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Analytical methodology for sampling and analysing eight siloxanes and trimethylsilanol in biogas from different wastewater treatment plants in Europe

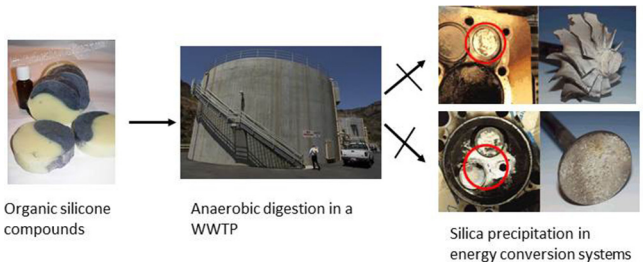
J. Raich-Montiu[a,*], C. Ribas-Font[b], N. de Arespacochaga[a], E. Roig-Torres[b], F. Broto-Puig[b], M. Crest[c], L. Bouchy[a], J.L. Cortina[a]

[a] CETaqua, Centro Tecnológico del Agua, Carretera d'Esplugues 75, 08940 Cornellà de Llobregat, Spain
[b] Dpto Química Analítica, Sección de Cromatografía, Institut Químic de Sarrià, Universitat Ramon Llull, Via Augusta 390, 08017 Barcelona, Spain
[c] CIRSEE, Suez-Environnement, 38 rue du Président Wilson, F-78230 Le Pecq, France

HIGHLIGHTS

- Siloxanes cause adverse effects on biogas utilisation for energetic purposes.
- Sampling and quantification of siloxanes in biogas were assessed.
- Reliable and robust analytical methodology was developed.
- Biogas from different WWTPs of different European countries was analysed.
- Siloxanes were over the limit of tolerance for most of energy recovery technologies.

GRAPHICAL ABSTRACT



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ABSTRACT

Siloxanes and trimethylsilanol belong to a family of organic silicone compounds that are currently used extensively in industry. Those that are prone to volatilisation become minor compounds in biogas adversely affecting energetic applications. However, non-standard analytical methodologies are available to analyse biogas-based gaseous matrixes. To this end, different sampling techniques (adsorbent tubes, impingers and tedlar bags) were compared using two different configurations: sampling directly from the biogas source or from a 200 L tedlar bag filled with biogas and homogenised. No significant differences were apparent between the two sampling configurations. The adsorbent tubes performed better than the tedlar bags and impingers, particularly for quantifying low concentrations. A method for the speciation of silicon compounds in biogas was developed using gas chromatography coupled with mass spectrometry working in dual scan/single ion monitoring mode. The optimised conditions could separate and quantify eight siloxane compounds (L_2, L_3, L_4, L_5, D_3, D_4, D_5 and D_6) and trimethylsilanol within fourteen minutes. Biogas from five waste water treatment plants located in Spain, France and England was sampled and analysed using the developed methodology. The siloxane concentrations in the biogas samples were influenced by the anaerobic digestion temperature, as well as the nature and composition of the sewage inlet. Siloxanes D_4 and D_5 were the most abundant, ranging in concentration from 1.5 to 10.1 and 10.8 to 124.0 mg Nm^{-3}, respectively, and exceeding the tolerance limit of most energy conversion systems.

* Corresponding author. Tel.: +34 660365321.
E-mail address: jordiraich@gmail.com (J. Raich-Montiu).

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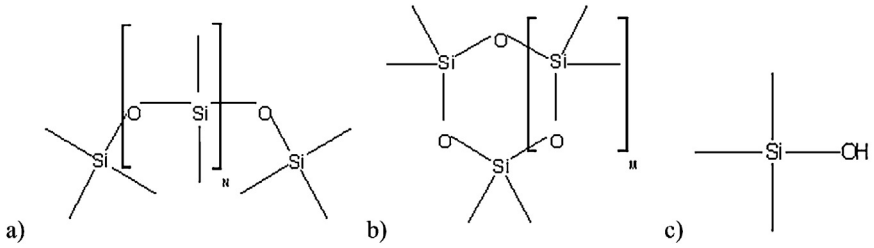

Fig. 1. General structure of siloxanes (a) linear compounds, (b) cyclic compounds and (c) trimethylsilanol.

1. Introduction

Due to the need to reduce greenhouse gas (GHG) emissions and the demand for renewable resources, using biogas is a relevant alternative for producing green energy [1]. Biogas is produced using farm biogas plants, mechanical biological treatment of municipal solid waste and, most commonly, waste water treatment plants (WWTPs) and landfills.

Biogas is composed of methane (CH_4) and carbon dioxide (CO_2), as well as other minor components, such as hydrogen sulphide, halogenated compounds and organosilicon compounds [2]. Although numerous technologies for biogas energy recovery, such as boilers, internal combustion engines (ICE), micro-turbines, fuel cells and Stirling engines have been developed, biogas contaminants hinder the efficiency and long-term performance of these systems. In particular, siloxanes adversely affect biogas usage [3], possibly damaging energy recovery technologies when silica is formed via combustion [4]. Siloxanes and trimethylsilanol (TMS) compose a family of compounds derived from the silicone derivatives widely used in cosmetics, oils, silicon production factories, electronics, paints, paper coatings and textiles. These compounds become volatile at relatively high operating temperatures (35–55 °C) during anaerobic digestion at waste water treatment plants and may be present in biogas as linear compounds, such as TMS, L_2, L_3, L_4, L_5, or cyclic compounds, such as D_3, D_4, D_5 and D_6 (see Fig. 1). Therefore, due to the high demand for biogas as a future energy source [5] and the extensive use of silicones, reliable analytical methodologies for analysing these compounds in biogas are critical. Currently, different analyses of the siloxanes in biogas [6–11], air [7,12–17], water [10,17–21], activated sludge [10,21–23] and soil samples [17,19,20,22,24] have already been published. Although gas chromatography–mass spectrometry (GC–MS) is most frequently used for these analyses [6,8–15,17–24], no standardised analytical methodologies have been reported in a gaseous matrix [25]. In addition, the most practical and reliable sampling technique has yet to be identified. Although several authors have already assessed using canisters [9], tedlar bags [6], sorbent tubes [8,23,24] or even on-line measurement techniques combining GC and Fourier transform infrared spectroscopy (FT-IR) [26] to analyse siloxanes, no studies have compared the different sampling techniques while analysing eight siloxanes and TMS.

This paper expands the analytical methodology used to quantify nine organic silicon compounds in biogas such as L_2, L_3, L_4, L_5, D_3, D_4, D_5, D_6 and TMS generated at five different WWTPs in Europe, while avoiding any undesired interference [27]. A rapid chromatographic separation and a reliable sampling technique were pursued for the siloxanes. The sampling techniques were compared by sampling sewage biogas directly from the waste water treatment plant or indirectly from a 200-L tedlar bag filled with homogenised biogas.

In addition, this study was also devoted to gaining further knowledge regarding the presence of siloxanes in biogas from different WWTPs. These important data should strengthen decision making related to selecting energy conversion systems (ECS) and designing biogas treatment technologies [28] used to prevent ECS breakdown. Five different WWTPs with different types of effluents, treatment processes and operational conditions were selected and studied in England, France and Spain. One site had already reported trouble with silica precipitation when biogas was used for energy production.

2. Materials and methods

2.1. Biogas samples

Biogas from five WWTPs located in Catalunya (NE of Spain), France and England was sampled in triplicate from the digester outlet streams or gas holder. The campaigns were performed during the spring and summer of 2011.

The different configurations of the sludge lines at the selected WWTPs are shown in Table 1. The role of five different parameters on siloxane concentration was studied: sludge type, sludge pre-treatment before digestion, operating temperature, retention time and sludge mixing. The type of sludge (primary, secondary or mixed sludge) strongly affects the biogas production and composition because the rate (kinetics) and extent (thermodynamics) biodegradability is different for each sludge type. Sludge is pre-treated (e.g. thermal hydrolysis) to break down organic matter before digestion to increase biogas production, converting large and non-volatile silicon compounds into lighter and more volatile compounds. The digestion temperature determines both the evaporation and stripping of silicon compounds. The retention time defines the extent of degradation for the organic matter in the reactor, linking this parameter to biogas production. Finally, the sludge mixing system (mechanical, sludge recirculation or biogas recirculation) prevents stratification, improving the anaerobic process and affecting the mechanism for siloxane transfer from the liquid to the gas phase.

2.2. Chemicals

TMS, L_2, L_3, L_4, L_5, D_3, D_4 and D_5 were supplied by Sigma–Aldrich (Steinheim, Germany); D_6 was supplied by TCI Europe (Zwijndrecht, Belgium). All purchased compounds were more than 97% pure. Table 2 shows some of the physico-chemical properties of these compounds.

Decane-d_{22} (Sigma–Aldrich, Steinheim, Germany, 99%) and a deuterated siloxane L_2–d_{18} (C/D/N Isotopes Inc., Quebec, Canada, 99.8%) were used as internal standards.

Trace substances typically found in biogas samples such as n-octane, n-decane, xylenes, ethylbenzene, cumene and α-pinene were supplied by Fluka (Steinheim, Germany), while trichloroethylene, tetrachloroethylene, and 1,2-dichlorobenzene were supplied by Merck (Darmstadt, Germany); toluene, and δ-limonene were supplied by Sigma-Aldrich and chlorobenzene was supplied by Panreac (Castellar del Vallès, Spain). All of these compounds had purities ranging from 98 to 99.5%.

Table 1
Description of the sludge line of the sites selected for the campaigns. AD: anaerobic digestion.

WWTP	1	2	3	4	5
Biogas Production	5750 m^3 day^{-1}	29,000 m^3 day^{-1}	5850 m^3 day^{-1}	29,500 m^3 day^{-1}	1560 m^3 day^{-1}
Sludge type	Mixed sludge	Indigenous and external mixed sludge	Secondary sludge	Mixed sludge	Mixed sludge
Sludge pre-treatment	None	Thermal hydrolysis (Cambi process)	None	None	None
AD temperature (regime)	37 °C (mesophilic)	42 °C (mesophilic)	37 °C (mesophilic)	55 °C (thermophilic)	36 °C (mesophilic)
AD retention time	19 days	26 days	21 days	21 days	25 days
AD mixing	Mechanical and sludge recirculation	Sludge recirculation	Sludge and biogas recirculation	Biogas recirculation	Mechanical and sludge recirculation

The standard solutions (0.04 to 60 mg L^{-1}) were prepared and stored in n-hexane because Ajhar et al. [6] reported that they were more stable in n-hexane than in methanol. n-Hexane was purchased from VWR international Eurolab S.L. (Llinars, Spain).

2.3. Sampling techniques

A 224-PCMTX8 air sampling pump (SKC, Palo Alto, USA) and a Defender 510-M primary gas flow calibrator (Mesa Laboratories, Colorado, USA) were used.

Different sampling techniques were studied: (1) large ORBO 32 adsorbent tubes with an activated coconut charcoal matrix (24–40 mesh) divided into beds A (400 mg) and B (200 mg) (Sigma–Aldrich); (2) 1 L tedlar bags with a single polypropylene septum fitting (SKC), (3) two 25 mL fritted impingers (A and B) (SKC) each containing 20 mL of n-hexane connected in series with polyethylene tubes and submerged into an ice-water bath.

A 200 L tedlar bag with a single polypropylene septum fitting (SKC) was used to contain a homogeneous biogas matrix.

A gas analyser 2000 plus (Royal Leamington Spa, United Kingdom) was used for on-site quantification of the CH_4, CO_2, O_2 and H_2S in the biogas. The results were validated by using a micro-GC with biogas samples in tedlar bags.

2.4. Sample preparation

The sampling techniques such as, tedlar bags, impingers and adsorbent tubes, were tested at the same WWTP using two different sampling configurations on two consecutive days. On day 1, the samples were taken directly from the biogas source. Triplicates for each technique were collected alternately to correct for any variations in biogas composition. On day 2, sampling was performed from a 200 L tedlar bag prefilled with biogas from the same day of the study and homogenised. In this case, the triplicate of each sampling technique was performed consecutively.

For both the adsorbent tubes and impingers, the samples were collected under optimised conditions: 1 L min^{-1} biogas over 10 min. The air pump was calibrated with a dry piston calibrator in order to set the flow. The biogas flow was controlled during sampling. The silicone-free plastic tubing connections were purged before its use. A condensate pot and a Peltier cooler were used when the biogas was wet.

The two sectors of adsorbent tubes (bed A and B) were transferred into two vials and independently desorbed with 2 mL of the internal standard solution in n-hexane. The vials were closed with a lid and manually shaken for 30 min. Finally, 2 μL were injected using a split/splitless injector into the GC–MS.

When the impingers were used, the absorption solutions (A and B) were transferred into two 25 mL volumetric flasks; internal standard solution was added and solutions were diluted to 25 mL with n-hexane. 2 μL were injected using a split/splitless injector into the GC–MS.

The tedlar bags were filled directly and the contents were manually injected (500 μL) into the GC–MS via the split/splitless injector.

2.5. Gas chromatography coupled to mass spectrometry

To optimise the chromatographic conditions, siloxanes and TMS were analysed using different stationary phases: (1) HP-5MS (5%diphenyl–95%dimethylpolysiloxane, 30 m × 0.25 mm i.d., 0.25 μm film thickness) from J&W Scientific (Folsom, CA, USA); (2) TRB-G43 (6%-cyanopropylphenyl–94%-dimethylpolysiloxane, 30 m × 0.53 mm i.d., 3 μm film thickness) from Teknokroma (San Cugat del Vallès, Spain); (3) DB-1701 (14%-cyanopropylphenyl–94%-dimethylpolysiloxane, 60 m × 0.25 mm i.d., 0.25 μm film thickness) from J&W Scientific (Folsom, CA, USA); (4) SUPELCOWAX 10 (100%-polyethyleneglycol, 30 m × 0.25 mm i.d., 0.25 μm film thickness) from Supelco Sigma–Aldrich; 5-DB-624 column (6%-cyanopropylphenyl–94%-dimetylpolysiloxane 30 m × 0.25 mm i.d., 1.4 μm film thickness) from J&W Scientific (Folsom, CA, USA). Agilent GC–MS equipment (6890N/5975B) was used.

The biogas samples were analysed using the DB-624 column. The average linear velocity was 36 cm s^{-1} and the split ratio was

Table 2
Physico-chemical properties of the compounds under study.

Sub index	Compound	Abbrev.	Chemical formula	Molar mass (g mol^{-1})	Melting point (°C)	Boiling point (°C)	Vapor pressure (kPa)
	Trimethylsilanol	TMS	C_3H_9SiOH	90	–	99	2.13
$N=0$	Hexamethyldisiloxane	L_2	$C_6H_{18}OSi_2$	162.38	−59	101	4.12
$M=1$	Hexamethylcyclotrisiloxane	D_3	$C_6H_{18}O_3Si_3$	222.46	50–64	134	1.14
$N=1$	Octamethyltrisiloxane	L_3	$C_8H_{24}O_2Si_3$	236.54	−82	153	0.52
$M=2$	Octamethylcyclotetrasiloxane	D_4	$C_8H_{24}O_4Si_4$	296.62	17–18	175	0.13
$N=2$	Decamethyltetrasiloxane	L_4	$C_{10}H_{30}O_3Si_4$	310.69	−68	194	0.07
$M=3$	Decamethylcyclopentasiloxane	D_5	$C_{10}H_{30}O_5Si_5$	370.77	−44	205	0.02
$N=3$	Dodecamethylpentasiloxane	L_5	$C_{12}H_{36}O_4Si_5$	384.84	−81	230	0.009
$M=4$	Dodecamethylcyclohexasiloxane	D_6	$C_{12}H_{36}O_6Si_6$	444.92	−3	245	0.003

Table 3
Optimised mass spectrometry conditions of the compounds under study.

Compound	Retention time (min)	Base peak	Selected ions (relative abundance > 2%)	Selected ions (relative abundance ≤ 2%)
TMS	5.1	75	–	73
L_2	5.6	147	73	75
D_3	7.2	207	191	73, 75, 147
L_3	7.8	221	73, 75, 147, 205	191, 207
D_4	8.7	281	73, 133, 207, 265	164, 295
Dd_{22}	8.9	82	164	–
L_4	9.4	207	73, 133, 295	265, 281
D_5	10.1	73	267, 355, 369	147, 281
L_5	10.5	147	73, 281, 369	267, 355
D_6	11.0	73	341, 429	–

SIM group	Time (min)	Selected ions
TMS, L_2, D_3, L_3	2.0–8.0	73, 75, 147, 191, 205, 207, 221
D_4, Dd_{22}, L_4	8.0–9.5	73, 82, 133, 164, 207, 265, 281, 295
D_5, L_5	9.5–10.5	73, 147, 267, 281, 355, 369
D_6	10.5–14.0	73, 341, 429

12:4:1. The column oven temperature ramped from 40 °C (2 min) to 60 °C at 12 °C min^{-1}, before increasing to 240 °C at 25 °C min^{-1} and held for 4.5 min. The total time was 14 min.

The injection occurred at 250 °C with helium (99.99% Air Products, Spain) as carrier gas. Bleed and temperature optimised septum (Agilent p/n 5183-4757) as well as focus liner (Agilent 210-4004) were used. The mass spectrometer was equipped with an electron impact ionisation source at 70 eV and 230 °C and a quadrupole analyser at 150 °C was operated simultaneously in full scan mode (m/z 70–450) and single ion monitoring mode (SIM). During SIM mode, the target ions for each compound were selected using mass spectra previously obtained in full scan mode (see Table 3). In SIM mode, the chromatogram was divided into four acquisition windows (SIM groups) where selected ions from TMS, L_2, D_3 and L_3 (m/z: 73, 75, 147, 191, 205, 207, 221), D_4, L_4 and D_{22} (m/z: 73, 82, 133, 164, 207, 265, 281, 295); D_5 and L_5 (m/z: 73, 147, 267, 281, 355, 369) and D_6 (m/z: 73, 341, 429) were monitored.

The compounds were identified by comparing the mass spectra and the ratio between the abundance of selected ions obtained in the samples and compared with the standards. The compounds were quantified by comparison of the sum of the selected ions included in the SIM group. When the ratio between some selected ions in the sample was not similar to the standard, those ions were discarded due to presence of interferences. In each sample, all siloxane compounds were quantified by calculating the average response factors of the two standard solutions with most similar concentrations.

2.6. Injection sequence

In order to minimise contamination problems with siloxanes released by the chromatographic system, the oven was heated at 260 °C for an hour. Afterwards, a suitability test conformed by analysing an instrumental blank, a solvent blank and five injections of a 3 mg L^{-1} standard solution was carried out. Finally, eight standard solutions and the sample solutions were injected. Each sample was injected twice. Between injecting different sampling materials, procedure blanks (solvent or nitrogen gas) and standard solutions were also injected.

2.7. Quality control

Siloxane concentration in the solvent blank was lower than 0.06 mg L^{-1}. The relative standard deviation (RSD) of the five area values for L_2 did not exceed 5%. The RSD of the ratio of the L_2 peak area to the internal standard peak area did not exceed 3%. The resolution between the peaks corresponding to decane-d_{22} and D_4 was at least 3. The D_3 peak was detected with a signal to noise ratio of at least 300. The mass of each siloxane found in the bed B (or impinger B) was lower than 10% of the content detected in bed A (or impinger A).

3. Results and discussion

3.1. Chromatographic separation

The chromatographic separation of eight siloxanes L_2, D_3, L_3, D_4, L_4, D_5, L_5, D_6 and TMS was optimised. A nonpolar capillary column (HP-5), two capillary columns with intermediate polarities (TRB-G43 and DB-1701) and a highly polar capillary column (Supelcowax-10) were assessed. The four columns utilised different stationary phases. Three of them (HP-5, DB-1701 and Supelcowax-10) had a 0.25 μm thick film and an internal diameter of 0.25 mm and three of them (HP-5, TRB-G43 and Supelcowax-10) had a column length of 30 m.

All the tested columns separate siloxane compounds according to their increasing boiling points, L_2, D_3, L_3, D_4, L_4, D_5 and L_5 (Fig. 2). The most volatile siloxane (L_2) was sufficiently retained as to elute after the solvent (n-hexane) in all columns, except in Supelcowax-10 column where it eluted at the solvent tail resulting in a complex quantification. TMS was not retained in the non-polar column (HP-5MS) and it eluted just before the solvent (n-hexane) due to its high volatility. It was sufficiently retained as to elute between the solvent (n-hexane) and the most volatile siloxane (L_2) with the intermediate polarity TRB-G43 column. TMS also eluted after siloxane L_2 with another intermediate polarity DB-1701 column. Finally, TMS was strongly retained in Supelcowax-10 column (high polarity) and it was eluted between siloxanes L_3 and D_4. TMS is a compound more polar than siloxanes and, consequently, it was peak delayed when the polarity of the stationary phase increased. The delay for TMS on the TRB-G43 column was partly due to the increased thickness of the stationary phase (from 0.25 to 3 μm). The best separation was achieved when using the two capillary columns with intermediate polarities (TRB-G43 and DB-1701). The time needed for analysis varied due to the length of the column (30 and 60 m, respectively). To include D_6 in the analysis without significantly increasing the analysis time, an intermediate polarity column (6%-cianopropilfenil–94%-dimethylpolysiloxane) with different column dimensions (30 m, 0.250 mm, 1.4 μm) was used.

The internal diameter was reduced from 0.530 to 0.250 mm and the thickness of the stationary phase from 3 to 1.4 μm decreasing the time of analysis and increasing the separation. However, when using this column, the peaks of decane-d_{22} and D_4 were overlapped. To separate these two compounds despite very similar boiling

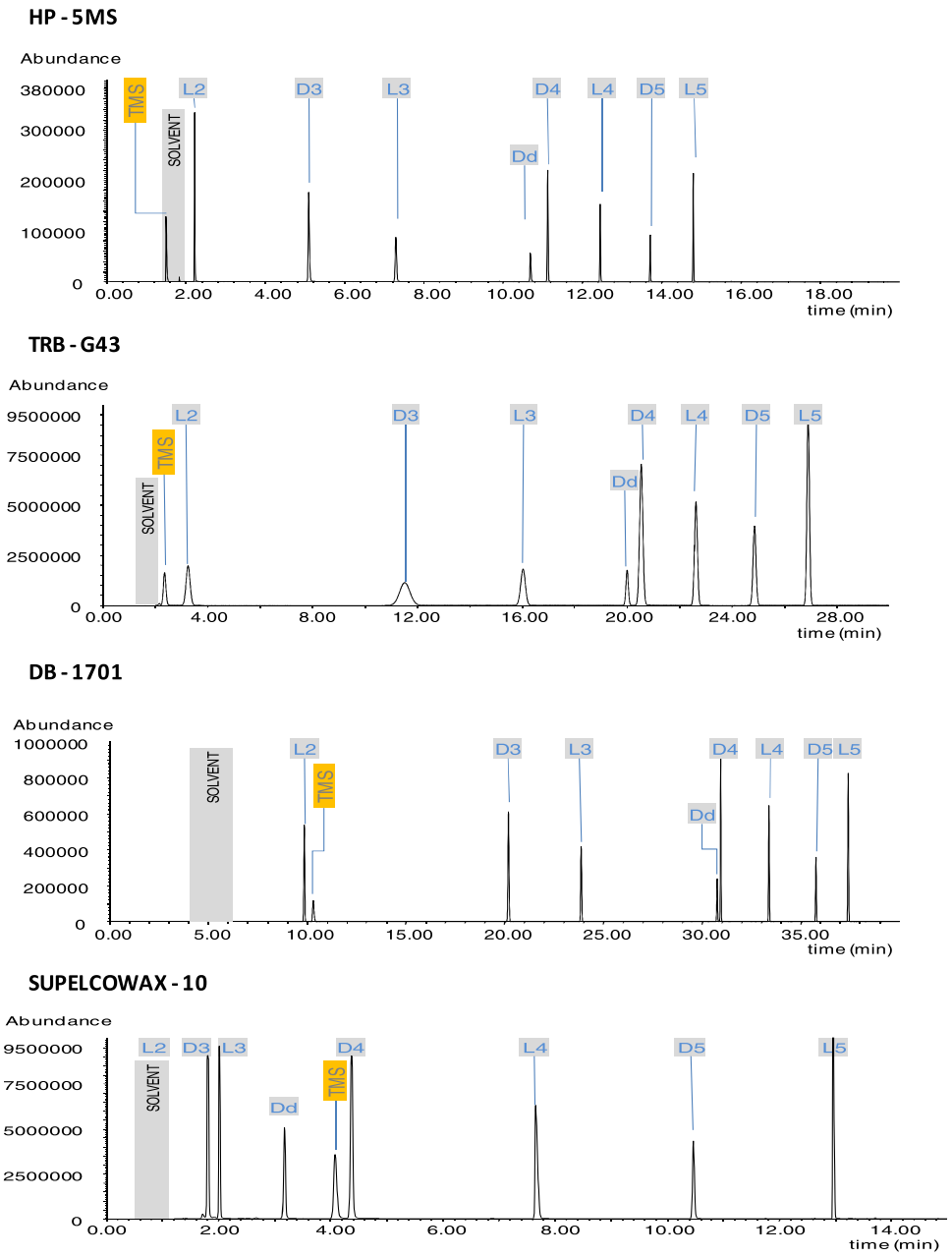

Fig. 2. Chromatograms obtained using GC–MS in SIM mode with four different columns: HP-5 MS; TRB G43; DB1701 and SUPELCOWAX-10.

points (174 and 175 °C, respectively), different temperature programs were assessed. When the elution temperature for decane-d_{22} and D_4 increased, their retention times decreased, affecting D_4 more strongly and allowing their separation. Under these conditions, the TMS still eluted between the solvent and L_2, and the resolution was good enough for all siloxanes. The separation was complete after 14 min. In addition, interference by other compounds often present in biogas matrices, such as linear aliphatic hydrocarbons (octane, decane), aromatic hydrocarbons (toluene, xylenes, ethylbenzene, cumene), chlorinated aliphatic hydrocarbons (trichloroethylene, perchloroethylene), chlorinated aromatic hydrocarbons (chlorobenzene, 1,2-dichlorobenzene) and terpenes (α-pinene, δ-limonene) were assessed. Chromatograms obtained when working in scan or SIM mode are shown in Fig. 3; the quantification of siloxanes was not affected.

Finally, eight standard solutions at different concentrations (0.04–60 mg L^{-1}) were injected five times. The limit of detection (LOD), repeatability and linearity of the method were determined. The LOD values (S N^{-1}: 3) were 0.04 ng injected for TMS and 0.02 ng injected for the siloxanes. The RSD of the peak area ratios between the analytes and the internal standard were lower than 5% for all compounds and concentrations. Equivalent RSD were obtained for both internal standards (L_2-d_{18} and decane-d_{22}). Decane-d_{22} was selected for further studies due to its low cost and peak placement in the middle of the chromatogram, as well as its excellent resolution. The calibration range was 0.08–60 mg L^{-1} for TMS and 0.04–60 mg L^{-1} for the siloxanes ($R^2 > 0.9995$).

3.2. Assessment of sampling methodologies

The precision of the two sampling configurations was assessed as described in Section 2.4 by direct sampling from the biogas source and indirect sampling from a 200 L tedlar bag filled with biogas. The standard deviations obtained after each sampling

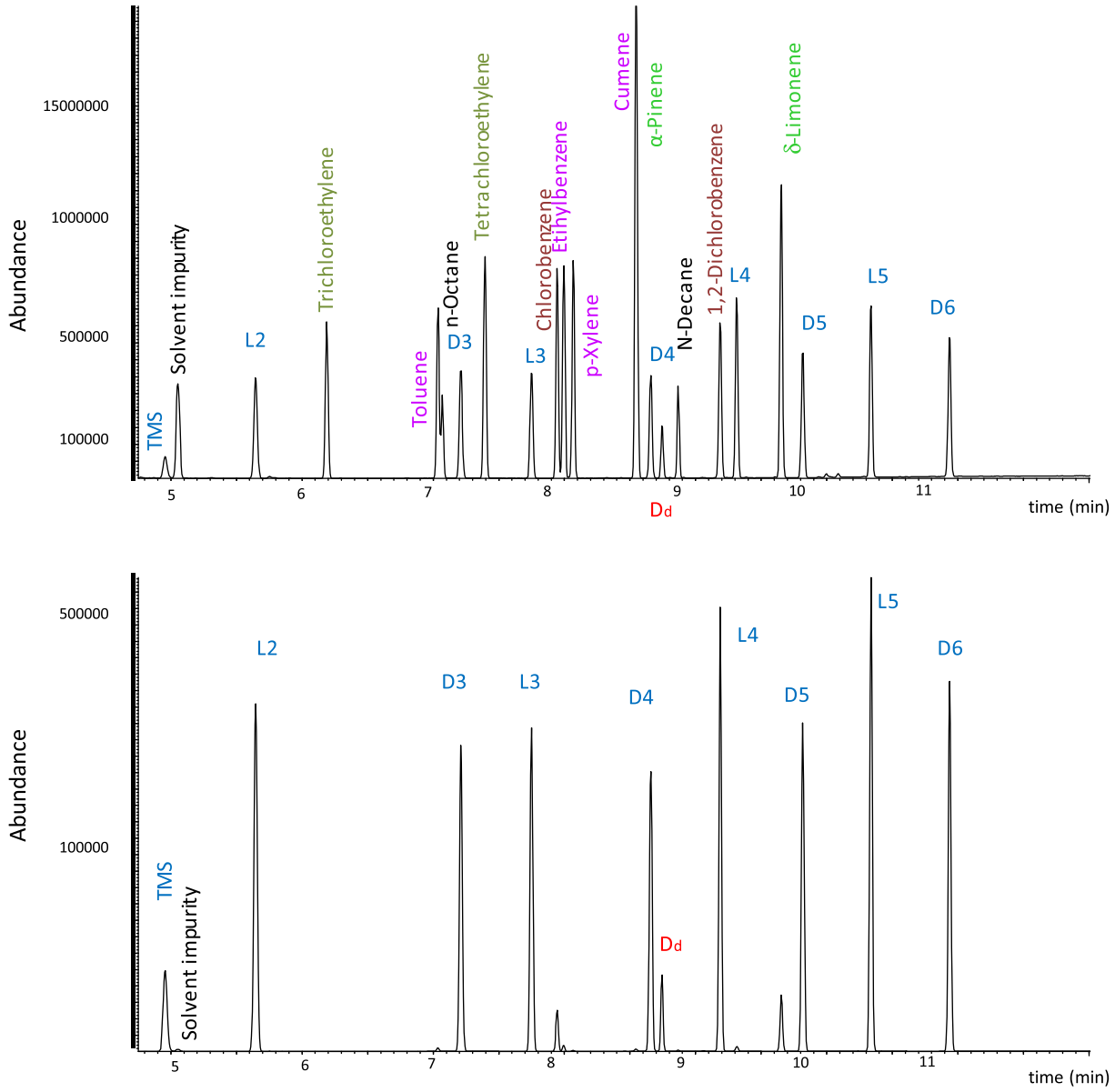

Fig. 3. Chromatogram of a standard solution of 60 mg L^{-1} each of TMS, L2, L3, L4, L5, D3, D4, D5 and D6 in SCAN mode (A) and SIM mode (B). Column: DB-624. D_d: deuterated decane.

technique for the most abundant siloxane compounds D_4 and D_5 (see Table 4) were compared. No significant difference was observed between sampling methods when using an *F*-test ($p < 0.05$). Therefore, direct sampling was chosen. However, when comparing the performance of these techniques, the tedlar bags showed higher standard deviations than the impingers or adsorbent tubes for both D_4 and D_5 in either configuration. This was partially caused by no adding internal standard before the injection into the GC–MS system when using the tedlar bags.

Table 4
Mean value of siloxane concentrations obtained when comparing different sampling methodologies and techniques in the WWTP-1. Standard deviation in brackets ($N = 3$).

Compound (mg Nm^{-3})	Configuration 1: prefilled and homogenised 200 L Tedlar Bag			Configuration 2: directly from the source		
	Tedlar bag	Impinger	Adsorbent tube	Tedlar bag	Impinger	Adsorbent tube
TMS	<0.4	<0.2	<0.02	<0.4	<0.2	<0.02
L_2	<0.2	<0.1	<0.01	<0.2	<0.1	<0.01
D_3	<0.2	0.1 (0.02)	0.05 (0.02)	<0.2	0.1 (0.02)	0.05 (0.01)
L_3	<0.2	<0.1	0.05 (0.01)	<0.2	<0.1	0.05 (0.02)
D_4	5.3 (0.8)	5.4 (0.1)	6.0 (0.3)	5.2 (0.7)	5.1 (0.3)	6.8 (0.2)
L_4	<0.2	0.1 (0.02)	0.08 (0.02)	<0.2	<0.1	0.08 (0.01)
D_5	14.3 (3.0)	11.8 (0.3)	10.8 (0.8)	14.8(2.3)	8.5 (0.9)	12.9(1.1)
L_5	<0.2	<0.1	0.03 (0.01)	<0.2	<0.1	0.04 (0.02)
D_6	0.7 (0.2)	0.5 (0.03)	0.4 (0.06)	0.7 (0.1)	0.3 (0.1)	0.5 (0.1)

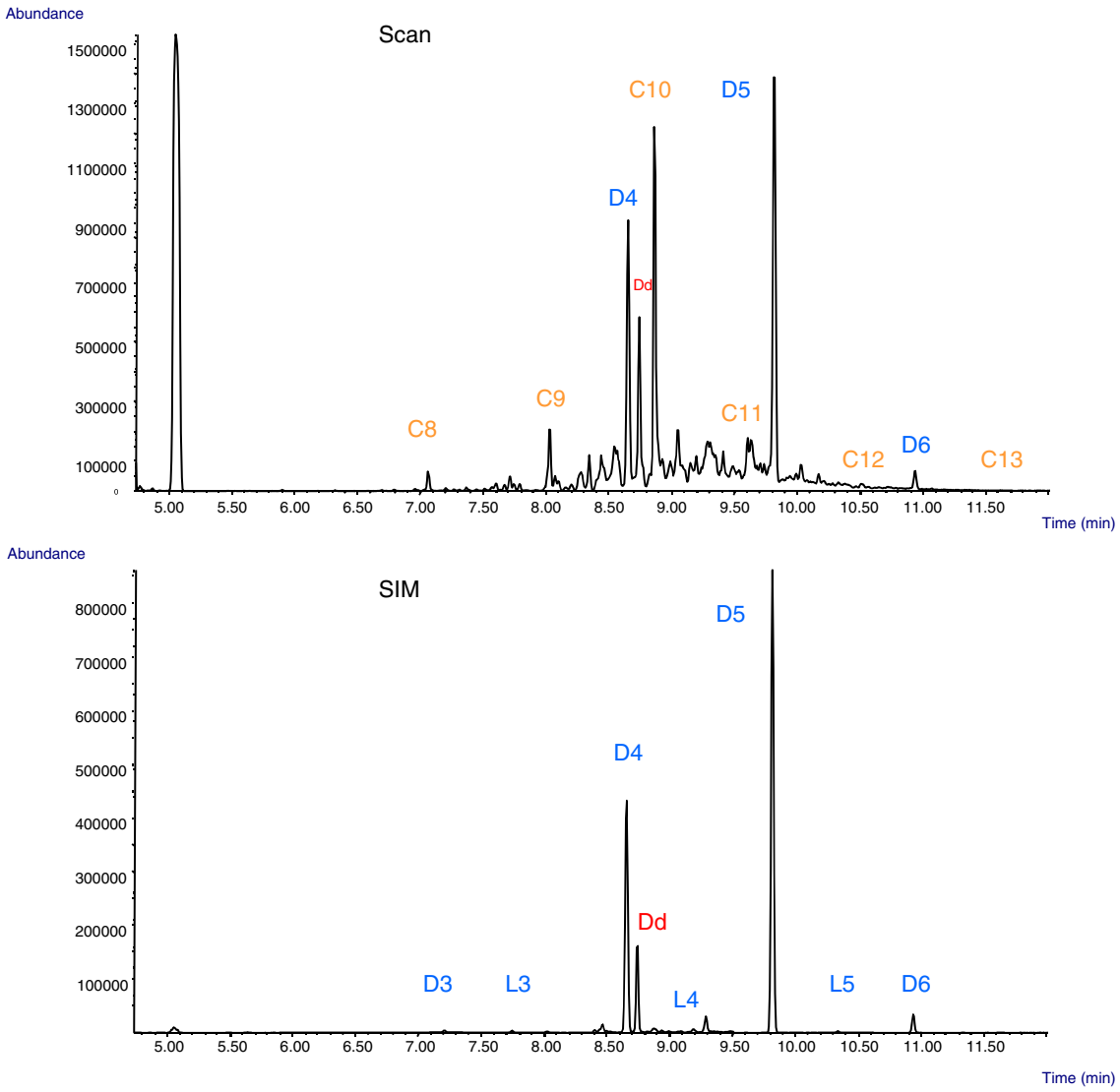

Fig. 4. Chromatogram (scan and SIM mode) of a biogas sample from a WWTP sampled directly from the source using adsorbent tubes. D_d: deuterated decane.

The LOQ for each sampling technique was determined as 10 times the signal to noise ratio (SN^{-1}). The LOQ for the tedlar bags was 0.4 mg m^{-3} for TMS and 0.2 mg m^{-3} for the siloxanes. The LOQ for the impingers was 0.2 mg m^{-3} for TMS and 0.1 mg m^{-3} for the siloxanes. Finally, the LOQ for the adsorbent tubes was 0.02 mg m^{-3} for TMS and 0.01 mg m^{-3} for the siloxanes. When sampling directly from the source, the adsorbent tubes reported higher concentrations than the impingers for D_4 and D_5. This result was important when avoiding possible underestimations of the total siloxane content as it might hinder the use of biogas with energy recovery technologies.

The selectivity was verified by comparing the whole mass spectra (scan mode) and ratio of the selected ions (SIM mode) from the signals obtained from samples and standards. All of the samples exhibited a ratio for the selected ions similar to those for the standards (L_2, D_3, L_3, D_4, D_5 and D_6). Mass spectra were compatible to standards with concentrations above 0.1 mg Nm^{-3} (D_4, D_5 and D_6). Signals corresponding to the Si – isotope cluster (^{28}Si, ^{29}Si, ^{30}Si) facilitated the comparison of their respective mass spectra. Chromatograms obtained from the three sampling techniques were similar and the signal of D_4 and D_5 siloxanes was predominant. Fig. 4 shows chromatograms obtained in scan and SIM modes from biogas sampled with an adsorbent tube. In scan mode (m/z 70–450), a complex mixture of linear and branched hydrocarbons (n-octane to n-tridecane) were detected in addition to siloxanes. Their signals notably diminished when using the m/z rang of 70–450 amu. n-Octane (112 amu) eluted with a slightly shorter retention time than D_3 (222 amu) and n-tridecane (184 amu) and exhibited a slightly longer retention time than D_6 (444 amu). Because the siloxanes coeluted with other lower molecular weight compounds, the selectivity was improved in scan and SIM modes.

TMS was not detected in the WWTP-1. In order to verify the correct functioning of the proposed method, landfill biogas samples were also analysed. D_4, L_2 and TMS were found to be the major compounds present in the matrix. Their mass spectra and the abundance ratio of selected ions were similar to those for the standards. In scan mode, the ions at m/z 73, 74, 75, 76 and 77 were taken into account to compare the TMS mass spectra. In SIM mode, the absence of ions at m/z 147, 191, 205, 207, 221 and the presence of ions at m/z 73 and 75 were noted and confirmed the presence of TMS.

Neither siloxanes nor the TMS were detected in bed B of the adsorbent tubes or in impinger B. Therefore, the loss of any target compounds during the sampling processes was impossible. Moreover, it also confirmed that the tube or the impinger was not polluted during sampling, storage or treatment pre-analysis.

Table 5
Mean value of siloxane concentrations in the different sites. Sampling performed with adsorbent tubes. Standard deviation in brackets ($N = 3$).

Concentration (mg Nm^{-3})	WWTP 1	WWTP 2	WWTP 3	WWTP 4	WWTP 5
TMS	<0.02	0.9 (0.1)	<0.02	<0.02	<0.02
L_2	<0.01	<0.01	<0.01	<0.01	<0.01
L_3	0.05 (0.02)	0.07 (0.02)	0.08 (0.02)	0.28 (0.03)	0.11 (0.01)
L_4	0.08 (0.02)	<0.01	<0.01	0.31 (0.02)	<0.01
L_5	0.04 (0.02)	<0.01	<0.01	0.8 (0.1)	<0.01
D_3	0.05 (0.01)	0.20 (0.03)	0.18 (0.03)	0.12 (0.02)	<0.01
D_4	6.8 (0.2)	10.1 (0.5)	1.5 (0.1)	1.9 (0.1)	2.5 (0.2)
D_5	12.9 (1.1)	43.8 (0.6)	12.5 (0.7)	124.0 (4.2)	13.1 (1.2)
D_6	0.5 (0.1)	–	–	–	0.4 (0.1)
Σ Siloxanes	18.5	55.1	14.3	127.4	16.1

Nevertheless, some cyclic siloxanes were detected in instrumental blanks with concentrations in the range of 0.04–0.06 mg L^{-1} for D_4, D_5 and D_6 and 0.01 mg L^{-1} for D_3. These compounds likely originated from the chromatographic system (septum and/or column). The amount of siloxane injected in the chromatograph was 12.5–20 times higher when the adsorbent tubes were used versus the impingers or tedlar bags. Consequently, the effect of the background (instrumental blank) was minimised.

The siloxane concentrations were quantified in the WWTP in agreement with Rasi et al. [8]. Both D_4 and D_5 were the siloxane compounds detected with higher concentration levels, followed by D_6.

The results from this study showed that direct sampling from the biogas source with adsorbent ORBO 32 tubes was reliable to quantify the siloxanes present in sewage biogas. Other criteria including storage, transportation and automated injection also confirmed the suitability of this sampling method.

3.3. Analysis of siloxanes from different WWTPs in Europe

The biogas from the different WWTPs located in England, France and Spain showed the following patterns during characterisation: CH_4: 55–66%, CO_2: 33–38% and O_2: 0.2–1%. H_2S presented highly variable concentrations from 260 mg Nm^{-3} to 3090 mg Nm^{-3}. A description of the sludge lines in the plants can be found in Table 1, summarising the different operational conditions (the nature of the sludge and the biogas production ranging from 1560 to 29,500 m^3 day^{-1}). The quantification of siloxanes in sewage biogas is presented in Table 5. In all WWTPs, D_4 and D_5 where the most abundant. Fig. 5 shows that the concentration of D_5 was related to the temperature of the anaerobic digestion at the WWTP, agreeing with previous works stating that the temperature of the anaerobic digestion favoured presence of siloxanes in biogas [4]. However, Dewil et al. did not report the operational conditions of the different WWTPs, or the concentration of each siloxane. For siloxane D_4, temperature of the anaerobic digestion did not affect its concentration in the biogas. Instead, the nature and pre-treatment of the anaerobic digestion inlet sludge seemed to affect the concentration of D_4. The higher concentration of D_4 in WWTP-2 compared to the other WWTPs was due to the thermal hydrolysis process. However, the high concentration of this compound in WWTP-1 was related to its shorter retention time in the digester; further research is necessary to confirm this result. Concentrations obtained for D_4 and D_5 were similar to those reported by Schweigkofler and Niessner [9] at two different German sewage treatment plants. However, concentration of D_5 in WWTP-2 and WWTP-4 was higher in this study. Such a high concentration of 124 mg Nm^{-3} for D_5 in WWTP-4 had never been published before. Less abundant siloxane compounds, such as L_2, L_3, L_4, L_5 and D_3, were detected at very low concentrations in some WWTPs, while remaining undetected in others. D_6 was only analysed at two of the five WWTPs at concentrations that were low and similar. TMS was only detected in WWTP-2 most likely due to the thermal hydrolysis process before sludge digestion. Although the mechanism for the breakdown of silicon compounds during the thermal hydrolysis processes was not studied, the presence of TMS and the higher concentration of D_4 in WWTP-2 was consistent with the proposed breakdown phenomenon. This WWTP treated approximately 50% of indigenous sludge and 50% external sludge, which might contribute to the presence of TMS to a lesser extent.

The total siloxane concentrations for all WWTPs other than WWTP-4 also agreed with the values presented by Dewil et al. [4], except for a WWTP in United Kingdom (up to 400 mg m^{-3}).

Other factors, such as the retention time or mixing, did not seem relevant for the biogas typologies regarding siloxanes content. Industrial effluents in the waste water lines might fluence the siloxane contents in the biogas; an additional study characterising the effluent should be undertaken. Moreover, analysing the siloxanes in sewage sludge should be undertaken to determine the mass balances.

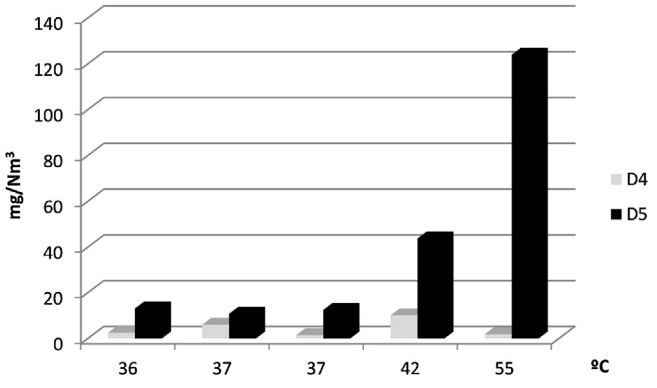

Fig. 5. Concentration of D_4 and D_5 as a function of the temperature of anaerobic digestion in the WWTP.

4. Conclusions

When using gas chromatography with a 6%-cyanopropylphenyl-94%-dimethylpolysiloxane column (30 m, 0.25 mm, 1.4 μm) eight siloxanes in addition to TMS could be separated in 14 min. ORBO 32 adsorbent tubes (activated coconut charcoal) were a reliable and easy-to-handle sampling technique for capturing siloxanes from biogas matrices. No significant differences were observed when sampling directly from the biogas source or through a filled and homogenised 200 L tedlar bag. The analytical methodology presented in this study is suitable for analysing the siloxanes in biogas from WWTPs. In addition, it was also used for landfill biogas with higher presence of L_2 and TMS.

High volatilisation of siloxane D_5, which was one of the less volatile siloxanes analysed, was detected in sewage sludge during

anaerobic digestion up to 55 °C. Nevertheless, further study is required to verify this behaviour and to assess the influence of other factors, such as retention time, mixing, sludge properties and industrial effluents on the siloxane concentrations in biogas. In addition, the siloxanes in sewage sludge should be analysed to determine the mass balances.

A reliable quantification of siloxanes in biogas was developed, demonstrating that the concentrations of siloxanes in biogas from WWTPs in different European countries were higher than the tolerance limit for most energy conversion systems. These results highlighted the need for siloxane removal technologies at WWTPs using biogas.

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