

Development of on-line FTIR spectroscopy for siloxane detection in biogas to enhance carbon contactor management

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Abstract

Activated carbon filters are used to limit engine damage by siloxanes when biogas is utilised to provide electricity. However, carbon filter siloxane removal performance is poorly understood as until recently, it had not been possible to measure siloxanes on-line. In this study, on-line Fourier Transform Infrared (FTIR) spectroscopy was developed to measure siloxane concentration in real biogas both upstream (86.1 – 157.5 mg m⁻³) and downstream (2.2 – 4.3 mg m⁻³) of activated carbon filters. The FTIR provided reasonable precision upstream of the carbon vessel with a root mean square error of 10% using partial least squares analysis. However, positive interference from volatile organic carbons was observed in downstream gas measurements limiting precision at the outlet to an RMSE of 1.5 mg m⁻³ (47.8%). Importantly, a limit of detection of 3.2 mg m⁻³ was identified which is below the recommended siloxane limit and evidences the applicability of on-line FTIR for this application.

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1 Introduction

Water utilities have considerable combined heat and power (CHP) engine capacity installed for electrical production. To illustrate, in 2013 UK Water Utilities generated 761 GWh from biogas arising from the anaerobic digestion of sewage sludge (DECC, 2013). To ensure this biogas is utilised economically, volatile methyl siloxanes (VMSs) must be removed as the VMS compounds can cause significant CHP engine damage following their oxidation during combustion which transforms the VMS compounds into silicon dioxide (Arnold, 2009). Some of this silicon dioxide is deposited in the engine as microcrystalline silica, where it abrades the inner surfaces of the combustion chamber (Schweigkofler and Niessner, 2001), clogs valves (Accettola et al., 2008) and reduces engine efficiency (Ohannessian et al., 2008). Damage caused by siloxanes is estimated to cost around £0.015 kWh⁻¹ (Lemar, 2005), or 16% of the current UK feed-in tariff for electricity from CHP engines (£0.094 kWh⁻¹, Read and Hofmann, 2011).

Current best practice for siloxane removal from biogas is pre-treatment using activated carbon (AC) filters (Ajhar et al., 2010a). Whilst many AC filters have been installed at sewage treatment works, there remains relatively little data relating to the effectiveness of these systems. This can, in part, be attributed to the difficulties in measuring siloxanes as until recently the most common methods involved discrete sampling using gas bags (Ajhar et al., 2010b) or canisters (Schweigkofler and Niessner, 1999), followed by analysis using gas chromatography-mass spectrometry (GC-MS) at an external laboratory. Not only is this expensive, at up to £100 per sample, but the data density provided is insufficient to fully characterise either the siloxane profile of the biogas or the performance of the AC filters. To illustrate, due to cost and logistical constraints, it is rare for biogas sampling to be carried out downstream of the carbon

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5 filters more than once per day. However, siloxane breakthrough from carbon filters has
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7 been noted to increase the carbon filter outlet siloxane concentration from the leakage
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9 concentration ($\approx 7 \text{ mg m}^{-3}$) to equal the inlet concentration ($\approx 100 \text{ mg m}^{-3}$) in less than
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11 four hours (Hepburn et al., 2015). This steep breakthrough curve is characteristic of gas
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13 adsorption processes (Wakao and Funazkri, 1978; Cooney, 1999) and emphasises the
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15 need to provide more frequent analytical measurement of siloxanes to ensure that the
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17 carbon vessels are appropriately managed to maintain a reliable barrier to siloxane
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19 penetration into the CHP engine.
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23 Arnold and Kajolinna (2010) and Bramston-Cook and Bramston-Cook (2012)
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25 were amongst the first to develop online siloxane detection to establish typical siloxane
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27 concentrations in real biogas. The authors used portable gas chromatography (GC) to
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29 characterise siloxane concentrations in untreated biogas at both sewage treatment works
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31 and landfill sites. Both groups demonstrated the ability of field GC to measure siloxanes
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33 in the complex biogas matrix, although Arnold and Kajolinna (2010) did note difficulty
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35 interpreting chromatograms due to the presence of other interfering volatile organic
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37 carbon species (VOCs). Whilst the authors' proved portable GC useful for both
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39 detection and speciation of siloxanes in real biogas, field GC techniques require regular
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41 calibration and specialist maintenance, which are practically constraining for more
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43 permanent installations to be operated by non-specialist staff. Oshita et al. (2010)
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45 applied Fourier Transform Infrared (FTIR) spectroscopy to determine the dynamic
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47 variation in siloxane concentration in biogas produced at a sewage treatment plant in
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49 Japan. The advantage of FTIR is that it requires only initial calibration, an annual
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51 maintenance cycle, and takes only around eight minutes to acquire background and
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53 sample spectrums (Bendini et al., 2007), making FTIR a more practicable technology
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5 for long term use by non-specialist operators, to monitor AC filter performance. Similar
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7 to Arnold and Kajolinna (2010), Oshita et al. (2010) found that in real biogas, the on-
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9 line results were higher than the results from laboratory GC-MS, and whilst VOCs were
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11 not measured directly, the authors also proposed that this was due to positive
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13 interference caused from VOCs. Nevertheless, Oshita et al. (2010) achieved a close
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15 correlation between on-line FTIR and laboratory GC-MS data in both synthetic and real
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17 biogas, despite the size of the siloxane peaks, which are approximately 1/50th of the
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19 height of the peaks caused by the bulk gases (see supplementary data, Figure S1).
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23 To date, each of the published studies using on-line detection for siloxane
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25 measurement have focused on quantitation of siloxanes in raw biogas, i.e. before biogas
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27 treatment by activated carbon. However, it is the siloxane data collected downstream of
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29 the carbon filter that is used to manage the process. The aim of this study is therefore to
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31 investigate the applicability of on-line FTIR for enhancement of carbon vessel
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33 management to further improve economic utilisation of biogas as a fuel. The objectives
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35 of this study are: (i) to calibrate an industrial FTIR spectrometer for siloxanes using
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37 synthetic reference gases; (ii) to investigate the applicability of FTIR for use on real
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39 biogas both upstream and downstream of an activated carbon filter; (iii) use laboratory
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41 based GC-MS methods to discriminate and diagnose field data; (iv) to refine calibration
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43 for use in real biogases and validate calibration using a certified primary reference gas
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45 mixture from a National Measurement Institute; and (iv) to develop some of the first
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47 seen breakthrough curves from full scale carbon vessels for siloxane removal to
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49 illustrate the utility of on-line siloxane measurement for enhancing carbon filter
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51 management.
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2 Materials and Methods

2.1 Instrument and set up

The Fourier Transform Infrared spectrometer was an Antaris Industrial Gas System (Thermo Fisher Scientific Inc, Waltham, MA). The gas cell had a 2 m path length and was operated at 80°C to minimise the probability of condensation within the cell. The mirrors within the gas cell were coated with gold to limit deposition of carbon fines introduced in the biogas. Background spectra (found by scanning with the gas cell evacuated) were subtracted from the sample spectrum and the reported value was ascertained from the average value of the scans, with cyclic siloxanes discriminated at 817 – 798 cm⁻¹. This region corresponds to the infrared (IR) absorbance caused by the Si-(CH₃)₂ group (Table 1) and was subject to integration to identify corresponding concentration.

2.2 Calibration and verification

Reference gas was generated by spiking a carrier gas (carbon dioxide or nitrogen) with D5 using the apparatus described in Supplementary Information. The test rig was connected directly to the inlet of the spectrometer gas cell, so that gas constantly flowed through the gas cell. To validate the FTIR results, gas samples (as biogas or synthetics gases produced in CO₂ or N₂) were collected downstream of the FTIR gas cell into Type 232 SKC gas bags (Tedlar body and polypropylene fitting) which Ajhar et al. (2010b) demonstrated to provide high and stable recovery of siloxanes from gas samples. Collected gas samples were subject to GC-MS analysis using an ISO17025 accredited method for siloxane determination. The method requires 100-250 ml of gas for transfer onto a Tenax adsorption tube at a flow rate of 30-50 ml min⁻¹. A stock standard

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5 containing eight siloxane species and toluene is used to prepare at least four calibration
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7 tubes. The samples, calibration standards, QC standards, drift checks and blanks were
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9 all analysed using a Markes Unity ATD system connected to an Agilent 5890/5973 GC-
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11 MS system (CERAM, 2012). The limit of detection was equivalent to 1 mg m^{-3} in the
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13 original sample. To verify the final method, the FTIR was challenged with a primary
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15 reference gas mixture (PRGM) supplied by the National Physical Laboratory (NPL,
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17 Teddington, UK) which had an amount fraction of $6.9 \text{ } \mu\text{mol mol}^{-1}$ of D5 in methane
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19 (110 mg m^{-3} of D5 in methane at standard temperature and pressure). Gas bag samples
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21 were also prepared with the PRGM and analysed using GC-MS, which evidenced an
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23 error between the measured and expected siloxane concentration of below 3% which
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25 confirmed gas sample stability within the bag samples taken.
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30 To evaluate the FTIR spectrometer on real biogas, the unit was moved to a large
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32 sewage treatment works and connected to gas sampling points upstream and
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34 downstream of a full-scale activated carbon vessel (6.76 m^3 , $3000 \text{ kg}_{\text{carbon}}$). The
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36 sampling lines were purged for two minutes (greater than three line volumes) before
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38 FTIR readings were taken. When undertaking measurements, sample gas was drawn
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40 through the gas cell by vacuum pump with 20 scans taken over 120 s. Bag samples were
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42 also collected for GC-MS analysis from the gas sampling lines upstream and
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44 downstream of the activated carbon vessel by disconnecting the sampling line from the
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46 inlet of the FTIR spectrometer immediately after taking a FTIR reading. Samples
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48 upstream and downstream of the carbon filter were also subject to analysis by GC-MS
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51 for a suite of VOCs using a UKAS accredited method.
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2.3 Data analysis

To distinguish trueness and precision for the produced FTIR data (using GC-MS data as the benchmark), two statistics have been used: the coefficient of determination (r^2) and the root mean square error (RMSE). The coefficient of determination is a measure of precision (Miller and Miller, 2005) where RMSE is a measure of overall accuracy, combining trueness and precision, and is commonly used for calibrating new FTIR methods (Bendini et al., 2007; Bertran et al., 1999):

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (y_{i,FTIR} - y_{i,GC-MS})^2}{n}} \quad (1)$$

where $y_{i,FTIR}$ is the FTIR reading for sample i , $y_{i,GC-MS}$ is the GC-MS results for sample i and n is the number of samples. The limit of detection (LOD) was given by:

$$LOD = y_B + 3s_B \quad (2)$$

where y_B is the blank signal, considered equal to the y-intercept of the line of regression, and s_B is the standard deviation of the blank signal, considered equal to $s_{y/x}$, the standard deviation of each data point in the y-direction (Miller and Miller, 2005).

3 Results

3.1 FTIR calibration using reference gas and real biogas

Decamethylcyclopentasiloxane (D5) was the dominant siloxane in the sewage sludge digester biogas, both upstream ($68.2 - 131.0 \text{ mg m}^{-3}$) and downstream ($2.2 - 4.3 \text{ mg m}^{-3}$) of the carbon vessel (Table 2). This correlates with other studies which also found D5 to be the most abundant siloxane in digester gas (Arnold and Kajolinna, 2010; Oshita et al., 2010; Rasi et al., 2010; Bramston-Cook and Bramston-Cook, 2012). Due to the dominance of cyclic siloxanes (85 - 95% of siloxanes in upstream samples and 100% in

downstream samples) this study used D5 to provide calibration of the FTIR instrument for cyclic siloxanes.

To establish responsiveness of the FTIR spectrometer to D5, reference gases were produced in an environmentally relevant concentration range, between 5 – 85 $\text{mg}_{\text{D5}} \text{m}^{-3} \text{carrier gas}$ (Figure 1). To illustrate FTIR responsiveness within different absorption regions, absorbance peak heights corresponding to the Si-O bond and Si-CH₃ bond were evidenced and indicated a strong correlation with the expected D5 concentration in the siloxane reference gas ($r^2 = 0.99$ for both correlations, Supplementary Information, Figure S2). To establish a preliminary calibration, the resultant integrated FTIR data at each estimated D5 concentration was ascertained ($r^2 = 0.97$, Figure 1). For external verification of the calibration, FTIR results were compared to those produced by GC-MS (Figure 2). A strong linear relationship was found, with $r^2 = 0.99$ for D5-spiked nitrogen and $r^2 = 0.98$ for D5-spiked carbon dioxide. In both reference gases the FTIR readings are higher than the GC-MS results, 60 – 120% higher for D5 in nitrogen and 30 - 80% higher for D5 in carbon dioxide.

When the FTIR system was applied for the determination of siloxanes in real biogas, D5 concentrations of 77 – 109 mg m^{-3} were recorded upstream of the AC filter. The FTIR data was subsequently compared to siloxane analysis by GC-MS, produced from the same biogas samples for external verification of FTIR accuracy in the complex biogas matrix (Figure 3). Upstream of the carbon filter, the correlation between FTIR and GC-MS data was strong ($r^2 = 0.86$, Figure 3a) although the FTIR data was 0 - 25% lower than the GC-MS data. The RMSE was 15.8 mg m^{-3} or 15.7%. In biogas samples downstream of the carbon vessel, the data range was narrow (6.4 – 7.9 mg m^{-3}) and the correlation between the two methods was weaker ($r^2 = 0.52$, Figure 3b). The FTIR data

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5 was 84 - 214% higher than the GC-MS data and the RMSE was 4.5 mg m^{-3} , although
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7 the higher relative RMSE (147%) can be anticipated in downstream samples due to the
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9 lower siloxane concentration.
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11 12 13 14 3.2 *Volatile organic carbons in biogas samples*

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16 A wide number of additional volatile organic carbon (VOC) compounds were found in
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18 the real biogas at concentrations ranging from 1.5 mg m^{-3} (cumene) to 54 mg m^{-3}
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20 (decane) (Figure 4). The VOC concentrations were almost all lower downstream of the
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22 carbon vessel, ranging from 1.3 mg m^{-3} (alpha-pinene) to 18.8 mg m^{-3} (m,p-xylene)
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24 (Figure 4a), indicating that the activated carbon also adsorbs the VOCs in addition to
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26 the target siloxanes. However, the molar ratio with respect to D5 of most species was
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28 higher downstream of the carbon vessel (Figure 4b). For example, the molar ratio of
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30 benzene to D5 upstream of the vessel was 0.69 and downstream of the vessel was 4.02,
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32 and for m,p-xylene, the molar ratio of m,p-xylene to D5 upstream and downstream of
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34 the carbon vessel were 3.32 and 9.12 respectively which confirms that the carbon filter
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36 was removing siloxanes preferentially to VOCs. Importantly, many of the determined
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38 VOC species absorb infrared radiation within the target region of the FTIR spectrum for
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40 siloxane quantitation (Table 3).
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48 49 3.3 *Partial Least Squares calibration and verification using primary reference gas*

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51 A new analysis using a Partial Least Squares (PLS) method was developed for the FTIR
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53 spectrometer with the collated spectra from real and synthetic biogas to provide an
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55 enhancement in resolution over the original method which used a Classical Least
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57 Squares (CLS) technique. A new region of the infrared absorbance spectrum was
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5 included at $1114.65 - 991.23 \text{ cm}^{-1}$, to utilise the absorbance peak caused by the
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7 stretching of the Si-O-C bond (Table 1). The region of the spectrum analysed to detect
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9 the Si-CH₃ bond was also expanded from $817.67 - 798.39 \text{ cm}^{-1}$ to $879.38 - 798.39 \text{ cm}^{-1}$.
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11 Re-evaluation of the original FTIR spectra was undertaken using the new PLS method
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13 and improved RMSEs to 9.8 mg m^{-3} (9.7%) and 1.5 mg m^{-3} (47.8%) for upstream and
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15 downstream data respectively, and the LOD was reduced from 6.9 mg m^{-3} to 3.2 mg m^{-3}
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17 (Table 4). The primary reference gas mixture ($110 \text{ mg}_{\text{D5}} \text{ m}^{-3}_{\text{CH4}}$) was used to verify the
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19 PLS calibration, and recorded a data range between 109.83 mg m^{-3} to 119.37 mg m^{-3}
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21 (mean 114.2 mg m^{-3}), only 3.8% higher than the expected value, which is within the
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23 uncertainty of the measurement (Table 4). For comparison, a concentration range of
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25 83.22 mg m^{-3} to 91.15 mg m^{-3} (mean 87.6 mg m^{-3}) was recorded for the original CLS
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27 method, around 20.4% lower than the expected value.
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3.4 *Application to full scale contactors*

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37 The FTIR spectrometer was used to construct a breakthrough curve for the full-scale
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39 carbon vessel at the sewage treatment works (Figure 5). The mass of siloxane passing
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41 into the engine can be calculated by integrating under the outlet concentration graph:
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43 0.94 kg of siloxane was found to have entered the engine before breakthrough (over a
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45 period of 18 days, light grey). When breakthrough begins, the cyclic siloxane
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47 concentration in the outlet gas rises from 18 mg m^{-3} to 101 mg m^{-3} in four hours. A
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49 further 0.94 kg of siloxane entered the engine during the three days after breakthrough
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51 (medium grey), which is equivalent to the minimum time typically required for external
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53 analysis of a grab sample taken at the point of breakthrough. The potential for siloxane-
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55 induced damage is therefore doubled if breakthrough is not measured using on-line
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analysis. However, at the case study sewage treatment works, on-line analysis was not used to inform when the carbon beds should be changed, and as the point of grab sampling did not correspond to breakthrough, the AC filter was operated for 29 days between carbon changes, during which an estimated total mass of 4.60 kg of siloxane entered the engine.

4 Discussion

This study has shown that FTIR spectroscopy can be applied for the quantitation of siloxanes in biogas both upstream and downstream of activated carbon vessels. In the initial FTIR assessment of biogas using a CLS method, data produced were predominantly within 95% confidence limits (Figure 3). The FTIR data demonstrated excellent linearity (r^2 0.98 – 0.99) for reference gases (Figure 2) and strong linearity for the real biogas sampled upstream (r^2 0.86). This is equivalent to the results of Oshita et al. (2010) who achieved r^2 0.98 – 0.99 for synthetic biogas and r^2 0.90 for real biogas using FTIR spectroscopy (which was not pre-treated with carbon) (Table 4). The RSME of 9.7% determined for upstream biogas data is comparable to the 10% error estimated by Arnold and Kajolinna (2010) using field GC with a photo-ionisation detector (Table 4).

However, biogas composition, including compositional variation in bulk gases, has an effect on the FTIR spectra. This was demonstrated through comparison of different carrier gases (N₂ and CO₂) in the reference gases (Figure 2) and was further evidenced in the real biogas evaluation (Figure 3) with the original CLS method where FTIR siloxane data was below the expected concentration in biogas based on GC-MS analysis, which indicated a negative bias when in the presence of carbon dioxide and

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5 other bulk gases. Nitrogen is a homonuclear diatomic molecule and therefore does not
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7 absorb infrared radiation (Stuart, 2004). However, when carbon dioxide was used as the
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9 carrier gas, the FTIR siloxane concentration readings were lower (Figure 2). Carbon
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11 dioxide and methane are known to cause interference during measurement of VOCs
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13 with FTIR. For example, Lechner et al. (2001) identified interference by carbon dioxide
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15 when measuring benzene in air near a paper mill. The effect of bulk gases depends on
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17 the temperature and pressure in the gas cell and on the relative sizes of the target and
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19 matrix molecules (Marshik and Perez, 2013), with negative bias being a common
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21 response to interference from non-target compounds (Lorberau, 1990; Williams et al.,
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23 2014). However, the proportion of bulk gases in biogas are reasonably stable (Rasi et
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25 al., 2010), thus the spectral interference imposed by the bulk gas matrix can be
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27 accounted for (Marshik and Perez, 2013). This is evidenced by the good correlation
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29 between FTIR and GC-MS results in real biogas (RSME = 15.7%, Figure 3a) which
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31 indicates that the interference imposed by bulk gases was consistent and can be
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33 compensated for through calibration.
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39 In this study, sixteen other non-target VOC species containing aliphatic =C-H
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41 bonds and/or aromatic C-H bonds (which absorb infrared radiation in the region 1000-
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43 600 cm^{-1} and 900-690 cm^{-1} respectively, Table 3) were identified in biogas at the case
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45 study site (Figure 4). The ratio of these non-target VOCs relative to the concentration of
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47 D5 was higher in biogas samples downstream of the carbon vessel (Figure 4).
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49 Interestingly, in the downstream biogas samples, FTIR siloxane data was higher than
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51 determined using GC-MS, without changes to bulk gas composition observed, and is
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53 counter to that observed upstream. It is therefore postulated that the higher
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55 VOC/siloxane molar ratio observed downstream of the carbon filter introduced positive
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5 interference to siloxane measurement in downstream samples. Whilst VOC analysis was
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7 not undertaken in their study, Oshita et al. (2010) also suggested positive interference
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9 from VOCs to explain the higher readings produced from on-line FTIR when applied to
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11 biogas with a lower siloxane concentration than observed in this study (Table 4).
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14 Lechner et al. (2001) also reported positive interference when developing a method to
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16 discriminate compounds which absorb in similar spectral regions, finding difficulty
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18 differentiating between different alcohols, acetates and methyl-alkanes in air from the
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20 production hall of a recycling centre. Such analyses ostensibly require more complex
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22 analytical methods to incorporate spectral correction that allows for interference (Li et
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24 al., 2002). Consequently, the infrared spectra in this study were reanalysed using a PLS
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26 method as this is considered to be more effective for complex mixtures (Stuart, 2004).
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29 The PLS method also incorporated a new region of the infrared absorbance spectrum:
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31 1114.65 – 991.23 cm^{-1} which includes the resonance frequency of the Si-O-C bond
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33 stretching. The Si-O bond absorbs infrared radiation strongly (Stuart, 2004; Coates,
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35 2000) resulting in a tall absorbance peak (see Supplementary Information, Figure S1),
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37 making siloxane quantitation easier. The systematic error was reduced by more than
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39 50%, enabling a lower limit of detection of 3.2 mg m^{-3} and the improved accuracy
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41 demonstrated with the PRGM (Table 4). Further enhancement of the LOD for field
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43 based FTIR could be achieved through increasing data density to refine the PLS method
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45 at the lower concentration limit. To illustrate, Marshik and Zemek (2012) achieved a
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47 LOD of 300 – 500 ppbv with FTIR through diluting biogas samples to ascertain trace
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49 siloxane concentrations sufficient for calibration at the lower concentration range.
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51 Importantly, the LOD determined in this study is below the siloxane limit set by CHP
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53 engine manufacturers for inlet gas quality of 6 mg m^{-3} (Deutz), 12 mg m^{-3} (Jenbacher,
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Caterpillar) and 30 mg m⁻³ (Waukesha), demonstrating the industrial applicability of on-line FTIR for AC filter management.

Preliminary cost savings can be evidenced by direct comparison with current bag sampling methods. The cost of a field ready FTIR unit is around £50,000 (including multi-sampling-point installation) which compares to an annual cost of around £36,500 for bag sampling (based on one sample per day), providing a payback period of 16 months. However, the total cost benefit for the implementation of FTIR is best described by the improvement in engine protection through better carbon filter management (Table 5). To illustrate, at the case study sewage treatment works, it was observed that whilst the carbon bed was operated for 29 days, carbon bed breakthrough occurs at around two weeks, after which the siloxane concentration exceeds the engine manufacturer's siloxane specification, which triggers carbon replacement (Figure 5). Replacing the carbon every two weeks (i.e. at breakthrough) instead of every four weeks, doubles carbon cost but suggests a reduction in the mass of siloxane which enters the CHP engine by up to 80% (Figure 5). Using data from site and from Tower and Wetzel (2006) to estimate the lower engine maintenance threshold that can be achieved through the use of FTIR to trigger carbon changes, indicates a net saving of £328,000 per year for the case study STW (saving of around £0.007 kWh⁻¹) or a payback period of two months for an FTIR spectrometer (Table 5).

5 Conclusions

Excellent linearity was found when on-line FTIR spectroscopy and laboratory GC-MS results from synthetic reference gas were compared and good linearity was found for real biogas samples upstream of the carbon vessel. Positive interference from VOCs

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5 limited precision in downstream gas samples, but introducing a partial least squares
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7 methodology to analyse the infrared spectra led to a limit of detection of 3.2 mg m^{-3}
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9 being achieved, indicating the FTIR analysis is industrially relevant. The improved
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11 carbon management that FTIR analysis can facilitate leads an estimated economic
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13 return of $\text{£}0.007 \text{ kWh}^{-1}$, or 50% of the estimated associated cost of siloxane damage.
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31 **References**

32
33 Accettola, F., Guebitz, G. M., Schoeftner, R., 2008. Siloxane removal from biogas by
34
35 biofiltration: Biodegradation studies. Clean Technol. Environ. Policy. 10 (2), 211-218.
36
37
38
39
40 Ajhar, M., Travesset, M., Yüce, S., Melin, T., 2010a. Siloxane removal from landfill
41
42 and digester gas - A technology overview. Bioresource Technol. 101 (9), 2913-2923.
43
44
45
46 Ajhar, M., Wens, B., Stollenwerk, K. H., Spalding, G., Yüce, S., Melin, T., 2010.
47
48 Suitability of Tedlar® gas sampling bags for siloxane quantification in landfill gas.
49
50 Talanta. 82 (1), 92-98.
51
52
53
54 Arnold, M., 2009. Reduction and monitoring of biogas trace compounds. VTT Research
55
56 notes, 2496 VTT, Espoo.
57
58
59
60
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64
65

Arnold, M., Kajolinna, T., 2010. Development of on-line measurement techniques for siloxanes and other trace compounds in biogas. *Waste Manage.* 30 (6), 1011-1017.

Bendini, A., Cerretani, L., Di Virgilio, F., Belloni, P., Bonoli-Carbognin, M., Lercker, G., 2007. Preliminary evaluation of the application of the FTIR spectroscopy to control the geographic origin and quality of virgin olive oils. *J. Food Quality.* 30 (4), 424-437.

Bertran, E., Blanco, M., Coello, J., Iturriaga, H., Maspoch, S., Montoliu, I., 1999. Determination of olive oil free fatty acid by Fourier transform infrared spectroscopy. *J. Am. Oil Chem. Soc.* 76 (5), 611-616.

Bramston-Cook, E., Bramston-Cook, R., 2012. Online, direct measurement of volatile siloxanes in anaerobic digester and landfill gases by gas chromatography with mass spectrometric detection, in: Air and Waste Management Association (ed.), Air Quality Measurement Methods and Technology Conference 2012, 24-26 April 2012, Durham, North Carolina, Curran Associates, New York, pp. 438-443.

CERAM, 2012. Analysis of landfill gas and biogas for siloxanes by automated thermal desorption-gas chromatography-mass spectrometry. CERAM, Stoke-on-Trent, UK.

Coates, J., 2000. Interpretation of infra-red spectra, a practical approach, in Meyer, R. A. (ed.) *Encyclopedia of Analytical Chemistry*. Wiley, Chichester, UK, pp. 10815-10837.

Cooney, D. O., 1999. Adsorption design for wastewater treatment. CRC Press LLC, Florida.

DECC 2013. Digest of United Kingdom energy statistics chapter six: Renewable sources of energy. DUKES, Department for Energy and Climate Change, London.

1
2
3
4
5 Hepburn, C. A., Martin, B. D., Simms, N., McAdam, E. J., 2015. Characterization of
6
7 full-scale carbon contactors for siloxane removal from biogas using online Fourier
8
9 transform infrared spectroscopy. *Environ. Technol.* 36 (2), 178-187.

10
11
12 Lechner, B., Paar, H., Sturm, P. J., 2001. Measurement of VOCs in vehicle exhaust by
13
14 extractive FT-IR-spectroscopy, in: Fujisada H., Lurie J.B., Ropertz A., Weber, K.,
15
16 (eds.), *Sensors, Systems, and Next-Generation Satellites IV*, SPIE, Barcelona, pp. 432.
17
18

19
20 Lemar, P., 2005. CHP systems for landfills and wastewater treatment plants.
21
22 Intermountain CHP Centre workshop, 11/08/2005, Salt Lake City, UT.
23
24

25
26 Li, Y., Wang, J. D., Huang, Z. H., Xu, H. Q., Zhou, X. T., 2002. Monitoring leaking
27
28 gases by OP-FTIR remote sensing. *J. Environ. Sci. Heal. A.* 37 (8), 1453-1462.
29
30

31
32 Lipp, E. D., Smith, A. L., 1991. Infrared, raman, near-infrared and ultraviolet
33
34 spectroscopy, in: Smith, A. L. (ed.) *The analytical chemistry of silicones*. Wiley, New
35
36 York, pp. 245-305.
37

38
39 Lorberau, C., 1990. Investigation of the determination of respirable quartz on filter
40
41 media using Fourier transform infrared spectrophotometry. *Appl. Occup. Environ. Hyg.*
42
43 5 (6), 348-350.
44

45
46 Marshik, B., Zemek, P. G., 2012. Real-time siloxanes measurements at landfill and
47
48 digester sites using FTIR, in: Air and Waste Management Association (ed.), *Air Quality*
49
50 *Measurement methods and Technology Conference*, 24-26 April 2012, Durham, North
51
52 Carolina, Curran Associates, New York, pp. 464-468.
53
54
55
56
57
58
59
60
61
62
63
64
65

- 1
2
3
4
5 Marshik, B., Perez, J. E., 2013. Novel improvements in FTIR analysis of specialty
6
7 gases, in: Geiger, W. M., Raynor, M. W. (eds.), Trace analysis of specialty and
8
9 electronic gases. Wiley, Hoboken, NJ, pp. 43-70.
10
11
12 Miller, J. N., Miller, J. C., 2005. Statistics and chemometrics for analytical chemistry,
13
14 fifth ed, Pearson Education, Harlow, UK.
15
16
17 Montanari, T., Finocchio, E., Bozzano, I., Garuti, G., Giordano, A., Pistarino, C., Busca,
18
19 G., 2010. Purification of landfill biogases from siloxanes by adsorption: A study of
20
21 silica and 13X zeolite adsorbents on hexamethylcyclotrisiloxane separation. Chem. Eng.
22
23 J. 165 (3), 859-863.
24
25
26
27 Ohannessian, A., Desjardin, V., Chatain, V., Germain, P., 2008. Volatile organic
28
29 silicon compounds: The most undesirable contaminants in biogases. Water Sci.
30
31 Technol. 58 (9), 1775-1781.
32
33
34
35 Oshita, K., Ishihara, Y., Takaoka, M., Takeda, N., Matsumoto, T., Morisawa, S.,
36
37 Kitayama, A., 2010. Behaviour and adsorptive removal of siloxanes in sewage sludge
38
39 biogas. Water Sci. Technol. 61 (8), 2003-2012.
40
41
42
43 Rasi, S., Lehtinen, J., Rintala, J., 2010. Determination of organic silicon compounds in
44
45 biogas from wastewater treatments plants, landfills, and co-digestion plants. Renew.
46
47 Energ. 35 (12), 2666-2673.
48
49
50
51 Read, A., Hofmann, F., 2011. Does biogas scrub up? In: Materials Recycling World,
52
53 2nd December 2011, EMAP Publishing, London.
54
55
56
57
58
59
60
61
62
63
64
65

Schweigkofler, M., Niessner, R., 1999. Determination of siloxanes and VOC in landfill
 gas and sewage gas by canister sampling and GC-MS/AES analysis. Environ. Sci.
 Technol. 33 (20), 3680-3685.

Schweigkofler, M., Niessner, R., 2001. Removal of siloxanes in biogases. J. Hazard
 Mater. 83 (3), 183-196.

Stuart, B., 2004. Infrared spectroscopy: Fundamentals and applications. Wiley,
 Chichester, England.

Tower, P. M., Wetzel, J. V., 2006. Making power generation make sense by removing
 siloxanes from digester gas. CWEA Annual Conference, 5-7 April, Sacramento, CA,
 California Water Environment Association.

Wakao, N., Funazkri, T., 1978. Effect of fluid dispersion coefficients on particle-to-
 fluid mass transfer coefficients in packed beds: Correlation of sherwood numbers.
 Chem. Eng. Sci. 33 (10), 1375-1384.

Williams, S., Leung, Y., Aleixo, J., Hu, R., 2014. Understanding FTIR formaldehyde
 measurement and its influence on the RICE NESHAP rule. DCL International, Ontario,
 Canada.

Figure 1. Reference gas D5 concentration (in CO₂) compared to D5 concentration measured by FTIR. The dashed line represents parity (y = x).

Figure 2. FTIR readings compared to GC-MS measurements in synthetic reference gas. $r^2 = 0.99$ for D5 in N₂ and $r^2 = 0.98$ for D5 in CO₂. The dashed line represents parity (y = x).

Figure 3. FTIR reading for cyclic siloxanes compared to total cyclic siloxanes measured from gas bag samples by GC-MS from biogas (a) upstream of carbon vessel and (b) downstream of carbon vessel. The dashed lines show the 95% confidence limits.

Figure 4. Volatile organic compounds determined in biogas samples upstream and downstream of a carbon vessel: (a) Concentration; (b) molar ratio to D5. Nonane, decane and carbon disulphide (Marked*), do not contain bonds which are thought to contribute to interference in the FTIR readings.

Figure 5. An example breakthrough curve for a carbon vessel (1.21 m³, 450 kg_{carbon}). The area under the outlet concentration graph can be used to calculate the mass of siloxane entering the engine as follows: light grey - 0.94 kg over 18 days before breakthrough; mid grey - 0.94 kg over three days after breakthrough; dark grey - a further 2.72 kg over eight days before the carbon is changed.

Table 1. Infrared absorbance peaks for siloxanes.

Bond	Molecules	Peak position	Reference
Si-O	All siloxanes	1150 – 1000 cm ⁻¹	(Oshita et al., 2010)
		1035 cm ⁻¹	(Montanari et al., 2010)
Si-O-Si	All siloxanes	near 1050 cm ⁻¹ (antisymmetric stretch)	
		1090 cm ⁻¹ (cyclotrisiloxanes)	
		1020 cm ⁻¹ (cyclotetrasiloxanes)	
		Broad doublet with maxima at 1020 and 1090 cm ⁻¹ for more than twenty coupled siloxane units	(Lipp and Smith, 1991)
		1095 – 1075 cm ⁻¹ and 1055 – 1020 cm ⁻¹	(Coates, 2000)
Si-O-C	All volatile methyl siloxanes	1300 – 1000 cm ⁻¹ (asymmetric stretching)	(Stuart, 2004)
		1110 – 1080 cm ⁻¹	(Coates, 2000)
		1110 – 1050 cm ⁻¹ (stretching)	(Stuart, 2004)
Si-CH ₃	Linear siloxanes	850 - 770 cm ⁻¹	(Oshita et al., 2010)
		818 cm ⁻¹	(Montanari et al., 2010)
		Near 775 cm ⁻¹	(Lipp and Smith, 1991)
		1280 – 1250 cm ⁻¹ (symmetric bending)	(Stuart, 2004)
Si-(CH ₃) ₂	Cyclic siloxanes	Near 805 cm ⁻¹	(Lipp and Smith, 1991)
Si-(CH ₃) ₃	Linear siloxanes	760 and 845 cm ⁻¹	(Lipp and Smith, 1991)
CH ₃	Siloxanes Many other organic compounds	1262 ± 5 cm ⁻¹ and around 800-900 cm ⁻¹	(Lipp and Smith, 1991)

Table 2. Speciated siloxanes in sewage treatment works biogas measured by GC-MS ($n = 9$).

Siloxane species	Upstream concentration (mg m ⁻³)*			Downstream concentration (mg m ⁻³)*		
	Mean	St. dev.	Range	Mean	St. dev.	Range
L2	10.0	3.2	5.3 – 15.2	<1.0	-	-
L3	1.3	0.14	1.0 – 1.5	<1.0	-	-
L4	<1.0	-	-	<1.0	-	-
D3	<1.0	-	-	<1.0	-	-
D4	13.4	1.5	10.7 – 16.0	<1.0	-	-
D5	87.7	21.0	68.2 – 131.0	3.1	0.62	2.2 – 4.3

*Method detection limit is 1 mg m⁻³. L – represents a linear siloxane compound (L2-L4): L2 – Hexamethyldisiloxane, L3 – Octamethyltrisiloxane, L4 – Decamethyltetrasiloxane. D – represents a cyclic siloxane compound (D3-D5): D3 – Hexamethylcyclotrisiloxane, D4 – Octamethylcyclotetrasiloxane, D5 – Decamethylcyclopentasiloxane.

Table 3. VOC species present in biogas samples and associated infrared absorbance peaks (Stuart, 2004). The italicised peaks may cause positive interference.

Species	Concentration (mg m ⁻³)	Bonds ^a	Peaks
Alkanes			
Nonane	6	-CH ₂ -	2930; 2850; 1465; 1305; 1300; 720
Decane	9		
Alkenes			
1-butene	3.4	=C-H	3100-3000; 1400; <i>1000-600</i>
		C=C	1680-1600
Aromatic hydrocarbons			
Benzene	3.6	C-H	3100-3000; 1275-1000; <i>900-690</i>
Toluene	25.3	C=C	1650-1430
Ethyl benzene	15.1	Substituted aromatic compounds will also have peaks similar to the aliphatic compounds above	
m,p-xylene	32.9		
o-xylene	11.		
o-ethyltoluene	16.2		
m-ethyltoluene	47.7		
p-ethyltoluene	21.0		
1,2,3-trimethylbenzene	5.7		
1,2,4-trimethylbenzene	44.5		
1,3,5-trimethylbenzene	22.2		
Cumene	10.9		
d-limonene	8.8		
Alpha-pinene	9.3		
Beta-pinene	3.1		
Sulphur compounds			
Carbon disulphide	2.2	C-S	700-600

^aBonds shown are representative of chemical groups

Table 4. Comparison of on-line analytical procedures for siloxane detection from the literature with the current study.

Gas	Total Siloxanes (mg m ⁻³)	On-line analysis	Calibration	Verification	Reference
Landfill ^f	1.6-7.9 ^a 0.1-1.3 ^b 0.2-4.3 ^c	Portable GC-PID Perkin Elmer Photovac Voyager (Speciated Siloxanes)	Reference gases from liquid standards (L2,L3,L4,D3,D4,D5) injected via syringe pump into a nitrogen flow using a Gasmeter TM calibrator. LOD = 0.01 ppm.	ATD-GC-MS (Perkin Elmer ATD400, HP5890/HP5972) Range (L2,L3,L4,D3,D4,D5) Standards prepared in methanol and preloaded onto Tenax TA adsorbent tubes Results obtained by direct GC measurement (GC-PID) higher than ATD-GC-MS. Some conformity noted. D4 around 10% difference; D5 comparable for concentrations >1-2 mg m ⁻³	Arnold and Kajolinna, 2010
Digester ^f	2.5-29.6 ^a 4.5-27.1 ^b				
Landfill ^f	4.9 ^{a,d} 4.6 ^{c,d}	GC-MS Bruker 451 GC/Scion SQ MS used with multi stream selector valve for automated switching between sample, standard, blank (hydrophobic mixed bed adsorbent trap)	Standards generated on demand with Dynacal® permeation tubes and a Dynacalibrator® calibration gas generator with N ₂ as dilution gas. LOD = 0.08 ppbv for D5.	None stated	Bramston-Cook and Bramston-Cook, 2012
Digester ^f	20.2 ^{a,d} 8.4 ^{c,d} 11.5 ^{b,d}	(Speciated Siloxanes)			
Digester ^f	32.2±13.3 ^a 25.5±11.4 ^b	FTIR VA-3001S, Osaka Gas Engineering (Total siloxanes)	Use of D4 Standard Gas 42.5ppmv/N ₂ prepared by Sumitomo Seika Chemicals Co. Level of determination = 0.6 mg m ⁻³ .	GC-MS (HP6890/HP5973) Range (L2,L3,L4,D3,D4,D5,D6) Close correlation identified between FTIR and GC-MS in both model biogas and real biogas	Oshita et al., 2010
Digester ^g	87.7 ^{b,e} 13.4 ^{c,e}	FTIR ThermoFisher Antaris IGS (Cyclic/linear siloxanes)	Reference gas from liquid standard (D5) produced from controlled volatilisation into CO ₂ / N ₂ flow. LOD = 3.2 mg m ⁻³ .	Tedlar bag samples loaded onto Tenax tubes and measured used GC-MS. Close correlation identified between FTIR and GC-MS. RMSE = 9.8 mg m ⁻³ (9.7%) and 1.5 mg m ⁻³ (48%) respectively for real biogas from upstream and downstream of a carbon vessel. Primary reference gas (110 mg _{D5} m ⁻³ _{CH4}). 4% error.	This study

^aTotal siloxanes; ^bD5 concentration. ^cD4 concentration. ^dUnits are ppmV. ^eMean based on initial speciation by GC-MS. ^fSiloxanes measured in untreated biogas. ^gSiloxanes measured upstream and downstream of carbon filter.

Table 5. Costs of siloxane monitoring, carbon replacement and CHP engine maintenance.

Scenario	Cost	No gas treatment		Carbon beds changed every four weeks		Carbon beds changed after breakthrough using FTIR	
		Frequency	Annual cost	Frequency	Annual cost	Frequency	Annual cost
Siloxane monitoring ^a							
Bag sampling	£100	Daily	£36,500	Daily	£36,500	-	-
FTIR service	£1,500	-	-	-	-	Annual	£1,500
Siloxane removal system ^a							
Replace GAC (3000 kg virgin GAC)	£5,052	-	-	700 hours	£63,000	400 hours	£110,000
Replace GAC (delivery/labour)	£3,000	-	-	700 hours	£39,000	400 hours	£62,000
Engine maintenance ^b							
Service	£225,000	5000 hours	£390,000	9000 hours	£220,000	20000 hours	£100,000
Decoke	£50,000	nd	nd ^c	3000 hours	£150,000	9000 hours	£50,000
Oil change	£7,500	250 hours	£260,000	500 hours	£130,000	1500 hours	£44,000
Spark plugs	-	500 hours	£15,000	1200 hours	£6,000	1500 hours	£5,000
Engine operation ^b							
Downtime	£80,000 per week	5 weeks per year	£400,000	1 week per year	£80,000	0.3 weeks per year	£24,000
Total			£1,251,500	£724,500		£396,500	
Annual saving (compared to no treatment)			-	£527,000		£855,000	
Annual saving (compared to bag sampling)			-	-		£328,000	
Payback period for FTIR spectrometer		£50,000	-	-		2 months	

nd = no data. ^aCosts based on case study sewage treatment works. ^bCosts estimated using data for Santa Cruz case study from Tower and Wetzel (2006) – pre-treatment cost, post-treatment low estimate and post-treatment high estimate. ^c£150,000 per annum used in total cost calculation. Biogas revenue is £0.19 m⁻³ (Read and Hofmann, 2011)

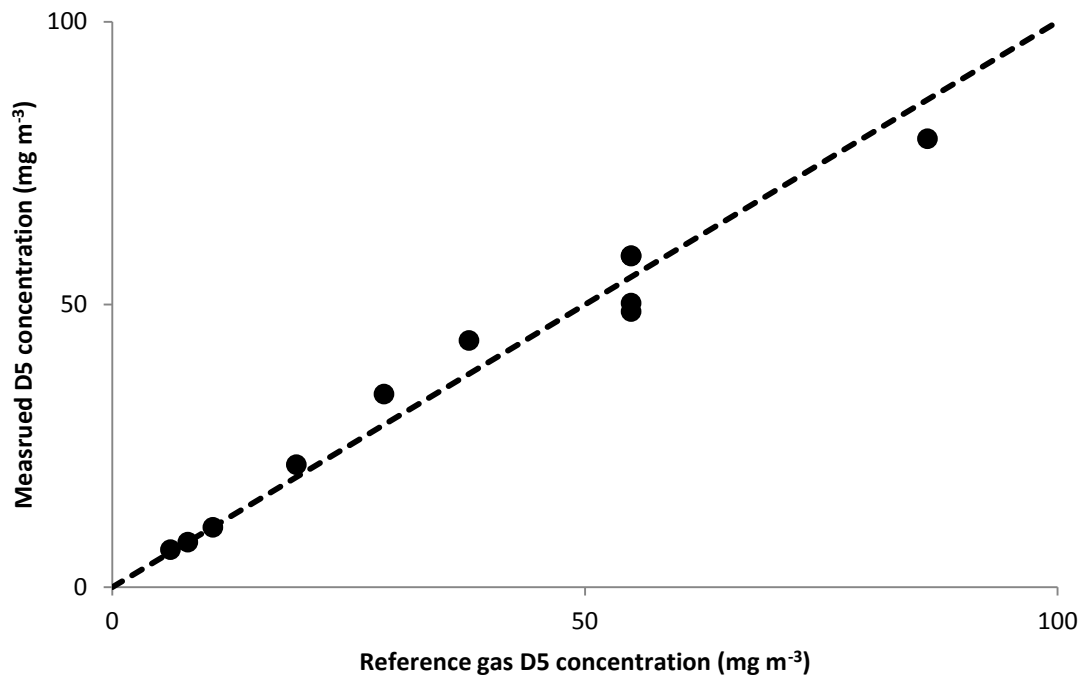


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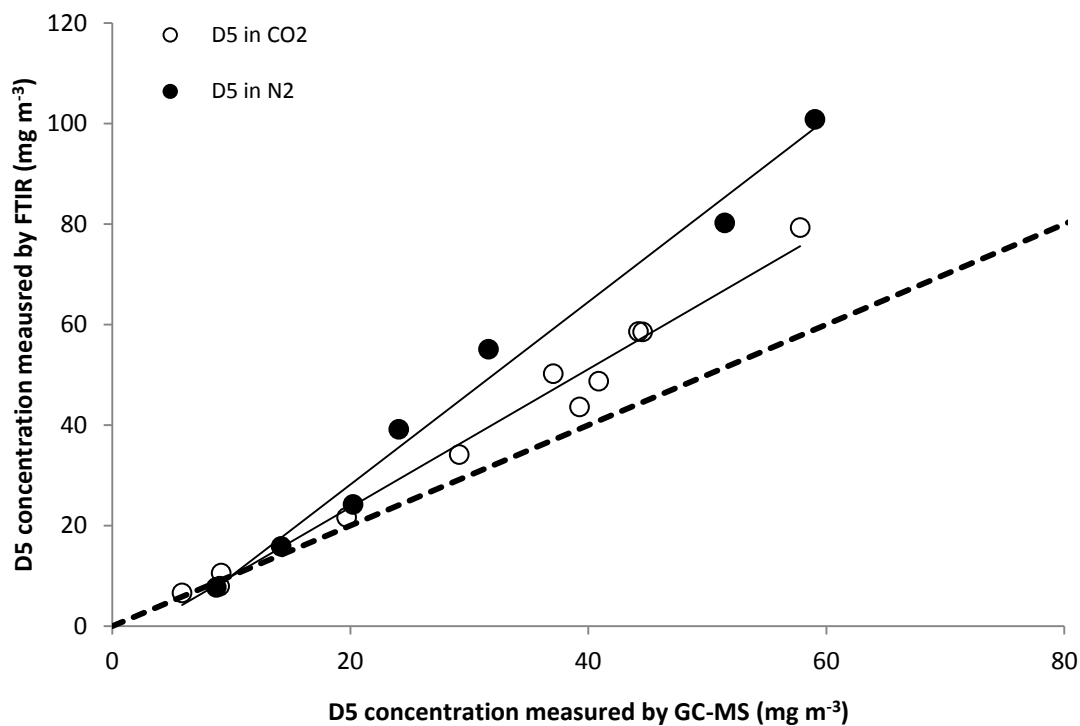


Figure 2. FTIR readings compared to GC-MS measurements in synthetic reference gas. $r^2 = 0.99$ for D5 in N₂ and $r^2 = 0.98$ for D5 in CO₂. The dashed line represents parity ($y = x$).

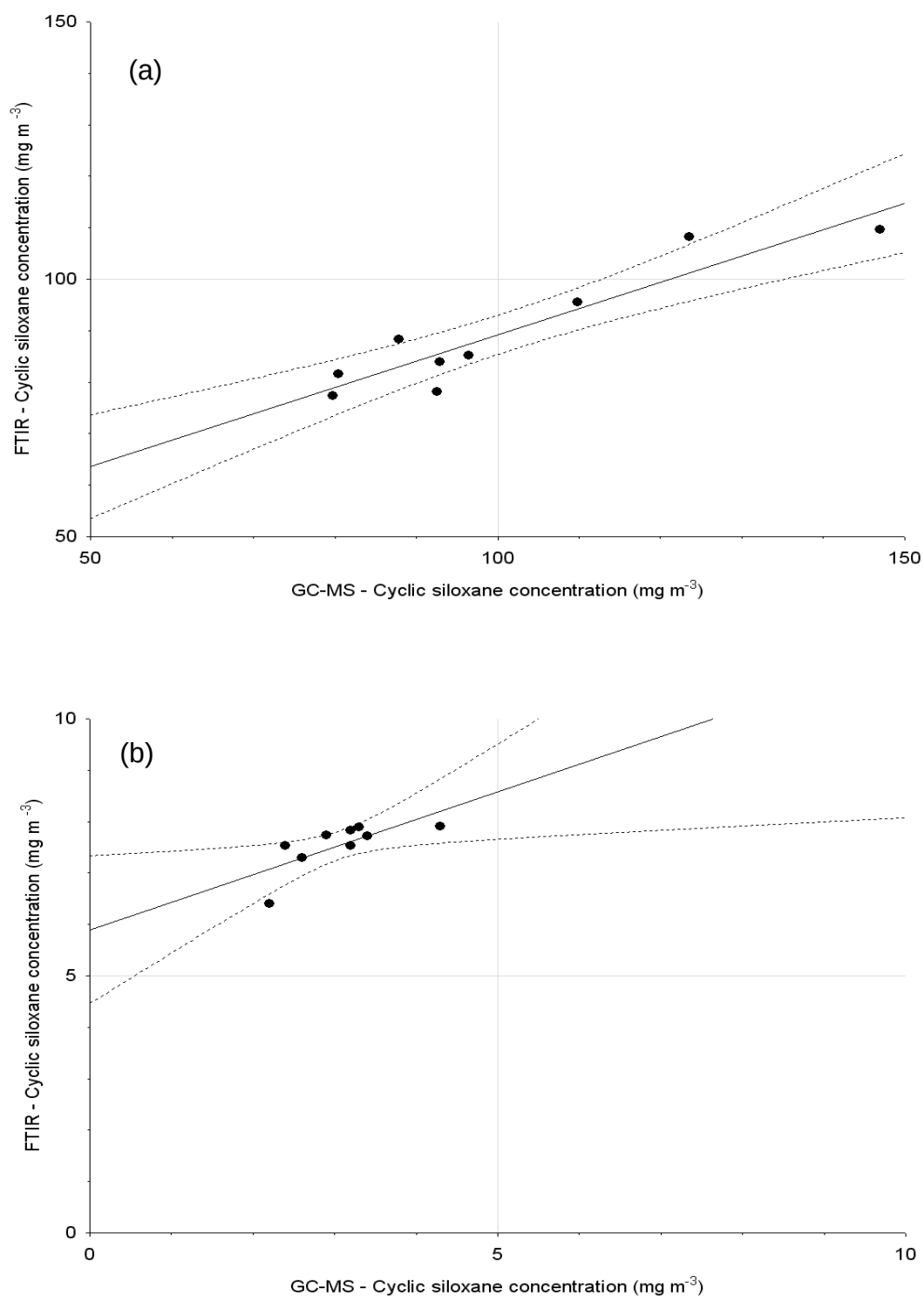


Figure 3. FTIR reading for cyclic siloxanes compared to total cyclic siloxanes measured from gas bag samples by GC-MS from biogas (a) upstream of carbon vessel and (b) downstream of carbon vessel. The dashed lines show the 95% confidence limits.

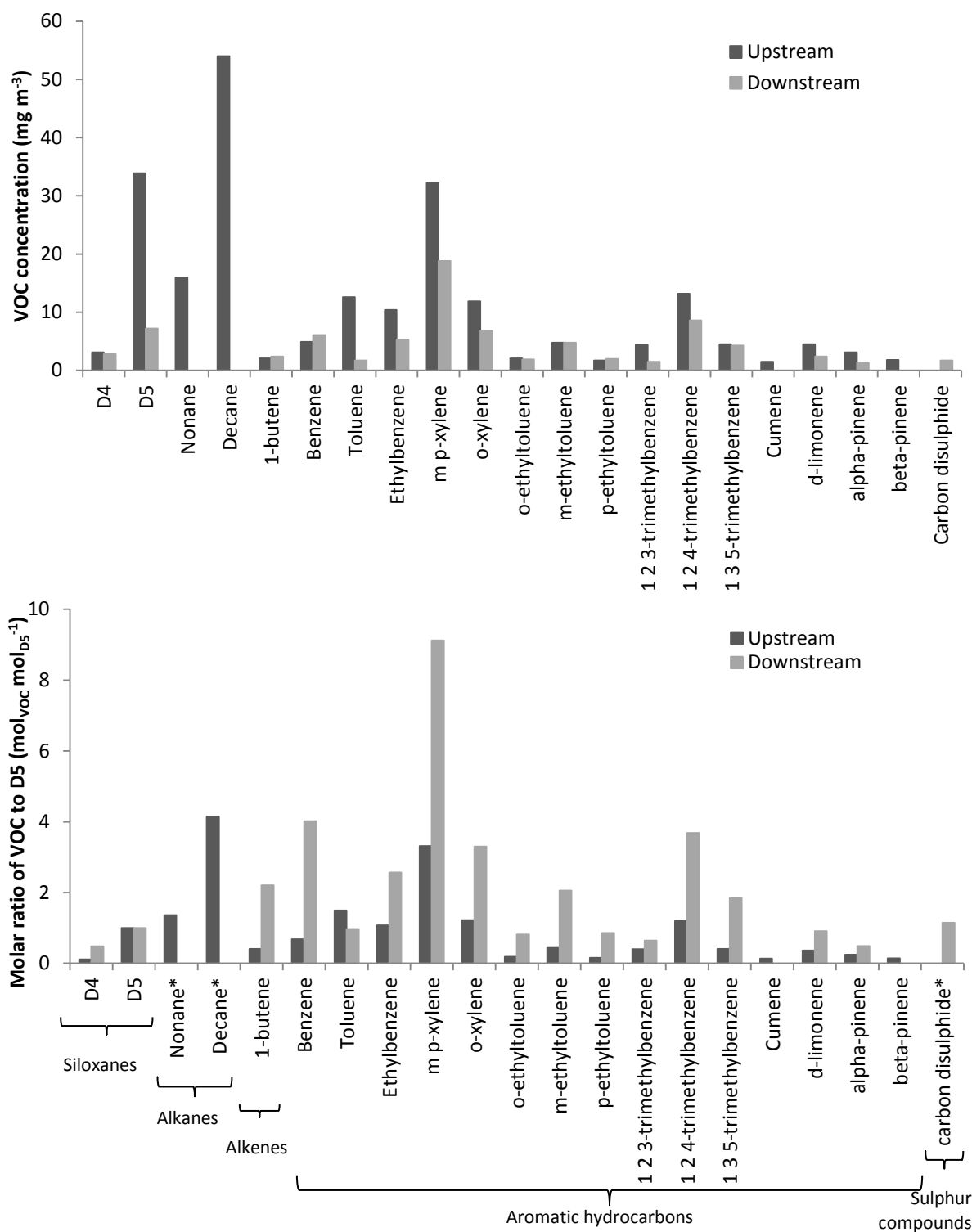


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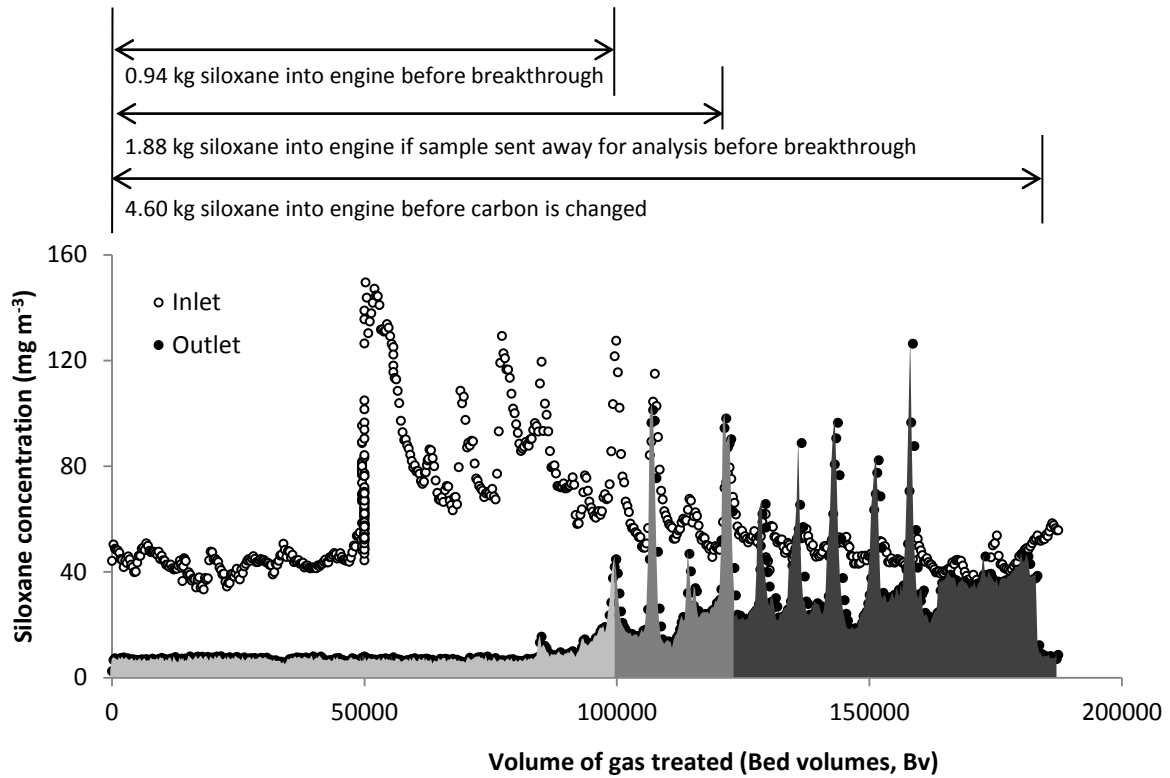


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Development of on-line FTIR spectroscopy for siloxane detection in biogas to enhance carbon contactor management

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