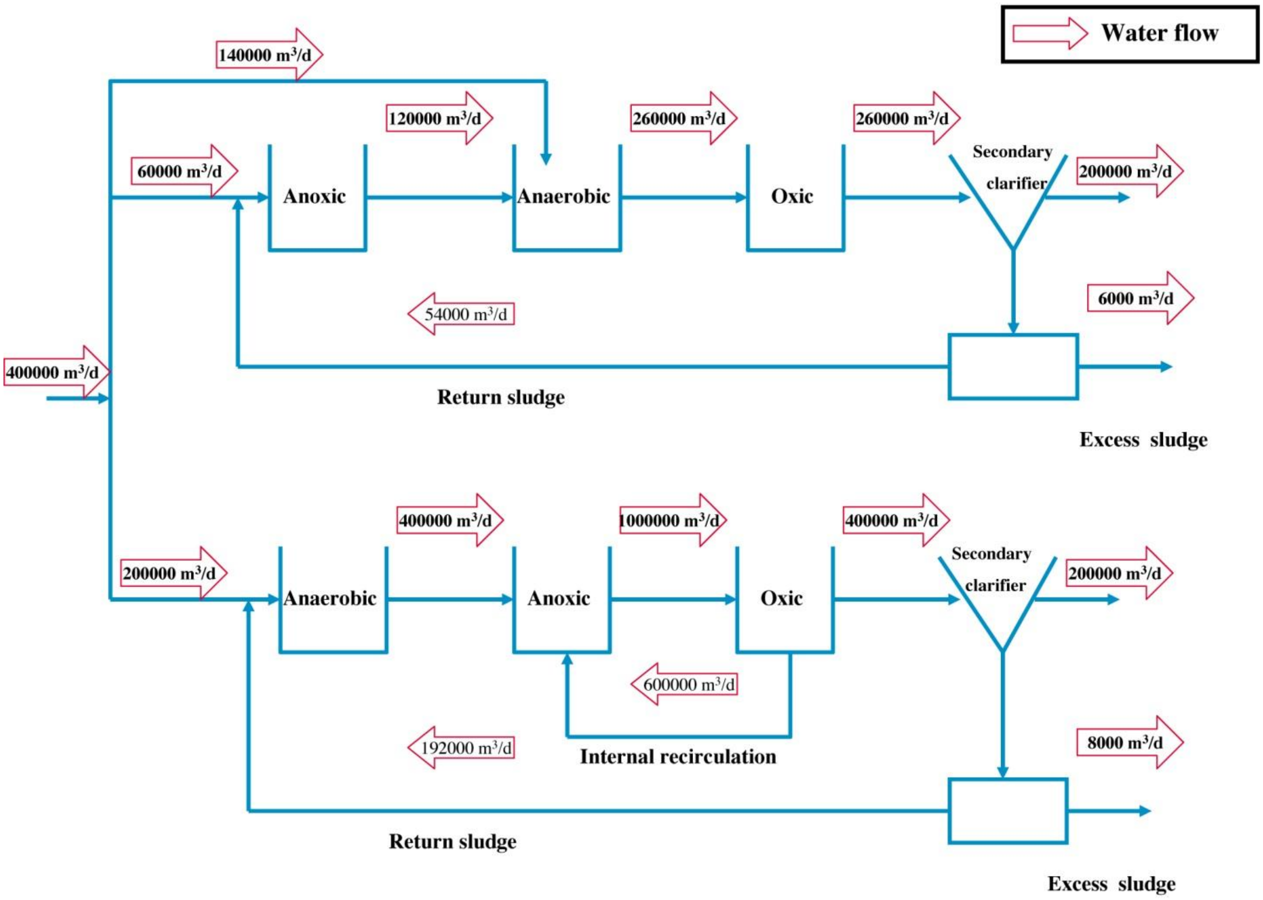


Figure captions reviewed

Figure 1. Structures of common siloxane compounds, adapted from Schweigkofler and Niessner [1]

Figure 2. Schematic of the contamination and decay rates and the equilibrium distribution between the particulate and dissolved fractions, adapted from Mueller et al. [90]

Figure 3. Flow scheme of the municipal WWTP in Beijing (China) (top: reversed A2O; bottom: A2O), adapted from Xu et al. [77]

Tables reviewed

Table 1. Selected physico-chemical properties of VMSs commonly found in biogas

	Abbreviation	Chemical formula	Molecular Weight (g/mol)	Boling point (ºC)	Water solubility (mg/L at 25ºC)
Hexamethyldisiloxane	L2	$C_6H_{18}OSi_2$	162	107	0.93
Octamethyltrisiloxane	L3	$C_8H_{24}O_2Si_3$	237	153	0.034
Decamethyltetrasiloxane	L4	$C_{10}H_{30}O_3Si_4$	311	194	0.00674
Dodecamethylpentasiloxane	L5	$C_{12}H_{36}O_4Si_5$	385	232	0.000309
Hexamethylcyclotrisiloxane	D3	$C_6H_{18}O_3Si_3$	223	135	1.56
Octamethylcyclotetrasiloxane	D4	$C_8H_{24}O_4Si_4$	297	176	0.056
Decamethylcyclopentasiloxane	D5	$C_{10}H_{30}O_5Si_5$	371	211	0.017
Dodecamethylcyclohexasiloxane	D6	$C_{12}H_{36}O_6Si_6$	444	245	0.005
Trimethylsilanol	TMOH	C_3H_9SiOH	90	99	42600

Table 2. Consumption of silicones and siloxanes in Western Europe in 2002 and expected fate as a function of field application, adapted from [17] and [30]

Silicone category	Applications	Consumption		Fate
		ktonnes	%	
Fluids	Processing aids	40	14	Incineration (as Municipal Solid Waste, MSW)
	Textile manufacturing (as softeners and wetting agents)	28.5	10	Softeners: wastewater Siloxanes in textiles: not identified
	Cosmetics and toiletries	25	8	Non-volatile siloxanes: wastewater Volatile siloxanes: air
	Health care: medical-pharmaceutical preparations			Major part: Incineration (as MSW or as medical waste)
	Paper coatings and antifoaming agents (mainly backing for self-adhesives)	17.5	6	Incineration (as MSW) Wastewater
	Surface treatment formulations: paints, coatings and waxes	11	4	Major part: Incineration, landfill Minor part: wastewater
	Mechanical and heat transfer fluids (hydraulic fluids and lubricants/greases)	9	3	Major part: chemical waste Minor part: soil, wastewater
	Other (cooking oils, processed/fast foods)	26	9	-
	Subtotal	*157*	*53*	
Elastomers (rubbers)	Sealants used in construction	78	26	Major part: incineration, landfill and recycling
	Special-purpose sealants and rubber	43	15	
	Subtotal	*121*	*41*	-
Resins	All applications (electrical insulating varnish, water-repellent paints)	18	6	Incineration (as MSW, electric and electronic waste), landfill
Total		296	100	-

Table 3. Review of the studies on the quantification of siloxanes in biogas samples

Siloxanes	**Sampling Technique**	**Analysis & Detection**	**Biogas site**	**Characteristics**	**Concentration**	**Reference**
L_2,L_3,L_4,L_5,D_3,$D_4$$D_5$ D_6,TM-OH	Canister	GC-MS/AES	1)Domestic waste disposals 2)Sewage treatment plants	------- -------	1)<0.01-8.8 mg/m^3 2)<0.01-9.7 mg/m^3	[1]
L_2,L_3,L_4,L_5,D_3,$D_4$$D_5$, TMS	Nalophan NA bags Absorbent tubes (Tenax GR 200 mg)	ATD-GC-MS	1)Landfills 2)WWTPs 3)Biogas plants	1)Gas recovery 1,7-60 million m^3/year 2)Production of 0,9-1,5 m^{3}biogas/year 3)Mesophilic and thermophilic	1)~0-5.25 mg/m^3 2)~0-12.50 mg/m^3 3)~0-5.50 mg/m^3	[7]
L_2,L_3,L_4,D_3,D_4,D_5	Tedlar bag (232 SKC, PP and SS fittings)	GC-MS	Landfill	From the pressurised line (approx. 1060 mbar) of a compressor station	--------	[12]
L_2,L_3,L_4,TMS,D_3,D_4, D_5	Adsorbent tubes (Tenax TA 60/80 mesh)	On-line Portable GC-PID ATD-GC-MS	1)Landfills 2)Bioreactors	1) 400-800 m^3/h 2) 0,1-400 m^3/h	1)<LOD(0.01)-4.3 mg/m^3 2)0.02-27 mg/m^3	[57]
L_2, L_3, L_4, L_5, D_3, D_4, D_5, D_6 and TM-OH	Tedlar bags (SKC, PP fittings) Impingers (n-hexane) Adsorbent tubes (ORBO 32 activated coconut, 24-40 mesh)	GC-MS	1) 5 WWTP in Spain, France and England 2) Landfill	Several configurations of anaerobic digesters were selected, based on temperature (mesophilic and thermophilic), retention time (19-26 days), sludge type and mixing (biogas, mechanical)	D_4: 1.5-10.8 mg/Nm^3 D_5: 12.5-124 mg/Nm^3	[58]
D_4,D_5	1) Gas streams with charcoal sorbent tubes (SKC) 2) n-heptane and mechanical shaking (48 h)	1) GC-MS 2) LSC	Pilot plant study (liquid and gas stream)	Primary and secondary clarifier, aeration basin receiving waste water from a full WWTP (average flow of 93000 m^3/day)	1) Primary clarifier 0.20-3.10 µg/L 2) Primary clarifier 38-129 µg/L	[59]
L_2,D_3,D_4,D_5,D_6, TMS	Comparison of six activated carbon tubes	SE-GC-MS	Landfill	Biogas production: 400 m^3/h	TMS:27-29 mg/m^3 VMS:19-39 mg/m^3	[61]
L_2,L_3,L_4,D_3,D_4,D_5	--------	On-line portable GC-PID	Anaerobic reactor (operating volume of 150 L)	T:35-37ºC 1-10 kgVS m^{-3}d^{-1} HRT:8 days	0.2-0.8 ppm	[62]
D_4,D_5	Teflon bags (Jensen Inert Products, Coral Springs)	APCI-MS/MS	Landfill	1) Well located in a landfill zone operated for 9 years (1991-2000) 2) Composite sample taken from the compressor room located between pumping station and electrical power plant	1) D_4: 1950 µg/m^3 D_5: 21 µg/m^3 2) D_4: 7850 µg/m^3 D_5: 107 µg/m^3	[64]

Table 4. Review of the studies on the quantification of siloxanes in air samples

Siloxanes	**Sampling Technique**	**Analysis & Detection**	**Matrix**	**Characteristics**	**Concentration-Recovery**	**Reference**
D_5	Two 10 mg ENV+ cartridges assembled in series	GC-MS	Air	Rural site 200 km west of Stockholm over a period of 4 months	0.7-8 ng/m^3	[40]
L_3,L_4,L_5,D_3,$D_4D_5D_6$	Passive air samplers comprising sorbent-impregnated polyurethane-foam	GC-MS	Air	1) Sites on the perimeter of two WWTPs and upwind of two landfills 2) On-site.	1) VMSs(WWTPs): 479 ng/m^3; VMSs (landfills): 333 ng/m^3 2) VMSs(WWTPs): 3980 ng/m^3; VMSs (landfills): 4670 ng/m^3	[65]
D_4,D_5	Teflon bags (Jensen Inert Products, Coral Springs)	APCI-MS/MS	Air	Compressed air sample	D_4:123 µg/m^3 D_5: 22 µg/m^3	[67]

Table 5. Review of the studies on the quantification of siloxanes in water, wastewater, soil and sludge samples

Siloxanes	**Solvent extracting agent and extraction technique**	**Analysis & Detection**	**Matrix**	**Characteristics**	**Concentration – Recovery**	**Reference**
D_4,D_5,D_6	Membrane-assisted solvent extraction (water) Liquid–solid extraction (sediment, soil, biota and biosolid)	LVI-GC-MS	Water, sediment, soil, biota and biosolids	Industrial wastewater, receiving water and biosolids collected from or near WWTPs	1) 78-136% (water) 2) 59-91% (sediment) 3) 79-103% (biota) 4) 82-146% (biosolid)	[26]
L_2,L_3,L_4,L_5,D_3,D_4,D_5, D_6	Vortex, thermostatic bath & HS-SPME	GC-MS	Surface waters	2 rivers	0,27-58,5 ng/L	[60]
L_2,D_3,D_4,D_5,D_6,	n-Hexane and vortex-mixed	GC-FID	Spiked Sludge samples	Activated sludge from a full WWTP. Samples were taken from the secondary clarifier.	74-100%	[63]
D_5	Thermostatic bath and mechanical vibration	HS-GC-MS	1) Surface water 2) Waste water	1) 2 rivers at different parts of its flow 2) Treated wastewater	1) 10-29 ng/L 2) 31-400 ng/L	[71]
TMS,L_2,L_3,L_4,L_5,D_3, D_4,D_5,D_6	Ultrasound-assisted dispersive liquid-liquid microextraction	GC-MS	Wastewater	Different points on two WWTPs in Murcia (Spain): influent, effluent, UV reactor inlet and UV reactor outlet	70-120%	[72]
L_5-L_{14}, D_4,D_5,D_6	n-Hexane and sonicated assisted extraction	GC-MS	Spiked Soil samples	Agricultural soils amended with sewage sludge and industrial soil	85-112%	[75]
TMS,L_3,L_4,L_5,D_3,D_4, D_5	N-Hexane liquid-liquid extraction + rotatory evaporator and drying with sodium sulphate	GC-MS/MS	Wastewater, surface water and river sediments	1) 17 WWTP 2) 2 rivers	1) Wastewater >70% for all siloxanes except D3 (40%) 2) Sediments: 80-108%	[76]

Table 6. Review of siloxane removal technologies and conclusions on the operating performance, energy consumption and running costs

Siloxanes removal technology	Reference	Experimental conditions and key findings	Operating performance	Energy consumption*	Investment and Operating Costs**
Adsorption (carbon-based materials)	[94]	2 types of AC showed adsorption capacities of 5.6 – 19.2% for D4 at 4500 mg/m^3 (N_2 dry matrix).	Removal efficiencies greater than 99% can be achieved with adsorbent materials with meso- and micro-porous structures. Adsorption capacities ranging 0.5 – 1.5% t are experimentally observed in real biogas matrices	Low. Pressure drops over adsorbent beds are approximately 0 – 40 mbar/m	Investment costs: low 38k€ for 190 Nm^3/h and 14 mg/Nm^3 siloxane [101] Operational cost: medium 4.5 k€/year for 190 Nm^3/h and 14 mg/Nm^3 siloxane [101] Adsorbent material approximately 0.5 – 1.5 €/kg and media disposal costs approximately 50 – 100 €/ton
	[95]	3 types of AC showed adsorption capacities of 15.5 – 30.7% for L2, D4 and D5 (1:1:1) (N_2 dry matrix).			
	[96]	11 types of AC showed adsorption capacities of 2.2 – 22.5% for D4 (synthetic dry CH_4:CO_2 mixture). AC with pore diameters of 1.7– 3.0 nm are the most favourable.			
	[100]	Graphite-based AC showed adsorption capacity of 0.5–1.5% exposed to real biogas at Calabasas WWTP, USA (4.8–25.2 bar and 4.4 ºC dew point).			
	[101]	Virgin AC showed an adsorption capacity of 0.5% exposed to real biogas at Mataró WWTP, Spain, with D4 and D5 12 – 15 mg siloxanes/m^3 (50.5% RH and 25ºC). Outlet concentrations were below 0.1 mg siloxanes/m^3.			
	[103]	12 types of AC showed adsorption capacities of 25 – 173% for D4 at 1000 ppm$_v$ (N_2 dry matrix).			
Adsorption (inorganic materials)	[4]	Silica gel (1-3 mm) showed adsorption capacity in the range of 1% exposed to real biogas with L2 and D5 16.2 and 14.8 mg/m^3 (50%).			
	[8]	Alumina allowed complete siloxane removal at high temperatures. If used coupled with high temperature fuel cells, the waste heat produced by the fuel cell can be used to preheat the gas.			
	[94]	Silica gel showed adsorption capacities of 10% at D4 concentrations of 4500 mg/m^3 (N_2 dry gas matrix).			
	[106]	Silica gel showed adsorption capacity of 25% at D4 concentrations of 400 mg/m^3 (25ºC; N_2 dry gas matrix).			
Absorption	[4]	Sulphuric, nitric and phosphoric acids were tested under different concentration and temperature conditions, showing removal efficiencies over 95% for D5 and L2 (H_2SO_4 at 48%/97% and 60ºC). Lower concentrations and temperatures reduced removal efficiencies to 50 – 70%.	Removal efficiencies over 95% with concentrated and hot acids and Selexol™ Water is not efficient for siloxanes scrubbing	Medium	Investment costs: medium Operational cost: high
	[12]	Selexol™ (polyethylene glycol or dimethyl ethers) showed removal efficiencies of 99% at pilot plant level.			
	[108]	Water scrubbing (pH = 7; column packed with Pall rings; liquid phase flow 5 – 10 L/min) was tested in a landfill site (Mustankorkea, Finland) at pilot level (gas flow 6 m^3/h) showing no removal of siloxanes from biogas (initial concentration 20 mg/m^3).			
Refrigeration – Condensation	[4]	Gas cooling to temperatures approximately 5ºC was not very efficient as the removal efficiencies of D5 from landfill gas (0.6 mg/m^3) and sewage gas (9.7 mg/m^3) were 12% and 18%, respectively.	Removal efficiencies approximately 5 – 20% (influence of gas temperature)	Medium	Investment costs: low Operational cost: medium
	[101]	Removal efficiencies of 5 – 15% for siloxanes were obtained when cooling the gas to 14ºC (initial concentration 12 – 15 mg siloxanes/m^3)			
Deep chilling	[99]	80 – 90% removal efficiency at – 30ºC for siloxanes concentrations 7 – 15 mgSi/m^3.	Removal efficiencies around 80 – 90%	High	Investment and operational costs: high
Membranes	[12]	Siloxanes removal efficiencies of 80% were observed with dense membranes.	Removal efficiencies not very well reported. Process performance not clear	Medium	Investment costs: high Operational cost: medium
	[110]	A PDMS membrane showed selectivity for siloxane 20 to 70 times bigger than for N_2. This membrane had also high permeability of water and other harmful organic compounds such as BTEX and halogenated hydrocarbons.			
Biological	[92]	A laboratory scale biotrickling filter (0.5 m height and 0.07 m diameter; Pall Rings 88% void volume and 350 m^2/m^3 specific surface) obtained removal efficiencies up to 20%. No siloxane removal was observed in the absence of the biomass, i.e., after the packing media was washed.	Removal efficiency of 10 – 40% Elimination capacity limited to 100 mg/m^3/h (very small compared to biological desulphurisation)	Low	Investment costs: medium Operational costs: low
	[98]	Removal efficiencies of 10 – 43% for D4 were observed in aerobic and anaerobic (N_2) gas-phase BTF (3.8 cm diameter, 390 mL packing volume), at a gas flow rate of 0.5 L/min and D4 concentration of 45 mg/m^3.			
	[115]	Removal efficiencies of 74% for D4 was observed in an aerobic gas at a lab-scale BTF (packed with porous lava			

		and inoculated with an effective strain of *Pseudomonas aeruginosa*) at empty bed residence time of 13.2 min. Dimethylsilanediol, silicic acid, CO_2 and methanol were the degradation products of D4.			

* Energy consumption (% of Lower Heating Value biogas): < 0.5 (low), 0.5 – 3 (medium), > 3 (high)

**Investment cost (k€/Nm^3/h): < 0.5 (low), 0.5 – 1 (medium), > 1 (high). Operating cost (c€/Nm^3): < 1.5 (low), 1.5 – 3 (medium), > 3 (high)

Table 7. Siloxane concentration limits for different Energy Conversion Systems (according to the manufacturers' specifications)

ECS	**Manufacturer/Model**	**Total Siloxane Limit (mg/m^3)**	**Suggested biogas treatment train**
Internal Combustion Engine	Jenbacher	12	Refrigeration/Condensation
	Caterpillar	28	
	Waukesha	30	
	Tech 3 Solution	5	
Micro-turbines	Capstone	0.03	Refrigeration/Condensation + adsorption
Fuel cells	PAFC	0.05 – 0.1	Refrigeration/Condensation + adsorption
	MCFC		
	SOFC		
Stirling Engine	Stirling Biopower	No limit	No treatment required
	Stirling Denmark		
	CleanEnergy		
Biomethane injection into the grid	Depending on each country	0.5 – 10	Refrigeration/Condensation + adsorption