Sewage sludge treatment: evaluation of the energy potential and methane emissions with COD balancing
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ABSTRACT
Sewage sludge is an important resource for the generation of electricity and heat within a wastewater treatment plant (WWTP). Taking a holistic approach to such use involves considering the greenhouse gas emissions. In particular, for anaerobic sludge treatment, methane emissions are a matter of concern. Therefore, the utilization of a carbon balance, based on the chemical oxygen demand (COD), will be a focus for evaluating the magnitude of methane losses within the sludge treatment. In addition to biogas production and use in combined heat and power plants (CHPs), dissolved methane in digested sludge, as well as the methane slip, have to be considered.
Measurements of dissolved methane concentrations in sewage sludge from digesters of various WWTPs show a concentration of about 17–37 mg CH₄/L. The COD balance indicates a ratio of the methane emissions (methane slip, dissolved methane and residual gas) of < 4% of the total methane production during digestion. Considering the electricity generation by CHPs and the higher global warming potential of methane, compared to carbon dioxide, emissions of approximately 300 g CO₂-eq./kWhₜₐₐₐ result, which is in a similar range to greenhouse gas emissions caused by electricity generation by fossil fuels.

Key words | digestion, greenhouse gas emissions, methane, sewage sludge

INTRODUCTION
Wastewater components eliminated during the treatment process are partly converted into gaseous substances and partly accumulated as sewage sludge. Because of the current focus on the sustainable use of resources, the use of sewage sludge for energy generation has become a particular concern. There is a significant demand for optimizing energy generation from organic matter contained in sewage sludge, or for minimizing the consumption of external energy sources for sewage sludge treatment and disposal. Therefore, the utilization of a carbon balance, based on the chemical oxygen demand (COD), is becoming an increasingly important issue; based on the stoichiometric calculation, the COD seems to be more appropriate for optimization than the commonly used total volatile solids (TVS) (Schaum et al. 2015).

Figure 1 shows, based on a specific COD load of 120 g COD/(PE-d), the COD balance in a conventional municipal wastewater treatment plant (WWTP) which consists of primary treatment, an activated sludge process and digestion (Meda et al. 2012; Svardal 2012). Approximately 55% of the COD load in the influent of the WWTP is directed to the digestion process via the primary and surplus sludge. The remaining 45% (approximately) is either converted to carbon dioxide during the biological wastewater treatment or can be found in the plant’s effluent. Digestion of the primary and surplus sludge produces 45% biogas (in terms of the COD load in the primary and surplus sludge, i.e. in the digester’s influent) that can be used in energy generation in combined heat and power plants (CHPs).

In view of the fact that methane is around 25–86 times more harmful for the climate than carbon dioxide (global warming potential, time horizon 100 and 20 years, respectively; IPCC 2013), any ecological evaluation of the COD balance must be expanded to include methane emissions.
produced by digestion or by the use of biogas. This is of particular importance with respect to greenhouse gas emissions; however, very few approaches to this issue have been published to date.

The following three aspects will be addressed:

• methane that is dissolved in the sludge and removed from the digester together with the sludge,
• residual gas potential that may be created in the thickener, and
• methane slip that may be released during the use of biogas in CHPs.

Because virtually no data about dissolved methane are available, the focus for both the theoretical considerations and the practical experiments will primarily address the determination of gas solubility.

Gas solubility in digested sludge – theoretical foundations

The theoretical solubility of methane in an aqueous phase can be calculated using Henry’s law. The solubility of a substance in pure water depends on the temperature, the concentration of the substance in the gas, and the pressure, therefore:

• the higher the concentration in the gas phase, the higher the concentration of dissolved methane,
• the greater the pressure, the higher the concentration of dissolved methane.

Figure 2 shows exemplarily the theoretical solubility of methane in pure water as a function of the temperature, using the following assumptions on the basis of a conventional anaerobic digestion process: methane concentration in the gas 60%; mean absolute pressure within the reactor 1,913 hPa; Henry’s constant, according to Haynes et al. (2010) and NIST (2014):

\[ k_H(T) = k_H^0 \cdot e \left( \frac{1}{T} - \frac{1}{298.15 K} \right) \]

with \( k_H^0 = 0.0014 \text{ mol/(kg × bar)} \); \( k = 1,600 \text{ K (NIST 2014)} \).

A further factor that influences gas solubility is the salt concentration, which can be used in the course of analyzing the dissolved methane in sludge. At 20°C, the saturation of sodium chloride is approximately 360 g/L, and the temperature has only a relatively small effect on the solubility (Lautenschläger 2001). For a Sechenov constant, which describes the solubility of 0.15 m³/kmol, calculated according to Hermann et al. (1995), only 10% is present as dissolved methane, compared to pure water. Even though the Sechenov constant is only moderately temperature dependent, Hermann et al. (1995) report a significance of ± 5 K. The shape of the curve in Figure 2 is thus only a theoretical representation.

These theoretical relationships make it clear that, at 37°C, the concentration of dissolved methane in digested sludge is approximately 22 mg CH₄/L. In a saturated NaCl
solution, the concentration decreases to approximately 2 mg CH₄/L, which is relevant for the development of methods to detect the concentration of dissolved methane. It should be noted that these theoretical considerations only apply to the boundary conditions listed above; possible effects of supersaturation, e.g. micro gas bubbles attached to the sludge, have been ignored.

MATERIALS AND METHODS

To evaluate the methane emissions that arise in the course of sewage sludge treatment, a COD balance was prepared. The amounts of dissolved methane and methane remaining in the digested sludge (residual gas potential) were measured experimentally, whereas the methane slip was estimated theoretically.

Digested sludge samples from several municipal WWTPs were investigated. The characterization of the digested sludge properties was carried out by measuring the total solids (TS), TVS, and COD, as well as pH, temperature, and conductivity.

One of the challenges associated with measuring the dissolved methane concentration in digested sludge is preventing an exchange of gases with the environment, i.e. as soon as the sludge leaves the digester, the dissolved methane is stripped into the atmosphere. In addition, the concentration of solids in samples taken from the sludge must also be considered, because it may influence the method employed (e.g. diameters of tubes and cannulas). A variety of methods has been developed for studying sewage and water samples (Walsh & McLaughlan 1999; Alberto et al. 2000; Foley & Lant 2009; Hatamoto et al. 2010; Shin et al. 2011; Souza et al. 2011; Daelman 2014); however, unification, or even standardization, are still lacking. For digestion and/or sewage, adaptation of the methodology is required for measurements in large-scale digester plants (connection to pipeline systems within diameters of 100–200 mm, pipeline pressure approximately 2,000 hPa, digested sludge at a concentration of 2–3% TS).

To determine the concentration of dissolved methane in the digested sludge, a modification of the salting-out method developed by Daelman et al. (2012) and Gal’chenko et al. (2004) was used. The samples (5 L of digested sludge) were taken directly at the outlet of the recirculation pipe of the digester, using a vacuum reactor that was specially developed and designed by the IWAR institute. After a reaction time of 30 minutes (with the temperature of the sludge about 35 °C), during which the reactor was shaken regularly, a sample was taken from the gaseous phase of the reactor’s headspace via a syringe. Measuring pressure and temperature, as well as the gas and sludge volumes, and using the...
general gas equation, makes it possible to calculate the concentration of dissolved methane in the sludge. In addition to the experiments at the 5-L scale, further experiments used 1-L gas flasks, with an analogous experimental setup and data analysis.

Henry’s law was used to determine the theoretical concentration of dissolved methane. The relevant pressures and temperatures were measured directly in the pipe with a manually operated instrument (Greisinger Co., Regenstauf, Germany). In addition, the process and structural parameters (circulation, depth of the sludge blanket, etc.) were collected.

Additional experiments have been carried out in order to strip the dissolved methane: the methane solubility equilibrium was shifted by adding sodium chloride up to saturation. The aim of adding the sodium chloride was also to inhibit microbiological activity.

The analysis of the gas samples was carried out with a gas chromatograph (FID-detector, Agilent Co., Santa Clara, USA).

For the determination of the residual gas potential of the digested sludge, anaerobic digestion tests were performed at mesophilic conditions (37 °C) in a water quench, via 1 L bottles in a batch-wise manner, in accordance with the VDI guidelines (VDI 2006).

**RESULTS AND DISCUSSION**

Validation of the method developed to measure the dissolved methane concentration

As part of the development of the method, the first 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 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: measurement for differing reaction times demonstrated that the solubility equilibrium was achieved relatively spontaneously; see Figure 3. Therefore, a reaction time of 30 minutes was chosen for subsequent experiments.

**Investigations of dissolved methane in various WWTPs**

Table 1 presents the experimental results, which demonstrate the following dependencies.

- In accordance with the theoretical considerations, using NaCl produced a clearly higher methane concentration, because the shift in solubility led to the complete stripping of the methane dissolved in the sludge. Approximately only 65%, on average, of the dissolved methane can be determined without the use of NaCl (measurements at 37 °C).
- In two WWTPs (#1 and #2), a comparison between measured (with NaCl) and calculated methane concentration yields values that are approximately 50% higher.

Supersaturation, i.e. where the measured methane concentration is higher than that calculated on the basis of theory, has also been observed in anaerobic sewage treatment plants (Hartley & Lant 2006), whereby the degree of supersaturation varies strongly with supersaturation ratios.
between 1.9 and 6.9 (Foley et al. 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 the 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, in the other WWTPs that were investigated, there was 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). This sensitivity is related to the fact that pressure is directly proportional to the dissolved methane concentration. Other factors, such as the temperature and methane concentration in the gas phase, can by contrast be accessed relatively 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 7.2 and 8.3 mS/cm, was not observed. The TS concentration in the investigated samples ranged from 2.3 to 3.5% (mean: 2.8%) with a TVS of 55–62% (mean 59%); technical process conditions produced an outlier of 71%. No dependency on the dissolved methane concentration was observed.

In all the investigated WWTPs, the circulation in the digester was achieved with external pumps, and the circulation rates were similar. Further investigations are needed to determine the effect of circulation, particularly when gas lifting is used. Circulation during digestion may influence the concentration of dissolved methane.

WWTP #3 operates three digestion tanks (tank 1: 5,500 m³; tanks 2 and 3: 3,250 m³ each) that are connected in series. The retention time in tank 1 is approximately 18 d. Samples for the determination of the dissolved methane concentration were taken from all three tanks; the methane concentration (with NaCl) in tanks 2 and 3 was 11 mg CH₄/L and 16 mg CH₄/L, respectively, and thus significantly less than in tank 1 (29 mg CH₄/L, see Table 1). This indicates a possible relationship between the dissolved methane concentration and the digestion procedure (operation in series, retention time) that requires validation in future experiments.

Table 2 presents changes in the concentration of dissolved methane during sewage treatment. Approximately 80% of the dissolved methane content in the digested sludge is immediately released into the atmosphere when
the sludge leaves the digester. The concentrations of dissolved methane in stored process water are \(<1\) mg/L, i.e. the methane that is dissolved in the digested sludge is released into the atmosphere during the subsequent processing steps.

### Comparison between measured and published values

Because the measurement of methane emissions is complex, data related to this parameter in the field of WWTPs are both scarce and vary greatly (see Table 3). Methane emissions in WWTPs without digestion can be identified close to the inlet pipes/canal and/or at locations where anaerobic conditions exist. In plants with digestion, the emissions are shifted to this area, or to digester constructions/machine technology located up- or downstream.

The average concentration of dissolved methane obtained in these investigations was approximately 29 mg CH\(_4\)/L (values for averaging were derived only from mesophilic digestion), which corresponds to an estimated yearly specific load of approximately 14–21 g CH\(_4\)/(PE·a) under the following assumption: amount of digested sludge per day 40–50 g TS/(PE·d), TS concentration 25–50 g TS/L. STOWA (2010) estimated yearly methane emissions from digestion to be 65 g CH\(_4\)/(PE·a); see Table 3, whereby the concentration of dissolved methane in digested sludge represents only one factor. Other factors include methane emissions from storage devices as well as methane slip, which is produced during combustion in CHPs.

### Results of measurements of the residual gas potential

In addition to methane losses due to its solubility, possible methane formation in the post-thickener, which can occur because of the residual methane potential of the digested sludge, has to be considered. The residual methane potential depends on several parameters, such as sludge retention time or volume load of the digester. For example, for WWTP #2, the batch test resulted in a methane production of approximately 30 NL CH\(_4\)/kg TVS\(_{\text{add}}\) after 5 d; i.e. during 2 d storage (e.g. over the weekend) on average about 15 NL CH\(_4\)/kg TVS\(_{\text{add}}\) residual gas is formed. Thus, if the retention time in the post-thickener is reduced, methane emissions could be reduced (Figure 4).

### COD balance for sewage sludge treatment

Figure 5 shows a simplified COD balance of the complete digestion system, whereby, as an extension of Figure 1, the following methane emissions were taken into account.

### Table 2 | Measured dissolved methane concentration of digested sludge (saturated with NaCl)

<table>
<thead>
<tr>
<th>Digestion (mg CH(_4)/L)</th>
<th>Post-thickener (mg CH(_4)/L)</th>
<th>Process water centrifuge (mg CH(_4)/L)</th>
<th>Process water storage (mg CH(_4)/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WWTP #1</td>
<td>37</td>
<td>7</td>
<td>4</td>
</tr>
</tbody>
</table>

### Table 3 | Methane emissions related to wastewater and sludge treatment

<table>
<thead>
<tr>
<th>CH(_4) emissions</th>
<th>CH(_4)/(PE·a)</th>
<th>CH(_4)/(L)</th>
<th>Brief description</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>14–21</td>
<td>(\approx 29)</td>
<td></td>
<td>6 German municipal WWTPs, only dissolved methane in the digester</td>
<td>Own measurement</td>
</tr>
<tr>
<td>39</td>
<td>–</td>
<td></td>
<td>WWTP Durham (NH, USA) wastewater treatment, aerobic sludge stabilization</td>
<td>Czepiel et al. (1995)</td>
</tr>
<tr>
<td>307 or 372(^a)</td>
<td>–</td>
<td></td>
<td>3 Dutch WWTPs with or without digestion (with digestion: 65 g CH(_4)/(PE-a))</td>
<td>STOWA (2010)</td>
</tr>
<tr>
<td>11</td>
<td>1.55 (\times 10^{-4})</td>
<td></td>
<td>WWTP Jinan (China), wastewater treatment including sludge thickening and sludge drying bed (no digestion)</td>
<td>Wang et al. (2011)</td>
</tr>
<tr>
<td>390(^b)</td>
<td>3.3</td>
<td></td>
<td>WWTP Kralingseveer (The Netherlands); wastewater treatment (activated sludge process) and sludge treatment via digestion</td>
<td>Daelman et al. (2015)</td>
</tr>
</tbody>
</table>

\(^a\) 7 g CH\(_4\)/(kg COD\(_{\text{rem}}\)) without digestion and 8.5 g CH\(_4\)/(kg COD\(_{\text{rem}}\)) with digestion; conversion with assumption of a specific COD load of 120 g COD/(PE·d); individual measurement data: WWTP Papendrecht 212 g CH\(_4\)/(PE·a), WWTP Kortenoord 153 g CH\(_4\)/(PE·a), WWTP Kralingseveer (with digestion) 438 (October 2008) and 230 (February 2009) g CH\(_4\)/(PE·a), cited in Daelman et al. (2013).

\(^b\) 1 g CH\(_4\)/(kg COD\(_{\text{rem}}\)) or 1.1% of the incoming COD; approximately 72 ± 23% of the total methane emissions originate in the sludge treatment (primary sludge thickener, digested sludge storage, dewatering, sludge storage, methane slip CHP) (Daelman et al. 2012).
Dissolved methane: 20 g CH\(_4\)/(PE·a) with the assumptions of 0.72 g CH\(_4\)/NL (in accordance with the ideal gas law) and 350 NL CH\(_4\)/kg COD yields a specific load of approximately 0.2 g COD/(PE·d).

Methane slip: in addition to the emission of dissolved methane, the combustion of digested gas causes a methane slip throughout the exhaust gas of CHPs. The methane slip is conservatively estimated to be approximately 1% of the amount of digester gas fed to the CHP (Liu 2006; SYLVIS 2009; Liebetrau et al. 2010); i.e. 31 g COD/(PE·d) of digester gas for the CHP results in a methane slip of approximately 0.3 g COD/(PE·d). In newer, more efficient CHPs, the methane slip can be significantly lower, e.g. approximately 0.3%, relative to the amount of digester gas for the CHP (SYLVIS 2009).

Residual gas potential after 2 days: 15 NL CH\(_4\)/kg TVS\(_{\text{add}}\) with a primary and surplus sludge quantity of 60 g TS/(PE·d), a combustive loss of approximately 70%, and 350 NL CH\(_4\)/kg COD results in 0.9 g COD/(PE·d). The formation depends on the boundary conditions of the procedure and the storage duration.

Additional methane emissions that can arise during the disposal, e.g. in agricultural settings, or incineration of digested sludge (SYLVIS 2009; Schaum et al. 2010), will not be considered within the framework of this investigation.

In terms of the COD balance, the ratio of methane emissions (methane slip, dissolved methane and residual gas) is <4% based on the total produced methane during digestion. Nevertheless, taking into account the global warming potential (GWP) of methane the relevance gets more significant. Figure 6 shows specific methane emissions as CO\(_2\)-equivalent per population equivalent (PE) and year for a time horizon of 100 and 20 years (depending on the GWP). About 4,400 (GWP\(_{100}\)) and 11,200 g CO\(_2\)-eq./(PE·a) (GWP\(_{20}\)), respectively, result considering total methane emissions of approximately 130 g CH\(_4\)/(PE·a). These are, on a time horizon of 100 years, about 300 g CO\(_2\)-eq./kWh\(_{\text{el}}\) based on a specific electricity production from biogas utilization by CHP of approximately 15 kWh\(_{\text{el}}\)/(PE·a) (assumptions according to Figure 1 and an electrical efficiency of 35%). Compared to specific emissions of approximately 500–1,000 CO\(_2\)-eq./kWh\(_{\text{el}}\) (FFE 2010) by fossil fuels, the methane emissions occurring due to the sewage sludge treatment have to be focused on and have to be reduced.

CONCLUSIONS

The energy generation 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. Methane emissions are of particular concern in anaerobic treatment. Therefore, the focus is on the utilization of a carbon balance, based on the COD, to evaluate the magnitude of methane losses during sludge treatment. In addition to biogas production and use, dissolved methane in digested sludge and the methane slip have to be considered when using CHPs. Measurements of dissolved methane concentrations at different WWTPs reveal a concentration range of approximately 17–37 mg CH₄/L. The COD balance indicates a ratio of the methane emissions (methane slip, dissolved methane, and residual gas) close to 4% of the total methane production during digestion. Considering the electricity generation by CHPs and the higher global warming potential of methane, compared to carbon dioxide, emissions of approximately 300 g CO₂-equ./kWh result, which is in a similar range to greenhouse gas emissions caused by electricity generation by fossil fuels.

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 the 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 treated or burned to avoid further emissions.

Further reductions of emissions due to methane slip can be achieved by employing catalysts or downstream incineration plants in the exhausts of CHPs.

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

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