Analysis of methane emissions from digested sludge
C. Schaum, T. Fundneider and P. Cornel

ABSTRACT

The energetic use of sewage sludge is an important step in the generation of electricity and heat within a wastewater treatment plant (WWTP). For a holistic approach, methane emissions derived from anaerobic treatment have to be considered. Measurements show that methane dissolved in digested sludge can be analyzed via the vacuum salting out degassing method. At different WWTPs, dissolved methane was measured, showing a concentration range of approximately 7–37 mg CH$_4$/L. The average concentration of dissolved methane in mesophilic digested sludge was approximately 29 mg CH$_4$/L, which corresponds to an estimated yearly specific load of approximately 14–21 g CH$_4$ per population equivalent. Comparisons between continuous and discontinuous digester feeding show that a temporary rise in the volume load causes increased concentrations of dissolved methane. Investigations using an industrial-scale digestion plant, consisting of three digestion tank operated in series, show comparable results.

Key words | digestion, dissolved methane, sewage sludge

INTRODUCTION

Wastewater and sewage sludge treatment systems of the future have to fulfill the requirements of health protection, water pollution control and resource conservation. Thereby, resource conservation includes questions of resource efficiency, meaning minimization of resource consumption (for example, energy and operating materials as well as minimization of environmental impact), resource recovery, meaning utilization of resources contained in wastewater or sewage sludge, in particular water, nutrients and energy (Schaum 2016).

From the energetic point of view, anaerobic sewage sludge treatment (digestion) becomes more important, as electricity and heat can be generated by using biogas. The used sewage sludge is then assessed as climate-neutral in terms of ‘renewable raw materials’. On the other hand, methane emissions from sewage sludge treatment get little attention and so far there are only few – highly variable – measurement data published (Foley et al. 2015); see Table 1.

Basically, methane emissions on wastewater treatment plants (WWTPs) without digestion will be identified mainly in the influent area, that is in areas with anaerobic processes (Foley et al. 2015). On WWTPs with digestion, the findings will shift towards the digestion plant, especially its upstream and downstream structures/facilities, see Table 1. Becker et al. (2012) identified sludge digestion as a main emitter of methane, whereby approximately 50% of the overall methane emissions were measured at the heads of the digester.

Table 1 shows that there are only few published data regarding methane emissions from wastewater treatment, and those that exist show a large range of data from 0.09 to 307 CH$_4$/(PE-a) (all without digestion). For the entire field of digestion (digestion, thickener.stack container, combined heat and power plant (CHP)), a range between 65 and 281 g CH$_4$/(PE-a) can currently be identified; mean value: 162 ± 87 g CH$_4$/(PE-a). Below, the main emission sources are listed (Schaum et al. 2015):

- Dissolved methane in digested sludge, discharged together with the digested sludge from the digestion unit.
- Residual gas potential that originates in the post-thickener and emits into the atmosphere.
- Methane slip, emitting from biogas utilization in the CHP.

The focus of this research will be on the measurement and assessment of dissolved methane emission from digestion:

- Development and validation of an analysis method for dissolved methane.
The higher the partial pressure in the gas phase, the higher the concentration of dissolved methane. Thereby, the partial pressure is the product of gas concentration and absolute pressure.

**GAS SOLUBILITY IN DIGESTED SLUDGE—THEORETICAL FOUNDATIONS**

The methane concentration in an aqueous phase can be calculated via Henry’s Law. The solubility of a substance in pure water depends on the concentration of the substance in the gas phase, gas pressure and temperature; see Figure 1. This means the following:

- The higher the partial pressure in the gas phase, the higher the concentration of dissolved methane.

**Table 1 | Methane emissions in the field of wastewater and sewage sludge treatment (in alphabetical order of authors); PE, population equivalent**

<table>
<thead>
<tr>
<th>CH4 emissions [g CH4/(PE·a)]</th>
<th>Technical description</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>31a</td>
<td>Municipal WWTP (without sewage sludge treatment, 210,000 PE, UK)</td>
<td>Abooobak et al. (2014)</td>
</tr>
<tr>
<td>280</td>
<td>WWTP &gt;10,000 PE and &gt;100,000 PE in North Rhine Westphalia (Germany); emissions 90% from sludge treatmentb</td>
<td>Becker et al. (2012)</td>
</tr>
<tr>
<td>39</td>
<td>WWTP Durham (UK), wastewater treatment, aerobic sewage sludge stabilization</td>
<td>Czepiel et al. (1993)</td>
</tr>
<tr>
<td>390c</td>
<td>WWTP Kralingseveer (The Netherlands); wastewater treatment (activated sludge process), sewage sludge treatment via digestion</td>
<td>Daelman et al. (2013); Daelman (2014)</td>
</tr>
<tr>
<td>300</td>
<td>Municipal WWTP (without sewage sludge treatment) (data from the Netherlands from 1991)</td>
<td>EEA (2015)</td>
</tr>
<tr>
<td>&lt;4–18a</td>
<td>WWTPs (France, details not published) &lt;0.1–0.4 g CH4/kg CODinfluent</td>
<td>Foley et al. (2015)</td>
</tr>
<tr>
<td>165</td>
<td>WWTP (320,000 PE) including digestion1; emissions &gt;98% from digestion</td>
<td>Gärtnert &amp; Hirschberger (2011)</td>
</tr>
<tr>
<td>110a</td>
<td>Methane emissions (measurement) Swedish WWTP with digestion (0.25% CODinfluent)</td>
<td>Gustavsson &amp; Tumlin (2013)</td>
</tr>
<tr>
<td>106</td>
<td>Digestion at municipal WWTP degassing of digested sludge: 30 g CH4/(PE·a) gas generation in stack container with 1 day retention time: 76 g CH4/(PE·a)</td>
<td>Leal Verdugo (2014)</td>
</tr>
<tr>
<td>0.09–0.18</td>
<td>WWTP Simmering (Austria), only activated sludge tank</td>
<td>Schmid &amp; Puxbaum (2000)</td>
</tr>
<tr>
<td>307 resp. 372c</td>
<td>3 Dutch WWTPs without and, respectively, with digestion (by digestion 65 g CH4/(PE·a))</td>
<td>STOWA (2010)</td>
</tr>
<tr>
<td>A: 251f B: 71f</td>
<td>Methane losses during digestion operation volatile emissions, residual gas, methane slip A = stock; B = new construction</td>
<td>UKWIR (2009)</td>
</tr>
<tr>
<td>11</td>
<td>WWTP Jinan (China), wastewater treatment incl. sewage sludge thickening and drying bed (no digestion)</td>
<td>Wang et al. (2011)</td>
</tr>
</tbody>
</table>

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- Analysis of dissolved methane depending on different operation conditions (for example, meso-/thermophilic, gas injection, digester feeding).

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**Figure 1 | Theoretical solubility of methane in the aqueous phase as a function of pressure, temperature (20 and 37 °C), salt concentration (0.2 mol/L NaCl (upper lines) and pure water (lower lines)) and methane concentration in the gas phase (60 and 70 vol-% CH4).**
• The higher the temperature, the lower the concentration of dissolved methane.

The calculation of the dissolved methane concentration is based on Henry's Law (Equation (1)) (Stephan et al. 2009; Sander 2014). Considering the influence of the temperature according to the van 't Hoff Equation (Sander 2014) leads to the combined equation Equation (2):

$$c_a = k_{H,pc} \cdot p \left[ \frac{mol}{m^3} \right]$$  

(Stephan et al. 2009)

$$k_{H,pc} = k_{H,pc,0} \cdot \exp \left( \frac{\zeta_G}{T} \left( \frac{1}{T_\Theta} - 1 \right) \right) \left[ \frac{mol}{m^3 \cdot Pa} \right]$$  

(Sander 2014)

Here, $c_a$ is the dissolved methane concentration in the aqueous phase [mol/m$^3$]; $p$ is the partial pressure in the gas phase under equilibrium conditions [Pa]; $k_{H,pc}$ are Henry's Law volatility constants [mol/(m$^3$·Pa)].

Method validation

Method validation was carried out via laboratory tests. A fully mixed reactor (reactor volume 12 L) was used in an experiment with pure water, where pressure (1,000–1,540 hPa), temperature (0.6–37 °C), salt concentration (sodium chloride (NaCl), 0–1 mol/L NaCl) and gas quality (99.5 vol-% CH$_4$ and a gas mixture of 60 vol-% CH$_4$ and 40 vol-% CO$_2$, both from Linde) were varied. The measured dissolved methane concentrations were measured and compared to the theoretically expected concentrations. All assessments are based on multiple measurements (at least three-fold determination).

WWTPs for measuring dissolved methane concentrations in digested sludge

The investigation on the concentration of dissolved methane in digested sludge was carried out at seven industrial-scale municipal WWTPs (hydraulic retention time (HRT) always >20 d), see Table 2.

In addition, at WWTP #3 and WWTP #7, the influence of mixing during digestion was investigated by means of gas injection (via lances).

Test plant for determining the effects of digested sludge feeding

A semi-industrial test plant with a digested sludge volume of 1 m$^3$ was used to investigate the influence of digested sludge feeding on the solubility of methane (HRT 20 d, mixing via stirrer). Thereby, the effects of continuous feeding of raw sludge were compared to those of discontinuous feeding.
In addition, the dissolved chemical oxygen demand (COD) was analyzed (cuvette test; Hach).

**Applied analysis methods**

Characteristic sewage sludge parameters were analyzed in the collected sewage sludge samples: total solids (TS) (DIN 2001), total volatile solids (TVS) (DIN 2012) and the chemical parameters pH-value (Knick Elektronische Messgeräte) and electrical conductivity (WTW).

The challenge in measuring the concentration of dissolved methane in digested sludge is to avoid gas exchange with the surrounding air: as soon as the digested sludge leaves the digester, methane stripping into the atmosphere occurs. Furthermore, one has to consider the content of TS in the digested sludge when sampling, due to its impact on the sampling method to be selected (diameter of tubes, etc.).

Several methods have been developed for water/wastewater, e.g. Daelman et al. (2012), Foley & Lant (2009), Alberto et al. (2000). However, there is no unification or even standardization. For the field of digestion for example, sewage sludge, method modifications are necessary for measurements in industrial-scale digestion plants, in particular regarding the connection to piping systems (circulation pipes) in the range of DN 100–200, pressure conditions in the pipes of approximately 1,800–2,600 hPa and the content of TS of 2–3% TS.

The vacuum degassing method according to Daelman (2014), Daelman et al. (2012) and Gal’chenko et al. (2004) was modified and applied for the measurement of dissolved methane concentrations in digested sludge. The method is based on headspace gas chromatography in combination with vacuum degassing and salting out for setting a new state of equilibrium.

The *in situ* measurement of solids-containing samples was carried out by means of two systems: 1 L glass flasks with GL thread connectors and a 12 L vacuum container. In Figure 2, the experimental setup of the vacuum container is depicted. Analogously, the applied 1 L glass flasks were equipped with respective entries/ exits.

The sampling of digested sludge (4–6 L and, respectively, 0.4–0.5 L containers/flasks) took place directly at the circulation pipe of the digestion unit (digestion units with gas injection, as well, are equipped with circulation pipes for heating the unit). A vacuum container (12 L and, respectively, 1 L containers/ flasks) was used to avoid methane stripping into the atmosphere. To shift the solubility of methane, sodium chloride (NaCl) was added (addition of...
400 g NaCl/L for a saturate solution) to strip the dissolved methane, as well as a 50% sodium hydroxide solution (approximately 20 ml/L sample volume) to inhibit microbiological activity. Following a reaction time of 30–60 min (Schaum et al. 2015), during which the container, or flask, was shaken at intervals, sampling of the gas phase was done via a septum. The sampled gas was analyzed by means of gas chromatography (flame ionization detector (FID); Agilent).

Then, the weight of the vacuum container or the glass flasks was determined. Subsequently, the gas space was completely filled with a saturated NaCl solution (density NaCl ≈ 1.2 kg/L at T = 20°C). The gas phase volume was calculated via the total weight of the container and the specific density of the NaCl solution.

By recording pressure and temperature as well as gas and sludge volume, one can calculate the concentration of dissolved methane in sludge via the ideal gas law. The determination of the theoretical concentration of dissolved methane follows Henry’s Law. The decisive pressure and temperature were measured directly in the pipes via a portable measuring instrument (Greisinger). Furthermore, processing and constructional parameters (circulation, height of the sludge level, etc.) were taken into account.

RESULTS AND DISCUSSION

Validation of the method developed for measuring dissolved methane concentrations

The evaluation of the validation results show that the measured concentrations of dissolved methane comply with the values according to the theories of Henry and Sechenov, thus confirming that the method qualifies for the complete detection of methane in aqueous phases; see Figure 3(a). The basis of the ten test settings (9–12 fold determination each) was the variation of the boundary conditions with regard to pressure, temperature, gas composition and NaCl concentration.

As part of the method development, the second step was to validate the experimental setup and procedure, whereby the following results were obtained:

- Multiple determinations (15 individual measurements, WWTP #1): mean: 36.9 mg/L; standard deviation: 3.4 mg/L (with NaCl), which provided confirmation for the high reproducibility of the experimental setup;
- Variations in the volumes of digested sludge samples: Figure 3(b) demonstrates the excellent correlation between variation in sample volume and dissolved methane. The concentration was 39.7 ± 1.9 mg/L CH₄;
- Variations in reaction times: measurements with differing reaction times demonstrate that the solubility equilibrium was achieved relatively spontaneously (Schaum et al. 2015). Therefore, a reaction time of 30–60 min was chosen for subsequent experiments.
Investigation of dissolved methane in various WWTPs

Table 3 presents the experimental results, which demonstrate the following dependencies:

- In accordance with the theoretical considerations, using salt (NaCl) produced a clearly higher methane concentration, because the shift in solubility led to the complete stripping of the methane dissolved in the sludge according to the theoretical solubility equilibrium (Hermann et al. 1995; Sander 2014); see also Figure 1. Approximately only 65%, on average, of the dissolved methane were detected without the use of NaCl (measurements at 37 °C).

- In two WWTPs (WWTP #1 and #2), a comparison between measured (with NaCl) and calculated methane concentration yields values that are approximately 50% higher for the measured concentrations.

Supersaturation, meaning the measured methane concentration is higher than that calculated on the basis of theory, has also been observed in anaerobic sewage treatment plants, whereby the degree of supersaturation varies strongly; supersaturation ratios are between 1.9 and 6.9 (Hartley & Lant 2009). Data for digested sludge are not yet available. Currently, and on the basis of recent results from anaerobic sewage treatment, it is only possible to speculate on the possible causes of supersaturation and the relevant mechanisms of action. For instance, sludge flocs and/or the related production or distribution of gas (micro gas bubbles) may lead to a shift in the solubility equilibrium. Further laboratory experiments that allow variations in defined boundary conditions will investigate possible effects on the solubility of methane.

By contrast, the other WWTPs that were investigated show close agreement between the measured and calculated concentrations.

Basically, calculating the concentration of the dissolved methane with Henry's Law provides a good first approximation for determining this concentration in digested sludge. The most sensitive factor in the determination of the dissolved methane concentration is the pressure that has to be applied, in particular because of possible measurement errors caused by the sampling location (e.g. pipeline layout, pump, etc.). This sensitivity is related to the fact that pressure is directly proportional to the dissolved methane concentration. Other factors, such as temperature, conductivity or methane concentration in the gas phase can, by contrast, be assessed exactly during data analysis.

- The mesophilic/thermophilic comparison reveals that methane has a low solubility in digested sludge, which is in accordance with theoretical calculations.

An influence of the pH, which ranged between 7.1 and 7.4 for all samples, as well as of the conductivity, which ranged between 6.3 and 9.8 mS/cm, was not observed. The TS concentration in the investigated samples ranged from 2 to 3% (mean: 2.8%) with a TVS of 55–62% (mean: 59%); technical process conditions produced an outlier of 71%. A dependency on the dissolved methane concentration was not observed.

Table 3 | Measured and calculated dissolved methane concentration of digested sludge

<table>
<thead>
<tr>
<th>Total pressure [hPa]</th>
<th>Measured (without NaCl) CH₄ [mg CH₄/L]</th>
<th>Measured (with NaCl) CH₄ [mg CH₄/L]</th>
<th>Calculated CH₄ [mg CH₄/L]</th>
<th>Supersaturation ratio measured (with NaCl) to calculated CH₄ [–]</th>
</tr>
</thead>
<tbody>
<tr>
<td>WWTP #1 2,360</td>
<td>23</td>
<td>37</td>
<td>27</td>
<td>1.37</td>
</tr>
<tr>
<td>WWTP #2 2,080</td>
<td>30</td>
<td>36</td>
<td>24</td>
<td>1.50</td>
</tr>
<tr>
<td>WWTP #3b 2,540</td>
<td>n.a.</td>
<td>29</td>
<td>29</td>
<td>1.00</td>
</tr>
<tr>
<td>WWTP #4 1,860</td>
<td>10</td>
<td>17</td>
<td>21</td>
<td>0.81</td>
</tr>
<tr>
<td>WWTP #5 2,200d</td>
<td>14</td>
<td>25</td>
<td>25</td>
<td>1.00</td>
</tr>
<tr>
<td>WWTP #6c 2,340</td>
<td>6</td>
<td>18</td>
<td>19</td>
<td>0.95</td>
</tr>
<tr>
<td>WWTP #7 2,340</td>
<td>n.a.</td>
<td>29</td>
<td>27</td>
<td>1.07</td>
</tr>
</tbody>
</table>

*Theoretical concentration of dissolved methane in digested sludge, based on pure water; Henry constant: k_H [35 °C] = 1.18 10⁻⁶ mol/m²·Pa; k_H [55 °C] = 8.57 10⁻⁶ mol/m²·Pa, Sander (2014), Stephan et al. (2009); pressure at the sample withdrawal location (pressure conduit) taken into account; methane concentration in the gas phase: 60% CH₄.

bMeasurement in digester tank 1 of 3 (series connection).

cThermophilic operating conditions (55 °C).
dMeasurement not possible; estimated via height of digester.
n.a., not analyzed.
Investigation on the influence of gas injection on dissolved methane

The mixing of the digestion in WWTPs #3 and #7 was carried out via interval gas injection; following 60 min of gas injection, generally there was a break time of 180 min. Based on the fact that biogas was used for gas injection to mix the digester, it was assumed that there is an impact on the concentration of dissolved methane. However, investigations at WWTPs #3 and #7 show that there was no significant impact of gas injection on the concentration of dissolved methane; see Figure 4. No change was observed in dissolved methane, neither before nor after gas injection. Due to a coarse-bubble gas injection, the influence to the methane solubility is low. Figure 4 also shows the comparison between calculated and measured concentrations of dissolved methane. It becomes clear that the results are comparable to those of Table 1.

Investigation on the influence of digester feeding on dissolved methane

In order to determine the influence of digester feeding on the concentration of dissolved methane, investigations were carried out in a semi-industrial plant with two parallel operating digesters (digester A and B). The type of feeding was varied. In Figure 5, the dissolved methane concentration is depicted as a factor of continuous (approximately 2.1 kg/h raw sludge), and discontinuous feeding (impact feeding of approximately 25 kg raw sludge within 30 min).

Due to the even feeding of digester A with raw sludge, a continuous gas production with comparable concentrations of dissolved methane and dissolved COD were observed within a period of 10 h, as had been expected. Caused by impact feeding with raw sludge, a significant increase in gas production immediately following the feeding of digester B was observed. With a certain time lag, hydrolysis leads to an increase in the concentration of dissolved COD, which subsequently is degraded again by conversion to biogas (Lensch et al. 2016). The dissolved methane concentration, as well as the supersaturation, correlates directly with the concentration of dissolved COD; see Figure 5.

Comparable effects were observed when analyzing the dissolved methane concentrations in the digester of WWTP #3. The digestion unit in WWTP #3 consists of three reactors operated in series. The measurements show that the dissolved methane concentrations decrease from reactor 1 to reactor 3 (digester 1: 29 mg/L CH₄; digesters 2/3: 11–16 mg/L CH₄). The two effects suggest that with the increase in volume load, both the concentration of dissolved methane and the supersaturation are increased. Parallel investigations of the Technische Universität Darmstadt, Institute IWAR show comparable effects in the anaerobic wastewater treatment via upflow anaerobic sludge blanket (UASB) and internal circulation (IC) reactors. The dissolved methane concentration correlates with the sludge bed (via reactor height) and the substrate gradient.

CONCLUSIONS

The energetic use of sewage sludge is an important step in the generation of electricity and heat within a WWTP. For a holistic approach, greenhouse gas emissions have to be considered. With anaerobic treatment, methane emissions are of particular concern.
The vacuum salting out degassing method can be applied to analyze methane dissolved in digested sludge. Method validation shows a high correlation between measured and calculated data (based on Henry’s Law).

Measurements of dissolved methane concentrations at different WWTPs reveal a concentration range of approximately 17–37 mg CH₄/L. The average concentration of dissolved methane in mesophilic digested sludge was approximately 29 mg CH₄/L, which corresponds to an estimated yearly specific load of approximately 14–21 g CH₄ per PE; under the following assumption: amount of digested sludge per day 40–50 g TS/(PE·d), TS concentration 25–30 g TS/L (Schaum 2015). This result is in the lower range of the latest literature research on methane emissions in the field of sewage sludge treatment of 65–281 g CH₄/(PE·a), see Table 1. However, one has to consider that the concentration of dissolved methane in digested sludge represents only one factor. Other factors include methane emissions from storage devices, as well as the methane slip during combustion in coupled heat and power plants (Schaum et al. 2015). Compared to the total digester gas production of about 2,800 g CH₄/(PE·a), the proportion of the dissolved methane is <1% (Schaum 2015).

The dissolved methane emissions of 14–21 g CH₄/(PE·a) corresponds to a global warming potential of 476–714 g CO₂ equivalent/(PE·a), considering a global warming potential of methane of 34 according to the Intergovernmental Panel on Climate Change (IPCC) (2015). For comparison: with the current German electricity mix, the global warming potential of the total electricity consumption of a municipal WWTP is about 8,400 g CO₂ equivalent/(PE·a) (Schaum 2015).

Vacuum degassing installations are able to abate emissions caused by dissolved methane. This technology has been installed in WWTP #5, with the aim of improving dehydration of sewage sludge. Initial studies demonstrate similar dissolved methane concentrations for the operation data of the full-scale vacuum degassing plant and the laboratory-scale results presented here. Nevertheless, the exhaust gas has to be incinerated to avoid further emissions.

Furthermore, the investigation shows that digester operation, in particular digester feeding, impacts the concentration of dissolved methane. Via respective operational measures, e.g. operation of several digesters, preferably operated in series rather than in parallel, concentrations of dissolved methane can be reduced.

In summary, the experimental results demonstrate the need for further measurements of dissolved methane in digested sludge. The focus should be on the interaction between biogas, water, and sludge flocs under various boundary conditions (pressure, temperature, circulation, etc.).

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